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Moisture and Oxygen Barrier Properties of Cellulose Nanomaterial-Based Films

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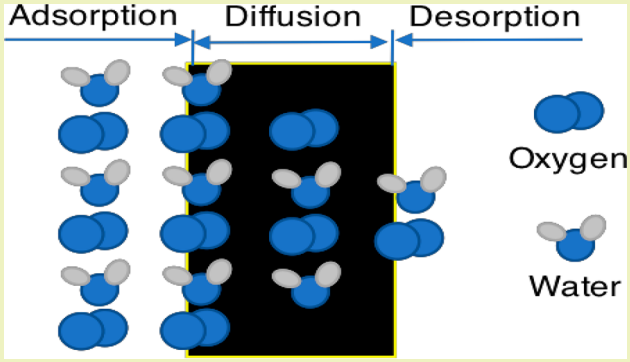
ABSTRACT: Applications of cellulose nanomaterials (CNMs) have attracted increasing attention in recent years. One conceivable path lies in their commercial applications for packaging, in which their barrier properties will play an important role in determining their competiveness with conventional materials. This review critically analyzes the performance of CNMs acting as a barrier against moisture and oxygen permeation in CNM films, CNM-coated polymers and papers, and CNM-reinforced polymer composites, gives some insights into remaining challenges, and brings an overall perspective of compositing CNMs with other materials to achieve balanced properties adequate for barrier packaging. In general, CNMs are a poor moisture barrier but excellent oxygen barrier in the dry state and are still good below 65% relative humidity. The addition of CNMs can improve the oxygen barrier of the resulting polymer composites; however, neat CNM coatings and films can afford better oxygen barrier properties than dispersed CNMs in coatings and nanocomposites. The morphology and surface functionality of CNMs can be tailored to maximize the barrier performance of materials comprising them. The higher the surface charge density is of CNMs, the better is the barrier performance of coated polymers. Like other oxygen barriers such as ethylene vinyl alcohol and cellophane, the moisture sensitivity and sealability of CNMs can be improved by sandwiching them with high moisture-resistant and sealable polymers such as a polyolefin. A multilayered structure with layers of CNMs providing oxygen resistance covered by other layers of polymers providing moisture resistance and sealability might be competitive in barrier packaging markets dominated by synthetic plastics.



KEYWORDS: *CNMs, Barrier, Multilayer film, Oxygen permeability, Water vapor permeability, Packaging*

INTRODUCTION

Barrier Packaging Materials and Trends. Food packaging can have a significant impact on food taste, quality, longevity and marketability. About 40% of all food produced spoils every year in the United States.[1] Technical limitations in harvesting, transporting, and storage contribute to food spoilage. It is believed that a major factor in preventing food loss lies in the use of quality packaging that prevents moisture and oxygen transmission between products and their environment. Loss or gain of oxygen and water is a major cause of food deterioration. Approaches to improve packaging in order to prolong the shelf life of products include the formation of airtight seals and the use of better barrier materials. Some packages contain desiccants, oxygen absorbers, or scavengers to help extend shelf life of foods, especially foods prone to rancidification; new trends are to control the permeation of gases through packaging and control the gas composition inside packages. In the past decades, globalization has made packaging touch every aspect of the industry in one way or another since most everything one buys is in a package. The disposal of used packages has caused great impacts on the environment. Therefore, packaging materials have been examined not only with respect to their performance in terms of strength, thermal, freezer-safety, or microwave-safety, and barrier properties, but also with respect to their sustainability in terms of life-cycle impacts, biodegradability, and compostability.

Glass, metal, and plastics are conventional packaging materials. Glass and metal containers provide excellent gas and water barrier properties and are dominant in alcoholic beverage packaging and the canning industry. However, glass and metal packaging increases transportation costs, has high energy costs to recycle, and does not decompose in landfills or

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the environment. Consumers of convenience foods prefer flexible packaging amenable to microwave operation and transparent enough to view the content over metal and glass counterparts. Polyvinylidene chloride (PVdC) is a conventional transparent barrier polymer with excellent barrier properties against both water vapor and oxygen. However, there is a desire to avoid the chlorine element in packaging materials, which may lead to the release of toxic dioxins at end-of-life incineration.

Other commodity plastics often have good water vapor barrier properties but poor oxygen barrier properties. One of the demands placed on plastic in packaging is the high barrier against oxygen. This requirement hinders the use of plastics for a number of applications. It is a huge challenge to develop plastic materials with oxygen barrier properties approaching those of glass. In practice, lamination and coating are two approaches to improve plastic barrier properties. Aluminum foil and metallized coatings provide excellent barrier properties attributable to their metallic crystalline structures and low porosity. However, these packaging systems are hard to recycle and do not break down in the environment, and materials like aluminum have a large environmental impact in its production. There are a lot of efforts in developing ceramic (SiO_x and AlO_x)-coated polymers to form high moisture and oxygen barrier materials,[2] but these coatings face challenges such as the presence of pinholes, brittleness, or poor flex crack resistance; i.e., they are sensitive toward thermal and mechanical perturbation which may limit their uses.

Generally, plastics are low weight and low cost but do not break down in the environment. Around 80% of all plastics end up in landfills or the natural environment causing problems such as plastic pollution on land and sea, impacting animals, clogging oceans, and killing marine life.[3] A challenge is to use sustainable materials for food packaging applications that can be recycled. However, poor mechanical and barrier properties of biopolymer-based packaging materials compared to those of nonbiodegradable materials have limited their widespread applications. The use of bioplastics as food packaging materials is constrained by their cost/performance characteristics, which are not comparable to conventional petroleum-based materials in several key properties. Polylactic acid (PLA), polyhodroxybutyrate (PHB), and thermoplastic starch are promising biomaterials for packaging applications. However, brittleness, thermal instability, low melt strength, difficult heat sealability, and high moisture and oxygen permeability restrict the use of PLA and PHB films for many food packaging applications.[2] The hydrophilic nature of thermoplastic starch packaging materials limits their long-term stability and mechanical properties in addition to challenges such as poor processability, brittleness, and vulnerability to degradation.[2] Therefore, current markets for these plastics are limited to biobags and mulch films for agricultural applications.[4] In addition, there are concerns on availability as well as on the use of land to produce feedstocks for these bioplastics.[5]

Although there are a variety of biopolymers available, cellulose stands out as a viable option for packaging beyond its current use in boxes and paper bags.[6] Cellulose derived from certified forests is abundant, renewable, and biodegradable making it a promising substitute with a high potential among emerging bioplastics. Current paper and boxes, that are not coated, have no barrier properties to oxygen or water vapor. Transparent cellulose-based films have also been used for packaging several food products. Cellulose acetate is the most common cellulose-based film and is commonly used for fresh produce and baked goods packaging that does not require a good barrier to oxygen.[7] Although a lot of cellulose derivatives are produced commercially and most of them have excellent film-forming properties, they are too expensive for bulk use.[5] Clear and transparent cellophane has been used for packaging since the middle of the 1920s, peaked in the 1960s, and gradually ceded to plastics since 1970. Its market volume has been limited by its hydrophilicity and its nonenvironmentally friendly production process.[8]

In the past two decades, several types of cellulose nanomaterials (CNMs) have been developed. These materials are low cost, have low environmental costs to produce and recycle, and will decompose in landfills or the environment. These CNMs also have demonstrated excellent oxygen barrier properties. The tensile strength of CNM films is in the range of 104−154 MPa, which is comparable to the tensile strength of cellophane of 125 MPa longitudinal and 75 MPa transversal, but the elastic modulus of CNM films can be much higher than that of cellophane (e.g., 15.7−17.5 GPa vs 3.7−5.4 GPa).[9] This may be attributable to the higher stiffness of crystalline cellulose fibrils in CNM films compared to the lower crystalline structure of cellophane films at around 27%.[10] Hence, they have been projected to have the largest market potential for barrier packaging among various applications.[11]

Barrier studies have been carried out on films prepared by various methods from several CNMs, generating varying barrier properties in the literature. It is noted that the barrier properties for the same material might not agree with each other in the literature, which might have reflected the difference of material compositions, processing histories, aging, test methods, and accuracy of measurements. It would be beneficial to analyze these data to understand uncertainties associated with these studies. Previous reviews of CNMs have contributed one or two paragraphs on the topic of barrier layers.[12,13] Others authors have provided good reviews on CNM barrier properties.[14−17] However, these reviews often lack identifying trends, connecting reported barrier properties to the requirements of potential applications, and clarifying factors among differing data.

The goal of this review is to evaluate and synthesize the findings of using CNMs as a gas barrier to understand their implications, challenges, and opportunities. The barrier property values reported in this review include only those obtained using a common oxygen permeability analyzer (MOCON); this is to remove questions around test methods associated with oxygen permeability. The values by alternative methods used in other publications[18−20] are not in the same order of magnitude as those tested using this common apparatus, but their comparative findings are still relevant and will be included in the discussion. In addition, barrier properties reported in different units were converted into the same units to allow for easy comparison. When the CNM barrier properties are discussed, they are always set in a context in contrast with the benchmarks of commercially important barrier materials to allow for easy identification of the strength and weakness of CNMs as barrier materials. The review starts with an introduction of barrier properties, classifications, and CNM terminology, followed with the barrier properties of three categorical CNM-based products: neat films, coatings on polymers or papers, and polymeric nanocomposites. Lastly, a potential way of using CNMs for barrier packaging is discussed. Specifically, the present review article has covered and

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Table 1. Barrier Parameters, Equations, and Units

Barrier Property	Equation	Unit
Water Vapor Transmission Rate (WVTR)	$\text{WVTR} = \frac{\text{weight passed through}}{\text{area}\cdot\text{time}}$	g/m^2·day
Water Vapor Permeability (WVP)	$\text{WVP} = \frac{\text{WVTR}\cdot\text{thickness}}{\text{saturated pressure}\cdot\Delta\%\,\text{RH}}$	g·μm/m^2·day·kPa
Oxygen Transmission Rate (OTR)	$\text{OTR} = \frac{\text{volume passed through}}{\text{area}\cdot\text{time}}$	cm^3/m^2·day
Oxygen Permeability (OP)	$\text{OP} = \frac{\text{OTR}\cdot\text{thickness}}{\text{oxygen partial pressure difference}}$	cm^3·μm/m^2·day·atm

Table 2. Barrier Classifications of Films Based on Oxygen and Water Vapor Permeability[a]

Grade	Oxygen Permeability (cm^3·μm/m^2·day·atm)	Example[b]	WVP (g·μm/m^2·day·kPa)	Example[b]
Poor	>40000	HDPE 43307, PP 59055, PS 170866, PHB 302555[c], LDPE 790000[d]	>3000	Silicone Elastomer 3502
Low	4000−40000	PVC 4252, BOPP 113204, PHA 150003, PLA 305005	1000−3000	PA 6 1253, PLA 11602
Medium	400−4000	EVOH wet 787, OPET 1181, PA 6 wet 1972, PET 3543	400−1000	PS 660, PHA 824[g] PLA 898[f]
High	40−400	PVdC 98, PA 6 dry 449	40−400	PAN 251, PVC 132, PET 79, LDPE 164[h]
Very high	<40	EVOH dry 3.93	<40	HDPE 23, PP 20, PVdC 17, OPET 4[i], BOPP 7[e]

[a]The number by the name is the permeability coefficient of that material at 23−25 °C for OP without specified RH%; 37.8 °C and 90%RH for WVP. BOPP: biaxially oriented polypropylene; EVOH: ethylene vinyl alcohol; HDPE: high density polyethylene; LDPE: low density polyethylene; OPET: oriented polyethylene terephthalate; PA 6: polyamide 6; PET: polyethylene terephthalate; PHA: polyhydroxyalkanoates; PHB: polyhydroxybutyrate; PLA: polylactic acid; PP: polypropylene; PVC: polyvinyl chloride; PVdC: polyvinylidene chloride; PS: polystyrene; PAN: polyacrylotrile. [b]Ref 30. [c]Ref 31. [d]Ref 32. [e]Ref 33. [f]Ref 34. [g]Ref 35. [h]Ref 36 at 25 °C, 84/22%. [i]Ref 37.

discussed moisture absorption equilibria and how they appear to be related to barrier properties as well as the effects of coating substrates and processing considerations on barrier performance. The discussion of effects of cations interacting with carboxylated cellulose nanomaterials is also a key contribution of this review article.

Barrier Properties. Gas phase permeation through a nonporous material occurs through adsorption at the leading interface, diffusion through the material, and desorption at the trailing interface and is often measured with three parameters: transmission rate, permeance, and permeability. Transmission rate is the volume or weight of a permeant (e.g., oxygen or moisture) passing through a film per unit surface area and time under equilibrium with testing conditions. Permeance is the transmission rate divided by the partial pressure difference of the permeant across the film. Permeability is the permeance multiplied by the thickness as shown in Table 1. Barrier properties are not only determined by the nature of a material, but are also a function of temperature, pressure, and relative humidity. Barrier properties are usually measured under equilibrium moisture conditions with a controlled environment.[21,22] It usually takes one or two days for a hygroscopic material to reach equilibrium. The accuracy and reproducibility depend on the precision of controlling test conditions and consistency of sample preparations. The transmission rate and permeance change with the thickness of a film and the level of partial pressure of the permeant and relative humidity across the test film. The permeability of a material can also be different if measured at two different thicknesses even though it is normalized to thickness. However, the permeability is expected to be independent of specimen thickness being tested for a thick film (e.g., >10 μm for glassy polymers)[23] for most gas phase permeations and thus can be used to roughly compare barrier performance among different materials if tested under similar conditions. Most oxygen and water vapor transmission rates in the literature were measured under 1 atm at a specific temperature and relative humidity. From test conditions and known thickness of the films, transmission rate, permeance, and permeability can be converted into each other even if a publication only reports one of the parameters.

The transmission rate of a substance through a specific material can be measured through numerous methods. The most commonly used oxygen permeation measurement follows ASTM standards[22,24] with an analyzer from the MOCON company;[25] the data measured with other operational principles might not be in the same order of magnitude.[18,19] Moisture transmission rate is typically measured per ASTM E96[21] using a gravimetric desiccant method. The SI units of mol/m s Pa and Barrers are used in literature, but cm^3 μm/m^2 day atm for oxygen permeability and g μm/m^2 day kPa for WVP are used more commonly because it is easily understandable with clear physical implications and convenient for dealing with a film thickness often measured in μm.

Barrier Classifications and Requirements. Rating various materials into a few grades by their permeability can explain quantities qualitatively and enhance the conceptual understanding of material barrier quality. But no specific rating scales have been promulgated to classify barrier grades. Hult et al.[26] defines a material as "high oxygen barrier" if its oxygen permeability is less than 75 cm^3·μm/m^2·day·atm at 25 °C and 50% of relative humidity. The ASTM standard[22] claims that films having transmission rates in excess of 200 cm^3/m^2·day·atm when tested with an oxygen partial pressure difference of 1 atm are defined as poor barriers and lists two examples of such materials as polyethylene (PE) and polystyrene (PS). Apparently, this definition is not sufficient because it depends

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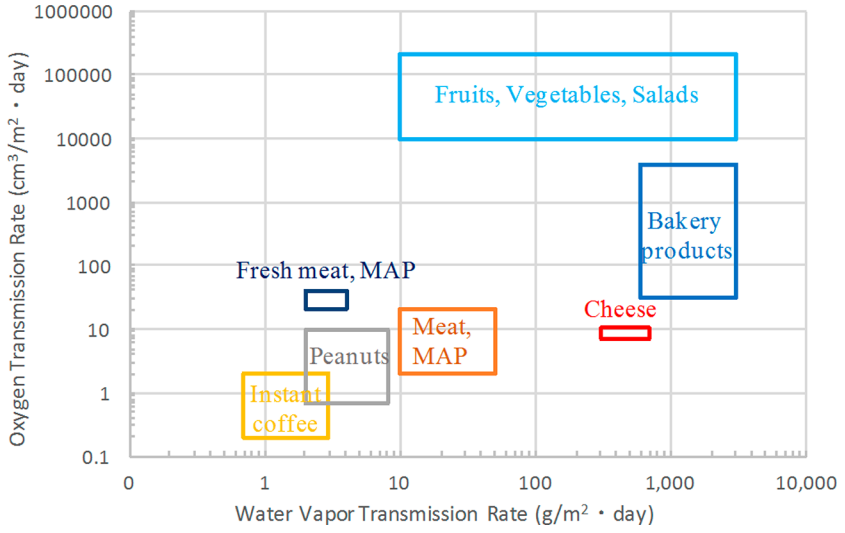

Figure 1. Packaging requirements of barrier films for selected food products.[38] MAP: modified atmosphere packaging.

on film thickness. Based on this understanding and the principles of similar materials falling into the same rank, we suggest a rough classification of commonly used polymeric packaging materials into five categories (Table 2), which intentionally classifies polypropylene (PP), PE, and PS into the poor oxygen barrier category. A similar classification philosophy is applied to classify moisture barriers. Table 2 shows that a good moisture barrier is typically not a good oxygen barrier except for PVdC. Good barriers to oxygen often have molecular structures with polar-to-polar interactions or hydrogen bonding (measurable by cohesive energy density or free volume), which usually result in high hydrophilicity, thus, poor water vapor barriers.[27,28] It is noted the listed barrier properties in Table 2 are nominal for that material; different grades, processing histories, and sources of material may result in different barrier values but should be in a similar order of magnitude.

Moisture and oxygen transmission rate requirements vary depending on the nature of foods that need to be protected (Figure 1). Package design needs to consider material and thickness as well as the temperature and humidity associated with its end-use to meet barrier requirements for a given application. For example, for the modified atmosphere packaging, the oxygen transmission rate should be below 10−20 cm^3/m^2·day.[29] A film made from the carboxyl CNFs (−COOH CNFs) (Table 4) needs to be 70 μm thick, but only 0.36 μm is needed with the calcium carboxylated CNFs (−COOCa CNFs) to meet this requirement. Typically, for a specific package, either increasing thickness or using high barrier materials can meet the requirements of gas transmission rates. Since customers do not like heavy packaging and manufacturers would like to reduce the use of materials, high barrier materials are preferable.

CNM Terminology. Cellulose macromolecules organize themselves into the form of long slender strands or fibrils in nature and are abundant in plant cell walls. Biologically, a fibril that was synthesized by a six-lobed rosette cellulose synthase complex is termed as a microfibril by biologists;[39,40] the one that was synthesized cooperatively by a group of densely packed cellulose synthase complexes is termed as aggregated microfibrils.[41] However, the terms of microfibril and aggregated microfibrils in biosynthesis studies are often called elementary fibril and microfibril by technologists, respectively, in studies developing the technology of cellulose products.[42,43]

Fibrils have been extracted from sulfite pulps and microcrystalline cellulose or other forms of purified cellulose by severe concentrated acid hydrolysis, intense mechanical shearing such as macrogrinding, beating, refining, microgrinding, microfluidization, and sonication, or assisted by light acid or enzymatic hydrolysis, chemical pretreatments creating negatively charged cellulose fibrils followed by gentle mechanical disintegration.[44] These different extraction methods with a continuous range and severity of treatment conditions remove the sheath around fibrils and break them down to a varying extent and have created technical products with different sizes, shapes, and compositions, which are generically termed as CNMs or nanocellulose.[45] Corresponding to three entities of cellulose in nature—microfibrils, elementary fibrils, and crystalline domains or crystallites—three forms of nanocellulose products can be isolated and are named as cellulose microfibrils, cellulose nanofibrils, and cellulose nanocrystals, respectively,[45] which were also lumped as cellulose nanoparticles in earlier publications.[12]

Typically, manufacturing methods are a defining factor to determine which form of CNMs will be obtained. Microgrinding and microfluidization promotes greater separation of fibrils than refining only; chemical pretreatments often lead to individualized fibrils and increased transparency for the resultant products.[46] Cellulose nanofibrils and cellulose microfibrils are sometimes loosely referred as cellulose nanofibrils, and microfibrilated, or nanofibrilated cellulose. Cellulose fibrils obtained with chemical pretreatment methods are also differentiated such as 2,2,6,6-tetramethylpiperidin-1-yl)oxyl, TEMPO-oxidized cellulose nanofibrils.[47] Sometimes, a product that is obtained from a series of chemomechanical treatments such as a combination of TEMPO-mediated oxidation and mechanical disintegration and that is hard to be distinguished between nanofibrils and nanocrystals or is a mixture of them is termed as nanofibers.[48]

The designations of CNMs in this review are in agreement with the publication by Moon et al.[45] Cellulose microfibrils (CMFs) are those CNMs with a diameter approximating the sum of a few elementary fibrils (10−100 nm wide, 0.5−10 μm long), widely distributed in size, sometimes networked, and

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with a low charge of less than 100 μmol/g,[49,50] which had been induced typically by pulping or bleaching procedures of their raw materials. Currently, CMFs are often obtained by mechanical treatments only or assisted with light chemical or enzymatic pretreatments. Cellulose nanofibrils (CNFs) are those CNMs with lateral dimensions approximating one or two crystal sizes, 5−30 nm in width, aspect ratio usually greater than 50, narrowly distributed in size, and often individualized, with an anionic charge from 300 to 1740 μmol/g depending on the severity of chemical treatments.[47,51] Currently, the properties corresponding to CNF dimensions are most often achieved by chemical pretreatments (oxidation or carboxymethylation) followed by mechanical disintegration. Cellulose nanocrystals (CNCs) are those CNMs with lateral dimensions approximating cellulose crystal size: 3−10 nm wide, aspect ratio of 5−50.[45] Currently, CNCs are most often obtained with concentrated acid hydrolysis methods with a undetectable charge for the hydrochloric acid hydrolyzed method and with a medium charge of 150 to 350 μmol/g for the sulfuric acid hydrolyzed method.[19,49]

Since a substantial portion of the reviewed literature does not provide size information, the designations in this review are mainly based on production methods and not size although each method results in a typical size range and morphology as defined above. The designations of CMFs, CNFs, and CNCs do not convey any information on surface chemistry that usually plays a large role in their applications. Charges and surface functionality are the results of preparation methods. Hence, CNMs are further differentiated based on hydroxyl derivatives and counterions. For example, TEMPO-mediated oxidized CNFs with a sodium counterion is labeled as sodium carboxylated CNFs, etc.

Moisture Absorption of CNMs. During storage or in service, cellulosic materials slowly absorb or desorb moisture from or to the surrounding air until they reach an equilibrium moisture content (EMC), a function of relative humidity and temperature of the surrounding air. Water sorption and retention greatly affect barrier properties and thus are examined first. Moisture adsorption isotherms at 25 °C are different from each other among different cellulosic materials (Figure 2). The wood isotherm was obtained by the Hailwood−Horrobin model with parameters from the EMC data of Sitka spruce wood,[52] while the three other isotherms were obtained by the GAB (Guggenheim−Anderson−de Boer) model[53] with parameters from Bedane et al.[54] These isotherm curves are characteristic of an inflection point at a different relative humidity, which is interpreted as the transition from monolayer to multilayer absorption.[55] EMC at an inflection point is termed as monolayer moisture content.[54] The monolayer moisture content and inflection points derived from Figure 2 are reported as follows: bleached Kraft paper 4% at 35% RH, wood 6% at 40% RH, regenerated cellulose 9% at 65% RH, and CNFs 12% at 70% RH.[54,56] The monolayer moisture content of the CNF film is three times larger than the one for the bleached Kraft paper sample and three times larger than that of the wood, indicating a large surface area with exposed hydrophilic sites. Above the monolayer moisture content, the absorption of water would expand gaps between fibrils resulting in a capillary network of water, which provides additional passages for moisture and oxygen beyond cellulose itself.

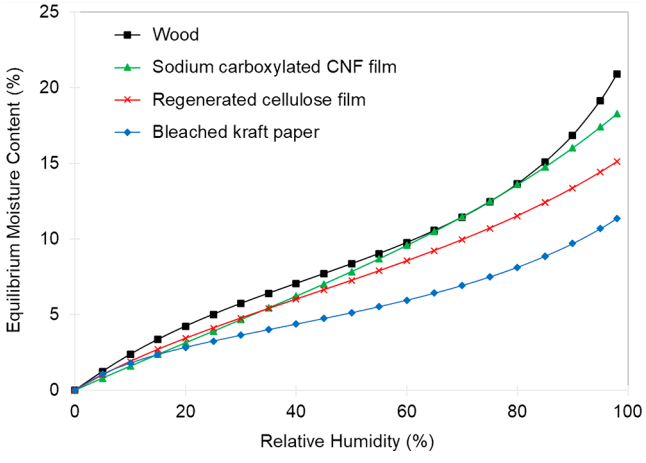

Figure 2. Moisture adsorption isotherms at 25 °C for wood[52] and other cellulosic materials.[54]

Figure 2 shows that the sodium carboxylated CNF film has a higher moisture adsorption capability than other forms of cellulose, especially in the high relative humidity range,[54] but slightly lower than wood adsorption.[55] It is understandable that wood absorbs more moisture than Kraft paper because it contains a much larger amount of hemicellulose capable of absorption except for cellulose. Regenerated cellulose generally has lower crystallinity, for example, 27% for lyocell,[10] than wood pulps, which has usually undergone a hornification process during the drying process resulting in higher crystallinity, and hence, the regenerated cellulose absorbs more moisture than the wood pulp. The high moisture absorbing ability of CNMs has been ascribed to their larger number of hydrophilic sites on the cellulose nanoparticle surface compared to other forms of cellulose.[54]

Other investigators[20,57,58] reported the absorption isotherms of films of CMFs and sodium carboxymethylated CNFs, and their glycerol plasticized films having similar shapes to wood isotherms with a transition point toward parallel to the moisture content axis at a high relative humidity. The carboxylated CNF films attained a higher equilibrium moisture content than the low-charged CMF films, and the plasticized films are higher than the unplasticized films. Nakagaito and Yano showed that the water retention of CMFs increased with an increasing degree of fibrillation.[59] The variations of reported CNM moisture absorption might reflect differences in morphology and surface functionality of CNMs.

CNM FILMS

Moisture Barrier Properties of CNM Films. Table 3 lists the WVP of several CNM films in contrast with paper, regenerated cellulose, biodegradable synthetic polymers, and commercially important moisture-resistant polymers. The WVP of CNMs ranges from 2882 to 27,750 g·μm/m^2·day·kPa, falling into the poor moisture barrier classification by comparing with the classifications in Table 2. The large variations were caused by variations mainly in test conditions, film density, and the nature of CNMs. It is observed that moisture permeates much faster from 100% to 50% RH than from 50% to 0% RH, although the moisture partial pressure difference is same in the two situations (Table 3).

Figure 3 shows that WVP does not increase with moisture content in the 0−40% RH range but decreases slightly with increasing RH for all cellulose films, which does not correlate well with moisture absorption isotherms that typically display nearly linear moisture content increase in this relative humidity

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Table 3. Water Vapor Permeability (WVP) of CNM Films Compared to Other Forms of Cellulose and Commercially Important Polymers

Material	WVP ($g \cdot \mu m/m^2 \cdot day \cdot kPa$)	Test Conditions[a]	Ref
Sodium carboxylated CNFs, Hardwood	2882	23 °C, 50/0%	60
Sodium carboxylated CNFs, softwood	3220	23 °C, 50/0%	60
Sodium carboxylated CNFs	22,854	25 °C, 90/0%	54
CMFs, softwood kraft pulp	6826	23 °C, 50/0%	61
CMFs, hardwood bleached kraft pulp	27,750	23 °C, 100/50%	50
Regenerated cellulose	3995	23 °C, 85/0%	62
Paper, 343 g/m^3	16,416	25 °C, 56/0%	63
Paper, bleached kraft pulp, 543 g/m^3	52,580	25 °C, 90/0%	54
Polyvinyl alcohol	41,904	38 °C, 90/0%	27
Ethylene vinyl alcohol	1468	38 °C, 90/0%	27
Polylactic acid, PLA	898	20 °C, 50/0%	34
Polylactic acid, PLA	1642	25 °C, 74/0%	63
Polycaprolactone, PCL	1510	25 °C, 60/0%	64
Polyhydroxyalkanoate, PHA	330−1253	38 °C, 90/0%	35
Polyethylene, PE	86	27 °C, 100/0%	65
Polyvinylidene chloride, PVdC	11	27 °C, 100/0%	65

[a]"/" indicates relative humidity levels across the test film.

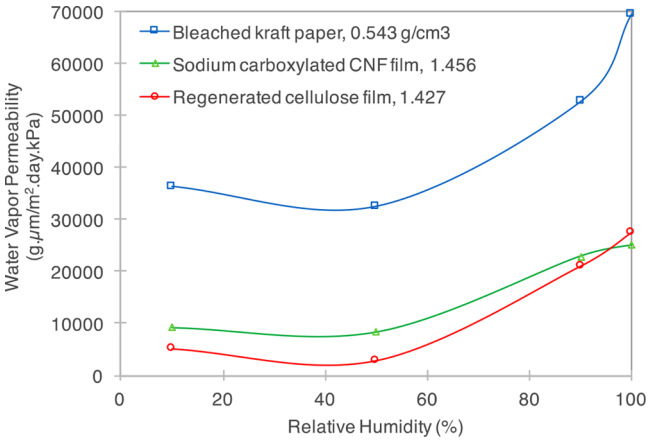

Figure 3. WVP of films of cellulosic materials tested by moisture permeating from different relative humidity levels to a dry condition. The figures in the legend are density. Recalculated and redrawn from Table 3 by Bedane et al.[54] Copyright 2015, with permission from Elsevier.

range. A similar trend was observed on EVOH films.[66] This trend may be attributed to the strong interaction of adsorbed water molecules with hydrophilic polymers such as cellulose and PVOH in the low moisture state. The moisture is absorbed onto high energy sites and is consequently immobilized and contributes little to the permeability.[66,67] It is also explained that the water molecules absorbed in low humidity fill free volume holes in EVOH or some other hydrophilic polymers thus decreasing the free volume fraction and hole size leading to the decreasing WVP.[68] In contrast, WVP increases rapidly with relative humidity in the higher relative humidity range above 50%, which might roughly correspond to the transition point from surface absorption to capillary condensation on a typical absorption isotherm; i.e., when the capillary condensation begins, interfibril interfaces are opened, and capillary pores increase rapidly with relative humidity, leading to increasing WVP. However, two other researchers show that the WVP of CNM films increased with relative humidity over the entire humidity range.[20,69] Kumar et al. also reported that if CNMs have a higher equilibrium moisture content it has a higher water vapor transmission rate.[60]

The CNM films have similar WVP to or slightly higher than the regenerated cellulose films but much lower than the paper. At high relative humidity, WVP of CNMs are very large but lower than the paper and PVOH—a water-soluble synthetic polymer. The large WVP of the paper might be partially attributed to its porous structure enabling direct diffusion of water vapor through the air in the pores and even convection as well or capillary flow at high relative humidity and the presence of hydroxyls. The size of cellulose fibrils and the interfibril cavities might render them to behave more like a polymer with hydroxyls such as PVOH. The presence of hydroxyl groups of CNMs and PVOH imparts to these materials the ability to form inter- and intramolecular hydrogen bonds resulting in high cohesive energy density, dense without large free volume, and the lowest reported oxygen permeability among existing barrier polymers in the dry state as discussed in the following sections. However, moisture can invade and replace some hydrogen bonds among themselves leading to the loss of gas and water vapor resistance.

Various attempts have been made to improve the WVP of CNMs. The acetylation of CMFs appeared not to significantly affect the moisture transmission rate.[61] The finding that the acetylation did not affect the moisture transmission rate implies that different mechanisms govern moisture uptake and moisture transmission since the acetylation effectively decreases moisture absorption and the equilibrium moisture content.[70] Decreasing moisture absorption capability does not necessarily decrease moisture permeability concomitantly. However, esterification with more carbon numbers of hexanoyl and dodecanoyl chloride decreased both the moisture and oxygen transmission rates of a regenerated cellulose.[71] Spence et al.[72] also found that a higher lignin content afforded CMF films higher contact angles but still higher WVTRs, which was explained by the presence of pores in the films resulting from higher lignin hydrophobicity. It seems reasonable to assume that the partial hydrophobization interferes with the structure of film: a resulting bulkier, more porous structure of the film might offset an apparent advantage of increased hydrophobic character. The competition of the two factors could be a logical

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ACS Sustainable Chem. Eng. 2018, 6, 49−70

Table 4. Oxygen and Moisture Permeability of CNM Films Compared to Those Made from Commercially Available Petroleum-Based Materials and Other Natural Polymers

Functionality		OP[a]	Conditions	WVP[b]	Conditions	Ref
Carboxymethylated CNFs, (−CH_2COONa CNFs)		0.061	23 °C, 0%	–	–	57, 73
		37−86	23 °C, 50%	–	–	57, 73
		3617	23 °C, 80%	–	–	57, 73
Carboxylated CNFs (−COO^- CNFs)	−COOH	700	23 °C, 50%	–	–	74
	−COONa	250	23 °C, 50%	–	–	74
	−COOAl	11	23 °C, 50%	–	–	74
	−COOCa	3.6	23 °C, 50%	–	–	74
Carboxylated CNFs (−COONa)		63−152	23 °C, 50%	2882−4220	23 °C, 50/0%[c]	60
CMFs (refining + grinding)		35−43	23 °C, 50%	916	23 °C, 50/0%[c]	60
CMFs (cut + homogenizing)		357−510	23 °C, 50%	–	–	9
CMFs (refining + homogenizing)		88	23 °C, 0%	6993	23 °C, 50/0%	61
Post-carboxylated CMFs		111	23 °C, 50%	7949	23 °C, 50/0%	49
CMFs		20	23 °C, 53%	27,750	23 °C 100/50%	50
		5573	23 °C, 96%	27,750	23 °C 100/50%	50
Wax dip coated CMFs (10 w/w% wax)		20	23 °C, 53%	1850	23 °C 100/50%	50
		1723	23 °C, 97%	1850	23 °C 100/50%	50
Bacteria Cellulose Nanocrystals (CNCs)		6.12	24 °C, 0%	3067	24 °C, 75/0%	75
		52,264	24 °C, 80%	3067	24 °C, 75/0%	75
tert-Butylamino CNCs		250	23 °C, 50%	3300	22 °C, 52/0%	76
		590	23 °C, 80%	3300	22 °C, 52/0%	76
Regenerated cellulose		0.5−1.2	23 °C, 0%	–	–	77
Amylopectin		1418	23 °C, 50%	124,000	23 °C, 85/50%	78
Amylose		709	23 °C, 50%	103,000	23 °C, 85/50%	78
Cellophane		263	23 °C, 0%	22,955	37.8 °C, 90/0%	36, 79−81
		25,470	23 °C, 95%	5962	25 °C, 84/22%	36, 79−81
Chitosan		112	25 °C, 0%	9198	100/50%	36, 79−81
		92,477	25 °C, 93%	9198	100/50%	36, 79−81
Polyethylene terephthalate (PET)		1000−5000	Unchanged over the entire RH[d]	4−79	37.8 °C, 90/0%	2, 66, Table 2
Polypropylene, PP		50,000−100,000	Unchanged over the entire RH[d]	7−20	37.8 °C, 90/0%	2, 66, Table 2
Polyethylene, PE		50,000−200,000		23	37.8 °C, 90/0%	2, 66, Table 2
polyvinylidene chloride, PVdC		10−300	23 °C, 50%	17	37.8 °C, 90/0%	2, 66, Table 2
Ethylene vinyl alcohol, EVOH		1−10	23 °C, 0%	20−50	35 °C, 90/0%	2, 66, Table 2

[a]OP: oxygen permeability in $cm^3 \cdot \mu m/m^2 \cdot day \cdot atm$. [b]WVP: moisture permeability in $g \cdot \mu m/m^2 \cdot day \cdot kPa$. [c]Difference of relative humidity across the film during the measurement. [d]OP of hydrophobic films such as PET, PLA, PP, and PE are almost unchanged over the entire RH range.[69]

reason that there is not a clear effect of hydrophobization on WVP in some cases. The biodegradable polymers such as PLA, PCL, and PHA fall into the medium or low moisture barrier classifications. It can be assumed that combining these biodegradable polymers with CNMs only moderately improve the moisture resistance of the composites.

Oxygen Barrier Properties of CNM Films. Various CNM films are comparable in oxygen permeability with some benchmark petroleum-based polymers and better than several

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relevant biopolymers (Table 4 and Figures 4 and 5). CNMs are outstanding oxygen barriers that perform better than EVOH

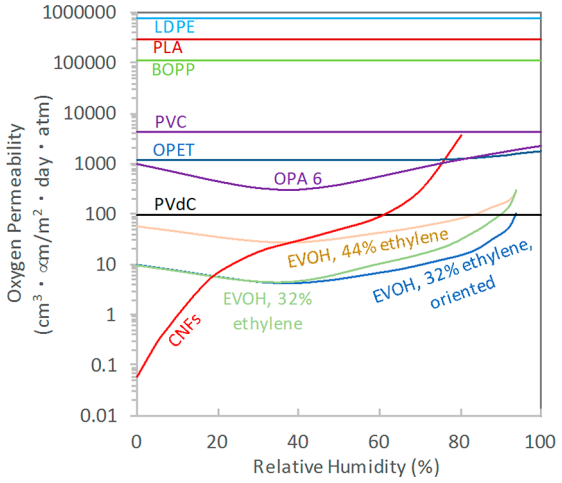

Figure 4. Oxygen permeability changes with relative humidity at 23−25 °C for films of carboxymethylated CNFs,[57,73] oriented polyamide 6 (OPA 6),[82] ethylene vinyl alcohol (EVOH),[66] and other polymers (Table 2).

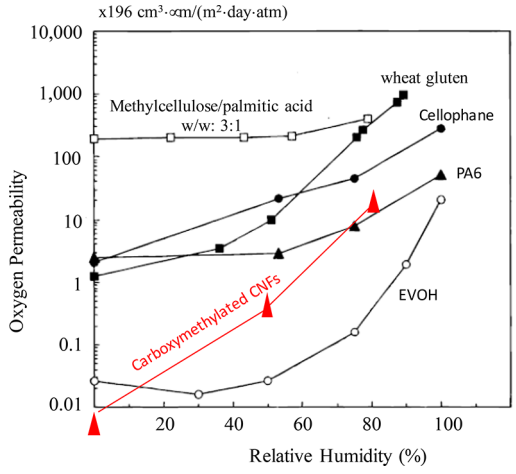

Figure 5. Oxygen permeability changes with relative humidity for natural and synthetic polymer films at 25 °C. Sources: sodium carboxymethylated CNFs;[57] other data.[81] PA 6: polyamide 6; EVOH: ethylene vinyl alcohol. Adapted with permission from ref 81. Copyright 1996, American Chemical Society.

and cellophane in the dry state. They fall into the high oxygen barrier classification with up to 65% relative humidity as seen by comparing oxygen permeability in Table 4 and Figures 4 and 5 to the classifications in Table 2, even though the oxygen permeability of CNM increases by a factor up to 1000 when the relative humidity increases from 0% to 65%. This suggests that CNMs may be ideally suited for packaging dry foods generally stored at low temperature and RH conditions. In this range of relative humidity, CNMs are competitive with synthetic polymers such as PVdC, which is one of the best barriers but contains chlorine atoms posing the potential for producing toxins at end-of-life incineration disposal. In addition, the oxygen permeability plotted as a function of RH for hydrophilic polymers such as OPA 6 and EVOH shows an upward concavity (Figures 4 and 5), suggesting a decrease in the oxygen permeability at low water concentration. It is considered that water molecules filling the free volume holes cause a decrease in the free volume in the low range of relative humidity and an increase in the free volume in the high humidity region,[68] leading to the change pattern of the oxygen permeability showing the similar trends as those in WVP (Figure 3). But there are not enough data points available to clearly indicate the changing pattern of oxygen permeability for CNMs along relative humidity. Three data points [(0% 0.061), (50% 50), and (80% 3617)] for carboxymethylated CNFs were from the literature (Table 4), and the curve was simulated as a sigmoid shape like the moisture absorption isotherm.

Effect of Moisture on Oxygen Permeation of CNM Films. The oxygen barrier properties of CNM films are outstanding at 0% RH but decline with increasing humidity and become extremely poor at higher levels of humidity. The oxygen permeability increases exponentially with relative humidity up to 65% RH and at a higher power (asymptotically) above 65% and essentially becomes transparent to oxygen at the higher relative humidity. For example, the oxygen transmission rate of a sodium carboxylated CNF-coated PET film at 35% RH increased approximately 2 orders of magnitude over that at 0% and was a poor barrier to oxygen above 75%;[69] the oxygen permeability of a carboxymethylated CNF film increased 3 orders of magnitude at 50% and five at 80% RH compared with that at 0%.[57] In another study, the oxygen permeability increased with relative humidity nonlinearly and at an accelerated rate starting at around 65−70% RH, corresponding to an equilibrium moisture content of 13% for a carboxymethylated CNF film.[57] This point correlated roughly with the monolayer moisture content of CNMs, corresponding to the occurrence of capillary condensation, which creates a network of capillary pores.

CNM films, fabricated from cellulose nanoparticles, are dense and highly crystalline in the dry state. It is noted that an increased crystalline structure improves barrier properties.[27] The film is rigid and vitreous at low moisture contents and rubbery and viscous at higher moisture contents. The presence of moisture softens polymer chains and increases interfibril free volume, which allows local deformation for oxygen molecules permeating through.

Effects of Surface Functionality on Barrier Properties of CNM Films. The three hydroxyls of each glucose unit on CNM surfaces, especially the C6 primary hydroxyl, can be modified during extraction processes—pulping, bleaching, and fibrillation. These processes create variations of hydroxyl, aldehyde, and carboxyl functional groups on cellulose chains, which affect the density and distribution of surface charges, their dispersion in solvents, and the structures of assembled CNMs, leading to different properties of films. Because acidic groups on CNM surfaces can become ionized, it is necessary to understand the role of cations as they act as counterions to these acidic groups. Different counterions contribute to variations of the resultant films' properties.[74,83] The performance of oxygen barriers of CNM was found to be in the following order: $H^+ < Na^+ < Al^{3+} < Ca^{2+}$.[74] CNM films with calcium and aluminum carboxylates were not as sensitive to moisture as other cations and had very low oxygen permeability of 8.1 and 150 $cm^3 \cdot \mu m/m^2 \cdot day \cdot atm$ even at 80% relative humidity, respectively. In addition, CNM films with Fe^{3+} and Al^{3+} ions had high wet tensile moduli and strengths of ∼3 GPa and 30−40 MPa, respectively. It was also reported that a film obtained by coating Na^+ carboxylated CNF on a PET film had a lower oxygen permeability than the one coated by H^+-CNF.[47]

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ACS Sustainable Chem. Eng. 2018, 6, 49−70

Xu et al.[84] also reported that the tensile strength of the Zn-cellulose films is enhanced in the presence of Ca^{2+} ions. Sirvio et al.[85] used Ca^{2+} to cross-link carboxylated CNFs and anionic polyelectrolyte sodium alginate leading to a film with excellent mechanical and grease barrier properties and reduced water vapor permeability. The cross-linking of alginate with multivalent ions dramatically decreased the water solubility of the alginate.[86] The mechanism of the ionic cross-linking of alginate has been delineated as the chelate complexation with Ca^{2+} in the center coordinating oxygen atoms on two adjacent alginate chains.[87] Although a detailed mechanism for the significantly different oxygen barrier properties with different counterions is unknown at present, the concept of producing water-resistant and high oxygen barrier CNM films might be realizable with interfibrillar cross-linkages coordinated through metal ions[74] in a similar way that Ca^{2+} working with alginate, taking advantages of chelation of multivalent ions and carboxylate end groups.

When cations are removed from pulp and replaced by a single cation species, it was found that the fiber saturation point increases in the order of $Al^{3+} < H^{+} < Mg^{+} < Ca^{+} < Li^{+} < Na^{+}$,[83] which is another evidence that counterions might come into play, influencing the self-assembly properties, phase behavior, and interaction forces of supramolecules. Protonated carboxyl groups (−COOH) might behave differently from carboxylate ion groups ($-COO^{-}$); multivalent metal ions such as Ca^{2+} and Al^{3+} might act as a cross-linker to render a more stable structure against moisture influence in contrast with monovalent Na^{+} that typically does not form coordinate chelation. These results present evidence that a common type sodium counterion is not good at moisture resistance, but the effect of the proton ion H^{+} on barrier properties needs further research. The sodium counterion rendering a better oxygen barrier than the carboxyl functionality is counterintuitive against the tendency of many sodium polyelectrolytes and carboxylates to absorb more water than carboxyl;[15,88] on the other hand, it might be attributable to the higher cohesive energy density[27] attributable in part to the sodium carboxylates and improved film integrity. It has been hypothesized that charge−charge repulsion would inhibit early strong adhesion between fibrils, thus allowing adjacent fibrils cooperative movement to self-organize themselves to some extent into a more favorable structure during the gradual drying and formation of a film.[15]

CNFs prepared by mechanical fibrillation of pulps typically bear a low charge, inherited from chemical pulps used to prepare CNFs.[50] Low-charged CNM films have an oxygen permeability of 20−510 $cm^3 \cdot \mu m/m^2 \cdot day \cdot atm$ at 23 °C and 50% RH,[9,50,60] which are categorized as a high barrier classification based on commonly used polymer film barrier performance metrics. The variations in permeability might be ascribable to the different film formation conditions. When films were formed by hot pressing, i.e., dense compressed and hornified (formation of irreversible hydrogen bonds), the oxygen permeability of CNFs decreased to below 20 $cm^3 \cdot \mu m/m^2 \cdot day \cdot atm$.[50]

It is not clear which is better with respect to barrier performance—low surface charge or ionized CNMs. On the one hand, negative charges help stabilize CNM suspensions and promote the coordinated structure formation of films during drying leading to the improvement of film integrity. On the other hand, the ionization of the acidic groups on CNM surfaces leads to a bulkier fiber structure when dried due in part to the electrostatic repulsion between the negatively charged carboxylate anions.[89] These opposite effects occurring simultaneously have resulted in conflicting reports. Some report that the films made from sodium carboxylated CNF are more sensitive to humidity[20] and had lower barrier properties against oxygen and moisture[60] than those made from low charged CNFs; the films made with very low surface charged CNCs prepared with hydrochloric acid hydrolysis displayed better oxygen barriers than those made with highly charged H_2SO_4 CNCs even though the surface of the former was rougher than that of the latter.[19] But others report that sodium carboxymethylated CNFs have a superior oxygen permeability.[73,79] In addition, sodium phosphorylated CNFs were found to exhibit significantly lower oxygen permeability at RH 80% than those of sodium carboxymethylated CNFs.[90] These conflicting findings would indicate that the dynamics of film forming, including what happens during CNM suspension application and during drying such as the events of nanoscale self-assembly, might be critical to the resulting film structures and might be investigated by some emerging tools.[91,92] It should be noted all these studies were conducted on a monovalent sodium ion, which might behave differently from multivalent ions as discussed in the previous section.

Moreover, Na^{+} was replaced with imidazolium or phosphonium cations using an ion exchange process; the resulting ion-exchanged CNCs were found to adsorb less water, and have thermal stabilities of up to 100 °C higher than those prepared from protonated CNCs (H^{+}-CNCs) and 40 °C higher than that of neutralized Na-CNCs. Methyl(triphenyl)phosphonium exchanged CNCs ($MePh_3P$-CNC) adsorbed 30% less water than Na-CNC and retained less water during desorption.[93,94] Although the literature data show the potential effect of the types of counterions and surface charges, it is inconclusive which surface functionality is the best in terms of oxygen and moisture barrier performance. This project will further the research systematically.

Oxygen barrier performance might also be enhanced by the formation of polyelectrolyte complexes of oppositely charged polyelectrolytes, which are normally prepared through layer-by-layer coating. Opposite ionic charges may enhance the cohesive energy density of the film, thus making it more resistant to gas permeation.[15] Negative charges of cellulose nanoparticles can be introduced by carboxymethylation,[57] TEMPO-mediated oxidation,[47] periodate oxidation,[95] etc. Cationization can be realized by depositing positively charged polyelectrolytes onto the surface of cellulose nanoparticles.[96] Low oxygen permeation was achieved at high relative humidity by the complexation of quaternized cellulose with glucuronoxylan[97] and also had a good adhesion and antibacterial effect by the complexation of quaternized chitosan deposited CNF and anionic polyelectrolyte sodium alginate.[98] Four bilayers (on both sides) of polycationic chitosan and negatively charged CNCs alternate formd a layer by layer coating on a PLA film and bottle and improved the water vapor permeability by 29% and 26%, respectively.[99] However, other studies generally found these polyelectrolyte complexes appeared not to upgrade moisture barrier performance substantially,[96,97] which reflects the pattern that a good oxygen barrier material might not be a high-grade water vapor barrier as shown in Table 2 because of different intrinsic molecular structure requirements for two characteristic permeants. Cellulose and chitin are the most and second most abundant natural biopolymers. The composition of these two materials via polyelectrolyte complexation may overcome each material disadvantages and create a moderate performance barrier packaging material but compostable.[99]

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Table 5. Oxygen and Moisture Permeability of CNM/Polymer-Coated Paper and Films[a]

Substrate	Coating	OP	Condition	WVP	Condition	Reference
Paper, 60 g/m^2, 63 μm	No coating, paper itself	Permeable	23 °C, 0%	2118	25 °C, 50/0%	26
	3.33 μm CMF	2,293,558	23 °C, 0%	2213	25 °C, 50/0%	26
	10.93 μm Shellac topcoat + 3.33 μm CMF basecoat	345,043	23 °C, 0%	319	25 °C, 50/0%	26
Unbleached Kraft Paper, 191 g/m^2, 263 μm	No coating, Kraft paper itself	–	–	26,198	23 °C, 80/0%	79
	2 μm $-CH_2COONa$ CNFs coating	–	–	12,256	23 °C, 80/0%	79
	4 μm $-CH_2COONa$ CNFs coating	–	–	12,704	23 °C, 80/0%	79
	19 μm alkyd resin coating	–	–	3624	23 °C, 80/0%	79
	19 μm alkyd resin topcoat, 2 μm $-CH_2COONa$ CNFs basecoat	–	–	2172	23 °C, 80/0%	79
	19 μm alkyd resin topcoat, 4 μm $-CH_2COONa$ CNFs basecoat	–	–	1615	23 °C, 80/0%	79
Paperboard, 178 g/m^2, 190 μm	No coating, paperboard itself	–	–	91,930	23 °C, 50/0%	107
	CMFs coating, 11 g/m^2, ~8 μm	–	–	13,800	23 °C, 50/0%	107
PLA, 25 μm	1.5 μm $-COONa$ CNFs	2/22,500	23 °C, 0%	74/75	23 °C, 90/10%	69
PET, 50 μm	1.5 μm $-COONa$ CNFs	4/1571	23 °C, 0%	4.6/5.5	23 °C, 90/10%	69
PET, 12 μm	1.5 μm coating of sulfate half ester CNCs	20/1380	23 °C, 0%	4.7/6	38 °C, 100/0%	100
OPP, 20 μm	1.5 μm coating of sulfate half ester CNCs	365/54,000	23 °C, 0%	1.2/1.6	38 °C, 100/0%	100
OPA,12 μm	1.5 μm coating of sulfate half ester CNCs	3/1020	23 °C, 0%	121/132	38 °C, 100/0%	100
Cell, 12 μm	1.5 μm coating of sulfate half ester CNCs	11/1320	23 °C, 0%	6.5/6	38 °C, 100/0%	100
PET, 12 μm	H_2SO_4 CNCs, 0.45 μm	76/1055	23 °C, 50%	–	–	110
	APS CNCs, 0.45 μm	43/1055	23 °C, 50%	–	–	110
CMFs, 65 μm	Wax dip coated CMFs (10 w/w% wax)	20/20	23 °C, 53%	1,850/27,750	23 °C, 100/50%	50
		1723/5573	23 °C, 96%	1,850/27,750	23 °C, 100/50%	50
Bacteria CNCs	PLA, 5 μm two sides (PLA film)	1,751 (15,583)	24 °C, 80%	1028 (1132)	24 °C, 75/0%	75
	VTMS, 0.8 μm two sides	48,237	24 °C, 80%	2833	24 °C, 75/0%	75
	APTS, 9 μm two sides	13,657	24 °C, 80%	1607	24 °C, 75/0%	75
	No coating, CNC film	52,264	24 °C, 80%	3067	24 °C, 75/0%	75
CNCs/PEG 900, w/w: 80/20	No coating, CNC film	62,770	24 °C, 80%	4156	24 °C, 75/0%	75
	PLA, 5 μm two sides	16,021	24 °C, 80%	1261	24 °C, 75/0%	75

[a]OP: oxygen permeability in cm^3·μm/m^2·day·atm, WVP: moisture permeability in g·μm/m^2·day·kPa; APS: ammonium persulfate, APTS: (3-aminopropyl) trimethoxysilane, Cell: cellophane, OPA: oriented polyamide, OPP: oriented polypropylene, PET: polyethylene terephthalate, VTMS: vinyltrimethoxysilane. In the columns of OP and WVP, the number before "/" is the OP or WVP of the coated sample, and the number after "/" is the OP or WVP of the substrate. In the column of WVP test condition, "/" indicates relative humidity levels across the test film.

Acetylation was found to affect barrier properties; the oxygen transmission rate of acetylated CMFs at the dry state increased with the degree of substitution.[61] The more hydrophobic nature of the modified cellulose decreases the cohesive energy density leading to increasing oxygen gas transmission.[27] Indeed, cellulose ester films have lower oxygen barrier properties than other cellulose derivative films with more hydrophilic functional groups.[7]

Effect of CNM Size and Type on Barrier Properties. There is not sufficient evidence to conclude the effect of sizes of CNMs on oxygen permeation. Research efforts on cellulosic films have mostly focused on fibril-based materials but less on neat CNC films. Belbekhouche et al.[18] reported that the oxygen permeability of the CNF films was lower than that of the CNC films, and this was attributed to the higher fibril entanglements and higher film density of the CNF films. Martinez-Sanz et al.[75] report that bacterial CNCs film had a much larger oxygen permeability at 80% humidity. These are cited as some evidence to conclude that CNF films have much lower oxygen permeability than CNC films.[17] Li et al.,[100] however, demonstrated that the short CNCs of 120 nm achieved high oxygen barrier properties, indicating that long entangled cellulose fibers are not the only crucial point in achieving a high oxygen barrier but CNCs may need a support substrate and a controlled process to collaborate each other to form a dense structure. Visanko et al.[76] developed butylamino-functionalized CNCs and self-standing CNC films with oxygen permeability approaching the high oxygen barrier classification

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even at 80% relative humidity, which might be an effect of polarity of butylamino pendants promoting nitrogen-hydrogen type hydrogen bonding and giving a higher cohesive energy density to the film material. The WVP of CNC films appears in the same magnitude as CNF films (Table 4).

While the transparency, surface smoothness, and mechanical properties of CNM films increase substantially with the decrease of CNM size, the oxygen permeability of CNM films is influenced to a greater extent by surface functionality (Table 4) and film densification or density than by size.[50,57,60,73] Fukuzumi et al. reported that there appeared some differences between the three-sized sodium carboxylated CNFs at 0% RH, but these differences became smaller above 75% RH.[69] The effect of particle dispersion and orientation on barrier properties is unclear. Several studies have demonstrated that particle morphology and size are less relevant to barrier properties of pure CNM films,[57] but there is not enough data to conclude the effect of particle morphology on composites either in coatings or in nanocomposites for which size and morphology of the CNM may affect interfacial properties thus adhesion and mechanical properties.

From Table 4, similar types of CNMs show varied oxygen permeability. This discrepancy may be attributable to differences in preparation of films, sampling, test methodology, or analysis of the data. Barrier properties obtained in different studies should be compared with some caution.

CNM COATINGS

Barrier Properties of CNM Coatings on Paper Substrates. Table 5 lists some results of CNM coatings on paper and polymer substrates. CNMs have been investigated for enhancing barrier properties of paper and paperboard in addition to improving printing and mechanical properties. Increasing coat weights of CNMs generally results in decreased air permeability and increased oil barrier properties due to the closure of open pores in the base paper and increased tortuosity (Figure 6).[9,57,101] However, an air permeability test is different from oxygen and water vapor permeation tests. The air permeability measures the volume of air flowing through the connected pores in a porous material such as uncoated paper under a pressure gradient. This is sometimes distinguished as penetration testing, probing defects such as cracks, pin holes, and pores in a material; small molecules are referred as the penetrant.[102] In contrast, oxygen and water vapor barrier properties are measured by a permeation testing under the static state flux; a partial pressure gradient of a permeant drives the molecules through nonporous materials by means of diffusion,[103] which is a cooperative movement between the permeant and polymer chains through dynamic free volume in polymers. Therefore, low air permeability does not necessarily translate into low oxygen and moisture permeability. In practice, a permeation testing might be greatly affected by penetration if the sample is defected, and thus, the resulting value might not represent the true one of that material. There may be no practical meaning to report the gas transmission rate for a porous material such as an uncoated paper other than air permeability. In addition, molecules might transport through a material in most cases by mixed modes of permeation and penetration; the distinction of penetration and permeation should be understood qualitatively which is dominated.

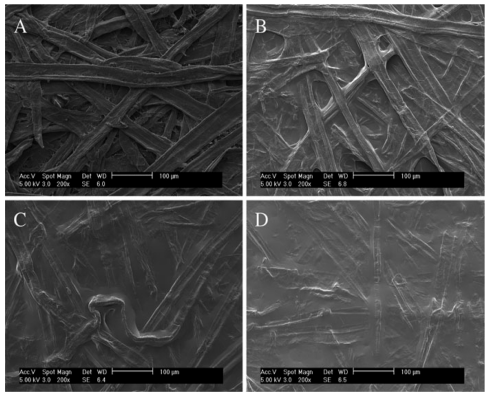

Figure 6. Surface structures of papers with CMF coat weights of 0 g/m^2 (a), 0.9 g/m^2 (b), 1.3 g/m^2 (c), and 1.8 g/m^2 (d), respectively. The increasing thickness of the coatings gradually closes the pores in the base paper decreasing air permeability. The scale bar is 100 μm. Reprinted with permission from ref 57. Copyright 2010, Springer Science + Business Media.

CMF coatings on cardboards[104] and CNCs coatings on base sheets of paper[101] did not adequately improve oxygen and water vapor barrier properties of the coated substrates. Although the coatings of CMFs on three bleached Kraft papers decreased oxygen permeability, the coated paper was still far from the requirements for a barrier material; moreover, the coatings did not significantly change moisture permeability compared to the base sheets of paper[26] because of CMF's hydrophilicity. Microscopic images disclosed that the CMF coatings did not completely restrict the base paper surface pores, which forms additional passages for gas penetration. Herrera et al.[105] found that thin spin-coated layers of CNMs did not cover the pores on the cellulose substrate with large pore size and that thicker dip-coated layers were delaminated from the mixed cellulose ester substrate with small pores. It was found that thinner coatings were very moisture sensitive. When the oxygen permeability was measured at above 50% RH, the materials lost their oxygen barrier properties completely, but the thicker coatings were less affected.

A base sheet of paper without precoating is a highly rough porous material and imposes a major challenge to obtain good surface coverage of coating.[4] In some applications, a thin coating layer is sufficient to change surface properties, while in other applications a thicker coating layer may be required, especially to form a continuous layer of CNFs if the surface of substrates is not smooth.[103] If the thickness of the coating is increased to cover all pores, the process economics may become a concern. Other materials may also be added to the coating. A study of PLA/CMFs blends coated on paper found that the addition of CMFs up to 10% in PLA did not significantly change the moisture transmission rate of the coated paper in comparison with the neat PLA coated paper.[106] For paperboards with a high WVP, a coating of CNMs decreased the WVP of the coated paperboards, but the coating with PLA, shellac, and alkyd resins was more effective by 1 order of magnitude.[26,79,107] Lavoine et al.[104] showed that in comparison with a base cardboard, moisture absorption increased for a cardboard coated with CMFs, while moisture absorption decreased if that same cardboard was coated with PE. Additions of carboxymethyl cellulose into CMF dispersions reduced viscosity, helped achieve higher coat weights and better coverage, and improved air permeability resulting from the closure of pores in paper substrates, but it did not significantly improve water vapor transmission rates of the coated papers,[108]

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ACS Sustainable Chem. Eng. 2018, 6, 49−70

which might be explained that the moisture permeation was not predominately determined by flowing through pores but diffusing through free volume of matrix. In sum, it appears that CNM coatings are not an effective way to bring oxygen and water vapor permeability of base papers to a useful range competitive with other conventional barrier materials.

Barrier Properties of CNM Coatings on Polymer Substrates. CNMs coated on polymer substrates have achieved remarkable oxygen barrier performance because of the smoothness of polymeric substrates (Table 5). The 1.5 μm coatings of sulfate half ester CNCs from cotton linters on PET, oriented PP (OPP), oriented PA (OPA), and cellophane, respectively, rendered an effective oxygen permeability of 2 $cm^3 \cdot \mu m/m^2 \cdot day \cdot atm$ on PET, 37 $cm^3 \cdot \mu m/m^2 \cdot day \cdot atm$ on OPP, 0.3 $cm^3 \cdot \mu m/m^2 \cdot day \cdot atm$ on OPA, and 1 $cm^3 \cdot \mu m/m^2 \cdot day \cdot atm$ on cellophane for the coatings only.[100] These values, in particular, the CNCs' coating on OPA, are comparable with that of commercialized oxygen barrier EVOH, though lower than those of carboxylated CNFs (Table 4) in the dry state. These results demonstrated that CNCs are therefore also considered to be a promising multifunctional coating for flexible food packaging. It is observed that a lower surface energy of the OPP film resulted in a much higher oxygen permeability, indicating the effect of the interactions between CNCs and substrates. Indeed, surface features of substrates have great influence on the oxygen barrier performance of thin coatings.[109] This implies that a surface treatment or a coupling agent is needed for bonding nonpolar polymers to CNMs for the greatest benefit. The addition of alkylketene dimer to the sodium carboxylated CNF coating was found to reduce moisture sensitivity.[48]

Effect of Surface Charge Strength on Oxygen Barrier Properties of Coated Polymers. Table 6 shows that a coating of TEMPO-oxidized sodium carboxylated CNFs on a 50 μm PET film achieved a barrier permeability of 0.17 for a 1 μm coating[47] and 4 for a 1.5 μm coating.[69] This discrepancy between two studies in the same laboratory might be attributable to the difference in the degree of oxidation as contrasted in Table 6. Indeed, the oxygen permeability of sodium carboxylated CNF-coated PET films decreased with increasing surface charges.[51] CNCs, produced through the ammonium persulfate treatment showed higher charge densities, likely due to the carboxylic groups formed during the process, resulted in a higher oxygen barrier of the coated PET film than CNCs produced by the H_2SO_4 treatment.[110] Plackett et al.[25] also found that the carboxymethylated CNFs-reinforced amylopectin had a lower oxygen permeability than the CMFs-reinforced amylopectin. Such a trend has not been obvious for the neat CNM films. It can be explained that a higher degree of carboxylation or carboxymethylation prior to fibrillation leads to a higher surface charge density, which leads to easier mechanical disintegration and thinner and better-dispersed fibrils in the solvents and on the polymer surface after solvent drying. Thus, the coatings were more uniform and better adhered to the polymer matrix when formed by solution casting, which led to improved oxygen barrier properties for higher oxidized samples coated on films.

Table 6. Characteristics of Sodium Carboxylated CNFs Coated on 50 μm PET Films at 23°C and 0% RH[a]

OP	Coating	Carboxylate	DPv	Density	Reference
0.17	1 μm	1.74 mmol/g	1440	1.47	47
4	1.5 μm	1.5 mmol/g	550	1.43	69
4	1 μm	1.4 mmol/g	400	1.45	51
10	1 μm	1.2 mmol/g	550	1.11	51
107	2 μm	0.8 mmol/g	690	1.10	51
1293	5 μm	0.3 mmol/g	920	1.13	51

[a]OP: oxygen permeability in $cm^3 \cdot \mu m/m^2 \cdot day \cdot atm$, DPv: viscosity-average degree of polymerization.

CNM NANOCOMPOSITES

Barrier Properties of CNM Polymeric Nanocomposites. Because a fully biodegradable packaging material is very attractive, CNMs have been used to reinforce biodegradable polymers and biopolymers with commercial potential such as PLA, PHB, and polysaccharides (starch, hemicellulose, cellulose, and chitosan). The assumptions are that acicular cellulose nanoparticles might be arranged parallel to the surface in the polymer matrix,[17] e.g., formed under the effect of shear flow when extruded, resulting in increased tortuosity, analogous to a mechanism of exfoliated platelets in clay nanocomposites where the platelet normal is coincident with the direction of diffusion.[111,112] They might serve as nucleation agents inducing high crystallinity in the matrix; they might also interact with the polymer matrix such as forming hydrogen bonding and inter-cross-linking through opposite charges. These effects will enhance gas barrier properties. In contrast, CNMs might not be compatible with the matrix resulting in interfacial defects that will adversely affect barrier and mechanical properties.

When CNMs are used as a dispersed phase, it has been shown to lower the oxygen permeability in most polymer systems. The degree of barrier performance improvement depends on the matrix to which the CNM is added and the dispersion of the CNM (Table 7). The oxygen permeability of CNM and hemicellulose composite films was statistically independent of their relative fractions in the films for carboxymethylated CNF reinforced birch xylan films.[113] The addition of 5% CNCs into spruce galactoglucomannan and konjac glucomannan, respectively, did not substantially change oxygen barrier properties (Table 7).[114] Their similar oxygen barrier properties and compatibility between CNMs and hemicellulose probably account for no apparent difference of their blends. The oxygen permeability of CMF/amylopectin films decreased with the CMF loading from 37 $cm^3 \cdot \mu m/m^2 \cdot day \cdot atm$ for a 15% CMFs to 16 for a 100% CMFs because cellulose is generally better than amylopectin in barrier properties.[25] The effect of the addition of CNCs to biodegradable polymers on oxygen barrier properties is not consistent among reported studies. Fortunati et al.[34] reported that a 5% CNC addition to PLA decreased the oxygen permeability to the half of neat PLA; however, Espino-Perez et al.[115] reported the addition of CNCs up to 15% to PLA generally increased the oxygen permeability. Dhar et al.[31] found that CNCs decreased the oxygen permeability of PHB films at the additions of 1% and 2% but increased oxygen permeability at 5% loading with the reported permeability of 172,988, 107,768, and 355,081 $cm^3 \cdot \mu m/m^2 \cdot day \cdot atm$, respectively, in contrast with 302,555 $cm^3 \cdot \mu m/m^2 \cdot day \cdot atm$ for pure PHB film. Comparing these decreased values with the barrier material classifications (Table 2), we can say that the addition of CNCs to PLA, PCL, or PHB did not upgrade their oxygen barrier classifications because these polymers themselves are low or poor oxygen barriers. The improvements are not enough to substantially change this characteristic.

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Table 7. Oxygen and Moisture Permeability of Cellulose/Polymer Nanocomposites

Formulation			OP	Conditions	WVP	Conditions	Ref
100% Bacteria CNCs/80% BCNCs + 20% PEG 900			6.1/3.6	24 °C, 0%	3067/4156	24 °C, 75/0%	75
			52,264/62,769	24 °C, 80%	3067/4156	24 °C, 75/0%	75
Birch Xylan: Carboxymethylated CNFs: Plasticizer (G: Glycerol, M: MPEG, S: sorbitol)		70/30/0	24	23 °C, 50%	1607	23 °C, 50/0%	113
		60/40/0	22	23 °C, 50%	1572	23 °C, 50/0%	113
		50/50/0	19	23 °C, 50%	2436	23 °C, 50/0%	113
		G: 35/35/30	981	23 °C, 50%	3672	23 °C, 50/0%	113
		M: 35/35/30	20,833	23 °C, 50%	8199	23 °C, 50/0%	113
		S: 35/35/30	8	23 °C, 50%	302	23 °C, 50/0%	113
70% CMFs + 30% Sorbitol			5200	23 °C, 80%	14,230	23 °C, 100/50%	124
Spruce galactoglucomannan (SGGM)/95% SGGM + 5% CNCs			700/700	22 °C, 50−75%	1700/2000	22 °C, 54/0%	114
			700/700	22 °C, 50−75%	33,000/37,000	22 °C, 86/32%	114
Konjac glucomannan (KGM)/95% KGM+5% CNCs			800/700	22 °C, 50−75%	3700/2600	22 °C, 54/0%	114
			800/700	22 °C, 50−75%	40,000/40,000	22 °C, 86/32%	114
50% ArabinoXylan + 50% Sorbitol/25% ArabinoXylan + 25% Sorbitol + 50% CNCs			18.2	–	32,870/46,470	37 °C, 100/0%	118,125
Arabinoxylan from wood			16.2	25 °C, 50%	–	–	126
90% ArabinoXylan +10% Sorbitol			324	20 °C, 50−75%	1100	23 °C, 50/0%	127
Polylactic acid (PLA)/ PLA + 5% CNCs			30,500/17,400	25 °C, 0%	898/855	20 °C, 50/0%	34
PLA/PLA + 15%CNCs			25,388/37,644	23 °C, 0%	1901/5622	25 °C, 50/0%	115
75%PLA + 25%PHB/71% PLA + 24% PHB + 5% CNCs			13,300/15,300	RT, 0%	–	–	122
Polycaprolactone (PCL)/ PCL + 5%CNCs			8750/7350	23 °C, 0%	1510/1220	25 °C, 60/0%	64
100% CMFs/67.5% CMFs + 32.5% Oxidized CNCs			91.2/101	25 °C, 50%	3283/2402	23 °C, 50/0%	49
100% CMFs/67.5% CMFs + 32.5% clay			91.2/101	25 °C, 50%	3283/1642	23 °C, 50/0%	49
CMFs/100% CMFs + 50% clay			Not detectable	23 °C, 0%	–	–	128
			48/45	23 °C, 50%	–	–	128
			17,800/3500	23 °C, 95%	–	–	128
Carboxylated CNFs/75% Carboxylated CNFs + 25% clay			5,066/304	23 °C, 50%	6032/4205	23 °C, 50/0%	129
50% CMFs + 50% PVOH/%25 CMFs + 25% PVOH + 50% clay			0.5/0.5	23 °C, 0%	22,056/12,237	23 °C, 100/50%	130
			6,790/190	23 °C, 90%	22,056/12,237	23 °C, 100/50%	130
PVOH/CMFs: PVOH, 1:100			45,000/50,000	23 °C, 90%	32,018/35,575	23 °C, 100/50%	120
Hydroxypropyl methylcellulose (HPMC)	Neat		–	–	10,560	25.3 °C, 82/0%	117
	CMFs	3:0.4	–	–	16,800	25.3 °C, 82/0%	117
	−COONa CNFs	3:0.4	–	–	18,960	25.3 °C, 82/0%	117
	CNCs	3:0.4	–	–	9120	25.3 °C, 82/0%	117
CMFs/Amylopectin, w/w (CNFs/Amylopectin, w/w)*		15:85	37 (34*)	23 °C, 50%	–	–	25
		50:50	20 (13*)	23 °C, 50%	–	–	25
		100:0	16 (13*)	23 °C, 50%	–	–	25

[a]OP: oxygen permeability in $cm^3 \cdot \mu m/m^2 \cdot day \cdot atm$, WVP: moisture permeability in $g \cdot \mu m/m^2 \cdot day \cdot kPa$, MPEG: methoxy polyethylene glycol, PEG: polyethylene glycol, PHB: polyhydroxybutyrate, PHOV: poly(vinyl alcohol). Slash symbol "/" separates two formulations: the base material and CNM composites. In the columns of OP and WVP, the number before "/" is the OP or WVP of the base material, and the number after "/" is the OP or WVP of the CNM composite. In the column of WVP test condition, "/" indicates relative humidity levels across the test film.

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ACS Sustainable Chem. Eng. 2018, 6, 49−70

As shown in Table 7, CNMs improved moisture barrier properties if the matrix was inferior to CNM in moisture barrier properties such as an amylopectin/CMFs system, in which amylopectin was more hygroscopic than the CMFs.[116] The addition of CNM increased the moisture permeability if the polymer matrices were superior to cellulose such as in the cases of the additions of CMFs or sodium carboxylated CNFs to the hydroxypropyl methylcellulose[117] and the carboxymethylated CNFs to the birch xylan.[113] The effect of CNC addition varied: it decreased the moisture permeability of hydroxypropyl methylcellulose and konjac glucomanann but increased those of spruce galactoglucomannans[114] and arabinoxylan.[118] The uses of CNCs as fillers that reduced moisture permeability were reported for PLA,[34] PCL,[64] and PVOH.[119] The suggested mechanism is the increased tortuosity resulting from high crystalline CNCs. However, it would seem somewhat unlikely that the rod shape of CNCs is inherently as efficient for blocking of water vapor permeation as thin platelets like montmorillonite. Other investigations found the addition of CNCs to PLA,[115] to PVOH,[120] and to rubber[121] resulted in increasing the WVP compared to neat polymers. The increase in WVP could also be explained by the high hydrophilic nature of the CNCs in comparison with the neat matrix. The incorporation of epoxy resin to CMFs/PVOH systems did not improve moisture barrier performance.[120] Saxena and Ragauskas[118] found that the incorporation of sulfate half ester CNCs into oat spelt xylan decreased WVP with increasing loadings up to 10% and then increased WVP with increasing loading and that the WVP of the composite at 50% CNC loading was larger than that of the neat xylan. Bras et al.[121] observed that the WVP values increased up to 7.5 wt % of CNCs and then decreased with loadings but were larger than the neat rubber in all loadings. The falloff at higher levels of the reinforcement is sometimes attributed to CNM agglomeration, which might introduce various defects to the composites.[15]

The contradicting results might reflect the effects of different preparation methods of the nanocomposites among the different studies, different interactions of specific CNM and the matrix, and different CNM loadings. Hubbe et al.[15] argues the levels of CNC inclusions in nanocomposites in most investigations would probably be insufficient to increase tortuosity significantly itself but whether the added CNCs aid the reduction of pores, cracks, or other defects in the film or whether they induce the increased crystallinity of matrix plays a large role in determining barrier properties of the composites. The synergistic interaction between the cellulose and the matrix such as hydrogen bonding might aid the formation of defect-free film structure and other factors such as incompatibility and high loading may result in defective films. It should be noticed that the CNM-coated polymers have slightly better moisture barrier performance than polymers themselves.[69,75,100] However, the addition of CNMs as a filler to a biodegradable polymer matrix generally did not upgrade its moisture barrier classification because the capacity of the CNM enhancement or detriment of barrier properties is limited when it is used as a dispersed phase. The permeability is predominantly decided by the matrix. It is probably because that the oxygen and moisture can bypass through the low barrier phases and through defected interfaces.

To improve the interfacial properties between CNMs and the matrix, several modifications have been studied. In one study, the surface modified CNCs did not provoke major changes in barrier performance by adding the mixture of a surfactant/CNCs in 1/1 (w/w) to PLA and PHB[122] and by adding n-octadecyl-isocyanate grafted CNCs to PCL[115] but improved barrier performance by adding the mixture of acid phosphate ester of ethoxylated nonylphenol/CNCs in a 1/4 (w/w) ratio to PLA[34] and by adding the CNC formate to PHBV (poly(3- hydroxybutyrate-*co*-3-hydroxyvalerate) up to 20%.[123] No significant differences were observed in the barrier performance between sulfate half ester CNCs and post-carboxylated CNCs as fillers in PVOH matrix.[119]

Effects of Additives on Barrier Properties of CNM Nanocomposites. Additives are universally used to improve nanocomposites. As fillers, different types of clays have been employed to enhance moisture and oxygen barrier performance. At the low humidity range, the addition of clay did not improve oxygen barrier properties.[49,128] In the high humidity range, the addition of clay upgraded the oxygen permeability of the resulting composites from the poor to medium classification.[49,128] Clay generally reduced moisture permeability of the resulting composites.[49,129] Moreover, Aulin et al. reported a more pronounced effect of a highly processed clay on oxygen and moisture barriers of carboxymethylated CNFs.[131] The improvement is ascribed to the exfoliated silicate platelets oriented parallel to the surface presenting a longer tortuous path for the diffusion of the permeants. However, at a low loading of clay, these improvements are still below the requirements of barrier materials; at a high loading of clay, the transparence, toughness, and flexibility, which are key requisites of many barrier packaging materials, are severely compromised by the clay.[128,132] In addition, from the processing perspective, the difficulty lies in dispersing clay in the matrix industrially to obtain intercalation and exfoliation, which is necessary for clay to perform.[2] The variations of the effect of clay on the barrier properties in the literature might reflect the quality of clay dispersion and clay platelet orientations in CNMs. Highly delaminated clays are necessary to achieve the desired strength and barrier properties.[133] It is concluded that the clay addition enhances the barrier properties but did not solve the problems alone.

Pure CNM films might be too brittle to be processed. It is necessary to plasticize CNM films to increase their flexibility. Plasticizers have two opposite effects on film barrier performance. Plasticizers interrupt interactions between polymer chains and increase the cooperative mobility of polymer chain segments leading to higher gas and moisture permeation locally on the one hand and potentially the reductions of defects in the whole film on the other hand, which improves barrier properties. For example, cellophane, a regenerated cellulose, has an oxygen permeability of 42 $cm^3 \cdot \mu m/m^2 \cdot day \cdot atm$ at 23 °C and 0% RH[134] in comparison with 963 for a glycerol plasticized cellophane at 23 °C and 50%.[135] Methoxy polyethylene glycol 350 increased the oxygen permeability of the plasticized composites by 3 orders of magnitude over the matrix.[113] In another effort, the moisture and oxygen permeability values of plasticized CNM films increased with glycerol and polyethylene glycol contents, but those of the carboxymethylated CNF films plasticized with 10−40 wt % sorbitol were significantly reduced.[113] The advantage of adding sorbitol was also realized in glyoxal-cross-linked spruce galactoglucomannan films[136] and corn hull arabinoxylan films.[137] The literature data suggests that sorbitol is a good plasticizer to reduce the film brittleness without compromising the barrier properties. This improvement might be ascribable to the reduction of defects in the films.

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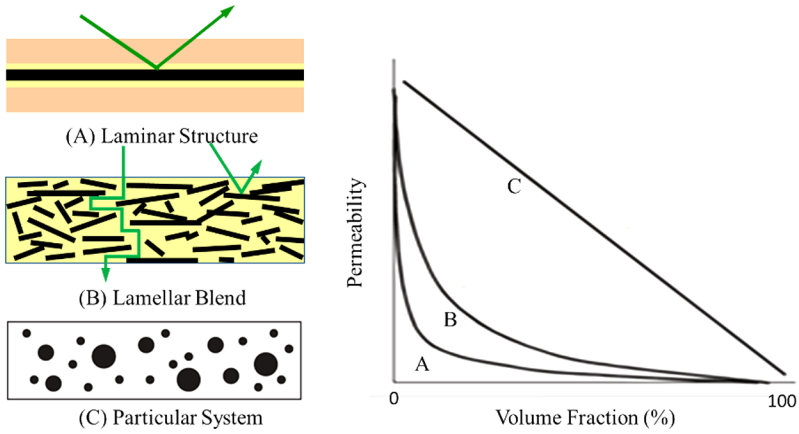

Figure 7. Schematic illustration of the permeability of a blend of a high-barrier material as indicated in black in a low-barrier matrix as a function of the morphology.[2] Adapted with permission from ref 2. Copyright 2003, John Wiley & Sons, Ltd.

Strength reinforcements may be added to improve mechanical properties. The addition of 1−5% w/w PVOH has a very significant improvement on the mechanical properties of CNM composites.[138,139] PVOH promotes the crystallization of the CNC matrix improving its mechanical properties.[140] CNM-PVOH-clay hybrid nanocomposites have synergistically improved oxygen and moisture barrier and thermomechanical properties.[130,141]

STRATEGIES TO IMPLEMENT CNM BARRIER PACKAGING

Methodology of Incorporating Barrier Materials. An ideal barrier packaging should be mechanically robust and thermally stable in addition to being able to protect the content from migration of its components and transmission of gases, moisture, and other harmful agents from the surroundings. The packaging must perform in commercial production as it moves through distribution onto the store shelf and into the consumer's hands. This broad spectrum of requirements of modern packaging explains why no single material can satisfy all the requirements simultaneously but is met practically by using multilayer structures containing a variety of polymers to perform different functions or combinations of functions. The right combination of materials is key to engineering better barrier packaging. Figure 7 schematically illustrates the barrier properties of a structure as a function of the morphology of each component. The multilayer structure where the barrier material is present as a continuous layer (Figure 7A) is more effective than the blend with lamellar or fibrillar morphology (Figure 7B); the latter are better than the particulate system (Figure 7C).[2] It is understandable that the blends have gaps between the barrier particles to form passages for gases to permeate through them, although the increased tortuosity slows gas permeation. This is why many food barrier packaging is multilayer films with thin layers of continuous phase barrier materials. Literature data reviewed have also shown that the continuous CNM phase in the neat and coated films performs better than the dispersed CNM phase in nanocomposites with respect to gas barriers.[16] Moreover, a good oxygen barrier is not usually a good water vapor barrier as shown in Table 2. Therefore, modern commercial packaging materials often consist of up to three to nine layers ranging from 10 to 100 μm in total thickness. Each layer performs a special function: an outer layer providing gloss and rigidity for infographic printing such as PET, a puncture-resistant layer such as oriented PA 6, a barrier layer such as metalized coatings, EVOH, and PVdC, and an inner sealing layer such as PP, PE, or other polyolefin copolymers. These multilayer films serve well for barrier packaging. But consumers are concerned about the waste generated after the use of such packaging. Environmentally conscious consumers are interested in using biobased packaging, which drives various efforts in incorporation of biopolymers into packaging materials.

Design of CNM-Based Structures for Moisture and Oxygen Barriers. The oxygen permeability of petroleum-based polar polymers such as EVOH and PA6 and most natural polymers such as cellophane, protein, starch, and xylan is also strongly influenced by relative humidity as shown in Figures 4 and 5. For example, the oxygen permeability of cellophane increases by a factor 20 when the relative humidity increases from 0% to 50%.[142] The oxygen permeability of wet EVOH is 2 orders of magnitude higher than dry EVOH.[30] Such behavior is typical of hydrophilic polymers. However, these materials are engineered for barrier packaging commercially by sandwiching them with moisture barrier polymers EVOH by PP and/or PE,[143] which both are very poor oxygen barriers as shown in Figure 4, and cellophane typically coated with nitrocellulose or PVdC.[144] These combinations create synergistic effects of both moisture and oxygen permeation resistance and allow heat sealing. The materials containing a xylan layer, a carbohydrate derived from grain husks, are claimed to provide an efficient barrier against oxygen, grease, and odor.[145]

The current paradigm to utilize cellulose in packaging is to coat cellulose with plastic polymers to provide a good barrier to moisture and liquids. Beverage cartons comprise layers of paperboard coated internally and externally with low-density PE, resulting in a carton that is impermeable to liquids and heat sealable; a thin layer of metalized coating may also be included acting as a gas and light barrier.[146] There exist various efforts to coat paper and paperboard with biodegradable polymers and biopolymers to improve target performance.[147,148] Cellophane is conventionally coated with PVdC and nitrocellulose to improve moisture barrier properties.[8] Various multilayer films of regenerated cellulose and other biopolymers have been assessed for barrier packaging of long shelf life food products.[145] NatureFlex 913 of starch/regenerated cellulose laminate film is certified according to the European (EN13432), American (ASTM D6400), and Australian (AS4736) standards for home compostable packaging.[6]

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ACS Sustainable Chem. Eng. 2018, 6, 49−70

The way in which these biopolymers are used may inspire a solution for utilizing moisture sensitive CNMs. A CNM film is different from paper and paperboard in that it acquires transparency and oxygen barrier properties. Several researchers recommended that a laminate structure with a layer of CNMs acting as the oxygen barrier covered with polymer layers acting as moisture resistance should provide a good combination with optimal functions for flexible barrier packaging, for which the transparency, flexibility, and barrier properties are valued.[15,103] Based on these observations, a laminate structure as shown in Figure 8 is a potential solution that combines two polymer

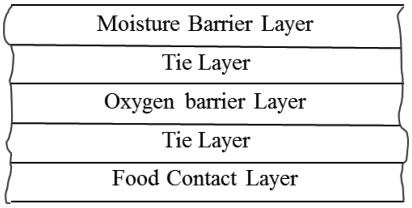

Figure 8. Schematic illustration of a typical transparent multilayer polymer/CNM barrier film with each layer performing a specific function.

layers sandwiching a CNM layer with two tie layers bonding them together. The polymers provide moisture barrier, flexibility, and sealability. The cellulose layer provides oxygen barrier and stiffness. Depending on market needs and marketing strategies, the polymers may be BOPP and PVdC to provide the highest moisture resistance, or PLA and PHA to provide biodegradable films with medium moisture resistance, or modified starch and other moisture-resistance-treated biopolymers to provide compostable films with reasonable moisture resistance. CNMs can also be laminated with other oxygen barrier materials such as polyglycolic acid,[149] EVOH, and PVOH to have a synergistic effect on oxygen permeation. The disadvantages of this system may include the increasing difficulties of processing and recycling. Even though it is protected, such a CNM layer will be very thin and have very little capacity to hold water molecules. So even a miniscule amount of moisture passing into that protected layer could, in principle, cause it to swell and become more permeable.[15] There would be a need to investigate the mechanism and effects of moisture absorption by protected CNM layers leading to a better understanding of their performance in various application environments.

Previous studies have shed valuable light on how effective the sandwich structure of CNM with moisture-resistant polymers is likely to be. A coating, comprising a 10 μm shellac top coat and 3 μm CNF base coat on a sheet of paper, upgraded the moisture barrier performance of the laminate from low grade to high grade classification; it substantially decreased oxygen permeability but remains too high to be considered as a high oxygen barrier material.[26] A dip coating of paraffin wax on CNF films decreased the oxygen permeability from 5571 to 1700 $cm^3 \cdot \mu m/m^2 \cdot day \cdot atm$ at 97.4% relative humidity and the water vapor permeability from 27,750 to 1850 $g \cdot \mu m/m^2 \cdot day \cdot kPa$.[50] A dip coating of beeswax on CNF films performed better in decreasing the moisture transmission rate than a paraffin wax dip coating, which was explained by beeswax's better wettability on cellulose and penetration into surface pores of the CNF films.[150] This study also found that the cooked starch coating on the CNF film decreased the moisture vapor transmission rate, but the addition of starch into the CNF film increased it. PLA and silane coatings on CNCs decreased moisture permeability of the resulting coated films to the level of polymers themselves.[75] These investigations have suggested that sandwiching CNM with high moisture barrier polymers might provide a potential to obtain low moisture and oxygen transmission rates even under high humidity conditions.[69,75,100] A three-layer structure of bio-HDPE (48 μm)/CNF (2 μm)/bio-LDPE (28 μm) decreased the oxygen transmission rate by 77% at 80% humidity compared with the one without a 2 μm CNF layer.[149] These films demonstrated promising oxygen barrier properties for demanding dry food products and modified atmosphere packaging.[151] However, it was not enough to render the film to meet high oxygen barrier classification at high humidity. The three-layer structure maintained the moisture resistance the same level as the polymers.[152] In summary, sandwiching CNM with polymers has demonstrated potential and needs further optimization.

CNM Adhesion in Layered Materials. Because of the incompatibility of hydrophobic polymers such as BOPP and hydrophilic cellulose, it is difficult to bond them intricately. Cellulose polymer compatibility has been improved by hydrophobically modifying CNMs.[153] However, cellulose modifications are typically not cost effective. In the industry practice of fabricating multilayer films, hydrophobic polymer and hydrophilic polymer are typically bonded by an adhesive, called a tie layer, which is essential to create an intricate interfacial phase even when polymers are corona or plasma surface treated. The adhesion occurring at the interfacial region where adhesive come into contact with cellulose and polymer surfaces may be classified as mechanical, adsorption, diffusion, chemical, or combinations of these types.[154] Adhesive molecular structures can be designed to implement select mechanisms to enhance the adhesion between adhesives and CNMs or polymers. It is likely that adhesive should be amphiphilic to accommodate opposite properties of polymers and cellulose. Anhydride-modified polypropylene such as maleic anhydride-grafted polypropylene has been proved to be an outstanding coupling agent between cellulose and polypropylene in wood plastic composites.[155] This type of tie layer can be applied via an extrusion coating process, in which the resin is melted and extruded onto a conveyed flat film on an industrial scale. Production processes of multilayer films are typically continuous processes of coating and laminating, differentiated by the type of adhesive used and how adhesives are applied and cured. Contact angles of water and other probing liquids have been measured with various techniques and used to derive an array of surface energy parameters, which can be used to analyze and identify promising formulations and processing conditions to improve adhesion and to reveal mechanisms of adhesion.[154]

Future Research Needs. Flexible packaging is expected to grow at an annual rate of 4.6% from 2016 to 2025. Stand-up pouches for food and beverage packaging are projected to increase rapidly in the near future.[156] With increasing consumer sustainability consciousness, corporations are looking for ways to increase their product biocontents. These trends may provide an opportunity for CNM-based films because stand-up pouches typically require stiffness (a rigid layer) and an oxygen barrier, for which cellulose is superior to plastics. However, one of the challenges is how to contain cellulose moisture effects. In the current technology, composition with water-resistant polymers represents the best opportunity to utilize CNMs for

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ACS Sustainable Chem. Eng. 2018, 6, 49−70

flexible films that require transparency and good moisture and oxygen barrier properties. The challenge of using biomaterials is to achieve equivalent or comparable technical properties to their petroleum-based counterparts, while ensuring that biomaterials are renewable, biodegradable, and/or compostable in accordance with recognized standards. In the transition time to a future fully biobased economy, a hybrid system of petroleum-based polymers and biopolymers may be marketable and practical, especially when petroleum-based products are still dominant. Using CNMs as oxygen-resistant layers will increase biocontents in barrier packaging materials with a high-volume market. Further, the use of CNMs in the continuous phase takes advantages of hornification in the drying process to form dense structure and avoids the need to distribute CNMs in a polymer matrix. Further research may be directed toward (i) understanding fundamental gas barrier mechanisms and processing/structure/property relations of the CNM phase across multiple length scales, (ii) tailoring morphology, crystallinity, and surface functionality and controlling processing conditions to achieve structures that have optimum nanoparticle packing, pores, and free volume as well as interactions between permeants and polymers, (iii) overcoming moisture effects and achieving more mechanical, chemical, and thermal robustness through hybridizing or compositing with other materials, and (iv) improving adhesion between polymers and cellulosic films using conventional surface treatment techniques such as corona and plasma treatments.

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ACS Sustainable Chem. Eng. 2018, 6, 49−70

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