Strength and Barrier Enhancements of Cellophane and Cellulose Derivative Films: A Review

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Cellulose derivatives, *i.e.* cellulose functionalized in a solvent state with various side groups, are an important source of biomaterials for food packaging. This review considers the following materials: i) cellophane, ii) cellulose acetate, iii) methylcellulose, and iv) carboxymethylcellulose. Mechanical and barrier properties are important for freestanding packaging films as well as for coatings. The potential of the selected cellulose derivatives and cellophane is thus examined from the viewpoint of their tensile properties as well as their moisture and oxygen barrier properties. The capacity of microcrystalline cellulose and nano-sized celluloses to reinforce the films and to help impede gas diffusion is examined for microfibrillar celluloses, nanocrystalline celluloses, and whiskers. Very good oxygen barrier properties have been reported for cellophane. Nanocellulose fillers have regularly been shown to enhance the tensile properties of several cellulose derivatives, but the effects on the water vapor permeability (WVP) have been studied less often.

Keywords: Cellulose derivatives; Cellophane; Cellulose acetate; Methylcellulose; Carboxymethylcellulose; Nanocomposites; Tensile properties; Water vapor permeability; Oxygen permeability; Food packaging

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INTRODUCTION

Cellulose derivatives are a class of natural polymers in which the cellulose is swollen and dissolved using a solvent before further processing to, *e.g.*, films, coatings, or filaments (Sjöström 1993). In the dissolved state, all the hydroxyl groups are accessible to the reactant molecules, and the swollen cellulose structure can be chemically modified to improve the processability and performance for particular uses. The approach is thus different from the surface modification of cellulose fibers, microfibrils, and crystals. Biodegradability, renewability, and worldwide abundance are the main benefits of cellulose as a raw material.

The three hydroxyl groups present on the anhydroglucose unit can be partially or totally reacted with various reagents to form derivatives, such as cellulose esters (*e.g.*, cellulose acetate, cellulose triacetate, and cellulose acetate butyrate) and cellulose ethers (*e.g.*, methylcellulose, hydroxypropyl methylcellulose, ethylcellulose, hydroxyethyl methylcellulose, carboxymethylcellulose, and hydroxyethylcellulose). Several of these modified forms of cellulose are important in food packaging (Allsopp *et al.* 2004), and their applications range from freestanding packaging films to edible films that are soluble in water. Derived celluloses are more resistant to microbial attacks and enzymatic cleavage than native cellulose (Allsopp *et al.* 2004).

Dissolving pulp, a refined bleached pulp that has high cellulose content, is used to manufacture cellulose derivatives and regenerated celluloses. In 2009, 3.6 million tonnes of dissolving pulp was produced worldwide. The production increased by 24% from 1998. Approximately 33% of dissolving pulp is used for derivative markets, such as esters and ethers, and 66% is used in regenerated cellulose markets. Cellulose ester and cellulose ether markets are expected to grow approximately 10% in size, and 40% in value from 2011 to 2015 (Higson and Smith 2011).

Any food packaging material has two functions that take precedence over all others. The packaging should provide sufficient mechanical protection and, at times, structural support to the food product. It should also prevent liquids, gases, and volatiles both from penetrating into or out of the package. The packaging material should have sufficient mechanical properties, and it should act as a barrier against oxygen, water and water vapor, carbon dioxide, light, microbes, and/or grease (Soroka 2009) because barrier properties increase the shelf life of food. In the form of freestanding wrapping films and edible coatings, cellulose derivatives are usually most relevant for packages that come into direct contact with foods (primary packaging). The other packaging functions that are traditionally connected with packaging, such as convenience of usage, information delivery, and sales promotion (Soroka 2009) generally do not require the use of cellulose derivatives. For such purposes, ordinary paper and paperboard can be used.

Edible films have traditionally been the area of use for cellulose derivatives. However, research is being done on blending, layering, or filling cellulose derivatives with other bio-polymers or synthetic polymers to enhance the mechanical and barrier properties, thus strengthening their position in competition against other packaging materials. Another research topic is the expansion of the raw material base for cellulose derivatives. Cellulose derivatives are mature substances with commodity character, but new production methods are being sought, especially for dissolving cellulose.

The following is an overview of the recent research on cellophane and three film-forming, traditional cellulose derivatives in the context of packaging: cellulose acetate (CA), methylcellulose (MC), and carboxymethylcellulose (CMC). Nanocellulose-reinforced cellulose derivatives are also discussed in a separate chapter. Research from approximately the last ten years is covered. The adaptation of these innovations into commercial use is not explored, and therefore patent literature is not included.

In this text, the potential of materials based on functionalized cellulose is evaluated against some commonly used petro-plastics in food packaging, such as the typical moisture barrier polymers high-density and low-density polyethylene (HDPE and LDPE, respectively), and the typical oxygen barrier polymer poly(ethylene terephthalate) (PET). Their tensile and water vapor barrier properties offer a common reference for comparing the properties of cellulose-based, freestanding packaging films, and edible films, even if LDPE and PET are not specifically used as edible films.

CELLOPHANE

The most commonly used cellulose-based food packaging film is cellophane, a versatile, non-plastic film that was invented in 1900. A peak in the number of publications on cellophane can be seen during the 1970s and 1980s. Commercial cellophane packaging films are clear and transparent.

During the manufacturing process for cellophane, cellulose is first derivatized with carbon disulfide and sodium hydroxide to an alkali-soluble sodium cellulose xanthate, commonly known as viscose, which is further dissolved in dilute sodium hydroxide. Dissolving pulps are often used as a raw material. The viscose liquid is extruded into a bath of sulphuric acid and sodium sulphate to reconvert it to solid cellulose. After completing the viscose process, cellulose is termed “regenerated cellulose”. In film form regenerated cellulose is called cellophane. This traditional viscose route generates hazardous byproducts (CS_2 and H_2S) during manufacturing, and alternative solvent systems have been developed to dissolve the cellulose.

Alkali/urea/H_2O (AU), a mixture with a weight ratio of 4.6:15:80.4, has been used successfully for dissolving cellulose (Yang *et al.* 2011). The films prepared from this AU cellulose were found to have superior oxygen barrier properties compared to traditional cellophane. The lowest oxygen permeability (OP) of $3.5 \cdot 10^{-17}$ $cm^3 \cdot m/m^2 \cdot s \cdot Pa$ (0% RH, 23 °C) was achieved for the film prepared from a 6 wt% cellulose solution by regeneration with acetone at 0 °C. The OP of the reference (traditional) cellophane was $5.6 \cdot 10^{-16}$ $cm^3 \cdot m/m^2 \cdot s \cdot Pa$ (0% RH, 23 °C). For comparison, the OP of commercial polyethylene terephthalates (PET) is typically $3.4 \cdot 10^{-14}$ to $5.7 \cdot 10^{-13}$ $cm^3 \cdot m/m^2 \cdot s \cdot Pa$ (0% RH, 24 °C) (The iDES Inc. 2012).

Another method for dissolving cellulose exploits enzymes. Hardwood dissolving pulp can be treated with purified *Trichoderma reesei* endoglucanases, which makes the pulp soluble to alkali (Rahkamo *et al.* 1996). This enzyme-assisted method can be used in an environmentally friendly way for preparing fibers (Vehviläinen *et al.* 2008), films such as cellophane, and membranes with cellulose or cellulose-containing composites in water-based solutions.

The third environmentally friendly approach to dissolve cellulose and produce regenerated cellulose is the so-called N-methylmorpholine-N-oxide (NMMO)-technology (Fink *et al.* 2001). NMMO is produced by the oxidation of the ternary amine N-methylmorpholine with hydrogen peroxide. Dissolving pulp is first dissolved without pretreatment in an NMMO-water mixture. Filtered cellulose solution is then extruded into a precipitation bath, where the cellulose is coagulated. After the process MNNO is recovered.

Improved barrier properties for cellulose have been presented. If cellophane films are esterified on the film surface in a controlled manner with two fatty acids, a decrease in the water vapor permeability (WVP) and the permeability of oxygen, nitrogen, and carbon dioxide is observed (Tomé *et al.* 2011). The fatty acid treatment decreased the WVP by 50% to the value of $8 \cdot 10^{-13}$ $g \cdot m/m^2 \cdot s \cdot Pa$ (0%/75% RH, 26 °C). The OP decreased by 8% to $3.7 \cdot 10^{-14}$ $cm^3 \cdot m/m^2 \cdot s \cdot Pa$ (0% RH, 25 °C). At wet stationary state (equilibrium with 100% RH), the OP is 400 times higher. The OP for LDPE is $2.2 \cdot 10^{-11}$ $cm^3 \cdot m/m^2 \cdot s \cdot Pa$ (0% RH, 25 °C). The films prepared with the AU method described above have considerably better oxygen barrier properties than the surface-modified commercial cellophane films in this experiment.

Recently, the performance of cellophane has been compared to other films for packaging of victuals in several studies (Allahvaisi *et al.* 2009a,b; Kantola and Helén 2001; Somboonkaew and Terry 2010). Cellophane maintains the color of the packed fruit well, but the respiratory product CO_2 accumulates inside the package. Compared to polyethylene and polypropylene, cellophane provided poor protection against tobacco beetle contamination of the packed food. The protection against the penetration of other insect species was better.

Cellophane has been rendered antibacterial by absorbing nisin onto the film (Guerra *et al.* 2005). Nisin is a polycyclic antibacterial peptide used as a food preservative. The bioactive cellophane wrap that contained 0.62 μg/cm^2 of nisin reduced the growth of the total aerobic bacteria in fresh veal meat by about 30 times during 12 days of storage at 4 °C compared to a non-treated cellophane wrap.

CELLULOSE ACETATE

Cellulose acetate (CA) is a general term for a variety of acetate esters of cellulose, and it was the raw material for one of the earliest commercially produced synthetic fibers (Allsopp *et al.* 2004). Cellulose acetate is widely used in food packaging as a rigid wrapping film, along with cellulose diacetate and cellulose triacetate. These materials have also been used extensively in other fields, such as membranes (Ren *et al.* 2008). In cellulose triacetate, at least 92% of the hydroxyl groups of the cellulose molecule are esterified (Doelker 1993). Cellulose diacetate (CDA) has, on average, two acetate groups in each anhydroglucose unit.

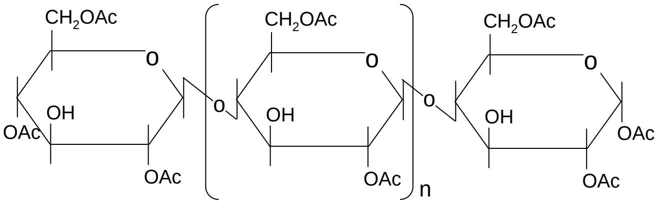

Fig. 1. Cellulose diacetate; Ac = $-COCH_3$

The tensile yield strength of generic commercial CA is 41 MPa to 87 MPa (23 °C, ISO 527-2), and the elastic modulus is 1.9 GPa to 3.8 GPa (23 °C, ISO 527-2). The WVP of vinyl-coated, freestanding CA films for packaging is $1.1 \cdot 10^{-12}$ to $1.7 \cdot 10^{-12}$ $g \cdot m/m^2 \cdot s$ Pa (22 μm, 90% RH, 38 °C) (The iDES Inc. 2012). Casted CA dense membranes have an OP of $3.7 \cdot 10^{-12}$ $cm^3 \cdot m/m^2 \cdot s$ Pa (20 °C, 0% RH) (Nakai *et al.* 2005). Commercial freestanding CA films are optically clear, printable, and available in different thicknesses.

Recent works on cellulose acetate in food packaging fall into the field of active packaging. CA films can be rendered antioxidant by adding L-lysozyme and L-tyrosine, which are naturally occurring antioxidants (Gemili *et al.* 2010). A more exotic type of active packaging is a film that reduces the bitterness of food. For this purpose, fungal-derived naringinase was immobilized on CA (Scares and Hotchkiss 1998). The films reduced the amounts of naringin and limonin that are the principle bitterness components of citrus juices. CA films have been made antimicrobial by adding the potassium salt of sorbic acid (potassium sorbate) (Uz and Altinkaya 2011), lysozyme (Gemili *et al.* 2009), or sodium proprionate (Soares *et al.* 2002).

Antimicrobial packaging materials affect the growth of pathogens in food, as the active agent is slowly released from the film and dissolved onto the surface of the food through direct contact. The aim is to extend the shelf life of the food product. The release rate of the active agent is thus critical, and several techniques can be used to achieve a controlled release. The porosity of the film is an important factor. Phase inversion covers a range of techniques for preparing polymer films with controlled morphology and permeability (Ren *et al.* 2008). CA films have been prepared by the dry phase inversion technique (Uz and Altinkaya 2011). Films with different porosities were created by changing the initial casting composition, wet casting thickness, and drying temperature. The degree of porosity in turn affected the crystallization of the antimicrobial agent (potassium sorbate) during drying. In dense films, the degree of crystallization was low. The release rate of potassium sorbate was controlled by the dissolution of the emerged crystals. The entrapping behavior of the active agents into pores of the film is specific to the particular molecule (Gemili *et al.* 2010). The release direction can be controlled by asymmetric films, where one side is more dense than the other (Gemili *et al.* 2009). The release kinetics of the active agent can also be manipulated, by changing the chemical linking of the active agent into the matrix. In multiple layer structures, some layers can act as barriers, while others contain the active agent.

CA can be used in combination with other polymers. Aluigi *et al.* (2008) recovered keratin from wool waste and created a keratin-filled translucent CA composite film that is suitable for compostable packaging. Suvorova *et al.* (2000) reported a study where cellulose diacetate (CDA) was mixed with potato or corn starch. The mixture was plasticized with triacetylglycerol and hot-molded into films. Potato starch formed more viscous composites with CDA than corn starch.

METHYLCELLULOSE

Methylcellulose (MC) is a simple, non-naturally occurring polymer, where one or several of the hydroxyl groups (-OH) in an anhydroglucose unit are replaced by a methoxide group (-OCH_3). The other two hydroxyl groups in the sugar unit can be replaced by, for example, an ethyl (-OC_2H_5) or a hydroxypropyl (-$OCH_2CH(OH)CH_3$) group, and the corresponding compound is called methylethylcellulose (MEC) or hydroxypropyl methylcellulose (HPMC). This section focuses on the cellulose ether methylcellulose.

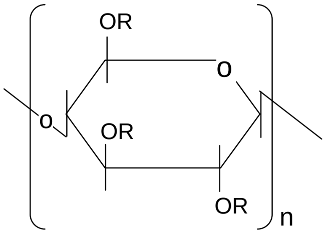

Fig. 2. Methylcellulose; R = –H or –CH_3

MC is soluble in cold water when the degree of substitution is within the range 1.4 to 2.0 (Sjöström 1993). It is non-toxic and forms continuous, flexible, transparent, tasteless films that have good oxygen barrier properties (Mura *et al.* 2011), but it is a poor barrier against water vapor. MC can be used as an edible film or coating, and as a component to modify the mechanical and barrier properties of layered or blended composites for packaging. MC has a wide range of uses other than packaging film: it acts as a thickener, emulsifier, binder, and a water-containing substance in cosmetics, food, pharmaceuticals, and construction materials.

Natural mono-biopolymer films have relatively poor mechanical and water vapor barrier properties compared to traditional petroleum-based polymeric packaging films, and any enhancements of these properties are of great interest. Improvements in barrier and mechanical properties are sought by compounding MC with other polymers. The oxygen barrier properties in starch-whey protein MC films could be predicted by the relative amounts of the components and their OTR (Yoo and Krochta 2012). Properties prediction, however, is not always possible due to the complex interactions between the components. MC was found to have a reinforcing effect due to its relatively high tensile strength and elastic modulus, but the observed improvements in those properties did not reflect the relative amounts of the components in the mixture.

Mechanical Properties

MC is a film-forming substance, and it enhances most mechanical properties in blends (Debeaufort *et al.* 2000) containing, for example, proteins, other polysaccharides, or lipids. The mechanical properties increase monotonically as a function of the MC content in the blends, but at the same time the resistance to water vapor penetration decreases (Zuo *et al.* 2009). Table 1 shows methods to enhance the tensile properties, and the values obtained for films containing MC in recent studies. The elastic modulus is seldom reported.

Table 1. Methods for Enhancing Tensile Properties of MC-Containing Films

		Reference				**Film**				
Components in Film	**Plasticizer**	**E [GPa]**	**σ_b [MPa]**	**ε_b [%]**	**Studied Factor(*)**	**E [GPa]**	**σ_b [MPa]**	**ε_b [%]**	**Test Conditions (T, RH, v)**	**Reference**
MC, corn starch (CS), whey protein isolate (WPI)	Glycerol (Gly)	--	--	--	Relative amounts (highest tensile strength at CS:MC:WPI 2:2:0 and CS-MC-WPI: Gly 3:1)	0.22	8.01	38	ASTM D882-91, 23°C, 50% RH, --	(Yoo and Krochta 2012)
MC	Glycerol	--	31	67	Ultrasound treatment	--	59	81	ASTM D882-02, 83%/min	(Ahmadi *et al.* 2011)
Glucomannan, MC, pectin	--	--	77	14	Gelatin (film-forming agent)	--	68	7	ASTM D882-98, 2%/min	(Chambi and Grosso 2011b)
Glucomannan, MC, pectin, gelatin (polysaccharides: gelatin 9:1)	--	--	46	6	Surfactant (sucrose ester)	--	55	14	ASTM D882-98, 2%/min	(Chambi and Grosso 2011a)
MC	Glycerol	--	17	47	Olive leaf extract oil	--	23	27	ASTM D638M, --	(Ayana and Turhan 2009)
MC: gluten (1:1), (annealing at 100 °C)	Glycerol	0.26	14	29	Annealing at 125°C	0.28	16	33	20°C, 26% RH, 50%/min	(Zuo *et al.* 2009)

σ_b = tensile strength at break, ε_b = strain at break
(*) The component added to the mixture, treatment, or manufacture method that affects the moisture permeation properties. The highest strength achieved in the experiment and corresponding mechanical parameters are given.

Increasing the amount of glycerol reduces the tensile strength, increases the elongation at break, and reduces the oxygen barrier (Yoo and Krochta 2012). The addition of lipids as a moisture barrier usually leads to a decrease in mechanical properties (Quezada Gallo *et al.* 2000). Unlike lipids, amphiphilic surfactants may blend better into the polysaccharide-containing, film-forming solution. The addition of gelatin to polysaccharide films improves the moisture barrier only at a certain pH and dosage (see Table 2) and reduces the mechanical properties in all cases (Chambi and Grosso 2011b). MC films, filled with microcrystalline cellulose at a loading level of 0.25% and above, improved the puncture strength by 117% and simultaneously decreased the water vapor permeability (WVP) by 26% (Khan *et al.* 2010).

Water Vapor Barrier Properties

Table 2 shows the WVP values of recently studied MC-based polymer blends and the methods to reduce the WVP. The WVP of MC films increases significantly as a function of the MC to the total polymer ratio in the blend, and as a function of relative humidity (Zuo *et al.* 2009). The intended application for MC films has almost exclusively been edible films.

Table 2. Methods for Enhancing Water Vapor Permeation Properties of Methylcellulose-Containing Films

			Reference		**Film**			
Components in Film	**Filler**	**Plasticizer**	**WVP [g·m/m^2·s·Pa]**	**Studied Factor**	**WVP [g·m/ m^2·s·Pa]**	**Change [%]**	**Test Conditions (T, RH)**	**Reference**
LDPE	--	--	9.14E-13	--	--	--	--	(García *et al.* 2009b)
HDPE	--	--	2.31E-13	--	--	--	--	(García *et al.* 2009b)
Poly(capro-lactone)	--	--	1.7E-11	MC, vegetable oil, surfactant Tween® 80 (plasticizer glycerol) in layered composites	3.0E-11	72	25 °C, 0%/60% RH	(Khan *et al.* 2012)
MC	--	Glycerol	4.8E-11	Ultrasound treatment	3.2E-11	-32	25 °C, 0%/100% RH	(Ahmadi *et al.* 2011)
MC, glucomannan, pectin, gelatin	--	--	8.3E-11	Surfactant	3.3E-11	-60	ASTM E96-95, 0%/75% RH	(Chambi and Grosso 2011b)
MC, vegetable oil, Tween® 80	--	Glycerol	7.3E-11	NFC filler	5.3E-11	-27	25 °C, 0%/60% RH	(Khan *et al.* 2010)
MC, vegetable oil, Tween® 80	NFC	Glycerol	6.8E-11	Gamma radiation	4.9E-11	-29	25 °C, 0%/60% RH	(Khan *et al.* 2010)
MC	--	Glycerol	2.1E-11	Olive leaf extract oil	1.4E-11	-33	25 °C, 0%/53% RH	(Ayana and Turhan 2009)
MC	--	--	3.5E-11	Stearic acid	1.3E-11	-63	25 °C, 0%/-- RH	(Ayranci and Tunc 2001)

MCC = microcrystalline cellulose

A recent study aimed to identify a biodegradable polymer candidate that could replace petroleum-based packaging materials. The useful properties of both MC and polycaprolactone (PCL), a thermoplastic biodegradable polymer, can be synergistically utilized by compounding them in a layered composite. PCL significantly lowers the WVP compared to lean MC ($7.3 \cdot 10^{-11}$ $g \cdot m/m^2 \cdot s \cdot Pa$), and MC increases the puncture resistance compared to lean PCL (Khan *et al.* 2012).

Chitosan-containing MC Films

Chitosan (CH), a polysaccharide derived from crustacean chitin, is of particular interest in food packaging. The second most abundant polysaccharide, CH is non-toxic, biocompatible, biodegradable, and cationic. Its antimicrobial activity against a large spectrum of bacteria and low toxicity toward mammalians has been known since the 1970s (Kong *et al.* 2010; Möller *et al.* 2004). The biggest drawback to utilizing chitosan is its cost.

CH has been blended with MC in binary blends (Cooksey 2005; García *et al.* 2009a; García *et al.* 2004; Khan *et al.* 2011; Mura *et al.* 2011; Pinotti *et al.* 2007; Sangsuwan *et al.* 2009; Vargas *et al.* 2011; Vargas *et al.* 2009; Yin *et al.* 2006), and in ternary blends with MC and poly(vinyl alcohol) to create packaging materials and edible films and coatings (Sugantha Kumari *et al.* 2012).

CH has been shown to increase the elastic modulus and tensile strength of the MC films (García *et al.* 2009a; Pinotti *et al.* 2007) due to its rigid character. MC brings high deformability to the blend due to its elongation at break value of 12.7%, *vs.* 3.9% for CH. The addition of CH has been seen to increase the solubility of the films in water (Mura *et al.* 2011) and decrease the WVP of the composite (García *et al.* 2009a; Khan *et al.* 2011). In some studies, the WVP of pure MC and CH have been essentially the same; $7.55 \pm 0.60 \cdot 10^{-11}$ $g \cdot m/m^2 \cdot s \cdot Pa$ and $7.24 \pm 0.81 \cdot 10^{-11}$ $g \cdot m/m^2 \cdot s \cdot Pa$, respectively (Pinotti *et al.* 2007). The mixtures did not have differing values, which can be understood as proof of the compatibility of the polymers. Treating the MC-CH films with an electrical field during drying decreased the WVP values and rendered the film structure more ordered (García *et al.* 2009a).

CH-containing MC can also act as a matrix in a composite and silica nano-particles have been used as filler (Mura *et al.* 2011). The films with a composition of CH:MC 50:50 and silica particles at a loading level of 1 w/v% showed improved tenacity (strength) values of 14,000 g, compared to 6000 g for non-filled composite in a dynamometric analysis.

Antimicrobial, CH-containing MC solutions inhibited the growth of *Listeria monocytogenes*, a virulent food-borne bacterium causing listeriosis (Cooksey 2005). Vanillin has been used as an antimicrobial agent in CH-MC-based films (Sangsuwan *et al.* 2009). The temperature, initial vanillin concentration in the film, and pH affected the release of the vanillin into food products. The diffusion coefficients followed the Arrhenius law.

Antimicrobial MC films containing no chitosan have been prepared with olive leaf extract (Ayana and Turhan 2009). The films contained glycerol and 0.5 to 3 w/v% of olive leaf extract (OLE), which contains physiologically active polyphenols. The OLE increased the tensile strength, but reduced the elongation at break and reduced the water vapor permeation and the growth of *Staphylococcus aureus* in cheese. Cinnamaldehyde, which is obtained from cinnamon bark, eugenol (Sanla-Ead *et al.* 2011), which is extracted from essential oils such as clove oil, and carvacol (Tunc and Duman 2011) have also been used as leaching antimicrobial agents in the MC matrix.

CARBOXYMETHYLCELLULOSE

Carboxymethylcellulose (CMC) is prepared by an alkali-catalyzed reaction with chloracetic acid ($ClCH_2CO_2H$), in which some of the hydroxyl groups of the glucopyranose units in cellulose are replaced by carboxymethyl groups. CMC absorbs moisture, dissolves easily in cold water, shows thermal gelatinization, and forms films. CMC finds its uses as a viscosity modifier, thickener, water retention agent, or a structural or adhesive component in various applications. Edible film is a common packaging-related application.

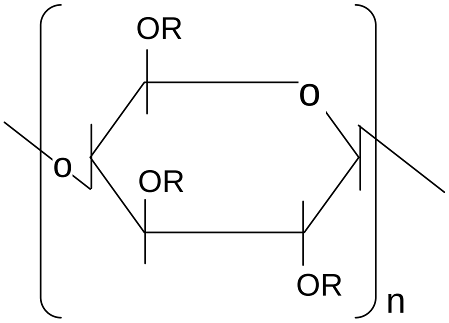

Fig. 3. Carboxymethylcellulose (CMC); R = –H or R = $–CH_2CO_2H$. CMC often refers to sodium carboxymethylcellulose (NaCMC) where the substituent is R = $–CH_2COO^- Na^+$.

Recently studied agricultural waste materials and alternative cellulose sources for preparing CMC include durian rind (Rachtanapun *et al.* 2012) and the invasive, weed-like tree *Mimosa pigra* (Rachtanapun and Rattanapanone 2011).

All of the CMC films surveyed in this study were prepared by suspension casting. CMC is first dispersed in the solute, often water, mechanically stirred, and sometimes sonicated. Thereafter, fillers and other additives are added. Then the films are cast onto a suitable flat surface such as a cellulose acetate sheet, a cellophane or acrylic plate, or a Petri dish. Emulsification can be used to incorporate hydrophobic lipids into hydrophilic CMC blends (Cheng *et al.* 2008).

CMC has been studied in combination with polymers such as chitosan, gelatin, starch, glucomannan, sodium caseinate, pullulan, PVA, polyvinylamine, and various other substances, such as sunflower oil and oleid acid. Sometimes the interaction between CMC and the copolymer(s) is identified as cross-linking, such as dialdehyde-CMC (DCMC) in gelatin-based films (Mu *et al.* 2012) or CMC in starch films (Ghanbarzadeh *et al.* 2011; Li *et al.* 2008). Cross-linking enhances the mechanical and barrier properties of the composites against water vapor or UV light.

CMC has recently been studied as a hydrogel polymer. Dry polymeric hydrogels are considered biodegradable alternatives to petro-plastic food packaging materials (Roy *et al.* 2012). Blend films prepared with synthetic polyvinylpyrrolidone (PVP) and CMC by solution casting are transparent and flexible, and have a tensile strength of 1.42 GPa. The films maintained their elastic properties for two weeks in a compost bed biodegradation experiment. The films are hygroscopic and will absorb the moisture released by packed foods such as fruits and vegetables.

Mechanical Properties

CMC, like other cellulose-based polymers and polysaccharides, is often used as a structural polymer or reinforcement in a film. The film-forming capabilities are due to the long chain length of the CMC molecules. As for other cellulose-based materials, the mechanical properties of CMC-containing films are lessened with increasing moisture content (Feng *et al.* 2006).

Table 3. Methods for Enhancing Tensile Properties of CMC-Containing Films

			Reference				**Film**				
Components in Blend/ Composite	**Filler**	**Plasticizer**	**E [MPa]**	**$\sigma\varepsilon_b$ [MPa]**	**ε_b [%]**	**Studied Factor**	**E [MPa]**	**σ_b [MPa]**	**ε_b [%]**	**Test Conditions (T, RH, v)**	**Reference**
CMC (20g cellulose/100 mL NaOH) (*)	--	--	--	141	2.3	NaOH concentration of etherification (30g/100mL)	--	256	2.2	27°C, 65% RH, 0.3%/s (ASTM D882)	(Rachtanapun *et al.* 2012)
PVP, CMC, PEG, agar (*)	--	Glycerin	1000	--	--	Proportions of components (best results PVP:CMC 1:4)	1420	21	10	25°C, 58% RH, 0.8%/s	(Roy *et al.* 2012)
Gelatin (*)	--	Glycerol	--	12	4	Adding of dialdehyde-CMC (cross-linking agent)	--	15	3	25°C, 50% RH, 6.7%/s	(Mu *et al.* 2012)
CMC, murta leaf extract	MMT	Glycerol	0.5	17	55	Adding filler	3	26	33	--, --, 1%/s (ASTM D882-91)	(Gutiérrez *et al.* 2012)
Sodium caseinate	MCC	Glycerol	171	4.7	24	Adding filler (3wt%)	310	6.6	16	23°C, --, 10mm/min (ASTM D1708-93)	(Pereda *et al.* 2011)
CMC	--	Glycerol	117	3	3.6	Addition of cashew tree gum	710	5.4	0.8	-- , --, --	(de Britto *et al.* 2012)
CMC	Chitosan nano-particles	--	408	5	6	Particle size of filler (highest σ_b with the size 110nm)	320	32	8.1	25° C, 34% RH, 0.8%/s	(De Moura *et al.* 2011)
CMC	--	Glycerol	--	17.6	6.6	Potassium sorbate conc. (active agent)	--	8.8	19	--, '--, 0.4%/s	(Sayanjali *et al.* 2011)
Cassava starch	--	Glycerol	--	2	85	Adding CMC (100% CMC)	--	24	30	25°C, 54% RH, 1.7%/s	(Tongdeesoontorn *et al.* 2011)
CMC, Tween 80 (emulsifier)	--	Glycerol	78	4.8	28	Adding oleic acid	22	4.7	78	25°C, 55% RH, 1.7%/s	(Ghanbarzadeh and Almasi 2011)
CMC, starch, citric acid (cross-linker)	MMT	Glycerol	--	9.8	64	Adding filler (7% MMT)	--	28	18	21°C, 55% RH, 0.17%/s	(Almasi *et al.* 2010)
CMC, glucomannan, potassium hydroxide	--	Moisture	3600	69	9	Palm olein, and moisture content	3100	53	13	21°C, 40% RH, 0.2%/s	(Cheng *et al.* 2008)

The highest strength achieved in the experiment and corresponding mechanical parameters are given. E = elastic modulus, σ_b = tensile strength at break, ε_b = strain at break, MMT = montmorillonite, MCC = carboxymethylated microcrystalline cellulose
(*) The reference includes the studied additive, and the lowest tensile strength observed in the test is given as reference.

The concentration of alkali during the functionalization of cellulose has a direct effect on the tensile properties of CMC films (Rachtanapun *et al.* 2012; Rachtanapun and Rattanapanone 2011). The alkali concentration affects the degree of substitution of the CMC molecules. The more carboxymethyl groups there are in the cellulose molecule, the stronger the CMC film is, due to strong intermolecular forces. At high alkali concentrations, sodium glycolate is formed, which reduces the strength properties.

Table 3 presents reported results on the tensile properties of CMC-containing films. In addition to using CMC in blends, CMC was filled with clay, microcrystalline cellulose, and chitosan. If the filler is well dispersed in the polymer matrix, an improvement in the mechanical properties is usually observed. Typically, the tensile strength and the E-modulus are increased, and the strain at break is reduced. Filling has other effects as well, *e.g.*, clay filler reduces the solubility in water as well as the moisture sensitivity of CMC-starch films.

Glycerol is a regularly used plasticizer in CMC-based films, as can be seen in Table 3. Increasing the amount of glycerol typically increases the ductility of the film significantly, but also leads to a decrease in the tensile strength and the modulus of elasticity.

Water Vapor Barrier Properties

CMC may reduce the WVP of the composite, depending on the other polymers included in it, such as for a starch/CMC material (Ghanbarzadeh *et al.* 2010). However, CMC films are generally permeable to water vapor, and several approaches have been tested to reduce their permeability. Lipids are among the potential additives that increase the barrier to water vapor in hydrophilic films. Increasing the mass fraction of lipids reduces the WVP of CMC films but also decreases the mechanical properties of the films. This behavior was observed, for example, with oleic acid in CMC films and palm olein in CMC/glucomannan blend films (Cheng *et al.* 2008; Ghanbarzadeh and Almasi 2011).

Table 4 shows methods for affecting the WVP of CMC films and the minimum WVP reached in recent works. The minimum WVP and the maximum tensile strength do not usually coincide. The preparation method, type, and amount of the CMC component in the blend can slightly reduce the WVP value, but greater reductions are achieved by using inorganic or organic fillers.

The degree of substitution (DS) of CMC affects the hydrophilicity of the film, which in turn is directly proportional to the WVP of the CMC films (Rachtanapun *et al.* 2012). At a certain alkaline concentration during the CMC preparation, the DS reaches its maximum, which coincides with the maximum permeability to water vapor.

Oxygen Barrier Properties

A non-cellulosic hydrolysate has been prepared from the non-purified wastewater of a wood pulping process (Edlund *et al.* 2010). The hydrolysate contained oligo- and polysaccharides and lignin. When mixed with CMC, homogeneous films or coatings with very low oxygen permeability can be created. The lowest OP reached was $9.3\cdot10^{-15}$ $cm^3\cdot m/m^2\cdot s\cdot Pa$ (23 °C, 760 mmHg) for a CMC/hydrolysate- (mixing ratio 1:1) coated PET. The OP of uncoated PET was $1.7\cdot10^{-13}$ $cm^3\cdot m/m^2\cdot s\cdot Pa$ (23 °C, 760 mmHg). A good oxygen barrier material has an OP smaller than $1.2\cdot10^{-13}$ $cm^3\cdot m/m^2\cdot s\cdot Pa$.

Table 4. Methods for Enhancing the Water Vapor Barrier of CMC-Containing Films

			Reference		**Film**			
Components in Blend/ Composite	**Filler**	**Plasticizer**	**WVP** $[g\cdot m/m^2\cdot s\cdot Pa]$	**Studied Factor(*)**	**WVP** $[g\cdot m/m^2\cdot s\cdot Pa]$	**Change [%]**	**Test Conditions (T, RH)**	**Reference**
CMC (50g/100mL NaOH)	--	--	WVTR 217g/d·m^2	NaOH concentration of etherification (60g/100mL)	WVTR 205g/d·m^2	-6	25°C, 0%/ 75% RH	(Rachtanapun *et al.* 2012)
Gelatin	--	Glycerol	1.80E-10	Adding dialdehyde-CMC (cross-linking agent)	1.50E-10	-17	20°C, 0%/100% RH	(Mu *et al.* 2012)
CMC, sunflower oil	--	Glycerol	1.26E-10	Murta leaf extract (antioxidant)	1.17E-10	-7	25°C, 0%/ 75% RH	(Ramírez *et al.* 2012)
CMC, murta leaf extract (active agent)	MMT	Glycerol	1.15E-10	Adding filler	5.00E-11	-57	20°C, 0%/ 75% RH	(Gutiérrez *et al.* 2012)
Sodium caseinate	MCC	Glycerol	8.70E-10	Adding filler	9.90E-10	14	18.5°C, 100%/73.5% RH	(Pereda *et al.* 2011)
CMC	Chitosan nano-particles	--	3.11E-07	Particle size of filler	1.81E-07	-42	25°C, 100%/ 0% RH	(De Moura *et al.* 2011)
CMC	--	Glycerol	1.37E-11	Potassium sorbate conc. (active agent)	8.74E-11	540	25°C, 0%/ 97% RH	(Sayanjali *et al.* 2011)
CMC, Tween 80 (emulsifier)	--	Glycerol	2.57E-10	Adding oleic acid	1.70E-10	-34	25°C, 0%/ 97% RH	(Ghanbarzadeh and Almasi 2011)
CMC, glucomannan, potassium hydroxide	--	Moisture	1.53E-11	Adding palm olein	1.19E-11	-22	30°C, 0%/ 22% RH	(Cheng *et al.* 2008)

(*) Component added to the mixture, treatment or manufacture method which affects moisture permeation properties.

The mechanical properties of the pure CMC/hydrolysate films were poor. Likewise, free-standing blend films prepared with CMC and hemicellulose (*O*-acetyl-galactoglucomannan), which was extracted from wastewater from a mechanical wood pulping process also had a low OP value of $1.5\cdot10^{-14}$ $cm^3\cdot m/m^2\cdot s\cdot Pa$ (Hartman *et al.* 2006). A plasticizer was needed to achieve sufficient film flexibility. Sorbitol achieved lower OP values than glycerol.

CMC in Active Packaging

An active packaging film carries property-changing agents that can be antimicrobial, antioxidant, or affect the flavor or other properties of the packed food. In general, the added compounds affect the barrier and mechanical properties of the packaging film due to chemical interactions between the polymer and the active compound.

Potassium sorbate has been studied as an antimicrobial agent in CMC films (Sayanjali *et al.* 2011). It provides the desired antimicrobial effect, but weakens the polymer structure. Water extracts from different types of murta leaves are antioxidant solutions from nature (Bifani *et al.* 2007; Gutiérrez *et al.* 2012; Ramírez *et al.* 2012). Murta is an evergreen shrub native to South America. The extracts give the CMC films a yellowish color. In addition to the antioxidative effect, the solids present in the extract may slightly reduce the WVP of the films, but significant reductions in the WVP are obtained by fillers. Murta extract plasticizes the CMC-matrix and thus reduces oxygen and CO_2 permeability. CMC itself has acted as an antioxidant agent and a scavenger of free oxygen radicals, both in whey protein and calcium caseinate-containing films (Tien *et al.* 2001).

NANOCELLULOSE-FILLED CELLULOSE DERIVATIVES

Nanocelluloses

If a cellulose particle has at least one dimension in the nanometer scale (1 nm to 100 nm), it is called nano-sized cellulose or nanocellulose. The other two dimensions can range from nanometers up to tens of micrometers. Nanocelluloses are divided into different classes, depending on the size and composition of the particles. Typically, a division into three classes is made of: i) individual microfibrils and microfibrillar (or microfibrillated) cellulose, ii) cellulose nanocrystals (CNC) and crystal aggregates, and iii) bacterial nanocellulose (BNC or BC) produced by bacterial synthesis. The nomenclature concerning nanocelluloses varies. Microfibrillated cellulose (MFC) may also be called nanofibrillar or nanofibrillated cellulose (NFC). Crystalline, straight cellulose particles are sometimes called nanorods, whiskers, nanowires, or cellulose nanocrystals. The typical size ranges of these particles are given in Table 5.

Table 5. Dimensions of Nano-sized Cellulose Types*

Nanocellulose Type	Diameter (d) (nm)	Length (L) (nm)	Aspect ratio (L/d)
Microfibril, an individual stable 'component' in a plant fiber	2-10	>10000	>1000
Microfibrillated cellulose (MFC)	10-40	>1000	100-150
Cellulose nanocrystal (CNC)	2-20	100-600	10-100
Microcrystalline cellulose (MCC)	>1000	>1000	~1

*Siró and Plackett 2010

It is typical of nano-sized cellulose materials that fibrils and crystals remain attached at least to some extent. MFC and NFC samples contain aggregates of individual microfibrils. A microfibril is a thread-like bundle of cellulose chains laterally stabilized by hydrogen bonds. The diameter of a microfibril is usually 2 nm to 10 nm, with a length up to several tens of microns. Several reviews are available on nanocelluloses in the literature (Hubbe *et al.* 2008; Klemm *et al.* 2011; Siró and Plackett 2010). Microcrystalline cellulose (MCC) contains individual crystals (CNC) or crystal aggregates, and its dimensions are in the micrometer scale, as the name suggests. In the following, cellulose derivative films having MCC as reinforcement fillers or additive are included.

The addition of nano-sized cellulose to a matrix is usually motivated by the modification of the stress-strain behavior of the matrix material. Certain unfilled biopolymers might show, for example, brittle failure, low strain at break, or inadequate tensile strength or elastic modulus. Reinforcing them with nanocellulose offers engineering possibilities concurrent to strength improvement, such as decreasing the oxygen permeability of the composite. Highly crystalline cellulose nanocrystals generally have the capacity to enhance the moisture barrier properties and decrease WVP

(Bilbao-Sáinz *et al.* 2011; George and Siddaramaiah 2012; Sanchez-Garcia and Lagaron 2010; Saxena *et al.* 2011).

Nano-sized cellulose can be used as filler in a cellulose derivative matrix. When using a water-soluble cellulose derivative like MC or CMC as a matrix, both of the phases are intrinsically polar, and thus compatible. Cellulose derivatives that are soluble in organic solvents, such as CA and cellulose acetate butyrate (CAB), have also been used as matrix material.

Mechanical Properties

MCC has been used as a reinforcement filler in hydroxypropyl methylcellulose (HPMC) (Bilbao-Sáinz *et al.* 2010; Dogan and McHugh 2007), cellulose acetate butyrate (CAB) (Petersson and Oksman 2006), and carboxymethylcellulose (CMC) (Choi and Simonsen 2006). Whiskers have been used as filler in HPMC (Bilbao-Sáinz *et al.* 2011), CAB (Ayuk *et al.* 2009; Petersson *et al.* 2009; Siqueira *et al.* 2011), and in CMC (Choi and Simonsen 2006). MFC has been used as a filler in cellulose acetate (CA) (Lu and Drzal 2010), and NFC has been used as a filler in hydroxyethylene cellulose (HEC) (Sehaqui *et al.* 2011) and hydroxypropylcellulose (HPC) matrices (Johnson *et al.* 2009). BC nanocrystals have been used as a filler in CAB matrix (Grunert and Winter 2002; Roman and Winter 2006). Natural hemp and sisal fibers have been coated with BC, and the resulting fibers have been used to fill a CAB matrix (Juntaro *et al.* 2007).

All the studies mentioned above report enhanced tensile properties. Nanowhisker addition (12 wt%) increases the elastic modulus by 83% and the tensile strength by 70% in CAB composites (Siqueira *et al.* 2011), and MCC increases the tensile strength by 53% in HPMC composites (Bilbao-Sáinz *et al.* 2010). MCC filling at a loading level of 5 wt% increased the tensile strength by 30%, toughness by 300%, and elongation at break by 135% of the CAB nanocomposites (Petersson and Oksman 2006).

It is known that addition of a reinforcement material to a matrix may reduce the strain at break, but nanowhiskers in a CAB matrix did not reduce the ultimate strain compared to neat CAB (Siqueira *et al.* 2011). CA-MFC composites at a loading level of 1 to 7 wt% also showed a larger elongation at break than the unfilled CA (Lu and Drzal 2010). The nanocellulose filling does not necessarily reduce the transparency of the composite (Petersson *et al.* 2009; Siqueira *et al.* 2011). The addition of a plasticizer can have a positive effect on the transparency of CAB-nanowhisker composites (Ayuk *et al.* 2009).

A particularly strong polymer material has been created by filling amorphous HEC with NFC at a high loading level of 10 to 60 v/v% (Sehaqui *et al.* 2011). NFC forms a load-carrying network, which is surrounded by soft HEC. The composite material sustains strains without visible cracks up to 10% to 20% strain. At loading levels of 35 to 52 v/v%, the strain at break is 19 to 25%, and at the same time the tensile strength of 147 to 181 MPa is obtained due to strain hardening. Tensile strength for the pure NFC film was 175 MPa.

Water Vapor Barrier Properties

Table 6 summarizes the WVP values of recently studied composites that had HPMC as a matrix material. To the knowledge of the author, the water vapor permeability of other nanocellulose-filled composites having a cellulose derivative as a matrix has not been studied.

Table 6. The Effect of Nanocellulose Additive on the WVP of Composites Having HPMC as a Matrix Material

	Matrix	**Reference**	**Additive Type; Origin of Nanocellulose**	**Addition [wt%]**	**Film**	**Conditions (T, RH)**	**Change [%]**	**Application**	**Reference**
		WVP [g·m/m^2·s·Pa]			**WVP, composite [g·m/m^2·s·Pa]**				
Plastics	LDPE	9.14E-13	--	--	--	--	--	--	(García *et al.* 2009b)
	HDPE	2.31E-13	--	--	--	--	--	--	(García *et al.* 2009b)
MFC	HPMC	1.22E-10	NFC; Eucalyptus sulphite pulp	2.6	1.36E-10	25°C, 0%/100% RH	11	Edible films, transparent films	(Bilbao-Sáinz *et al.* 2011)
	HPMC	1.22E-10	TEMPO-oxidised NFC; Eucalyptus sulphite pulp	2.6	2.08E-10	25°C, 0%/100% RH	70	Edible films, transparent films	(Bilbao-Sáinz *et al.* 2011)
MCC	HPMC	1.22E-10	Whiskers; MCC (non-specified)	11.8	1.06E-10	25°C, 0%/100% RH	-14	Edible films, transparent films	(Bilbao-Sáinz *et al.* 2011)
	HPMC	1.31E-10	Lipid coated MCC (commercial); --	21	6.39E-11	25°C, 0%/87% RH	-51	Edible film	(Bilbao-Sáinz *et al.* 2010)
	HPMC	3.33E-10	MCC (commercial); --	14	2.78E-10	25°C, 100%/50% RH	-17	Edible film	(Dogan and McHugh 2007)

The minimum WVP and the corresponding level of filling are given.

Nanofibrillar celluloses do not improve the moisture barrier performances of the HPMC composites. Entangled nanofibrillar fillers form aggregates and create pathways for moisture, thus increasing the permeability. However, highly crystalline cellulose nanocrystals have the capacity to enhance the moisture barrier properties and decrease the WVP of biopolymer materials (Bilbao-Sáinz *et al.* 2011; George and Siddaramaiah 2012; Sanchez-Garcia and Lagaron 2010; Saxena *et al.* 2011). The enhancement is based on the crystallinity of cellulose, the density of the film, and the dispersion of the filler in the matrix. The MCC and CNC filler slightly reduce the WVP of HPMC composites. Surface treatment of the filler is a method for reducing the WVP of composites. A lipid-coated MCC filler provided an additional 10% reduction in the WVP of the HPMC-based composite compared to non-treated MCC fillers. There are examples of minimal or no improvements with other surface treatments, such as the oxidation of hydroxymethyl groups of NFC to carboxylic groups in a HPMC-NFC composite.

DISCUSSION

A gas may be transported through a polymer film by two main mechanisms. Gas molecules absorb and dissolve into the solid polymer phase and diffuse in the solid phase throughout the film. On the other hand, gas diffusion occurs in pores and along material surfaces. Factors such as interactions between the permeating molecules and the polymer and the porosity of the film affect the solubility. The migration of the penetrant inside the film is affected by the size and shape of the molecules and the packing of the polymer molecules.

In Table 7, the studied cellulose derivatives are organized according to their WVP and OP values. The method of permeability determination and the measurement conditions greatly affect the individual results, but certain regularities can be observed.

Table 7. The WVP and OP of the Surveyed Monopolymer Cellulose Derivative Films in Increasing Order

WVP [g·m/m^2·s·Pa]

CA $1.1\cdot10^{-12}$	<	Cellophane $2.4\cdot10^{-12}$ (Tomé *et al.* 2011)	<	CMC $1.4\cdot10^{-11}$ (Sayanjali *et al.* 2011)	<	MC $2.1\cdot10^{-11}$ (Ayana and Turhan 2009)

OP [cm^3·m/m^2·s·Pa]

Cellophane (0% RH) $3.5\cdot10^{-17}$ (Yang *et al.* 2011)	<	Cellophane (100% RH) $1.2\cdot10^{-13}$ (Tomé *et al.* 2011)	<	MC (75% RH) $1.5\cdot10^{-12}$ (Pastor *et al.* 2012)	<	CA (0% RH) $3.7\cdot10^{-12}$ (Nakai *et al.* 2005)	<	CMC (100% RH) $1.4\cdot10^{-10}$ (Gutiérrez *et al.* 2012)

The polar molecules of water are soluble in cellulose, which always contains polar groups. In Table 7, MC that has low polar methoxide groups has the largest WVP. The diffusion of water inside the cellulose derivatives is greatly affected by the interactions between the polymer and the water molecules.

Several methods have been tried to enhance the water vapor barrier without decreasing the mechanical properties at the same time. Adding lipids with long hydrocarbon chains and fatty acids decreases the WVP but usually reduces the strength properties. With a fatty acid treatment, cellophane films reached the water vapor barrier ($8\cdot10^{-13}$ g·m/m^2·s·Pa) corresponding to the WPV of LDPE films (~$9\cdot10^{-13}$ g·m/m^2·s·Pa). Lipids may have adverse effects on optical or organoleptic properties. The cellulose derivative can also be compounded with another polymer with a lower WVP, such as MC with PCL. Using mineral or cellulosic fillers may be a solution for enhancing the water vapor barrier. However, there is a risk that macro-pores that increase vapor diffusion will be created. Filling the MC-matrix with MCC improved both the tensile properties and the WVP. For CMC, fillers reduced the WVP of the composite by approximately 50%, while with other techniques the reduction was between 5% and 30%.

The non-polar oxygen molecules have low solubility to cellulose-containing polar groups. Even if the functional groups are of low polarity, the degree of substitution is seldom close to 3. As a consequence, the packing of the cellulose chains and the porosity of the polymer films are vital. Large polar functional groups, such as carboxymethyl and acetate, increase the porosity of the cellulose films, which provides pathways for oxygen to diffuse and increase the OP. Smaller but non-polar groups have the same effect. At 0% RH, there is no simultaneous oxygen and vapor sorption and no bound water present in the polymer, which would affect oxygen transport. As can be seen in Table 7, the oxygen permeation in cellophane in a dry state is very low. The solubility is low, and the hydroxyl groups of regenerated cellulose pack tightly and do not create void volume for oxygen to diffuse.

Cellulose derivatives are film-forming substances that are commonly used as structural components in polymeric blends. The properties of the blend reflect the properties of the components, although the properties do not always reflect the relative amounts of components in the blend. Increased tensile properties are thus commonly reported. Glycerol typically reduces the tensile strength, but other methods, such as adding a cross-linking agent or a filler, applying ultrasound treatment to the films, or certain changes in the manufacturing process increase the tensile strength. Often the ductility of the composite is decreased as the strength increases. If the nanocellulosic reinforcement filler is well distributed in the matrix, then the tensile strength is reported to increase by 30% to 70%.

Active packaging is a current research topic, and the range of potential active agents is large, covering both synthetic and natural compounds. Out of the four studied materials, cellophane has been rendered antimicrobial by using nisin, CA by using potassium sorbate, lysozyme, or sodium proprionate, MC by using chitosan and vanillin, olive leaf extract, cinnamaldehyde, eugenol, or carvacol, and CMC by using murta leaf extract or potassium sorbate. Antioxidant and bitterness-reducing properties have also been created for films. The active agents often change the mechanical and barrier properties of the films.

Cellulose derivatives are materials that have been used in food packaging since the early 1900s. In search of new bio-based alternatives, these materials and their preparation methods, especially methods to effectively dissolve cellulose, are gaining new interest. The availability of raw materials and natural qualities of the films and coatings produced are some of the advantages. Cellulose and its derivatives have a capability to mechanically reinforce and enhance the oxygen barrier properties of polymer materials.

ACKNOWLEDGMENTS

The author would like to acknowledge Prof. Øyvind Gregersen at Norwegian University of Science and Technology (NTNU) in Trondheim for the comments on the manuscript and NTNU for financing the project. She also thanks Ms. Eymann Smalø for proofreading this text.

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Article submitted: Sept. 4, 2012; Peer review completed: Oct. 15, 2012; Revised version received and accepted: March 29, 2013: Published: April 3, 2013.