

REVIEW

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High performance green barriers based on nanocellulose

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Abstract

With the increasing environmental concerns such as sustainability and end-of-life disposal challenges, materials derived from renewable resources such as nanocellulose have been strongly advocated as potential replacements for packaging materials. Nanocellulose can be extracted from various plant resources through mechanical and chemical ways. Nanocellulose with its nanoscale dimensions, high crystalline nature, and the ability to form hydrogen bonds resulting in strong network makes it very hard for the molecules to pass through, suggesting excellent barrier properties associated with films made from these material. This review paper aim to summarize the recent developments in various barrier films based on nanocellulose with special focus on oxygen and water vapor barrier properties.

Keywords: Green barriers, Nanocellulose, Cellulose nanofibrils, Cellulose nanocrystals

Introduction

Packaging materials are widely used to prevent food and drink, healthcare, cosmetics and other consumer goods against physical, biochemical, and microbiological deterioration. They should provide sufficient barrier against oxygen, water vapor, grease, and microorganisms. Currently, the packaging materials are largely based on glass, aluminum and tin, and fossil derived synthetic plastics. These materials possess high strength and barrier properties. However, they are unsustainable, some are fragile such as glass, and their weight adds to energy costs for shipping [1-6]. The global consumer packaging demand is valued at approximately US\$400b-\$500b and is one of the faster-growing markets, forecasted to grow at ~4% per year until 2015 [7].

With the increased environmental concerns over sustainability and end-of-life disposal challenges, materials derived from renewable resources have been strongly advocated as potential replacements [8]. Cellulose is the most abundant polymer in nature and accounts for approximately 40% of lignocellulosic biomass. Cellulose paper-based packaging is lightweight, low-cost, and

most important, sustainable. Unfortunately, common paper made from lignocelluloses does not provide sufficient barrier for water, oxygen or oil. Currently, paper based packages are made with unsustainable coatings of wax, plastics, or aluminum. Cellophane is the only cellulose based material (not modified or coated) currently used for barrier packaging due to its high gas barrier. However, the production of cellophane is via a viscose route which produces byproducts and uses reagents (CS₂ and H₂S) that are harmful to the environment [9].

The production of cellulose nanomaterial such as cellulose nanofibrils (CNFs) and cellulose nanocrystals (CNCs) have opened vast possibilities of utilizing cellulose based materials for packaging. Cellulose nanomaterial has diameter in the range of 2–50 nm with large surface area [10-12]. The ability to form hydrogen bonds resulting in strong network makes it very hard for the molecules to pass through, excellent for barrier applications [13]. This review paper aim to summarize the recent developments in various barrier films based on nanocellulose with special focus on oxygen and water vapor barrier properties.

Nanocellulose and its preparation

Cellulose nanofibrils (CNFs) or microfibrils have diameter in the range of 2–50 nm and lengths up to several

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micrometers depending on their origin [10-12]. CNFs have exceptional optical and mechanical properties, and therefore can be used as a building block for a variety of high-performance materials [14-16]. Intensive mechanical treatment is required to disintegrate the cellulose fiber to nanofibrils [17]. Several methods of mechanical fibrillation have been used for the production of CNFs such as homogenizers [18,19], microfluidizers [20], and grinders [21,22]. Cellulose nanocrystals (CNCs) are often prepared by treating cellulose fiber with sulfuric acid or hydrochloric acid. Strong acidic condition leads to aggressive hydrolysis to attack the noncrystalline fractions within the cellulose fiber which results in the formation of low aspect cellulose fibril aggregates known as CNCs [23-25].

Mechanical fibrillation of cellulose fibers to CNFs are very energy intensive with reported values ranging from 4500–10000 kWh/tonne [21,22]. Chemical pretreatments and enzymatic pretreatments before mechanical fibrillation have been used to reduce this energy consumption. Cellulose fibers were oxidized by a 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated system. These treated fibers were further mechanically fibrillated to CNFs while reducing the energy costs [26]. Aulin et al. [27] carboxymethylated softwood pulp and then fibers were mechanically fibrillated using a high-pressure fluidizer to produce CNFs of diameter of 5–10 nm. Enzyme pretreatment of biomass followed by mechanical homogenization has been used as an environmentally friendly alternative to chemical pretreatment for nanocellulose production [28-30]. Figure 1 shows the morphological difference between the CNCs and CNFs.

Migration process of molecules through nanocellulose film

Migration of molecules between two adjacent volumes separated by a thin film of solid polymer or membrane occurs in three basic steps. In the first step, the diffusing

molecule is adsorbed on to the sample surface. In the second step, the molecule then diffuses through the film or membrane. Finally, the diffusing molecule exits the sample by desorbing from the surface. The gas permeability through a nanocellulose film mainly depends on the dissolution of gas and its rate of diffusion in the film. Thus, permeability of gas molecules through nanocellulose film can be expressed as:

$$P = DS \quad (1)$$

Where P is the permeability, D is the diffusion coefficient, and S is the solubility coefficient.

The permeability coefficient P is obtained from the application of Henry's law of solubility to Fick's law of diffusion,

$$P = DS = ql/At\Delta p \quad (2)$$

Where q is the amount of material passing through the film, l is the thickness, A is the cross sectional area, t is time, and Δp is the pressure difference between the two sides of film.

The gas molecules should be first dissolved in the membrane or film before diffusing. Even though the surface of films influences the permeating gas molecules, the most dominant factor in molecular migration is bulk flow, i.e., rate of molecule diffusion in the membrane or film [31]. The good oxygen barrier properties of nanocellulose can be attributed to the dense network formed by nanofibrils with smaller and more uniform dimensions. Considering this fact, the pores within the films serve as the major path for permeating oxygen molecules. The dense nanofibrils forms more complex and smaller pores compared to pure cellulose fibers which are in micro scale. This complex dense network increases the tortuosity within the film and thereby decreases the permeability within the films [13]. Figure 2 shows a schematic

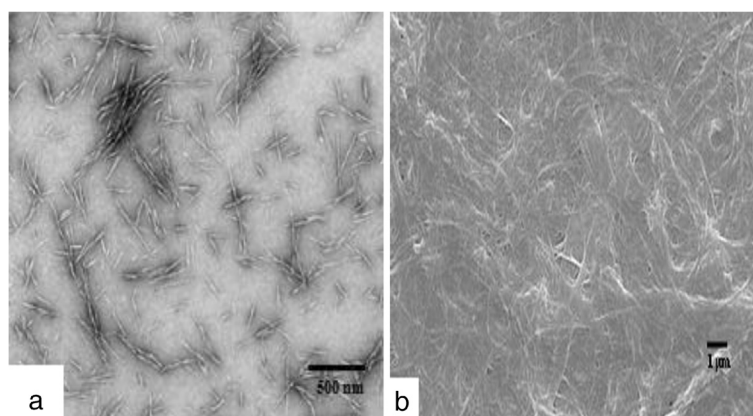


Figure 1 Images of (a) CNCs [24], and (b) CNFs [18].

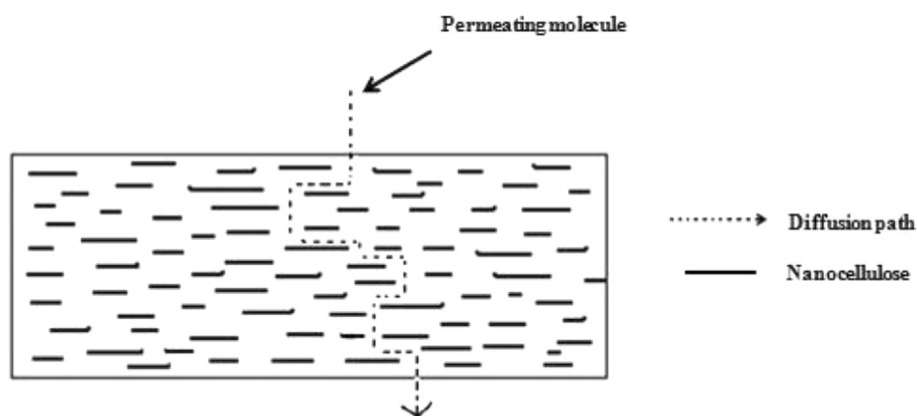


Figure 2 Shows schematic representation of increased diffusion path within the nanocellulose films.

representation of increased diffusion path within the nanocellulose films. Also, the high crystalline structure within the nanofibrils or whiskers contributes to the gas barrier properties [23,31]. Cellulose is composed of both crystalline and disordered regions. High crystallinity ranging from 40-90% has been reported for the nanocellulose, with CNCs showing higher crystallinity than the CNFs because strong acid hydrolyzes disordered cellulose to result in highly crystalline CNCs [21,32]. Even though the CNCs have higher crystallinity than CNFs, mechanically fibrillated CNF films were found to have much lesser oxygen permeability than CNCs. Both showed similar solubility, but the oxygen molecules penetrated more slowly through the CNF films. This is mainly due to the structural organization within the films. The CNF films have higher entanglements within the film which increased the tortuosity factor or increase the diffusion path [33]. Even though nanocellulose provides a high barrier for oxygen, the water vapor barrier properties are low. This is mainly due to high affinity between water and the nanocellulose film. Nanocellulose is much better water vapor barrier than cellulose fiber. Nanocellulose has a strong reducing effect on water vapor diffusion due to its size, and swelling constraints formed due to rigid network within the films. However, at a high relative humidity these structural organizations can be disrupted due to high swelling and can lose barrier properties for both oxygen and water vapor [34].

CNFs for barrier application

CNFs is a strong gas barrier material. Compared to CNCs, CNFs consists of crystalline and disordered regions. In most of the cases, crystallinity ranging from 40-75% has been reported for the CNFs obtained from softwoods and hardwoods [11,12,21,22]. Saito and Isogai (2004) showed that the degree of crystallinity varied from 78-91% for

CNFs produced from TEMPO oxidation of cotton linter [35]. Films made purely of mechanically fibrillated CNFs have very high air and oxygen barrier property. The oxygen transmission rates (OTR) of CNF films with thickness of 21 μm were as low as $17 \pm 1 \text{ ml m}^{-2} \text{ day}^{-1}$. These values are competitive with other best synthetic polymers such as ethylene vinyl alcohol (EVOH) ($3\text{--}5 \text{ ml m}^{-2} \text{ day}^{-1}$) and polyvinylidene chloride (PVdC) coated polyester films ($9\text{--}15 \text{ ml m}^{-2} \text{ day}^{-1}$) of approximately same thickness with respect to OTR [13]. Recently, Osterberg et al. [36] demonstrated a rapid method of making robust CNF films with high oxygen barrier property. The CNF solutions were first filtered followed by hot pressing at high pressure followed by air drying. At a relative humidity below 65%, the oxygen permeability of these films was below $0.6 \text{ cm}^3 \mu\text{m m}^{-2} \text{ d}^{-1} \text{ kPa}^{-1}$. However, oxygen permeability of CNF films increases with the increase in relative humidity. This is mainly due to the plasticizing and swelling of nanofibrils through the adsorption of water molecules at high relative humidities.

CNFs also have tunable barrier properties. Rodionova et al. [5] showed that both pure and partially acetylated CNF films can be used for modified atmosphere packaging (MAP) with permeability below $10\text{--}20 \text{ mL m}^{-2} \text{ day}^{-1}$. Similarly, carboxymethylated CNF films with thicknesses of 2.54 and 3.19 μm have very low oxygen permeability of 0.009 and 0.0006 $\text{cm}^3 \mu\text{m m}^{-2} \text{ day}^{-1} \text{ kPa}^{-1}$, respectively [27]. High oxygen performance barrier films with permeability of 0.007 $\text{cm}^3 \mu\text{m m}^{-2} \text{ day}^{-1} \text{ kPa}^{-1}$ can be made by controlled thermal treatment at different temperatures. It was demonstrated that after thermal treatment at 175°C , the oxygen permeability of the CNF films was reduced by 96% compared to the films without heat treatment [37]. Table 1 shows the oxygen permeability of films made from nanocellulose compared with those from commercially available petroleum based materials and other polymers. Also, CNFs are used to coat the surface of films to

Table 1 Oxygen permeability of nanocellulose film compared to those made from commercially available petroleum based materials and other polymers

Material	Oxygen permeability (cc.μm/m ² .day.kPa)	References, conditions
CNF	0.6	[35], at 65% RH
CNF (carboxymethylated)	0.0006	[27], at 0% RH
CNF (carboxymethylated)	0.85	[27], at 50% RH
Cellophane	0.41	[46], at 0%RH
PVdC	0.1-3	[47], at 50% RH
Polyvinyl alcohol (PVOH)	0.20	[47], at 0% RH
EVOH	0.01-0.1	[47], at 0% RH

enhance the barrier properties. Fukuzumi et al. [38] prepared high oxygen barrier CNF films by TEMPO mediated oxidation. The 0.1 μm thick CNF film when coated on a polylactic acid film, reduced the oxygen permeability from 746 ml m⁻² day⁻¹ Pa⁻¹ for pure PLA film to 1 ml m⁻² day⁻¹ Pa⁻¹ for PLA film with CNF layer. The oxygen barrier of PET films was raised by more than 350 times through a 1 μm thick layer of the same TEMPO-oxidized CNFs [39]. Similarly, Fujisawa et al. [40] found that the use of TEMPO-oxidized CNFs with sodium carboxylate groups improved the oxygen barrier of PET films more than when coated with TEMPO-oxidized CNFs with carboxyl groups. Hult et al. [41] showed that the oxygen transmission rate of paper substrates were decreased by several logarithmic units by the deposition of CNFs and shellac coating layers. CNFs have also been used as filler material to obtain a nanocomposite material. Plackett et al. [42] showed that the addition of 15 wt% of CNFs substantially increased the oxygen barrier of amylopectin films. The use of CNFs in xylan films showed very low oxygen permeability of 0.19 cm³ μm m⁻² day⁻¹ kPa, which is comparable to previously reported values for 100% CNF films [43]. Several studies have been conducted on making composites using CNF with nanoclay [44], and talc [45]. Oxygen barrier properties of these composites were highly competitive and much better than various synthetic polymers currently used in the packaging industry.

Even though the oxygen barrier properties of CNF films are competitive with current commercial films made from synthetic polymers, their water vapor barrier remains very low or the water vapor transfer rate remain very high. Table 2 shows the water vapor transmission rate (WVTR) of nanocellulose films than those of commercially available films from petroleum based materials and other polymers. This is mainly due to the strong hydrophilic nature of the cellulose nanofibers. However, the water vapor transmission rate (0.02 g/m² day/m) was significantly lower compared with films made from

bleached softwood fibers (0.11 g/m² day/m). The CNF film structure is more compact, therefore less water can penetrate through the film compared to the films made of cellulose fibers. The water contact angle was substantially increased for the CNF film compared to films made from bleached softwood film. The hydrophilic nature is not the only important criteria for water vapor barrier property. The films with high lignin content created more hydrophobic surface with higher water contact angles but showed the least water vapor barrier enhancement. However, the CNF films without lignin produced a more compact structure. The presence of lignin hindered the hydrogen bonding and created more hydrophobic pores which aided in more water vapor transmission [34]. Recently, researchers have modified the properties of CNFs using various pretreatments to enhance the water vapor barrier property. Sharma et al. [37] showed that the water vapor permeability was reduced by 50% upon heat treatment at 175°C for 3 hours as compared to the untreated CNF films. They attributed that the enhancement in barrier property was mainly due to increase in hydrophobicity as evidenced by the increase in water contact angle and reduced porosity by heat treatment. Rodionova et al. [5] showed that the WVTR of pure CNF films (234 g m⁻² day⁻¹) was reduced to 167 g m⁻² day⁻¹ by 30 mins of acetylation treatment. The acetylation created a much higher hydrophobic film surface indicates by higher water contact angles. Minelli et al. [48] showed that the use of carboxymethylated pretreated CNFs produced a more homogenous and less porous film than enzyme pretreated CNFs and showed a much enhancement in water vapor barrier property below 80% relative humidity. Recently, the water vapor permeability of the paper substrates was substantially decreased with a multilayer coating of nanocellulose and alkyd resins. The WVTR reached very low and reached values considered as high barriers in packaging applications [49].

CNCs for barrier application

Contrary to CNFs, very few studies have been directed toward study of 100% pure CNC film or treated CNC films. Belbekhouche et al. [33] compared the gas barrier properties between CNF and CNC films. They found that the films made of CNCs were more permeable to oxygen than those made of CNFs. The oxygen molecules penetrated much more slowly within CNF film due to the higher fibril entanglements within the film which increased the tortuosity factor. CNCs, which have crystallinity greater than 60% combined with their ability to form a dense hydrogen bonded network can increase gas barrier property. Bacterial cellulose nanocrystals (BNCs) films present excellent oxygen barrier at low relative humidity, but their high moisture sensitivity results in dramatically decreased barrier when the

Table 2 WVTR of nanocellulose compared to commercially available petroleum based materials and other polymers

Material	Water vapor transmission rate (WVTR) (g/m ² day)	Average thickness of the film (μm)	References, conditions
CNF	234	42	[5], 50% RH
CNF (acetylated for 0.5 h)	167	46	[5], 50% RH
PVdC	3.07	12.7	[50], 100% RH
Polyethylene (PE)	16.8	18.3	[50], 100% RH
Plasticized polyvinyl chloride (PVC)	118.56	12.7	[50], 100% RH

relative humidity is higher than 70%. The oxygen permeability of 6.99×10^{-22} m³ m/m² s Pa at 0% humidity increased to 5.97×10^{-18} m³ m/m² s Pa at 80% humidity. However, this permeability was reduced by 97% and 74% when BNC films were coated with annealed PLA electro spun nanostructured fibers and 3-aminopropyl trimethoxysilane (APTS), respectively [51]. Herrera et al. [52] studied thin spin coated films made from CNCs prepared with sulfuric acid and hydrochloric acid. The hydrochloric acid made CNCs resulted in films with low permeability for oxygen, while the sulfuric acid made CNCS resulted in films with higher permeability.

CNCs have been studied as filler for various natural polymers for enhancing the barrier properties. Saxena et al. [23] produced nanocomposite film with low oxygen permeability by casting an aqueous solution containing xylan, sorbitol and nanocrystalline cellulose. Oxygen permeability of films prepared from xylan, sorbitol and 50% by weight of sulfonated CNC exhibited a significantly reduced oxygen permeability of 0.1799 cm³ μm/m².d.kPa compared with films prepared solely from xylan and sorbitol with an oxygen permeability of 189.1665 cm³ μm/m². d.kPa. Poly lactic acid (PLA) nano-biocomposites containing 5 wt% of nanocrystals exhibited the highest oxygen barrier. The OTR for PLA nanocomposites with 5% w/w of unmodified CNCs was 17.4 ± 1.4 cm³ mm m⁻² day⁻¹, while that for modified CNCs with an acid phosphate ester of ethoxylated nonylphenol in a 1/4 (wt/wt) ratio was 15.8 ± 0.6 cm³ mm m⁻² day⁻¹ [53]. Addition of 1 wt% of silver nanoparticles to these modified CNC- PLA composites further decreased the OTR to 12.6 ± 0.1 cm³ mm m⁻² day⁻¹ [54]. The OTR values of ternary systems consisting of PLA, PHB (poly hydroxybutyrate) and 5 wt% unmodified CNCs was 15.3 cm³ mm m⁻² day⁻¹, while that for modified CNCs with an acid phosphate ester of ethoxylated nonylphenol in a 1/1 (wt/wt) ratio was 13 cm³ mm m⁻² day⁻¹. Water contact angle measurements showed that the ternary system had high hydrophobicity and the presence of sulphate groups with low polarity on the surface of CNCs increased the surface hydrophobicity of the final composite material [55].

CNCs were used as fillers in polyvinyl alcohol (PVOH) matrix. The addition of 5 wt% CNCs decreased the WVP of pure PVOH films from 0.61 ± 0.04 g.mm/kPa.h.m² to 0.44 ± 0.01 g.mm/kPa.h.m² [56]. The reinforcement of natural biopolymers with CNCs was found to reduce WVTR of the resulting nanocomposites. The films prepared using xylan as reinforcement polymer with 10% sulfonated CNCs exhibited a 74% reduction in specific water transmission properties compared with the film without CNCs and a 362% improvement compared with xylan films reinforced by 10% softwood kraft fibers. The xylan/sulphonated CNC nanocomposites showed a WVTR of 174 g/hm² [57]. They also compared xylan films reinforced with CNC made from hydrochloric acid with those reinforced with sulphonated CNC. Even though, films showed a significant reduction in water transmission, the reduction was not as significant as those using sulfonated CNCs. The xylan/ hydrochloric acid made CNC films showed a WVTR of 281 g/hm² [58]. Khan et al. [59] showed that the values of water vapor permeability (WVP) decreased sharply as the content of CNCs increased in the methyl cellulose based films. The WVP of control films (without CNCs) was 6.3 g.mm/m². day.kPa, while those films in cooperated with 1 wt% CNC showed a permeability of 4.7 g.mm/m².day.kPa.

Conclusions

Nanocellulose such as CNFs and CNCs have opened vast possibilities of utilizing cellulose based materials. The use of CNFs in films, composites, and coatings has found to substantially reduce the oxygen permeability within these materials. The oxygen barrier efficiency of pure CNF films is highly competitive and even be comparable with commercial synthetic polymers. The improvement of oxygen barrier properties by CNFs can be attributed to the dense network formed by nanofibrils with smaller and more uniform dimensions. Even though CNCs have higher crystallinity than CNFs, mechanically fibrillated CNF films were found have much lesser oxygen permeability than CNCs. The CNF films have higher entanglements within the film which increases the diffusion path for gas molecules. Also, nanocellulose has a strong reducing effect on water vapor diffusion due to its size,

and swelling constraints formed due to rigid network within the films compared to cellulose fibers. The use of CNFs and CNCs in various natural polymer based composites has found to substantially reduce the gas permeability within these composites.

Competing interests

The authors declared that they have no competing interests.

Authors' contributions

All the authors have contributed to the literature review and manuscript writing. All authors read and approved the final manuscript.

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