Chapter 5
Recent Trends on Nano-biocomposite Polymers for Food Packaging

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Abstract In recent years, much attention has been focused on research to replace petroleum-based polymers by biodegradable materials. Specify, polymer from natural sources have been considered as the most promising materials for this purpose. However, materials manufacture from natural polymers (e.g. polymeric films) generally present poor mechanical and high water sensibility. A recent alternative to improve the physical properties of natural polymeric films is a reinforcement with nanoparticles, producing nano-biocomposite polymers. The present chapter reviews the state-of-the-art with regard to the use of polymers obtained from biomass and their reinforced with nanoparticles, aiming food packaging applications. This chapter, especially include information about: (1) the use of casein, collagen/gelatin, chitin/chitosan, gluten, soya, starch, whey and zein as macromolecules to manufacture polymeric films, (2) the use of carbon nanotubes, chitin whiskers, metal nanoparticles, nanocellulose, nanoclays and starch nanocrystals to reinforced polymeric films, (3) the main physicochemical properties of nano-biocomposite polymers. The use of casting, tape casting, thermoforming and extrusion to manufacturing polymeric films; as well as the recent applications of nano-biocomposite polymers as food packaging and active/intelligent food packaging materials. Others topics such as nanoparticle migration, future prospects and limitations in nano-biocomposite polymers will be included in this chapter.

Keywords Biomass · Food applications · Nanoparticles · Nanotechnology · Polymers

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5.1 Introduction

Petroleum-based polymers have been the most used materials for manufacture films[1] in food packaging industry due to their good mechanical, optical and gas barrier properties (Embuscado and Huber 2009). However, petroleum-based polymers are:

- Nonbiodegradable materials and may cause environmental and ecological problems due to the accumulation of waste polymers in living and non-living systems (Vieira et al. 2011; Benjakul et al. 2016).
- Produced from non-renewable resources, therefore, they are exhaustible raw materials that are subject to great price fluctuations (Gómez-Estaca et al. 2016).

New strategies are oriented to regarding the manufacture of packaging films using renewable polymers that could lead to crucial reductions of environmental and economic problems (Li et al. 2015a).

Polymers from natural sources or biopolymers can be classified in three categories, such as: polymers from biomass, polymers synthetized by means of microbial routes and polymers chemically synthesized using monomers from agro-resources (Vieira et al. 2011). Due to the abundant, renewable and inexpensive biomass characteristics (Ali and Ahmed 2016), most studies have been addressed to manufacture food packaging materials using polymers from biomass (Li et al. 2015a; Abreu et al. 2015; Montero et al. 2017; Belyamani et al. 2014; Colak et al. 2016; Balakrishnan et al. 2017; Huang et al. 2016; Oechsle et al. 2016; Etxabide et al. 2016; Matet et al. 2015; Mendes et al. 2016; Garrido et al. 2016; Wang and Padua 2003; Valencia et al. 2016). Polymers from biomass can be classified in two groups: polysaccharides and proteins, both isolated from animal or plant sources (Fig. 5.1) (Vieira et al. 2011).

Biopolymer-based films usually present some good functional or physical properties but are very sensitive to environmental conditions, as relative humidity, and are affected by several factors such as pH, heat treatment, addition of plasticizers, ion concentration, biopolymer concentration and its molecular conformation (Nisperos-Carriedo 1994; Arvanitoyannis 2002; Gutiérrez and Alvarez 2017a). An alternative to enhance the biopolymer-based films properties is their reinforcement with nanoparticles, producing a material often called as nano-biocomposite polymers or only nanocomposites (Lagaron et al. 2005). Thus, the nano-biocomposite polymer films are thin materials formed by a biopolymer matrix reinforced with a dispersed nanoscale filler (Gutiérrez et al. 2016).

The present chapter aims to reviews the recent trends about the use of polymers produced from biomass and used to manufacture nano-biocomposite polymer films; the main techniques used to manufacture nano-biocomposite polymer films (casting, tape casting, thermoforming and extrusion); the use of nanoparticles to manufacture nano-biocomposite and active nano-biocomposite polymer films; the nanoparticle

[1] Films are continuous polymeric materials with thickness less than 0.3 mm (Embuscado and Huber 2009).

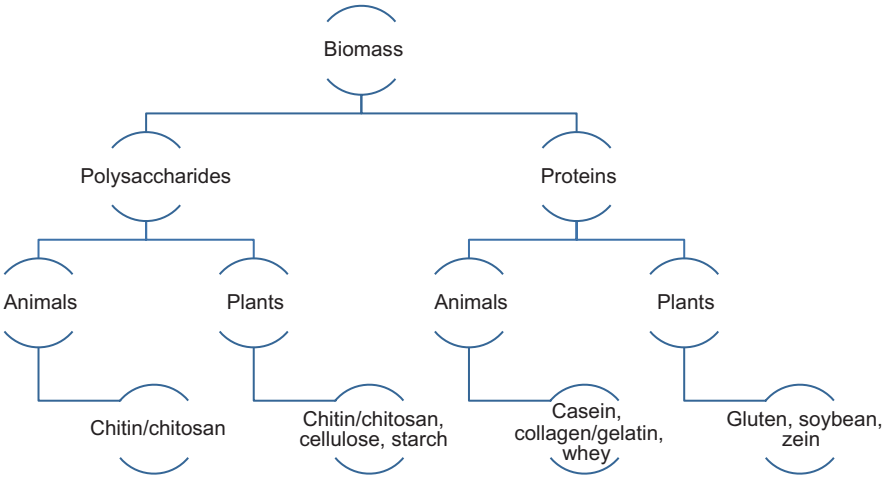

Fig. 5.1 Examples of polymers produced from biomass (adapted from Vieira et al. (2011))

migration from nano-biocomposite polymer films to food products; and the prospects of nano-biocomposite polymer films in food industry.

5.2 Main Polymers Isolated from Biomass

In this section, the main biopolymers produced from biomass and used to manufacture nano-biocomposite polymer films will be presented. These biopolymers are:

5.2.1 Chitin/Chitosan

Chitin is a N-acetylglucosamine mainly found in cell walls of fungi and exoskeleton of arthropods such as shrimps shell, carapace of crabs, epidermis and trachea of insects (Ali and Ahmed 2016; Kumar 2000; Usman et al. 2016; Merzendorfer and Zimoch 2003; Gutiérrez 2017). The chemical structure of chitin consists of 2-acetamido-2-deoxy-β-D-glucose through a β (1 → 4) linkage and its molecular weight (MW) varies between 1.030 and 2.500 kDa (Kumar 2000). Depending of the degree of hydration, size of unit cell, and number of chitin chains per unit cell, chitin can has a α, β, or γ crystalline structure. This polymer is broadly used in pharmaceutic and chemical industries (Ali and Ahmed 2016; Merzendorfer and Zimoch 2003).

Chitosan is a linear and partially acetylated (1–4)-2-amino-2-deoxy-β-D-glucan obtained by de-acetylation of chitin (Ali and Ahmed 2016). The MW of chitosan can varies between 100 and 500 kDa (Kumar 2000). Chitosan is a biodegradable polymer, non-toxic, biocompatible and displays antimicrobial properties against

several microorganisms. Chitosan exhibits good filmogenic properties, allowing the manufacture of films with low barrier to oxygen and water vapor (Martínez-Camacho et al. 2013; Bonilla et al. 2014). More detailed characteristics and/or properties of chitin and chitosan can be found in the specialized literature (Ali and Ahmed 2016; Kumar 2000; Usman et al. 2016; Merzendorfer and Zimoch 2003).

5.2.2 Cellulose/Cellulose Derivatives

Cellulose is considered the polysaccharide most abundant in biomass (Gutiérrez and Alvarez 2017b). This is a crystalline biopolymer produced from plants, principally from cotton and wood, with molecular weight (MW) between 460 and 520 kDa (Ali and Ahmed 2016; Kathirgamanathan et al. 2017). Cellulose is composed of D-glucopyranose units linked by β(1 → 4)-glycosidic bonds (Ali and Ahmed 2016; Park et al. 2010). Hydrogen groups in cellulose can conform several intra- and intermolecular hydrogen bonds, resulting in different crystalline structures (I, II, III and IV) (Park et al. 2010).

Cellulose is a biopolymer insoluble in water due to its molecular and supramolecular structure (Mischnick and Momcilovic 2010). Modifications of cellulose are performed under controlled conditions aiming to destroy the crystalline structure of cellulose, hence, D-glucopyranose units should become equally accessible. In sequence, solvents are added to modify the swelling properties, followed by the addition of an alkyl halide or by an oxirane, obtaining cellulose derivatives (Mischnick and Momcilovic 2010; Doelker and Geneva 1993).

Cellulose derivatives have a MW less than 150 kDa, they may be water soluble and are used in a large number of pharmaceutical, cosmetic and food industrial applications (Kulicke et al. 2005; Kalyuzhnaya et al. 2015). The cellulose derivatives most used to manufacture biopolymer films are the methylcellulose (MC), carboximethylcellulose (CMC), hydroxypropylcellulose (HPC), hydroxypropylmethylcellulose (HMC) (Mischnick and Momcilovic 2010; Kulicke et al. 2005; Kalyuzhnaya et al. 2015). Cellulose derivatives have a good film-forming performance and its films are transparent and have a high mechanical strength and low barrier to oxygen and water vapor (Kalyuzhnaya et al. 2015; Deng et al. 2016; Yang et al. 2011). More detailed characteristics and/or properties of cellulose and cellulose derivatives can be found in several works (Kathirgamanathan et al. 2017; Park et al. 2010; Mischnick and Momcilovic 2010; Doelker and Geneva 1993; Kulicke et al. 2005; Kalyuzhnaya et al. 2015; Deng et al. 2016; Yang et al. 2011).

5.2.3 Starch

Starch is a polysaccharide conformed of amylose and amylopectin, in which amylose is the predominantly linear (1 → 4)-linked α-glucan, while, amylopectin has a linear (1 → 4)-linked α-glucan with many ramifications by means α-(1 → 6) branch points

(Álvarez et al. 2017; Gutiérrez et al. 2017a). The MW of amylose and amylopectin varies between 150 and 400 kDa; and between 10,000 and 15,000 kDa, respectively (Cornell 2004; Pérez et al. 2009). Amylose and amylopectin conform starch granules with different shapes such as spheres, ellipsoids, polygons, platelets, irregular tubules and sizes between 0.1 to at least 200 μm, depending on the botanical source (Cornell 2004; Pérez et al. 2009). Starch granules are partially crystalline with A, B or C crystalline structure (Gutiérrez et al. 2015; Gutiérrez and Álvarez 2016; Gutiérrez 2018). These granules are mainly found in roots, tubers and seeds and to a lesser extent in stems, leaves, fruits and pollen (Pérez et al. 2009). The amount of the amylose in starch granules oscillates between 15 and 40% (Tester et al. 2004). Starch has the ability to form a continuous matrix, allowing the manufacture of films where the mechanical, barrier and film formation properties are improved with the increasing in amylose content (Azevedo et al. 2017; Valencia et al. 2018). The main functional and physical properties of starch has been reviewed by many authors (Ali and Ahmed 2016; Cornell 2004; Pérez et al. 2009; Tester et al. 2004).

5.2.4 Casein and Whey

Casein and whey are milk proteins. Milk proteins constitute approximately 3.2% of bovine milk (Guo and Wang 2016). Casein constitute approximately 75% of the total proteins in milk, which precipitates at pH 4.6. The protein remaining in milk serum (~25%) are called whey protein (Guo and Wang 2016; Morgan et al. 2005).

In its native state in milk, casein is mostly a random coil with a high proline content, highly phosphorylated for calcium binding, existing in the form of a "micelle" structure with a MW of ~10^5 kDa, and comprising four different casein subunits (α-, β- and κ-casein) and calcium phosphate (Guo and Wang 2016; Morgan et al. 2005). The proportion of α-, β- and κ-casein varies among species. The MW of α-, β- and κ-casein are approximately 23, 25, 24 and 19 kDa, respectively (Gómez-Estaca et al. 2016; Morgan et al. 2005; Wang et al. 2013; Bonnaillie et al. 2014).

Whey proteins are ordered secondary structures, which is described as a "cup" or "calyx" shaped three-dimensional structure and with a low proline content, is non-phosphorylated, and has small soluble proteins (Guo and Wang 2016). The β-lactoglobulin (MW ≈ 18 kDa) is the dominant protein in whey, which accounts for about 50% of total whey proteins (Guo and Wang 2016). Other proteins such as α-lactalbumin (MW ≈ 14 kDa) and bovine serum albumin (MW ≈ 66 kDa) also are found in whey protein (Gómez-Estaca et al. 2016; Schmid et al. 2012).

Casein and whey have good film-forming performance and their films have a good barrier to oxygen and they can form flavourless, flexible and transparent films (Bonnaillie et al. 2014; Schmid et al. 2012; Wagh et al. 2014). More detailed characteristics and/or properties of casein and whey proteins can be found in the specialized literature (Guo and Wang 2016; Morgan et al. 2005; Wang et al. 2013; Bonnaillie et al. 2014; Schmid et al. 2012).

5.2.5 Collagen/Gelatin

Collagen is comprised of homotrimers and heterotrimers that are formed by three polypeptide chains called α-chains (collagen triple helix), each one, with a MW between 345 and 360 kDa (Vieira et al. 2011; Gómez-Estaca et al. 2016; Mouw et al. 2014). To date, some 28 different types of collagen have been identified, classified as type I, II, II… XXVIII (Schrieber and Gareis 2007; Shoulders and Raines 2009). Type I collagen is formed by two α-1 chains and one α-2 chain, this protein exhibits primary, secondary, tertiary and quaternary structure and it has several industrial applications (Mouw et al. 2014; Schrieber and Gareis 2007).

Collagen is the primary fibrous protein present in the extracellular matrix of animals and is a major component of tendon, cartilage, bone and skin. Principally, this protein is produced from mammalian (bovine, goat, porcine and ovine) and non-mammalian (amphibian and fish) animals (Fauzi et al. 2016; Stylianou and Yova 2013). This protein is not water soluble, however, after a number of separations and hydrolysis, the collagen becomes a hydrocolloid, exhibiting filmogenic properties (Wolf et al. 2009).

Collagen can be hydrolyzed under thermal treatments, in acidic or alkaline conditions, obtaining type A or B gelatin, respectively (Schrieber and Gareis 2007). Depending of hydrolysis type, the isoelectric point (IEP) and MW of gelatins are altered. Hence, the IEP for type A and B gelatins are ranged between 8 and 9, and between 4.8 and 5.5, respectively (Schrieber and Gareis 2007), while MW of type A and B gelatins are 30–300 kDa, and ~100 kDa, respectively (Djabourov et al. 2013). The hydrolysis type of collagen results in gelatin with different amino acid composition, altering the viscosity and gelling properties of gelatin (Schrieber and Gareis 2007). Gelatin has an excellent filmogenic properties which allows the production of films with excellent optical properties (Valencia et al. 2016).

Collagen and gelatin films are good barrier to oxygen, carbon dioxide and oils (Chen et al. 2013). The functional and physical properties of collagen and gelatin have been reviewed by many authors (Mouw et al. 2014; Schrieber and Gareis 2007; Shoulders and Raines 2009; Djabourov et al. 2013).

5.2.6 Gluten

Gluten is a protein fraction from several cereal seeds such as wheat, rye, barley, oats or their crossbred varieties and derivatives (Rzychon et al. 2017). Gluten proteins can be divided in gliadins and glutenins, being that both fractions have high glutamine and proline contents. Gliadins are mainly monomeric proteins with a MW between 28 and 55 kDa and can be classified according to their different primary structures into the α/β-, γ- and ω-type. Glutenins are comprised of aggregated proteins linked by interchain disulphide bonds with MW varying between 500 and more than 10,000 kDa (Wieser 2007). Glutenin subunits can be obtained reducing

disulphide bonds in glutenins. The resulting glutenin subunits are soluble in aqueous alcohols, similar to gliadins. Depending of primary structure, glutenins subunits can be classified in high-molecular-weight (HMW) and low-molecular-weight (LMW), with MW between 67 and 88 kDa; and between 32 and 35 kDa, respectively (Wieser 2007; Tilley et al. 2001).

Several researches have studied the gluten film-forming performance, particularly, its viscoelastic properties, ability to cross-link upon heating, low water solubility, low cost and availability as a co-product of the wheat starch industry (Tilley et al. 2001; Ansorena et al. 2016; Tanada-palmu and Grosso 2003). Gluten films are good barrier to oxygen, carbon dioxide and oils (Chen et al. 2013). Most information about the functional and physical properties of gluten can be found in the specialized literature (Wieser 2007; Tilley et al. 2001; Gras et al. 2001; Shewry et al. 2002).

5.2.7 Soybean/Soybean Derivatives and Zein

Soybean proteins are composed of a mixture of globular proteins such as albumins (10–50%) and globulins (50–90%) (Qi et al. 2011), with MW between 140 and 170 kDa; and between 340 and 375 kDa, respectively (Nehete et al. 2013). Globulin is the dominant storage protein in soybean (50–90%), this protein is composed of two major components: glycinin (11S) and β-conglycinin (7S). The 11S:7S proportion depend of the botanical origin, varying from 1:3 to 3:1 (Qi et al. 2011; Singh et al. 2015). Two proteins derivatives can be obtained from soybean protein: soy protein concentrate (SPC) and soy protein isolate (SPI). The difference between SPC and SPI is based on the protein content, hence SPC is defined as an protein product with a protein content ≥65%, whereas SPI is a product with a protein content ≥90%, both on dry weight basis (Wang et al. 2004). SPC and SPI are prepared in different process involving insolubilization of the protein to remove soluble sugars, whereas, SPI preparation involves solubilization of the protein to remove the insoluble fiber and then precipitation to remove soluble sugars (Wang et al. 2004; Tsumura 2009).

On another side, zein is a protein (prolamine) from maize with MW between 14 and 27 kDa (Wang and Padua 2003; Argos et al. 1982; Thompson and Larkins 1989). This protein displays significant hydrophobic properties due to the amino acid composition, having a large amount of strong or somewhat hydrophobic residues such as glutamine, proline, leucine and alanine (Matsushima et al. 1997). According to the solubility properties, zeins can be classified as α, β, γ and δ. Hence, α-zeins (MW between 19 and 22 kDa) can be extracted by aqueous alcohol alone, whereas β (MW ~ 14 kDa), γ (MW between 16 and 27 kDa) and δ-zeins (MW ~ 10 kDa) are solubilized by the addition of a reducing agent to aqueous alcohol. The β, γ and δ-zeins exhibit little charge heterogeneity and are probably single polypeptides (Thompson and Larkins 1989).

Films based on soybean/soybean derivatives proteins and zein have excellent water-resistance, as well as good mechanical and optical properties (Chen et al.

2013; Li et al. 2016). Most information about the functional and physical properties of soybean/soybean derivatives proteins (Qi et al. 2011; Singh et al. 2015; Wang et al. 2004; Tsumura 2009; Li et al. 2016), as well for zein (Wang and Padua 2003; Argos et al. 1982; Thompson and Larkins 1989; Matsushima et al. 1997) can be found in the specialized literature.

5.3 Main Techniques Used to Manufacture Nano-biocomposite Polymer Films

In general, films manufactured with biopolymers from biomass are sensitive to water vapor, thus limiting their food industrial applications (Valencia et al. 2016; Azevedo et al. 2017; Chen et al. 2013; Ansorena et al. 2016). Then, in the next sections we will discuss some new strategies to improve physicochemical properties (e.g. water vapor barrier, mechanical, optical and thermal properties) in films based on biopolymers from biomass. There are two common technologies to manufacture biopolymer films and nano-biocomposite polymer films: wet and dry processes.

5.3.1 Wet Process

In the wet process, solvents are used for the dispersion of biopolymer to obtain a film-forming solution (FFS). Then the desired additives, such as plasticizers, to allow the production of flexible films; cross-linkers, to produce films with modified biopolymers; antimicrobials/antioxidants, to produce active films; or, nanoparticles, when we are interested in to produce nano-biocomposite polymer films, are added to FFS. Finally, FFS is dried to remove the solvent and form a continuous film (Benjakul et al. 2016).

Wet process comprises casting and tape-casting techniques. In casting, FFS is poured onto the support, and then, the film thickness is a function of the weight of dry matter poured onto the support (Valencia et al. 2016, 2018). Casting is the most used technique to manufacture biopolymer films at laboratory-scale. This technique has been used for manufacture biopolymer films based on chitosan (Bonilla et al. 2014; Ma et al. 2016), cellulose (Yang et al. 2011), starch (Abreu et al. 2015; Valencia et al. 2018), casein (Bonnaillie et al. 2014; Wagh et al. 2014), whey (Wagh et al. 2014), collagen (Wolf et al. 2009), gelatin (Valencia et al. 2016), gluten (Fakhouri et al. 2018), soybean (Ma et al. 2016) and zein (Matthews et al. 2011), among others.

Tape-casting, or spread casting or knife-coating, is a well-known technique to manufacture paper, plastic and ceramics (Richard and Twiname 2000). In this technique, FFS is placed in a reservoir with a blade, whose height can be adjusted with micrometric screws (Fig. 5.2). The FFS is cast as a film on a tape or support, due to the movement of the doctor blade, in batch process; or the movement of the carrier

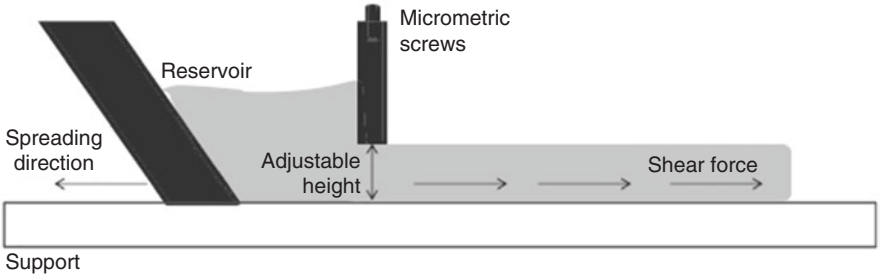

Fig. 5.2 A schematic illustration of the tape-casting process (adapted from De Moraes et al. (2013))

tape, in continuous process (De Moraes et al. 2013). FFS is dried on the tape, resulting in a reduction of its thickness, hence, the film thickness is a function of the weight of dry matter poured onto the tape, which can be controlled knowing the dry matter of FFS and the height of the blade (Flaker et al. 2015). Principally, tape-casting has been used to manufacture biopolymer films based on starch (De Moraes et al. 2013, 2015) and gelatin (Flaker et al. 2015). The disadvantage of tape-casting technique is that FFS must have a shear-thinning behavior with viscosity values that allow the flow of FFS to high- or low-shear stresses (De Moraes et al. 2013).

In the wet process (casting and tape-casting), the selection of solvents is one of the most important factors. Normally, solvents are water and mixtures of water/ethanol or water/acetic acid (Benjakul et al. 2016; Bonilla et al. 2014). The type of solvent, its pH and temperature can affect the biopolymer network during its dispersion. For example, chitosan, collagen and some proteins are dispersed in acid conditions (Bonilla et al. 2014; Wolf et al. 2009; Li et al. 2012); whereas, starch and gelatin can be dispersed using only hot water (Valencia et al. 2016, 2018).

By means of wet process, it is possible to manufacture biopolymer films with better barrier properties (e.g., oxygen, water, light), however, other physical properties such as mechanical properties, thermal sealebility and printability are not necessarily improved (Gómez-Estaca et al. 2016).

5.3.2 Dry Process

In the dry process or thermal process, solvents are not necessary needed, thus, from economic and environmental viewpoints, this process is interesting to manufacture biopolymer films in an industrial-scale (Bouvier and Campanella 2014). In dry process, heat is applied to increase the temperature above the glass transition (T_g) and/or the melting (T_m) temperatures of biopolymer and then promoting the material flow (Benjakul et al. 2016; Gómez-Estaca et al. 2016). Normally, biopolymer film formation can be carried out using thermoforming and extrusion (Bouvier and Campanella 2014; Gutiérrez and Alvarez 2017c, d).

Thermoforming is a high-temperature process where the biopolymer is forced to form a specific shape in a mold. Normally, this process is done under high pressure and high temperature, promoting important changes in the molecular network of biopolymer due to the thermal transitions and even by the formation of covalent and cross-linking bonds (Ansorena et al. 2016; Bouvier and Campanella 2014). The principal disadvantage of thermoforming is that materials are manufactured in batch process (Ansorena et al. 2016; Bouvier and Campanella 2014).

The principal variables to manufacture biopolymer films by thermoforming are temperature and pressure molding, as well process time, depending of the biopolymer to be manufactured (Table 5.1). Sothornvit et al. (2007) observed that to produce compression-molded whey protein films is necessary a minimum temperature of 104 °C. However, a temperature higher than 140 °C lead to the polymer degradation. In this same research, these authors observed that continuous polymeric material were obtained using pressures between 0.8 and 2.2 MPa.

In the last years, most researchers have studied the extrusion because materials can be manufactured in a continuous process (Bouvier and Campanella 2014). Extrusion is widely used in polymer industry to manufacture plastic packaging and recently used to manufacture biopolymer films (Hanani et al. 2013).

Extrusion is a thermomechanical process based on combination of multiple unit operations such as the transport, mixing, shearing, plasticizing, melting, polymerization, and fragmentation (Emin and Schuchmann 2017). Extrusion uses one or two co-rotating twin screws fitted in a barrel in order to gradually increase the pressure and push forward and mix the ingredients required to manufacture the product through a die section where expansion may take place (Fig. 5.3) (Hanani et al. 2013; Emin and Schuchmann 2017). Actually, extruders allow extensive variation in thermal and mechanical energy inputs, control of the residence time and efficient of mixing ingredients (Bouvier and Campanella 2014). The principal disadvantage of extrusion is that several parameters control the process, hence slight variations in processing conditions can have a considerable effect on physicochemical properties of biopolymer films (Bouvier and Campanella 2014).

The principal variables to manufacture biopolymer films and nano-biocomposite polymer films by extrusion are screw speed, temperature profile in screw section (e.g. temperature 1/temperature 2, etc) and temperature in die section (temperature at the end of extruder) (Table 5.2).

Extrusion can cause chemical reactions or reorganization of the chain structure in biopolymers, allowing to improve some physicochemical properties in biopolymer films (Garrido et al. 2016; Hanani et al. 2012). Hanani et al. (Hanani et al. 2012) developed films based on gelatins from beef, pork and fish sources using twin-screw extrusion (Table 5.2). These authors observed that as the screw speed increased up to 300 rpm, the tensile strength (TS) of films based on gelatin from beef and pork increased, however, at 400 rpm, the TS values of both films decreased. Also, as the screw speed of the extruder was increased, from 100 to 300 rpm, an increase in elongation at break (EB) for fish gelatin films was observed. These authors observed that higher screw speed provoked the gelatin melting by friction and lead to most homogeneous films due to the better compound mixture. Also,

Table 5.1 Principal thermoforming variables used to manufacture biopolymer films and nano-biocomposite polymer films

Biopolymer	Thermoforming variables			Film thickness (mm)	Reference
	Temperature (°C)	Time (min)	Pressure (kPa)		
Cellulose derivatives	100	8	6863	0.08	Shih et al. (2009)
	160	2	3000	0.3	Ortega-toro et al. (2014)
Starch	110 to 170		29 to 69	Not informed	Guimarães et al. (2010)
	110	3	7400	0.3	Hietala et al. (2013)
	140	6	14,706	0.1	López et al. (2015)
	160	2 and 6	5000 and 15,000	0.2 to 0.3	Ortega-Toro et al. (2015)
	180	15	10,000	0.7	Gutiérrez and Alvarez (2017)
Whey	150	5	20,000	Not informed	Sharma and Luzinov (2013)
Gelatin	80	2	64	1.0	Krishna et al. (2012)
Casein	70 to 140	7	50,000	0.5	Colak et al. (2016)
Gluten	80	10	1	Not informed	Zubeldía et al. (2015)
	100	10	1	Not informed	Ansorena et al. (2016)
Soybean derivatives	150	2	12,000	0.7	Guerrero et al. (2011)
	150	2	13,000	0.4	Garrido et al. (2016)

higher screw speed increased extruder shear rate and decreased the viscosity of gelatin solutions. These authors concluded that the mechanical properties of films based on fish gelatin decreasing when the processing temperature increased from 90 to 120 °C, due to thermomechanical process that disrupt the structures of the protein from fish gelatin. Water vapor permeability (WVP) values in gelatin films decreased with the increasing in extrusion screw speeds due to the decreasing in the molecular size of gelatin. Finally, the water solubility in gelatin films increased with the extrusion screw speeds and with the processing temperature due to the modifications in secondary and tertiary structures of proteins into films.

Hanani et al. (2014) studied the effect of the processing temperature on the mechanical and water vapor barrier properties of extruded gelatin films (Table 5.2) and observed that temperature had a significant effect on the mechanical and WVP properties in composite films. Hence, TS values for gelatin films increased, from 1.4 to 5.4 MPa, as temperature increased until 120 °C. This could be attributed to the melting protein at higher temperature, which also contributed to tighter compact protein networks. Also, EB was not altered with temperature in screw section (EB = 2.1%). WVP values decreased from $9.3x10^{-10}$ to $4.6x10^{-10}$ g·m/m²·s·Pa, as

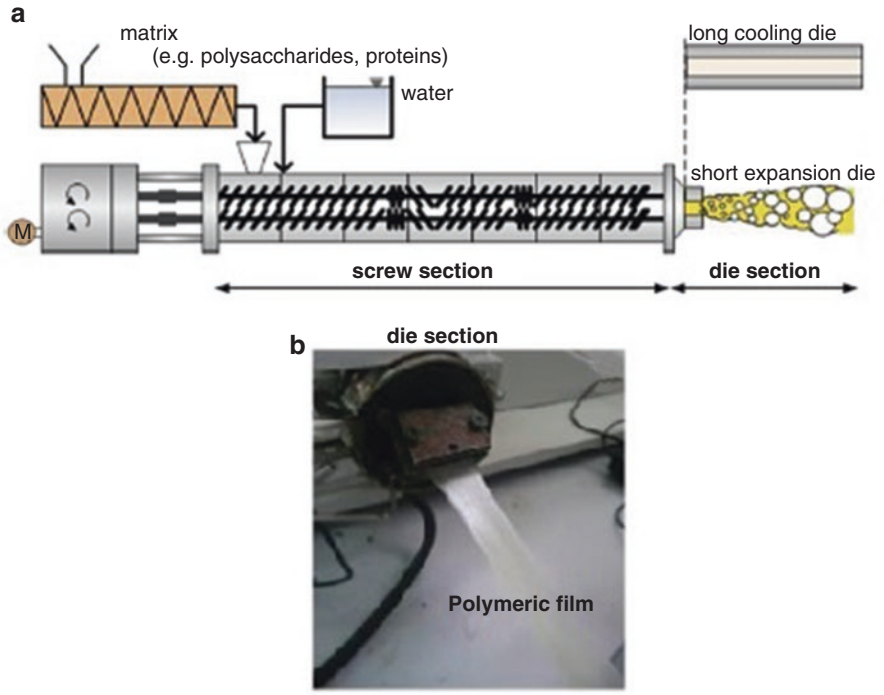

Fig. 5.3 (**a**) A schematic illustration of twin screw extrusion with the principal sections (adapted from Emin and Schuchmann (2017)). (**b**) A photography of a polymeric extruded film (adapted from Camacho et al. (2013))

temperature increased, from 90 °C until 120 °C, in screw section. Similar results were observed by Krishna et al. (2012), working with extruded gelatin films, which also observed that the T_g values in extruded gelatin films increased with increase in extrusion temperature, from 110 °C (T_g = 11.6 °C) to 120 °C (T_g = 26.3 °C). This behavior was due to the decreasing in films moisture content with the increasing of processing temperature (Krishna et al. 2012).

Andreuccetti et al. (2012) compared the casting and extrusion process to manufacture gelatin films. These authors observed that extruded films showed much better elongation at break and lower WVP that those manufactured by casting. Similar results were observed by Guerrero et al. (2010) and Yan et al. (2012), both, comparing the casting and extrusion process to manufacture soybean and corn starch films, respectively.

However, others researchers have been observed that extrusion process not necessarily improve the physicochemical properties of biopolymer films when compared with the same films manufactured by means of wet process. These behavior could be due to the biopolymer degradation during extrusion process (Krishna et al. 2012; Yan et al. 2012; Andreuccetti et al. 2012; Park et al. 2008).

Table 5.2 Principal extrusion variables used to manufacture biopolymer films and nano-biocomposite polymer films

Biopolymer	Extruder	Extrusion variables			Film thickness (mm)	Reference
		Screw speed (rpm)	Temperature profile (°C)			
			Screw section	Die section		
Chitosan	Single-screw	120	150/160/160	160	0.3	Martínez-Camacho et al. (2013)
	Single-screw	40	130	140	1.5	Quiroz-Castillo et al. (2014)
	Twin-screw	170	90/95/105/110/115/120/120/120/120	125	Not informed	Shih et al. (2009)
	Single-screw	35 to 45	130–140	150	0.3	Dang and Yoksan (2016)
Cellulose derivatives	Twin-screw	150	185	185	Not informed	Quintana et al. (2016)
Starch	Twin-screw	30	95 to 125	Not informed	0.1	Yan et al. (2012)
	Twin-screw	300	90/90/90/100/110/110	100	0.2	Hietala et al. (2014)
	Twin-screw	200	80/90/90/100/100/110	110	0.3	Hietala et al. (2013)
	Single-screw	Not informed	120	125 to 130	0.1	López et al. (2013)
	Twin-screw	35	100/140/140	140	0.3	Ayumi et al. (2013)
	Single-screw	40 to 80	160 to 190	Not informed	Not informed	Zepon et al. (2013)
	Single-screw	35 to 45	130/140/140/140	150	Not informed	Dang and Yoksan (2015)
Casein	Twin-screw	45	80	80	0.3	Belyamani et al. (2014)
	Twin-screw	Not informed	65	80	0.5	Colak et al. (2016)
Collagen	Single-screw	65	5	5	0.6	Oechsle et al. (2016)

(continued)

Table 5.2 (continued)

Biopolymer	Extruder	Extrusion variables			Film thickness (mm)	Reference
		Screw speed (rpm)	Temperature profile (°C)			
			Screw section	Die section		
Gelatin	Twin-screw	100 to 400	90 (all sections)	Not informed	0.04	Hanani et al. (2012)
	Twin-screw	300	90/120/90/90	Not informed	0.022	Hanani et al. (2013)
	Twin-screw	300	90/90–130/90/90	Not informed	0.025	Hanani et al. (2014)
	Twin-screw	70	90	90	3.8	Etxabide et al. (2016)
Zein	Twin-screw	100	80	80	Not informed	Chen et al. (2013)
	Single-screw	12 to 115	105/132/145	145	No informed	Selling and Utt (2013)

5.4 Main Nanoparticles Used to Manufacture Nano–biocomposite Polymer Films

The use of nanoparticles is a recent alternative to improve the physicochemical properties of biopolymer films (Valencia et al. 2016; Flaker et al. 2015; Perotti et al. 2014), and even to manufacture active packaging[2] (Krepker et al. 2017). Nanoparticles are characterized by having at least one dimension in nanometric scale, i.e. between 1 and 100 nm (Aouada et al. 2011). Hence, when the particle size is equivalent to the dimension of a molecule, the atomic and molecular interactions can have a significant influence on the macroscopic properties of liquid and solid systems (Valencia et al. 2015). It is important that nanoparticles are well-dispersed in the biopolymer network to enhance the contact area between nanoparticle and biopolymer chain and then improve the physicochemical properties of nano-biocomposite polymer films (Valencia et al. 2016; Flaker et al. 2015; Yamakawa et al. 2017; Ghelejlu et al. 2016).

The principal nanoparticles used in studies about nano-biocomposite polymer films are:

5.4.1 Carbon Nanotubes

Carbon nanotubes (CNTs) are sheets of graphite that has been rolled into a tube, forming cylinders in nanometric scale (Belin and Epron 2005). There are two types of CNTs: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) (Zhanjun et al. 2011). SWCNTs have a well-defined atomic structure, with high length to diameter ratio, having a diameter between 0.8 and 1.2 nm and length between 100 and 1000 nm. MWCNTs are elongated cylindrical nanoparticles made of sp^2 carbon, having a diameter between 3 and 30 nm and length of several cm long, thus their aspect ratio can vary between 10 and ten million. CNTs have electronic properties and can be either metallic or semiconducting depending on their geometry (Belin and Epron 2005).

CNTs have been broadly used in electrical applications due to its high electrical conductivity (Yamakawa et al. 2017). Most recently, CNTs have been used as reinforcement load for biopolymer films due to its high mechanical properties (elastic modulus, EM = 0.91 TPa and tensile strength, TS = 0.15 TPa) and thermal stability (Ortiz-Zarama et al. 2014). Zhanjun et al. (2011) manufactured nano-biocomposite polymer films based on corn starch containing until 3% of CNTs (based on the mass of biopolymer) and observed that the weight loss of nano-biocomposite polymer films, analyzed by thermogravimetric analysis (TGA), decreased with CNTs con-

[2] Active packaging: active packaging are materials that contain deliberately incorporated components intended to release (controlled) or absorb substances into or from the packaged food or from the environment surrounding the food (Krepker et al. 2017).

centration, in the temperature between 260 and 315 °C. However, the CNTs decreased the compatibility between corn starch with other compounds such as polyols (e.g. glycerol) used to plasticizer the biopolymer.

Famá et al. (2011) developed nano-biocomposite polymer films based on tapioca starch containing until 0.055% of MWCNTs (based on the mass of biopolymer) and observed that nano-biocomposite polymer films exhibited highly improved tensile and impact properties, with increments of approximately 70% in stiffness, 35% in ultimate tensile strength and 50% in tensile toughness, keeping deformations higher than 80% without break. Similar results were observed by Jose et al. (2015) and Ortiz-Zarama et al. (2014), working on nano-biocomposite polymer films based on corn starch or bovine gelatin, both containing until 2% of CNTs (based on the mass of biopolymer), respectively.

However, the high price and toxicity concerns are the principals disadvantages of CNTs, thus limiting its applications in nano-biocomposite polymer films for food industry (Famá et al. 2011).

5.4.2 Chitosan Nanoparticle

Chitosan nanoparticles (CNPs) have spherical shape with diameters less than 100 nm (Hosseini et al. 2015), with are produced from chitosan by means of several methods such as emulsion crosslinking, reverse micelles, precipitation, ionotropic gelation, among others (Gomathi et al. 2017). CNPs are broadly used for various applications due to their biodegradability, high permeability through biological membranes, non-toxicity to human, cost effectiveness and broad antifungal activities (Dananjaya et al. 2017; Ma et al. 2017a).

In the nano-biocomposite polymer film domain using CNPs. Hosseini et al. (2015) developed nano-biocomposite polymer films based on fish gelatin containing until 8% of CNPs (based on the mass of biopolymer) and observed that the addition of CNPs caused remarkable increase in TS and EM in nano-biocomposite polymer films when compared with control films (gelatin films without CNPs). Also, the addition of CNPs decreased in approximately 50% the WVP and the transparency at 600 nm of values of nano-biocomposite polymer films when compared with control films (without CNPs). The improvement of mechanical and barrier (WVP) properties of nano-biocomposite polymer films with the CNPs concentration was due to the decreasing in the free volume between gelatin chains caused by an increase in intermolecular attractive forces, making the gelatin network highly dense and thus less permeable. CNPs were not dissolved into biopolymer matrix, hence, nano-biocomposite polymer films were most opaque with CNPs, reflecting the UV light.

Barreras et al. (2016) observed that CNPs enhanced the antibacterial activity of nano-biocomposite polymer films based on collagen, suggesting that CNPs could be used to develop active packaging with food applications (Krepker et al. 2017).

5.4.3 Metal Nanoparticles

The most common nanoparticles from noble metals are silver and gold. Silver (AgNPs) and gold (AuNPs) nanoparticles are synthetized by chemical reactions from silver nitrate and chloroauric acid, respectively. Normally, AgNPs and AuNPs have a spherical form with diameters less than 100 nm (Valencia et al. 2013, 2014a; Cheviron et al. 2014; Ji et al. 2016).

AgNPs are known to have inhibitory and antimicrobial properties and low toxicity, receiving special attention in food packaging industry. These nanoparticles have an absorbent effect, being applied in food packaging to absorb moisture and fluids exuded from foods such as meat and fish (Abreu et al. 2015). AgNPs are broadly used to develop active food packaging (Carbone et al. 2016).

Regarding nano-biocomposite polymer film loaded with AgNPs, Abreu et al. (2015) developed nano-biocomposite polymer films based on corn starch containing until 1.7% of AgNPs (based on the mass of biopolymer) and observed that this material had antimicrobial activity against *Staphylococcus aureus*, *Escherichia coli* and *Candida albicans* without significant differences between AgNPs concentrations in nano-biocomposite polymer films. Similar results were observed in nano-biocomposite polymer films based on chitosan (Gabriel et al. 2017), starch (Valencia et al. 2013; Cheviron et al. 2014; Ji et al. 2016; Ortega et al. 2017) and gelatin (Kanmani and Rhim 2014) loaded with AgNPs.

Ortega et al. (2017) developed also nano-biocomposite polymer films based on corn starch containing until 0.02% of AgNPs (based on the mass of biopolymer) and observed that the nano-biocomposite polymer films extended the shelf-life of fresh cheese samples for 21 days due to the antimicrobial activity of AgNPs.

Moreover, AgNPs can cause an increasing in opacity and thermal stability, as well as decreasing in mechanical properties and WVP in nano-biocomposite polymer films (Ji et al. 2016; Ortega et al. 2017; Kanmani and Rhim 2014).

Regarding gold nanoparticles (AuNPs), Abdel-Raouf et al. (2017) and Mohamed et al. (2017) recently observed that this nanoparticle had antibacterial activity against Gram-positive and Gram-negative bacteria. In addition, Bumbudsanpharoke and Ko (2018) observed also antioxidant properties in nano-biocomposite polymer films charged with AuNPs and explained this behavior by the electron configuration of AuNP, allowing accept or donate an electron to quench radicals. However, AuNPs are less investigate in food packaging research due to its high price. Most research about AuNPs are focused on the development of drug delivery systems (Pooja et al. 2015) and biosensors (Valencia et al. 2014b).

5.4.4 Cellulose Nanowhiskers or Nanocrystals

Cellulose nanowhiskers (CNWs) or cellulose nanocrystals (CNCs) can be obtained by strong acid hydrolysis of cellulose fibres from cotton, hemp, flax, microcrystalline cellulose and bacterial cellulose, using sulfuric acid under controlled

conditions, such as temperature, agitation and time, producing highly crystalline rod-like nanostructures (Alves et al. 2015; Cano et al. 2015). Thus, CNWs are from renewable, sustainable and abundant resources. CNWs have a needle shaped with the length between 10 and 400 nm and the diameter between 3 and 30 nm, depending on the chemical reaction (Wang et al. 2017; Soni et al. 2016).

Cano et al. (2015) developed nano-biocomposite polymer films based on pea starch containing until 5% of CNWs (based on the mass of biopolymer) and observed that the incorporation of CNWs lead to phase separation between CNWs and starch. These authors also observed that CNWs did not improved water vapor barrier in nano-biocomposite polymer films.

Noshirvani et al. (2018) developed nano-biocomposite polymer films based on potato starch containing until 20% of CNWs (based on the mass of biopolymer) and observed that nano-biocomposite polymer films showed a decreasing in solubility, water absorption, WVP and EB values with CNW concentration, and that contact angle, TS, T_g and T_m values increased with CNW concentration. The physicochemical modifications in nano-biocomposite polymer films with CNWs was due to the three-dimensional networks of intermolecular hydrogen-bonding interactions between CNW and potato starch matrix. CNW has also a crystalline nature with high aspect ratio, altering the films crystallinity and then their physical properties (Noshirvani et al. 2018). Similar results have been obtained in nano-biocomposite polymer films based on chitosan containing CNWs (Soni et al. 2016; Mujtaba et al. 2017; Ma et al. 2017b; Llanos and Tadini 2018).

In the same sense, Soni et al. (2016) observed that CNWs improved the thermal stability in nano-biocomposite polymer films based on chitosan due to the presence of the crystalline structure and great compactness between both chitosan and CNWs. Ma et al. (2017b) observed that CNWs improved barrier properties against UV light in nano-biocomposite polymer films based on chitosan as a consequence that CNWs hinder light transmission in the near ultraviolet range (between 300 and 400 nm). These results may be due to the interaction between the CNWs and chitosan matrix. Mujtaba et al. (2017) observed that CNWs improved the antimicrobial properties in nano-biocomposite polymer films based on chitosan against *Escherichia coli* ATCC 35218, *Pseudomonas aeruginosa* ATCC 27853, *Enterococcus faecalis* ATCC 29212, *Staphylococcus aureus* ATCC 25923 and *Listeria monocytogenes* ATCC 7644.

5.4.5 Nanoclays

Nanoclays are nanoparticles of layered mineral silicates, that can be classified as natural and synthetic nanoclays (Bracone et al. 2016; Gutiérrez et al. 2017b). The most common natural and synthetic nanoclays used to manufacture nano-biocomposite polymer films are montmorillonite (Mnt) and laponite (Lap), respectively (Valencia et al. 2016, 2018; Flaker et al. 2015; Llanos and Tadini 2018). Mnt and Lap have a disk-shape with a thickness of approximately 10 nm for Mnt and 1 nm for Lap, and a diameter of approximately 1000 nm for Mnt and 25 nm for Lap (Cummins 2007; Cadene et al. 2005).

Chung et al. (2010) developed nano-biocomposite polymer films based on corn starch containing until 7% of Mnt or Lap (based on the mass of biopolymer) and observed that nanoclays improved EM and TS in nano-biocomposite polymer films. Nanoclays can improve others physical properties such as thermal stability (Perotti et al. 2014; Aouada et al. 2011; Gutiérrez and Alvarez 2018), water vapor barrier and water solubility (Flaker et al. 2015; Barreras et al. 2016; Tang and Alavi 2012) in nano-biocomposite polymer films. Optical properties of nano-biocomposite polymer films were not altered by nanoclays as a consequence of well dispersed nanoclays (exfoliated) into biopolymer matrix (Valencia et al. 2016, 2018).

About the antibacterial activity, Hong and Rhim (2008) observed that natural Mnt (Cloisite Na^+) did not show any antibacterial activity. However, modified Mnt (Cloisite 20A and Cloisite 30B) displayed antimicrobial effect against Gram-positive and Gram-negative bacteria. Liu et al. (2014) observed that films based on synthetic polymer containing modified Mnt (I.34TCN) displayed antimicrobial activity against Gram-positive bacteria (i.e., *Listeria monocytogenes* and *Staphylococcus aureus*). Nanoclays can also have antioxidant effect. Echeverría et al. (2018) observed that the presence of Mnt in polyethylene films was able to decrease microbial growth and also the lipid autoxidation of tuna fillets during the storage period studied (17 days of storage at 2 °C). Li et al. (2015a) developed nano-biocomposite polymer films based on gelatin containing until 20% of Lap (based on the mass of biopolymer) and observed that Lap avoided lipid oxidation and protein decomposition of meat during storage due to the barrier capability of Lap. In this way, nanoclays are important candidates to manufacture active food packaging, however, the main disadvantage is that nanoclays are not from renewable sources, neither biodegradables (Abdollahi et al. 2013).

5.4.6 Starch Nanocrystals

Starch nanocrystals (SNC) can be obtained from native starch by strong acid hydrolysis, using HCl or H_2SO_4, under controlled conditions such as temperature, agitation and time. SNC has crystalline platelets with a length between 20 and 40 nm, a width between 15 and 30 nm, and a thickness between 5 and 7 nm (Gong et al. 2016). The main advantage is that SCN are from renewable sources and are biodegradables (González and Igarzabal 2015).

SNC has been used to improve the physicochemical properties of nano-biocomposite polymer films. Li et al. (2015b) developed nano-biocomposite polymer films based on pea starch containing until 9% of SNC (based on the mass of biopolymer) and observed that SCN improved some physicochemical properties in nano-biocomposite polymer films such as mechanical properties, water vapor barrier and thermal stability. González & Igarzabal (2015) also developed nano-biocomposite polymer films based on soybean protein isolate containing until 40% of SNC (based on the mass of biopolymer). These authors observed that the opacity, degree of crystallinity and mechanical properties in nano-biocomposite polymer films increased with SNC. The moisture content, total soluble matter and swelling

in water showed also a marked effect on SNC additions. As the amount of SNC increased, the nano-biocomposite polymer films exhibited less affinity for water. These authors observed that nano-biocomposite polymer films containing SNC sequester cholesterol when brought into contact with cholesterol-rich food such as milk. Hence, SNC can also be used to develop active food packaging.

5.5 Nanoparticle Migration

As previously described, nanoparticles can improve several physicochemical properties and provide active properties in biopolymer films. However, the use of nanoparticles to manufacture nano-biocomposite polymer films for food packaging applications is a recent technology and can have several risks associated with the potential ingestion of nanoparticles migrated from films to drinks and foods (Carbone et al. 2016). To date, the toxicity, genotoxicity and carcinogenicity effect of nanoparticles in humans is not clear (Dimitrijevic et al. 2015).

The European Union (EU) and Switzerland are the only world region where nano-specific provisions have been incorporated in legislation. In other regions, nanomaterials are regulated more implicitly by mainly building on guidance for industry (Amenta et al. 2015). European Food Safety Authority (EFSA) did not approve the use of nanomaterials in food packaging (Carbone et al. 2016; Amenta et al. 2015).

Actually, nanoparticle migration into drinks and foods is studied based on overall migration limit (OML) proposed by European directives on food packaging normative (Commission Regulation No. 10/2011) (European Food Contact Materials Legislation 2002). For that, the OML in plastic materials due be less than 60 mg (of substances)/kg (of foodstuff or food simulant) for all substances. However, this normative is not specify for nanoparticles migration.

There are a limited number of studies about nanoparticle migration from nano-biocomposite polymer films. In some studies, the AgNPs and Mnt migration into foods have been studied. Abreu et al. (2015) studied the AgNPs migration from nano-biocomposite polymer films based on corn starch to food simulants and observed that the OML was less (42.9 mg/kg) than that OML proposed by European directives on food packaging normative. Similar results were observed by Metak et al. (2015) who studied the AgNPs migration from polyethylene packaging to different food simulants and real foods samples. These authors concluded that polymer films containing nanoparticles appears to be safe for food packaging since insignificant levels of AgNPs were released.

Echeverría et al. (2018) studied the Mnt migration from polyethylene films to tuna fillets during the storage period studied (17 days of storage at 2 °C) and did not observe significant migration of Mnt compounds (Mg, Al, Si) to tuna fillets, proving that polymer films containing Mnt can be used as food packaging.

However, it is necessary to study the nanoparticle migration in extreme conditions of temperature, pH and time, as well as in most liquid and solid foods. Several

nanoparticles have been proposed as possible nanomaterials to manufacture nano-biocomposite polymer films for future food packaging applications (e.g. carbon nanotubes, chitosan nanoparticles, cellulose nanowhiskers, starch nanocrystals and some nanoclays such as laponite and modified Mnt), however, any study about the nanoparticle migration into food systems were reported to date. Finally, it is necessary to quantify the OML permissible of each nanoparticle into foods. For that, is necessary to understand the nanoparticle accumulation in biosystems and its toxicity, genotoxicity and carcinogenicity effects (Carbone et al. 2016).

5.6 Prospects in Nano-biocomposite Polymer Films

Aiming the improvement of physicochemical properties in nano-biocomposite polymer films, some authors have charged more than one nanoparticle in the same biopolymer matrix. Thus, Abreu et al. (2015) and Kanmani and Rhim (2014) developed nano-biocomposite polymer films based on starch or gelatin, both loaded with Mnt and AgNPs. In these research, AgNPs provided antimicrobial properties, whereas Mnt improved some mechanical and water barrier properties in the nano-biocomposite polymer films. Hence, these authors developed active nano-biocomposite polymer films with better physicochemical properties when compared with control films (without nanoparticles).

Other mixtures of nanoparticles such as CNTs and CNWs (Yamakawa et al. 2017), CNPs and AgNPs (Dananjaya et al. 2017) and SNC and Mnt (Orsuwan and Sothornvit 2017) have been charged in nano-biocomposite polymer films with better physicochemical and antimicrobial properties. Nevertheless, according to Yamakaka et al. (2017), these nanomaterials should have a similar diameter and similar aspect ratio to improve the nanoparticle compatibility into biopolymer matrix.

Another approach to improve physicochemical properties of nano-biocomposite polymer films is to blending biopolymers or biopolymers/synthetic polymer in presence of nanoparticles (Ortega-Toro et al. 2015; Jose et al. 2015; Alves et al. 2015; Noshirvani et al. 2018; Tang and Alavi 2012; Taghizadeh and Favis 2013). However, the phase separation between nanoparticle and biopolymer/polymer matrixes is a problem frequently observed (Li et al. 2015a; Valencia et al. 2018; Flaker et al. 2015; Cano et al. 2015; Tang and Alavi 2012). A recent alternative to improve compatibility between biopolymer/polymer and nanoparticles is the use of reactive extrusion (Gutiérrez and Alvarez 2017; Quintana et al. 2016; Dhar et al. 2016). Reactive extrusion is a process where chemical reactions are controlled during extrusion process (Bouvier and Campanella 2014). To blending biopolymer by reactive extrusion it is necessary that biopolymers or biopolymer/synthetic polymer have similar melting temperatures (Quintana et al. 2016).

5.7 Conclusions

Based on the economic and environmental viewpoints, biopolymer films are probably the future materials to be used in food industry. In nature, there are several biopolymers able to be used in manufacture process of biopolymer films. However, it is necessary to understand as biopolymer films can become materials with important characteristics to food industry. The use of news manufacture process and/or nanomaterials can improve the mechanical, thermal, optical and barrier (to water, oxygen and UV/light) properties of biopolymer films. Particularly, the use of nanoparticles can introduce new properties such as antimicrobial and antioxidant activity as well as sequester effects in biopolymer films, opening a windows of news applications as active packaging films for food industry. However, the toxicity, genotoxicity and carcinogenicity effects of nanoparticles are not clear to date. Hence, it is necessary most studies about the nanoparticle migration into drinks and foods as well as its risks associated with the potential ingestion, before the nanoparticle application in industrial food packaging.

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