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Contents

Articles

- 1 Modeling and simulation of liquid metal battery (LMB) materials development using statistical package for social sciences (S.P.S.S.) Simon Ejededawe Igberaese
- **10** Underwater implosion behavior of 3D-printed polymer structures Nathan Grantham-Coogan, Craig Tilton, Helio Matos, Arun Shukla

30 Collagen derived from a giant African snail (*Achatina achatina*) for biomedical applications

Dustin Pomary, Belinda Selase Korkor, Bernard Owusu Asimeng, Solomon Kingsley Katu, Lily Paemka, Vitus Atanga. Apalangya, Bismark Mensah, E. Johan Foster, Elvis K. Tiburu

- **43** Low-cost ternary composite photocatalysts consisting of TiO₂, kaolinite and cement for an efficient organic waste decontamination in water *Kohobhange Karunadasa, Pannilage Madhushanka, Chinthan Manoratne*
- **59** An analysis of temperature control for electromagnetic induction heating of CFRP based on sparrow search algorithm *Ning Yang, Tianyu Fu*
- **70** Assessing the rheological properties of bio modified asphalt cement Saad Issa Sarsam

80 The potential of DNA from industrial vegetables byproducts for the preparation of sustainable materials

Tatiane Zucchini de Souza, Priscila Nishizaki Borba, Bruna Fernandes Antunes, Deliane da Silva Cabral, Antonio José Felix Carvalho, Eliane Trovatti

89 Mechanical strength investigation of chemically reinforced sandy soil using organic copolymers for geotechnical engineering applications

Mohan Raj Krishnan, Edreese Housni Alsharaeh

99 Unnotched impact toughness of polybutylene terephthalate/polyamide 6/carbon black blends

Quoc Bao Ngo, Phan Hieu Hua, Thi Hong Nga Pham, Minh Trong Tin Vo, Thanh Tan Nguyen, Quan Anh Pham, Van Huong Hoang, The San Tran, Sy Hung Ho, Khac Nhan Nguyen

Reviews

- **106** Solid waste recycling and organic particulate hybrid nanocomposite technologies for sustainable infrastructure—A comprehensive review Lucky Ogheneakpobo Ejeta, Ehiaghe Agbovhimen Elimian
- 128 Zein—A plant protein as a promising biopolymer for biomedical applications: A perspective

Anns Raju Reshma, M. R. Rekha

161 Modeling and formulation/process parameters design methodological approaches for improving the performance of biocomposite materials for building, construction, and automotive applications: A state-of-the-art review

Lucky Ogheneakpobo Ejeta

177 Advancements in nanohybrids: From coordination materials to flexible solar cells

Shahab Khan, Inam Ullah, Salman Khan, Sanila Ajmal, Najmus Saqib, Faizan Ur Rahman, Shahid Ali

194 Recent advancements in nanocellulose synthesis, characterization, and application: A review

Shamim Ahsan, M. S. Rabbi

227 Footsteps of graphene filled polymer nanocomposites towards efficient membranes—Present and future

Ayesha Kausar, Ishaq Ahmad

251 Sustainable membrane technology for water purification—Manufacturing, recycling and environmental impacts

Ayesha Kausar



Modeling and simulation of liquid metal battery (LMB) materials development using statistical package for social sciences (S.P.S.S.)

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Abstract: There are a number of input parameters that are considered in relation to the stimulatory possibility of constructing a Liquid Metal Battery (LMB). This paper talks about the modeling approach possible for use in LMB research work. Equivalent Circuit Modeling (ECM) is the most common method used to analyze input data or parameters. In analyzing some of the basic elements, such as electrical capacitance, electrical resistance, open circuit voltage, terminal voltage, temperature, time response, time constants, State of Charge (SOC), etc., the cell impedance could be calculated by predicting the system elements that would play key roles in the determination of the parameter identification method for the battery's Equivalent Circuit Model. Secondly, each element in the model has a known behaviour, which mainly depends on the element type and the values of the parameters that characterize that element. In EIS software, the Graphical Model Editor could be used to build an equivalent circuit model, or the befitting model could be carefully and properly selected. Thirdly, in fitting the Equivalent Circuit Model (ECM) to the initial data or parameters, one must take note that the parameters are strongly dependent on temperature, heat, and losses. Such are: the Open Circuit Voltage (OCV), which is strongly dependent on the temperature, the loss processes depend on temperature; losses produced by the loss processes are dissipated as heat energy; the heat generated or consumed by the electrochemical reactions during normal operation has a defined temperature; and a system with a defined temperature window with safe, stable, and efficient operation is achievable. At the end of this research, the simulation of Lithium (Li) and Cadmium (Cd) was found to be in the proportion of 67:33, which is used to determine the strength of the reactivity of the metals. It can be informed in this article that the Bi and Li chemical compositions of the metals are equal to 49 for Li and 51 for Bismuth, which makes the overall reactivity very high, which could be used for LMB development.

Keywords: LMB; energy; Lithium; Cadmium; Antimony; Bismuth; estimation; storage; development

1. Introduction

Despite the known problems of power unavailability due to power outages or insufficiencies, the development of alternative solutions is necessary. The alternative solution needed for electrical energy storage is the LMB [1]. This is mainly done in three ways: the design of batteries with a greater energy density; and the reduction and optimization of dynamic modes of charging/discharging of the LMB. Liquid Metal Batteries (LMBs) compared to other battery types have a number of advantages, which are: greater efficiency, increased energy density, increased nominal voltages, increased lifetime, faster and more efficient charging, no need for routine maintenance, and greater resistance to external conditions [2]. One of the peculiar advantages of LMB is that it does not completely discharge like other conventional batteries. In the

field of battery modeling, many different battery models have been proposed in the literature. The battery models can be divided into analytical, electrochemical, and electrical circuit models or a combination of the model types. Analytical models do not give a good outlook on the electrochemical processes occurring in the cell. Electrochemical models require a large amount of computational power to solve the time-varying partial differential equations and cannot be directly linked to the rest of the system [3]. Combined analytical and electrochemical models also suffer from high complexity and poor system modeling compatibility. On the other hand, electrical circuit models can easily be connected to the rest of the electronic systems. However, to model the general behavior of the battery, electrical circuit models are sufficient [4]. Most electrical circuit models can be classified as impedance or thevenin models. Impedance models require Equivalent Circuit Modeling (ECM) to determine the circuit components that are related to the electrochemical processes in the cell [5]. The goal of this paper is to provide a tool for simulating the behaviour of LMB parameters such as the electropositive metal, the electronegative metal, and the suitable molten salt electrolyte under possible simulating conditions, especially with simulation programs such as Matlab software.

2. Battery modelling consideration

Because of the complex charging/discharging characteristics and relative damageability of batteries generally, it is necessary to establish accurate battery models, which can help the design of charging stations more proficiently and dependably. Researchers around the world have developed a wide variety of battery models with varying degrees of impedance. The two primary modeling strategies are the mathematical and circuit-oriented modeling strategies. Conventionally, mathematical battery models are developed based on primary forecast system-level behaviour such as battery runtime, efficiency, or capacity levels [6].

Many recent mathematical battery models have been significantly improved by adding and modifying the terms of conventional battery models to relax the assumptions of the model. This is considered to be able to represent the battery voltage dynamics more accurately when the current varies, as well as when considering battery age and charge/discharge dynamics. Circuit-oriented battery models are electrical equivalent models using a combination of voltage sources, resistors, etc., which are normally used by electrical engineers for designing and co-simulating with other electrical circuits and systems. In modeling generally, a substantial clarification can be made between the electric circuit components of the model and the actual battery dynamics consideration. An equivalent circuit model needs to be built primarily to match experimental data. Such a model provides adequately correct information that serves the need for a real-time battery management approach when properly designed [6].

3. Criteria for battery modelling

To achieve the objectives of the study, the following criteria need to be set according to the different model characteristics, which are presented as follows:

Criteria 1: The model should be able to determine the development of input battery parameters, including terminal voltage, open circuit voltage, the state of health, resistance, etc., which explain the state of the battery for a dynamic discharging condition. It should also be able to adequately represent dynamic processes while the battery is discharging [7].

Criteria 2: The complication of the model should adequately suit Criteria 1 but must also be executable in real-time for a model-based system [7].

Criteria 3: The output of the battery model should be comprehensible to battery operators and technicians, as well as significant to those who do not have any background in battery technologies [7].

4. Different battery model criteria

Many electrochemical factors contained in the electrochemical model are immaterial to the external circuit, and some of the key parameters, like the internal resistance, are hard to explain in an electrochemical model. Therefore, this model technology is not able to meet Criteria 1. However, the solutions in the electrochemical model are not complicated. Criteria 2 can therefore be satisfied by an electrochemical model of a battery. Criteria 3 might be difficult to obtain for an electrochemical model because the understanding of the outputs for an electrochemical model usually requires some background knowledge of the battery chemistry. As a result, the electrochemical model was not chosen for this research work. Physical models can give a good understanding of the battery's important parameters so that Criteria 1 can be satisfied. Criteria 3 can also be met, as the terminal voltage can be determined as the output with the knowledge of these parameters. One significant disadvantage is that the physical models involve a huge amount of calculation in analysis which is quite timeconsuming. In finite element or Computational Fluid Dynamics (CFD) methods, a large non-linear system of equations is solved iteratively, and it could take much Central Processing Unit (CPU) time, especially when the system has more than two dimensions. However, the physical modeling methods could also meet Criteria 2, though a fast response is required.

Therefore, Criteria 1 can be satisfied by the equivalent circuit model. The model's ease is due to its low computational time (Criteria 2) and therefore it can be suitable for online implementation [7]. Furthermore, the basic battery parameters like internal resistance, terminal voltage, State of Charge (SOC), etc. can be chosen as the main output of the model to meet Criteria 3.

5. Battery modelling techniques

A number of diverse types of battery models include Electrochemical Model (EM), Computational Fluid Dynamics Model (CFD), Finite Element Model (FEM) and Equivalent Circuit Model (ECM). This part gives a summary of the above-named four various types of battery models and the problems that are solved by each of them. In this part, every battery model technology is judged based on the general criteria.

5.1. Electrochemical model (EM)

The electrochemical model (EM) deals with electrochemistry, which is a division of chemistry that involves chemical reactions that take place in a solution at the interface of an electron conductor (a metal or a semiconductor) and an ionic conductor (the electrolyte). The reactions involve electron transfer between the electrode and the electrolyte. The behaviour of the battery is dependent not only on how it is used but also on a number of construction factors, which are the thickness of the plates, the active mass density of the active material, the concentration of the overall solution, and the nature of the electrodes [8].

5.2. Physical model (PM)

(a) The finite element method (FEM) is that part of the physical model, which deals with numerical analysis techniques for finding estimated solutions to partial differential equations as well as integral equations. The basic principle of the Finite Element Model (FEM) is to divide the problem into elements (parts or portions), and each element or part is a smaller problem to be solved so that they can be analyzed separately. The 'elements' are then assembled together to restore the initial problem. Finite element analysis is a very popular method of analysis in areas with complex geometries like the Liquid Metal Battery (LMB), and it is excellent at stress and thermal analysis of the LMB. The Finite Element Model (FEM) application for batteries could help, especially with a good knowledge of heat loss. There are also attempts to analyze the current density on the positive terminal of the LMB using the FEM analysis tool [8].

(b) Computational Fluid Dynamics (CFD) technology is a well-established tool for the physical analysis and optimization of fluid flow, mass and heat transfer, and related phenomena (e.g., chemical reactions) that may simultaneously take place in a complex system. Therefore, such modeling is able to give an excellent understanding of the battery parameters and detailed characteristics of battery dynamics [8].

5.3. Equivalent circuit model

An equivalent circuit refers to the simplest form of a circuit that retains all of the electrical characteristics of the original circuit. In its most common form, an equivalent circuit is made up of linear, passive elements. However, more complex equivalent circuits are used to approximate the non-linear behaviours of the original circuit. The extensively used equivalent circuit model consists of the battery's Open Circuit Voltage (OCV), ohmic resistance (R0) of the connectors, electrodes, electrolyte, and two parts of parallel resistor-capacitor combinations R1, C1, and R2, C2, representing both the mass transport and the double layer characteristics [8].

$$Vt = V0C - V0 - V1 - V2$$
(1)

$$V0 = iR0 \tag{2}$$

$$C1\frac{dv1}{dt} + \frac{V1}{P1} = I$$
(3)

$$\frac{dt}{C2}\frac{dv_2}{dv_2} + \frac{V_2}{V_2} = I$$
(4)

$$\frac{dt}{dt} + \frac{dt}{R2} = 1 \tag{4}$$

From the Equivalent Circuit Model stated in **Figure 1** above, it was assumed that the battery was de-energized by opening the circuit. A step change in the magnitude

of current, occurs for the current, I at t = T0 = 0. The corresponding battery voltage would immediately drop at time, T0 due to the ohmic resistance. Hence, when the circuit is energized due to the closure of the circuit, the current pulse ends at t = T1, which means that the battery voltage has an automatic increment, which is again due to the ohmic resistance factor. Finally, it moves into the time-off stage, where the battery is not charging or discharging. The voltage levels differ exponentially at the time-off stage. Assume that the data is recorded until t = T2.

$$Voc = Vt (T0-)$$
(5)

To ascertain battery models of superior worth, model parameters need to be correctly calculated from experimental data. To recognize the parameters, usually specific tests such as constant current pulse discharge and charge tests at various SOC and current levels are performed. The ohmic resistance R0 can be easily considered based on the instant battery voltage change before and after the current step. However, the other parameters (R1, C1, and R2, C2) are more difficult to identify because two-time constants are involved in the model.



Figure 1. Battery equivalent circuit model [9].

6. Modelling of the battery cell voltage (CV)

The modeling of the battery cell is voltage-based, and it is a function of Discharge Capacity (DC), Charge time (Ct), and Charge Capacity (CC).

$$CV = f(DC, Ct, CC)$$
(6)

$$CV = \alpha 0 + \alpha 1DC + \alpha 2Ct + \alpha 3CC$$
(7)

$$CVe = \alpha 0e + \alpha 1DCe + \alpha 2Cte + \alpha 3CCe$$
(8)

where, CV = Cell Voltage, DC = Discharge Capacity, Ct = Charge time, CC = Charge Capacity, and α signifies a specified constant, which ranges from 0, 1, 2, 3 ... ∞ .

Equations (6–8) are the model for the battery and the model operates with the parameters CV, DC, Ct, and CC.

Temperature (T) =
$$f$$
 (time) (9)

Open Circuit Voltage (OCV) =
$$f$$
 (State of Charge) or f (SOC) (10)

Resistance (R) =
$$f(SOC)$$
 (11)

Capacitance (CP) =
$$f(SOC)$$
 (12)

$$Fine \text{ constant (TC)} = f(SOC)$$
(13)

Hence,

$$SOC = f(OCV, R, CP, TC)$$
 (14)

$$\frac{dE}{dt} = \left(\frac{dE}{dt}\right)\text{gen.} + \left(\frac{dE}{dt}\right)\text{loss} + \left(\frac{dE}{dt}\right)\text{in} + \left(\frac{dE}{dt}\right)\text{out}$$
(15)

Table 1 shows the estimated parameters of the Liquid Metal Battery (LMB) with four (4) samples of Liquid Metal Battery developmental parameters, which gives a breakdown into electrode composition, operating temperature, electrode area, interelectrode distance, charge-discharge current, coulombic efficiency, voltage efficiency, average discharge voltage, theoretical capacity, discharge capacity, voltage input, and voltage output.

Design parameters	Li//Cd-Sb	Li//Cd-Bi	Li-Bi	Li-Cd
Electrode composition in moles	47-36-17 48-36-16 49-35-16 50-34-16	42-38-20 47-33-20 45-35-20 44-32-24	45-55 40-60 50-50 48-52	70-30 60-40 50-50 65-35
Operating temperature in O °C	450–500	400–500	350-400	300-400
Electrode area in cm ²	1.30-2.50	1.00-1.50	1.00-2.00	1.50-2.00
Inter-electrode distance in cm	1.00-1.50	1.00-2.00	1.50-2.00	1.50-2.00
Charge-discharge current, A	0.34-0.55	0.34-0.55	0.34-0.55	0.34-0.55
Coulombic efficiency in %	80–99	80–99	80–99	80–99
Voltage efficiency in %	65-80	65–80	65-80	65-80
Average discharge voltage in Volts	0.65-0.75	0.65-0.75	0.65-0.75	0.65-0.75
Theoretical capacity in Ah	0.75-0.90	0.75-0.90	0.75-0.90	0.75-0.90
Discharge capacity in Ah	0.55-0.80	0.55-0.80	0.55-0.80	0.55-0.80
Voltage input in Volts	12.0 12.1 12.3 11.9	12.5 12.6 11.8 12.0	11.6 11.7 11.9 12.1	11.5 11.6 11.8 11.7
Voltage output in Volts	220 215 225 235	225 220 230 230	230 225 235 225	235 230 240 220

Table 1. Estimated parameters for the LMB.

7. Simulation and analysis of the liquid metal electrodes

From **Figure 2**, a comparison of the reactivity dynamics between the two metals, Bismuth (Bi) and Lithium (Li) shows a variation in the extent of reactivity of the metals involved. From the graph, Lithium is more reactive than Bismuth, which therefore implies that the selection of Lithium metal is suitable. However, the reactivity level of Bismuth was characterized by a slow reaction at the beginning and a spontaneous reaction occurring at the end, though the electrode compositions of Li and Bi are not the same.



Figure 2. Simulated graph of Bismuth and Lithium metals.

In **Figure 3**, a comparison of the reactivity dynamics between the two metals, Bismuth and Antimony, was done in order to establish the compatibility of both metals. From the graph, Antimony is more reactive than Bismuth, which gives rise to the selection of Antimony metal over Bismuth in terms of the suitability of both metals involved. However, the reactivity level of Antimony was characterized by a fast reaction occurring during the reaction process.



Figure 3. Simulated graph of Bismuth and Antimony metals.

In **Figure 4**, the reactivity dynamics of three metals are x-rayed. The metals are Lithium, Antimony, and Bismuth. The strength of the reactions of the different metals is displayed in the graph above. Lithium indicated in red is highly reactive due to its usual property of being extreme in terms of reactivity. Lithium is followed by Antimony, which is moderately reactive in its alloy combinations in order to decrease the temperature of its overall reactants to give the desired products.



Figure 4. Simulated graph of Bismuth, Lithium, and Antimony metals.

In **Figure 5**, the reactivity of the two metals was examined. The Lithium and Bismuth metals are displayed in the graph above. The Lithium indicated with a red line was moderately reactive. Lithium is followed by Antimony, which is moderately reactive in its alloy combinations, and it helps to decrease the temperature of its overall reactants to give the desired products.



Figure 5. Simulated graph of Bismuth and Lithium metals.

In **Figure 6**, the composition of Lithium (Li) and Cadmium (Cd) was on the premise of 67:33 in order to determine the strength of the reactivity of the metals. From the Bi and Li metals, the chemical composition is almost equal at a ratio of 49 for Li and 51 for Bismuth. The overall reactivity is going to be very high. Thus, the values of the composition are not fit for use in the LMB construction.



Figure 6. Simulated graph of Lithium and Cadmium metals.

8. Conclusion

From the simulated graphical analysis in this research work, it was deduced that the dynamic characteristics of the LMB metals, which were carefully analyzed, show that the metals Li//Sb-Bi are the most suitable electrodes that could be used among the varieties of proposed metals being examined. The possibility of examining varying salt electrolytes was carried out, and it was discovered that the LiCl-LiF-LiI salt electrolyte is one of the best alternative chemistries. In this paper, the electropositive metal, the electronegative metal, and the molten salt electrolyte were carefully identified and simulated. Based on the simulated results, LMB development is achievable.

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Article

Underwater implosion behavior of 3D-printed polymer structures

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Abstract: This study experimentally investigates the failure behavior of 3D-printed polymer tubes during underwater implosion. Implosion is a prevalent failure mechanism in the underwater domain, and the adaptation of new technology, such as 3D printing, allows for the rapid manufacturing of pressure vessels with complex geometries. This study analyzes the failure performance of 3D-printed polymer structures to aid in the future development of 3Dprinted pressure vessels. The 3D-printed tube specimens analyzed were fabricated using digital light synthesis (DLS) technology and included four different case geometries. The geometries consist of three cylindrical shells of varying diameter and thickness and one double hull structure with a cylindrical gyroid core filler. These specimens were submerged in a pressure vessel and subjected to increasing hydrostatic pressure until implosion failure occurred. High-speed photography and Digital Image Correlation (DIC) were employed to capture the collapse event and obtain full-field displacements. Local dynamic pressure histories during failure were recorded using piezoelectric transducers. The findings highlight that the 3D-printed polymers underwent significant deformation and failed at localized points due to material failure. The fracture of the specimens during failure introduced inconsistencies in pressure and impulse data due to the chaotic nature of the failure. Notably, the energy flow analysis revealed that the proportion of energy released via the pressure pulse was lower than in traditional aluminum structures. These findings contribute to our understanding of the behavior of 3D-printed polymers under hydrostatic pressure conditions.

Keywords: 3D printed polymers; structural failure; implosion; cylindrical shells; double hull structures

1. Introduction

Undersea structures, such as unmanned underwater vehicles (UUVs) and underwater pipelines, are susceptible to failure when exposed to high hydrostatic pressure at greater operational depths. These failures can occur due to pressures exceeding their critical failure limit or dynamic loads from events in their immediate surroundings. To enhance the safety and efficiency of undersea operations, exploring innovative technologies capable of designing more robust underwater structures is crucial. One such technology is 3D printing, which offers numerous advantages such as design flexibility, customization, lightweight construction, simplified assembly, cost and time efficiency, and on-site production and repair capabilities [1]. By leveraging these benefits, 3D printing has the potential to revolutionize certain aspects of underwater operations by delivering improved performance, enhanced reliability, and cost-effectiveness. To aid in this development, this work analyzes the failure mechanisms of 3D-printed structures within a high-pressure underwater environment.

Extensive research has been conducted on hydrostatically induced failures over

the past century. The implosion of objects emits pressure waves that can damage nearby structures [2,3], making implosion a subject of intense study. Early studies focused on the implosion of glass spheres [2–4], while NASA demonstrated interest in implosion studies for space vehicles [5]. More recently, there has been significant research on the implosion of cylindrical shells [6–8]. Researchers like Turner and Ambrico have characterized the pressure pulse of cylindrical metallic structures and developed accurate numerical models of the implosion process [6]. Additionally, composite materials have gained interest for their collapse mechanism, critical collapse pressure, and energy emitted during the implosion process [7,9,10].

Researchers have recently explored double-hull structures to enhance structural efficiency and mitigate energy during implosion events. However, most studies on cylindrical double-hull structures have focused on their performance under blast loading rather than hydrostatic loading [9,11,12]. While the study by DeNardo et al. examined hydrostatically induced failure in composite structures with foam as the filler material between the two shells [9], no research has been conducted on double hull structures with seamlessly connected shells and filler material. Li et al. investigated double hull structures using auxetics as the filler material and employed a numerical approach to study their post-buckling behavior [13].

This study aims to investigate the failure of 3D-printed double-hull structures by exploiting a 3D printer's capability to produce advanced structures, which have not been explored in the literature. The investigation involves four specimens, including three cylindrical tubes and one double-hull structure. These specimens were subjected to increasing hydrostatic pressure until failure occurred, and their behavior was observed using high-speed cameras, Digital Image Correlation (DIC) analysis, and dynamic pressure sensors. The resulting data provided insights into the implosion characteristics of the material and enabled the calculation of the energy released during the implosion event. Furthermore, these experimental results were compared to numerical models created in Abaqus for specimen design.

2. Experimental procedures

2.1. 3D printing material

The specimens utilized in this study were produced using a carbon M2 resin printer. This printer has a build volume of $7.4 \times 4.6 \times 12.8$ inches and can produce parts with relatively isotropic properties. The printing process involved using urethane methacrylate resin (UMA 90). A summary of the cured resin properties is presented in **Table 1** below.

Property	Value
Elastic modulus	1400 MPa (~200,000 psi)
Poisson's ratio	0.4
Yield stress	30 MPa (~4350 psi)

Table 1. Material properties of UMA 90 are provided by carbon.

To ensure consistent quality, each UMA 90 part undergoes a post-processing

procedure in accordance with the instructions provided in Carbon's technical sheet [14]. This procedure includes an IPA bath to remove excess resin, followed by one minute of UV light exposure on each side of the specimen using an APM LED UV-Cube-II.

2.2. Structural system

Four different specimen structures were considered in this study. The first three structures consist of cylindrical shell tubes with varying diameters and thicknesses. The fourth structure is a double hull design that combines two shells from the previous cases. The unsupported length of the tube structures is 25.4 cm in all cases. To prevent water penetration, each tube system is equipped with endcaps that seal its air interior from the underwater environment. The end caps are machined from aluminum 6061-T6 to have a snug fit to the inner tube surface and a 20 mm overlap with the tube's inner surface. In addition, an O-ring seal is placed between the end cap and the tuber's inner surface to prevent leakage during pressurization. **Figure 1** provides a visual representation of the longitudinal cross-sectional view of the four specimens, while **Table 2** presents the specific measurements of the first three cylindrical shell tubes.



Figure 1. Specimen layouts for single shell and double hull specimens.

Experimental designation	Structure type	Outer diameter (cm)	Inner diameter (cm)	Total thickness (cm)
Case A		5.08	4.45	0.32ª
Case B	Single shell	2.54	2.23	0.16 ^a
Case C		5.08	4.09	0.50 ^a
Case D	Double hull	5.08	2.23	1.43 ^b

 Table 2. Cylindrical shell specimen details.

a) The wall thickness of a single shell.

b) The wall thickness of two shells plus the core thickness.

The double hull structure is 3D printed as a single unit using a gyroid core filler, as illustrated in **Figure 1**. The gyroid shape was chosen because it is a common filler structure for 3D printing while highlighting the uniqueness of 3D printing to print complex geometries. To maintain the cylindrical shape, the gyroid structure was designed to bridge the outer and inner shells with a cell size of 1.27 cm (1/2 inch). The equation for a single gyroid unit shell in cartesian coordinates is represented in Equation (1).

$$0 = \cos(\omega x)\sin(\omega y) + \cos(\omega y)\sin(\omega z) + \cos(\omega z)\sin(\omega x)$$
(1)

In Equation (1), ω represents the gyroid unit cell's period, and *x*,*y*, and *z* represent the position in space in the cartesian coordinate system. To create the gyroid as a cylindrical shape, the gyroid is represented using polar coordinates. This transformation and mapping can be done similarly to a previous study by Wang et al. [15]. A MATLAB code that can recreate the cylindrical gyroid used in this study is in the Appendix and illustrated in **Figure A1** of the Appendix.

The unsupported length of the specimen, which measures 25.4 cm, was divided into twenty gyroid cells, resulting in a height of 1.27 cm for each cell. For the gyroid cylinder to connect properly, its circumference must consist of nine gyroid cells. Therefore, the circumference of each gyroid cell measured 1.33 cm (0.523 inches). The gyroid thickness, determined through the numerical model procedure, is 0.762 mm (0.03 inches). These dimensions and design considerations ensure the gyroid-filled double hull specimen's appropriate connection and structural integrity. Lastly, the thicker-walled cylindrical structure was designed for equivalent collapse pressure and displaced volume as the gyroid double hull structure.

2.3. Experimental setup

The experiments were conducted in the University of Rhode Island implosion tank facility. This facility comprises a semi-spherical pressure tank with a diameter of 2.1 m and is equipped with two high-speed cameras, as illustrated in **Figure 2**. The tank can handle pressures up to 6.9 MPa (1000 psi). During the experiments, the specimen was suspended in the center of the tank. The tank was then filled with water and pressurized using compressed nitrogen gas. To record the emitted signatures, three to four PCB 138A05 dynamic pressure transducers manufactured by PCB Piezotronics, Inc. (Depew, NY) were used to record pressure data at 2 MHz.



Figure 2. URI's implosion tank facility schematic.

The placement of the pressure sensors was determined to capture the implosion behavior and pressure signatures of each specimen, considering their respective outer diameters and dimensions. The schematic for the sensor locations is displayed in **Figure 3**.



Figure 3. Sensor locations inside pressure tank.

2.4. Digital image correlation

High-speed cameras captured the implosion process at 40,000 frames per second. Each specimen was coated with a random DIC (Digital Image Correlation) pattern to facilitate accurate measurements of deformation. The speckle was high-contrast and randomized using a white UMA base and a random black speckle pattern using flat black paint.

Commercially available VIC-3D 9 software from Correlated Solutions, Inc. (Columbia, SC) was used for image analysis. The software enabled the extraction of out-of-plane displacements by comparing common pixel subsets between original undeformed and subsequent deformed images. Before usage, the system was calibrated using a 12×9 dots calibration grid with 18 mm spacing and periodically captured calibration grid images while translating and rotating the grid in all six degrees of freedom. This procedure is outlined in previous work [16–18]. Before pressuring the implosion tank at the beginning of the experiments, the calibration was validated by calculating the outer radius of the submerged cylinder using DIC (yielding errors of 5% or less). This validation procedure is also shown in previous work in more detail [19].

2.5. Post-processing calculations

2.5.1. Normalizing results

The results were normalized using the Buckingham-Pi theorem to facilitate effective comparison between all the cases. This normalization approach was initially made for energetic systems by the seminal work of GI Taylor [20]. It is now being adapted to the normalized pressure (π_p), in which the pressure (P) is multiplied by the cube of the sensor distance from the center of the implodable (R_s) and divided by the energy in the system (E_o), given by Equation (2). This value results in a dimensionless representation of the pressure energy relative to the initial energy of the implodable. Since sensor locations and initial energy vary between cases, this normalization is an important tool to assess the relative change between the cases. In addition, the initial potential energy in the implodable system was determined by multiplying the critical collapse pressure (P_{cr}) by the collapsible volume of the implodable (V_c), given by Equation (3).

$$\pi_P = \frac{PR_s^3}{E_o} \tag{2}$$

$$E_o = P_{cr} V_c \tag{3}$$

Similarly, the time history (t) was also normalized using the critical collapse pressure (P_{cr}), the collapsible volume (V_c), and the density of water (ρ_o), as given by Equation (4). The normalized time, π_p , represents the time it takes for the pressure wave generated by the implosion event to move in a particular medium relative to the size of the implodable (which affects how long the pressure wave is) and the initial pressure (which affects collapse velocity).

$$\pi_t = t P_{cr}^{\frac{1}{2}} V_{cr}^{-\frac{1}{3}} \rho_o^{-\frac{1}{2}}$$
(4)

2.5.2. Energy flux potential

To assess the damage potential of a failing implodable structure, the energy emission is calculated using the pressure signatures from the pressure transducers. Previous studies on implosion energy [10,21] performed these calculations by assuming a spherical pressure pulse to calculate energy flow. A spherical pulse is the general solution for a point source pressure pulse. However, a point source pulse is not a good assumption for the cases in this study when accounting for the tube geometry relative to the sensor location. In this work, an elliptical pressure wave surface is used to accommodate the cylindrical shape of the implodable. The ellipsoidal surface, SA, is calculated using the unsupported length of the implodable structure, UL, and the sensor location relative to the center of the implodable, Rs, as its major axis, given by Equation (5).

$$SA = 4\pi \left(\frac{2\left(\frac{UL}{2}R_s\right)^{1.6} + (R_s^2)^{1.6}}{3}\right)^{\frac{1}{1.6}}$$
(5)

To determine the maximum potential energy flux at the sensor location, E_{pf} , at the specific location, the potential energy in the system is divided by the surface area, as given by Equation (6). Note that E_o is a relatively high estimate for the actual energy release because (1) the pressure decreases during the collapse process, and (2) not the entire internal volume collapses during an implosion [10]. Previous work [10] accounted for the pressure decrease by calculating E_o as $\frac{1}{2}P_{cr}V^*$, where the $\frac{1}{2}$ term accounts for the pressure drop and V^* is the collapsible volume of an assumed collapsed shape. However, the pressure is also not uniform throughout the wavefront surface area, close to the implosion event. Hence, SA is also a relatively high estimate for surface area if used with a point pressure measurement. Since E_o and SA are both overestimated, these overestimation factors will partially cancel out the calculation for the potential energy flux at the sensor location, E_{pf} .

$$E_{pf} = \frac{E_o}{SA} \tag{6}$$

2.5.3. Impulse and energy flux

The specific dynamic impulse, I, of the pressure generated during the implosion event, is calculated as the integral of the dynamic pressure signature, given by Equation (7), where t_i is the time in which the implosion initiates, and t_f is the time

in which the low-pressure signatures of the implosion end (and the high-pressure starts).

$$I = \int_{t_i}^{t_f} (P - P_{cr}) dt \tag{7}$$

Lastly, earlier work on explosives by Aarons and Yennie [22] calculated the flow energy generated by an explosive bubble's collapse. Previous work [21] has leveraged these solutions by treating the implodable as a collapsible cavity. The energy flux generated by a collapsible cavity can be calculated using the impulse of the pressure signature, fluid properties, and measurement location as given by Equation (8).

$$E_f = \frac{I^2}{2\rho_o R_s} \tag{8}$$

Furthermore, the energy flux released can be normalized by dividing Equation (8) by Equation (6) to quantify the relative change in implosion pressure energy from different cases, providing valuable insights into the energy mitigation capabilities of the imploding structures.

As mentioned, the pressure is not uniform throughout the wavefront surface. Hence, Equation (8) gives a representative value that can be used to compare with other cases that use the same procedure to calculate E_f . A sensor array that can capture the pressure distribution would be needed for a better solution for total energy at the implosion wavefront. Another option is to use one sensor farther away from the implodable, in which case the point source spherical wavefront assumption becomes a valid option. The challenge with this latter option is having a sensor that has high sensitivity as well as having an implosion facility large enough to support a larger reflection-free window between t_i and t_f .

3. Preliminary analysis

3.1. Computational model

The double hull structure was a major design consideration when developing the implodable cases (Case D in **Table 2**). The inner and outer hulls are coupled through the core structure in the double hull structure. Unlike the single shell cases, where analytical tools such as the Von Mises buckling equation [23] can predict the collapse pressure, a computational model is required to design the implodable system for the desired collapse pressure given the displaced volume. Abaqus CAE 2022 was used to construct all the models, using the non-linear Riks solver to determine the collapse pressure.

3.1.1. Single shell

The material model used for the UMA 90 is given in **Table 1**, and the tube specimens were modeled using shells (for Cases A and B) and solid elements (for Case C). A unit pressure load was applied to the shell's exterior to simulate hydrostatic pressure. An equivalent force from the pressure around the endcaps was also applied to the ends of the tubes. Boundary conditions were implemented to model the endcaps, where the radial motion was fixed at the ends of the tube. The critical collapse pressure of the tubes was then determined by the maximum load

proportionality factor (LPF) output. **Figures 4a** and **4b** illustrate the model for cases C and D, respectively, showcasing the boundary conditions and load application.



Figure 4. (a) Single and (b) double hull tube structures model in Abaqus CAE.

3.1.2. Double hull structure

In Abaqus CAE, the double-hull structure was designed to maintain consistent boundary and loading conditions as in the single-shell simulations (as shown in **Figure 4a**). The gyroid core was also modeled using solid elements (shown in **Figure 4b** between the inner and outer shells as dark red). This is doable after simplifying the structural geometry and applying an effective bulk property to the double hull core.

Generally, single-shell simulations are relatively straightforward, but the double-hull structures were a challenge due to the structural complexities of the core. For complex structures, some validation tests representative of the mechanics should be made so the model can be calibrated to the validation test. Bending tests were performed for this work, as outlined in the following section. Another option would be to adopt a multiscale simulation approach, where the cores are simulated independently from the bulk structure (not used in this study).

3.1.3. Core properties

To determine the effective bulk property of the gyroid core structure, a series of 3 3-point bending (3PB) tests were performed in accordance with ASTM D5023. During these tests, sandwich beam structures with gyroid cores of the same cell size, periodicity, and total thickness as the double hull structure were performed with varying gyroid wall thickness. These tests were re-created using Abaqus CAE (as illustrated in **Figure 5**). Then, an iFEA approach was implemented to determine the effective elastic modulus for the given thickness to match the beam's flexural modulus (assuming Poison's core ratio is zero). **Table 3** summarizes the results for effective core properties as a function of gyroid thickness.



Figure 5. 3 Point bending (a) Abaqus model layout (b) experimental setup.

Tuble of Effective cole property.			
Gyroid thickness (mm)	Effective elastic modulus in MPa		
0.762	10.34		
1.524	34.47		
2.286	60.87		
3.048	64.33		

Table 3. Effective core property.

Lastly, a parametric study was performed using varying core elastic moduli, ranging from 10.34 to 64.33 MPa, to determine and estimate collapse pressure as a function of core wall thickness to determine the appropriate wall thickness that will yield a collapse pressure for the experimental facility (the facility limit is 6.9 MPa, but experiments were designed with a 75% cap on the limit for safety).

3.2. Computational design

After running Abaqus simulations of all cases and determining the appropriate wall thickness, the resulting collapse pressures for the designs are shown in **Table 4**.

Experimental designation	Structure type	Computation design collapse pressure (MPa)	Experimental collapse pressure (MPa)	Prediction accuracy Error
Case A		0.7998	0.855	6.5%
Case B	Single shell	0.793	0.752	5.5%
Case C		3.792	4.551	16.7%
Case D	Double hull	3.758	4.029	7.2%

 Table 4. Specimen collapse pressures.

These results show errors ranging from 5 to 17% compared to the true collapse pressure observed in experiments. Different factors contribute to the prediction discrepancy of 3D printed structures. These factors should be considered when 3D printing structures with geometry and property sensitivity. These factors include the material residue after 3D printing, which can increase the overall thickness. Post-processing the part removes the residual for the most part, but post-processing is a very meticulous process. Also, when printing the different cases, even though they have the same height, the printing time was longer for the thicker shell, and the material was exposed to UV curing for longer. Hence, there can be a slight variation in mechanical properties in one-part thermoset materials, which are highly dependent on UV curing. Lastly, the print is being done from an STL file, which alters the circular shape into a polygon shape. Most CAD software (such as SolidWorks, which was used in this study) offers the option of a fine STL export, but a fine export is not on par with what is considered a fine mesh by FEA standards.

4. Results and discussion

4.1. Pressure results

In this study, the pressure data analysis focuses on the sensor located at one outer diameter of the specimen. It has been observed that as the collapse pressures decrease, this sensor registers higher spikes in pressure. As a result, the noise levels recorded by this sensor are lower than those located farther away from the specimen.

4.1.1. Cylindrical shells

This study's 3D-printed polymer material exhibits a different failure behavior than metal tubes or stronger materials. For metal tubes with relatively thin wall thickness, failure initiates due to the instability of the load relative to what the structure can support [7–10]. Instead of this instability failure, the failure initiates with plastic deformation of the specimen (before implosion—also referred to as preimplosion deformation or pre-deformation), leading to imperfection and stress concentration on the lobes of the deformed tube. After reaching a critical stress, the implosion occurs after a crack propagates from the high-stress imperfections. These observations indicate that the implosion from these polymeric structures shows a material failure initiation, unlike traditional thin-walled structures, which fail with an instability initiation.

Figure 6 illustrates the implosion characteristics observed in the three shell tubes labeled based on their inner diameter. Critical instances during the implosion process are labeled in a sequence from A to E, from initiation to catastrophic implosion failure. The colormap overlayed on the tube's surface is the 3D DIC results for displacement, which show the change in radius relative to the center of the tube in millimeters. The corresponding pressure graphs for these trials are also presented with indicators A to E, showing what the structure looked like at these particular time instances. Each plot combines three trials, with the pressure data normalized by dividing it by the critical collapse pressure of each trial. For each plot, the average of all trials is shown as a solid line, and the sample standard deviation is given as the shaded area (this format is consistent for subsequent plots). The alignment of the pressure graph and accompanying photos is based on the implosion initiation, which sets the time to zero for each trial.



Figure 6. Normalized collapse pressure data for **(a)** Case A, **(b)** Case B, and **(c)** Case C.

The implosion initiates in time instance A, set to t = 0 in **Figure 6**. The first visible crack typically occurs along the top or bottom of the specimen and propagates longitudinally until it branches off and spreads throughout the specimen (B). This stage is characterized by major fracturing and increasing pressure variations between trials. The shell then undergoes implosion until wall contact occurs near the initial crack (C). At this point, the pressure pulse plateaus briefly as the rest of the specimen collapses. Subsequently, the specimen fractures into numerous pieces (D), and crack propagation continues until all the energy is released, resulting in the complete propagation of cracks (E).

Case C, which consists of the tube with a 4.089 cm (1.61 inch) inner diameter, exhibits a similar collapse behavior. Still, due to its thicker shell and higher collapse pressure, the pressure pulse data shows more consistency across different trials. Unlike Case A, which consists of a 4.45 cm inner diameter tube, a crack propagates during the implosion event along the center of the specimen (B) rather than the top or bottom. The collapse is also asymmetrical, with the side where the initial crack occurs experiencing a larger radial change than the other side, resulting in the walls not meeting in the middle.

The collapse characteristics of Case B, which is the tube with a 2.235 cm (0.88 inches) inner diameter, differ from those of the larger inner diameter tubes mentioned earlier. These tubes experience much greater deformation. The tube walls appear to be in contact even before the collapse is triggered (A). Failure begins with the formation of a crack at the top or bottom of the specimen, which propagates longitudinally (B). This is accompanied by a drop in pressure data and the formation and propagation of cracks throughout the specimen. At this stage, the walls in the center of the tube are completely in contact (C). Following the initial pressure spike, the rest of the specimen starts to collapse, resulting in additional spikes, as shown by D and E in **Figure 6c**.

The data were normalized using the Buckingham-Pi theorem to compare the results of all three trials. The normalized collapse pressure data for all three trials are presented in **Figure 7**. This normalization allows for a direct comparison of the collapse behavior and provides valuable insights into the implosion characteristics of the different tube specimens.

Among the three trials, the specimen with a 2.23 cm inner diameter (Case B) produced the lowest pressure pulse. This can be attributed to the high degree of deformation observed before the collapse in these experiments. With less distance for the walls to travel when instability occurs, the velocity of the shell walls is lower upon contact, resulting in a smaller pressure pulse.

In contrast, the inner diameters of the specimens at 4.09 cm (Case C) and 4.45 cm (Case A) exhibit significantly different characteristics in the under-pressure region during the collapse. This difference can be attributed to the fracture behavior observed in these trials, with the 4.09 cm specimen remaining more intact during the implosion event. Despite the variation in the under-pressure regions, the peak pressure pulse emitted from each experiment occurs at approximately the same location.



Figure 7. (a) Pressure vs. time for all cylindrical tubes (b) Normalized time vs. normalized pressure for all cylindrical tubes.

These variations in collapse characteristics among the three specimens highlight the complexity of predicting the exact outcome of a 3D-printed structure under hydrostatic pressure, especially when using a purely polymer structure. The additional complexities in failure mechanisms, coupled with the fact that polymers are inherently orders of magnitude weaker than metallics, make un-reinforced 3D printed polymer hull systems a unique choice for pressure hulls that may have a different application space (e.g., near-surface underwater vehicles with complex shapes that need rapid design and deployability). In addition, polymer parts of underwater structures are still necessary for non-structural applications in many undersea systems due to their lower impedance relative to metallics. Hence, these observations and findings are important in understanding the underwater structural behavior of 3D-printed polymer parts.

4.1.2. Double hull pressure data

The critical collapse pressure for the double hull, Case D, is 4.029 MPa with a standard deviation of 0.116 MPa. The collapse pressure shows a variation of 6%, which is relatively consistent compared to the shell tubes, which exhibited a percent error of 9%. This indicates a higher level of reliability and repeatability in the collapse behavior of the double-hull structure.

However, no notable data was recorded when analyzing the dynamic pressure sensors. This is due to the implosion behavior of this 3D-printed double-hull structure, driven by local failure (illustrated in the subsequent sections). This leads to water penetration at the local failure location and into the specimen. Water rushed inside the specimen, and a hammer occurred at the end cap locations. The pressure emitted from the local failure and internal hammer was negligible outside the specimen relative to the hydrostatic collapse pressure. For this reason, the collapse of this double-hull specimen cannot be accurately characterized using traditional cylindrical tube collapse analysis.

4.2. Displacement/DIC

4.2.1. Cylindrical shell displacement data

Table 5 presents the pre-deformation radius measurements obtained using DIC for the cylindrical shell specimens in different trials. The 3D DIC software directly measures the tube radius. The original radius, minimum radius before implosion is initiated (before any notable drop in hydrostatic pressure), and maximum radius percent change are provided for each trial. The measurements highlight the significant plastic deformation experienced by the specimens before failure, contributing to the variations in collapse pressure and failure characteristics.

Experiment	Original radius (cm)	Average minimum radius before implosion (cm)	Max radius percent change
Case A	5.54	0.957 ± 0.294	$62.3 \pm 11.6\%$
Case B	1.27	0.140 ± 0.139	$89.0\pm11.0\%$
Case C	2.54	1.62 ± 0.17	$36.2\pm6.8\%$

Table 5. Cylindrical shell pre-deformation gathered using DIC.

For case A, the radius change of 62.3% indicates a substantial shell deformation, leading to variations in collapse pressure and failure behavior among the trials. Similarly, case B undergoes significant deformation, with the walls almost touching before failure. The radius change of 89.0% indicates a high level of plastic deformation. In contrast, case C, the thicker shell specimen, exhibits comparatively lower deformation before failure.

These measurements highlight the influence of plastic deformation on the collapse behavior of the cylindrical shell specimens. The variations in deformation and collapse pressure among the trials can be attributed to factors such as fracture properties, plastic deformation properties, and material defects that may have been introduced during the 3D printing process. The observed pre-deformation provides insights into the complex nature of failure in these specimens and underscores the challenges of accurately predicting collapse behavior.

4.2.2. Double hull displacement data

Figure 8a illustrates the collapse process of the double hull structure. Before applying hydrostatic pressure, the structure is in its initial state. As the pressure increases, localized deformation occurs due to the presence of the gyroid structure providing structural support (0 ms). Once the critical point is reached, a crack forms at the point of maximum deformation, initiating the collapse (1 ms). The entry of water into the specimen causes significant damage to the affected region (2 ms). Unlike the shattered cylindrical shells, a significant portion of the double hull structure remains intact after the initial local failure.

In different trials, the initial failure points on the specimen vary. In **Figure 8b**, Trial 2 and Trial 3 specimens are shown before the collapse, with P0 representing the center point of the tube and P1 indicating the point of maximum deformation. In both trials, the failure initiates at the rear end of the specimen, which is not visible in the images. The presence of material imperfections is likely the primary factor contributing to the collapse of these specimens. As the hydrostatic pressure increases, these imperfections become more pronounced and lead to failure.



Figure 8. (a) Double hull structure collapse mechanism (b) Failure starting points for different experiments.

The average radius change before collapse for the double hull structure was 20.6%, with a standard deviation of 4.7%. As a result of localized failures, the specimens mostly remained intact during these trials. These observations demonstrate the influence of material imperfections and localized failure on the collapse behavior of the double hull structure. The variations in failure points and deformation patterns highlight the complex nature of collapse in these specimens and the challenges associated with predicting their behavior accurately. Interestingly, this type of implosion failure mechanism has little damage potential to its surroundings due to its low-pressure emissions.

4.3. Energy flow

Figure 9a illustrates the impulse behavior of the three single-shell tubes. The impulse values obtained from the experiments are used in Equation (8) to calculate the energy flux. The highest impulse value for each trial is selected to determine the energy flow, illustrated in **Figure 9b**.

Figure 10 presents the ratio of the maximum energy flow to the potential energy flux from Equation (6). This ratio represents the proportion of energy released through the pressure pulse. To facilitate comparison, the results from Pinto et al. have been adjusted to match the methodology described in this paper (using an elliptical area instead of the spherical area used in previous work [21]).



Figure 9. (a) Impulse behavior of the three shell tubes (b) Energy behavior in Joules of the three shell tubes.



Figure 10. Flow energy as a percentage of the potential energy of each shell tube type compared with aluminum [21] results.

The results show that the polymer shell tubes exhibit lower energy flow than conventional aluminum tubes and carbon/epoxy specimens. It also shows comparable energy emissions to the Glass/PE specimens. The lower energy emission of Glass/PE tubes was attributed to the delamination/fracture damage induced during implosion. Similarly, the urethane polymer structures had a lot of fracture damage, which is energy-consuming. The polymer tubes also exhibit greater plastic deformation before implosion occurs. Among the shell tubes, the 2.23 cm inner diameter shell (Case B) displays the lowest energy flow to the potential energy average (as a variation), primarily due to the significantly higher pre-deformation observed in this specimen.

These findings highlight the unique behavior of the polymer shell tubes compared to other materials and provide insights into their energy dissipation characteristics during collapse. The differences in energy flow indicate the distinct failure mechanisms and deformation patterns exhibited by the polymer tubes, emphasizing the importance of considering the material properties and behavior when analyzing collapse phenomena.

5. Conclusion

This experimental investigation examined the behavior of 3D-printed polymer structures under critical hydrostatic pressure conditions. These structures' failure mechanisms and energy dissipation characteristics were analyzed using high-speed photography, the Digital Image Correlation (DIC) technique, and dynamic pressure sensors. The study yielded the following key conclusions:

- Significant deformation occurs in the polymer tubes before failure, resulting in inconsistent critical collapse pressures. The variation in deformation contributes to the difficulty in accurately predicting the collapse behavior and emphasizes the importance of considering material properties and structural characteristics.
- 2) The fracture and deformation of the polymer material during implosion lead to lower energy flow emissions than traditional aluminum tubes. The unique properties of polymers result in a higher energy requirement for fracture and increased plastic deformation before implosion occurs.
- 3) The localized failure observed in double-hull structures is attributed to material imperfections. This type of implosion failure has negligible pressure signatures compared to its single hull equivalent system (Case C).

These findings provide valuable insights into the behavior of 3D-printed polymer structures under critical hydrostatic pressure. Understanding the failure mechanisms and energy dissipation characteristics is crucial for designing and engineering such structures and predicting their performance under extreme conditions.

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Data availability: The data that supports the findings of this study may be available upon request from the corresponding author. The data are not publicly available due to data control restrictions.

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Appendix

Core for double hull structure: clear all; clc;

% Define resolution for the grid (complex number to specify the number of points) res = 100i;% Define lattice parameters a = 1;b = 1;c = 1;% Calculate reciprocal lattice parameters kx = 2*pi / a;ky = 2*pi / b;kz = 2*pi / c;% Create the grid in cylindrical coordinates [r aux, phi, z] = ndgrid(linspace(0, a, imag(res)), ... linspace(0, b, imag(res)), ... linspace(0, 20*c, imag(res))); % Convert r aux range to actual radii r1 = 0.5;r2 = 0.875;r = (r2 / a) * r aux + (r1 / a) * (1 - r aux);% Define the gyroid function $Gyroid = @(x, y, z) (\cos(kx^*x).*\sin(ky^*y) + \dots$ $\cos(ky^*y).*\sin(kz^*z) + ...$ $\cos(kz^*z)$. $\sin(kx^*x)$; % Compute data for the cylindrical gyroid % r aux is x, phi * 12 is y, and z is z fun values = Gyroid(r aux, phi * 9, z); % Compute Cartesian coordinates for grid points $x = r \cdot \cos(phi * ky);$ $y = r \cdot sin(phi * ky);$ % Create the structured grid grid = struct('x', x(:), 'y', y(:), 'z', z(:), 'vol3', fun_values(:)); % Reshape the data for isosurface num points per axis = imag(res);x reshaped = reshape(x, num points per axis, num points per axis, num points per axis); y reshaped = reshape(y, num points per axis, num points per axis); z reshaped = reshape(z, num points per axis, num points per axis); fun values reshaped = reshape(fun values, num points per axis, num points per axis); % Create an isosurface

iso_value = 0;

fv = isosurface(x_reshaped, y_reshaped, z_reshaped, fun_values_reshaped, iso_value);

% Extract the vertices and faces from the isosurface data

vertices = fv.vertices; faces = fv.faces;

% Calculate colors based on the z-coordinate of vertices colors = vertices(:, 3);

% Plot the cylindrical gyroid fig = figure; patch('Faces', faces, 'Vertices', vertices, ... 'FaceVertexCData', colors, 'FaceColor', 'interp', 'EdgeColor', 'none'); xlabel('X'); ylabel('Y'); zlabel('Y'); zlabel('Z'); colormap jet; colorbar; axis equal; grid on; view(3);



Figure A1. Gyroid core coordinates (in inches).


Article

Collagen derived from a giant African snail (*Achatina achatina*) for biomedical applications

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Copyright © 2024 by author(s). Journal of Polymer Science and Engineering is published by EnPress Publisher, LLC. This work is licensed under the Creative Commons Attribution (CC BY) license. https://creativecommons.org/licenses/ by/4.0/ Abstract: Achatina achatina (AA) is a rich source of collagen due to its large size, but it is underutilized. Type I collagen was extracted from AA to serve as an alternative to existing collagen sources. The collagen was extracted at varying alkaline and temperature conditions to determine the optimal parameters that would give a high yield of acid-soluble collagen. The extracted collagen was characterised using X-ray diffraction, Fourier transform infrared (FTIR) spectrometry, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) to confirm the integrity and purity of the extracted collagen. The type of collagen was determined using sodium dodecyl sulphate-polyacrylamide gel electrophoresis. The α -1, α -2, and dimer electrophoresis bands confirmed that the collagen is type I, and the XRD data supported the findings. The highest collagen yield was obtained at 4 °C for 48 h, which decreased with increasing temperature due to the instability of the protein in acid at high temperatures. A cytotoxicity test was conducted using an Alamar blue assay. The AA collagentreated normal prostate cell line (PNT2) showed no significant difference from the untreated control cells. The high-quality type I collagen extracted from AA has the potential for biomedical and other industrial applications.

Keywords: Achatina achatina; Type I collagen; characterisation

1. Introduction

Collagen is a triple helix of three polypeptide chains of molecules, mainly glycine, proline, and hydroxyproline. It is found in the extracellular matrix (ECM) of connective tissues, including tendons, ligaments, bone, and skin, in humans and other organisms [1]. Collagen in the ECM maintains structural integrity and also helps in the transmission of cellular signals [2,3]. Collagens are mainly produced within connective tissue by fibroblasts [4]. The literature reports 28 different types of collagens, which are grouped according to their function, composition, and location in the body.

Collagen is extracted from bovine and swine for biomedical applications for a variety of reasons, including aging and accidents [5]. For example, in the area of tissue engineering and regeneration, collagen is used in the design of artificial ECM

(scaffolds) to generate new tissues for the replacement of diseased or damaged tissues and/or organs in the human body [6]. In cosmetics, collagen is used to develop skin care products [7], among others. However, most of the existing and known sources of collagen extraction are notably expensive [5,8]. Literature reports on other low-cost sources of extracting collagen. These are poultry, fish, marine snails, and other marine animals. The yield of collagen extracted from these organisms is considerably small [9]. Moreover, the pre-treatment parameters and extraction conditions of collagen vary from one organism to another, depending on the organism from which it is extracted [10].

Non-collagenous proteins are removed from organic raw materials by breaking cross-links to allow acid to penetrate and extract collagen molecules. The physical swelling of the samples indicates adequate alkaline absorption, allowing the cleavage of crosslinks between other proteins in the samples [11–13]. In the extraction of collagen, the type and concentration of reagent used are also varied depending on the organism from which the collagen is being extracted [10]. The pre-treatment time also varies from a few hours up to two days [14,15]. Such noted variation in the temperature conditions is due to the temperature of the habitat of the organism from which the collagen is being extraction temperature conditions and the respective durations for which various extractions are carried out also vary. The most preferred temperature for extracting collagen is 4 °C. However, there are also reports of collagen extraction carried out at 8 °C, 25 °C, 37 °C, and 50 °C [16].

Literature reports of the extraction of gelatin from marine snails (*Hexaplex trunculus*), which are molluscs and bear some level of structural similarity to giant African snails (*Achatina achatina*). Therefore, we extracted collagen from an onshore source, *Achatina achatina*, to validate the pre-treatment and extraction conditions. The giant African snail is rich in protein [17] and mostly regarded as a pest [18,19] in some parts of sub-Sahara African while others consume its meat as a delicacy [17]. This research seeks to use the giant African snail as a replenishable and more affordable source of collagen due to its abundance and comparatively high reproductive rate [20,21].

The snail foot muscle (meat) was removed from the snail shell, washed, minced, and pre-treated with alkaline at different molar concentrations for different time intervals, after which the collagen extraction was achieved at different temperatures. The extracted collagen was characterised using X-ray diffractometry (XRD), Fourier transform infrared (FTIR) spectrophotometry, thermal gravimetric analysis (TGA), and differential scanning calorimetry (DSC) to determine the phase purity, functional groups, and thermal stability of the extracted collagen, respectively. Also, sodium dodecyl sulphate-polyacrylamide gel electrophoresis (SDS-PAGE) was used to determine the type of collagen present, after which a cytotoxicity test was performed.

2. Materials and methods

2.1. Materials

The materials included acetic acid (99% purity), sodium hydroxide (NaOH) and butanol (C₄H₉OH) (Philip Harris Education, Cheshire, England), hydrochloric acid (HCl) (WWR International Ltd., Fontenay-sous-Bois, France), sodium chloride (NaCl), trizma-hydrochloric (trizma HCl) acid, proteases, glycerol, sodium dodecyl sulphate (SDS), Coomassie blue (Merck KGaA, Darmstadt, Germany), tris acetate EDTA (TAE) and tris borate EDTA (TBE) (Central Drug House, P, Ltd., New Delhi, India), and lysis buffer (Thermo Fisher Scientific, Waltham, Massachusetts, United States).

2.2. Pre-treatment and extraction

Achatina achatina (AA) snail was obtained from the Ashaiman local market in Ghana. The shells were removed, and the meat was washed with chilled, doubledistilled water. The foot of the snail meat was shredded into 0.5×0.5 cm² pieces using a scalpel blade and stored at 4 °C until it was ready for use. A mass of 30 mg each of the minced meat (MM) was added to four different concentrations of NaOH (0.05, 0.1, and 0.2 M, respectively) at a ratio of 1:20 (w/v). The mixture was stirred at 4 °C using a Stuart Magnetic Heat Stirrer-UC152 (Cole-Palmer, Staffordshire, United Kingdom) for 6, 12, 24, and 48 h. The mixture was maintained at 4 °C in a 1500-mL beaker. The ice was crushed into the beaker using an Ice Crusher IC20 (Waring Commercial, USA) to create an ice bath. The NaOH was replaced every 3 h, and the MM was continuously observed for sufficient physical swelling. The MM was sieved with a double cheesecloth and rinsed thoroughly with chilled (4 °C) double distilled water to remove NaOH and obtain a pH of 7.3. The pH was monitored with a Mettler Toledo pH metre (N.V. Mettler-Toledo, Zaventem, Belgium), and the respective level of observable swelling of the MM within the given duration was noted.

Fats and pigments were removed from the pre-treated minced foot muscle (PMM) using 10% butanol at 4 °C under continuous stirring in the ratio 1:20 (w/v) [16,22]. The butanol was replaced every 2 h for 6 h. A double cheesecloth was used to sieve the PMM, which was then thoroughly rinsed with chilled double-distilled water to remove the butanol and obtain a defatted and decoloured minced foot muscle (DMM) of the PMM. The DMM was weighed with a Denver Instrument electronic balance (Cole-Palmer, Court Vernon Hills, IL, USA) to obtain the wet weight.

The extraction of collagen from DMM was carried out using 0.5 M acetic acid at a ratio of 1:20% (w/v). Four sets of extraction were carried out at varying temperatures (4, 8, 16, and 32 °C) for four different durations (12, 24, 36, and 48 h), respectively, in 250-ml beakers [23,24]. For 4 °C collagen extraction, 20 g of the DMM was used for 12, 24, 36, and 48 h. An ice bath was created using a 1500-mL beaker, and a 250mL beaker containing the DMM and 0.5 M acetic acid was placed into it. For 8 and 16 °C, the temperature was controlled in the ice bath. For 32 °C, DMM in the beaker was placed on a Stuart Magnetic Heat Stirrer (UC152) (Cole-Palmer, Staffordshire, United Kingdom) and stirred for all durations (12, 24, 36, and 48 h). The DMM was sieved using double cheesecloth, and the filtrate was collected after the respective durations. The filtrate in each case was precipitated with 2.5 M NaCl in the presence of trizma-HCl and centrifuged at 10,000 rpm for 10 min. The residue was collected in the form of collagen concentrate (CC). The CC was dialyzed against 0.1 M acetic acid using a cellophane dialysis tube for 24 h and dialyzed again against double-distilled water for 36 h. The dialysis was carried out at 4 °C [25,26] and the dialyzed CC was lyophilized to obtain collagen powder using a vacuum freeze dryer (Laconco Corporation, Kansas City, U.S.A.). The collagen powder (CP) in each case was weighed to obtain the dry mass. The wet yield of the collagen in Equation (1) was obtained by dividing the weight of the collagen obtained after freeze-drying by the wet weight and multiplying the result by 100.

$$Yield = \frac{(\text{weight of collagen obtained})}{(\text{wet weight})} \times 100 \tag{1}$$

2.3. Characterization techniques

X-ray diffractometry (XRD, PANalytical Empyrean, Netherlands) was used to determine the phase purity of the extracted collagen. The XRD pattern of the collagen was obtained using CuK α radiation of wavelength, $\lambda = 1.5406$ Å. CP were scanned from 5° to 100° with a scan step size of 0.05°. Fourier transform infrared spectrometry (FTIR) data was recorded with a Nicolet MAGNA-IR 750 spectrometer (Nicolet Instrument Co., Madison, WI, USA). The analysis was done from 450 to 4000 cm^{-1} and the data was analysed. The CP thermal profile was analysed using a thermogravimetric analyzer and differential scanning calorimetry (TGA-DSC, Q600 SDT, TA instrument). The thermal profiles were obtained at a temperature range of 0 to 700 °C at a heating rate of 10 °C/min under nitrogen gas at a flow rate of 100 cm³/min. The type of the CP was determined using sodium dodecyl sulphate polyacrylamide gel electrophoresis (SDS-PAGE), and the Laemmli method was used with a little modification [27]. This modification entailed mixing the extracted collagen with Tris-HCl buffer containing 2% mercaptoethanol and 0.016% bromophenol blue to reach a final collagen concentration of 1 mg/mL and boiling the mixture for 5 min at 95 °C. Each boiled EC (15 μ L) was injected into the stacking gel and electrophoresed under a current of 12 mA. The gel was stained for 45 min in the presence of a 0.25% Coomassie Brilliant Blue R-250 solution and destined for a 5% methanol/7.5% acetic acid solution until the bands were clear. Two gel densities, 16% and 12%, were used for the electrophoresis. The device used was a BIO-RAD mini-PROTEAN Tetra System (Bio-Rad Laboratories, Dubai, U.E.A.) [28,29].

2.4. Cell viability assay (Alamar Blue assay)

The effect of the extracted collagen on cell viability and proliferation was determined using an Alamar Blue assay. The normal prostate cell line PNT2 (Sigma Aldrich) was seeded at 10⁴ cells/well into a 96-well plate and incubated for 24 h. AA collagen was then administered to the cells in varying concentrations for 24, 48, and 72 h. After time elapsed, Alamar Blue[®] reagent was added to each well, including the negative controls and blanks, and incubated for 4 h at 37 °C away from light. Using the VarioskanTM LUX multimode microplate reader, fluorescence at an excitation wavelength of 560 nm and an emission wavelength of 590 nm was obtained. The cell viability was calculated using the formula

% Cell viability = $\frac{\text{Relative fluorescence units of tested sample}}{\text{Relative fluorescence units of untreated cell control}} \times 100$ (2)

2.5. Statistical analysis

A two-way ANOVA Sidak's multiple comparisons was used to determine the

statistical significance, which was determined at a confidence level of p < 0.05. All the data presented were averages (mean) with their standard deviations as errors.

3. Results

3.1. Pre-treatment

A 0.05 M NaOH lower concentration used led to low swelling of the MM. However, the MM treated with 0.1 M NaOH for 6 h swelled moderately, and for 12 h, the swelling was highly significant. From 12 to 24 h, the physical structure of the MM started to overs well and become gel-like. A 0.2 M NaOH concentration led to the swelling of MM early on in the experiment, but the sample started to physically dissolve gradually into the solution, thereby making the solution cloudier from around 12 to 24 h.

3.2. Extraction of collagen

The highest quantity of collagen weighed was obtained at 4 °C for 48 h followed by 8 °C for 48 h, and the least quantity obtained was at 32 °C for 12 h. At 36 and 48 h, no significant quantity of collagen was obtained at 32 °C, as most of the MM started to gelatinize in the acetic acid, turning it into jelly. Collagen extracted at 8 and 16 h for various durations resulted in comparatively lower yields. **Figure 1** shows the average yield of collagen extracted at the respective temperatures.



Figure 1. Graphical representations of the collagen yield extracted at 4, 8, 16, and 32 °C.

3.3. XRD results

Figure 2 shows the XRD pattern of CP extracted from *Achatina achatina*, AA. The patterns possess three main peaks occurring at 2θ /degrees (8.3°, 21.8°, and 32.1°) and correspond to XRD patterns of standard collagen [30]. The first peak that occurs at 8.3° is the highest, and it indicates the distance between the molecular chains with the triple helical amino acid. This peak is, however, not visible in the pattern of collagen extracted at 32 °C. The peak of the CP, occurring at 21.8°, is broader than the other two peaks and corresponds to the amorphous scattering that resulted from disorganised components of the collagen fibres. The smallest peak on the pattern

occurring at 32.1° is due to the typical triple-helix structure occurring in collagen [31]. A similar peak is also seen in the XRD spectrum of collagen extracted from fish [32].



Figure 2. XRD spectrum of collagen extracted from Achatina achatina.

3.4. FTIR results

Figure 3 shows the FTIR spectrum of CP extracted from AA at 4, 8, 16, and 32 °C. The spectra show bands identical to those of the golden apple snail (*Pomacea canaliculata*) [33]. The CP extracted from the four main temperatures showed characteristic patterns in regions of amide A, amide I, amide II, and amide III. The amide A bands occurring around $3600-2300 \text{ cm}^{-1}$ occur as a result of N–H stretching, while the amide I bands, which are formed at $1656-1644 \text{ cm}^{-1}$ are due to C=O stretching. The bands at $1560-1335 \text{ cm}^{-1}$ are amide II, occurring because of N–H bending and C-N stretching vibrations. The amide III bands at $1240-670 \text{ cm}^{-1}$ resulted from an intricate system associated with CH₂ residual groups from glycine and proline [34].



Figure 3. FTIR spectrum of collagen extracted from *Achatina achatina* at various temperatures.

3.5. TGA-DSC

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to determine the thermal stability of the extracted collagen. **Figure 4** depicts a DSC plot of heat flow (blue) versus temperature, with the CP beginning to receive heat (endothermic reaction) at 31.3 and rising to 229.5 to achieve a stable heat flow up to 700. The derivative heat flow (red) shows a corresponding chemical component that was given out from the heat reaction. At 51.25, the collagen started denaturing and losing structure water at 112.1.



Figure 4. Shows the TGA-DSC profile of the derived collagen.

3.6. SDS-PAGE

CP with a gel [density of 12%] had its α -1 and α -2 chains occurring at 110 and 80 kDa, respectively, while the β -dimer occurred at 200 kDa. Other peptides also occurred in the CP in strong and weak bands. These bands occurred around molecular weights of 160, 44, 43, and 25 kDa, as shown in **Figure 5**. According to the literature [35], Sheep Trail Tendon, a type I collagen, has three signature bands on SDS-PAGE: the α -1 chain, the α -2 chain, and the β dimer. The bands are present in the CP extracted from AA [36,37]. The intensity of the α -1 chain band of the collagen extracted appears almost twice as heavy as what appears in the α -2 chain. The chains occur at ~115 and ~110 kD for the α -1 chains, and ~129 and ~125 kDa for the α -2 chains.



Figure 5. SDS-PAGE pattern of collagen extracted from Achatina achatina.

3.7. Cytotoxicity

The effect of AA collagen on the PNT2 cell line viability was determined using an Alamar Blue assay for 24, 48, and 72 h and showed no cytotoxicity in vitro. The plot in **Figure 6** shows various extract variations in Alamar blue with no significant toxic effect on PNT2. On high extract variation, a slightly significant difference was observed at 24 and 72 h.



Figure 6. The effects of *Achatina achatina* foot muscle collagen on the normal prostate cell line PNT2 viability using the Alamar blue assay.

There was no significant effect (no *) of AA collagen at most concentrations on the cell line. A significant proliferation was observed only at the highest concentration. * = significant, **** = highly significant, CTRL = untreated control.

4. Discussion

Achatina achatina has been identified through studies to serve as both a host and an immediate vector for some parasitic species [38]. The link between Achatina achatina and parasites occurs through feeding and direct contact with the source of these parasites [39]. Works done [40] in different local government areas in Nigeria on the parasitic profile of five species of terrestrial Achatina snails indicated that parasitic prevalences with different species were different for the respective localities from which the snail samples were obtained, and the prevalence of parasites of Achatina achatina is dependent on the proximity of the parasite source. Achatina achatina has a comparatively high reproduction rate and is often reared in sub-Saharan Africa for consumption as food. Achatina achatina reared domestically will be less susceptible to parasite infestation than those captured from the wild.

NaOH was preferred for MM pre-treatment because HCl pre-treatment at 0.1 M results in an extremely low collagen yield. A higher concentration also produced a physical breakdown of the MM structure in the reagent. The pre-treatment was carried out to remove non-collagenous proteins from the MM, making it easy for the extraction of collagen [13,16]. Three factors that mainly influenced the pre-treatment of the MM were the concentration of NaOH, the duration for the MM to swell, and the temperature at which the swelling occurs. However, excessive swelling of the MM leads to the cleaving of cross-link chains in the non-collagenous proteins and peptide bonds in the collagen. The cleaving is temperature, concentration, and time-dependent. Comparatively long exposure to NaOH concentration at 4 °C led to the dissolution of MM under preferential conditions of 0.1 M NaOH for a duration of 12 h. The poor swelling observed in the MM pre-treated in 0.05 M NaOH is a result of the low concentration of the reagent used since a low temperature, less concentrated

NaOH, and relatively short duration of treatment also lead to poorly cleaved crosslinks, poor swelling of the MM, and subsequently a low collagen yield [13,16]. A concentration that is higher than 0.05 M and a suitable duration and temperature would also aid in the considerable swelling of the AA MM. The 0.1 M NaOH pre-treatment produced a significant swelling within the first 12 h of continuous stirring at 4 °C. Other concentrations of the alkaline used to pre-treat the MM were therefore not appropriate because they either led to over-swelling or insufficient swelling. The appropriate swelling directly translates into collagen yield. The pre-treatment process used in this study contrasts with the pre-treatment process for the Hexaplex trunculus [36]. In their study, the sample was soaked in 0.02 M NaOH for 60 min at room temperature. In a study conducted [41], the collagen source was from the skin of the red snapper and was pre-treated with 0.1 NaOH for 12 h. Here, the study reported, after carrying out a quantitative analysis with Bradford and bovine serum albumin (BSA) tests, that the concentration of non-collagen protein was impacted. NaOH was also used by Blanco et al. [42] for the pre-treatment of their sample, and further multivariate analysis of their sample showed that temperatures around 4 °C and an alkaline concentration of 0.1 M led to a high yield of collagen during extraction. In their study, Blanco et al. [42], however, gave a range of 0.05 M to 0.1 M and temperatures from 4 to 20 °C for alkaline pre-treatment, depending on the source of collagen being extracted. The fat content in snail muscle is generally low [43]. Therefore, the procedure was geared more towards the removal of pigments, as Xu et al. [22] used H_2O_2 to decolor their sample, using a sample-to-solution ratio of 1:20 at 4 °C for 24 h, and suggested that the decoloring and degreasing process enhanced the purity level of the collagen extracted. Studies carried out by Kaewdang et al. [37] also used butanol to remove fats from yellowfin tuna samples before proceeding with the extraction process.

The extraction at 4 °C had the highest yield of around 1.44%, and the acid concentration and duration of the extraction were consistent with what was reported by Kaewdang et al. [37]. They also determined the yield of acid-soluble collagen extracted using the dry weight of yellowfin tuna to be 1.07%. The extraction of collagen from *Sheep tail tendon* carried out acid extraction and reported a yield of 9.7% which was obtained from 1.651 g of the dry weight of the tendon [44], while acid soluble collagen extracted from the mesoglea of jellyfish gave 0.12% of the wet weight [45]. A study that extracted acid-soluble collagen from Indonesian local goat skin estimated a yield of 7.35%, which was obtained after 48 h of treatment with acid [46]. The yield of collagen extracted from three different types of fish, namely common carp, red snapper, and milkfish was estimated to be between 0.8%–2.1% [45]. The differences in yields can be attributed to the different collagen structures in different organisms, the varying crosslinking of collagen [13].

A study conducted by Matmaroh et al. [47] reported the wet weight of collagen extracted from the cartilage of brown-banded bamboo sharks to be 1.27% [37].

Collagen extracted from various sources using the acid extraction method provides a fair idea with regards to the amount (yield) and abundant information about the nature (characteristics) of collagen that is present in a particular source. However, this method is not employed as a quantitative extraction method for collagen because the literature provides evidence that the entirety of collagen present in a particular source cannot be extracted using only the acid extraction method. Other methods need to be used, or employed to complement this method, to obtain full quantitative information about collagen from a given source [27,48]. Acid extraction gives a low yield, while other extraction methods give higher yields. Examples of extraction methods that provide full quantitative information about collagen extracted from various sources include enzymatic and ultrasonic extraction methods.

The phase composition, functional groups, and thermal stability data from the XRD, FTIR, and TGA-DSC revealed that the extracted CP from the AA is collagen, specifically type I collagen, as indicated by the results from the SDS-PAGE. The most common types of collagens in the human body are types I, II, III, IV, and V. Type I collagen is the most abundant type (about 90%) in the human body and is found in the scar tissue, bone, tendons, ligaments, and the skin in the arteries to support smooth, firm, and strong body tissues [49,50]. The results show that the extracted collagen has no significant toxic effect on the PNT2 cell line. Most cell lines are cultured in collagen-coated vessels, and they have been found to be a suitable modification for culture vessels [51]. Compared to the untreated control, collagen increased proliferation of the cell line at the highest concentration, which corresponds to results found in the literature [52].

5. Conclusion

Collagen was extracted from the foot muscle of the giant African snail (Achatina achatina) using the acid-soluble extraction method. The giant African snail serves as a viable source of collagen for biomedical and other applications. The optimum pretreatment was a 0.1 M NaOH solution for 12 h at 4 °C under constant stirring. The other pretreatment conditions lead to the cleaving of cross-links, which swells the sample too fast and thus damages it. The extraction was done using 0.5 M acetic acid at 4 °C for 48 h, and the highest yield of the extraction was 1.44%. The phase purity, functional groups, and thermal stability of the extracted collagen were characterised diffractometry transforms by X-ray (XRD), Fourier infrared (FTIR) spectrophotometry, thermal gravimetric analysis (TGA), and differential scanning calorimetry (DSC), respectively, whereas sodium dodecyl sulphate-polyacrylamide gel electrophoresis (SDS-PAGE) determined that the collagen was type I. The collagen had no significant effect on the normal prostate cell line, PNT2.

Author contributions: Conceptualization, BOA and DP; methodology, DP, SKK and BSK; software, BOA; validation, BOA, DP, SKK and BSK; formal analysis, BOA, DP and BSK; investigation, DP and BSK; resources, BOA, BM, VAA; data curation, BOA; writing—original draft preparation, BOA, DP, LP and BSK; writing—review and editing, BOA, EJF and EKT; visualization, BOA; supervision, BOA, LP and EKT; project administration, BOA; funding acquisition, BOA, DP and EKT. All authors have read and agreed to the published version of the manuscript.

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Low-cost ternary composite photocatalysts consisting of TiO₂, kaolinite and cement for an efficient organic waste decontamination in water

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Abstract: The present study demonstrates the fabrication of heterogeneous ternary composite photocatalysts consisting of TiO2, kaolinite, and cement (TKCe), which is essential to overcome the practical barriers that are inherent to currently available photocatalysts. TKCe is prepared via a cost-effective method, which involves mechanical compression and thermal activation as major fabrication steps. The clay-cement ratio primarily determines TKCe mechanical strength and photocatalytic efficiency, where TKCe with the optimum clay-cement ratio, which is 1:1, results in a uniform matrix with fewer surface defects. The composites that have a clay-cement ratio below or above the optimum ratio account for comparatively low mechanical strength and photocatalytic activity due to inhomogeneous surfaces with more defects, including particle agglomeration and cracks. The TKCe mechanical strength comes mainly from clay-TiO₂ interactions and TiO₂-cement interactions. TiO₂-cement interactions result in CaTiO₃ formation, which significantly increases matrix interactions; however, the maximum composite performance is observed at the optimum titanate level; anything above or below this level deteriorates composite performance. Over 90% degradation rates are characteristic of all TKCe, which follow pseudo-first-order kinetics in methylene blue decontamination. The highest rate constant is observed with TKCe 1-1, which is 1.57 h^{-1} and is the highest among all the binary composite photocatalysts that were fabricated previously. The TKCe 1-1 accounts for the highest mechanical strength, which is 6.97 MPa, while the lowest is observed with TKCe 3-1, indicating that the clay-cement ratio has a direct relation to composite strength. TKCe is a potential photocatalyst that can be obtained in variable sizes and shapes, complying with real industrial wastewater treatment requirements.

Keywords: TiO₂; kaolinite; cement; composite photocatalyst; industrial wastewater treatment

1. Introduction

Rapid industrialization, agrochemical consumption, and limited disposal space have all contributed to the accumulation of organic waste in water bodies, which is responsible for significant environmental pollution [1]. Traditional wastewater treatment methods (alkaline hydrolysis) are less viable due to drawbacks such as high alkaline consumption, low treatment efficiency, and environmental pollution caused primarily by alkaline disposal [1]. The photo-catalyzed advanced oxidation method outperforms conventional treatment methods for organic waste decontamination in water. Photocatalytic degradation is a well-known advanced oxidation process due to its high efficiency and environmental friendliness when compared to other advanced oxidation processes, including the Photo-Fenton technique, which requires additional reagents [2]. TiO_2 is a well-known semiconductor photocatalyst that can decontaminate a wide range of organics and microorganisms while producing inorganic species that are naturally harmless. This is mainly achieved via advanced oxidation, where organic waste decontamination is initiated by electron-hole pair generation under sunlight/UV irradiation, which is often used to mineralize a variety of organic pollutants in wastewater. Because of its high photocatalytic activity/stability, chemical/biological inertness, and low cost, TiO₂ has been widely used.

Photocatalysts can be utilized as a powder, membrane (immobilized on the surface of a suitable substrate), or composite material. TiO₂ powder is less effective as a photocatalyst alone because of its small specific surface area, low adsorption ability, photocatalyst agglomeration, and post-separation issues [1]. A supportive substrate that has a large surface area and a high adsorption capacity should be used to immobilize TiO_2 powder, which is an essential step to overcome these limitations. Photocatalyst immobilization can be accomplished on a variety of substrates. Powder/pellets, soft/thin, and rigid substrates are the three major classes that have often been used [3]. Activated carbon, clay, and volcanic ash are the best powder/pellet substrates for immobilizing photocatalysts. The soft/thin substrates fall within a broad range, including alumina, polyvinylidene difluoride, glass filters, cellulose fibers, and sponges [4-7]. TiO₂ can be immobilized on a substrate using one of two methods, including binders' incorporation or physically anchoring TiO₂ particles on a substrate [1]. Poor TiO_2 immobilization is caused by the use of organic/inorganic binders, including polyester resin, polyethylene, polypropylene, polyethylene glycol, and silicon adhesive [8–10]. Because the binders are typically organic in nature, they are highly susceptible to self-degradation (by TiO₂) when exposed to sunlight/UV light. TiO₂ particles, on the other hand, can submerge and agglomerate within the binder, resulting in decreased photocatalytic activity. The coating preparation is also imperfect and complex, resulting in a number of difficulties in controlling the uniformity and durability.

Apart from binder-based TiO₂ immobilization, clay is a better supportive substrate than many other types, making it a promising raw material for hybrid photocatalysts. TiO₂-clay photocatalysts differ in terms of both preparation and morphology [1]. The sol-gel process, which involves growing and anchoring nanosized TiO₂ particles on the clay surface, has been widely used to produce claybased photocatalysts. Despite the basic characteristics of the sol-gel process, preparation methods involve a diverse set of techniques and raw materials, resulting in a highly diversified synthesis process. Titanium butoxide, TiCl₄, TiOSO₄, and titanium tetra-isopropoxide are common titanium precursors used in the sol-gel process [11–20]. The various techniques that are often used in sol-gel synthesis, including hetero-coagulation, hydrothermal treatment, calcination, ultrasonic agitation, supercritical drying, and intercalation, make the preparation significantly diverse [11–20]. The well-known clay types that are frequently used in TiO_2 -based hybrid photocatalysts are kaolinite, hectorite, rectorite, palygorskite, montmorillonite, vermiculite, and allophane [11-16]. However, because these clay-based products are primarily in powder/particle/aggregate forms, commercial applications are limited due to constraints associated with the implementation of large-scale reactors [11–20]. High manufacturing costs, post-separation issues, short-term durability, and installation difficulties, particularly in large industrial treatment tanks, are major limitations of existing TiO_2 -clay-based photocatalysts [1]. The latter highlights the importance of hybrid photocatalysts that can be easily integrated with commercial wastewater treatment units.

Existing techniques are limited to laboratory scale or prototypes, and their commercial applications are imperfect. Due to the low stability/durability of the photocatalysts and engineering constraints that are related to reactor design, they fail to meet industrial waste disposal standards. From an industrial standpoint, low-cost, long-lasting photocatalysts that can be easily integrated into commercial wastewater treatment units are essential. Furthermore, having a readily available photocatalyst that can be easily synthesized on a large scale is more important. The authors of the present study recently developed a novel composite preparation method based on mechanical compression and heat treatment, resulting in a stable binder-free graphite and clay composite electrode [21–25]. Following a similar technique, authors recently developed efficient binary photocatalysts that are composed of raw materials, including TiO₂ and clay (kaolinite/MMT), resulting in improved photocatalytic activity and mechanical strength [26,27]. However, authors also found that ternary composites that are related to graphite-clay composite electrodes outperform the binary electrodes, revealing that such ternary composites result in matrix enhancements [23,24]. Based on a similar hypothesis, the current study demonstrated the fabrication of a ternary TiO₂-clay-cement composite photocatalyst (TKCe) for the first time. The TKCP offers numerous advantages, including high photocatalytic activity, mechanical stability, mouldability, chemical-free surface regeneration, and long shelf life, resulting in an effective photocatalyst that can bridge the gap between lab scale and commercial products.

2. Material and methods

2.1. Materials

Nippon Aerosil Co. Ltd., Japan, provided TiO_2 (Degussa P25 powder) with 56 nm particles. Sigma-Aldrich Ltd., USA, provided the raw minerals, including kaolinite (>99%, 1.2 μ m particles) and methylene blue (>99%). The cement (>98%, average particle size 1.5 μ m) was obtained from the Department of Geology at the University of Peradeniya in Sri Lanka.

2.2. TKCe block fabrication

To prepare composite suspensions, a fixed amount of TiO_2 (80%) was mixed in distilled water with various clay and cement (total 20%) ratios and then continuously stirred at 1000 rpm using an overhead agitator (IKA, Germany) for 3 h. TKCe 1-3, TKCe 1-1, and TKCe 3-1 were prepared in 25 g by combining kaolinite and cement in the following ratios: 1:3, 1:1, and 3:1. TKCe blocks with dimensions of 4 cm × 4 cm × 0.8 cm were fabricated by applying a 125,000 N vertical ram force for 30 min to a partially dried composite material that was uniformly packed inside a specially designed steel mould. TKCe blocks were then calcined for 2 h at 600 °C in a high-temperature furnace (Nebertherm), resulting in a TiO₂-kaolinite-cement heterogeneous photocatalyst (**Figure 1**). The TKCe photocatalytic activity was

determined using modified blocks with an untreated top surface. To accomplish this, the TKCe blocks' side and bottom surfaces were uniformly painted, except the top surface, which serves as the active exterior, facilitating photocatalytic disintegration.



Figure 1. TKCe blocks prepared with different kaolinite and cement ratios.

2.3. TKCe block characterization

To characterize the TKCe blocks and raw materials, an X-ray diffractometer (Rigaku Ultima IV, Japan) equipped with a copper target X-ray generator ($\lambda_{CuK\alpha l}$ -0.154056 nm), a secondary beam curved graphite monochromator, and a D/tex Ultra detector were used. An X-ray beam generated under standard tube conditions, including a 40 kV tube voltage and a current of 30 mA, was used to analyze the powdered samples. The samples were scanned between 15° and 80° at 2° min⁻¹ to obtain diffractograms. The X-ray beam geometry was carefully optimized, with the divergence, scattering, and receiving slits all fine-tuned by 2/3°, 2/3°, and 0.45 mm, respectively. The Rietveld refinement on XRD profiles was performed using an advanced WPPF (whole powder pattern fitting) component that was integrated with the PDXL X-ray powder diffraction software. The refined diffractograms were analyzed with the PDXL integrated X-ray powder diffraction software, which was linked to the ICDD (International Centre for Diffraction Data) database. The composition analysis was achieved via the Relative Intensity Ratio (RIR) module that is available with powder diffraction software. The crystallite size estimation related to both anatase and rutile was carried out accurately by analyzing refined diffractograms using the Halder-Wagner model available with PDXL software.

The flexural strength was calculated by substituting the force at rupture of a TKCe strip that was measured using a universal testing machine (Testometric, UK). To accomplish this, the TKCe strip was carefully placed horizontally on the Testometric universal testing machine's supporting stage, and the force at the fracture point was measured upon collision with a load that was vertically lowered at a rate of 2 mm min^{-1} .

$$F_f = (FL / 2bd^2) \tag{1}$$

where σ_f , F, L, b, and d stand for flexural strength, force at the fracture point, supporting span length (2.00 cm), TKCe strip width (1.3 cm), and TKCe strip depth (0.8 cm), respectively [28].

The TKCe series was examined using a scanning electron microscope (ZEISS EVO LS15, Germany), which produced well-resolved images at a constant accelerating voltage of 20 kV. The FT-IR spectra were collected in an attenuation total reflection module (ATR) with a diamond puck (sample compartment) using a Bruker Tensor 27 spectrometer (Germany). The samples were scanned between 600 and 4000 cm⁻¹ at a resolution of 4 cm⁻¹, yielding a transmittance spectrum from which the vibration frequencies corresponding to IR bands were obtained. TGA/DSC analysis

(TA Instruments SDTQ600, USA) was used to determine the thermal profile and stability of kaolinite.

2.4. TKCe photocatalytic activity determination

Methylene blue degradation in the presence of TKCe was measured using a UVvisible spectrophotometer (UV-1800 Shimadzu, Japan, at $\lambda_{max} = 664$ nm). Each TKCe block was placed in a crystallization flask (150 mL), followed by 100 mL of methylene blue solution (1.56×10^{-5} mol dm⁻³). The reaction vessels were exposed to sunlight for 2.5 h, with absorbance measurements taken every thirty minutes (**Figure 2**). The dye concentration (C_{MB}) after each consecutive irradiation was determined carefully using a calibration plot that was preliminarily constructed with known methylene blue concentrations. The calibration plot was constructed using the UVProbe software, which is interfaced with the UV-Vis spectrophotometer. The irradiated methylene blue concentration was determined directly from the previously installed calibration plot. The entire experiment was conducted in direct sunlight, with an average irradiation of 400 W m⁻² (intensity). After determining the methylene blue concentration in relation to the control sample, the percentage degradation (D_R) and the pseudo-first-order rate constant (k) were calculated using the following relationships [29].

$$D_R = [(C_0 - C_{MB}) / C_0] \times 100\%$$
(2)

$$lnC_{MB} = -kt + lnC_0 \tag{3}$$

where C_0 (1.56 × 10⁻⁵ mol dm⁻³), C_{MB} , and t denote the initial concentration of methylene blue, concentration at time t, and time, respectively.



Figure 2. TKCe photocatalytic activity determination under natural sunlight.

3. Results and discussion

According to previous studies, the TiO_2 amount that can effectively be incorporated into a binary TiO_2 -clay-based composite photocatalyst is found to be 60%, greater than which the composite stability is drastically reduced, causing multiple surface cracks [26]. In the present study, the TiO_2 percentage that can be incorporated into the composite photocatalysts is greater than the previously fabricated binary composite photocatalyst. This is mainly due to cement incorporation as an additional mineral phase, which results in high TiO_2 loading capacity without deteriorating the composite mechanical strength. The clay itself can only increase the TiO_2 loading capacity up to some extent, but the clay-cement combination makes the composite architectural framework quite stronger, which results in stable ternary composite photocatalysts. The high TiO_2 loading capacity is an advantage that makes TiO_2 surface concentration very high, resulting in a high photocatalytic activity. This is a good indication for the advancement of solid-state composite engineering, which highlights the incorporation of minerals together, including clay and cement, that can significantly improve the photocatalysts' properties and performance.

The clay firing is a major step that led to a strong photocatalyst matrix, which mainly resulted from the dehydroxylation, integrating the clay mineral with other composite components. Among the many clay types available, kaolinite was chosen in the current study due to its low cost, high abundance, and platy sheet-like structure, which allow easy processing of the material at high compressibility [26]. **Figure 3** exhibits a TGA/DTA thermogram, which reveals that kaolinite typically undergoing dehydroxylation at 500 °C, resulting in a rigid clay matrix. Therefore, the firing temperature was set at 600 °C to ensure complete dehydroxylation. It also reveals that spinal crystallization takes place at 1000 °C, followed by mullite and crystobalite formation, which typically occurs above 1100 °C.



Figure 3. TGA-DSC curves related to kaolinite.

The TKCe photocatalytic activity and the mechanical strength are both important factors that determine the industrial-level feasibility. TKCe 1-1 accounts for the highest photocatalytic activity and mechanical strength, revealing that the 1:1 kaolinite to cement ratio resulted in an effective composite matrix (**Table 1**). Over 98% degradation rate (D_R) is observed with TKCe 1-1, which is the highest among all binary composite photocatalysts that are fabricated previously and raw TiO₂ [26,27]. The authors' previous study observed a very low D_R (72.5%) and pseudo-first-order rate constant (k = 0.28 h⁻¹) related to raw TiO₂ when used in powder form, which is

mainly due to the ultra-fine particle nature of TiO_2 , which results in a colloidal suspension where the tiny particles are dispersed throughout the entire solution [26]. This is caused by poor sunlight penetration and scattering through the suspension, which results in ineffective sample irradiation [26]. TKCe 1-1 also accounts for the highest pseudo-first-order rate constant (k), which is higher than binary composites, and many photocatalysts test against methylene blue, including TiO₂ nanotrees (0.346 h^{-1}), TiO₂ nanobelts (0.026 h^{-1}), multilayer TiO₂ coating on HDPE (0.27–0.43 h^{-1}), and GO-ZnO-Cu nanocomposite (0.246 h^{-1}) [26,30–32] (see Table 1 and Figure 4). The plots (C vs. time and 1/C vs. time) both account for a nonlinear relationship, which confirms the deviation from the zero and the second-order reaction kinetics (Figure 4). TKCe 1-3 and TKCe 3-1 both accounted for a higher %degradation and k compared to previously developed binary TiO₂-kaolinite (TKCP) and TiO₂-kaolinite-MMT composite (TKMCP) photocatalysts. These binary composites have shown a less than 95% degradation rate in comparison to TKCe, which exhibits a $D_R > 98\%$ (Table 1). TKCe 1–1 rate constant, which is 1.57 h^{-1} , is quite similar to that of TKMCP (1.55 h^{-1}) and is greater than that of TKCP (0.58 h^{-1}) [26,27].



Figure 4. TKCe kinetic studies related to methylene blue degradation (a) $\ln C_{MB}$ vs. time (C_{MB} -Methylene blue concentration); (b) C_{MB} vs. time; (c) $1/C_{MB}$ vs. time.

Composite	D _R (%)	k (h ⁻¹)	σf (MPa)	
TKCe 1-3	91.4	0.94	6.44	
TKCe 1-1	98.4	1.57	6.97	
TKCe 3-1	95.8	1.22	5.67	

Table 1. TKCe flexural strength, DR, and pseudo first-order rate constant.

The mechanical strength of TKCe follows a similar trend as photocatalytic activity, with the highest observed with TKCe 1-1 (6.97 MPa), implying that the optimal cement percentage is critical for a better composite matrix (Table 1). The much lower or higher cement percentages result in comparatively deteriorated properties and performance of TKCe. In that sense, the highest D_R , σ_f , and k were observed in TKCe 1-1, which is considered the composite with the optimum kaolinite to cement ratio; the composites that deviate from the optimum ratio account for comparatively low D_R , σ_i , and k (see **Table 1**). Among the rest of the TKCe composites, the composite with more cement accounts for a stronger matrix than the one with the lowest cement fraction, which is TKCe 3-1. In contrast, the composite with a high clay fraction results in better photocatalytic activity than the one with a low clay fraction, which is TKCe 1-3 (Table 1). TKCe 1-1 mechanical strength is greater than that of binary composites, including TKCP (3.55 MPa) and TKMCP (5.83 MPa), that were fabricated previously [26,27]. Therefore, an optimum clay-cement combination simultaneously results in high photocatalytic activity and mechanical strength, which is observed in TKCe 1-1, revealing that proper raw material combinations can have a significant impact on composite properties.

The improved photocatalytic activity and mechanical strength related to TKCe 1-1 can be explained by considering four factors, including anatase to rutile ratio, crystallite size, calcium titanate percentage, and morphology. The anatase to rutile ratio in each composite is determined using an X-ray diffraction analysis, and the results are given in **Table 2**. The authors of the current article revealed that the same TiO₂ powder underwent a measurable phase transition at low temperatures, resulting in a composition change of approximately 25% at 650 °C [33]. Such phase transitions are prevented in binary composites that are fabricated using clay. This is because clay eventually acts as a phase transformation barrier and predominantly undergoes dehydroxylation, preventing anatase from rutile transformation [26,27]. In the present study, kaolinite also acts as a barrier for anatase to rutile conversion, preventing the phase transformation, which results in a marginal change in rutile percentage (**Table 2**). Kaolinite not only serves as a phase transition barrier but also provides an architectural framework for strengthening the composite matrix.

Composite	Compositi	on (%)	D _{cryst} (nm)	D _{cryst} (nm)		
	Anatase	Rutile	CaTiO ₃	CaCO ₃	Anatase	Rutile
TKCe 3-1	81.6	14.5	2.9	1.1	16.7	21.1
TKCe 1-1	78.9	14.6	4.5	2.0	17.0	24.0
TKCe 1-3	68.2	13.8	12.2	5.8	11.3	22.1

Table 2. TKCe composition and crystallite size (anatase and rutile).

Dcryst - Crystallite size.

TKCe composites are negative for characteristic kaolinite XRD peaks, indicating that dehydroxylation occurred completely, resulting in metakaolinite, which is amorphous in nature (please see **Figures 5** and **6**). The FT-IR spectra related to TKCe provide clear evidence for the amorphization of kaolinite, which is confirmed by the absence of characteristic kaolinite IR bands between 1250–600 cm⁻¹ (in-plane Si-O stretching vibration at 1114 and 1007 cm⁻¹, OH vibration of inner and outer Al-OH bonds at 912 cm⁻¹, Si-O-Al stretching vibration at 788 and 748 cm⁻¹) and emergence of an amorphous SiO₂ peak at 1070 cm⁻¹ (**Figure 7**). This anti-symmetric Si-O stretching band is unique to metakaolinite, and the absence of bands in composites at 3689 and 3619 cm⁻¹, which correspond to the stretching vibration of hydroxyl, ensures complete dehydroxylation [34].



Figure 5. X-ray diffractograms of raw materials at room temperature (a) TiO₂; (b) kaolinite; (c) cement.



Figure 6. X-ray diffractograms of TKCe (a) TKCe 1-3; (b) TKCe 3-1; (c) TKCe 1-1.



Figure 7. FT-IR spectra of raw materials and composites.

However, the situation is somewhat different when incorporating cement as a ternary phase that consumes anatase to produce calcium titanate (CaTiO₃) instead of undergoing phase transformation, resulting in a considerable reduction in anatase percentage (**Table 2**). This is clearly reflected by the anatase and rutile percentages that are observed in composites and raw TiO₂, exhibiting a significant reduction in anatase percentage unlike rutile, which is quite similar in magnitude (**Table 2**). The calcium titanate formation typically occurs at high temperatures, which are above 900 °C [35]. In the present study, CaTiO₃ emerged at 600 °C, revealing that such formation is likely induced by a highly compressed matrix, which is responsible for low-temperature titanate formation. This is a good indication of mechanical activation that mainly results from the highly compressed matrix, which triggers the thermal conversion of minerals within the composite even at low to moderate temperatures. CaTiO₃ formation begins with the thermal decomposition of calcite, which results in CaO (calcite from cement, see **Figure 5**). However, calcite decomposition is a high-temperature process that typically occurs above 700 °C [36].

In the present study, mechanical compression is implemented as a fabrication technique that leads to a highly compressed material matrix, which eventually experiences very high matrix stress. The composite heating also accounts for the further increase in matrix stress where the composite matrix tries to regain stability via either thermal decomposition or matrix distortion. The thermal decomposition is more effective than the matrix deformation, where matrix stability is likely achieved via material loss, resulting in a low matrix stress [36,37]. This explains why calcite is decomposed even at temperatures that are well below the typical decomposition temperature. The CO₂ removal during calcite decomposition is likely to reduce the matrix stress by increasing the internal space, which is mainly caused by material loss [36]. Therefore, unlike non-compressed materials, materials that are under high compression strain can easily undergo thermal conversions even at low to moderate temperatures.

The reaction between CaO and TiO₂ produced orthorhombic CaTiO₃, which is the stable phase below 1200 °C; this is more pronounced in TKCe, which contains more cement (**Figure 6** and **Table 2**). During CaTiO₃ formation, the reaction is most likely propagated in the following sequence [35,36].

$$At \ 600 \ ^{\circ}\text{C}(2 \ h)$$

$$CaCO_{3(s)} \xrightarrow{\Delta} CaO_{(s)} + CO_{2(g)}$$

$$CaO_{(s)} + TiO_{2(s)}(anatase) \xrightarrow{\Delta} CaTiO_{3(s)}$$

The TKCe X-ray diffractograms provide clear evidence for titanate formation and the amorphization of certain cement phases that are available at room temperature. The absence of characteristic cement phases in TKCe, including calcium silicate and aluminates, is a better indication for cement amorphization, which is also reflected in TKCe FT-IR spectra (**Figure 7**). Raw cement exhibits the characteristic vibrational modes at 871, 1083, and 1425 cm⁻¹, which are corresponded to CO_3^{2-} stretching (outof-plane), Si-O-Si stretching, and CO_3^{2-} stretching (asymmetric) modes, respectively (**Figure 7**) [38]. These modes are mainly caused by primary constituents in cement, including CaCO₃ and calcium silicate (**Figure 6**). A low, intense, broad titanate FT-IR vibration band can be seen in all composites (1455 cm⁻¹), but it is more pronounced in TKCe 1-3, which has the highest titanate percentage (**Figure 7**) [39]. The most distinctive cement IR bands, which correspond to calcite CO_3^{2-} vibrations, and CaTiO₃ fingerprint bands are masked by a broad Ti-O-Ti stretching vibration band that typically appears between 900 and 600 cm⁻¹ (see **Figure 7**) [26,27].

In TiO₂-clay binary composites that are recently developed, the dehydroxylation typically results in Ti-O-Si and Al-O-Ti bond formation that ensures a strong composite matrix [26,27]. However, in the present study, CaTiO₃ is directly involved in the material architectural framework, increasing the mechanical strength in addition to the Ti-O-Si and Al-O-Ti formations that are reflected by TKCe's very high flexural strength (**Tables 1** and **2**). However, CaTiO₃ in excess can negatively affect the matrix uniformity, which results in the lowest flexural strength and photocatalytic activity that are clearly noticeable in TKCe 1-3 (**Tables 1** and **2**). This indicates that an optimum CaTiO₃ level is important to have a uniform composite matrix with improved properties. Numerous studies have revealed that anatase itself is a relatively poor photocatalyst, but anatase and rutile mixtures are better photocatalysts with a wide range of applications [40]. The optimum titanate level also accounts for the proper anatase to rutile ratio, which is quite essential to obtaining an efficient photocatalyst with high activity, which is clearly reflected in TKCe 1-1 (**Table 1**).

Anatase crystallite size and photocatalytic activity have a direct relationshp that is well noticeable in TKCe 1-3, which has the smallest anatase crystallites, resulting in the lowest catalytic activity. The more cement in TKCe can produce excess CaTiO₃, during the production of which anatase crystallites are greatly consumed upon the reaction with CaO that likely damages the crystallites, resulting in small anatase crystallites. A small anatase crystallite size is a strong indication of the matrix defects that are typically generated during titanate formation. The titanate formation via anatase incorporation is confirmed by a significant decrease in anatase size and a marginal change in rutile crystallite size, indicating that rutile is less important in titanate formation, most likely due to structural disparity and low abundance (see **Table 2**). However, up to a certain level, the titanate formation is positively affected by TKCe properties and performance, resulting in improved mechanical strength and catalytic activity. This is in better agreement with the high DR observed with TKCe 1-1, which has the largest anatase crystallites (**Table 2**). However, this is somewhat opposite when the titanate percentage increases above the optimum level, where the excess CaTiO₃ is likely to damage the composite matrix, destabilizing the anatase lattice, which results in small crystallites.

The TKCe composition-matrix correlations are clearly reflected in SEM micrographs, which reveal the structural alterations that occurred under mechanical and heat treatment. The SEM images reveal that a uniform composite surface is more pronounced in TKCe 1-1 compared to both TKCe 1-3 and TKCe 3-1, which have somewhat less uniform surfaces. In contrast to binary TiO₂-clay composite photocatalysts, cement incorporation induces raw material amalgamation, resulting in small spherical composite particles that are packed together, resulting in a compressed composite matrix (**Figure 8**).



Figure 8. SEM images exhibiting TKCe surface (a) TKCe 3-1; (b) TKCe 1-1; and (c) TKCe 1-3. The particle agglomeration and surface defects are more pronounced in both TKCe 1-3 and TKCe 3-1 compared to TKCe 1-1. TKCe 1-1 exhibits a uniform matrix with fewer surface defects, facilitating a highly compressed surface for effective photocatalytic activity.

The nature of the composite particles, including shape and size, is important in determining the composite's compressibility under hydraulic pressing. However, it is obvious that the size of such composite particles is determined by their composition, particularly the ratio of kaolinite to cement.

The TKCe 1-1 SEM micrograph clearly exhibits fewer surface defects and a wellorganized, uniform composite matrix, which explains the improved mechanical strength and photocatalytic activity of TKCe 1-1. In contrast to TKCe 1-1, both TKCe 1-3 and TKCe 3-1 have partially compressed matrixes with more surface defects, including particle agglomerates and cracks. This explains why mechanical compression and heat treatment are more effective when the optimal matrix composition is used, resulting in a uniform matrix with low surface defects. It is important to have composite particles that can undergo effective mechanical compression (high compressibility), resulting in a highly compressed matrix. In contrast, both TKCe 1-3 and TKCe 3-1 resulted in poor compressibility, leaving more surface defects, including particle agglomerates and cracks. Therefore, the deviation from optimum raw material ratios accounted for a less uniform composite matrix with comparatively higher surface defects, which are mostly particle agglomerations, forming as a result of low compressibility. The latter accounts for partially compressed composite particles that are still noticeable in both TKCe 1-3 and TKCe 3-1 SEM micrographs.

The TiO₂ immobilization technique described here is very useful for large-scale commercial photocatalyst fabrication, with a focus on high-capacity wastewater treatment plants that are powered by renewable sunlight or UV irradiation. The simple chemical-free fabrication process makes commercial-level TKCe production more feasible, requiring minimal supervision and machinery and yielding a high output. TKCe has several advantages, including easy fabrication, low cost, free of hazardous chemicals, high production capacity with minimal machinery/supervision, non-self-degradability, easy disposal, easy installation in pilot-scale reactors, compatibility with both batch and flow reactors, and environmental and user-friendliness.

4. Conclusions

An industrially feasible TiO₂-kaolinite-cement composite photocatalyst is prepared using inexpensive raw materials via a straightforward method. The fabrication route is intended to avoid additional reagents, making the process more economical, faster, and environmentally friendly (green technology). The TKCe can be manufactured in a variety of shapes and sizes to match the reactor dimensions, reducing engineering constraints when upgrading the lab-scale product to pilot-scale reactors. The physical properties of TKCe are primarily determined by the claycement ratio, where the optimum ratio, which is 1:1, exhibits the highest photocatalytic activity and flexural strength. This is mainly due to a uniform TKCe matrix with fewer surface defects, which resulted from its high compressibility. Composites with claycement ratios below or above the optimum ratio exhibit lower mechanical strength and photocatalytic activity due to an inhomogeneous surface with more defects, such as particle agglomeration and cracks. TKCe mechanical strength is primarily derived from clay-TiO₂ interactions and TiO₂-cement interactions. TiO₂-cement combination results in CaTiO₃, which significantly improves matrix interactions; however, the best composite performance is achieved at the optimal titanate level; anything above or below this level negatively affects composite performance. The TiO₂ immobilization technique that is described here is very useful for large-scale commercial photocatalyst fabrication, with a focus on high-capacity wastewater treatment plants powered by renewable sunlight or UV irradiation. The simple chemical-free fabrication process enables commercial-scale TKCe production with minimal supervision and machinery, resulting in a high production capacity.

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An analysis of temperature control for electromagnetic induction heating of CFRP based on sparrow search algorithm

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Copyright © 2024 by author(s). Journal of Polymer Science and Engineering is published by EnPress Publisher, LLC. This work is licensed under the Creative Commons Attribution (CC BY) license. https://creativecommons.org/licenses/ by/4.0/ **Abstract:** Accurate temperature control during the induction heating process of carbon fiber reinforced polymer (CFRP) is crucial for the curing effect of the material. This paper first builds a finite element model of induction heating, which combines the actual fiber structure and resin matrix, and systematically analyzes the heating mechanism and temperature field distribution of CFRP during the heating process. Based on the temperature distribution and variation observed in the material heating process, a PID control method optimized by the sparrow search algorithm is proposed, which effectively reduces the temperature overshoot and improves the response speed. The experiment verifies the effectiveness of the algorithm in controlling the temperature of the CFRP plate during the induction heating process. This study provides an effective control strategy and research method to improve the accuracy of temperature control in the induction heating process of CFRP, which helps to improve the results in this field.

Keywords: carbon fiber; temperature control; temperature field distribution

1. Introduction

The superior physical and chemical properties of CFRP make it increasingly widely used in daily life, especially in the fields of aerospace, automobiles, and energy, where the application scope of CFRP is constantly expanding and its consumption is increasing year by year. This puts forward higher standards for the heating rate, energy utilization, and pollutant emission of CFRP in the curing process. For this purpose, scholars have proposed many innovative curing and molding methods, such as infrared thermal radiation, resistance heating, ultraviolet light, induction heating, etc. Among them, induction heating technology has many advantages, such as high efficiency, energy savings, a small footprint, non-contact, etc. Combining it with the curing and molding of CFRP can significantly improve the heating rate of the material, reduce manufacturing costs, and reduce the intrusion of external impurities. However, the arrangement of carbon fibers inside the material directly affects the heating effect and the distribution of the temperature field during the heating process, and the distribution of the temperature field directly affects the molding quality of the composite material. Therefore, it is necessary to explore the spatiotemporal variation of the temperature field generated by CFRP with different fiber arrangement modes in the induction heating process.

The application of induction heating technology in CFRP curing and molding is increasing, which has attracted the high attention of scholars in the industry, and they have conducted in-depth research on the heating principle and temperature distribution of CFRP in the induction heating process. Fink et al. [1] discussed that the condition for forming an eddy current in CFRP during induction heating is that there is an effective closed circuit between the fibers. For this purpose, carbon fiber bundles need to be cross-woven in other ways to form the laminated structure of CFRP. Yarlagadda et al. [2] analyzed the three overlapping contact modes of fiber bundles during weaving, which correspond to three heating modes of resistance heating, capacitance heating, and resistive-capacitive heating, respectively, affecting the heat generation and heating rate at the nodes. Kim et al. [3]. studied the method to determine the dominant heating mechanism of carbon fiber induction heating under different weaving/overlapping modes, and established a numerical analysis model of CFRP induction heating including three heating mechanisms. Lundström et al. [4]. established a finite element simulation model of CFRP induction heating, and studied the influence of carbon fiber volume fraction, laying mode, and fiber orientation on the temperature field distribution of CFRP induction heating.

When induction heating CFRP, the heating process, temperature regulation speed, and temperature value accuracy of the temperature field directly determine the molding quality of CFRP, so the control algorithm is very important for the production of induction heating CFRP. The performance of the controller is affected by the parameter adjustments [5,6]. In order to find the suitable controller parameter set, there are many methods proposed, such as the Ziegler-Nichols method [7], the ant colony optimization algorithm [8,9], and the neural network method [10]. However, the model of the induction heating system changes with the environment, induction coil, and workpiece. Therefore, the neural network lacks a pre-trained data set. Some studies [5,11,12] show that a fuzzy PID controller that combines the structure of a PID controller and the expert knowledge of FIS, has excellent control performance. Soyguder et al. [13] designed an adaptive fuzzy PID controller, which adjusts the PID parameters online according to the temperature error and error change rate of the HVAC system, and achieves the minimum setting time and zero steady-state error. Chang et al. [14] deeply analyzed all the quantization factors and developed a selftuning module that used finite element analysis to simulate the control ability of a selftuning fuzzy logic controller and conducted experiments on the induction heating system, verifying the effectiveness of the method. Chowdhury et al. [15] proposed a fuzzy self-tuning PID controller for a preheating recovery system, tested the set point tracking and disturbance suppression ability in steady-state and transient heat cases, and found that the fuzzy self-tuning PID controller greatly reduced the calculation time and significantly improved the control performance. Wang et al. [16] proposed a temperature control method of induction heating system based on a variable domain fuzzy controller, and the simulation results showed the effectiveness and superiority of the temperature control system. These studies prove the effectiveness of fuzzy PID in temperature control systems, but for induction heating CFRP, which is a fast heating system, the accurate mathematical model and robustness of the temperature control system are very important.

In order to avoid falling into the local optimum and ensure control accuracy and optimization performance, this paper proposes a PID control algorithm based on sparrow search (SSA-PID) and compares SSA-PID with particle swarm optimization PID algorithm (PSO-PID) and PID control. The conclusion is that SSA-PID has a smaller overshoot and faster adjustment time than the other two algorithms.

2. CFRP induction heating principle and analysis

Alternating magnetic field generates an induced electric field E(V/m) in carbon fiber structure, which can be expressed in the form of frequency as follows:

$$= -j\omega A \tag{1}$$

In the equation, $j^2 = -1$, $\omega = 2 * \pi f(rad/s)$ is the angular frequency, and f(Hz) is the magnetic field frequency.

The total current sum generated in the fiber structure consists of conduction current $J_i = \sigma E$ and displacement current $J_d = j\omega D$:

$$J_t = J_t + J_d = \sigma E + j\omega D \tag{2}$$

The eddy current in the fiber structure and the Joule heat generated by its own resistance are the heating heat sources of CFRP, where the heat source $Q_{rh,i}$ (W/m³) can be expressed as follows:

$$Q_{rh,i} = J_t \cdot E \tag{3}$$

When the power supply is activated, the heat generated by the induced current in the fiber bundle is transferred to the surrounding fiber bundle, resin, and ambient air. The heat conduction of the fiber part can be expressed by Fourier's law of heat conduction:

$$\rho C_p \frac{\partial T}{\partial t} + \nabla \cdot (-k \nabla T) = Q \tag{4}$$

In the equation, $\rho(\text{Kg/m}^3)$ is the density of the material, $C_p(J/\text{kg}\cdot\text{K})$ is the specific heat capacity of the material, $k(W/m\cdot\text{K})$ is the thermal conductivity of the material, and $Q(W/m^3)$ is the heat emitted by the heat source.

As epoxy resin is a phase change material, it releases heat during the curing process from liquid to solid. The heat conduction equation when the phase change occurs in the resin is as follows:

$$oC_p \mu \cdot \nabla T + \nabla \cdot (-k\nabla T) = Q \tag{5}$$

In the equation, $\mu(m/s)$ is the flow velocity of the resin when heated.

The resin gradually releases latent heat L(J/Kg) during the process of gradually changing from the liquid phase to the solid phase during heating. Since we only consider the heat release of the material during heating, in order to make it easier to calculate, we assume that the phase change temperature of the resin occurs between $T_{pc} - \Delta T/2$ and $T_{pc} + \Delta T/2$. In the interval of phase change reaction, the material is modeled by a smooth function; θ represents the fraction of phase in the transition process, from $\theta = 0$ when the temperature is $T_{pc} - \Delta T/2$, to $\theta = 1$ when the temperature reaches $T_{pc} + \Delta T/2$. In the equation, ρ is the density of the material, and H is the specific enthalpy, which will be expressed as follows:

$$C_p = H + C_L(T) = \frac{1}{\rho} (\theta \rho_1 C_{p1} + (1 - \theta) \rho_2 C_{p2}) + L \frac{\partial \alpha}{\partial T}$$
(6)

The latent heat distribution C_L can be expressed as follows:

$$C_L = L \frac{\partial \alpha}{\partial T} \tag{7}$$

The total heat released per unit volume during phase change is equal to the latent heat:

$$\int_{T_{pc}-\frac{\Delta T}{2}}^{T_{pc}+\frac{\Delta T}{2}} C_L(T) dT = L \int_{T_{pc}-\frac{\Delta T}{2}}^{T_{pc}+\frac{\Delta T}{2}} \frac{d\alpha}{dT} dT = L$$
(8)

In the induction heating process, when the temperature of the object is higher than the external environment, the heated object exchanges heat with the surrounding environment after heating, and the exchange with the air is the most important, so the convective heat flux of the air needs to be considered:

$$-k\nabla T = h(T_{amb} - T) \tag{9}$$

In the equation, $h(W/m^2K)$ is the heat transfer coefficient determined by the boundary type and surface properties, T_{amb} is the external air temperature, and T is the surface temperature of the heated material.

When the temperature gradually rises, the thermal radiation generated by the material needs to be considered, and the diffuse surface uniformly releases radiation intensity in all directions. The surface radiation intensity of the material is:

$$-k\nabla T = \varepsilon\gamma (T_{amb}^4 - T^4) \tag{10}$$

In the equation, ε is the emissivity of the material surface, and γ is the Boltzmann constant.

This study uses COMSOL as the simulation platform and establishes a finite element analysis model with the plain weave structure of CFRP as the geometric model, as shown in **Figure 1**. The size of CFRP in the model is 60 mm × 60 mm × 5 mm, the induction coil size is $\varphi 30 \times 20$ mm, the number of turns is 50, the current size is 16A, the frequency size is 13 kHz, the external environment temperature is 20 °C, and the distance between the coil and the carbon fiber surface is 2.5 mm. The parameters assigned to each material in the geometric model are shown in **Table 1**, and the parameters are obtained from the CFRP manufacturers and the COMSOL material library.



Figure 1. Finite element analysis model of plain weave structure CFRP.

	Air	Carbon fiber bundle	Resin	Coils
Thermal Conductivity (W/(m·K))	N/A	30	0.2	N/A
Heat Capacity (J/(kg·K))	N/A	1000	1000	N/A
Density (kg/m ³)	N/A	1500	1200	8960
Electrical Conductivity (S/m)	0	$6.4 \times E^4$	$1 \times E^{-2}$	$6 \times E^7$
Relative Permittivity	1	_	3.2	1
Relative Permeability	1	1	1	1

 Table 1. Simulation parameters.

From the simulation results in **Figure 2**, it can be seen that when induction heating CFRP, the temperature rise of the material mainly occurs in the heat source area near the outer circle of the induction coil in the initial stage and presents a ring-shaped temperature field distribution. With the increase in heating time, the heat transfers along the fiber bundle direction, making the overall temperature of the material rise. The temperature field distribution also gradually changes from ring-shaped to cross-shaped, spreading along the X-axis and Y-axis directions. The center area of the material heats up the fastest and finally reaches the same temperature as the heat source area, and the value is the largest.



Figure 2. Change rules of temperature field of CFRP induction heating.

3. Induction heating temperature control

3.1. Sparrow search algorithm principle

In the induction heating process, the mixing mode of the resin matrix and fiber structure in carbon fiber composite material, as well as the interlayer heat conduction process, will cause a difference between the temperature value recorded by the infrared sensor and the actual internal temperature value of the material. In addition, the inherent lag of the temperature control system makes it more challenging to control the temperature of CFRP during heating. This is especially important in the curing and molding process of CFRP because a high temperature value will affect the molding quality of the material. Therefore, reducing overshoot in the material heating process is essential for improving the quality of material curing and molding. In order to realize the quantifiable optimization of control factors and improve control accuracy, this study adopts a sparrow search algorithm to optimize the PID control method. The schematic principle of the control method is shown in **Figure 4**.



Figure 3. Schematic diagram of PID algorithm optimized by the sparrow search algorithm.



Figure 4. PID control algorithm flow chart optimized by the sparrow search algorithm.

First, calculate the current fitness value of each sparrow and store the individual and position information in the local extremum. Traverse the individual extremum, select the optimal individual information, and store it in the global extremum. In order to ensure that the parameters have good selectivity, the fitness function defined in this paper is as follows:

$$f(x) = \sum_{i=1}^{d} x_i^2$$
(11)

where x represents the position of the sparrow, and d represents the dimension. Then, update the weight and learning factor, and modify the critical value of the crossover probability. The crossover probability here is not a fixed value but is adjusted according to the size of the population difference to avoid falling into the local optimum in the later stage of evolution. By increasing the crossover probability in the later stage, we can effectively escape from the local optimum. In addition, the equation for updating the weight is as follows (12), the equation for updating the learning factor is as follows (13 and 14), and the equation for modifying the adaptive crossover probability is as follows (15).

$$w = w_{max} - \frac{w_{max} - w_{min}}{iter_{max}} \cdot iter$$
(12)

$$c_1 = c_{1max} - \frac{c_{1max} - c_{1min}}{iter_{max}} \cdot iter$$
(13)

$$c_2 = c_{2max} - \frac{c_{2max} - c_{2min}}{iter_{max}} \cdot iter$$
(14)

$$p_c = 0.5 + \frac{0.5}{1 + \exp\left(-\frac{f_g - f_w}{f_g + f_w + \varepsilon}\right)}$$
(15)

where, w represents the inertia weight, w_{max} and w_{min} respectively represent the maximum and minimum values of the inertia weight, *iter* represents the current iteration number, *iter_{max}* epresents the maximum iteration number, c_1 and c_2 respectively represent the first and second learning factors, c_{1max} and c_{1min} respectively represent the initial and minimum values of the first learning factor, c_{2max} and c_{2min} respectively represent the initial and minimum values of the first learning factor, c_{2max} and c_{2min} respectively represent the crossover probability, f_g and f_w respectively represent the global optimal fitness value and the global worst fitness value, ε represents a small constant, used to avoid the denominator being zero.

Then, update the speed and position of the sparrows according to Equations (16) and (17). Next, calculate the new fitness value matrix of the individuals in the population, and prepare for the subsequent genetic algorithm. If the sparrows are out of bounds, randomly generate new positions and speeds within the specified range, and replace the current positions and speeds.

$$v_{i,j}^{t+1} = w \cdot v_{i,j}^{t} + c_1 \cdot R_1 \cdot \left(x_{p,j}^t - x_{i,j}^t\right) + c_2 \cdot R_2 \cdot \left(x_{g,j}^t - x_{i,j}^t\right)$$
(16)
$$x_{i,j}^{t+1} = x_{i,j}^t + v_{i,j}^{t+1}$$
(17)

where, $v_{i,j}^t$ represents the speed of the *i*-th sparrow in the *j*-th dimension, $v_{i,j}^{t+1}$ represents the updated speed of the *i*-th sparrow in the *j*-th dimension, $x_{i,j}^t$ represents the position of the *i*-th sparrow in the *j*-th dimension, $x_{i,j}^{t+1}$ represents the updated position of the *i*-th sparrow in the *j*-th dimension, $x_{p,j}^t$ represents the position of the *o*ptimal explorer in the *j*-th dimension, $x_{g,j}^t$ represents the position of the global optimum in the *j*-th dimension, R_1 and R_2 respectively represent the uniform random numbers in (0, 1].

In addition, a danger warning mechanism is introduced. When there are predators around, the sparrows will change their positions to avoid being preyed upon. The position update equation for the danger warning is as follows:

$$x_{i,j}^{t+1} = \begin{cases} x_{best,j}^{t} + N(0,1) \cdot |x_{i,j}^{t} - x_{best,j}^{t}| & \text{if } f_{i}^{t} > f_{g}^{t} \\ x_{i,j}^{t} + K \cdot \left(\frac{|x_{i,j}^{t} - x_{worst,j}^{t}|}{f_{i}^{t} - f_{w}^{t} + \varepsilon}\right) & \text{if } f_{i}^{t} = f_{g}^{t} \end{cases}$$
(18)

where, $x_{i,j}^t$ represents the position of the *i*-th sparrow in the *j*-th dimension, $x_{best,j}^t$ represents the position of the best sparrow in the *j*-th dimension, $x_{worst,j}^t$ represents the position of the worst sparrow in the *j*-th dimension, f_i^t represents the fitness value of the i-th sparrow, f_g^t represents the global optimal fitness value, f_w^t represents the global worst fitness value, N(0,1) represents a standard normal distribution random number, *K* represents a random number in [-1,1], ε represents a small constant, used to avoid the denominator being zero.

Finally, repeat the above steps until the stopping condition is met, which is usually reaching the maximum number of iterations or reaching the preset target value.
Output the position and fitness of the best sparrow as the optimal solution or approximate optimal solution of the optimization problem.

3.2. Induction heating temperature control analysis

According to prior knowledge, the mathematical model of the CFRP induction heating system can be expressed as a first-order inertia system with a lag link, and its equation is as follows:

$$G(s) = \frac{K}{Ts+1} \cdot e^{-Ls} \tag{19}$$

where K represents the inertia gain, T represents the inertia time constant, and L represents the lag time.

This experiment is based on open-loop induction heating for data collection. The temperature value is collected every 0.5 seconds, and the total heating time is 2000 seconds. A genetic algorithm is used to identify and fit the parameters. The final transfer function equation for the system is as follows:

$$G(s) = \frac{195.78}{221.1s+1} \cdot e^{-11.82s}$$
(20)

In order to study the accuracy and anti-interference ability of SSA-PID control in the temperature control of CFRP induction heating, this paper uses MATLAB/Simulink as the simulation platform and establishes the control model of the induction heating CFRP temperature control system. In the same simulation environment, PID, the PSO-PID algorithm, and SSA-PID are compared and analyzed. The Simulink model is shown in **Figure 5**, where line 1 represents PID control and line 2 represents PSO-PID and SSA-PID, respectively.



Figure 5. Simulation of induction heating temperature control simulink.

Figure 6 shows the fitness value and parameter change curve obtained by the simulation model of the PID temperature control method optimized by the sparrow search algorithm. It can be seen from the figure that with the increase in iteration times, the proportion, integral, and differential coefficients are gradually adjusted and finally stabilized, indicating that the sparrow search algorithm has good adaptability and anti-interference characteristics in the CFRP induction heating control process. In addition, the PID parameters will be automatically adjusted with the change in temperature conditions.



Figure 6. Change curve of proportional, integral, and differential coefficients.

As shown in **Figure 7**, the comparison of the three control algorithms for the CFRP induction heating system shows that all three control algorithms eventually achieved stable control. The traditional PID control system reached a steady state in 142.5 s, the PSO-PID control system reached a steady state in 99 s, and the SSA-PID control system reached a steady state in 91.5 s. Compared with the traditional PID control, the PSO-PID control system and the SSA-PID control system both have faster response speeds and smaller overshoots. By comparing the PSO-PID and SSA-PID control system, it can be seen that the SSA-PID control system is superior to the PSO-PID control system, mainly manifested in the SSA-PID control system has a faster response speed and a smaller overshoot. Under the fact that the SSA-PID control method, the temperature rise time, overshoot, adjustment time, and steady-state error are minimized. This indicates that this control method has better dynamic performance than the traditional control method, effectively improving the material forming quality.



Figure 7. Adaptive response of three control methods.

4. Conclusion

In order to improve the temperature control accuracy and reduce the errors caused by the heating lag of carbon fiber cloth and the inherent delay of the temperature control system, this paper uses COMSOL as the platform, performs temperature field analysis and calculation on the induction heating CFRP temperature control system, collects the temperature output data from the initial state to the steady state of the induction heating system, and uses a genetic algorithm to identify the system mathematical model of the induction heating CFRP system. Matlab is used to simulate and verify the temperature control model, and the simulation results of the PID, PSO-PID, and SSA-PID algorithms are compared and analyzed. It is observed that the SSA-PID controller has good performance, obtaining the minimum overshoot, the shortest rise time, and the minimum adjustment time. Compared with the traditional PID control method, SSA-PID shows significantly improved stability and accuracy, which also indicates that the SSA-PID established in this study can more effectively adjust the heating curve in the CFRP heating process.

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Assessing the rheological properties of bio modified asphalt cement

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Copyright © 2024 by author(s). Journal of Polymer Science and Engineering is published by EnPress Publisher, LLC. This work is licensed under the Creative Commons Attribution (CC BY) license. https://creativecommons.org/licenses/ by/4.0/ Abstract: The production of asphalt cement binder in Iraq is conducted through the distillation of crude oil. The byproduct of such distillation is asphalt cement, which does not practice any further processing. Further processing of the binder is considered vital to controlling its physical properties and chemical composition. The implementation of biomodifiers before using such asphalt cement binder for paving work is a sound practice to enhance its sustainability and reserve the required rheological properties. In the present study, the asphalt cement binder was modified by the implementation of extender oil (used diesel engine oil) and scrap tire rubber. The aim of this work is to improve and provide a sustainable and proper rheological quality of the binder for paving work. Various percentages of scrap tire rubber and extender oil have been tried to optimize the modifiers that can exhibit a suitable control on the required rheological properties of the asphalt binder, such as the stiffness modulus, its temperature susceptibility in terms of penetration index, and penetration viscosity number, and the temperature of the equivalent stiffness of the binder. The stiffness of asphalt cement binder was digested in hot, moderate, and cold environments. It was observed that the implementation of extender oil was able to reduce the penetration index (PI) by 36.3%, 54.5%, and 27.2% when 15%, 10%, and 5% of extender oil by weight of the mixture were added, respectively, to the control binder. The addition of scrap tire rubber to the binder-oil mixture was able to reduce the PI by up to 10% of the rubber content and exhibited further control over the temperature susceptibility of the binder. It can be revealed that the extender oil increases the negative values of penetration viscosity number (PVN), while the scrap tire rubber can improve the PVN of the binder. When a high percentage of extender oil (15%) is implemented, the stiffness of the binder declines by 50%, 90%, and 75% when the testing temperature changes from 4 to 25, and 60 °C, respectively. It was concluded that the inclusion of 15% scrap tire rubber and 15% extender oil in the asphalt cement binder produced by Qayarah oil refinery is recommended to provide a sustainable binder for pavement, control its temperature susceptibility, and provide a binder that is less susceptible to pavement distress.

Keywords: extender oil; scrap rubber; asphalt cement; rheological properties; sustainability; stiffness

1. Introduction

The feasibility of using high-density polyethylene (HDPE) waste as an asphalt binder modifier was evaluated by Mainieri et al. [1]. It was revealed that the waste HDPE could increase the binder's stiffness and slightly improve its ductility and elasticity. It was concluded that using a waste HDPE-modified binder is recommended for improving resistance to moisture-induced damage and adhesion. Sarsam [2] assessed the possibility of implementing extender oil (used oil) and scrap tire rubber to improve the physical qualities of the asphalt cement. It was revealed that a combination of 15% scrap rubber and 10% extender oil provided a suitable

control on the softening point, ductility, penetration, and viscosity of the binder. However, the stiffness of the asphalt concrete mixture provides a suitable resistance to deformation in hot, moderate, and cold environments. It was concluded that the implication of such a combination of additives in asphalt cement can create a sustainable green binder for pavement. Al-Harbi [3] investigated the influence of implementing crumb rubber on the physical properties of asphalt binder. It was concluded that 12% of crumb rubber has the best content and exhibits higher fatigue resistance, lower rutting depth, and higher stability as compared with the control asphalt mixtures. Sarsam [4] studied the impact of polymer-based additives on the quality of asphalt binder using the surface-free energy concept. It was revealed that crumb rubber can provide higher surface free energy and contact angle as compared with the control binder when the sessile drop technique is implemented, regardless of the additive content. Lyu et al. [5] assessed the implications of extender oil (bio-oil made from biomass waste) and scrap tire rubber to create bio-modified rubberized asphalt for roadway paving construction. It was revealed that this technique can promote a clean and sustainable manufacturing process when turning two waste streams (rubber and biomass waste) into a product that supports resource conservation and sustainability. Nanjegowda and Biligiri [6] used scrap tire rubber to develop the modified asphalt-rush green paving mixture, which is considered superior to conventional asphalt-rubber mixtures. The modified asphalt concrete mixture was verified under the stiffness modulus test. It was revealed that the developed mixture exhibits an insignificant rate of change in viscosity with increasing temperatures; however, the rubber particles can provide the additional resilience required to endure the mix performance for the entire design life. The rheological properties and adhesion characteristics of modified asphalt cement binder were investigated by He et al. [7]. The modification was conducted using various crumb rubber powder contents and foamed binder. The temperature sensitivity and the viscoelastic characteristics of each asphalt binder sample were studied. The results showed that it was difficult to foam successfully when the rubber powder content was higher than 15%. Nassar et al. [8] investigated eco-friendly alternative asphalt binders for pavement construction. Green bio-additives were prepared using waste cooking oil and waste polystyrene and styrene-butadiene rubber and mixed with asphalt binder to prepare a green alternative binder. The physical properties of the modified binder, including softening point, penetration index, penetration temperature susceptibility, and penetration, were investigated. Mashaan et al. [9] assessed the impact of waste polyethylene terephthalate plastic on paving asphalt binder. Test results revealed that waste plastic can improve aging and rutting resistance. It was concluded that the application of plastic waste on pavements can reduce costs, conserve natural resources, and improve sustainability despite environmental impact. Pasetto et al. [10] stated that synthetic binders may be implemented in place of conventional and sustainable binders. A rheological study was conducted to characterize such materials. It was revealed that using non-linear data, the functions of temperature and strain rate can be modeled to evaluate the rheological response of the modified binders, which can exhibit complex behaviors. Wang et al. [11] investigated the possibility of using waste polyethylene as an additive to the asphalt cement binder. A positive impact could be noticed by such an

additive on the rheological properties of asphalt binder. It was noted that the use of plastic modifiers leads to an overall higher softening point and complex shear modulus. It was stated that uneven dispersion of plastic material at high temperatures could exhibit scatter in the data. The modified binder, neat rubber, and complex modified binder were visually identified based on different rheological behaviors. Sarsam [12] assessed the changes in the aging index of asphalt cement binder after modification with polymeric additives such as polyethylene and crumb rubber. The aging index was evaluated through various physical testing procedures. It was revealed that the aging index declined after the addition of crumb rubber. However, the aging index increases after implementing polyethylene into the asphalt binder. It was stated that the implication of crumb rubber in the asphalt binder is beneficial from the point of view of resistance to oxidative aging.

The aim of the present assessment is to evaluate, improve, and provide a sustainable and proper rheological quality of the binder for paving work by enhancing the rheological properties of bio-modified asphalt cement. Asphalt cement binder will be digested with various percentages of extender oil and scrap tire rubber. The variations in the rheological properties of the modified asphalt cement binder will be evaluated.

2. Materials properties and testing methods

2.1. Scrap tire rubber

The scrap tire rubber in powder form was obtained from the Diwaniya tire plant, south of Baghdad. The specific gravity of the powder is 0.421 gram/cm³. The grain size distribution of the rubber powder is demonstrated in **Figure 1**.



Figure 1. Grain size distribution of the rubber powder.

2.2. Extender oil (used oil)

The implemented extender oil was obtained from a diesel truck that used oil after a 1500 km run; the saybolt furol viscosity of the oil is 56 s at 60 °C.

2.3. Asphalt cement binder

The asphalt cement binder was obtained from Qayarah oil refinery, north of Baghdad, its softening point is 44 °C while the penetration value is 48. The chemical

composition of the binder consists of 16.5% nitrogen base, 40% asphaltenes, 30% acidifies, and 13.5% paraffin. All of the testing procedures have been conducted according to ASTM [13].

2.4. Preparation of modified binder mixture

The preparation of the modified binder mixture was conducted using the wet process technique. The control asphalt cement binder was heated to 150 °C, and the pre-determined scrap tire rubber percentage was added with continuous stirring. Five percentages of rubber have been implemented: 3%, 5%, 7%, 10%, and 15% by weight of the asphalt binder. The blend was maintained at 150 °C for 30 min and subjected to stirring several times until a homogeneous mixture was achieved. Such preparation techniques for the modified binder in such an environment were conducted to promote the expected physical and possible chemical bonding between rubber and the binder. The extender oil was added to the blend with continuous stirring to promote the required workability and control the viscosity of the modified binder. Three percentages of extender oil were implemented: 15%, 10%, and 5% by weight of the binder. A control binder was reserved (with no extender oil or scrap tire rubber) for comparison. A similar preparation procedure was implemented by Sarsam and Lafta [14].

2.5. Testing for the rheological properties

The modified and control binders were tested for rheological properties such as stiffness of the binder, penetration viscosity number (PVN), penetration index (PI), and temperature of equivalent stiffness (TES). The shell nomograph [15] was utilized for evaluation of the test results.

3. Results and discussions

3.1. Influence of binder modification on penetration index (PI)

Norhidayah et al. [16] addressed the fact that the penetration index (PI) is considered a good measure of the temperature susceptibility of the viscosity of the asphalt binder. However, it can provide a measure of its deviation from Newtonian behavior, as stated by Bose and Jain [17]. The penetration index can be derived mathematically from the penetration and softening point test values. Asphalt binders with a PI value range between (-2) and (+2) exhibit normal susceptibility to the change in temperature. Asphalt binders with a PI below (-2) are brittle at low temperatures. Asphalt cement with PI between (+1 and -1) is normally used for pavement construction, as addressed by Button et al. [18]. In addition, the negative sign of PI can indicate that asphalt cement is highly susceptible to the change in temperature. Figure 2 demonstrates the variation in the penetration index values after modification of the asphalt binder with extender oil and scrap tire rubber. It can be noticed that the asphalt-rubber mixture exhibits mostly negative values of PI. The negative values of the penetration index decline sharply as the rubber content rises. After reaching 0.075 of the rubber/asphalt ratio, the rate of variations in the PI values shows a gentle trend with further increments in the rubber content. When the extender oil is introduced, a further decline in the negative values of PI could be observed. It can be revealed that as the extender oil content increases, the temperature susceptibility of the rubber-treated asphalt binder declines regardless of the rubber content. It can be noticed from **Figure 2** that the control binder (without rubber or extender oil) exhibits high susceptibility to temperature, and the PI is -2.75. The addition of extender oil was able to reduce the PI by 36.3%, 54.5%, and 27.2% when 15%, 10%, and 5% of extender oil were added, respectively.



Figure 2. Influence of binder modification on penetration index.

However, the addition of scrap tire rubber exhibits further control of the temperature susceptibility and was able to reduce the PI up to 10% of rubber, further increments in the rubber content exhibit no significant impact on the PI regardless of the extender oil content. It can be concluded that the scrap tire rubber and extender oil additives can improve the resistance of the control asphalt cement binder to variations in temperature.

3.2. Influence of binder modification on temperature of equivalent stiffness (TES)

The temperature of equivalent stiffness TES is the temperature at which the stiffness of asphalt is 138 MPa at 2.77 h of loading time, as mentioned by the Shell Nomograph [15]. It can be noticed from **Figure 3** that the control binder (without rubber or oil) exhibits the lowest TES of (-21) among the modified binder mixtures. The implications of scrap tire rubber further decline the TES to (-29) at 15% rubber content. However, the implication of extender oil was able to significantly increase the negative values of TES, while the rubber content did not exhibit significant variation in TES. Such behavior agrees with Sarsam [19].



Figure 3. Influence of binder modification on temperature of equivalent stiffness.

3.3. Influence of binder modification on the penetration viscosity number (PVN)

The penetration viscosity number of asphalt binder PVN is calculated based on the empirical correlation between viscosity at 60 °C and penetration at 25 °C which are usually specified as a requirement for asphalt binders suitable for paving work, as stated by Beaty and Sunjaya [20]. The lower the PVN, the higher its temperature susceptibility. Most of the suitable paving asphalt binders have a PVN between +0.5and -2, as reported by Rusbintardjo et al. [21]. It can be observed from Figure 4 that the negative values of PVN decline after the implementation of scrap tire rubber, regardless of the rubber or oil content, while the negative values of PVN increase as the extender oil is implemented in the mixture. The control binder (without rubber or extender oil) exhibits a PVN value of (-0.6), and it declines by 33% after implementing 15% rubber into the mixture. When the extender oil is added to that combination, the negative PVN values increase by (1.6, 1.3, and 1) folds when 15%, 10%, and 5% of the extender oil are added, respectively. When 15% of scrap tire rubber was implicated in the binder, the negative PVN values increased by (2, 1.5, and 0.5) folds when 15%, 10%, and 5% of extender oil were added respectively. It can be revealed that the scrap tire rubber can decline the negative values of PVN in the binder, while the extender oil increases the negative values of VPN.



Figure 4. Influence of binder modification on the penetration viscosity number.

It can be concluded that lower negative values of both PI and PVN can show higher temperature susceptibility of the binder and are supposed to exhibit more imperviousness to breaking and rutting, as expressed by Fazaeli et al. [22]. One remarkable contrast between PI and PVN is that the PI changes because of the maturing process (during blending and in this manner in assistance), while the PVN esteem remains significantly similar.

3.4. Influence of binder modification on the stiffness of the binder

The stiffness of asphalt cement binder is considered a simple means for characterizing its consistency over a wide range of environmental conditions. Figure 5 demonstrates the influence of binder modification on stiffness in a cold environment of 4 °C. It can be observed that the stiffness of the binder increases sharply as the rubber content rises. However, when the extender oil is implemented, the stiffness of the control binder declines by 50% while the stiffness of the rubber-binder mixture declines by 100%. This may be attributed to the change in the viscosity of the binder after digestion with rubber and oil. When the testing was conducted at a moderate environment temperature of 25 °C, a similar trend of change in stiffness could be detected, and the influence of extender oil was more pronounced at high rubber content, as exhibited in **Figure 6**.



Figure 5. Influence of binder modification on the stiffness of a cold environment.



Figure 6. Influence of binder modification on the stiffness at moderate environment.

The stiffness of the control binder declines by 97% when the testing temperature rises from 4 to 25 °C, while it declines by 96% for a mixture of binder and 15% rubber as compared with the testing condition in a cold environment.

Figure 7 demonstrates the influence of binder modification on the stiffness in a hot environment. It can be observed that the implementation of scrap tire rubber exhibits a more pronounced influence on the stiffness of the binder at such a high testing temperature, while the addition of 15% of extender oil exhibits a significant change in the (rubber-asphalt) binder stiffness. It can be observed that for the control binder (no rubber and no oil), the stiffness increases by 99% and 500% when the testing temperature declines from 60 to 25, and 4 °C, respectively. However, when the 15% extender oil is implemented, the stiffness of the binder declines by 75%, 90%, and 50% when the testing temperature declines from 60 to 25, and 4 °C, respectively.



Figure 7. Influence of binder modification on the stiffness of a hot environment.

It can be observed that the testing temperature has a more detrimental impact on the asphalt cement binder mixture. This could be attributed to the possible scattering of rubber material due to stirring at high temperatures, which causes the dissipation of its impact. It can also be seen that the change in the testing environment does not affect the shape of the asphalt binder stiffness function but shifts it sharply along the y-axis after the implementation of extender oil and shifts it along the x-axis when scrap tire rubber was implemented. However, as the extender oil was introduced, the influence of variations in rubber content on the binder stiffness was not significant regardless of the testing environments. This may be attributed to the significant decline in the viscosity of the asphalt-rubber structure after the implementation of extender oil. Khairuddin et al. [23] and Gatoto et al. [24] reported similar behavior.

4. Conclusions

The following conclusions are addressed based on the limitations of testing and materials:

1) Implementation of extender oil declined the penetration index by 36%, 54%, and 27% when 15%, 10%, and 5% of extender oil were added to the control

binder, respectively. However, implementations of scrap tire rubber exhibit further control of the temperature susceptibility of the binder.

- 2) The implication of scrap tire rubber declines the temperature of equivalent stiffness to -29 at 15% rubber content. The implication of extender oil was able to increase the negative values of TES.
- 3) The penetration viscosity number of the binder declined by 33% after implementing 15% rubber. When the extender oil is added, the negative PVN values increase by (1.6, 1.3, and 1) fold when 15%, 10%, and 5% of the extender were added, respectively.
- 4) When 15% of extender oil is implemented, the stiffness of the binder declines by 75%, 90%, and 50% when the testing temperature declines from 60 to 25, and 4 °C, respectively.
- 5) The implication of 15% scrap tire rubber and 15% extender oil in the asphalt cement from Qayarah refinery is recommended to control temperature susceptibility and provide a sustainable binder for pavement.

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Article

The potential of DNA from industrial vegetables byproducts for the preparation of sustainable materials

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Copyright © 2024 by author(s). Journal of Polymer Science and Engineering is published by EnPress Publisher, LLC. This work is licensed under the Creative Commons Attribution (CC BY) license. https://creativecommons.org/licenses/ by/4.0/ Abstract: Vegetable byproducts from the food and agroforestry industries are a source of several molecules and macromolecules that can find application in the development of high-value materials because of their intrinsic properties. Deoxyribonucleic acid (DNA) is found in all living systems and is widely available in nature. It is a macromolecule well known for its biological function related to carrying and transmitting genetic information. The chemical composition and arrangement of this macromolecule can generate new materials with noble properties that are still being explored for applications apart from their biological function. The purpose of this work was to study the film formation and its properties using the DNA extracted from the food industry byproducts, namely orange and banana, in order to evaluate their properties. The material was capable of forming large films with green, mild, and easy processing techniques. The films were characterized by mechanical tensile tests, Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA), indicating their potential as an alternative natural material for developments in composite and biomedical fields.

Keywords: DNA; biomass; film; sustainable materials

1. Introduction

The interest in using materials from renewable resources and biodegradable materials has been increasing in an attempt to explore their potential new properties. Its use can reduce waste disposal in the environment and avoid accumulation problems [1]. The agroforestry industry generates large amounts of biomass composed of by-products, residues, and derivatives of vegetables from food industries, papermaking, and others [2]. The vegetable biomass from the food industry has been extensively studied, and the components found in small amounts can represent the source of raw material with superior properties; however, they are few studied because of their low yield. These waste materials with superior properties can be useful to generate products with low production costs and high value-added applications [2,3].

Deoxyribonucleic acid (DNA) is found in any living organism, and thus it is available in fresh waste vegetables, an abundant source of raw materials from the agroforestry industry. The DNA molecule displays a double helical structure composed of nitrogenous base pairs (adenine, thymine, cytokine, and guanine) that provides stability to the molecule for the storage of the genetic code [4]. Apart from its biological function as the genetic material in living systems, the most promising DNA application is in the development of tools for diagnosis and disease treatment [5], which has created possibilities to revolutionize clinical practice [6]. In cell-related applications and biomedical applications, it can be used for the immuno-modeling process, for protein production [7] and to manufacture DNA-based nanostructures such as aptamers, tetrahedrons, molecular beacons, nanoflow, nanotubes, dendrimers, scaffolds [8], hybrid devices [9–11], composites [12] and structured DNA nanoparticles [5]. It was also used for the preparation of thin films [13,14] for use in electronic and optoelectronic devices; however, to the best of our knowledge, much remains to be explored with respect to its structure, morphology, and properties, not deeply studied for application in material development. Thus, a strategy to increase the competitiveness of this unique material would be the study of its intrinsic features, such as its capability of forming films and its mechanical properties, aiming to widen its range of applications and generate high-value products.

Residues from the fruit processing industry could be effectively used in this context. For instance, oranges (*Citrus sinensis* L.) and bananas (*Musa sapientum* L.) are among the most consumed fruits worldwide and generate high amounts of residues, including whole fruits. Orange worldwide production in 2024 is 48.8 million tons [15], and about 115 million tons in 2017–2019 [16].

In this vein, the objective of this work is to evaluate the properties of the DNA from two abundant fresh vegetable wastes, the orange and banana, as the raw material for the preparation of films and to characterize the films, aiming to show their physicchemical properties. The reuse of these raw materials represents an upgrade of these residues, contributing to the gradual implementation of the biorefinery concept in the food industry. In this perspective, after separating the DNA, their yield and capability of forming films were tested, and then the film properties were characterized by FTIR, tensile tests, and thermal analysis.

2. Materials and methods

2.1. DNA extraction

The whole waste oranges (1 kg) were peeled, cut, and ground using a high-speed kitchen blender (Arno, Power Max LN50, Brazil) for 5 min. A lysis solution was prepared by mixing 100 mL of sodium lauryl sulfate solution (5 wt%), 40 g of sodium chloride (NaCl), and distilled water to complete 600 mL. The lysis solution (600 mL) was added to 1000 g of the milled orange and kept resting for 3 min. The suspension was filtrated into a Becker cup using a sieve, and the filtrate was used for DNA precipitation. Cold ethanol (150 mL) was slowly added (with a pipette) to the edges of the Becker cup. The precipitated DNA was then visualized at the top of the mixture and separated using a glass rod. The precipitated DNA was washed with deionized water (100 mL), followed by cold ethanol (100 mL), and the washing process with water followed by ethanol was repeated twice. DNA from a waste peeled banana (1 kg) was extracted using exactly the same process; however, on the first step, the peeled fruit pulp was handily crushed within a plastic bag, handily homogenized for 5 min and stored at 8 °C.

2.2. DNA film preparation

The extracted DNA dispersed in ethanol was poured into Petri dishes and dried at room temperature (25 °C) until the mass was stable, giving rise to the film.

2.3. DNA yield

The wet DNA (after washing with ethanol) was weighed, dried as described in item 2.2, and weighed on an analytical balance (final mass). The initial mass corresponds to the whole peeled vegetables before the extraction described in item 2.1. The mass values were used to calculate the yield, as shown in Equation (1):

 $\eta = (M_{\rm F} \times 100)/M_{\rm i} \tag{1}$

where: η = yield (%), $M_{\rm F}$ = Final mass (g), $M_{\rm i}$ = Initial mass (g).

2.4. DNA film characterization

The chemical structure of DNA was analyzed using FTIR, their thermal and mechanical properties were determined using Differential Scanning Calorimetry (DSC), Thermogravimetric analysis (TGA) and tensile tests, respectively.

2.4.1. Fourier transform infrared (FTIR)

The dried films were used for the analyses using a Perkin-Elmer Spectrum 100 FT-IR Spectrometer equipped with an attenuated total reflectance (ATR) device of diamond coated with zinc selenide crystal. The spectra were in the range of 650 to 4000 cm^{-1} , with 4 cm⁻¹ resolution after 16 spectrum scans, and the spectral outputs were recorded in transmittance.

2.4.2. Differential scanning calorimetry (DSC)

The samples were cut in a circular shape with approximately 8 mg and analyzed using a Perkin-Elmer DSC 8000 calorimeter calibrated with indium. The analyses were carried out in a nitrogen atmosphere at a 50 mL·min⁻¹ flow rate. The heating and cooling cycles ranged from -25 to 200 °C at a scan rate of 10 °C min⁻¹ using 40 µL aluminum standard pans.

2.4.3. Thermogravimetric analysis (TGA)

Analyzes were performed using a Perkin Elmer Thermogravimetric Analyzer Pyris 1 TGA at 20 mL/min nitrogen flow atmosphere. The samples (3–8 mg) were heated at 10 °C min⁻¹ in the temperature range from 25 to 600 °C, using a platinum crucible as a sample holder.

2.4.4. Mechanical tests (tensile tension)

Mechanical tests were performed in an Instron Universal Testing Machine, model 5969, with a 0.5 kN load cell and a deformation rate of 50 mm·min⁻¹. Six specimens $(9 \times 1 \times 0.1 \text{ cm})$ of each sample were tested. The samples were kept at 25 °C and 50% RH for 72 h before the tests. Young's modulus, stress at break, and elongation at break were calculated using the resulting curves from the mechanical tests.

3. Results and discussion

3.1. DNA extraction, film preparation and yield

DNA extraction followed the conventional approach reported for extraction, in which the surfactant (sodium laurel sulfate) was used to disrupt the lipid bilayer cell membrane, releasing the DNA; NaCl was used to remove the proteins bound to the DNA and keep them soluble in the aqueous medium; and ethanol was used for precipitation and separation of the DNA. **Figure 1** shows the extraction (A and B) and double washing with ethanol, showing the cleaner appearance of the DNA after treatment.



Figure 1. DNA extraction. (A, B) DNA extraction; (C) washed DNA in cold ethanol; (D) orange DNA film; (E) banana DNA film.

After extraction and washing, the films were prepared for further characterization. The films from banana and orange, after drying, were similar in visual appearance, showing a white, opaque color, a rough surface, and about 0.5 mm of thickness, as shown in **Figures 1D and 1E**. The solvent evaporation from the suspension of the precipitated DNA strands gave rise to the films. The ethanol evaporation led the DNA macromolecules to approximate each other; the molecules bind each other by intermolecular forces, including hydrogen bonds and van der Waals. These weak bonds are responsible for the intrinsic properties of the DNA, such as the mechanical strength and melting point [17].

The yield of the DNA extraction from the waste fruits was calculated using Equation (1), and the yields were 6 wt% for bananas and 4.5 wt% for oranges. Even with its low yield when compared to other natural products, such as cellulose (about 40 wt%), it can be seen as a potential source of material with noble properties for the search for novel applications.

3.2. Fourier transform infrared (FTIR)

The infrared absorption spectrum in both experiments showed the typical bands of the DNA functional groups, as shown in **Figure 2** for the banana film. The presence of intense bands in the region of 1009 cm⁻¹ corresponds to the vibrations of the furan ring breath present in the deoxyribose; in the regions near the wavelength of 1630 cm⁻¹ corresponds to the vibrations of the primary amides in nitrogenous bases; at 1735 cm⁻¹ correspondent to the C=O groups, 1076, corresponding to the vibrations of the C–O– C; at 764 to the vibrations of the C=C bonds; at 1235 cm⁻¹ correspondent to the phosphate ions vibrations; the peaks at 2930 and 2855 cm⁻¹ corresponding to the free NH₂ of the nitrogenous bases [18]. The band at 3280 cm⁻¹ corresponds to the OH groups. The FTIR spectra of banana and orange DNA films are similar, suggesting the DNA structure dominates the spectrum, and no detectable impurities were revealed by this analysis. Also, both spectra are similar to the pure DNA spectrum from the literature [19,20].



Figure 2. Infrared absorption spectrum (FTIR) of banana DNA.

The cell disruption using surfactant (sodium lauryl sulfate) was useful to separate the DNA from other cell components, including macromolecules such as cellulose and hemicelluloses, which are present in the cell wall and are not solubilized by surfactants. In agreement, the FTIR spectrum revealed no typical peaks for cellulose. The salt NaCl kept the proteins soluble even after the treatment with ethanol; thus, most of the proteins were separated from the DNA at this step, as revealed by the absence of the typical peaks of proteins in the spectrum.

3.3. Differential scanning calorimetry (DSC)

The DSC thermograms of DNA samples are shown in Figure 3. The results indicated an endothermic transition at about 80 °C for banana DNA and at about 100 °C for orange DNA, as the result of their intrinsic sequence of nitrogen bases, which can drive the force between the DNA strands. The DSC measurement determines the heat flow and the temperature associated with the changes in the structural/conformational state of the molecules and, for DNA, especially to study the nucleic acid-folding transitions [21,22]. The DNA molecule is formed by a double strand of nitrogenous bases. The two strands are stabilized by hydrogen bonds, which start to break when the temperature increases and result in their separation. The temperature at which half of the DNA is unwound or separated into single strands is called the melting temperature (T_m) [21,22]. The T_m depends on the composition of the DNA. The DNA double strand is formed by the intermolecular interaction of the base pairs A-T and C-G. The A-T base pairs interact via two hydrogen bonds, and the C-G base pairs interact, forming three hydrogen bonds. Each DNA species has a typical composition in A-T and C-G base pairs and a typical T_m. The higher the content of G-C base pairs, the higher their T_m because C-G base pairs require more energy to dissociate than A-T base pairs [22]. The DSC heating curves of the DNA indicated the endothermic event at the region of DNA typical T_m , indicating the heat treatment partially separated the DNA. The temperature effect was most intense for the banana

DNA. The slight event shown by the orange DNA can be the result of a molecule rich in C-G nitrogenous base pairs, indicating the heating DSC treatment separated just small parts of the DNA strands. The DSC thermogram profiles and the temperature revealed here for banana and orange DNA are in agreement with the DSC data range for DNA from other sources described in the literature [14].



Figure 3. DSC curves of the DNA films.

3.4. Thermogravimetric analysis (TGA)

The TGA tracing of DNA is shown in **Figure 4**, showing the thermal stability and degradation profiles of the materials. The loss of mass (about 2 wt%) up to 100 °C can be attributed to water evaporation. The two samples showed a two-step loss of mass (about 60 wt%), which starts at 200 °C, displaying the first peak at 220 °C and the second at 380 °C. This two-step event can be attributed to the separation of the double-stranded DNA, followed by its degradation. The thermal decomposition process of both samples presented a single weight loss step profile.

The two-step degradation, most evident for the orange DNA, is strictly related to its structure, possibly because its composition is rich in C-G nitrogenous base pairs, which requires more energy to be broken when compared to the A-T-rich base pairs of the banana DNA, in agreement with the DSC results.



Figure 4. Thermogravimetric analysis (TGA); (A) orange and banana TGA curves; (B) orange and banana derivative.

The thermal features of the DNA indicated its good thermal stability, starting to degrade above 250 °C, similar to other natural polymers such as cellulose and nanofibrillated cellulose, which start to degrade at about 285 °C and 320 °C, respectively [23,24], pullulan, which starts to degrade at about 317 °C [25] and starch, which starts to degrade at about 325 °C [26]. The high thermal stability results reported here certainly reflect the excellent properties of DNA from waste fruits as a potential material to be used as reinforcing nanostructures/nanofibers for composite materials, for natural or synthetic matrices, replacing the conventional natural polymers.

3.5. Mechanical tests

The stress- strains of the DNA samples are shown in **Figure 5**. Both DNAs showed an almost linear behavior with fractures without large plastic deformations. The DNA samples display a stress-strain profile of a relatively brittle material. The most relevant differences between the DNA materials are the higher modulus and tensile strength of banana DNA with respect to orange DNA. Data for young modulus, tensile strength, and elongation at break are shown in **Table 1**. These mechanical properties of the films can determine their applications. The results showed the low elongation at break of both films and their relatively high Young's modulus, suggesting applications as reinforcing materials for composite materials because of their high modulus and their use in new packaging or coatings because they self-assemble and are natural sources.

Table 1. Results of the mechanical tests of DNA films, mean and SD.

Results	Banana	Orange
Tensile strength (MPa)	2.16 ± 0.90	7.04 ± 1.59
Elongation at break (%)	2.45 ± 1.56	1.63 ± 0.31
Young's modulus (MPa)	157.50 ± 69.78	705.47 ± 90.75



Figure 5. Stress-strain curves for DNA films.

In general, the results showed the use of biomass from the food and agroforestry industries to prepare self-assembled DNA films. The findings match the demand for the production of new sustainable materials using green methods. The methods for extraction and preparation are totally free of organic solvents and drastic procedures, contributing to the green tendency in material preparation. In addition, solvent-free methods widen the range of applications of the material for use in medicine, food, and packaging. Its physicochemical properties also suggest its use in fields such as construction, transport, and manufactured goods. In addition, the sustainable utilization of biomass represents a strategy to valorize vegetable raw materials.

4. Conclusion

The extraction of DNA from bananas and oranges was efficient and cost-effective based on the yield, which was about 5 wt%. The characterization of DNA showed it can form films, and its thermal and mechanical properties are adequate for application in the materials science field. Its chemical structure and properties suggest it can be a potential raw material for innovative applications. In addition to the potential for the development of new materials, the reuse of vegetable residues can contribute to decreasing their disposal in nature, decreasing their associated environmental problems. In addition, the preparation of new materials from vegetable DNA can generate high-value products and contribute to the circular economy.

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Mechanical strength investigation of chemically reinforced sandy soil using organic copolymers for geotechnical engineering applications

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Copyright © 2024 by author(s). Journal of Polymer Science and Engineering is published by EnPress Publisher, LLC. This work is licensed under the Creative Commons Attribution (CC BY) license. https://creativecommons.org/licenses/ by/4.0/ **Abstract:** The chemical reinforcement of sandy soils is usually carried out to improve their properties and meet specific engineering requirements. Nevertheless, conventional reinforcement agents are often expensive; the process is energy-intensive and causes serious environmental issues. Therefore, developing a cost-effective, room-temperature-based method that uses recyclable chemicals is necessary. In the current study, poly (styrene-co-methyl methacrylate) (PS-PMMA) is used as a stabilizer to reinforce sandy soil. The copolymer-reinforced sand samples were prepared using the one-step bulk polymerization method at room temperature. The mechanical strength of the copolymer-reinforced sand samples depends on the ratio of the PS-PMMA copolymer to the sand. The higher the copolymer-to-sand ratio, the higher the sample's compressive strength. The sand (70 wt.%)-PS-PMMA (30 wt.%) sample exhibited the highest compressive strength of 1900 psi. The copolymer matrix enwraps the sand particles to form a stable structure with high compressive strengths.

Keywords: sand; copolymer; polystyrene; polymethyl methacrylate; soil reinforcement; geotechnical

1. Introduction

Natural sandy soils are unsuitable for geotechnical engineering applications due to their low strength, loose structure, and high saturated liquefaction potential [1–3]. Therefore, chemical reinforcement of sandy soil is widely employed in geotechnical engineering [4]. The traditional sand reinforcement agents are lime [5], fly ash [6], gypsum [7], cement [8], zeolite [9–11], etc. Though these reinforcement agents for improvement have apparent advantages, the modifications made using these chemical additives often increase the modified sand's pH value and cause groundwater pollution and other environmental issues [4]. To overcome these potential limitations of conventional soil reinforcement agents, non-conventional chemical additives such as polymers [12], resins [13], enzymes [14], ions [15], and lignin derivatives [16]-based reinforcement agents are developed to meet the physical and engineering requirements of the sandy soil for different engineering purposes [17].

Various polymer systems have been systematically studied for successful sand reinforcements [18,19]. Polymer and polymer nanocomposite materials are found to be potential candidates for improving the compressibility strength of sandy soil [20] and various other applications [21–43]. Also, the polymer materials can enwrap the sand particles and improve their strength by filling the void spaces between them [44]. Krishnan et al. recently reported a series of research works to improve the crush resistance of sand particles by dual polymer nanocomposite coating onto the sand surfaces [45–49]. Krishnan et al. also reported sand particle modifications with

polyacrylamide (PAM) gels at elevated temperatures for petroleum and natural gas engineering applications [50–56]. The same group reported various significant works of different industrial importance processes based on polymer composite systems [51,54,57–60]. The PAM-modified sand particles are also used for agricultural purposes in deserts [45,60]. Xanthum gum, an eco-friendly organic polymer, was also studied for coastal agriculture, reducing coastal erosion issues. Naeini et al. studied the mechanical strength improvement of sand particles by epoxy resin modification. It was also found that the modification of epoxy resin in sand particles enhanced elastic modulus under wet and dry conditions. Yang et al. reported polyaspartic acid resin as a novel sand-fixing agent. As evident from the recent research reports, polymeric materials can act as a potential reinforcement agent for sandy soil.

The current work aims to study the effect of PS-PMMA copolymer as a chemical reinforcing agent for sandy soil. The compressibility strengths of the PS-PMMA copolymer-reinforced sand samples were evaluated. Different concentrations of PS-PMMA copolymer and sand were chosen to determine the effect of the copolymer on the sand's compressibility and strength enhancement. The results and associated discussion provide information on the chemical stabilization mechanisms of polymer-reinforced sand for researchers and practicing engineers.

2. Experimental

2.1. Materials

Styrene (S; >99% purity) was purchased from Sigma Aldrich. Methylmethacrylate (MMA; 99% purity) was purchased from Aldrich. Benzoyl peroxide (BPO; >90% purity) was purchased from Loba Chemie. Dimethyl-p-toluidine (DMPT; >99% purity) was purchased from Alfa Aser. All the chemicals are of analytical grade and used as received. Sandy soil samples (70/40 mesh) were collected from the Saudi Desert.

2.2. Methods

2.2.1. Preparation of PS-PMMA reinforced sandy soil



Figure 1. Cylindrical blocks of PS-PMMA reinforced sandy soils of different heights. (a) 10 cm; (b) 7 cm; and (c) 3 cm.

To prepare PS-PMMA-reinforced sandy soil, the sand particles were well mixed to a 30 wt.% of a 1:1 wt.% co-monomer mixture of S and MMA along with BPO (0.01 wt.% related to the monomers) and 0.001 wt.% of DMPT at room temperature. The mixed sand samples were aged 10–15 min for the completion of the polymerization

reaction. The sand samples were prepared in a cylindrical glass tube to prepare the cylindrical-shaped samples (**Figure 1**). After the sand samples were hardened, the glass tubes were broken to retrieve the sand samples.

2.2.2. Calculation of bulk volume, grain volume, and pore volume

The samples' bulk volume (cc), pore volume, and grain volumes are calculated using Equations (1)–(3).

Bulk volume of the cylindrical sample = $\pi r^2 h$ (1) 'h' is the height of the cylindrical sample.

The samples' pore volumes (cc) were determined by the liquid saturation method. The samples are initially immersed in methanol, and after 60 min, the excess methanol is decanted, and the sample is weighed again. The pore volume of the sample is calculated using the initial and liquid pore-filled sample weights (Equation (2)).

 $The pore volume of the sample = \frac{Weight of the MeOH saturated sample-Weight of the dried sample}{Density of MeOH} (2)$

Grain Volume = Bulk Volume - Pore volume(3)

2.2.3. Compressibility tests



Figure 2. Compressibility test of the copolymer-reinforced cylindrical sand blocks. The inset shows the cracked block after the block is compressed.

The compressibility test has been carried out using a Specac mechanical compressor (**Figure 2**). The cylindrical sample block is placed on a supporting bottom, and specific pressure is applied through a circular pressure head. The pressure rises

and suddenly drops when the block starts cracking (**Figure 2**). The maximum pressure the sample block tolerated before cracking down is calculated as its compressibility strength (Equation (4)).

$$Pressure = Force/Area \tag{4}$$

3. Results and discussion

3.1. PS-PMMA copolymer reinforced sand blocks

The stepwise preparation of PS-PMMA copolymer-reinforced sand blocks at room temperature is schematically illustrated in **Figure 3**. The sand particles were mixed with the required amount of a co-monomer mixture of S, MMA, BPO, and DMPT to prepare the samples. This subsequently allowed for random copolymerization at room temperature. The BPO undergoes decomposition in the presence of DMPT and produces BPO free radicals. The co-monomer molecules were synchronously transformed into co-monomer free radicals with the aid of the BPO initiator radicals. After that, the co-monomer free radicals became radical donors to the neighboring co-monomer molecules. Consequently, a chain propagation of S and MMA monomers took place, which resulted in the growth of PS-PMMA random copolymer chain radicals [61,62]. Finally, the copolymer chain radicals were terminated either by dimerization or disproportionation. The formed PS-PMMA copolymer on sand surfaces efficiently wraps the sand particles.



Figure 3. Schematic illustration of the preparation of PS-PMMA copolymer reinforced sand (sand-(PS-PMMA) cylindrical block).

3.2. Bulk, grain, and pore volumes of PS-PMMA copolymer-reinforced sand

Photographs of PS-PMMA copolymer-reinforced sand samples are shown in **Figure 4**. As evident from **Figure 4a–c**, when the copolymer concentration is low relative to sand (i.e., 1 wt.%, 5 wt.%, and 10 wt.%), the sand particles either remain free or agglomerated, while if the concentration is increased to 15 wt.% and above (20 wt.% and 30 wt.%), sand-polymer blocks are obtained. When the PS-PMMA concentration is increased beyond 30 wt.% to sand, the sand particles are well-buried into the polymer matrix, which is no longer a homogenous composite of sand-PS-PMMA copolymer. The shape of the blocks can be manipulated using respective shaped templates. In this study, we prepared the samples in cylindrical geometries to evaluate the bulk, grain, and pore volumes and the effect of PS-PMMA copolymer

concentration on these structural parameters (**Figure 5**). In the sample with 15 wt.% of PS-PMMA, the bulk, grain, and pore volumes are 50 cc, 32 cc, and 18 cc, respectively. At the same time, for the sample with 20 wt.% PS-PMMA, the bulk, grain, and pore volumes are 50 cc, 40.8 cc, and 9.2 cc, respectively, while for the sample with 30 wt.% PS-PMMA, the bulk, grain, and pore volumes are 50 cc, 46.1 cc, and 3.9 cc, respectively. The geometric and pore characteristics of the samples are summarized in **Table 1**. For the fixed bulk volume of the copolymer-reinforced sand blocks, with an increase in the polymer concentration, the porosity decreases while the grain volume increases. The samples' increased grain and decreased pore volumes are attributed to the successful coating of the copolymer onto the sand particles while efficiently wrapping them.



Figure 4. Photographs of Sand-Copolymer samples prepared at room temperature. (a) Sand (99%)-(PS-PMMA)(1%); (b) Sand (95%)-(PS-PMMA)(5%); (c) Sand (90%)-(PS-PMMA)(10%); (d) Sand (85%)-(PS-PMMA)(15%); (e) Sand (80%)-(PS-PMMA)(20%); (f) Sand (70%)-(PS-PMMA)(30%).



Figure 5. Bulk, grain, pore volumes, and porosity of sand (85%)-(PS-PMMA)(15%), sand (80%)-(PS-PMMA)(20%), and sand (70%)-(PS-PMMA)(30%) samples.

The calculated geometric and pore characteristics of the PS-PMMA copolymerreinforced sand samples are summarized in **Table 1**.

lume (cc)

Table 1. Geometric and pore characteristics of the PS-PMMA copolymer-reinforced sand samples.

3.3. Compressibility strength of PS-PMMA copolymer-reinforced sand

Figure 6 shows the compressibility strengths of the PS-PMMA copolymerreinforced samples—the compressibility strengths for the sand samples with 1 wt.%, 5 wt.%, and 10 wt.% PS-PMMA copolymers were not determined as they are either free or agglomerated particles. The compressibility strengths of sand (85%)-(PS-PMMA)(15%), sand (80%)-(PS-PMMA)(20%), and sand (70%)-(PS-PMMA)(30%) are evaluated to be 224 psi, 1500 psi, and 1900 psi. The compressibility strengths of PS-PMMA copolymer-reinforced sand samples are summarized in **Table 2**. If the copolymer concentration of the reinforced sand samples was high, the compressibility strengths were also found to be high [63]. This increase in the samples' mechanical strength is attributed to the addition of high-strength thermoplastic polymers to the sand and the successful cross-linking of copolymers with the sand surfaces [30,31,33,34,40,45–50,55,56,60].



Figure 6. Compressibility strength of sand (85%)-(PS-PMMA)(15%), sand (80%)-(PS-PMMA)(20%), and sand (70%)-(PS-PMMA)(30%) samples.

S.No. Sa	ample	The shape of the sample	Compressibility strength (psi)
1. Sa	and (99%)-(PS-PMMA)(1%)	Individual Grains	-
2. Sa	and (95%)-(PS-PMMA)(5%)	Individual Grains	-
3. Sa	and (90%)-(PS-PMMA)(10%)	Agglomerated Grains	-
4. Sa	and (85%)-(PS-PMMA)(15%)	Cylindrical	224
5. Sa	and (80%)-(PS-PMMA)(20%)	Cylindrical	1500
6. Sa	and (70%)-(PS-PMMA)(30%)	Cylindrical	1900

Table 2. Compressibility strengths of the PS-PMMA copolymer-reinforced sand samples.

4. Conclusion

The current work reports a cost-effective preparation method of mechanically reinforced sand particles using PS-PMMA copolymer. A one-step bulk polymerization technique was used to coat the sand particles with the PS-PMMA copolymer. When the BPO is in contact with DMPT at room temperature, the BPO instantaneously decomposes to form free radicals. The free radicals react with the monomers and form co-monomer free radicals. The co-monomer free radicals randomly react to form the co-polymer onto the sand particles. The compressibility strength of the copolymer-reinforced sand blocks is directly proportional to the sand-to-copolymer ratio. The higher the sand-to-copolymer ratio, the higher the strength of the sand block. Simultaneously, the porosity is inversely related to the sand-to-copolymer ratio. The sand (70 wt.%)-PS-PMMA (30 wt.%) sample exhibited a high compressive strength of 1900 psi. The copolymer matrix enwraps the sand particles to form a stable structure with high compressive strengths.

Author contributions: Experimental studies, MRK; data analyses, MRK and EHA; original manuscript writing, MRK and EHA; supervised the project, EHA. All authors have read and agreed to the published version of the manuscript.

Data availability statement: The data will be available based on a request from the corresponding author.

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Article

Unnotched impact toughness of polybutylene terephthalate/polyamide 6/carbon black blends

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Copyright © 2024 by author(s). Journal of Polymer Science and Engineering is published by EnPress Publisher, LLC. This work is licensed under the Creative Commons Attribution (CC BY) license. https://creativecommons.org/licenses/ by/4.0/ **Abstract:** The combination of polybutylene terephthalate (PBT) and polyamide 6 (PA6) plastic mixture was taken from waste from the table production process along with carbon black (CB) reinforcement with the desire to create a potential plastic mixture widely used in many fields. The PBT/PA6/CB mix is created by injection molding with a CB weight ratio of 0%, 4%, 8%, and 12%. This study has shown the change in plastic's mechanical properties when adding CB to the mixture by testing the unnotched impact toughness according to ASTM D256 standards. Research results show that the unnotched impact toughness was gradually reduced when increasing the CB content in the mixture from 0% to 12% CB. Specifically, at 0% CB, the resulting unnotched impact toughness was 12.85 kJ/m², reduced to 4.78 kJ/m².

Keywords: PBT; PA6; carbon black; PBT/PA6 blend; unnotched impact toughness

1. Introduction

Annual plastic waste from human activities is one of the causes of global warming and is seriously threatened [1]. This problem also gives scientific researchers a headache when studying how to handle that amount of plastic waste to prevent direct discharge into the environment and protect the human living environment. Currently, researchers around the world are working on doing that. The research team researched the recycling of PBT and PA6 materials for clean and green earth. The idea for this research originated from knowing that toothbrush bristles are usually made of two main types of plastic: PBT and PA. During production, a large amount of plastic waste is created from the cutting process for fur shaping. That plastic will no longer be used, causing a waste of resources and costs for waste treatment. The research team aims to use the discarded plastic waste after recycling it to be used in the electrical, automotive, and household appliances industries.

PBT is a thermoplastic that belongs to the polyester terephthalate family. PBT is also very popular due to its outstanding properties, such as good mechanical performance, electrical insulation, and water resistance [2,3]. From the above points, the research team sees this plastic material's high practicality and benefits. However, in addition to the advantages of PBT, there are still disadvantages, such as low heat distortion temperature and ease of flexural. It is warping due to mold shrinkage, low solvent absorption, and low unnotched impact toughness. Therefore, the application of PBT is limited by working conditions with solid impacts or some harsh conditions, such as high-temperature environments [4,5].

PA6 is a widely used semi-crystalline polymer due to its technical benefits, such as its high heat distortion temperature, good chemical resistance, high strength and

hardness, and abrasion resistance. In contrast to PBT, PA6 has superior mechanical properties.

The research team used mixing two types of plastic, PBT and PA6, to improve their disadvantages while maintaining the good properties of each kind of plastic [6– 9]. However, the compatibility between these two types of plastic, PBT and PA6, could be better, leading to the low durability of this mixture. Therefore, a study is needed to improve this plastic mixture to enhance its mechanical properties and meet the technical requirements of the product. In this study, the research team used CB as a filler. Reinforcement for the PBT/PA6 plastic mixture. CB is a relatively new filler in the plastics industry, so more detailed research is needed on this type of filler. This filler is also a big challenge for the research team. However, detailed information about this type of filler is essential for today's plastic recycling industry, where the source of recycled materials is highly abundant. Information about the influence of CB on the PBT/PA6 mixture helps plastic recycling businesses have a better basis to perfect their products and improve economic efficiency from recycled materials. This study will minimize the negative impact of plastic waste on the environment and contribute to sustainability in production.

In short, this research can solve the remaining PBT and PA6 wastes to create usable products. Furthermore, this study provides more detailed information about the PBT/PA6/CB mixture, a reference source that contributes to the basis for future research on polymer blends.

Revolving around the issue of improving the properties of polymer mixtures, many researchers have implemented a third method of adding fillers. Typically, in the study of Nga et al. [10], researchers have shown that glass fiber combined with the PBT/PA6 mixture gives this plastic mixture better tensile strength and more durability. Fire resistance is thanks to the properties of fiberglass. In the research paper by Nga [11], the author concluded that activated carbon makes the microstructure smaller and finer, enhances cohesion, and improves the mechanical properties of the PBT/PA6 mixture. This study shows that each type of filler will change the internal structure, leading to different physical and mechanical properties. Research by Li et al. [12] has investigated PBMMA particles as strength modifiers and compatibilizers used to harden the PA6/PBT mixture to increase the unnotched impact toughness of this mixture. Research continues to demonstrate fillers' role in improving the mechanical properties of PBT/PA6 composites. However, this study still needs some information about mechanical and flexural properties. In the paper of Jubinville et al. [13], researchers reported that the compatibility and tensile strength of the PBT/PA6 blend were improved by adding the renewable bio-derived PA11 compatibilizer. However, the research team found that the most significant barrier to this research is the high cost of PA11, leading to low production feasibility.

Meanwhile, the research paper of Li et al. [14] presented research results on a PBT/PA6 mixture combined with carbon black as a filler, helping to improve tensile strength when mixed with 6% CB. However, this study does not specifically state or provide more detailed information about the effects of CB on the entire plastic mixture; instead, it simply studies the electrical conductivity of the entire plastic mixture. In the article on the non-isovolumic viscoelastic properties of PBT/PA6 [15], researchers have shown that the Poisson's ratio when plastic deformation of PBT/PA6

is less than 0.5 and the plastic properties of PBT and PA6 are not isovolumic. The article by Yang et al. [16] has successfully researched the PA6/GF mixture that can increase fire resistance and is environmentally friendly with fireproof properties and a fireproof index reaching UL94-V0. From previous studies, the research team realized that studying the influence of CB on the PBT/PA6 mixture is necessary to have a more detailed view of this new material.

This research holds immense potential for the recycling of plastic waste from PBT and PA6 sources. By ensuring the production of high-quality products with excellent mechanical properties, we can significantly enhance the economic value of plastic recycling businesses. Moreover, our ultimate aim is to reduce costs associated with plastic waste treatment and make a substantial contribution to environmental protection, a cause we all deeply care about.

To achieve this purpose, the following objectives need to be achieved:

- To find the CB ratio in the PBT/PA6 mixture that provides the best mechanical properties, the research team will create durability test samples with CB ratios of 0, 4, 8, and 12% by injection molding.
- The research team tested and analyzed the results to determine the unnotched impact toughness of the entire PBT/PA6/CB mixtures.

2. Materials and methods

8CB

12CB

Research uses three types of materials: PBT, PA6, and carbon black. The materials used in the study are shown in **Figure 1**.



Figure 1. Materials used in research: (a) PBT; (b) PA6; (c) black.

Through research, choose the plan and mix it according to the ratio in Table 1.

Samples	PBT (wt.%)	PA6 (wt.%)	Carbon black (wt.%)		
0CB	75	25	0		
4CB	72	24	4		

23

22

Table 1. Mixing ratio of PBT/PA6/CB blend

The machine used to measure unnotched impact toughness is shown in Figure 2.

8

12

Before measuring, after performing injection molding, randomly select five samples for each ratio. Before performing the measurement, ensure that the measurement environment is at a temperature of 23 ± 2 °C and a relative humidity of

69

66


50% \pm 5%. Laboratory samples should be stored for at least 40 h.

Figure 2. Tinius Olsen impact testing machine for measuring sample unnotched impact resistance.

Your role in this process is crucial. The first step is to enter measurement parameters into the machine at a 1.59 mm/min speed. To measure, you need to carefully place the part on the machine table and position it securely. Then, measure and record the final result. Take the part out of the machine. Repeat this for each case, ensuring accuracy and consistency in your measurements.

3. Results

3

The sample used to measure unnotched impact toughness is shown in Figure 3.



Figure 3. Sample used to measure unnotched impact toughness.

 Table 2 shows the description of the unnotched impact toughness parameters of the sample.

75PBT/25PA6/CB.					
Sample	0% CB	4% CB	8% CB	12% CB	
1	13.64	6.33	10.41	5.63	
2	10.17	9.68	9.07	5.09	

9.74

5.75

5.82

Table 2. Unnotched impact toughness parameters of each sample75PBT/25PA6/CB.

16.06

Sample	0% CB	4% CB	8% CB	12% CB	
4	14.00	9.09	7.06	6.09	
5	15.33	12.35	6.80	7.17	
6	11.37	8.10	7.26	4.15	
7	17.03	9.52	7.23	2.54	
8	13.28	9.10	7.29	3.98	
9	9.87	12.62	8.88	2.540	
10	7.70	10.31	7.91	4.75	
Average	12.85	9.69	7.77	4.78	
Standard deviation	3.00	1.84	1.34	1.51	

Table 2. (Continued	l).
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The average display of unnotched impact toughness is depicted in Figure 4.



Figure 4. Average unnotched impact toughness of the sample.

Table 2 and **Figure 4** show that the unnotched impact toughness is clearly reduced when carbon black is involved. Initially, the unnotched impact toughness of PBT/PA6 is 12.85 kJ/m², and when CB is reinforced at a rate of 4%, 8%, and 12%, the unnotched impact toughness of the sample decreases by 9.69 kJ/m², 7.77 kJ/m², and 4.47 kJ/m², respectively. It can be said that CB can induce variation in the mechanical properties of plastics, but the reinforcement may not be flexible and effective. This result can reduce impact toughness, especially as CB content increases.

Adding the CB measurement function causes the unnotched impact toughness to decrease, as shown in **Figure 4**. It can be said that CB can create a change in the mechanical properties of the plastic, but the reinforcement may not be flexible and effective. This result can reduce impact toughness, especially as CB content increases. Similar research [17] shows that when the PB content increases from 10 to 70% by weight, the unnotched impact toughness of the composite decreases by 72%. When the PB concentration increases, the toughness of the composite material decreases. Incorporating PB particles into HDPE created stress concentration zones requiring less energy to create cracks in the composite, thus reducing unnotched impact toughness.

This effect may indicate reaching the limit when the CB content is excessive. The change of CB into the mixture is similar to the research results [18], showing that the PB content increases by 10%–30%–50% by weight, the flexural strength of the composite increases, and the flexural strength of the material increases. PB/HDPE composite was reduced to 70 wt% PB content, demonstrating that 70 wt% PB content is unsuitable for molding PB/HDPE composites. Thus, we see that the higher the % CB, the more it affects the tensile strength of the material and the flexural strength.

The research results are explained by the factors affecting the mechanical properties of materials when mixed with PBT/PA6/CB. The interaction between CB and polymer affects the flexural strength of the mixture. The limitations of this research are that more than the research time is needed to monitor material changes over a long period, and secondly, due to limited research environmental conditions and costs. To solve the above problems, we need time to monitor the process of changing materials and find the best funding source and research location so that the research process can happen in the best way.

This research and development direction is to expand its scope into the fields of research and production to serve the daily needs of people and today's industries. The difficulties encountered when doing extensive research are difficulties in finding documents, foreign languages, and data processing, in addition to difficulties in finance, equipment, and human resources in expanding research.

4. Conclusion

Overall reliability is improved when adding CB to PBT/PA6, following an increasing and then decreasing trend as CB becomes higher. Therefore, if we want to improve the material, we can add a reasonable CB content with the condition that CB must be less than 12%.

The consistent decrease in unnotched impact toughness with increasing CB content is a crucial finding. It indicates a potential for enhanced durability. Therefore, if the aim is to improve durability and impact, it's advisable to avoid adding CB. This direct influence of CB content on the material's unnotched impact toughness is a key factor to consider, offering a pathway to achieve optimal performance. Furthermore, this research paves the way for exciting future developments in the application of PBT/PA6 materials containing CB in various industries.

Author contributions: Conceptualization, THNP and PHH; methodology, QBN; software, TTN; validation, THNP, PHH and QBN; formal analysis, PHH; investigation, QBN; resources, QAP and MTTV; data curation, PHH; writing—original draft preparation, QBN; writing—review and editing, THNP; visualization, TST; supervision, SHH; project administration, KNN; funding acquisition, VHH. All authors have read and agreed to the published version of the manuscript.

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Review

Solid waste recycling and organic particulate hybrid nanocomposite technologies for sustainable infrastructure—A comprehensive review

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Copyright © 2024 by author(s). Journal of Polymer Science and Engineering is published by EnPress Publisher, LLC. This work is licensed under the Creative Commons Attribution (CC BY) license. https://creativecommons.org/licenses/ by/4.0/ Abstract: Solid waste has become a major environmental concern globally in recent years due to the tremendous increase in waste generation. However, these wastes (e.g., plastics and agro-residues) can serve as potential raw materials for the production of value-added products such as composites at low cost. The utilization of these waste materials in the composite industry is a good strategy for maintaining the sustainability of resources with economic and environmental benefits. In this report, the environmental impacts and management strategies of solid waste materials are discussed in detail. The study described the benefits of recycling and reusing solid wastes (i.e., plastic and agro-waste). The report also reviewed the emerging fabrication approaches for natural particulate hybrid nanocomposite materials. The results of this survey reveal that the fabrication techniques employed in manufacturing composite materials could significantly influence the performance of the resulting composite products. Furthermore, some key areas have been identified for further investigation. Therefore, this report is a state-of-the-art review and stands out as a guide for academics and industrialists.

Keywords: solid waste; value-added products; sustainable infrastructure; nanocomposite technologies; organic particulate

1. Introduction

Solid waste management has been a major concern globally in recent years due to the increasing waste generation. Examples of solid waste materials include plastic waste, food waste, chemicals, glass, and metal waste [1], and agro-waste. Solid wastes are known to cause pollution issues that act as threats to human health and the ecosystem [2]. The increasing amount of municipal solid waste (MSW) is ascribed to the rapid socio-economic growth and improvements in the standard of public living in a country like China, as reported [3]. However, the efforts to manage these waste materials are low compared to the quantity of MSW generated [1]. Therefore, efforts should be intensified by employing various waste management strategies, especially sustainable approaches.

Agro-waste such as coconut husk, cotton stalk, corn husk, rice husk, and wood waste is eco-friendly, cheap, nonabrasive, sustainable, and biodegradable. The materials are usually burned or destined for landfills, thereby posing pollution issues [2]. However, several researchers [4–6] have proven the feasibility of using these materials as reinforcements for polymer matrices in the polymer industry. Despite the numerous benefits of these materials, they are still regarded as waste materials and are therefore left to decay or burn after the harvest season. Kang et al. [7] reported that over 20 million tons (dry weight) of cotton stalks are generated in China per year, the

majority of which are either burned or left to decay without being fully utilized. The utilization of these biomass materials as reinforcing agents for polymer matrix in the composite industry could be a good strategy for waste management as well as providing additional income to rural farmers.

Petroleum-based plastics are commonly used to produce household materials such as bottles, cups, and pipes due to their lightweight and durability. These plastic materials are estimated to generate about 150 million tons per year as plastic solid waste at the global level [2]. However, this large volume of plastics commonly regarded as household waste could serve as matrices for organic fillers if properly sorted and recycled. The utilization of these plastics in the polymer industry will prevent resource depletion and offer both economic and environmental benefits [2,8] compared to their virgin counterparts.

Nanoclay is gaining attention in the polymer industry as a modifier due to its enhancement properties, such as thermomechanical properties, barrier properties, fire retardancy, and thermomechanical properties [2]. Nanoclay as a layered silicate in the nanoscale diameter range is reported in the literature [6] to significantly improve the performance of plastic materials at a small quantity (≤ 5 wt%) due to its large aspect ratio. Some examples of nanoclays include saponite, hectonite, montmorillonite (MMT), and nontronite.

The mechanical performance of biocomposite products depends on the nature of the components as well as the processing techniques. For example, a good dispersion of fibre/filler in a composite system that will ultimately improve the tensile and flexural properties can be obtained through injection molding [9]. Therefore, choosing an appropriate fabrication technique is critical to the development of improved biocomposite products. The commonly known processing techniques as well as novel approaches reported in the literature are discussed in this review.

Although several solid waste materials and their treatment technologies are reviewed in published papers [1]. Other reviews [10–12] that discussed the fabrication techniques of natural fibre-reinforced composites exist in the literature. However, not all techniques used in natural fibre-reinforced composite production are suitable for natural particulate hybrid nanocomposites. For example, the compression molding manufacturing process is suitable for composites containing long fibre lengths but may not be appropriate for particulate filler-filled reinforced composites. Therefore, a review of the emerging technologies for the production of natural particulate hybrid nanocomposite from plastic waste, nanoclay, and organic filler particles (i.e., from agro-waste) is critical, as the performance of the developed composites is dependent on the manufacturing process employed. This paper seeks to review the recent advances in fabrication technologies involving the use of plastic waste and agro-waste as promising raw materials for the production of natural particulate hybrid nanocomposites for sustainable infrastructural applications. Therefore, the objectives of this work are to:

- Discuss the environmental impacts and management of solid waste materials.
- Discuss solid waste materials (i.e., plastic and agro-waste) as emerging raw materials in the polymer industry.

Review the emerging fabrication approaches for organic particulate hybrid nanocomposites.

2. Environmental impacts of solid waste materials

Emission of greenhouse gases (GHGs) such as carbon dioxide, methane, volatile organic compounds, nitrous oxide, and sulfur dioxide are caused by inappropriate management of municipal solid waste [13,14]. The atmospheric methane concentration is increasing at a rate of 2% per year, making it one of the major contributors to the greenhouse effect [15]. Methane emissions from landfills comprised 3%–9% of global anthropogenic sources [16]. Despite claims that methane is not harmful to plants, vegetation in areas affected by landfill gas emissions experiences negative effects. When landfill waste decomposes, methane displaces oxygen in the atmosphere, while carbon dioxide leads to a condition where plants experience oxygen deficiency in their root environment [17]. On the contrary, studies have demonstrated that plants can thrive when exposed to carbon dioxide concentrations below 5%, even though the soil typically contains less than 2% of this gas [18]. However, it is important to note that higher concentrations of carbon dioxide, exceeding 20%, are considered phytotoxic and can have detrimental effects on plant growth and health [19]. Landfils elevated carbon dioxide levels can threaten nearby plants, especially their delicate roots, even with sufficient soil oxygen [20]. Approximately 60% of methane and 40% of carbon dioxide (CO₂) emissions from organic materials in waste dumps and landfills occur during anaerobic decomposition [21]. This process also generates trace gases such as carbon monoxide, nitrogen, oxygen, hydrogen, and hydrogen sulfide [22,23] and is regarded as environmentally dangerous [19].

Furthermore, the accumulation of municipal solid waste can indeed cause leachate plumes. Leachate is the liquid that forms when water percolates through waste materials in a landfill or dumpsite. It contains various pollutants and can pose a significant threat to groundwater and surface water if not properly managed. Leachate plumes commonly contain high concentrations of organic carbon, including ammonium and dispersed phenols [24]. Leachate plume generation is affected by different variables such as waste composition, temperature, precipitation, population densities, and amount of moisture [25]. The composition of leachate and the contaminant itself significantly influence pollutant migration. Similar chemical pollutants in leachates, complex mixtures of compounds and pollutants, may behave similarly due to co-contaminant influence [26].

Leachate can seep into the surrounding soil and contaminate groundwater. This can happen due to factors such as inadequate landfill liners, the absence of leachate collection systems, and improper waste disposal practices. Leachate plumes can develop when water-carrying pollutants from the waste site move through the soil, spreading the contamination [27]. Researchers identified two distinct leachate transport routes within the landfill after further investigations [28,29]. The movement of pollutants through defective soil membranes can occur via advection and dispersion, while organic pollutants can move through soil membranes via diffusion. Improper garbage disposal has a growing impact on the environment and human

health, especially in developing countries. To mitigate greenhouse gas (GHG) emissions and acidification of ecosystems caused by ammonia release, environmentally friendly municipal solid waste (MSW) management techniques are being implemented.

3. Municipal solid management techniques

Waste management practices that follow the principles of sustainable development and recognize waste as a valuable resource are essential. Municipal solid waste management has gained significant attention due to the production of approximately 450 million tonnes per year [30]. To achieve an effective waste management system, it is necessary to consider specific factors such as waste characteristics, efficient collection systems, appropriate processing infrastructure, proximity of materials for recovery, adherence to emission standards, costeffectiveness, and community involvement [30,31]. Waste management methods worldwide primarily include landfilling, composting, recycling and reuse, and incineration, as shown in Figure 1. The solutions for proper waste treatment are influenced by factors such as population density, income levels, and available infrastructure. Landfilling remains the most used approach, responsible for approximately 40% of global waste disposal [32]. Approximately 19% of waste undergoes recycling and composting for recovery, while 11% is treated through modern incineration methods [33]. Regrettably, a portion of waste is still handled through open dumping and burning practices. The various solid waste management approaches, as well as their merits and limitations, are presented in Figure 1 and Table 1, respectively.



Figure 1. Different management approach for solid municipal waste.

Types of technique	Merits	Limitations
Composting	It has cost benefits due to its low operational costs. It can serve as a	It is suitable for only organic waste and this is a
	source of organic manure.	limitation.
Anaerobic digestion	Emission of greenhouse gases is low. Biogas can be utilized for power generation.	It requires high operational costs and maintenance.
Landfilling	It requires low operational costs. Landfill gas can be used for electricity generation. It can be used for any type of waste stream.	It poses the risk of groundwater and soil contamination. It leads to land degradation and reclamation of such land requires huge capital.
incineration	Easy setup and fast treatment. Energy/steam production from the heat generated. Suitable for any type of solid waste.	It is a source of pollution.
Recycling and reuse	It is a sustainable approach with both economic and environmental	Sorting of waste materials is very cumbersome and
	benefits.	therefore, requires lots of effort.

Table 1. Merits and limitations of the different treatment technicities.

3.1. Landfills

Landfills are traditionally designed to ensure the safe storage and disposal of waste materials [34]. Landfill characteristics are influenced by a range of environmental factors. However, the primary challenge with landfills lies in identifying a suitable location due to the increased disruptions in the physiochemical properties of the soil compared to the surrounding land [35]. Modern engineered landfills utilize a waste control liner system to create a protective barrier separating the waste from the surrounding environment. These landfills are equipped with gas and leachate collection systems to effectively manage these byproducts. After the waste deposition is complete, a final cover is implemented [36]. The management of closed landfills involves the continuous monitoring and regulation of emissions like gas and leachate, as well as the assessment of factors such as surface water, groundwater, soil, and air quality [37]. Additionally, it is crucial to maintain a stable facility for the collection of leachate and waste gas.

The landfills are classified into different categories by the Environmental Protection Agency of the United States.

- Municipal Solid Waste Landfills (MSWLFs): Household, commercial, and nonhazardous materials are among the waste categories that are accepted at these sites. These landfills are subject to operating, closure, and post-closure care requirements, which are governed by the state in which they are located [37,38]. Closure involves implementing a final cover system to minimize liquid infiltration and soil erosion. Post-closure care aims to prevent the release of hazardous constituents by monitoring and maintaining the landfill diligently [39].
- Bioreactor landfill sites: Bioreactor landfills are a type of municipal solid waste landfill (MSWLF) that uses liquid additions to promote waste breakdown by bacteria [40]. This differs from traditional dry landfills. The introduction of liquids and air enhances microbial processes, resulting in increased waste degradation and stabilization [40]. The advantages of bioreactor landfills include accelerated waste decomposition, potential space savings (up to 30% compared to traditional landfills), and cost-effectiveness [41]. However, the increased moisture content may impact the landfill's structural stability by increasing pore water pressure [40,42]. Proper management is crucial, including liquid addition and other strategies like waste shredding, pH adjustment, nutrient balance, and temperature control. Successful operation requires focused plans to optimize bioprocesses and ensure effective functioning [42].
- Sanitary landfills: Industrial waste landfills are designated areas where nonhazardous industrial waste, including solid waste from manufacturing, is disposed of. These landfills are capable of handling substantial amounts of waste, including construction and demolition waste and hazardous waste [43]. The primary objective of industrial waste landfills is to create a controlled environment that ensures proper waste disposal and minimizes any negative impacts on the ecosystem. They adhere to engineering and sanitary landfill principles, incorporating modern design, stricter regulations, and specific operational procedures. Design specifications for these landfills include the use

of compactors, plastic coverings, double liners, gas, and leachate collection systems, as well as the monitoring of groundwater quality [44].

Hazardous Waste Landfills: Hazardous waste landfills are specifically designed facilities that prioritize the safe disposal of non-liquid hazardous waste, ensuring no chemical release into the environment [45,46]. These landfills adhere to design standards, including leak detection and collection systems, as well as measures to prevent any potential issues. Closure and post-closure care, such as maintaining a final cover, operating the leachate collection system, and monitoring groundwater quality, are also essential requirements [46,47]. It is important to note that hazardous waste landfills differ from municipal solid waste landfills, as they are subject to separate regulations [48].

Landfills are responsible for the production of methane, nitrogen dioxide, sulfur dioxide, ammonia, carbon monoxide, hydrogen sulfide odor, and particulate matter. These pollutants present a significant hazard [49]. Moreover, the constraints on available land and the recognition of waste as a valuable resource are compelling factors that drive the transition from traditional landfilling practices to more sustainable waste management strategies.

3.2. Composting

Among the various components of municipal solid waste, which encompass domestic waste, agricultural waste, yard debris, and process waste, organic waste, which encompasses domestic waste and agricultural waste materials constitutes the largest proportion of the total solid waste generated [50]. Effectively managing organic solid waste is crucial for achieving sustainable and environmentally friendly waste disposal practices [51]. Composting, as a simple technique for managing organic waste as shown in **Figure 2** [52], involves the controlled decomposition of organic matter by microorganisms such as bacteria, fungi, algae, and protozoa [53]. This process yields compost, which serves as a beneficial soil amendment [54]. The composting processes are influenced by multiple factors based on the composition of the composting mixtures and environmental conditions (temperature, oxygen content, and pH levels) [55,56].



Figure 2. Compositing process of Municipal solid waste [52] with modification.

Composting can be conducted aerobically or anaerobically, depending on oxygen availability. Aerobic composting involves the aerobic microbial oxidation of organic materials, resulting in the production of carbon dioxide, nitrite, and nitrate. Under specific aerobic conditions, biological processes regulate organic matter to generate valuable products [57]. Microorganisms reduce and break down organic molecules in anaerobic environments. The resulting product slightly oxidizes when applied to the land. Municipal solid waste composting provides a reliable source of manure for crop growth. Common aerobic composting techniques include windrow composting and vermicomposting [58]. Composting facilitates the reduction of waste volume, eliminates weeds, and kills harmful bacteria [59]. Composting municipal solid waste enhances soil nutrients, soil organic carbon (SOC), and the biomass and activity of soil microbes. Furthermore, it is essential for controlling the cycles of phosphorus (P), nitrogen (N), and carbon (C) by affecting the activity of important enzymes [60].

Despite the advantages of composting, there are several drawbacks to consider. The challenges include greenhouse gas emissions (methane and nitrogen oxide), nitrogen release as ammonia gas, and potential environmental hazards from contaminants in compost substrates [57,61]. To mitigate these issues, various approaches are being explored, such as implementing different aeration methods, using bulking agents, and optimizing the formulation of the substrate and feedstock to ensure optimal conditions for sustainable composting. The composting sector is experiencing industrialization, characterized by the expansion of operations and the production of superior-quality products. However, compost needs to adhere to specific criteria to guarantee its safety and appropriateness as a biofertilizer for soil. The focus on quality control has led to the establishment of new alliances between composters and other businesses, which encourages creativity in the creation of customized compost materials appropriate for a range of agricultural uses, such as mulching, general purpose farming, and vegetable farming. Even though industrial composting has received a lot of attention, small-scale home composting must also be acknowledged.

3.3. Anaerobic digestion

The process of anaerobic digestion, also known as bio-methanation, breaks down organic molecules in the absence of oxygen, producing methane and carbon dioxide as important byproducts (Figure 3). The resulting residue, referred to as digestate, is highly valuable and can be effectively repurposed as a potent fertilizer or enhancer for soil quality. One of the most impressive aspects of anaerobic digestion is its remarkable capacity to produce a significant quantity of methane, constituting approximately 55%–60% of the overall output. This method is particularly employed for solid waste generated by agriculture-based industries to produce fertilizer and biogas. The primary outcome of bio-methanation is biogas, which comprises 25% of CO₂, 60% of methane, and 15% of other gases like H₂S and NH₃ [62]. This biogas serves as a versatile resource, capable of being utilized as both electricity and cooking fuel. Approximately 2040 W and 2014 W of electricity can be generated from 1 m³ of biogas through anaerobic digestion [63] and bio-methanation [64] at a conversion efficiency of 35%. Several studies have suggested that the co-digestion of municipal

solid waste (MSW) with food waste can enhance biogas production [65]. Purifying biogas generated from anaerobic digestion improves its quality and makes it a viable substitute for natural gas in industrial and household applications. Anaerobic digestion is widely used for energy recovery from high-moisture municipal solid waste (MSW), particularly in developing countries, and is applied in the treatment of animal and plant waste as well as sewage [66]. Therefore, anaerobic digestion is an effective technique for energy recovery.



Figure 3. Anaerobic digestion process [67].

3.4. Incineration

The process of incinerating garbage involves burning organic materials at a high temperature to produce fly ash and bottom ash as byproducts. In contrast to biomethanation, incineration typically occurs at temperatures ranging from 800 °C to 1200 °C in the presence of air and excess oxygen. The waste undergoes multiple steps to transform it into CO₂, water, non-combustible products, and solid residues. To highlight the significance of moisture content, the first step involves removing excess water from the biomass. During the devolatilization process, the biomass is broken down to produce carbon dioxide, water vapor, hydrogen, carbon monoxide, and methane. These organic compounds can be further oxidized to generate heat, while the carbon and hydrogen components produce CO_2 and water [68]. The incineration process can effectively treat all types of waste with a high calorific value and low moisture content.

Due to limited land availability for landfilling, alternative waste disposal methods such as incineration have been adopted. Incineration helps mitigate issues such as land degradation, methane gas production, and leachate generation that are often associated with inadequate landfilling practices. It is particularly efficient in managing non-biodegradable waste with low moisture content [69]. Incineration is a valuable method for both volume reduction and energy recovery, as it can reduce waste volume by 70%–90% while capturing energy for power generation [70].

The drawback of incineration is the significant expenses associated with the technical, and operational aspects of incineration plants, particularly for lower- to middle-income countries that may struggle to afford the establishment and maintenance of such facilities [71,72]. This results in the production of poisonous gases such as NO_x and CO_2 [73]. However, there are technologies readily available to control gaseous emissions and mitigate the environmental impact caused by these gases.

3.5. Reuse and recycle approach

Solid waste management options also consist of recycling and reuse [74]. Recycling is a method of managing waste that entails gathering, treating, and converting waste materials into fresh items. Its goal is to decrease landfill waste, conserve natural resources, and mitigate environmental harm. Recycling enables the recovery and reutilization of materials like paper, plastics, glass, and metals, reducing the necessity for raw material extraction and energy consumption. This waste reduction approach not only aids in waste management but also supports the development of a sustainable and circular economy [75]. Recycle rates are often greater and more effective in developed countries than in underdeveloped ones. This is mostly because there are excellent collecting services and facilities with the necessary equipment for sorting and processing. These recycling facilities are widespread, subject to regulations, and outfitted with cutting-edge technology in industrialized countries. On the other hand, developing nations frequently lack the infrastructure necessary for garbage recycling and treatment, which leads to the open disposal of waste into the environment [76]. The recycling process is commonly carried out informally.

Reusing is a waste management strategy that involves finding new ways to use items or materials instead of throwing them away. It is a sustainable approach that aims to extend the lifespan of products and reduce the amount of waste generated. Reusing helps protect the environment, save energy, and conserve resources. Reuse can take many forms, such as repairing broken items, donating unwanted items to others, or repurposing materials for different purposes. It is a crucial tactic in the hierarchy of waste management because it fosters a more sustainable and circular economy by lowering the demand for new production and consumption [75]. Composting and vermicomposting are popular methods for reusing organic solid waste. The resulting composts and vermicomposts can be used as manure for agricultural purposes. These methods are cost-effective and well-suited for managing solid waste in developing countries, where there is a high proportion of organic waste. Developed countries have witnessed a rise in composting facilities, with certain European countries experiencing composting rates increasing by over 50% between 1995 and 2007 [77]. The implementation of these principles is beneficial in reducing waste generation from various sources, while also mitigating the associated risks to human health and the environment.

4. Solid waste materials as emerging raw materials in the polymer industry

Plastic and agricultural wastes are solid waste materials that are emerging as potential raw materials for the production of composite products in the polymer industry owing to global environmental and resource problems. According to Nassar et al. [78], the efficient utilization of solid wastes leads to the reduction of environmental degradation and waste hazards, which in turn improves the quality of the ecosystem. Meanwhile, Deka et al. [79] have stated that one of the processes to reduce environmental pollution issues is recycling and reusing. Recycling enables the various properties of recycled plastic materials to be improved by combining them

with biomass materials. Thus, taking into account the benefits of recycled plastics and agro-residues, these solid waste materials can be used to produce low-cost, sustainable, and eco-friendly composite products, as illustrated in **Figure 4**.



Figure 4. Biocomposite products from solid waste materials.

An investigation by Kazemi et al. [80] revealed that the tensile, flexural, and torsion modulus of the un-compatibilized wood plastic composites (WPCs) were higher than those of the neat polymer due to the stiffness invoked by the wood flour. However, the inclusion of wood filler led to a decrease in the tensile strength, elongation at break, and notched impact strength due to the poor interfacial interactions between the wood flour and the plastic matrix. It was further reported that the addition of compatibilizing agents led to an increase in the tensile strength even as filler loading increased, which was contrary to the case of uncompatibilized ones. The improvement in tensile strength is due to the enhanced interfacial bonding brought about by the reduction of the interfacial tension through the treatment with the compatibilizing agents, as revealed by the scanning electron micrographs (see Figures 5 and 6). Overall, the authors have demonstrated the possibility of using wood dust and municipal plastic wastes for the production of wood plastic composites.



Figure 5. Typical SEM micrographs of the recycled light fraction plastics: (a) without compatibilizer and (b) with 5 wt% of EOC. The arrows indicate typical domain sizes in SEM micrographs [80].



Figure 6. SEM micrograph of composites with 40 wt% wood flour: **(a,c)** without coupling agents and **(b,d)** with additives [5 wt% of EOC and 5 wt% (MAPE/MAPP: 80/20)] at different magnifications [80].

4.1. Agricultural residues as reinforcing agents in composite production

Biomass waste materials are unavoidably generated and are usually destined for landfills or burning, thereby constituting a significant part of the pollution problem. However, the utilization of these materials for the production of value-added products (e.g., biocomposites) can contribute to a safer environment [81] with economic benefits. Literature shows that these cheaply available bioresources are yet to be fully utilized in the research community. These biomass materials, commonly regarded as agro-residues, could potentially serve as raw materials for composite production with sustainable structural applications. Therefore, there should be a continuous effort to utilize these agricultural waste materials as fillers (either in a single or combined form) in the composite industry for the benefit of mankind.

The use of natural fillers (obtained from agro-waste) as reinforcing materials in the polymer matrix stems from the present demand for high-performance green composites [82]. Countries such as China, the USA, the UK, Europe, and other government agencies encourage the use of green composites with several natural sources [83–87]. Due to the global emergency of energy and the dangers of CO_2 emissions, there is an urgent need to develop composite materials that are sustainable and environmentally benign. This has necessitated scientists in the field of green composites to produce new materials from nature itself that allow for the reduction of the carbon emission effect [88–91] and energy demand at the lowest cost of production. As such, the use of green fillers as reinforcement materials is increasingly gaining attention as substitutes for their synthetic counterparts (e.g., glass, carbon, aramid, etc.) in composite material production. The commonly available green fillers include; agro-residue powder (cotton stalk powder, coconut shell powder, rice husks, date seed, cashew nuts powder,), bast fibers (hemp, kenaf, flax, abaca, jute, banana bark, cotton stalk bark), grass fiber (bamboo, vetiver grass, elephant grass, napier grass), and leaf fiber (sisal, pineapple) [82,92–95]. Natural plant-derived fillers, in comparison to other fillers, are generally suitable for reinforcing plastics due to their relatively high specific strength and modulus, lightweight, good biodegradability, environmental benignity, renewability, low cost, low density, and low carbon dioxide emissions, which are very desirable these days [82,86]. Thus, green product-based polymeric matrices have become the emerging innovative products and potential candidates for the replacement of synthetic composites in structural and semistructural applications like construction, aviation, and automobile industries, as well as in sporting facilities, decking, furniture, and several electronic appliances [82,85,96]. The use of lignocellulose fibres/fillers as reinforcements for plastics will continue to be an important area of research as the demand for biocomposite products is on the increase due to the numerous benefits they possess [97]. However, these natural fillers/fibers have some setbacks that limit their widespread application in the polymer composite industry [82]. These limitations include poor compatibility, poor thermal stability, hydrophilicity, low durability [85], and lower mechanical properties when compared with synthetic fibers/fillers [82]. The weak interfacial properties and poor moisture resistance of the green fillers are the results of the hydrophilicity of the biological organic materials due to the presence of hydroxyl functionalities in them [82], which are incompatible with the polymer matrix being hydrophobic. So, when the natural filler/fibre is incorporated into the polymer matrix, a poor fibre/matrix interfacial bond strength is formed due to the differences in the polarities of the biomass material and the polymer matrix [2]. Furthermore, water or moisture may easily penetrate the inside of the composites through the matrix/filler interface and affect both the short- and long-term properties of the polymer composites [82]. As a consequence, there is a high tendency for polymer-based composites to undergo degradation if used for outdoor applications [98].

Due to the drawbacks mentioned above, Nourbakhsh and Hosseinzadeh [99] suggested two possible ways of improving the mechanical integrity of filler-filled polymer-based composites, namely, by altering the filler's particle size via size reduction and by applying compatibilizing agents. These treatment approaches are discussed in detail in the published literature [2].

4.2. Plastic waste as structural matrices for natural filler/fibre in composite production

Plastics are classified into two main groups, namely, thermoplastics and thermosets [2], which are used in the manufacturing of biocomposite products. However, due to the low degradation temperature (about 220 °C) of the biomass material, thermoplastics are preferable. Elsheikh et al. [11] suggested that to avoid the disintegration of the cellulose chains of the natural filler/fibre, the processing temperature of the plastic materials should not exceed 200 °C. Examples of such polymers include high-density polyethylene (HDPE), polypropylene (PP), polyvinyl chloride (PVC), acrylonitrile butadiene styrene (ABS), polystyrene (PS), and low-density polyethylene (LDPE). The waste materials of these plastic products, which

contribute to a significant volume of municipal solid waste, can be used as structural matrices in composite manufacturing when sorted and recycled. These plastic wastes, when recycled and reused can offer cost and environmental benefits as well as resource sustainability. Singh et al. [100] stated in their report on recycling plastic solid waste that the production of virgin plastics is energy-demanding and has the capacity to eliminate fossil fuels. Similarly, Kreiger et al. [101] reported that the annual production of virgin plastics (in the form of stored potential energy) requires about 1.3 billion barrels of crude oil, which is estimated to be 4% of the world's oil production. Also, it was noted in the published work [100] that plastics, which constitute a major part of MSW, are increasing daily as new plastic products emerge in the market. This poses a threat to the environment with the consequence of releasing CH_4 and CO_2 (i.e., greenhouse gases). Nevertheless, several environmental advantages can be obtained by using recycled plastic in the production of composite materials, including an extension of the plastic's service life, a reduction in waste, the avoidance of resource depletion, and a contribution to the advancement of waste recycling [8]. Thus, the utilization of recycled plastic waste as a matrix in natural particulate-reinforced polymer composites is a good way to obtain economic and environmental benefits.

The feasibility of using municipal plastic waste materials for the production of low-cost composite products is reported in the literature. For example, Turku et al. [102] investigated the possibility of using recycled plastic waste in the fabrication of wood plastic composites (WPCs). It was reported that the strength of the composites containing recycled plastic waste was inferior to that of the virgin composites. However, the stiffness of the recycled composites was superior to that of the reference. In another study, it was reported that recycled blends of low-density polyethylene (LDPE) and polypropylene (PP) exhibit tensile properties similar to their virgin counterparts, with PP giving more rigidity to the blend and acting as reinforcement in the LDPE matrix [103]. A research study carried out by Schürmann et al. [104] revealed that the impact strength of the blends of high-density polyethylene (HDPE) and isotactic polypropylene (ipp) in a mixing ratio of 60:40 wt% doubled that of pure ipp.

5. Nanoclay as a component of hybrid nanocomposite material

Nanoclays play an essential role in the improvement of the mechanical, thermal, and barrier properties of hybrid nanocomposite materials. The size, shape, filler loading, as well as compatibility with the polymer matrix, are the critical factors that determine the reinforcement property of nanoclay in hybrid nanocomposite products [105]. Therefore, the aforementioned factors should be optimized to obtain maximum performance of the resulting nanomaterials. The feasibility of using nanoclay as a reinforcement for the enhancement of the performance properties of the developed hybrid material is reported [4,6,106]. In the report of Zhong et al. [6], it was stated that a small quantity of nanoclay of approximately 5 wt% is sufficient to greatly improve the performance of the resulting nanocomposite products without affecting the processability and density. Detailed information on nanoclay exists in published reviews [2,105].

6. Fabrication technologies

The use of organic particulate fillers as replacements for their inorganic counterparts is gradually gaining momentum in the scientific community due to their economic and environmental benefits [2]. The performance of the resulting composite products is influenced by the component elements and processing techniques employed. The selection of the type of fabrication technology to be used will be a decision based on a careful evaluation of the various manufacturing methods.

6.1. Adhesive mechanism between the plastics and fillers during the fabrication process

The fabrication process can be defined as the process of manufacturing composite materials by reinforcing polymeric matrices with fillers. The formation of composite products is made possible because, during the manufacturing process, heat is generated, which melts the thermoplastic [2] to become fluidized and then wets the filler particle surfaces [107]. Following wetting, the polymer will spread over the particle surface to form a continuous phase and consolidate. Upon conditioning, good adhesive bond strength at the interface between the polymer and the filler particles is realized.

6.2. Types of processing techniques

There are several processing methods employed in the fabrication of natural particulate hybrid nanocomposite products. These include powder impregnation through compression molding, extrusion followed by injection molding, extrusion followed by compression molding, and solution blending. The various processing technologies and their merits and demerits are herein discussed.

6.2.1. Extrusion followed by injection molding

This method involves two stages, namely, extrusion and injection molding. In the first stage, both the filler and the plastic materials are fed into the hopper of the extrusion machine (e.g., a twin screw extruder) and then pass to the heating barrel, where the melting of the polymer occurs. Upon melting, the plastic material will become fluidized and then wet the filler (e.g., wood waste) particle surfaces. Following wetting, the polymer will spread over the particle surfaces through the mixing occurring in the extruder. After spreading, the polymer will penetrate the porous structure of the filler particles [107] to form a blend that is extruded through the die as extrudates in the form of strands. These strands are then passed through a water bath or air cooling unit. Upon cooling, the interfacial bond strength between the fibre/matrix brought about by mechanical interlocking is strengthened. The cooled strands are then pelletized to form composite granules. The second stage involves the use of an injection molding machine. Injection molding of composite products is a manufacturing process by which a known quantity of mixture that contains molten polymer and fibre/filler is forced into mold cavities [12]. Before injection molding, it is always advisable to dry the composite granules to remove any moisture that might interfere with the mechanical properties of the resulting composite products. So, the dried granules are fed into the hopper of the injection molding machine. Upon reaching the heating barrel, the plastic component will melt and mix sufficiently with the filler by the shear forces of the machine and consolidate. The blend of the mixture will be injected through the mold in the form of a dumbbell shape as an injection molded sample for mechanical testing. According to Liu et al. [9], injection molding will promote good dispersion of the filler particles in the polymer matrix, thereby leading to improvements in the tensile and flexural properties. Mohanty et al. [108] stated that the intimate mixing of fibre/filler and matrix, which promotes interfacial adhesion during the extrusion-injection molding process, is one of the major advantages of the technique. However, the shear forces of the machine can damage fibres with long lengths. Therefore, this method is suitable for the manufacturing of natural particulate filler-reinforced polymer composites.

6.2.2. Extrusion followed by compression molding

This manufacturing process also involves two stages, namely, extrusion and compression molding. The first stage is the extrusion process, which has already been discussed above. The second stage is the formation of composite panels from the resulting granules with the aid of an electrically heated platen press, which was conditioned before mechanical testing. During compression molding, it is believed that the plastic will undergo melting and wet the filler. The plastic will consolidate upon cooling, forming a protective covering for the filler in the composite system. The disadvantage of compression molding is that there is no proper mixing of the filler and matrix. Consequently, hollow features are formed on the developed composite product. During mechanical testing, these voids and holes act as stress concentrations, resulting in poor mechanical properties. According to Ho et al. [12], various minor defects such as residual stress, warpage, voids, fibre breakage, scorching, and sink marks could lead to a reduction in the mechanical performance of the composite material. Thus, to reduce the possibility of flaws appearing, material, process, and geometric parameters should be optimized.

Liu et al. [9] in their work on thermal and mechanical properties of kenaf fiber reinforced biocomposites based on injection and compression molding after extrusion revealed that samples prepared by compression molding after extrusion had the same storage modulus as those of injection molded samples at room temperature (i.e., 25 °C). However, higher heat of deflection temperature (HDT) and superior notched impact strength were observed with compression molded samples.

6.2.3. Solution blending

In this manufacturing process, a suitable solvent that can dissolve the plastic material and cause the swelling of clay is used, and a homogeneous three-component mixture of an appropriate composition is produced with the aid of heating and mechanical and/or ultrasonic stirring. Then polymer/clay composites are obtained by removing the solvent either by precipitation or evaporation [109,110]. The main disadvantage of this method is that it uses solvents that are not environmentally friendly [79]. However, recovering and reusing such solvents is a good approach to remedying the environmental impact. Several researchers [79,109,110] have demonstrated the feasibility of using solution blending in their investigations.

6.2.4. Powder impregnation through compression molding

In this manufacturing process, natural fibres/fillers are mechanically mixed with cellulosic plastic and liquid plasticizer to form biocomposite products. Mohanty et al. [108] investigated the mechanical performance of composites made from cellulosic acetate plastics and chopped hemp natural fibre. The biocomposites were fabricated using two different approaches, namely, extrusion followed by injection molding and powder impregnation through compression molding. It was reported that biocomposite products fabricated through extrusion followed by injection molding exhibited better flexural strength and modulus properties than those made by powder impregnation through compression molding. The better performance obtained is due to the sufficient shear forces for the intimate mixing of the composite elements. This is contrary to the report of Liu et al. [9], who reported the modulus did not change for both compression and injection molded samples. Due to this discrepancy, further research work is needed to provide more evidence for researchers in this field. Such studies are ongoing in our laboratory and will be published soon.

7. Applications of natural particulate hybrid nanocomposites

As a class of structural and infrastructural materials, particulate-reinforced composite materials have received wider engineering applications due to their sustainability, ease of preparation, cost, and environmental benefits [2,111,112]. Higher stiffness can be provided by particle fillers due to their large surface area, which is available for effective interactions compared to their fibre counterparts. Natural particulate-filled hybrid nanocomposites have found applications in various sectors, including building, construction, and automobiles [2].

8. Conclusion/future perspective

Plastic waste and agro-residues have been identified as major sources of municipal solid waste in the world today, which requires urgent management attention. The recycling and reuse of these waste materials in the polymer industry is a good management approach that offers economic and environmental benefits. However, compared to the huge amount of waste generated, only a small amount finds its way into the polymer industry, while the majority is either burnt or destined for landfill. Therefore, efforts should be intensified for the full utilization of these waste materials in the engineering fraternity.

Various processing techniques for biocomposite material manufacturing appear in the literature. However, this study has identified extrusion followed by injection molding as the best manufacturing method that could be used to obtain good mechanical performance in natural particulate hybrid nanocomposites due to its ability to promote good interfacial bonding through adequate wetting and mixing as well as good consolidation. The study also identified that a limited amount of research on the mechanical performance of natural particulate hybrid materials based on processing techniques is available. Therefore, more research studies are needed in this area, as we cannot use the research on fibre-reinforced composites based on manufacturing techniques to account for particulate-reinforced composites. This is because the length of the fibre in the injection molding machine is always affected by the shear forces of the instrument; hence, compression molding is preferable. However, this is not the case with particulate fillers.

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Abbreviations

Acrylonitrile butadiene styrene = ABS Greenhouse gases = GHGs High-density polyethylene = HDPE Low-density polyethylene = LDPE Montmorillonite = MMT Municipal solid waste = MSW Municipal Solid Waste Landfills = MSWLFs OFMSW = Organic food Municipal Solid Waste Landfills Polypropylene = PP Polyvinyl chloride = PVC Polystyrene = PS Soil organic carbon= SOC Wood plastic composites = WPCs

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Review

Zein—A plant protein as a promising biopolymer for biomedical applications: A perspective

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Copyright © 2024 by author(s). Journal of Polymer Science and Engineering is published by EnPress Publisher, LLC. This work is licensed under the Creative Commons Attribution (CC BY) license. https://creativecommons.org/licenses/ by/4.0/ **Abstract:** Recent technological advances in the fields of biomaterials and tissue engineering have spurred interest in biopolymers for various biomedical applications. The advantage of biopolymers is their favorable characteristics for these applications, among which proteins are of particular importance. Proteins are explored widely for 3D bioprinting and tissue engineering applications, wound healing, drug delivery systems, implants, etc., and the proteins mainly available include collagen, gelatin, albumin, zein, etc. Zein is a plant protein abundantly present in corn endosperm, and it is about 80% of total corn protein. It is a highly renewable source, and zein has been reported to be applicable in different industrial applications. Lately, it has gained attention in biomedical applications. This research interest in zein is on account of its biocompatibility, non-toxicity, and certain unique physico-chemical properties. Zein comes under the GRAS category and is considered safe for biomedical applications. The hydrophobic nature of this protein gives it an added advantage and has wider applications in drug delivery. This review focuses on details about zein protein, its properties, and potential applications in biomedical sectors.

Keywords: zein; drug delivery; nanoparticles; tissue engineering; wound healing; biopolymers

1. Introduction

The emergence of biopolymers has prompted a wave of exploration into the development of biomaterials possessing an array of characteristics that find value across a broad spectrum of biomedical applications. Notably, the biomaterials sector has witnessed significant advancement as these fabricated materials, with their diverse attributes, have contributed to progress in the medical and healthcare industries [1]. Biopolymers are employed in a wide range of applications, such as gels used to maintain moisture in eye drops or as laxatives for flexible scaffolds used for replacing different tissues, rigid materials that are required for support structures, and so on [2]. Furthermore, a variety of synthetic and natural polymers have been utilized in biomedical applications, such as surgical meshes, hard contact lenses, heart valves, enteric pharmaceutical coatings, drug encapsulation, wound dressings, and bone tissue regeneration, among others [3].

Protein-based polymers are being explored on a growing basis for use in biomedical applications owing to their superior processability, biocompatibility, and biodegradability [4]. Proteins are preferred over carbohydrates because they contain a variety of functional groups, such as carboxyl and amino groups, which can be exploited for labeling targeting molecules of interest or facilitate rapid and stable crosslinking during the development of three-dimensional scaffolds. Furthermore, proteins possess an adaptable framework that allows them to easily and dynamically interact with lipids and carbohydrates, thanks to their amphipathic nature [5].

Zein is a biodegradable plant protein obtained from maize (*Zea mays*), an abundant and sustainable agricultural source [6]. Zein is a class of prolamin-rich alcohol-soluble protein that forms the major storage protein in the endosperm of corn, comprising almost 80% of the whole protein content of corn [7,8]. Considering that the corn market is massively widespread on a global scale, accounting for an annual production of over 1 billion tons, zein becomes readily available in the environment as organic waste [6]. Zein was previously thought of as more of a byproduct of the corn processing industries; general agreement suggested that zein was a low-value material with few practical technological applications. However, nowadays, there is a new perspective towards zein and zein-based materials, considering them as more valuable materials due to several recent technologies and developing processes allowing zein's applications in different sectors [7].

Zein is currently drawing research interest on account of its unique properties, such as biocompatibility, resistance to heat, water, abrasion, and humidity. It can be readily processed and can be applied to create films, sheets, microspheres, nanoparticles (NPs), and nanofibers, among others [4,8]. Zein has the potential to be used to generate biodegradable chewing gum, fibres, adhesives, coatings, ceramics, inks, cosmetics, and textiles. Zein finds applications in biomedical as well as pharmaceutical sectors. Zein-based biodegradable materials are most effectively employed in the food and pharmaceutical industries [7]. Moreover, zein was approved as a Generally Recognized as Safe (GRAS) excipient in 1985 by the United States Food and Drug Administration (USFDA, 21CFR184.1984) for application in the film coating of pharmaceuticals [6,8].

To improve the mechanical, physical, and biological properties of zein-based biomaterials, a number of chemical modifications, including plasticizing and crosslinking, as well as combinations with other materials, including biopolymers and inorganic materials, are being investigated. Inorganic fillers, like bioactive ceramics, glasses, and clays, are promising substances being combined with zein and zein-based biopolymers. Through this composite approach, zein can attain antibacterial, antioxidant, and anti-inflammatory functionalities [4]. Furthermore, zein protein can increase the possibility that the biomolecules will endure a longer shelf life. Zein is therefore regarded as a novel material that holds tremendous potential for advanced biomedical applications like tissue engineering, delivery systems, and wound healing. Numerous biomedical domains take advantage of zein, and research on its various characteristics is nowadays extensively prolific [8].

In this review, we attempt to highlight and describe general aspects of biomaterials and their contribution to biomedical research, focusing mainly on biopolymers, updating information concerning the source, structure, and general properties of zein, and potential applications of zein and zein-based materials in the fields of drug delivery, tissue engineering, and wound care.

2. Biomaterials and biomedical applications

A biomaterial is any material, synthetic or natural, that can be applied in medical

applications to carry out a bodily function or replace a tissue or body part. In 1987, the European Society for Biomaterials defined "biomaterial" as a non-biological material used in a medical device with the objective of interacting with biological systems [9]. Different biomaterials are designed based on their intended applications. It may be used as a potential carrier system for drugs or bioactive molecules, or it can act as a support matrix, providing a suitable microenvironment for cell growth and survival, etc. [10]. A biomaterial must be biocompatible, which means it should be friendly with the biological system without causing adverse effects on the cellular or system level [11].

2.1. Types of biomaterials and their biomedical applications

Broadly, biomaterials can be grouped into four major categories: i) metals; ii) ceramics; iii) composites; iv) and polymers [11].

2.1.1. Metals

Intrinsic properties of metals such as high mechanical strength, reliability, corrosion and wear resistance, toughness, elasticity, and thermal and electrical conductivity make them ideal for biomedical applications. The first successful implants were made of stainless steel and chromium alloys [12].

Pure titanium and titanium-aluminium-vanadium alloys (Ti-6al-4V) find application in dental implants, bolts and column slips, pacemaker housings, artificial heart valves, screws, and bone fixation staples as part of knee, hip, shoulder, elbow, and wrist joints. Chromium-cobalt alloys are also used in dental applications, artificial joints, and implants [13]. Gold is widely used in wiring for pacemakers, dental crowns, and other stomatological applications. Silver is used to treat burns, coat surgical instruments, in stethoscope diaphragms, in fibers used for wrapping wounds to prevent infections, etc. Platinum is incorporated as electrodes in pacemakers for stabilizing cardiac rhythm and in hearing aids. Metal alloys with memory capacity are used in orthopedic and orthodontic applications [9].

2.1.2. Ceramics

Ceramics exhibit properties such as resistance to wear, corrosion, and compression biocompatibility, low thermal and electrical conductivity, shinier surfaces, hardness, brittleness with minimum deformation, and greater density as compared to metals [9,10,14]. Ceramics are mainly used in the repair, regeneration, and augmentation of hard tissue, in particular in non-load-bearing applications or as metal implant coatings [11].

Alumina is employed in wear surfaces in joint prostheses such as the acetabulum and femoral heads in hip arthroplasty [9]. Polycrystalline tetragonal zirconia is used in prosthetic equipment, mainly in femoral heads [15]. Ceramic hydroxyapatite is ideal for application in dental implants, knee and hip replacement, polymeric prostheses, or metal coatings, as it releases calcium and phosphate ions into the body [9].

Carbon-derived materials such as carbon nanotubes, graphene, fullerene, quantum dots, non-crystalline diamond films, carbon nanofibers, etc. are promising materials for cancer diagnosis, bioimaging purposes, etc. [10]. Graphene and its associated materials are employed in biosensors, cancer therapy, imaging, tissue engineering applications, etc. [9].

2.1.3. Composites

A composite material is a heterogeneous material formed from the combination of two or more materials with different characteristics, with the aim of developing a novel material possessing properties superior to those of its individual materials [9]. For example, a combination of polymer and carbon fibre (like carbon-fiber-reinforced polyetheretherketone) is used in the development of screws for orthopedic purposes [10]. Ceramic microparticle polymer composites with polymers and bioactive glass as individual components have been applied in the orthopedic regeneration of tissue [16,17]. Hydroxyapatite/zirconia promotes the mechanical properties of HA, maintaining the properties of adhesion to bone tissue [18].

One of the recently emerged nanocomposite biomaterials is nanocomposite hydrogel. They can be developed as promising scaffolds due to their tailorable properties, and they closely mimic the ECM environment, thus providing a hydrated three-dimensional network. This network of nanocomposite hydrogels supports the transport of nutrients and promotes cell growth and maturation. The ability to selfheal in response to mechanical abrasion is one of the important features of nanocomposite hydrogels [19].

2.1.4. Polymers

Polymers, or polymeric biomaterials, are extensively used in biomedical uses such as cardiovascular, neural, and dermal tissues [10]. The biocompatibility of polymers depends on their chemical composition, molecular weight, solubility, geometry, water or liquid absorption, erosion or degradation processes, etc. [9]. Polymeric biomaterials can be degradable or non-degradable, synthetic or natural, or a combination of both [20].

Polymers can be classified into two categories: natural polymers and synthetic polymers. Natural polymers comprise proteins, polysaccharides, decellularized matrices of tissues, etc., and synthetic polymers include polyethylene, polyurethane, polyamide, polytetrafluoroethylene, polymethylmethacrylate, synthetic rubber, polystyrene, etc. An advantage of natural polymers over synthetic polymers is their non-toxic properties for our bodies [9,10].

Synthetic polymers such as PTFE have been employed in vascular graft applications as soft tissue fillers; PVC is used in tubes, blood bags, and catheters; silicon is used in ophthalmological aids; and encapsulation is formed in breast implants, Polymethyl methacrylate finds uses in orthopedic applications such as bone cement and ophthalmological applications such as contact lenses and intraocular lenses. Polyamides or nylon are used in suture lines, and a combination of nylon and polyurethane is used in balloons or catheters in angioplasty. Polyurethane is used as a coating in breast implants, aortic balloons, gastric balloons, male contraceptives, surgical gloves, etc. Ultra-high molecular weight polyethylene (UHMWPE) is used on sliding surfaces of artificial joints, surgical cables in bone fracture, high-strength orthopedic sutures for repair of soft tissues, catheters, stent-grafts, heart valves, and disc replacement for spinal issues [9].

3. Biopolymers as biomaterials

Biopolymers are a class of polymers that are produced by living organisms. They are also called polymeric biomolecules [21]. Natural polymers are non-toxic, biocompatible, biodegradable, and readily available from renewable sources such as plants, animals, microorganisms, etc. [9]. They possess properties such as low antigenicity, high bioactivity, providing support for cell growth and proliferation, appropriate mechanical strength, and processability for complicated shapes with sufficient porosity. Biopolymers can be classified based on different criteria. They can be classified based on the monomeric units present in them. These include polynucleotides (made up of nucleotide polymers like DNA or RNA), polypeptides (made up of short polymers of aminoacids), and polysaccharides (made up of different bonded monosaccharides). Biopolymers can be classified based on their origin or source of isolation. Polysaccharides of bacterial origin include xanthan, dextran, gellan, polygalactosamine, cellulose, etc. Fungal-based polysaccharides include pullulan, elsinan, yeast glucans, etc. Biopolymers such as starch, cellulose, agar, alginate, carrageenan, and pectin fall under plant or algal polysaccharides. Polysaccharides of animal origin are chitin and hyaluronic acid. Lignin, tannin, and humic acid are a category of polyphenols [21].

3.1. Polysaccharides

Biopolymers provide a plethora of applications in the biomedical sector. It includes drug delivery systems, wound dressings, tissue engineering, etc. [21]. Polysaccharide biopolymers that are employed in the biomedical sector include cellulose, chitosan, xylan, alginate, carrageenan, pectin, hyaluronic acid, etc. [9]. Cellulose is the most predominant polysaccharide found in nature. They are the main constituents of plants, and some bacteria, such as *Acetobacter xylinum*, can synthesize cellulose. Cellulose ether is used in solid tablets, enabling the swelling-driven release of the drug in the body [21].

Chitosan, a derivative of chitin, is present in the exoskeletons of crustaceans and insects [22]. Chitosan exhibits excellent biocompatibility, high bioactivity, biodegradability, selective permeability, polyelectrolyte action, antimicrobial and anti-inflammatory activity, gel and film formation, chelation, and adsorptive capacity, due to which it can be developed as a carrier for controlled release of the drug, promote osteogenesis, healing of lesions and ulcers, etc. [23]. A hydrogel sheet made up of powdered alginate, chitin, chitosan, and fucoidan is developed as a functional wound dressing to create a moist environment for rapid wound healing [24]. The chitosan/hydroxyapatite composite shows promise to mimic the organic portion as well as an inorganic component of bones. Chitosan gel is used in the prevention and treatment of dental caries [21].

Xylan, a hemicellulose, is a suitable biopolymer for developing drug delivery systems for the colon, as it gets degraded by colonic microflora enzymes. Pentosan polysulfate, a glucoxylan derivative anti-coagulant in gel form, can be applied in the treatment of infusion thrombophlebitis [25]. Alginate, a hydrocolloid polysaccharide extracted from sea weed, is used as a support matrix or delivery system for tissue repair and regeneration. Alginate is a US-FDA-approved polymer and finds application in

nutrition supplements. They are employed in making tooth impressions in dental clinics. Sodium and calcium-incorporated alginate-based wound dressings provide a moist environment at the wound bed, absorb the exudate, relieve wound pain, reduce the bio-burden around it, absorb proteinases, reduce odor, and help achieve hemostasis and wound closure. Wound dressings based on alginate formed as hydrogel, electrospun mats, or sponges have gel forming ability upon absorption of wound exudates and hemostatic ability. Moreover, alginate is used as a carrier to immobilize or encapsulate drugs [21].

Carrageenan is a polysaccharide present in seaweeds belonging to the class Rhodophyceae. It exhibits anticoagulant activity by inhibiting thrombin. They are also a potential substitute for gelatin in hard and soft gel capsules. Its addition to the glycerin-water mixture reduces the chalkiness of antacid gels. It is used in suppository or topical bases. It acts as a thickening agent and binder in dentifrices [21]. Pectin, is a heteropolysaccharide present in the primary cell wall of plants. Pectin in combination with Carbopol and chitosan, is employed in making mucoadhesive patches. It acts as a prophylactic substance against poisoning with cations, which are toxic. Pectin-based hydrogels have been used in tablet formulations as agents for binding and carrier material in colon-specific drug delivery systems. Hyaluronic acid is a biocompatible mucoadhesive polysaccharide with a negative charge. In the late 1950s, it was applied as a substitute for the vitreous humor of the eye during eye surgery [26]. Other applications include wound healing, epithelial regeneration, treatment of dry eye and Sjogren syndrome, osteoarthritic problems, preventing bacterial adhesion in dental implants, intraocular lenses, and catheters, etc. [27].

Gum Arabic is an edible gummy exudate from the stems and branches of the plant *Acacia Senegal*. Studies reported that gum Arabic could prevent the formation of dental plaque and improve tooth remineralization. These properties are due to the high content of Ca²⁺, Mg²⁺, and K⁺ salts [28]. Xanthan gum is a bacterial polysaccharide widely used in tooth pastes and cosmetics. The addition of xanthan gum to emulsions or suspensions of pharmaceutical formulations prevents the separation of insoluble components [29].

3.2. Proteins

Protein-based biopolymers applied in biomedical applications include collagen, gelatin, zein, etc. Collagen film/sheet/disc is used for the treatment of corneal tissue or liver cancer. A collagen-based soluble ophthalmic insert in the form of film or wafer was developed as a drug delivery system for the delivery of antibiotics such as gentamicin to treat corneal tissue infection. A collagen film matrix is employed as a gene delivery system for bone formation. Collagen-based wound dressings in the form of sponges, membrane sheets, and powder are used to manage severe burns. Nanoparticles based on collagen find use in sustained-release formulations for antimicrobial agents or steroids [30]. Gelatin, formed by partial hydrolysis of collagen, is used as a forming, emulsifying, and wetting agent in pharmaceutical applications due to its surface active properties [31]. Zein is another biopolymer abundantly present in nature. Its source is corn, and it comprises about 80% of total corn protein. Zein has been reported to be applicable in different biomedical applications such as drug

delivery, tissue engineering, wound healing materials, etc. This can be attributed to its unique properties such as hydrophobicity, biocompatibility, film formation properties, glossy, tough, and greaseproof nature, and water vapour permeability [7]. This review focuses on details about zein protein, its properties, and potential applications in the biomedical sector.

4. Zein

4.1. Zein—Source, structure and properties

Since the early twentieth century, zein has been investigated as a potential raw material for polymer applications. John Gorham first characterized zein from maize (*Zea mays*) in 1821 and named it 'zeine'. Gorham described zein as a soft, ductile, tenacious, and elastic protein resembling bees' wax. It resembled resin and possessed some of the qualities of wheat gluten. Ritthausen coined the term 'maize fibrin' to describe the same material. Chittenden and Osborne classified zein as a prolamine, as it is now [32]. Zein is abundant in maize and accounts for 44% to 79% of the endosperm content [33].

Unlike corn gluten, zein is not widely produced on a large scale, due to the high cost of the conventional extraction process [7]. The conventional process involves extraction in an aqueous alcohol solution and then clarification by centrifugation, followed by chilling to precipitate out zein. The composition, with respect to the relative proportion of different fractions of zein and the fine structure of zein, is affected by raw material, solvent type, method of extraction and purification, concentration, temperature of alkali or other reducing agent used, drying method, etc. [34–36].

Zein is commercially available in two forms: yellow zein and white zein [37]. Yellow zein has a purity range of 88%–90%. It carries a high concentration of xanthophyll with lutein, zeaxanthin, and β -cryptoxanthin [38]. The presence of xanthophyll bound to zein has a significant impact on the solubility of zein and is responsible for the large particle size distribution and low drug encapsulation in the zein matrix during nanoparticle formation. On the other hand, white zein has a purity of more than 96%. It is obtained from the decolourization of yellow zein and has negligible xanthophyll content [39].

Zein is found in whole maize as a heterogeneous mixture of aggregates linked by disulfides, with an average molecular weight of 44 kDa. Zein truly represents a combination of distinct peptides that have differing molecular sizes, charges, and solubility. Zein is classified into four types based on its molecular weight and solubility: α -zein, β -zein, γ -zein, and δ -zein. With a molecular weight of 19–22 kDa and soluble in 70%–95% aqueous ethanol solution, α -zein accounts for 35% of total zein content as well as 80% of prolamine content. β -zein is made up of α -zein linked by disulphide bonds, so its molecular weight is higher. In reducing SDS PAGE studies, β -zein displayed 3 distinct bands of 14 kDa, 22 kDa, and 24 kDa. It is soluble in 60% ethanol and insoluble in 95% ethanol [40,41]. β -zein has a high content of methionine. δ zein is the minor fraction with 10 kDa. The solubility of β -zein and δ -zein is comparable with that of α -zein. The γ -zein consists of two parts: 27 kDa and 18 kDa [37]. More than 50% of zeins' amino acid residues are hydrophobic—20% leucine,

9%–10% proline, and 10%–14% alanine. It also possesses 21%–26% of glutamine, a hydrophilic amino acid [7,40,41].

Various models to interpret the tertiary structure of α -zein have been proposed, including the cylinder model, ribbon-like model, hairpin model, super helical structural model, etc. [42]. Argos et al. [43] proposed the molecular structure of zein to be a helical wheel conformation, in which the protein is believed to possess nine homologous consecutive units stacked in an anti-parallel manner, stabilized by hydrogen bonds, and exhibit asymmetric geometry. According to the circular dichroism and optical rotatory dispersion measurements, the helical content of zein ranges between 50%–60% in 80% ethanol [43–45]. The α and β zeins are present almost in the same proportion. Zein takes on a globular structure in non-aqueous solutions with conformational properties comparable to those of other globular proteins like insulin and ribonuclease [45]. The primary structure of each zein molecule consists of 20 amino acid units that are repeated nine times. Physical characteristic analysis (hydration potential, polarity, turn, and helix formation tendency) reveals that the amino acid sequence, including the repeat fragments, is made up of α -helixes with turn areas on both sides [42].

The helix comprises several polar amino acids as well as numerous hydrophobic amino acid residues, whereas the turn regions are rich in glutamine. The van der Waals force and intra- and intermolecular hydrogen bonds tend to stabilize this structure. The glutamine-rich turns are present between the helix and the cylindrical cap, assisting the intermolecular stacking into a plane by the interaction between side chains [43]. On the contrary, Matsushima et al. [44] modified the model proposed by Argos et al. on the basis of small angle X-ray scattering studies and proposed that reduced α -zein exists as asymmetric particles of length 13 nm with an elongated prism-like molecular structure with an axial ratio of 6:1 [44].

This ribbon-like model of zein defines it to be 9–10 topologically antiparallel homologous helices, clustered and arranged adjacently to form a slender rectangular prism-like structure possessing an edge length of 13 nm, 3 nm, and 1.2 nm and an axial ratio of 6:1. The side chain residues in the helices accumulate into the hydrophobic exterior as a result of intermolecular hydrophobic aggregation. Thus forms the zein structure of considerable stability with both hydrophilic and hydrophobic sides. The two-dimensional ribbon-like model of zein is extensively used to demonstrate various orientations of zein molecules on hydrophilic and hydrophobic surfaces and their self-assembly from single molecules to nanoparticles [42,44].

Furthermore, the hairpin model of zein is primarily based on nuclear magnetism resonance (NMR), small angle X-ray diffraction (SAXS), and Fourier transform infrared spectroscopy (FTIR). According to this model, zein is made up of a succession of helix configurations. Unlike the previous two models, these helix structures are connected and stretched in the shape of rings, sheets, or loops, allowing zein to fold or expand in diverse ways in different solvent systems. At the same time, it is assumed to be related to zein's fibrillation ability [46]. Regardless of disparities in the molecular models of zein, it is widely assumed that zein exhibits a slender confirmation formed by a large number of alpha-helical structures [42].

The characterization of α -zein by FTIR is well-studied. The amide A band between 2800 cm⁻¹ and 3500 cm⁻¹ corresponds to N-H stretch and O-H stretch in

amino acid residues. The carbonyl, C=O stretch of amide groups appears at 1650 cm⁻¹ and is referred to as amide I. The band at 1540 cm⁻¹ is named amide II and corresponds to the angular deformation vibration of the N-H bond, whereas the band at 1230 cm⁻¹ defines the axial deformation vibrations of the C-N bond [47,48].

Different factors affect the 3-dimensional structure of zein, particularly the solvent type. The somewhat larger sizes of α -zein in acetic acid, 70%, and 80% ethanol aqueous solutions imply that the α -zein structure is locally unfolded in these solutions when compared to the folded structure model. The circular dichroism data reveal that the secondary structure of α -zein does not change much in acetic acid or in 70% and 80% ethanol aqueous solutions, which might possibly be due to local unfolding occurring largely in the coil area. The size of α -zein in acetic acid is bigger than in ethanol aqueous solutions, showing that the degree of α -zein expansion and swelling is greater in the presence of acid. The conformation and dissolution behavior of alpha-zein vary with the nature of the solvent. This may be attributed to three main causes. The dissolution behavior of α -zein is closely related to the solvent polarity, hydrophilicity/hydrophobicity of the protein surface, its protonation, etc. [49].

Zein behaves as an amphiphilic protein but also displays a hydrophobic nature [40]. Therefore, zein is soluble in ethanol, acetone, or acetylacetone and insoluble in water. This characteristic property is due to the presence of more hydrophobic nonpolar amino acids than polar hydrophilic amino acids. The existence of numerous uncharged amino acid residues also reinforces this property. Studies showed that zein is approximately 50 times more hydrophobic than albumin and fibrinogen [40]. Although zein is insoluble in water, it becomes soluble in the presence of alcohol, a high concentration of urea, reducing agents, anionic surfactants, or a pH above 11 [37]. The presence of the following functional groups determines zein's solubility and chemical reactivity: amines, amides, hydroxyls, carboxylates, and phenols. Because of the presence of such various types of groups, zein can be physically and chemically transformed to enhance its functional qualities. The addition/grafting of groups with adequate hydrophilicity may be applied to control zeins' hydrophilicity/hydrophobicity. Chemicals such as formaldehyde, glutaraldehyde, citric acid, and others may trigger cross-linking between zein molecules [32].

Despite zein's poor water solubility, low nutritional value, and unequal amino acid composition, its unique solubility allows it to self-assemble into micro- or nanoparticles. In this context, zein serves as an excellent carrier for hydrophobic bioactive molecules. Moreover, it is less digestible than other proteins, which makes it suitable as an oral delivery carrier [50]. As the isoelectric point of zein is 6.2, colloidal systems prepared at neutral pH or in PBS pH 7.4 tend to aggregate and display a large size distribution. This can be overcome by the addition of a moderate concentration of stabilizers or surfactants such as casein, lecithin, tween 20, and polyvinylpyrrolidone, thus altering the surface charge of the preparation medium and facilitating the formation of more stable zein micro- or nanoparticle dispersion [37,51].

Zein has grease-proof properties and low water vapor permeability. Zein is a completely amorphous polymer with plasticizing viscoelasticity and a glass transition temperature (Tg) of about 165 °C, although its Tg decreases significantly with increasing degree of plasticization. Zein exhibits a thermal degradation temperature of

320 °C, a degree of polymerization of 210–245, and a partial specific volume of 0.771 [48].

Zein finds application in various industries. Zein films appear tough with glossy surfaces, and so they find application in the food and pharmaceutical industries. Zein is modified for the delivery of drugs and vaccines owing to its mucoadhesiveness and ability to withstand gastric conditions. The brick-like structure of the protein offers adequate space for drug entrapment [37]. The gel-forming capacity of zein, with or without other polymers, has been exploited for the delivery of active biomolecules. In recent years, zein has attracted the attention of the pharmaceutical sector due to its important qualities, such as its natural renewable origin, biodegradability, non-toxicity, and biocompatibility [33]. **Figure 1** depicts the biomedical applications of zein.



Figure 1. Schematic diagram of different biomedical applications of zein.

4.2. Zein-based drug delivery systems

Drugs are compounds used to prevent, control, and treat diseases. Drug delivery systems (DDS) have several advantages over conventional drug delivery methods and have now reached the third generation of DDS. With DDS, therapeutic efficacy is increased significantly, and there are advances in developing potential drugs with the help of bioinformatics. Even with the use of technological advances, there are still limitations in terms of solubility, stability, toxicity, and bioavailability. Scientists have been motivated by this situation to come up with technologies for enhancing therapeutic efficiency by developing novel carriers that release the molecule at a regulated pace while posing minimal toxicity. Among the widely explored new carriers, the demand for zein formulations to convey bioactive ingredients has continued to grow. Zein-based formulations were developed based on the many features of this natural substance for use in medication and biological delivery systems. Its resistance to heat, moisture, abrasion, and humidity increases the probability that the formulated product will have a longer shelf life. Moreover, zein consists of a large number of non-polar amino acids with aggregation formation ability, which in turn helps in the entrapment of drugs. These physical properties of zein allow for a wide range of usage in different formulations, including films, fibers, gels, controlled drug delivery systems such as tablets, and micro- or nano-particulate systems.
4.2.1. Zein nanoparticles

Zein is one of the most intensively investigated plant proteins for drug delivery applications due to its amphiphilic nature, bio-adhesive properties, and tendency to self-assemble into nanoparticles of sufficient stability. Nanoparticles are used to encapsulate, protect, and deliver therapeutic agents. For effective delivery of active ingredients, nanoparticles should withstand environmental stresses and effectively release the active material at the desired site [52]. Protein-based nanoparticles offer advantages over other materials in terms of biodegradability, safety status, and commercial scale-up [37].

Zein nanoparticles have been found to be effective in cancer therapy. In general, nanoparticles exhibit the ability of size dependent passive targeting through leaky tumor capillary fenestrations into the tumor vasculature through enhanced permeability and retention effects. As a result, tumour cells carry elevated concentrations of loaded cytotoxic agents, thereby facilitating the rapid and effective death of cancer cells. In a study, Lai et al. encapsulated 5-fluorouracil, an anticancer drug, into zein nanoparticles via the phase separation method for liver targeting and reported more than 31% targeting efficiency. The relative uptake of the loaded nanoparticle in the liver was reported to be 2.79 times greater than that of the 5-fluorouracil drug solution when administered through the intravascular route [53].

Resveratrol is a drug that displays poor solubility and bioavailability but has the potential to treat cancer. It is naturally present in grapes, berries, and peanuts, but after consumption, it is quickly metabolized into glucuronides and sulfates and excreted. Moreover, resveratrol can be degraded by heat, light, and enzyme exposure. To circumvent this problem, resveratrol can be preserved by nanoencapsulation, which will improve the drug's oral administration. In this regard, Huang and colleagues developed zein-pectin core/shell nanoparticles loaded with resveratrol by combining antisolvent precipitation and electrostatic deposition. It was found that the antioxidant activity of resveratrol was greatly improved when it was encapsulated into biopolymer-based nanoparticles. With the help of a pectin-based shell, the zein can act as a core and avoid aggregation caused by pH, high salt concentrations, and high temperatures [54].

A novel drug delivery system where the drug, honokiol, was encapsulated in a zein/hyaluronic complex was developed by Zhang et al. [55]. The complex exhibited anti-carcinogenic activity against breast carcinoma and anti-inflammatory, antioxidant, and neuroprotective properties. Honokiol targets the CD44 receptors that are overexpressed in cancer cells. Hyaluronic acid-zein-honokiol complex reduces tumor growth by 77.3% when compared with free honokiol with only 25.8% of tumor inhibition.

Nanoparticles have been shown to improve the oral bioavailability of compounds, either by protecting them from degradation by the gastric environment, improving the solubility of less water soluble drugs, or improving drug permeability through the intestinal lumen. Zein nanoparticles can also be utilized for enhancing the oral bioavailability of therapeutic molecules [56]. Zou et al. [56] generated zein nanoparticles and emulsified these particles with a surface active agent, D- α -tocopheryl polyethylene glycol succinate (TGPS), to form TGPS emulsified zein

nanoparticles and employed them for oral administration of daidzin, which is an isoflavone 7-glycoside with poor bioavailability in mice. It was inferred from the results that zein nanoparticles enhanced the bioavailability (2.64 times higher), and the cellular uptake and drug release were elevated in the Caco-2 cell line. It was reported that the enhanced absorption of the drug was due to P-glycoprotein inhibition by TGPS and transcytosis of particles.

According to Lee et al. [57], zein nanoparticles synthesized by the phase separation method have the ability to protect therapeutic proteins, antioxidant enzymes such as catalase, and SOD from digestion by pepsin and acidic conditions in the stomach. Zein NPs were loaded with SOD and catalase to protect them from gastrointestinal degradation following oral administration and also to target them to activated macrophages through folate receptors. The particle size of this system was 255.21 nm, with a loading efficiency of 30%–50%. The encapsulation of these enzymes into zein increased the proteins' therapeutic function from 5%–10% with free catalase and SOD to 40%–60%. The complex is believed to protect the loaded enzymes from pepsin as well as the acidic conditions of the stomach.

Moreover, the antioxidant compound, procyanidin, extracted from cranberries, was successfully loaded into zein nanoparticles by employing the liquid-liquid dispersion method. The procyanidin-zein nanoparticle showed an average size of 392 nm to 447 nm, and cell culture studies reported the cytotoxicity of procyanidins in promyelocytic leukemia L-60 cells in comparison with plain procyanidin solution [58]. Similarly, using the liquid-liquid dispersion method, essential oils such as thymol and carvacrol, were encapsulated in the zein nanoparticles. The morphology, structure, antioxidant capacity, and antibacterial activity of the nanoparticles with respect to different pH conditions were studied. Samples under neutral and basic conditions formed nanoparticles. Ferric ion spectrophotometric assay and DPPH analysis were used to evaluate the antioxidant qualities. Depending on the formulation, DPPH was lowered by 24.8%–66.8%, and samples quenched more than 65% of the hydroxyl free radicals. Furthermore, it was reported that *Escherichia coli* reductions of 0.8–1.8 log CFU/mL were achieved in the presence of essential oil-encapsulated nanoparticles [59].

Drugs can be encapsulated in zein nanoparticles. A zein-based hollow nanoparticle with sodium carbonate as a template has been employed in the delivery of the anti-diabetic drugs, metformin. A phase separation technique was used to fabricate these hollow zein nanoparticles. The development of sacrificial cores from sodium carbonate (2.0–9.1 wt%) and the precipitation of zein onto cores were the two steps involved in the preparation of hollow zein nanoparticles. The dissolved zein polymers were found to be attached to sodium carbonate nanocrystals, thereby preventing their agglomeration. The mixture was added to 200–500 g of distilled water in various proportions to precipitate sodium carbonate-cored zein nanoparticles. The sodium carbonate cores exhibited high water solubility, causing them to disintegrate quickly when the zein polymers on the surface precipitated, creating hollow zein nanoparticles [60].

In the studies conducted by Podaralle and Perumal, zein nanoparticles were fabricated using a pH-controlled nano-precipitation method. The model hydrophobic drug, 6,7-dihydroxy-coumarin (DHC) was encapsulated. It was observed that DHC, in spite of being a hydrophobic drug, exhibited 78% encapsulation efficiency with white zein [61]. Luo et al. developed zein nanoparticles coated with carboxy methyl chitosan (CMC) and further encapsulated with vitamin D3. On comparing CMCs-coated zein nanoparticles with plain zein nanoparticles, the former displayed an encapsulation efficiency of 87.9% and sustained release in PBS medium [62]. Retinol, one of the hydrophobic vitamins, was effectively encapsulated into zein chitosan nanoparticles. Before chitosan coating, the retinol-loaded zein nanoparticles had a particle size of about 6 nm; however, after coating, the particle size increased to about 400 nm. As the concentration of zein increased, the encapsulation efficiencies marginally increased from 66.2% to 72.8%. These findings indicate that processing parameters such as the molecular weight of chitosan and a ratio of weight of zein/chitosan may have a significant impact on the characteristics of zein-chitosan nanoparticles [63]. **Table 1** summarizes some of the zein nanoparticle-based drug delivery systems.

Carrier system	Approach/Method	Drug/bioactive compound	Biomedical applications	Reference
Zein	Phase separation	5-Fluorouracil (5-FU)	Liver targeting	[53]
Zein/Pectin	Anti-solvent precipitation and electrostatic deposition method	Resveratrol	Oral delivery system, Improved bioavailability	[54]
Zein/Hyaluronic acid	Anti-solvent precipitation and electrostatic deposition method	Honokiol	Delivery system for metastatic breast cancer therapy	[55]
Zein/D-α-tocopheryl polyethylene glycol succinate (D-α-TGPS)	Antisolvent precipitation method	Daidzin	Improving oral bioavailability of isoflavone glycosides	[56]
Zein	Phase separation method	Catalase, superoxide dismutase (SOD)	Reactive oxygen species (ROS) scavenging, targeting activated macrophages	[57]
Zein	Liquid-liquid dispersion method	Cranberry Procyanidins	Leukemia treatment	[58]
Zein	Liquid-liquid dispersion method	Thymol, carvacrol	Antioxidant, anti-microbial activity	[59]
Zein	Phase separation method with nucleation	Metformin	High payload, intracellular delivery	[60]
Zein	pH-controlled nanoprecipitation	6,7-Dihydroxy coumarin	Optimization of formulation factors	[61]
Zein/Carboxymethylcellulose (CMC)	Phase separation method	Cholecalciferol (Vitamin D3)	Delivery system for hydrophobic nutrients/drugs	[62]
Zein/Chitosan	Anti-solvent precipitation and solvent evaporation	Retinol	Increasing nanoparticle stability	[63]
Zein/Sodium caseinate	Modified anti-solvent approach	Thymol	Anti-microbial, antioxidant activity	[64]
Zein	Solution-enhanced dispersion by supercritical fluids	Lutein	Controlled drug release	[65]
Zein	Anti-solvent precipitation method	Hyperoside	Oral delivery system	[66]

 Table 1. Zein nanoparticle-based drug delivery systems.

4.2.2. Zein based nanofibers

Nanofibers find diversified uses in the biomedical sector. The natural origin polymeric nanofibers incorporated with different therapeutics, growth factors, vitamins, etc. have been investigated for various delivery applications through various administration routes such as oral, pulmonary, transdermal, and ocular routes [67]. Zein fibres can be fabricated using two different techniques. Melt-spinning is applied for the preparation of conventional fibres whereas electrospinning is used for nanofibers. The nanofibrous structure of electro-spun nanofibres, mimics the ECM environment, offers a large surface area for drug loading and cell attachment, and hence is more advantageous in biomedical applications than conventional fibres [68]. Moreover, electrospinning is the most widely used technique for the fabrication of nanofibers from natural as well as synthetic sources for controlled delivery of drugs, gene delivery, tissue engineering, etc. [69]. However, poor morphological stability and low mechanical strength of zein in wet conditions are limitations of native zein fibers [70].

Many attempts are being made by scientists to amplify its mechanical strength by making use of other polymers with zein or chemical crosslinking agents, which include formaldehyde or glutaraldehyde. The latter is toxic for human use and, hence, not preferable. Citric acid was used as a crosslinker for zein electrospun fibers. It was observed that the crosslinked electrospun fibers were able to maintain their ultrafine fibrous structure in phosphate-buffered saline at 37 °C up to 15 days [70]. In another similar study, citric acid cross-linked electrospun zein scaffolds exhibited better biocompatibility, attachment, migration, and proliferation of fibroblast cells than uncross-linked electrospun zein fibers, cross-linked zein films, and electrospun polylactide fibers [71]. Similarly, zein/citric acid crosslinked fibers catalyzed by sodium hydroxide exhibited a drug-loading efficiency of 58% along with a prolonged release of drug in artificial gastric juice. The mechanical properties, such as dry and wet tensile strength, increased by 183% and 448%, respectively [70]. Gallic acid, a food-grade antioxidant, when electrospun into zein produced ultra-fine fibers of diameters of 327 to 387 nm and an in vitro DPPH assay concluded that loaded gallic acid could preserve its phenolic character and retain its antioxidant activity after electrospinning [72].

Nanofibers based on zein, poly (ethylene oxide), and chitosan (zein/PEO/CS fibres) were synthesised by Wongsasulak et al. and exhibited good mucoadhesion features in the gastrointestinal tract. Wetting and swelling of the fiber's polymeric molecular chains caused a molecular interaction between the fiber and mucin molecules, (a glycoprotein found in epithelial tissues) due to the gastro-mucoadhesion [73]. Similarly, Wang and Chen formulated hordein-/zein-based nanofibers. These fibers with 30% zein content demonstrated a well-interconnected network, sufficient tensile strength, and stability in water. The release profile experiments revealed that the three-dimensional porous structure of the fibers may possibly serve as carriers for the regulated release of bioactive substances such as riboflavin in phosphate-buffered saline. Interestingly, the fibers were found to be stable in simulated gastric fluid as they were found to be resistant to pepsin, but underwent digestion in simulated intestinal fluid (where they are normally absorbed), thereby progressively releasing the incorporated compound [74].

Zein/Eudragit S 100 was electrospun to generate composite nanofibers that were utilised for carrying pantoprazole and aceclofenac simultaneously. Aceclofenac was readily loaded into zein, while Eudragit S 100 was intended to deliver pantoprazole,

an acid labile proton pump inhibitor that inhibits gastric acid secretion. The medication was then loaded into nanofibers after the development of nanocarriers using a singlenozzle electrospinning technique. Both in vitro and in vivo studies revealed sustained drug release for up to 8 h; hence, it was concluded that NSAIDs with controlled release triggered less toxicity in the GI tract. The electrospun composite zein/eudragit nanofibers developed by Karthikeyan et al. [75] aimed to simultaneously deliver two distinct drugs that would mitigate or lessen the side effects of NSAIDs. In this study, a single nozzle electrospinning process was applied to generate zein/Eudragit S 100 nanofibers loaded with aceclofenac and pantoprazole. Pantoprazole is an acid-labile drug, and hence, to prevent its degradation in an acidic environment, Eudragit S 100 was used as a carrier for its delivery via the oral route. The effectiveness of the developed fibers to sustain the release of both drugs for up to eight hours was demonstrated by in vitro release studies. It was observed that the co-administration of pantoprazole and aceclofenac lessened the NSAID-induced gastrointestinal toxicity, as further evidenced by in vivo animal studies. Zein nanofiber-based drug delivery systems are listed in Table 2.

Carrier system	Fiber type	Drug/bioactive compound	Biomedical applications	Reference
Zein	pure	Citric acid	Improving cytocompatibility	[70]
Zein	pure	Citric acid	Sustained drug release, improved mechanical properties	[71]
Zein	pure	Gallic acid	Antioxidant activity	[72]
Zein/Poly (ethylene oxide) (PEO)/Chitosan	Hybrid	-	Gastro mucoadhesive delivery vehicle improves bioavailability	[73]
Zein/Hordein	Hybrid	Riboflavin	Intestine-targeted drug delivery systems, delivery of bioactive compounds for wound healing	[74]
Zein/Eudragit S100	Hybrid	Pantoprazole, Aceclofenac	Oral drug delivery, sustained release of non-steroidal anti-inflammatory drugs (NSAIDs)	[75]
Zein	Core sheath	Ferulic acid	Sustained drug release	[76]
Zein	Pure	Curcumin	Sustained drug release	[77]
Zein/Polycaprolactone	Hybrid	Tetracycline	Sustained antibiotic release	[78]
Zein/Polyurethane/Cellulose Acetate	Hybrid	Streptomycin sulphate	Antimicrobial activity	[79]
Zein/Collagen	Hybrid	Berberine	Antibacterial activity, sustained drug release	[80]

 Table 2. Zein nanofibers as drug carriers for drug delivery systems.

4.2.3. Zein based microspheres

Protein-based microspheres and microparticles are used in mucoadhesive vaccine delivery, depot preparations, and controlled release in the GI tract [37,81–83]. Zein microspheres were developed by Mehta et al. in which various antitubercular drugs such as rifampcin, isoniazid, and pyrazinamide were loaded using a solvent evaporation technique. Among these drugs, rifampicin and isoniazide exhibited higher and lower encapsulation, respectively, than others [84]. Similarly, α -tocopherol was encapsulated in zein/chitosan to form a complex possessing a size of 200–800 nm and a zeta potential of 22.8 to 40.9 mV. It was reported that electrostatic interactions and hydrogen bonding aided the complex formation. This complex provided better

protection to this antioxidant from adverse conditions in the GI tract as compared with plain zein nanoparticles, thereby revealing their potential efficacy in delivering hydrophobic drugs [85].

Researchers developed a novel delivery system consisting of chitosan/zein nanoin-microparticles loaded with DNA. The chitosan/DNA particles represented the core, which was encapsulated in zein microspheres. The study revealed the protective nature of zein microspheres towards the encapsulated DNA in a harsh GI environment [86]. Zein-based microspheres were conjugated with the chemoimmunotherapy drug polysaccharide-Kureha used for cancer treatment [87]. In a similar study, antitumor drugs such as mitomycin C, daunomycin hydrochloride, and peplomycin sulfate were successfully conjugated with zein microspheres using a DMSO-water solvent system [88]. Zein-based microspheres for controlled delivery of antibiotics such as ciprofloxacin have also been reported [89]. In a study conducted by Liu et al. [90], the phase separation method was used to generate a novel microsphere drug delivery system for ivermectin, an antiparasite drug, by making use of zein. Release studies of this model drug from zein microspheres as well as from tableted microspheres were carried out in vitro. The outcomes demonstrated that the tableted and zein microspheres are appropriate for use as a sustained-release form of ivermectin. As the diameters of microspheres are suitable for macrophage phagocytosis, it could be helpful in drug targeting systems.

In the same study, the release kinetics of tableted microspheres were explored [90]. Pepsin enzyme degraded tableted microspheres exhibited zero order kinetics for drug release. Hence, the formulation can be applied to orally administer drugs to maintain a constant concentration of drug in plasma in vivo. Furthermore, they could be developed as scaffolds consisting of microspheres that can steadily release bioactive compounds that could promote cell differentiation in tissue engineering applications. Muthuselvi and Dhathathreyan [91] formulated simple coacervates of zein to encapsulate a cardiotonic glycoside, gitoxin. Zein microspheres and gitoxinloaded zein microspheres were prepared using different solvents such as methanol, ethanol, and isopropyl alcohol. In-vitro release studies of gitoxin from zein microspheres developed in ethanol were best suited as the sustained release form of gitoxin. **Table 3** summarizes some of the zein microsphere-based drug delivery systems.

Carrier system	Approach/method	Drug/bioactive compound	Biomedical applications	Reference
Zein	Emulsification and solvent evaporation method	Antituberculosis drugs – Rifampicin, Isoniazid, pyrazinamide	Tuberculosis chemotherapy	[84]
Zein/Chitosan	Anti-solvent precipitation and solvent evaporation	α-tocopherol	Hydrophobic drug delivery to the GI tract	[85]
Zein/Chitosan	Water in oil emulsion	DNA	Oral gene delivery	[86]
Zein	High dilution process	Polysaccharide-K	Cancer immunotherapy	[87]

 Table 3. Zein microsphere-based drug delivery system.

Carrier system	Approach/method	Drug/bioactive compound	Biomedical applications	Reference
Zein	Emulsification	Antitumour drugs –Mitomycin C, Daunomycin, Peplomycin sulphate	Cancer immunotherapy	[88]
Zein	Phase separation method	Ivermectin	Drug targeting system	[90]
Zein	Coacervation	Gitoxin	Sustained drug release	[91]
Zein	Coacervation method	Ovalbumin	Vaccine delivery, to improve adjuvanticity and immunogenicity	[92]
Zein	Emulsification and solvent evaporation method	Aceclofenac sodium	Sustained delivery systems for NSAIDs	[93]

Table 3. (Continued).

4.2.4. Zein based films

Zein can be developed into films either by interaction with other materials or by a chemical or heat-based crosslinking procedure. This property is attributed to the presence of numerous amino acid side chains. Zein films are tough, glossy, hydrophobic, biodegradable, resistant to microbial attack, and safe for internal human use [7,37,94,95]. Wang et al. [96] reported zein films to be biocompatible with human umblical vein endothelial cells (HUVECs). Zein microspheres as well as heparinloaded zein microspheres suspended in a 40% ethanol solution were prepared and subsequently volatilized at 37 °C to form zein microsphere films. It was observed that zein films and heparin-loaded zein microsphere films were able to suppress platelet adhesion. Moreover, heparin-loaded zein film exhibited better anti-coagulation properties. It was reported in a study that ciprofloxacin-loaded zein films could possibly prevent bacterial infection on implanted devices [89]. Singh et al. [97] prepared zein films loaded with salicylic acid and acetyl salicylic acid, with or without glycerol. The resultant films containing glycerol, salicylic acid, and acetylsalicylic acid showed a decrease in tensile strength. Studies reported that oleic acid plasticized zein films withstand gastric fluids and are soluble in intestinal fluids [98].

Zein films were investigated for their ability to enhance the resistance of cells to flow-shear-stress after the implantation of vascular implants. The films were made of three types of zein, collagen, and poly-L-lactic acid. The flow shear stress resistance of NIH3T3 and EA.hy926 cell lines on films was studied. It was observed that cell retention of EA.hy926 on zein film with a rough surface was better than that of films with a flat surface. The cell retention of NIH3T3 on a rough surface was better under flow-shear stress for 6 hours. This study concluded that zein films with more roughness could possibly enhance the cell's flow shear stress resistance and may be applied to vascular implant coatings [99]. Another study has reported that zein-based films act as a good matrix for the sustained release of drugs such as nisin, iodine, thymol, catechin, lysozyme, and gallate esters [100]. A novel technique was developed by Gao et al. for the preparation of films from zein thermo-modified starch by using dry heating of starch or di-starch phosphate with zein. It was observed that the dry heating reduced the pasting properties of zein and distarch phosphate. These zein/starch films exhibited good compatibility, a higher water contact angle, and tensile strength, implying that dry heating is a possible method to improve the properties of starch films [101].

4.3. Zein in tissue engineering

The extracellular matrix (ECM), as is well known, is made up of a variety of biomolecules, notably proteins, and polysaccharides such as hyaluronic acid, chondroitin sulphate, heparin, heparin sulphate, etc. [102], and proteoglycans, among others, which aid cell attachments as well as proliferation, differentiation, and migration [33]. Tissue engineering typically involves the culturing of living human cells, usually in polymeric (ceramic) scaffold materials, ex vivo, and eventually permitting them to develop into a three-dimensional tissue. With the use of tissue engineering, it is possible to regenerate tissues that have been damaged by disease or trauma, and in some situations, to develop new tissues or substitute failing or malfunctioning internal organs. Degradable biomaterials generally serve this purpose by either promoting the ingrowth of surrounding tissue and cells or acting as temporary scaffolds on which transplanted cells can adhere, proliferate, and retain their differentiated functions. Hence, biomaterials play a transient but vital role in the success of tissue engineering [103]. Therefore, in the tissue engineering process, cells are exposed to a fabricated scaffold that mimics the ECM, and under this new and artificial environment, the cells are expected to carry out the same functions and regenerate or heal the damaged tissue [33,102].

It is feasible to elaborate the extracellular matrix by different methods to produce fibers, both from natural and synthetic sources. Fibers from natural sources are biocompatible but show low mechanical firmness. Although the synthetic fibers lack cell binding and acid production ability, they show sufficient mechanical stability. The nanofibers from natural and synthetic sources can be combined to fabricate an ECM matrix by different methods, thus providing a synergetic effect. Zein has been shown to be an exceptional biopolymer in tissue engineering on account of its flexibility, resistance to microorganisms, compatibility with the human body, and biodegradability [33].

The successful implementation of tissue engineering depends on the choice of scaffold, which has a sponge-like structure with high porosity and optimum thickness. Three-dimensional porous zein fibers have also been manufactured to replicate the structure of human tissue as scaffolds for tissue engineering [37]. Zein scaffolds were developed in combination with other fibers such as cellulose acetate, polyurethane, and gum Arabic [33]. Rad and colleagues designed and characterized an electrospun nanocomposite scaffold for skin tissue engineering using polycaprolactone/zein/gum Arabic. Zein and gum Arabic provide protein and polysaccharide content, respectively, for the regeneration of skin, while PCL provides mechanical stability. The PCL/zein/gaum Arabic scaffold exhibited high hydrophilicity, a tensile strength of 1.36-3 MPa, and an elongation of 19.13%-44.06%, thus making it ideal for skin tissue engineering applications. In addition, the porosity of the scaffold was greater than 77%, which was appropriate and suggested for cell infiltration. Furthermore, due to the presence of cyanogenic glycosides in gum Arabic, the composite scaffolds showcased antimicrobial characteristics as well as improved hydrophilicity, which in turn enhanced cell viability and proliferation [104].

Dong et al. prepared zein films using solutions of varying concentrations, and by SEM analysis, it was found that these films were formed of zein particles with varying

sizes ranging from 100-500 and 500-2500 nm in diameter. Human liver cells (HL-7702) and mouse fibroblast cells (NIH3T3) were cultured in these films, and the ability of cells to adhere, grow, and proliferate on zein films served as a measure of their biocompatibility. The results showed the attachment of more than 60% of cells to zein films at 3 h after seeding [105]. Zein exhibited excellent biocompatibility with platelets and human umbilical vein endothelial cells. This property was explored by Wang et al. [96] to develop zein film as a coating material. It was observed that platelet adhesion was suppressed by both zein film and heparin-loaded microsphere film, while the latter showed anticoagulation properties. In another study conducted by Dhandayuthapani et al., a novel fluorescent nanocomposite nanofiber made up of cadmium sulphate and zein was developed through an electrospinning technique. These composites tend to support the mesenchymal stem cells and fibroblasts for their attachment and proliferation. It was further noted that these cells hold normal cell shapes and merge well with surrounding fibers, emphasizing the importance of quantum dot-encapsulated fluorescent zein nanofibers as scaffolds for tissue engineering [106].

Studies have reported that three-dimensional fiber scaffolds developed from a homogeneous blend of gelatin/zein (1:4) via the force-spinning technique exhibited improved tensile strength and good hydrophobic properties, with a water contact angle of 115° and low cytotoxicity in human fibroblasts, and facilitated sustained release of the drug berberine for over 15 days [107]. The gelatin ought to be responsible for the scaffold's improved elastic modulus, hydrophilicity, and cytocompatibility [108]. In a study conducted by Saowakon et al. [109], ultrafine zein-based electrospun composite fibers with mucoadhesive properties were developed. The fibers were composed of zein, polyethylene oxide, and chitosan in the ratios 87.5, 10, and 2.5, respectively. A hydrophobic antioxidant compound, $-\alpha$ tocopherol was added 20 wt% into the fiber matrix. This fiber displayed adequate gastro-mucoadhesive and release characteristics, which makes it capable of delivering hydrophobic compounds to the GI tract.

As is well known, the crosslinking method and the addition of plasticizers can strengthen the mechanical properties of membranes. For example, hexamethylene diisocyanate is often used as a crosslinker agent for zein-based nanofibers. Besides, zein nanofibers in combination with palmitic acid/zein (1:2) and stearic acid/zein (1:4) displayed better mechanical stability, as palmitic acid contributes to its plasticization property. Likewise, the addition of mica, kaolinite, montmorillonite, and zeolite to zein fibers enhanced their mechanical properties [4].

Zein is an excellent choice for fabricating biomaterial scaffolds for bone regeneration due to its biocompatibility, biodegradability, remarkable mechanical properties (including strength, flexibility, and compressibility), antioxidant capacity, and microbial resistance. It has been established that scaffolds made of zein-based composites enhance osteogenesis differentiation, which renders them ideal for bone tissue regeneration [4]. Because of probable interactions between cells and the protein layer, zein-based biomaterials are favourable for cell adhesion [110].

Periodontitis is a prevalent dental disease in which electrospun NFs could provide effective treatment and aid in the recovery of the paradentium. Yang et al. [108] employed the co-electrospinning method to develop zein/gelatin nanofibres using 1,1,1,3,3,3-hexafluoro-2-propanol as the solvent. The fibers were characterized, and

human periodontal ligament stem cells were used to evaluate the cell affinity towards zein/ gelatin nanofibers. On comparison with the native zein scaffold, the zein/gelatin scaffold demonstrated good cytocompatibility, and the addition of gelatin promoted the development of periodontal ligament stem cells. Furthermore, by altering the gelatin-to-zein ratio, surface shape, and fibre diameter, the mechanical performance and cell adhesive capacity in vitro may be easily adjusted. In addition, the constructed scaffold promoted cell adhesion and expedited periodontal ligament stem cell development.

Shrestha et al. [111] succeeded in the development of a novel bone regenerating scaffold using a zein/chitosan/polyurethane composite membrane incorporated with functionalized multiwalled carbon nanotubes using the electrospinning method. The obtained scaffold exhibited good antibacterial efficacy against bacterial strains such as *Escherichia coli*, *Staphylococcus aureus*, *Micrococcus luteus*, and *Staphylococcus epidermis*. According to in vitro investigations, it was observed that the scaffold significantly enhanced the regenerative effect of pre-osteoblast (MC3T3-E1) by facilitating rapid cell-to-cell communication through a bio-interface and promoting cell growth, proliferation, and differentiation. The excellent osteoinductive properties of the scaffold were indicated by the nucleation of hydroxyapatite nanocrystals and the expression of osteogenic markers, as confirmed by Alizarin red staining analysis, alkaline phosphatase activity, and western blotting. These findings suggested that the designed PU/Zein/CS-carbon nanotube fibrous scaffold has the biological properties necessary to function as an artificial bone extracellular matrix, ensuring bone cell regeneration.

The solvent casting particulate leaching method was applied to fabricate a zein/poly(caprolactone) biocomposite scaffold with sodium chloride particles as porogen. This scaffold enhanced hydrophilicity, and faster in vitro degradation as compared to the PCL scaffold. In addition, the in-vitro degradation behaviour of scaffolds in PBS was studied for 28 days and reported a slight weight loss of the zein/PCL scaffold with increasing the zein content in the composite. These studies concluded that zein/PCL biocomposite could be a promising material for bone tissue engineering [112]. The zein-based scaffold generated by Yan-Zhi et al. [113] exhibited better porosity, an open pore wall structure, and excellent biocompatibility with periodontal ligament cells, and hence was applied for periodontal tissue healing.

Moreover, zein blended with poly (glycerol sebacate) finds application in soft tissue engineering [114]. The incorporation of hydroxyapatite (HA) improves tissue regeneration as well as minimizes scaffold degradation rate. In this regard, zein with hydroxyapatite has proven to improve osteoblasts [115]. Yao et al. [116] and Zhang et al. [117] developed nanofibers of zein/hydroxyapatite with a reasonable tensile strength and subsequently utilized these materials as scaffolds for tissue reconstruction in separate investigations. The mineralized zein nanofibrous membranes had an excellent impact on osteoblast growth and did not generate cytotoxicity, as demonstrated by osteoblast adhesion tests and in vitro cytotoxicity experiments. The zein/HA membrane had distinct nanofibrous structural properties, and a coating of HA nanocrystallites can be used in bone repair and regeneration, indicating that the electrospun zein/HA fibrous membranes show potential for bone tissue engineering applications.

Poly (3-hydroxubutyrate-co-4hydroxubutyrate) (PHB), a bacterial thermoplastic, when incorporated with zein in appropriate concentrations (20%–80%) and subsequently electrospun, formed ultrathin fibres (60–650 nm in diameter) with a tensile strength of 4.8–7.1 MPa and elongation at break between 15%–69%. The invitro experiments demonstrated that the blended scaffolds are non-cytotoxic for NIH3T3 fibroblast cells and MG-63 osteoblast cells and offer support for cell adhesion, distribution, and proliferation [118].

A three-dimensional zein porous scaffold with and without rabbit mesenchymal stem cells was assessed for its osteogenic activity by Tu et al. [119]. Earlier studies from this group proved that zein scaffolds have good mechanical properties suitable for bone-tissue engineering applications, and their porous nature encouraged cell migration and ingrowth [120]. In this study, mesenchymal stem cells were seeded onto zein scaffolds, and the cell-seeded scaffold was evaluated for the formation of ectopic bone in the thigh muscle pouches' model of nude mice. Further to this, the MSC-seeded zein scaffolds were implanted into a segmental bone defect of 1.5 cm length created in the middle of the radial shafts. These studies revealed that MSC-seeded zein scaffolds could successfully induce ectopic bone formation in the thigh muscle pouches of nude mice, and they also demonstrated a good ability to repair rabbits' critical-sized radial bone defects, which were accompanied by blood vessel formation. These findings suggest that stem cell-seeded zein scaffolds could be a promising strategy for treating bone abnormalities [119].

A three-dimensionally stable zein scaffold with an interconnective and open pore structure was produced using the salt leaching process. The particle size and porosity of the scaffold were 300 mm and 75.3%–79.0%, respectively. The mechanical properties, such as Young's modulus and compressive strength, of the scaffold were comparable to those of the cancellous bone, implying its possible application in non-load-bearing regions. Additionally, in-vitro cell culture studies showed that rat mesenchymal stem cell adhesion, growth, and proliferation could be successfully achieved on zein porous scaffolds and that these scaffolds possessed demonstrable osteoconductive qualities in the presence of dexamethasone, further indicating zein as a promising material for bone tissue engineering [121].

Hadavi et al. synthesized a zein nanoparticle-based delivery system incorporated with bone morphogenic protein-6 (BMP6), which is a peptide growth factor in bone formation, using a liquid-liquid phase separation method. This was investigated for its in vitro osteoinduction property in mouse myoblast C2C12 cells. The study reported 72% encapsulation and a prolonged release pattern of the loaded peptide, as well as high biocompatibility of the BMP-6 loaded zein, with 90% cell viability after 48 and 96 h incubation. Furthermore, on day 14 after incubation, the level of enzyme alkaline phosphatase, an osteocyte marker, in C2C12 cells treated with BMP-6-loaded nanoparticles and those treated with blank nanoparticles was compared, and an elevated level of ALP was observed in the former. The BMP6 peptide-loaded zein nanoparticles substantially improved Runx2, a transcription factor for osteoblast differentiation gene, expression compared to blank nanoparticles, implying that the BMP pathway was active. The study suggested that BMP6 peptide-loaded zein nanoparticles may be a good candidate for bone regeneration [122].

In a study conducted by Turner et al. [123], to improve hydrolytic stability, zein was cross-linked with trimethylolpropane triglycidyl ether to form a fibrous scaffold using the electrospinning method. The scaffolds were characterized and assessed for their ability to support the osteogenic differentiation of MC3T3-E1 cells. It was observed that even in the absence of induction factors, MC3T3-E1 cells were able to grow and differentiate on the zein scaffolds, as evidenced by the early upregulation of Runx2 gene expression and increased alkaline phosphatase activity. These studies show that zein fibrous scaffolds promote cell growth and differentiation without the aid of growth factors, and these cross-linked scaffolds are stable and are proposed to be useful in bone repair applications.

According to recent research, the bioactive glass-based scaffold covered with zein excels the bare scaffold in bone regeneration. Arango-Ospina et al. [124] created a multifunctional bone regeneration scaffold using a foam-replica approach by coating bioactive glass with zein and Manuka honey. The study aimed at combining the biodegradability and biocompatibility of zein with the bioactive properties of bioactive glass and the antimicrobial effect of manuka honey. This scaffold outperformed uncoated bioactive glass scaffolds in terms of mechanical properties; the compressive strength of the uncoated scaffold was as low as 0.04 ± 0.01 MPa, whereas it increased to 0.14 ± 0.05 MPa for the coated one. The increased compressive strength of the coated scaffolds might be linked with the reinforcement effect of the infiltration of the polymer into the cracks and open hollow struts of bioactive scaffolds. The uncoated scaffolds had a porosity of $95.6\% \pm 0.3\%$, while the scaffolds coated with zein and 20 wt.% Manuka honey had a porosity of $77.0\% \pm 3.0\%$. The formation of a hydroxycarbonate-growing apatite layer on the surface of scaffolds was detected using an SEM and FTIR analysis as a part of bioactivity studies in simulated bodily fluid. The coated scaffolds generated an apatite-like layer on their surfaces after 1 week of incubation, but the untreated scaffolds developed the apatite layer after only 1 day. The release studies showed a fast release of honey from the scaffold within 1 hour.

It is worth mentioning the studies carried out by Eldeeb et al. [125], in which the dual-drug-loaded implant was developed using a zein matrix to deliver pitavastatin calcium, an osteogenic drug, and tedizolid, an antibiotic for bone regeneration. In order to improve the bone proliferative effect of the formulated implants, a titanium-doped bioactive glass was used, as well as sodium hyaluronate, which served as a porogenic agent to produce the porosity essential for cellular infiltration and proliferation. The fabricated implant demonstrated persistent release of both drugs for 28 days. Besides, in vivo studies in Sprague Dawley rats showed a strong bone regenerating effect.

A study conducted by Mariotti et al. [126] applied electrospinning to generate fiber mats of zein mixed with non-doped or copper-doped bioactive glass. A 14-day degradation study in DMEM media revealed a slow development of halite crystals with a gradual loss of fibrous structure of the scaffolds; nonetheless, some fibers contained bioactive glass at the end of the study, indicating that the scaffolds were sufficiently strong. In vitro cell viability investigations, using zein fiber mats loaded with copper-doped bioactive glass indicated enhanced cell proliferation of up to 61% on the human osteosarcoma cell line MG-63 and 59% on the mouse muscle cell line C2C12 after 7 days.

Another study was conducted by Ranjbar et al. [127], in which a permeable scaffold was constructed from 58S bioactive glass with zein to strengthen its mechanical properties and serve as a medium for the controlled release of the drug kaempferol. The scaffolds coated with a 7% w/v zein solution possessed superior mechanical strength and an extremely porous structure. Furthermore, the data suggested that the generated scaffolds could promote optimal kaempferol release and a favorable environment for cell adhesion. In summary, zein-based composite scaffolds can be utilized as promising and nontoxic alternatives in bone tissue regeneration. The hybrid zein-based fibrous scaffold has the potential to serve as a future biomaterial for the repair of a wide range of tissue defects.

4.4. Zein in wound dressings

Over the past few years, scientists have tried to make advanced wound dressings from zein-based biomaterials due to their specific properties, including biodegradability, biocompatibility, film formation, and antioxidant capacity [128]. Zein can be fabricated as films or bandages that bind to the wound, form a protective barrier, and expedite wound healing. This can help save a moist wound environment and promote a natural healing process.

An ideal wound dressing for commercial use ought to promote the natural healing process of the wound while also protecting it from external conditions. The wound dressing should maintain an appropriate moist environment that prevents the wound from drying out, and it must not create excessive moisture that can lead to bacterial growth. Another property of wound dressing is its ability to absorb excess exudate and prevent leakage to the surrounding healthy skin. The commercial wound dressing should also be easy to apply, remove, and dispose of, possessing antimicrobial properties to manage infection in the wound area. Moreover, the dressing material should be biocompatible, non-toxic, non-allergenic, and cost-effective. The combination of these properties can help promote wound healing, reduce pain, and thereby improve the quality of patients' lives [129]. These dressings can be customized for different types of wounds, including acute and chronic wounds [130].

Proteins in the form of film or nanofibrous scaffolds have been explored for wound healing applications [125,126]. Recently, the function of nanofiber membranes designed through an electrospinning process in accelerating wound healing has attracted wide attention [132]. A blend combination of zein and poly(ethylene oxide) (PEO) fabricated by coaxial electrospinning, in which zein occupied the core and PEO in the shell, also exhibited wound healing properties. Interestingly, it was found that the electrospun formation of zein improved with the addition of PEO and increased the elasticity of these microfiber mats [133].

Miyoshi et al. reported [134] that when zein was hydrolyzed with thermolysin, angiotensin inhibitory peptides, mainly tripeptides, were produced, and further oral administration of these hydrolysates of α -zein to hypertensive rats brought about a reduction in their blood pressure. Further studies from the same group reported that this inhibitor, when administered topically and orally, hastens wound closure and prevents the formation of scar tissue by inhibiting angiotensin receptors or by converting angiotensin I to angiotensin II [130]. Interestingly, the wound site showed

more structurally organized collagen fibers that resembled normal skin texture. This might be due to inhibition of expression of TNF- α , fibroblast proliferation, and collagen production after ACEI production.

Antimicrobial wound dressing using electrospun zein, along with synthetic polymers like polycaprolactone (PCL), poly(ethylene oxide) (PEO), polyurethane (PU), and polylactic acid (PLA), and natural polymeric substances like gum arabic, hyaluronic acid, cinnamaldehyde, gum tragacanth, etc., were explored for their wound care properties. A wide range of antibiotics, antibacterial nanoparticles, and antimicrobial plant extracts could be incorporated into zein-based fibers. The role of zein-based electrospun nanofibers in combination with antimicrobial agents in enhancing wound healing is widely studied [131]. In a study conducted by Dashdorj et al. [135], silver nanoparticles loaded with electrospun zein fibers exhibited higher cytocompatibility and showed antibacterial effects against *Staphylococcus aureus* and *Escherichia coli*.

Ghalei and collaborators developed a bioactive nanofiber wound dressing matrix from poly (vinyl alcohol) PVA/zein nanoparticles loaded with diclofenac (DLF) by the single jet electrospinning method. The drug loading efficiency was reported to be 47.80%. According to release profile studies, incorporation of zein nanoparticles (NP) into PVA nanofibers ensured a slower, sustained, and controlled release of the drug with prolonged release time instead of burst release of the drug. This makes PVA/zein NPs/DLF nanofibers a promising drug delivery system. Moreover, the cytotoxicity tests of PVA, PVA/zein NPs, and PVA/zein NPs/DLF nanocomposite dressings in L929 cell lines showed no signs of toxicity, and the addition of NPs to PVA fibers led to better cellular proliferation [136].

In a study conducted by Kimna et al. [130], gentamicin-loaded zein fibers were fabricated by electrospinning on the surface of the membrane. These fibers, which possessed a film thickness ranging from 311 to 361 µm and a fiber diameter between 350 and 425 nm, displayed structural features comparable to the layers of skin tissue. Moreover, the mechanical characteristics of the fiber were compatible with the skin tissue. Furthermore, membranes exhibited antimicrobial activity against *Escherichia coli* and *Staphylococcus aureus*. Gentamicin displayed a sustained cumulative release of 94%. According to the in-vitro cell culture results, membranes were found to be non-toxic, and proliferation of NIH/3T3 and HS2 cell lines was observed in each layer of the fiber, mimicking the multilayer skin tissue. These studies shed light on the possibility of developing a zein-based bilayer as a potential antimicrobial wound dressing for skin tissue regeneration.

Zein, in combination with other polysaccharides, also displayed wound-healing properties. Nanofibrous membranes of zein/collagen exhibited better surface wettability, mechanical and in vitro degradable properties, and cell adhesion ability [137]. In a study conducted by Unnithan et al. [138], the electrospinning method was adopted for the fabrication of a streptomycin sulfate-loaded composite nanofiber blend composed of polyurethane (PU), cellulose acetate (CA), and zein. Here, PU was used as the core polymeric component, while CA and zein were intended to improve hydrophilicity, permeability to air and moisture, cell attachment, proliferation, and blood thickening ability. The in-vitro antimicrobial activity of the nanofiber membranes was evaluated for use in wound dressings. There was a favorable

interaction of cells with the PU-CA-zein-drug composite scaffold. These scaffolds showed enhanced blood clotting and platelet activation. To add to above-mentioned properties, CA and zein also increased liquid uptake and created a moist environment for the wound, which is necessary to hasten wound recovery.

Application of natural medicinal extracts such as essential oils can enhance the antibacterial properties of zein-based wound dressings significantly. Thyme oil incorporated zein wound dressing was prepared by the in-situ electrospinning method. These fibres exhibited superhydrophilicity with a 0° contact angle and a gas permeability of 154 ± 20.9 m², as well as antibacterial activities. The in-vivo experiment data revealed that the fibres hastened wound recovery in mice within 11 days [139]. In a study carried out by Qin et al. [140], an antibacterial wound dressing was fabricated by incorporating clove essential oil (CEO) into the fibrous membranes of zein and deposited directly on the wound area of experimental mice via the in situ electrospinning method. The wound healing process was observed to be promoted as the zein/CEO fibrous membrane exhibited sufficient porosity, good gas permeability $(168.2 \pm 43.3 \text{ mm s}^{-1})$, biocompatibility, and an antibacterial effect. Moreover, higher hydrophilicity to absorb wound exudate was observed. Zinc oxide nanoparticles and aloe vera incorporated in zein/PCL/collagen electrospun nanofibers were studied by Ghorbani et al. [141]. The developed mats had strong mechanical properties, conductivity, antibacterial qualities, and a unique surface for cell adhesion and growth. They also exhibited outstanding biocompatibility.

An interesting study was conducted by Gunes et al. [142], in which a novel hybrid bilayer wound dressing was designed from zein. The upper layer, composed of zein film with montmorillonite (MMT) nanocomposite incorporated with *Hypericum perforatum* oil, and three-dimensional electrospun zein/MMT nanofibers represented the bottom layer. This layer induced wound healing with the controlled release of *H. perforatum* oil. The bilayer composites proved to have appropriate gas barrier properties, surface wettability, and antimicrobial efficacy against *Esherichia coli, Staphylococcus aureus*, and *Candida albicans*. The cell culture studies indicated no signs of toxicity on NIH3T3 mouse fibroblast and HS2 keratinocyte cell lines. The scratch wound assay indicated a wound-healing effect by enhancing fibroblast attachment, proliferation, and collagen secretion.

One of the drawbacks of electrospun zein matrices is their poor mechanical stability. This limitation can be overcome by mixing zein with other compatible polymers or cross-linking. Surendranath et al. [143] have reported post-electrospinning UV-mediated crosslinking for the zein/PEO blend wound dressing matrix to achieve mechanical stability and water resistance. Furthermore, the fabricated membrane elevates collagen production and aids in wound healing in human dermal fibroblast cells with no in-vitro cytotoxicity.

Zein has been explored for its efficacy in treating diabetic wounds. Liu and team developed a cellulose acetate-zein composite nanofiber incorporated with 5% sesamol for the treatment of diabetic wounds. This membrane turned down the expression of inflammatory cytokines IL-10 and sesamol, up-regulated IL-6 expression, and stimulated TGF- α signaling pathway transduction, and together enhancing the growth and proliferation of keratinocytes in diabetic mice [132]. A study conducted by Gough

et al. revealed air-jet spun zein nanofibers to be an effective carrier of sodium citrate that is applied topically to treat diabetic ulcers [144].

Attempts have been made by Wang et al., to develop composite films of zein and hydrogel poly (acrylic acid) to heal skin burns. These composite films showed better elasticity, better adhesiveness to human finger skin, and stretching properties under strenuous joint exercises. The burn wound in vivo data indicated that film improved wound healing properties and suggested that it could be a promising wound dressing material [145].

5. Conclusion

Biomedical applications based on protein-derived materials are of great interest now. Proteins, particularly those derived from plants, have tunable properties, safety, and biocompatibility characteristics that render them suitable for biomedical purposes. The efficiency of zein in being shaped and chemically handled provides an incredible tool for the biomedical world. The physical and chemical characteristics and unique structure (at molecular, nano, and micro levels) indicate that zein is inherently superior to many other natural as well as synthetic polymers. The chemical modification of zein is a critical aspect that could be improved in every scope, which is crucial to work on the zein-based biomaterial for enhancing the mechanical properties of biomaterials. Thanks to its remarkable physicochemical properties, zein protein has a glowing future in the intracellular delivery of therapeutic peptides and genetic materials, making it a viable substitute for the currently employed synthetic polymers. Moreover, the attempt to create zein-based 3D structures also sheds light on zein as a very promising material in regenerative medicine and tissue engineering. New research focusing on the chemical modification of zein, biodegradability, and cytotoxicity of zein-based materials is still required. The fact is that the biodegradability and biocompatibility of zein and other inherent characteristics associated with zein's chemistry allow various applications of zein and zein-based biomaterials with great potential in the near future.

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Review

Modeling and formulation/process parameters design methodological approaches for improving the performance of biocomposite materials for building, construction, and automotive applications: A state-of-the-art review

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Copyright © 2024 by author(s). Journal of Polymer Science and Engineering is published by EnPress Publisher, LLC. This work is licensed under the Creative Commons Attribution (CC BY) license. https://creativecommons.org/licenses/ by/4.0/ Abstract: In today's manufacturing sector, high-quality materials that satisfy customers' needs at a reduced cost are drawing attention in the global market. Also, as new applications are emerging, high-performance biocomposite products that complement them are required. The production of such high-performance materials requires suitable optimization techniques in the formulation/process design, not simply mixing natural fibre/filler, additives, and plastics, and characterization of the resulting biocomposites. However, a comprehensive review of the optimization strategies in biocomposite production intended for infrastructural applications is lacking. This study, therefore, presents a detailed discussion of the various optimization approaches, their strengths, and weaknesses in the formulation/process parameters of biocomposite manufacturing. The report explores the recent progress in optimization techniques in biocomposite material production to provide baseline information to researchers and industrialists in this field. Therefore, this review consolidates prior studies to explore new areas.

Keywords: optimization techniques; formulation; process design; natural fibres; plastics; biocomposite material

1. Introduction

The demand for eco-friendly materials due to environmental concerns and fossil fuel depletion has recently increased [1,2]. As such, biocomposite materials are increasingly gaining attention over their synthetic counterparts in the composite industry based on their attributes such as eco-friendliness, cost-effectiveness, and renewability. Natural plant fibres are used as reinforcing materials for making biocomposite materials due to their good thermal insulation properties, lightweight, good mechanical properties, low price, durability, sustainability, and biodegradability [3,4]. Examples of plant fibres/fillers include wood powder, coconut husk, cotton stalk, shells of nuts (coconut, palm kernel), banana, hemp, flax, jute, and sisal [2,5]. Most of these biomass materials are often regarded as waste and are mostly burnt or find their destination in landfills, thereby constituting pollution [2,6,7]. However, the utilization of these agricultural materials in the polymer industry has both economic and sustainable benefits [2].

Petroleum-based plastics have been beneficial to humanity [8] in several ways, specifically in the polymer industry, where they are used to produce various polymeric goods like silicone heart valves, bottles, pipelines, plastic bags, epoxy glue, and

polyethylene cups [2,9]. Compared to other materials, polymers possess better resistance to corrosion and chemicals, have a lower density, and have good thermal and electrical insulating properties [9]. However, their non-biodegradable nature and the tendency to contribute a large volume of environmental pollutants, with an annual estimation of 150 million tons globally [2], have called for great concern recently. Therefore, recycling and reusing them in the polymer industry as matrices for fibres/fillers has both environmental and economic benefits.

Recently, the field of material design has seen a remarkable transformation of biocomposite materials, which are extensively used in applications such as construction, automotive, sports, and aviation. Nevertheless, biocomposites, like every other material, are continually subjected to market competition across the globe, and this calls for continuous research [10,11] to meet customers' demands. Improvements in mechanical properties are the major concern of composite materials. However, on the premise that a single application may require several properties (such as strength, resilience, toughness, stiffness, and so on), these improvements must take into consideration the overall performance of the materials [10]. The mere mixing of components and the characterization of the properties of the resulting biocomposite materials [11] are not enough to define the overall improvement. Also, as stated by Toupe et al. [10], it is not possible to improve a particular property without influencing others. Therefore, techniques that take into consideration the simultaneous optimization of multiple responses are desirable. Generally, the mechanical performance of any biocomposite material is affected by the process parameters employed during manufacturing [10] as well as the formulation parameters, as proven by several authors [10,12–14]. To have improved performance properties, it is critical to optimize these parameters by applying the appropriate optimization technique involving mathematical modeling. However, as noted in the literature, while the majority of the studies on natural filler/fibre-reinforced polymer composites reported in published works are limited to experimental investigation, research involving empirical modeling of biocomposite is limited [15]. This claim is justified by a database search carried out in this survey. A total of 7524 research articles were retrieved from the Web of Science within the last two decades (2000-2023) for the topic "biocomposites", whereas only about 60 studies involved "response surface methodology". In this regard, it is essential to intensify research efforts. The trend of the indexed articles containing "response surface methodology" is presented in Figure 1.

In general, a single property of a product is not sufficient to define its quality in the presence of multiple characteristics. Also, the optimization of a specific property in the presence of multiple responses cannot be achieved without affecting others negatively [12] if a suitable optimization technique is not employed. Such a conflicting situation is usually known as a multiple-response problem. To solve such problems, a methodology that can simultaneously optimize all the responses into a single performance is required. Some authors [10,12,16], in an attempt to solve multiple response problems, have employed response surface methodology (RSM) in their research studies in the field of composites. Experimentation and modeling were used to optimize the processing and formulation conditions, as reported in the previous studies. However, the review to consolidate these prior research studies is lacking in this field. Therefore, this report presents a review of the modeling and optimization of formulation conditions as well as process parameters of manufacturing techniques based on RSM approaches for improved performance properties (mechanical, tribological, physical, and surface properties) of biocomposite materials. The study will provide researchers with the baseline information needed for the advancement of this field.



Figure 1. Trend of indexed research articles containing "response surface methodology" from 2000–2023 (Source of data: Web of Science Core Collection, accessed in December 2023).

2. Experimental design, modeling and prediction

The design of experiments (DOEs), modeling, and prediction are becoming critical aspects of product design. This is because they are suitable tools for understanding the factors-response relationships and establishing optimal conditions for maximum product quality. With such tools, robust experimentation and convincing conclusions can be reached. However, the conventional approach of mere mixing of composite elements and characterization without involving these tools can lead to inconclusive results or misleading conclusions. The reason is that the traditional method deals with the linear/main effects of the factors on the response while ignoring the quadratic and interaction effects. For example, in a study [17] on the influence of compatibilizers on the performance of WPCs, the authors concluded that it is still unknown whether the observed enhancements in the material strength are from better dispersion of wood, improved interfacial bonding, or changes in the morphology of the plastic material. However, in such a mixture experiment, non-linear behaviour like interaction amongst factors is expected to occur because most factors do not blend linearly. Such behaviour cannot be predicted by a pure factor response. Additionally, the quadratic/interaction terms of the factors can influence the response variable. Therefore, to have a better understanding of the relationships between the factors/responses, it is necessary to consider both linear and non-linear behaviours using the aforementioned tools.

2.1. Experimental design

The design of experiment (DOE) is defined as a branch of applied statistics that deals with how input factors are manipulated to examine their impacts on a

performance metric by carrying out investigations of a system, process, or product. In this technique, experiments are planned, and executed, and results are analyzed and interpreted [18]. The design of the experiment is therefore a crucial aspect of experimentation and therefore should not be overlooked. Proper experimental design will promote the efficiency of the process at a reduced cost as the number of trial and error experiments is reduced.

There are two main designs of experiments, namely, one factor at a time and a factorial design. In the design of the one factor-at-a-time approach, one parameter is varied at a time while others are constrained [18]. The major drawback of this approach is that it does not involve the interactions amongst all the factors, which can automatically prevent the overall effects of all the parameters on the performance response. The factorial design is often seen as a robust method. In this approach, the total effects of the factors under consideration are observed on the performance metric. Factorial and fractional designs [19] are common examples of this approach. Many reviews [18,19] on experimental design already exist in published literature, which are also applicable in this field.

2.2. Modeling and prediction

Modeling and prediction are integral parts of optimization techniques involving the response surface methodology approach. By modeling, the relationship that exists between the factors and the quality characteristic can be established. In other words, the effects of the input variables on the performance metric can be observed.

The goodness of fit or predictive ability of a model is determined by the coefficient of correlation: R-squared (R^2) and the adjusted coefficient of correlation: R-squared adjusted R^2 (adj). A model is said to have a good fit when the R^2 and R^2 (adj) values are greater than 0.8 [12] and the absolute average deviation (AAD) between the experimental values and predicted data must be as low as possible [20]. Removal of non-significant factors from the original model [21] can be carried out to obtain the best R^2 and R^2 (adj) values. This process is called model refinement. However, care should be taken when carrying out model refinement because some factors that appear to be insignificant may have positive quadratic/interaction effects. It was reported in a previous study [10] that, based on the ordinary least square (OLS) assumptions, insignificant factors were allowed to remain in the model. Therefore, in model refinement, the total effects (main/linear, quadratic, and interactions) of all factors on the response should be considered.

3. Optimization of performance properties of biocomposites

Optimization techniques are methods that can be used to establish optimum conditions/parameters for performance improvement from a set of experimental trials. The purpose of carrying out the optimization process is to achieve maximum improvement in performance properties, including mechanical, tribological, physical, and surface characteristics, at reduced experimental trials and costs. According to Bhaskar and Sahoo [22], optimization plays a key role in the decision-making process in an industrial manufacturing process by maximizing one or more process parameters while keeping other factors within the constraints. Therefore, the importance of

optimization cannot be over-emphasized as far as the manufacturing of improved products is concerned.

3.1. Types of optimization techniques

In an attempt to increase the performance of biocomposite products, several optimization techniques have been reported in the published literature, including the Taguchi method (i.e., one response-at-a-time approach) and the response surface methodology approach (viz., simultaneous optimization approaches). The various types of optimization techniques, including the Taguchi method and response surface methodology (RSM), are presented in **Figure 2**.



Figure 2. Types of optimization strategy.

3.1.1. Taguchi method

This is also called the one-response-at-a-time technique. It is the conventional approach of identifying optimal parameters while maintaining the other variables at a constant level [20] within the boundary conditions. In many single-response problems, the Taguchi method has been employed to find the best parameter setting, reduce response variation, and simultaneously change the mean to the desired value. Using a fractional factorial experimental design known as orthogonal arrays (OAs), it decreases the number of experimental trials within acceptable reliability and uses signal-to-noise ratio (SNR) to evaluate the performance of the responses [23,24]. The Taguchi technique offers a simple and efficient integrated method for selecting the best possible designs in terms of quality, performance, and computational cost. In this technique, parameter design is a crucial step. With the least amount of noise sensitivity, the input parameters are meant to optimize the response variables [24].

Several research studies reported in the published literature have proven that the Taguchi method, including its analysis, is a feasible and effective strategy for optimizing the formulation/process parameters for mechanical performance enhancement. For example, many researchers have reported the process conditions of injection molding technique for thin wall parts [25–28] as well as in recycled plastic products [29] for a single response problem. The major setback of this technique is that it does not involve the optimization of multiple responses simultaneously, as reported in the literature.

Most Taguchi practitioners/industrial engineers still base their decisions on mere human judgment and past experience in establishing optimal settings for multiple responses, as reported in the work of Antony [30]. The uncertainty of such a decisionmaking process is debatable as to whether or not the decision-maker might interfere with the process. However, product design is becoming increasingly complicated due to the intense competition in today's manufacturing sector, and therefore, the optimization of multiple responses to a product is critical [31]. The separate analysis of conflicting responses could yield incompatible solutions, and they should be optimized simultaneously [32]. For multi-response problems, the Taguchi method is insufficient due to the increasing complexity of the problem with correlated responses [23]. Therefore, to solve this problem, a response surface methodology strategy is required to establish optimal settings that will ensure simultaneous optimization of all responses.

Signal-to-noise (S/N) ratio

To evaluate the robustness of the quality characteristic (response), a signal-tonoise (S/N) ratio is introduced by Taguchi. The S/N ratio is a performance metric aimed at producing goods and processes that are not sensitive to noise factors. A higher S/N ratio suggests that the signal is stronger than the random impacts of the noise factors [24,29].

According to the Taguchi technique, the S/N ratio is classified into three categories: the smaller the better, the nominal the better, and the greater the better [24,27,29], as shown in Equations (1), (2), and (3), respectively.

$$S/N = -10\log_{10}\left[\frac{1}{n}(\sum_{i=1}^{n} y_i^2)\right]$$
(1)

$$S/N = -10\log_{10}\left[\frac{1}{ns}(\sum_{i=1}^{n} y_{i}^{2})\right]$$
(2)

$$S/N = -10\log_{10}\left[\frac{1}{n}(\sum_{i=1}^{n} 1/y_i^2)\right]$$
(3)

where, y_i represents the value of the performance for the ith experimental setting, n denotes the total number of experimental trials, and s is the y_i standard deviation. However, the choice of using any of Taguchi's equations depends on the aim of the study. For example, in a work aimed at maximizing the mechanical properties of biocomposite materials, the signal characteristic of the larger is better (i.e., Equation 3) is recommendable.

3.1.2. Response surface methodology and their relevant literature

One of the major issues facing the manufacturing sector today is the problem of multi-responses due to their conflicting nature, as earlier mentioned. For instance, improving one response in multi-response problems can decrease the performance of one or more responses [33]. A methodology that can simultaneously optimize all the responses into a single response to give better performance at optimum formulation/processing conditions at a reduced cost is preferable. The multivariate strategy for solving such multiple response problems is known as response surface methodology (RSM).

Response surface methodology is a combination of mathematical and statistical methods that can be used to describe the relationships between the response and the independent variables. These interactions can be defined, either singly or in combination with the input variables. This experimental approach produces a mathematical model in addition to examining the effects of the independent variables. The name "response surface methodology" was coined as a result of the mathematical model's graphical perspective [20]. The relationship between the independent variable

and the response can be expressed mathematically in the form of a quadratic Equation (4) [20].

 $Z=a+b_1y_1+b_2y_2+\ldots+b_{12}y_1y_2+b_{13}y_1y_3+\ldots+b_{11}y_1^2+b_{22}y_2^2+\ldots$ (4) where, Z is the response, $y_1, y_2, y_3...$ are the independent variables, a is a constant (also called the Z-intercept), $b_1, b_2, b_{12}, b_{22}...$ represent the coefficients.

There are three main stages involved in the optimization study by RSM. The RSM optimization study is divided into three primary phases. The first stage consists of the preliminary work/screening experiment, whereby the independent parameters and their levels are determined. The selection of the experimental design, prediction, and validation of the model equation make up the second stage. The final step is to determine the optimal points and obtain the response surface plot/response contour plot as a function of the input factors, as detailed in the report by Baş and Boyacı [20]. The flowchart for the optimization study using response surface methodology is shown in **Figure 3**. However, this may vary slightly relative to the optimization technique used.



Figure 3. Optimization flowchart for RSM.

3.1.2.1. Principal component analysis

This is a multivariate approach that is suitable for combining highly interrelated criteria into a single response that includes multilateral data. It is employed in multivariate analysis to reduce the dimensionality [34] of a data set that contains highly correlated variables [24]. The data set is transformed into a new set of variables called the principal components (PCs), which are uncorrelated, orthogonal, and ordered so that the first few retain most of the variation present in the original variables. The advantage of this method is that it is sensitive to the relative scaling of the initial variables [35]. However, only components of eigenvalue (≥ 1) are extracted, and this

cannot account for the total response variance since only a small number is used to represent the whole of the original data set.

Several authors have attempted to solve multi-response problems using principal component analysis (PCA). For example, Su and Tong [36] proposed a systematic procedure for optimizing multiple responses in the manufacturing process based on PCA. They concluded that the proposed strategy yields a satisfactory result. However, in their analysis, one component that had an eigenvalue greater than or equal to one was considered. Another study was carried out to solve the multiple response optimization problem of welding parameters in a submerged arc-welding process using Taguchi's quality loss function and principal component analysis [30]. Although the author stated that the procedure was successful, it was reported that only one component had an eigenvalue greater than or equal to one. Consequently, only one component was extracted. In most of today's complex production processes, this is no longer applicable [37].

In an attempt to extract more than one principal component, the use of the Taguchi-integrated PCA method with a coefficient of determination approach was reported [37]. The authors employed this methodology for the process parameter optimization of an injection molding technique for glass fibre-reinforced polybutylene terephthalate. Two out of four eigenvalues were found to be greater than one. However, since the principal components of all the quality characteristics were not considered, it is still arguable that the optimal condition was obtained subjectively. Additionally, in this type of approach, the total response variable might not be considered, and this could lead to an unsatisfactory compromise solution.

However, in their findings, only components that have eigenvalues greater than or equal to 1 were considered, and hence, the total response variances were not included. This might lead to an unsatisfactory compromise solution and increase the uncertainty of the result as to whether it is optimal or not which is a limitation of this method. Furthermore, the application of PCA and grey relational analysis (GRA) for the optimization of correlated multiple response processes was reported [38]. Nevertheless, the starting process conditions were assumed to be known, which is not good for designing new processes as commented by Sibalija and Majstorovic [23].

Overall, although PCA appears in the published literature as an effective and feasible technique to jointly optimize multiple responses, the objectiveness of the method is still debatable. This is because only components that have eigenvalues greater than or equal to 1 are extracted, and hence, the total response variances may not be considered. This might lead to an unsatisfactory compromise solution and increase the uncertainty of the result as to whether it is optimal or not.

3.1.2.2. Desirability function analysis

Desirability function analysis (DFA) is a simple and effective method of solving multi-objective problems. In practice, it optimizes more than one response simultaneously [22]. DFA is a less sophisticated method that is easy to understand [32] and does not involve complex mathematics or computation [39]. Thus, it is simple and can be used even by non-statisticians. Although it is claimed in the literature [30] that analysis involving relative weights of responses is often quite subjective in nature. However, using an objective weighting method such as criteria importance inter-

criteria (CRITIC) [40] that is not based on the preference of the decision maker will lead to a compromise solution in an objective manner.

Many researchers have proven the feasibility and effectiveness of this technique as a method for solving multiple response problems in process engineering for the optimization of various machining process parameters, including electric discharge machining of Inconel 718 material [41], milling of glass fibre-reinforced composites [39], end milling of Inconel 718 super alloy [42], milling of rice husk fibre-reinforced composites [43], wire cut electrical discharge machining [44], drilling of polymer composite reinforced with jute fibre [45], and drilling process parameters of polymer composite reinforced with Washintonia filifera [46]. Despite the effectiveness and simplicity of this method, very few studies have employed this strategy to solve multiresponse problems in the concept of biocomposite manufacturing. For example, the use of the desirability function approach for the optimization of drilling parameters of rice-husk fibre-reinforced composite (RFRC) was described [43]. The authors found that 120 mm/min was the optimal feed rate to reduce roughness as well as the input and output delamination factors. In addition, the trials' optimal point had a reasonably high desire factor of 0.678. The optimal conditions included roughness (1.75 lm), input delamination factor (1.30), and output delamination factor (1.54). The feed speed (120)mm/min), spindle speed (800 rpm), drill type (Kevlar), and type of resin (polyester) are the control parameters at the optimal point. To the author's knowledge, only Toupe et al. [12] reported the use of the Box-Behnken experimental design and desirability function approach (Derringer-Suich and Ch'ng et al. models) to establish the optimum formulation conditions based on the quality/cost ratio for flax/recycled plastic biocomposite. Using such models will require high computational skills and also involve the interference of the decision maker in terms of assigning objective weights during the process. However, DFA can be used simply and effectively by integrating the Taguchi method into it and using a weight-determining method such as criteria importance through inter-criteria correlation (CRITIC), which does not involve the preference of the decision maker. We are currently investigating such studies on biocomposite material production for improved performance in our laboratory. There are three kinds of desirability functions; nominal-the-best, larger-the-better, and smaller-the-better, as detailed in Bhaskar and Sahoo [22].

3.1.2.3. Computational-based approaches

Computational-based strategies include all approaches that involve the use of complex mathematics/computational skills. Examples include neural networks [47,48], goal programming [49], and physical programming [50,51]. Several researchers have employed the computational-based approach in their studies in an attempt to solve multi-response problems. For example, the use of an artificial intelligence (AI)-based gene expression programming (GEP) technique to predict the performance of biocomposite materials was studied [15]. The authors found that the GEP-AI model results were more accurate with strong and better predictability compared to the regression analysis techniques. In another study reported in published work, an artificial neural network (ANN) was employed to optimize the thermophysical properties of a bio-unsaturated polyester (BUP) composite [52]. In the investigation, response surface methodology (RSM) was used in the design of the experimental study

plan, and both ANN and RSM approaches were used to analyze the results. The authors stated that the reliability of the theoretical model study was enhanced by comparing the results with the ANN, even though the RSM approach was used in the experiments to determine the optimization assessment. In an attempt to identify the effect of fibre loadings on the wear property of cotton fibre polyester composites, an artificial neural network was employed as the optimization technique [53]. The results of the conformation test showed that the ANN was a more useful tool than a general regression model for predicting the material's wear behaviour. Furthermore, it was reported that an artificial neural network was successfully used to estimate the specific wear rates of walnut shell powder-reinforced polyester composites [54]. Although each of these methods has its benefits, their sophisticated nature (complex mathematics/statistics), lack of algorithms used, and absence of proper guidelines make some of them unattractive and not highly practicable to practitioners, particularly non-statisticians [32].

In summary, although the computer-based approach seems promising, its complicated nature is a disadvantage since it can only be used by people with high computational/mathematical skills. Designing a mathematical model for multiple response problems that can be used by statisticians and non-statisticians and does not require complex mathematics/computational skills is most desirable in today's manufacturing sector. This will save computational costs, time, and energy and increase production outputs.

3.2. Summary of previous studies involving the optimization of biocomposites using RSM

 Table 1 presents some research studies regarding the use of response surface

 methodology as reported in the published literature. This is to give insight into prior

 research in order to discover new research areas.

Author (s)	Input factors	Response (s)	RSM technique	Remarks/results of the study
[43]	Screw speed, feed rate, resin type, and drill bit.	Ra, Fde, and Fds.	DFA approach.	The optimal point of the drilling process was found at the desirability of 0.678 with input variables at; spindle speed (800 rmp), feed rate (120 mm/min), resin type (polyester), type of drill bit (Kevlar) and response variables at; Ra (1.75 μ m), Fde (1.30), and Fds (1.54).
[10]	Extrusion profile temperature, barrel heating temperature, and mold temperature.	Flexural modulus, tensile modulus, impact strength, and tensile stress at yield.	DFA approach using the Derringer-Suich model.	The authors reported that the optimum condition at; extrusion profile temperature is 145 °C–175 °C, barrel heating temperature of 190 °C–160 °C, and temperature of mold 35 °C.
[55]	Fibre loadings for each natural fibre (hemp, ramie, and pineapple).	Tribological properties.	CRITIC and MEW approach.	The author reported that the formulation containing 5 wt% ramie fibre is the best option for maximizing Tribological performance for the automotive braking application.
[56]	Wood waste of various amounts.	Physical, mechanical, and Wear properties.	Hybrid entropy-simple additive weighting method.	The authors reported that the best combination was found with a composite containing 2.5 wt% of wood waste.
[12]	Flax fibres, coupling agent, and impact modifier.	Flexural modulus, tensile modulus, impact strength, and tensile stress at yield.	DFA approach using the Derringer-Suich model.	The optimal formulation was obtained at; 45 wt% of flax fibre, 4 wt% of coupling agent, and a 25 wt% of impact modifier.
[57]	RWF, Rpp, MAPP, and UV stabilizer. The lubricant was kept constant.	Mechanical properties.	D-optimal mixture experimental design approach.	The authors reported that the optimal formulation was found at 50.3 wt% Rpp, 44.5 wt% RWF, 3.9 wt% MAPP, 0.2 wt% UV stabilizer, and 1.0 wt% lubricant.
[43]	Screw speed, feed rate, resin type, and drill bit.	Ra, Fde, and Fds.	DFA approach.	It was reported that the optimal point was found at Ra $1.75 \ \mu$ m, Fde 1.30, and Fds 1.54 with a desirability index of 0.678.

Table 1. Summary of previous literature involving response surface methodology.

To have a robust and quality product, the optimization techniques must be suitably reviewed and designed. Although there is no universal guideline for choosing the best optimization strategies for a given application [58], a proper selection of the optimization techniques and design of experiments will yield high-performance properties for the resulting product. A simple and effective method that does not involve the preference of the decision-maker and could be used by both statisticians and non-statisticians is highly recommended. The desirability function-integrated Taguchi approach fits into this description based on this survey.

3.3. Applications of biocomposite materials

Biocomposite products have found wider applications as a class of infrastructural and structural materials in various sectors, including building, construction, and automobile industries, owing to their sustainability, ease of production, as well as their cost and environmental benefits [2]. Compared to wood, wood-plastic composites (WPs) are receiving more attention as building materials in applications such as decking and flooring owing to their better mechanical properties and stability [7]. Decking is the major market for WPCs. There are growing numbers of applications in the areas of residential, automotive, infrastructural, and railroad ties [59]. According to Mohanty et al. [60], biocomposites are emerging as a viable substitute for glass fibre-reinforced polymer composites in the automobile industry because of their favourable non-brittle fracture upon impact-a feature that is necessary for the passenger compartment and lightweight. Also, the automobile sector is taking big steps in the transition to a more environmentally friendly supply chain by using natural fibers as base materials for auto parts like boot linings, door panels, spare tires, and seat backs [61]. Natural fiber composites have been employed in structural and infrastructure applications to produce load-bearing components such as beams, roofs, multipurpose panels, water tanks, and pedestrian bridges [62]. Examples of biocomposite materials are presented in Figure 4. From the survey, it is evident that there is a growing market for biocomposite materials globally, which requires more research efforts. However, to have a good quality product that meets customers' demands, employing a suitable optimization technique in the product design is critical.



Building and Construction

Automobile Parts



Figure 4. Biocomposite materials [2].

4. Conclusion/future perspective

In order to have robust and good mechanical performances of biocomposite products suitable for use in the building, construction, and automobile sectors, the optimization techniques must be suitably reviewed and designed. Proper selection of the optimization methods and design of experiments will yield composite materials with improved performance properties. Therefore, the decision maker must be prudent in selecting the optimization techniques and design without interference. From the survey, it seems that DFA-integrated Taguchi with CRITIC methodology is a better option when considering optimization techniques. This is because such a methodological approach is feasible, effective, and objective in nature. Additionally, it involves the total response variable, unlike the PCA, where only components with eigenvalues greater than or equal to one are extracted. Compared to computer-based approaches like neural networks or goal programming, DFA-integrated Taguchi with the CRITIC method does not require complex mathematics/computational skills and can be carried out using Minitab software and Excel.

Response surface methodology approaches have been frequently used in process engineering; however, only a few research studies have been reported on the concept of polymer-based biocomposites, considering the myriad of natural fibres/fillers. Most composite designers/industrial engineers today still base their engineering judgment on the Taguchi method of single optimization of response and past experience. However, in today's world of manufacturing, industries are being faced with multiresponse problems, and only the Taguchi technique is not enough to solve such complex challenges. Also, employing past experience in the decision-making process is debatable, as the preference of the decision-maker cannot possibly be avoided. To overcome these challenges, a response surface methodological approach is required. However, the methodology for optimizing the multiple performance of a product is yet to be fully explored in the field of biocomposite, as very few studies involving the use of mathematical modeling of performance properties compared to the traditional experimental investigation approach are reported in the literature to the best of the author's knowledge. From the survey, it appears that the desirability function-Taguchi approach is a better optimization approach for multiple responses due to its simplicity, effectiveness, feasibility, and economic benefits. Also, there is no defined standard rule for choosing the best optimization technique for a given application. Therefore, efforts should be intensified to improve on the existing methodology and discover new ones to achieve quality biocomposite products for building, construction, and automobile applications.

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Abbreviations

RWF: Rubberwood flour. Rpp: Recycled polypropylene. MAPP: Maleic anhydride polypropylene. UV: Ultraviolet. Ra: Roughness. Fde: Input delamination factor. Fds: Output delamination factor. CRITIC: Criteria importance through inter-criteria correlation. MEW: Multiplicative exponent weighting. RSM: Response surface methodology. DFA: desirability function analysis. PCA: Principal component analysis. GRA: Grey relational analysis. WPCs: Wood plastic composites. PBT: Polybutylene terephthalate. GEP-AI: Gene expression programming-artificial intelligence

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Advancements in nanohybrids: From coordination materials to flexible solar cells

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Copyright © 2024 by author(s). Journal of Polymer Science and Engineering is published by EnPress Publisher, LLC. This work is licensed under the Creative Commons Attribution (CC BY) license. https://creativecommons.org/licenses/ by/4.0/ Abstract: This comprehensive review explores the forefront of nanohybrid materials, focusing on the integration of coordination materials in various applications, with a spotlight on their role in the development of flexible solar cells. Coordination material-based nanohybrids, characterized by their unique properties and multifunctionality, have garnered significant attention in fields ranging from catalysis and sensing to drug delivery and energy storage. The discussion investigates the synthesis methods, properties, and potential applications of these nanohybrids, underscoring their versatility in materials science. Additionally, the review investigates the integration of coordination nanohybrids in perovskite solar cells (PSCs), showcasing their ability to enhance the performance and stability of next-generation photovoltaic devices. The narrative further expands to encompass the synthesis of luminescent nanohybrids for bioimaging purposes and the development of layered, two-dimensional (2D) material-based nanostructured hybrids for energy storage and conversion. The exploration culminates in an examination of the synthesis of conductive polymer nanostructures, elucidating their potential in drug delivery systems. Last but not least, the article discusses the cutting-edge realm of flexible solar cells, emphasizing their adaptability and lightweight design. Through a systematic examination of these diverse nanohybrid materials, this review sheds light on the current state of the art, challenges, and prospects, providing valuable insights for researchers and practitioners in the fields of materials science, nanotechnology, and renewable energy.

Keywords: coordination materials; nanohybrids; advanced energy storage; solar cells

1. Introduction

Coordination materials-based nanohybrids represent a fascinating frontier in materials science, where the synergy between organic ligands and metal ions creates versatile structures with multifunctional properties. These nanohybrids, often designed at the molecular level, leverage the unique coordination chemistry of metal ions to impart specific functionalities to the resulting materials. One of the distinctive features of coordination materials is their ability to form well-defined structures through coordination bonds, leading to the assembly of organized and tailored architectures. In the realm of nanohybrids, coordination materials find application in a myriad of fields, ranging from catalysis and sensing to drug delivery and energy storage [1]. The controlled synthesis of these hybrids allows for the precise incorporation of organic ligands and metal ions, enabling the fine-tuning of their properties for targeted applications. For instance, the incorporation of luminescent metal complexes into coordination nanohybrids has paved the way for advanced imaging and sensing

technologies, capitalizing on the inherent properties of the metal ions to emit light under specific conditions. Moreover, coordination materials-based nanohybrids exhibit remarkable catalytic activities owing to the inherent reactivity of metal centers. The well-defined coordination environments provide an ideal platform for catalytic reactions, and these hybrids have been employed as efficient catalysts in various chemical transformations. The modular nature of coordination materials allows for the incorporation of different metal ions and ligands, enabling the development of catalytic nanohybrids with tailored reactivity and selectivity. In the realm of drug delivery, coordination materials-based nanohybrids offer a unique combination of biocompatibility and controlled release properties. The metal-ligand coordination bonds can be designed to respond to specific stimuli, such as pH or temperature, triggering the release of encapsulated therapeutic agents at targeted sites. This precise control over drug release enhances therapeutic efficacy while minimizing side effects. Furthermore, the advent of coordination materials-based nanohybrids has made significant strides in the development of advanced energy storage and conversion systems. Metal-organic frameworks (MOFs), a subclass of coordination materials, have emerged as promising candidates for applications in batteries and supercapacitors due to their high surface areas and tunable porosities [2].

The unique properties of these nanohybrids position them as model support structures for developing nanomaterials with extraordinary performance features [3]. The design of luminescent nanohybrids for bioimaging purposes has been explored through various approaches in the literature. Silica luminescent nanohybrids containing Eu³⁺-complexes were synthesized using three distinct methods to determine the most efficient approach for obtaining highly emissive final hybrids suitable for cell imaging applications, leveraging the luminescent probe properties of Eu³⁺. The synthesis process involved the transformation of dense Stober silica nanoparticles (SiO₂) into luminescent hybrids through a series of well-defined steps. The surface of SiO_2 was first functionalized with APTES, and the amine group subsequently reacted with salicylaldehyde to form a Schiff base ligand (SB), resulting in the SiO₂-SB system. The coordination of Eu³⁺ ions to SB, followed by the displacement of coordinated water molecules with dibenzoylmethane (DBM), led to the creation of the hybrid SiO₂-[Eu1]. Tris-[Eu(DBM)₃] complexes coordinated to the imine groups grafted on the SiO₂-SB surface were employed to generate the SiO₂-[Eu] hybrid. A novel Eu³⁺-Schiff base combination with a triethoxysilyl group was grafted onto the SiO₂ surface to produce the third hybrid, SiO₂-[Eu].

All three luminescent hybrids exhibited red emission, extended lifetimes (0.34– 0.61 ms), and remarkable photostability under continuous 340 nm UV light exposure. Characterized by a spheroidal form and a size of 100 nm, the hybrids were evaluated using the LUMPAC software program and the Horrocks equation to determine quantum efficiency (QE) and the quantity of coordinated water molecules (qH₂O) to the Eu³⁺. While all three synthesis methods showed promise, SiO₂-[Eu] emerged as the optimal hybrid based on photophysical results, boasting higher QE and color purity values. Moreover, SiO₂-[Eu] demonstrated non-toxicity (**Figure 1**), as evidenced by its bio-viability in CHO-k1 cells at various dosages. The effectiveness of SiO₂-[Eu] as a luminous stain for cell imaging was further validated through exploratory cell imaging assays, where the internalization of nanoparticles within the cells was confirmed by Eu^{3+} (${}^{5}D_{0}$ ${}^{7}F_{J}$) narrow emission bands, showing distinct cell marking in proximity to the nucleus. In conclusion, SiO₂-[Eu] exhibited favorable characteristics in terms of form, size, optical properties, and biocompatibility, positioning it as a promising candidate for use as a luminous stain in cell imaging applications [4].



Figure 1. Three approaches for Silica luminescent nanohybrids containing Eu^{3+} -complexes SiO₂ [Eu] in CHO-k1 cells [4].

2. Synthesis of CPs nanostructures

The synthesis of conductive polymers (CPs) nanostructures involves crafting nanoscale architectures with enhanced electrical conductivity and distinctive properties, combining the electrical characteristics of metals with the mechanical features of polymers. The synthesis process encompasses several key steps. Firstly, an appropriate monomer, such as aniline, pyrrole, or thiophene, is selected based on the desired properties of the final nanostructure. Various polymerization methods, including chemical oxidation, electrochemical polymerization, and oxidative polymerization, offer tailored approaches to CPs nanostructure production. Chemical oxidation, utilizing agents like ammonium persulfate, is apt for bulk synthesis, while electrochemical methods, involving an electrode for precise control, offer advantages in size and morphology modulation. Oxidative polymerization, with agents like ferric chloride or bromine, allows for specific shape and size control. Template-assisted synthesis, utilizing porous materials or nanostructures, and surfactant-assisted synthesis, employing stabilizing surfactants, contribute to dimension and shape regulation. Doping, a crucial step employing acids, salts, or electron-accepting molecules, enhances electrical conductivity. Thorough characterization using techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR) evaluates size, morphology, crystallinity, and chemical structure. Finally, exploring applications in sensors, flexible electronics, energy storage devices, and emerging technologies leverages the unique electrical and mechanical properties of CPs nanostructures. Through meticulous control of synthesis parameters,

researchers can tailor CPs nanostructure properties for specific applications, contributing to advancements in materials science and electronic devices. The structure and morphology of the CPs sensing layers, which are the result of structural effects, are intimately connected to the sensing responses. To meet the needs of various types of sensor setups, a variety of procedures have been investigated to construct 0D, 1D, 2D, and 3D CPs nanostructures. Thus, the process used to create the CPs nanostructures is crucial for the integration of sensors [5]. Research interest has been growing in the "MXene" family of massive, recently discovered 2D materials. The substance has good optoelectronic, physicochemical, thermoelectrical, and mechanical capabilities [6] and is made up of transition metal carbides and nitrides. The formula Mn + 1XnTx, where n = 1, 2, or 3, may be used to show MXene. M stands for a transition metal (such as Mn, Sc, Cr, Nb, Ta, Mo, and Hf), X for a C or N element, and T for various surface functional groups or atoms (-OH, O, or F). The predecessors of MXene are MAX phases, which have the common formula Mn + 1AXn, where A is any element from groups IIIA and/or IVA of the periodic table. X indicates a C and/or N element, and *n* = 1, 2, 3, 4, and 5 [6].

3. Properties of coordination material-based nanohybrids

The properties of coordination material-based nanohybrids underscore their significance in the realm of materials science. These nanohybrids exhibit a remarkable interplay between organic ligands and metal ions, giving rise to a diverse range of functionalities [7]. Their unique coordination chemistry enables the formation of well-defined structures, allowing for precise control over their size, shape, and composition. Coordination material-based nanohybrids often boast enhanced mechanical, thermal, and electrical properties, making them versatile candidates for various applications. The tunability of these properties is further augmented by the choice of metal ions and ligands during the synthesis process. Additionally, coordination nanohybrids frequently exhibit superior catalytic activities, making them valuable in catalysis and sensing applications. Their inherent biocompatibility and tailored release mechanisms also position them as promising candidates for drug delivery systems. As the exploration of these nanohybrids advances, their properties continue to be fine-tuned, paving the way for innovations in fields such as energy storage, biomedical applications, and catalysis [8].

4. Emerging solar cell technologies

4.1. Lead-based perovskite materials

Lead-based perovskite materials have emerged as a transformative force in the fields of photovoltaics and optoelectronics. These materials, typically adopting the ABX₃ crystal structure, where A is a cation, B is a metal cation, and X is an anion, exhibit exceptional optical and electronic properties. Particularly, lead halide perovskites, such as methylammonium lead iodide (MAPbI₃), have demonstrated outstanding power conversion efficiencies in solar cells, rivaling traditional silicon-based technologies. The facile and cost-effective fabrication processes, including solution-based deposition techniques, make lead-based perovskites attractive for large-scale production. However, their commercial viability is tempered by concerns

regarding the toxicity of lead, urging researchers to explore alternative compositions, such as tin-based perovskites. Ongoing research endeavors focus on enhancing the stability, scalability, and environmental impact of lead-based perovskite materials, aiming to unlock their full potential for clean energy applications. Despite challenges, the rapid progress and immense promise of lead-based perovskite materials continue to drive innovation and reshape the landscape of renewable energy technologies. Kojima et al. employed MAPbI₃ and MAPbBr₃ as the first perovskite materials to be used in DSSCs as sensitizers, and Pb-halide-based perovskites have since drastically changed the field of PVs [9]. The photovoltage and photocurrent of the device are significantly altered by the employment of I and Br ions as halide anion in the PSCs. Pb-based perovskites have a number of exceptional qualities that make them suited for optoelectronic uses. They are semiconductors with an almost perfect direct band gap (1.6 eV), and for single-junction solar cells, the Schockley-Queisser gap is 1.43 eV. They have an extremely high absorption coefficient ($a = 5 \times 10^4 \text{ cm}^{-1}$), which is nearly 25 times more than Si's and even better than GaAs [10]. Because e- and h+ have balanced, very tiny effective masses for enhanced conveyance using charge carriers [11], with a 1 m diffusion length, photo-generated charge carriers have a long lifespan. Planar and lateral structures are the two forms of architecture that may be employed in the creation of perovskite single-crystal devices. A planar or conventional sandwiched structure is an example of the solar cell architecture that is most often used. Malinkiewicz et al. [12] created a planarly structured single crystal device; in this work, the team combined fullerene derivatives with MAPbI3 as a donor material. Their planar devices were made using a thermally deposited 285 nm MAPbI3 thin film at ambient temperature. Sandwiched between materials that act as an electron acceptor (PCBM) and an electron blocker (polyTPD) is a film. The manufactured device established a benchmark PCE of 12% for an organic solar cell based on fullerene [13], and since then, additional small-molecule-based hybrid solar cells have reached PCEs of 18% [12,14]. In contrast to the typical arrangement of a planar-structured device, lateral-structured single-crystal devices exhibit improved thermal and mechanical characteristics, providing the device with more stability.

4.2. Dye-sensitized solar cells (DSSCS)

The dye-sensitized solar cell (DSSC) provides a practical and effective technology for the delivery of energy in the future. It offers comparable power conversion efficiency (PCE) to traditional silicon solar cells at cheap manufacturing and material costs. Titanium oxide (TiO₂) is a common, affordable, and environmentally safe DSSC material. In order to print DSSCs on the mass production line, a roll-to-roll method might be used since DSSC materials are less prone to contamination and processable at room temperature. DSSCs are a great option for interior applications since they work better in lower light intensities. The development of molecular engineering has led to the introduction of colorful and transparent thin films to increase their aesthetic qualities. Such advantages have so far sparked a lot of research interest and commercialization activity. This study considers device modeling, cutting-edge methodologies, and unique device topologies to explore advanced approaches and research trends for this promising technology [15]. As a result, the dye-sensitive solar cells (DSSC) (**Figure 2a**) [16], a novel form of solar cell

consisting of a counter electrode, an electrolyte containing iodide-triiodide ions, and a nanocrystalline porous semiconductor electrode that absorbs dye [17], have been thoroughly researched. Based on photosensitization caused by the dyes on the wideband-gap mesoporous metal oxide semiconductors [18], it is a device for converting visible light into electricity. Due to the dye's absorption of a portion of the visible light spectrum, this sensitization has occurred. Sensitized dye functions by receiving solar energy and transforming it into electrical energy. Figure 3b illustrates the DSSC's basic operating concept. It falls under the following categories of flows: 1) an electron went through an excitation cycle; 2) TiO_2 was injected into, and iodine was reduced at the counter electrode; 3) an electron performed external work [19]; 4) the electrolyte was diffused; and 5) the oxidized dye was restored. Due to its potential uses in environmental protection and energy production, titanium dioxide (TiO₂) has recently attracted the attention of researchers from all over the world. It has been used primarily in DSSC due to its nanocrystalline mesoporous nature, which translates to a high surface area for dye adsorption [20]. The solar energy may then be used to excite the absorbed dye molecules to create electron-hole pairs that are then divided and transported into the TiO_2 lattice. The dye's absorption spectrum and its anchoring to the surface of TiO_2 are crucial factors in determining the cell's effectiveness [21]. The comparison of semiconductor solar cells and DSSCs is given in Table 1. Much attention has been paid to the dye since it is crucial for absorbing visible light and converting photon energy into electricity, paid to survey the effective sensitizer dyes [22]. Porphyrins [23], platinum complexes [24], and other organic dyes have been created and utilized as sensitizers together with other metal complexes [25]. Ru-based complex sensitizers are often employed because of their superior effectiveness and long lifespan. These benefits, however, are outweighed by their high price and propensity to degrade in the presence of water [26]. Additionally, it is considered to be extremely poisonous and carcinogenic.

 Table 1. Comparison between semiconductor-based solar cells and dye-sensitive solar cells (DSSC) [16].

	Semiconductor solar cells	Dye-sensitized solar cells
Transparency	Opaque	Transparent
Pro-environment (material & process)	Normal	Great
Power generation cost	High	Low
Power generation efficiency	High	Normal
Color	Limited	Various



Figure 2. (a) the structure of DSSC; (b) the mechanism of DSSC [16].

The dye-sensitized solar cell (DSSC), one of the several solar technologies, holds out the most hope for a low-cost, highly-manufacturable answer to an energy economy free of fossil fuels and their negative effects. The overall conversion efficiency of DSSCs documented in the literature, however, has only grown by 4% in the last 25 years. This chapter gives a general overview of the DSSC architecture, discusses the state of the technology today, and considers the causes that have prevented cell efficiency from improving despite enormous amounts of effort. in advancing technologies. It emphasizes the extremely difficult and complicated nature of DSSC optimization as well as the necessity of multiscale first principles mathematical modeling of DSSCs to fully comprehend the physics, dynamics, and interactions [27] of internal DSSC components. These models enable in silico design and DSSC optimization and can characterize cellular activities at various temporal and geographical dimensions [28].

4.3. Coordination material-based nanohybrids in DSSCS

A sensitizer molecule (often several dye molecules) is used in dye-sensitized solar cells (DSSCs), a solar photovoltaic device that transforms solar energy into electrical energy. The cost of manufacturing DSSCs is much cheaper than that of traditional silicon-based solar cells since they do not include pricey silicon. Their commercial usage has been hindered despite the cost benefit by their generally poor chemical stability and low photo conversion efficiency (PCE). The two most costly components of PV technology, the platinum counter electrode (CE) and ruthenium-based dyes, may be replaced with less expensive ones; however, some recent advances showing PCE in the region of 15% imply that DSSCs can be a low-cost alternative to PV technology. In the DSSC, the material choice for the CE is critical. performance because its primary function is to draw electrons from the outside circuit and catalyze a redox process to decrease the electrolyte ions. Due to their intriguing catalytic activity and intriguing physicochemical features, transition metal chalcogenides (sulfides/selenides), among others, have lately gained significant study attention as CE materials as an alternative to platinum. This chapter begins with an explanation of the

fundamental operation of the DSSC, with a focus on the function of the CE. This is followed by a summary of the typical procedures for the synthesis of sulfides and selenides-based CE for DSSC application. We next compare output metrics, including PCE, stability, and fill factor, to the literature on the state of the art for DSSCs made with sulfides/selenides-based CEs. Finally, we summarize the overall conclusion and discuss the scope for future research [29].

4.4. Organic solar cells (OSCS)

A promising new low-cost thin-film photovoltaics technology is the organic solar cell (OSC). With the advancement of low-bandgap organic material synthesis and device processing technologies, the power conversion efficiency (PCE) of OSCs has surpassed 16% for single junction and 17% for organic-organic tandem solar cells. The OSCs' lackluster device stability is the biggest impediment to their commercial applications. The elements affecting OSC stability are enumerated here. Oxygen, water, radiation, heating, metastable morphology, diffusion of electrode and buffer layer materials, and mechanical stress are the stability-limiting elements. The most recent developments in methods to strengthen the stability of OSCs are reviewed, including material design, active layer device engineering, employing stable electrodes and encapsulating materials, inverting the shape, and improving the buffer layers. Also included are the guidelines from the International Summit on Organic Photovoltaic Stability. The different research approaches that may be used to attain the necessary device efficiency and stability are outlined, opening up prospective routes for the successful commercialization of OSCs [30].

The most promising organic solar cells (OSCs) for use in wearable energy resources and photovoltaics incorporated into buildings are those that are flexible and semitransparent. As a result, the development of novel flexible bottom or top transparent electrodes, the design and synthesis of high-performance photoactive layer and low-temperature processed electrode buffer layer materials, and the engineering of device architecture have all contributed to the rapid development of flexible and semitransparent OSCs in recent years. Flexible OSCs have the best power conversion efficiency at over 10%, while semitransparent OSCs have the highest at 7.7% with an average visual transmittance of 37%.

4.4.1. Factors limiting the stability of OSCS

The stability of OSCs in the real world might be limited by a variety of circumstances, which is different from the research setting in labs. In this section, we go over the elements—metastable morphology, electrode and buffer layer diffusion, oxygen and water, radiation, heating, and mechanical stress—that affect OSC stability over the course of their whole lifetimes (**Figure 3**). The essential element of OSCs is an active layer, which typically consists of two or three phases (donor phase, acceptor phase, and mixed donor/acceptor phase) [31]. Because organic components [32,33] move around so much, phase separation is always metastable. Micro-focused grazing incidence small-angle X-ray scattering (mGISAXS) was utilized by Muller-Buschbaum. To examine the metastable morphology of a polymer/fullerene mix. A morphological deterioration model was put out by them (**Figure 3a–d**), in which the



donor domains drift apart from one another (smaller domains disappear while bigger ones increase) [34].

Figure 3. Organic solar cells (OSCS); (a) schematic diagram of the factors limiting the stability of OSCs; (b) schematic diagram of the device under mechanical stress; (c) schematic diagram of the diffusion of electrodes and buffer layers; (d) schematic diagram of the diffusion of oxygen and water [35].

The efficiency of bulk heterojunction (BHJ)-based organic solar cells (OSCs) has significantly increased during the past several years. However, more advancements are required for precision device fabrication and large-scale roll-to-roll (R2R) manufacture of this technology. The essentials of a BHJ OSC, including its operating principle and performance traits, are highlighted in this article. Different degradation variables impacting the operational life of OSCs are explored, and the significance of stability for device longevity is supported. Last but not least, methods to increase OSC stability include encapsulating the device, controlling morphology in the BHJ layer, and interfacial engineering using buffered layers. The emphasis is placed on the utilization of inverted geometry and different electrode materials. In addition, a straightforward mathematical model of OSC deterioration trends is suggested. This study covers practically all of the major factors that are thought to be crucial for understanding the current condition of BHJ OSCs regarding stability and deterioration [36,37].

4.5. Coordination material-based nanohybrids in PSCS

Coordination material-based nanohybrids have emerged as promising components in the development of perovskite solar cells (PSCs), offering innovative solutions to enhance their performance and stability. PSCs, with their remarkable light-absorption properties and cost-effective fabrication methods, have gained attention as next-generation photovoltaic devices. Integration of coordination nanohybrids into PSCs involves incorporating tailored nanoscale architectures, often derived from metal-organic frameworks (MOFs) or other coordination materials, to

address challenges associated with PSCs. The unique properties of coordination nanohybrids contribute significantly to PSCs. These materials can serve as electron or hole transport layers, enhancing charge carrier mobility within the solar cell. Their tunable structures and functionalities allow for precise control over interfaces, leading to improved charge separation and reduced recombination losses. Additionally, coordination nanohybrids can function as stabilizing agents, mitigating the notorious issue of perovskite material degradation due to moisture or temperature fluctuations. In the quest for efficient and stable PSCs, the incorporation of coordination materialbased nanohybrids has shown promising results. Researchers are exploring various strategies, such as incorporating nanohybrids as interlayers or modifying the perovskite layer itself, to optimize device performance. By leveraging the unique properties of coordination nanohybrids, PSCs can potentially achieve higher efficiencies, enhanced long-term stability, and reduced manufacturing costs, paving the way for the widespread adoption of this renewable energy technology. As advancements in materials science and nanotechnology continue, coordination material-based nanohybrids stand at the forefront of innovations in PSCs, bringing us closer to a sustainable and efficient future for solar energy.

High-performance perovskite solar cells (PSCs) require a substantial amount of hole-transporting material (HTM). HTMs based on inorganic, organic, and hybrid (organic-inorganic) materials have been effectively produced and studied throughout the years. With the use of 2,2',7,7'-tetrakis (N,N-di-p-methoxyphenylamine) and 9,9spirobifluorene (spiro-OMeTAD) as HTM, perovskite solar cells today achieved an efficiency of 22.1%. Alternative materials are needed since the synthesis and price of organic HTMs provide a significant challenge. Inorganic HTMs have significantly improved in stability and power conversion efficiency (PCE) during the last few years. CuOx just attained the PCE of 19.0% with more consistency. These discoveries demonstrate that for next-generation PSCs, inorganic HTMs are superior to organic HTMs. In this paper, we primarily concentrated on the most recent developments in inorganic and hybrid HTMs for PSCs and emphasized how the stability and efficiency of PSCs were increased by switching from metal oxides to HTMs. Therefore, we anticipate that the energy levels of these inorganic HTMs will fit the valence band of perovskites extremely well, and increased efficiency will aid in the practical deployment of low-cost PSCs in the future [38].

4.6. Silicon solar cells

Historical advancements that led to the creation of high-efficiency crystalline silicon solar cells are recognized and explained. Despite the development of laboratory cells that perform close to their theoretical maximum, commercial cell designs still need to undergo substantial development in order to reach their full potential. To achieve commercial devices of 20% efficiency from solar-grade substrates, in particular, the development of cell structures and processes that enable fully activated device volumes in conjunction with well-passivated metal contacts and front and rear surfaces is crucial (yet not particularly difficult). Manufacturers will be forced to adapt their designs in this way by the inevitable trend toward smaller substrates if they don't want to suffer significant performance losses. Thin-film crystalline silicon cells, which

are a kind of thin-film technology, are anticipated to take over at some point. a credible candidate. It is especially important to achieve devices with fully activated volumes (diffusion lengths much greater than device thicknesses), well-passivated metal contacts and surfaces, and the crucial inclusion of light trapping because current commercial techniques and processes are generally unsuitable for thin-film fabrication. A key characteristic of this laboratory cell is its extremely good light trapping, which disproves the long-standing criticism of crystalline silicon regarding its poor absorption properties and, correspondingly, perceived inability to achieve high-performance thin-film devices. The recent achievement of 21.5% efficiency on a thin crystalline silicon cell (less than 50 urn thick) adds credibility to the pursuit of crystalline silicon in thin films. The parallel-multijunction cell is a low-cost, low-quality polycrystalline silicon material. Over the next 10 years, structure may offer a method for attaining fully active cell volumes with the ability to reach acceptable efficiencies at a low cost.

First silicon cells, 1940–1950

Russell Oh1 of Bell Laboratories discovered a clearly defined barrier while researching recrystallized melts of commercially high-purity silicon. Fortunately, impurity segregation during the recrystallization process led to the formation of these natural connections. He referred to one side of the junction as "positive" or "*p*-type" and the other as "*n*-type" (the functions of acceptors and donors were not understood at the time). The computation of cell voltage polarity has been made easier for future generations thanks to this lucky naming decision! Because of the absence of control over the junction position and the caliber of the crystalline silicon material, Russell Ohl was unable to create functional cells from these natural connections, as illustrated in **Figure 2**, with efficiencies significantly below 17 [39].

By better utilizing the solar spectrum, it is possible to increase the cell efficiency of silicon solar cells in three different ways: photoluminescence (shifting photons into wavelength ranges better accepted by the solar cell), down-conversion (cutting one high-energy photon into two low-energy photons), and up-conversion (combining low-energy photons into one high-energy photon). This study discusses the appropriateness of current materials for use with silicon solar cells and presents the state-of-the-art of these three approaches [14].

The crystalline silicon (c-Si) solar cell has been recognized as the only affordable, long-term, sustainable, and environmentally acceptable renewable energy source to displace fossil fuels since its invention. Si-based photovoltaic (PV) technology has advanced at a pace that is sufficient for the job. It has increased to 55 GW, controls 90% of the market, and has an admirable track record of price reductions (**Figure 4**). By 2020, it is predicted that the market will expand by 20 to 30 percent and produce 100 gigawatts (WP) annually [1]. Cost reduction to compete with fossil fuels has been the main driver of Si PV's industrial growth. Solar cell production costs have decreased from \$76/WP in 1977 to \$0.3/WP in 2015. This cost is still 3–4 times higher than carbon-based fuels [40].



Figure 4. (a) PV growth from 2010–2015; **(b)** crystalline Si PV market share; **(c)** reduction in PV module price [40].

4.7. Tandem solar cells

Tandem solar cells represent a cutting-edge advancement in solar photovoltaic technology, aiming to maximize energy conversion efficiency by stacking multiple layers of solar cell materials with complementary absorption spectra. Unlike traditional single-junction solar cells that are limited by the Shockley-Queisser efficiency limit, tandem solar cells leverage the concept of spectral utilization to capture a broader range of solar radiation. In a tandem configuration, each layer is designed to absorb a specific portion of the solar spectrum, ensuring that a larger fraction of sunlight is converted into electricity. This tandem architecture typically combines materials with varying bandgaps, allowing them to absorb light at different wavelengths. Common tandem cell designs include the integration of silicon-based cells with thin-film technologies like perovskite or organic photovoltaics. One of the primary advantages of tandem solar cells is their potential to achieve efficiencies beyond what is possible with standalone solar cells. By efficiently utilizing a broader range of the solar spectrum, tandem cells have demonstrated the ability to surpass the limitations imposed by individual materials. Moreover, tandem configurations can be tailored for specific applications, such as space exploration or terrestrial power generation, by optimizing the choice of materials and bandgap combinations. While tandem solar cells hold great promise for significantly improving energy conversion efficiencies, challenges remain, including the development of stable and scalable manufacturing processes, managing the complexities of integrating different materials, and addressing cost considerations. Nevertheless, ongoing research and development efforts continue to propel tandem solar cells toward commercial viability, offering a path toward more efficient and sustainable solar energy utilization in the future [41].

4.8. Quantum dot solar cells

Quantum dot (QD) solar cells have the capacity to use hot photogenerated carriers to produce larger photovoltages or higher photocurrents, which has the potential to raise the maximum thermodynamic conversion efficiency of solar photon conversion up to roughly 66%. In order to gather hot carriers in QD array photoelectrodes before they relax to the band margins by phonon emission, the first effect relies on miniband transport. The latter effect relies on using hot carriers in QD solar cells to improve impact ionization processes and produce and collect more electron-hole pairs. The three QD solar cell configurations—photoelectrodes with QD arrays, QD-sensitized nanocrystalline TiO₂, and QDs distributed in a mixture of hole- and electronconducting polymers—are all explained. These high-efficiency setups call for and we report preliminary findings on slower hot electron cooling in InP QDs [42] for slow hot carrier cooling durations. Quantum dot (QD) solar cells have the capacity to use hot photogenerated carriers to produce larger photovoltages or higher photocurrents, which has the potential to raise the maximum thermodynamic conversion efficiency of solar photon conversion up to roughly 66%. In order to gather hot carriers in QD array photoelectrodes before they relax to the band margins by phonon emission, the first effect relies on miniband transport. The latter effect relies on using hot carriers in QD solar cells to improve impact ionization processes and produce and collect more electron-hole pairs. The following three QD solar cell arrangements are described: (1) photoelectrodes with QD arrays; (2) nanocrystalline TiO₂ that has been QD-sensitized; and (3) QDs that are disseminated in a mixture of hole- and electron-conducting polymers [43]. We report preliminary findings on slower hot electron cooling in InP QDs, which are necessary for these high-efficiency designs [44,45].

4.9. Flexible solar cells

Flexible solar cells represent a revolutionary development in solar photovoltaic technology, offering a versatile and adaptable approach to harnessing solar energy. Unlike traditional rigid solar panels, flexible solar cells are fabricated on flexible substrates, such as plastics or thin metal foils, allowing them to conform to curved or irregular surfaces. This flexibility opens up a wide range of applications, including integration into wearable devices, roll-able solar blankets, and other unconventional surfaces. The most common materials used in flexible solar cells include thin-film technologies like amorphous silicon, organic photovoltaics (OPV), and emerging materials such as perovskites. These materials provide the flexibility needed for the solar cells to bend and conform without compromising their energy conversion efficiency. One of the key advantages of flexible solar cells lies in their lightweight and portable nature, making them ideal for applications where traditional, rigid solar panels would be impractical. The flexibility also enables seamless integration into various surfaces, expanding the possibilities for solar energy harvesting in unconventional environments. Furthermore, flexible solar cells are particularly wellsuited for portable and off-grid power solutions. They can be easily rolled up or folded, making them compact and easy to transport. This makes them valuable for applications such as camping, outdoor activities, and emergency power supplies. Despite the promising advantages, challenges remain in terms of achieving high efficiency and maintaining durability over extended periods, especially in outdoor conditions. Researchers are actively working on improving the stability and efficiency of flexible solar cells through advancements in materials and manufacturing processes. It has been stated that the electron is the supreme form of money in contemporary culture. Electricity is the most often utilized source of energy since it is silent, clean, portable, and quickly transformed into labor. However, except for a 16% contribution from nuclear fission, we mostly generate power by burning hydrocarbons and, ironically, far less expensive coal. For instance, coal accounted for over half (49%) of the 4.1 trillion kWh of power produced in the US in 2006. China alone will need to add around

25 GW of new capacity annually over the next ten years to keep up with demand, which is the equivalent of building one sizable coal power plant every week. Unfortunately, coal releases a lot of CO₂ that alters the climate, and it also includes mercury. Ocean and food chain contamination is being brought on by combustion. The largest challenge of our time is to generate power only from solar energy in order to reduce emissions and avert climate change [46]. Flexible thin-film solar cells are compact and strong mechanically. Flexible solar panels are anticipated to provide specialty items that call for lightweight, mechanical flexibility, and moldability into complicated designs, such as roof panels for electric cars, foldable umbrellas, camping tents, etc., with fast-expanding battery technology. In this article, we offer a thorough analysis of pertinent materials that may be used to create flexible solar cells. Metals, ceramics, glasses, and polymers have all been examined as substrate materials. In terms of active materials, we mainly concentrate on recently developed novel semiconductors such as organometal halide perovskites, conjugated donor/acceptor polymers, and tiny organic donor/acceptor molecules. the electrode Materials such as thin metal films/nanowires, conducting polymers, nanocarbons, carbon nanotubes [47,48], and transparent conducting oxides are discussed in the literature, along with the advantages, disadvantages, and potential of these materials for creating flexible photovoltaics of the future [49].

5. Conclusion

This review provides a comprehensive exploration of the diverse and dynamic landscape of nanohybrid materials, encompassing coordination material-based nanohybrids, luminescent nanohybrids, conductive polymer nanostructures [43], and the revolutionary realm of flexible solar cells. The synthesis methods, properties, and applications of these nanohybrids have been elucidated, highlighting their significant contributions to catalysis, sensing, drug delivery, and energy storage. The integration of coordination nanohybrids in perovskite solar cells (PSCs) emerged as a promising avenue, showcasing their potential to enhance device performance and stability. Furthermore, the synthesis of luminescent nanohybrids for bioimaging purposes and the development of layered 2D material-based nanostructured hybrids for advanced energy storage and conversion underscore the breadth of applications for these innovative materials. The exploration of conductive polymer nanostructures in drug delivery systems revealed their potential for controlled release and targeted therapeutics. The final segment of the review explores the transformative field of flexible solar cells, emphasizing their adaptability and lightweight design. The potential applications of flexible solar cells in portable and off-grid power solutions open new frontiers in solar energy harvesting. While these nanohybrid materials exhibit remarkable properties and hold promise across various domains, challenges such as stability, scalability, and environmental impact remain areas of ongoing research. Nevertheless, the collective advancements showcased in this review underscore the potential of nanohybrid materials to revolutionize materials science, nanotechnology, and renewable energy. As researchers continue to innovate and address existing challenges, these nanohybrids stand poised to contribute significantly to the advancement of technology and the realization of sustainable and efficient solutions for numerous applications.

Conflict of interest: The authors declare no conflict of interest.

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Review

Recent advancements in nanocellulose synthesis, characterization, and application: A review

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Copyright © 2024 by author(s). Journal of Polymer Science and Engineering is published by EnPress Publisher, LLC. This work is licensed under the Creative Commons Attribution (CC BY) license. https://creativecommons.org/licenses/ by/4.0/ **Abstract:** Cellulose nanocrystal, known as CNCs, is a form of material that can be produced by synthesizing carbon from naturally occurring substances, such as plants. Due to the unique properties it possesses, including a large surface area, impressive mechanical strength, and the ability to biodegrade, it draws significant attention from researchers nowadays. Several methods are available to prepare CNC, such as acid hydrolysis, enzymatic hydrolysis, and mechanical procedures. The characteristics of CNC include X-ray diffraction, transmission electron microscopy, dynamic light scattering, etc. In this article, the recent development of CNC preparation and its characterizations are thoroughly discussed. Significant breakthroughs are listed accordingly. Furthermore, a variety of CNC applications, such as paper and packaging, biological applications, energy storage, etc., are illustrated. This study demonstrates the insights gained from using CNC as a potential environmentally friendly material with remarkable properties.

Keywords: Cellulose Nanocrystal (CNC); manufacturing; characterization; application

1. Introduction

Nowadays, each and every living thing is deeply concerned about the condition of the environment. Throughout history, several artificial products and substances have been created in order to fulfill the needs and desires of individuals. These synthetic materials have the potential to adversely affect both the environment and our way of life. Given these concerns and the growing scarcity of non-renewable resources, there is a growing focus on renewable resources and bio-based materials as viable alternatives for producing valuable commodities. Nanocellulose, derived from lignocellulosic sources, is a plentiful and eco-friendly substance. The material has garnered significant attention from both the scientific and industrial sectors due to its exceptional mechanical capabilities, extensive surface area, ample hydroxyl groups for modification, and inherent environmentally friendly properties [1–3]. Cellulose, an abundant and renewable constituent obtained from biodiversity, is commonly acknowledged as the major component among its equivalents. It is well acknowledged as a plentiful and abundant source of raw materials. The presence of this phenomenon is widespread among a diverse array of organisms, including plants, tunicates, algae plants, and certain bacteria [4,5]. The intrinsic adaptability of the material enables several changes and functionalizations, rendering it extremely suitable for various industrial applications. Current study endeavors persist in revealing novel understandings and progressions in the domain of cellulose, hence necessitating further investigation and recognition [6–8]. The benefits of cellulose can be augmented by the aggregation of cellulose chains, leading to the creation of highly structured domains that can be synthesized as nanoparticles from cellulose. Cellulose nanocrystaline (CNC), referred to as nanocelluloses, has received considerable interest in the realm of advanced materials due to their distinctive physicochemical characteristics [9]. In addition, it is important to underscore that these compounds demonstrate chemical inertness, low mass density, notable rigidity, exceptional resilience, a minimal thermal expansion coefficient, and the capacity to modify their surface chemical properties [10-13]. Nanocellulose exhibits a range of favorable properties in comparison to its bulk equivalent, owing to its nanoscale dimensions. These include the nanoscale effect, surface chemical reactivity, biocompatibility, crystallinity, purity, biodegradability, and high mechanical strength, as well as being environmentally friendly and non-toxic [14–16]. Nevertheless, the characteristics of nanocellulose, including yield, surface chemistry, physicochemical, dimensions and morphology, crystallinity, physicochemical, as well as thermal properties, can be customized for specific applications through variations in the sources, isolation procedure, conditions, and various treatments. This customization enables the development of novel materials and devices, offering a wide array of possibilities [17,18].

Examples of nanostructured materials include microcrystals and microfibrils of cellulose, whereas examples of nanofibers include bacterial cellulose, nanofibrils of cellulose, and nanocrystals of cellulose [19-21]. There are numerous diverse varieties of nanocellulose that can be generated through the use of many different processes. These nanocelluloses are derived from many different kinds of cellulose [11,22,23]. The exploration of producing nanocellulose with a diverse assortment of physical attributes is considered a captivating area of research, as it offers the opportunity to explore underutilized biomass resources. Significant benefits may be gained by using nanocellulose due to its 3-dimensional hierarchical nanostructure and its nanoscale physicochemical features, as investigated in distinctive studies [13,22,24,25], which suggest intriguing potential for diverse applications. Nanocellulose, a material currently undergoing mass production at an industrial level of multiple metric tons per day, exhibits a diverse array of uses across multiple disciplines. The range of applications for nanocomposite materials is extensive and encompasses various fields such as biomedical products, wood adhesives, supercapacitors, templates for electronic components, batteries, electroactive polymers, continuous fibers and textiles, food coatings, barrier/separation membranes, antimicrobial films, paper products, cosmetics, cement, and other emerging uses [26,27]. There has been a noticeable increase in the publication of literature review articles in recent years, with a predominant focus on the production, modification, and applications of nanocellulose [8,24,28–35]. This study is intended to provide a concise summary of the scholarly investigations carried out on nanocelluloses, with a specific focus on CNCs, and to emphasize their recent progress in many fields of application. The text begins by presenting a succinct introduction to cellulose, referred to as nanocellulose, and discusses the techniques used to extract it from different sources. In the subsequent sections, an overview will be presented of contemporary trends and recent scholarly investigations concerning the application of nanocellulose. The scope of this study encompasses a targeted examination of the various uses of this material, with particular emphasis on its

utilization in various sectors. This review is expected to make a valuable contribution to the progress of preparation techniques for CNC and the development and assembly of innovative products derived from CNC. The overarching objective is to facilitate a greater profusion of CNC-fabricated substances in cutting-edge applications.

2. Nanocullose details

Cellulose structure and source

One of the most common polymeric resources on Earth is cellulose, a renewable feedstock with a large supply. It is reported that the projected yearly production varies between 10¹⁰ and 10¹¹ metric tons [7]. Surprisingly, a relatively small quantity of approximately 6×10^9 tons is being utilized throughout many industrial sectors, including minerals, chemicals, paper, and textiles. The phenomenon of underutilization continues to exist, even after the molecular structure of this white biomacromolecule was clarified by Herman Staudinger a few years following its original isolation by Anselme Payen in 1838 [36]. Cellulose mostly consists of anhydroglucose units (AGUs), which are comprised of repeated β (1,4)-linked D-glucopyranosyl units. The units are arranged in a conformation referred to as a ${}_{1}^{4}C$ -chain. According to the findings of Gopi et al., the polymer's helical structure is a result of the 180° twist that each monomer unit undergoes in relation to the neighboring units [37]. The aforementioned anhydroglucose units (AGUs) undergo a process of chemical bonding to produce cellobiose units. These cellobiose units then aggregate to form the crystalline structure of cellulose, known as primary fibrils. The phenomenon of fibril bundling initiates the generation of microfibrils, which subsequently assemble to become cellulose fibers, often known as macro-fibrils. Cellulose possesses distinct properties like hydrophilicity, chirality, simple chemical modification, and infusibility. The existence of intramolecular and intermolecular chemical groups within the cellulose structure is responsible for these characteristics [38]. The length of cellulose chains is mostly determined by the degree of polymerization. Cellulose derived from wood generally comprises approximately 10,000 AGUs, whereas cellulose derived from cotton consists of approximately 15,000 units. The features of cellulose are determined by the degree to which it has been polymerized as well as the length of the chain it contains. The degree of crystallinity of natural cellulose can range anywhere from around 40% to about 70%, depending on where the cellulose comes from and how it was extracted. In the literature, it has been noted that amorphous regions, which lack a distinct crystalline structure, demonstrate greater reactivity with other molecular groups and possess a lower density when compared to regions characterized by a crystalline structure [39–41].

Crystalline domains demonstrate enhanced resistance to mechanical, chemical, and enzymatic interventions in comparison to amorphous regions. Cellulose has a diverse array of polymorphic forms, including cellulose I, II, III_I, III_I, IV_I, and IV_{II}. The alteration of these structures can be achieved using either thermal or chemical methodologies. The alterations witnessed in this specific setting are impacted by a variety of factors, including the orientations of molecules, the existence of van der Waals forces, and both intra- and intermolecular interactions. Moreover, the methodologies employed for the segregation and administration of these modifications play a pivotal role in their development [42-44]. The hydrolytic activity is facilitated by the lowered steric barrier and kinetic considerations, allowing for the dispersion of areas of disorder as chain dislocations among segments of the elementary fibril. On the other hand, the domains that are arranged in an orderly manner demonstrate a higher level of resistance to the hydrolysis process and do not experience any changes. Subsequently, the cellulose fibrils undergo transverse cleavage, leading to the generation of CNC characterized by a substantially elevated level of crystallinity. However, after this subsequent phase, further steps such as washing, solvent removal, neutralization, purification, filtration, centrifugation, sonication, dialysis, fractionation, surface modification, and drying (specifically spray-drying and freeze-drying) are necessary to recover the CNC product following the hydrolysis process.

A low-cost method for removing lignin and other impurities from the surfaces of natural fibers is alkali treatment. Surface treatment of thermosets and thermoplastics with alkaline fibers is common. The process of this treatment causes an increase in surface roughness by breaking hydrogen bonds. The rough texture of natural fibers makes them ideal matrix materials for attachment. Alkaline treatments have the potential to improve mechanical properties while having a negative effect on tensile strength. Surface roughness and cellulose content of fibers are both enhanced by alkaline treatment [45]. The interlocking of polymer resins is improved by an alkaline treatment, which raises the crystallinity index, lowers the spiral angle, and removes cementing components from the fibers. The index and crystallinity of natural fibers are proportional to the percentage of solution [46]. To improve the wettability of epoxy resin, alkali was used to decrease the intercrystalline and intercrystalline lignin in sisal fibers [47]. To determine the ideal concentration of the treatment fluid to eliminate impurities while diminishing surface quality, researchers employed scanning electron microscopy [5,48].

Several theories describe the mechanisms by which the interfacial bonding of silane coupling agents enhances the mechanical properties of biocomposites. Adding salt to fiber-polymer composites makes them stickier. The matrix system determines the salinity level. Composites benefit more from a salt treatment than an alkaline one in terms of Young's modulus [49]. Saline coupling agents significantly enhanced the interlocking of fibers and polymers. In 80 min, coupling agents are dissolved by air-

drying sisal fibers immersed in a 2% aminosaline solution. Also examined are saline solutions in water and ethanol at concentrations of 0.033% and 1% [5,50].

The hydrophobicity of fibers is enhanced through acetylation and other surface changes. Through this modification, acyl groups are substituted for lignocellulosic hydroxyl groups. Acetylation is a surface modification process that uses acetates such as acidic anhydride and acetyl chloride. For 1 h at 30 °C, researchers submerged sisal fibers in 5% and 10% NaOH solutions; for 1 h, alkaline-treated fibers were immersed in glacial acetic acid; and for 1 h, pretreatment fibers were immersed in acetic anhydride with one drop of concentrated H₂SO₄ [51]. Cellulose gains additional adhesive bonding sites for polymer resins when lignin and hemicellulose are removed from fibers through acetylation. The amount of time a fiber is soaked is also crucial when changing its surface. Polymer resins bind with fibers less effectively after prolonged soaking. The bending strength and modulus of sugar palm fibers treated with 4% acetyl acid were maximal before they began to decrease [52].

The hydrophobicity of natural fibers is decreased and matrix interaction is increased by benzoyl chloride. When compared to untreated fibers, those treated with benzoyl showed a 25% increase in thermal diffusivity and a 16% increase in conductivity [53]. Benzoyl treatment altered the surface properties and visual appearance of sisal fibers. The surfaces of the fibers are chemically roughened by reacting with benzoyl chloride [54]. Benzoylation improves thermal stability, decreases water absorption, and reinforces fiber-matrix bonding. Benzoyl chloride and sodium hydroxide are used to treat the surface of Sansevieria ehrenbergii fibers. Composites produced from treated fibers demonstrated superior thermal stability compared to those made from untreated fibers [55].

The process of copolymerization between cellulose hydroxyl groups and permanganate ions is initiated by potassium permanganate in acetone to improve the surface features of natural fibers. The mechanical and thermal properties of biocomposites are enhanced when lignin and permanganate ions are used to remove lignin from fiber cells. Natural fiber KMnO₄ oxidation was employed in the treatment. When the concentration of KMnO₄ is increased, the hydrophobicity of natural fibers is reduced [56]. The fiber surfaces are degraded due to the long soaking time and high KMnO₄ concentration. Although KMnO₄-treated sisal fibers showed an initial increase in crystallinity, this effect was attenuated as concentration increased [57]. The surface properties are affected by the chemical reactions that take place between the cellulose fibers. Compared to NaOH, the tensile, flexural, and impact strengths of sugar palm fibers treated with KMnO₄ concentrations, which in turn reduces the flexural and impact strengths of the biocomposites [58].

3. CNCs preparation

After undergoing pretreatment, the fibers are put through a controlled procedure that involves the hydrolysis of strong acids. During the CNC fabrication process of strong acid hydrolysis, hydronium ions are able to break through the cellulose chain in both the aromatic and amorphous regions. Infiltration leads to the creation of cellulose crystallites, which in turn are caused by the hydrolysis of glycosidic linkages. When the cellulose nanoparticles created by this process are suspended in water, they are referred to as cellulose nanocrystals (CNCs) and cellulose nanowhiskers (CNWs), which are also common names for nanoparticles [59]. The following subsections illustrate the various types of acid hydrolysis along with their corresponding advantages and disadvantages.

3.1. Sulfuric acid hydrolysis

The successful application of sulfuric acid hydrolysis for the synthesis of sulfonated cellulose nanocrystals (SCNCs) from cellulosic biomass sources was not achieved until 1947. The weight percentage (wt%) of sulfuric acid is a crucial metric that must be taken into account while treating the SCNCs. According to Nagarajan et al., insufficient acid hydrolysis may result in the formation of a high-amorphous zone containing low-crystalline particles when the acid concentration is below 63-64 wt% [60]. This process leads to a lower dissolution of amorphous and aromatic polymers. The production of SCNCs exhibits higher yields when the acid content falls within the range of 63 to 64 wt% and the temperature is maintained between 45 °C and 60 °C for a duration of 30 to 120 min. It can be inferred that when the concentration of acid exceeds 64 wt%, there is a likelihood of swelling and partial breakdown occurring in the crystalline areas [38,61]. The disordered components inside cellulose fibrils were effectively dissolved using the process of sulfuric acid hydrolysis [62]. Nevertheless, the α -cellulosic crystalline regions inside the cellulosic fibrils exhibit no chemical reaction with sulfuric acid and remain intact. Consequently, the cellulose fibrils undergo transverse cleavage, resulting in the formation of rod-shaped CNC with dimensions ranging from 2.3 to 60 nm in width and 100 to 500 nm in length. These CNCs exhibit a relatively high level of crystallinity and possess exceptional mechanical characteristics [60,30]. A random replacement process with sulfate ester is carried out on the hydroxyl groups that are located on the surface of the CNC. Ultimately, it is observed that the hydrolysis event results in the formation of negatively charged semiconductor nanocrystals (SCNCs), hence contributing to the establishment of a colloidal suspension with enhanced stability. Nevertheless, the thermal stability of SCNCs is quite low as a result of the sulfate group present on their surface [63]. Moreover, the process of neutralizing sulfated cellulose nanocrystals (SCNCs) using sodium hydroxide (NaOH) contributes to the restoration and enhancement of the thermal properties of CNCs produced by hydrolysis with sulfuric acid [64,65].

3.2. Hydrochloric acid hydrolysis

One well-known and often-utilized method for producing cellulose nanocrystals (CNCs) is the hydrolysis of hydrochloric acid. The HCL hydrolysis method involves much longer optimal reaction times (2–4 h) and temperatures (60–105 °C) compared to H₂SO₄ hydrolysis. Keeping the acid concentration between 2.5 and 6.0 N is optimal for CNC yield efficiency [66]. A high degree of crystallinity is produced as α -cellulose during the HCl hydrolysis. This α -cellulose exhibits rod-like, structured

CNCs with diameters ranging from 10 to 12 nm and lengths ranging from 285 to 304 nm [67]. Isolated CNCs tend to clump together when they come into contact with solvents or polymers because they do not possess adequate negative charges. As a direct consequence of this, there is an extensive network of hydrogen bonding connections both inside the molecule itself and between the molecules that make up the complex. This is a direct result of the extremely high concentration of hydroxyl groups that the surface possesses. It has been discovered that CNCs obtained through HCL hydrolysis are more thermally stable than those acquired through H₂SO₄ hydrolysis [68]. Furthermore, the CNCs produced by this hydrolysis exhibit the ability to create stable interfaces between oil and water, known as Pickering emulsions. On the other hand, nanocrystals that have a carboxyl group on their surface don't respond in this way when they come into contact with an interface [69,70].

3.3. Phosphoric acid hydrolysis

Phosphoric acid is a type of mineral acid that is often used to prepare CNCs from biomass. Using a concentration of phosphoric acid that is between 70 and 75 weight percent in this acid hydrolysis process results in an increase in the efficiency with which CNCs are produced from fibers. Notably, the temperature is kept between 100–120 °C, and the duration of the hydrolysis process is typically between 80 and 120 min [71]. One of these benefits is the potential use of the material in applications involving bone scaffolding. In these settings, the material can encourage the formation of new bone while simultaneously delivering greater thermal stability and flame resistance. The isolated CNCs exhibit a rod-like shape, distinguished by a diameter that ranges from 15 to 32 nm and a length that ranges from 238 to 475 nm [72]. During the process, the surfaces of α -cellulosic nanocrystals acquire a charge on their phosphate groups. The extracted CNCs possess a tiny zeta potential, which indicates their low colloidal stability characteristic [73,74].

3.4. Organic acid hydrolysis

Recent research has revealed that CNCs can be isolated from organic acids such as, formic acid, maleic acid, citric acid, and oxalic acid as alternatives to mineral acid. CNCs are obtained using a process of FeCl₃-catalyzed hydrolysis of organic-based formic acid. It is shown that the utilization of FeCl₃ as a catalyst leads to improved production of CNCs due to better hydrolysis efficiency [75]. The entire process taken 6 h with 88 wt% of formic acid and the temperature is maintained 95 °C. The post-processing procedure resulted in a notable enhancement in the crystalline indices of the CNCs. Additionally, despite their diminutive size, the CNCs exhibited remarkable thermal stability.

Chen et al. used a toluenesulfonic acid solution at 50 wt% as a strong organic acid to speed up the separation of CNCs [76]. By maintaining ambient pressure and heating the eucalyptus pulp to 100 °C for 45 min, the acid easily passes through the cellulosic microfibril bundles and into the amorphous zone. Subsequently, CNCs are separated in a longitudinal orientation along the fibrils.

Researchers have used a 70% oxalic acid solution to isolate CNCs. CNCs can be isolated from eucalyptus pulp. This method exhibits a quicker approach with only half an hour at a temperature of 100 °C. The isolated CNCs are found to be more stable at high temperatures than their non-isolated counterparts. This is because CNCs and water don't come into as much physical contact.

Seta et al. applied a maleic acid solution with a high concentration to perform hydrolysis on ball-milled bamboo pulp [77]. The pulp is treated with a liquid solution whose weight-to-pulp's weight ratio was 100:1, yielding a maleic acid concentration of 75 wt%. The hydrolysis process was completed at a temperature of 110 °C for 3 h while ensuring steady stirring. The CNCs obtained exhibit favorable thermal stability at a temperature of 291 °C with a rod-shaped morphology of lengths ranging from 105.6 to 223.8 nm. In contrast, the yield of cellulose nanocrystals (CNCs) obtained through this particular procedure is somewhat lower (24%) in comparison to the hydrolysis method with formic acid.

The utilization of organic acid hydrolysis technologies demonstrates a higher degree of environmental sustainability in comparison to traditional mineral acid hydrolysis techniques. The utilization of organic acids in recycling processes has several advantages, including reduced corrosion of equipment utilized in the operation. Hence, the current trends greatly endorse and facilitate the achievement of CNCs' industrialization through the utilization of organic acid hydrolysis. **Table 1** presents a comprehensive overview of the acids employed in the hydrolysis process, including their ideal working conditions and notable properties.

Sl No	Name of the acid hydrolysis	Concentration of acid (wt%)	Reaction temperature (°C)	Reaction time (min.)	Post-processing method	Nature of CNCs	Size of CNCs (nm)	Ref.
01	Hydrochloric acid hydrolysis	37	50	60	Centrifugation and sonication	Rod like structure	10 ± 2 (Width) 285 ± 58 (Length)	[78]
02	Sulfuric acid hydrolysis	64	45	60	Centrifugation, dialysis tube and sonication	Rod like structure	12 ± 1.2 (Width) 280 ± 20 (Length)	[38]
03	Phosphoric acid hydrolysis	80	50	420	Centrifugation, dialysis tube and sonication	Rod like structure	2–6 (Width) 100–330 (Length)	[79]
04	Formic acid hydrolysis (organic)	88	92	720	Centrifugation	Rod like structure	5–20 (Width) 50–200 (Length)	[75]

Table 1. Comparative study of several key characteristics of different acid hydrolyzed CNCs.

4. Surface modification of CNC

Surface chemistry can be altered through chemical manipulation, physical interactions, and biological means [80]. The presence of OH groups on the surface of nanocellulose has the effect of making it very hydrophilic. The surface functionalization of nanocellulose can be accomplished either during the manufacturing process or after it has been completed [81–84]. Their performance in a particular application is improved as a result of these modifications, which achieve desirable attributes. According to George and Sabapathi, incorporating any chemical functionality into a nanocellulosic material allows for the surface of the material to

be modified such that it reacts differently with outer molecules [85]. The change of the surface of polysaccharide nanocrystals can lead to the formation of polymeric matrices that have greater reinforcing, which means that they have improved thermal and mechanical properties, as stated by Lin et al. [81].

As stated in earlier works, the most common methods for chemically altering the surface of cellulose nanocrystals are covalent surface modifications such as sulfonation, polymer grafting, oxidation, esterification, nucleophilic substitution, and etherification. These modifications modify the surface of the nanocrystals in a variety of different ways [80,82-86]. Polyacrylamide was grafted onto cellulose nanocrystals (CNC) and subsequently integrated into polyvinyl alcohol (PVA) in a recent study that used a solution-casting process to reinforce nanocomposite films. Polyacrylamide was then included in the PVA. With cinnamoyl chloride and butyryl chloride grafted onto them, hydrophobically modified cellulose nanofibrils displayed good surface qualities and were able to stabilize oil-water emulsions, as demonstrated by research conducted by Tong et al. [87]. Due to the fact that they are unable to stabilize Pickering emulsions, nanocelluloses that have a high surface charge density are not suitable for use as interfacial stabilizers. The surfaces of nanocelluloses can be changed by grafting hydrophobic polymers onto them in order to reduce the amount of interfacial tension that exists between them. Because of this, they become more wettable when exposed to the oil phase. According to Kaboorani and Riedl, polymer coatings and adsorbing surfactants have also been employed in this research [88].

Irradiation, surface fibrillation, ultrasonic treatment, and electric discharge (plasma treatment) are some of the available therapies for physical surface functionalization [80]. All of these treatments are possible. Afrin and Karim, for instance, used enzymes to modify the surface of nanocellulose in two different ways: (a) direct modification, in which the enzyme comes into direct contact with the nanocellulose; and (b) indirect enzyme-mediated modification [82]. Both of these enzyme-based approaches were utilized. It was determined by them that the enzymatic technique for creating nanocellulose and functionalizing it further is a more sustainable alteration method than the chemical modification strategy. This was the result that they arrived at. In order to maintain the integrity of the crystal structure, the approach must only alter the surface of the cellulose nanofibrils (CNF) without altering the morphology. This is one of the most significant obstacles that must be overcome when attempting to alter the CNF. According to Robles et al., the creation of hydrophobic surfaces of CNC and CNF through surface modification with silanes results in an increase in the stability of these materials [89]. Figure 1 provides a schematic representation of the most widely used techniques for modifying the surface of nanocellulose. Table 2 demonstrates the impact of surface treatments on natural fibers.



Figure 1. Schematic representation of the most commonly used surface modification routes for nanocellulose [7].

Table 2. The consequences of surface treatments on natural fibers.

Surface Treatment	Treatment effect	References
Plasma treatment	The surface roughness of plant fibers is increased by etching, leading to a more mechanically interlocking interaction with the matrix.	[90], [91], [92], [93], [94]
Vacuum Ultraviolet Irradiation treatment	Enhances the surface characteristics encompassing adhesion, wettability, tribological properties, fouling resistance, barrier performance, insulating capacity, dye absorption, and biocompatibility.	[95]
Ozone treatment	Contributes to the preservation of its physical attributes.	[96]
Corona treatment	Increase the basicity and acidity of the fiber surface	[97], [98], [99]
γ -Ray treatment	The structural integrity of natural fiber is shown to increase as a result of exposure to gamma radiation, which induces intercross-linking between adjacent cellulose molecules.	[100], [101], [102], [103]
Laser treatment	Reducing the concentration of lignin while simultaneously enhancing the structural characteristics of the fibers.	[104], [105], [106]

5. Characterization methods

5.1. Fourier-transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) is widely recognized as a nondestructive analytical technique that offers both quantitative and qualitative information about natural fibers. The chemical contents of natural fibers are analyzed to obtain an infrared absorption spectrum. The major range of frequency for observing infrared spectra derived from natural fibers is typically between 400 and 4000 cm^{-1} [107,108]. The FTIR peak positions on the natural fiber, along with the accompanying chemical stretching mode vibrations, are shown in **Table 3**.

Wave number (cm ⁻¹)	Allocations
3600–3500	O–H stretching oα-cellulose
3500–3300	N-H stretching (Amine)
3500	N-H stretching (Amine)
3100–3000	C=C-H stretching
2960–2850	C–H stretching
2590–2540	S–H stretching
1740–1720	C=O stretching of hemicelluloses
1685–1655 & 1600	α , β unsaturated stretching
1680–1650	N=O stretching
1650–1630	OH (Absorbed water)
1600	C=O stretching (Amide)
1600,1580,1500,1450	C=C stretching
1450–1400	CH ₂ Symmetric bending
1567,1380	NO ₂ stretching
Above 1500	C=O, NH, C=C, C=N functional group stretching
Below 1500	Single bonds and bending vibrations
1395–1385	t-butyl stretching
1365	CH bending (deformation)
1350–1260	C–O stretching
1150–1070	C–O–C stretching
1050–1020	Symmetric C-OH stretching of lignin
815-750	N–O stretching
800–600	C–S stretching
770–735	C–C deformation
520-420	S–S stretching

Table 3. FTIR peak locations and the vibrations of the associated chemical stretching mode [109–115].



Figure 2. FTIR spectra of (a) raw fibers, (b) alkali-treated fibers, (c) bleached fibers, and (d) CNC [123].

C=O bond stretching vibrational modes in carboxylic acids and hemicellulose esters, C=C bonds in lignin's benzene rings, and the C=O bonds of lignin's acetyl group are all effectively blocked, as was the infrared absorption spectrum of natural fibers (A), pre-treated fibers (B), and bleached fibers (C), as well as cellulose nanocrystal (D). This discovery demonstrates that the processing of CNC resulted in the removal of hemicellulose and lignin from the CNC [116]. The spectral range from 1635 to 1640 cm⁻¹ has been identified to include vibrational modes of OHgroup stretching and bending in absorbed water [117,118]. Vibrations of the OHgroup, the most abundant organic group in the stem, are attributed to the spectral region between 3300 and 3400 cm⁻¹. The observed peaks within the spectral range of 2800–2900 cm⁻¹ can be attributed to the stretching vibrations of C-H bonds [119,120]. Additional peaks are seen in the raw fibers' spectra at 1730 and 1250 cm⁻¹. The C=O bond stretching vibrations in the acetyl and C-O bond stretching vibrations in the aryl groups account for the observed peaks. Lignin and hemicellulose both include these functional groups [120-122]. The aforementioned compounds are found to be completely absent in fibers that underwent alkali treatment and bleaching. Chemical treatments have a clear effect on the chemical composition of fibers, as evidenced by the differences in peak intensities between raw fibers and CNC in the spectrum areas of 2700 to 3600 cm⁻¹ and 850 to 1500 cm⁻¹. In addition, the 850 to 1500 cm⁻¹ transmittance peaks, which are characteristic of the cellulose material's crystal structure, were not observed in the CNC. With each successive treatment, the height of these peaks diminished. The absence of lignin, hemicellulose, and wax in the fibers suggests that they have been processed. Figure 2 presents a visual representation of the Fourier Transform.

5.2. X-ray powder diffraction (XRD) analysis

X-ray diffraction, often known as XRD, is a non-destructive and expeditious type of analytical technique that is frequently utilized for the determination of the chemical properties of natural fibers [107,124,125]. The spectrum obtained from the experiments, which corresponds to a specific fiber, exhibits the diffraction peaks associated with both the amorphous and crystalline areas. The crystallinity index (CI) is determined using the formula,

$$CI = \left(1 - \frac{I_{AM}}{I_{00}}\right) \times 100\%$$

where I_{AM} represents the intensity of the amorphous phase and I_{00} represents the intensity of the fully crystalline phase [126]. Figure 3 displays a comparison of the diffractograms of cellulose following each chemical treatment. The peaks is identified at a 20 angle of 14.7°, 22.6°, and 34.4° are indicative of the normal cellulose I structure. The CNC exhibited a distinct and pronounced peak at an angle of 22.6°. Wax, hemicellulose, and lignin are found to be present in a unique zone that was indicated by the wide pattern of the diffractogram that was acquired from the raw fibers.



Figure 3. The X-ray diffraction (XRD) pattern of natural fibers (**A**), pre-treated fibers (**B**), bleached fibers (**C**), and cellulose nanocrystals (CNC) was analyzed [127].

It was found that the crystallinity improved by using the alkali treatment due to the fact that the lignin and hemicellulose components were removed by the treatment. After going through the acid hydrolysis procedure, the nanocrystals had a crystallinity of around 64.2%, which is just marginally greater than the crystallinity of the bleached fibers. Because alkali treatment results in the formation of cellulose nanofibrils rather than cellulose crystals, the change in crystallinity index that occurs between acid hydrolysis and alkali treatment is almost insignificant [116]. The amorphous component included within the amorphous region was successfully extracted using the chemical treatment [128]. The degree of crystallinity showed a significant increase of 252% when comparing the raw fibers (18.2%) to the fully treated fibers (64.2%) [116]. The study reported an observed crystallinity of 69% for derived nanofibers made from poplar wood [129]. The increase in crystallinity seen in the fiber after treatment is documented in the literature, with values ranging from 78% for banana rachis [116] to as high as 450% for banana peel bran [128].

5.3. Scanning electron Microscope (SEM) analysis

A scanning electron microscope (SEM), which is one of the most flexible pieces of equipment that is now accessible, can be used to facilitate the surface topography assessment of the micro and nanostructure morphologies of cellulosebased nanocomposites. This assessment and differentiation of objects on a nanoscale can be accomplished. The use of SEM is the most effective method for illustrating the properties of nanocomposite materials as a function of nanofiber dimensions, shapes, orientations, and interactions between the matrix and nanofibers [130]. In order to map out the topography of the material as it travels across its surface, it makes use of electron beams that have been carefully focused during the process.

It is possible for the electron beam to penetrate the sample to a depth of a few microns when it hits the surface; this is contingent upon the accelerating voltage as well as the density of the sample. A multitude of signals, such as X-rays and secondary electrons, are produced as a result of this interaction contained within the sample. Several studies have found that the resolution of SEM images is typically associated with the size of the electron beam spot, which is smaller at higher

acceleration voltages (AV). This is the case whenever the acceleration voltage is increased [131–134].

In order to prepare nanocomposite samples for electron irradiation without causing electrostatic charges to form on the surface, the samples must have surfaces that are electrically conductive and must be grounded to a sample holder. SEM imaging of cellulose nanocomposites can result in a number of undesirable consequences, including scanning errors, picture distortions, and nanocomposite charging. This is due to the fact that CNCs are not conductive. Sample preparation is an essential step in the process of creating nanocomposites, which are frequently sputtered in a vacuum with an extremely thin layer of conductive materials such as carbon, gold, or platinum [135]. When working with cellulose nanocrystals, scanning electron micrographs are typically utilized for the purpose of evaluating the surface morphology of nanocomposites as well as the interaction between polymers and CNCs [132,134,136]. For instance, SEM is frequently utilized for the purpose of analyzing the fracture surface of nanocomposites that have been manufactured, as well as for determining the dispersion of CNCs inside a host polymer matrix when subjected to tensile or impact stresses [131,133]. As shown in Figure 4, SEMs of CNCs that were manufactured with various acid concentrations are exhibited.



Figure 4. SEM images of as-synthesized CNCs at (a) 50 μ m; (b) 1 μ m; and (c) 2 μ m scale [137].

5.4. Atomic force microscopy (AFM) analysis

The technique known as atomic force microscopy (AFM) makes it possible to capture surface profile details with a granularity that is frequently greater than one micron. AFM has the capability to directly quantify the predominant forces involved in adhesion processes, as demonstrated by studies conducted by Balnois et al. [138] and Ben Sghaier et al. [139]. This approach necessitates the scanning of a sharp-tipped cantilever over the fiber. The deflection of the cantilever is facilitated by the repulsive forces generated upon contact between the cantilever tip and the fiber. The AFM has the capability to analyze and describe the surface properties of fibers in three dimensions [140]. The AFM topography, as illustrated in **Figure 5**, exhibits the presence of fibers at the macro, micro, and nanoscales [141].



Figure 5. The atomic force microscopy micro-, nano-, and macro-fiber topographies of a banana pseudo stem [141].

The mean diameter of the nanofibers was calculated to be around 30 nm. Microand nanofibers are formed more effectively by removing the intermediate lamella and main cell walls. Consequently, the surface has been enriched with a higher concentration of cellulose, and the dimensions of the fibers have been effectively reduced to the nanoscale. According to the findings of Chokshi et al. [142], the microfibrillar angle is identified as the key determinant of the intrinsic fiber strength properties. It is reported that achieving high fiber strength requires an increased proportion of cellulosic content and a decreased value of MFA. The key factors contributing to the poor elongation of banana fibers are the lower microfibrillar angle (11°) and the relatively high percentage of crystallinity [143].

5.5. Transmission electron microscope (TEM) analysis

Transmission electron microscopy (TEM) micrographs provide accurate measurements of the fiber diameters and are useful for studying the axial thickness of a cell wall and its component sublayers [144]. Nevertheless, the use of these techniques necessitates a rigorous procedure for the processing of samples. The fibers are subjected to a double boiling process using an excessive 1% NaOH solution for a duration of 3 h. Subsequently, a solution of HCL with a concentration of 0.05 M is applied to the fibers, and then they are thoroughly rinsed with water. The fibers are immersed in distilled water for a duration of 4 h, facilitating the creation of a sample that enables meticulous study of the structural characteristics of the fibers using TEM [145]. Images captured using an electron microscope The TEM images present in **Figure 6** illustrate the structural characteristics of distinct nanocellulose samples derived through varying acid hydrolysis conditions.



Figure 6. TEM images of nanocellulose samples using different acid hydrolysis conditions [146].

6. Application of CNCs

CNCs are considered a promising and environmentally friendly alternative to inorganic materials. The principal utilization of CNC is in the reinforcement of thermoplastic nanocomposites, owing to their advantageous mechanical characteristics and convenient modification. A diverse assortment of polymers has been widely studied as the host matrix for many applications, including a wide spectrum of functions.

6.1. Packaging

Food packaging materials have a twofold function: firstly, to protect food from external factors that may interfere with or contaminate it, and secondly, to improve the nutritional quality of the food by preventing the migration of small molecules. Although polymer materials are widely used in the packaging industry, they are not completely impervious to small molecules, including gases, organic compounds, and water vapor. This deficiency in their barrier properties might have adverse effects on their appropriateness for particular applications. Numerous methodologies have been explored in order to mitigate the limitations associated with polymer matrices. The utilization of CNC as reinforcing agents and permeability enhancers is a commonly employed strategy for enhancing the barrier characteristics of polymer matrices. In recent decades, numerous scientists have integrated CNC into various polymers to create nanocomposite films that exhibit exceptional performance. These films have found applications in the food packaging industry. Extensive literature has documented several significant avenues for enhancing packaging materials that incorporate CNC. Yadav and Chiu conducted a study whereby they investigated the impact of incorporating different weight percentages of CNC into glycerol films containing κ -carrageenan [147]. The study revealed a significant reduction of 52% in water vapor permeability (WVP) due to the physical impediment generated by CNC, which restricts the flow of water across the packing film. Furthermore, a significant rise in permeability was noted in the nanocomposite films. Salmieri et al. developed oregano essential oil that incorporated PLA-CNC nanocomposite films with antibacterial properties. It was found that there was a noticeable increase in the tensile strength of nanocomposite films after including CNC in packaged food goods, which increased their water absorption capacity [148].

de Oliveira et al. derived CNC from oats and eucalyptus to fabricate aerogels for use as absorbers in the food packaging industry. Hey reported a decrease in water absorption characteristics, which can be attributed to the presence of larger pore sizes. Hence, the utilization of aerogels with reduced crystallinity has been proposed as a means to mitigate moisture accumulation in food packaging applications, particularly in the context of meat packing, with the objective of minimizing water condensation [149]. **Table 4** provides an overview of how CNC is used in the food packaging business in conjunction with various polymer matrices.
CNC content	Polymer matrix	Thickness	RH (%)	Oxygen barrier property	Property	Ref.
30	Edible coating on alginate film	-	0 50 70	92 (mL. <u>μm</u> 250 1427	• The lipid oxidation of chicken has a low level during the initial three-day period of storage.	[150]
4	PET film	1 μm.	0 20 40 60 70 80	0.38 (mL. m ⁻² d ⁻¹ bar ⁻¹) 1.03 2.05 23.07 56.41 83.97	• Reduced CO ₂ barrier when relative humidity is high	[151]
0.20	Hybrid PVA cellulose bioactive aerogels	-	-	0.38 (mL m ⁻² d ⁻¹ bar ⁻¹)	 Bioactive chemicals are released in a controlled manner. Enhanced water absorption; maintained material integrity while submerged 	[152]
1.2 2.4 3.6	Chitosan-nano clay film	40 µm	50	8.1 (mL. m ⁻² d ⁻¹ atm ⁻¹) 5.4 7.2	 Enhanced tensile modulus and strength Increased resistance to heat 	[153]
5 7 11	Starch-glycerol- montmorillonite film	-	-	35.26 (mL. m ⁻¹ d ⁻¹ Pa ⁻¹) 37 38.5	 Improvement in tensile strength and tensile Modules Improvement in barrier properties Incrementing disintegrability 	[154]
1 5	PLA-Ag	200–220 µm	-	16.5 (mL. min. m ⁻² day ¹	 Raised the degree of crystallinity in general The barrier effect is effective Lessening of vapor transmission through the material 	[155]

Table 4	CNC na	nocomposite	examples	in the	food	nackaging	industry
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6.2. Drug delivery

Over the course of the last decade, researchers have focused their attention on several methodologies within the pharmaceutical industry. These methodologies include compression, spray and dip coating, and encapsulation, all of which aim to incorporate particular drugs into polymeric structures for the purpose of targeted distribution and/or controlled release. The utilization of coating materials to encapsulate the medicine is strongly advised in order to get a sustainable, controlled release within a specified timeframe [156,157].



Figure 7. Visual representation of in vitro drug release profiles of PHBV/CNC-g-PDMAEMA composite membranes at varying pH levels [160].

According to the most recent research, CNC has a significant amount of potential both as a medicinal substance and as a carrier for drug delivery systems. Because of its one-of-a-kind characteristics, CNC can be loaded with both charged and neutral medications, released in a controlled manner, and transported to specific cells, where they can have the greatest impact [158,159]. Chen and colleagues investigated the potential uses of poly (3hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) electrospun composite membranes that were reinforced with poly (dimethylaminoethyl methacrylate) (PDMAEMA)-grafted CNC. A visual representation of such a structure is depicted in Figure 7. The goal of the project was to develop membranes that, when subjected to PDMAEMA in a gamma configuration, would enable the controlled and prolonged release of a model drug [160].

Because of their hydrophilic properties and porous structures, which are both made possible by their chiral nematic structures, CNC are ideally suited for use as active components in medicinal products [161], especially in terms of hydrogels. The key factors contributing to the enhancement of drug absorption and dissolution through the integration of CNC into porous hydrogels are CNC's notable hydrophilicity and its tendency to undergo swelling in the presence of water. CNC hydrogels have been widely utilized in many applications due to their high permeability, particularly in converting chemicals [162] as well as thermal [163], hence facilitating drug release in CNC hydrogels. Among these stimuli, pH has been shown to be the most prevalent trigger.

Ooi et al. effectively synthesized semi-interpenetrating network (IPN) hydrogels composed of gelatin and CNC that exhibit stimulus-responsive behavior in response to variations in pH. The use of unadulterated CNC with a strong affinity for water played a crucial role in regulating the porous microarchitecture of the hydrogels. This, in turn, influenced the swelling properties and the rate at which drugs were released under varying pH conditions [164].

However, the hydrophilic characteristics and strongly negative surface properties of virgin CNC limit its potential use for hydrophobic medicines, including anticancer treatments. Consequently, further surface modification techniques can be employed to control the characteristics of CNC in order to facilitate the binding of non-ionized or hydrophobic medicines that would typically not adhere to untreated CNC surfaces. Castro et al. endeavored to functionalize CNC using β -cyclodextrin (β -CD) in order to introduce novel active substances onto the CNC surface and enable the sustained release of antibacterial agents [165]. A schematic representation of propargyl group functionalization in CNC for use in nanomedicine is shown in **Figure 8**. In an alternative study, the surface of CNC was subjected to functionalization by the incorporation of propargyl groups. This modification was carried out with the purpose of producing nanomedicine containing radionuclides, which may be utilized in the context of radio-immune treatment. In the study, the researchers introduced oligoethylene glycol methacrylate and aminopropyl methacrylamide into CNC to create a limited quantity of primary amine pendant groups that had the ability to transport pharmaceutical substances. The investigation into the cellular uptake behavior of CNC conjugates in the context of nanomedicines revealed that ovarian cancer cell lines exhibited uptake of these conjugates. The human breast cancer cell line exhibited a diminished capacity for internalizing CNC conjugates [165].



Figure 8. Propargyl group functionalization in CNC for nanomedicine applications [165].

6.3. Wound dressing

Wound dressing materials are specifically engineered to fulfill many crucial functions, including the provision of a protective barrier against bacterial infiltration, facilitation of gaseous exchange, management of wound infections, and facilitation of the wound healing process. There has been a shift in recent years towards using polymers derived from natural sources and hybrids thereof in the field of medical dressings. This trend may be attributed to their inherent biocompatibility, biodegradability, and comparatively less cytotoxic effects. The utilization of CNC in wound dressing materials has been seen, wherein they serve as either a reinforcing agent or a major element. This is mostly attributed to their widespread availability and remarkable mechanical properties [166,167].

In their research, Zhang et al. developed a nanocomposite hydrogel that repairs itself by combining modified CNC carboxymethyl chitosan (CMC) [168]. The goal of developing this hydrogel is to create a more comfortable environment for severe burn wound beds by absorbing and retaining exudate. Analysis of the healing process revealed that, compared to chitosan-based hydrogels, CMC-DACNC hydrogels had better self-healing characteristics. As depicted in **Figure 9**, this may be a result of DACNC's reinforcing effects.



Figure 9. Gel formation and the self-healing process of carboxymethyl cellulose (CMC) and dialdehyde cellulose nanocrystals (DACNC) [168].

Huang et al. described a simple method for synthesizing cellulose nanocrystal (CNC) films, which serve as a delivery mechanism for antimicrobial medications in the setting of diabetic wound dressings [168]. CNC's presence in the PVA-CNC film facilitates a robust connection between curcumin and the film, which in turn protects the curcumin from being washed away.

Cheng et al. conducted a comprehensive investigation to learn more about the effects of TEMPO treatment on modifying CNC by adding carboxyl groups [169]. Calcium ions (Ca^{2+}) are employed as a cross-linking agent in this process. The findings of their study demonstrate that the composite components did not have any impact on the physiological activity of the blood cells.

6.4. Tissue engineering

Biomedical engineering has become more popular over the past ten years, and the use of naturally occurring plastics in tissue engineering has become an important area of study [170]. Within the field of tissue engineering, a pivotal consideration in the identification of suitable synthetic tissues for transplantation into human or animal organs is the advancement of a permeable membrane characterized by meticulous geometric properties and a linked network of pores. The hydrophilic hydroxyl groups found in CNC have been demonstrated in multiple studies published in the literature to have the ability to form a permeable, flexible membrane with a multi- and ultrafine open-pore structure. This unique characteristic of CNC enables enhanced cell adhesion and promotes cell survival, hence facilitating the regeneration of damaged tissues or organs [171]. Lam et al. utilized CNC derived from sugarcane bagasse as a raw material to fabricate porous nanocomposite scaffolds composed of polyvinyl alcohol (PVA) and CNC. These scaffolds are specifically designed for the cultivation of human skin cells. The studies documented the development of porous scaffolds that exhibited no cytotoxic effects and had a cell survival rate of 82%. The pore size of these scaffolds was shown to be significantly influenced by the concentration of CNC. The elevated levels of CNC content led to an enhancement in pore size as a consequence of a decrease in the proportion of free PVA volume. The presence of a larger concentration of CNC led

to an observed increase in the degree of swelling, as the CNC particles restricted the mobility of the polymer chains [172].

Gao et al. conducted a study to examine the effects of integrating the in-situ composite process with freeze-drying methodology [173]. This modification, the inclusion of CNC in the nanocomposite scaffolds, led to an enhancement in the surface hydrophilicity of the scaffolds. The enhanced hydrophilicity facilitated favorable interactions between cells and the scaffold, promoting cell development and proliferation.

6.5. Organic photovoltaic (OPV) cells

Organic photovoltaic (OPV) cells are types of solar cells that utilize organic absorbing layers composed of polymers or tiny molecules. These absorbing layers have the ability to capture incident light and convert it into electrical energy through the process of fluorescence absorption and subsequent conversion. CNC nanosheets exhibit inherent traits related to transparency and dispersion of light, making them highly appealing as substrates for efficient organic photovoltaic cells that possess improved light management capabilities. Conversely, the attainment of robust hydrophobic properties and superior mechanical properties is vital for OPV cells [153,174].

6.6. CNC nanocomposites for supercapacitors

Materials possessing a substantial capacity and a swift charging cycle comprise supercapacitors. CNC does not possess inherent electrical conductivity. Nevertheless, they may be utilized as environmentally sustainable and recyclable materials in the fabrication of composite supercapacitors. Chen et al. conducted a study wherein they achieved a uniform distribution of metal nanoparticles (MNPs) on CNC. The application of melamine-formaldehyde (MF) resin to CNC has the dual purpose of protecting CNC from oxidation and facilitating the development of a porous structure with nitrogen functions, which in turn promote the deposition of more metal [175]. Another study synthesizes core-shell PPy/PVP/CNC nanorods by physically adsorbing PVP onto CNC. This technique modified CNC hydrophilicity and promoted pyrrole formation. The core-shell system's specific capacitance increased by 35%, according to a study [176].

6.7. Smart materials

In recent times, there has been a significant allocation of research efforts towards the advancement of renewable smart materials utilizing biobased components such as CNC [177]. CNC's large surface area, controlled shape, and structure make it a promising bio-sensing component stabilizer. CNCs are ideal for bioactive chemical immobilization due to their unique properties [178,179]. Furthermore, a wide range of noncovalent surface modification techniques can be employed to modify the structure of CNC by introducing specific functional groups.

The sensitivity of nanocomposites to variations in temperature is primarily determined by either the lower critical solution temperature (LCST) or the upper critical solution temperature (UCST), which is referred to as the critical temperature

range. Two critical temperatures, known as the lower critical solution temperature (LCST) and the upper critical solution temperature (UCST), have a substantial impact on the phase behavior and miscibility of polymer solutions. These critical temperatures demarcate distinct regions whereby the aforementioned properties exhibit divergent characteristics, depending on whether they are above or below these thresholds. In this regard, Kato et al. developed a new and efficient solution. A mechanically durable and thermoresponsive nanocomposite film is fabricated via a solvent casting technique, employing poly(2-phenylethylmethacrylate)-grafted CNC as the primary material. It is suggested to use nanocomposite films in thermal cutoff safety devices, such as thermal fuses, that need to reduce conductivity below the lower critical solution temperature (LCST) [180]. Specifically, it was discovered that transparency or semi-transparency occurred below the lower critical solution temperature (LCST), but light scattering and consequent opacity were detected above the LCST [181].

The literature has documented that prior to utilizing CNC as a pH-sensitive system, some preparatory procedures must be undertaken to include pH-sensitive connections onto the surface of CNC [182,183]. The use of CNC in intrinsically pH-sensitive polymers is a method commonly applied for the synthesis of pH-sensitive CNC nanocomposites [184]. The primary reaction of hydrogels to diverse external stimuli is swelling and deswelling, which is caused by the creation of hydrogen bonds between water molecules and the hydrophilic components of the hydrogel. Targeted drug release can be facilitated by adding diverse functional groups to the surface of CNC to cause specific gelation characteristics in response to the pH gradient within the human body [185]. For example, the pore size of pH-responsive CNC hydrogels decreases in acidic settings and increases in alkaline conditions as the hydrogel's pH changes.

7. Challenges of using CNC and recommendations

This review provides an in-depth analysis of recent advancements in the synthesis, modification, and utilization of nanocellulose, and cellulose nanocrystals in particular, as active components in a wide variety of novel and fascinating applications. These findings have the potential to act as a driving force behind additional research in this field. In particular, it is necessary to address certain challenges, particularly in the areas of surface and end-reducing modifications, the scaling up of production, and the methods and techniques that are used to describe cellulose nanocrystalline (CNC). Over the last decade, a multitude of research and review articles have been written on this subject, and an abundance of methods and tactics for the characterization of CNC have been developed and published. For cellulose nanocrystalline (CNC), these characterization approaches yield information on various aspects, including their size (length, diameter, and aspect ratio), shape, surface charge, surface chemistry, crystallinity, mechanical qualities, and rheological features. NC properties and, by extension, characterization methodologies are significantly influenced by several factors, including the production method (mechanical, chemical, or biological), the cellulose source material (wood, pulp,

recycled paper, bamboo, agricultural wastes, cotton, or other biomass sources), and the final use.

The realistic transfer of lab-scale manufacturing to industrial or commercial scale, the achievement of material feasibility, and the introduction of these products to the market are all areas that require additional research to address the existing knowledge gaps. These include, but are not limited to, the optimization of the entire process, the development of new techniques to make new materials based on NC, and the reduction of the amount of energy and time that is consumed by NC-based products.

In industrial contexts, there are currently no technologies that can provide fast and accurate characterization, making it impossible to guarantee CNC quality and reliability. Additionally, the methods of nano-characterization that are now in use have some restrictions and downsides that must be considered. These approaches are dependent on off-line measurements that are carried out in laboratories. These measurements require a significant amount of post-processing and analysis, in addition to a substantial financial commitment and personnel that have received intensive training. On top of that, monitoring and control routines are unable to be applied in CNC production processes due to the significant delay in information collection that is brought about by the absence of real-time characterization methods. This section provides an overview of the most significant limitations and flaws associated with the CNC category in question.

8. Conclusion

Today's scientists, researchers, and academics are mostly focused on creating eco-friendly and bio-based nanomaterials to shield the planet from negative impacts. Derived from several lignocellulosic fiber types, nanocellulose is regarded as a sustainable and adaptable resource. It can be applied as a reinforcing material in a variety of industries, including food packaging, printed electronics, paper manufacture, and structural applications. This review article's objective is to give readers a full grasp of nanocellulose, in particular cellulose nanocrystals (CNCs), as well as the major properties of CNCs and prospective applications for these qualities. The following are the main findings from this review:

Because they contain large levels of noncellulosic components, including hemicellulose, lignin, and waxes, raw lignocellulosic fibers are not appropriate for use as reinforcement in a variety of applications. To effectively remove these noncellulosic elements from biomass and improve the physical structure of nanocellulose, chemical pretreatment is essential.

The conventional method of separating CNCs, mineral acid hydrolysis, has a number of drawbacks, including poor thermal stability of the CNCs, excessive water use for neutralization, and environmental problems. For the time being, researchers are focusing their efforts on organic acid hydrolysis and mixed acid hydrolysis, both of which involve the utilization of only a minute quantity of mineral acids. Organic acid hydrolysis is one of these techniques; it yields CNCs with better colloidal stability, less equipment corrosion, excellent thermal stability, and acid reusability. The need for environmentally sustainable materials has led researchers worldwide to investigate nanocellulose materials and their potential uses in a range of industries. Studying the surface and morphological behavior of these materials is crucial to understanding them completely and making appropriate use of them. This article serves as a useful resource for aspiring CNC researchers by highlighting significant characterization approaches used to analyze the microstructure of CNCs.

There is only a limited application of bio-based products for sustainable purposes. Researchers, scientists, and academics must have a broad perspective in order to create environmentally acceptable nanocellulose composites that do not harm ecosystems or the environment. The usage of CNCs in a variety of bio-based goods is examined in this article, along with their potential application in the creation of ecologically friendly products in the future.

In conclusion, this review paper offers a thorough overview of the methods used to process nanocellulose and is an invaluable resource for long-term expansion in the manufacturing of high-grade nanocomposite materials. Presently, governments and enterprises across the globe are allocating substantial financial resources to scientists and researchers working on nanotechnology applications in order to boost productivity and encourage environmental sustainability. The study concludes that research on nanotechnology is growing rapidly and has a lot of potential to support commercial and sustainable uses in the future.

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Footsteps of graphene filled polymer nanocomposites towards efficient membranes—Present and future

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Copyright © 2024 by author(s). Journal of Polymer Science and Engineering is published by EnPress Publisher, LLC. This work is licensed under the Creative Commons Attribution (CC BY) license. https://creativecommons.org/licenses/ by/4.0/ Abstract: Due to rising global environmental challenges, air/water pollution treatment technologies, especially membrane techniques, have been focused on. In this context, air or purification membranes have been considered effective for environmental remediation. In the field of polymeric membranes, high-performance polymer/graphene nanocomposite membranes have gained increasing research attention. The polymer/graphene nanomaterials exposed several potential benefits when processed as membranes. This review explains the utilization of polymer and graphene-derived nanocomposites towards membrane formation and water or gas separation or decontamination properties. Here, different membrane designs have been developed depending upon the polymer types (poly(vinyl alcohol), poly(vinyl chloride), poly(dimethyl siloxane), polysulfone, poly(methyl methacrylate), etc.) and graphene functionalities. Including graphene in polymers influences membrane microstructure, physical features, molecular permeability or selectivity, and separations. Polysulfone/graphene oxide nanocomposite membranes have been found to be most efficient with an enhanced rejection rate of 90%–95%, a high water flux >180 L/m²/h, and a desirable water contact angle for water purification purposes. For gas separation membranes, efficient membranes have been reported as polysulfone/graphene oxide and poly(dimethyl siloxane)/graphene oxide nanocomposites. In these membranes, N₂, CO₂, and other gases permeability has been found to be higher than even >99.9%. Similarly, higher selectivity values for gases like CO₂/CH₄ have been observed. Thus, high-performance graphene-based nanocomposite membranes possess high potential to overcome the challenges related to water or gas molecular separations.

Keywords: graphene; nanocomposite; membrane; water purification; gas separation

1. Introduction

Generally, membrane-based technologies have been used to remove toxic nanomaterials from the environment [1]. Among membrane materials, polymericbased materials and nanomaterials have been adopted for separation purposes [2,3]. Owing to the technical benefits of nanocarbons, graphene, fullerene, and carbon nanotubes have been adopted as unique and valuable nanostructures [4,5]. Graphenederived nanomaterials possess fine tendencies toward separation applications [6]. Especially, graphene has been reinforced in polymers to form high-performance nanocomposite membranes [7]. Polymer- and graphene-derived nanocomposite membranes have been efficiently used for the separation of hazardous molecules [8]. For the fabrication of polymer/graphene membranes, facile processing approaches have been used [9]. Solution processing, the phase inversion method, the infiltration technique, and other facile methods have been reported [10,11]. Polymer/graphene

membranes have been developed using polymers like polyamides, polysulfone, poly(dimethyl siloxane), poly(methyl methacrylate), and several others [12]. The nanocomposite membranes possess superior nanofiller dispersion, pore sizes, molecular permeation, and selectivity properties [13]. Owing to their effective characteristics, polymer/graphene nanocomposite membranes have been applied for technological sectors focusing on water, gaseous, and chemical separations [14]. The resulting membranes have been applied in commercial-scale water purification systems, gas sensing, and separation systems, fuel cell systems, and a myriad of other technical areas [15,16]. Most importantly, polymer- and graphene-based nanocomposite membranes have been fabricated for gas and water purification. Graphene mostly develops torturous pathways in the matrices to facilitate gas- or water-based ionic or molecular diffusion processes [17]. Homogeneous graphene dispersion in polymeric membranes has been used to enhance the separation of impurities and toxic molecules from air mixtures or contaminated water [18,19]. In this regard, several membrane processes have been studied, like nanofiltration, microfiltration, ultrafiltration, and reverse osmosis [20-22]. Afterward, graphenederived nanocomposite membranes have been efficiently used for removing pollutants [23]. The polymer/graphene nanocomposite membranes have structural advantages relative to reported nanocomposite membrane designs in terms of facile processing and resulting performance benefits [24]. Research progressions have led to the advancement of efficient air/water membranes [25].

For efficient graphene membrane fabrication, membranes, and mechanisms of molecular transport need to be thoroughly understood. The self-standing nanocomposite membranes must be researched for new design novelties [26]. In addition to graphene, graphene derivatives like graphene oxide, reduced graphene oxide, etc. may widen the potential of these membranes. The ultimate thinness of the membranes has been desirable to allow high flux [27]. The narrow pore size distribution and surface chemistry have been identified as desirable factors to promote molecular sieving and diffusion through the membranes. According to the literature, the interlayer spacing between graphene nanosheets can promote molecular transportation through the membrane [28]. To better withstand the high temperature, pressure, and humidity conditions, membrane support materials must be used [29]. Such efforts fill gaps between the membrane designs, large-scale productions, and commercialization of the novel graphene nanocomposite membranes.

This review article discusses the developments of graphene nanocomposites towards efficient membrane applications. The inclusion of graphene in polymers has improved the membranes' permeation and selectivity properties for water purification and gaseous molecular separation. In this article, the design, structure, and properties of polymeric membranes filled with graphene or graphene oxide nanofillers have been scrutinized. Subsequently, the microstructure, durability, stability, permeability, and other membrane properties have been used. The competence of nanocomposite membranes has been studied for gas or water purification, especially for the separation of toxins, pollutants, and unwanted species. The polymer and graphene-based nanomaterials have a high surface area and exceptional structure for efficient membrane performance. Accordingly, the formation of polymer/graphene membranes has extended the scope of air purification and water management. To the best of my knowledge, this article is ground-breaking in presenting efficient graphene-based membranes. The review outline, including literature, as well as relevant discussions, is novel and based on recent research assumptions for graphene-based membranes. Moreover, hardly any recent topical comprehensive review reports have been observed on the polymer/graphene nanocomposite membranes. The need for this review article also arises due to remarkably increased research reports on graphene nanocomposite membranes in the past two to three years. Hence, there is the utmost need for a recent innovative review on polymer/graphene nanocomposite membranes, it can be stated that substantial progress has been made in this field up until now. This article will definitely be beneficial for field scientists/researchers to expand their research toward the future success of high-performance industrial-scale nanocomposite membranes.

2. Graphene

Graphene is a one-atom-thick nanosheet of sp² hybridized carbon atoms [30]. **Figure 1** shows the structure of graphene and related derivative forms. This remarkable nanocarbon was discovered in 2004 [31].



Figure 1. Graphene and related derivative forms.

Graphene has been developed using various techniques such as graphite exfoliation, plasma processes, chemical vapor deposition, and chemical or organic synthetic strategies [32]. It is a transparent carbon nanostructure [33] having a high thermal conductivity of 3000–5000 W/mK [34], Young's modulus of ~1 TPa [35], and weak van der Waals forces [36]. Graphene oxide is a graphene-based nanocarbon that is usually formed through the oxidation and stripping of graphite. This graphene derivative has a graphene nanosheet structure with carboxylic, hydroxyl, carbonyl, or other oxygen-containing surface groups [37]. Graphene and graphene oxide have been employed to form nanocomposite materials [38]. Graphene nanocomposites have been studied for their high electron conductivity, thermal and chemical stability, and physical properties [39]. In addition, the high-tech potential of graphene has been developed for coatings, membranes, energy devices, and biomedical sectors [40].

Graphene is composed of a single carbon atom layer arranged in a twodimensional honeycomb lattice. A wide range of two-dimensional nanomaterials like graphene, graphene, nanoclays, MXenes, silicane, hexagonal boron nitride, transition metal dichalcogenides, etc. have been reported. A two-dimensional carbon nanostructure like graphene has probabilities to tailor and functionalize through surface defects, modified groups, number of layers, morphology, etc. Graphene has been explored for doping, modification, strength, conductivity, and other physical characteristics, relative to other two-dimensional nanomaterials. Consequently, graphene has been found to be stronger than other zero-, one-, or two-dimensional materials due to its structural strength. Especially compared with other carbon nanomaterials like carbon nanotubes (one-dimensional) and fullerene (zerodimensional), graphene nanosheets have revealed remarkable potential due to their high surface area nanostructures and better compatibility with polymer matrices. Research has realized the importance of graphene two-dimensional monolayers in several fields, with a special emphasis on their benefit to our society.

3. Polymer nanocomposite based membranes

Polymer-based membranes have been produced using a range of polymer matrices and preparation approaches [41]. Numerous carbonaceous nanoparticles and inorganic nanofillers were filled in the different polymeric matrices to develop the nanocomposite membranes [42]. The combination of these nanoparticles with polymers resulted in the formation of membranes with significant physical characteristics [43]. The resulting properties depend upon the nanoparticle type, nanoparticle amount, and polymer types as well [44]. These nanocomposite membranes have fine microstructure and separation properties for different types of molecules [45,46]. In other words, polymeric nanocomposite membranes act as molecular sieves for molecular separations [47]. The molecular permeation mechanisms depend on the interactions between the polymer and nanoparticles and their mutual effects [48]. In inorganic nanoparticle-filled membranes, silica nanoparticles have been used as nanofillers [49,50]. For silica-filled membranes, permeation and selective separation of O_2 , CO_2 , and N_2 gaseous molecules have been studied. Functional silica nanoparticle-filled poly(vinylidene-fluoridehexafluoropropylene) membranes were prepared through the phase separation method [51]. The molecular separation of CO_2 molecules was studied. The nanocomposite membrane with 40 wt.% nanoparticles revealed a CO₂ uptake of 33.75 mg/g [52,53]. Silica nanoparticles developed fine pathways for gas diffusion [54,55]. Titania nanofiller [56] and zinc oxide nanoparticles [57] have also been used with the polymers. Such membranes may have high structural robustness and CO₂/H₂ selectivity of 2.77.

In addition, carbon nanoparticles have been reinforced in the polymeric membranes [58]. Various nanocarbon nanoparticles have been used as efficient nanofillers with polymers like carbon nanotube, nanodiamond, fullerene, etc. to form nanocomposite membranes. Graphene-based nanomaterials have a high surface area-to-volume ratio, light weight, facile processing, and structural flexibility [59]. The inclusion of very minor amounts of graphene nanofiller in the nanocomposites has been found to enhance the physical features due to their interfacial properties [60]. Interfacial bonding has been found to directly affect the mechanical and thermal properties of the nanocomposites. As compared to zero- and one-dimensional nanocarbons like fullerene and carbon nanotubes, graphene nanostructure has an advantageous two-dimensional nanostructure with a light and strong nanosheet

nanostructure and intrinsic charge mobility and permeability features [61]. Therefore, graphene nanocomposites reveal a range of potential applications and remarkable properties, from high-performance nanocomposites to technical nanostructures like membranes. In nanocomposites membranes, graphene has a better alignment, dispersion, porosity, and tortuous pathway formation than one-dimensional nanostructures for better molecular permeability [62]. The polymer-based nanocomposite membranes have been applied for water purification and gas permeation purposes [63–65].

4. Efficiency of graphene nanocomposite membranes for water or gas separations

Owing to the lack of inherent robustness, and structural, and fouling drawbacks, polymeric membranes have been continuously replaced with nanocomposite membranes for better performance [66,67]. Consequently, nanocomposite membranes have been recognized for their controlled and advantageous thermal stability, selectivity, and permeability features [68]. For water remediation applications, solution processing, blading, phase separation, and related membrane fabrication strategies have been focused on [69]. Membrane matrices like poly(vinyl alcohol), polysulfones, nylons, and numerous others [70,71]. Graphene and graphene oxide nanofillers have been used for the development of efficient membranes. Polystyrene, polysulfone, and polyethersulfone have been widely used as ultrafiltration membranes due to their fine strength, durability, pH operating range, and chemical stability [72]. However, their uses in water treatment have been restricted due to their hydrophobicity and related reduced permeability properties. Widely used ultrafiltration polymeric membrane materials have hydrophobic properties. Poly(vinyl fluoride), poly(vinyl chloride), and poly(methyl acrylic acid) have been adopted for these membranes. Membrane hydrophobicity has been found to decrease the water flux due to the organic compound accumulation on the membrane surface. In this regard, polymer modification has been suggested to induce membrane hydrophilicity to enhance the membrane antifouling properties for enhanced water filtration processes. The future of polymer-based water treatment membranes relies on the adoption of new modified polymer matrices as well as nanoparticle nanofillers in the nanocomposite matrices.

Most membranes have been used to remove soluble and non-soluble impurities through the processes of ultra-filtration, reverse osmosis, nanofiltration, microfiltration, etc. [73]. Ultrafiltration membranes have pore sizes of $0.01-0.1 \mu m$, which are smaller than microfiltration membranes. However, these pores are larger than the pores of nanofiltration ($0.0001 \mu m$) and reverse osmosis membranes. Nanofiltration has been used to remove small organic molecules, like viruses. Ultrafiltration has been found to remove bacteria, microbes, and suspended solids from the water. Reverse osmosis works like filter media which attracts contaminants. The efficiency of the membrane filtration processes depends on the polymer type, surface functional groups, and physical characteristics of the polymeric membranes. The polymer modification has been used to attain efficient membrane separation processes and desired membrane performance. The modification may involve the incorporation

of copolymers and nanoparticles into the polymeric membranes to form blends or nanocomposites.

For the fabrication of polymer/graphene nanocomposite membranes, efficient techniques have been used [74,75]. The solution-casting technique follows the principle of Stokes' law [76]. In this technique, the polymer is dissolved in a solvent. The nanoparticles are also dispersed in a solvent. Both the polymer solution and the nanoparticle solution are mixed to form a homogeneous phase. Later, the solution phase is evaporated to form a polymer film or membrane. The phase inversion technique has also been focused on polymer/graphene nanocomposite membranes [77]. In this process, the controlled transformation of polymers is performed from the liquid to the solid phase. Consequently, steps like precipitation, controlled evaporation, and immersion precipitation are involved in this method. Furthermore, the polymer/graphene nanocomposites have been formed by interfacial polymerization [78]. Interfacial polymerization involves steps like the oil phase, emulsification, and solvent evaporation. All these technologies have been used to form nanocomposite membranes with finely dispersed graphene and derived nanofillers.

Consequently, poly(vinyl alcohol) and poly(vinyl chloride) matrices have been considered important as important matrices for graphene nanofillers [79-81]. Production and properties of poly(vinyl chloride) and graphene oxide nanocomposite membranes have been produced through the phase inversion method [82]. According to microscopic studies, these membranes revealed a macro-void structure. The nanocomposite membranes were investigated to remove bovine serum albumin from water. The separation performance was observed due to the hydrophilic nature of the membranes. Poly(vinyl alcohol) matrix has been filled with graphene or graphene oxide nanoparticles [83]. These nanomaterials based on poly(vinyl alcohol) and graphene oxide possess hydrogen and hydrophilic binding interactions. Moreover, the membrane design based on poly(vinyl alcohol) and graphene oxide was reported by Castro-Muñoz and researchers [84]. The poly(vinyl alcohol)/graphene oxide-based mixed matrix membranes were prepared using dense-film casting and solvent evaporation methods. The inclusion of 1 wt.% graphene oxide in the membrane resulted in a permeate flux of 0.14 kg m⁻²h⁻¹. Sun and co-workers [85] used the pressure-assisted filtration process for the production of a poly(vinyl alcohol)/graphene oxide system. Including 10 wt.% nanoparticles caused superior water flux and salt rejection of 98 kgm⁻²h⁻¹ and 99.9%, respectively. Thakur and coresearchers [86] utilized the direct laser writing method to form laser-induced graphene-based three-dimensional porous carbon nanomaterial. Three-dimensional laser-induced graphene had superior electron conductivity. Then, nanocomposite of poly(vinyl alcohol) and laser-induced graphene have been prepared for the formation of membranes. The poly(vinyl alcohol)/laser-induced graphene nanocomposites own fine mechanical, physical, and surface wettability characteristics. Figure 2 displays a scheme for the development of poly(vinyl alcohol) and laser-induced graphene nanocomposite derived nanocomposite based water treatment membranes for nt. Consequently, the ultrafiltration poly(vinyl alcohol)/laser-induced graphene nanocomposite membranes showed separations of solute particles and bacterial species. Figure 3 specifies the construction of poly(vinyl alcohol)/laser-induced graphene nanocomposite membranes.



Figure 2. Schematic of poly(vinyl alcohol) and laser induced graphene nanocomposite membranes for water remediation [86]. Reproduced with permission from ACS.



Figure 3. (a) Laser-induced graphene (LIG) is generated on UP 010 membranes through 10.6 μ m CO₂ laser; **(b)** scanning electron microscopy images of as-prepared LIG including cross-section (inset); **(c)** fabrication technique for laser-induced graphene and poly(vinyl alcohol) (LIGPVA-4) membrane showing excess of poly(vinyl alcohol) (PVA) solution removal with a rubber roller; and **(d)** scanning electron microscopy images of LIG-PVA-4, including cross-section (inset) [86]. Reproduced with permission from ACS.

Initially, laser-induced graphene was coated on a polyethersulfone substrate. Then, the laser-induced graphene was coated with poly(vinyl alcohol) to form the nanocomposite membrane. Scanning electron microscopic studies on laser-induced graphene and poly(vinyl alcohol)/laser-induced graphene nanocomposite membranes revealed the development of a porous three-dimensional network with consistent pore size distributions. The rejection rate was found to be 99.9%.

The polysulfone and graphene-derived nanocomposites formed some advantageous membrane design combinations [87]. Zinadini et al. [88] reported on polysulfone and graphene oxide-derived membranes. The addition of nanoparticles to the membrane systems resulted in a unique microstructure and high water flux [89]. The polysulfone/graphene oxide-derived membranes revealed a contact angle of 55° – 65° and a water flux of >20 kg/m²h. Hydrogen bonding interactions have also been observed between the polysulfone matrix and graphene oxide, leading to the formation of efficient hydrophilic membranes. Here, the wet phase inversion method has been preferred for the fabrication of polysulfone and graphene oxide-derived membranes [90]. Rezaee and co-workers [91] reported on polysulfone/graphene oxide

nanocomposite membranes using the solution technique. **Table 1** demonstrates the influence of adding graphene oxide amounts on the pure water flux, porosity, and pore structure of the membranes. Enhancing the graphene oxide contents from 0.5 to 1 wt.% enhanced the pure water flux from 20 to 50 L/m²h. The membrane porosity was also enhanced from 78% to 87%.

Table 1. Effect of GO content on pure water flux and pore structure parameters of the prepared membranes [91]. GO = graphene oxide; PSF = polysulfone; PSF/GO = polysulfone/graphene oxide. Reproduced with permission from Springer (Creative Commons CC BY).

Membrane	Pure water flux (L/m ² h)	Porosity (%)	Pore diameter (nm)
Pure PSF	19.7 ± 3.2	48.3 ± 2.6	6.9 ± 0.56
PSF/GO 0.5	32.3 ± 3.5	77.9 ± 2.2	8.3 ± 0.31
PSF/GO 1	49.9 ± 2.6	86.5 ± 1.8	9.1 ± 0.63
PSF/GO 2	46.4 ± 2.0	82.1 ± 2.6	8.7 ± 0.42

Adding 1 wt.% graphene oxide caused higher pure water flux, porosity, and pore diameter properties relative to the neat polymer and other nanofiller loaded membranes. The effect of a change in pH on the rejection rate was studied for membranes with different nanofiller contents (**Figure 4**). Better arsenate rejection performance was observed for 1 and 2 wt.% nanoparticle loading. Consequently, the nanofiller addition caused high separation efficiency due to homogeneous membrane structure, morphology, pore sizes, and optimum porosities [92]. Hence, polymer/graphene and polymer/graphene oxide nanocomposites have been studied for water remediation and filtration [93]. However, these membranes need further research efforts to resolve the challenges of low membrane stability and fouling effects.



Figure 4. Percentage rejection of As (V) at different pHs by prepared membranes with various graphene oxide (GO) contents. (Operating pressure = 4 bar; initial As (V) concentration = $300 \pm 10 \mu g/L$; feed temperature = $25 \pm 0.5 \text{ °C}$) [91]. As = arsenate; PSF = polysulfone; PSF/GO = polysulfone/graphene oxide. Reproduced with permission from Springer (Creative Commons CC BY).

Tulugan et al. [94] formed polysulfone/graphene nanocomposite-derived nanofiltration membranes. The water flux of the neat polysulfone membrane (33.2

 $L/m^2/h$) was improved with the inclusion of graphene to 183.6 $L/m^2/h$. Moreover, the nanofiltration membranes have a high adsorption rate of 79.8%, relative to neat polymer membranes (26.7%). Alshahrani et al. [95] used the interfacial polymerization method for polysulfone/reduced graphene oxide membrane fabrication. Including 0.015% nanofiller in polyamide led to a water permeability of 48.9 L/m^2 h, higher than the neat polyamide membrane (25.0 L/m^2 h). In addition, these membranes have a high salt rejection of 80–95%. Yu et al. [96] developed polyamide-polysulfone membranes through interfacial polymerization. The water permeability of membranes was found to be 48.90 L/m^2 h at 22 bar, which was superior to the neat polyamide membrane of 25.0 L/m^2 h. Salt rejection was observed in the range of 80%–95%.

In addition to water permeation or desalination membranes, polymer/graphene membranes have been frequently investigated for gas molecule transportation [97]. Koenig and colleagues [98] formed pristine graphene membranes on a silicon substrate for the separation of H₂ and CO₂ gases. The structure and morphology of membranes have been reported. In addition, membranes have been studied for CO_2/CH_4 , CO_2/O_2 , and CO₂/N₂ permeation and separation processes [99]. The performances were found to be related to membrane pore sizes as well as affinity towards different molecular species [100]. Subsequently, graphene designs have been investigated for fine gas separations [101]. To improve the properties of graphene towards gas permeation, polymer and graphene-based membranes have been reported [102]. Li and researchers [103] fabricated the polymer/graphene nanocomposite membranes with a pore size of 0.34 nm. The membranes were tested for high selectivity for H_2/CO_2 and H_2/N_2 gases. These membranes still need to be focused on improving pore sizes towards CO_2 sieving [104]. For gas separation membranes, poly(dimethyl siloxane) has been considered [105]. Ultrathin membranes of poly(dimethyl siloxane) have been designed to focus on the carbon dioxide and other toxic gases removal [106]. Nevertheless, pristine poly(dimethyl siloxane) membranes have certain drawbacks due to a lack of structural robustness. In this regard, reports on poly(dimethyl siloxane) and graphene oxide-derived nanocomposite membranes have been found in the literature [107]. Such nanocomposite membranes have been prepared using ultrasonication and solvent-based methods. The poly(dimethyl siloxane)/graphene oxide membranes have fine CO_2 permeability and CO_2/CH_4 separation characteristics. Poly(methyl methacrylate) is a thermoplastic polymer widely applied for membrane applications [108]. Baldanza and researchers [109] produced poly(methyl methacrylate) and graphene-based nanocomposite membranes through a wet deposition technique. The 'lift-off/float-on' method was used for the formation of these membranes [110]. Figure 5 shows the formation of poly(methyl methacrylate) and twenty layers of graphene-based nanocomposite membrane. The membrane thickness and nominal volume fraction were observed at around 550 nm and 0.06%, respectively. According to scanning electron microscopy, a regular lamination sequence was observed. Neat poly(methyl methacrylate) and poly(methyl methacrylate)/graphene membranes were studied for the permeability coefficients of humidified CO_2 and O_2 (Figure 6). The nanocomposite membrane had significantly low permeability properties. Adding graphene nanofiller reduced the CO2 and O2 permeability coefficients of the membrane to 1.30×10^{-17} and 0.21×10^{-17} mol·m·m⁻²·Pa⁻¹·s⁻¹, respectively (**Table** 2). The property was declined owing to the development of diffusion pathways in the



membrane. These membranes had high permeability coefficients suitable for commercial scale uses of poly(methyl methacrylate)/graphene membranes [111].

Figure 5. (a) Schematic illustration of the iterative 'lift-off/float-on' process combined with wet depositions adopted to produce the Gr-PMMA nanolaminates; (b) Thickness evaluation of the single Gr-PMMA layer deposited on a Si wafer: representative cross-section of the scratch and atomic force microscopy image as inset; and (c) scanning electron microscopy image in the cross-section plane of the nanolaminate [109]. Gr = graphene; Gr-PMMA = poly(methyl methacrylate/graphene nanocomposite); APS = ammonium peroxydisulfate.

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Figure 6. Gas permeability coefficients at 25 °C through poly(methyl methacrylate) (PMMA) (blue bars) and Gr-PMMA (poly(methyl methacrylate/graphene nanocomposite)) (red bars) for **(a)** CO₂ and humidified CO₂ and **(b)** O₂ and humidified O₂ [109]. Reproduced with permission from MDPI.

Table 2. Permeability coefficients of CO_2 or O_2 through the nanocomposite at different R.H. levels [109]. PMMA = poly(methyl methacrylate); Gr-PMMA = poly(methyl methacrylate/graphene nanocomposite). Reproduced with permission from MDPI.

Nanolaminate/ permeating gas	$\mathbf{P} [\mathbf{mol} \cdot \mathbf{m} \cdot \mathbf{m}^{-2} \cdot \mathbf{Pa}^{-1} \cdot \mathbf{s}^{-1}]$	P [Barrer]
PMMA/CO ₂	$21.9 (\pm 0.8) \times 10^{-17}$	$6.5 (\pm 0.2) \times 10^{-1}$
Gr-PMMA/CO ₂	$1.30 (\pm 0.1) \times 10^{-17}$	$0.39~(\pm 0.03) imes 10^{-1}$
PMMA/O ₂	$4.79(\pm 0.01) \times 10^{-17}$	$1.434(\pm 0.003) \times 10^{-1}$
Gr-PMMA/O ₂	$0.21 \ (\pm 0.01) \times 10^{-17}$	$0.063 (\pm 0.003) \times 10^{-1}$

Polysulfone is also an important thermoplastic polymer for gas purification membrane systems [112]. In this contest, the mixed matrix membranes of polysulfone have been reported [113]. These membranes have been reported for the separation or selective separation of CO₂ and other noxious gases [114]. Sainath and co-workers [115] produced the mixed matrix polysulfone/graphene oxide membrane for the selective separation of gases. Adding 0.25 wt.% graphene oxide caused 3-4 times higher CO₂/CH₄ selectivity relative to the pristine membrane. The results were obtained due to better nanofiller dispersion and the formation of diffusing routes in the nanocomposite membranes [116]. Gas separation membranes of copolymers have also gained success in gas separation applications such as poly(1-trimethylsilyl-1propyne)/graphene oxide [117–119] and poly(phenyl sulfonepyridine)/graphene oxide nanocomposites [120]. Similarly, poly(2,6-dimethyl-1,4-phenylene oxide) has been adopted for gas separation membrane matrix [121–123]. Rea and co-workers [124] fabricated the poly(2,6-dimethyl-1,4-phenylene oxide) and graphene-based nanocomposite membranes. The 0.3-15 wt.% nanoparticle contents were filled in the membranes. Figure 7 shows the morphology of the poly(2,6-dimethyl-1,4-phenylene oxide)/graphene nanocomposite membrane. A few layers of graphene were observed in the polymer matrix, showing layered morphology and fine dispersion.



Figure 7. Scanning electron microscopy image of PPO and a few-layer graphene membrane [124]. PPO = poly(2,6-dimethyl-1,4-phenylene oxide). Reproduced with permission from MDPI.



Figure 8. Gas permeability before (a) 35 °C; (b) 65 °C; and after graphene addition (c) 35 °C; (d) 65 °C, as a function of graphene loading in the poly(1-trimethylsilyl-1-propyne) matrix [124]. Reproduced with permission from MDPI.

The gas permeability was found to decrease at 35 and 65 °C with the addition of graphene (**Figure 8**). The effect on the permeation properties was observed due to the variation in loading level and dispersion in the polymer matrix. Hence, numerous polymeric membranes have been prepared with graphene or graphene oxide nanofillers for gas permeation [125]. The gas permeability and selectivity properties rely on the nanoparticle alignment in the matrices, which may affect the membrane pore sizes and microstructures [126,127].

5. Important prospects

Numerous polymer/graphene nanocomposite membrane systems have been proposed for superior water permeation, desalination, gas separation, and selective separation characteristics. Key points of this review article include the (i) fundamentals of graphene; (ii) fundamentals of polymer membranes; (iii) efficiency of graphene nanocomposite membranes for water remediation or gas separations; (iv) important aspects of the nanocomposite membranes; (v) graphene amount and dispersion; (vi) graphene interactions with membrane matrix; (vii) membrane porosity, morphology, and surface properties; and (viii) membrane permeability and selectivity properties. Additionally, graphene-based systems have advanced mechanical stability and thermal stability properties. Generally, fine graphene dispersion in matrices has been considered for fine molecular transportation characteristics such as barrier, permeation, and selective separation (**Figure 9**). These membrane properties can be limited due to poor nanoparticle dispersion, surface properties, and imperfect membrane pore formation. Another limiting factor is the fabrication of graphene-based membranes on industrial or commercial levels. The large-scale processing depends upon technique, polymer/nanofiller types, and functionalization affecting the microstructure, durability, and water/gaseous molecular transportation.



Figure 9. Graphene for gas separation membranes.

According to a literature comparison (**Table 3**), polysulfone nanocomposite membranes have been prepared with carbon nanotubes [128], zeolites [129], and silicon dioxide [130]. The polysulfone/graphene or graphene oxide-based membranes revealed better nanoparticle dispersion, antifouling, water flux, and permeability properties. By comparing the utilization of graphene or graphene oxide nanofillers in the water purification membranes, most of the membranes have been prepared using the graphene oxide nanofiller. The inclusion of graphene oxide or reduced graphene oxide in membranes led to superior water flux, permeability, and rejection properties. The reason seems to be the functionalization of graphene nanosheets, which causes better interactions and dispersion with the polymers relative to neat graphene nanofillers.

Solution casting, phase inversion, and ultrasonication. Techniques that have been frequently used include gas separation polymer/graphene and polymer graphene oxide membranes. As compared to polysulfone/graphene and polysulfone/graphene oxide membranes [115,131], lower CO₂ permeability and ideal CO₂/CH₄ selectivity of 4.2% and 2.7%, respectively, were observed for commercial polysulfone/zeolite membranes [132]. For gas separation membranes, both graphene, graphene oxide, and modified graphene oxide have been applied. A number of studies have been reported on graphene and derivative-based membranes [133]. By comparing various studies on graphene and graphene-derived membranes (Table 4), graphene oxide-based

membranes were found to have higher selectivity and permeability values than graphene-based systems. For example, the polysulfone [103] system revealed much higher gas selectivity than the corresponding graphene-based membranes [115,131]. The reason seems to be the nanostructure of graphene, which has impermeability towards molecular passage. However, the formation of graphene oxide or modified graphene nanostructures may cause surface defects, leading to better compatibility, interactions, and interface formation. Consequently, superior permeability and selectivity of graphene oxide membranes reveal better gas separation properties to overcome the tradeoffs between permeability and selectivity of the nanocomposite membranes. Nevertheless, these membranes are still in their developmental stages, and further studies have been desirable to understand the transport mechanisms as well as the structural specifications.

Polymer	Nanofiller	Fabrication route	Membrane properties	Ref
Poly(vinyl alcohol)	Graphene oxide	Mixed matrix membranes; dense-film casting technique; solvent evaporation	Permeate flux 0.14 kg m ^{-2h^{-1}; permeation rate 75%}	[84]
Poly(vinyl alcohol)	Graphene oxide	Pressure-assisted filtration process	water flux 98 k gm ⁻² h ⁻¹ ; salt rejection 99.9%	[85]
Poly(vinyl alcohol)	Laser-induced graphene	Ultrafiltration, direct laser writing method	Three-dimensional network; consistent pore size distribution; rejection rate 99.9%	[86]
Polysulfone	Graphene oxide	Phase inversion method	Water flux >20 kg/m ² h; contact angle 55°–65°	[89]
Polysulfone	Graphene oxide	Solution casting	Pure water flux 20–50 L/m ² h; porosity 78%–87%.	[91]
Polysulfone	Graphene oxide	Nanofiltration	Contact angle 7°; water flux 33.2 183.6 L/m ² /h; adsorption rate 79.8%	[94]
Polysulfone	Reduced graphene oxide	Interfacial polymerization	Water permeability 48.9 L/m ² h; permeability 25.0 L/m ² h; salt rejection 80%–95%	[95]
Polysulfone-polyamide	Sulfonated graphene oxide	Interfacial polymerization	Fluorine treatment; F ⁻ retention effect; water flux 83.2%	[96]

Table 3. Specifications of polymer/graphene nanocomposite membranes for water separation.

Here, research progress in the field of polymer/graphene nanocomposite membranes needs to be analyzed according to the membrane design, type, and specific end application in order to assess the crucial difficulties in this field. Research progress in the field of polymer/graphene membranes can be primarily categorized as desalination or separation membranes for the removal of salts, biological, and organic pollutants by attaining optimally high water flux. The design and essential characteristics of polymer/graphene nanocomposite-based water permeation membranes have been studied. The nanocomposite membranes have been investigated for their morphological properties, permeability, flux, desalination, and toxin removal.

Table 4. Specs of	f polymer/g	graphene nano	composite mem	branes for gas	s separation.

Polymer	Nanofiller	Fabrication route	Physicochemical properties	Membrane properties	Ref
Polymer	Graphene or graphene oxide	Solution casting	Ion-molecule interaction; 1.8–20 nm thickness	H ₂ /N ₂ selectivity 900; H ₂ /CO ₂ selectivity 3400; pore size ~0.34 nm	[103]
Polysulfone	Graphene oxide	Solution route; N- Methyl-2-pyrrolidone solvent	Physical interaction between oxygenated functional groups of graphene oxide and polymer; Interactions between functional groups of nanocomposites and gas molecules	CO ₂ /CH ₄ selectivity ~45	[115]
Polysulfone	Graphene	Phase inversion; hollow fiber mixed matrix membrane	Nanosize synthesized graphene; Interfacial interaction between graphene and polymer matrix	CO ₂ /N ₂ selectivity 158%; CO ₂ /CH ₄ selectivity 74%	[131]
Polysulfone	Zeolite	Mixed matrix membranes	Interlinked morphology	CO ₂ permeability and ideal CO ₂ /CH ₄ selectivity were slightly 4.2% and 2.7%, respectively	[132]
Polyphenylsulfone- pyridine	Graphene oxide	Vacuum infiltration technique	Wettability and surface charge response to pH; acidic pH = 3 form hydrophilic state contact angle 63.3° ; alkaline pH = 11 form hydrophobic state contact angle 106.5°; charge-density-tunable nanoporous; power of ≈ 0.76 W m ⁻²	Dispersion; morphology	[120]
Poly(dimethyl siloxane)	Graphene	Solution casting; p-xylene solvent	π - π interactions in matrix- nanofiller	0.2 wt.% nanofiller; N ₂ , CO ₂ , Ar, and CH ₄ permeation 60%; CO ₂ /CH ₄ selectivity 4.2	[134]
Poly(dimethyl siloxane)	Graphene oxide	Solution/ ultrasonication methods; tetrahydrofuran solvent	Interfacial interactions between functional groups of graphene oxide and polymer; density 1.09–1.12; Thickness 1.9–2.8 nm	5 wt.% nanofiller; CO ₂ /CH ₄ selectivity 112%; CO ₂ permeability 29%.	[107]
Poly(dimethyl siloxane)	Graphene oxide	Solution casting	Matrix-nanofiller interactions; interaction between graphene oxide and polymer	8 wt.% nanofiller; H ₂ , O ₂ , N ₂ , CH ₄ and CO ₂ permeability 99.9%	[135]
Poly(methyl methacrylate)	Graphene	Wet deposition method	Water adsorption, membrane wrinkles; degree of dispersion/orientation of the graphene nanosheet, structure organization of polymeric chains at the interface with graphene nanosheet	$\begin{array}{l} CO_2 \text{ permeability coefficient} \\ 1.30 \times 10^{-17} \\ \text{mol}\cdot\text{m}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}\cdot\text{s}^{-1}; \\ O_2 \text{ permeability coefficient} \\ 0.21 \times 10^{-17} \\ \text{mol}\cdot\text{m}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}\cdot\text{s}^{-1} \end{array}$	[109]

Polymer	Nanofiller	Fabrication route	Physicochemical properties	Membrane properties	Ref
Poly(1-trimethylsilyl-1- propyne)	Graphene oxide	Solution casting; chloroform solvent	Anchoring of graphene oxide nanosheets lowers membrane flexibility; and less free volume; covalent cross-linking of polymer	1 wt.% graphene; diffusion coefficient of CO ₂ (25%); N ₂ (14); CH ₄ (9%)	[118]
Poly(1-trimethylsilyl-1- propyne)	Graphene	Solution route	Interaction between filler and polymer matrix; 0.93–1.36 MPa; 38–44 MPa	$\begin{array}{l} 0.05 \text{ wt.\% nanofiller;} \\ CO_2 \text{ permeability } 3.5 \ \times \ 10^3 \\ Barrer \end{array}$	[119]
Poly(2,6-dimethyl-1,4- phenylene oxide)	Graphene	Solution route	Void formation at the interface; glassy polymer filled with graphene; graphene inclusion for the physical constraint to relaxation of polymer chains	0.3–15 wt.% nanofiller reduced permeability	[124]

 Table 4. (Continued).

The mechanical properties like flexibility, strength, toughness, and other important properties of membranes have been deliberated. Graphene nanoparticle dispersion has been found to be important in enhancing the matrix-nanofiller interactions and improving the final membrane characteristics. In this context, compatibility between the polymer and graphene nanoparticles may cause better nanoparticle dispersion and miscibility effects. The molecular diffusion and permeability properties rely on the pore size, shape, and nanoparticle dispersal in the polymeric matrices. All these properties not only affect the selectivity/permeability features but also the membrane strength and functional life for membrane applications. Major challenges identified in this sector have been found to be complications owing to poor nanoparticle dispersion, phase separation, optimum fabrication parameters, and the identification of perfect membrane designs for commercial-scale production of these membranes. In this way, desirable barrier effects can be achieved for selective molecular transportation through the membranes to separate the salts, toxic ions, biological species, and other toxins. Thus, not much research has been observed regarding the separation mechanisms and overcoming the challenges of fabricating well-defined designs for commercial-level use. Future research in the mentioned directions will be beneficial for the formation of efficient water separation membranes.

Secondly, an important application of polymer/graphene nanocomposite membranes has been observed for gas separation. Here, matrices like polysulfone, poly(dimethyl siloxane), poly(methyl methacrylate), and other block copolymers have been used and filled with graphene nanofillers using facile solution, sonication, phase inversion, infiltration, and other techniques. For this application, efficient design combinations have been observed for separating the toxic or desired gas from gaseous mixtures. The resulting membrane must have optimum porosity, permeability, selectivity, and other membrane features for the separation of molecular species. As discussed above, all the membrane characteristics have been found to be dependent upon the processing, nanoparticle alignment, functionality, and compatibility with the polymer phases. By controlling all these features, complex gas mixtures can be separated using novel membrane designs. In addition, membrane thicknesses have also been found to be important to control not only the gas transport and flux characteristics, but also the membrane durability and cyclic performance. For gas separation, identification of the perfect processing technique, membrane parameters, and ultrathin polymer/graphene nanocomposite membrane formation have been found to be limiting factors or challenges. In this field, there is a lack of research regarding the separation mechanisms, structure-property relationships, and well-defined membrane designs for the separation of specific gaseous pollutants. Hence, due to a lack of targeted research in this area, desired permeability, selectivity, and working life have been found challenging. More focused research efforts have definitely been needed in these directions to form high-performance membranes through facile processing with welldefined parameters.

6. Conclusions

Hence, this article presents the gas separation performance of polymer/graphene nanocomposite membranes, keeping in view the important literature reports. Graphene as well as modified graphene nanoparticles have been filled in the nanocomposite membranes. The resulting membrane systems have been analyzed for fine water and gas molecular separation as well as permeation properties. The polymer/graphene nanocomposite membranes have been examined for the nature of pores, microstructure, sturdiness, and gas or water molecular separation efficiencies. Various combinations of polymers and graphene, or modified graphene, have been developed for the formation of efficient membrane systems. Nevertheless, there are several challenges in the way of the formation and application of polymer/graphene nanocomposite membranes. The related challenges may be comprised of polymer type, nanoparticle modification, nanoparticle dispersion, and nanoparticle interaction with the polymer. Despite the advantages, there are numerous problems limiting the rapid development of graphene-based nanocomposite membranes. Even though facile solution methods have been used, no perfect design with all the defined parameters, high surface area, and even thickness has been identified so far for large-scale functioning. Facile methods have been found to be ineffective in producing membranes with all defined membrane parameters on a large scale. Pore clogging and membrane fouling (biofouling, micro fouling, macrofouling) due to the presence of organic/inorganic pollutants (dyes, metal particles, microbes, bacteria, etc.) have been found to prevent rapid water purification. Hence, the development of evenly structured ultrathin, enduring, lightweight, low price, antifouling, and extended life polymer/graphene membranes has been found difficult to attain for large-scale commercial systems. Overcoming all these challenges may yield fine future opportunities for high-tech, commercial-grade graphene-filled membranes.

Thus, the research progress on graphene nanocomposite membranes led to several advances in types, designs, and applications to overcome the challenges in this field. For an increase in physical properties, nanoparticle dispersion has been found to be important for matrix-nanofiller interactions, microstructure, mechanical features, and for advanced membrane characteristics. Consequently, the compatibility of matrix graphene has been recommended to improve for better miscibility and reinforcing effects. The membrane performance also depends upon the pore shapes, sizes, and distribution in the matrices. The random nanofiller dispersion or pore distribution in membranes may influence the strength, durability, and life of the membranes. For commercial-scale membrane production, membrane design features must be analyzed. Hence, future research must resolve the challenge of identifying directions for highperformance gas separation membranes.

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Review

Sustainable membrane technology for water purification—Manufacturing, recycling and environmental impacts

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Abstract: Water pollution has become a serious threat to our ecosystem. Water contamination due to human, commercial, and industrial activities has negatively affected the whole world. Owing to the global demanding challenges of water pollution treatments and achieving sustainability, membrane technology has gained increasing research attention. Although numerous membrane materials have focused, the sustainable water purification membranes are most effective for environmental needs. In this regard sustainable, green, and recyclable polymeric and nanocomposite membranes have been developed. Materials fulfilling sustainable environmental demands usually include wide-ranging polyesters, polyamides, polysulfones, and recyclable/biodegradable petroleum polymers plus non-toxic solvents. Consequently, water purification membranes for nanofiltration, microfiltration, reverse osmosis, ultrafiltration, and related filtration processes have been designed. Sustainable polymer membranes for water purification have been manufactured using facile techniques. The resulting membranes have been tested for desalination, dye removal, ion separation, and antibacterial processes for wastewater. Environmental sustainability studies have also pointed towards desired life cycle assessment results for these water purification membranes. Recycling of water treatment membranes have been performed by three major processes mechanical recycling, chemical recycling, or thermal recycling. Moreover, use of sustainable membranes has caused positive environmental impacts for safe waste water treatment. Importantly, worth of sustainable water purification membranes has been analyzed for the environmentally friendly water purification applications. There is vast scope of developing and investigating water purification membranes using countless sustainable polymers, materials, and nanomaterials. Hence, value of sustainable membranes has been analyzed to meet the global demands and challenges to attain future clean water and ecosystem.

Keywords: sustainable; membrane technology; polymer; recycling; water purification

1. Introduction

For the purification of globally produced wastewater, membrane technology has been found most effective not only for treating the desired pollutants but also for largescale processing [1]. However, previously synthesized and used water permeation membranes have low sustainability due to the non-green materials used. The entire life cycle assessment results also revealed the low sustainability of commercially used water-treating membranes [2]. The design of sustainable membranes obviously depends upon the use of green and recyclable raw materials like green polymers and biodegradable petroleum-derived polymers and non-hazardous solvents. Using sustainable materials based membranes can easily reduce the disposal burdens at the life cycle end as well as the expected environmental risks of non-degradable materials [3]. Therefore, there is need of replacing the traditional commercial materials by using sustainable recyclable materials and green solvents for the membrane fabrication [4–6]. The recyclability studies of water purification polymeric membranes through mechanical, chemical, or thermal processes have pointed ways to future sustainable environmental materials [7].

Briefly, this review critically assesses recent developments towards the sustainability of membrane technology including nanofiltration, reverse osmosis, ultrafiltration, and other techniques. The use of degradable materials (polymers, solvents, chemicals) may lead to the transformations of the advanced membrane industry according to circular economy concept and safe ecosystem.

2. Sustainable water purification membranes

Membrane technology has played important part globally in efficient waste water management through superior separation efficiency consuming less energy [8–10]. This technology has further employed the microfiltration, nanofiltration, ultrafiltration, and reverse osmosis membrane processes for efficient water cleaning. Different membrane materials have been pragmatic so far to develop the water purification membranes [11–13]. **Table 1** exhibits examples of few membrane designs and specifications involved in the water treatment modules. Recent membrane technology has moved towards the green separation approaches due to the environment friendly and sustainability demands [14–16]. To enhance the membrane separation performances, modification routes have been preferred in this field [17,18]. At the end of membrane service, life cycle management techniques have been cast-off. In addition to the use of sustainable polymers, non-toxic solvents must be adopted for membrane processing [19–21].

Polymeric material	Diameter/Size	Voltage requirement	Physical properties	Membrane flow rate	Reference
Polyethylene terephthalate with graphene nanoparticles	-	-	Percolation threshold 0.2 Scm^{-1}	Air gap ~3 cm; pressure 25 psi	[22]
Polyamide with graphene nanoparticles	76–338 nm	8–10 kV	113% increased Young's modulus and 250% rise in fracture toughness	$0.05 \text{ mL } h^{-1}$	[23]
Aramid with carbon nanoparticles	~8 nm	-	Ultimate tensile stress increase by 700%	$2-6 \text{ mL } h^{-1}$	[24]
Poly(ε-caprolactone) with graphene	100–130 nm	12 kV	304% increased tensile strength	$1 \text{ mL } h^{-1}$	[25]
Poly(ε-caprolactone) with nanoparticles	121–154 nm	15–17 kV	Young's modulus 3771 MPa	$0.8-1 \text{ mL } h^{-1}$	[26]

Table 1. Design and specifications of few water purification membranes.

Polyesters have been identified as sustainable green materials for membranes [27–29]. Polyethylene membranes especially recycled membranes from petroleum products have advantages of antifouling, chemical. and chlorine resistance. These membranes have high separation ability towards water pollutants, organic wastes, salts, etc. Ma et al. [30] performed life cycle assessment of polyesters. These polymeric membranes had facile processing and sustainability opportunities. Park et al. [31] developed nanofiltration polyester membranes for desalination and dye removal. The

polyester membrane design and salt or dye removal towards water purification is given in **Figure 1**. The physicochemical features of polyester membranes and salt or dye rejection efficiencies for polluted water have been assessed.



Figure 1. Polyester membrane for water purification by desalination and dye removal [31]. Reproduced with permission from Elsevier.

Donnakatte Neelalochana et al. [32] produced sustainable polyethylene terephthalate based anion exchange membranes. These water purification membranes have alkaline stability and ionic conductivity of about 432 h (1 M KOH) and $5.3 \times 10^{-2} \,\mathrm{S} \cdot \mathrm{cm}^{-1}$, respectively. The membrane degradation pathways and mechanisms have been investigated in the alkaline conditions. Fan et al. [33] designed the polyester membrane with superior physicochemical properties for drinking water purification. High-performance membranes have fine chlorine resistance and antifouling performance.

Polypropylene based sustainable water purification membranes [34–36]. Particularly such membranes have been industrialised for oil-water separations. However, these membranes have high prices, low efficiency, and limited environmental pollutant removal for industrial oil-water separations [37–39]. Yuan et al. [40] fabricated the membranes based on polypropylene wood pulp fiber composite nonwoven fabric for kerosine-water separations. Figure 2 shows gravity-driven oilwater separation system, oil-water separation device, and gravity-driven oil-water separation vs. time. Kerosine oil was stained with oil red. Oil-water mixture was gradually poured in the designed separation device. Upon passing through polypropylene membrane, oil-water separation may efficiently occur which can be visualized in photographs. Scanning electron microscopy images of polypropylenewood pulp fiber composite nonwoven membrane are given in Figure 3. The micrographs of the wood pulp fiber side and polypropylene fibres side of the polypropylene wood pulp fiber composite nonwoven fabric samples were scanned. The diameter of polypropylene fibres was observed at 10 μ m, which was much lesser than that of the wood pulp fiber (35 µm). In these composites, oil-water separation was observed in the range of 50%-75%. Figure 4 depicts a simple design used for polypropylene membranes for oil-water separation.

The oil-water contact interface was found to be affected by the polypropylenewood pulp fiber nonwoven membrane was found depending upon the nature and diameter of fibers used in the composites. The membranes revealed high efficiency towards oily wastewater purification.

Polysulfone-based sustainable membranes have been found effective for waste water treatment [41–43]. Huang et al. [44] designed the thin film nanocomposite membrane using polysulfone with cellulose nanocrystals and piperazine through

interfacial polymerization technique (**Figure 5**). These membranes have sufficient hydrophilic surfaces with optimum water permeation flux pf about 10 $\text{L}\cdot\text{m7}^{-2}\cdot\text{h}^{-1}$. High salt rejection was observed in the range of 96%–99% for MgSO₄, Na₂SO₄, and related salts. Thus, the nanocomposite membranes have been active water desalination and refinement effects.



Figure 2. (a) schematic of the gravity-driven oil-water separation; **(b)** lab made oilwater separation device; **(c)** gravity-driven oil-water separation experiments as a function of time. In the experiment, kerosene was stained with Oil Red O, whereas water was stained blue with industrial water-based pigment [40]. Reproduced with permission from ACS.



Figure 3. (a) scanning electron microscopy (SEM) image of the wood pulp fibres side of polypropylene-wood pulp fiber composite nonwoven fabric (PWNF); (b) SEM image of the polypropylene fibres side of PWNF. The green arrow indicates the intertwined structure; (c) SEM image of a single ribbon of a wood pulp fibre; (d) SEM image of a single cylindrical polypropylene fibre [40]. Reproduced with permission from ACS.



Figure 4. Polypropylene membrane for oil water separation [40]. Reproduced with permission from ACS.



Figure 5. Sustainable thin film polysulfone (PSf) nanocomposite membranes with cellulose nanocrystals (CNC) and piperazine (PIP) [44]. Reproduced with permission from ACS.

Polyamide matrices have been employed for sustainable water purification membranes [45–47]. Polyamide membranes have been explored for durability, facile processing, superior water flux, and salt rejection as well as pollutant removal characteristics. Zhao et al. [48] fabricated the polyamide-derived water purification membranes using tannic acid functional carbon nanotube and silver nanoparticles. The interfacial polymerization method was used for the fabrication of reverse osmosis membranes (**Figure 6**). In these membranes, hydrogen binding and π - π stacking interactions were perceived between the matrix nanofiller. The polyamide nanocomposite membranes have high water permeability of about 5 L m⁻² h⁻¹ bar⁻¹ and NaCl salt rejection of 50%–99%. These membranes have fine antibacterial effects due to silver nanoparticles and also the bio-fouling effects.



Figure 6. Schematic of tannic acid functionalized carbon nanotubes embedded with silver nanoparticle membranes for water purification [48]. Reproduced with permission from ACS.

3. Environmental impact assessment of sustainable water purification membranes

After membrane filtration processes for waste water, environmental impact assessments need to be analysed at the end-of-life management [49–51]. Here, environmental and sustainability demands need the treatment of large amounts of wastes from water pollution. **Figure 7** shows waste management opportunities in a hierarchal order. Specifically, the parameters regarding reverse osmosis membranes have been focused.



Figure 7. (**A**) waste management hierarchy from most to least preferred options; (**B**) composition of a typical reverse osmosis (RO) membrane element [52]. Reproduced with permission from Elsevier.



Figure 8. Membrane life cycle [53]. Reproduced with permission from Elsevier.

In majority of practices, solid wastes are used to be disposed in landfills. Sustainable strategies need to be applied to dispose the water wastes. Safe management approaches must be adopted on priorities to meet the sustainable environmental needs [52]. The components of reverse osmosis membranes after recycling have been extracted and recycled through chemical or mechanical recycling processes. Lawler et al. [53] studied a normal membrane lifecycle leading from raw material extraction to end-of-life possibilities (**Figure 8**). Furthermore, greenhouse gas emissions resulting from disposal reverse osmosis membranes have been portrayed (**Figure 9**). Membrane processes as well as transportation contribute towards the gaseous and disposes emissions to environment. The entire membrane model can be seen as raw material extraction, synthesis or engineering, packaging, and delivery or transport processes. Major impacts of membrane disposition and recycling have been

assessed on climate changes and fossil fuel deletions. All the recycling emissions have affected the environmental sustainability scenarios.



Figure 9. (**A**) greenhouse gas emissions and resource depletion for the disposal of one reverse osmosis (RO) membrane element. Results are displayed in terms of relative offset of membrane production; (**B**) contribution of transportation and process to the climate change emissions of the different scenarios [52]. Reproduced with permission from Elsevier.

4. Sustainable membrane recycling

Polymers especially the petroleum derived polymers have been recycled using efficient techniques such as mechanical recycling, chemical recycling, and thermal recycling [54–56]. Soundness of membrane recyclability processes depends upon the membrane material used for water purification [57–59]. Most widely used process is mechanical recycling including physical grounding of plastics or membranes and contaminant separation based on particle sizes [60–62]. The mechanically recycled material can be used for producing new desired products [63]. The economic viability of the mechanical recycling process has been found important to consider in addition to environmental safety [64,65]. Polymers like polypropylene, polyamide, and polysulfone are chemically resistant and may need toxic solvents for degradation, therefore mechanical recycling is preferred for these membranes [66–68]. Similarly, polyester can be better recycled using the mechanical processes [69]. The recycled membrane materials have been studied for maintained physical properties to be further employed for technical uses [70].

Second important recycling method used is chemical recycling of the membrane materials [71–73]. This technique involves the degradation or depolymerisation of membranes into valuable raw materials for petrochemical uses. The plastic material is usually degraded to small molecules or chains which can be easily recycled or used. Polyesters based membranes have been degraded easily through the chemical route via polycondensation reaction [74]. However, using chemical recycling on the contaminated materials may result into the production of ecologically hazardous products [75]. Consequently, materials need to be pre-treated before the chemical recycling.

Another important recycling process used is thermal recycling of the membrane materials [76]. Thermal recycling may involve the pyrolysis in the absence of oxygen and through gasification processes [77]. This method has been found safe depending

upon the nature of material recycled. Here, gasification typically includes the simple waste residue treatments with less toxic emissions. Mixed plastic wastes based on recyclable green polymers can be easily processed using thermal method. Hence, different water purification polymeric membranes can be easily recycled to attain sustainable processing [78–80].

5. Future and conclusions

Design and essential properties of water permeation membranes have been scrutinized in this article. After developing the sustainable water purification membranes, permeability, desalination, salt removal, dye elimination, toxic ion removal, and antibacterial effects have been studied. The microstructure, water flux, and flow rate of the membranes have been considered important for pollutant removal. Moreover, major functional demands of water purification membranes include durability and strength while filtration. According to the modern global sustainability and environmental demands of waste water treatment, recyclable and degradable membrane materials have been focused. Various sustainable membrane designs with polymers based on polyesters, polyamides, and other green polymers and efficient techniques (micro-, nano-, ultra-, reverse osmosis, etc.) have been considered. Appropriate membrane fabrication process may lead to well defined membrane structure and optimum membrane properties. Subsequently, smooth molecular transportation, superior flux, and barrier features were observed for membranes. After designing and successful use, recycling of polymeric membranes through appropriate processes has been found desirable. Here, according to the material type, heat, mechanical, or chemical routes have been applied for degrading the membrane material. The choice of membrane material as well as recycling process have been found challenging. The detailed overall life cycle assessments of the membranes must be carried out to resolve the sustainability and environmental challenges in this field.

Hence, current and future research on water purification membranes must focus on various parameters like the (i) development of efficient ecofriendly ultrafiltration, reverse osmosis, nanofiltration, and microfiltration processes; (ii) sustainable membrane manufacturing; (iii) choice of sustainable polymers like polyesters, polyamide, polysulfone, and others; (iv) choice of non-toxic solvent; (v) impact of membrane processes on the desalination or other filtration processes; (vi) recycling through mechanical, chemical, or thermal processes; (vii) use of life cycle assessment tool; and (viii) environmental impact of using sustainable water purification membranes.

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