REVIEW ARTICLE **bioresources.com**

Nanocellulose in Thin Films, Coatings, and Plies for Packaging Applications: A Review

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This review article was prompted by a remarkable growth in the number of scientific publications dealing with the use of nanocellulose (especially nanofibrillated cellulose (NFC), cellulose nanocrystals (CNC), and bacterial cellulose (BC)) to enhance the barrier properties and other performance attributes of new generations of packaging products. Recent research has confirmed and extended what is known about oxygen barrier and water vapor transmission performance, strength properties, and the susceptibility of nanocellulose-based films and coatings to the presence of humidity or moisture. Recent research also points to various promising strategies to prepare ecologically-friendly packaging materials, taking advantage of nanocellulose-based layers, to compete in an arena that has long been dominated by synthetic plastics. Some promising approaches entail usage of multiple layers of different materials or additives such as waxes, high-aspect ratio nano-clays, and surface-active compounds in addition to the nanocellulose material. While various high-end applications may be achieved by chemical derivatization or grafting of the nanocellulose, the current trends in research suggest that high-volume implementation will likely incorporate water-based formulations, which may include water-based dispersions or emulsions, depending on the end-uses.

Keywords: Barrier properties; Water vapor transmission; Food shelf life; Oxygen transmission; Packages; Cellulose nanomaterials

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INTRODUCTION

There has been explosive growth in the publication of peer-reviewed articles that combine key words related to "packaging" and "cellulose," in combination with the terms "nanocellulose," "nanocrystal*," or "nanofibril*". As of November 2016, a search of this combination of terms showed about as many publications since the start of 2015, compared to all preceding years combined. Given such an acceleration of research around the world, it makes sense to ask whether this high amount of research effort has yet borne significant fruit. In light of this question, the emphasis of this review article is on research publications that shed light on known challenges to the successful implementation of nanocellulose products to enhance the performance of packaging.

In principle, a nanocellulose-based film, coating, or intermediate layer, in addition to being light in weight, can provide benefits of renewability, recyclability, processability, and compatibility with health and the environment. In particular, very high performance, relative to plastic-based materials, has been reported for the oxygen permeation resistance of certain nanocellulose-based films (Fukuzumi *et al.* 2009; Syverud and Stenius 2009; Aulin *et al.* 2010a; Hult *et al.* 2010; Plackett *et al.* 2010; Chinga-Carrasco and Syverud 2012; Rodionova *et al.* 2012a,b; Shimizu *et al*. 2016). While a high level of resistance to oxygen permeation has been reported, many other studies have revealed much lower performance of cellulose-based films and coatings in terms of resistance to water vapor transmission. In many applications it would be very important to hold out gases and water vapor under both dry and humid or wet conditions. Future successful implementations of nanocellulose-based films are most likely to take advantage of inherent positive attributes of cellulose-based films, while compensating for or overcoming product requirements that are inherently difficult or expensive to achieve with a nanocellulose-based film structure.

Several important review articles provide a starting platform and raise some important issues to be further considered in this article. The general subject area of packaging materials involving biomaterials has been the focus of numerous review articles and monographs (Lagaron *et al.* 2004; Rhim 2007; Rhim and Ng 2007; Chiellini 2008; Johansson *et al.* 2012; Tang *et al.* 2012; Paunonen 2013a). For example, Krochta and DeMulderJohnston (1997) reviewed research related to edible and biodegradable films for packaging applications. Also, there has been much interest and research related to cellulose fiber usage in composite materials for packaging (Johansson *et al.* 2012; Faruk *et al.* 2014). Research related to the use of nanocellulose in packaging applications also has been reviewed (Turbak *et al.* 1983; Dufresne 2008, 2012; Hubbe *et al.* 2008; Azeredo 2009; Eichhorn *et al.* 2009; Oksman *et al.* 2009; Habibi *et al.* 2010; Siqueira *et al.* 2010; Siro and Plackett 2010; Moon *et al.* 2011; Olsson *et al.* 2011; Petersen and Gatenholm 2011; Faruck *et al.* 2012; Huber *et al.* 2012; Khalil *et al.* 2012, 2014; Lavoine *et al.* 2012; Freire *et al.* 2013; Lopacka 2013; Paunonen 2013a,b; Sandquist 2013; Cowie *et al.* 2014; Khan *et al.* 2014a; Tammelin and Vartiainen 2014; Mihindukulasuriya and Lim 2014; Azizi Samir *et al.* 2015; Hannon *et al.* 2015; Li *et al.* 2015a; Simao *et al.* 2015; Gomez *et al.* 2016; Khalil *et al.* 2016). In particular, Lindström and Aulin (2014) reviewed research progress up to 2014, emphasizing some of the key unmet issues that are likely to continue to slow down progress in production-scale implementation of nanocellulose in packaging. The cited article will be used in the present article as a kind of benchmark by which to judge whether or not meaningful progress has been achieved more recently. Near to the end of this article, a list of unresolved issues highlighted by Lindström and Aulin (2014) will be considered again, with attention to whether or not the challenges have been addressed in the intervening two years. While the articles mentioned in this paragraph mainly concerned technical feasibility, Shatkin *et al.* (2014) reviewed the potential market projections for cellulose nanomaterials and came to the conclusion that the greatest volume potential for nanocellulose lies in paper and packaging applications.

Motivations to Employ Nano-scale Cellulosic Particles in Packaging

The aforementioned published literature points to two classes of motivating factors favoring efforts to use cellulosic nanomaterials for enhancement of packaging. Firstly, there is a widespread desire to replace petroleum-based materials with renewable, biodegradable, and life-friendly nature-based materials. In addition, there is fast-accumulating information regarding the performance of nanocellulose-containing packaging structures relative to end-use requirements such as barrier properties, appearance, and strength. Some general directions for the development of barrier films already had been well established before nanocellulose films were even considered for such applications (Lagaron *et al.* 2004), and these goals have been extended to systems that can involve cellulosic nanomaterials (Moon *et al.* 2011; Paunonen 2013b). The subsections below further expand upon such aspects.

Mechanical and barrier properties

During the early development of cellulosic nanomaterials there was much attention paid to the superior tensile modulus and other strength attributes that can be achieved upon the drying of such materials (Nakagaito and Yano 2004). The individual crystals of nanocellulose exhibit elastic modulus and breaking strength characteristics that are among the highest listed, per unit mass, for common materials (Eichhorn *et al.* 2009). Furthermore, as a result of extensive hydrogen bonding and high density, the tensile strength of nanocellulose-based thin films can reach values that approach those of metals and advanced synthetic polymer materials (Qing *et al.* 2012).

A high proportion of articles dealing with nanocellulose materials for packaging have been focused on barrier properties. Figure 1 represents four kinds of barrier properties that have potential to be important in various applications of nanocellulose films in packaging.

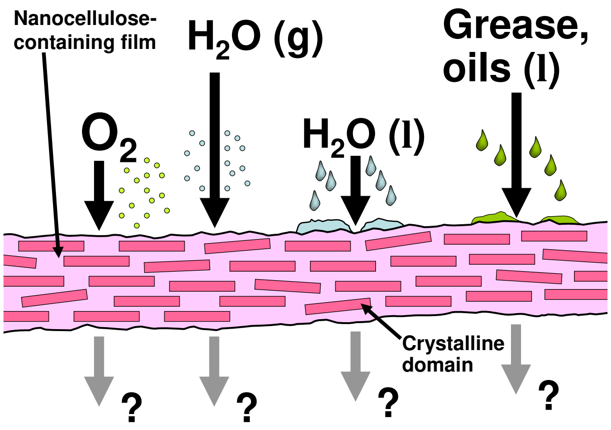

Fig. 1. Four types of barrier performance often studied relative to packaging film requirements

Oxygen barrier

Foremost among the concerns regarding packaging applications has been a motivation to limit the permeation of oxygen and other gases and volatile compounds through the barrier layers of packages. In this way, nanocellulose-related films have the potential to either increase the shelf life of foods, to prevent the accumulation of unwanted odors or contamination of the food, or conversely to avoid the escape of food odors. The following articles indicate strong performance of nanocellulose-containing films as oxygen barriers (George *et al.* 2005; Pääkkö *et al.* 2007; Fukuzumi *et al.* 2009; Syverud and Stenius 2009; Aulin *et al.* 2010a; 2012; Edlund *et al.* 2010; Hult *et al.* 2010; Plackett *et al.* 2010; Sanchez-Garcia and Lagaron 2010; Yang *et al.* 2011; Charani *et al.* 2013; Chinga-Carrasco and Syverud 2012; Fortunati *et al.* 2012b; Martínez-Sanz *et al.* 2012; Rodionova *et al.* 2012a,b; Savadekar *et al.* 2012; Stevanic *et al.* 2012; Espino-Pérez *et al.* 2013; Li *et al.* 2013a; Martínez-Sanz *et al.* 2013a; Österberg *et al.* 2013; Paunonen 2013a,b; Iotti 2014; Kumar *et al.* 2014; Lavoine *et al.* 2014c; Liu *et al.* 2014; Miettinen *et al.* 2014; Ibn Yaich *et al.* 2015; Rojo *et al.* 2015; Cheng *et al.* 2016; Shimizu *et al.* 2016).

Oils, grease barrier

In a fundamental sense, the hold-out of greases and oils is closely related to the holdout of nonpolar gases such as oxygen. The key is that neither oxygen gas nor greases and oils interact strongly with the hydrogen-bonded structure of a cellulose-based barrier film. Due to the importance of the topic for such applications as food packaging, several studies have focused on oil resistance (Aulin *et al.* 2009b, 2010a; Österberg *et al.* 2013; Kumar *et al.* 2014; Sirviö *et al.* 2014; Kisonen *et al.* 2015; Raghu 2015). Interestingly, several of these studies showed that the same systems providing superior oil hold-out also acted as superior barriers for oxygen permeation (Aulin *et al.* 2010a; Österberg *et al.* 2013; Kisonen *et al.* 2015). Researchers also have made efforts to further improve oil-holdout from nanocellulose-based films by rendering them oleophobic. This can be achieved by derivatization with very low surface energy substances, such as fluorocarbons; such effects can be enhanced if a surface is pretreated with nanoparticles to impart nano-scale roughness prior to perfluorosilane treatment (Kisonen *et al.* 2015).

Water vapor barrier

It would be a great advantage if a thin, eco-friendly barrier layer would also provide full resistance to moisture and high humidity. Cellulosic materials are inherently sensitive to the presence of both gaseous and liquid water (Spence *et al.* 2010a,b, 2011a,b; Belbekhouche *et al.* 2011; Ferrer *et al.* 2012a,b; Abdollahi *et al.* 2013a; Bai *et al.* 2015; Ferrer *et al.* 2015, 2016b; Rojo *et al.* 2015; Lundahl *et al.* 2016). There also have been efforts to modify nanocellulose-based systems so as to improve barrier performance in key areas. It is a challenge to prevent permeation of water vapor (Belbekhouche *et al.* 2011; Spence *et al.* 2011b; Paunonen 2013b; Lu *et al.* 2014, 2015). At high humidity, or when wet, typical cellulose-based films lose much of their ability to prevent the permeation of oxygen (Aulin *et al.* 2010a). Studies addressing these issues will be considered in the course of this review article.

Moisture sensitivity also can be a key concern when water-soluble polymeric substances are used to prepare thin films and their materials. In some such cases the inclusion of cellulosic reinforcing materials, at suitable levels, has been shown to reduce moisture-sensitivity (Cao *et al.* 2008; Azeredo *et al.* 2009; Bilbao-Sáinz *et al.* 2010; Sanchez-Garcia *et al.* 2010; George and Siddaramaiah 2012; Johnsy and Siddaramaiah

2012; Savadekar *et al.* 2012; Follain *et al.* 2013; Dehnad *et al.* 2014a; Peresin *et al.* 2014; Santos *et al.* 2014). Similar effects have been found when cellulose nanocrystals were used to reinforce a natural rubber matrix (Bras *et al.* 2010) or poly-lactic acid (PLA) (Sanchez-Garcia and Lagaron 2010; Hossain *et al.* 2011; Fortunati *et al.* 2012b; Martínez-Sanz *et al.* 2012; Song *et al.* 2014). However, Pereda *et al.* (2011) reported no beneficial effects relative to water vapor penetration or other attributes when including nanocellulose in a sodium caseinate-type protein film. Presumably any beneficial effects of reinforcements in limiting water vapor transmission may be due to either an improvement in film integrity, such as resistance to swelling in moist environments, or to the vapor-impermeable nature of crystalline cellulose.

Aqueous liquid barrier

Resistance to penetration of packaging materials by aqueous solutions is important in many applications, and several studies involving nanocellulose have focused on this issue (Choi and Simonson *et al.* 2006; Chinga-Carrasco *et al.* 2012; Yang *et al.* 2012; Follain *et al.* 2013; Kisonen *et al.* 2015; Shimizu *et al.* 2016). Liquid water is an especially challenging fluid from the perspective of cellulose-based films due to the fact that it has the potential to invade and replace hydrogen bonds connecting adjacent cellulosic surfaces in the film. It follows that it is not sufficient just to focus on achieving a dense layer without large pores. Rather, efforts to minimize penetration by aqueous fluids generally have focused on decreasing the water-wettability of the nanocellulose-based barrier films (Yang *et al.* 2012; Kisonen *et al.* 2015). Measurements of the contact angle of water have been employed as a criterion for identifying promising formulations to achieve resistance to liquid water (Spence *et al.* 2010b; Rodionova *et al.* 2011, 2012a; Yang *et al.* 2012; Pereda *et al.* 2014; Kisonen *et al.* 2015; Rojo *et al.* 2015; Visanko *et al.* 2015).

Drug release and antimicrobial packaging

The controlled release of drugs is another application for which the use of nanocellulose barrier layers has been considered (Kolakovic *et al.* 2012; Lavoine *et al.* 2014b, 2016). In these applications, the nanocellulose-based film appears to function as a barrier to the contained pharmaceutical compounds. Kolakovic *et al.* (2012) used a filtration procedure to form the nanocellulose film and then to collect a model drug compound. Lavoine *et al.* (2014b) coated nanofibrillated cellulose onto a caffeine-impregnated paper base. In these studies, the rate of release of the confined material was shown to be slowed down by the presence of a nanocellulose-based layer.

Several researchers have evaluated strategies to impart antimicrobial properties to packaging with systems that involve nanocellulose (Andresen *et al.* 2007; Dobre *et al.* 2012; Boumail *et al.* 2013a,b; Cozzolino *et al.* 2013; Costa *et al.* 2014; Dehnad *et al.* 2014b; Salmieri *et al.* 2014a,b; El-Wakil *et al.* 2015; Saini *et al.* 2015, 2016a,b; Amini *et al.* 2016; Hu and Wang 2016; Jebel and Almasi 2016; Padrao *et al.* 2016; Yan *et al.* 2016). Of particular interest are treatments with food-grade compounds such as sorbic acid (Dobre *et al.* 2012) or the bio-based cationic polymer chitosan (Tome *et al.* 2013; Velasquez-Cock *et al.* 2014; Li *et al.* 2015b), which nevertheless can improve the ability of the package to protect the food inside it against decay. Also, there has been much interest in utilizing nanomaterials such as colloidal silver particles in combination with nanocellulose for antimicrobial activity in packaging (Amini *et al.* 2016; Yan *et al.* 2016).

Transparency

In addition to the barrier properties and related functional capabilities of nanocellulose-based layers, much research has focused on desirable attributes such as transparency (Yano *et al.* 2005; Petersson and Oksman 2006; Nordqvist *et al.* 2007; Shimazaki *et al.* 2007; Ayuk *et al.* 2009; Fernandes *et al.* 2009, 2010; Fukuzumi *et al.* 2009; Kim *et al.* 2009; Nogi *et al.* 2009; Petersson *et al.* 2009; Sehaqui *et al.* 2010; Hassan *et al.* 2011; Pereda *et al.* 2011, 2014; Stevanic *et al.* 2011; Yang *et al.* 2011; Aulin *et al.* 2012; Hu *et al.* 2013; Li *et al.* 2013a; Tome *et al.* 2013; Khan *et al.* 2014b; Kumar *et al.* 2014; Kurihara and Isogai 2014; Tammelin and Vartiainen 2014; Ambrosio-Martin *et al.* 2015b; Honorato *et al.* 2015; Oun and Rhim 2015; Toivonen *et al.* 2015a,b). Hu *et al.* (2013) showed that nanocellulose films could be rendered conductive by deposition of tin-doped indium oxide, while still retaining their transparency; solar cells prepared with such films were successfully demonstrated. In general, it has been found that good transparency can be achieved as long as the cellulosic material is small enough, fully wetted by the matrix material (if any) in the layer, and not clumped up or entangled. Simao *et al.* (2015) carried out related work in which the band gap of optical absorption was determined for nanocellulose thin films. By contrast, more opaque films have been achieved in cases where cellulose reinforcements were either poorly wetted, agglomerated (Santos *et al.* 2014; Ambrosio-Martin *et al.* 2015b), or simply large relative to the wavelength of light (Kumar *et al.* 2014). Toivonen *et al.* (2015a) demonstrated for the first time that transparent films can be achieved even in the case where aerogel technology had been used in the initial film formation; subsequent compaction yielded transparent, flexible films.

Edibility

In potential applications where a nanocellulose-based film is applied directly to food, researchers have been concerned about the edibility of such films (Dogan and McHugh 2007; Azeredo *et al.* 2009, 2010; Bilbao-Sáinz *et al.* 2010; George and Siddaramaiah 2012; Johnsy and Siddaramaiah 2012; Pereda *et al.* 2014; Oun and Rhim 2015; George *et al.* 2016). In none of these cited studies was edibility actually evaluated; rather edibility was assumed based on the ubiquitous character and natural source of the cellulose.

Biodegradation properties

Nanocellulose is generally regarded as biodegradable for two reasons: As a type of cellulose, one can expect it to be susceptible to cellulase-producing fungi and bacteria, which are present throughout the biosphere (Rabinovich *et al.* 2002; Sukumaran *et al.* 2005). Secondly, the tiny dimensions of nanocellulose imply a high exposure to its surroundings. The issue of biodegradation has been emphasized in studies in which nanocellulose was used in composite structures with other natural film-forming materials (Lu *et al.* 2008; Ma *et al.* 2008; Cheng *et al.* 2009; Wan *et al.* 2009; Azeredo *et al.* 2010; Bras *et al.* 2010; Khan *et al.* 2010, 2012, 2014b; Siro and Plackett 2010; Chinga-Carrasco and Syverud 2012; da Silva *et al.* 2012; George and Siddaramaiah 2012; Hassan *et al.* 2012; Johnsy and Siddaramaiah 2012; Tang *et al.* 2012; Baheti and Militky 2013; Chinga-Carrasco *et al.* 2013; Ollier *et al.* 2013; Bhardwaj *et al.* 2014; Dehnad *et al.* 2014a; Fortunati *et al.* 2014; Ghaderi *et al.* 2014; Khalil *et al.* 2014; Kumar *et al.* 2014; Lu *et al.* 2014; Marais *et al.* 2014; Rafieian and Simonsen 2014; Reddy and Rhim 2014; Song *et al.* 2014; Yang *et al.* 2014; Azizi Samir *et al.* 2015; Feng *et al.* 2015a; Figueiredo *et al.* 2015; Honorato *et al.* 2015; Lavoine *et al.* 2015; Li *et al.* 2015a; Lu *et al.* 2015; Youssef *et al.*

2015; Cheng *et al.* 2016; Shankar and Rhim 2016). According to Lindström and Aulin (2014), biodegradability can be regarded as a more important issue for packaging, when compared to the displacement of petroleum-derived plastic materials.

Types of Nanocellulose to Consider for Packaging

Up to this point in this article there has been little emphasis on the different available types of nanocellulose. Now, to lay the groundwork for a discussion of how to improve the performance of nanocellulose applications in packaging, some more attention will be paid to that issue. As mentioned before, the three types of nanocellulose products that mainly are being studied for packaging are cellulose nanocrystals (CNCs), nanofibrillated cellulose (NFC), and bacterial cellulose (BC). Though the term "cellulose nanofibrils" has sometimes been used as an alternative to NFC, the latter term is preferred in the present article to emphasize the fact that the nanofibrillated material is often not completely separated into individual fibrils. These categories of nanocellulose, which will be discussed below, are sketched in Fig. 2. Overviews that describe all three of these products have been published (Siro and Plackett 2010; Nelson *et al.* 2016).

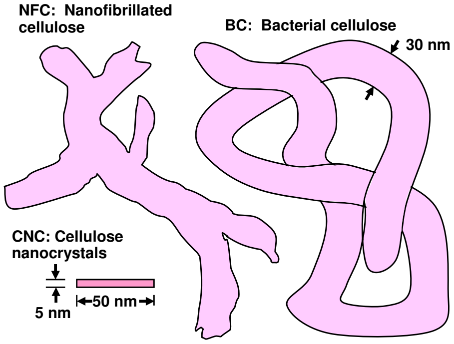

Fig. 2. Sketches of the three major types of nanocellulose, showing some typical dimensions. Please note that the lengths of some NFC and especially BC can be many times longer than what is represented in the figure. Also, CNCs in some cases can exceed 1000 nm in length.

Cellulose nanocrystals

If one processes plant-based material to remove the lignin and then treats the isolated cellulose with a strong acid or other suitable reagents to degrade and remove the less crystalline domains and any residual hemicelluloses, then, by optimizing the conditions of treatment, one can obtain a suspension of cellulose crystallites (Mariano *et al.* 2014; Nelson *et al.* 2016). Typical sizes of cellulose crystallites range from about 3 to 30 nm in thickness and few hundreds of nm in length, depending on the plant source (Elazzouzi-Hafraoui *et al.* 2008; Eichhorn 2011). Nanocellulose crystals also can be obtained from other cellulose sources such as algae (Feng *et al*. 2015b; Hai *et al*. 2015; Chen *et al.* 2016b), tunicin (Dufresne 2012; Piao and Zhang 2016), and bacteria (discussed in a different section). Studies related to the use of CNCs in packaging are listed in Table A in the Appendix of this article (see first column, in which the type of nanocellulose is identified). Table B in the Appendix provides a summary of barrier performance findings for oxygen and water vapor transmission in films composed primarily of nanofibrillated cellulose.

Relative to the production of cellulose-containing packaging materials, CNCs represent the smallest, most fundamental option. The crystalline content of cellulose in raw biomass ranges from about 25 to 75% (Xu *et al.* 2013), whereas the crystallinity of CNCs has been reported as about 85% according to X-ray diffraction tests (Aulin *et al.* 2009a). The CNC particles resulting from the hydrolysis of native cellulose are rigid and relatively straight, with aspect ratios generally in the range of 11 to 67 (Bras *et al.* 2011). These dimensions have two implications regarding thin film structures. On the one hand, they set a practical lower limit on the conceivable thickness of thin films comprising CNCs. On the other hand, they entail a large ratio of surface area to mass; this implies that any surface treatments of the CNCs are likely to be demanding, if needed.

The surface chemistry of CNCs has been found to be dependent on the mode of isolation. Sulfuric acid digestion of cellulose to obtain CNCs yields a negative surface charge, which is due to the presence of sulfate half-ester groups (Mascheroni *et al.* 2016). The cited authors showed that higher negative charge density can be achieved by using ammonium persulfate as the oxidant during the treatment of cellulose to release the nanocrystals. In that case, dissociation of surface carboxylic acid groups would account for the negative charge. Alternatively, a negative charge can be imparted by phosphorylation (Naderi *et al.* 2016). The negative charges can be beneficial in aqueous media as a means of keeping the CNCs in stable suspension. Other modes of digestion such as HCl or enzymes do not impart the negative charge to the surfaces, though negative charges can result from secondary treatment, as with TEMPO-mediated oxidation (George *et al.* 2010). Chen *et al.* (2016a) employed difunctional carboxylic acids to impart a strong negative charge to both CNC and NFC.

Highly fibrillated cellulose

The term "highly fibrillated" is used here in recognition of the difficulty in drawing a clear differentiation within a broad, continuous range of possible mechanical treatments (Kangas *et al.* 2014; Khalil *et al.* 2014). In addition to refining, homogenizing, and grinding procedures, NFC also can be prepared by "counter-collision" of aqueous streams (Jiang *et al.* 2016). The terms "nanofibrillated cellulose" (NFC) (Siro and Plackett 2010; Lavoine *et al.* 2012; Sandquist 2013) and "microfibrillated cellulose" (MFC) (Aulin *et al.* 2012; Österberg *et al.* 2013; Khalil *et al.* 2014; Simao *et al.* 2015) are both used in the literature, with an implied understanding that the widths of fibrils ought to determine which term is more appropriate. In either case, both the lengths and widths of component fibrils are substantially larger than those of the CNCs already discussed. According to Chinga-Carrasco and Syverud (2010), the individual fibrils within NFC are typically in the range of 20 to 30 nm in width. Aulin *et al.* (2009a) found highly fibrillated cellulose samples to have crystallinities in the range of 60 to 70%. Another difference is that highly fibrillated fibers will clearly contain higher amounts of non-crystalline cellulosic matter. Thus, in general, highly fibrillated celluloses will tend to be more flexible in the wet state when compared to a crystalline cellulose structure. The term "nanocellulose aggregate" has sometimes been used to draw attention to some preparations of highly fibrillated cellulose in which bunches of fibrils remain attached together (Ambrosio-Martin *et al.* 2015a). According to Cowie *et al.* (2014), the market potential of highly fibrillated cellulose products is much greater than that of CNCs.

Regarding the preparation of nanocellulose films, various studies have indicated that the flexible nature of NFC gives it the potential to achieve high density in cross-linked structures that are formed, achieving low porosity and high resistance to air permeation (Aulin *et al.* 2010a). Belbekhouche *et al.* (2011) observed higher resistance to air permeation in films prepared from NFC relative to films prepared from CNC suspensions.

Table A lists some essential information about numerous studies in which highly fibrillated cellulose (MFC or NFC) has been considered for films or layers for packaging.

Bacterial cellulose

In theory, bacterial cellulose (BC) has some important inherent advantages in terms of preparation of nanocellulose material. Unlike biomass derived from wood and other plant sources, bacterial cellulose contains neither lignin nor heteropolysaccharides (Feng *et al*. 2015c). The properties of BC are highly dependent on the bacterial source, and fibrils having widths in the range of 10 to 50 nm have been reported (Moon *et al.* 2011). The BC particles are very long and flexible in the wet state. Studies in which bacterial cellulose was evaluated for its properties in packaging applications are listed in Table A.

Because certain purified bacterial cellulose products have been regarded as "food grade," BC has been considered for direct application in food items, such as vegetables, fruits, and meat, as edible films (George and Siddaramaiah 2012; Johnsy and Siddaramaiah 2012; George *et al.* 2016; Padrao *et al.* 2016).

NANOCELLULOSE IN FILMS AND COATINGS

An important function of a package can be to inhibit the passage of gases or liquids into or out from the contained products. Nanocellulose has potential usage in various layers or coatings, which may contribute to barrier properties. This section will deal with some contrasting types of nanocellulose-based layer types and some markedly different means of achieving them. Four of the most widely studied means of preparing these films or "nanopapers" that contain nanocellulose are illustrated schematically in Fig. 3.

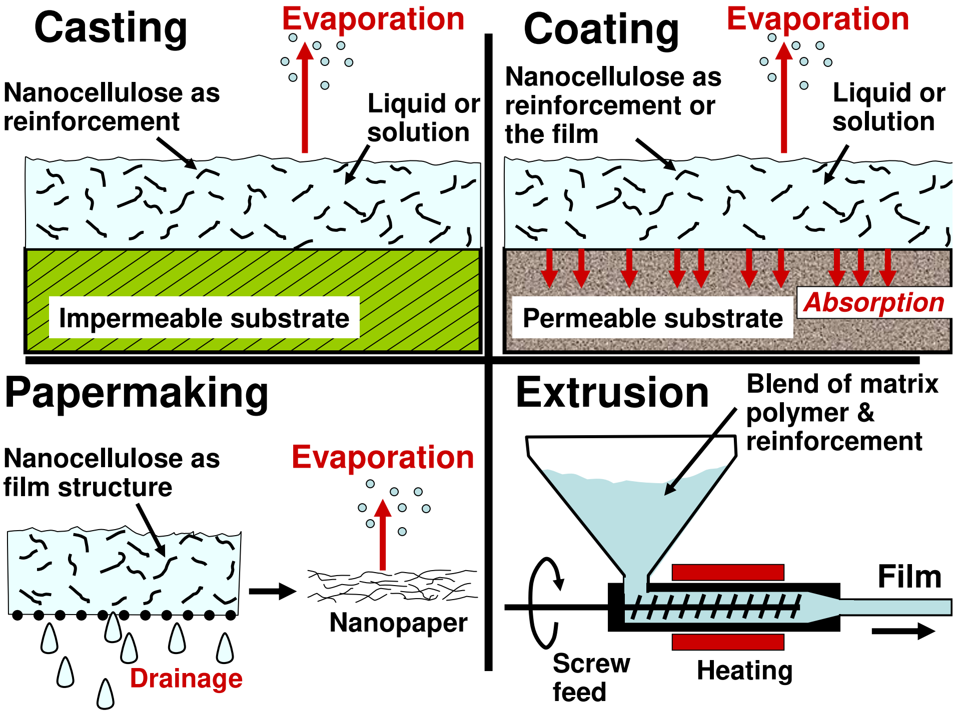

Fig. 3. Schematic illustration of four primary means of preparing thin films that contain nanocellulose, emphasizing differences in how liquid (if any) is mainly withdrawn during preparation of the film or nanopaper

These ways of forming films can be called casting, coating, papermaking, and extrusion. Extrusion will be considered first, then cast film processes, processes that resemble papermaking, and then coating processes.

Extruded Films

Extrusion can be defined as a process in which a substance or mixture is forced through a die at high pressure and temperature to form a sheet, fiber, filament, or other continuous form. This type of forming is widely used in preparation of lamination for packaging based on synthetic plastic materials. When employing nanocellulose for such strategies, some key issues might include breakage, thermal degradation, alignment of nanocellulose, and high viscosity due to the high aspect ratio of the particles. Another key aspect is the manner in which one achieves a solid-type layer after having essentially handled the composition as a liquid in the course of the extrusion. Thus, the subsections that follow will deal with such options as cooling (after having melted a matrix material) or undergoing a chemical reaction to cure the composition. In other words, the resulting layer may be either a thermoplastic or a reactive system.

Melt extrusion

Melt processing has been employed in numerous research projects in which nanocellulose was used as a minor component to reinforce a thermoplastic resin (Seydibeyoglu and Oksman 2008; Martínez-Sanz *et al.* 2012, 2013a,b,c; Suzuki *et al.* 2013, 2014; Fortunati *et al.* 2014; Ambrosio-Martin *et al.* 2015a; Arrieta *et al.* 2015; Ferrer *et al.* 2016a; Herrera *et al.* 2016; Lendvai *et al.* 2016). After emerging from the die of the extruder, the material cools below the melting point of the matrix polymer. Generally, it has been found that inclusion of nanocellulose increases the modulus of elasticity in such applications. Relatively low-melting polymers are often preferred in order to avoid thermal damage to the cellulosic reinforcement during compounding. Alternatively, researchers who want to utilize nature-based products have selected poly-(lactic acid) (Martínez-Sanz *et al.* 2012) or thermoplastic starch mixtures (Lendvai *et al.* 2016) as the matrix. Herrera *et al.* (2016) showed that the results were strongly affected by the rate of cooling in the case of poly-lactic acid film reinforced with CNC. Rapid cooling yielded more amorphous, transparent, and compliant films.

Curing

By relying upon a reaction, rather than cooling to solidify the extruded film, there can be an opportunity to avoid the high temperatures required for melting or the high shear stresses associated with the high viscosity of a fully polymerized matrix. Aulin and Ström (2013) considered such a system in which autoxidation of an extruded film brought about solidification. A patent by Schade *et al.* (2015) lists a “curing agent” as an option to cure a nanocellulose-reinforced film in the course of its extrusion. Curable resins such as epoxy also have been impregnated into pre-formed cellulosic films (Lee *et al.* 2012)

Pre-milling and pre-mixing

As a way to improve the performance of extrusion operations, efforts to improve the initial blending of ingredients can be important. Ambrosio-Martin *et al.* (2015b) used ball milling to improve the incorporation of freeze-dried CNC aggregates in a more fully dispersed form. In a related work (Ambrosio-Martin *et al.* 2015a), it was shown that more favorable properties could be achieved by pre-blending reinforcement with the matrix prior to extrusion. Though freeze drying is preferred as a means of minimizing aggregation of nanocellulose, the relatively pure cellulosic surfaces of CNC are highly prone to the development of mutual hydrogen bonding upon drying (Sanchez-Garcia and Lagaron 2010; Baez *et al.* 2014; Lindström and Aulin 2014).

Casting of Nanocellulose Films from Liquids

When one's goal is to prepare a nano-cellulose-based film or layer having either 100% or a high proportion of nanocellulose in it, then extrusion may not be practical due to poor flow characteristics at moderate to high solids levels. Instead, it makes sense to suspend the nanocellulose in a suitable liquid or solution that can be subsequently evaporated. Two main classes of such "casting from solution" systems can be differentiated: casting from aqueous solution (or pure water) and casting from a non-aqueous liquid. The former case, using water, has the potential advantage of allowing strong hydrogen bonding to take place among the cellulose nanoparticles during the course of drying. Alternatively, non-aqueous casting systems have a potential advantage of allowing dissolution of various water-insoluble matrix materials that may influence the properties of a resulting layer or film. In either case, the proportion of solids relative to the evaporable liquid will depend on such factors as being able to uniformly disperse particles of relatively high aspect ratio, while on the other hand having to evaporate a lot of liquid.

Aqueous media

Numerous researchers have prepared nanocellulose-based films from aqueous media, including aqueous solutions and suspensions. The following studies pertain to preparation of relatively pure cellulose films, using plain water as a casting medium: (Dufresne *et al.* 1997; Yano and Nakahara 2004; Fukuzumi *et al.* 2009; Aulin *et al.* 2010a; Minelli *et al.* 2010; Rodionova *et al.* 2012a,b; Tammelin *et al.* 2013; Palaninathan 2014; Lu *et al.* 2015).

Notably, Dufresne *et al.* (1997) discovered that the pectin component of their highly fibrillated sugar beet cellulose played a key role in strength development of the sheets formed when the cast film was dried. Yano and Nakahara (2004) observed a doubling of yield strain and bending strength upon addition of 2% oxidized starch to the formulation, on a dry basis. Thus, even in compositions that are mostly cellulose, it can be advantageous to have some amount of water-soluble or water-swellable polymer present that can function as a binder. It appears that more research related to this topic is merited.

When an aqueous solution of a soluble polymer is employed in a casting and evaporation procedure, the dissolved matter becomes incorporated into a composite product. Many studies related to this were found in the present search of the literature. Table 1 lists such studies according to the type of solvent (if any) that was dissolved in the aqueous solution.

The presence of nanocellulose as reinforcement in a polymer film can have diverse effects on the subsequent processing and properties. López-Rubio *et al.* (2007) discovered that microfibrillated cellulose could play a role analogous to that of a plasticizer, replacing glycerol in facilitating the preparation of high-quality films from amylopectin. In the absence of MFC it was not possible to prepare the highly uniform, strong films without the addition of glycerol. Tammelin *et al.* (2013) described how the application of a water-based nanocellulose formulation to a support surface, followed by drying in place, can be a convenient way to avoid problems of shrinkage in separately-prepared films. Toivonen *et al.* (2015a) showed that the transparency of films could be retained effectively by using a solvent-exchange process as a means of drying. The nanocellulose in those products made it possible to maintain a stable mesoporous structure, and the films showed promise for use in air filtration.

Table 1. Solutes Employed in Studies of Aqueous "Cast Film" Procedures

Agar
Reddy and Rhim 2014
Shankar & Rhim 2016

Alginate
Abdollahi *et al.* 2013a
Abdollahi *et al.* 2013b
Liu *et al.* 2013
Khan *et al.* 2014b
Sirviö *et al.* 2014

Carboxymethylcellulose
Choi and Simonsen 2006
Sharmin *et al.* 2012
El Miri *et al.* 2015
Oun & Rhim 2015
Youssef *et al.* 2015

Carrageenan
Sanchez-G. *et al.* 2010
Savadekar *et al.* 2012

Caseinate (Na)
Pereda *et al.* 2011

Chitosan
Li *et al.* 2009
Azeredo *et al.* 2010
Fernandes *et al.* 2010
Hassan *et al.* 2011
Khan *et al.* 2012
Liu *et al.* 2013
Tome *et al.* 2013
Dehnad *et al.* 2014a,b
Dong *et al.* 2014
Pereda *et al.* 2014
Velasquez-Cock *et al.* 2014
Feng *et al.* 2015a
Li *et al.* 2015b

Gelatin
George & Siddaramaiah 2012
Santos *et al.* 2014

Gluten
Rafieian *et al.* 2014
Rafieian & Simonsen 2014
El-Wakil *et al.* 2015

Guar
Cheng *et al.* 2016

Guar, hydroxypropyl
Dai *et al.* 2015

Hemicelluloses
Mikkonen *et al.* 2011
Peng *et al.* 2011
Stevanic *et al.* 2011
Stevanic *et al.* 2012

Hydroxy-prop-methylcellul.
Bilbao-Sáinz *et al.* 2010

Latex (PLA)
Larsson *et al.* 2012

None
Johnson *et al.* 2009
Khan *et al.* 2010

Polyacrylamide
Kurihara & Isogai 2014
Mandal & Chakrabarty 2015

Polyethylene oxide
Azizi Samir *et al.* 2004b

Polyvinyl alcohol
Zimmermann *et al.* 2004
Chakraborty *et al.* 2006
Lu *et al.* 2008
Cheng *et al.* 2009
Lee *et al.* 2009
George *et al.* 2010
Souza *et al.* 2010
Baheti & Militky 2013
Ollier *et al.* 2013
Pereira *et al.* 2014
Bai *et al.* 2015a,b
Li *et al.* 2015b
Mandal & Chakrabarty 2015
Noshivani *et al.* 2016

Pullulan
Trovatti *et al.* 2012a,b
Cozzolino *et al.* 2014

Starch
Dufresne & Vignon 1998
Angeles & Dufresne 2000
Dufresne *et al.* 2000
Angeles & Dufresne 2001
López-Rubio *et al.* 2007
Svagan *et al.* 2007
Cao *et al.* 2008
Mathew *et al.* 2008
Wan 2009
da Silva *et al.* 2012
Tome *et al.* 2013
Salehudin *et al.* 2014
Yang *et al.* 2014
Noshivani *et al.* 2016

Xylan
Hansen *et al.* 2012

Non-aqueous media

When the matrix phase to be reinforced by nanocellulose is too hydrophobic to dissolve in water, non-aqueous solvents have been employed in the preparation of such films and coatings (Grunert and Winter 2002; Petersson and Oksman 2006; Sanchez-Garcia *et al.* 2008; Ayuk *et al.* 2009; Petersson *et al.* 2009; Hossain *et al.* 2011; Fortunati *et al.* 2012b; Hassan *et al.* 2012; Salmieri *et al.* 2014b; Song *et al.* 2014; Fortunati *et al.* 2015; Kiziltas *et al.* 2015; Urbina *et al.* 2016). By employing a solvent with a sufficiently low boiling point, the film preparation can be carried out with good distribution of the reinforcement, suitably low viscosity to allow easy spreading of the film, ready evaporation of the solvent from the film, and avoidance of the need for elevated temperatures, since the matrix polymers are dissolved rather than melted. Likewise, Aulin *et al.* (2013) regarded solvent-cast poly-lactic acid films as a leading "benchmark" of performance, which they attempted to improve upon by further surface treatments.

One of the challenges faced by researchers employing non-aqueous solvent-casting with the inclusion of nanocellulose solids is the incompatibility of ordinary cellulose surfaces with relatively non-polar matrix polymers such as poly-lactic acid (PLA) and cellulose acetate butyrate (CAB). Grunert and Winter (2002) pioneered the modification of nanocellulose for such systems, using trimethylsilane to make the surface of bacterial cellulose less hydrophilic. Several other research groups have employed related strategies to hydrophobically modify nanocellulose materials for use in solvent-casting with a hydrophobic matrix (Hassan *et al.* 2012; Song *et al.* 2014). Alternatively, Fortunati *et al.* (2012b) found that uniform mixing of un-modified nanocellulose in such a system could be achieved by adding a surfactant, due to reduction in surface energy of nanocellulose by surfactants.

Filtration and Papermaking Processes

Papermaking can be described as a process in which a suspension of cellulosic fibrous matter is collected on a screen, followed by drying and the development of inter-fiber hydrogen bonding. A number of researchers have demonstrated such a process when using nano-fibrillated cellulose (Nakagaito and Yano 2004, 2005, 2008a,b; Henriksson *et al.* 2008; Nogi *et al.* 2009; Syverud and Stenius 2009; Sehaqui *et al.* 2010, 2011; Larsson *et al.* 2012; Hu *et al.* 2013; Rojo *et al.* 2015). Keshvarzi *et al.* (2015) prepared paper-like films from a gelled mixture of nanocellulose and zeolites. These films were found to have a high ability to absorb odors. Such preparation methods generally can achieve relatively high strength, high resistance to oxygen, and high transparency (Klemm *et al.* 2011; Lindström and Aulin 2014).

Alternatively, nanofibrillated or microfibrillated cellulose has been added to suspensions of ordinary wood-pulp fibers in order to achieve higher strength of the resulting paper (Ahola *et al.* 2008a,b; Eriksen *et al.* 2008; Schlosser 2008; Syverud *et al.* 2009; Guimond *et al.* 2010; Song *et al.* 2010; Taipale *et al.* 2010; Gao *et al.* 2011; Husband *et al.* 2011; González *et al.* 2012; Johansson *et al.* 2012; Charani *et al.* 2013; Ankerfors *et al.* 2014). Slower dewatering during paper forming has been observed (Taipale *et al.* 2010), though residual lignin and added cationic polymers have been found to be helpful to promote dewatering in such cases. Otherwise, the dewatering is too slow due to the high surface area of nanocellulose, which has more capacity to hold water than conventional cellulose (Taipale *et al.* 2010; Rojo *et al.* 2015).

Coating Processes

A coating process can be defined as the application of a slurry onto a porous surface, such that the solid contents are converted into a film that has good adhesion to the underlying matter. The liquid suspending medium may be partly absorbed into the underlying material, and the rest is typically evaporated directly. According to Kiviranta (2000), most of the paper and board products currently being used for food packaging already have some kind of coating. Accordingly, the presence of nanocellulose in coatings for paper deserves consideration.

In cases of particular interest to packaging, the support surface can be paper or paperboard, and the absorption of solution into the pores can provide a primary means of initially draining the suspending medium from the coating layer (Lindström and Aulin 2014). Coatings of nanocellulose suspensions onto paperboard have been reported, and the topic has been reviewed by Rastogi and Samyn (2015). Table 2 lists such studies based on the type of nanocellulose.

Table 2. Studies in which Micro- or Nanocellulose Was Applied as a Coating

Microfibrillated cellulose	**Nanofibrillated cellulose**	**Cellulose Nanocrystals**
Syverud *et al.* 2009 Syverud and Stenius 2009 Aulin and Ström 2013 Ridgeway & Gane 2012, 2013 Dimic-Misic *et al.* 2014 Lavoine *et al.* 2014b,c Liu *et al.* 2014 Lavoine *et al.* 2015 Salo *et al.* 2015 Cozzolino *et al.* 2016	Hamada *et al.* 2010 Freire *et al.* 2013 Hu *et al.* 2013 Ridgeway & Gane 2012, 2013 Dimic-Misic *et al.* 2014 Iotti 2014 Rautkoski *et al.* 2015 Salo *et al.* 2015 Amini *et al.* 2016 Dimic-Misic *et al.* 2016 Kumar *et al.* 2016 Vartiainen *et al.* 2016	El-Wakil *et al.* 2015 Mascheroni *et al.* 2016

In addition to the listed studies, Nygårds *et al.* (2011) employed an offset printing approach to apply various nanocellulose-based barrier coatings. A potential advantage of this kind of system is that absorption of water by the underlying paper can rapidly immobilize the coating. Kumar *et al.* 2016) demonstrated the feasibility of a roll-to-roll coating system with non-contact infra-red drying and air drying to apply a CNF coating to paper at speeds up to 30 m/min.

According to Lindström and Aulin (2014), the inherently high viscosity of suspensions of nanofibrillated cellulose pose great challenges to the industrial implementation of such technology. In some coating systems it may be necessary to lower the solids in the formulation in order to achieve suitable flow properties. Salo *et al.* (2015) found that highly fibrillated cellulose could serve the role of "water retention aid" in a coating formulation, helping to promote the leveling of the coating after its application to a paper surface. As noted by Syverud and Stenius (2009), such coating layers can increase paper strength and reduce oxygen transmission through the paper. Charani *et al.* (2013) compared the effects of adding microfibrillated cellulose to the fiber slurry or as a coating on paper. The coating approach was found to be more effective in reducing air permeability.

Due to their lower aspect ratios, typical cellulose nanocrystals do not pose such great challenges related to rheology of their suspensions as do highly fibrillated cellulose materials at similar solids levels. Li *et al.* (2013a) applied cellulose nanocrystal suspensions to various substrates, including regenerated cellulose film. Liu *et al.* (2015) prepared composites of nano-Fe_3O_4 with CNC and used these nanocomposites to prepare conductive paper by a coating method. Yang *et al.* (2014) reported the preparation of starch solutions containing CNC at the 0.3% level on starch solids; their application to paper in a size press operation had a favorable effect on paper strength and resistance to air permeation.

Coating from non-aqueous solution onto a paper substrate has already been mentioned in the context of casting of films (Song *et al.* 2014). The cited authors applied blended mixtures of surface-hydrophobized nanocellulose in a solution of poly-lactic acid onto paper. The presence of 1% CNC in the cast-coated PLA film resulted in a low water vapor transmission rate.

Impregnation of Nanocellulose Films

Several researchers have explored procedures similar to coating in which the applied fluid was able to permeate a previously-prepared film of nanocellulose. For instance, the following authors reported improvements in various barrier and strength properties of the thin films achieved through such treatments (Wan *et al.* 2009; Lee *et al.* 2012; Aulin and Ström 2013; Barud *et al.* 2013). Nakagaito and Yano (2004, 2005, 2008a) reported similar work in which fibrillated kraft pulp impregnated with phenolic resin was compressed under very high pressure to make high-strength nanocomposites. By using impregnation of an existing nanocellulose film with nanofillers, high contents of cellulose can be achieved. Also, the impregnant may be able to aid in sealing off some pores.

Layer-by-Layer Processes

Using a sequential adsorption of oppositely charged polyelectrolytes, it is possible to build up well-organized multilayers having very uniform and controllable thickness (Decher 1997). Some researchers have applied the same approach to preparing films incorporating nanocellulose, essentially substituting the nanocellulose suspension in place of the negatively charged polyelectrolyte solutions typically used in such procedures (Wågberg *et al.* 2008; Aulin *et al.* 2009b, 2010b, 2013; de Mesquita *et al.* 2010; Li *et al.* 2013b; Marais *et al.* 2014). Alternatively, it is possible to convert nanocellulose to a positively charged form and make the opposite substitution (Aulin *et al.* 2010b). Aulin *et al.* (2010b) discovered that such films exhibited considerable strength even before the film was dried, *i.e.* a kind of "green strength." The cohesion of the undried films was attributed to electrostatic attraction between oppositely charged surfaces. Aulin *et al.* (2013), who prepared 50-pair-layer structures (nanofibrillated cellulose and polyethyeneimine in each bilayer), were able to exceed the oxygen permeability resistance of solvent-cast NFC films through this route. Ankerfors *et al.* (2016) demonstrated the application of microfibrillated cellulose layers onto mechanical pulp fibers, with the incorporation of charged starch derivatives and poly-(amidoamine epichlorohydrin) wet-strength resins. The CTMP pulp, treated in this way, gave high levels of strength to the paper.

A positive attribute of polyelectrolyte multilayer deposition as a way to create nanocellulose-containing thin films is its great flexibility to achieve a wide range of properties, which can be extremely uniform down to nanometer dimensions. For instance, Aulin *et al.* (2009b) prepared superoleophobic (contact angle with glycerol >90) films by deposition of cellulose nanocrystals onto a silica substrate, followed by a layer of fluoropolymer. Aulin *et al.* (2013) were able to tune the barrier properties of the films by varying the procedural details of successive adsorption of polyethyleneimine and nanocellulose. Marais *et al.* (2014) demonstrated unusually high straining ability of such films. They also demonstrated a large difference in properties, depending on which of the successive layers was the last to be deposited in a multilayer film structure. By incorporating tin-doped indium oxide, carbon nanotubes, and silver nanowires into a multilayer structure with nanocellulose, Hu *et al.* (2013) prepared films that were electrically conductive, in addition to being transparent.

Application procedures for polyelectrolyte multilayer deposition are inherently slow, relative to high-speed manufacturing processes. Time is required at each step for the respective polyelectrolyte to diffuse from a solution and form a charged complex with the opposite charges of the substrate or of a previous deposited layer. Most procedures used for polyelectrolyte multilayer preparation call for a rinsing step between each adsorption step.

Foam Structure Preparation

Many of the same factors already discussed in the context of thin films also have relevance to the preparation and properties of foam materials, which can be envisioned as structures formed from the thin film walls of bubbles (Lindström and Aulin 2014; Ago *et al.* 2016). For instance, Tchang Cervin *et al.* (2014) patented the preparation of a foam composition including nanofibrillated cellulose. Through the incorporation of a hydrophobic amine additive, the foam was rendered resistant to water, and it also was claimed to be effective as a gas barrier. The incorporation of the nanocellulose into a foam wall structure provides rigidity to the material (Pääkkö *et al.* 2008; Srinivasa *et al.* 2015). To avoid the collapse of such foams during drying, freeze-drying is the usual approach in the cited works.

Curing Processes

As a means to achieve the desired properties, some form of heating or drying is often the final step in the preparation of a thin film incorporating nanocellulose. Such "curing" steps are considered below.

Several research teams have described procedures whereby nanocellulose-containing films have been heated or subjected to photo-initiation in order to bring about chemical reactions that cure the films (Shimazaki *et al.* 2007; Stoica-Guzun *et al.* 2013; Bai *et al.* 2015a,b; Schade *et al.* 2015). For example, the article and patent by Bai *et al.* (2015a,b) describe the use of UV light to cure a formulation that included nanofibrillated cellulose, polyvinyl alcohol, a cross-linking agent, and a photo-initiator. A patent by Schade *et al.* (2015) describes a similar approach, but the curable matrix consists of either a phenol-formaldehyde resin or an isocyanate formulation.

Hot-pressing is another well-known curing strategy, which recently has been applied in the preparation of films and layers containing nanocellulose (Larsson *et al.* 2012, 2016; Qing *et al.* 2012; Khan *et al.* 2013; Österberg *et al.* 2013; Figueiredo *et al.* 2015; Schade *et al.* 2015). Larsson *et al.* (2012) and Figueiredo *et al.* (2015) took advantage of the thermoplastic nature of polylactide and polycaprolactone, respectively, in heat-preparation of a composite films with nanocellulose. Österberg *et al.* (2013) found that heating was able to increase the water-resistance of films prepared from nanofibrillated cellulose, and that water-resistance could be further enhanced by wax coating.

A specialized drying procedure can sometimes be used if there is a motivation to preserve a high surface area or other specialized effects in a nanocellulose-based thin film. Thus, Sehaqui *et al.* (2011) exchanged the water in nanofibrillated cellulose hydrogels with liquid CO_2, supercritical CO_2, and tert-butanol, followed by drying by sublimation. The resulting films had a high porosity (*e.g.* 56%) and a high specific surface area (as high as 480 m^2/g). Bardet *et al.* (2015) used vacuum drying (75 °C, 1 h) to remove sulfate ester groups from the CNC surfaces in the film. Rodionova *et al.* (2012a) discussed hornification effects, *i.e.* a loss of re-swelling ability, which can take place during routine drying of nanocellulose-based films. Effects of different drying methods on the properties of bacterial cellulose were reported by Feng *et al.* (2015a). Freeze drying, relative to conventional oven drying, yielded much lower watering holding capacity (about 6000% in comparison to 12,000%) but a much higher water absorption rate (about 880% *vs.* about 140%).

As noted by Tammelin *et al.* (2013), nanocellulose-based films have the potential to shrink greatly during evaporative drying from an aqueous suspension. To avoid this, Baez *et al.* (2014) evaluated different modes of restraint of the dimensions during drying. Stretching of the films prior to drying yielded the highest alignment of fibrils within the structure. It also yielded the highest directional strength and stiffness in the stretched direction. Fully restrained drying achieved a non-aligned film with relatively high strength characteristics relative to an unrestrained sample. Lindström *et al.* (2012) investigated the effects of cyclic exposure to different humidities. The nanocellulose films and aerogels showed substantial creep behavior, indicating that creep was dominated by local events within the film during changes in humidity.

BARRIERS AND PATHS TO IMPLEMENTATION

Based on literature already cited, there are many ongoing concerns related to performance issues of nanocellulose-based films, coatings, and layers. These are summarized in Table 3, along with some ways that researchers have attempted to address those concerns. The final section of the review article will discuss progress that has been made relative to the challenges posed in Table 3. Emphasis will be placed on work related to resistance to oxygen and water vapor diffusion through the films, especially in humid or wet environments.

Oxygen Barrier Performance Concerns

Oxygen barrier issues will be considered first here, mainly in recognition of the outstanding performance levels reported by some authors (Fukuzimi *et al.* 2009; Syverud and Stenius 2009; Aulin *et al.* 2010a; Cozzolino *et al.* 2014; Kisonen *et al.* 2015). It seems likely that at least part of the recent spurt of academic and industrial attention directed toward nanocellulose films in packaging can be traced to a superior ability to block the passage of oxygen.

A high level of success, in any arena, can entail a subsequent higher level of scrutiny. There can be concerns that maybe, by modest modifications in procedures or composition, it might be possible to make very large improvements in the first-generation films created in the laboratory thus far. On the other hand, high levels of oxygen hold-out achieved in the lab might not hold true when attempting to implement the same scheme on an industrial scale. For instance, defects and leakage past the barrier might become an important issue when trying to coat large areas or when trying to form films rapidly. Issues related to effects of humidity and moisture will be considered subsequently.

As can be recognized by inspecting the corresponding entries in Table A (see Appendix), a great many researchers have reported on the ability of nanocellulose-based films to limit or to almost prevent the passage of oxygen. Some key examples are listed by Aulin *et al.* (2010a). The performance of various nanocellulose-based films to resist permeation by oxygen is summarized in Table B of the Appendix.

Table 3. Challenges Concerning the Performance of Nanocellulose-based Thin Films, Coatings, and Layers for Packaging

Key Challenges	Strategies to Overcome Challenges
Oxygen barrier is inadequate to meet the stretch goals of package designers.	Selection of nanocellulose type (Siro and Plackett 2010) Tortuosity enhancement (Wu *et al.* 2012; Visanko *et al.* 2015) Enhancement of hydrogen bonding (Angles & Dufresne 2001) Oxidation and related (Chinga-Carrasco & Syverud 2012)
Films fail to block wetting or leakage of a liquid.	Use of a separate moisture barrier (Lagaron *et al.* 2004) Chemical modification of the cellulose (Visanko *et al.* 2015) Coupling agents (Eichhorn *et al.* 2009; Faruk *et al.* 2012) Waxes on NFC film (Spence *et al.* 2011b) Plasticizer in NFC film (Bayati *et al.* 2014; Arrieta *et al.* 2015) Curable cross-linking (Fernandez *et al.* 2008; Raghu 2015)
Film performance is compromised by high humidity or moisture.	Chemical modification of the cellulose (Tome *et al.* 2010) Use of additives to the film (Pereda *et al.* 2014) Waxes and other coatings on the film (Kisonen *et al.* 2015) Curable cross-linking treatments (Aulin and Ström 2013) Allow residual lignin in the composition (Rojo *et al.* 2015)
Films break due to stress above their strength at the weakest point.	Selection of fibers and matrix (Siro and Plackett 2010). Plasticizer use to increase compliance (Alves *et al.* 2015) Strategies related to coupling agents (Suzuki *et al.* 2014) Avoid agglomeration with low reinforcement (Sandquist 2013).
Films crack due to bending stresses and inadequate flexibility.	Strategies related to plasticization (Azeredo *et al.* 2010) Type of polymeric matrix material (Oun and Rhim 2015) Tuning of modulus & bondedness (Yano & Nakahara 2004) Strategies for drying the films (Toivonen *et al.* 2015a)
Films lack transparency, which may be required in some applications.	Disperse nanocellulose well (Ambrosio-Martin *et al.* 2015a) Mill nanocellulose clusters (Ambrosio-Martin *et al.* 2015b) Use surfactants to get uniform dispersion (Fortunati 2015) Derivatize the cellulosic surfaces (Hu & Wang 2016)
Film manufacturing rate is slow relative to the competition, *e.g.* plastic films.	How to prepare layers at high speed (Aulin & Ström 2013) Spray-coating issues (Hult *et al.* 2010; Yu *et al.* 2016) Self-assembly issues (Habibi *et al.* 2010; Moon *et al.* 2011) Dewatering issues (Dimic-Misic *et al.* 2016)

Some key factors accounting for the ability of nanocellulose films to block gas transport will be summarized. As noted already by Lagaron *et al.* (2004), one of the essential principles underlying resistance to diffusion of gases through packaging materials is to have a very low solubility of the gas in the material. In general terms, very low solubility implies a large difference in factors such as hydrogen bonding ability. Both oxygen and nitrogen gases are non-polar compounds, whereas cellulose is rich in polar, hydrogen-bonding –OH groups. The other key factor noted by Lagaron *et al.* (2004) is a high cohesive energy density, which again can be attributed to the hydrogen bonding. According to Lagaron *et al.* (2004), resistance to gas permeation through a solid film is often correlated with the glass transition temperature; a high T_g value implies a generally immobile nature of molecular segments, so that gas diffusion through the material is not facilitated. As long as the film is uniform and defect-free, effective barrier performance can be expected.

As noted by Aulin *et al.* (2010a), nanofibrillated cellulose, when dried as a film from aqueous solution, can form a very dense structure. The high level of hydrogen bonding within the structure, involving a high density of cohesive energy, may be important not only in achieving higher film density, but also in avoiding gaps in such films.

As illustrated informally in Fig. 4, due to the hydrogen bonding between the molecular chains, cellulose has sufficient cohesive energy density to hold the material together as a film that is sufficiently dense, on a molecular level, to be able to block gas molecules. Such film characteristics can be effective for impeding the permeation of oils as well as gases (Aulin *et al.* 2010a).

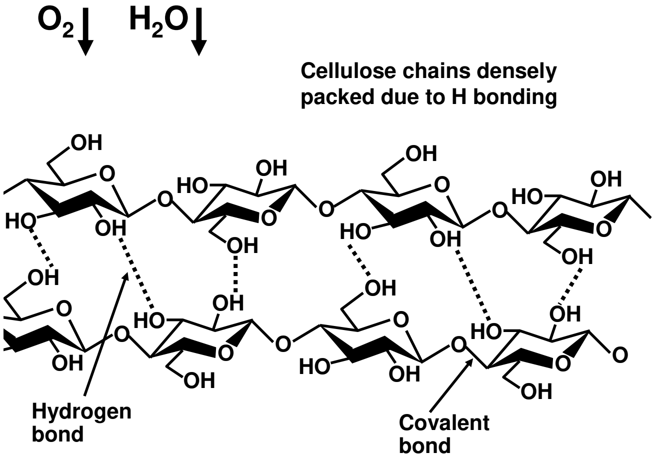

Fig. 4. Concept of hydrogen bonding within a nanocellulose film, leading to a highly dense structure that can block gas molecules

Hansen *et al.* (2012) found that whereas pure cellulose films, prepared from NFC, were highly resistant to oxygen, such resistance was seriously hurt by the incorporation of plasticizers in the formulation of the films. Such observations can serve as confirmation of the hypothesis that hydrogen bonding and a high energy of interaction among the cellulosic elements in the film are mainly responsible for the ability to resist oxygen. A plasticizer, which by its nature has much less ability to hydrogen bond, would provide less-bonded regions that could locally reduce the solid density, which would be more conducive for the diffusion of gas. This concept is illustrated in Fig. 5.

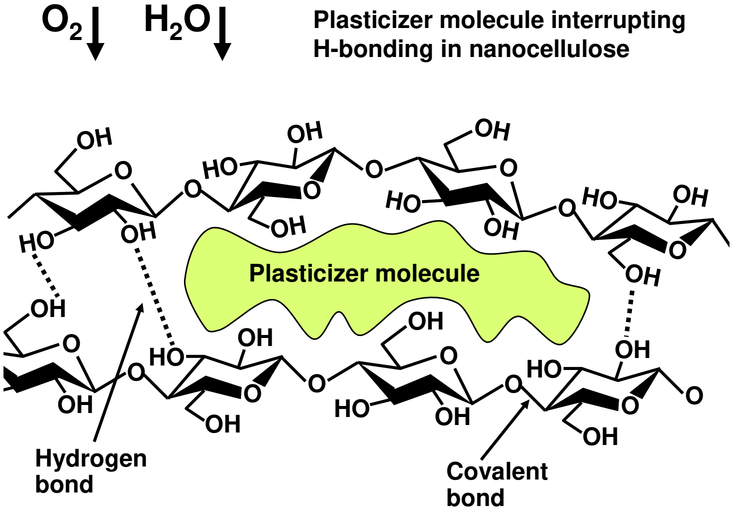

Fig. 5. Concept that the presence of plasticizer molecules can be expected to interrupt the network of hydrogen bonding within a nanocellulose film

Type of nanocellulose vs. O_2 barrier performance

Belbekhouche *et al.* (2011) prepared thin films from cellulose nanocrystals and microfibrillated cellulose, both obtained from sisal fibers. The film prepared from the CNC was much more permeable to gases, and the difference was attributed to a more porous nature of such films. Thus, the inherently higher flexibility of nanofibrillated cellulose may be essential if the goal is to achieve high resistance to air permeation through a film composed only of cellulose. Indeed, high levels of resistance to oxygen have been reported from studies focusing on NFC (Fukuzimi *et al.* 2009; Syverud and Stenius 2009; Aulin *et al.* 2010a; Cozzolino *et al.* 2014; Kisonen *et al.* 2015).

In light of the findings just cited, one might expect that such resistance might increase with increased fibrillation. Siro *et al.* (2011) found otherwise. Oxygen permeability was not significantly influenced by the number of times the material had been passed through a homogenizer. Such results suggest that the lowest level of microfibrillation considered by the cited authors was already sufficient to impart enough flexibility into the wet material in order to be able to form a dense, air-impermeable structure upon drying.

Oxidation and negative surface charges vs. O_2 barrier performance

Many researchers aiming to achieve oxygen barriers with nanocellulose particles have employed underivatized NFC. Visanko *et al.* (2015) followed a contrasting approach, starting with CNC, then derivatizing the cellulose with TEMPO-mediated oxidation, followed by reductive amination to connect butylamino groups. High resistance to oxygen transport was observed even at 80% relative humidity. Likewise, Chinga-Carrasco and Syverud (2012) employed TEMPO oxidation to produce CNF, which was then used to form films that exceeded the oxygen barrier performance of parallel samples prepared without oxidation. The authors attributed the high performance to the dense nature of the resulting films. Both of these effects, as cited above, may be regarded as consequences of the polar nature of carboxylic acid groups, which in principle might give a higher cohesive energy density to the film material.

Mascheroni *et al.* (2016) observed strong resistance to oxygen permeation when CNC was applied as a coating to poly(ethylene terephthalate) films. Notably, better blocking of oxygen transport was achieved by the use of CNCs produced by ammonium persulfate (APS), rather than the usual sulfuric acid. The results were attributed to a higher negative charge density induced by the APS, in the form of carboxylate groups on the CNC. Related and confirmatory results were obtained by Naderi *et al.* (2016), who phosphorylated NFC in order to increase its negative surface charge. Again, substantially lower oxygen permeabilities were observed when compared to the default NFC.

One can hypothesize that negative charges induced by the oxidation would inhibit early strong adhesion between cellulosic surfaces, thus allowing adjacent chains to organize themselves more densely during the gradual drying of a film (Hubbe and Rojas 2008). In other words, charge-charge repulsion between particles helps the particles to avoid forming clumps, and thus a denser, less permeable dry coating layer will have been formed once the drying process has been completed.

Tortuosity enhancement vs. O_2 barrier performance

It has been widely assumed that gas diffusion cannot take place at all within or through crystalline domains of cellulose. It is reasonable to suspect that the direct blockage of gas diffusion by crystalline regions can account for at least part of the observed ability of nanocellulose films to impede passage of oxygen (Fukuzimi *et al.* 2009; Syverud and Stenius 2009; Aulin *et al.* 2010a; Lindstrom and Aulin 2014).

Figure 6 presents a view of how tortuosity may play a significant role in limiting gas diffusion through nanocellulose films. In this figure the film is assumed to be comprised of NFC. Each fibril in the structure is understood to be made up of cellulose nanocrystals (shown with darker shading) that are connected or surrounded by non-crystalline regions (shown without shading). The structure as a whole is assumed to be tightly bonded together, on account of the high flexibility of the individual NFCs in the wet state, before drying of the film. A gas molecule, when passing through the film, would be blocked each time that it encounters a crystalline region, which may occupy the majority of the volume. The lengthening of the diffusion paths would imply a slower rate of gas transport.

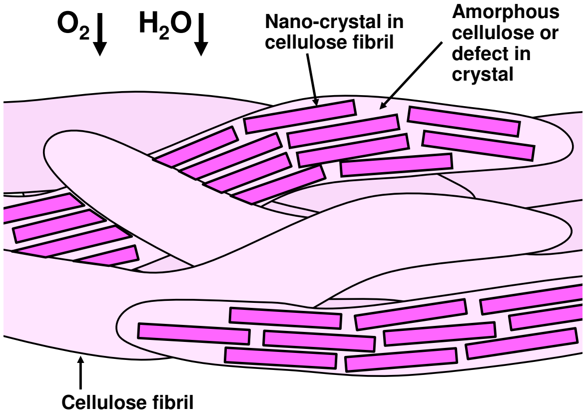

Fig. 6. Concept that crystalline regions inherent in native cellulosic structures are likely to play a role in impeding the diffusion and permeance of oxygen and water vapor, both of which would have to pass around the outsides of any crystalline domains

The very thin, platy nature of montmorillonite (*i.e.* bentonite) particles can be used advantageously in various films to reduce the permeation of gases (Rhim *et al.* 2013). The idea is that the crystalline nature of the particles precludes air passage through the particles, and their wide, flat shapes mean that gas molecules must take a longer path during their diffusion through the matrix polymer. Wu *et al.* (2012) found montmorillonite particles to be highly effective for decreasing the oxygen-permeability of films formed from TEMPO-oxidized NCFs.

Induced crystallinity vs. O_2 barrier performance

Various researchers have shown that the addition of nanocellulose reinforcement in polymer films also has the ability to decrease gas permeation (Paunonen 2013a; Ambrosio-Martin *et al.* 2015a; Dhar *et al.* 2015). As discussed above, such results might be partly attributed to the relatively high crystallinity of most types of nanocellulose (Aulin *et al.* 2009a; Xu *et al.* 2013), which can help to explain their apparent ability to block oxygen permeation when present in certain polymeric matrices (Ambrosio-Martin *et al.* 2015a). Dhar *et al.* (2015) attributed the strong gas-barrier properties to the effective hydrogen bonding between cellulose and the matrix, as well as the more tortuous path required for diffusing gas molecules. Visanko *et al.* (2015) observed resistance to O_2 permeability even at relatively high humidity when using periodate-oxidized-aminated

CNC to form a single-component film. The promising results were attributed to tortuosity, giving rise to longer diffusion paths through the dense film.

Though mechanisms based on tortuosity have been shown to be valid in other circumstances, it seems doubtful that CNC would be greatly effective in blocking the progress of gas molecules when present at a relatively low percentage in a polymer matrix. The columnar shape of a CNC particle does not seem nearly as well suited for such purposes as, for instance, montmorillonite clay (Liu and Berglund 2012). Another possible explanation for enhanced barrier properties upon addition of CNC to a matrix polymer melt is that the crystalline regions could have functioned as nucleation sites for crystallization of the matrix polymer. If such a process leads to higher overall crystallinity, while still preserving a defect-free structure, then the barrier properties might be enhanced. In support of this concept, Camarero-Espinoza *et al.* (2015) reported that CNC induced increased crystallinity of poly-lactide after heating. Gas permeability was not measured in that study, though higher storage modulus was observed. Lu *et al.* (2016) also observed an increased rate of crystallization of poly-(lactic acid) with the inclusion of nanocellulose formate in the composite. Further studies are needed in order to determine whether such induced crystallinity can be used as a strategy to decrease gas permeability, when using nanocellulose reinforcement in thermoplastic matrix polymers.

Additives and coatings vs. O_2 barrier performance

Increased resistance to oxygen transmission has been achieved by adding shellac, along with MFC (Hult *et al.* 2010). Though shellac forms a relatively water-repellent film, the main ingredients are rich in hydrophilic carboxyl and hydroxyl groups (Sharma *et al.* 1983). Hansen *et al.* (2012) found that high oxygen resistance was maintained when preparing composite films of xylan (hemicellulose) with NFC. These are examples of combining two ingredients, both of which have substantial hydrogen bonding ability, to achieve high-performing films.

Hambardzumyan *et al.* (2015) showed that films with promising O_2-barrier performance could be prepared from lignins in combination with CNC. Fenton's reagent was used to promote grafting of lignin onto the CNC surfaces. Related work was reported by Yang *et al.* (2016), who used CNC and lignin nanoparticles together in poly-(lactic acid) matrix; the two types of nano-reinforcement appeared to be acting synergistically.

Promising results have been found in some cases where a thin coating was applied on top of highly fibrillated cellulose films. Spence *et al.* (2011b) found that the application of a surface coating of wax on top of a microfibrillated cellulose layer achieved oxygen-resistance that exceeded that of low-density polyethylene. Kisonen *et al.* (2015) applied coatings of either native galactoglucomannan (GM) or a succinic ester of GM onto the surface of composite films of NFC and O-acetyl galactoglucomannan. Both coatings increased resistance to oxygen permeation, and they also more effectively prevented grease penetration. Such results suggest that NFC and the hemicellulose layer may constitute a synergistic pair, in which the NFC provides a stable structure and the hemicellulose, being more fluid, can seal any holes that may be present in the NFC film structure. This concept is illustrated in Fig. 7, where a wax is assumed. The promising nature of the results described in this paragraph, coupled with the simplicity of the preparation of such bilayer systems, suggests that this is a very promising area for future research.

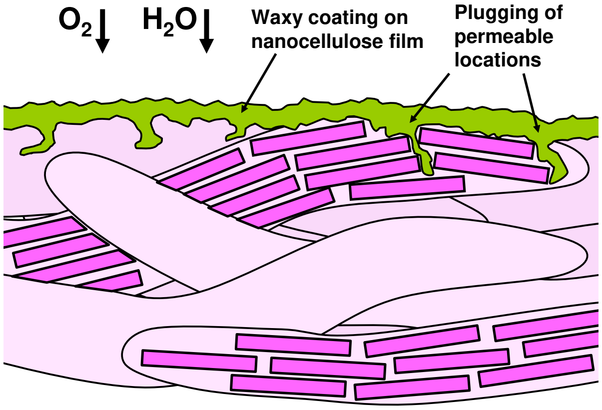

Fig. 7. Concept of a coating material that serves to "plug" locations in a nanocellulose film that may be defective or may offer higher gas permeability due to their amorphous nature

Fortunati *et al.* (2012a,b, 2013, 2015) obtained promising results for surfactant-modification of CNC. The surfactant employed was an acid phosphate ester of ethoxylated nonylphenol. The modified CNC was used as a reinforcement in poly-(lactic acid) (PLA) films. The surfactant tended to improve the distribution of CNC in the matrix, and the system also led to increased crystallinity of the PLA.

Polyelectrolyte complexes vs. O_2 barrier performance

Some studies have reported enhancements of oxygen barrier performance with the formation of polyelectrolyte complexes (PECs) from aqueous solutions during the preparation of the film. For instance, in the following studies, the nanocellulose reinforcements had an opposite ionic charge from a polyelectrolyte, which would eventually play the role of matrix in the formed composite films (de Mesquita *et al.* 2010; Khan *et al.* 2012; Liu *et al.* 2013; Dong *et al.* 2014; Velasquez-Cock *et al.* 2014; Ibn Yaich *et al.* 2015; Li *et al.* 2015b). However, only in a few of these cases were the oxygen or grease permeability evaluated (Ibn Yaich *et al.* 2015; Shimizu *et al.* 2016). Liu *et al.* (2013) reported a system in which the positively charged polyelectrolyte chitosan was precipitated onto the surface of bacterial cellulose by adding phosphate ions; then, the chitosan-treated BC was combined with the anionic polyelectrolyte sodium alginate. Good strength and antibacterial effects were reported. Sirviö *et al.* (2014) used calcium ions to create complexation within a mixture of negatively charged sodium alginate and strongly negatively charged (carboxylated) NFCs. Excellent resistance to grease and water vapor permeation were observed. Shimizu *et al.* (2016) created complexes by adding multivalent cation solutions to TEMPO-oxidized NFC and achieved very low oxygen permeability through the resulting films.

Presumably, the strong contribution of opposite ionic charges to bonding might be expected to enhance the cohesive energy density of a PEC film, thus making it more difficult for gas molecules to pass. The concept is illustrated in Fig. 8, which emphasizes the ionic interaction between positively charged ionic groups on a polyelectrolyte and anionic groups at the surface of nanocellulose particle. Because their energy content can be much larger than hydrogen bonds, ionic interactions seem worthy of consideration, as a way to achieve high bonding within a nanocellulose-containing film. However, since the oxygen or grease permeability was evaluated only in a few cases (Ibn Yaich *et al.* 2015; Shimizu *et al.* 2016), there is a need for further research.

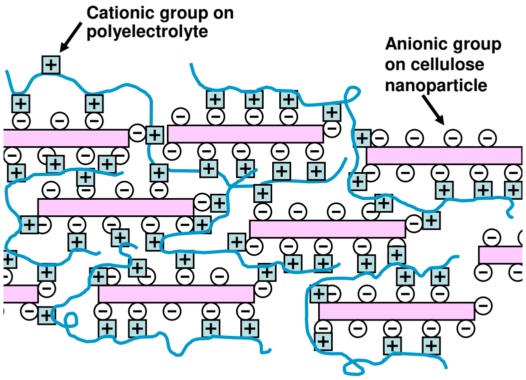

Fig. 8. Conceptual sketch of ionic bonding within a film comprised of anionically substituted nanocellulose particles complexed with a cationic polyelectrolyte, then dried

Plasticizers vs. O_2 barrier performance

Some conflicting results have been obtained regarding the effects of plasticizing agents on oxygen permeability in different circumstances. As a general rule, plasticizers tend to hurt the cohesive energy density of a material. As a result, they tend to hurt resistance to permeation (Lagaron *et al.* 2004). Positive effects of plasticizers on oxygen or water vapor barrier performance have been reported by some authors (Bayati *et al.* 2014; Arrieta *et al.* 2015). Hansen *et al.* (2012) found that various hydrophilic plasticizers increased the equilibrium moisture content as a function of relative humidity, but that one of the plasticizers that they tested (sorbitol) reduced O_2 permeability. In systems containing only MFC and optional glycerol, Minelli *et al.* (2010) found that glycerol was helpful for achieving uniform films. These films showed high resistance to gas permeability under very dry conditions. However, under humid conditions the barrier performance was decreased dramatically. Such varied findings suggest that there is a subtle balance between the conflicting effects of surfactants – at once tending to improve the uniform distribution of the cellulosic nanoreinforcement but simultaneously tending to interrupt the dense hydrogen bonded film structure depending on the chemical structure of plasticizers.

Moisture Sensitivity Concerns

Moisture sensitivity of O_2 barrier performance

Sensitivity to moisture, including the effects of high humidity, is clearly a major obstacle to many potential applications of nanocellulose-based barrier films. Numerous researchers have discovered that resistance to oxygen permeation falls rapidly when the relative humidity rises (Martínez-Sanz *et al.* 2013a; Cozzolino *et al.* 2014; Miettinen *et al.* 2014; Tammelin and Varianen 2014). For instance, Cozzolino *et al.* (2014) found roughly 20 times higher oxygen transmission through MFC-based films at 80% relative humidity in comparison to completely dry conditions.

Lagaron *et al.* (2004) attributed such effects to the plasticizing effect of water within the cellulosic material; just like an organic plasticizer, the level of water molecules associated with high humidity conditions can be sufficient to weaken the film cohesion, thus speeding up the rate of gas diffusion. This effect is depicted schematically in Fig. 9. Though water molecules would be expected to be involved in hydrogen bonding, such bonds are not drawn into Fig. 9 due to their expected short lifetimes, compared with the stability of hydrogen bonds that are associated with dense polysaccharide structures.

Miettinen *et al.* (2014) noted that film thickness tended to increase with increasing relative humidity, *i.e.* a swelling effect. The observed increasing oxygen permeability was consistent with the increased molecular-scale porosity of the NFC films that they studied.

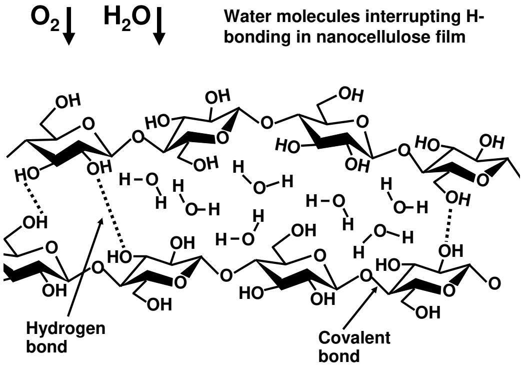

Fig. 9. Schematic picture of how the presence of water molecules within a nanocellulose film can be expected to interrupt the hydrogen bonds among –OH groups along the polymer chains

Using layers to overcome moisture sensitivity

A number of researchers have demonstrated packaging strategies in which cellulosic material is employed in a layered system, isolated from a humid environment, and thereby protecting the vulnerable material from the effects of moisture (Lagaron *et al.* 2004; Boumail *et al.* 2013b; Chinga-Carrasco *et al.* 2013; Österberg *et al.* 2013; Shade *et al.* 2015; Vartiainen *et al.* 2016). Despond *et al.* (2005) protected a bilayer of chitosan on a paper substrate by applying an outer layer of wax. The patent by Schade *et al.* (2015) describes the use of a multi-layered structure in which a layer with NFC is protected by water-resistant plastic layers. Österberg *et al.* (2013) found that very high resistance to oxygen could be maintained, even at high relative humidity, by coating of an NFC film with wax. Such systems are represented, in cross-sectional view, in Fig. 10.

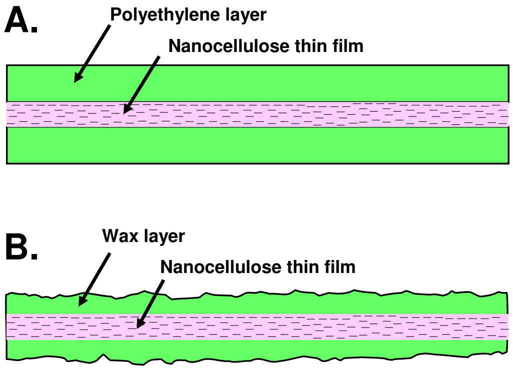

Fig. 10. Schematic views of "sandwich" type film structures in which a nanocellulose film (offering high resistance to oxygen permeation when dry) is sandwiched between a pair of highly water-resistant layers

A question that appears to merit further research is whether such structures, as illustrated in Fig. 10, will gradually fail during long-term exposure due to eventual equilibration with a humid environment, even when the rates of water vapor permeability through the outer layers may be very low. It is reasonable to expect the moisture content of a thin nanocellulose layer to change significantly, even with just a minor influx of water molecules, due to the layer's low mass.

Chemical modification to overcome moisture sensitivity

Ibn Yaich *et al.* (2015), who studied polyelectrolyte complexes involving cationically modified cellulose and an anionic xylan in aqueous solution, reported low oxygen permeability even at a relative humidity of 80%. Likewise, Shimizu *et al.* (2016) reported the persistence of strong resistance to oxygen passage at high humidity in the case of a TEMPO-oxidized cellulose film that had been soaked in solutions of salts of various multivalent ions, thus forming complexes. These results seem surprising given the tendency of many polyelectrolyte complexes to absorb water (Bajpai *et al.* 2016). Clearly more experimental investigation is warranted.

Balan *et al.* (2015) carried out studies in which MFC was used in combination with different types of the chitosan. Though chitosan has a positive charge, one of the modifications involved quaternization, making the polymer yet more cationic and fully water-soluble. Alternatively, chitosan was derivatized with C8 alkyl chains (alkyl chitosan) or carboxymethyl cellulose (CMC chitosan). Both the alkyl chitosan and the CMC chitosan improved the barrier to water vapor.

Another chemical approach that achieved high resistance to oxygen permeation even at high relative humidity was the butylamino functionalization of CNC (Visanko *et al.* 2015). From one perspective, the more hydrophobic nature of the modified nanocellulose would render it less sensitive to water molecules. But on the other hand, one is left to wonder how such modified nanocellulose would still be capable of achieving a high cohesive energy density, which is essential in order to effectively block oxygen gas (Lagaron *et al.* 2004).

Dufrense *et al.* (2000) observed beneficial effects of glycerol, as a plasticizer, on the water vapor barrier performance of starch films formed with or without NFC reinforcement. Performance increased by a factor of about five as the level of NFC was increased from zero to 20%. Incorporation of 30% glycerol in the formulation led to a further decrease in moisture diffusion by as much as a factor of five. Minelli *et al.* (2010) found that although glycerol plasticizer improved water vapor sorption at low levels of humidity, it had the opposite effect when the humidity was high.

Nanocellulose reinforcement to overcome moisture sensitivity

Under some circumstances the reinforcement of a thermoplastic matrix with nanocellulose has been found to decrease the film's sensitivity to moisture. For instance, the presence of bacterial cellulose reinforcement in a thermoplastic poly-lactic acid (PLA) matrix was found to improve resistance to oxygen permeation at a relative humidity of 80% (Ambrosio-Martin *et al.* 2015a). The cited authors proposed that the effect was due to blockage of gas molecules by the cellulose itself. However, the content of cellulose in the composite films was, at most, 5%. Hence, it appears that the nano-reinforcement within the PLA matrix aided in the formation of a dense, defect-free layer, and that blockage of gas by cellulose crystalline domains probably played only a supplementary role. In addition, as mentioned earlier, the crystalline nature of the nanocellulose might have been affecting the extent of crystallinity in the matrix material as it cooled.

Related results have been achieved with elongated CNC, *i.e.* tunicin whiskers. Angles and Dufresne (2001) found that such reinforcement in a starch matrix helped achieve a strong and continuous film. The cited authors proposed that the good film properties, when combining starch with cellulosic nanoreinforcement, could be attributed to hydrogen bonding. Da Silva *et al.* (2012) used CNCs to reinforce cassava starch in the presence of sugars as plasticizers; the nanocellulose helped to reduce the extent of swelling and solubility in water. Follain *et al.* (2013) observed improved resistance to water vapor with the addition of CNC to poly(epsilon-caprolacone) films; the effect was attributed to tortuosity, *i.e.* a longer diffusion path for water molecules in the film. Saxena and Ragauskas (2009) showed that incorporation of CNC in a xylan film reduced the water vapor transmission by 74%. Cozzolino *et al.* (2014) observed excellent oxygen barrier performance with a film prepared from pullulans with an MFC reinforcement. However, the presence of the MFC did not prevent a sharp lessening of resistance to oxygen permeability at higher humidity levels, such as 65% and 80%. Dhar *et al.* (2015) found that CNC improved the oxygen barrier properties of poly(3-hydroxybutyrate) films, an effect that they attributed to good hydrogen bonding between the cellulose and the matrix.

To account for the effects in the reports cited above, one likely explanation is illustrated in Fig. 11. In part A of the figure, the polymer matrix is shown as being defective in some way, possibly due to its brittleness or due to problems related to film formation. In part B of the figure, the CNC particles are envisioned as helping to tie the nanostructure together as a defect-free continuum. In this type of mechanism, the level of CNC would probably be insufficient to have a significant effect on the lengths of diffusion paths by which gas molecules can pass through the film. Rather, the effect of the CNC on barrier performance would be attributed to a reduction in pores, cracks, or other defects in the film.

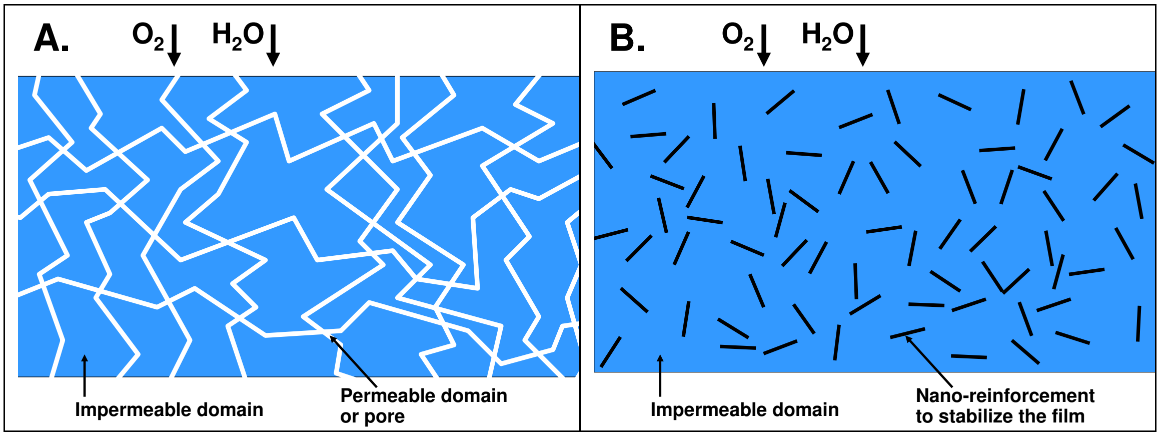

Fig. 11. Concept of how CNC reinforcement may, in some cases, improve barrier performance of a polymer film by decreasing the frequency of defects in the film

Montmorillonite and water-resistance

Several researchers have studied the influence of montmorillonite clay or related materials on the water-resistant properties of thin films that involved cellulose nanomaterials (Liu and Berglund 2012; Abdollahi *et al.* 2013b; Gamelas and Ferraz 2015; Noshirvani *et al.* 2016). Aulin *et al.* (2012) found greater oxygen resistance even at relatively high humidity when vermiculite nanoparticles were incorporated into NFC films. Liu and Berglund (2012) reported much lower oxygen transmission rates at 90% relative humidity upon the addition of either montmorillonite clay or a combination of the nanoclay and chitosan. Abdollahi *et al.* (2013b) found that both the CNC and the nanoclay decreased the water-solubility of alginate films, though the nano-clay was more effective for this purpose. Noshirvani *et al.* (2016) compared CNC and montmorillonite in starch-polyvinyl alcohol films and judged that the montmorillonite was more effective for improving strength and thermal stability.

Curing for water-resistance

Chemical reactions to cure and insolubilize a matrix polymer, usually by some form of cross-linking, have been used as a means to decrease the moisture-sensitivity of nanocellulose-containing barrier layers (Fernandez *et al.* 2008; Aulin and Ström 2013; Raghu 2015). Fernandez *et al.* (2008) employed gamma irradiation to cure ethylene vinyl alcohol films incorporating MFC as a reinforcement. The water barrier properties of the films were enhanced by the gamma radiation treatment. Aulin and Ström (2013) employed alkyd resins and cured the film by auto-oxidation. Choi and Simonsen (2006) found that simply heating a carboxymethyl cellulose (CMC) film, prepared with microcrystalline cellulose, resulted in water resistance. One possible explanation is that the heat was sufficient to promote esterification within the film, including the possibility of ester linkages between the CMC and the cellulose. Österberg *et al.* (2013) observed that the simple heating of NFC films imparted wet strength. Formation of ester cross-linking would seem unlikely in such a system, though the observed effects may have been due to coalescence of the adjacent cellulosic surfaces, an effect sometimes termed "aggregation" of the nanocellulose fibrils (Pönni *et al.* 2012).

Susceptibility to Wetting by Liquids

Hydrophobization to overcome adverse effects of wetting by water

If a liquid is not able to wet a porous barrier layer, then, as long as there are no serious defects, theories of capillary penetration predict that the liquid will not be able to pass through it (Hubbe *et al.* 2015a). Accordingly, various researchers have explored ways to render cellulose-based films resistant to wetting (Aulin *et al.* 2009b; Spence *et al.* 2010b; Rodionova *et al.* 2011; Yang *et al.* 2012; Abdollahi *et al.* 2013b; Kisonen *et al.* 2015; Visanko *et al.* 2015). Spence *et al.* (2010b) and Rojo *et al.* (2015) showed that contact angles of water on cellulosic films tend to increase with increasing lignin content within the range from about 1 to 14% lignin. Contact angles were reduced, thereby increasing water-wettability in cases where the films had been extracted with a benzene/ethanol mixture. Thus, if one's aim is to resist water wetting, it makes sense to prepare highly fibrillated cellulose from raw biomass that still has lignin and extractive materials present in it.

Even though CNCs are composed of cellulose, which is very rich in water-loving –OH groups, the use of CNC's as reinforcement in a hydrophilic polymer film sometimes can decrease the wettability. Thus, Abdollahi *et al.* (2013b) rendered alginate films increasingly resistant to wetting by incorporation of CNCs that had been prepared by sulfuric acid digestion of microcrystalline cellulose. The water contact angle increased from about 41° to about 74° as the CNC content was raised from 0 to 5%. Notably, the addition of sodium montmorillonite, over the same range, merely made the alginate film slightly more wettable by water. This may be another case in which the observed changes might be explained by the ability of the crystalline cellulosic material to induce increased crystallinity in the matrix material; it would be interesting to carry out additional research to determine whether the alginate films were more highly crystalline after having been dried in the presence of the CNCs. Pereda *et al.* (2014) achieved strong resistance to aqueous wetting by a combination of CNC incorporation and olive oil treatment of chitosan films.

Derivatization to resist wetting

As has been described in more detail in earlier review articles (Hubbe *et al.* 2015a,b), cellulosic surfaces can be changed from hydrophilic to hydrophobic by chemical derivatization. The following authors reported the hydrophobization of nanocellulose-based thin films by the covalent attachment of hydrophobic groups to the cellulose (Rodionova *et al.* 2011; Chinga-Carrasco *et al.* 2012; Yang *et al.* 2012; Follain *et al.* 2013; Visanko *et al.* 2015). Tchang Cervin *et al.* (2014) used a similar approach to achieve a hydrophobic solid foam of NFC; the hydrophobic treatment of the cellulose rendered the product hydrophobic.

Tome *et al.* (2010) derivatized bacterial cellulose membranes by esterification with hexanoyl chloride. The water contact angle was increased, along with resistance to water and gas diffusion. Rodionova *et al.* (2011) rendered MFC hydrophobic by acetylation; remarkably, this treatment did not seem to hurt inter-fibril bonding within the MFC films. Related results were obtained by Yu *et al.* (2014b) and Trifol *et al.* (2016a,b). Hu and Wang (2016) achieved hydrophobicity of polyvinyl alcohol films by reinforcing them with MFC that had been derivatized with hydroxypropyltrimethylammonium chloride. The derivatized CNC retained sufficient hydrogen bonding capability so that good dispersion was obtained, leading to increased strength. Kisonen *et al.* (2015) achieved a much higher level of hydrophobicity by coating a film of NFC and hemicellulose by use of an alkylsuccinic ester of the hemicellulose.

Superhydrophobicity and related

Extremely high resistance to wetting often can be achieved by a combination of nano-scale roughness and low-energy surface modification (Song and Rojas 2013; Hubbe *et al.* 2015a,b). Yang *et al.* (2012) demonstrated such an approach using CNC that was derivatized in various ways. Final treatment with a silane reagent rendered the films superhydrophobic by covalently bonding CNC and acrylic acid chains via silane bridges, meaning that contact angles of water droplets were greater than 150 degrees. Aulin *et al.* (2009b), taking a much more aggressive approach, used a polyelectrolyte layer-by-layer deposition approach to incorporate CNCs into a thin film. This was followed by treatment with fluorinated trichlorosilane. The result was a super-oleophobic surface that was able to even prevent wetting by oils.

More recent work (Guo *et al.* 2016) presents a facile process for tailoring the surface wettability and functionality of NFC films by a fast and versatile approach. Firstly, the NFC films were coated with a layer of reactive nanoporous silicone nanofilament by polycondensation that afforded reactive vinyl groups, thereby enabling simple UV-induced functionalization with various thiol-containing molecules *via* the photo "click" thiol-ene reaction. Modification with perfluoroalkyl thiols resulted in robust superhydrophobic surfaces, which could then be further transformed into transparent slippery lubricant-infused NFC films that displayed repellency against both aqueous and organic liquids with surface tensions as low as 18 $mN \cdot m^{-1}$. Transparent and flexible NFC films incorporated hydrophilic micropatterns by modification with OH, NH_2, or COOH surface groups, enabling space-resolved superhydrophobic-hydrophilic domains.

Weakness of Barrier Films

In addition to holding out gases or liquids, another realistic expectation of nanocellulose-based barrier films is that they should have sufficient strength. These issues will be considered in three parts, starting with situations where failure might be caused by tensile or shearing stresses above a critical value, continuing with concerns about the modulus of elasticity, and finishing with concerns about toughness and stretchability.

Concerns about tensile stress to breakage

In some applications a barrier film may have to contribute to the resistance to tensile stresses. Authors have shown that, when suitably formed, nanocellulose-based films can have remarkably high ability to resist such stresses. Qing *et al.* (2012) reported that neat NFC films were able to resist up to 232 MPa of tensile stress. Yano and Nakahara (2004) reported bonding strength up to 250 MPa in plant microfiber structures, even without the use of a binder. Addition of just 2% oxidized starch improved that value to 310 MPa.

In light of these high values, obtained under ideal conditions, it is important to emphasize that failure is likely to occur at points of weakness or defects, such as thin areas, places where the film or underlying material may have been cut, or places where the structure may have become wet, *etc.* Thus, the uniformity of the preparation of barrier layers could be important for product strength in some applications.

Percolation threshold and agglomeration issues

When nanocellulose is being used as a reinforcement within a continuous polymeric matrix, many studies have reported a maximum of strength at a certain level of reinforcement, followed by a decline in strength at higher levels of nanocellulose (Zimmermann *et al.* 2004; Martínez-Sanz *et al.* 2013c; Rafieian and Simonsen 2014). The optimum point is often said to be associated with a percolation threshold, *i.e.* the proportion of fibers, of a given aspect ratio, that is just sufficient to fill the volume with an inter-connecting structure (Dufresne 2008; Moon *et al.* 2011; George and Siddaramaiah 2012; Baheti and Militky 2013). The fall-off at higher levels of the reinforcement is sometimes attributed to "agglomeration" (Abdollahi *et al.* 2013a; Sandquist 2013; Rafieian and Simonsen 2014), which appears to be a problem especially in systems where there is incomplete wetting and contact between the phases. This situation is illustrated schematically in Fig. 12.

In practical terms, a cluster of cellulosic particles or fibrils within a composite structure can be expected to introduce points of weakness, especially if there are air-filled gaps or direct contact between the cellulosic particles with no intervening matrix polymer. Since a continuous network of fibers becomes highly probable above the percolation threshold, it also makes sense to expect more entanglements or flocs among those fibers, especially when flow is present. As the mixture is sheared, elongated particles are forced to collide and become entangled, leading to increased levels of clustering. Composites based on thermoplastic polymers such as polyethylene are typically prepared under dry conditions in which there is little opportunity for the cellulosic particles to become held together by extensive hydrogen bonding. This is a different situation compared to a sheet of paper, wherein extensive hydrogen bonding contributes to the inter-fiber bonding (Davison 1980). Thus, cellulose-to-cellulose contact within a composite prepared under nonaqueous conditions can be expected to contribute points of weakness in the structure.

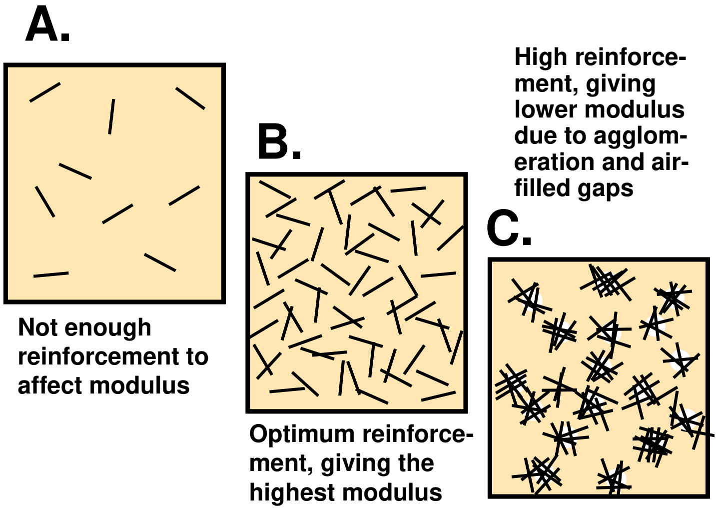

Fig. 12. Schematic illustration of common finding that agglomeration of fibrillary reinforcement particles becomes important above a threshold level, such that the elastic modulus is typically highest at an intermediate level of reinforcement

Concerns about elastic modulus

The achievement of a high modulus of elasticity in a barrier film may be important in some applications where the package, as a whole, needs to be stiff, or where the film itself needs to resist stretching or sagging. Factors affecting the modulus of elasticity (MoE) of nanocellulose-based films have been widely studied (Dufresne *et al.* 1997; Yano and Nakahara 2004; Nakagaito and Yano 2005; 2008a; Yano *et al.* 2005; Nogi *et al.* 2009; Qing *et al.* 2012; Visanko *et al.* 2015; Shimizu *et al.* 2016). Also, several studies have shown that the Young's modulus of different polymeric films can be increased by the addition of nanocellulose reinforcements (Cao *et al.* 2008; Azeredo *et al.* 2009, 2010; Martins *et al.* 2009; Bras *et al.* 2010; Fernandes *et al.* 2010; Bilbao-Sáinz *et al.* 2011; Mikkonen *et al.* 2011; Bulota *et al.* 2012; Trovatti *et al.* 2012a,b; Wu *et al.* 2012; Tome *et al.* 2013; Dehnad *et al.* 2014a; Kurihara and Isogai 2014; Pereira *et al.* 2014; Salehudin *et al.* 2014; El-Wakil *et al.* 2015). In general, these studies showed increases in the elastic modulus upon the addition of optimized levels of nanocellulose to a matrix polymer. Notably, however, Nordqvist *et al.* (2007) found that MFC had little or no effect on the modulus of chitosan-based films. Capadona *et al.* (2009), who prepared CNC-reinforced nanocomposites in such a way as to avoid the possibility of CNC agglomerate formation, observed a continuous increase in modulus with increasing CNC content, and the results were in reasonable agreement with predictions based on a percolation model.

Brittleness of Reinforced Matrix

Solid materials also fail as a result of being changed in dimensions beyond their limits of stretching or compression. In other words, they may be too brittle to meet the requirements of certain applications such as folding cartons. This is a particularly important issue in the case of fiber-reinforced plastic composites that combine cellulosic fibers and relatively soft matrix materials. In such cases, though the composites might have much higher modulus than the polymer alone, the elongation or distortion before failure can be much lower (Martins *et al.* 2009; Pereda *et al.* 2011; George *et al.* 2012; Rafieian *et al.* 2014; Salehudin *et al.* 2014; Santos *et al.* 2014; Oun and Rhim 2015).

By contrast, certain other composites incorporating cellulose display high toughness, meaning that a high amount of energy is expended in bringing about their fracture (Zimmerman *et al.* 2004; Qing *et al.* 2012). Zimmerman *et al.* (2004) attributed the toughness of their specimens to the compliant nature of their matrix polymer, hydroxypropyl cellulose, which was plasticized by the presence of water. On the other hand, Nakagaito and Yano (2008b) showed that higher work to failure could be achieved by NaOH treatment of microfibrillated cellulose; those results were attributed to changes in the amorphous regions of the cellulose, *i.e.* formation of a highly networked structure.

Use of plasticizer vs. mechanical poperies

The tolerance of many polymeric materials to changes in dimension before breakage can be increased by the addition of plasticizing agents, which can usually be described as organic compounds having a high solubility in the polymer. Several studies have shown that plasticizers can be used at controlled levels to adjust the degree of compliance or rigidity of films that contain nanocellulose reinforcements (Angles and Dufresne 2000; Dufresne *et al.* 2000; López-Rubio *et al.* 2007; Svagan *et al.* 2007; Azeredo *et al.* 2010; Mikkonen *et al.* 2011; Peng *et al.* 2011; Hansen *et al.* 2012; Trovatti *et al.* 2012ab; Barud *et al.* 2013; Fortunati *et al.* 2014; Pereda *et al.* 2014; Alves *et al.* 2015).

The importance of glycerol as a plasticizer was shown in a study by Angles and Dufresne (2000), who prepared starch films reinforced by cellulose nano-whiskers (unusually long nanocrystals) obtained from tunicins. Without the plasticizer, the starch would have been too rigid. The glycerol was found to be enriched in the interfacial zone close to the nanocellulose. Azeredo *et al.* (2010) found that chitosan films reinforced with nanocellulose achieved their best overall properties when the glycerol content was about 18%. Fortunati *et al.* (2014) showed that the addition of limonene to poly-lactic acid (PLA) films reinforced with CNC tended to decrease the glass transition temperature of the PLA. Thus, by adjusting the levels of plasticizer and reinforcement, one can obtain various levels of compliance before failure, as well as other properties.

López-Rubio *et al.* (2007) found that it was not possible to cast neat amylopectin films of high uniformity with less than 38% glycerol plasticizer. But when MFC was added, it appeared to play the role of plasticizer, making it possible to achieve high-quality films with no glycerol at all. Moreover, the MFC-reinforced films without glycerol were not brittle. The researchers attributed this to the increased moisture associated with the cellulose. Because it is not usual to achieve plasticizer-like effects by the use of nanomaterials, future studies are recommended in order to more fully illuminate the underlying mechanisms.

Degraded Transparency When Adding Reinforcement

In some potential applications it might be important to preserve the transparency of composite films. As mentioned earlier, many previous reports have made assertions regarding the high transparency achieved with the use of nanofibrillated cellulose (see, for instance, Yano *et al.* 2005).

In principle, as long as the matrix polymer by itself can form a transparent film, the next step is to incorporate the reinforcement particles in such a way as to not disturb that desired condition. Light scattering generally can be avoided if there are no air gaps between the phases and if the refractive indices of the phases are similar. Since the refractive index of cellulose (about 1.6) is similar to that of commonly used plastics, it follows that incompatibility between the phases, leading to gaps, may be a main contributor to the opacity of reinforced composite films.

Another principle is that light scattering becomes significant when particles in a continuous medium are larger than about 0.2 times the wavelength of light (Hu *et al.* 2013), which works out to about 80 to 140 nm within the visible range of light. Thus, superior transparency of films incorporating fibrillated cellulose has been reported mainly in cases where the cellulose has been thoroughly broken down to a very small size (Nogi *et al* 2009; Plackett *et al.* 2010; Siro *et al.* 2011). Siro *et al.* (2011) found that multiple passes through a homogenizer device during the preparation of NFC tended to improve the transparency of the resulting films. Ambrosio-Martin *et al.* (2015b) ensured that nanocellulose was present as individual particles rather than as clusters by the ball-milling of bacterial cellulose before its incorporation into poly-lactide films.

Progress has been achieved with respect to ensuring that nanocellulose is truly of "nano" size when applied as a reinforcement. Bilbao-Sáinz *et al.* (2011) showed that CNCs could be incorporated in a hydroxypropylmethylcellulose (HPMC) film with only 3 to 6% loss in transparency.

High transparency has been especially achieved when NFC films are formed separately, rather than incorporating the nanocellulose within a matrix. This approach has been extended in a few studies in which a pure NFC film was used as a coating or layer. Cozzolino *et al.* (2014) found that better transparency could be achieved when MFC was used as a coating, rather than incorporating it into a pullulan film. Aulin *et al.* (2013) suggested that the high transparency of films prepared from nanofibrillated cellulose may be due to the high nano-scale uniformity that can be achieved in such films.

End of Life Issues

Packaging materials are well represented not only in typical batches of household garbage, but also in roadside litter. Some of the non-biodegradable plastic debris from packaging ends up in the ocean, where it can harm fish and other organisms (Gregory 2009). According to Lindström and Aulin (2014), less than 4% of the consumption of fossil gas and oil resources goes into the production of plastics. It follows that even a complete switching to fully bio-based packaging would only slightly affect the overall consumption of fossil resources. Therefore, the cited authors proposed that emphasis be placed on biodegradability and various adverse effects of litter.

Possible adverse effects of nanomaterials have received much attention from regulatory agencies, and there is much uncertainty regarding future regulations (Hannon *et al.* 2015; Shatkin and Kim 2015; Gomez *et al.* 2016). Shatkin and Kim (2015) expressed greatest concern regarding respiratory issues. The small size of nanomaterials, especially during manufacturing operations, makes it likely that they can remain airborne and pass into people's lungs. Future studies will be needed to quantify any tendency of the nanocellulose to later become released into the air during usage or final deconstruction of the composite materials. Also, there has been concern about food contact safety. Hannon *et al.* (2015) considered gaps in knowledge about risks and considered ways of carrying out risk assessments when nanomaterials are employed in food-contact applications. Future studies are needed in order to ensure that nanocellulose-containing films live up to their potential as non-toxic materials, especially when pure.

Recyclability

Individually, just about every material that has been mentioned in this article can be recycled. Problems arise, however, when materials of different types are so intimately or finely mixed that they are no longer practical to separate. Many packaging structures involve laminations or composite mixtures that are quite well bonded together. Efforts to recycle the components materials in packages have been reviewed (Arvanitoyannis and Bosnea 2001; Cimpan *et al.* 2015). Also, the value of used packaging as a fuel source has been considered (Arvanitoyannis and Bosnea 2001). These are challenging issues that will require much research.

Figure 13 envisions a situation likely to occur with increasing frequency if or when it becomes common to add nanocellulose as a reinforcement in the production of petroleum-derived plastic materials. Part A of the figure represents the current situation in which plastic material, after their automated separation according to type, can be used in the manufacture of secondary plastic material and products. Part B represent a hypothetical future situation in which nanocellulose present in a fraction of the collected waste material has potential to interfere with unit operations in the recycling and remanufacturing processes. Due to the likelihood of increased operational problems during separation and reprocessing of the waste material, as well as the degraded character of the final product, it becomes less likely that anyone will choose to continue recycling this waste stream.

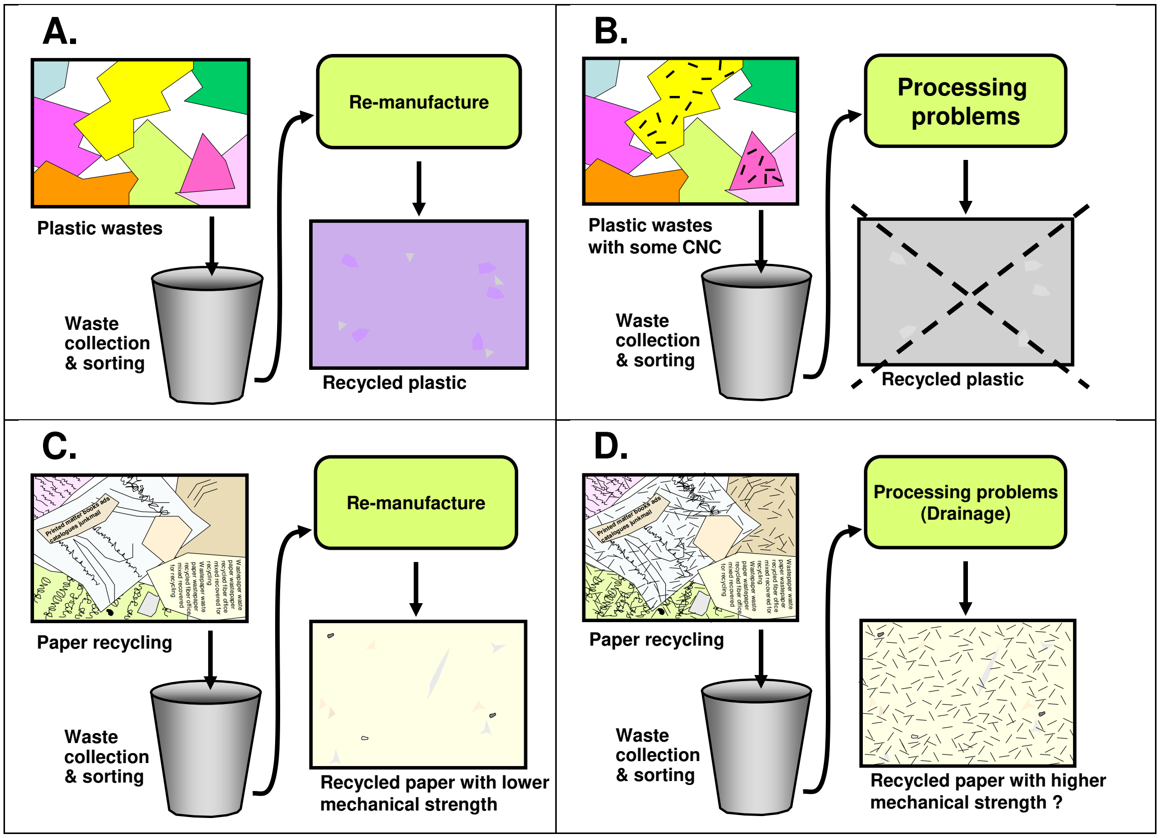

Fig. 13. Nanocellulose reinforcement and the recycling of used plastics and paper. **A and C:** Representation of the current situation, in which waste plastic and paper are recycled into usable products; **B and D:** Hypothetical future situation in which there is enough nanocellulose-containing respective material in the waste streams to that it is no longer practical to try to run reprocessing operations, due to operational problems in the attributes or variability of the final product but at the same time it can be help in improving strength properties in the case of paper.

Biodegradability

Several authors cited already in this article have used "biodegradability" as one of their motivations for selecting nanocellulose as a candidate for the reinforcement of films or layers in packages (da Silva *et al.* 2012; Abdollahi *et al.* 2013b). Azeredo *et al.* (2010) had a further requirement that the materials all be suitable for eating. The US Food and Drug Administration has a category of substances that, based on their long history of usage in foodstuffs, are "generally recognized as safe" (FDA 2006). According to Ludwicka *et al.* (2016), bacterial cellulose is included on that list.

Other authors have shown that their packaging structures conformed to biodegradability standards (Avella *et al.* 2005). Kibedi-Szabo *et al.* (2012), on the other hand, demonstrated the biodegradability of composite materials comprised of poly-(vinyl alcohol), bacterial cellulose, and chitosan. Biodegradation was observed to take place within the composites, not just at their surface. Luzi *et al.* (2015) likewise demonstrated the biodegradability of composites comprising CNC and poly-(lactic acid). Machado *et al.* (2012) designed a package to be biodegradable, using starch as the matrix; during storage it was found that the packaging materials became oxidized, thus serving as a sacrificial material to minimize oxidation of the contents of the package. The study of related issues can be expected to expand in the coming years, as policy-makers seek to implement practical, integrated systems for collection, selective recycling, composting, and other forms of minimizing the adverse environmental effects of disposal.

SUMMARY COMMENTS

In their review article of 2014, Lindström and Aulin identified some key challenges that might block or delay industrial implementation of nanocellulose in packaging applications. While progress has been made in addressing some of the challenges considered in that article, some important issues seem to pose intractable problems. Table 4 lists some such challenges and suggests possible kinds of research that could be carried out.

As is apparent from Table 4, some serious and perhaps insurmountable challenges face those who wish to implement various aspects of nanocellulose usage in packaging. However, as shown in many articles cited in this review, important progress is being made. Nanocellulose therefore can be expected to play an increasingly important role in future packaging systems.

In addition to the continuing challenges just discussed, there are practical issues that need more attention with respect to scale-up and implementation of nanocellulose technologies for packaging. Future studies and articles are needed that allow better estimates of the likely future costs and available amounts of nanocellulose. Also, given the expectation that nanocellulose costs will tend to remain high and supplies will remain constrained in the near future, some analysis is needed to identify the high-added-value applications of nanocellulose that are most likely to become implemented first. These analyses should include consideration of competing technologies, including competing nanomaterials that might be used for packaging films. Projections of market share, based on various assumptions, could be helpful. And finally, continuing work is needed with respect to life cycle analysis of nanocellulose-based packaging film technologies.

Table 4. Some Key Challenges Noted by Lindström and Aulin (2014)

Challenge	Possible Research Paths (and relevant citations)
How to disperse inherently hydrophilic cellulosic nanomaterials in inherently hydrophobic polymer matrices?	Using the date of the Lindström and Aulin review article (2014) as a benchmark, it seems that mainly incremental progress has been achieved since then. The main challenge of uniform dispersion remains. Maybe the most significant progress has been the demonstration of surfactant and emulsion-based systems as a way to improve nanocellulose dispersion in a matrix and achieve superior overall properties (Arrieta *et al.* 2014a,b; Carrillo *et al.* 2016).
How to avoid un-wanted hornification and shrinkage-related effects during drying of nanocellulose before use?	Possibly the most important work related to this challenge has been that of Ambrosio-Martin *et al.* (2015b), who demonstrated the effectiveness of mechanical milling (ball-milling) of dried bacterial cellulose to break up clumps and restore its "nano" character. Other aspects of hornification remain challenging, and maybe it will be fruitful to focus on applications where the attributes of dried nanocellulose may offer advantages.
How to deal with the tendency of nanocellulose to absorb a lot of water from the atmosphere, *i.e.* its hygroscopic character?	As was noted by Lindström and Aulin (2014), the uptake of moisture from the surroundings tends to be one of the most intractable problems associated with the maintenance of superior barrier properties. Though there has been some progress in addressing such problems by inherently expensive routes (Visanko et al. 2015), based on the present review it seems that layered structures, basically protecting the nanocellulose-rich layer from moisture (Schade *et al.* 2015; Vartiainen *et al.* 2016), hold great promise.
How to deal with the potential high expense and environmental costs of drying highly water-swollen matter?	It appears that Lindström and Aulin (2014) put their fingers on an intractable issue – the high energy associated with drying of a water-loving film constituted of nano-size elements. Since so far no fully satisfactory resolution to this challenge has been presented, one answer may be to focus future efforts on end-uses in which a very thin layer is sufficient, and in which the value of the application justifies the relatively high input of energy.

ACKNOWLEDGMENTS

The authors are grateful for the following sources of support for this work: The Buckman endowment, which supports the work of Dr. Hubbe; the Department of Forest Biomaterials and College of Natural Resources, which supports Dr. Pal, The NCSU Provost's Fellowship Award, which supports the work of Preeti Tyagi, the Hallburton project, which supported the work of Ana Ferrer, and the Graduate Student Innovation Plan of Jiangsu Province of China (KYLX16_0790), which supports Yuanyuan Yin. Dr. Rojas acknowledges the Academy of Finland's Centers of Excellence program (project 264677, HYBER) for their support. The authors also wish to thank Justin Zoppe and Miha Humar for their comments, which helped to improve the quality of the work.

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APPENDIX

Table A. Publications Describing Nanocellulose-containing Barrier Layers, Films, or Coatings

Type of Nano-cellulose	**Category of Layer**	**Fluid Medium Used**	**Matrix Polymer**	**Key Additives & Conditions**	**Key Findings**	**Literature Citation**
CNC	Cast	Aqueous	Alginate	Addition level: 0 to 10%	Decreased water vapor permeability; became more opaque when CNC was >10%.	Abdollahi *et al.* 2013a
CNC	Cast	Aqueous	Alginate	Montmorillonite addition too	CNC addition made the film less hydrophilic; montmorillonite had the opposite effect.	Abdollahi *et al.* 2013b
NFC	Cast	Aqueous	Starch	Lignin containing NFC	Lower water uptake was attributed to the nature of lignin	Ago *et al.* 2016
NFC	Paper additive	Aqueous	None	Wet-strength polymer	Sequential addition of cationic polymer, then NFC, gave high-strength paper.	Ahola *et al.* 2008a
NFC	Spin-coat films	Aqueous	None	Cationic silane on silica	Highly charged fibrils formed a denser network of cellulose I.	Ahola *et al.* 2008a
BC	*In-situ* biosynth.	Aqueous	None	Montmorillonite hybrid films	The MMT inclusion gave higher water vapor and O_2 barrier performance.	Algar *et al.* 2016
CNC	Cast	Aqueous	Starch & gelatin	Starch & gelatin proportions	Homogeneous and cohesive films. CNC increased strength and elongation to break.	Alves *et al.* 2015
BC	Extruded	Melt	PLA	Grafting lactic acid oligomers onto BC	Pre-incorporation gave the best increase in modulus and tensile strength. High resistance to both water vapor and oxygen were achieved.	Ambrosio-Martin *et al.* 2015a
BC	Extruded	Melt	PLA	Ball-milling of freeze-dried BC	The milling led to better dispersion of the BC in the PLA, giving the best oxygen barrier even at 80% rel. humidity.	Ambrosio-Martin *et al.* 2015b
NFC	Coating on paper	Water	None	Colloidal silver	Antibacterial, greaseproof, and tensile strength properties increased relative to the uncoated paper.	Amini *et al.* 2016
MFC	Cast	Water	None	Quaternary hydro-phobe grafting	Antimicrobial films that did not leach were prepared.	Andresen *et al.* 2007
CNC from tunicin	Cast	Aqueous	Starch	Glycerol plasticizer	Plasticizer accumulated at the interfacial zones.	Angeles & Dufresne 2000
CNC from tunicin	Cast	Aqueous	Starch	Glycerol plasticizer	Effects could be interpreted in terms of a percolation involving a structure of long CNC whiskers.	Angeles & Dufresne 2001

Type of Nano-cellulose	**Category of Layer**	**Fluid Medium Used**	**Matrix Polymer**	**Key Additives & Conditions**	**Key Findings**	**Literature Citation**
MFC	Multi-layer	Aqueous	None	Alternate layers made cationic	Best strength with alternating layers of cationic wet-strength polymer and anionic MFC.	Ankerfors *et al.* 2016
MFC	Paper additive	Aqueous	None	Cationic starch	Increased dry strength properties were achieved.	Ankerfors *et al.* 2014
CNC	Extruded	Melt	PLA	Plasticizer used	Oxygen barrier and stretchability were achieved with use of CNCs and acetyl(tributyl citrate) plasticizer.	Arrieta *et al.* 2015
CNC	Extruded	Melt	PLA/PHB	Surfactant	Surfactant improved the uniformity of blending and the consequent film properties.	Arrieta *et al.* 2014a
CNC	Extruded	Melt	PLA/PHB	Surfactant	Improved mechanical stiffness and stretchability were achieved with the surfactant-treated CNC. It also resisted water vapor and oxygen.	Arrieta *et al.* 2014b
Spin-coat; MFC, CNC	Multilayer; Spin-coat; Cast	Aqueous	None	Different film-forming methods	Film character was consistent with the size and nature of the component cellulosic elements.	Aulin *et al.* 2009a
MFC	Coating on paper	Water	None	Carboxymethylation of the MFC	There was low O_2 permeability at low relative humidity, but exponential increase with increasing humidity.	Aulin *et al.* 2010a
MFC	Layer by layer	Water	None	Anionic & cationic MFC layers	Multilayers with PEI and anionic MFC were the densest and strongest.	Aulin *et al.* 2010b
NFC	Layer by layer	Water	PLA substrate	CMC and PEI	Some multilayers outperformed cast NFC films in terms of oxygen barrier performance.	Aulin *et al.* 2013
NFC	Cast	Solvent	None	Vermiculite	Nanoclay addition improve oxygen barrier performance while maintaining transparency.	Aulin *et al.* 2012
MFC	Coating on paper	Water	None	Alkyd resin coated on top of the NFC	The alkyd resin improved water barrier performance.	Aulin & Ström 2013
CNC	Multilayer	Water	Polyelec-trolytes	Fluorosilane treated	Highly non-wetting, porous surfaces were created.	Aulin *et al.* 2009b
CNC	Cast	Acetone	Cellulose acetate-butyrate	Optional plasticizer	Plasticizer use increased transparency due to better dispersion of CNC.	Ayuk *et al.* 2009
CNC	Cast	Aqueous	Chitosan	Glycerol as plasticizer	Good dispersion of CNC was found; composition was optimized.	Azeredo *et al.* 2010

Type of Nano-cellulose	**Category of Layer**	**Fluid Medium Used**	**Matrix Polymer**	**Key Additives & Conditions**	**Key Findings**	**Literature Citation**
CNC	Cast	Aqueous	Mango puree	-	The CNC increased tensile strength, modulus, and water vapor barrier performance.	Azeredo *et al.* 2009
MFC, CNC	Cast	Melt	Thermo-plastics	-	The intertwined microfibrils in the parenchyma cell wall gave rise to high-performance materials.	Azizi Samir *et al.* 2004a
CNC from tunicate	Cast	Aqueous	PEO	-	Increased crystallization of the matrix	Azizi Samir *et al.* 2004b
NFC	Cast	Water	None	TEMPO-oxidation; Drying restraint	Strength was improved in the restrained directions, which was consistent with nanofiber alignment.	Baez *et al.* 2014
NFC	Cast	Aqueous	PVOH mulch	Wet *vs.* dry milling	Modulus was increased by NFC inclusion.	Baheti & Militky 2013
MFC, NFC	Cast	Aqueous	PVOH	Cross-linking (HEMA)	Crosslinking reduced water vapor permeability.	Bai *et al.* 2015a
MFC	Cast	Aqueous	PVOH	Cross-linking (HEMA)	Patent.	Bai *et al.* 2015b
MFC	Cast	Aqueous	Chitosan derivatives	Alkyl, quaternary, or carboxymethyl	Alkylchitosan, with or without MFC, improved water and water vapor barrier performance.	Balan *et al.* 2015
CNC	Cast	Aqueous	None	Remove sulfonation by vacuum & heat	Films made from CNC were ground to form iridescent pigment.	Bardet *et al.* 2015
BC	Cast	Acetone	Polycapro-lactone	-	Cellulose I was preserved, giving clear, stretchable films.	Barud *et al.* 2013
CNC	Cast	Aqueous	Hydroxy-propxylan	Sorbitol as plasticizer	Transparent, rigid films prepared showed low diffusion of water.	Bayati *et al.* 2014
CNC, MFC	Cast	Aqueous	None	Type of cellulose	Diffusion was controlled by the film surface, more so than its core. MFC films were less permeable to gas than CNC.	Belbekhouche *et al.* 2011
CNC	Cast	Solvent exchange	Polyhydro-xybutyrate	Polyhydroxyalkan-oate addition	Solvent exchange-cum-casting is demonstrated as a cost-effective way to prepare films.	Bhardwaj *et al.* 2014
MCC	Cast	Aqueous	Hydroxy-propylmethylcellulose	Lipid coating	Reinforcing effects were observed. Moisture permeability was reduced by the MCC, and additionally by the lipid coating	Bilbao-Sáinz *et al.* 2010
NFC, CNC	Cast	Aqueous	None	TEMPO oxidation of the CNC	A reinforcing effects was observed. CNC (whiskers) improved water barrier performance.	Bilbao-Sáinz *et al.* 2011

Type of Nano-cellulose	Category of Layer	Fluid Medium Used	Matrix Polymer	Key Additives & Conditions	Key Findings	Literature Citation
CNC	Cast	Aqueous	Methyl-cellulose	Enclosed within PCL layers.	Gas barrier and controlled release properties were demonstrated.	Boumail *et al.* 2013a
CNC	Cast	Aqueous	Methyl-cellulose	Enclosed within PCL layers.	Antimicrobial formulations in the CNC/methylcellulose layers were demonstration.	Boumail *et al.* 2013b
CNC	Cast	Aqueous emulsion	Natural rubber	-	The CNC reinforced the rubber above its softening point.	Bras *et al.* 2010
CNC	Cast	Aqueous	None	Aspect ratio varied	Film stiffness depended on CNC aspect ratio.	Bras *et al.* 2011
CNC	Cast	Chloro-form	PLA	Acetylation of the nanocellulose	Acetylation increased the performance for tensile break and toughness, as well as modulus.	Bulota *et al.* 2012
BC	Cast	Chloro-form	Polyhydro xybutyrate	-	The film was transparent with enhanced mechanical properties.	Cai & Yang 2011
CNC	Cast	Dimethyl formamide	PLA	Isothermal treatment	The CNCs promoted a lamellar structure during isothermal annealing, leading to higher modulus.	Camarero-Espinosa *et al.* 2015
CNC	Cast	Aqueous	Plasticized starch	Loading level of CNC	Homogeneously distributed CNC led to increased glass transition temperature, tensile strength, and modulus.	Cao *et al.* 2008
CNC	Cast	Solvent exchange	PEO epi-chlorohydr.	Template approach	Maximum in mechanical reinforcement was consistent with a percolation threshold.	Capadona *et al.* 2009
MFC	Cast	Aqueous	PVOH	-	Highest tensile strength and stiffness achieved at 5% MFC. The aspect ratio of the MFC was critical.	Chakraborty *et al.* 2006
CNC	Extruded	-	PLA	Mica	Reinforcement improved the thermal stability, strength, and UV-shielding ability. Best at 7% CNC.	Chang *et al.* 2013
MFC	Coating, paper	Aqueous	-	Consistency of refining for MFC	Coating of the MFC onto paper gave best decrease in air-permeability.	Charani *et al.* 2013
CNC	Cast	Aqueous	Guar gum		Improved optical and mechanical properties as well as O_2 barrier, with a completely water-soluble film.	Cheng *et al.* 2016
MFC	Cast	Aqueous	PVOH	Ultrasonic making of MFC	Mechanical properties were improved in most cases.	Cheng *et al.* 2009
MFC	Cast	Aqueous	-	Unbleached *vs.* TEMPO-oxidized MFC	Layered structures with different MFC types gave promising results.	Chinga-Carrasco *et al.* 2013

Type of Nano-cellulose	**Category of Layer**	**Fluid Medium Used**	**Matrix Polymer**	**Key Additives & Conditions**	**Key Findings**	**Literature Citation**
MFC	Cast	Aqueous	-	Bleached *vs.* unbleached MFC	Unbleached MFC gave higher O_2 barrier performance, lower wettability, and higher tensile strength. Carboxy-methylation rendered the fibrillation easier.	Chinga-Carrasco *et al.* 2012
NFC	Cast	Aqueous	-	-	The nanomaterials and films were characterized by scanning electron microscopy, and profilometry. Fibril diameters were quantified.	Chinga-Carrasco *et al.* 2010
MFC	Cast	Aqueous	-	-	Good oxygen barrier performance was attributed to the dense film structure. This was modeled.	Chinga-Carrasco & Syverud 2012
CNC	Cast	Aqueous	Carboxy-methyl-cellulose	Glycerol as plasticizer	Higher strength and stiffness were achieved with CNC. Heat-treatment yielded water resistance.	Choi and Simonsen 2006
CNC	Cast	Aqueous	Starch	Glycerol as plasticizer	Reinforcement increased strength and reduced water permeability.	Costa *et al.* 2014
MFC	Coating	Aqueous	Pullulan	Borax	Increased oxygen barrier performance, especially when dry. Spectroscopic analysis suggests curing reaction.	Cozzolino *et al.* 2016
MFC	Coating	Aqueous	Pullulan	-	Increased oxygen barrier performance, especially when dry. Spectroscopic analysis suggests curing reaction.	Cozzolino *et al.* 2014
MFC	Coating	Aqueous	-	Lysozyme microbial agent contained.	Release rates of the lysozyme were quantified.	Cozzolino *et al.* 2013
CNC	Cast	Aqueous	-	Carboxylation CNCs	The tensile strength, modulus, and elongation at break were increased.	Criaclo *et al.* 2016
NFC	Cast	Aqueous	Hydroxypropyl guar	TEMPO-oxidized nanofibers	Physical and oxygen barrier performance increased. High flexibility and transparency achieved.	Dai *et al.* 2015
CNC	Cast	Aqueous	Starch	Sucrose and invert sugar plasticizers	Water resistance (solubility and swelling) has enhanced. Network formation was proposed. Strengthening.	da Silva *et al.* 2012
CNC	Cast	Acidic aqueous	Chitosan	Ultrasonic treatment	Higher mechanical properties and water vapor barrier were achieved.	Dehnad *et al.* 2014a
CNC	Cast	Acidic aqueous	Chitosan	Glycerol plasticizer	Antimicrobial properties were demonstrated.	Dehnad *et al.* 2014b

Type of Nano-cellulose	Category of Layer	Fluid Medium Used	Matrix Polymer	Key Additives & Conditions	Key Findings	Literature Citation
CNC	Layer by layer	Aqueous	Chitosan	-	Electrostatic interactions were proposed to be important for the layering.	de Mesquita *et al.* 2010
CNC	Cast	H_2O, acetone, chloroform	Polyhydroxybutyrate	Solvent exchange.	Low O_2 transmission rates were obtained, as well as resistance to migration of polar and nonpolar food simulants.	Dhar *et al.* 2015
NFC	Paper-making	Aqueous	-	*In-situ* precipitated calcium carbonate	The *in-situ* precipitated calcium carbonate had a favorable impact on dewatering rate when using NFC.	Dimic-Misic *et al.* 2016
NFC, MFC	Coating	Aqueous	-	As thickener or co-binder *vs.* CMC	The fibrillated cellulose can function as a water retention agent, thickening agent, and co-binder in coating colors.	Dimic-Misic *et al.* 2014
BC	Cast	Aqueous	PVOH	Grinding of the BC; Sorbic acid added	Antimicrobial capability found. Release rates were studied.	Dobre *et al.* 2012
MCC	Cast	Aqueous	Hydroxypropylmethyl cellulose	Size of the MCC	Mechanical properties increased with decreasing size of the MCC. The authors attributed this to greater surface area per unit mass.	Dogan & McHugh 2007
NFC	Cast	Aqueous	Chitosan	Ultrasonication of MCC	Enhanced mechanical properties found, including wet tensile strength. Better barrier properties achieved.	Dong *et al.* 2014
NFC	Cast	Aqueous	Pectins	Purification, extent of fibrillation	The presence of the pectins was important for achieving high strength in the films.	Dufresne *et al.* 1997
MFC	Cast	Aqueous	Starch	Glycerol as plasticizer	The MFC decreased the water-sensitivity, maintaining mechanical properties to higher humidity.	Dufresne *et al.* 2000
MFC	Cast	Aqueous	Starch	-	The MFC decreased the water-sensitivity, maintaining mechanical properties to higher humidity.	Dufresne & Vignon 1998
CNC	Cast	Aqueous	CMC/ Starch mix		An entangled network structure was found, with shear-thinning behavior. Lower water vapor permeability found.	El Miri *et al.* 2015
CNC	Coating on paper	Aqueous	Wheat gluten	Also TiO_2 nanoparticles	Layers coated onto paper increased breaking length and showed resistance to microbes.	El-Wakil *et al.* 2015
MFC	Added in paper	Aqueous	-	Thermomechanical pulp furnish	Tensile strength and air resistance were increased.	Eriksen *et al.* 2008
CNC	Cast	Chloro-form	PLA	Grafting with octa-decyl isocyanate	The grafting did not improve the water vapor permeability resistance.	Espino-Pérez *et al.* 2013

Type of Nano-cellulose	Category of Layer	Fluid Medium Used	Matrix Polymer	Key Additives & Conditions	Key Findings	Literature Citation
Nano cellulose	Cast	Ethanol, acetic acid	Chitosan	Silane coupling agent	The patent claims good tensile strength and resistance to oxidation.	Feng *et al.* 2015a
BC	Cast	Aqueous	-	-	The bacterial cellulose obtained from mutated bacteria gave good strength and thermal stability.	Feng *et al.* 2015b
NFC	Cast	Aqueous	Chitosan	-	The transparent films exhibited improved strength and modulus, as well as thermal stability.	Fernandes *et al.* 2010
MFC	Cast	Aqueous	Ethylene vinyl alcohol	Ionizing radiation (gamma)	The MFC led to decreased water resistance properties, but this was overcome by irradiation curing of the film.	Fernandes *et al.* 2008
BC	Cast	Aqueous	Chitosan	DP of the chitosan	The transparent films had higher strength.	Fernandes *et al.* 2009
NFC	Extruded	Melt	Polypro-pylene	Freeze-milling	The lignin-containing nanofibrils were suitable for reinforcement of polypropylene.	Ferrer *et al.* 2016a
BC	Hot press	Dry	Polycapro lactone	-	The films were prepared without the usual solvent requirement, which is great for food applications.	Figueiredo *et al.* 2015
CNC	Cast	Dichloro methane	Polycapro lactone	Long-chain graft of isocyanate	Water permeability resistance was attributed to tortuosity.	Follain *et al.* 2013
CNC	Extruded	Melt	PLA	Surfactant-modified CNCs, Ag particles	Surfactant help the dispersion and nucleation; anti-bacterial effects were observed.	Fortunati *et al.* 2012a
CNC	Extruded	Melt	PLA	Limonene as plasticizer	Limonene acted as a plasticizer.	Fortunati *et al.* 2014
CNC	Cast	Chloro-form	PLA	-	Surfactant helped the dispersion and nucleation.	Fortunati *et al.* 2015
CNC	Cast	Chloro-form	PLA	Surfactant	The surfactant-modified CNC was very effective for O_2 barrier enhancement and migration resistance.	Fortunati *et al.* 2012b
CNC	Cast	Chloro-form	PLA	Surfactant, Ag particles	The combination of surfactant-modified CNC and Ag nanoparticles increased the barrier performance.	Fortunati *et al.* 2013
NFC	Coating	Aqueous	Pullulan	Various	Review article; various systems described	Freire *et al.* 2013
CNC	Cast	Aqueous	-	TEMPO-oxidized cellulose	The clear films had good oxygen barrier performance.	Fukuzumi *et al.* 2009
CNC	Cast	Aqueous	PVOH	HCl digestion of BC to make CNC	Mechanical and thermal performance of the films was increased by including the CNC.	George *et al.* 2010

Type of Nano-cellulose	Category of Layer	Fluid Medium Used	Matrix Polymer	Key Additives & Conditions	Key Findings	Literature Citation
CNC	Cast	Aqueous	Hydroxy propyl methyl cellulose	-	Modulus was increased, but the films were more brittle with the inclusion of CNC; moisture adsorption was decreased.	George *et al.* 2014
CNC	Cast	Aqueous	Hydroxy propyl methyl cellulose	-	The addition of CNC reduced the moisture sensitivity and contributed to strength.	George *et al.* 2016
CNC	Cast	Aqueous	PVOH	Ag nanoparticles	The Ag nanoparticles helped overcome the embrittling effects of the CNC.	George *et al.* 2012
CNC	Cast	Aqueous	Gelatin	-	Percolated networks improved the strength, decreased moisture uptake, and reduced water vapor permeability.	George & Siddaramaiah 2012
NFC	Paper making	Aqueous & I.L.	-	Partial dissolution with ionic liquid	Dissolution time was correlated with increasing water permeability. Tough and biodegradable films achieved.	Ghaderi *et al.* 2014
NFC	Paper making	Aqueous	-	NFC as paper additive	The NFC has similar effects as refining of the main pulp; thus less refining was required of the main furnish.	González *et al.* 2012
BC	Cast	Acetone	Cellulose acetate butyrate	Trimethylsilytated CNCs	The unmodified CNCs exhibited better reinforcement capabilities.	Grunert & Winter 2002
NFC	Cast	Solvents	Lubricant	Thiolene NFC modification	Slippery, superhydrophobic films were prepared	Guo *et al.* 2016
NFC	Paper making	Aqueous	-	NFC as paper additive	-	Hamada *et al.* 2010
CNC	Coating or cast	Aqueous	Organosolv lignin	Lignin as a grafting additive	Fenton's reagent was used to graft the lignin onto the CNC.	Hambardzumyan *et al.* 2015
NFC	Cast	Aqueous	Xylan	With or without plasticizers	Plasticizers gave rise to less brittle films, and the oxygen barrier properties were promising.	Hansen *et al.* 2012
CNC	Cast	Toluene	Polycapro lactone	Derivatization with octadecyl isocyanate	Very low moisture uptake was observed, regardless of whether then CNC was derivatized.	Hassan *et al.* 2012
MFC	Cast	Aqueous	Chitosan	Loading levels.	Alkali treatment of the MFC gave higher strength of the transparent films.	Hassan *et al.* 2011

Type of Nano-cellulose	Category of Layer	Fluid Medium Used	Matrix Polymer	Key Additives & Conditions	Key Findings	Literature Citation
NFC	Paper making	Aqueous	-	-	The nanopaper showed high strength.	Henriksson *et al.* 2008
CNC	Compress molded	Melt	PLA	Plasticized with citrate	Mechanical properties were improved by the CNC.	Herrera *et al.* 2016
NFC	Cast	Aqueous	Clay or $CaCO_3$	TEMPO oxidation to make the NFC	Clay-containing films were reasonably tough and useful.	Honorato *et al.* 2015
CNC	Cast	Chloro-form	PLA	-	Water uptake was increased with CNC content.	Hossain *et al.* 2011
MFC	Cast	Aqueous	PVOH	Quaternization of the cellulose	A reinforcing effect, hydrophobicity, and reduced swelling were attributed to hydrogen bonding effectiveness.	Hu & Wang 2016
NFC	Paper making	Aqueous	-	Conductive materials	Transparent and conductive films were prepared.	Hu *et al.* 2013
MFC	Cast	Aqueous	-	Shellac coating on the MFC film	The shellac coating was extremely effective in reducing water permeation.	Hult *et al.* 2010
Cellulose	Cast	Aqueous	Glucurono xylan	Quaternized cellulose	Low oxygen permeation was achieved even at 80% relative humidity when using the cationized cellulose.	Ibn Yaich *et al.* 2015
Nano-cellulose	Coating	Aqueous	-	Cationic surfactant	The patent claims low oxygen permeability.	Iotti 2014
NFC	Paper making	Aqueous	Hemi-celluloses	Degree of grinding to make NFC	Hemicelluloses inhibited the coalescence of microfibrils during drying.	Iwamoto *et al.* 2008
BC	Multi-layers	Aqueous	-	ZnO	Controlled release of the ZnO particles was demonstrated for antimicrobial effect.	Jebel & Almasi 2016
NFC	Cast	Aqueous	-	Degree of fibrillation	Their appearance suggests high fracture toughness of the films.	Johnson *et al.* 2009
CNC	Cast	Aqueous	Gelatin	-	Edible high performance films were prepared with improved properties.	Johnsy & Siddar-amaiah 2012
NFC	Cast	Aqueous	-	TEMPO oxidizing to make the NFC	Ca^{2+} induced gelation of NFC. Zeolites provided odor absorption;	Keshavarzi *et al.* 2015
CNC	Cast	Aqueous	Chitosan	Level of CNC	Water vapor permeability was decreased by the CNC, and there was less swelling.	Khan *et al.* 2012
CNC	Compress molding	Heated	Polycapro lactone	-	The CNC lowered the oxygen transmission rate.	Khan *et al.* 2013

Type of Nano-cellulose	Category of Layer	Fluid Medium Used	Matrix Polymer	Key Additives & Conditions	Key Findings	Literature Citation
MFC	Cast	Aqueous	Alginate	Level of MFC	The MFC was an effective reinforcement.	Khan *et al.* 2014b
CNC	Cast	Aqueous	-	Vegetable oil, glycerol, surfactant	Gamma irradiation slightly hurt mechanical properties but improved water vapor resistance.	Khan *et al.* 2010
BC	Cast	Aqueous	PVOH, chitosan	-	Biodegradability was quantified.	Kibedi-Szabo *et al.* 2012
BC	Cast	Aqueous	PLA	-	A reinforcing effect of the BC was observed.	Kim *et al.* 2006
NFC	Paper making	Aqueous	Acetyl-glu-comannan	Acetylation of the matrix	High resistance to oxygen and grease were observed with NFC addition.	Kisonen *et al.* 2015
NFC, CNC, BC	Cast	Acetone	PMMA	Loading (up to 0.5%)	Increased strength and elastic modulus were observed.	Kiziltas *et al.* 2015
NFC	Paper making	Aqueous	_	Water-insoluble drugs	Drug delivery was sustained over a three-month period.	Kolakovic *et al.* 2012
NFC MFC	Cast	Aqueous	-	TEMPO oxidation as an option	The MFC films showed superior O_2 barrier performance; the NFC films had higher transparency and strength.	Kumar *et al.* 2014
NFC	Coating	Aqueous	-	Roll-to-roll coating	Coatings were applied at high speed to paper, imparting strength and barrier to water and heptane.	Kumar *et al.* 2016
NFC	Cast	Aqueous	PAM	TEMPO oxidized	Large increases in modulus and strength, as well as high transparency of the films, were observed.	Kurihara & Isogai 2014
NFC	Paper making	Aqueous	PLA latex	Hot pressing	Adding NFC conferred high modulus and strength, and high cellulose levels could be achieved.	Larsson *et al.* 2012
MFC	Coating	Aqueous	-	Bar coating	The coating conferred bending stiffness to the paperboard but it did not contribute to barrier properties.	Lavoine *et al.* 2014a
MFC	Coating	Aqueous	-	Caffeine impregnation	Controlled release of caffeine was demonstrated.	Lavoine *et al.* 2014b
MFC	Coating	Aqueous	-	Different coating processes	Bar coating was more promising than size-press coating.	Lavoine *et al.* 2014c
MFC	Coating	Aqueous	-	Antibacterial agent impregnation	Gradual release of the antimicrobial compound was demonstrated.	Lavoine *et al.* 2015

Type of Nano-cellulose	**Category of Layer**	**Fluid Medium Used**	**Matrix Polymer**	**Key Additives & Conditions**	**Key Findings**	**Literature Citation**
BC, NFC	Paper making	Aqueous	Epoxy resin	Impregnation of resin into cellulose	The two types of nanocellulose yielded similar nanocomposite materials.	Lee *et al.* 2012
CNC	Cast	Aqueous	PVOH	-	Tensile and thermal properties of the PVOH films were enhanced.	Lee *et al.* 2009
MFC	Extruded	Aqueous	Thermopl. starch	Glycerol & water as plasticizers	Mechanical reinforcement was found to depend on the aspect ratio of the nanocellulose.	Lendvai *et al.* 2016
CNC	Cast	Aqueous	Poly-saccharides	Sorbitol plasticizer as an option	The best films contained more than 30% CNC.	Le Normand *et al.* 2014
CNC	Coating	Aqueous	-	On various film surfaces	High oxygen barrier was achieved, along with high transparency.	Li *et al.* 2013a
CNC	Layer by layer	Aqueous	Chitosan	Number of layers, pH of deposition	The system seemed promising for gas barrier; results could be tuned by adjusting the pH.	Li *et al.* 2013b
CNC	Cast	Aqueous	PVOH, chitosan	Complexation interactions	Antimicrobial, oxygen barrier, and mechanical property improvements were demonstrated.	Li *et al.* 2015b
CNC	Cast	Aqueous	Chitosan	-	The CNC enhanced mechanical properties and conferred water resistance.	Li *et al.* 2009
NFC	Cast	Aqueous	Talc	Oxidation to make the nanocellulose	The films were flexible and showed good oxygen barrier ability. The talc decreased moisture uptake.	Liimatainen *et al.* 2013
NFC	Cast	Aqueous	-	Creep behavior; TEMPO oxidation	Microstructures of intermediate size appeared to govern the mechanosorptive creep behavior.	Lindström *et al.* 2012
NFC	Paper making	Aqueous	Chitosan	Montmorillonite co-addition	The chitosan acted as a dewatering aid, allowing the preparation of high-filler nanopaper.	Liu & Berglund 2012
MFC	Cast	Aqueous	Chitosan, alginate	Benzalkonium chloride	Tripolyphosphate was used to coagulate the cationic matrix; the MFC gave higher strength of the anti-bacterial films.	Liu *et al.* 2013
CNC	Coating	Aqueous	Fe_3O_4 nanopart.	Coating level *vs.* conductance	The magnetite NPs were precipitated in the presence of CNC to make conductive paper.	Liu *et al.* 2015
MFC	Coating	Aqueous	-	TEMPO oxidation	High folding endurance and resistance to air permeability were achieved.	Liu *et al.* 2014
MFC	Cast	Aqueous	Amylo-pectin	Glycerol as a plasticizer	The use of MFC made possible the casting of high-quality films without the use of the plasticizer.	López-Rubio *et al.* 2007

Type of Nano-cellulose	Category of Layer	Fluid Medium Used	Matrix Polymer	Key Additives & Conditions	Key Findings	Literature Citation
Spherical NC	Cast	Chloro-form	PLA	Spherical nanocell-ulose formate	The nanoparticles induced higher tensile strength, modulus, and thermal stability, which were attributed to higher crystallinity of the PLA in the films.	Lu *et al.* 2016
MFC	Cast	Aqueous	PVOH	Level of MFC	The MFC yielded stronger PVOH films.	Lu *et al.* 2008
NFC	Cast	Aqueous	-	Coating with acryl-ated soy oil, silane	The hydrophobic coating on the NFC film yielded a transparent, hydrophobic film.	Lu *et al.* 2015
NFC	Cast	Aqueous	Beeswax latex	Coating with acryl-ated soy oil, silane	The hydrophobic coating on the NFC film yielded a transparent, hydrophobic film.	Lu *et al.* 2014
CNC	Cast	Chloro-form	PLA	Surfactant use	Biodegradability of the films was demonstrated.	Luzi *et al.* 2015
MCC	Extruded	Aqueous	Starch & CMC	Glycerol plasticizer	The cellulose increased the storage modulus and decreased water vapor permeability.	Ma *et al.* 2008
CNC	Cast	Aqueous	Starch	Glycerol plasticizer	The package components were oxidized sacrificially, protecting the contents of the package.	Machado *et al.* 2012
CNC	Cast	Aqueous	PVOH & PAM	-	The interpenetrating network, with the CNC, gave low water vapor transmission and improved strength.	Mandal & Chakrabarty 2015
NFC	Paper making	Aqueous	-	Layer-by-layer PEI, NFC on pulp fibers	Higher strength when the PEI was on the outside of the layered structure.	Marais *et al.* 2014
CNC	Cast	Aqueous	Rubber latex	Oxidation of the natural rubber latex	Intermediate levels of oxidation were optimal at a fixed level of 5% CNC, which prevented disruption of the film.	Mariano *et al.* 2016
BC	Melt com-pounding	-	PLA, EVOH	Pre-dispersion of nanocellulose	Properties maximized at 2-3% BC for strength and reduced water permeability, but less barrier to oxygen.	Martínez-Sanz *et al.* 2012
CNC from BC	Cast	Chloro-form	PLA	Grafting of BC with PGMA	Both neat and PGMA-grafted BC reduced oxygen permeability; grafting reduced the adverse effect of moisture on oxygen permeability.	Martínez-Sanz *et al.* 2013a
CNC	Melt or cast	Melt, or aqueous	EVOH	Pre-dispersion of CNC in EVOH	Up to 4% loading was achieved without substantial agglomeration.	Martínez-Sanz *et al.* 2013b
CNC	Melt com-pounding	-	EVOH	Plant or BC sources for CNC	Poor dispersion during direct compounding of dried CNC gave poor water barrier performance.	Martínez-Sanz *et al.* 2013c

Type of Nano-cellulose	Category of Layer	Fluid Medium Used	Matrix Polymer	Key Additives & Conditions	Key Findings	Literature Citation
BC	Injection molded	Aqueous	Starch	Glycerol as plasticizer	The BC caused the composites to be much higher in modulus and less stretchy.	Martins *et al.* 2009
CNC	Coating	Aqueous	PET	CNC made with sulfuric or APS	Higher charge density was achieved with ammonium persulfate preparation of CNC. These authors suggest sandwiching the NC layer between plastic films.	Mascheroni *et al.* 2016
CNC	Cast	Aqueous	Starch	Sorbitol plasticizer	Mechanical strength increased in proportion to CNC loading, but results were highly humidity-dependent.	Mathew *et al.* 2008
NFC	Layer-by-layer	Aqueous	Polyvinyl amine	Manipulation of the pH to control the layer thickness	High strength and modulus films were achieved; the films were ductile when wet. Water acted as a plasticizer.	Merindol *et al.* 2015
NFC	Cast	Aqueous	-	TEMPO oxidation	Low oxygen transmission was achieved at humidity levels below 60%. Higher humidity caused film swelling.	Miettinen *et al.* 2014
MFC	Cast	Aqueous	Galacto-gluco-mannans	Glycerol plasticizer	MFC reduced moisture uptake, increased strength, and increased modulus. It was possible to form films with low plasticizer content when using MFC.	Mikkonen *et al.* 2011
MFC	Cast	Aqueous	-	Glycerol plasticizer, optional	The dry films showed high barrier to oxygen, but this was lowered by plasticizer and by high humidity.	Minelli *et al.* 2010
CNC	Cast	Aqueous	Starch	Glycerol plasticizer or lignin	Strength and elasticity were both increased by the CNC, with glycerol and lignin.	Miranda *et al.* 2015
NFC	Cast	Aqueous	-	Phosphate functionalization	The phophorylated cellulose, when microfluidized to make NFC, gave lower oxygen permeability films.	Naderi *et al.* 2016
BC	Paper making	Aqueous	Phenolic resin	Pressure impreg. of the phenolic resin	The BC imparted greater Young's modulus.	Nakagaito *et al.* 2005
NFC	Paper making	Aqueous	Phenolic resin	Pressure impreg. of the phenolic resin	A threshold of refining and fibrillation was needed to achieve high strength. WRV is a good control measure.	Nakagaito & Yano 2004
MFC	Paper making	Aqueous	Phenolic resin	Pressure impreg. of the phenolic resin	Outstanding strength properties were achieved.	Nakagaito & Yano 2005
MFC	Paper making	Aqueous	Phenolic resin	Pressure impreg. of the phenolic resin	There was a linear increase in modulus with increasing MFC up to 40%.	Nakagaito & Yano 2008a

Type of Nano-cellulose	Category of Layer	Fluid Medium Used	Matrix Polymer	Key Additives & Conditions	Key Findings	Literature Citation
MFC	Paper making	Aqueous	Phenolic resin	NaOH treatment of the MFC	The alkali treatment of the fibers led to greatly increased ductility.	Nakagaito & Yano 2008b
MFC	Paper making	Aqueous	-	NFC from kraft pulp & Matsuko grinder	The nanopaper exhibited high Young's modulus, strength, and foldability, but now thermal expansion.	Nogi *et al.* 2009
MFC	Cast	Aqueous	Chitosan	Chitosan with acetic acid	The use of MFC made it unnecessary to buffer the pH to get good films.	Nordqvist *et al.* 2007
CNC	Cast	Aqueous	Starch & PVOH	Montmorillonite (MMT) co-addition	The nano-reinforcements decreased moisture affinity and increased tensile strength. The MMT worked best.	Noshivani *et al.* 2016
MCC	Cast	Aqueous	PVOH	-	The films were judged to be suitable for packaging.	Ollier *et al.* 2013
BC	Cast	Aqueous	Starch & glycerol	*In-situ* preparation of BC in starch	The films showed good interfacial behavior, water stability, and mechanical properties.	Osorio *et al.* 2014
NFC	Cast & hot press	Aqueous	-	Surface wax coating	Better resistance to oxygen and grease was achieved by hot pressing and by wax coating.	Österberg *et al.* 2013
NFC	Cast	Aqueous	CMC	-	High strength & modulus films formed with NFC present. A low NFC content decreased water vapor permeability.	Oun & Rhim 2015
MFC	Cast	Aqueous	-	Cellulase treatment employed for MFC	Aerogels with high flexibility were prepared, in which the MFC was resistant to collapse during drying.	Pääkkö *et al.* 2008
BC	Cast	Aqueous	-	Edible ingredients employed	The films showed potential to protect sausages by contributing strength and resistance to water vapor.	Padrao *et al.* 2016
BC	Cast	Aqueous	-	Acetosulfation of the BC	The films were smooth, with good mechanical properties and biocompatibility.	Palaninathan *et al.* 2014
CNC	Cast	Aqueous	Starch & PVOH	-	On optimum CNC level maximized strength and minimized water sensitivity.	Panaitescu *et al.* 2015
NFC	Cast	Aqueous	Xylan-rich hemicellul.	Sorbitol as plasticizer	Incorporation of NFC led to enhanced film properties, with increased strength and film integrity.	Peng *et al.* 2011
MCC/CNC	Cast	Aqueous	Sodium caseinate	Glycerol as plasticizer	Cellulose addition initially improved barrier properties, but not when added at higher levels.	Pereda *et al.* 2011
CNC	Cast	Aqueous	Chitosan	Glycerol and olive oil	The additives affected the opacity, contact angle, and mechanical properties of the mixture.	Pereda *et al.* 2014
CNC	Cast	Aqueous	PVOH	-	Increasing CNC tended to increase the water vapor barrier, while maintaining transparency.	Pereira *et al.* 2014

Type of Nano-cellulose	Category of Layer	Fluid Medium Used	Matrix Polymer	Key Additives & Conditions	Key Findings	Literature Citation
CNC	Cast	Ethanol	Cellulose acetate butyrate	-	Transparent films were prepared having improved storage modulus over a wide temperature range due to the presence of the CNC.	Petersson *et al.* 2009
MCC	Cast	Chloro-form	PLA	MCC swollen, freeze-dried, then sonicated in $CHCl_3$	Montmorillonite in the PLA matrix reduced oxygen permeability, but the sonicated MCC did not.	Petersson & Oksman 2006
MFC	Cast	Aqueous	Amylo-pectin	MFC from sulfite or form carboxymethyl dissolving pulp	The pure MRC films achieved low oxygen permeability compared to other films.	Plackett *et al.* 2010
NFC	Paper making	Aqueous	Xyloglucan coating	Enzymes used with nanofibrillation	The xyloglucan coating of the nanofibrils gave superior mechanical performance of the films.	Prakobna *et al.* 2015
NFC	Paper making	Aqueous	PF resin	TEMPO oxidation	The resin increased film toughness to high values and decreased hygroscopicity.	Qing *et al.* 2012
CNC	Cast	Aqueous	Gluten	Carboxylated CNC loadings	Breaking length & storage modulus increased with increasing CNC. Water vapor permeability decreased.	Rafieian *et al.* 2014
CNC	Cast	Aqueous	Gluten	TEMPO oxidized CNC	Tensile strength peaked at 5% load; higher loading gave agglomerates. CNC raised water vapor permeation.	Rafieian & Simonsen 2014
NFC	Coating	Aqueous	Latex	-	NFC acted as a thickener in a coating formulation, but its thickening effects were too strong.	Rautkoski *et al.* 2015
CNC	Cast	Aqueous	Agar	-	Blending with 3% CNC decreased water vapor permeation; modulus & strength also increased.	Reddy and Rhim 2014
NFC, MFC	Coating	Aqueous	Calcium carbonate	-	The nanocellulose coating on paper improved smoothness and barrier properties.	Ridgway and Gane 2012
NFC, MFC	Coating	Aqueous	Calcium carbonate	-	The NFC tends to be held out near the surface of paper, since it is too big to permeate into pores of paper.	Ridgway and Gane 2013
MFC	Paper making	Aqueous	-	Surface acetylation of MFC	Hydrophobicity was increased, and strength was not hurt by acetylation of the MFC before film forming.	Rodionova *et al.* 2011
MFC	Cast	Aqueous	-	Optional TEMPO oxidation	Layering of films yielded low oxygen permeation; drying caused hornification and lowered film properties.	Rodionova *et al.* 2012a

Type of Nano-cellulose	Category of Layer	Fluid Medium Used	Matrix Polymer	Key Additives & Conditions	Key Findings	Literature Citation
NFC	Cast	Aqueous	-	TEMPO-oxidized production of NFC	Increased oxidation of NFC decreased oxygen permeability and gave high tensile strength.	Rodionova *et al.* 2012b
NFC	Paper making	Aqueous	-	NCF prepared with different lignin amounts	The lignin tended to seal up the porosity of the nanopaper. Surface energy was lowered by lignin. Oxygen barrier behavior was improved by lignin content.	Rojo *et al.* 2015
NFC	Coating	Aqueous	-	Laccase modif. with dodecyl gallate	The dodecyl gallate treatment reduced hydrophilicity.	Saastamoinen *et al.* 2012
MFC	Cast	Aqueous	-	Surface-cationized	Anti-microbial activity was shown.	Saini *et al.* 2016a
MFC	Cast	Aqueous	-	Surface-cationized	Static tests shown strong antibacterial activity.	Saini *et al.* 2015
MFC	Cast	Aqueous	-	Nisin anchored	The grafted nicin showed antimicrobial activity.	Saini *et al.* 2016b
CNC	Cast	Aqueous	Starch	-	The films had high tensile strength and modulus, but both decreased above 2% CNC loading.	Salehudin *et al.* 2014
CNC	Compress molding	-	PLA	Nisin, heating to 180 °C	Film was stable after storage; the film showed antibacterial effectiveness.	Salmieri *et al.* 2014a
CNC	Compress molding	-	PLA	Oregano essential oil release	The film completely inhibited bacteria on vegetables.	Salmieri *et al.* 2014b
MFC, NFC	Coating	Aqueous	CMC, poly acrylates	-	Double coating was effective to avoid sagging; the nanocellulose acted as a water retention aid.	Salo *et al.* 2015
CNC	Cast	Chloro-form	PLA	-	Adding 3% CNC decreased water and oxygen permeabilities, which was the optimum.	Sanchez-G. & Lagaron 2010
CNC	Cast	Aqueous	Carrageenan	-	Adding 3% CNC reduced water vapor permeability and solubility of the films.	Sanchez-G. *et al.* 2010
CNC	Cast	Aqueous	Fish gelatin	-	The CNC improved the water vapor barrier. Sonication improved transparency.	Santos *et al.* 2014
NFC	Cast	Aqueous	Carrageenan	-	Adding 0.4% NFC increased tensile strength and water vapor and oxygen barrier properties.	Savadekar *et al.* 2012
MFC	Paper making	Aqueous	-	Paper sheet cured at 93 °C & pressure	Relatively large nanocellulose sheets can be made quickly by papermaking, using a membrane filter.	Sehaqui *et a.* 2010
NFC	Paper making	Aqueous	-	Evaporation after solvent exchange	TEMPO-oxidized NFC yielded a high surface area nanopaper after the specialized drying.	Sehaqui *et a.* 2011

Type of Nano-cellulose	**Category of Layer**	**Fluid Medium Used**	**Matrix Polymer**	**Key Additives & Conditions**	**Key Findings**	**Literature Citation**
MFC, NFC	Compres. molding	-	Thermoplastic PU	Layer of nanocel. between PU	Improved mechanical and thermal properties of the films were achieved.	Seydibeyoglu & Oksman 2008
NFC	Cast	Ethanol	Zein	-	The NFC achieved flexible, transparent films with better properties than unfilled films.	Shakeri & Rad-manesh 2014
NFC	Cast	Aqueous	Agar	Glycerol as plasticizer	Cellulose was regenerated from NaOH, then sonicated; 3% NFC helped strength and water vapor barrier.	Shankar & Rhim 2016
NFC	Cast	Aqueous	-	Heating of the film after preparation	Increasing the heating temperature after formation of the NFC films increased oxygen barrier performance.	Sharma *et al.* 2014
CNC	Cast	Aqueous	CMC	Glycerol & and acrylate monomer	Up to 1% CNC improved mechanical and barrier properties.	Sharmin *et al.* 2012
NFC	Paper making	Aqueous	Epoxy resin	Impregnation of NFC sheet by resin	Thermal stability was improved by the NFC addition.	Shimazaki *et al.* 2007
NFC	Cast	Aqueous	-	TEMPO-mediated oxidation	Calcium or aluminum counter-ion usage led to very low oxygen permeabilities.	Shimizu *et al.* 2016
NFC	Cast	Aqueous	-	Moisture cycles	Reversible control of cellulose film properties with changing humidity was observed by a new method.	Simao *et al.* 2015
NFC	Cast	Aqueous	-	Carboxylation of the NFC	Film opacity decreased and strength increased with increasing homogenization of the NFC.	Siro *et al.* 2011
NFC, MFC	Cast	Aqueous	Alginate	Dicarboxylate NFC also evaluated	NFC increased the strength greatly, and ionic crosslinking further increased strength. High resistance to grease and water vapor were demonstrated.	Sirviö *et al.* 2014
MFC	Coating	Aqueous	Anionic starch	TMP base-sheets were coated	The MFC coating greatly decreased the linting tendency of the paper. MFC together with starch worked best.	Song *et al.* 2010
MFC	Coating	THF	PLA	Coated onto paper handsheets	Low values of water vapor transmission were achieved.	Song *et al.* 2014
Nano-cellulose	Cast	Aqueous	PVOH	-	Good interfacial compatibility was achieved due to the polar nature of the matrix.	Souza *et al.* 2010
MFC	Cast	Aqueous	-	Extractives, lignin, hemicellulose	Lignin content led to increased film toughness; drying did not result in any adverse effects on the films.	Spence *et al.* 2010a

Type of Nano-cellulose	**Category of Layer**	**Fluid Medium Used**	**Matrix Polymer**	**Key Additives & Conditions**	**Key Findings**	**Literature Citation**
MFC	Cast	Aqueous	-	Extractives, lignin, hemicellulose	Processing (energy) led to decreased water absorption and transmission; wax helped block water vapor.	Spence *et al.* 2010b
MFC	Cast	Aqueous	-	Mineral fillers and wax coating	Addition of mineral fillers reduced the water vapor transmission; coating with wax or cooked starch greatly reduced water vapor transmission.	Spence *et al.* 2011
NFC	Cast	Aqueous	-	Foams prepared by freeze-drying	Mechanical attributes were evaluated and modeled.	Srinivasa *et al.* 2015
NFC	Cast	Aqueous	Arabino-xylan	-	The NFC decreased moisture uptake and increased stiffness, strength, and flexibility of the films.	Stevanic *et al.* 2012
BC	Cast	Aqueous	Arabino-xylan	Enzymatic debranching of AX	The NFC decreased moisture uptake and increased strength, and flexibility of the films.	Stevanic *et al.* 2011
BC	Cast	Aqueous	PVOH	-	Swelling behavior was compared.	Stoica-Guzun *et al.* 2013
MFC	Melt extrusion	-	Polyprop-ylene	MFC prep during compounding	MFC greatly increased the modulus and tensile strength.	Suzuki *et al.* 2013
MFC	Melt extrusion	-	Polyprop-ylene	MAPP & cat. poly coupling agents	The system with both coupling agents showed greatest strength.	Suzuki *et al.* 2014
MFC	Cast	Aqueous	Amylo-pectin	Glycerol (50%)	High tensile strength and modulus were achieved.	Svagan *et al.* 2007
MFC	Cast, paper, coated	Aqueous	-	-	High strength and low permeability were observed with three kinds of application approaches.	Syverud *et al.* 2009
MFC	Paper making	Aqueous	-	Also as a coating on paper	High tensile strength, density, and elongation of the films were observed; low oxygen transmission was observed.	Syverud & Stenius 2009
NFC	Cast	Aqueous	-	-	This patent claims the preparation of an NFC film by application of a suspension to a surface and drying.	Tammelin *et al.* 2013
NFC	Cast	Aqueous	Chitosan	Chitosan identified as a crosslinker	Raising the pH precipitates the chitosan and imparts strength even before drying the film.	Toivonen *et al.* 2015b
BC	Cast	Aqueous	Freeze-dried	Esterification with hexanoyl chloride	The esterification, after forming and drying the films, decreased the transport of both gas and water.	Tome *et al.* 2010

Type of Nano-cellulose	**Category of Layer**	**Fluid Medium Used**	**Matrix Polymer**	**Key Additives & Conditions**	**Key Findings**	**Literature Citation**
BC, NFC	Cast	Acidic aqueous	Starch, chitosan	Optionally, a more cationic chitosan	Addition of the chitosan improved the transparency; the nanocellulose improved physical properties.	Tome *et al.* 2013
NFC	Cast	Dichloro-methane, or others	PLA	Optionally with montmorillonite; acetylation of NFC	Oxygen transmission was reduced the most with mercerized, bleached, and acetylated NFC; also the water vapor transmission was reduced.	Trifol *et al.* 2016a
NFC, CNC	Cast	Dichloro-methane, or others	PLA	Acetylation	The montmorillonite and nanocellulose were synergistic for reducing oxygen transmission	Trifol *et al.* 2016b
BC	Cast	Aqueous	Pullulan	Glycerol as plasticizer	The nanocellulose gave rise to improved mechanical properties of translucent films.	Trovatti *et al.* 2012a
NFC	Cast	Aqueous	Pullulan	Glycerol as plasticizer	Increased Young's modulus and tensile strength were achieved by use of the nanocellulose and glycerol.	Trovatti *et al.* 2012b
BC	Impreg-nation	Chloro-form	PLA	Polyethylene glycol as plasticizer	The composite showed better transparency and enhanced water barrier properties.	Urbina *et al.* 2016
NFC	Cast	Aqueous	PGA layer	Layering	Multilayers with NFC layers and polyglycolic acid (PGA) resisted oxygen even at elevated humidity.	Vartianen *et al.* 2016
BC	Cast	Aqueous	Chitosan	Type of acid: acetic *vs.* lactic	5% BC gave the highest tensile strength; results depended on the type of acid employed.	Velasquez-Cock *et al.* 2014
CNC	Paper-making	Aqueous	Membrane filtration	Butylamino func-tionalized CNC	Periodate oxidation, followed by reductive amination led to films with high resistance to oxygen.	Visanko *et al.* 2015
MFC	Layer-by-layer	Aqueous	-	Carboxymethylated MFC	Smooth films were prepared with controlled layering. Cationic polyelectrolytes were used for the other layers.	Wågberg *et al.* 2008
BC	Cast	Aqueous	Starch	-	The BC improved tensile properties and resistance to moisture sorption.	Wan 2009
NFC	Cast	Aqueous	With mont-morillonite	TEMPO-mediated oxidation of NFC	The transparent, flexible films resisted oxygen permeation.	Wu *et al.* 2012
NFC, MFC	Paper-making	Aqueous	-	Silver nanoparticles	The incorporation of silver nanoparticles rendered antimicrobial properties.	Yan *et al.* 2016
CNC	Paper-making	Aqueous	Membrane filtration	Negative charge added in 3 ways	The films were highly transparent. Aldehyde treatment increased strength. Hydrophobic films were made.	Yang *et al.* 2012

Type of Nano-cellulose	**Category of Layer**	**Fluid Medium Used**	**Matrix Polymer**	**Key Additives & Conditions**	**Key Findings**	**Literature Citation**
CNC	Coating	Aqueous	Starch	-	Mechanical properties and resistance to air were improved by the CNC addition.	Yang *et al.* 2014
CNC	Reactive extrusion	Melt	PLA	GMA-grafting of the PLA	Masterbatch preparation increased crystallization, improving the heat resistance of the films.	Yang *et al.* 2015
CNC	Reactive extrusion	Melt	PLA GMA-grafted	With lignin nano-particles	The lignin showed a synergistic influence, including UV blocking, higher crystallinity, strength, & modulus.	Yang *et al.* 2016
MFC	Molding	Aqueous	2% oxidiz. starch	-	A 2% level of oxidized starch doubled the yield strain and gave high bending resistance.	Yano & Nakahara 2004
BC	Impreg-nation	-	Epoxy, PF, acryl. resin	Pressed & dried BC	High strength and transparency were achieved even with 70% cellulose content of the films.	Yano *et al.* 2005
NFC	Cast	Aqueous	Starch	Freeze drying to make foams	The NFC made it possible to create the stable foams with good structural integrity.	Yildirim *et al.* 2014
CNC	Cast	Aqueous	CMC	-	Carboxymethylcellulose films were reinforced, achieving higher tensile modulus and strength.	Youssef *et al.* 2015
CNC	Cast	Chloro-form	PHBV	Silver nanohybrids	Poly-hydroxybutyrate-co-hydroxyvalerate films showed reduced water uptake and permeability.	Yu *et al.* 2014a
CNC	Cast	Chloro-form	PHBV	Methylated CNC	The methylated CNC did not require a stabilizer to be dispersed in the matrix and gave high crystallinity, strength, and barrier properties.	Yu *et al.* 2014b
CNC	Cast	Chloro-form	PLA	Formated CNC; sprayed Ag layer	Water vapor permeability was reduced by the CNC; the Ag imparted antibacterial effects.	Yu *et al.* 2016
CNC, NFC	Cast	Aqueous	PVOH	-	The NFC films outperformed the CNC films, giving higher elongation to rupture (toughness).	Zimmermann *et al.* 2004

Table B. Compilation of Reported Oxygen and Water Vapor Barrier Performance of Nanocellulose Films

Nanocellulose Type	***Modification/ Addition***	**Substrate/ film type**	***Thickness [µm]***	***RH [%]***	***OP without modification [ml.mm/m^2/ d/Pa]***	***OP with modification [ml.mm/m^2/d/Pa]***	***Reduction in WVTR [%]***	***Reference***
CNC	Alginate film with CNC	Solvent casted film	-		-	-	18 %	Abdollahi *et al. 2013a*
BC	BC film with 9%MMT	Prepared with hydraulic press	-	50	2.8 X 10^{-6}	0.41 X 10^{-6}	70 %	Algar *et al. 2016*
CNC	Phosphorylated-CNC + PHB	Extrusion based film	30	50	3.05 X 10^{1}	1.3 X 10^{1}	-	*Arrieta et al. 2014b*
MFC	10X homogenized	Solvent casted film	3.19	0	-	6.0 X 10^{-7}	-	Aulin *et al.* 2010a
MFC	10X homogenized	Solvent casted film	3.19	50	-	8.5 X 10^{-4}	-	Aulin *et al.* 2010a
CNF	20% Vermiculite	Solvent casted film	5.8	50	5.2 X 10^{-7}	7.0 X 10^{-8}	-	Aulin *et al.* 2012
CNF	20% Vermiculite	Solvent casted film	5.8	80	2.5 X 10^{-5}	1.5 X 10^{-6}	-	Aulin *et al.* 2012
CNF	LbL PEI/NFC	Layer by layer deposition	113	50	7.1 X 10^{-7}	3.4 X 10^{-7}	-	Aulin *et al.* 2013
CNF		Dispersion film	-	42	-	-	-37 %	Azeredo *et al.* 2009
CNF	MMT	Solvent casted film	40	50	9.0 X 10^{-7}	10 X 10^{-7}	-50 %	Bardet *et al.* 2015
CNF	Carboxymethylated-CNC	Film	37	50	9.0 X 10^{-7}	10 X 10^{-7}	-26.9 %	Bardet *et al.* 2015

Nano-cellu-lose Type	***Modification/ Addition***	**Substrate/ film type**	***Thick-ness [µm]***	***RH [%]***	***OP without modification [ml.mm/m^2/ d/Pa]***	***OP with modi-fication [ml.mm/m^2/d/Pa]***	***Reduc-tion in WVTR [%]***	***Reference***
MCC	Hydroxypropyl methyl cellulose reinforced with MCC	Solvent casted film	20-25	0	-	-	-40 %	Bilbao-Sainz *et al.* 2010
MFC	2X Homogenized and hexamethyldisilazane treatment	Coated on paper	15-17	50	6.0 X 10^{-7}	5 X 10^{-7}	-	Chinga-Carassco *et al.* 2012
NFC	TEMPO oxidized NFC films	Solvent casted film	20	50	-	4.0 X 10^{-7}	-	Chinga-Carassco and Syverud, 2012
MFC	Pullolan matrix reinforced with MFC and borax	Coating on plastic film	20	0	1.73X10^{-4} (No MFC)	5.9 X 10^{-7}	-	Cozolino et al 2016
MFC	Pullolan matrix reinforced with MFC and borax	Coating on plastic film	20	80	1.73X10^{-4} (No MFC)	3.8 X 10^{-5}	-	Cozolino *et al.* 2016
CNF	Hydroxypropyl guar/TEMPO oxidized CNF composite	Solvent casted film	70-106	40	8.55 X 10^{-7} (No CNF)	3.96 X 10^{-7} (70% CNF)	+39 %	Dai *et al.* 2015
CNC	PHB/CNC reinforced matrix	Film	-	0	2.99X10^{-3} (Pure PHB)	1.06X10^{-3} (2%CNC)	-	Dhar *et al.* 2015
CNC	CMC/starch matrix reinforced with CNC	Solvent casted film	-	100	-	-	-70 %	El Miri *et al.* 2015
CNC	Wheat Gluten (WG)/CNC nanocomposite	Solvent casted film	-	100	-	-	-37 % (12.5%CNC)	El-Wakil *et al.* 2015

Nano-cellu-lose Type	***Modification/ Addition***	**Substrate/ film type**	***Thick-ness [µm]***	***RH [%]***	***OP without modification [ml.mm/m^2/d/Pa]***	***OP with modi-fication [ml.mm/m^2/d/Pa]***	***Reduc-tion in WVTR [%]***	***Reference***
CNC	PLA film reinforced with octadecyl isocynate (ICN) grafted-CNC	Solvent casted film		50	-	-	-26 % (Reinforcement with 15% CNC (grafted vs not grafted)	Espino-Pèrez *et al.* 2013
CNC	Polycaprolactone film reinforced with octadecyl isocynate grafted CNC	Solvent casted film	350	50	-	-	-66 % (Reinforcement with 12 % CNC (grafted vs not grafted)	Follain *et al.* 2013
CNC	PLA-s-CNC composite	Film	40	50	3.05 X 10^1 (No CNC)	1.58X10^1 (5%CNC)	-34 %	Fortunati *et al.* 2012b
CNF	TEMP-oxidized CNF	Coated on PLA film (PLA film thickness: 25 µm)	0.4	50	1.865X10^1	2.54X10^{-2}	-	Fukuzami *et al.* 2009
CNF	Sorbitol plasticized Xylan-CNF composite film	Film	15-35	50	1.9X10^{-7}	8.3X10^{-8}	-88 %	Hansen *et al.* 2012
CNF	Glycerol plasticized Xylan-CNF composite film	Film	15-35	50	1.9X10^{-7}	6.9X10^{-7}	-46%	Hansen *et al.* 2012

Nano-cellu-lose Type	***Modification/ Addition***	**Substrate/ film type**	***Thick-ness [µm]***	***RH [%]***	***OP without modification [ml.mm/m²/ d/Pa]***	***OP with modi-fication [ml.mm/m²/d/Pa]***	***Reduc-tion in WVTR [%]***	***Reference***
Cellulose	Polyelectrolyte complexes films prepared using quaternized cellulose(QC) with glucurono xylan	Solvent casted film	-	50	-	1.0 X 10^{-7} (with wood hydrolysate & 40% QC-L)	-	Ibn Yaich *et al.* 2015
Cellulose	Polyelectrolyte complexes films prepared using quaternized cellulose(QC) with glucurono xylan	Solvent casted film	-	80	-	6.2 X 10^{-7} (with wood hydrolysate & 40% QC-L)	-	Ibn Yaich *et al.* 2015
CNC	Chitosan reinforced with CNC	Solvent casted film	20	-	-	-	-27 % (5% CNC reinforcement)	Khan *et al.* 2012
CNF	O-acetyl galactoglucomannon-succinic ester(GGM-Su) coating on CNF-GGM composite film	GGM-Su coating on CNF-GGM film	35-49	50	5.0 X 10^{-7} (No Coating)	1.0 X 10^{-7} (Coating)	-	Kisonen *et al.* 2015
CNF	Bare CNF films produced by homogenizing HW pulp	Solvent casted film	25	50	4.02 X 10^{-6} (one pass homogenization)	0.92 X 10^{-6} (one pass homogenization)	22 %	Kumar *et al.* 2014

Nano-cellu-lose Type	***Modification/ Addition***	**Substrate/ film type**	***Thick-ness [µm]***	***RH [%]***	***OP without modification [ml.mm/m^2/ d/Pa]***	***OP with modi-fication [ml.mm/m^2/d/Pa]***	***Reduc-tion in WVTR [%]***	***Reference***
CNF	Bare CNF films produced by homogenizing SW pulp	Solvent casted film	25	50	0.62 X 10^{-6} (one pass homogenization)	1.5 X 10^{-6} (one pass homogenization)	12 %	Kumar *et al.* 2014
CNC	CNC-noncellulosic polysaccharide composite plasticized with sorbitol	Film	17-22	50	5.4 X 10^{-5} (30%CNC)	2.7 X 10^{-7} (50%CNC+Sorbitol)	-	Normand *et al.* 2014
CNC	CNC-noncellulosic polysaccharide composite film	Film	17-22	80	2.72X 10^{-4} (30%CNC)	6.5 X 10^{-6} (50%CNC)	-	Normand *et al.* 2014
CNF	CNF with TEMPO-CNF	Solvent casted film	15-18	50	4.12X10^{-6} (Pure CNF)	6.0X10^{-7} (70%CNF+30%TEMPO-CNF)	-	Miettinen *et al.* 2014
CNF	Wax treatment over CNF film	Solvent casted film	-	96	5.3 X 10^{-5}	1.7 X 10^{-5}	-93 %	Österberg *et al.* 2013
MFC	Amylopectin reinforcement in sulfite pulp MFC	Solvent casted film	-	50	3.7X10^{-7} (15%MFC)	1.6X10^{-7} (100%MFC)	-	Plackett *et al* 2010
MFC	Amylopectin reinforcement in carboxymethylated-MFC	Solvent casted film	15-18	50	3.4X10^{-7} (15%MFC)	1.3X10^{-7} (100%MFC)	-	Plackett *et al.* 2010
CNF	CNF reinforcement in kappa-carrageenan (KCRG) matrix	Solvent casted film	58-61	50	7.8X10^{-3} (Pure KCRG film)	1.5X10^{-3} (+0.4%NFC)	88%	Savadekar *et al.* 2012

Nano-cellulose Type	***Modification/ Addition***	**Substrate/ film type**	***Thick-ness [µm]***	***RH [%]***	***OP without modification [ml.mm/m^2/ d/Pa]***	***OP with modification [ml.mm/m^2/d/Pa]***	***Reduction in WVTR [%]***	***Reference***
CNF	CNF reinforcement in PLA film	Solvent casted film	-	50	2.2X10^1 (Pure PLA film)	5.1X10^0 (3%CNC)	46%	Trifol *et al.* 2015
CNC	CNC reinforcement in PLA film	Solvent casted film	-	50	2.2X10^1 (Pure PLA film)	5.6X10^0 (3%CNC)	48%	Trifol *et al.* 2015
	MMT reinforcement in PLA film	Solvent casted film	-	50	2.2X10^1 (Pure PLA film)	16X10^0 (3%CNC)	39%	Trifol *et al.* 2015