Chapter 3
Cellulose Reinforced Biodegradable Polymer Composite Film for Packaging Applications

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Abstract This chapter provides a broad overview of bionanocomposite film prepared from various biodegradable polymers reinforced with nanocellulose. In nature, biodegradable polymer exhibits relatively weaker properties than the synthetic polymers. Incorporation of cellulose into the biopolymer matrix has improved the mechanical, thermal, and barrier properties of the resulting biopolymer film significantly. This achievement has encouraged their application as packaging material. Since they have a huge potential in the future, further investigation of this composite material is crucial.

Keywords Cellulose · Biodegradable polymer · Composite film · Reinforcement · Packaging

3.1 Introduction

"Packaging" can be described as a material that uses to protect the packed products against any physical, chemical, or biological hazards. Plastic is among the materials (i.e., wood, paper, metals, and glass) that commonly used in packaging due to its softness, lightness, and transparency. Petrochemical-based plastics such as polyethylene terephthalate (PET), polyvinylchloride (PVC), polyethylene (PE), polypropylene (PP), polystyrene (PS), and polyamide (PA) are the common materials for manufacturing packaging films. These materials are chosen probably due to their abundant availability, low cost, excellent mechanical, and barrier properties. However, the increase of using these synthetic packaging films has led

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to serious municipal waste disposal problem, which attributed by the materials' non-degradable characteristic (Siracusa et al. 2008). Therefore, the biodegradable polymer becomes more attention as green materials for packaging applications.

Biodegradable polymers can be derived from renewable resources (biomass) and microorganisms or synthesized from bio-derived monomers (Vieira et al. 2011). Polymers from biomass such as polysaccharides, proteins, and lipids are the most basic (common) materials utilized to form edible and/or biodegradable films. Polysaccharides have good film forming properties, but their moisture barriers are weak, while the protein-based films usually have better mechanical and barrier properties than that of the polysaccharide-based films. Although lipid films exhibit good moisture barrier properties, they can cause textural and organoleptic problems (Vieira et al. 2011). Since these biodegradable polymer films possess certain unfavorable physicochemical properties, which may restrict their applicability and feasibility on edible or non-edible packaging applications, development of composite film is an alternative approach to solving this issue.

Cellulose is one of the polysaccharides that largely available in the world. In comparison with other biopolymers, cellulose is neither meltable nor soluble in water or any common organic solvents. Thus, chemical modification of cellulose surface is generally required to form soluble cellulose (i.e., cellulose derivatives), which is suitably used as film-forming materials for packaging. Since cellulose exhibits excellent mechanical performance, it has gained more significant interest and attention as reinforcement in the biodegradable polymer film. It is well known that incorporation of cellulose into a biodegradable polymer film can be an effective way to overcome the poor properties of the biodegradable polymer and meanwhile, obtain desired function and properties (Hu et al. 2016; Phan The et al. 2009).

This chapter highlights the important role of cellulose used as reinforcement material in packaging applications. Literature review on cellulose reinforced biopolymer-based biodegradable packaging film is the main focus in this chapter. Hence, the first section of this chapter briefly summarizes the chronological events of cellulose fiber as reinforcement in composite materials, whereas the second section describes the characteristics and properties of different (micro-/nanoscale) cellulose as reinforcing materials. Thereafter, the following section comprehensively discusses the preparation and properties of the composite film with cellulose reinforced plastics by using the biodegradable polymer as a matrix. The criteria of this composite film as packaged material are also highlighted in the last section of this chapter.

3.2 Chronological Events of Cellulose Fiber as Reinforcement in Composite Materials

Since cellulosic fiber consists of specific benefits over the synthetic fibers (i.e., carbon and glass fibers) such as renewability, abundant availability, inexpensive and acceptable specific strength, as well as non-hazardous, cellulosic natural fiber as

Table 3.1 Chronological events of the development of cellulose fiber as reinforcement in composite materials

Year	Progress and development	References
1838	First introduction of cellulose	Bledzki and Gassan (1999)
1908	Cellulose from paper or cotton reinforced phenol or melamine formaldehyde matrix as sheet for electronic purpose	Bledzki and Gassan (1999)
1978	Jute fiber reinforced polyester as construction material for building	Bledzki and Gassan (1999)
1987	Cellulosic pulp fiber reinforced thermoplastic composite	Boldizar et al. (1987)
1995	First introduction of "all-organic" nanocomposite: cellulose whickers from sea animal reinforced polymer nanocomposite film	Favier et al. (1995)
1996	Cellulose whickers from wheat straw reinforced thermoplastic nanocomposite film	Helbert et al. (1996)
1999	Green composite: cellulosic pineapple leaf fiber reinforced Poly (3-hydroxybutyrate-co-3-hydroxyvalerate) biodegradable composite film	Luo and Netravali (1999)
2000	Cellulose microfibrils from potato tuber cells reinforced starch film for packaging	Dufresne et al. (2000)
2001	Cellulose fiber reinforced starch composite film for thermoforming packaging	Moroa (2001)
2004–2005	First introduction of "all-cellulose" composite: native cellulose fiber reinforced cellulose matrix	Nishino et al. (2004), Gindl and Keckes (2005)
2005	Microcrystalline cellulose (MCC) reinforced Polylactic acid (PLA) biodegradable composite film for packaging	Mathew et al. (2005)
2007	MCC reinforced hydroxypropyl methylcellulose (HPMC, a cellulose derivative) film for food packaging	Dogan and McHugh (2007)
2008	Carboxymethyl cellulose (CMC) reinforced pea starch composite film for food and biodegradable packaging	Ma et al. (2008)
2009	Cellulose whiskers reinforced chitosan composite film for food packaging	Li et al. (2009)
2009	Cellulose nanofiber reinforced mango puree composite film for food packaging	Azeredo et al. (2009)
2009	Microfibrillated cellulose reinforced PLA composite film for packaging applications	Suryanegara et al. (2009)
2010	Cellulose nanofiber reinforced PLA composite film for packaging applications	Jonoobi et al. (2010)
2010	Bamboo cellulosic crystal reinforced starch composite film for packaging applications	Liu et al. (2010)
2010	Bagasse cellulose whickers reinforced natural rubber composite for packaging films and tapes	Bras et al. (2010)

(continued)

Table 3.1 (continued)

Year	Progress and development	References
2011	Different cellulose nanoparticles reinforced HPMC composite film for packaging	Bilbao-Sainz et al. (2011)
2011	Nanocrystalline cellulose reinforced xylan composite film for packaging applications	Saxena et al. (2011)
2012	Nanocrystalline cellulose reinforced chitosan composite film for food packaging	Khan et al. (2012)
2013	Cellulose nanowhiskers reinforced cellulose acetate composite film for packaging	Yang et al. (2013)
2014	Cellulose reinforced alginate composite film for packaging	Sirviö et al. (2014)
2015	Recycle cellulose reinforced starch–gelatin composite film for packaging	Rodríguez-Castellanos et al. (2015)
2016	Bacterial cellulose nanowhiskers reinforced thermoplastic corn starch nanocomposite film for food packaging	Fabra et al. (2016a)
2016	MCC reinforced polypropylene composite for microwavable packaging	Ummartyotin and Pechyen (2016)

reinforcement for composite material and their utilization in various applications have been widely studied in the past few years (Jawaid and Khalil 2011). Table 3.1 illustrates the chronological events of the development of cellulose fiber as reinforcing materials including its modification and applications. As can be seen, cellulose as filler in the composite material is mainly focused on the field of packaging. Since the year 1999, researchers are started paying attention to renewable and sustainable packaging materials.

3.3 Cellulose: A Biodegradable Polymer Reinforcement

Cellulose can be obtained from wood or non-wood plant biomasses. It is a linear carbohydrate polymer chain that consists of units of glucose connected through (1,4)-β-D linkages (Tye et al. 2016). Moreover, it is among the constituents (i.e., hemicellulose and lignin) of lignocellulose biomass that largely available with a content approximately about 45%. In the plant cell wall, the crystalline fraction of the plant is contributed only by cellulose, whereas hemicellulose and lignin are amorphous. Since a lot of hydroxyl groups in the crystalline phase of cellulose form many hydrogen bonds, and these hydrogen bonds construct a huge network that directly contributes the compact and highly ordered crystal cellulose structure, cellulose is very stable and difficult to break apart. Therefore, with this crystalline part, cellulose has outstanding mechanical properties, which is interesting to be used as reinforcement in polymer composite (Zimmermann et al. 2010). Nevertheless, the mechanical properties of cellulose are strongly depended on the cellulose type (Brinchi et al. 2013). Cellulose fibers are assembled in a hierarchical and multi-level ordered structure, where microfibrils (basic fibrils) in the nano-sized scale formed by the cellulose chains are packed into larger units called macrofibrils. Therefore, different kinds of nanocellulose fillers can be extracted such as cellulose nano-structured materials (i.e., microcrystalline cellulose and microfibrillated cellulose) and cellulose nanofibers (i.e., nanocrystalline cellulose and nanofibrillated cellulose) (Osong et al. 2016).

3.3.1 Cellulose Nano-structured Materials

Within the microfibrils in the plant cell wall, cellulose exhibits both crystalline and amorphous regions. Since it is known that crystalline cellulose is much stronger and stiffer than the amorphous cellulose and cellulose itself, the production of microcrystalline cellulose (MCC) can be a better reinforcing agent than cellulose (Ashori and Nourbakhsh 2010). Microcrystalline cellulose (MCC) or known as cellulose microcrystal is a crystalline cellulose. It is generally produced from the acid hydrolysis of cellulosic pulp fiber to remove the amorphous region of cellulose (Ashori and Nourbakhsh 2010; Siqueira et al. 2010). The resulting particles are porous, insoluble in water, possess high cellulose content, high aspect ratio (>1000), and high crystallinity (Moon et al. 2011; Osong et al. 2016). In comparison with other synthetic polymers such as glass fiber, MCC is cheap, has low density, and is renewable as well as biodegradable. Moreover, the high crystallinity of MCC delivers a strong reinforcing ability due to the high modulus. The longitudinal modulus for MCC is about 150 GPa, which is capable of improving the mechanical properties of the resulting biocomposites. Therefore, MCC has been widely used as fillers in various polymers composite (Ashori and Nourbakhsh 2010; Rico et al. 2016).

Microfibrillated cellulose (MFC) is cellulose microfibrils that can be extracted by a mechanical disintegration process (consisting of refining and high-pressure homogenizing) with or without chemical/enzymatic pretreatment from cellulosic pulp fiber (Siró and Plackett 2010). Besides, there are also several kinds of mechanical treatment such as microfluidization, super-grinding, cryo-crushing, steam explosion, and high-intensity ultrasonication (HIUS), which can be used to reduce the particle size of fibers to micro- or nanoscale (Osong et al. 2016). The resulting particles are spaghetti-like in shape, long, flexible, and composed of more or less individualized cellulose microfibrils (width: 10–100 nm, length: 0.5–10 mm) and pure cellulose that contains both crystalline and amorphous regions (Moon et al. 2011; Siqueira et al. 2010). Moreover, MFC has a very good ability to form the web-like network and high elastic modulus ($\sim$150 GPa), which is attracted to be used as reinforcement materials in composite films (Siqueira et al. 2010).

3.3.2 Cellulose Nanofibers

Nanofibrillated cellulose (NFC) is cellulose nanofibrils or finer cellulose fibrils produced by high shearing forces of disintegration leading to a high degree of fibrillation from cellulosic pulp fiber. Similar to MFC, the resulting NFC particles consist of pure cellulose from both crystalline and amorphous regions and have the ability to create entangled networks (Kalia et al. 2014). However, NFC has a relatively high aspect ratio (width: 4–20 nm wide, length: 500–2000 nm) than MFC (Moon et al. 2011). The wide range of size distribution for NFC usually dependent on the energy input to disintegrate the cellulose fibers and on the pretreatment utilized to facilitate the disintegration process (Kalia et al. 2014). Besides, nanocrystalline cellulose or known as cellulose nanocrystal is stiff-rod (‘rice-like’) or whisker-shaped particles produced after acid hydrolysis of MCC or cellulose fiber (Siqueira et al. 2010). Similar to MCC, the resulting particles are crystalline cellulose with a high crystallinity of 54–88%. Nevertheless, NCC has a relatively higher aspect ratio than MCC (width: 3–5 nm, length: 50–500) (Moon et al. 2011).

3.4 Cellulose Reinforced Biodegradable Polymer Composite Film

The reason for using biodegradable polymers is to reduce the amount of synthetic polymer required for packaging applications, but not to completely replace the synthetic plastic. Nevertheless, the commercial use of biodegradable polymer films has been limited due to their poor mechanical and barrier properties when compared to synthetic polymers. The incorporation of reinforcing component to polymer has recently proposed to improve the poor properties of this biopolymer film. However, many reinforced materials especially the macroscopic reinforcing components present poor interfacial adhesion with the polymer matrix (Azeredo et al. 2009). Therefore, there has been a growing interest from industry to use nano-sized cellulose as reinforcement materials in packaging applications. Nanocellulose materials are usually having a high aspect ratio, which is capable of providing better reinforcing effects. Hence, a high strength, stiffness, and transparency film can be produced due to the uniform dispersion of nanoparticles in a polymer matrix (Besbes et al. 2011).

3.4.1 Types and Properties of Biodegradable Polymer

Unlike non-renewable petroleum-based biodegradable polymer, biodegradable polymers can be naturally derived from renewable resources. The renewable biodegradable polymer can be categorized into three groups depending on the

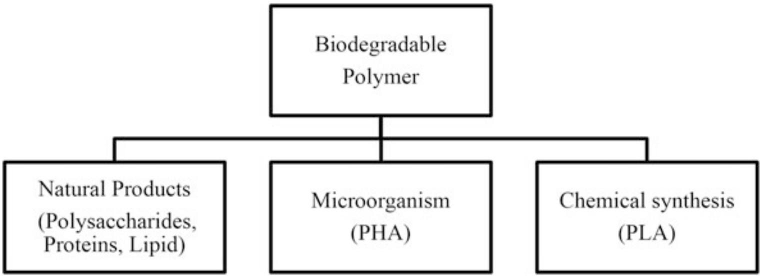

Fig. 3.1 Classification of renewable biodegradable polymers (Othman 2014)

origin of the biopolymers: (1) natural biopolymers extracted from natural products, (2) synthetic biopolymers from microbial production or fermentation, and (3) synthetic biopolymers conventionally and chemically synthesized from biomass (Fig. 3.1).

3.4.1.1 Polysaccharides

Polysaccharides, proteins, and lipid are the common biodegradable polymer that extracted from plants or animals. Among the biopolymers, polysaccharides such as starch, cellulose, seaweed, and chitosan are widely used as polymer film in packaging applications due to they are typically cheap and abundantly available.

Starch is derived from cereal grains and tubers like corn, wheat, potato, tapioca, and rice. Generally, it consists of two kinds of molecules such as amylose (about 20–30%) and amylopectin (about 70–80%), in which amylose was the primary molecule for filmmaking. The edible film with high amylose content is flexible, oxygen impermeable, oil resistant, heat sealable, and water soluble. Moreover, starch is extensively used as a replacement for plastic polymer due to both having similar characteristics, which are transparent, odorless, tasteless, colorless, non-toxic, biologically absorbable, semipermeable to CO_2, and resistant to the passage of O_2. In addition, edible starch-based films can hinder microbial growth by lowering the water activity within the package (Shit and Shah 2014). Although starch is edible, safe, and degradable, it has low mechanical properties. Therefore, previous studies have proposed that starch mechanical properties can be improved by incorporation with plasticizer and/or nanofillers (Jiménez et al. 2012; Othman 2014).

Cellulose and starch are two very similar polymers. Both of them are made from glucose and have the same glucose-based repeat units. The main difference between cellulose and starch is that cellulose contains beta glucose, while starch is made of alpha glucose. Because of this difference, both differ in their chemical and physical properties. In comparison with starch, cellulose from lignocellulosic biomass is a more sustainable material as it does not disturbs the food sources such as wheat, maize, and potatoes, which are mainly used to derive the starch. Unlike starch, only cellulose-derived polymers (cellulose derivatives) have the film-forming ability because native cellulose is water-insoluble compound. Hydroxypropyl cellulose (HPC), hydroxypropyl methylcellulose (HPMC), carboxymethylcellulose (CMC), and methylcellulose (MC) are the common cellulose derivatives that used for polymer coatings or films. The cellulose derivatives' films exhibit moderate strength, flexibility, transparency, flavorless, colorless, tasteless, and moderate barriers to oxygen as well as resistant to oils and fats. Nevertheless, similar to starch, they possess poor mechanical and water vapor barrier properties. A way to improve weak properties would be the addition of filler to develop a composite film (Shit and Shah 2014).

Besides plant-derived polysaccharides, marine-derived polysaccharides such as alginate, carrageenan, and agar have a potential to form biopolymer film because of their unique colloidal properties, which commonly used as a thickening, stabilizing, and suspending agent in food industry. Alginate, carrageenan, and agar are seaweed derivatives. Agar and carrageenan can be extracted from red seaweed, while alginate from brown seaweed. Since seaweed derivatives are a water-soluble polymer, they exhibit poor water resistance because of their hydrophilic nature. Although edible films prepared from these seaweed-derived polymers have strong potential to be used in wide range of applications, they usually lack the desired mechanical properties, such as high strength that are needed for certain packaging application (Joye and McClements 2014; Shit and Shah 2014).

Chitin is a linear polysaccharide comprised of β-1,4-N-acetylglucosamine, which is extracted from shells of crustaceans and cell walls of fungi. Similar to cellulose, chitin is insoluble in common solvents because of its high crystalline structure and hydrogen bonding between carbonyl, hydroxyl, and acetamide groups. Therefore, chitin is generally used for the production of chitosan by deacetylation (Abdul Khalil et al. 2016). Chitosan is biodegradable, non-toxic, and low-cost as well as has good film-forming properties. The edible film prepared from chitosan exhibits excellent O_2 and CO_2 permeability and antimicrobial activity against bacteria, yeasts, and molds (Shit and Shah 2014). However, similar to other polysaccharides, their poor mechanical and thermal properties have restricted its widespread applications. Thus, the chitosan film properties can be improved by reinforcement of nano-sized cellulose (Abdul Khalil et al. 2016).

3.4.1.2 Proteins

Proteins used to produce edible film can be divided into animal- and plant-derived proteins. Plant origin proteins are corn zein, wheat gluten, soy protein, pea protein, sunflower protein, peanut protein, and cotton protein, whereas animal origin proteins are keratin, collagen, gelatin, fish myofibrillar protein, egg white protein, and casein as well as whey protein (Ogur and Erkan 2015). Generally, animal-derived protein (the fibrous protein) is water insoluble, while plant-derived protein (the globular protein) can soluble in water or aqueous solutions of acids, bases, or salts. The chemical and physical properties of these proteins are highly depending on the relative amounts of component amino acid residues and their placement along the protein polymer chain (Wittaya 2012).

Among the biodegradable polymer films, protein-based films are the most attractive. It has the impressive gas barrier and better mechanical properties as compared with other biodegradable polymer films due to proteins have a unique structure (based on 20 different monomers), which can form bonds at different positions and offer high potential for forming numerous linkages. However, similar to other biodegradable polymers, the protein-based film has a poor water vapor barrier (contain predominantly hydrophilic amino acid residues) and mechanical strength as compared with synthetic polymers, which limits its application. These properties can be improved by modifying properties of the protein by chemical and enzymatic methods, combining with the hydrophobic material or some polymers, or by using a physical method (Bourtoom 2009).

3.4.1.3 Lipid

Lipid compound consists of acetylated monoglycerides, natural wax, and surfactants. Parrafin wax and beeswax are the lipid substances that widely used as edible film. Although lipid-based film is capable of inhibiting the passage of moisture, its hydrophobic character usually forms thicker and brittle film. Therefore, it usually mixes with other film-forming agents such as polysaccharides, to provide mechanical strength, while maintaining its characteristics (Shit and Shah 2014).

3.4.1.4 Polyhydroxyalkanoates (PHA)

Different from other biodegradable polymers, polyhydroxyalkanoates (PHA) is a family of bio-polyesters, which derived from the microorganism. PHA is biodegradable. However, it is costly (Yang et al. 2002). Since PHA presents a relatively wide range of properties depending on the hydroxyvalerate (HV)-to-hydroxybutyrate (HB) ratio, several studies were conducted using homopolymer polyhydroxy butyrate (PHB), the most common member of the PHA family, as a biomaterial for in vitro and in vivo studies (Martínez-Sanz et al. 2016). Although it presents mechanical properties similar to those synthetic thermoplastics such as polyethylene and polypropylene, it has relatively high glass transition and melting temperatures, leading to excessive brittleness due to its highly crystalline characteristics. In order to reduce the excessive brittleness and low thermal stability, copolymers of PHB with hydroxyvalerate, which commonly known as PHBV, have been developed to enhance the properties of this bio-polyester. Nevertheless, they still present an insufficient barrier to substitute other synthetic polymers commonly used for food packaging applications. Hence, the addition of fillers is an alternative way in order to make this biopolymer more suitable for food packaging applications (Yang et al. 2002; Fabra et al. 2016b).

3.4.1.5 Polylactic Acid (PLA)

Polylactic acid (PLA) is among the most common synthetic biopolymers. PLA is produced from lactic acid through fermentation of carbohydrate from plant resources, for instance, sugar beet and corn. It is biodegradable and offers good stiffness and strength. However, it possesses low heat distortion temperature, low resistance to extreme heat and humidity, and low flexibility (Mathew et al. 2005; Othman 2014). Therefore, PLA mainly used in products with not very high performance such as plastic bags for household wastes, barriers for sanitary products and diapers, planting, and disposable cups and plates. Hence, the incorporation of renewable reinforcement can be of great interest in order to enhance some limitation of PLA (i.e., low toughness and thermal stability) while maintaining their transparency and biodegradability properties (Mathew et al. 2005; Haafiz et al. 2016).

3.4.2 Properties of Biodegradable Polymer-Cellulose Composite Film

To understand the performance of cellulose fiber reinforced biopolymer film, it becomes necessary to determine the mechanical, physical, and chemical properties of this developed composite film. According to Table 3.2, biopolymers, which derived from natural products (i.e., polysaccharides and proteins), are among widely used with cellulose as reinforcement material in packaging applications.

Although amylose from starch can form gels and films, starch has poor mechanical, thermal, and barrier properties when compared with petroleum-based polymers. The dispersion of filler reinforcement from micro- or nanoscale such as microcrystalline cellulose (MCC), cellulose nanoparticles (CN), and microfibrillated cellulose (MFC) into a starch biopolymer matrix has been reported as one of the most promising approaches for improving the mechanical and water vapor barrier properties of the starch film (Table 3.2). However, the starch bionanocomposite films increased in tensile strength but decreased in elongation at breaks of composites. The increase in tensile strength is directly related to the hydrogen bonds formed between the starch and cellulose structures. A good interfacial interaction between cellulose and starch matrix is most probably due to their chemical similarity (both are polysaccharides). Moreover, the presence of these micrometric or nanometric particles also is capable of reducing the water vapor diffusion through the matrix and thus, decreasing the water vapor permeability of the starch films (Guimarães et al. 2016).

In general, the native starch in a granular structure can be processed into thermoplastic materials for expanding starch processability and applications. Thermoplastic starch (TPS) usually formed when the presence of a suitable plasticizer (i.e., water, polyols, and amides), temperature, and shear. Then, the starch

Table 3.2 Properties of cellulose reinforced biopolymer film by casting method

Biodegradable polymer (matrix)	Type of cellulose (reinforcement)	Film characteristics and improvement	References
Starch	MCC	Addition of MCC improved tensile strength and water resistance of starch film	Wittaya (2009)
	Cellulose nanoparticles (CN)	Addition of CN improved the tensile strength, thermal stability, and water vapor barrier of starch film	Chang et al. (2010)
	MFC	Addition of MFC increased the tensile strength and decreased the water vapor permeability	Guimarães et al. (2016)
Thermoplastic Starch (TPS)	MCC	Addition of MCC improved the thermal stability, tensile strength, dynamic mechanical and water vapor barrier properties of TPS film	Ma et al. (2008), Rico et al. (2016)
	Cellulose nanocrystals (CNC)	Addition of CNC improved the tensile strength and water vapor permeability of TPS film	González et al. (2015)
	Cellulose nanofiber (CNF)	Addition of CNF improved the mechanical and water vapor barrier properties as well as storage modulus and degradation rate of TPS film	Babaee et al. (2015)
Alginate	NCC	Incorporation of NCC improved film mechanical (except elongation), water vapor permeability, and thermal properties	Huq et al. (2012)
	NFC	Incorporation of CNF improved film water resistance and mechanical properties as well as decreased biodegradation time	Deepa et al. (2016)
Kappa-carrageenan	NCC	Incorporation of NCC showed good dispersion, superior mechanical properties, and thermal stability of film	Zarina and Ahmad (2015)
	NFC	Addition of CNF improves the tensile strength, water vapor transmission rate, and oxygen transmission rate of film	Savadekar et al. (2012)
Agar	NCC	Film transparency decreased. Addition of NCC improved film mechanical, thermal, and water vapor barrier properties	Rhim et al. (2015), Shankar and Rhim (2016)

(continued)

Table 3.2 (continued)

Biodegradable polymer (matrix)	Type of cellulose (reinforcement)	Film characteristics and improvement	References
Chitosan	Cellulose nanoparticles (CN)	Chitosan/CN indicated excellent antimicrobial properties and thermal stability	Dehnad et al. (2014)
	Cellulose whiskers (CW)	Addition of CW increased tensile strength of chitosan film. This nanocomposite film displayed excellent thermal stability and water resistance	Li et al. (2009)
	Nanocrystalline cellulose (NCC)	Addition of NCC improved the tensile strength water vapor barrier properties of chitosan film	Khan et al. (2012)
	MFC	Addition of MFC increased the tensile strength, storage modulus and glass transition temperature of chitosan film	Hassan et al. (2011)
Protein	Cellulose pulp fiber	Cellulosic pulp fiber as reinforcement improved mechanical properties (except elongation at breaks) of castor bean cake protein film	Oliveira et al. (2015)
	MCC	Addition of MCC improved the tensile strength, oxygen, and water barrier properties of soy protein isolate (SPI) film	Wang et al. (2013)
	CW	CW/SPI composite film showed greater tensile strength, young modulus, and water resistance as well as thermal stability	Wang et al. (2006)
	CW	CW/fish gelatin composite film exhibits good mechanical properties (except elongation) and water vapor barrier	Santos et al. (2014)
	MFC	Addition of MFC improved the mechanical strength and reduced the water vapor permeability (WVP) and water absorption of gelatin film	Fadel et al. (2012)
	Bacterial cellulose nanocrystal (BCNC)	Addition of BCNC improved the moisture sorption, WVP behavior, mechanical and thermal properties of gelatin film	George and Siddaramaiah (2012)

(continued)

Table 3.2 (continued)

Biodegradable polymer (matrix)	Type of cellulose (reinforcement)	Film characteristics and improvement	References
PHB	CNC	Addition of CNC improved gas barrier and migration properties of PHB film	Dhar et al. (2015)
PHBV	MCC or ultrasound modified bacterial cellulose (us-BC)	Us-BC/PHBV show higher tensile strength and modulus than MCC/PHBV	Panaitescu et al. (2013)
	CW	CW/PHBV exhibit good mechanical and thermal properties	Ten et al. (2010, 2012)
PLA	MCC	Addition of MCC improved the thermal stability and young modulus, but decreased the tensile strength and elongation of PLA film	Mathew et al. (2005), Haafiz et al. (2013)
	Cellulose nanofibril	The mechanical properties of cellulose nanofibril/PLA are lower than poly (ethylene glycol)/PLA film	Qu et al. (2010)

granules can be fragmented, swelled, and melted, and consequently, the hydrogen bonds among the starch molecules can be disrupted. This modified starch is capable of being processed and with similar applications as conventional thermoplastic materials (Rico et al. 2016). Nevertheless, TPS still exhibits problems such as high water absorption and low mechanical properties, which are highly affected by the relative humidity. Previous studies have reported that the incorporation of natural bio-fillers such as MCC, cellulose nanofiber (CNF), and cellulose nanocrystals (CNC) is one of the methods to enhance the performance of TPS films and develop inexpensive starch biocomposite (Table 3.2). Similar to native starch film, TPS film reinforced with these cellulosic fibers, whiskers, and nanofibers is capable of enhancing the tensile strength and water vapor permeability of TPS film. Surprisingly, in an addition of these cellulose reinforcement materials to TPS matrix, other properties like thermal stability, storage modulus, and degradation rate of TPS films are improved as well (Table 3.2).

Similar to starch, seaweed derivatives (alginate, carrageenan, and agar) are ideal film-forming materials. It also lacks sufficient mechanical and water vapor properties. Since cellulose possesses outstanding characteristics and properties, the incorporation of cellulose reinforcing materials such as NCC and NFC into seaweed matrix is capable of increasing the seaweed derivatives' film mechanical properties and water resistance as well as thermal properties of the seaweed film remarkably (Table 3.2). This phenomenon is actually expected due to both seaweed and cellulose are a chemical similarity. Hence, the improvement in mechanical strength and water vapor barrier properties are largely due to strong hydrogen bond networks between cellulose and seaweed and good dispersion of cellulose in the seaweed film (Deepa et al. 2016; Huq et al. 2012).

Different from starch and seaweed, chitosan is natural antimicrobial polysaccharides that can fight against a wide variety of microorganisms (i.e., bacteria, yeast, and molds), and thus, it has been successfully used as packaging material for the preservation of food quality (Dehnad et al. 2014). However, the inherent water sensitivity and relatively low mechanical properties of chitosan have restricted it applications especially in the wet or moist conditions (Li et al. 2009). To solve these problems, chitosan is mixed with nanoparticles, which having at least one dimension in nanoscale (i.e., CN, CW, NCC, and MFC) to prepare composite materials with improved properties. Since chitosan and cellulose are structural similarities, they are compatible, and thus, the composite film exhibits excellent mechanical, thermal, and water vapor barrier properties as well as the capability for further extending the food shelf-life (Table 3.2).

Soy protein isolate (SPI) is one of the proteins that often used to develop edible materials for diverse applications. However, SPI application is limited by poor mechanical properties (especially flexibility) and the water sensitivity of soy protein-based materials. Although the brittleness of SPI film can be reduced by employing plasticizer, this phenomenon will lead to a significant decrease in the tensile strength and increase in the water sensibility as well (Wang et al. 2006, 2013). Therefore, to obtain flexible SPI plastic with an acceptance tensile strength, several kinds of reinforcement materials such as cellulosic pulp fiber, MCC, and CW have been studied (Table 3.2). Surprisingly, these reinforcement materials improve the tensile strength and water resistance as well as the thermal stability of SPI films. However, the incorporation of cellulosic pulp fiber in the SPI matrix is less effective as compare to the nanocellulose materials (MCC and CW) due to the load with cellulosic pulp fiber is not able to transform the composite film in a high water vapor barrier (Oliveira et al. 2015). Therefore, it is believed that nanoscale cellulose, which contained smaller particle size, larger surface area, and more free hydroxyls on the surface, is capable of forming a crosslinking network by hydrogen bonds between the nanocellulose materials and the SPI matrix. Hence, this phenomenon improved the film's abilities as a water vapor and oxygen barrier (Wang et al. 2006, 2013).

Besides, gelatin is another protein that is widely used as a food ingredient. It can be extracted from collagen, which exists in skin, bones, and animal tissue, by boiling them after alkali or acid pretreatment. However, the source, age of the animal, and type of collagen will affect the properties of the gelatin. Therefore, most of the gelatin exhibits poor mechanical properties and water sensitivity. Studies have reported that the use of nanocellulose materials as reinforcement has markedly improved the moisture sorption, water vapor permeability behavior, and mechanical as well as thermal properties of gelatin film, as shown in Table 3.2.

PHA (polyhydroxyalkanoates) and PLA (polylactic acid) are both bio-polyesters that have attracted special interest recently due to they are synthesized from renewable resources and possess excellent properties. For PHA, the homopolymer poly(3-hydroxybutyrate) (PHB) has been more extensively studied since it presents mechanical properties similar to those of conventional petroleum-based polymers. Although PHB exhibits a relatively high melting and glass transition temperature as well as great stiffness, it presents some drawbacks like brittleness and low thermal stability and thus, making it unstable during melt processing and limiting its applicability (Martínez-Sanz et al. 2014). The reinforcement of PHB with CNC has further improved the properties like a gas barrier of PHB film as crystalline cellulose has the capability to form a network-like structure within biopolymer matrix (Table 3.2). Besides, the toughness of PHB can be enhanced by forming a copolymer of hydroxybuterate and hydroxyvalerate (HV)—PHBV. Although PHBV exhibits low stiffness, low brittleness, and low melting temperature without reducing the thermal stability of the material, it rather low crystallinity due to the present of HV content will impair the barrier properties of the polymeric materials. Recent studies have reported that MCC, ultrasound modified bacterial cellulose (us-BC), and CW are capable of enhancing this limitation (Table 3.2). This is due to the strong interaction between the nanocellulose materials and their high aspect ratio.

Similar to other biopolymers, PLA has its own drawbacks such as low thermal stability, low water vapor, and gas barrier properties, as well as it possesses limited use in the high-temperature environment. Reinforcing fillers such as MCC and cellulose nanofibrils are capable of improving PLA properties (Table 3.2). However, the mechanical properties decreased with increasing MCC content due to poor dispersion of MCC in PLA matrix and subsequent chain restriction movement, respectively (Haafiz et al. 2013). In contrast, the mechanical properties are increased when the cellulose nanofibrils and poly(ethylene glycol) (PEG) are added to the PLA matrix. This phenomenon shows that addition of PEG gives positive effects to the mechanical properties of the composite film. Besides using as a plasticizer, PEG also acts as a compatibilizer between PLA matrix and cellulose nanofibrils to improve their interaction and prevent the aggregation of nanofibrils (Qu et al. 2010).

3.5 Packaging Applications

Today, biopolymer films, which derived from renewable resources, have been increasingly used as packaging materials, because of their great advantages as follows (Ogur and Erkan 2015):

- edible and biodegradable
- supplement the nutritional value of foods
- enhance organoleptic characteristics of food, such as appearance, odor, and flavor
- reducing packaging volume, weight, and waste
- incorporate antimicrobial agents and antioxidants
- extended shelf-life and improved quality of usually non-packed items
- control over inter-component migration of moisture, gases, lipids, and solutes
- individual packaging of small particulate foods (i.e., nuts and raisins)
- function as carriers for antimicrobial and antioxidant agents
- for microencapsulation and controlled release of active ingredients
- have a possible utilization in multilayer food packaging materials together with non-edible film
- low cost and abundant.

Moreover, a good packaging film for food, pharmaceutical, and electronic device packaging applications should meet below criteria (Tharanathan 2003):

- allow for a slow but controlled respiration (reduced O_2 absorption) of the commodity
- allow for a selective barrier to gases (i.e., CO_2) and water vapor
- creation of a modified atmosphere with respect to internal gas composition, thus regulating the ripening process and leading to shelf-life extension
- lessening the migration of lipids in confectionery industry
- maintain structural integrity (delay loss of chlorophyll) and improve mechanical handling
- serve as a vehicle to incorporate food additives (flavor, color, antioxidant, antimicrobial agent)
- prevent or reduce microbial spoilage during extended storage.

All the above criteria can be met with by biopolymers from agricultural feedstocks and other resources providing they mixed with other materials such as other biopolymers, plasticizer, and additives due to their uncertain limitations. Owing to the advantages of nano-sized cellulose, these bio-nanocomposites packaging materials have great potential in enhancing the food quality, safety, and stability as an innovative packaging and processing technology. The unique benefits of the natural biopolymer packaging may open a new possibility product development in various edible and non-edible packaging industries.

3.6 Conclusion and Future Perspective

This chapter shows that nanocellulose reinforced biodegradable polymer-based film is of great potential and benefit to use as packaging material. Nevertheless, the development of bionanocomposite film is still at the initial stage. In order to widen the application of bio-nanocellulose composite packaging films across various industries, several aspects regarding their quality, cost, and utility must be considered for future development and application.

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References

Abdul Khalil HPS, Saurabh CK, Adnan AS et al (2016) A review on chitosan-cellulose blends and nanocellulose reinforced chitosan biocomposites: Properties and their applications. Carbohydr Polym 150:216–226

Ashori A, Nourbakhsh A (2010) Performance properties of microcrystalline cellulose as a reinforcing agent in wood plastic composites. Compos Part B Eng 41(7):578–581

Azeredo H, Mattoso LHC, Wood D et al (2009) Nanocomposite edible films from mango puree reinforced with cellulose nanofibers. J Food Sci 74(5):N31–N35

Babaee M, Jonoobi M, Hamzeh Y et al (2015) Biodegradability and mechanical properties of reinforced starch nanocomposites using cellulose nanofibers. Carbohydr Polym 132:1–8

Besbes I, Alila S, Boufi S (2011) Nanofibrillated cellulose from TEMPO-oxidized eucalyptus fibres: effect of the carboxyl content. Carbohydr Polym 84(3):975–983

Bilbao-Sainz C, Bras J, Williams T et al (2011) HPMC reinforced with different cellulose nano-particles. Carbohydr Polym 86(4):1549–1557

Bledzki AK, Gassan J (1999) Composites reinforced with cellulose based fibres. Prog Polym Sci 24(2):221–274

Boldizar A, Klason C, Kubat J et al (1987) Prehydrolyzed cellulose as reinforcing filler for thermoplastics. Int J Polym Mater 11(4):229–262

Bourtoom T (2009) Edible protein films: properties enhancement. Int Food Res J 16(1):1–9

Bras J, Hassan ML, Bruzesse C et al (2010) Mechanical, barrier, and biodegradability properties of bagasse cellulose whiskers reinforced natural rubber nanocomposites. Ind Crops Prod 32 (3):627–633

Brinchi L, Cotana F, Fortunati E (2013) Production of nanocrystalline cellulose from lignocellulosic biomass: technology and applications. Carbohydr Polym 94(1):154–169

Chang PR, Jian R, Zheng P et al (2010) Preparation and properties of glycerol plasticized-starch (GPS)/cellulose nanoparticle (CN) composites. Carbohydr Polym 79(2):301–305

Deepa B, Abraham E, Pothan LA et al (2016) Biodegradable nanocomposite films based on sodium alginate and cellulose nanofibrils. Mater 9:1–11

Dehnad D, Mirzaei H, Emam-Djomeh Z et al (2014) Thermal and antimicrobial properties of chitosan–nanocellulose films for extending shelf life of ground meat. Carbohydr Polym 109:148–154

Dhar P, Bhardwaj U, Kumar A et al (2015) Poly (3-hydroxybutyrate)/cellulose nanocrystal films for food packaging applications: Barrier and migration studies. Polym Eng Sci 55(10):2388–2395

Dogan N, McHugh TH (2007) Effects of microcrystalline cellulose on functional properties of hydroxy propyl methyl cellulose microcomposite films. J Food Sci 72(1):E016–E022

Dufresne A, Dupeyre D, Vignon MR (2000) Cellulose microfibrils from potato tuber cells: processing and characterization of starch–cellulose microfibril composites. J Appl Polym Sci 76(14):2080–2092

Fabra MJ, López-Rubio A, Ambrosio-Martín J et al (2016a) Improving the barrier properties of thermoplastic corn starch-based films containing bacterial cellulose nanowhiskers by means of PHA electrospun coatings of interest in food packaging. Food Hydrocolloid 61:261–268

Fabra MJ, Pardo P, Martínez-Sanz M et al (2016b) Combining polyhydroxyalkanoates with nanokeratin to develop novel biopackaging structures. J Appl Polym Sci 133(2):1–12

Fadel SM, Hassan M, Oksman K (2012). Improving tensile strength and moisture barrier properties of gelatin using microfibrillated cellulose. J Compos Mater 47(16):1977–1985

Favier V, Chanzy H, Cavaille JY (1995) Polymer nanocomposites reinforced by cellulose whiskers. Macromolecules 28(18):6365–6367

George J, Siddaramaiah (2012) High performance edible nanocomposite films containing bacterial cellulose nanocrystals. Carbohydr Polym 87(3):2031–2037

Gindl W, Keckes J (2005) All-cellulose nanocomposite. Polym 46(23):10221–10225

González K, Retegi A, González A et al (2015) Starch and cellulose nanocrystals together into thermoplastic starch bionanocomposites. Carbohydr Polym 117:83–90

Guimarães IC, dos Reis KC, Menezes EGT et al (2016) Cellulose microfibrillated suspension of carrots obtained by mechanical defibrillation and their application in edible starch films. Ind Crops Prod 89:285–294

Haafiz MM, Hassan A, Zakaria Z et al (2013) Properties of polylactic acid composites reinforced with oil palm biomass microcrystalline cellulose. Carbohydr Polym 98(1):139–145

Haafiz MM, Hassan A, Khalil HA et al (2016) Exploring the effect of cellulose nanowhiskers isolated from oil palm biomass on polylactic acid properties. Int J Biol Macromolec 85:370–378

Hassan ML, Hassan EA, Oksman KN (2011) Effect of pretreatment of bagasse fibers on the properties of chitosan/microfibrillated cellulose nanocomposites. J Mater Sci 46(6):1732–1740

Helbert W, Cavaille JY, Dufresne A (1996) Thermoplastic nanocomposites filled with wheat straw cellulose whiskers. Part I: processing and mechanical behavior. Polym Compos 17(4):604–611

Hu D, Wang H, Wang L (2016) Physical properties and antibacterial activity of quaternized chitosan/carboxymethyl cellulose blend films. LWT—Food Sci Technol 65:398–405

Huq T, Salmieri S, Khan A et al (2012) Nanocrystalline cellulose (NCC) reinforced alginate based biodegradable nanocomposite film. Carbohydr Polym 90:1757–1763

Jawaid MHPS, Khalil HA (2011) Cellulosic/synthetic fibre reinforced polymer hybrid composites: a review. Carbohydr Polym 86(1):1–18

Jiménez A, Fabra MJ, Talens P et al (2012) Edible and biodegradable starch films: a review. Food Bioprocess Tech 5(6):2058–2076

Jonoobi M, Harun J, Mathew AP et al (2010) Mechanical properties of cellulose nanofiber (CNF) reinforced polylactic acid (PLA) prepared by twin screw extrusion. Compos Sci Technol 70(12):1742–1747

Joye IJ, McClements DJ (2014) Biopolymer-based nanoparticles and microparticles: fabrication, characterization, and application. Curr Opin Colloid Interface Sci 9(5):417–427

Kalia S, Boufi S, Celli A et al (2014) Nanofibrillated cellulose: surface modification and potential applications. Colloid Polym Sci 292(1):5–31

Khan A, Khan RA, Salmieri S et al (2012) Mechanical and barrier properties of nanocrystalline cellulose reinforced chitosan based nanocomposite films. Carbohydr Polym 90(4):1601–1608

Li Q, Zhou J, Zhang L (2009) Structure and properties of the nanocomposite films of chitosan reinforced with cellulose whiskers. J Polym Sci Part B Polym Phys 47(11):1069–1077

Liu D, Zhong T, Chang PR et al (2010) Starch composites reinforced by bamboo cellulosic crystals. Bioresour Technol 101(7):2529–2536

Luo S, Netravali AN (1999) Interfacial and mechanical properties of environment-friendly “green” composites made from pineapple fibers and poly (hydroxybutyrate-co-valerate) resin. J Mater Sci 34(15):3709–3719

Ma X, Chang PR, Yu J (2008) Properties of biodegradable thermoplastic pea starch/carboxymethyl cellulose and pea starch/microcrystalline cellulose composites. Carbohydr Polym 72(3):369–375

Martínez-Sanz M, Villano M, Oliveira C et al (2014) Characterization of polyhydroxyalkanoates synthesized from microbial mixed cultures and of their nanobiocomposites with bacterial cellulose nanowhiskers. N Biotechnol 31(4):364–376

Martínez-Sanz M, Lopez-Rubio A, Villano M et al (2016) Production of bacterial nanobiocomposites of polyhydroxyalkanoates derived from waste and bacterial nanocellulose by the electrospinning enabling melt compounding method. J Appl Polym Sci 133(2):1–14

Mathew AP, Oksman K, Sain M (2005) Mechanical properties of biodegradable composites from poly lactic acid (PLA) and microcrystalline cellulose (MCC). J Appl Polym Sci 97(5):2014–2025

Moon RJ, Martini A, Nairn J et al (2011) Cellulose nanomaterials review: structure, properties and nanocomposites. Chem Soc Rev 40(7):3941–3994

Moroa L (2001) Starch-based biodegradable materials suitable for thermoforming packaging. Starch/Stärke 53:368–371

Nishino T, Matsuda I, Hirao K (2004) All-cellulose composite. Macromolecules 37(20):7683–7687

Ogur S, Erkan N (2015) The physicochemical properties of edible protein films. Ital J Food Sci 27 (1):1F

Oliveira TG, Makishi GLA, Chambi HNM et al (2015) Cellulose fiber reinforced biodegradable films based on proteins extracted from castor bean (Ricinus communis L.) cake. Ind Crops Prod 67:355–363

Osong SH, Norgren S, Engstrand P (2016) Processing of wood-based microfibrillated cellulose and nanofibrillated cellulose, and applications relating to papermaking: a review. Cellulose 23 (1):93–123

Othman SH (2014) Bio-nanocomposite materials for food packaging applications: types of biopolymer and nano-sized filler. Agric Agric Sci Procedia 2:296–303

Panaitescu DM, Casarica A, Stanescu PO et al (2013) Comparative analysis of bacterial and microcrystalline celluloses as reinforcements for poly (3-hydroxybutyrate-co-3-hydroxyvalerate). Mater Plast 50(4):236–240

Phan The D, Debeaufort F, Voilley A et al (2009) Biopolymer interactions affect the functional properties of edible films based on agar, cassava starch and arabinoxylan blends. J Food Eng 90:548–558

Qu P, Gao Y, Wu G et al (2010) Nanocomposites of poly (lactic acid) reinforced with cellulose nanofibrils. BioResources 5(3):1811–1823

Rodríguez-Castellanos W, Flores-Ruiz FJ, Martínez-Bustos F et al (2015) Nanomechanical properties and thermal stability of recycled cellulose reinforced starch–gelatin polymer composite. J Appl Polym Sci 132(14):1–7

Rhim JW, Reddy JP, Luo X (2015) Isolation of cellulose nanocrystals from onion skin and their utilization for the preparation of agar-based bio-nanocomposites films. Cellulose 22:407–420

Rico M, Rodríguez-Llamazares S, Barral L et al (2016) Processing and characterization of polyols plasticized-starch reinforced with microcrystalline cellulose. Carbohydr Polym 149:83–93

Santos TM, de Sá Men, Filho MS, Caceres CA et al (2014) Fish gelatin films as affected by cellulose whiskers and sonication. Food Hydrocoll 41:113–118

Savadekar NR, Karande VS, Vigneshwaran N et al (2012) Preparation of nano cellulose fibres and its application in kappa-carrageenan based film. Int J Biol Macromolec 51:1008–1013

Saxena A, Elder TJ, Ragauskas AJ (2011) Moisture barrier properties of xylan composite films. Carbohydr Polym 84(4):1371–1377

Shankar S, Rhim JW (2016) Preparation of nanocellulose from micro-crystalline cellulose: the effect on the performance and properties of agar-based composite films. Carbohydr Polym 135:18–26

Shit SC, Shah PM (2014). Edible polymers: challenges and opportunities. J Polym 2014:1–13

Siqueira G, Bras J, Dufresne A (2010) Cellulosic bionanocomposites: a review of preparation, properties and applications. Polym 2(4):728–765

Siracusa V, Rocculi P, Romani S et al (2008) Biodegradable polymers for food packaging: a review. Trends Food Sci Tech 19(12):634–643

Siró I, Plackett D (2010) Microfibrillated cellulose and new nanocomposite materials: a review. Cellulose 17(3):459–494

Sirviö JA, Kolehmainen A, Liimatainen H et al (2014) Biocomposite cellulose-alginate films: promising packaging materials. Food Chem 151:343–351

Suryanegara L, Nakagaito AN, Yano H (2009) The effect of crystallization of PLA on the thermal and mechanical properties of microfibrillated cellulose-reinforced PLA composites. Compos Sci Technol 69(7):1187–1192

Ten E, Turtle J, Bahr D et al (2010) Thermal and mechanical properties of poly (3-hydroxybutyrate-co-3-hydroxyvalerate)/cellulose nanowhiskers composites. Polym 51 (12):2652–2660

Ten E, Bahr DF, Li B et al (2012). Effects of cellulose nanowhiskers on mechanical, dielectric, and rheological properties of poly (3-hydroxybutyrate-co-3-hydroxyvalerate)/cellulose nanowhisker composites. Ind Eng Chem Res 51(7):2941–2951

Tharanathan RN (2003) Biodegradable films and composite coatings: past, present and future. Trends Food Sci Technol 14(3):71–78

Tye YY, Lee KT, Abdullah WNW et al (2016) The world availability of non-wood lignocellulosic biomass for the production of cellulosic ethanol and potential pretreatments for the enhancement of enzymatic saccharification. Renew Sustain Energy Rev 60:155–172

Ummartyotin S, Pechyen C (2016) Microcrystalline-cellulose and polypropylene based composite: a simple, selective and effective material for microwavable packaging. Carbohydr Polym 142:133–140

Vieira MGA, da Silva MA, dos Santos LO et al (2011) Natural-based plasticizers and biopolymer films: a review. Eur Polym J 47(3):254–263

Wang Y, Cao X, Zhang L (2006) Effects of cellulose whiskers on properties of soy protein thermoplastics. Macromol Biosci 6(7):524–531

Wang Z, Sun XX, Lian ZX et al (2013) The effects of ultrasonic/microwave assisted treatment on the properties of soy protein isolate/microcrystalline wheat-bran cellulose film. J Food Eng 114 (2):183–191

Wittaya T (2009) Microcomposites of rice starch film reinforced with microcrystalline cellulose from palm pressed fiber. Int Food Res J 16(4):493–500

Wittaya T (2012) Protein-based edible films: characteristics and improvement of properties. INTECH Open Access Publisher, Rijeka, pp 44–46

Yang X, Zhao K, Chen GQ (2002) Effect of surface treatment on the biocompatibility of microbial polyhydroxyalkanoates. Biomaterials 23(5):1391–1397

Yang ZY, Wang WJ, Shao ZQ et al (2013) The transparency and mechanical properties of cellulose acetate nanocomposites using cellulose nanowhiskers as fillers. Cellulose 20(1):159–168

Zarina S, Ahmad I (2015) Biodegradable composite films based on k-carrageenan reinforced by cellulose nanocrystal from kenaf fibres. BioResources 10:256–271

Zimmermann T, Bordeanu N, Strub E (2010) cellulose). Properties of nanofibrillated from different raw materials and its reinforcement potential. Carbohydr Polym 79(4):1086–1093