Chapter 4
Properties of Micro- and Nano-Reinforced Biopolymers for Food Applications

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Abstract Food packaging implies a significant consumption of different materials, of which plastics are the second most widely used. So, the development of biopolymers for food packaging applications is critically important. Although several biopolymers are available for different applications, they have some drawbacks and their functional properties need to be adapted for food packaging requirements. The incorporation of micro- and nano-fillers into the biopolymer matrix has proven to be an alternative means of improving their mechanical and barrier properties. In composites, the polymer forms the continuous matrix while the dispersed filler phase helps to positively modify the functional characteristics of the material. Different kinds of fillers have been used which modify the material characteristics as a function of their content and filler-matrix interactions. The particle size and shape, the amount and distribution and the chemical nature of the fillers are key factors in the final properties of the composite. In general, thermomechanical processes with high shearing forces and temperatures for the required time are needed to guarantee the convenient dispersion of the filler within the polymer matrix. In this chapter, the different kinds of fillers used in biopolymer composites have been summarized. The relevant surface properties and the changes induced by fillers on the mechanical, barrier and thermal properties of micro- and nano-composites have been discussed, with emphasis on food packaging applications. The processing techniques, formulation and final structure of materials have also been reviewed, as well as the influence of the fillers on the biodegradation behaviour of composites.

Keywords Biodegradability · Functional properties · Micro- and nanocomposites · Thermomechanical process

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Abbreviations

AFM	Atomic Force Microscopy
Ag-NPs	Ag nanoparticles
ATBC	Acetyltributyl citrate
BCNW	Bacterial cellulose nanowhiskers
ChNC	Chitin nanocrystals
CMC	Carboxymethyl cellulose
CNC	Cellulose nanocrystals
CNF	Cellulose nanofibrils
DSC	Differential Scanning Calorimetry
FESEM	Field emission scanning electron microscopy
FTIR	Fourier-transform infrared spectroscopy
GTA	Glycerol triacetate
HPMC	(Hidroxypropil)metil cellulose
MC	Methylcellulose
MCC	Microcrystalline cellulose
Mnt	Montmorillonite
NCC	Nano-crystalline cellulose
PBS	Poly(butylene succinate)
PBTA	Poly(butylene adipate co-terephthalate)
PCL	Polycaprolactone
PEG	Polyethylen glycol
PHA	Polyhydroxyalcanoates
PHB	Polyhydroxybutyrate
PHBV	Polyhydroxyl-3-butyrate-co23-valerate
PHBV12	Polyhydroxybutyrate with 12 mol% of valerate and containing 10 wt% of the plasticizer citric ester
PLA	Poly(lactic) acid
PLLA	Poly(L-lactide)
PVA	Poly(vinyl alcohol)
SEM	Scanning Electron Microscopy
TPCS	Thermoplastic corn starch
TPS	Thermoplastic starch
WSNC	Waxy starch nanocrystals

4.1 Introduction

Of all the materials available for food packaging, plastics have increased exponentially over the past two decades, with an annual growth of approximately 5%. It is estimated that worldwide annual plastic production exceeds 300 million tonnes, and was about 59 million tonnes in Europe in 2014. In fact, nowadays, plastics represent almost 40% of the European packaging market (Muller et al. 2017a). Of the plastic

materials, petroleum-based plastics, such as polyethylene (PE), polypropylene (PP), polyamide (PA), are widely used as packaging materials due to their ready availability at relatively low cost, good mechanical and barrier properties, thermoprocessing ability and chemical characteristics, which make them suitable for food packaging. However, despite their good properties, their use and accumulation imply serious environmental problems and a dependence on fossil fuels. Around 63% of the current plastic waste comes from packaging applications, and it is estimated that less than 14% is recyclable. Taking this scenario into account, and bearing in mind the growing environmental awareness, research has focused on the development of alternative bio-packaging materials, derived from renewable sources, which are biodegradable or compostable.

Biopolymers can be used for food packaging applications or food coating purposes, reducing the environmental impact and oil-dependence (Rivero et al. 2017; Emadian et al. 2017). They can be divided into three main categories, on the basis of their origin and biodegradable nature. Together with the conventional, non-biodegradable, oil-based plastics, there are biobased-non-degradable bioplastics (e.g. polyethylene terephthalate: PET), biobased-biodegradable bioplastics (e.g. polylactic acid: PLA, starch and other polysaccharides, or proteins) or fossil-based biodegradable bioplastics (e.g. polycaprolactone: PCL, polyvinyl alcohol: PVA, or polybutylene succinate: PBS). So, biopolymers are biodegradable, biobased or both and can be classified as those directly obtained from biomass (polysaccharides and proteins), synthetic biopolymers from biomass or petrochemicals (e.g. PLA, PCL) or those obtained by microbial fermentation (polyhydroxyalcanoates: PHA and bacterial cellulose) (Nair et al. 2017). The former are directly extracted from biological and natural resources and they are hydrophilic and somewhat crystalline in nature, making an excellent gas barrier. Biodegradable polyesters (synthetic or biosynthesized) are more hydrophobic and constitute better barriers to water vapour. In general, the functional properties of biopolymer-based materials in terms of their mechanical and barrier properties need to be adapted to food requirements by using different strategies, such as physical or chemical modifications (crosslinking), blending with other components, fillers, plasticizers or compatibilizers (Ortega-Toro et al. 2017).

The industrial uses of biopolymers have been restricted because of their usually poor mechanical, barrier or thermal properties, and high price. The incorporation of micro- and nano-reinforcing agents into the matrix for the purposes of obtaining composites has been seen to improve their functional properties and so their competitiveness in the plastics market. Composites are made up of a continuous polymer matrix in which the filler particles are dispersed, thus contributing to a modification of the functional characteristics of the material (Azeredo 2009). Fillers differing in size, shape, amount, distribution and chemical nature have been used. Lignocellulosic or cellulosic materials obtained from agro-waste have been widely studied as organic micro-fillers (Gutiérrez and Alvarez 2017). Fibres from cotton (Ludueña et al. 2012), garlic straw (Kallel et al. 2016), rice husk (Johar et al. 2012), wheat straw (Berthet et al. 2015) or coffee silverskin (Sung et al. 2017), have been used as reinforcing agents in different biopolymer films. Micro-particles significantly improved the elastic modulus of composites while providing great thermal

resistance to the matrices due to the presence of hydroxyl groups interacting with the biopolymer network (Ludueña et al. 2012; Berthet et al. 2015). Different organic nano-fillers can be obtained, mainly from cellulose (cellulose nanocrystals or nano-fibres), chitin/chitosan nanocrystals from crustacean waste (Gutiérrez 2017) or starch nanoparticles. These nano-reinforcing agents improve the tensile strength and elastic modulus when they have a proper distribution, chemical affinity with the polymer and high aspect ratio. The crystalline structure of nanofillers enhances the tortuosity factor for the mass transport of gas molecules into the biopolymer matrix, contributing to the formation of a hydrogen-bonded network (Ng et al. 2015; Azeredo 2009; Azeredo et al. 2017). On the other hand, inorganic particles are relevant as filling agents in food packaging materials due to the enhancement of the mechanical and barrier properties (MgO, silicon carbide or nano-clays) Some of them also exhibited antimicrobial activity, such as Ag, TiO_2 and ZnO nanoparticles (Gutiérrez et al. 2017; Azeredo 2009).

It is remarkable that biodegradation behaviour is a crucial factor in the development of composites. The biodegradation process takes place in aerobic conditions by the action of a microorganism, which identifies the polymer as a source of energy to produce organic residues from the packaging material. The incorporation of nano-fillers can affect the biodegradability of composites (Gutiérrez 2018). In this sense, cellulose nanocrystals (CNC) promoted the material's water intake due to their hydrophilic nature, contributing to an acceleration of the biodegradation process (Ludueña et al. 2012; Luzi et al. 2016). Some inorganic nano-fillers could also affect the disintegration processes, such as what occurs with Ag nanoparticles (Ramos et al. 2014; Cano et al. 2016), or nano-clays, whose hydroxyl groups react with the chains of the polymer matrices (montmorillonite and fluorohectorite, Fukushima et al. 2013).

This chapter reviews the potential use of reinforcing agents of differing natures and sizes in biopolymer materials that are potentially useful for food packaging, analysing their effect on the mechanical and barrier properties and on the thermal resistance of the material. The surface properties and biodegradation behaviour were also analysed in different kinds of composites.

4.2 Bioplastics for Food Packaging

Over the last decade, several bioplastics, bio-based, biodegradable, or both, have been available as a suitable alternative to conventional plastics for food packaging applications (Fabra et al. 2014; Ortega-Toro et al. 2017). At least 90% of natural or synthetic biodegradable polymers decompose in less than 180 days (ASTM 2003). Figure 4.1 shows the main polymers of potential use in food packaging. Of the natural polymers, different polysaccharides and proteins and microbially-produced biopolymers have been extensively studied for food packaging applications. Starch is a promising polymer, suitable for processing by means of different techniques, such as the casting method (Moreno et al. 2017), compression moulding (Muller et al. 2017b), extrusion (Gutiérrez and Alvarez 2018) or injection moulding (López et al.
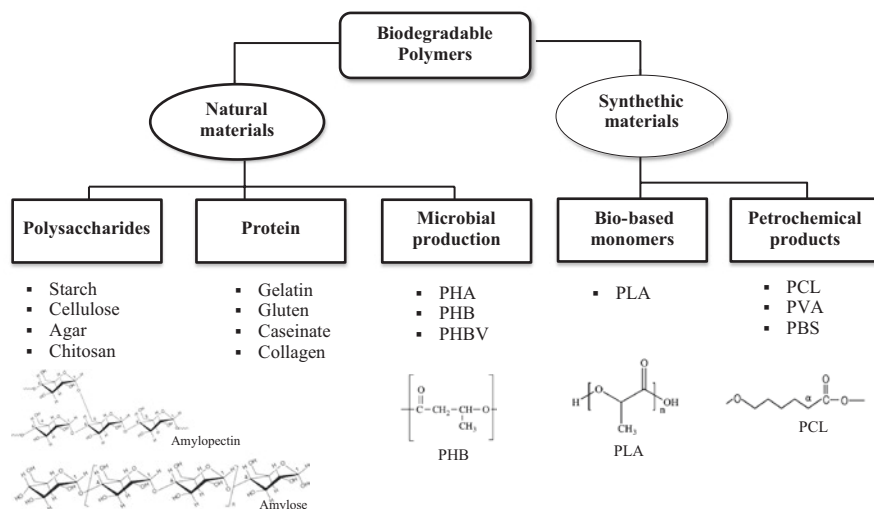
Fig. 4.1 Main biopolymers with potential application in food packaging. Some molecular structures are included

2015). Starch is naturally highly abundant, low cost and renewable. Cellulose, constituted by glucose units via β-1,4-glycosidic bonds, is the most naturally abundant carbohydrate (Xiao et al. 2014). This polymer is usually used as micro-filler or nano-filler (Shankar and Rhim 2016) in the composite formulation. These could be processed by compression moulding and injection moulding (Graupner et al. 2016) to obtain semi-rigid packaging (trays). On the other hand, agar is a fibrous polysaccharide obtained from marine algae, such as *Gelidium* sp. and *Gracilaria* sp., consisting of a mixture of agarose and agaropectin, which is slightly branched and sulphated. This is thermoplastic polysaccharide, biodegradable and biocompatible, which exhibits great mechanical strength with moderate water resistance (Giménez et al. 2013). Chitosan, the second most naturally abundant polysaccharide, has non-toxic, biodegradable, and antimicrobial characteristics, which are of great interest for packaging purposes (Leceta et al. 2013). Chitin, the precursor of chitosan, is a linear polymer of mainly β-(1 → 4)-2-acetamido-2-deoxy-ᴅ-glucopyranose units and low amounts of β-(1 → 4)-2-amino-2-deoxy-ᴅ-glucopyranose residues (Van den Broek et al. 2015). Others relevant natural polymers are proteins, such as gelatin or collagen, gluten proteins and dairy proteins. Gelatin is an animal protein obtained by the hydrolysis of the fibrous insoluble collagen from skins and bones of different animals. It is well known for its film-forming properties. It is abundantly available, low cost, and easily biodegradable and biocompatible (Kanmani and Rhim 2014). On the other hand, wheat gluten (constituted by gliadins and glutenin proteins) is an inexpensive protein from the milling process, which allows the production of membranes that are semipermeable to water vapour, oxygen and carbon dioxide molecules. This polymer can be applied as a food coating or edible film on different foods (Rocca-Smith et al. 2016), or processed by compression moulding (Zubeldía et al. 2015) and extrusion (Rombouts et al. 2013) for the purposes of developing flexible or

semi-rigid packaging. Caseinates have been proposed as raw materials for food packaging development, since this protein exhibited good film-forming ability with good mechanical properties (Fabra et al. 2012; Arrieta et al. 2014a; Jiménez et al. 2013). The use of caseinates could be considered an alternative means of obtaining a high degree of protection from oxygen in modified atmosphere packaging (Arrieta et al. 2014a). Biopolymers obtained from several microorganisms, such as poly-hydroxyalkanoates -PHA-, poly-hydroxybutyrate -PHB-, or poly- hydroxybutyrate-co-hydroxyvalerate -PHBV-, are a family of biodegradable thermoplastic polymers. The polymer is produced in the microbial cells through a fermentation process and then collected by solvents, like chloroform. More than 100 PHA are identified, of which PHB is the most common (Peelman et al. 2013). PHB is a biopolymer produced from renewable sources and fermentation by certain micro-organisms, like *Halomonas hydrothermalis* and *Burkholderia sp.* and *Chelatococcus daeguensis*, inter alia (Bera et al. 2015). In addition to being biodegradable, PHB exhibits some properties similar to some synthetic polymers, especially polypropylene (PP) (Heitmann et al. 2016). PHBV is a copolymer of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid produced directly by microorganisms. This polymer is less brittle and more stretchable than PHB (Requena et al. 2017).

Other biodegradable polymers are obtained by synthesis from biobased monomers (e.g. PLA) and non-biobased monomers (e.g. PCL, PVA or PBS). PLA is the most common synthetic polymer obtained from biobased monomers. The synthetic routes to obtain PLA are through the ring-opening polymerisation of the esters of the acid and the direct condensation of the free acid (Cheng et al. 2009). PLA is of great potential to the packaging industry because of its mechanical, barrier and optical properties. It can be processed using readily available production technologies, and exhibits good thermal behaviour and water vapour barrier properties, although it is brittle and only a moderate gas barrier (Bonilla et al. 2013).

In the category of biodegradable synthetic petroleum-based polymers, PCL, PVA and PBS are the most representative. PCL is a linear, semicrystalline hydrophobic polyester, highly flexible, tough and thermally stable (Correa et al. 2017). In contrast, PVA is a synthetic, water soluble polymer which forms translucent films with good tensile strength, elongation at break and barrier properties (Dominguez-Martinez et al. 2017). PVA has been used in polymeric blends, with glycerol as a proper plasticiser because of its chemical affinity. PBS is another biodegradable thermoplastic polymer which has desirable melt processability and good mechanical properties, which are closely comparable to those of widely-used polyethylene (PE) or polypropylene (PP) (Mizuno et al. 2015).

4.3   Micro and Nano-Reinforcing Agents

An alternative means of improving the properties of biopolymers for food packaging applications, and reducing some of their drawbacks, is by the incorporation of micro- or nano-fillers to the matrix for the purposes of obtaining micro- and

nano-composites. Composites have immiscible phases constituted by the polymer continuous network in which the filler particles are dispersed, thus generating new structures with different properties to those of the original polymer matrix. The filler can positively modify the functional characteristics of the material, depending on the filler polymer network interactions. Different kinds of fillers have been used, which modify the material characteristics as a function of the filler-matrix interactions. The size, shape, amount, distribution and chemical nature of the fillers are crucial factors in the final properties of the composite.

Many studies reported the use of different kinds of fillers. As is shown in Table 4.1, cellulose has been frequently used as a reinforcing agent in different forms, such as cellulosic fibres (Martino et al. 2015; Moustafa et al. 2016; Ludueña et al. 2012), bacterial cellulose (Fabra et al. 2016), nano-cellulosic fibres (Abdul Khalil et al. 2016) or cellulose nanocrystals (El-Hadi 2017; Fortunati et al. 2013a; Follain et al. 2013). In the polymer matrices, the incorporation of cellulosic fillers directly affects the mechanical and barrier properties depending on the particle size (micro or nano), which is a significant factor. As has been observed by various authors, particle size has differing effects on the mechanical properties. Cho et al. (2006) studied the effect of the particle size on the mechanical properties of polymeric composites with spherical micro (0.5 mm) and nano (15 nm) particles. They observed that, at nano-scale, Young's modulus and tensile strength increased as the particle size decreased. As regards the barrier properties, it is expected that nano scale and a homogeneous distribution increases the tortuosity factor for the migration of molecules through the composite, decreasing the permeability of both water vapour and gases. On the other hand, the amount of filler included significantly affects the composite properties. At high concentrations, the polymer matrix could lose cohesiveness and continuity which could lead to a loss in functional properties (mechanical and barrier). In this sense, Maqsood et al. (2016) studied the reinforcing capacity of enzyme-hydrolysed longer jute micro-crystals in polylactic acid matrices. The elastic modulus and tensile strength increased by 40% and 28% respectively, once the filler loading rose to 5% with respect to neat PLA. However, a filler loading of 10% led to a decrease of 32% in the elastic modulus and 33% in tensile strength with respect to materials containing 5% of fillers. Other organic fillers are chitin nanocrystals (Herrera et al. 2016) from crustacean waste that improve the mechanical properties and transparency of neat PLA. Also, starch nanocrystals are frequently added to several biopolymers, improving the mechanical and barrier properties and decreasing the biodegradation time (Mukurubira et al. 2017; Le Corre and Angellier-Coussy 2014).

Some inorganic particles have been extensively studied as fillers in food packaging materials. Some of these, such as MgO, (Sanuja et al. 2014); silicon carbide, (Dash and Swain 2013) and nano-clays (Cavallaro et al. 2013; Majeed et al. 2013; Abdollahi et al. 2013), enhanced the mechanical and barrier properties of the films. Additionally, other ones can provide antimicrobial activity to the material, as occurs with Ag nanoparticles (Carbone et al. 2016; Gutiérrez

Table 4.1 Main inorganic and organic reinforcing agents used as fillers in biopolymer matrices and main provoked changes in the matrix

Micro- and nano-fillers	Filler information	Polymer matrix	Main provoked changes	Applications	Reference
Organic fillers					
Lignocellulosic fibres	Natural Lignocellulosic material	PHBV/wheat straw	– Decrease cost – Increase EM – Decrease deformation	– Food Packaging	Martino et al. (2015)
	Natural by-product	PBAT/coffee ground	– Compatibiliser not necessary – Improve mechanical properties	– Food packaging	Moustafa et al. (2016)
Cellulosic fibres	Natural Previously alkali treated agro-waste	PCL/cotton	– Improve mechanical properties and biodegradation in soil	– Food packaging	Ludueña et al. (2012)
Bacterial cellulose	Obtained from bacterial strain *Gluconacetobacter xylinus* 7351	TPS, PHB	– Improve mechanical and barrier properties	– Food packaging	Fabra et al. (2016)
Nanocellulosic fibres	Natural Glucose units (beta-1,4 glycosidic linkages) $(C_6H_{10}O_5)n$	TPS, PLA	– Improve mechanical, thermal and barrier properties	– Food packaging – Pharmaceutical and industrial packaging – Medical application	Abdul Khalil et al. (2016)
Cellulose nanocrystal	Natural Obtained from agro-wastes	PHB and PLA	– Reduce Tg, Tc and Tm – Improve mechanical properties	– Food packaging	El-Hadi (2017)
		PVA	– Increase tensile strength	– Food packaging	Fortunati et al. (2013a)
		PCL	– Decrease WVP	– Food packaging	Follain et al. (2013)

Table 4.1 (continued)

Micro- and nano-fillers	Filler information	Polymer matrix	Main provoked changes	Applications	Reference
Chitin nanocrystals	Powder from crustacean waste	PLA	– Improve mechanical properties and transparency	– Packaging and food packaging	Herrera et al. (2016)
Starch nanocrystals	Amadumbe corms Botanical sources: normal maize, waxy maize, amylomaize, potato, rice, oat, peas or beans	TPS PLA, PVA, PBS, natural rubber, pullulan, carboximethyl chitosan	– Increase barrier properties – Improve mechanical properties – Increase the biodegradability	– Food packaging –Water treatment – Adhesive applications – Medical application	Mukurubira et al. (2017) and Le Corre and Angellier-Coussy (2014)
Inorganic fillers					
Ag nanoparticles	Metal	– Cellulose – HPMC – Pullulan – TPS – Alginate – Agar	– Provide antimicrobial and antiviral properties – Decrease WVP	– Fresh food packaging: meat, fruit and dairy products – Food packaging – Agricultural – Food packaging	Carbone et al. (2016) and Gutiérrez et al. (2017) Rhim et al. (2014)
TiO₂ nanoparticles	Oxide	Several polymers TPS	– Provide antimicrobial properties – Change colour	– Food packaging; active and intelligent packaging – Food packaging – Agricultural	He et al. (2015) and Gutiérrez et al. (2017)
ZnO nanoparticles	Oxide	TPS	– Provide antimicrobial properties	– Food packaging – Agricultural	Gutiérrez et al. (2017)
MgO nanoparticles	Oxide	Chitosan	– Increase tensile strength and deformation – Decrease water solubility	– Food packaging	Sanuja et al. (2014)

Table 4.1 (continued)

Micro- and nano-fillers	Filler information	Polymer matrix	Main provoked changes	Applications	Reference
Silicon carbide	SiC Melting point: 2730 °C Molar mass: 40.11 g/mol	Starch	– Decrease OP	– Food packaging – Industrial packaging	Dash and Swain (2013)
Nano-clays	Phyllosilicates $Al_2Si_2O_5(OH)_4$ Specific gravity: 2–2.65	Pectin/PEG/hallosyte	– Decrease water uptake capacity – Increase EM	– Industrial packaging	Cavallaro et al. (2013)
	$M_x(A_{l4}\text{-}xMg_x)Si_8O_{20}(OH)_4$	Several polymers/Mnt	– Increase barrier properties – Improve mechanical properties	– Food packaging – Industrial packaging	Majeed et al. (2013)
		Alginate	– Reduced water solubility – Decrease elongation and increase tensile strength – Decrease WVP	– Food packaging	Abdollahi et al. (2013)

et al. 2017), TiO$_2$ nanoparticles (He et al. 2015; Gutiérrez et al. 2017) and ZnO nanoparticles (Gutiérrez et al. 2017).

4.4 The Effect of Reinforcing Agents on the Functional Properties of Biopolymers

In the following sections, the effect that micro- and nano-fillers have on the tensile behaviour, barrier properties, thermal resistance and biodegradability of biopolymer matrices is discussed, taking the processing method into account.

4.4.1 Processing Methods

In general, thermomechanical processes (melt compounding, extrusion and compression moulding) with high shearing forces, temperature and adequate time are necessary to guarantee the convenient dispersion of the filler in the polymer matrix. However, the casting of polymer-filler dispersions is an alternative method to obtain nano-composites, due to the high aggregation tendency of nanoparticles, which are better maintained in liquid dispersions. Table 4.2 shows some recent studies on composite materials, including micro- or nano- fillers of differing characteristics, using different processing methods.

Berthet et al. (2015) studied the properties of PHBV composites containing wheat straw micro-fibres (10, 20 and 30 wt%). Compounding was carried out with a lab-scale twin-screw extruder, using a temperature profile from the polymer feeding to the die of 180–160 °C. Composite films were obtained by compression moulding at 170 °C. The mechanical and barrier properties of composites were poorer than those of neat PHVB, although the authors point that the obtained materials could be applied as packaging for respiring fresh products. Melt compounding using a Plastograph mixer (16 cm^3) for 4 min at 160 °C was also applied to obtain PHBV composites with micro-particles of keratin at 0.5, 1, 3, 5, 10, 25 and 50 wt%. The composites exhibited improved mechanical and water vapour and oxygen barrier properties with only 1 wt% of micro-filler (Pardo-Ibáñez et al. 2014). Moustafa et al. (2016) studied the use of roasted coffee grounds as micro-reinforcing agent to produce high-quality biodegradable Polybutylene adipate co-terephthalate (PBAT) composites for food packaging applications. The composites were extruded at 160–165 °C with a screw speed of 100 rpm for 5 min mixing. The films were obtained by a special die attached to the mixing chamber. The authors observed an increase in the hydrophobicity and thermal stability compared to the control films without fillers. A compatibiliser was not necessary to obtain a filler-polymer matrix with suitable interfacial adhesion, especially at low filler content (<30%), which was attributed to the good grindability of roasted coffee, which improved compatibility and filler dispersion during processing.

Table 4.2 Recent studies on composite materials including micro- or nano- fillers of different nature, applying different processing methods

Composite material	Filler content	Processing method	Effect of filler	Possible application	Reference
Polymer/micro-filler					
PHBV/ wheat straw fibres	10, 20 and 30 wt% filler with different preparation process	Extrusion and compression moulding	– Increased the water vapour transmission – Decrease ultimate tensile strength	– Food packaging materials to respiring fresh products	Berthet et al. (2015)
PHBV/ keratin	0.5, 1, 3, 5, 10, 25 and 50 wt% filler	Melt compounding	– Reduction WVP and OP – Improve mechanical properties	– Packaging	Pardo-Ibáñez et al. (2014)
PBAT/ roasted coffee ground	10, 20 and 30 wt% filler with roating process at 250 and 270 °C	Extrusion	– Increase hydrobicity – Increase thermal stability – Compatibiliser is not necessary	– Food packaging	Moustafa et al. (2016)
Polymer/nano-filler					
PCL-MC/ NCC	2 wt% NCC	Casting and compression moulding	– Increased the tightly of the matrix – Increased stability of active components – Increased the rough and density of the matrix	– Vegetable packages	Boumail et al. (2013)
PLA/CNC from MCC and Ag-NPs	1 and 5 wt% CNC with/ without surfactant and 1 wt% Ag nanoparticles	Casting	– Increase barrier effect – Antimicrobial effect	– Food active packaging	Fortunati et al. (2013b)
Agar/ Ag-NPs	20, 40 and 80 mg Ag-NPs	Casting	– Increase thermal stability – Barrier properties to water vapour increase slightly – Mechanical strength and stiffness decreased slightly – Antimicrobial activity against Listeria monocytogenes and Escherichia coli O157:H7	– Food packaging	Rhim et al. (2014)

Table 4.2 (continued)

Composite material	Filler content	Processing method	Effect of filler	Possible application	Reference
Alginate/ nano-clays Mnt and CNC from MCC	1, 3 and 5 wt% fillers	Casting	– Decrease water solubility – Increase surface hydrophobicity with CNC and decrease of this parameter with nanoclays addition – Reduction in WVP – Tensile properties improved	– Food packaging	Abdollahi et al. (2013)
Chitosan/ MgO	0.1 g MgO/g chitosan	Casting	– Improve mechanical properties – Increase opacity – Decrease swelling, permeability and solubility – Antimicrobial properties	– Food active packaging	Sanuja et al. (2014)
Starch/ Silicon carbide	1, 2, 5, 8, 10 wt% filler	Casting	– Increase thermal stability – Reduce OP	– Adhesive application – Covering and protecting applications – Food packaging	Dash and Swain (2013)
Pectin-PEG/ Halloysite nanotubes	5, 10, 15, 20, 30 and 50 wt% filler	Casting	– Decrease wettability – Improve mechanical properties	– Coatings for food conservation	Cavallaro et al. (2013)

As concerns the incorporation of nano-fillers in composites, casting is the most commonly used method due to the better dispersion (more limited aggregation) of nano-particles in a liquid medium. Casting is suitable for the obtaining of coatings, mulch films and flexible films. In some cases, this technique has been used as a preliminary test to study the filler effect before thermomechanical processing with actual industrial applications. Boumail et al. (2013) characterized trilayer antimicrobial films based on methylcellulose and PCL composites with 2% of cellulose nanocrystals (CNC). These were prepared under stirring before sonication at room temperature for 30 min and the subsequent casting of the PCL-CNC dispersion. The trilayer films were obtained by compression moulding at 120 °C. An increase in the matrix toughness and greater stability of active components was found by the filler addition. Fortunati et al. (2013b) incorporated the CNCs and Ag-NPs PLA films

obtained by casting, leading to improved barrier properties and antimicrobial activity in the composites. Ag-NPs (20, 40 and 80 mg Ag-NPs) have also been included in other polymers, such as agar matrices; although a significant increase in the thermal stability of the material was obtained, with improved water vapour barrier properties and antimicrobial activity against *Listeria monocytogenes* and *Escherichia coli* O157:H7, the mechanical strength and stiffness of the composites slightly decreased with respect to filler-free polymers (Rhim et al. 2014). Chitosan composites with MgO nano-filler, obtained by casting, also exhibited antimicrobial properties. In addition, the metallic oxide improved the mechanical properties and reduced the water swelling capacity and solubility and water vapour permeability of the films, which became less transparent.

Other nanocomposites with organic (CNC) or inorganic nano-clays:Mnt) obtained by casting, using an alginate matrix, exhibited improved functional properties with respect to the net polymer matrix (Abdollahi et al. 2013). The addition of both nano-fillers improved the tensile properties of the material and promoted a decrease in water solubility and water vapour permeability, whereas the surface hydrophobicity increased with the use of CNC but decreased with nano-clays. In the same way, nanoparticles of silicon carbide increased the thermal stability and reduced the oxygen permeability in starch composites (Dash and Swain 2013). This material could be used as adhesive and coating in food applications. Halloysite nanotubes promoted a decrease in film wettability and improved the mechanical properties in composites of pectin and polyethylene glycol blends (Cavallaro et al. 2013).

4.4.2   *The Effect on Tensile Properties*

In this section, the changes in the tensile properties of some biopolymers caused by incorporating nano- and micro-fillers of differing characteristics are analysed, as summarized in Table 4.3. The main mechanical properties characterized in plastic packaging materials are elastic modulus (EM) and the tensile strength (TS) and elongation (ε) at break, which provide information about the rigidity and resistance to deformation and break of the material, respectively.

The changes in the polymer's functional properties caused by filler addition are strongly associated with surface properties and polymer-filler interfacial interactions. In this sense, the effects caused by fillers on the mechanical properties of polymer are not always positive. The main reason is the interruption of the polymer matrix continuity, but this effect could be diminished if the polymer and fillers have chemical affinity or an interfacial agent is added into the composite formulation. As previously mentioned, Berthet et al. (2015) found a deterioration in the tensile properties of neat PHBV when wheat straw fibres were added to the matrix. Strain and stress at break decreased by 61% and 63%, respectively, with 30 wt% filler in the composite. However, Young's modulus increased by 13% with 20 wt% filler. Moustafa et al. (2016) found different trends in the tensile strength with the varia-

Table 4.3 Changes in tensile properties of some biopolymers by incorporating micro- or nano-fillers of different nature

Composite material	Filler content	Plasticizer/ equilibrium RH	Thickness (µm)	TS (MPa)	EM (MPa)	ε (%)	Reference
Polymer/micro-filler							
PHBV/wheat straw fibres	10, 20 and 30 wt% filler with different preparation process	–	–	2.2–3.13	14.4–39.2	0.89–2.3[a]	Berthet et al. (2015)
PBAT/ roasted coffee ground	10,20 and 30 wt% filler with roasting process at 250 and 270°°C	/50%	300–400	6.8–18.2	–	98–1545[a]	Moustafa et al. (2016)
PHBV / keratin	0.5, 1, 3, 5, 10, 25 and 50 wt% filler	–	100	–	540–600	2.9–5.5[a]	Pardo-Ibáñez et al. (2014)
Polymer/nano-filler							
PCL-MC/ NCC	7.7 wt% NCC	Glycerol/	225–280	20.3[a]–24.0	175.2–218.3[a]	–	Boumail et al. (2013)
PLA/CNC and ChNC	1 wt % nanocrystals	Triethyl citrate	100	15.8[a]–24.2	300[a]–1200	16–309	Herrera et al. (2016)
Corn starch-gelatin/CNC from eucalyptus wood pulp	0.44, 1.5, 2.56; 3% CNC and 20% plasticizer	Glycerol/50%	50–140	11–49	–	1.24–38	Alves et al. (2015)
Alginate/ nano-clays Mnt and CNC from MCC	1, 3 and 5 wt% fillers	Glycerol/53%	–	CNC: 18[a]–23	150[a]–270	9–12[a]	Abdollahi et al. (2013)
				Mnt: 17–19	150[a]–210	8–12[a]	
Pectin-PEG/ Halloysite nanotubes	5, 10, 15, 20, 30 and 50 wt% filler	/53%	60	25–26	2.6[a]–4.1	0.9–1.5[a]	Cavallaro et al. (2013)
Chitosan/ MgO	0.1 g MgO/g chitosan	–	220–470	30[a]–60	–	7.5[a]–15	Sanuja et al. (2014)
Agar/ Ag-NPs	20, 40 and 80 mg Ag-NPs	Glycerol/50%	62.2–65.8	45.2–49.6[a]	1290–1460	19.0–23.6[a]	Rhim et al. (2014)

TS tensile strength; *EM* young's modulus; *ε* elongation at break

Data show the range in the values of each property reported for the different formulations

[a]Identifies the value for the control sample (without filler), when it is in the edge of the range

tion in filler content, using differently roasted coffee ground (CG) in PBAT matrices. As compared with neat PHBV, the best tensile behaviour was obtained with 10% of filler roasted at the highest temperature (270 °C), while the worst behaviour was observed for 30% of non-roasted CG powder. As the authors mentioned in their study, roasted CG showed a better affinity with PBAT compared to untreated CG when obtaining green composites without the need for a compatibiliser. This is important because the greater chemical affinity among the components led to stronger structures and better tensile properties of the composites. The values of the strain at break were lower than in the net polymer films for every composite. Pardo-Ibáñez et al. (2014) also found a decrease in the elongation at break of PHBV composites in line with differing quantities of keratin microparticles, but the elastic modulus at low loading was significantly improved. The content of filler greatly affected the tensile behaviour of composites and, in general, low filler contents improved both tensile strength and elastic modulus.

As regards nano-fillers, different studies have shown the improvement in tensile strength and elastic modulus when nanoparticles are incorporated into the polymer matrices. This effect is enhanced by a good particle distribution, a chemical affinity between filler and polymer and a high aspect ratio of the particles and filler-polymer contact area (more interactions). However, the processing conditions and the filler-polymer ratio must be taken into account to optimize the composite properties. Excessively high filler content results in the polymer matrix interruption and formation of micro- nano-cracks. Herrera et al. (2016) studied the effect of the incorporation of CNCs and chitosan nano-crystals (ChNC) into PLA films obtained by extrusion and compression moulding using fast and slow cooling rates. The tensile properties of composites were affected by both the chemical nature of the filler and processing conditions. Strength at break was improved by CNC incorporation, both at fast and slow cooling rates, but ChNC only improved the film strength when processing at a slow cooling rate. Young's modulus increased and elongation at break decreased after the addition of both nanoparticles at both processing cooling rates. Alves et al. (2015) studied the effect of CNC and gelatin on corn starch plasticised films. Nanocrystals were added at 0.44, 1.5, 2.56 and 3% with respect to the polymers. They found a significant increase in the film resistance when the CNC ratio rose, with a slight fall in the elongation values. Similar results were obtained in nanocomposites based on pectin/polyethylene glycol blends containing halloysite nanotubes (Cavallaro et al. 2013). The incorporation of nanotubes led to significantly more rigid films, but reduced the elongation capacity of the material.

Metallic oxide nanoparticles have been used as a suitable option to improve the mechanical properties of biopolymers. Sanuja et al. (2014) reported a significant increase in both the tensile strength and elongation at break of chitosan composites with 10% magnesium oxide, obtained by casting. Abdollahi et al. (2013) compared fillers of differing chemical characteristics (Mnt and CNC) added to alginate matrices at 1, 3 and 5%. The tensile strength values exhibited a constant growth as the CNC content increased but this parameter decreased when the content of Mnt was higher than 1%. Young's modulus also behaved differently, depending on the filler. The composite stiffness was higher as the CNC content increased from 0 to 5%, but decreased when the Mnt content rose from 3 to 5%. However, the elongation values

exhibited the same trend for both kinds of nanocomposites; decreasing when both CNC and Mnt contents increased.

4.4.3   The Effect on Barrier Properties

Some biodegradable materials need to improve the gas and water vapour permeability because it is a fundamental property in packaging (Ng et al. 2015). The incorporation of micro- and nano-fillers, of organic or inorganic nature, to biodegradable polymer matrices can modify the barrier properties (oxygen permeability: OP and water vapour permeability: WVP). The barrier properties of polymers containing fillers depend on their chemical nature, the particle size and shape of the particles, as well as other factors such as polarity, hydrogen bonding capacity and polydispersity (González et al. 2015; Pardo-Ibáñez et al. 2014). Table 4.4 summarizes the different effects several fillers were observed to have on the barrier properties of some biopolymer matrices. In every case, the addition of fillers can improve the oxygen permeability and the values of the control samples (without filler) were in the range of the corresponding composites or at the high end, especially when CNC fillers were used. Fabra et al. (2016) studied the incorporation of bacterial cellulose nanowhiskers (BCNW) into thermoplastic corn starch matrices (TPCS) and a 95% decrease in OP was obtained with 15% of filler with respect to the TPCS sample. The reinforced TPCS was assembled in multilayer PHB films to obtain more hydrophobic matrices and to improve the film performance. The best functional properties of multilayers were obtained with 15% BCNW-TPCS composite inner layer and PHB outer layers. Luzi et al. (2016) observed a reduction of 47% in OP with the incorporation of 3 wt% CNC from *Carmagnola* carded hemp fibres and a commercial surfactant into a PLA-PBS matrix. The addition of a surfactant could contribute to a better dispersion of the CNCs and PBS. They observed that the CNCs were well dispersed in the polymer matrices, through the Atomic Force Microscopy (AFM) analysis of surface roughness.

As regards values, analyses of WVP in composites provide similar tendencies to those OP values. In most cases, WVP was reduced after the incorporation of fillers, especially nano-size ones. Table 4.4 shows the different effect of micro- and nano-fillers on this barrier property for several biopolymer matrices. Raw lignocellulosic fibres (Berthet et al. 2015) or cellulose fibres obtained after chemical treatments (Ludueña et al. 2012) only slightly decreased, or did not affect, the WVP of some composites due to their hydrophilic nature. However, Pardo-Ibáñez et al. (2014) observed a 59% reduction in WPV of the PHVB matrices with 1 wt% of keratin micro-filler, while no significant differences were obtained with a filler load higher than 5 wt%. They detected a homogenous particle distribution in the matrix at 1 wt% filler, where the micro-particles are not aggregated, causing an increase in the tortuosity factor for the diffusion of gas molecules, which reduced the permeability values. On the other hand, the incorporation of nano-filler into different polymer matrices, especially CNCs, improved the WVP values. The crystalline structure of

Table 4.4 Changes in barrier properties (oxygen and water vapour permeability) of some biopolymers by incorporating micro- or nano-fillers of different nature

Composite material	Filler content	Processing method	Plasticizer/equilibrium RH	OP (m³.m/m².Pa.s)	WVP (kg.m/Pa.s.m²)	RH (%)	T (°C)	Thickness (µm)	Reference
Polymer/micro-filler									
PHBV/wheat straw	10, 20 and 30 wt% filler with different preparation process	Extrusion and compression moulding	–	–	$1.26 (10^{-7})^a$–$1.27 (10^{-6})$ (kg/m².s)	100	20		Berthet et al. (2015)
PHBV/keratin from poultry feathers	0.5, 1, 3, 5, 10, 25 and 50 wt% filler	Brabender Plastograph mixer and compression moulding	–	$1.0 (10^{-18})$–$3.2 (10^{-18})$	$3.1 (10^{-15})$–$62.0 (10^{-15})$	40	24	100	Pardo-Ibáñez et al. (2014)
PCL/cellulose fibres from cotton	5 and 15 wt% filler	Brabender Plastograph mixer and compression moulding	–	–	$1.6 (10^{-14})^a$–$1.7 (10^{-14})$	68	–	–	Ludueña et al. (2012)
Polymer/nano-filler									
Corn starch-gelatin/CNC from eucalyptus wood pulp	0.44, –1.5, 2.56; 3% CNC	Casting	Glycerol/50%	–	$5.21 (10^{-14})$–$6.99 (10^{-14})^a$	50	37.8	90–140	Alves et al. (2015)
Pea starch-PVA/CNC from MCC	1, 3 and 5 wt% CNC	Casting	/53%	–	$2.32 (10^{-11})$–$2.43 (10^{-11})$	100	25	1000	Cano et al. (2015)
TPS/CNC from gravata fibres	0.5, 1, 2 and 3 wt% CNC	Casting	Glycerol and lignin/	–	$1.27 (10^{-13})$–$2.67 (10^{-13})^a$	100	25	–	Miranda et al. (2015)
Starch-CMC/CNC from sugarcane bagasse	0.5, 2.5 and 5 wt% CNC	Casting	Glycerol/	–	$9.72 (10^{-14})$–$3.75 (10^{-13})^a$	50	32	–	El Miri et al. (2015)
TPS/WSNC	1, 2.5 and 5 wt% WSNC	Casting	Glycerol/	$8.79 (10^{-16})$–$3.07 (10^{-15})$	$57.3 (10^{10})$–$66.7 (10^{10})$ (kg/m².s.Pa)	50	23	–	González et al. (2015)

Composite material	Filler content	Processing method	Plasticizer/ equilibrium RH	OP (m³.m/ m².Pa.s)	WVP (kg.m/ Pa.s.m²)	RH (%)	T (°C)	Thickness (μm)	Reference
TPCS-PHB/BCNW	2, 5, 10, 15, 20 and 25 wt% CNC	Brabender Plastograph internal Mixer, compression moulding and Electrospinning	Glycerol/0%	2.03 (10^{18})–41^a ± 2.3 (10^{18}) (80% HR)	6.42 (10^{13})–15.52 $(10^{13})^a$	0–100	25	–	Fabra et al. (2016)
Chitosan/ Commercial CNC	1, 3 and 5 wt% CNC	Casting	–	–	2.62 (10^{-7})–4.20 $(10^{-7})^a$ (kg.d.m/m².Pa)	75	25	50	Corsello et al. (2017)
Wheat gluten/CNC and CNF from sunflower stalks	1 and 3 wt% CNC or CNF	Casting	/53%	CNC 1 (10^7)–1.21 $(10^7)^a$ CNF 1.08 (10^7)–1.37 (10^7)	CNC 1.40 (10^{-11})–1.55 (10^{-12}) CNF 1.39 (10^{-12})–1.55 (10^{-12})	53	25	–	Fortunati et al. (2016)
PLA-PBS/CNC from *Carmagnola* carded hemp fibres	1 and 3 wt% CNC with/without surfactant	Casting	–	1.05 (10^{-6})–1.98 $(10^{-6})^a$	1.52 (10^{-14})–2.41 (10^{-14})	53	25	–	Luzi et al. (2016)
PVA/CNC from potato peel waste	1 and 2 wt% CNC	Casting	Glycerol/50%	–	1.25 (10^{-5})–1.33 (10^{-5}) (kg/m².s)	50	23	150	Chen et al. (2012)
Alginate/ nano-clays Mnt and CNC from MCC	1, 3 and 5 wt% fillers	Casting	Glycerol/53%	–	1.6 (10^{-13})–1.99$(10^{-13})^a$	20	1.5	–	Abdollahi et al. (2013)
Agar/Ag-NPs	20, 40 and 80 mg Ag-NPs	Casting	Glycerol/50%	–	1.38(10^{-12})–1.52 $(10^{-12})^a$	–	–	–	Rhim et al. (2014)

OP oxygen permeability; *WVP* water vapour permeability; *RH* equilibrium relative humidity of samples; *T* temperature of the analysed samples

Data show the range in the values of each property reported for the different formulations

[a]Identifies the value of the control sample (without filler) when it is in the edge of the range

nanocrystals makes it difficult for certain molecules (O_2, CO_2, H_2O) to diffuse into the biopolymer matrix because of the formation of a hydrogen-bonded network (Brinchi et al. 2013; Ng et al. 2015), which favours the development of a percolation network, as reported by Miranda et al. (2015); the incorporation of 1 wt% of CNC from gravata fibres into thermoplastic corn starch matrices, provoked a 30% decrease in WVP. The addition of 2.5 wt% of CNC from sugarcane bagasse into matrices made up of corn starch and CMC decreased WVP by 50% due to the impermeable crystalline structure of CNC and a good dispersion of CNCs, creating a highly tortuous path for water vapour transfer (El Miri et al. 2015).

The use of inorganic fillers had similar effects on barrier properties to those of organic nano-fillers. The improvement in the barrier properties is due to the increased tortuosity factor for the gas molecule mass transport in the matrix and the impermeable nature of fillers, as reported by Abdollahi et al. (2013) in alginate films with 5% of Mnt nano-clays, where WVP decreased by about 20%. Studying agar films reinforced with Ag-NPs, Rhim et al. (2014) observed that the dispersed phase of Ag-NPs in the polymer impeded the mobility of its chains, inducing an improvement in WVP of the composites.

4.4.4 The Effect on Thermal Properties

The effects of micro- and nano-fillers of differing characteristics on the thermal properties of some biopolymers have been studied by several authors. Table 4.5 shows the main calorimetric parameters obtained from Differential Scanning Calorimetry (DSC) and the thermal stability of different materials obtained by Thermogravimetric Analysis (TGA) for different biopolymers and composites. Information about glass transition temperature (T_g), crystallisation temperature (T_c), melting temperature (T_m), melting enthalpy (ΔH_m), onset temperature (T_{onset}) and peak temperature (T_{peak}) of thermodegradation are given in the Table 4.5.

In general, the addition of micro- or nano-fillers can modify the Tg and crystallization/melting properties (T_c, T_m, ΔH_m) of polymer in line with the established interactions between particles and polymer chains. As expected, the addition of plasticizers to the filler-biopolymer blends decreases both the Tg and melting point (T_m). In this sense, Martino et al. (2015) analysed the effect of different plasticisers, such as ATBC (acetyltributyl citrate), GTA (glycerol triacetate) and PEG (polyethylen glycol) in PHVB films with 20 wt% of wheat straw fibres. Blends with ATBC showed the strongest Tg reduction due to its non-polar nature and great affinity with the polymer. Similar effects were observed in both polymer and composites. Cano et al. (2015) observed a ~5 °C reduction in Tg of pea starch-PVA (1:1) matrices after the addition of 3 wt% of CNC from MCC. This was related to the partial inhibition of the PVA crystallisation and to the lower mean molecular weight of the amorphous PVA fraction.

As regards the thermal degradation of materials, the addition of fillers generally improves the thermal stability of composites for both micro or nano fillers. The

Table 4.5 Changes in thermal behaviour (calorimetric parameters and thermal degradation) of some biopolymers by incorporating micro- or nano-fillers of different nature

Composite material	Filler content	Processing method	Plasticizer/ equilibrium RH	Calorimetric parameters				Thermal degradation		Reference
				T_g (°C)	T_c (°C)	T_m (°C)	ΔH_m (J/g)	T_{peak} (°C)	T_{onset} (°C)	
Polymer/micro-filler										
PHBV/wheat straw fibres	10, 20 and 30 wt% filler with different preparation process	Extrusion and compression moulding	–	–	–	–	–	273–315[a]	227–276[a]	Berthet et al. (2015)
PHBV/wheat straw fibres	20 wt% fibres	Extrusion and compression moulding	ATBC, GTA and PEG/	–14–3[a]	–	161–170[a]	70–95	–	–	Martino et al. (2015)
PHBV/keratin from poultry feathers	0.5, 1, 3, 5, 10, 25 and 50 wt% filler	Brabender Plastograph blending and compression moulding	–	–	101.9–103.3	147.1–148.3	35–49.9	–	–	Pardo-Ibáñez et al. (2014)
PBAT/coffee ground	10,20 and 30 wt% filler with roasting process at 250 and 270 °C	Extrusion with die attached with the mixing chamber	–	–	80.7–88.1	95.8–115.1	6.3–6.7	334.7–404.8[a]	278.5–353.3[a]	Moustafa et al. (2016)
Mater Bi–KE/ cotton, kenaf, and hemps fibres	10% (w/w) fibres	Extrusion and compression moulding	–	–	41.85[a]–46.65	62.85[a]–67.95	61.1[a]–68.8	335[a]–356	319[a]–334	Moriana et al. (2011)
PCL/cellulose fibres from cotton	5 and 15 wt% filler	Brabender Plastograph blending and compression moulding	–	–	–	–	–	354–417[a]	–	Ludueña et al. (2012)

(continued)

Table 4.5 (continued)

Composite material	Filler content	Processing method	Plasticizer/equilibrium RH	Calorimetric parameters				Thermal degradation		Reference
				T_g (°C)	T_c (°C)	T_m (°C)	ΔHm (J/g)	T_{peak} (°C)	T_{onset} (°C)	
Polymer/nano-filler										
Corn starch-gelatin/CNC from eucalyptus wood pulp	0.44, 1.5, 2.56 and 3% CNC	Casting	Glycerol/	–	–	–	–	296.39–298.47[a]	248.34–304.13	Alves et al. (2015)
Pea starch-PVA/CNC from MCC	1, 3 and 5 wt% CNC	Casting	Glycerol/53%	73.9–78.6[a]	200.7[a]–202.3	225.6–227.04[a]	61–108[a]	419[a]–431.9	–	Cano et al. (2015)
PLA–PHB/CNC from MCC	5% CNC	Extrusion and compression moulding	–	55.3–62.5		148.6–150.2	17.7[a]–28.6	267–357[a]	278[a]–280	Arrieta et al. (2014b)
PLA–PHB/CNC from MCC	1 and 5 wt% CNC 15 wt% plasticizer	Electrospinning Extrusion and compression moulding	ATBC/	27.1–51[a]	80.7–107.6[a]	147.5–155[a]	35–48[a]	332–340	76[a]–141.1	Arrieta et al. (2015)
PLA-PBS/CNC from *Carmagnola* carded hemp fibres	1 and 3 wt% CNC with/without surfactant	Casting	–	46.9–54.6	–	138.6–138.6[a]	21.5–30.3	344–364[a]	–	Luzi et al. (2016)
PLA/CNC from *Posidonia oceanica* plant waste	1 and 3 wt% CNC	Casting	–	40.6–54.3	91.5–118.6[a]	157.2–164.1	37.4[a]–40.4	313–332	240–270[a]	Fortunati et al. (2015)
PLA/CNC from *Phormium tenax* leaves	1 and 3 wt% CNC with or without 20 wt% plasticizer	Extrusion and compression moulding	Limonene	31.6–59.6	92.6–112.6[a]	143.2–147.9[a]	29.1[a]–44.0	352–357[a]	–	Fortunati et al. (2014)
PLLA/CNC from eucalyptus wood pulp	10 wt% CNC	Casting	–	59[a]	98–100[a]	160–162[a]	41[a]–48	–	–	De Paula et al. (2016)

Composite material	Filler content	Processing method	Plasticizer/equilibrium RH	Calorimetric parameters				Thermal degradation		Reference
				T_g (°C)	T_c (°C)	T_m (°C)	ΔHm (J/g)	T_{peak} (°C)	T_{onset} (°C)	
PLA/CNC from MCC	1 and 3 wt% CNC-g-PLLA	Grafting Extrusion and compression moulding	–	57.7–60.4[a]	96.2–100.5[a]	166–168.8	42.4–47.9	300–310	–	Lizundia et al. (2016)
Poly(butylene/triethylene succinate)/CNC from MCC	1 and 5 wt% CNC with surfactant	Extrusion and compression moulding	–	–40–33	50–89[a]	84–114[a]	27–63	402–407	–	Fortunati et al. (2017)

T_g glass transition temperature; T_c crystallisation temperature; T_m melting temperature; ΔHm melting enthalpy; T_{peak} peak temperature in DGTA; T_{onset} onset temperature in DTGA

Data show the range in the values of each property reported for the different formulations

[a]Identifies the value of the control sample (without filler) when it is in the edge of the range

network of the matrices becomes more resistant to heat based on the inherently high heat resistance of organic and inorganic fillers. Lignocellulosic fillers, such as wheat straw fibres (Berthet et al. 2015; Martino et al. 2015), kenaf fibres (Moriana et al. 2011), garlic straw (Kallel et al. 2016), rice husk (Johar et al. 2012), sisal fibres (Santos et al. 2015), pineapple leaf fibres (Shih et al. 2014), soy hull (Flauzino Neto et al. 2013), rice straw (Boonterm et al. 2015), coconut husk fibres (Rosa et al. 2010) or banana peel waste (Hossain et al. 2016) decompose in the temperature range of 150–500 °C: specifically, hemicellulose decomposes mainly from 150 to 350 °C, cellulose at between 275 and 350 °C and lignin undergoes gradual decomposition in the range of 250–500 °C. This high/wide range of decomposition temperatures promotes the greater thermal resistance of composites. Moriana et al. (2011), found a T_{peak} increase of 6% when natural micro-fibres (cotton, kenaf and hemp fibres) were incorporated into starch-based composites. The greatest increase was obtained with kenaf fibres, probably due to the better compatibility between this filler and the starch matrix. This was associated with the higher content of hemicellulose, which promotes the hydrogen bonding between the fibres and the matrix, improving the interfacial adhesion and thermal stability. However, with other biopolymer matrices, the addition of micro-fibres did not affect the thermal stability as described by Berthet et al. (2015) for PHBV-wheat straw micro-fibres blends. The presence of lignocellulosic micro-fibres could contribute to a reduction in the mean polymer molecular weight of the blend, reducing the overall thermal stability, as was also observed by Ludueña et al. (2012) in PCL-cotton micro-fibre films.

The particle size reduction from micro- to nano-scale of fibres (e.g. by means of alkali and bleaching treatments of lignocellulosic material and acid hydrolysis to obtain pure cellulose nanocrystals (Brinchi et al. 2013; Jonoobi et al. 2015; Zhou et al. 2016), implies a high yield in thermal resistance, as well as in the previously mentioned barrier and mechanical properties. The incorporation of CNCs into biopolymer composites improved their thermal stability due to the crystalline structure and compact chains present in the nanocrystals, which are not easily dissociated by heating, increasing the thermal stability (Ng et al. 2015). Arrieta et al. (2014a, b and 2015) reported greater thermal stability in PLA-PHB blends reinforced with 1 or 5 wt% of CNC, from commercial MCC, obtained by electrospinning or extrusion processes. Similar behaviour was observed by Cano et al. (2015) in PVA-starch matrices with 1, 3 and 5 wt% of the same reinforcing agent.

As concerns the influence of inorganic nano-fillers on the thermal properties of composites, they also enhanced the thermal stability of biopolymer matrices. Rhim et al. (2014) studied the use of Ag nanoparticles in glycerol plasticised agar matrices obtained by casting. The thermogravimetric analysis exhibited a high residual mass of the composite films due to the inclusion of the more thermally stable metallic nanoparticles. Cavallaro et al. (2013) obtained pectin-PEG blends with nano-clays, specifically hallosyte nanotubes, at 5, 10, 15, 20, 30 and 50 wt% by casting. The thermal degradation analyses reflected the fact that nano-composites had a high degree of thermal resistance in comparison with the control sample, which was attributed to the fact that the nano-clay lumen can encapsulate the pectin degradation products delaying the process. Moreover, the good dispersion of the nano-filler inside the polymer matrix improved the thermal stabilization of the biopolymer.

4.5 The Surface Properties of Micro- and Nano-Reinforced Polymers for Food Applications

In this section, recent studies into the effect of the addition of micro- and nano-fillers of differing characteristics on the surface properties of some biopolymers are analysed, and summarised in Table 4.6. The main changes in biopolymer functional properties caused by the addition of a filler are strongly associated with surface properties and the interfacial interactions between biopolymer and filler. Several methods have been used to characterise the morphology and the surface composition/structure of biomaterials, such as contact angle, electron spectroscopy for chemical analysis (ESCA) or X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS), scanning electron microscopy (SEM), atomic force microscopy (AFM) (Gutiérrez et al. 2018). The surface properties of the composites can directly impact on the macroscopic observation of the material gloss, which can have notable influence on their practical applications. In this section, recent studies into the effect of different fillers on the surface hydrophobicity (contact angle), topographic analysis (AFM) or sample gloss are discussed and summarised in Table 4.6.

The contact angle (θ) of a liquid in contact with a solid material mainly depends on the balance between the adhesive liquid-solid forces and the cohesive forces of the liquid (Gutiérrez et al. 2018). Aqueous or organic solvents can be used on a determined material in order to characterise the relative affinity of the material for polar or non-polar systems, thus obtaining information about its respective wettability properties according to the hydrophobic-hydrophilic nature of the surface. The θ values vary according to the type of biopolymer and nature of the filler (organic/inorganic). The inorganic fillers, such as nano-clays, could negatively affect the surface hydrophobicity of matrices due to their great water affinity, as reported by Abdollahi et al. (2013) for matrices of alginate-Mnt nano-clays at 1, 3 and 5 wt%. The film's surface was more hydrophilic than the control sample mainly due to the hydrophilic nature of the Mnt also present at surface level. However, the same authors observed an 87.5% increase in hydrophobicity when they used CNC from commercial MCC in the same matrices. Films with 5 wt% CNC exhibited the highest degree of hydrophobicity, which was associated with the high ratio of CNCs at surface level and their crystalline nature, with lower water affinity than the alginate matrix. Similar results are reported by Slavutsky and Bertuzzi (2014) for thermoplastic starch (TPS) matrices reinforced with CNCs from sugarcane bagasse. The water contact angle increased (rise in the surface hydrophobicity) when CNCs were incorporated into TPS, while strong interactions and the formation of hydrogen bonds between the starch chains and CNCs are expected. These strong internal bonds could also reduce the surface interactions between water molecules and the material. Cao et al. (2008) obtained nanocomposites with TPS and CNCs from hemp fibres and they also observed an increase in the water contact angle or surface hydrophobicity of the matrices. On the contrary, the incorporation of CNCs into hydrophobic polymer matrices, such as PBS, enhanced the water wettability of the films (decrease in contact angle). This could be expected from the surface presence

Table 4.6 Effect of fillers on surface properties of different composite films

Composite material	Formulation	Processing method	Surface analysis	Effect on polymer matrix	Reference
Polymer/micro-filler					
PHBV/wheat straw fibres (WSF)	20 wt% fibres 10 wt% plasticizer (ATBC, GTA or PEG)	Extrusion and compression moulding	– Surface hydrophobicity (contact angle reference liquids: distilled water, diiodomethane ethylene glycol and glycerol)	Contact angle values of the plasticized composite with WSFs were lower than that of the PHBV matrix	Martino et al. (2015)
Polymer/nano-filler					
Alginate/ nano-clays Mnt and CNC from MCC	1, 3 and 5 wt% fillers	Casting	– Surface hydrophobicity (contact angle)	Composites with Mnt had more hydrophilic surface Composites with CNC had more hydrophobic surface due to their highly crystalline nature	Abdollahi et al. (2013)
Pea starch-PVA/CNC from MCC	1, 3 and 5 wt% CNC	Casting	– Gloss	The incorporation of filler do not affect gloss in composites	Cano et al. (2015)
TPS/CNC from sugarcane bagasse	Appropriate amount of CNC suspension and glycerol as plasticizer	Casting	– Surface hydrophobicity (contact angle)	Contact angle increased with CNC addition Strong interactions between starch chains and CNC, which reduced the water affinity of the film surface	Slavutsky and Bertuzzi (2014)

Table 4.6 (continued)

Composite material	Formulation	Processing method	Surface analysis	Effect on polymer matrix	Reference
Wheat gluten/ CNC and CNF from sunflower stalks	1 and 3 wt% CNC or CNF	Casting	– Gloss – AFM topographic analysis	Good distribution of CNC into the matrix and some regions with aggregated CNF CNC promoted gloss a function of filler content CNF decreased gloss as a function of filler content	Fortunati et al. (2016)
Poly(butylene/ triethylene succinate)/ CNC from MCC	1 and 5 wt% CNC, with surfactant	Extrusion and compression moulding	– Gloss – Surface hydrophobicity (contact angle)	Decreased the gloss value as the amount of CNC increased Higher contact angle values for 1% filler	Fortunati et al. (2017)
PLA-PHB/ CNC from MCC	1 wt% and 5 wt% CNC 15 wt% plasticizer	Extrusion and compression moulding	– Topographic analysis by AFM	Presence of aggregated and individualized CNC The surfactant allowed for the polymer chain penetration between the cellulose structures	Arrieta et al. (2014b)

of the cellulose hydroxyl groups, which favour water affinity at the surface (Fortunati et al. 2017).

From the AFM analyses, the presence of nanoparticles on the composite surface and their aggregation/isolation state can be assessed, while their effect on the surface roughness can be verified. Arrieta et al. (2014b) studied the surface properties of PLA-PHB matrices containing CNCs from MCC. The AFM analysis showed the presence of some agglomerated and individualised CNCs in matrices. The aggregation of nanoparticles was reduced by the use of surfactants, which allowed for a better polymer chain interaction with the cellulose nanostructure. Nevertheless, an opposite effect was deduced by Fortunati et al. (2016) from the AFM images for CNCs in wheat gluten matrices, probably due to the different kinds of interactions between cellulose and the amphiphilic protein chains. The tendency of nanocrystals

to aggregate has been widely found in numerous studies (Brinchi et al. 2013; Ng et al. 2015; Zhou et al. 2016) due to the spontaneous tendency to reduce the interfacial free energy of the system, accumulated at the contact surface area. The aggregated nanocrystals can be successfully dispersed and homogenised by strong mechanical shearing effects into a homogeneous suspension (Ng et al. 2015) or with the incorporation of surfactants to achieve a good dispersion in the matrices (Hu et al. 2015; Kaboorani and Riedl 2015); all of this is dependent on the nature of the polymer and filler and the processing conditions.

The influence of fillers on the material gloss is related with the surface topography achieved in the composite. Materials with aggregated fillers exhibit greater surface roughness so that they are less bright than other homogeneous material with a smoother surface. Fortunati et al. (2016) studied the homogeneity of CNC and cellulose nano-fibril (CNF) dispersion in wheat gluten composites and observed changes in the material gloss as a function of the filler. In the case of bionanocomposites that are reinforced with CNC, the values of gloss increase as a function of the filler percentage while the opposite behavior was observed in the CNF-reinforced materials. This could be related with the presence of CNF aggregates on the composite surface, evidenced by optical microscopy, whereas in CNC nanocomposites, nanoparticles were homogeneously distributed in the matrix. Cano et al. (2015) observed that the addition of CNCs to pea starch-PVA matrices did not affect the gloss values, as compared with the control samples, which was attributed to the good CNC dispersion in the biopolymer blends, with strong adhesion forces between the filler and the matrix.

4.6 The Effect of Reinforcing Agents on the Material Biodegradability

The disintegration and biodegradation behavior of the materials is analyzed through their composting under controlled aerobic processes, designed to produce organic residues from the biodegradable parts of the material, by the action of microorganisms. In this sense, ISO standards establish methodologies, where specific disposal pathways, specific time frames and criteria are indicated in order to unify a proper composting analysis (Cano et al. 2016). The biodegradation behavior is a crucial factor for the purposes of developing environmentally-friendly packaging materials. Biodegradable polymers are able to decompose in the medium by the enzymatic action of microorganisms in a defined period (Nair et al. 2017). In the disintegration and biodegradation processes produced by the action of microorganisms (bacteria, fungi and algae), these identify the polymer as a source of energy to produce organic residues from the biodegradable materials. These chemically react under the microbial enzymatic action and the polymer chains are fragmented (Cano et al. 2016; Nair et al. 2017).

Table 4.7 shows the effect of some reinforcing agents on the composite disintegration or biodegradation|, using different composting conditions. The degradation rate of the materials varies according to the type of polymer and reinforcing agent.

Table 4.7 Effect of reinforcing agents on the material biodegradability

Composite material	Formulation	Processing method	Biodegradation test	Control method	Effect of filler on biodegradation of polymer matrix	Reference
Polymer/micro-filler						
PCL/cellulose fibres from cotton	5 and 15 wt% filler	Brabender Plastograph blending and compression moulding	– Samples: 10 mm × 20 mm × 0.3–0.5 mm – Compost material: natural microflora present in soil (Pinocha type) – Incubation: 20 °C, 40% HR under aerobic conditions – Time tested: 6 months	– Average weight loss (%WL)	The high hydrophilicity of the natural fibres promoted the water intake and provides a rougher support for microbial growth	Ludueña et al. (2012)
Polymer/nano-filler						
PCL/CNC from cotton	5 and 15 wt% filler	Brabender Plastograph mixer and compression moulding	– Samples: 10 mm × 20 mm × 0.3–0.5 mm – Compost material: natural microflora present in soil (Pinocha type) – Incubation: 20 °C, 40% HR under aerobic conditions – Time tested: 6 months	– Average weight loss (%WL)	The crystalline structure of CNC promoted the water intake	Ludueña et al. (2012)
PLA-PHB/CNC from MCC	1 and 5 wt% CNC 15 wt% ATBC as plasticizer	Electrospinning	– Sample: 15 mm × 15 mm – Compost materials: 10% compost, 30% rabbit food, 10% starch, 5% sugar, 1% urea, 4% corn oil, 40% sawdust and 50 wt% of water content – Incubation: 58 °C, under aerobic conditions – Time tested: 28 days	– Photographs of physical changes – SEM analysis	The presence of nano-filler speeded up the disintegration process Matrices became breakable after 10 days of composting	Arrieta et al. (2015)

Table 4.7 (continued)

Composite material	Formulation	Processing method	Biodegradation test	Control method	Effect of filler on biodegradation of polymer matrix	Reference
PLA/PVAc/CNC from Whatmann paper	3 wt% CNC and 10 wt% Glycidyl methacrylate resect to PVAc	Extrusion	– Samples: – – Compost material: sawdust, rabbit food, starch, sugar, oil and urea – Incubation: 58 °C, 50% humidity under aerobic conditions – Time tested: 60 days	– Disintegration value	Variation in terms of mass loss was limited because the water attack starts on the more susceptible component with hydroxyl groups available on the surface	Haque et al. (2017)
PLA/CNC from *Phormium tenax* leaves	1 and 3 wt% CNC with or without 20 wt% limonene as plasticizer	Extrusion and compression moulding	– Samples: 15 mm × 15 mm × 0.05 mm – Compost material: compost inoculum, sawdust, rabbit food, starch, sugar, oil, urea and 50 wt% water of content – Incubation: 58 °C, under aerobic conditions – Time tested: 14 days	– Photographs of physical changes – FESEM – FTIR – Disintegration value	The CNCs increased the crystallinity and inhibited water diffusion into the material, causing a lower disintegration rate	Fortunati et al. (2014)
PLA-PBS/CNC from *Carmagnola* carded hemp fibres	1 and 3 wt% CNC with/without surfactant	Casting	– Samples: 15 mm × 15 mm × 0.03 mm – Compost material: sawdust, rabbit food, compost inoculum, starch, sugar, oil and urea – Incubation: 58 °C, 50%HR under aerobic conditions – Time tested: 90 days	– Photographs of physical changes – Degree of disintegration (D)	CNCs benefited disintegration process due to their hydrophilic nature Hydrophilic surfactant improved the CNC dispersion in the matrices and the D parameter	Luzi et al. (2016)

Composite material	Formulation	Processing method	Biodegradation test	Control method	Effect of filler on biodegradation of polymer matrix	Reference
PLA/Ag-NPs	1 wt% CNC and 2 ratio of antioxidant	Extrusion and compression moulding	– Samples: $15 \times 5 \times 2$ mm^3 – Compost material: sawdust, rabbit food, starch, oil and urea-Incubation: 58 °C, under aerobic conditions – Time tested: 35 days	– DSC – FTIR – FESEM – Disintegration test	Ag-NPs and thymol (plasticizer) accelerated the PLA hydrolysis process Ag atoms could catalyse the disintegration process	Ramos et al. (2014)
Starch-PVA/ Ag-NPs	0.6, 6, 16 and 32% respect to starch ratio	Casting	– Compost material: organic fraction of solid municipal waste and vermiculite – Incubation: 58 °C, under aerobic conditions – Time tested: 45 days	– CO$_2$ produced – Disintegration test	Ag-NPs enhanced film disintegration due to the incorporation of structural discontinuities in the composite network Low Ag-NPs concentrations are recommended to avoid alterations in the bio-degradation process	Cano et al. (2016)
PLA/ Montmorillonite and Fluoro-hectorite nano-clays	5 and 10 wt% filler	Extrusion and compression moulding	– Samples: 75 mm × 0.5 mm – Compost material: pruning residues – Incubation: 40 °C, 50 70% RH under aerobics conditions – Time tested: 35 days	– Photographs of physical changes – DSC – Tensile properties	The hydroxyl groups of silicate layers and/or of their organic modifiers promoted biodegradation of the PLA matrix	Fukushima et al. (2013)

Table 4.7 (continued)

Composite material	Formulation	Processing method	Biodegradation test	Control method	Effect of filler on biodegradation of polymer matrix	Reference
Methyl cellulose/ Montmorillonite	1, 2, 3, 5 and 10 wt% filler	Casting	– Samples: 5 g of fragmented samples – Compost material: 70% topsoil and 30% composted manure. 80–100% moisture content – Incubations: 25 °C in dark cabinet – Time tested: 42 days	– CO$_2$ produced	The filler improved the composite barrier properties, restricting the segmental movement at the interface The silicate layers on the film surface could hide part of the polymer chains, making biodegradation more difficult	Rimdusit et al. (2008)
Alginate/Chitin whiskers	0.1 and 2 wt% filler	Extrusion	– Medium: Tris-HCl buffer solution (pH =7.4) or buffer solution containing 0.4 mg/mL of lysozyme (pH = 7.4) – Incubation: Shaking incubator at 37 °C – Time tested: 5 days	– SEM – Mechanical integrity	Biodegradation process was improved by lysozyme Surface of the samples was smoother and weight loss was higher	Watthanaphanit et al. (2008)
Poly(butylene/ triethylene succinate)/CNC from MCC	1 and 5 wt% CNC, with surfactant	Extrusion and compression moulding	– Samples: 20 × 30 mm and ~35 mg of weight – Compost material: 22.08% organic carbon, 13.44% humic and fulvic carbon – Incubation: 58 °C – Time tested: 30 days	– Residual mass – Visual observations – SEM	The surface hydrophilicity increased when the CNC content rose. This provoked higher resistance to water uptake and diffusion, delaying disintegration process	Fortunati et al. (2017)

Ludueña et al. (2012) analysed the biodegradation behavior of PCL composites containing cotton fibres and CNC from cotton fibres at 20 °C and 40% relative humidity (RH), using compost material with the natural microflora present in soil (Pinocha type). The analysis was carried out throughout 6 months by controlling the average weight loss of the samples. They observed that the biodegradability of the reinforced material was enhanced with the addition of both kinds of fillers, which was attributed to the high hydrophilicity of the natural fibres, which promoted water transport and provided a rougher support for microbial growth. PCL is semicrystalline polyester and the reduction in the degree of crystallinity benefits the biodegradation process, since the amorphous regions are more quickly attacked by microorganisms. Similar conclusions were reported by Luzi et al. (2016), for PLA-PBS composites reinforced with CNC from *Carmagnola* carded hemp fibres submitted to composting in sawdust, rabbit food, compost inoculum, starch, sugar, oil and urea, at 58 °C and 50% HR throughout 90 days. The authors evaluated the degree of disintegration (D) and the physical changes and observed that the presence of CNC in the matrices benefited the biodegradation process. Likewise, the use of a hydrophilic surfactant improved the dispersion of cellulosic nano-fillers in the matrices and the D parameter. The biodegradation in blends with PBS was retarded due to the more hydrophobic and semicrystalline nature of PBS. However, Fortunati et al. (2014) observed CNC from *Phormium tenax* leaves had the opposite effect on PLA composites. The presence of CNCs increased the crystallinity of the composites, limiting the water transport through the PLA matrices. When limonene was incorporated as plasticiser in the PLA composites, an increase in the biodegradation rate was observed due to an improvement in the chain mobility, which favoured the polymer erosion. Nevertheless, each sample was 90% disintegrated after 14 days of composting, which is within the limit defined by the ISO 20200. In PBS composites containing CNC from MCC, similar behavior was observed, but the hydrophobic nature of PBS and the degree of crystallinity slowed down the biodegradation process (Fortunati et al. 2017).

The addition of inorganic nano-fillers provoked similar effects to those brought about by organic fillers in the biodegradation process of composites. Ramos et al. (2014) studied the effect of Ag nanoparticles on the disintegrability of PLA composites at 58 °C, using a compost media made from sawdust, rabbit food, starch, oil and urea, throughout 35 days. They assumed that Ag atoms could catalyse the disintegration process and the synergies between the Ag-NPs and thymol could accelerate the hydrolysis process. The presence of homogeneously dispersed thymol in the PLA matrix could promote the polymer chain mobility and thus, diffuse the water molecules through the PLA structure. Cano et al. (2016) also observed an increase in the film disintegration rate when different ratios of Ag-NPs were incorporated in starch-PVA composites. Nevertheless, the generation of CO_2 as the result of total carbon conversion was notably reduced when the Ag ratio increased, probably due to its antimicrobial effect on the microorganisms responsible for the biodegradation process. Fukushima et al. (2013) also observed an increase in the disintegration rate of PLA composites with Mnt and fluorohectorite nano-clays at 5

and 10 wt%. The biodegradation of PLAl matrices was enhanced by the catalytic effect of the hydroxyl groups of silicate layers.

It is remarkable that many factors can affect the degradation rate of composites. The environmental conditions have a significant impact on microbial growth and parameters, such as humidity, temperature, pH, salinity, oxygen pressure, and microbial nutrients, have a great influence on the microbial degradation of polymers. The biodegradation process also depends on the chemical and physical characteristics of the biopolymer. Nair et al. (2017) report that the enzymatic degradation implies the binding of the enzyme to the bioplastic surface, followed by hydrolytic split; biopolymers are degraded into low-molecular-weight oligomers, dimers, monomers and finally mineralised to CO_2 and H_2O. For instance, the biodegradation of PLAl starts with the hydrolysis of the polymer chains promoted by the water diffusion in the matrices. When the molecular weight reaches about 10,000–20,000 g mol^{-1}, microorganisms, such as fungi and bacteria, can metabolise the macromolecules, converting them into carbon dioxide, water and humus (Luzi et al. 2016; Fortunati et al. 2014; Fukushima et al. 2013). Several microorganisms are able to decompose biomaterials, such as *Tritirachium album, Amycolatopsis* strain 41*, Amycolatopsis* sp. strain 3118*, Kibdelosporangium aridum* for PLA, *Penicillium* sp. strain 26–1 (ATCC 36507), *Aspergillus* sp. strain ST-01*, Clostridium* sp. for PCL or *Pseudomonas* sp., *Bacillus* sp., *Streptomyces* sp., *Aspergillus* sp. for PHB (Nair et al. 2017).

4.7   Final Remarks

The incorporation of reinforcing agents of different natures (organic or inorganic) and size (micro or nano-sized) represents a good strategy for the purposes of improving the functional properties of biopolymers. In general, improved barrier and mechanical properties can be achieved when compatible micro or nano particles are adequately dispersed in the polymer matrix. Nano-particles are generally more effective, but their natural tendency towards aggregation makes the dispersion process difficult, requiring carefully designed dispersion techniques. To a great extent, the surface interactions of the filler with the polymer matrix define the effectiveness of the reinforcement and the promotion of barrier properties. Therefore, if materials with optimal functionality are to be obtained, it is of relevance to make an adequate selection of both the filler for a determined polymer matrix and the processing conditions necessary to ensure high dispersion levels of the particles. Composite biodegradability is generally enhanced by the presence of the filler dispersed particles. However, the total conversion of carbon to CO_2 through the action of microorganisms could be limited when the filler exhibits antimicrobial action.

References

Abdollahi M, Alboofetileh M, Rezaei M et al (2013) Comparing physico-mechanical and thermal properties of alginate nanocomposite films reinforced with organic and/or inorganic nanofillers. Food Hydrocoll 32:416–424

Abdul Khalil HP, Davoudpour Y, Saurabh C et al (2016) A review on nanocellulosic fibres as new material for sustainable packaging: process and applications. Renew Sust Energ Rev 64:823–836

Alves JS, dos Reis KC, Menezes EGT et al (2015) Effect of cellulose nanocrystals and gelatin in corn starch plasticized films. Carbohydr Polym 115:215–222

Arrieta M, Peltzer M, López J et al (2014a) Functional properties of sodium and calcium caseinate antimicrobial active films containing carvacrol. J Food Eng 121:94–101

Arrieta MP, Fortunati E, Dominici F et al (2014b) Multifunctional PLA–PHB/cellulose nanocrystal films: processing, structural and thermal properties. Carbohydr Polym 107:16–24

Arrieta MP, López J, Kenny JM et al (2015) Biodegradable electrospun bionanocomposite fibers based on plasticized PLA–PHB blends reinforced with cellulose nanocrystals. Ind Crop Prod 96:290–301

ASTM (2003) Standard test method for determining aerobic biodegradation of plastic materials under controlled composting conditions, incorporating thermophilic temperatures. Standards designations: D5338. In: Annual book of ASTM standards. American Society for Testing and Materials, Philadelphia, PA

Azeredo HMC (2009) Nanocomposites for food packaging applications. Food Res Int 42:1240–1253

Azeredo HMC, Rosa MF, Mattoso LHC (2017) Nanocellulose in bio-based food packaging applications. Ind Crop Prod 97:664–671

Bera A, Dubey S, Bhayani K et al (2015) Microbial synthesis of polyhydroxyalkanoate using seaweed-derived crude levulinic acid as co-nutrient. Int J Biol Macromol 72:487–494

Berthet MA, Angellier-Coussy H, Chea V et al (2015) Sustainable food packaging: valorising wheat straw fibres for tuning PHBV-based composites properties. Compos Part A Appl Sci Manuf 72:139–147

Bonilla J, Fortunati E, Vargas M (2013) Effects of chitosan on the physicochemical and antimicrobial properties of PLA films. J Food Eng 119(2):236–243

Boonterm M, Sunyadeth S, Dedpakdee S et al (2015) Characterization and comparison of cellulose fiber extraction from rice straw by chemical treatment and thermal stem explosion. J Clean Prod 134:592–599

Boumail A, Salmieri S, Klimas E et al (2013) Characterization of trilayer antimicrobial diffusion films (ADFs) based on methylcellulose−polycaprolactone composites. J Agric Food Chem 61:811–821

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

Cano A, Fortunati E, Cháfer M et al (2015) Effect of cellulose nanocrystals on the properties of pea starch–poly(vinyl alcohol) blend films. J Mater Sci 50:6979–6992

Cano A, Cháfer M, Chiralt A et al (2016) Biodegradation behaviour of starch-PVA films as affected by the incorporation of different antimicrobials. Polym Degrad Stab 132:11–20

Cao X, Chen Y, Chang PR et al (2008) Green composites reinforced with hemp nanocrystals in plasticized starch. J Appl Polym Sci 109(6):3804–3810

Carbone M, Donia DM, Sabbatella G et al (2016) Silver nanoparticles in polymeric matrices for fresh food packaging. J King Saud Univ Sci 28:273–279

Cavallaro G, Lazzara G, Milioto S (2013) Sustainable nanocomposites based on halloysite nanotubes and pectin/polyethylene glycol blend. Polym Degrad Stab 98:2529–2536

Chen D, Lawton D, Thompson MR et al (2012) Biocomposites reinforced with cellulose nanocrystals derived from potato peel waste. Carbohydr Polym 90:709–716

Cheng Y, Deng S, Chen P et al (2009) Polylactic acid (PLA) synthesis and modifications: a review. Front Chem China 4(3):259–264

Cho J, Joshi MS, Sun CT (2006) Effect of inclusion size on mechanical properties of polymeric composites with micro and nano particles. Compos Sci Technol 66(13):1941–1952

Correa JP, Molina V, Sanchez M et al (2017) Improving ham shelf life with a polyhydroxybutyrate/polycaprolactone biodegradable film activated with nisin. Food Packaging Shelf Life 11:31–39

Corsello FA, Bolla PA, Anbinder PS et al (2017) Morphology and properties of neutralized chitosan-cellulose nanocrystals biocomposite films. Carbohydr Polym 156:452–459

Dash S, Swain SK (2013) Synthesis of thermal and chemical resistant oxygen barrier starch with reinforcement of nano silicon carbide. Carbohydr Polym 97:758–763

De Paula EL, Roig F, Mas A et al (2016) Effect of surface-grafted cellulose nanocrystals on the thermal and mechanical properties of PLLA based nanocomposites. Eur Polym J 84:173–187

Dominguez-Martinez B, Martínez-Flores H, Berrios J et al (2017) Physical characterization of bio-degradable films based on chitosan, polyvinyl alcohol and opuntia mucilage. J Polym Environ 25(3):683–691

El Miri N, Abdelouahdi K, Barakar A et al (2015) Bio-nanocomposite films reinforced with cellulose nanocrystals: rheology of film-forming solutions, transparency, water vapor barrier and tensile properties of films. Carbohydr Polym 129:156–167

El-Hadi A (2017) Increase the elongation at break of poly (lactic acid) composites for use in food packaging films. Sci Rep 7:46767. https://doi.org/10.1038/srep46767

Emadian SM, Onay TT, Demirel B (2017) Biodegradation of bioplastics in natural environments. Waste Manag 59:526–536

Fabra MJ, Talens P, Gavara R et al (2012) Barrier properties of sodium caseinate films as affected by lipid composition and moisture content. J Food Eng 109(3):372–379

Fabra MJ, López-Rubio A, Lagaron JM (2014) Biopolymers for food packaging applications. In: Aguilar de Armas MR, Román JS (eds) Smart polymers and their applications. Elsevier, Amsterdam, pp 476–509

Fabra MJ, López-Rubio A, Ambrosio-Martín J et al (2016) 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 Hydrocoll 621:261–268

Flauzino Neto WP, Silvério HA, Dantas NO et al (2013) Extraction and characterization of cellulose nanocrystals from agro-industrial residue soy hulls. Ind Crop Prod 42:480–488

Follain NG, Belbekhouche S, Bras J et al (2013) Water transport properties of bionanocomposites reinforced by Luffa cylindrica cellulose nanocrystals. J Membr Sci 427:218–229

Fortunati E, Puglia D, Luzi F et al (2013a) Binary PVA bio-nanocomposites containing cellulose nanocrystals extracted from different natural sources: part I. Carbohydr Polym 97:825–836

Fortunati E, Pelltzer M, Armentano I et al (2013b) Combined effects of cellulose nanocrystals and silver nanoparticles on the barrier and migration properties of PLA nano-biocomposites. J Food Eng 118:117–124

Fortunati E, Luzi F, Puglia D et al (2014) Investigation of thermo-mechanical, chemical and degradative properties of PLA-limonene films reinforced with cellulose nanocrystals extracted from Phormium tenax leaves. Eur Polym J 56:77–91

Fortunati E, Luzi F, Puglia D et al (2015) Processing of PLA nanocomposites with cellulose nanocrystals extracted from *Posidonia oceanica* waste: innovative reuse of coastal plant. Ind Crop Prod 67:439–447

Fortunati E, Luzi F, Jiménez A et al (2016) Revalorization of sunflower stalks as novel sources of cellulose nanofibrils and nanocrystals and their effect on wheat gluten bionanocomposite properties. Carbohydr Polym 149:357–368

Fortunati E, Gigli M, Luzi F et al (2017) Processing and characterization of nanocomposite based on poly(butylene/triethylene succinate) copolymers and cellulose nanocrystals. Carbohydr Polym 165:51–60

Fukushima K, Tabuani D, Arena M et al (2013) Effect of clay type and loading on thermal, mechanical properties and biodegradation of poly(lactic acid) nanocomposites. React Funct Polym 73:540–549

Giménez B, López de Lacey A, Pérez-Santín E et al (2013) Release of active compounds from agar and agar–gelatin films with green tea extract. Food Hydrocoll 30:264–271

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

Graupner N, Ziegmann G, Wilde F et al (2016) Procedural influences on compression and injection moulded cellulose fibre-reinforced polylactide (PLA) composites: influence of fibre loading, fibre length, fibre orientation and voids. Compos Part A Appl Sci Manuf 81:158–171

Gutiérrez TJ (2017) Chitosan applications for the food industry. In: Ahmed S, Ikram S (eds) Chitosan: derivatives, composites and applications. Wiley-Scrivener, Beverly, MA, pp 183–232. EE.UU. ISBN: 978-1-119-36350-7. https://doi.org/10.1002/9781119364849.ch8

Gutiérrez TJ (2018) Biodegradability and compostability of food nanopackaging materials. In: Cirillo G, Kozlowski MA, Spizzirri UG (eds) Composite materials for food packaging. Wiley-Scrivener, Beverly, MA, pp 263–289 EE.UU. ISBN: 978-1-119-16020-5. https://doi.org/10.1002/9781119160243.ch9

Gutiérrez TJ, Alvarez VA (2017) Cellulosic materials as natural fillers in starch-containing matrix-based films: a review. Polym Bull 74(6):2401–2430. https://doi.org/10.1007/s00289-016-1814-0

Gutiérrez TJ, Alvarez VA (2018) Bionanocomposite films developed from corn starch and natural and modified nano-clays with or without added blueberry extract. Food Hydrocoll 77:407–420. https://doi.org/10.1016/j.foodhyd.2017.10.017

Gutiérrez T, González P, Medina C et al (2017) Effect of filler properties on the antioxidant response of thermoplastic starch composites. In: Thakur V, Thakur M, Kessler M (eds) Handbook of composites from renewable materials. Wiley, New York, pp 337–369. https://doi.org/10.1002/9781119441632.ch14

Gutiérrez TJ, Ollier R, Alvarez VA (2018) Surface properties of thermoplastic starch materials reinforced with natural fillers. In: Thakur V, Thakur M (eds) Functional biopolymers. Springer series on polymer and composite materials. Springer, Cham, pp 131–158. https://doi.org/10.1007/978-3-319-66417-0_5

Haque MM, Puglia D, Fortunati E et al (2017) Effect of reactive functionalization on properties and degradability of poly(lactic acid)/poly(vinyl acetate) nanocomposites with cellulose nanocrystals. React Funct Polym 110:1–9

He J, Chong Yap R, Wong S et al (2015) Polymer composites for intelligent food packaging. J Mol Eng Mater 3(1):1–12

Heitmann A, Patrício P, Coura I et al (2016) Nanostructured niobium oxyhydroxide dispersed poly (3-hydroxybutyrate) (PHB) films: highly efficient photocatalysts for degradation methylene blue dye. Appl Catal B Environ 189:141–150

Herrera N, Salaberria AM, Mathe A et al (2016) Plasticized polylactic acid nanocomposite films with cellulose and chitin nanocrystals prepared using extrusion and compression molding with two cooling rates: effects on mechanical, thermal and optical properties. Compos Part A 83:89–97

Hossain ABMS, Ibrahim N, AlEissa MS (2016) Nano-cellulose derived bioplastic biomaterial data for vehicle bio-bumper from banana peel waste biomass. Data Brief 8:286–294

Hu Z, Ballinger S, Pelton R et al (2015) Surfactant-enhanced cellulose nanocrystal pickering emulsions. J Coll Interface Sci 439:139–138

Jiménez A, Fabra MJ, Talens P et al (2013) Physical properties and antioxidant capacity of starch–sodium caseinate films containing lipids. J Food Eng 116(3):695–702

Johar N, Ahmad I, Dufresne A (2012) Extraction, preparation and characterization of cellulose fibres and nanocrystals from rice husk. Ind Crop Prod 37:93–99

Jonoobi M, Oladi R, Davaoudpour Y et al (2015) Different preparation methods and properties of nanostructured cellulose from various natural resources and residues: a review. Cellulose 22:935–969

Kaboorani A, Riedl B (2015) Surface modification of cellulose nanocrystals (CNC) by a cationic surfactant. Ind Crop Prod 65:45–55

Kallel F, Bettaieb F, Khiari R et al (2016) Isolation and structural characterization of cellulose nanocrystals extracted from garlic straw. Ind Crop Prod 87:287–296

Kanmani P, Rhim JW (2014) Physicochemical properties of gelatin/silver nanoparticle antimicrobial composite films. Food Chem 148:162–169

Le Corre D, Angellier-Coussy H (2014) Preparation and application of starch nanoparticles for nanocomposites: a review. React Funct Polym 85:97–120

Leceta I, Guerrero P, de la Caba K (2013) Functional properties of chitosan-based films. Carbohydr Polym 93(1):339–346

Lizundia E, Fortunati E, Dominici F et al (2016) PLLA-grafted cellulose nanocrystals: role of the CNC content and grafting on the PLA bionanocomposite film properties. Carbohydr Polym 142:105–113

López OV, Ninago MD, Soledad Lencina MM et al (2015) Thermoplastic starch plasticized with alginate–glycerol mixtures: melt-processing evaluation and film properties. Carbohydr Polym 126:83–90

Ludueña L, Vázquez A, Alvarez V (2012) Effect of lignocellulosic filler type and content on the behavior of polycaprolactone based eco-composites for packaging applications. Carbohydr Polym 87:411–421

Luzi F, Fortunati E, Jiménez A (2016) Production and characterization of PLA PBS biodegradable blends reinforced with cellulose nanocrystals extracted from hemp fibres. Ind Crop Prod 93:276–289

Majeed K, Jawaid M, Hassan A et al (2013) Potential materials for food packaging from nanoclay/natural fibres filled hybrid composites. Mater Des 46:391–410

Maqsood HS, Baheti V, Wiener J et al (2016) Reinforcement of enzyme hydrolyzed longer jute micro crystals in polylactic acid. Polym Compos 39:1089–1097. https://doi.org/10.1002/pc.24036

Martino L, Berthet MA, Angellier-Coussy H et al (2015) Understanding external plasticization of melt extruded PHBV–wheat straw fibers biodegradable composites for food packaging. J Appl Polym Sci 41611:2–11

Miranda CS, Ferreira MS, Magalhães MT, Santos WJ et al (2015) Mechanical, thermal and barrier properties of starch-based films plasticized with glycerol and lignin and reinforced with cellulose nanocrystals. Mater Today Proc 2:63–69

Mizuno S, Maeda T, Kanemura C et al (2015) Biodegradability, reprocessability, and mechanical properties of polybutylene succinate (PBS) photografted by hydrophilic or hydrophobic membranes. Polym Degrad Stab 117:58–65

Moreno O, Gil A, Atarés L et al (2017) Active starch-gelatin films for shelf-life extension of marinated salmon. LWT Food Sci Technol 84:189–195

Moriana R, Vilaplana F, Karlsson S et al (2011) Improved thermo-mechanical properties by the addition of natural fibres in starch-based sustainable biocomposites. Compos Part A 42:30–40

Moustafa H, Guizani C, Dupont C et al (2016) Utilization of Torrefied coffee grounds as reinforcing agent to produce high-quality biodegradable PBAT composites for food packaging applications. ACS Sustain Chem Eng 5(2):1906–1916

Mukurubira AR, Mellem JM, Amonsou EO (2017) Effects of amadumbe starch nanocrystals on the physicochemical properties of starch biocomposite films. Carbohydr Polym 165:142–148

Muller J, González-Martínez C, Chiralt A (2017a) Combination of poly(lactic) acid and starch for biodegradable food packaging. Materials 10. https://doi.org/10.3390/ma10080952

Muller J, González-Martínez C, Chiralt A (2017b) Poly(lactic) acid (PLA) and starch bilayer films, containing cinnamaldehyde, obtained by compression moulding. Eur Polym J 95:56–70

Nair NR, Sekhar VC, Nampoothir KM et al (2017) Biodegradation of biopolymers. In: Pandey A, Negi S, Soccol CR (eds) Current developments in biotechnology and bioengineering. Elsevier, Amsterdam, pp 739–755

Ng HM, Sin LT, Tee TT et al (2015) Extraction of cellulose nanocrystals from plant sources for application as reinforcing agent in polymers. Compos Part B 75:176–200

Ortega-Toro R, Bonilla J, Talens P et al (2017) Future of starch-based materials in food packaging. In: Vilar M (ed) Starch-based materials in food packaging: processing, characterization and application. Academic Press, London, pp 257–312

Pardo-Ibáñez P, López-Rubio A, Martínez-Sanz M et al (2014) Keratin–polyhydroxyalkanoate melt-compounded composites with improved barrier properties of interest in food packaging applications. J Appl Polym Sci 39947:1–10

Peelman N, Ragaert P, Meulenaer B et al (2013) Application of bioplastics for food packaging. Trends Food Sci Technol 32(2):128–141

Ramos M, Fortunati E, Peltzer M et al (2014) Influence of thymol and silver nanoparticles on the degradation of poly(lactic acid) based nanocomposites: thermal and morphological properties. Polym Degrad Stab 108:158–165

Requena R, Vargas M, Chiralt A (2017) Release kinetics of carvacrol and eugenol from poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) films for food packaging applications. Eur Polym J 92:185–193

Rhim JW, Wang LF, Lee Y et al (2014) Preparation and characterization of bio-nanocomposite films of agar and silver nanoparticles: laser ablation method. Carbohydr Polym 103:456–465

Rimdusit S, Jingjid S, Damrongsakkul S et al (2008) Biodegradability and property characterizations of methyl cellulose: effect of nanocompositing and chemical crosslinking. Carbohydr Polym 72:444–455

Rivero CP, Hu Y, Kwan TH et al (2017) Bioplastics from solid waste. In: Wong JWC, Tyagi RD, Pandey AR (eds) Current developments in biotechnology and bioengineering. Elsevier, Amsterdam, pp 1–26

Rocca-Smith J, Marcuzzo E, Karbowiak T et al (2016) Effect of lipid incorporation on functional properties of wheat gluten based edible films. J Cereal Sci 69:275–282

Rombouts I, Lagrain B, Delcour J et al (2013) Crosslinks in wheat gluten films with hexagonal close-packed protein structures. Ind Crop Prod 51:229–235

Rosa MF, Medeiros ES, Malmonge JA et al (2010) Cellulose nanowhiskers from coconut husk fibers: effect of preparation conditions on their thermal and morphological behavior. Carbohydr Polym 81:83–92

Santos RPO, Rodrigues BVM, Ramires EC et al (2015) Bio-based materials from the electrospinning of lignocellulosic sisal fibers and recycled PET. Ind Crop Prod 72:69–76

Sanuja S, Agalya A, Umapathy MJ (2014) Studies on magnesium oxide reinforced chitosan bionanocomposite incorporated with clove oil for active food packaging application. Int J Polym Mater Polym Biomater 63:733–740

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

Shih YF, Chang WC, Liu WC et al (2014) Pineapple leaf/recycled disposable chopstick hybrid fiber-reinforced biodegradable composites. J Taiwan Inst Chem Eng 45(4):2039–2046

Slavutsky AM, Bertuzzi MA (2014) Water barrier properties of starch films reinforced with cellulose nanocrystals obtained from sugarcane bagasse. Carbohydr Polym 110:53–61

Sung SH, Chang Y, Han J (2017) Development of polylactic acid nanocomposite films reinforced with cellulose nanocrystals derived from coffee silverskin. Carbohydr Polym 169:495–503

Van den Broek L, Knoop R, Kappen F et al (2015) Chitosan films and blends for packaging material. Carbohydr Polym 116:237–242

Watthanaphanit A, Supaphol P, Tamura H et al (2008) Fabrication, structure, and properties of chitin whisker-reinforced alginate nanocomposite fibers. J Appl Polym Sci 110:890–899

Xiao S, Liu B, Wang Y et al (2014) Efficient conversion of cellulose into biofuel precursor 5-hydroxymethylfurfural in dimethyl sulfoxide–ionic liquid mixtures. Bioresour Technol 151:361–366

Zhou Y, Fan M, Chen L (2016) Interface and bonding mechanisms of plant fibre composites: an overview. Compos Part B 101:41–45

Zubeldía F, Ansorena M, Marcovich N (2015) Wheat gluten films obtained by compression molding. Polym Test 43:68–77