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REVIEW ARTICLE

A review study of the structure, properties and general application of poly(methyl methacrylate)

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ABSTRACT

Poly(methyl methacrylate) (PMMA) is a versatile and widely used polymer that has gained significant attention in various industries due to its unique combination of properties and ease of processing. PMMA, also known as acrylic or plexiglass, is a transparent thermoplastic with exceptional optical clarity, high-impact resistance, and excellent weatherability. This scholarly article endeavors to offer an exhaustive examination of the composition, characteristics, and broad utilization of poly(methyl methacrylate) (PMMA). This study aims to conduct an in-depth analysis of the molecular composition and chemical attributes inherent to PMMA. Furthermore, it intends to examine the mechanical and physical attributes exhibited by PMMA meticulously. Additionally, an exploration of varied methodologies employed in the processing and fabrication of PMMA will be undertaken. The extensive array of applications of PMMA spanning multiple industries will be underscored, followed by a comprehensive discourse on its merits, constraints, contemporary advancements, and prospective avenues. Understanding the properties and applications of PMMA is crucial for engineers, scientists, and professionals working in fields such as automotive, aerospace, medical, and signage, where PMMA finds extensive use.

Keywords: Poly(methyl methacrylate); Structure; Properties; Application; Polymer

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1. Introduction

1.1 Poly(methyl methacrylate) (PMMA)

The discovery of poly(methyl methacrylate) (PMMA) was attributed to two British chemists, both Rowland Hill and John Crawford, in the 1930s. However, its maiden implementation was in 1934 by German chemist Otto Rohm[1]. PMMA, commonly referred to as acrylic resin, is typically produced through the radical polymerization of methyl methacrylate (MMA), although anionic and coordination polymerization methods are also viable alternatives. PMMA is a transparent thermoplastic material that exhibits desirable properties such as impact resistance, weather resistance, and chemical resistance. It is often utilized as a substitute for inorganic glass due to its optical clarity and durability[2]. PMMA is recognized for its exceptional optical properties, rendering it an excellent polymer for optical applications. It exhibits a remarkable visible light transmittance of 92%, surpassing that of glass. Additionally, PMMA possesses the ability to withstand ultraviolet (UV) radiation and harsh outdoor conditions, making it an ideal glass substitute (see **Figure 1**). PMMA further demonstrates advantageous attributes as a low-cost, non-toxic, environmentally friendly, recyclable, and highly biocompatible polymer. These remarkable characteristics have propelled PMMA's extensive utilization in diverse fields such as aviation, construction, automotive, advertising, medicine, and the electronics industry[3]. High tensile strength and roughness, high resistance to chemicals, and low-cost production as a result of its properties [R6]. PMMA, also known as plexi-glass or acrylic glass, is a polymer whose monomer structures are demonstrated in **Figures 1** and **2**, respectively[4,5].

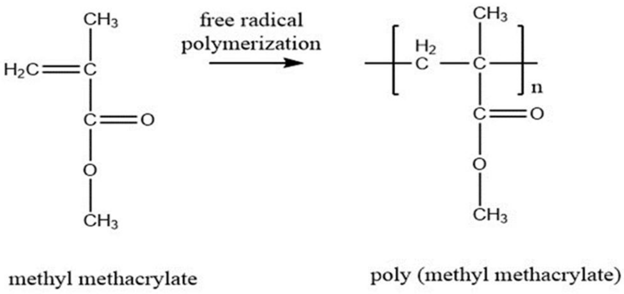

Figure 1. The chemical structures of PMMA and its monomer MMA.

Figure 2. PMMA crystalline fashion.

1.2 Distinct structural forms of PMMA: Isotactic, syndiotactic, and atactic

In an academic context, polymer tacticity refers to the spatial arrangement of neighboring chiral centers within a polymer, with particular emphasis on vinyl polymers. The physical characteristics and properties of a polymer are significantly influenced by the composition of its monomer and its overall molecular structure[6]. The isotactic state occurs upon the addition of adjacent monomer groups in a meso diad mode, with the ester groups located on the successive asymmetrical carbons on the same side of the polymeric chain[7]. In contrast, the syndiotactic state occurs when the addition of the monomer groups is in a racemic diad mode and the ester groups on successive asymmetric carbons are projected in a regular alternation method on both sides of the plane of a polymeric chain. Similarly, the atactic state represents another racemic diad mode, but it differs in the distribution of the ester groups located on the successive asymmetrical carbons, which are showcased in a random method on either of the plane sides of a polymeric chain, as illustrated in **Figure 3**[8,9].

Through the employment of radical polymerization (control/living), anionic polymerization, and reversible addition-fragmentation chain transfer techniques, PMMA can be synthesized in its pure form, exhibiting isotactic, syndiotactic, and atactic configurations, contingent upon the specific initiator, monomer feed, and solvent utilized[8,10].

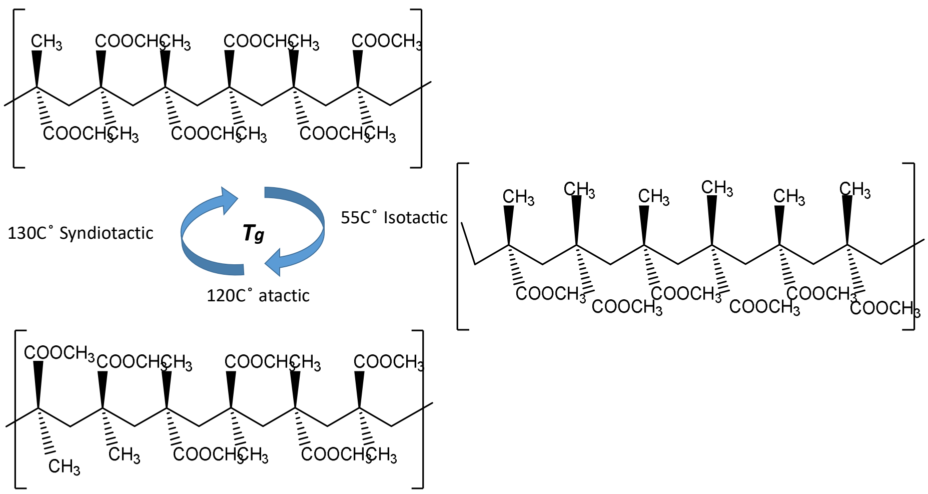

Figure 3. The different tacticities of PMMA[11].

1.3 Lifetime and degradation science: Applicability to polymers

In the pursuit of understanding the degradation mechanisms arising from weathering of PMMA, data-driven techniques from the interdisciplinary area of data science were employed. Specifically, Lifetime and Degradation Science (L & DS) were utilized, employing a stressor, mechanism, and response framework, to quantify the correlation between environmental stresses and the resulting degradation accumulation caused by distinct degradation mechanisms during the weathering process (**Figure 4**). The weathering data encompassed the monitoring of physical and chemical alterations in PMMA under varying exposure conditions, such as irradiation, temperature, and moisture. To gauge the physical and chemical degradation of PMMA, non-destructive measurements like Fourier-transform infrared spectroscopy (FTIR), colorimetry, and UV-Vis spectroscopy were employed[11].

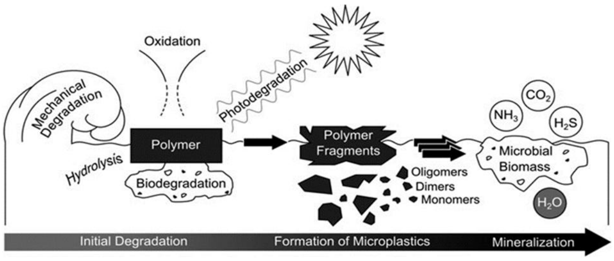

Figure 4. weathering process.

Depolymerization reaction of PAAM

The transformative procedure of depolymerization involves disassembling a polymer into constituent monomers or smaller molecular units[12]. The depolymerization phenomenon concerning PMMA holds considerable research interest, primarily due to its extensive spectrum of industrial applications and the potential it harbors for chemical recycling endeavors[13]. PMMA embodies a polymer characterized by an aliphatic foundational structure, contributing to its robust chemical and thermal stability[14]. The deliberate disintegration of PMMA can be instigated through thermal or chemical methodologies[13].

Thermal pathways for PMMA depolymerization encompass diverse postulations[15]. One articulated mechanism, as proposed by Kashiwagi *et al*.[16], involves cleavages occurring within the principal PMMA chain. Another theoretical framework put forth by Manring contemplates homolytic cleavages of adjoining methoxycarbonyl groups nestled within the PMMA structure[17]. Notably, the rate constants and activation energies associated with the thermal deterioration of PMMA exhibit variance, thereby engendering distinctions in the effectiveness of the depolymerization process[18].

Nonetheless, consensus aligns with the notion that PMMA's thermal decomposition transpires via a biphasic sequence[19]. In the primary stage, there emerges a stochastic degradation of polymer chains, culminating in the generation of diminutive fragments[12]. Subsequently, the secondary stage heralds depolymerization, wherein both the initial chains and the fragments undergo rupture, culminating in the formation of monomers[12]. The trajectory of PMMA's depolymerization is intrinsically molded by an amalgamation of factors, encompassing temperature, bond cleavage proclivities, and the presence of inhibitory agents[19].

1.4 Applications of PMMA

PMMA found its initial significant application during World War II, where it was employed as aircraft windows and bubble canopies for gun turrets[20]. The suitability of PMMA for these applications hinged on achieving the appropriate weight, composition, and thickness tailored to its intended purposes. Some other studies highlight the essential characteristics of PMMA, with the representative values corresponding to new and unexposed material. Furthermore, **Figure 5** illustrates the various applications contributing to the global demand for PMMA[21,22].

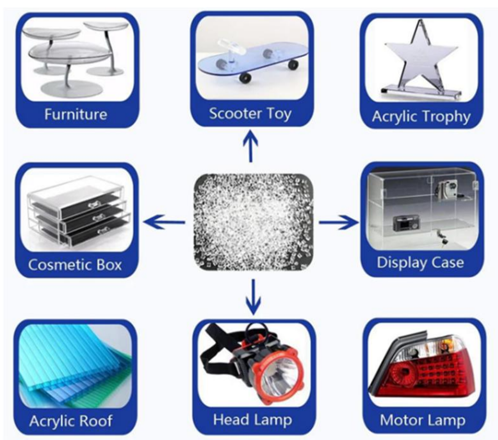

Figure 5. Some application of glass replacement.

Figure 6 shows the applications for global PMMA demand.

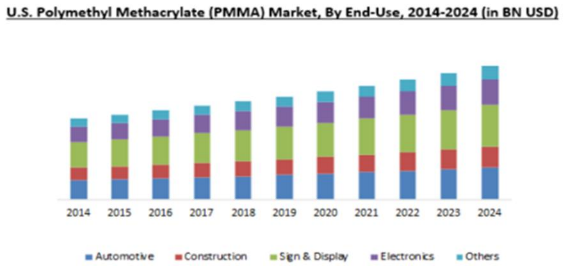

Figure 6. Applications for global PMMA demand since 2014–2024.

1.4.1 Applications of solar technology

In the quest for developing a quasi-solid-state dye-sensitized solar cell (DSSC) with a high-conductivity polymer gel electrolyte, the selection of a suitable polymeric material as a host matrix within the composite was crucial[23]. Consequently, PMMA emerged as a favorable and compatible choice for this application[24]. This selection was attributed to PMMA's advantageous mechanical strength, compatibility, and optical clarity properties[23]. Recently, Shen *et al*.[22] presented a pioneering study reporting the hydrothermal synthesis of europium ion (Eu+3)-doped sodium gadolinium fluoride ($NaGdF_4$: Eu) nanocrystals (NCs). For the first time, a down-conversion (DC) layer comprising PMMA doped with luminescent $NaGdF_4$: Eu was prepared and affixed to the rear of TiO_2 anodes to enhance the efficiency of dye-sensitized solar cells (DSSCs)[23]. The evaluation of the impact of doped and undoped $NaGdF_4$ nanocrystal layers on the photovoltaic device, with incident-photon-to-current efficiency (IPCE) as the parameter of comparison, revealed that the DSSC incorporating a doped $NaGdF_4$: Eu DC-PMMA layer exhibited an improved photoelectric conversion efficiency by 4.5%[23]. In another study, Yan *et al*.[25] conducted successful preparations of a polymer gel electrolyte employing a blend of PMMA, ethylene carbonate, 1,2-propanediol carbonate, dimethyl carbonate, and sodium iodide/iodine as the source of I-/I-3[26]. This specific polymer electrolyte, denoted as PMMA-EC/PC/DMC-NaI/I2, exhibited a remarkable ionic conductivity of 6.89 mS cm^{-1}. The researchers further utilized this high-conductivity electrolyte to fabricate a quasi-solid-state dye-sensitized solar cell (DSSC), which displayed impressive long-term stability and achieved a notable light-to-electrical energy conversion efficiency of 4.78%[27]. Moreover, Hammam *et al*.[24] fabricated a fluorescent PMMA film incorporating a commercial coumarin dyestuff (MACROLEX Fluorescent Red G) via a flow-spin coating technique. The dye concentration within the film was adjusted to achieve the maximum intensity, and its emission characteristics were optimized to align with the absorption bands of chlorophyll (650–680 nm) for greenhouse applications[28]. Remarkably weather-resistant, this fluorescent film proves suitable for deployment in growing rooms dedicated to commercial plant cultivation[29].

1.4.2 Applications in optics

Optical science plays a vital role across various disciplines, including engineering, medicine, pure science, and astronomy[29]. Its practical applications encompass a wide range of technologies, such as lenses, microscopes, lasers, fibers, and polymers[30]. In particular, the optical activity of materials is an outcome observed when they interact with light, and this activity can be quantified through the refractive index[31].

In the case of PMMA, its optical applications are primarily attributed to its favorable refractive index, excellent resistance to UV light, chemical durability, and commendable mechanical properties[32]. Moreover, organic polymers offer advantages like cost-effectiveness, lightweight nature, and ease of processing, rendering them well-suited for immobilizing semiconductors in heterogeneous photocatalytic applications[33].

Recently, Camara *et al*.[34] conducted an investigation involving eleven synthetic polymers capable of being coated with TiO_2. These coated polymers were exposed to solar radiation for 150 days, both with and without the TiO_2 layer, to study the weathering effects[28]. Such studies contribute to a better understanding of how polymers respond to environmental exposure and play a crucial role in advancing practical applications and innovations in the field of optical materials[31].

Upon careful observation, it was found that among the studied materials, only PMMA exhibited excellent retention of both the optical and mechanical properties of titania after undergoing natural weathering[32]. Consequently, PMMA emerges as the most promising candidate for effectively immobilizing TiO_2 in applications related to photocatalytic treatment[33].

1.4.3 Application in dentistry

Thermoplastic resins have a long-standing history of utilization in dentistry, characterized by their ability to undergo multiple cycles of softening through heating and hardening via cooling without undergoing chemical alterations[35]. These resins consist of polymer chains, composed of diverse lengths and molecular weights, organized into bundles. Four broad classifications of thermoplastic resins include thermoplastic acetal, thermoplastic polycarbonates, thermoplastic acrylic, and thermoplastic nylon[36].

In particular, thermoplastic acetal exists in both homo-polymer and copolymer forms, with the latter exhibiting superior long-term stability compared to its homopolymer counterpart[37]. Its resistance to occlusal wear makes it highly suitable for preserving the vertical dimension during provisional restorative therapy[37]. However, when compared to thermoplastic acrylic and polycarbonate, thermoplastic acetal lacks the natural translucency and vitality, making it more suitable for short-term temporary restorations[38].

Thermoplastic polycarbonates, composed of bisphenol-A carbonate polymer chains, find ideal applications in provisional crowns and bridges, yet are not well-suited for partial denture frameworks[39]. However, dentists have long been using thermoplastic acrylic, which is shown in **Figure 7**, for temporary crowns and as a base plate material for partial and complete dentures[39]. Nevertheless, thermally polymerized PMMA does exhibit certain drawbacks, such as high porosity, water absorption, volumetric changes, and residual monomer[40].

Figure 7. Temporary crowns.

Due to their limited impact resistance, tensile strength, and flexural strength in various applications, the use of traditional thermoplastic resins faces challenges[41]. Consequently, for specific circumstances that demand enhanced flexibility, improved resistance to flexural fatigue, and superior impact strength, the adoption of improvised thermoplastic nylon can present a valuable alternative to polymethylmethacrylate[42].

1.4.4 Applications of the viscosity

In the realm of fluid dynamics, viscosity represents the extent of a fluid's resistance to flow when subjected to applied shear stress[43]. When considering polymeric melts or solutions, they exhibit non-Newtonian behavior, meaning that the shear stress is not directly proportional to the shear rate[44]. However, polymers possess an intrinsic viscosity, serving as an indicator of their capacity to enhance the viscosity of another fluid[45]. As a result, a high-molecular-weight polymer can effectively modify or influence the viscosity of low molecular weight polymers. PMMA, due to its compatibility and ease of processing, proves valuable for developing viscosifier copolymers in conjunction with natural polymers[46].

In a study conducted by Mishra and Sen, the grafting of PMMA onto guar gum was accomplished using a microwave-initiated method. The investigation focused on the correlation between the percentage of grafting and the intrinsic viscosity of the resulting product. The findings demonstrated that the modified product could serve as a superior viscosifier compared to guar gum in its pristine form[47].

1.4.5 Nanotechnology applications

The interplay between polymers and nanomaterials has revolutionized the field of nanotechnology, leading to the development of polymer nanocomposites[48]. These composites exhibit significant enhancements in material properties despite incorporating only minute amounts of nanoparticles. The improvements encompass a wide range of characteristics, including mechanical strength, solubility, electrical conductivity, optical properties, scratch resistance, thermal stability, and flame retardation, among others. The extensive application potential of nanocomposites in nanotechnology has attracted considerable research attention towards their fabrication and diverse applications[49].

Perween *et al.*[31] explored the utilization of

PMMA and graphite in the production of plastic chip electrodes (PCEs) using a straightforward solution casting technique. The resulting electrodes were cost-effective, versatile, and dispensable for various applications. Microscopy (SEM and AFM), thermal properties (TGA), and mechanical and electrical analyses were conducted to characterize the fabricated electrode.

In a novel approach for preparing nanocomposites involving nanoparticles, the combination of covalent and noncovalent interactions was found to be highly beneficial. Wang *et al*.[32] investigated the effect of SiO_2 nanoparticles on SiO_2/PMMA composites. The fabrication involved a two-step process: noncovalent modification of SiO_2 nanoparticles with tetraoctylammonium bromide to facilitate their dispersion in the solvent, and covalent process through radical suspension polymerization with MMA monomer, leading to the formation of silicon oxide/PMMA nanocomposite. This method aimed at enhancing the mechanical properties of PMMA for broader applications. The study revealed remarkable improvements in tensile strength and flexural strength, with enhancements of up to 80.6% and 127.3% compared to pure PMMA, respectively.

Surface functionalization of nanoparticles through polymer grafting holds significant importance in the design of both organic and inorganic nanocomposites. Atom Transfer Radical Polymerization (ATRP) has emerged as a leading method due to its superior control over molecular weight and low polydispersity. The surface-initiated ATRP technique is widely adopted for grafting homopolymers, diblock copolymers, graft copolymers, star polymers, and branched polymers from various nanoparticles, such as nanotubes, nanowires, and nanoclays[26]. PMMA has been successfully grafted into carbon nanotubes (CNTs) to improve the solubility and processability of CNTs. This is significant considering the exceptionally low density, mechanical, electrical, and thermal properties of CNTs, which are hindered by limited solubility due to π-π bond interactions.

1.4.6 Applying thick PMMA layers onto conductive metal substrates

Three distinct methods are available for the application of thick PMMA layers onto a conducting metal substrate: multilayer coating, casting, and sheet adhesion. Among these, casting and commercial sheet adhesion are the most frequently employed techniques[50].

1.4.7 Application of PMMA in the construction of microanalytical separation apparatus

PMMA possesses several advantageous characteristics that render it a suitable substrate for the fabrication of microanalytical separation devices. Its ease of machinability using various methods, such as laser ablation, injection molding, imprinting, and hot embossing, allows for efficient device production. Additionally, molds produced through the LIGA process, which is a German acronym for lithography, electroplating, and moulding (Lithographie, Galvanik und Abformung), have been effectively employed to create PMMA microanalytical separation devices. The material's optical properties enable analyte detection using fluorescence and visible spectroscopies[46].

Furthermore, PMMA demonstrates the ability to withstand high electric fields and effectively dissipate heat, making it a desirable choice for applications in the microanalytical separation device industry. With a glass transition temperature (Tg) of –100 °C in commercially available PMMA sheets, microdevices fabricated from PMMA can be thermally sealed using a PMMA top plate via thermal bonding procedures. Notably, PMMA exhibits solubility in various organic solvents while remaining insoluble in polar solvents like water and alcohols, which are commonly employed in conventional CE and CEC solvent systems. Likewise, it remains insoluble in nonpolar solvents such as hexanes and cyclohexane[42,43].

1.4.8 PMMA as a significant resist material in microelectronic applications

PMMA has garnered considerable significance as a pivotal resist material within the realm of microelectronic applications. Its prominence arises from its capability to form ultra-thin, coherent films and its susceptibility to etching processes in lithographic operations due to its notable depolymerization proficiency[28–35]. Notably, PMMA demonstrates a distinct characteristic in facilitating controlled solvent mobility over its polymeric matrices, owing to the facile manipulability of its dissolution kinetics. This attribute has enabled the achievement of highly defined edges with desired slopes in the imagery of the resist material when employing a PMMA matrix[28,36]. The rate of PMMA dissolution during photoresist development is notably contingent upon parameters such as molecular weight and molecular weight distribution, both of which significantly impact the fabrication of diverse optical elements[45]. Consequently, PMMA serves as a benchmark against which the efficacy of resistive materials can be measured. While numerous alternative polymers have been unveiled, many surpass PMMA in terms of sensitivity. Nonetheless, the amalgamation of attributes encompassing stability, sensitivity, contrast, adhesion, and solubility has perpetuated PMMA's preeminence[28,47–49]. Consequently, renewed interest has arisen in the innovative synthesis of PMMA. Photoresists founded on photoinduced free-radical chemistry have garnered escalating attention within the sphere of microelectronic applications[50]. Researchers have successfully used the solution casting technique to synthesize PMMA and Rhodamine-B fluorescent dye-doped PMMA[51]. The researchers meticulously recorded the UV-visible spectra of these films[52]. They then utilized the spectral data to derive various optical properties, including band gap, refractive index, and metallization criterion[52]. Notably, the investigation revealed that while the band gap generally diminishes with increasing dopant concentration, the direct band gap exhibited a gradual reduction, whereas the indirect band gap displayed an initial moderate decline that transitioned into a more pronounced reduction beyond a dopant concentration of 10 wt%[51]. This discernment underscores the potential for precise modulation of PMMA's optical characteristics through judicious doping with Rhodamine B dye[53].

1.5 Further positive sides of PMMA

The commendable attributes of poly(methyl methacrylate) (PMMA) find significant relevance within diverse academic and industrial spheres, substantiated by empirical evidence:

1) Exceptional Transparency: PMMA's exceptional transparency, allowing the transmission of up to 92% of visible light, is well documented[54]. This unique property positions PMMA as a preferred choice for applications necessitating unimpeded clarity and visibility, such as optical lenses, display panels, and windows[54].
2) Resilience to Weather Elements: PMMA's remarkable resistance to UV radiation is extensively recognized[55]. This characteristic endows PMMA with suitability for outdoor deployment, as it resists yellowing or degradation under prolonged sunlight exposure, thereby maintaining optical integrity over time[55].
3) Vigorous Impact Endurance: Studies affirm PMMA's superior impact resistance compared to glass[56]. This intrinsic property fosters its adoption in scenarios demanding shatterproof or impact-resistant attributes, ensuring safety in contexts predisposed to high winds or unintended collisions[57].
4) Featherweight Composition: The lightweight nature of PMMA has been acknowledged in both academic and industrial realms[58]. This feature enhances its handling ease, transportation convenience, and capacity to contribute to weight reduction in diverse structures, thereby exemplifying its pertinence in industries like automotive and aerospace[58].
5) Adaptability and Dexterity: PMMA's adaptability, facilitated shaping, and facile fabrication processes are well-documented[59]. This versatility translates into various forms, including sheets, rods, and intricate designs, thereby spanning applications in architecture, medical equipment, and consumer goods[59].
6) Chemical Endurance: Extensive research underscores PMMA's commendable chemical resistance to acids, alkalis, and solvents[60]. This property positions it favorably in settings involving chemical exposure, such as laboratory equipment and chemical storage containers[60].
7) Simplicity in Upkeep: Scholarly work corroborates the ease of maintenance of PMMA[57]. Its potential for polishing to mitigate surface imperfections and reduced susceptibility to staining compared to other materials support its longevity and cost-effectiveness[60].

The confluence of these positive attributes underscores PMMA's indispensability within a myriad of industries and applications. A dynamic equilibrium between optical performance, resilience, and adaptability substantiates PMMA's continued prominence.

2. Conclusions

In conclusion, poly(methyl methacrylate) (PMMA) is a remarkable polymer with a wide range of applications and unique properties. Its transparent nature, excellent mechanical strength, and ease of processing make it highly valuable in industries such as automotive, aerospace, medical, and signage. While PMMA offers numerous advantages, it also has certain limitations that need to be considered in specific applications. Ongoing research and development efforts continue to explore new manufacturing processes and expand the potential applications of PMMA. Further research should focus on enhancing its properties, improving its sustainability, and exploring novel applications in emerging fields. With its versatility and promising future prospects, PMMA remains an important material in the polymer industry.

Author contributions

Conceptualization, SS and EY; methodology, SS; software, SS; validation, SS, EY and KZ; formal analysis, SS; investigation, SS; resources, SS; data curation, EY; writing—original draft preparation, SS and KZ; writing—review and editing, KZ; visualization, EY and KZ; supervision, EY; project administration, SS and EY. All authors have read and agreed to the published version of the manuscript.

Conflict of interest

The authors declare no conflict of interest.

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