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ORIGINAL RESEARCH ARTICLE

Water vapor permeability of smooth cellulose nanofiber film prepared via spraying

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ABSTRACT

Eco-friendly and greener barrier materials are required to replace the synthetic packaging materials as they produce a threat to environment. These can be fabricated by natural polymers such as cellulose nanofiber (CNF). The sustainability of CNF was so amazing due to its potential for circular economy and provides alternative platform for synthetic plastics. The challenging task to fabricate CNF films still existed and also current methods have various limitations. CNF films have good oxygen permeability and the value was lower than synthetic plastics. However, CNF films have poor water vapour permeability and higher than that of synthetic plastics. The fabrication method is one of strong parameters to impact on the water permeability of CNF films. The deposition of CNF suspension on the stainless-steel plate via spraying, is a potential process for fabrication for CNF films acting as barrier material against water vapour. In spraying process, the time required to form CNF films in diameter of 15.9 cm was less than 1 min and it is independent of CNF content in the suspension. The uniqueness of CNF films via the spraying process was their surfaces, such as rough surface exposed to air and smooth surface exposed to stainless steel. Their surfaces were investigated by SEM, AFM and optical profilometry micrographs, confirming that the smooth surface was evaluated notable lower surface roughness. The spray coated surface was smooth and glossy and its impact on the water vapor permeability remains obscure. The spraying process is a flexible process to tailor the basis weight and thickness of CNF films can be adjusted by the spraying of CNF suspension with varying fibre content. The water vapour permeability of CNF films can be tailored via varying density of CNF films. The plot between water vapour transfer rate (WVTR)/water vapour and density of CNF films has been investigated. The WVP of spray coated CNF films varied from 6.99 ± 1.17 × 10^{-11} to 4.19 ± 1.45 × 10^{-11} g/m.s.Pa. with the density from 664 Kg/m^3 to 1,412.08 Kg/m^3. The WVP of CNF films achieved with 2 wt% CNF films (1,120 Kg/m^3) was 3.91 × 10^{-11} g/m.s.Pa. These values were comparable with the WVP of synthetic plastics. Given this correspondence, CNF films via spraying have a good barrier against water vapour. This process is a potential for scale up and commercialization of CNF films as barrier materials.

Keywords: Cellulose Nanofiber (CNF); Spray Coating; Water Vapour Permeability; Water Vapour Transfer Rate (WVTR); Synthetic Plastics

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1. Introduction

Cellulose nanofiber (CNF) is a type of nanomaterial derived from natural cellulose fibres, which is the main component of plant cell walls. The notable properties of CNF are high mechanical strength, high surface area, biodegradability, and biocompatibility[1]. There are several types of nanocellulose, including cellulose nanocrystals

(CNCs), cellulose nanofibrils (CNFs), and bacterial cellulose (BC)[2]. CNCs were produced from acid hydrolysis of cellulose fibres and are typically rod-shaped with dimensions on the order of 5–20 nm in diameter and several hundred nanometres in length[2]. CNFs were also produced by mechanical processing of cellulose fibres from the wood pulp and non woody pulp and the size of CNF typically has widths ranging from 5 to 50 nm and lengths ranging from several microns to several millimeters. Bacterial cellulose is produced by bacteria and has similar properties to plant-derived cellulose, but with higher purity and consistency[3].

Cellulose nanofiber (CNF) is a sustainable fibrous nanomaterial used as feed stock for the fabrication of free-standing films and composite with various nano-inorganic materials. Past decade, CNF was getting improved attention to play as alternative for synthetic plastics in packaging application. CNF has a good potential for recyclability and biodegradability. CNF was produced by the fibrillation of cellulose pulps from lignocellulosic biomass through mechanical process such as homogenization, chemical process such as Acid Hydrolysis and TEMPO and enzymatic process. CNF has low density and toxicity and provides a platform for sustainability and circular economy. The film prepared from cellulose nanofibrils has translucency and good strength[3]. CNF films were reported as a good barrier against oxygen, however poor barrier against water vapour. The challenge in this area is to bring the value of water vapour permeability (WVP) of free-standing CNF films near to synthetic plastics. The fabrication of CNF films is one of the strong parameters controlling the water vapour barrier performance of the film[2].

The reported fabrication methods for CNF films were solvent casting, hot pressing, Roll to Roll (R2R) coating, vacuum filtration and spray coating[3]. Vacuum filtration is the most common process for fabricating CNF films. In this method, the filtration time to form CNF films exponentially increased with CNF suspension consistency. The time for forming CNF films on the filter mesh consumes 10 min[4] to 4 h[3]. The filter marks were appeared on CNF films when the film was peeled from the filter mesh. These marks affect the uniformity of the film indirectly effects on the barrier properties and mechanical properties of CNF films. Solvent casting is a laboratory scale method to fabricate CNF films for various applications. However, the evaporation of water from CNF suspension consumes time more than a day to form the film on the Petri dish. The limitation of cast CNF films consists of shrinkages which affects the uniformity and various properties of CNF films. This method has time constraint and not fit for scale up for commercialization via large scale production[3].

Recently, spraying CNF suspension on the polished metal surface is a novel process for fabrication of free-standing CNF films[5,6]. In the spraying process, CNF suspension was deposited on the stainless-steel plate via spray coating and then allowed to dry in standard laboratory conditions. Dried CNF films were smoothly and easily peeled from the stainless-steel plate. In the case of fabricating CNF films via spraying, the thickness and basis weight of CNF films can be tailored via spraying CNF suspension with various fibre content. The operation time for spraying CNF suspension was independent of their solid content. The spraying process was rapid in the formation of wet CNF films[6]. The mechanical and barrier properties of the film can be tailored via spraying various concentration of CNF on the stainless-steel plate[2].

Even though the film made from CNF has a good barrier against oxygen and also incomparable with synthetic plastics[7]. CNF films have poor barrier properties against water vapour due to high affinity between cellulose nanofibrils and water molecules. CNF is a highly hydrophilic polymer and capable for susceptible to water molecules. But CNF is much better than nominal cellulose fibres such as paper and paper board substrates in terms of water vapour permeability[3]. This is why cellulose nanofiber was used as high-performance barrier material as it forms a compact network/mesh of cellulose nanofibrils to free standing CNF films[6]. Apart from this, CNF films have very minute pores and complex tortuous pathway for water vapour and air than that of normal cellulose substrates[1,8].

It was noticed that the fabrication methods also control the WVP of CNF films and other barrier properties of CNF films, such as air permeance and oxygen permeability[3]. Having spraying process for scale up potential, the WVP of spray coated CNF films should be investigated and their water vapour transfer mechanism across CNF films should be investigated. This paper deals the effect of CNF films density on the water vapour transfer rate and the water vapour permeability of CNF films and the WVP of CNF films was compared with CNF films from synthetic plastics.

2. Materials and methods

The number of terminologies for cellulose nanofiber (CNF) has been mentioned in various scientific literatures. Generally, cellulose nanofibers are also called as nano-fibrillated cellulose, cellulose nano-fibrils, micro fibrillated cellulose and nanocellulose, etc. But in this scientific study, cellulose nanofiber/nanocellulose has been reported throughout in this paper[2]. The CNF was used as a feed stock for fabrication of CNF films. The used raw CNF is KY 100S received from DIACEL Chemical Industries, Japan. The CNF content in KY100S was 25 wt.% and the mean diameter of cellulose nanofibrils in CNF was 73 nm. The aspect ratio of Raw CNF (KY100S) was investigated to be 142 ± 28 and the crystallinity index of the KY 100S was evaluated to be 78%. The SEM micrographs of the Raw CNF have been shown in **Figure 1**[6].

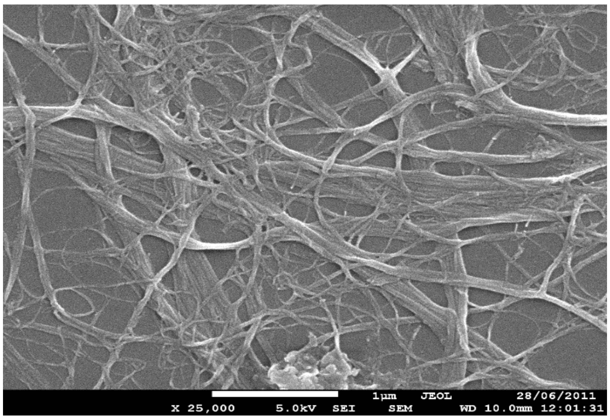


Figure 1. SEM micrograph of cellulose nanofiber (KY 100S)—Diacel Chemical Industries, Japen.

2.1 Preparation of CNF suspension for spraying

The CNF suspension was prepared with concentration varying from 1 wt.% to 2 wt.% of CNF content in the water. The raw CNF quantity of interest was added into the double distilled water and disintegrated at 15,000 RPM for 15 min to make CNF suspension of Interest. In this way, the CNF suspension from 1 wt.% to 2 wt.% was produced for spraying process.

2.2 Fabrication of CNF films via spraying

The experimental set up for spray system was shown in **Figure 2**. The CNF suspension was sprayed on the polished stainless-steel plate via the professional Wagner spray system. The process conditions for spraying process have been followed as per the reported in our previous scientific literature. There are two important parameters in the spray coating experimental system to control/tailor the thickness and basis weight of CNF films were velocity of the conveyor and CNF suspension consistency. In this study, the velocity of the conveyor was maintained a constant parameter at a velocity of 0.32 cm/sec and then CNF suspension was varied from 1 wt.% to 2 wt.% for spraying on the stainless-steel plate. The spray distance between spray tip to the circular stainless-steel plate was 30 ± 1 cm. The diameter of the orifice in spray nozzle was 0.38 mm and produces elliptical pattern and spray width of 50 cm[6].

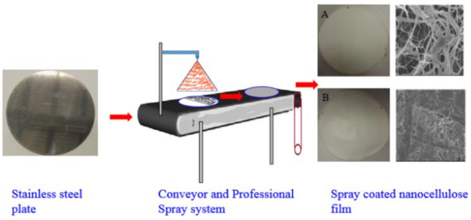


Figure 2. Experimental system for spray coating setup.

2.3 Drying of CNF films and its characterization

The wet film on the stainless-steel plate was formed and dried under standard laboratory conditions. In drying spray coated wet CNF films, the film was kept in Laminar flow chamber with constant flowrate for faster removal of water from the wet film. The dried film was easily peeled from the stainless-steel plate and subjected to the measurement of thickness and basis weight of the film. The apparent density of CNF films was evaluated from its thickness and basis weight of the film. The surface topography and morphology of spray coated CNF films was evaluated by scanning electron microscopy as per the reported procedure previously[2]. The surface roughness of CNF films was evaluated by atomic force microscopy and optical profilometry[6].

2.4 Evaluation of water vapour barrier of spray coated CNF films

The water vapour barrier of CNF films was performed as the per standard of ASTM E96/E96M-05[9]. The films/specimen size having diameter of 76 mm was used as specimen and dried in an air oven at a temperature of 105 °C for 4 h. This would help the complete removal of moisture from the specimen to evaluate water vapour permeability of the film perfectly. As per the ASTM standard, the brass cups were filled with dried anhydrous calcium chloride and then covered with CNF films as experimental cups and cups covered without $CaCl_2$ as control in the experimental study. This test was carried out at 23 °C and 50% RH and the weight of the cup was increased/measured due to the absorption of water vapour across CNF films. From the data, the water vapour transmission rate (WVTR) is the slope derived from the plot between weight of the cup and time[2,9,10].

$$WVTR = \frac{G}{t \times A}$$

where G/t refers to the slope of a straight line (g h^{-1}) and A is the surface area of the films (m^2).

The water vapour permeability of CNF films was evaluated from the WVTR normalized with thickness of CNF films.

The permeance of CNF films was found to be:

$$Permeance = \frac{WVTR}{S(R1 - R2)}$$

where S is the saturation vapor pressure per mmHg (1.333×10^2 Pa) at the tested temperature, $R1$ is the relative humidity of the source and $R2$ is the relative humidity of the vapor sink, expressed as a fraction.

Finally, the WVP of the films can be evaluated as

$$WVP = Permeance \times Thickness\ of\ CNF\ film$$

The mean of WVP from three replicates in the experiment was reported in this work. The value of WVP of CNF films was compared with the synthetic plastics to show the potential of CNF films as a good barrier against water vapour.

3. Results and discussion

Spraying nanofibers is a new concept for fabrication of film for various applications[11–13]. Nanofiber spraying has several advantages over traditional fibre production methods, including a higher surface area to volume ratio, enhanced mechanical properties, increased porosity, and improved biocompatibility[3]. Applications of nanofiber spraying include drug delivery, tissue engineering, air filtration[1,8], and energy storage such as fabrication of sustainable electrodes[13,14]. However, there are still challenges in scaling up nanofiber spraying for commercial production and optimizing the process parameters[6] for specific applications such as food packaging and barrier materials[7,10].

Spraying CNF suspension on the polished stainless-steel plate is a flexible method to fabricate CNF films with unique surfaces[6]. The spray coated CNF has two unique surfaces namely rough surface exposed to air and smooth surface exposed to the stainless-steel plate. Spraying CNF suspension on the metal surface produce the film with glossy and shiny and the smoothness of the film was replicated from the stainless-steel plate[6]. **Figure 3** shows the spray coated CNF films and shows the two surfaces of the film.

Spray coated CNF films have very compact and cellulose nanofibrous network[6]. The basis weight and the thickness of CNF films were tailored by varying CNF suspension for spraying[10]. The compactness of CNF films was achieved via the coalescence of the atomized CNF suspension from the spray jet in the spraying process. The atomized CNF suspension formed together via forming hydrogen bonds between the hydroxyl group of the cellulose nanofibrils, results in forming the compact film[3,11].

3.1 Scanning electron microscopy micrograph

Figure 4 reveals the rough and smooth surface of spray coated CNF films. The rough side of CNF films was porous and high surface roughness. The roughness of the film was high due to the distribution of various fibres. The smooth side of CNF films was glossy and shiny. The surface roughness of the film on the smooth side was very low and fibres compressed and mimics the surface smoothness of the film from stainless steel plate. However, the effect of surface roughness on the barrier performance of CNF films remains obscure[10].

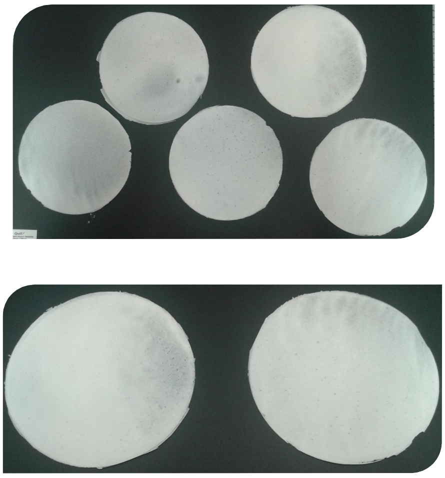
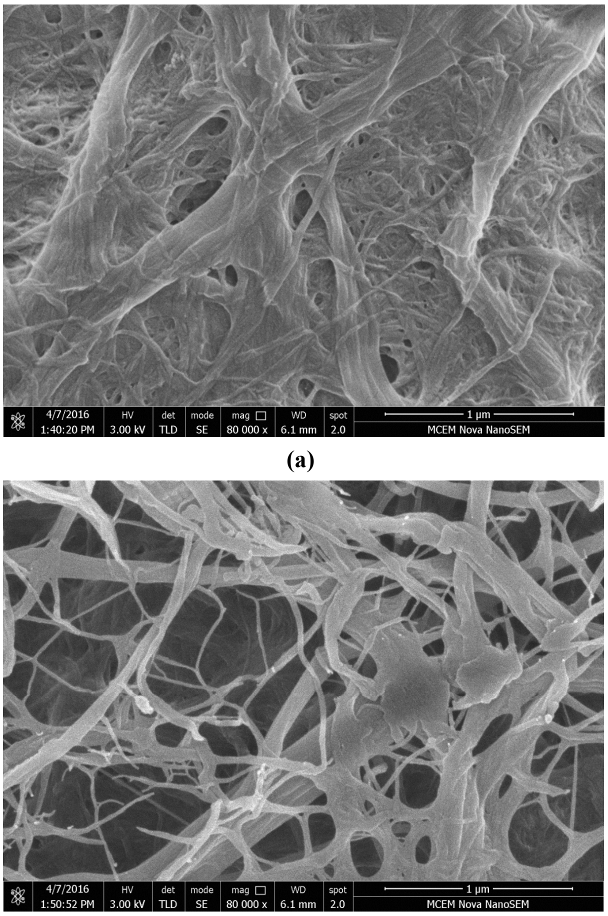


Figure 3. Spray coated CNF films.



(a)

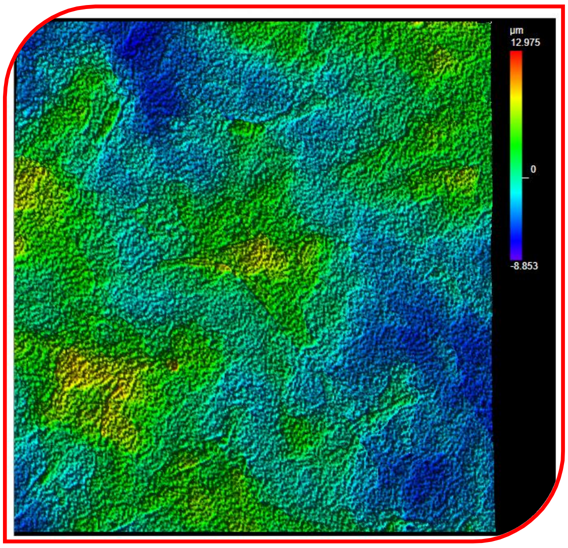
(b)

Figure 4. (a) Rough surface of spray coated CNF films' SEM micrographs. **(b)** Smooth surface of spray coated CNF films' SEM micrographs.

3.2 Optical profilometry images

Figure 5a–b reveals the optical profilometry of CNF films confirming the rough surface and smooth surface of CNF films. In this investigation, the RMS of both surfaces were evaluated. The

RMS of rough and smooth side was reported to be 2000 nm and 400 nm, respectively[6,10]. The effect of surface roughness on the rough side and surface smoothness on the smooth side of CNF films were obscure on the barrier performance against water vapour.



(a)

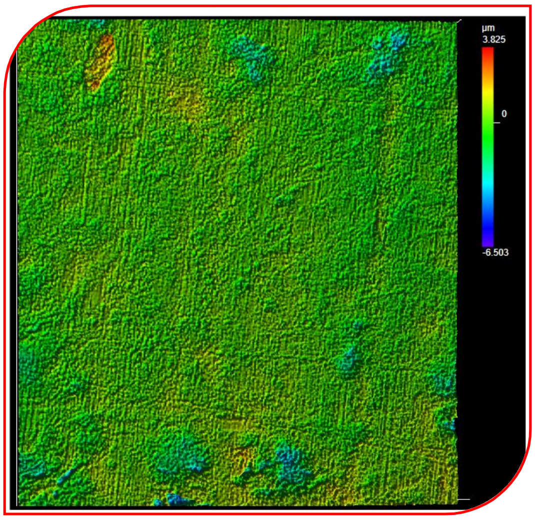
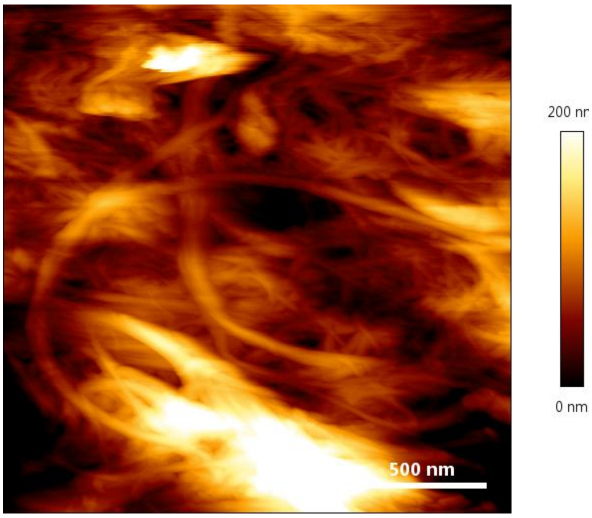


Figure 5. (a) Optical profilometry image of rough side of CNF films. **(b)** Optical profilometry image of smooth side of CNF films.

3.3 Atomic force microscopy images

AFM micrographs of CNF films confirms the surface roughness of the both surfaces at nanoscale dimension. It confirmed that the rough side of the film was very porous and high surface roughness due to various size distribution of cellulose nanofibrils. The smooth side of the film was very glossy and shiny and their surface roughness was too low. The RMS for rough surface and smooth surface was reported to be 51.4 nm and 16.7 nm[6]. See **Figure 6a–b**.



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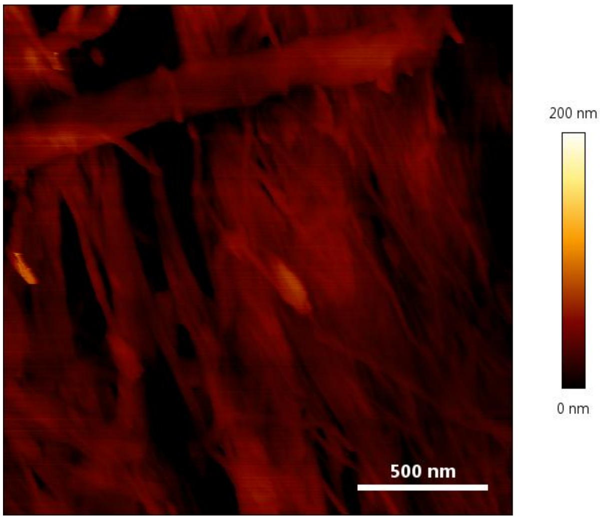

Figure 6. (a) AFM micrograph of rough side of spray coated CNF film. **(b)** AFM micrograph of smooth surface of CNF films.

3.4 Water vapour barrier performance of CNF films

Water vapour permeability (WVP) refers to the ability of a material to allow the passage of water vapour through it. This property is important in packaging, as it affects the moisture resistance of the material. The WVP of a material depends on their structure, thickness, and other factors. The performance of CNF films as water vapour barriers has been attributed to their ability to form dense, nano porous networks that impede the movement of water molecules. It has been noticed that the fabrication method for CNF films is one of the main criteria for controlling water vapour barrier performance of the films.

Figure 7 reveals the effect of film's density on the water vapour transmission rate of CNF films. The apparent density of CNF films is defined as the ratio between basis weight and thickness of CNF films[6]. The basis weight and thickness of the CNF can be tailored by varying CNF suspension concentration for spraying process to fabricate the CNF[6]. The relationship between thickness and basis weight of CNF films was linear[6]. As a result, the water transmission rate of CNF films was tailored via thickness and basis weight of the film[10]. The WVTR of CNF films was comparable with synthetic plastics. The WVTR was normalized with thickness of CNF films to give the value of WVP[2].

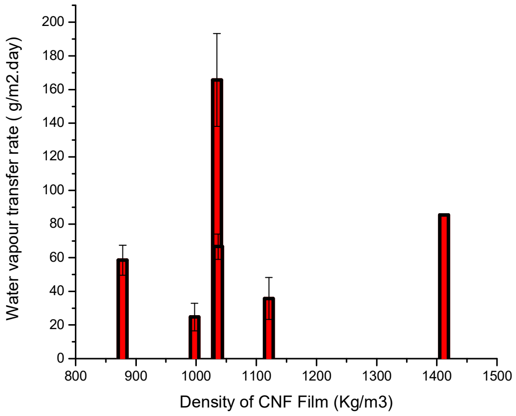

Figure 7. Effect of film's density on water vapour transfer rate.

Figure 8 shows the effect of apparent density on the WVTR of CNF films. The spraying process was carried out in two different conditions. One of the conditions from fixed CNF concentration and varied velocity of the conveyor in the experimental set up was performed[2]. The other was from the fixed velocity of the conveyor and varied CNF suspension concentration from 1 wt.% to 2 wt.% was carried out to fabricate the CNF films. This plot confirms that the lower density of CNF films gives good barrier against water vapour.

Figure 9 shows the effect of density on the water vapour permeability of CNF films. It is noted that the WVP of CNF films was comparable with synthetic plastics. The lower density of the film gives good barrier against water vapour. However, the higher density of CNF films has poor barrier performance against water vapour[2].

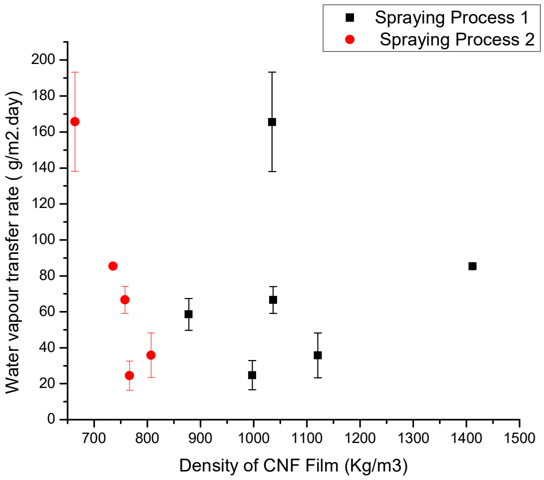

Figure 8. Effect of density on water vapour transmission rate.

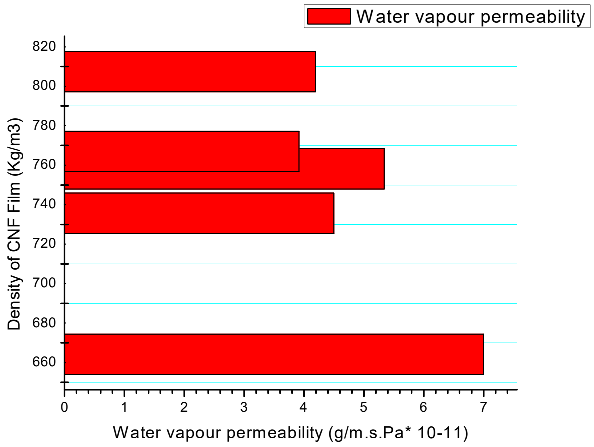

Figure 9. Effect of density on the water vapour permeability of the CNF films.

Figure 10 shows the effect of cellulose nanofibrils on the water vapour permeability. This is due to the reducing effect of cellulose nanofiber. It means that cellulose nanofibrils is a hydrophilic polymer, reduced the water vapour permeability of the film when fibre diameter reduced. When the fibre diameter of CNF is reduced, the water vapour diffusion rate was increased across the tortuous pathway in the film. CNF films with lowest fibre diameter forms rigid fibrous network which acts as a good resistance against gaseous substances including water vapour[15]. The diameter of CNF reduction was performed by the mechanical process such as high-pressure homogenization, chemical methods such as acid hydrolysis and enzymatic process[16]. The data in **Figure 10** was derived from the spraying of high pressure homogenized CNF suspension on the stainless-steel plate to fabricate CNF films which acts as high-performance barrier against water vapour[10].

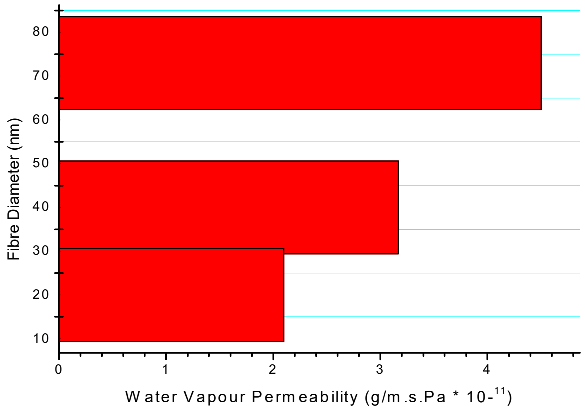

Figure 10. Effect of fibre diameter on the WVP of CNF films.

3.5 Comparison with synthetic plastics

Figure 11 reveals the potential of spray coated CNF films as a good water vapour barrier and comparable with synthetic politics. However, the thickness of packaging film also decides the barrier performance of the film against water vapour. This is why water vapour permeability was used to describe the water vapour barrier performance of the film and this value was calculated via the normalizing thickness of the film with their WVTR values. **Figure 12** shows the comparison of spray coated CNF films with synthetic plastics in terms of WVP. This plot confirms that the WVP of spray coated CNF films has comparable with synthetic plastics[17]. Apart from this advantage, CNF is an eco-friendly friendly nanomaterial that has capacity to degrade in environment[18,19].

3.6 Barrier mechanism of CNF films

Figure 13 reveals the mechanism of water vapour passage across the spray coated CNF films. The nanocellulose/CNF suspension was well mixed during the spraying process and sprayed on the stainless-steel plate[6,12]. It results in the formation of smooth CNF films[6]. It has been concluded that CNF films are an effective barrier against water vapour due to its physical and mechanical properties[17]. The barrier mechanism of CNF films can be commented as the following factors. The nanostructure of CNF films is a predominant reason for good barrier mechanism even though CNF is a hydrophilic polymer[20,21]. Generally, CNF has high aspect ratio and high surface area to volume ratio[24]. This unique nanostructure

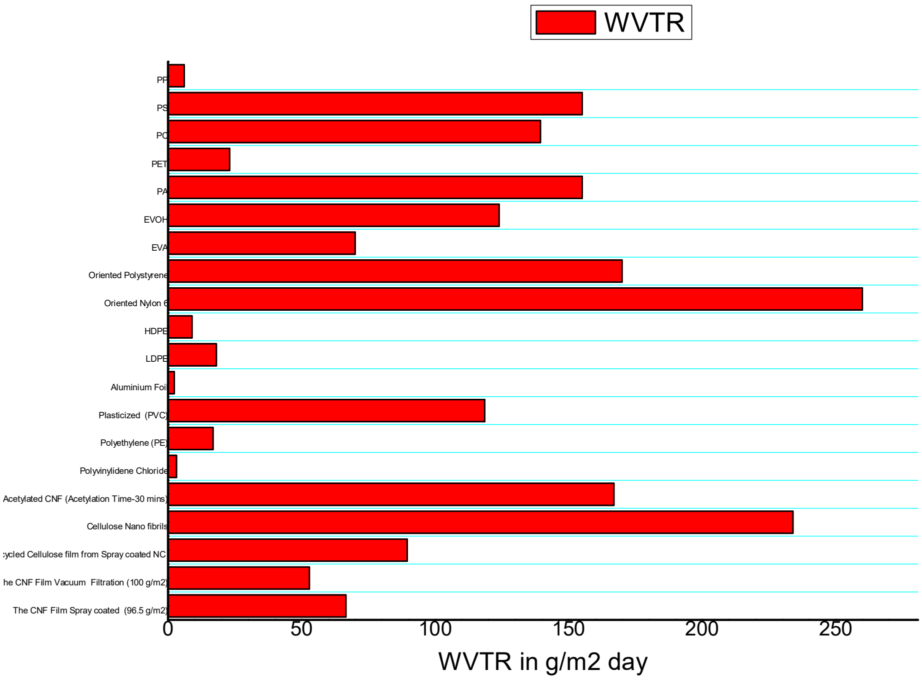

Figure 11. Comparison of WVTR of CNF films with conventional synthetic plastics.

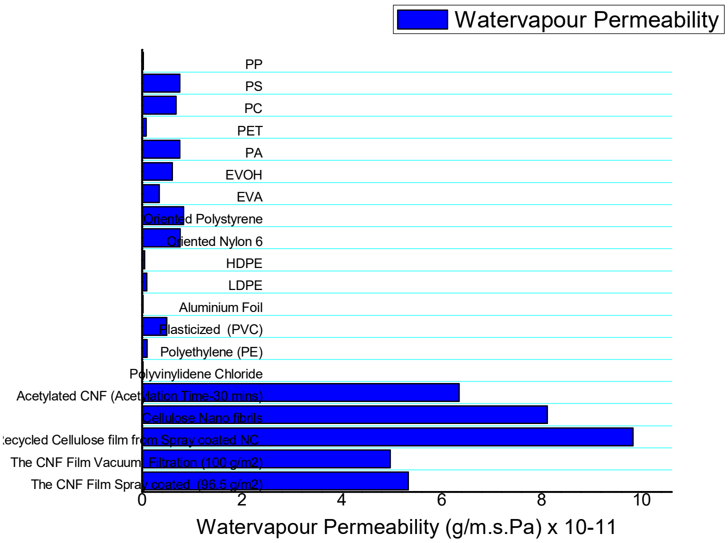

Figure 12. Comparison of WVP of CNF films with synthetic plastics.

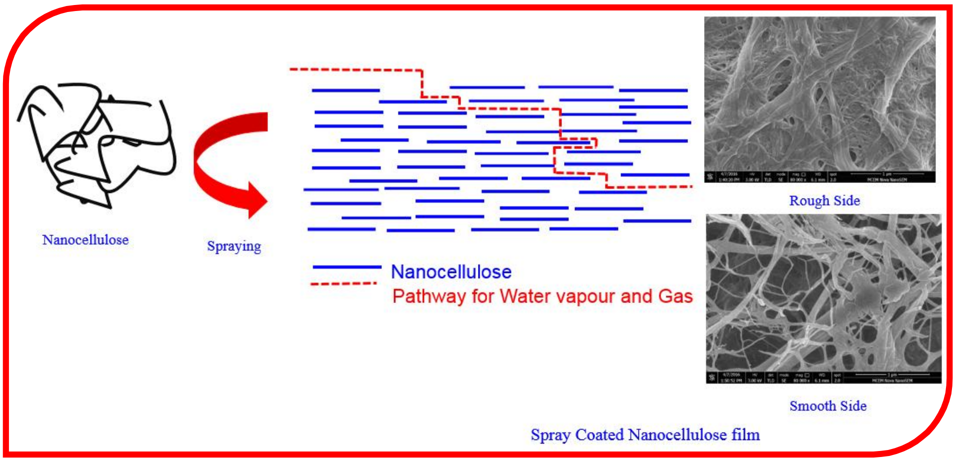

Figure 13. Water vapour barrier mechanism of spray coated cellulose nanofiber film.

of CNF forms a compact network of cellulose nanofibrils during the fabrication of CNF films via spraying[6]. It results a compact and dense film which acts as barrier against gaseous molecules. The dense packing of CNF produces a tortuous pathway for diffusion of water vapours, which reduces the permeability of the film to water vapour[21,22].

CNF has high source of hydroxyl groups (–OH) present in their surface of cellulose nanofibrils and offers for strong intermolecular hydrogen bonding between adjacent fibres[18]. In addition to that, CNF films were densified via crosslinking of the fibres via hydrogen bonding and it strengthens the intermolecular and intramolecular hydrogen bonds in the film[23]. As water vapour is polar in nature and forms hydrogen bonds, the strong intermolecular hydrogen bonding between the cellulose nanofibers creates a strong barrier to water vapour diffusion. Overall, the combination of the unique nanostructure and the strong intermolecular hydrogen bonding in cellulose nanofiber films results in a highly effective water vapour barrier, making it an ideal material for a wide range of applications where water vapour barrier properties are required[17,21,22].

3.7 Recommendations for improving the WVP of CNF films

The following recommendations have been mentioned to improve the water vapour barrier performance of CNF films.

1) Use a higher concentration of cellulose nanofibers: Increasing the concentration of cellulose nanofibers in the film can lead to smaller pores and increased density, improving the film's ability to block water vapour[6,10].

2) Incorporate hydrophobic materials: Adding materials that repel water, such as hydrophobic nanoparticles like silica or graphene or montmorillonite[24], can improve the water vapour barrier properties of the film[25,26].

3) Modify the surface of the cellulose nanofibers: The surface of cellulose nanofibers can be modified with various chemicals to increase the surface charge or to introduce hydrophobic/hydrophilic functionalities. This can help to alter the water interactions of the film[24].

4) Increase the number of layers: Building up multiple layers of cellulose nanofiber films can reduce the size of the film's pores, improving its water barrier properties[21,22].

5) Increase the degree of orientation: By subjecting the cellulose nanofiber films to mechanical or thermal treatments, it is possible to achieve higher degrees of alignment in the fibres, which can improve water vapour barrier properties[27].

6) Add plasticizers: Incorporating plasticizers, such as glycerol or sorbitol, can improve the flexibility of the cellulose nanofiber film, reducing the possibility of cracks or gaps that can allow water vapour to pass through[28].

3.8 CNF for packaging applications

Cellulose nanofibers (CNFs) are a promising natural and renewable material for use in packaging. The unique properties of CNFs, including their high strength, low weight, and excellent barrier properties, make them an attractive alternative to other packaging materials such as plastics[7]. Several packaging applications of CNFs have been explored, including: 1) food packaging: CNFs have been used to produce films and coatings for food packaging, providing excellent barrier properties against oxygen and water vapor. CNF-based packaging can also prolong the shelf life of food products, preventing spoilage. 2) Biodegradable packaging: CNFs can be used to produce biodegradable packaging materials that are environmentally friendly and fully compostable. This makes them an excellent alternative to traditional plastic packaging, which can take hundreds of years to decompose. 3) Medical packaging: CNFs have been used for the packaging of medical devices and other healthcare products due to their excellent biocompatibility and low toxicity. 4) Electronics packaging: CNFs can also be utilized in electronic packaging due to their excellent electrical insulation properties. CNF-based packaging can help protect electronic devices from moisture, dust, and other environmental contaminants. Overall, the use of CNFs in packaging can reduce the environmental impact of packaging while providing excellent protection to the packaged product. As the demand for sustainable packaging continues to grow, CNFs are likely to play a significant role in the future of packaging materials[7,22].

4. Conclusion

The spray coated cellulose nanofiber (CNF) film is a renewable, biodegradable and sustainable material that has attracted attention for its unique mechanical properties, high surface area, and good barrier properties. The film is produced by a process called spray coating, which involves spraying cellulose nanofibers onto a stainless-steel surface to form a compact film which has a notable smoothness on the spray coated side. The resulting film has two unique surfaces, potential barrier against water vapour. It is a sustainable material that can be produced in large quantities via spraying, a scalable process, making it an attractive alternative to petroleum-based materials in conventional packaging. The water vapour permeability of CNF films can be tailored by varying the density of the film through tailoring the thickness and basis weight of the film. It can be done by spraying various CNF concentration on the stainless stee plate to fabricate the film. Given this correspondence, spraying CNF suspension on the polished stainless steel surface is a flexible process for fabrication of CNF films and capacity to tailor barrier properties of the film.

Conflict of interest

The authors declare no conflict of interest.

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