

Biodegradable Starch Nanocomposites

N.L. García, L. Famá, N.B. D'Accorso and S. Goyanes

Abstract Biodegradable thermoplastic materials offer great potential to be used in food packaging or biomedical industry. In this chapter we will present a review of the research done on starch and starch nanocomposites. In the case of nanocomposites based on starch, special attention will be given to the influence of starch nanoparticles, cellulose whiskers, zinc oxide nanorods, antioxidants, and antimicrobial inclusion on the physicochemical properties of the materials. The discussion will be focused on structural, mechanical, and barrel properties as well as on degradation, antibacterial and antioxidant activities. Finally, we will discuss our perspectives on how future research should be oriented to contribute in the substitution of synthetic materials with new econanocomposites.

Keywords Starch • Nanocomposites • Starch nanoparticles • Cellulose • Layered silicate • Antioxidant nanofillers • Antimicrobial nanofillers

Abbreviations

σ	Tensile strength
Ag-NP	Silver nanoparticles
B-NC	Bamboo nanocrystals
C-NC	Cellulose nanocrystals
C-NF	Cellulose nanofibers
C-NW	Cellulose nanowhiskers
CH	Chitosan

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CH-NP	Chitosan nanoparticles
CA-S-NP	Citric acid-modified starch nanoparticles
CO ₂	Carbon dioxide
CMC	Carboxymethylcellulose sodium
D	Diameter
DAS	Dialdehyde starch
F-CN	Flax cellulose nanocrystals
HC-NC	Hemp (<i>Cannabis sativa</i>) cellulose nanocrystals
<i>k</i>	Aspect ratio
<i>L</i>	Length
MCC	Microcrystalline cellulose
MEO	Pennyroyal
MFC	Microfibrillated cellulose
MMT	Montmorillonite
PLA	Polylactic acid
PO ₂	Oxygen permeability
PVA	Polyvinyl alcohol
REX	Reactive extrusion
RTE	Ready-to-eat
S-NP	Starch nanoparticles
SME	Specific mechanical energy
<i>T_d</i>	Decomposition temperature
<i>T_g</i>	Glass transition temperature
TiO ₂	Titanium oxide
TiO ₂ -NP	Titanium oxide nanoparticles
<i>T_m</i>	Melting temperature
TPS	Thermoplastic starch
WVP	Water vapor permeability
UV	Ultraviolet spectroscopy
wt%	Weight percentage
ZEO	Zataria multiflora Boiss
ZnO	Zinc oxide
ZnO-NP	Zinc oxide nanoparticles
ZnO-NP-CMC	Zinc oxide nanoparticles-carboxymethylcellulose sodium
ZnO-NR	Zinc oxide nanorods

1 Introduction

Nowadays, petroleum-derived polymers are the most widely used materials in the packaging industry. However, there are important problems related with their use, such as no renewability, high costs, and potential pollution they can create (Thakur et al. 2012a, b, c, d, e). The extensive degradation time associated to these

materials, which take hundreds of years and involves the production of high CO₂ levels, is the main cause of the environmental pollution and residues accumulation produced (Chaudhry et al. 2008; de Azedero 2009; Arora and Padua 2010; Vieira et al. 2011; González Seligra et al. 2013). A new generation of materials based on biopolymers will reduce the polymers and plastics industry dependency on petroleum, creating more sustainable alternatives (Thakur et al. 2014a, b, c, d, e).

Bio-based polymers are derived from renewable resources such as plant and animal mass from CO₂. They can be divided into two groups: natural or synthetic polymers. Natural bio-based polymers are polymers synthesized by living organisms such as animals, plants, algae, and microorganisms. The most abundant bio-based polymers in nature are polymers from biomass (from gro-resources) as polysaccharides: starches (Famá et al. 2005, 2006; Rojas-Graü et al. 2007; Flores et al. 2007; Ma et al. 2008a; Jiménez et al. 2013; Lamanna et al. 2013; Souza et al. 2013), lignocellulosic products (Santiago-Silva et al. 2009; Sayanjali et al. 2011; Pastor et al. 2013) and others as pectin, chitosan/chitin, and gums (Norajit et al. 2010; Martins et al. 2012; Elsabee and Abdou 2013; Rubilar et al. 2013), protein and lipids (Bourtoom 2009; Jiménez et al. 2010; Murillo-Martínez et al. 2011), and plants (Orliac et al. 2003; Bertan et al. 2005). In particular, polysaccharides have been the focus of research in recent decades as base materials for the development of biodegradable products (Xie et al. 2011a; Thakur et al. 2014a; Thakur and Thakur 2014a). These are a good alternative to perform biodegradable formulations due to their “green” connotation (environmentally friendly material): they are biodegradable, edible, and compostable (Ptaszek et al. 2013; He et al. 2014).

Another topic that was exhaustively investigated during the last few years was the development of biorenewable polymers-based hydrogels. They have attracted great interest for miscellaneous applications including biomedical, toxic ion removal, and water purification (Thakur and Thakur 2014a, b, c).

Constant demands for biodegradability in many products lead to the search for materials that can be produced in significant amounts and are versatile in terms of their properties and potential applications (Singha and Thakur 2009a, b, c, d, e). In this context, recent innovations in polymer materials are widely discussed in the literature, presenting improvements in packaging, surgery, pharmaceutical, biomedical, hygiene, and food industrial uses (Bierhalz et al. 2012; Bouyer et al. 2012; Prajapati et al. 2013; Ghorl et al. 2014; Suvakanta et al. 2014; Famá et al. 2014). In particular, cellulose and clays are two of the more common fillers used in the development of biodegradable compounds (Tjong 2006; Lu and Mai 2007; Thakur et al. 2010a; Müller et al. 2011; Sadegh-Hassani and Nafchi 2014; Thakur et al. 2014b; Thakur et al. 2014b).

One of the most used polymers for the development of biodegradable materials is the starch, mainly due to its low cost and the possibility of obtaining it from several renewable resources (Tharanathan 2003; Lu et al. 2005; Romero-Bastida et al. 2005; Sorrentino et al. 2007; Talja et al. 2007). The use of different starches in their natural form or as modified by chemical cross-linking has been extensively investigated. Some of the advantages of modified starch-based films are the improvement of mechanical and barrier properties, as well as thermal stability

(Ghanbarzadeh et al. 2011; Zuraida et al. 2012; Olsson et al. 2013; Gutiérrez et al. 2014a, b).

In order to help food preservation, several researches have considered the use of many additives or food components into biodegradable starch films as a way of improving food shelf life (García et al. 1998; Petersson and Stading 2005; Famá et al. 2010, 2011; Gutiérrez et al. 2014a, b). The great research boom in the use of starch-based composites is reflected in the significant number of patents and papers in the literature (Arvanitoyannis et al. 1998; Rindlav-westling et al. 1998; Myllärinen et al. 2002; Famá et al. 2007; Hansen and Plackett 2008; Ma et al. 2008a; Famá et al. 2009a, b; Goyanes et al. 2010; Li et al. 2011b; García et al. 2011; Famá et al. 2012).

However, so far there are few applications that have been accomplished. Although starches have many advantages over synthetic materials, their use is still strongly limited because they have worse mechanical properties and higher permeation compared to other nonnatural polymers (Hansen and Plackett 2008; Dhakal and Zhang 2012). The incorporation of micro- and nano-sized fillers into starch materials has been the topic of many studies in order to overcome these disadvantages (Ma et al. 2009; Famá et al. 2009a, b, 2010, 2011, 2012; Cheviron et al. 2014; Lopez et al. 2014).

Many packaging industries are trying to implement composites based on starch as new technologies in bags, plates, cups, bowls, and coatings (Wong et al. 2003; Avérous and Boquillon 2004). In addition, the biomedical industry has shown a great interest in the development of starch nanocomposites for their use as sensors or stimulators of bone cells (Torres-Castro et al. 2011; Xie et al. 2011a, b). However, there are increasing scientific evidences reporting that nanoparticles can cross cellular barriers and may lead to oxidative damage and inflammatory reactions (Chaudhry et al. 2008; Lewinski et al. 2008; Bouwmeester et al. 2009).

It has been well established that the filler properties and size greatly influences mechanical properties of the final composite (Lin et al. 2011a, b). In general, smaller sized fillers improve mechanical, electrical, and thermal properties (Biercuk et al. 2002; Kilbride et al. 2002; Wei et al. 2002; Sandler et al. 2003) of the composites.

Besides improving physicochemical properties of biomaterials, the addition of certain nanofillers with antimicrobials and/or antioxidants characteristics can bring important properties such as good resistance to bacteria, mildew, and insect attack; and can also alter nutrition, flavor, texture, heat tolerance, and shelf life of the product (Lu et al. 2006; Zhao et al. 2011; Li et al. 2012; Liu and Kim 2012; Martinez-Gutierrez et al. 2012; Pérez Espitia et al. 2012).

In this chapter, a review of several researches done on the development and characterization of nanocomposites based on starch will be presented. Special attention will be given to the influences of the incorporation of starch, cellulose, layered silicate, and antioxidant and/or antimicrobial nanofillers on the physicochemical properties of the composites. The discussion will be focused on structural, mechanical, and barrel properties as well as on degradation, antibacterial and antioxidant activities.

2 Starch

2.1 Characteristics and Properties

The scientific and business community finds in starch a good alternative for biodegradable packaging applications, as it is a renewable resource widely available that can be obtained from different agricultural surplus and industrial leftovers from raw materials processing. Besides, among all biodegradable polymers, its cost is relatively low. Starch naturally occurs in a variety of botanical sources such as cereal grains (corn, wheat, and rice), seeds, legumes (lentils), and tubers (potato and cassava). In addition it is completely compostable without toxic residues, odorless, tasteless, colorless, nontoxic, and biologically absorbable (Wong et al. 2003).

Starch is a polymeric carbohydrate composed of anhydroglucose units, which is deposited in plant tissues as insoluble semicrystalline granules that vary in shape, size and structure, depending on their origin. Usually, it is mostly composed by a mixture of two biopolymers (glucans): amylose (straight chain) and amylopectin (branched chain). The structure of the starch granule depends on the way in which amylose and amylopectin are associated and distributed (Zavareze and Guerra Días 2011). The ratio between amylose and amylopectin varies depending on the starch source. In regular starches, amylose constitutes about 15–30 % of total starch (Hoover et al. 2010).

Amylose is essentially a linear structure of α -1,4 linked glucose units (Fig. 1a). The large number of hydroxyl groups in its structure confers hydrophilic properties to the polymer, resulting in a material with high affinity for moisture. Because of its linear nature, mobility and the presence of many hydroxyl groups along the

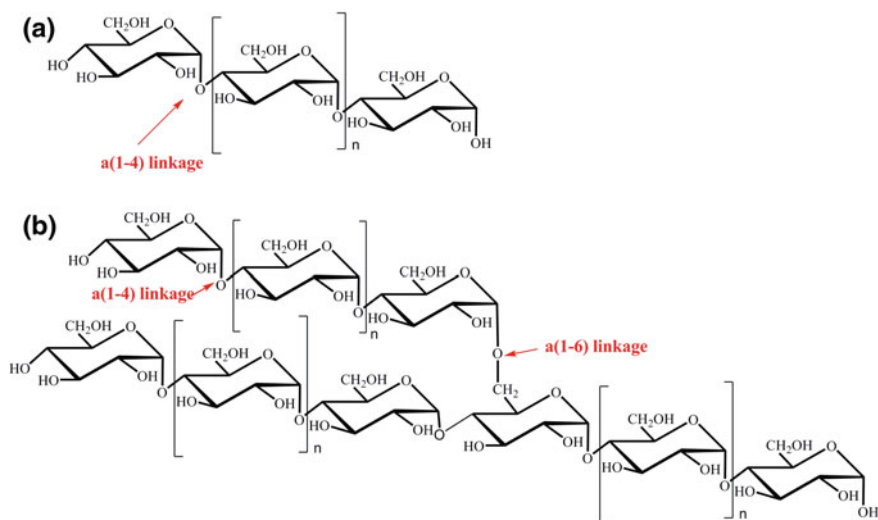


Fig. 1 Chemical structures of amylose (a) and amylopectin (b)

polymer chains, amylose molecules tend to orient themselves parallel to each other and approach each other near enough to allow formation of hydrogen bonds between adjacent chains. It is widely accepted that the most favorable three-dimensional conformation for amylose is a double helix, which is able to pack into regular arrays (Zobel 1994).

Amylopectin is a highly branched structure of short α -1,4 chains linked by α -1,6 bonds containing 10–60 glucose units and side chains with 15–45 glucose units with an average of 5 % of links α -(1–6) in branching points (Fig. 1b) (Van der Maarel et al. 2002). The molecular weight of amylopectin is about 1000 times the molecular weight of amylose and ranges from 1×10^7 to 5×10^8 g/mol (You et al. 2002). Amylopectin chains are arranged radially within the granule with their nonreducing terminal ends oriented toward the surface. These are composed by alternating crystalline areas (as a double helix) and amorphous areas with regions of branching points (Zavareze and Guerra Dias 2011).

Amylose content and branches length and placement in amylopectin are the major determinant factors of starch functional properties, such as water absorption, gelatinization and pasting, retrogradation, and susceptibility to enzymatic attack (Jane 2007; Copeland et al. 2009). According to their origin, starches possess differing amylose and lipid-complexed amylose contents, amylopectin chain-length distributions, relative crystallinity, microstructures, swelling behavior, gelatinization properties, and pasting/rheological characteristics (Bertolini et al. 2003; Kim and Huber 2008; Salman 2009). Due to their strong and flexible structure, transparency (derived from the linear structure of amylose), and their resistant to fats and oils, starch films are useful for numerous applications in food industry. Their functional properties depend on the source but are also affected by other factors like chemical modification, system composition, pH, and ionic strength of the media.

Table 1 shows the amylose and amylopectin content of starches from different sources.

Table 1 Amylose and amylopectin content of starch from different sources

Type of starch	Amylose (%)	Amylopectin (%)	References
Amylomaize	48–77	23–52	Cuq et al. (1977); Takeda et al. (1989)
Banana	17–24	76–83	Cuq et al. (1977); Moongngarm (2013)
Corn	17–25	75–83	Cuq et al. (1977); Sandhu et al. (2007)
Cush-cush Yam	9–15	85–91	Gutierrez et al. (2014a); Pérez et al. (2012)
Chickpeas	30–40	60–70	Cuq et al. (1977); Polesi et al. (2011)
High-amylose corn	55–70	30–45	Sandstedt (1961); Halsall et al. (1948); Cuq et al. (1977)
Potato	17–24	76–83	Rosin et al. (2002); Svegmarm et al. (2002); Vasanthan et al. (1999)
Rice	15–35	65–85	Cuq et al. (1977)
Sorghum	25	75	Cuq et al. (1977)
Tapioca (cassava)	19–22	28–81	Cuq et al. (1977); Pérez et al. (2012); Gutierrez et al. (2014a)
Wheat	20–25	75–80	Cuq et al. (1977)
Waxy	<1	>99	Cuq et al. (1977)

Starches also contain minor components such as protein (0.05–0.5 wt%), lipids (0.1–1.7 wt%), inorganic substances (0.1–0.3 wt% of ash), and non-starch polysaccharides (Liu 2005), which can interact with many additive components (Baker et al. 1994; Garcia et al. 1998). This makes them widely used in packaging industry, because in addition to protecting the products against shock and vibration that occur during transport, they can impart antioxidant and/or antimicrobial properties.

In recent years, several attempts have been made to apply starch in the manufacture of films. However, even today, industrial products associated with the production of starch films are scarce, frequently due to problems related to the extrusion of starch, which results much more complex for this polymer than for traditional plastics.

2.2 Processing

Similar and adapted techniques to those used for processing conventional synthetic thermoplastics have been used to process starch. Those include solution casting, internal mixing, extrusion, injection molding, and compression molding (Shank and Kong 2012). However, in the case of starch, one important factor to consider in all processes is the presence of water. Water and/or plasticizers are essential for starch processing. The dry starch melting temperature (T_m) is generally bigger than its decomposition temperature (T_d), as it was shown in the works of Liu et al. (2008) and Russel (1987). However, as moisture content increases, water acts as a plasticizer decreasing the T_m gradually, allowing starch treatment. One important problem that could influence the mechanical properties of the final material is the water evaporation during starch processing, which generates instabilities and occluded bubbles. The materials processed exclusively with water are usually brittle. For that reason, not easily evaporated plasticizers, such as polyols, are employed.

More emphasis will be made on the starch processing by casting and extrusion, being them the most used at laboratory and industrial scale.

2.2.1 Casting

The most widely used technique for the laboratorial production of starch-based films is casting (Vicentini et al. 2002; Mali et al. 2005; Famá et al. 2006, 2011, 2012; Müller et al. 2008; García et al. 2009a). The production of films by the classical casting technique consists in pouring on small plates or molds, an aqueous suspension of gelatinized starch, plasticizer and other additives, followed by a drying process where water is evaporated. The starch granule gelatinization is achieved heating the suspension before pouring it (Fig. 2). The average thickness of the resulting films is controlled by the mass of suspension poured on the plate. Several studies report that suspension's drying takes place at room temperature or in

Fig. 2 Pouring suspension of starch gelatinized



Fig. 3 Film of thermoplastic starch detached from its mold once the drying process is finished



ovens with forced air circulation at moderate temperatures (30–50 °C), requiring drying times of 10, 24, or 48 h (Godbillot et al. 2006; Müller et al. 2009; García et al. 2011 among others). The reported average size of films is diverse, and varies according to the size of the mold used.

Figure 3 shows how these films can be easily detached from its mold once the drying process is finished according to the different techniques of evaporation applied.

The main advantage of this method is its simplicity. Besides, the films obtained by casting are in general adequate testing structures for determination of barrier, mechanical, and other relevant properties.

Different and varied techniques are applied on the preparation of starch suspensions for the casting method. For example, Wang et al. (2014) gelatinized a mild oxidized cornstarch with urea contents between 0 and 50 wt%, relative to the total dry basis, at 90 °C for 90 min. The obtained suspension was poured in glass dishes and dried at room temperature.

López and García (2012) gelatinize ahipa and cassava starch at 90 °C for 20 min; for the filmogenic suspension onto Petri dishes and dry them in ventilated oven at 60 °C for 2 h.

Ghasemlou et al. (2013), transferred a potato starch and glycerol suspension to a water bath at 90 °C for 10 min, and agitated by magnetic stirrer at 500 rpm. After cooling at room temperature, about 70 mL of the sample was spread evenly over a Teflon casting plate (15 cm of diameter) placed on a leveled surface. The drying process continued for 48 h at 30 % RH and 20 °C.

García et al. (2009) and Famá et al. (2006), emphasize that before the casting procedure, the air bubbles contained in the starch suspension must be removed. This can be achieved lowering the pressure in the suspension's container using a vacuum mechanical pump. Once the removal is complete, the suspension is poured in a plastic mold and dried in an air convection oven at 50 °C for 24 h.

In general, optimal film formation, where a film is easily removable from the mold and immediately suitable for further studies, is strongly influenced by the starch source and preparation conditions of the film such as glycerol content, heating time, and heating temperature. Koch et al. (2010) examined the effects of manufacturing time, processing temperature, and plasticizer content on the molecular structure of high-amylose maize starch films. They demonstrated that glycerol played an important role in film formation. In particular, for films prepared at 140 °C for 15 min, when no glycerol was added a non-cohesive, wavy film with curled up areas was obtained (Fig. 4d). In contrast, films prepared under the same conditions but with a glycerol content of 30 % showed cohesivity, but kept exhibiting highly curled up borders (Fig. 4b). Slightly higher glycerol content (34 wt%) was required for smooth, even, and cohesive films (Fig. 4c). On the other hand, the heating time and heating temperature also showed detrimental effects on film formation. In particular, for samples with 34 wt% of glycerol, heating the starch slurry for 30 min instead of 15 min at 140 °C resulted in wavy and non-cohesive films (Fig. 4e), while highly fragmented films (Fig. 4f, g) resulted from heating at 150 °C for 5 and 15 min.

An important disadvantage of the casting technique lies on the fact that it is a batch method that is not able to be industrially replicated which does not allow an easy control on the sample film thickness and uniformity, and rarely allows samples larger than 100–200 cm². The sample with the mildest treatment (Fig. 4a), i.e., lower temperature but the same heating time as sample (Fig. 4b), was a cohesive film.

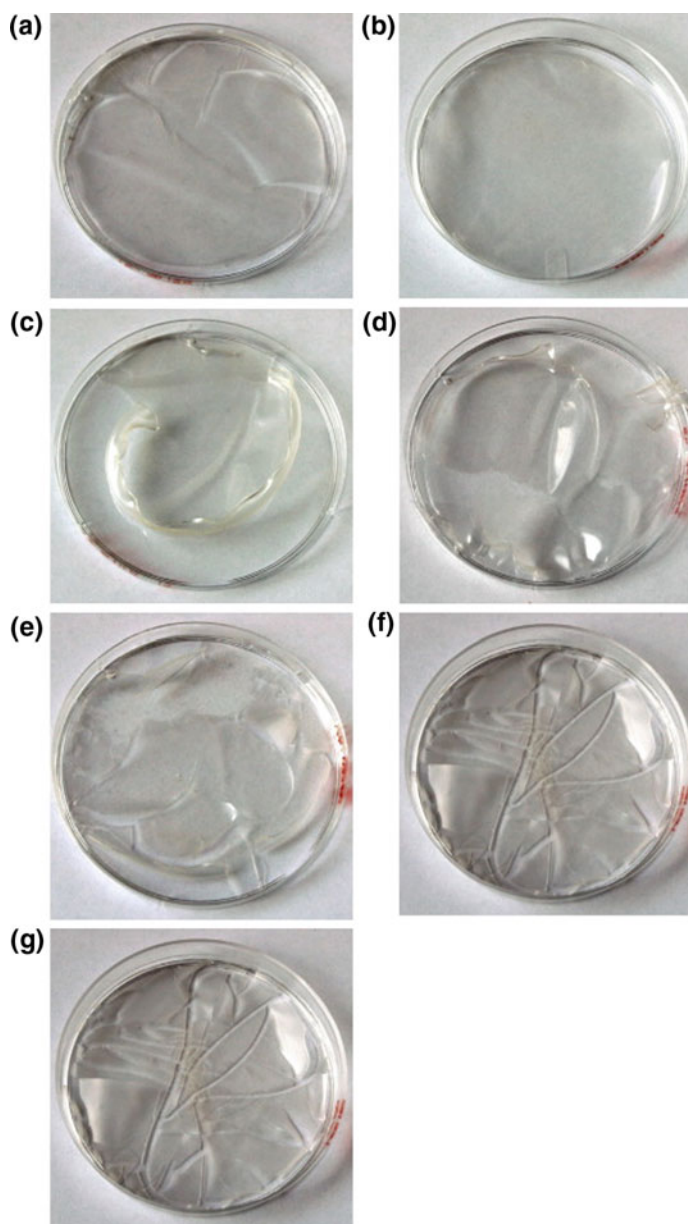


Fig. 4 Digital images of solution-cast high-amylose maize starch films prepared under different experimental conditions. Reproduced with permission from Koch et al. (2010). © 2013, Elsevier Ltd

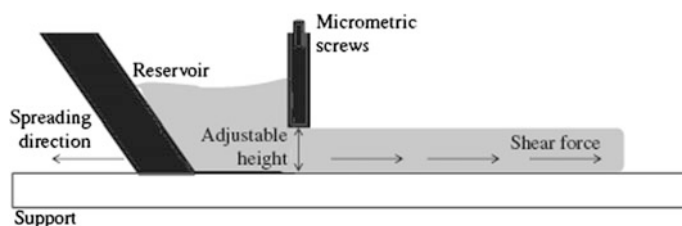


Fig. 5 Sketch of the tape casting process [adapted from Wonisch et al. (2011)]. Two micrometric screws control the gap between the doctor blade and the support. Reproduced with permission from Oliveira de Moraes et al. (2013). © 2013, Elsevier Ltd

An alternative to produce biodegradable films with controlled thickness is a technique named tape casting. This technique (also known as spread casting or knife coating) is well known in paper, plastic, ceramics, and paint manufacturing industries (Richard and Twiname 2000). In tape casting process a suspension is placed in a reservoir with a blade, whose height can be adjusted with micrometric screws (Hotza 1997). The suspension is cast as a thin layer on a support (tape) due to the movement of the carrier tape (continuous process) or the movement of the doctor blade (batch process) (Larotonda 2007). The equipment consists in a constant speed guide driving a knife maintained at an adjustable gap from the film support. This technique allows a very strict control over the thickness and film length. The spreading of the film forming solution (or suspension) can be done on larger supports or on a continuous carrier tape.

The formed film is dried on the support, by heat conduction, circulation of hot air (heat convection) and infrared, resulting in a reduction of its thickness.

A sketch of the tape casting process (adapted from Wonisch et al. 2011) is presented by Oliveira de Moraes et al. (2013) and can be observed in Fig. 5. They obtained, through this technique, cassava–glycerol films reinforced with cellulose fibers. The results showed that tape casting is a suitable technology to scale-up the production of starch-based films.

However, despite these possible methods for forming scalar thermoplastic films, for large-scale manufacture, an extrusion process is usually used.

2.2.2 Extrusion

In gelatinization, when native starch granules are heated in water, their semicrystalline nature architecture is gradually disrupted, resulting in the phase transition from an ordered granular structure into a disordered state in water (Lelievre 1974; Atwell et al. 1988; Ratnayake et al. 2008). This is an irreversible process that includes granular swelling, native crystalline melting (loss of birefringence), and molecular solubilisation in time–temperature sequence (Sullivan and Johnson 1964). Therefore, the gelatinization/melting behavior of starch is quite different when shear treatment is imposed (Xie et al. 2006).

Extrusion is an energy efficient system able to break down the starch granule structure through a combination of high shear, temperature and pressure and can successfully melt starch. Typical single or double screw extruders, in general form consists of a hopper, barrel, feed screw, thermocouples, and dies.

In the bibliography, there are two main types of extrusion: reactive extrusion and extrusion-cooking.

The reactive extrusion (REX) is used primarily in the chemical modification of starch, and to add cross-link agents or to make copolymers. The grafting of monomers from starch as single units, such as ring-opening of epoxides, esterification (with lactones, anhydrides, acids, halides, or vinyl esters), phosphorylation, and silylation; graft polymerization from starch by radical-induced grafting or the ring-opening polymerization of lactones; reactive compatibilization with polyesters and polyolefins by grafting to or from starch; cross-linking of starch with epichlorohydrin or by phosphorylation; and the degradation of starch thermally or catalyzed by acid or enzymes are some of the processes that use REX (Moad 2011). The use of extrusion can be used to produce modified starches in a continuous process with a more consistent product quality. The extruder has the advantage of a being an excellent mixing device and is particularly suitable for processing highly viscous fluids (such as gelatinized starch). Thus, with the use of REX, starch modification can be performed in a homogeneous medium.

There are several studies on the extrusion of modified starches. Chemical starch modifications, such as esterification, etherification, or oxidation before thermoplasticization process, reduce water sensibility and enhance mechanical behavior of the obtained thermoplastic starch (TPS) materials (Gaspar et al. 2005). Likewise, Thunwall et al. (2008) reported that the use of oxidized and hydroxypropylated starches, as well as high plasticizer content could increase the TPS melt tenacity (ability of the melt to deform without rupture), one of the potential limitations in their processing. Different formulations based on native and acetylated cornstarches and glycerol were made by López et al. (2013), who could obtain biodegradable films from thermoplastic native and acetylated cornstarches and glycerol as plasticizer, employing the blowing technique.

Generally, extrusion technology used in food industry is referred as extrusion-cooking. It has been employed for the production of so-called engineered food and special feed. Extrusion-cooking of vegetable raw materials consists in the extrusion of grinded materials at barothermal conditions. With the help of shear energy, exerted by the rotating screw, and additional heating by the barrel, the food material is heated to its melting point or plasticizing point (Moscicki and Van Zuilichem 2011). In this changed rheological status, the food is conveyed under high pressure through a die or a series of dies, and the product expands to its final shape. This results in different physical and chemical properties of the extrudates in comparison to raw materials used.

Nowadays, extrusion-cooking is used for the production of different food stuff, ranging from the simplest expanded snacks to the highly processed meat analogues. The most popular extrusion-cooked products are: direct extrusion snacks, RTE (ready-to-eat) cereal flakes and diverse breakfast foods produced from cereal

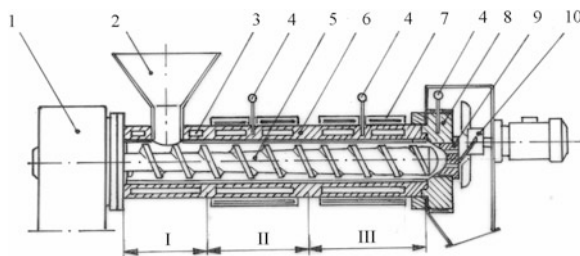


Fig. 6 A cross section of a single-screw extrusion-cooker: 1 engine, 2 feeder, 3 cooling jacket, 4 thermocouple, 5 screw, 6 barrel, 7 heating jacket, 8 head, 9 net, 10 cutter, I transport section, II compression section, III melting and plasticization section. Reproduced with permission from Moscicki et al. (2013). All published manuscripts are licensed under a Creative Commons Attribution 3.0 Unported License

material and differing in shape, color and taste, snack pellets—half products suitable for fried or hot air expanded snacks, precooked pasta, baby food, precooked flours, instant concentrates, functional components, pet food, aquafeed, feed concentrates and calf milk replacers, among others.

A cross section of a single-screw extrusion-cooker is shown in Fig. 6 (Mościcki et al. 2013).

Mitrus y Moscicki (2014) showed, for example, that the application of extrusion-cooking technique to process starch–plasticizer mixtures can be one of the most economical and efficient ways to produce TPS loose-fill foams. Then extrusion-cooking technique can be successfully employed for starch-based foams production.

Application of food extruders gives much better results in processing of starch-based materials than conventional plastic extruders due to the plant origin of the biopolymer. Most of the experimental works which apply extrusion-cooking for the production of starchy loose-fill foams started in the Department of Food Process Eng., Lublin University of Life Sciences in 2012. Their objective is to achieve commercially acceptable biodegradable products based on locally produced potato, corn- and wheat starch, which can replace popular expanded polystyrene loose-fill foam products. Results of the first phase of this study are presented in their work (Mitrus and Moscicki 2014).

More recently, Zhang et al. (2014) presented a new gelatinization technology, the improved extrusion-cooking technology, which is reconstituted from traditional single-screw extruders. Conventional extrusion-cooking is a continuous high-temperature and short-time process, which physically modifies moistened expansible starchy and proteinaceous materials, causing them to swell through the use of the unique combination of high temperature, pressure, and shear forces. Compared to the traditional extrusion-cooking machines, single-screw extruder transformed by Zhang et al. (2014) shows the characteristics of a longer screw (1950 cm), longer residence time (40–68 s), higher die pressure (13.4–19.1 MPa), lower temperature (69.8–120.2 °C), and lower screw speed (20.1–32.6 rpm) than traditional

extrusion-cooking extruders. Furthermore, a new forming mold and a rotary cutting knife which are not included in traditional extruders are added (Liu et al. 2011). The retrogradation behavior of rice starch with high amylose content treated by improved extrusion-cooking technology was investigated by morphologic studies, retrogradation enthalpy, percentage of retrogradation, relative crystallinity, and FTIR absorbance ratio.

It is well known that in the plasticization of starch, a phase transition occurs and the phase transition degree determines the process ability and the final product properties. Xie et al. (2014) claim that during the processing of starch, it is also important to know and control the rheological behavior of plasticized starch to prevent flow engineering problems and maintain the final product quality (Xie et al. 2012). Then, in processed plasticized starch-based materials, the phase transition and rheology are the two most important aspects to take into account, and the understanding of the materials melt flow results necessary.

In general form, it is considered that plasticized starch melt has a shear-thinning behavior, which can be expressed in the power-law equation:

$$\eta s = K \dot{\gamma}^{(n-1)} \quad (1)$$

where ηs is the viscosity, $\dot{\gamma}$ is the shear rate, K is the consistency coefficient, and n is the power-law index (<1). The K value is dependent on thermomechanical treatment, temperature and plasticizer content, which can be expressed as (Tajuddin et al. 2011):

$$K = K_0 \exp\left(\frac{E}{RT} - \alpha MC - \alpha' GC - \beta SME\right) \quad (2)$$

where MC is the moisture content, GC is the glycerol content, SME is the specific mechanical energy, T is the temperature, E/R is the reduced flow activation energy, and K_0 , α , α' , and β are coefficients.

During extrusion processing, the structural modification of starch, which is directly related to the viscosity, depends on the specific mechanical energy, feeding rate, screw speed, screw profile, and barrel pressure in the extruder.

SME is the amount of mechanical energy (work) dissipated as heat inside the material, expressed per unit mass of the material. Specifically, it is the work input from the drive motor into the material being extruded and thus provides a good characterization of the extrusion process, then it is an important process parameter influencing the final product characteristics such as solubility, extrudate density, expansion index, hardness, etc. (Godavarti and Karwe 1997). This energy input into the material is an important parameter because it is related with the product physical and chemical transformations. The heat generated due to viscous dissipation is proportional to the material's volume. In a corotating twin screw extruder, viscous dissipation of the mechanical energy predominates, especially at low moisture contents, making the extrusion process highly energy efficient and cost-effective (Guerrero et al. 2012).

One of the more straightforward SME calculations is as follows:

$$\text{SME} = \frac{P \times \tau \times \frac{\text{RPM}_{\text{act}}}{\text{RPM}_{\text{rated}}}}{\dot{m}} \quad (3)$$

where P is the motor power, expressed in kW, τ is the difference between the running torque and the torque when the extruder is running empty divided by the maximum allowable torque, RPM_{act} is the actual screw RPM, $\text{RPM}_{\text{rated}}$ is the maximum allowable screw RPM, \dot{m} is the mass flow rate of the system (kg/sec).

The output of the calculation will be in kJ/kg (Plattner et al. 2011).

Vergnes y Berzan (2010) founded that starch transformation can be predicted with an error of less than 10 %. They have showed that starch transformation during twin screw extrusion can be accurately predicted using dedicated software in which viscosity and SME are coupled. This may allow the processing conditions or screw profile to be optimized and scale-up problems to be solved.

Mitrus and Moscicki (2014) reported the value of SME in extrusion of starchy components for production of starchy loose-fill foams which can replace expanded polystyrene loose-fill foam products. They prepared blends of different starches mixed with up to a 20 wt% of glycerol; with functional additives such as talc, polyvinyl alcohol, and foaming agent. During the extrusion-cooking process, energy consumption was measured with a wattmeter connected to the extruder and the specific mechanical energy (SME) input was calculated (Janssen et al. 2002). Average value of SME for extrusion-cooking of TPS-based foams was in the order of $2.52 \times 10^5 \text{ J kg}^{-1}$, which is equivalent to $0.07 \text{ kW h kg}^{-1}$. They concluded that the SME value depended on the material composition, temperature, and the screw rotation speed used during processing.

Zhu et al. (2010) extruded blends of high-amylose cornstarch and soy protein concentrate. The increasing SME with increasing screw speed observed in this work is in agreement with previous reports (Jin et al. 1994; Akdogan 1996; Gropper et al. 2002; Schmid et al. 2005; de Mesa et al. 2009).

Besides rheology, there are other aspects to consider in the extrusion of starch which have already been widely studied and are important to emphasize.

In order to produce starch-based materials the starch has to be processed with a plasticizer. Water and glycerol are the most commonly used plasticizers. The use of plasticizers in the extrusion technique is very common because the starch cannot be thermally processed without water since the melting temperature of dry starch is often higher than its decomposition temperature, as it was previously explained.

Plasticizers combinations are reported in literature as well as the use of additives and lubricants, which can be included before entering the extruder. For example, Yan et al. (2012) made mixtures of starch, glycerol (25, 30, 35, 40, 45, 50 wt% of starch), pullulan (5 wt% of starch), stearic acid (1 wt% of starch), and glyceryl monostearate (0.5 wt% of starch) in a mixer at room temperature for 30 min. Blended mixtures were stored in polyethylene bags at room temperature overnight to equilibrate all components and finally after this procedure the extruder was fed with these mixtures.

López et al. (2013) mixed starches powders with glycerol, in different proportions, by hand to achieve plasticizer incorporation and homogeneous mixtures. The mixtures were conditioned for 12 h at ambient temperature before submitting them to the extrusion process.

In a work by Wang et al. (2012), pea starch was fed into the extruder at a rate of 350 g/h using a MT-1 twin screw volumetric feeder. In this case, water was injected into the extruder with a liquid pump at a rate of 85–158 g/h, so that the final mixture had moisture content in the range of 30–40 %.

Mościcki et al. (2012) extruded starch–glycerol mixtures without the addition of water. SEM micrographs of the obtained samples showed many of untreated starch granules inside its structure, evidencing the presence of ungelatinized zones. Li et al. 2011b compared the results of extruding starch powder and inject water at the extrusion barrel with the ones of extruding a premix of water and starch. They show that, in the first case gelatinization is not homogeneous and instabilities in the torque are generated during extrusion, while premixing leads to a homogeneous material. They also report that without a gases venting step, the extruder cannot work with higher water content than 40 %. Huneault and Li (2012) obtained an extruded homogeneous material feeding the extruder with a slurry composed of 50 wt% starch, 25 wt% water, and 25 wt% glycerol prior. They gelatinized starch during extrusion at 140 °C and then applied two-stage vent. In the last one, residual water was extracted by mechanical pump.

The importance of the plasticizer for the processes following extrusion, such as blowing and injection molding techniques, is exposed in the work of Moscicki et al. (2012). Various blends of potato starch mixed with glycerol were extrusion-cooked to obtain good quality TPS pellets, which were later processed using film blowing and injection molding techniques. It was noticed that with the full range of processing temperatures, independently of the mixtures composition used, the maximal elongation values coincided with increasing injection temperature and glycerin content in the sample. Results of the mechanical properties measurements showed that the extrusion processing parameters, the presence of plasticizer, and the blowing conditions have a critical impact on the film strength and elongation.

3 Starch Nanocomposites

3.1 Characteristics and Properties

As it was previously mentioned, the starch materials are strongly limited due their poor mechanical properties and high permeation. In this context, and in order to solve this problem, the incorporation of different fillers such as fibers, flakes, platelets, and particles into starch matrices (García et al. 2009a, 2011; Siqueira et al. 2009; Famá et al. 2010, 2011, 2012), or the starch blending with other polymers, have been the topic of many investigations. It has been well established that the

filler size greatly influences physicochemical properties of the final composite. Smaller size fillers have serious advantages over micro-sized particles. For example, when nanofillers are used, the relationship between the area of the interface and the volume of the reinforcement is much higher than in the case of micro or conventional reinforcements. On the other hand, microfillers scatter light and therefore the composites lose transparency, obtaining composites with high opacity. This behavior does not occur in the case of nanofillers. Moreover, the optimal effect is achieved when the light reflection coefficient of the filler is similar to that of the material used as matrix.

In addition, the use of nanofillers improve several mechanical properties, such as Young's modulus, tensile strength, deformations, and toughness (García et al. 2009b; Famá et al. 2011), as well as electrical (Kilbride et al. 2002; Sandler et al. 2003) and thermal properties (Biercuk et al. 2002; Wei et al. 2002). The high aspect ratio ($k = L/d$) and large surface area per unit volume of same nanofiller result in a very good transfer of their properties to the polymer matrix. The effect of the incorporation of nanofillers in the starch retrogradation has also been investigated by some researches who found that the addition of nanoparticles diminishes the retrogradation of the polymer (Angellier et al. 2006; Cao et al. 2007; Ma et al. 2008b).

Interfacial adhesion between filler and matrix plays a vital role in the final properties of polymeric composites. The physicochemical properties of a composite material depend not only on the properties of its components, but also on the bonding between matrix and filler. When nanofillers are used, the ratio between the area of the interface and the volume of the reinforcement is much greater than in the case of micro-sized fillers. Furthermore, in the case of nanometric fillers, a high fraction of the atoms are in the surface resulting in increased reactivity. If good nanofillers dispersion is achieved, the interface region is maximized allowing the conformation of an interfacial percolation network that can improve different properties of the nanocomposite (Qiao and Brinson 2009).

There are different ways to improve the filler–matrix interaction in the interface. The most popular ones between them are:

- Mechanical bonding: Roughness between both surfaces leads to bonding, being better when higher roughness is observed. This type of bonding is ineffective for tensile but effective for shear improvements.
- Electrostatic bonding: This type of bonding occurs when both surfaces are charged, one positively and the other negatively.
- Chemical bonding: It occurs when the surface of the reinforcement has chemical groups compatible with the chemical groups of the matrix. The strength depends on the number of bonds per unit area.
- Bonding by interdiffusion: In this type of bonding, the surfaces of the reinforcement and of matrix have chains that spread between them. The strength of this bond depends on the number of entanglements between chains and increases with the addition of solvents or plasticizers.

In many cases certain drawbacks such as incompatibility with the polymer matrix due to hydrophilicity differences, tendency to form aggregates during processing, and poor resistance to moisture greatly reduce the potential of the filler to be used as reinforcement in polymer composites. Interfacial coupling agents are often used to improve interfacial properties and control the morphologies of polymeric composites. Coupling agents make the fillers compatible with organic polymers since they are hybrids of organic molecules and minerals; and, as they have reactive functional groups, they are able to generate in situ formation of blocks or grafted copolymers at the interface by hot-melting blending. It has been proven that the addition of these coupling agents generates compatibilization between fillers and matrix, being an effective method for morphology control in a variety of composite systems (Son et al. 2000; Kim et al. 2001; Pagnoulle and Jerome 2001; Wang et al. 2001).

3.2 Processing

Processing nanocomposites results much more complex than neat starch due to the inherent complications related to the nanofillers use. Its high surface/volume ratio makes the electrostatic interactions between them, such as Van der Waals interactions, maximized, generating a large amount of agglomerates which are too difficult to break during processing. Furthermore, most of the employed loads in starch composites are hydrophilic and therefore show strong hydrogen bridge interactions, contributing to the agglutination problem. For that reason, different strategies have been developed in order to incorporate nanofillers to the matrix, with a special focus on a good dispersion achievement.

In the next sections we briefly discuss the processing of nanocomposites by the casting and extrusion techniques.

3.2.1 Casting

Casting is one of the most common techniques for processing lab scale starch composites. Different types of polysaccharide nanofillers such as cellulose from flax, wood, hemp ramie, cassava bagasse, wheat straws, starch from waxy maize, regular maize, and chitin, chitosan, among others; were used to fabricate starch nanocomposites by the solution casting method.

The main drawback associated with this method is that polysaccharide nanofillers tend to agglutinate due to the strong hydrogen bonding interactions between them (especially cellulose nanowhiskers (C-NW) (Cao et al. 2008a; b; Kaushik et al. 2010) and starch nanoparticles (S-NPs) (Angellier et al. 2006; Viguié et al. 2007; García et al. 2009a, 2011).

In general for the dispersion of these fillers in starch solutions, some additional treatments, such as ultrasonication, sonication and homogenization, are required

(Chang et al. 2010a; Kaushick et al. 2010). In some cases special considerations need to be taken into account. Starch nanoparticles (S-NP), for example, must be added at reduced temperature to avoid the gelatinization of their amorphous component and the destruction of their special structure, which affect their reinforcing ability (Xie et al. 2014). A possible attempt to solve this problem was proposed by Ma et al. (2008c), who modified starch nanoparticles with citric acid by dry preparation technique. These modified nanoparticles dispersed in distilled water were added before gelatinization at 90 °C. In this case they reported that S-NP could not be swelled or gelatinized in hot water due the cross-linking induced by the citric acid.

In the case of starch or cellulose nanocrystals obtained by the sulfuric acid treatment, and prepared in aqueous condition, the suspension experiences neither sedimentation nor flocculation, as a consequence of charge repulsion due to the sulfate groups created on their surface. This feature makes it easier to add them into to the starch solution (Angles et al. 2000; Mathew and Dufresne 2002; Angellier et al. 2006; Lu et al. 2006; Viguié et al. 2007; Cao et al. 2008a, b; Chen et al. 2009a, b; García et al. 2009, 2011).

The way in which different nanofillers are added into the matrix varies according to different authors. For example, Viguié et al. (2007) added a nanoparticle suspension of waxy maize starch to gelatinized starch, but they do not specify the suspension preparation protocol.

García et al. (2009), adding the suspension of waxy maize starch nanocrystals in the desired quantities to gelatinized matrix of cassava starch, and then the mixture was stirred for 10 min at 250 rpm and degassed for another 1 h.

Piyada et al. (2013) prepared a rice starch solution with a concentration of 3 % (w/v) in distilled water. They heated the dispersion with continuous stirring until it was completely gelatinized (85 °C for 5 min), and finally cooled it to 45 ± 2 °C. Subsequently, previously lyophilized nanocrystals were dispersed in water, and incorporated to the gelatinized starch suspension.

By contrast, some authors add the suspension together with the starch before gelatinization. In the work by Kaushik et al. (2010), prepared TPS nanocomposites reinforced with cellulose nanofibers (C-NF) extracted from wheat straw. They shear mixed maize starch and glycerol (30 %) for 10 min using a Fluko FA25 homogenizer (10,000 rpm) and prepared a C-NF water dispersion using a bath sonicator for 3 h. The C-NF dispersion was added to the starch–glycerol mixture and the final product was subjected to further shear mixing for 20 min. Finally, the starch + glycerol + C-NF mixture was continuously stirred (at 80–100 rpm) using a mechanical stirrer and heated at 75 ± 3 °C. Noteworthy that these authors mix the starch nanofillers suspension employing high shear.

In the case of Ma et al. (2008c), as already described, added citric acid-modified starch nanoparticles (CA-S-NP) into a water, glycerol, and starch mixture, prior to gelatinization.

Cao et al. (2008a), used starch, glycerol, a cellulose nanocrystallites suspension and distilled water mixed together to obtain a homogeneous dispersion and fabricate plasticized starch/flax cellulose nanocrystals (S/FC-NC) composite films.

The glycerol content was fixed at 36 wt% based on the dry starch matrix. Then this mixture was poured into a flask equipped with a stirrer and heated at 100 °C for 30 min to gelatinize starch. The same procedure is used for the fabrication of the Hemp (*Cannabis sativa*) cellulose nanocrystals and potato starch nanocomposite films S/HC-NC (Cao et al. 2008b).

Summarizing, in the preparation of starch-based nanocomposites by casting technique it is generally necessary take into account how to prevent the nanoparticles clumping.

3.2.2 Extrusion

The problems associated with starch extrusion are increased when starch nanocomposites are processed using hydrophilic fillers. As it was explained before, although these fillers are compatible with starch and glycerol, they tend to clump together obstructing their dispersion in the matrix.

Some authors propose the preparation of a dry starch, glycerol, and nanofiller mixture without water addition (only the starch moisture is used) to be extruded (Galicía-García et al. 2012; Müller et al. 2012; Pelissari et al. 2012); while others, underline the problem of the hydrophilic fillers and propose their incorporation into water suspensions, either by pumping the solution to the molten polymer into a subsequent extrusion stage (Vasquez et al. 2012), or by feeding the extruder with the mixture of all the components with water (Ayadi and Dole 2011; Martínez-Bustos et al. 2011). For example, Mitrus y Moscicki (2014), reported two types of food extruders that were used for processing of prepared blends of starchy components mixed with glycerol added up to 20 % in weight; functional additives like talc, polyvinyl alcohol, and foaming agent (PLASTRONFOAM PDE). The additives were added up to 3 % in weight, while water up to 5 % in weight. The blends were extruded at temperature range 80–170 °C, variable screw rotational speed up to 150 rpm, and die pressure of 12 till 18 MPa.

Hietala et al. (2013), premixed starch, plasticizer, lubricant, and cellulose nanofiber (C-NF) gels with high water contents and then extruded the obtained dispersions. The authors prepared nanocomposite with 0, 5, 10, 15, and 20 wt% of cellulose nanofiber. In order to remove the water excess, an extruder barrel equipped with two atmospheric vents and vacuum ventilation was proposed.

Yurdakul et al. (2013), proposed to mix starch, carbon nanotubes, water and glycerol, gelatinize the obtained suspension and introduce it manually into the extruder.

The extrusion process was performed between 25 and 75 rpm with temperatures between 110 and 140 °C. The obtained material showed a good filler dispersion and improvements in stress and strain at break for filler contents smaller than 1 wt%.

Regardless of the variations in the methodology chosen for the components addition in the extruder, it is important to note that the filler can be dispersed in starch during the gelatinization extrusion process. It is advantageous to use a twin screw extruder with multiple inlet ports so that gelatinization, plasticizer, and filler

addition can be separated processing steps within one extrusion cycle. The production of TPS pellets in common plastic extruders is generally not recommended due to the need of a different machine design and processing difficulties.

4 Nanocomposites

4.1 Starch/Starch

Starch nanocrystals or nanoparticles can be prepared principally by four different methodologies, (1) by hydrolysis including acid or enzymatic hydrolysis (nanocrystals), (2) by regeneration using cocrystallization (Kim and Lim 2009), or cross-linking (Tan et al. 2009; Ma et al. 2008), and (3) using gamma radiation (Lamanna et al. 2013) mechanical treatment with a microfluidizer (Le Corre et al. 2010).

It is noteworthy that both amorphous and crystalline particles are obtained in the final reaction of the methods 2 to 4, while method 1 produces preferably nanocrystals.

The mechanical treatment is performed analogously to the production of microfibrillated cellulose. Liu et al. (2011) intended to produce starch nanoparticles by fluidization. They found that crystalline microparticles turned into amorphous nanoparticles with increasing run numbers. The hydrolysis methodology consists basically in removing starch amorphous regions. Attempts to produce starch nanocrystals by enzymatic hydrolysis were reported by Kim et al. (2008), it is believed that the process leads to blocklets rather than nanoparticles. Kim and Lim (2009) reported the preparation of nanocrystals by complex formation between amylose and *n*-butanol, thereafter enzymatic hydrolysis was used to selectively keep crystalline particles. Ma et al. (2008) reported the production of starch nanoparticles by precipitation of gelatinized starch in nonsolvent followed by a cross-linking reaction.

There are other methodologies as used by Lamanna et al. (2013); who obtained starch nanoparticles (S-NP) applying gamma radiation. Another environmental-friendly mechanical method to obtain nanoparticles is extrusion. Eugenius et al. (2000) patented a starch nanoparticles preparing method based on reaction extrusion. Using this technology, commercial product EcoSphere is produced by Ecosynthetix.

In the same way, Song et al. (2011), reported starch nanoparticles prepared by reactive extrusion method. Their results indicate that with the addition of an appropriate cross-linker, starch nanoparticles with an average size of 160 nm could be obtained.

Le Corre et al. (2011), propose another technique against limitations of the acid hydrolyses process for producing starch nanocrystals. Protocol using acid hydrolysis is only for producing small quantities of S-NC and renders a limited yield (10–15 %) after a production time of (5 days). They proposed a continuous extraction technique:

hydrolyzed from wheat starch and filtered using a microfiltration unit equipped with ceramic membranes to assess the cross-flow membrane filtration potential of S-NC suspensions. They show to be an efficient continuous operation for separating S-NC from the bulk suspension whatever the ceramic membrane pore size (0.2–0.8 μm).

Therefore, starch nanoparticles look like a good alternative for developing starch-based nanocomposites with high transparency. This was reported in the study of Gonçalves et al. (2014), with nanocrystals obtained from the seeds of pinhão (*Araucaria angustifolia*). The greater solubility and reduced turbidity are interesting from a commercial standpoint, indicating that pinhão starch nanoparticles could be useful for development of coating materials or films composites.

However, there are two fundamental problems to solve in order to develop composites using starch nanoparticles: the high agglomeration between them and the degradation possibility due to temperature or shear employed in processing method.

Furthermore, it is well known that the nanoparticles shape plays a very important role in the improvement of barrier properties. Platelet-shaped particles are preferred because they are thought to alter the diffusion path of penetrant molecules and improve the barrier properties of the material. Nanoparticles with this geometry create a sort of winding road hindering and delaying the passage of gases and water.

The nanofillers having these latest features are clays and starch nanocrystals, therefore, both could be fitted for flexible food packaging applications.

The use of starch nanoparticles is receiving a significant amount of attention because of the abundant availability of starch, low cost, renewability, biocompatibility, biodegradability, and nontoxicity (Chakraborty et al. 2005).

Starch nanocrystals has been used in different environmental-friendly polymers such as waterborne polyurethane (Chen et al. 2008) (also called organic solvent free polyurethane), starch (waxy maize, Angellier et al. 2006; Viguié et al. 2007; García et al. 2009a), pullulan (Kristo et al. 2007) (obtained by starch fermentation), PLA (Yu et al. 2008), polyvinyl alcohol (PVA) (Chen et al. 2008), and soy protein isolate (Zhen et al. 2009), but we will focus on its use on starch matrices.

The most common sources of starch to develop the nanocomposites matrix are pea starch, waxy maize starch, cassava starch, normal maize and potato starch. (Chen et al. 2009; García et al. 2009a, b; Jayakody and Hoover 2002; He et al. 2012).

In most publications, authors have opted for a simple casting–evaporation method in the preparation of starch-based nanocomposites. The general method consists in dispersing the nanocrystals in aqueous solution and adds this suspension to the mixture of starch and other components which will be then gelatinized. Other authors prefer to add the suspension after the gelatinized starch. This was already discussed in section casting of nanocomposites.

Other conditions have caught significant attention during investigations, for example, Garcia et al. (2009a) taking care of degassing thermoplastic cassava starch solution before and after the introduction of starch nanoparticles.

The potential use of starch nanocrystals as a reinforcing phase in a polymeric matrix has been evaluated from a mechanical point of view in several publications.

Angellier et al. (2006) showed that the reinforcing effect of starch nanocrystals is more significant in TPS than in other matrices. This is probably a consequence of the strong interactions between the filler and amylopectin chains and a possible crystallization at the filler/matrix interface (Angellier et al. 2006). Besides, the reinforcing effect of S-NC within a TPS matrix was higher than that of other fillers, such as tunicin or sugarcane bagasse cellulose whiskers.

Other authors reported the same reinforcing effect (Viguié et al. 2007; Ma et al. 2008c; García et al. 2009). In particular, Viguié et al. (2007) showed that for higher plasticizer contents (35 wt% sorbitol) the reinforcing relative effect was higher. The Young's modulus and the strength of a film reinforced with 15 wt% starch nanocrystals increased by a factor 7 and 12, respectively, when plasticized with 35 wt% of sorbitol, and only by a factor 2.7 and 4.2, respectively, when plasticized with 25 wt% sorbitol.

Garcia et al. (2009), reported an increase of 380 % of the rubbery storage modulus (at 50 °C), in nanocomposites of cassava starch reinforced with waxy starch nanocrystals.

On the other side, starch nanocrystals' surface can be chemically modified. These modifications consist in transforming the polar hydroxyl group sitting at the surface of starch nanocrystals into moieties capable of enhancing interactions with nonpolar polymers (Labet et al. 2007; García et al. 2012).

Modifications in order to improve starch matrix–starch nanoparticles nanocomposites were also proposed. For example, Ma et al. (2008c), proposed the fabrication and characterization of citric acid-modified starch nanoparticles/plasticized pea starch composites. In dynamic mechanical thermal analysis, the introduction of CA-S-NP could improve the storage modulus and the glass transition temperature of pea starch/CA-S-NP composites. The tensile yield strength and Young's modulus increased from 3.94 to 8.12 MPa and from 49.8 to 125.1 MPa, respectively, when the CA-S-NP contents varied from 0 to 4 wt%.

On the other hand, nanoparticle's moisture resistance was reported by different authors and an important characteristic in many nanocomposites potential applications. The improvements in the water vapor permeability (WVP) of nanocomposites with starch nanoparticles are associated to the introduction of a tortuous pathway for water molecules to pass through, as it was mentioned before. Garcia et al. (2009a) reported a WVP reduction of a 40 % in cassava starch matrix composites reinforced with 2.5 wt% starch nanoparticles respect to the starch matrix. However, in waxy starch matrix composites the permeability to water vapor increased (by 79 %) upon the addition of only 2.5 wt% waxy maize starch nanocrystals. This result is opposite to the cassava starch, where the nanocrystals were well distributed (García et al. 2011). These results are due to the fact that it is considered that starch–SNC is a complex system governed apparently both by the nanocrystals and the plasticizer. García et al. (2011), proposed that the higher density of –OH groups on the surfaces of S-NPs, which were mainly the crystalline zones of hydrolyzed waxy starch, led to more association of the S-NPs with glycerol molecules. Consequently, more –OH groups of the matrix result available

to interact with moisture, and a nanometric fibrillar preferential path for water vapor diffusion was formed, resulting in an increase in the moisture sensitivity.

In composites, starch nanocrystals (S-NC) are candidates of growing interest, for this reason recently has been studied in detail in a recent European Project (FlexPakRenew-FP7/2007-2013—no. 207810).

4.2 Nanocomposites: Starch/Cellulose

Natural cellulose fibers from different biorenewable resources have considerable attraction of research community due to their unique intrinsic properties such as biodegradability, easy availability, environmental friendliness, flexibility, easy processing, and impressive physicommechanical properties (Singha and Thakur 2008a, b, 2010a, b; Thakur et al. 2010a; Thakur and Thakur 2014a, b, c). In addition, considerable efforts are currently being directed toward improving the quality of the interfacial bonding between polymers and fibers by chemical surface modifications (Singha et al. 2009; Thakur et al. 2010b, 2011, 2012).

Moreover, cellulose nanofillers such as nanorod, rod-like cellulose microcrystals, nanowires, and long and straight crystals were investigated.

Since the first announcement cellulose whiskers application as reinforcing phase by Favier et al. in 1995, new nanocomposite materials with original properties were obtained using cellulose nanowhiskers (C-NW) and microfibrillated cellulose (MFC) and led to the development of studies on chitin whiskers.

The C-NW can be obtained from different sources like cassava baggage (Texeira et al. 2009), ramie (Lu et al. 2006), hemp (Cao et al. 2008b), flax (Cao et al. 2008a), peal hull (Chen et al. 2009a, b), jute (Cao et al. 2012), tunicate (Angles et al. 2000; Angles et al. 2001; Mathew et al. 2002; Mathew et al. 2008) (sea animal) or from microcrystalline cellulose (MCC) (Kvien et al. 2007; Chang et al. 2010a). Recent publications also reported cellulose nanocrystals from sweet potato residue and bamboo (Lu et al. 2013; Zhang et al. 2014).

Different methods are presented in literature to obtained cellulose nanowhiskers: chemical hydrolysis, high-pressure homogenization, and enzymatic hydrolysis.

In a classical hydrolyses is obtained cellulose rod-like nanocrystals or nanocrystal systems from hardwood and softwood (Beck-Candanedo et al. 2005); or whiskers (Bondenson et al. 2007) or rod-like nanoparticles (Mesquinfam et al. 2011)

These nanofillers are usually obtained by acid hydrolysis under specified conditions of temperature and processing time, allowing the decrease of the amorphous regions, resulting in a highly a crystalline material. The subsequent procedure to acid hydrolysis consists in a wash by centrifugation, then dialyzed against distilled water and ultrasonicated. The surface grafted sulfate groups, negatively charged, provide that nanocrystals form stable layers at the air–water interface, then the nanofiller is prepared in aqueous condition, with well dispersion and without sedimentation or flocculation. This is an advantage in the preparation of

nanobiocomposites, because the suspension can be incorporated directly into the starch solutions. (Angles et al. 2000; Lu et al. 2006; Cao et al. 2008a; Chen et al. 2009; García et al. 2009a, 2011).

Using high-pressure homogenization of wood fibers in water, MFC, composed of liberated semicrystalline microfibrils, is obtained. MFC was first introduced by Turbak et al. (1983), who reported that the fibrils width was between 25 and 100 nm, while the length was longer.

Similarly MFC were obtained applying a high-pressure homogenizer to commercial microcrystal cellulose previously dispersed by a Turrax. The cellulose fibrils were in the range from 28 to 100 nm (Lee et al. 2009).

A novel concept to prepare nanocellulose fibrils has been reported, where enzymatic hydrolysis was used in combination with mechanical shearing and high-pressure homogenization to produce defibrillation of the fiber wall and obtain fibrils with a diameter of around 5–6 nm and aggregates of around 10–20 nm (Paakko et al. 2007).

Recently novel techniques for obtaining of cellulose nanocrystals have appeared in the literature. Cao et al. (2012) showed a controllable method to fabricate cellulose nanowhiskers from jute fibers with a high yield (over 80 %) via a 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)/NaBr/NaClO system selective oxidation combined with mechanical homogenization.

Haafiz et al. (2014) showed an isolation method of C-NW from MCC and a detailed characterization of the new filler. MCC was produced from oil palm empty fruit bunch chlorine free pulps. It was swelled and partly separated to whiskers by chemical and ultrasonication treatments using the same method as described by Pereda et al. (2011) based on original procedures described by Oksman et al. (2006).

An exhaustive economic analysis for the production of cellulose nanowhiskers as a coproduct in an ethanol biorefinery and an ASPEN Plus-based process model (<http://www.aspentech.com/core/aspent-plus.cfm>) was developed to evaluate ethanol production from wheat straw. All the collected data on cellulose nanocrystals in terms of production, characterization, and application suggest that this nanomaterial could be easily extrapolated to bioethanol production (Duran et al. 2011).

The relative degree of crystallinity and the geometrical aspect ratio of obtained cellulose nanocrystals, depend on cellulose origin and the processing conditions, such as time, temperature, and original raw material purity.

The principal characteristics observed with the addition of cellulose nanocrystals to starch-based materials led to improvements in the mechanical properties, thermal properties (represented by an increase in the glass transition temperature, T_g), and moisture resistance.

Several publications reported these effects. In the works of (Cao et al. 2008a), cellulose crystals, prepared by acid hydrolysis of flax fiber (F-CN), were added to a potato starch (PS) matrix, the nanocomposite films exhibited a significant increase in tensile strength and Young's modulus from 3.9 to 11.9 MPa and from 31.9 to 498.2 MPa, respectively, with increasing F-CN content from 0 to 30 wt%.

The resulting nanocomposite films also showed a higher water resistance and the nanocomposite water uptake decreased as the filler content increased. The fillers addition did not change the transition temperature for the glycerol-rich phase, but the T_g value of the starch-rich phase shifted to higher temperatures from 43.3 to 48.8 °C, indicating that F-CN restrict the mobility of starch chains. This can probably be explained by the reinforcement effect from the homogeneously dispersed high-performance F-CN fillers in the PS matrix and the strong hydrogen bonding interaction between F-CN and PS molecules.

The reason for the nanocomposites increased thermal properties is associated to the relocation of the plasticizer(s), water inclusive, from the starch matrix to the cellulose nanocrystals surfaces, which decreases the plasticization effect on the amorphous regions (Angles and Dufresne 2000, 2001). They proposed the formation of the transcrystalline zone, around the cellulose nanofillers in order to explain the results obtained in plasticized waxy maize starch reinforced with tunicin nanowhiskers. This effect is caused by the recrystallization of amylopectin chains assisted by the plasticizer accumulation and the nucleating effect of C-NW.

The improvement in mechanical properties of starch due to the addition of different cellulose nanofillers was reported in different works: Hemp nanocrystals in TPS (Cao et al. 2008b); nanofibrils of wheat starch in regular maize starch (Kaushick et al. 2010); ramie crystallites in commercial industrial-grade wheat starch (Lu et al. 2006), nanofibrils in cassava starch (Texeira et al. 2009), tunicin whiskers in plasticized starch (Angles et al. 2000), between others. The explanation for this effect is ascribed to the formation of a rigid network of nanofillers, the mutual entanglement between the nanofiller and the matrix, and the efficient stress transfer from the matrix to the nanofiller (Kaushik et al. 2009; Siqueira et al. 2009). In works of Mathew and Dufresne (2002) and Mathew et al. (2008), the authors propose an increase in the overall crystallinity of the system resulting from the nucleating effect of the C-NW, this effect can be beneficial for mechanical properties.

Slavutsky and Bertuzzi (2014) recently showed cellulose nanocrystals (C-NC) obtained from sugarcane bagasse. They formulated starch/C-NC composites and their water barrier properties were studied. The measured film solubility, contact angle, and water sorption isotherm indicated that reinforced starch/C-NC films have a lower affinity to water molecules than starch films. The same effect was observed in studies by Savadekar and Mhaske (2012). They studied the effect of C-NC incorporation on TPS matrix and found that the nanofillers addition improved their barrier and mechanical properties.

The main causes for the improved moisture resistance exhibited by the nanocomposites are the less hydrophilic nature of cellulose and the geometrical impedance created by the C-NW, the constraint of the starch swelling due to the presence of the C-NW network, the resistance of the diffusion of water molecules along the nanofiller–matrix interface, and the reduced mobility of the starch chains, resulting from an increase in the T_g or the crystallinity.

4.3 Nanocomposites: Starch/Layer Silicates

Polymer nanocomposites reinforced with layer silicates are very common because the first application of these fillers was in the automotive industry. The packaging industry has focused its attention principally on layered inorganic fillers like clays and silicates due to their low cost, availability, significant augment, and considerably simple processability (Le Corre et al. 2010).

Clay minerals, the micas, chlorite, serpentine, talc, between them can also find within the group of minerals phyllosilicates or layered silicates. They all have different morphology, structure, and texture (Bergaya et al. 2009). The some representative layer silicates used mainly in nanocomposites-based starch are listed in Table 2. It is important to note that the some phyllosilicates do not display a normal layered structure, for example, the sepiolite shows a fibrous structure meanwhile halloysite has spheroidal aggregates morphology (Duquesque et al. 2007; Bergaya et al. 2009).

Many organophilic nanoclays, therefore, have already been studied, and some of their products are already marketed on an industrial scale (Park et al. 2002; Turrit al. 2008). The variation in the fillers dimensions depends on the clay source, particulate silicate and preparation technique, but all these layers have a very high aspect ratio (length/thickness) and surface area (Reedy et al. 2013).

The crystal arrangement in the silicate layers is made up of two tetrahedrally coordinated atoms fused to edge-shared octahedral sheets. These sheets are made up either of magnesium or aluminum hydroxide. Their thickness is about 1 nm and their tangential dimensions range from 300 Å to a few microns. The van der Waals gap between these layers is due to the regular layers stacking; this gap is known as inter-gallery spacing. Each of these layers is negatively charged, and the excess charge is balanced by alkali cations, such as Na^+ , Li^+ or Ca^{2+} , that reside in these inter-gallery space between the aluminosilicate layers (Ray and Okamoto 2003; Majdzadeh-Ardakani et al. 2010). To improve their dispersability, clays are often modified with conventional organomodifiers, many of them are surfactants, which are typically the quaternary ammonium salts of long fatty acid chains. These organomodifiers decrease the surface tension of the aluminosilicate particulates, which in turn reduces the mixing endothermic enthalpy.

Table 2 Representative layer silicates used mainly in nanocomposites based starch

Group	Nanofiller	Dimensional type	Matrix starch	Load (%)	References
Kaolinite	Kaolinite	Nanolayer	Cassava	2–6	Mbey et al. (2012)
Kaolinite	Halloysite	Nanotubes	Potato	5	He et al. (2012)
Smectite	Montmorillonite	–	Wheat	3–6	Chivrac et al. (2010)
			Corn	0–5	Aouada et al. (2011)
Sepiolite	Sepiolite	Nanolayer	Potato	–	Du et al. (2013)
Smectite	Hectorite	Nanolayer	Yam	<30	Wilhelm et al. (2005)
Synthetic clay	Somasif	Nanolayer	PLA	–	Borges et al. (2012)
Mica	Laponite	–	Corn	1–5	Aouada et al. (2011)

The most commonly used strategy to increase the interlayer spacing (Lagaly et al. 1986) is the chemical modification of the phyllosilicate surface by cationic exchange using the quaternary ammonium salts of long fatty acid chains. From this technique, different organomodified clays can be obtained.

In nanocomposites-based starch, the most widely studied type of clay is montmorillonite (MMT) or modified montmorillonite, among which the main difference is the nature of the counterion and the cationic exchange capacity (CEC).

In literature, natural Montmorillonite MMT or MMT- Na^+ , can also be found under the following names: Cloisite® Na^+ , Dellite® LVF, Dellite® HPS, Nanofil® 757, BH Natural. When different counterions are used in order to modify MMT, the trade names used which can be found are: Cloisite® 30B, Cloisite® 10A, Cloisite® 25A, Cloisite® 93A, Cloisite® 20A, Nanomer® I.30E, Nanofil® 784, Nanofil® 804, Nanofil® 948, natural calcium hectorite and Bentone® 109 (all are commercial names registered). The principal counterions used to modify MMT are listed and the synonyms names associated with them are showed in Table 3.

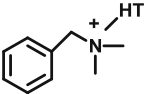

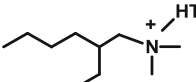
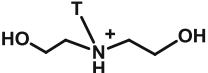

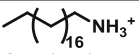
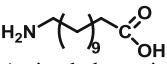
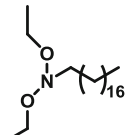
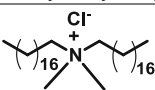
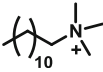
However, some these chemical modifications increase the hydrophobicity of the phyllosilicate, resulting in a reduction of the compatibility with the hydrophilic starch matrix. The surface hydrophobicity of Cloisite MMT nanofillers follows an order: Natural sodium MMT is less hydrophobic than Cloisite® 30B. In turn, Cloisite® 30B is less hydrophobic than Cloisite 10 A, and thereby the order is as follows: 10A < 25A < 93A < 20A < 15A < 6A (Xie et al. 2012).

The dispersion state of a typical phyllosilicate (except sepiolite and halloysite) in a matrix polymer depends on the preparation conditions and the matrix–nanolayer affinity. This effect determines the structure of the resulting composites, which can be either phase separated composites (microcomposites), intercalated nanocomposites, or exfoliated nanocomposites (Alexandre and Dubois 2000).

In nanocomposites, several studies have reported the efficiency of nanoclay incorporation in improving mechanical properties and decreasing water vapor (Müller et al. 2011; Sadegh-Hassani and Nafchi 2014), and oxygen permeability (O_2P) (Tjong 2006; Lu and Mai 2007).

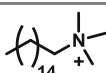
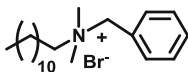
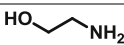
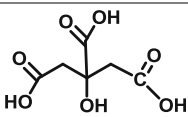
Particularly, starch nanocomposites reinforced by phyllosilicates show generally an increase in tensile strength (σ), Young's modulus (E), storage modulus (measured by dynamic mechanical analysis), thermal stability, moisture resistance, oxygen barrier property (Zeppa et al. 2009), and biodegradation rate (Magalhaes and Andrade 2009). For example, green nanocomposites were prepared by solution induced intercalation method using starch, jute, glutaraldehyde, nanoclay (Montmorillonite K-10) and glycerol. The addition of glutaraldehyde and nanoclay has been found to improve the thermal stability, flame retardancy, dimensional stability, and mechanical strength of the prepared composite. The values for tensile strength changed from 18.62 MPa (0 wt% filler) to 40.63 MPa for 5 wt% of addition filler, and the modulus value changed from 1117 MPa for the matrix to 2344 Mpa for the nanocomposite (Iman and Maji 2012). On the other hand, Sadegh-Hassani et al. (2014), reported bionanocomposite films prepared by the casting method from potato starch with halloysite nanoclay as the reinforcing materials. The composition included potato starch with 40 wt% of a mixture of

Table 3 List of the principal counterions used to modify MMT and the synonyms names associated with them

Counter-cation	Name
Na^+	Natural sodium MMT; MMT- Na^+ ; Cloisite® Na^+ ; Dellite® LVF; Dellite® HPS; Nanofil® 757; BH Natural
 Dimethyl-benzyl-hydrogenated-tallow ammonium	Cloisite® 10A; Bentone® 111; Dellite® 43B
 Dimethyl-dihydrogenated tallow ammonium	Cloisite® 20A; Cloisite® 15A; Cloisite® 6A; Dellite® 67G; Dellite® 72T
 Dimethyl-hydrogenated tallow-2-ethylhexyl ammonium	Cloisite® 25A
 Methyl-tallow-bis-2-hydroxyethyl ammonium	Cloisite® 30B
 Methyl-dihydrogenated tallow ammonium	Cloisite® 93A
 Octadecyl ammonium	Nanomer® I.30E
 Aminododecanoic acid	Nanofil® 784
 Stearyl-dihydroxyethyl ammonium	Nanofil® 804
 Distearyl dimethyl ammonium chloride	Nanofil® 948
 Dodecyl trimethyl ammonium	

(continued)

Table 3 (continued)

Counter-cation	Name
 Hexadecyl trimethyl ammonium	
 Dodecyl benzyl dimethyl ammonium bromine	
 Etanolamine	
 Citric acid	
Ca ²⁺	Natural calcium hectorite; Bentone EA-163

sorbitol/glycerol (weight ratio of 3–1 as plasticizer) with nanoclay (0–5 wt%). The clay nanoparticles incorporation decreased permeability of the material to gaseous molecules and improved the mechanical properties. Tensile strength increased from 7.33 to 9.82 MPa, and elongation at break decreased from 68.0 to 44.0 % with the filler addition. Matsuda et al. (2013) presented biodegradable trays of cassava starch and organically modified montmorillonite (Cloisite® 10A and 30B) using a baking process. The stress at break of the samples was strongly affected by the nanoclay additions for different RH conditions. In addition, independently of the nanoclay type or concentration used, the stress at break was significantly increased. The stress at break value for the control sample was 13.26 MPa while for the nanocomposite at 33 % RH it was 108.18 MPa.

The improvements observed in these properties are due to the good dispersion of silicate layers in the starch matrix, the high aspect (width-to-thickness) ratio and thus accessible exposed surface of the montmorillonite nanofiller, and the strong hydrogen bonding interactions.

4.4 Nanocomposites: Starch/Antioxidants and/or Antimicrobials

In food packaging and medical industry, biodegradable thermoplastic materials require the possibility to add antimicrobial and/or antioxidant agents to limit microbial activity.

Antimicrobial agents are additives that may retard microbial growth or cause microbial death, being the main targets of action pathogenic microorganisms producing toxins or causing infections and deteriorative microorganisms whose metabolic end products cause odors and flavors or texture and discoloration problems, in particular in food (Davidson and Zivanovic 2003). In medical science, antimicrobial components contribute to the elimination of infections and stimulate the immune system.

In the case of food, antioxidants are substances with the ability to delay or prevent the development of rancidity and deterioration of sensory attributes related to flavors and aroma; and also function as oxidation inhibitors or retarders. The effectiveness of these additives depends on a number of factors, like: intrinsic factors, such as the composition (lipids, carbohydrates and proteins), pH, water activity and oxide reduction potential; extrinsic factors, such as temperature, storage time, and humidity and atmospheric conditions; processing factors; and microbial factors, such as the type and quantity of microorganisms, resilience microorganisms and cellular composition (Davidson and Taylor 2007).

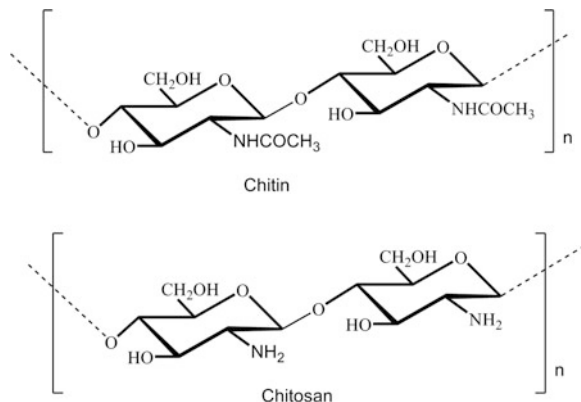
Different studies have shown that starch films are excellent intermediates for transporting antimicrobials and antioxidants. However, although the incorporation of organic compounds such as essential oils (Tripathi and Dubey 2004), organic acids (Schirmer et al. 2009), enzymes like lysozyme (Appendini and Hotchkiss 1997) and bacteriocins (Han 2005; Gálvez et al. 2007) is effective to improve the quality and safety, and/or to slow the oxidation of a product, typically deplete mechanical resistance and barrier properties (Raybaudi-Massilia et al. 2009). To solve this problem, nanofillers with antimicrobials and/or antioxidants characteristics have been used, to contribute their important antimicrobial properties, without diminishing general properties of the product (Pérez Espitia et al. 2012). The advantage of nanotechnology, which involves nano-sized products, has brought great opportunities for the development of antimicrobial agents with new properties.

The increasing number of studies in the nanocomposites field is probably due to the strong antibacterial activity achieved at low filler concentrations, caused by the high surface area to volume ratio, unique chemical and physical properties (Rai et al. 2009), and stability in extreme conditions (Sawai 2003).

These additives can be classified into two major groups: synthetic and natural nanofillers. The former has been used for many years and they have been generally produced by chemical synthesis. Such classification does not imply that synthetic preservatives are more effective from a microbiological point of view than those of natural origin, or vice versa (Davidson and Taylor 2007; Raybaudi-Massilia et al. 2009).

Natural fillers have low-cost, low density, high specific properties and, also, they provoke a great acceptance between consumers. They are particularly biodegradable and nonabrasive, unlike other reinforcing materials. Besides, they are readily available and their specific properties are comparable to those of other fillers used as reinforcements.

Fig. 7 Chemical structures of chitin and chitosan



Among possible natural nano-sized additives with antimicrobial character, chitosan nanoparticles (CH-NP) have been the focus of discussion of some investigators due to their high compatibility with starch, as both polysaccharides are structurally related (Yumin et al. 1997; Li et al. 2013) (Fig. 7). Chitosan is the main derivative of chitin, which is part of the carapace of crustaceans, mollusks, insects, and other living things. It is nontoxic, biodegradable, biofunctional and biocompatible and has the structure of a linear copolymer of glucosamine and *N*-acetylglucosamine units linked by β -1,4 glycoside linkages. Chitosan has the advantage of having antibacterial activity (Dutta et al. 2009), which makes it very promising for applications in the previously mentioned industries (Chang et al. 2010b, c).

In order to obtain nanocomposites with potential applications in medicine, agriculture, drug release and edible films packaging, Chang et al. (2010b) fabricated glycerol plasticized starch matrix films reinforced with different concentrations of chitosan nanoparticles. They prepared the nanoparticles by physical crosslinking (electrostatic interaction) between tripolyphosphate and protonised chitosan, instead of chemical crosslinking, obtaining CH-NP from about 50 to 100 nm. For the lower nanofiller contents (0, 2, 4 and 6 wt%) a good degree of dispersion was achieved, and the tensile strength and storage modulus increased in more than four times respect to the matrix. A decrease in the elongation at break was also exhibited, but it was of nearly a third of the matrix value. The similar polysaccharide structures of chitosan and starch and their great interaction were the reasons of that mechanical behavior (Yu et al. 2008). When 8 wt% of CH-NP were used, nanoparticles agglomerations were detected and the tensile strength resulted worse than that of the others composites. The glass transition temperature resulted also sensitive to the chitosan nanoparticles presence. With their addition, the T_g shifted to a higher temperature, indicating that the filler improved the intermolecular interaction in the matrix, reducing the free volume. On the other hand, water vapor permeability of composites decreased, probably due to the introduction of a tortuous path for the water molecules to pass through, in the case of the major concentration (Yu et al. 2008). These nanoparticles also modified the decomposition temperature of the

films. The degradation of the composites resulted at higher temperatures respected to that of the matrix. The increment of the thermal stability has been attributed to the better thermal stability of CH-NP, and the better interfacial interaction between the filler and the matrix.

In their work, (Chang et al. 2010b, c) found that the incorporation of chitin nanoparticles uniformly dispersed in a starch matrix at low loading levels (till 5 wt %) led to improvements in mechanical parameters (tensile strength, elastic modulus, and T_g) and water vapor permeability. For higher filler contents, agglomeration occurred, but good interfacial interactions between the nanofiller and the starch could be observed.

Woranucha and Yoksana (2013) conducted a thorough study about the possibility of using chitosan nanoparticles and eugenol-loaded chitosan nanoparticles as antioxidants to obtain active bio-based packaging materials by extrusion. They used a mixture of cassava, rice, and waxy rice flours as base material. The studies of the nanocomposites antimicrobial activity revealed that both chitosan and eugenol-loaded chitosan nanoparticles exhibited high antimicrobial. The incorporation of less than 6 wt% of nanoparticles did not greatly affect the crystallinity of the material. However, some physicochemical properties of these composites were changed by the incorporation of the nanofiller. The degradation and melting temperature of the matrix tended to decrease when CH-NP and eugenol-CH-NP were used, leading to a reduction in thermal stability of composites. The addition of only 3 wt% of this filler did not significantly changed tensile strength and elastic modulus respected to the matrix, but provoked a great reduction on the elongation at break. Although the eugenol has characteristics of plasticizer, which could lead to decrements in tensile strength and modulus and an increment in elongation at break, the incorporation of eugenol-loaded chitosan nanoparticles did not significantly change these mechanical parameters, because of the small amount of eugenol in the final material. In contrast, in composites with CH-NP, the elongation at break behaved as the matrix, but both tensile strength and modulus, decreased considerably, probably due to the particle agglomerations which might cause poor interfacial interaction between CH-NP and matrix as well as induce structural fragility. The incorporation of these nanoparticles caused a reduction of WVP, indicating that this property was enhanced by the incorporation of the nanofillers. Probably, the improvement might be due to the fewer free hydroxyl groups available in the matrix because of H-bond formation with the nanoparticles; and a more tortuous path for water molecules to pass through (Chang et al. 2010; Ghanbarzadeh et al. 2011). In the case of the incorporation of eugenol-CH-NP, WVP resulted lower and O_2P higher than those of starch/C-NP, due to the hydrophobicity of liberated eugenol in the extrusion process.

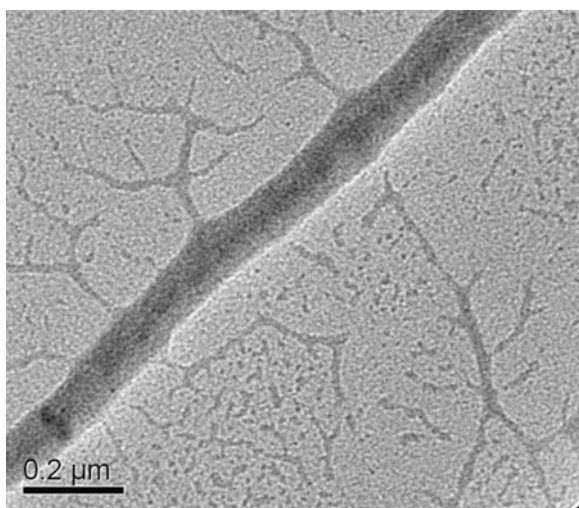
On the other hand, wood fibers are being used as natural reinforcement of composites in a large number of applications because of their low cost and readily availability. Recently, some researchers have explored the use of bamboo nano-size fibers into polymer materials (Takagi and Takura 2003; Takagi and Ichihara 2004; Ghavami 2005; Liu et al. 2010). Bamboo is a renewable natural bioresource abundant in tropical and subtropical regions of the world (Ghavami 2005). It has

several advantages respect to others wood fibers including small environment load, rapid growth, renewability, relatively high strength, and good flexibility (Liu et al. 2010).

Presently bamboo is considered as an important source of fibers. Their fibers are mainly composed by cellulose, hemicelluloses and lignin. There are, in minor concentration, other constituents as protein, fat, pectin, tannins, pigments and ash. These constituents play an important role in the physiological activity of the fibers. The nature of bamboo fibers is one of the most attractive characteristic of this material. This makes bamboo fibers promising alternatives, among the many types of natural fibers, for their use as bio-based composites reinforcements (Jindal 1986; Amada et al. 1997; Kitagawa et al. 2005). Particularly, it is deemed to have one of the most favorable combinations of low density and good mechanical properties (specific strength and stiffness) (Dieu et al. 2004).

Starting from bamboo fibers, a combined nitric acid–potassium chloride treatment and sulfuric acid hydrolysis can be used to obtain bamboo nanocrystals (B-NC). Liu et al. (2010) investigated the effect of B-NC (Fig. 8) incorporation on starch-based materials conformed by casting. The fractured surface of neat starch films was rather smooth, but when the starch matrix contained 1 wt% of the nanofiller, small leaves were pulled out of the matrix surface. The leaves kept increasing on the rugged fracture surface, due to good surface bonding between starch and low-level B-NC. In samples with high concentration of the filler, the interface was smooth with white dots. When filler level increased from 10 to 20 wt %, the composites exhibited increased groups of agglomerates. Micrographs finally detected that the suspended crystals kept their one-dimensional nano-size morphology at low concentrations of the bamboo reinforcement, but at high concentration levels, the crystals congregated into microparticles. With the addition of low filler concentrations (<8 wt%), the humidity content of the nanocomposites greatly

Fig. 8 TEM micrograph of bamboo nano crystals (B-NC). Reproduced with permission from Liu et al. (2010). © 2010, Elsevier Ltd



decreased, however in the case of the materials containing more than 8 wt% of B-NC, the decrease was much slower. Mechanical properties depended on the composites filler's content. Till 8 wt%, tensile strength and Young's modulus increased one order of magnitude, and the elongation at break decreased with increasing B-NC content. When the reinforcement was higher, no improvements were observed for all of these parameters. In that case, the interface adhesion had not been enough to withstand the imposed high stretching forces, resulting in diminished tensile strength. For all the composites, the relaxation transition temperatures shifted toward lower temperatures, what was attributed to the incorporation of a significant degree of crystallinity by the B-NC. The authors concluded that the addition of 8 wt % of bamboo cellulose crystals was quite sufficient to get an important reinforcing effect on a starch-based composite.

Different-sized bamboo fillers were obtained and incorporated into starch matrices. In this context Takagi and Ichihara (2004) investigated the effect of the dimension of short bamboo fibers and their concentration on mechanical properties of a starch–resin material. When bamboo fibers with smaller lengths than 15 mm were used, both tensile and flexural strengths of the composites tended to increase with the increment of the fiber dimensions. The authors also observed that this significant increment in the strengths parameters was experienced for samples with filler contents of up to a 10 wt%, but it did not happen in the cases of composites containing more than a 20 wt% of bamboo fibers.

On the other hand, when Takagi and Takura (2003) analyzed biodegradable composites fabricated with starch and bamboo powder of 500 μm in diameter, they found that the resultant materials had acceptable high bending strength and modulus.

As it was previously explained, many additives studied in order to provide antimicrobial and/or antioxidant properties to polymeric films were detrimental to some basic physical properties of composites. However, in several cases, when these additives were incorporated in powdered form instead of oil, some of them did not cause damage to the characteristics of the final material. One case is the work of Ghasemlou et al. (2013), who studied starch films containing *Zataria multiflora* Boiss (ZEO) or pennyroyal (MEO). The addition of both ZEO as MEO produced a decrease in water vapor permeability, while it had not lead to significant differences in O_2P , except with the incorporation of the highest concentration of both components. Following to Han et al. (2006), they suggested that the oxygen could have penetrated between the additives particles, facilitating its path for the case of higher concentrations. Another explanation was developed by the authors: in the starch films with ZEO smooth surfaces were observed, however, fine particles and holes distributed homogeneously in the polymer matrix had been found. In the case of the addition of high concentrations of MEO, a thicker microstructure had been seen, probably due to possible agglomerations.

Biocomposites with garlic powder added on glycerol–cassava starch films were studied by Famá et al. (2009b) and Famá et al. (2010). When the structure was evaluated, the authors observed a homogeneous distribution of nano/micro fibers that was attributed to the fact that garlic powder has a high percentage of water

soluble components (DTU Food 2009), detecting fibrils in the remainder of the solubilisation process. Due to the high number of hydroxyl groups present in this fiber (Sato et al. 2006; Corzo-Martínez et al. 2007), the number of groups available to be involved in exchange with water increased. Similar values of T_g were reported for both matrix and composites; however, composite presented slightly wider peak. This trend was ascribed to the occurrence of two opposite effects: first, the addition of a filler shifts the T_g to higher temperatures (Wollerdorfer and Bader 1998; Van de Velde and Kiekens 2002) and broadens peaks associated with it, but garlic powder contains chemical moieties that possess hydroxyl and amino groups (Sato et al. 2006; Corzo-Martínez et al. 2007) capable of forming hydrogen bonds, affecting the polymeric network formation, developing a plasticizing action (Chartoff 1981).

The development of new resistant bacteria to existing antibiotics (Singh et al. 2008) led to the search for other types of antibacterial substances that can effectively reduce the harmful effects of microorganisms. In the last years, the advent of nanotechnology made that some investigations focused on the development of inorganic fillers nanostructures. There are lots of inorganic composites that are considered nontoxic and contain mineral elements essential to the human body (Roselli et al. 2003). Most antibacterial inorganic materials are metallic nanoparticles and metal oxide nanoparticles such as silver, copper, titanium oxide, gold and zinc oxide (Sondi and Salopek-Sondi 2004; Cioffi et al. 2005; Chaudhry et al. 2008; Bradley et al. 2011). Besides their promising use in industries such as food or medicine, metal nanoparticles have been attractive because of their unique size-dependent optical (Norman et al. 2002; Ung 2002) and electronic properties (Wessels et al. 2004; Schmid and Simon 2005). In addition, they promise environmental benefit due to the possibility of their applications on nanoscience/nanotechnology, including new catalysts for environmental improve (Kamat et al. 2002), photovoltaic (Hasobe et al. 2003), thermoelectric materials for cooling without refrigerants (Venkatasubramanian et al. 2001), nanocomposite materials for vehicles (Lloyd and Lave 2003), sensors (Macanás et al. 2006; Muraviev et al. 2007), packaging in food industry (Varaprasad et al. 2010), and biomedical applications (Stodolak et al. 2009).

When an inorganic nanofiller is incorporated in a starch matrix, uniform dispersions and strong interfacial adhesion through hydrogen bonding between the metal and the matrix could be achieved due to the similar chemical structures of the stabilizer and the matrix (Chang et al. 2009; Ma et al. 2009; Yu et al. 2009; Liu et al. 2011). As a result, increments in mechanical properties (Wu et al. 2009; Yun et al. 2011), WVP (Yu et al. 2009; Liu et al. 2011), and UV absorbance (Chang et al. 2009; Ma et al. 2009), can be observed.

Oxide nanoparticles such as zinc oxide are a very innovative alternative for use as antibacterial agents to prevent bacterial growth (Moezzi et al. 2012). Research on zinc oxide (ZnO) as an antimicrobial agent started in mid-twentieth century. However, their real use for this application was late last century (Sawai 2003). Currently, ZnO is *generally recognized as safe* material by the U.S. (FDA 2011). It is an essential micronutrient and has important and critical roles in growth and development in humans and animals (Shi et al. 2008). In addition to its important

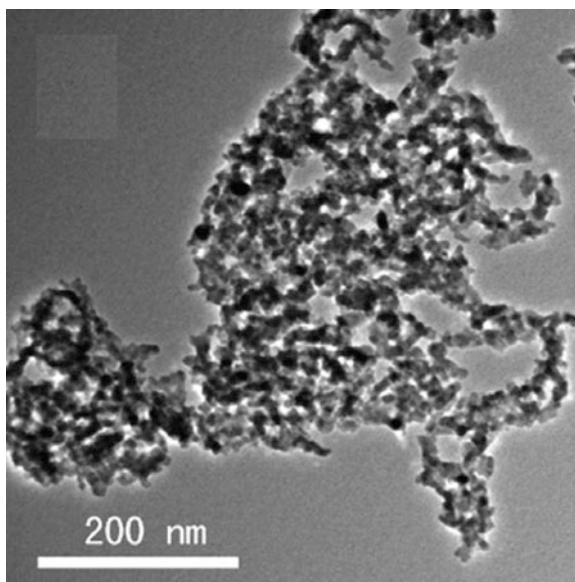
antimicrobial properties, there is a wide interest in ZnO is for its fundamental characteristic, which lead to potential applications in electronic, structural and biomaterials (Wang et al. 2004). Microelectromechanical devices, sensors, transducers and biomedical applications are a few among the spectrum of applications for ZnO.

Today, the major uses of zinc oxide are in the rubber industry, followed by ceramics (International Zinc Association-Zinc Oxide Information Center 2011), drilling fluids for the oil and gas industry (Lau et al. 1997; Sayyadnejad et al. 2008), LEDs, transparent transistors, solar cells and memory devices (Ozgur et al. 2005; Klingshirn 2007a), pigments (Auer et al. 2005), as an energy-saving coating on windows (Klingshirn 2007b), and as the basis of a transparent conducting oxide for consumer devices, for example in food packaging or medicine (Ellmer et al. 2008; Tankhiwale and Bajpai 2012).

In medicine, ZnO has been in use at least since year 2000 as a constituent of medicinal treatment of boils and carbuncles (Frederickson et al. 2005; Halioua and Ziskind 2005). In vitro tests have shown that zinc oxide nanoparticles (ZnO-NP) have antitumor activity against human colon carcinoma cells (De Berardis et al. 2010). ZnO-NP have been considered to be used for the prevention of infectious diseases through their antimicrobial effects (Zhang et al. 2008; Li et al. 2010; Rajendra et al. 2010).

Yadav et al. (2006) reported that ZnO-NP (Fig. 9) possess higher antibacterial effects on microorganisms *S. aureus* and *Salmonella* than other metal oxide nanoparticles (Jones et al. 2007), and fair activity against *E. coli* and *Bacillus phaeus* (Tam et al. 2008). The antimicrobial activity of these nanoparticles is attributed to several mechanisms, including the release of antimicrobial ions (Kasemets et al. 2009),

Fig. 9 TEM images of zinc oxide nanoparticles (ZnO-NP). Reproduced with permission from Pantani et al. (2013). © 2013, Elsevier Ltd



interaction of nanoparticles with microorganisms, subsequently damaging the integrity of bacterial cell (Zhang et al. 2008) and the formation of *reactive oxygen species* by the effect of light radiation (Jalal et al. 2010).

In this context, in order to improve the properties of glycerol plasticized starch films, Yu et al. (2009) prepared pea starch-based nanocomposites by casting containing ZnO-NP stabilized by carboxymethylcellulose sodium (CMC). A few agglomerations of the nanofiller with CMC appeared in the composites with higher filler concentrations (more than 5 wt%). The incorporation of the nanofiller at lower concentrations enhanced the pasting viscosity, storage modulus, glass transition temperature and the tensile strength of the nanocomposites. At these filler concentrations, the tensile strength increased more than 100 %, while an important decrement in the elongation at break to nearly half of the matrix value was observed. Besides, the glass transitions shifted to higher temperature with increasing contents of ZnO-NP. The authors explained this behavior in the same way as Chang et al. (2010b) in their investigation of starch/CH-NP nanocomposites, attributing it to the fact that ZnO-NP improved the intermolecular interaction of the matrix, reducing the free volume and increasing the glass transition temperature of composites. WVP of these composites decreased with the increasing of ZnO-NP concentration. This behavior was more marked at very low contents of filler, while for the higher concentrations the decrease of WVP resulted less evident. The addition of these nanoparticles probably introduced a tortuous path for water molecule to pass through (Kristo and Biliaderis 2007), as their water resistance was better than the matrix one. Since ZnO-NP-CMC could achieve a good dispersion degree in the starch matrix at low concentrations, there were few paths for water molecules to pass through. An important conclusion of these authors was that the ZnO-NP protected by CMC could be easily integrated into some relevant systems for pharmaceutical (drug release) and biomedical applications, as well as for agriculture, and packaging fields.

Parallel to the study of Yu et al. (2009), a bionanocomposite based on glycerol plasticized-pea starch containing ZnO-NP stabilized by soluble starch as filler, was developed by Ma et al. (2009). In this work, the authors showed that the incorporation of this nanofiller led to improvements in the pasting viscosity, storage modulus, glass transition temperature and UV absorbance. In the same way of Yu et al. (2009), the authors attributed the results to the interaction between ZnO-NP and starch matrix. Soluble starch played an important role in the stabilization of the filler and in the fabrication of starch/ZnO-NP composites. The strong interaction between the filler and the matrix contributed to the improvement in the bionanocomposite properties.

In the recently years some researches demonstrated the important effect of zinc oxide nanorods (ZnO-NR) incorporating them in a thermoplastic sago starch-based material (Nafchi et al. 2012, 2013; Rahman et al. 2013). In particular, (Nafchi et al. 2012, 2013) investigated physicochemical properties of nanocomposites formed by sago starch and different concentration of ZnO-NR (1–5 wt%). The incorporation of low concentration of this nanofiller significantly increased the viscosity of the solution and decreased water vapor permeability of the composites to less than one

third of the matrix one. These behaviors were attributed to the greater water resistance of the filler compared with the matrix, and the introduction of a tortuous pathway for water vapor molecules to pass through (Yu et al. 2009). Solubility, moisture content, and monolayer water content also decreased with the addition of ZnO-NR. According to Tunç and Duman (2010), the increment of the ZnO-NP concentration, results in the formation of more hydrogen bonds between the filler and the matrix components, making that free water molecules cannot interact as strongly with the nanocomposite than with the matrix. Besides, increasing the ZnO-NR content in starch films led to a greater contact angle, indicating greater hydrophobicity of the surface. The authors indicated that contact angle results were consistent with the decrease in water absorption tendency because the surfaces of the composites became more hydrophobic. Finally, these nanofiller did not modify UV transmittance of the films (0 %), and were able to absorb more than 80 % of Near Infrared spectra (Nafchi et al. 2012).

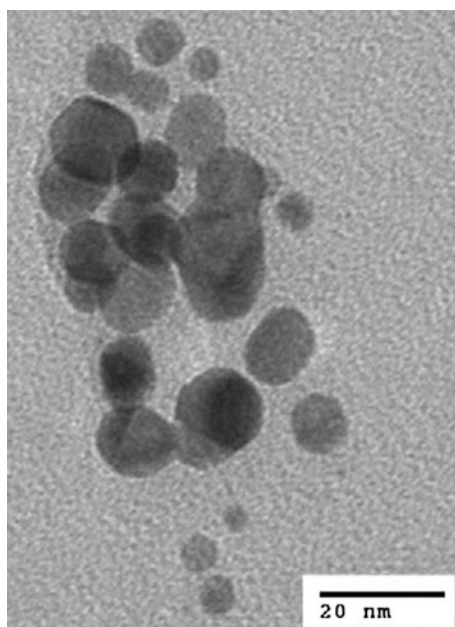
Similar behavior on water absorption capacity, WVP and water solubility of sago starch-based composites containing 0, 1, 3 and 5 wt% of ZnO-NR was reported by Alebooyeh et al. (2012): all these properties decreased by increasing concentration of the nanofiller. In particular, these authors observed that when ZnO-NR content was only 1 wt%, these parameters showed a more marked decrease, especially WVP. Furthermore, the addition of the nanorods demonstrated a decrease in the microbial activity, in particular, the composites showed antimicrobial properties against *E. coli*, which was very important even with the addition of the lowest concentration of ZnO-NR. In other investigation of Nafchi et al. (2013), mechanical, thermal and antibacterial properties of starch/ZnO-NR films were exposed. Significant increments in tensile strength and elastic modulus were observed when the nanorod concentration increased, while elongation at break decreased in all the studied composites. The authors explained that this phenomenon could have been due to two possible reasons. The first is related to the decrease in moisture content with the ZnO-NR addition. Water plays opposite roles in a biopolymer matrix: as plasticizer and as antiplasticizer, decreasing the flexibility of the films (Cheng et al. 2006; Müller et al. 2011). The second reason is related to the interfacial interaction between the nanorods and the starch matrix. In these work, the authors predicted the mechanical parameters of the composites, showing that the experimental values resulted higher than those data predicted, suggesting that there was a significant interaction between the sago starch matrix and the ZnO-NR. Dynamic mechanical properties indicated that the addition of the filler had significantly increased T_g . This behavior resulted consistent with the moisture content reported for this composite (Abdorreza et al. 2011; Nafchi et al. 2012).

Sago starch with ZnO-NR films exhibited excellent antimicrobial activity against *S. aureus*, suggesting these nanocomposites have potential applications as active packaging materials in the pharmaceutical and food industries. Rahman et al. (2013) used concentration of ZnO-NR between zero and 10 wt% to incorporate into a thermoplastic sago starch matrix. Initially, the authors showed no filler particles agglomeration in all film samples indicating an uniform distribution of the nanorods into the starch film. Unusually, FTIR analysis revealed that there was no presence

of new functional groups after the incorporation of the ZnO-NR, indicating that the interaction between the filler and the starch was physical or no covalent. By increasing the amount of filler, the authors observed a huge difference in the studied properties, especially on relative dielectric constant and electrical conductivity. When ZnO-NR concentration increased, the electrical conductivity and relative dielectric constant of the composites increased, becoming around 53 and 60 % in the case of the material with highest filler content, respectively. Similar to Nafchi et al. (2012), ultraviolet absorbance showed zero light transmission below 380 nm independently of the filler concentration. The authors concluded that that ZnO-NR can provide UV-shielding properties to TPS materials. When loss tangent with frequency less than 1 Hz was investigated, a decrement in the T_g was observed with the filler addition. In general, $\tan \delta$ values are expected to increase as concentration of filler increase. The opposite behavior observed in this case was explained taking into account the charge transport through the different chains or interfaces and to some defects as some agglomerations. The authors concluded that the antibacterial mechanism of starch/ZnO-NR composites could preclude the growth of bacteria.

Other metal as silver (Ag) is economical and has important antimicrobial activity properties (Sharma et al. 2009). However, the use of Ag as a reinforcement of thermoplastic materials requires a pretreatment of the metal, due to its natural size and its propensity to form agglomerates in the composite material. Improved properties are generally obtained when small dispersed nanodomains are observed (Wiley et al. 2007). In order to reduce the particle size, some authors synthesized silver nanoparticles (Ag-NP) (Fig. 10). Controllable synthesis of this metal is the

Fig. 10 TEM image of silver nanoparticles (Ag-NP). Taken from Seo et al. (2012). © 2012, Elsevier Ltd



first key challenge to achieve their better applied characteristics (Wiley et al. 2007). Silver nanoparticles can be prepared by physical, biological and chemical methods. Generally, the modification of this metal implies a large number of stabilizers, such as surfactants, proteins, peptides, polymers, oligonucleotides, carbohydrates, plants extracts, and organic solvents (Xie et al. 2007; Sharma et al. 2009). Ag-NP have attracted considerable interest in biological studies because of their easy preparation, good biocompatibility, and relatively large surface area (Wiley et al. 2004; Xie et al. 2007). Additionally, for their potential antibacterial characteristics (Huang et al., 2006), they are used as a sterilizer for removing bacteria from food (Creutz 1981; Davies 1992).

The incorporation of Ag-NP into biodegradable polymers for their potential applications in biotechnology has been a great interest topic in the last years (Huang et al. 2004; Narayanan and El-Sayed 2005; Murugadoss and Chattopadhyay 2008; Sanpui et al. 2008; Rhim et al. 2013; Cheviron et al. 2014). The carbohydrates can act as a reducing and/or stabilizer agent, and also have the possibility to carry Ag-NP with excellent antibacterial activity. The formed nanocomposites result safe, biocompatible, nontoxic, and environmentally friendly (Rhim et al. 2013).

Among all the studies about composites with silver nanoparticles, very few have concerned about the preparation of biodegradable starch–silver nanoparticles nanocomposites for green applications.

Cheviron et al. (2014) prepared environmentally friendly nanocomposite films based on potato starch/glycerol reinforced by colloidal Ag-NP by solution casting. In order to correctly disperse the nanofiller into the biodegradable matrix, the authors used water, glucose and soluble starch as solvent, reducing and stabilizing agent respectively. Two different populations with distinct Ag-NP particle size (diameters: 5 nm and 20–50 nm) were distinguished in their observations. They concluded that the starch presence in the colloidal nanoparticles allows a better dispersion of them in the starch matrix due to their similar chemical structure and the high molar mass polymer chains of potato starch.

Starch-based composites were developed by Khachatryan et al. (2013) using Ag-NP with dialdehyde starch (DAS) in order to reduce and protect agents. Micrographs confirmed formation of spherical Ag-NP of size within 10 and 15 nm, and with crystalline characteristics. TGA curves showed that the incorporation of the filler presented materials with approximately 1 % less water than matrix. It was also possible to note that the decomposition of the materials with the nanoparticles occurred in slightly smaller temperatures than that of DAS.

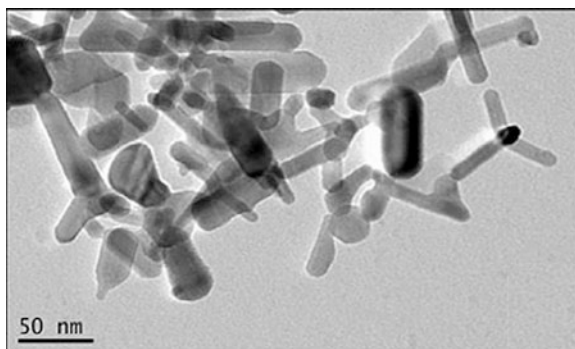
Yoksan and Chirachanchai (2010) used γ -ray irradiation reduction of silver nitrate in a chitosan solution to obtain Ag-NP with the objective of incorporating them into a starch-based matrix. TEM images showed that after the synthesis, silver nanoparticles presented a spherical shape with size between 20 and 25 nm. γ -ray irradiated chitosan solution containing Ag-NP exhibited an important antimicrobial activity against *E. coli*, *S. aureus* and *B. cereus*. When color was evaluated, matrix resulted transparent and slightly yellowish, while composites were pale brown; and the color difference of the film increased with the concentration of Ag-NP. Physicochemical behavior of these composites was not the most desired

compared with that reported in the literature (Khachatryan et al. 2013; Cheviron et al. (2014). In particular, films containing low concentrations of nanoparticles presented not markedly differences in tensile strength and elongation at break respect to the matrix, and a slightly improvement was achieved with the highest filler content, suggesting that the incorporation of Ag-NP could somewhat improve the tensile properties of starch-based films but not with low concentrations of the filler. However, in the case of the elastic modulus, a slight increase was observed for all composites. The addition of Ag-NP slightly increased WVP, probably due to the obstruction of intermolecular hydrogen bond formation between polymer molecules by Ag-NP, causing the incompatibility of the film matrix, adsorption of water vapor at the hydrophilic sites of polysaccharide molecules, and penetration of moisture (Shelma et al. 2008). The best result showed by these authors was the enhancement of O₂P properties of the composites with the addition of the silver nanoparticles.

Some authors have investigated the properties of starch/Ag-NP composites incorporating a biopolymer as part of the matrix or as an additive, for its antimicrobial contribution (Arockianathan et al. 2012; Zepon et al. 2013). The attributes of excellent biocompatibility of biopolymers with versatile biological activities and in some cases antimicrobial activity, have provided great opportunities to improve the properties of nanocomposites, obtaining functional biomaterials of high potential in various fields. In particular, in the investigation of Arockianathan et al. (2012) sago starch-based composite films impregnated with different concentrations of CH-Ag-NP were developed using casting method. FTIR spectrum validated chemical interaction between the polymers. The authors showed that the better composite was the one containing 10 wt% of CH-Ag-NP mix, which increased tensile straight without decreasing elongation at break, and its water absorption capacity after 24 h was lower than the matrix one. The authors used this nanocomposite and the starch matrix as wound dressing materials in experimental wounds of rats, and evaluated the healing pattern, observing faster healing in the cases treated with the material containing CH-Ag-NP compared to the control. They finally suggested that starch/CH-Ag-NP nanocomposite could have possibilities as a dressing material for wound healing applications.

Among the various semiconductor photocatalysts, titanium oxide (TiO₂) is one of the most popular and promising materials because it is stable in various solvents and it is commercially available (Sepone and Pelizzetti 1989; Schiavello 1997). It is also efficient to adsorb light energy. In particular, titanium oxide nanoparticles (TiO₂-NP) have been incorporated in polysaccharide based thermoplastic materials (Miao et al. 2008; Hejri et al. 2012; Nuryetti and Nasikin 2012; Sreekumar et al. 2012; Yun et al. 2012) (Fig. 11). TiO₂-NP have potential remarkable applications as an attractive filler for multifunctional materials, due to their unique properties such as higher stability, long lasting, safe and broad-spectrum antibiosis (Roessler et al. 2002; Cai et al. 2006). Their most striking characteristics are their photocatalytic activities (Kanehira et al. 2008; Wang et al. 2008), related to their microstructure and the powder purification (Weibel et al. 2006; Verran et al. 2007). Common preparation of these types of bionanocomposites included hydrolysis of the metal compounds and dehydration (Montoya et al. 1992), sol-gel (Barringer and Bowen 1982),

Fig. 11 TEM image of titanium oxide nanoparticles (TiO_2 -NP). Reproduced with permission from Miao et al. (2008). © 2008, Elsevier Ltd



a hydrothermal method (Kondo et al. 1994), or modification of commercially available TiO_2 .

Two methods are the most frequently used to perform a polymer-based biocomposites containing TiO_2 -NP. The filler is directly added into the starch matrix solution (Yun et al. 2011), or directly synthesized in a starch dispersion, which acts not only as the stabilizer but also as the matrix (Liao and Wu 2008).

In plants it has been demonstrate that TiO_2 -NP could increase the nitrate reductive enzyme, increase the abilities to absorb and use water and fertilizer, promote antioxidant system, and accelerate germination (Lu et al. 2002; Zheng et al. 2005; Navarro et al. 2008). In particular these effects can be because titanium oxide nanoparticles have high specific surface area.

One example of starch composites formed with TiO_2 -NP was the reported by Nuryetti and Nasikin (2012). They prepared tapioca starch matrices containing different concentrations of this filler (1, 3, 5 and 7 wt%) using a melt process, in order to investigated structure, energy band gap, and electrical conductivity of the composites. The energy gap range for the composites with TiO_2 -NP resulted very closed in number (3.30–3.22 eV), and similar to the values of the energy gap of semiconductors (Poole and Owens 2003; Sing et al. 2010). UV tests showed that tapioca starch/ TiO_2 -NP were effective as barriers for UV wavelength range (315–280 nm) (Kim et al. 2000). The incorporation of filler concentrations till 3 wt% resulted in a small increase of the electrical conductivity of the composites, while in the case of 5 wt%, the increment was sharp. However, a decrease in electrical conductivity of the composite with 7 wt% of filler was observed. Finally, taking into account the conductivity behavior, starch/ TiO_2 -NP presented percolation thresholds when concentrations of the oxide were between 3 and 5 wt%.

5 Conclusions and Future Perspective

In this chapter a review of the most important and recent researches on development and characterization of biodegradable nanocomposites based on starch reinforced by different types of nanofillers were exposed. Particularly, the investigation was

focused on the influence of the incorporation of starch, cellulose, layered silicate, and antioxidant and/or antimicrobial nanofillers on the physicochemical properties of the composites.

Some different methods for processing both starch matrix and nanocomposites were discussed. Significant attention was paid on the variables involved in casting and extrusion techniques, being these the most used methods at laboratory and industrial scale processes.

Several physicochemical properties as structure, mechanics and barrier, as well as degradation, antibacterial and antioxidant activity have been presented. There is agreement in the literature about improvements in barrier, thermal and mechanical properties of starch by the addition of nanofillers, only in the cases in which they are well dispersed and are compatible with it. In some cases the methodology for the nanofiller obtaining generates reactive groups that help the filler dispersion in the starch matrix, whereas in other cases it is necessary to functionalize them. In particular in the case of clays, they are usually modified by organic surfactants. Furthermore, the interface between filler and matrix plays a crucial role in the final properties of the composite. Besides, the researches on nanofillers with antibacterial characteristics as chitosan, garlic, bamboo, zinc oxide, silver and titanium oxide, demonstrated that the incorporation of this kind of reinforcement in a starch material serves to retard the growth and the action of pathogenic microorganisms whose produce toxins or cause infections. On the other hand, in some cases the degradation of the composites results at higher temperatures due to the characteristics of the nanofiller.

From the results reported in the different works cited in this chapter, it can be concluded that in order to improve the barrier, mechanical and thermic properties of a starch matrix, the next considerations need to be taken into account: (a) morphological and chemical characteristics of the employed nanofillers; (b) the reactive groups in their surface, as well as their crystalline fraction (this depends on the methodology employed for their obtaining); (c) the variables involved in the biodegradable nanocomposites manufacture.

Taking into the account the serious problems that have been caused by mis-treatment ecology due to the increasing use of synthetic materials, necessary awareness must be given to the replacement of these treacherous by materials that are friendly to both the environment and human health. Furthermore, the increasing use of synthetic polymers or plastics as a result of the growing human population and standard of living will result in higher demands on oil production and will contribute to a possible depletion of crude oil before the end of the century. The implement of the bio-based polymers use will reduce the dependency on the plastics derived from the petroleum industry, creating more sustainable alternatives. Nowadays, there are few companies that use starch-based polymer materials in the packaging industry and food products. For example, Biostarch (Singapour), Plantic (Australia), Novamont (Australia), BIOP Biopolymer Technologies (Germany) and Sphere (France) manufacture disposable products as dishwasher tablets, plates, cutlery, glasses, thermoformed trays, film to cover food, packaging, bags for agriculture, etc.

Based on the literature, several nanofillers showed that they can improve the properties of biodegradable starch-based polymers making possible their use in numerous applications.

In particular, nowadays industries with high demand for materials with these nanocomposites' characteristics, such as packaging or biomedicine, do focus on them to be implemented in daily life.

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