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REVIEW PAPER

Polysaccharide nanocrystals as fillers for PLA based nanocomposites

Roberto Scaffaro · Luigi Botta · Francesco Lopresti · Andrea Maio · Fiorenza Sutera

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Abstract The development of green nanocomposites based on biopolymers and bio-based nanofillers has attracted over the recent years the attention of academic and industrial research. Indeed, these nanocomposites could replace some oil-derived polymers and thus helping to overcome environmental problems. In this regard, PLA as matrix and polysaccharide nanocrystals as fillers are the most promising components to obtain high-performance green bio-nanocomposites suitable for different applications, particularly for packaging and biomedical applications. Indeed, at present, due to its processability, mechanical and biological properties, as well as its commercial availability, poly(lactic acid) (PLA) possesses one of the highest potentials among biopolymers whereas polysaccharide nanocrystals can be considered the most promising bio-based reinforcements due to their availability, renewability, versatility, biodegradability and high aspect ratio. Aim of this review is to give an overview on the preparation routes and main properties of PLA/polysaccharide nanocomposites highlighting the main differences among the three main polysaccharide nanocrystals, i.e. cellulose, chitin, and starch.

Keywords Poly(lactic acid) (PLA) · Nanocomposites · Polysaccharide nanocrystals · Cellulose nanocrystals (CNCs) · Chitin nanocrystals (ChNCs) · Starch nanocrystals (SNCs)

Introduction

Several inorganic nano-sized particles, such as layered silicates, metals, carbon nanomaterials, silica nanoparticles, have been extensively studied in the field of nanocomposites and nanohybrids (Paul and Robeson 2008; Chen et al. 2010; Zhu et al. 2012; Gu et al. 2013, 2016; Maio et al. 2014, 2016a; Gedler et al. 2016; Guan et al. 2016; Guo et al. 2016; Liu et al. 2016a; Scarfato et al. 2016; Sirin et al. 2016). Indeed, it is well known that nanocomposites, i.e. polymers filled with particles having at least one dimension in the nanoscale range (i.e. <100 nm), show unique properties because of the peculiar increase of the matrix-filler interface (Botta et al. 2007, 2010; Scaffaro et al. 2009, 2010, 2011a, b, 2013a, b; Maio et al. 2014; Thakur and Kessler 2015). However, due to growing concerns over sustainability and environmental protection, many efforts have been carried out for the development of eco-friendly nanoparticles. Among these ones, polysaccharide nanocrystals (PNs) can be considered the most promising nanofillers due to their availability, renewability, versatility, biodegradability and high aspect ratio. Polysaccharide nanocrystals can

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R. Scaffaro (✉) · L. Botta · F. Lopresti · A. Maio · F. Sutera
Dipartimento di Ingegneria Civile, Ambientale, Aerospaziale, dei Materiali, UdR INSTM di Palermo, Università di Palermo, Viale delle Scienze, 90128 Palermo, Italy
e-mail: roberto.scaffaro@unipa.it

be obtained by a simple process based on the acid hydrolysis of biomass under controlled conditions. Multiple new techniques to isolate polysaccharide nanocrystals were recently developed (Bogdanova and Chvalun 2016).

PNs exhibit a varied morphology, high specific strength, high rigidity and high specific surface area and in general, as reported in Table 1, properties comparable to those of some commonly used inorganic fillers that however are neither biodegradable nor renewable. PNs include rod-like or spherical cellulose nanocrystals, rod-like chitin nanocrystals, and platelet-like starch (Hu et al. 2014). These three abundant renewable polysaccharides have similar building blocks, even if they show quite different properties because of the existing differences in molecular structure leading to different arrangements and supramolecular structures.

The potential of these nanoparticles has been proved for special functional nanomaterials but they have attracted significant interest as a bio-based reinforcing nanofillers for polymer nanocomposites (Dufresne and Lin 2014). Although several polymers have been used as matrices, including oil-based synthetic polymers, the optimum is to incorporate PNs into biopolymers since the latter ones possess properties comparable to traditional polymers but are renewable and biodegradable (Van de Velde and Kiekens 2002; Morreale et al. 2008a, b; Thakur et al. 2012a, b; 2013b, d, 2014a, b, d; Wang and Mao 2012; Scaffaro et al. 2013c, 2015, 2016a, f, g; Thakur and Thakur 2014, 2015). Indeed, as well known, a broad use of biopolymers is often restricted by the need of improving some functional properties and an effective way to improve their properties, thus enhancing their commercial potential, is to incorporate into the polymeric matrix, fibers or particles including nanosized ones (Bordes et al. 2009; Raquez et al. 2013; Thakur et al. 2013a, c, e, 2014c; Scaffaro et al. 2014; Fiore et al. 2014; Botta et al. 2015a, b; La Mantia et al. 2015; Pappu et al. 2015).

Poly(lactic acid) (PLA) can be considered one of the most attractive biopolymers due to its physical properties, renewability, biodegradability (Auras et al. 2004; Jamshidian et al. 2010; Rasal et al. 2010; Inkinen et al. 2011; Lopes et al. 2012; Scaffaro et al. 2016b, e). Moreover, PLA can be processed with a large number of techniques and it is commercially available in a wide range of grades making it suitable for several applications (Auras et al. 2004; La Mantia et al. 2012; Lopes et al. 2012; Lo Re et al. 2015; Scaffaro et al. 2016c, d).

The incorporation of polysaccharide nanocrystals to PLA allow obtaining nanocomposites that could overcome environmental problems since both the matrix and the filler are renewable and biodegradable. Furthermore, polysaccharide nanocrystals may improve the mechanical, thermomechanical and barrier properties of PLA and enhance its surface appearance thus making PLA/PNs nanocomposites suitable for different applications, particularly for packaging and biomedical applications. However, the main challenges are the achievement of a homogeneous dispersion within a polymeric matrix and the improvements of its usually poor interfacial adhesion with cellulosic particles.

Although, several reviews are focused on polymer nanocomposites with reinforcements from renewable sources (Moon et al. 2011; Abdul Khalil et al. 2012; Miao and Hamad 2013; Morán et al. 2014; Ching et al. 2016; Dufresne and Castaño 2016; Oksman et al. 2016; Bogdanova and Chvalun 2016; Panaitescu et al. 2016) or on PLA nanocomposites (Singh and Ray 2007; Jamshidian et al. 2010; Lagarón 2011; Balakrishnan et al. 2012; Armentano et al. 2013; Raquez et al. 2013; Brzeziński and Biela 2014; Norazlina and Kamal 2015), the attention is paid particularly only on nanocellulose and at the best of our knowledge, no review reports the status of the research on the nanocomposites based on PLA and polysaccharide nanocrystals, i.e. cellulose, chitin, and starch, providing a comparison among them. In particular, aim of this review is to give an overview on the preparation routes and main properties of PLA/polysaccharide nanocomposites highlighting the main differences among the three polysaccharide nanocrystals.

Poly(lactic acid)

PLA is an aliphatic polyester derived from 100% renewable resources (Auras et al. 2004; Jamshidian et al. 2010; Rasal et al. 2010; Inkinen et al. 2011; Lopes et al. 2012). It was first synthetized by Carothers (DuPont) in 1932 although only in 1954 Du Pont produced PLA with higher molecular weight that was eventually patented.

PLA can be synthetized through different polymerization routes of lactic acid monomers, i.e. ring

Table 1 Main properties of polysaccharide nanocrystals and of some common nanoparticles used as fillers for polymer based nanocomposites

Nanofiller	Geometry	Elastic modulus (GPa)	Biodegradability	Biocompatibility	Renewability	Antimicrobial properties	Wettability	Problems related to dispersability
CNTs	1D	270–900 GPa (Yu et al. 2000; Demczyk et al. 2002)	No	No (Chang et al. 2011)	No (Prasek et al. 2011)	Yes (Kang et al. 2007)	Hydrophobic (Scaffaro and Maio 2012)	Bundling (Scaffaro et al. 2012; Maio et al. 2014)
Graphene, GNP	2D	1000 (Maio et al. 2015)	No	No (Chang et al. 2011; Wojtoniszak et al. 2012; Scaffaro et al. 2016)	No (Choi et al. 2010)	Yes (Liu et al. 2011)	Hydrophobic (Mohd Zubir et al. 2016; Park et al. 2016)	Stacking (Yang et al. 2011)
GO	2D	200–300 (Zhu et al. 2010)	Moderate (Kotchey et al. 2012)	Yes (Chang et al. 2011; Wojtoniszak et al. 2012; Scaffaro et al. 2016g)	No (Zhu et al. 2010)	Yes (Chen et al. 2014)	Amphiphilic (Maio et al. 2016a, b; Mohd Zubir et al. 2016)	Stacking, crumpling (Maio et al. 2015; Scaffaro and Maio 2017)
Nanoclay	2D	168–265 (Rhim et al. 2009)	No (Le Corre et al. 2013)	Yes (Nitya et al. 2012)	No (Le Corre et al. 2013)	Yes (Rhim et al. 2009)	Hydrophilic (Rhim et al. 2009)	Stacking (Scaffaro et al. 2009)
CNC	0D; 1D	200 (Dufresne and Lin 2014)	Yes (Spinella et al. 2015)	Yes (Blaker et al. 2010)	Yes (Dufresne and Lin 2014)	No (Dufresne and Lin 2014)	Hydrophilic (Dufresne and Lin 2014)	Bundling (Peng et al. 2013)
CNF	1D	200 (Dufresne and Lin 2014)	Yes (Zeng et al. 2016)	Yes (Cho et al. 2012)	Yes (Dufresne and Lin 2014)	No (Dufresne and Lin 2014)	Hydrophilic (Dufresne and Lin 2014)	Bundling (Spinella et al. 2015)
CNW	0D	200 (Dufresne and Lin 2014)	Yes (Dufresne and Lin 2014)	Yes (Blaker et al. 2010)	Yes (Dufresne and Lin 2014)	No (Dufresne and Lin 2014)	Hydrophilic (Dufresne and Lin 2014)	Bundling (Fragal et al. 2016)
Chitin	1D	100–150 (Paillet and Dufresne 2001)	Yes (Paillet and Dufresne 2001)	Yes (Paillet and Dufresne 2001)	Yes (Paillet and Dufresne 2001)	Yes (Paillet and Dufresne 2001)	Hydrophilic (Paillet and Dufresne 2001)	Bundling (Ifuku et al. 2015)
Starch	2D	>100 (Hu et al. 2014)	Yes (Le Corre et al. 2013)	Yes (Le Corre et al. 2013)	Yes (Le Corre et al. 2013)	No (Le Corre et al. 2013)	Hydrophilic (Le Corre et al. 2013)	Stacking (Angellier-Coussy and Dufresne 2013)

opening polymerization (ROP), polycondensation and direct methods like azeotropic dehydration and enzymatic polymerization (Jamshidian et al. 2010; Inkinen et al. 2011). Nevertheless, polycondensation of lactic acid does not allow to obtain high molecular weight PLA that, on the contrary, can be obtained through ROP of lactide (Lopes et al. 2012). ROP can be performed in the melt, in solution, or in bulk and by anionic, cationic, and coordination-insertion mechanisms depending on the catalyst. Stannous octoate is usually preferred as catalyst since it provides high conversion rate, high reaction rate, and high molecular weights, even under rather mild polymerization conditions (Lopes et al. 2012).

Several companies such as Cargill Dow Polymer LLC, Shimadzu Corp, Mitsui Chemicals, Musashino Co. are now producing PLA-targeting markets for packaging, films, textiles, along with pharmaceutical products and biomedical devices. The US Food and Drug Administration (FDA) and European regulatory authorities have already approved the PLA resins for all food type applications and some chirurgical applications such as drug releasing systems (Auras et al. 2004; Lopes et al. 2012).

Due to the chirality of the lactic acid molecule, PLA has stereoisomers, such as poly(L-lactide) (PLLA), poly(D-lactide) (PDLA), and poly(DL-lactide) (PDLLA).

The properties of PLA are affected by several factors such as the source, the component isomers, the annealing time, the processing routes, the molecular weight (Van de Velde and Kiekens 2002; Nampoothiri et al. 2010; Raquez et al. 2013; Scaffaro et al. 2014; Fiore et al. 2014; Botta et al. 2015a, b; Farah et al. 2016). In general, PLA crystallinity, and consequently its properties, is strongly influenced by the stereochemistry and thermal history. PLA with PLLA amount higher than 90% tends to be crystalline, while the lower optically pure is substantially amorphous. Both melting temperature (T_m) and glass transition temperature (T_g) of PLA decrease on decreasing the content of PLLA (Auras et al. 2004). In Table 2 the main physical properties of PLA, PLLA and PDLLA are reported (Van de Velde and Kiekens 2002).

PLA degradation occurs mainly by hydrolysis, after several months exposure to moisture. In particular, it degrades in two stages: in the first stage, random non-enzymatic chain scission of the ester groups leads to a decrease of molecular weight; in the second, the molecular weight is reduced until the lactic acid and low molecular weight oligomers are naturally metabolized by microorganisms to finally yield carbon dioxide and water (Auras et al. 2004; Oyama et al. 2009). PLA degradation rate is strongly affected by several factors such as temperature, moisture, amount of isomer, crystallinity, residual lactic acid concentration, molecular weight, water diffusion and metal impurities from the catalyst (Auras et al. 2004; Lopes et al. 2012).

The mechanical properties of semi-crystalline PLA are attractive, and, in particular its elastic modulus make it an excellent substitute of commodity polymers such as polyethylene (PE), polypropylene (PP), polystyrene (PS) and polyethylene terephthalate (PET) in short-time packaging. Nevertheless and similarly to PS, the poor impact strength of PLA represents one of its main limitations for its sustainable development (Auras et al. 2004). Furthermore and in addition to these limits, the main issue about commercial PLA is related to its low crystallization ability and degree, that strongly limits its industrial implementation in different applications, particularly in durable applications like automotive and electronics (Rasal et al. 2010). A solution for overcoming the problem, widely used over the past years, consisted in the incorporation of nanosized reinforcements within the polymeric matrix, yielding so-called nanocomposite materials (Bordes et al. 2009; Raquez et al.

Table 2 Main physical properties of PLA, PLLA and PDLLA

Polymer	E (GPa)	TS (MPa)	EB (%)	T_m (°C)	T_g (°C)
PLA	0.35–3.5	21–60	2.5–6	150–162	45–60
PLLA	2.7–4.14	15.5–150	3.0–10.0	170–200	55–65
PDLLA	1–3.45	27.6–50	2.0–10.0	Amorphous	50–60

Elastic modulus (E), tensile strength (TS), elongation at break (EB) melting temperature (T_m) and glass transition temperature (T_g) (Van de Velde and Kiekens 2002)

2013). Different kinds of nanofillers have been considered as reinforcing agents to PLA matrix in order to enhance its thermo-mechanical properties as well as to provide additional functionalities like fire-resistance.

Polysaccharide nanocrystals

Differently from traditional and most common used inorganic nanoparticles, polysaccharide nanocrystals (PNs), are renewable and biodegradable. Moreover, PNs exhibit a varied morphology, high specific strength, moduli in the range 100–200 GPa (i.e., high rigidity), and high specific surface area (usually several hundred square meters per gram) (see Table 1). PNs are generally extracted by acid hydrolysis; the different methods of extraction and sources affect the structure, morphology, and surface properties of PNs.

Cellulose nanocrystals

Cellulose can be considered one of the most important renewable materials of the current century, owing to several factors. First, it is the most widely and abundantly spread organic material on the Earth (Kim et al. 2015). The most relevant sources are plant fibers, whose cellulose is the main skeletal component, however it is possible to extract it even from microbes (acetobacter) and animals (ascidian) (Takagi 2014).

Cellulose provides several benefits in terms of sustainability, renewability and biodegradability, thus fulfilling the current requirements of eco-friendly and biocompatible products (Johari et al. 2016). It displays high versatility, since it can be used either as a polymer (i.e. in its raw form) (Persenaire et al. 2016) or as a nanofiller (via isolation of the crystalline domains from cellulose sources) (Dufresne 2013). Furthermore, cellulose possesses fascinating structure and chemical-physical properties.

Indeed, from a chemical point of view, cellulose is an organic homopolymer, constituted by 1,4-anhydroglucopyranose repeating units. The sequence of cyclic poly(hydroxyl) building blocks determines that all the –OH moieties are equatorial with respect to the six-membered ring, as well as the 1–4 acetal links. The pendant equatorial hydroxyl groups provide the formation of intramolecular hydrogen bonds along the axis of the chain between neighboring glucose units, thus hindering the rotation of the chain about the 1–4 acetal links. The combination of ring structures and intramolecular hydrogen bonding confer high rigidity, crystallinity and close packing to linear stiff-chain cellulose molecules. The structure of cellulose macromolecules can be considered as the renewable equivalent of aramids, by replacing benzene with glucose. As a consequence, the density and the mechanical features of the two materials are quite similar. A perfect cellulose crystal possesses a Young's modulus (E) of about 200 GPa and a tensile strength (TS) ranging from 2 to 10 GPa (Dufresne 2013).

Furthermore, if compared to other nanofillers currently attractive for polymeric nanocomposites, cellulosic nanocrystals display mechanical properties similar to those of graphene oxide and oxidized carbon nanotubes (Maio et al. 2014, 2015, 2016a; Scaffaro and Maio 2017). Owing to these considerations, cellulosic nanofillers may represent an ecofriendly, renewable alternative to oxidized graphene-related materials, especially for those applications where renewability and biocompatibility are preferred to electrical properties, being equal or substantially similar either mechanical performance and gas permeability.

Based on the geometric features, it is possible to categorize cellulosic compounds into "micro" cellulosic products, whose particle size lays in the scale of several microns, and "nano" cellulosic products, characterized by at least one or two dimensions in the scale of nanometers. Hence, the aspect ratio is a crucial parameter to better identify the different types of cellulose nanoparticles which are generally categorized as (Le Corre and Angellier-Coussy 2014):

(1) nano crystalline cellulose (NCC) or cellulose nanocrystals (CNCs), $D < 10$ nm, $L/D = 20$–40;
(2) hydrolyzed cellulose whiskers or cellulose nanowhiskers (CNWs), $D = 5$–10 nm, $L/D = 3$–10
(3) nanofibrillated cellulose (NFC) or cellulose nanofibers (CNF), $D = 100$–1000 nm, $L/D = 20$–200
(4) bacterial cellulose, $D = 50$–100 nm, $L/D = 300$–800

The source of cellulose nanoparticles affects their distinctive sizes and aspect ratios (see Fig. 1).

Another key factor to be considered is the degree of polymerization (DP) of the different forms of

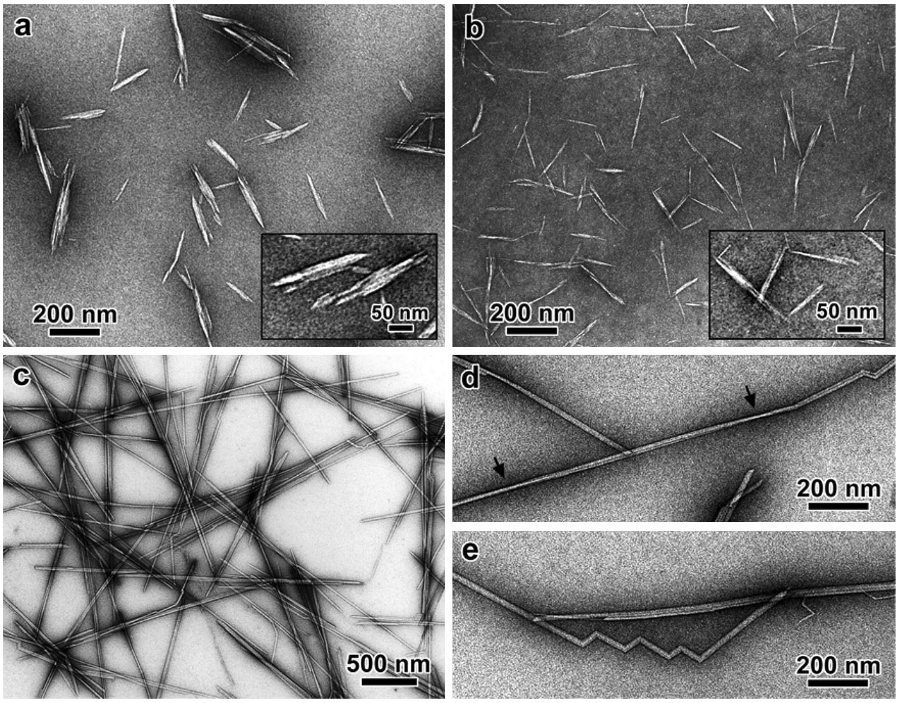

Fig. 1 TEM micrographs of negatively stained cellulose nanowhiskers obtained by sulfuric acid hydrolysis of cotton (**a**), Avicel (**b**), and tunicate (**c**–**e**) cellulose. *Insets* enlarged views of some characteristic particles. Reprinted with permission from (Elazzouzi-Hafraoui et al. 2008). Copyright (2008.) American Chemical Society

cellulose. DP depends on the source material (cotton, softwood, hardwood, etc.) and on the intensity of chemical and/or mechanical treatments: the stronger chemical treatment the lower the DP; the higher the L/D the higher the DP (Aspler et al. 2013). Cellulose is also prone to be superficially modified by several reaction paths, thus extending the range of its possible application fields. Currently, cellulose-based materials find a wide variety of applications, such as biomedical uses (wound dressing, nanocarriers for drug delivery, scaffolds for tissue engineering), environmental remediation (water treatment), energy and electronic applications (energy harvesters, paper transistors, OLED) and materials science (fillers for polymer nanocomposites) (Kim et al. 2015). In the recent years, the surface derivatization and graft copolymerization of cellulosic nanomaterials gained much concern.

Indeed, the intrinsic hydrophilicity of cellulose hinders its dispersion in both hydrophobic solvents and molten matrices. Thus, surface modification with hydrophobic monomers (Petersson et al. 2007) represents the most widely employed strategy to lower the interfacial associative tensions, yielding a surface capable to improve the affinity towards nonpolar compounds, without affecting the mechanical properties of the bulk nanocellulose. In this direction, several methods were reported, including the use of surfactants, graft copolymerization, surface derivation, corona or plasma discharges (Anirudhan and Rejeena 2012; Wolf et al. 2013; Cunha et al. 2014; Hoeng et al. 2016).

Chitin nanocrystals

In the past recent years chitin nanocrystals (ChNCs) were developed due to their excellent properties including biocompatibility, nontoxicity, and biodegradability. As matter of fact, they can play a key role in a variety of areas such as biomedical applications, water treatment, agriculture, and attractive component for natural nanocomposites processing (Zeng et al. 2012).

After cellulose, chitin is the second most abundant biopolymer occurring in nature since it is biosynthesized by many living organism such as shellfish, crabs, shrimp, insects, mushrooms and algae. The chitin's molecular structure is characterized by the repeating units along the *N*-acetylglucosamine structure.

Chitin's crystalline domains are characterized by high modulus but natural chitin is a semicrystalline material. In order to remove the amorphous domains and isolate the nanoscaled crystalline domain, chitin is usually chemical treated in acid environment (Zeng et al. 2012).

Nanocrystalline chitin shows usually a whiskers morphology with size in the range of 4–30 nm for the cross-sectional width and 50–500 nm for the length, as shown in Fig. 2 (Revol and Marchessault 1993; Paillet and Dufresne 2001; Gopalan Nair and Dufresne 2003; Goodrich and Winter 2007; Fan et al. 2008, 2010; Yamamoto et al. 2010; Guan and Naguib 2014). The Average value of the literature for β chitin longitudinal elastic modulus is 150 GPa while the transverse modulus taken as the lowest value of the two transverse modulus (by analogy with cellulose whiskers) is around 15 GPa (Paillet and Dufresne 2001).

Crystalline chitin presents three polymorphic forms: α-, β-, and γ-chitins, this last occasionally found as a transformation of the α structure (Atkins 1985). The most abounding chitin form, α-chitin, is usually derived from crab and shrimp. This is the most stable arrangement because this form is favorable for the formation of strong intermolecular hydrogen bonding.

ChNCs are often derived from living tissues so the presence of impurities, such as proteins, require particular purification steps. The structural properties and the degree of crystallinity are strongly affected by the extraction method and the chitins source. Acid hydrolysis is the method most commonly used to prepare ChNCs. Usually the common preparation steps are (1) hydrolysis with strong acid; (2) mechanical disintegration; (3) reflux of the solution in an alkaline solution to remove various proteins and (4) purification, filter and dispersion in distilled water (Revol and Marchessault 1993; Paillet and Dufresne 2001; Guan and Naguib 2014).

Another synthetic route to prepare highly crystalline α- and β-ChNCs is provided by TEMPO-mediated oxidation of crab shells and squid pen respectively (Fan et al. 2008, 2009).

Morin and Dufresne prepared long ChCNs whiskers (500–10,000 nm) by riftia tubes (a marine invertebrate) extraction with HCL hydrolysis (Morin and Dufresne 2002). The ChNCs cristallinity is usually around 84% (Goodrich and Winter 2007) and very high (94%) in the case of TEMPO-mediated oxidation of crab shells (Fan et al. 2008).

Starch nanocrystals

Starch nanocrystals (SNCs) have attracted considerable interest in bio-based nanofillers production thanks to easiness to chemically modify (Le Corre et al. 2010) and semi-crystalline structure that gives interesting property (Huang et al. 2013).

Starch is an abundant, biodegradable, biocompatible, non-cytotoxic, and low cost carbohydrate polymer produced in nature (Mathew and Dufresne 2002).

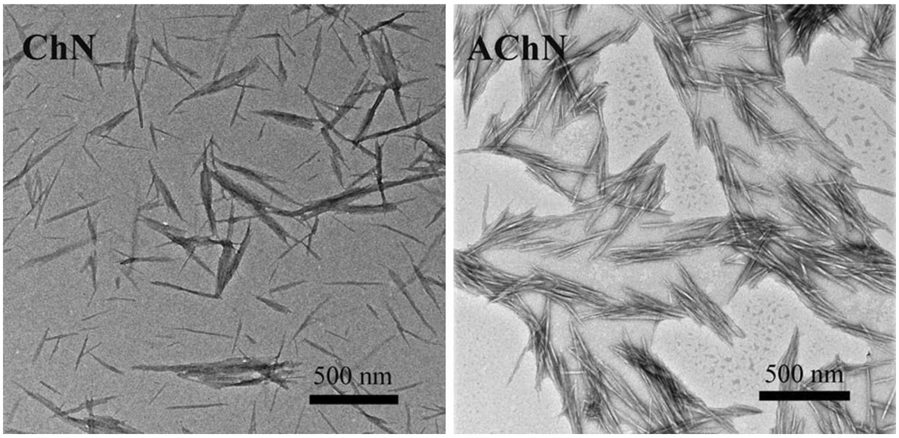

Fig. 2 TEM micrographs of chitin nanocrystals (ChN) and acetylated chitin nanocrystals (AChN). Reprinted from (Zhang et al. 2014), Copyright (2013), with permission from John Wiley and Sons

It consists of two main components: amylose, a mostly linear or slightly branched macromolecule; and amylopectin, a highly branched macromolecule. The ratio between both molecules depends on the botanical origin (Ashwar et al. 2016).

The “native starch” is used as extracted from roots of green plants, corn, wheat, rice, potato and tapioca (Smith et al. 1967), while the “modified starch” is chemically treated to improve its specific properties (Mary et al. 2013). As extracted from plants, the starch granules are in the form of a white powder with diameter in the range 2–100 μm, insoluble in cold water. The shape and particle size of granules depends strongly on its sources. A generally accepted model refers to a multiscale structure. The granule (2–100 μm) is composed by alternating amorphous and semicrystalline growth rings (120–500 nm) consisting of blocklets (20–50 nm); these blocklets are composed of amorphous and crystalline lamellae (9 nm) containing amylopectin and amylose chains (0.1–1 nm) (Le Corre et al. 2010). Being derived from the crystalline regions of the original starch granules, starch nanocrystals differ from starch nanoparticles, which can be even amorphous (Angellier-Coussy and Dufresne 2013).

Depending on the treatment technique of native starch granules, it is possible to obtain several type of nanosized starch: nanocrystals, nanoparticles, nanocolloids and nanomicelles.

According to the scientific literature, the most common method to prepare CSNCs refers to acidic hydrolysis with hydrochloric acid or sulfuric acid (Buléon et al. 1998; Putaux et al. 2003; Rajisha et al. 2014), although it is possible to achieve CSNCs even by enzymatic hydrolysis (Cai et al. 2010). Starch nanocrystals can be also obtained by co-crystallization combined with the regeneration process (Kim and Lim 2009). As reported by Putaux et al. (Fig. 3), SNCs display a platelet-like morphology (Putaux et al. 2003).

Starch nanoparticles are obtained by regeneration and precipitation with or without cross-linking (Ma et al. 2008) or by reactive extrusion; the presence of cross-linking increases the stability of the formed structure (Valodkar and Thakore 2010).

Finally, nanocolloids and self-assembled nanomicelles are produced by microfluidization (Liu et al. 2009) and by chemical modification of starch granules (Han et al. 2008), respectively.

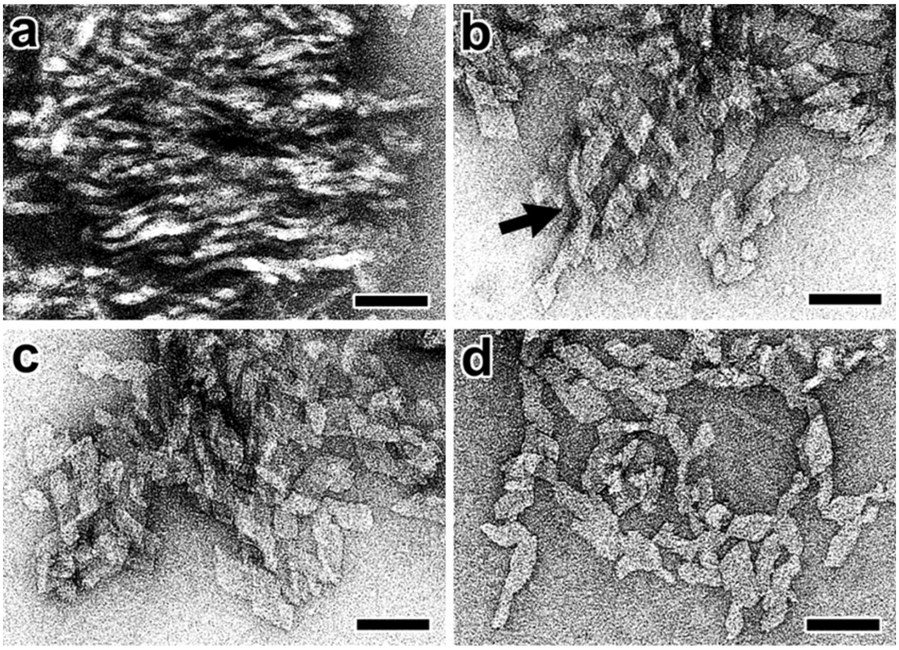

Fig. 3 TEM micrographs of negatively stained waxy maize starch samples: **a**–**c** fragments of waxy maize starch granules after 2 weeks of hydrolysis; **d** nearly individual waxy maize starch nanocrystals obtained after 6 weeks of hydrolysis (*scale bars* 50 nm). Reprinted with permission from (Putaux et al. 2003). Copyright (2003) American Chemical Society

Depending on the different methods used, the properties, the crystallinity and shape of the nano-sized starch particles obtained are found to vary. The yield and the structure of nanocrystals depend both on origin of native granules, and on process variables of the acid hydrolysis, with stron repercussions on type of crystallinity, amylose to amylopectin ratio and morphology (Kargarzadeh and Ahmad 2015).

Starch nanocrystals have great potential application as reinforcing fillers in the preparation of fully renewable and biodegradable nanocomposites, since they were found to enhance either mechanical and barrier properties of biopolymers, without altering their eventual biocompatibility. All of these features make SCNCs and relative polymer-based bio-nanocomposites particularly suitable for a wide range of application fields, ranging from the traditional industrial applications, such as food packaging and agriculture, to advanced uses, such as biomaterials for drug release or tissue regeneration (Dufresne 2008; Ma et al. 2008; Zheng et al. 2009; García et al. 2011; Huang et al. 2013).

PLA/polysaccharide nanocrystals nanocomposites

Cellulose-containing nanocomposites

Preparation routes

Basically, the most common methods to prepare PLA-cellulose nanocomposites can be divided into three approaches: melt processing, wet processing or their combination. Each preparation technique presents its own advantages and disadvantages. PLA-based nanocomposites can be prepared by melt processing, since PLA requires melting and molding temperature of 170–190 °C. Indeed, cellulose is stable up to 200 °C, thereafter its chemical dehydration, owing to the loss of physically and chemically bonded water, determines the yellowing and further darkening of the cellulose fibers with consequent embrittlement (Dufresne 2008). Nevertheless, the shear forces present in a batch mixer or in an extruder could not be able to avoid reaggregation phenomena of the nanoparticles. In this context, wet mixing (i.e. solvent casting, solvent foaming, etc.) ensures a higher level of dispersion but, conversely, requires toxic and/or dangerous solvents for dissolving PLA. The well-known difficulty to remove solvent residuals poses a serious issue when these materials are addressed to certain uses (food packaging, biomedical devices, etc.).

Another problem is related to the strong hydrophilicity of the nanofiller, leading to poor dispersion and weak interfacial adhesion with hydrophobic polymers, such as PLA. In order to overcome the aforementioned issues, the surface of cellulosic nanomaterials is usually functionalized as summarized in the following.

2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation This synthetic pathway represents a selective and green method to introduce carboxyl and aldehyde moieties onto the C-6 glucose units and leads to an extremely individualized cellulose nanofibrils. De Nooy and his group were the first who introduced this method to convert C-6 primary hydroxyl groups of water soluble polysaccharides to C-6 carboxylates by applying TEMPO/NaBr/NaClO oxidation under basic conditions (pH = 9–11) (De Nooy et al. 1995).

Bulota et al. (2012) synthesized TEMPO-oxidized fibrillated cellulose (TOFC) from bleached birch Kraft pulp for preparing a PLA-based film.

Urethanization This approach exploits the alcoholysis reaction between isocyanate moieties and hydroxyl groups, leading to urethanes. Owing to covalent bonds with hydroxyl groups, urethanization can be considered as a suitable alternative for esterifying agents. Siqueira et al. (2009) modified nanocellulose extracted from sisal by *N*-Octadecyl isocyanate in toluene via a multistep procedure, involving several solvent exchanging (ethanol to dichloromethane), centrifugation, sonication, filtration and washing steps.

The grafting of isocyanate moieties was found to improve the dispersion of nanofillers in organic solvents. The results put into evidence that the well dispersed nanocellulose fillers act as nucleation sites in PLA, thus increasing glass transition, crystallization, and melting temperatures as well as the degree of crystallinity. They also demonstrated that the efficiency of the surface modification strongly depends on the nature of the nanoparticle, in terms of specific area, peeling capacity, and solvent dispersion (Siqueira et al. 2010). Differently, Yu et al., used methylenediphenyl diisocyanate as a compatibilizer for PLA-starch blends loaded with cellulose. The enhancement of mechanical properties was explained by hypothesizing the in situ formation of a block copolymer (Yu et al. 2007).

Acetylation Acetylation method exploits the reaction between cellulose surface hydroxyl (OH) and acetyl groups, leading to cellulose plasticized fibers (Lee et al. 2014; Lin et al. 2011; Myoung et al. 2016). Bulota et al. (2012) used acetic anhydride in acetylation process of mechanically derived NFC. In this latter work, NFC were immersed in ethanol and subsequently in toluene and acetic anhydride. The reaction was performed at 105 °C for 30 min. The results of FTIR tests demonstrated the presence of a band located at 1740 cm^{-1}, ascribed to the insurgence of acetyl groups. Mechanical properties of the nanocomposites prepared with PLA also revealed that E increased by approximately 70% and the TS increased by approximately 60% at 20% NFC content.

Carboxymethylation This derivatization technique allows obtaining a cellulose with negatively charged surface when the pH is above about 3.5 and the groups are in the carboxylates conjugated base form, leading to nanosized, highly hydrophilic cellulose fibers stable in aqueous solutions. Aulin et al. (2013) successfully adopted this method to deposit a coating made by negative charged carboxymethylated cellulose and a cationic polyelectrolyte on flexible PLA substrates.

Silylation Nanocellulose surface modification by silane or its derivatives is a well-known route to replace the hydrophilic surface of fibers with a hydrophobic one.

This path can be followed even in the absence of water, since at temperature higher than 80 °C the presence of moisture promotes the silanol groups hydrolysis, thus increasing their reactivity toward cellulose.

CNFs were treated with 3-aminopropyltriethoxysilane (Frone et al. 2013) and with 3-methacryloxypropyltrimethoxysilane (Qu et al. 2012). Studies carried out on the influence of treated and untreated nanoparticle on morphology and thermal properties of PLA–based nanocomposites demonstrated that silylation allows enhancing CNF-PLA affinity.

Polymer grafting The affinity towards PLA can be dramatically enhanced by grafting hydrophobic monomers, polymers or by polymerizing PLA itself onto the cellulose surface (Peltzer et al. 2014; Hua et al. 2016). In some works the surface of nanometric cellulose was successfully functionalized either by polymerizing PLA (Goffin et al. 2011; Habibi et al. 2013) via ROP in the presence of stannous octoate or by covalently attaching LA monomer via Fischer esterification to increase PLA-cellulose compatibility (Spinella et al. 2015). Poly(butylene succinate) (PBS) was successfully grafted onto CNC by in situ polymerization by Zhang and Zhang (2016), aiming at enhancing the compatibilization of PLA/PBS blends. The authors reported that the size of PBS droplets in PLA was decreased by the addition of PBS-g-CNC, with positive repercussions on thermal and mechanical properties of the materials.

Phosphorylation Beyond the paths used to improve cellulose affinity to PLA, in the scientific literature there are reported even derivatization strategies aiming at providing cellulose with additional properties. In this context, Costes et al. prepared phosphorylated cellulose by reacting cellulose microparticles with phosphorous acid in molten urea to enhance the flame retardant properties of PLA (Costes et al. 2016).

Processing techniques

PLA/CNC nanocomposites can be melt processed either by using an internal batch mixer (Khoshkava and Kamal 2013; Kamal and Khoshkava 2015; Piekarska et al. 2016) or by a twin-screw extruder (Oksman et al. 2006; Jonoobi et al. 2012). Jonoobi et al. evaluated the influence of the surface chemistry of cellulose (pristine or acetylated) on the properties of PLA, in nanocomposite prepared by melt extrusion (Jonoobi et al. 2012), clearly showing that the acetylation of cellulose leads to a strong enhancement of mechanical performance of the nanocomposite. Furthermore, adding acetylated CNC in the melt was found to increase PLA crystallinity (Arrieta et al. 2014a, 2015). Similar results were reported when CNWs were incorporated into PLA by using a twin-screw extruder in the presence of compatibilizers (Oksman et al. 2006) or by using a masterbatch (Jonoobi et al. 2010) prior to melt processing. Indeed, a two-steps processing, combining wet and melt mixing, was often adopted to enhance the dispersion of the nanofillers (Eyholzer et al. 2012; Arias et al. 2014). Eyholzer et al. (2012) prepared a masterbatch by mixing in water and freeze-drying polyethylene oxide (PEO) and NFC functionalized with hexanol moieties, then diluted with PLA and melt mixed; Bitinis et al. (2013) adopted a similar two-steps method (solvent casting plus melt extrusion) to prepare PLA/natural rubber/CNC bionanocomposites in order to prevent the degradation of the moieties grafted on CNC, derivatized by PLA (PLA-g-CNCs) or by alkyl chains (C18-g-CNC) and to obtain a good dispersion of the fillers within the matrix constituted by immiscible polymers. Although the CNCs evidenced no significant effect on the compatibilization of PLA and rubber, the different surface chemistry of the CNC was found to affect the morphology of the blend, since PLA-g-CNCs were located in the PLA phase while C18-g-CNCs were present in the rubbery phase. A suitable strategy to maximize the compatibility between nanocellulose and PLA is represented by directly polymerizing D-lactide onto CNC surface in toluene, and then melt-blend the nanohybrids with PLA in a mini-extruder (Goffin et al. 2011, 2012; Habibi et al. 2013). It was also demonstrated the possibility to improve PLA-CNC mechanical performance by grafting even different monomers (Spinella et al. 2015) or by adopting a reactive extrusion approach to graft polyvinyl alcohol (PVA) onto CNC, thus enhancing its dispersion within PLA (Pracella et al. 2014).

Melt processing was successfully used even to prepare ternary hybrids, where PLA and nanocellulose were combined with nanoclays (Hong and Kim 2013), silver nanoparticles (Fortunati et al. 2012a, b, 2014) and poly(hydroxybutyrate) (Arrieta et al. 2014a, b).

Blaker et al. (2014) prepared aligned unidirectional PLA/bacterial cellulose nanocomposite fibers by melt spinning. The addition of 7 wt% of cellulose determined improvements of up to 175% in terms of storage moduli (E') with respect to pure PLA.

Ambrosio-Martin et al. (2015a, b) used ball milling to prepare PLA/bacterial cellulose nanocrystals (BCNC) nanocomposites. They demonstrated that this technique permits to break up a very large extent of the freeze-dried nanocellulose aggregates, leading to a significant dispersion of the BCNC filler within a PLA matrix when compared to direct addition of freeze-dried nanocellulose in a melt mixing process. Improved thermo-mechanical and barrier properties were observed for nanocomposites as compared to the neat PLA.

Conversely, solvent mixing approach is used especially when it is crucial to preserve the stability of components subject to thermal degradation, as in the case of antimicrobial PLA-CNC nanocomposites loaded with oregano essential oil for food packaging (Salmieri et al. 2014). Among the wet mixing techniques, solvent casting is the most used one. Petersson and Oksman (2006) used unmodified cellulose and nanoclay as fillers for PLA by solvent casting in chloroform and their effect on the performance of ultimate materials was compared, showing that both mechanical and barrier properties of PLA were worsened by cellulose, likely due to the lack of affinity between cellulose and the host polymer. On the other hand, by using the same technique, Arjmandi et al. (2015) partially replaced montmorillonite with CNW on PLA nanocomposites, thus demonstrating that the addition of small percentage of CNC in combination with nanoclay increases tensile strength and modulus, with respect to pure matrix and PLA-nanoclay systems. The dispersion of nanocellulose within PLA matrix can be improved by adding low molecular polyethylene glycol (PEG) as plasticizing agent (Qu et al. 2011) or surfactant-modified cellulose nanocrystals (Fortunati et al. 2012c). As already discussed in the case of melt-processed nanocomposites, the grafting of polymer onto nanocellulose surface dramatically enhances the ultimate performance of PLA-based nanocomposites. CNW were surface-grafted with polycaprolactone via microwave-assisted ring-opening polymerization (Lin et al. 2009), or with PLLA by polymerizing L-lactide (Braun et al. 2012) and then added to PLA by solvent casting. The same approach was adopted to prepare PLA-based nanocomposites with hydrophobic-modified CNF (Song et al. 2014), CNW grafted Poly(glycidyl methacrylate) (Martínez-Sanz et al. 2013), CNC functionalized with fatty acids (Almasi et al. 2015). In all the cases, it was observed a strong improvement of mechanical and thermal resistance of the materials, owing to the enhanced matrix-filler compatibility in terms of interfacial adhesion and dispersion. Furthermore, the hydrophobic modification of CNW was found to decrease the water vapour permeability (Espino-Pérez et al. 2013). Baheti et al. (2014) carried out an interesting study focused on the influence of cellulose purity on the ultimate properties of PLA-CNC nanocomposites produced by solvent casting. In particular, the authors investigated the effect of noncellulosic contents present in cellulose produced by nanoscale refinement of waste jute fibers and reported that higher degree of purity of cellulose results in a stronger interphase and, as a consequence, in higher ultimate performance, as confirmed by tensile and dynamic-mechanical tests (Baheti et al. 2014).

Cellulose-reinforced PLA nanocomposites were prepared even with unusual solvent-based techniques. Wang and Drzal (2012) employed a water-based approach, commonly used for drug microencapsulation, in order to suspend PLA in water as microparticles, amenable to be mixed with the CNFs by high-pressure homogenization. The authors report that CNFs improved both the stiffness and strength of the polymer, especially after the amorphous polymer transitioned into the viscous region above its T_g, due to the formation of a stiff CNF network.

PLA latex/NFC cellulose bionanocomposites were produced by using a straightforward wet mixing method similar to papermaking (Larsson et al. 2012). In this case, the mechanical properties of the bionanocomposites were found to be a linear combination of those of PLA and NFC within the whole range of concentration.

PLA/CNFs microcellular foams were successfully prepared with a batch foaming technique, using supercritical CO_2 as a plasticizer and blowing agent (Cho et al. 2012; Dlouhá et al. 2014).

PLA-CNC fibers were prepared via electrospinning for controlled release of nonionic compounds (Xiang et al. 2013), and for bone tissue engineering (Pirani et al. 2013; Zhou et al. 2013; Zhang et al. 2015), since the incorporation of CNC allows improving the mechanical properties of PLA without affecting biocompatibility and biodegradability.

Main properties

Mechanical and thermomechanical properties The addition of cellulose nanofillers generally determines an increase of crystallinity (Kose and Kondo 2013) and of mechanical and thermomechanical properties of PLA (Kowalczyk et al. 2011; Abdulkhani et al. 2014; Lu et al. 2016; Oksman et al. 2006; Hossain et al. 2012; Wang and Drzal 2012; Haafiz et al. 2016; Pracella et al. 2016). Table 3 provides a summary of the main achievements in terms of mechanical and thermomechanical properties registered for various types of PLA-nanocellulose systems. As clearly visible, the extent of improvements strongly depends on the filler content, as well as on the technique used for the preparation of nanocomposites and surface treatments, able to improve both interfacial adhesion and dispersability (Graupner et al. 2016; Mukherjee et al. 2016). Generally, the introduction of nanocellulose to a PLA matrix leads to improvements ranging from 50% to 200% in terms of elastic modulus and the strongest enhancement in tensile properties is usually achieved at a loading level of 5%. Due to the aforementioned bad affinity between nanoparticles and matrix and to the well-known tendency of CNC to re-aggregate spontaneously, their incorporation may have a negligible or even negative effect on mechanical properties of PLA (neat or plasticized by PEG) whether a poor dispersion is observed (Jonoobi et al. 2010; Sanchez-Garcia and Lagaron 2010; Espino-Pérez et al. 2013). On the other hand, in the case of nanocomposites prepared by electrospinning, it is possible to observe exceptionally higher improvements, due to the higher stiffness contrast between electrospun matrix and filler. Indeed, the elastic modulus of PLA-based electrospun fibers loaded with 5% CNC was found to increase by 22-fold with respect to that of the pure matrix (Shi et al. 2012), whereas at a filler content of 10% a dramatic loss in mechanical performance was observed, due to the re-aggregation of nanoparticles. As before discussed, the specific surface treatment of the cellulosic nanoparticles can be a useful strategy to limit the bundling phenomena affecting filler dispersion at high loadings. In this context, a strong increase of both mechanical and thermomechanical properties was observed with the addition of surface treated cellulose, especially when cellulose was functionalized with LA moieties (LA-CNC) (Gårdebjer et al. 2015; Spinella et al. 2015). In particular, storage modulus was found to increase monotonically (up to 400%) with the filler content up a loading level of 20%, thus confirming the poor tendency to re-aggregate of LA-CNC nanoparticles.

The enhancement of the thermo-mechanical properties of cellulose-reinforced and partially crystallized PLA composites could enable PLA/cellulose

Table 3 Main achievements in terms of mechanical and thermomechanical properties registered for various types of PLA-nanocellulose systems

Type and weight content of cellulose	Filler modification	Other components	Preparation method	Main results	References
CNF (up to 5%)	Acetylation	–	Solvent casting	E up to +200%; TS up to +100%; WVP up to +38%	Abdulkhani et al. (2014)
CNF (up to 12%)	Fatty acids grafting		Solvent casting	E up to +250%	Almasi et al. (2015)
BCNW (5%)	Grafting of OLLA	–	In situ polymerization + melt mixing	E up to +52%	Ambrosio-Martín et al. (2015b)
CNW (up to 5%)	–	MMT	Solvent casting	EB up to +79%	Arjmandi et al. (2015)
Nanofibrils from waste jute (3%)	–	–	Solvent casting	E = +207.69% TS = 168.67%	Baheti et al. (2014)
CNC (7%)	Esterification	–	Melt-spinning + layer-by-layer	E′ up to +175%	Blaker et al. (2014)
CNW (15%)	Acetylation	–	Solution polymerization	HDT up to +220%	Braun et al. (2012)
CNF (3%)	Acetylation	–	foaming	Toughness up to +300%	Dlouhá et al. (2014)
CNW	–	–	Solvent casting	TS −125%/−260%	Espino-Pérez et al. (2013)
CNW	Urethanization	–	Solvent casting	TS up to +127%	Espino-Pérez et al. (2013)
NFC (7.5%)	Carboxymethylation	–	Melt extrusion	E up to +10%	Eyholzer et al. (2012)
CNC	–		Solvent casting	TS −66%; E up to +179%	Fortunati et al. (2012b)
CNC	Surfactant		Solvent casting	TS up to +167%; E up to +164%	Fortunati et al. (2012b)
CNW (up to 4%)	PLA grafting		Melt blending	E′ up to around +60% in the rubbery zone	Goffin et al. (2011)
CNW (up to 5%)	–	–	Solvent casting	TS up to +85%	Haafiz et al. (2016)
CNC (up to 10%)	PLLA grafting	–	Melt extrusion	E′ up to +41%	Habibi et al. (2013)
CNF	–	Glycerol triacetate	Extrusion with liquid feeding	Toughening +800%	Herrera et al. (2015a)
CNC	–	Triethyl citrate	Extrusion with liquid feeding	EB +300%	Herrera et al. (2015b)
CNW (up to 5%)	–	–	Solvent casting	TS up to +34%; E up to 31%	Hossain et al. (2012)
CNW	MPLA	nanoclay	Melt mixing	E up to +100%	Hong and Kim (2013)
CNF (5%)	–	–	Two-step (solvent + melt mixing)	E and TS up to +20%	Jonoobi et al. (2010)
CNF (5%)	Acetylation	–	Two-step (solvent + melt mixing)	E′ up to +81%	Jonoobi et al. (2012)

Table 3 continued

Type and weight content of cellulose	Filler modification	Other components	Preparation method	Main results	References
CNC (7%)	–	–	Spray drying + melt extrusion	E′ up to +200%	Kamal and Khoshkava (2015)
CNF (2%)	–	–	Two-step (solvent + melt)	TS up to + 50%	Kowalczyk et al. (2011)
NFC (up to 99 wt/wt%)	–	–	Wet mixing + centrifugation	Mechanical properties up to +700%	Larsson et al. (2012)
CNW (3%)	Acetylation	–	Solvent casting	TS up to +25.6%	Lee et al. (2014)
CNW (up to 8%)	PCL grafting	–	Solvent casting	EB up to +1070%	Lin et al. (2009)
CNC (6%)	Acetylation	–	Solvent casting	TS up to +61.3%	Lin et al. (2011)
CNW (3%)	Grafting Of Glycidyl Methacrylate	–	Solvent casting	TS up to +20%	Martínez-Sanz et al. 2013
CNC (0.5%)	Acetylation	Silica	Solvent casting	TS up to +65%	Myoung et al. (2016)
CNW (up to 17%)	Swelling by dimethylacetamide	PEG	Melt extrusion	EB up to +800%	Oksman et al. (2006)
CNW (5%)	Grafting of tert-butanol	–	Solvent casting	E′ up to +64%	Petersson et al. (2007)
MCC (up to 5%)	–	Bentonite	Solvent casting	TS = −12%	Petersson Oksman (2006)
CNC (2%)	–	–	Electrospinning	E = +150%	Pirani et al. (2013)
CNC (up to 6%)	GMA grafting	PVAc	Reactive melt extrusion	E′ up to +90% in rubbery region	Pracella et al. (2014)
CNW	–	PEG	Solvent casting	TS +56.7% EB +48%	Qu et al. (2011)
CNF (1%)	Silanization	–	Solvent casting	E′ up to +33%	Qu et al. (2012)
CNW (3%)	Amino-based	–	Melt blending	E′ up to +190%	Raquez et al. (2012)
CNW (3%)	n-Propyl-based	–	Melt blending	E′ up to +230%	Raquez et al. (2012)
CNW (3%)	Methacrylic-based	–	Melt blending	E′ up to +235%	Raquez et al. (2012)
CNW (3%)	Acrylic-based	–	Melt blending	E′ up to +217%	Raquez et al. 2012
CNW (up to 5%)	–	–	Solvent casting	E from −35 to −85%	Sanchez-Garcia and Lagaron (2010)
CNC (5%)	–	–	Electrospinning	E up to +2200%; TS up to +500%	Shi et al. (2012)
MFC (up to 20%)	–	–	Solvent casting	E′ up to +250%	Suryanegara et al. (2009)
CNC (up to 20%)	LA grafting		Extrusion	E′ up to +450%	Spinella et al. (2015)
CNW (2%)	–	–	Solvent casting	TS = −12.5%	Wang et al. (2014)

Table 3 continued

Type and weight content of cellulose	Filler modification	Other components	Preparation method	Main results	References
CNW (2%)	–	PEG, $M_w = 1000$	Solvent casting	TS = +37.5%	Wang et al. (2014)
CNW (2%)	–	PEG, $M_w = 4000$	Solvent casting	TS = +25%	Wang et al. (2014)
CNW (2%)	–	PEG, $M_w = 6000$	Solvent casting	TS = +6.25%	Wang et al. (2014)
CNF	–	–	Microemulsion + high pressure homogenization	E up +58%; TS up to +210%	Wang and Drzal (2012)
CNC (5%)	Grafting of PEG	–	Electrospinning	TS up to +170%	Zhang et al. (2015)
CNC (0.2%)	Grafting of PBS	PBS	Melt blending	IS up to +1296%	Zhang and Zhang (2016)
CNC (5%)	Grafting of MA	–	Electrospinning	TS up to +1000%	Zhou et al. (2013)

nanocomposites to replace fully crystallized neat PLA for high temperature applications (Suryanegara et al. 2009, 2010).

Indeed, studies on the thermal and structure properties of CNW/PLA nanocomposites mixed with three different molecular weight of PEG, put clearly into evidence that all the nanocomposites displayed a good thermal stability in the region between 25 and 245 °C (Wang et al. 2014). Although the thermomechanical properties of PLA-CNW were found to be enhanced when silanized CNWs were used as nanofillers (Raquez et al. 2012, 2013), the optimization of nanofiller dispersion due to particular techniques (Wang and Drzal 2012), as previously discussed, can determine increases in the flexural modulus and strength (up to 58 and 210%, respectively) even with unmodified CNF, as clearly visible in Fig. 4.

It was demonstrated that CNWs improve the thermal stability of the PLA compared to montmorillonite (Arjmandi et al. 2015; Trifol et al. 2016a), while CNFs, especially at high loading levels, are prone to make a network within the polymer matrix, thus behaving as carbon nanotubes (CNTs). The formation of a stiff network is hypothesized to determine the strong increase of the stiffness in the temperature region above the glass transition of PLA (Wang and Drzal 2012).

Furthermore, Trifol et al. (2016a) hypothesized two different mechanism acting in thermomechanical reinforcement of cellulosic nanofillers based on their geometrical features: CNF shows a better dispersability; CNC can form stronger percolated networks due to stronger hydrogen bonding interaction between fillers. Nevertheless, the final effect is substantially the same.

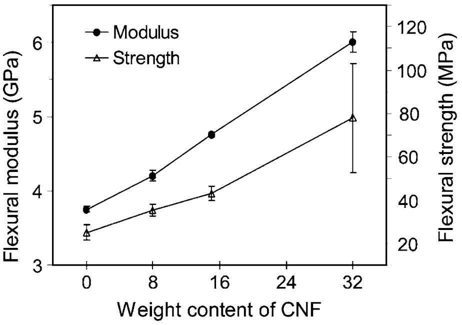

Fig. 4 Flexural modulus and flexural strength of PLA/CNF nanocomposites as a function of the CNF content. Reprinted with permission from (Wang and Drzal 2012). Copyright (2012) American Chemical Society

Barrier properties Aulin et al. (2013) adopted a deposition method to obtain a laminate constituted by alternating layers of nanofibrillated cellulose or carboxymethyl cellulose (CMC) with a cationic polyelectrolyte, on flexible PLA substrates, thus achieving optically transparent films with tunable gas barrier properties. Generally, CNWs were found to enhance the barrier properties of PLA. Even at low loading levels (3 wt%), CNWs and bacterial CNWs strongly reduced PLA permeability towards oxygen

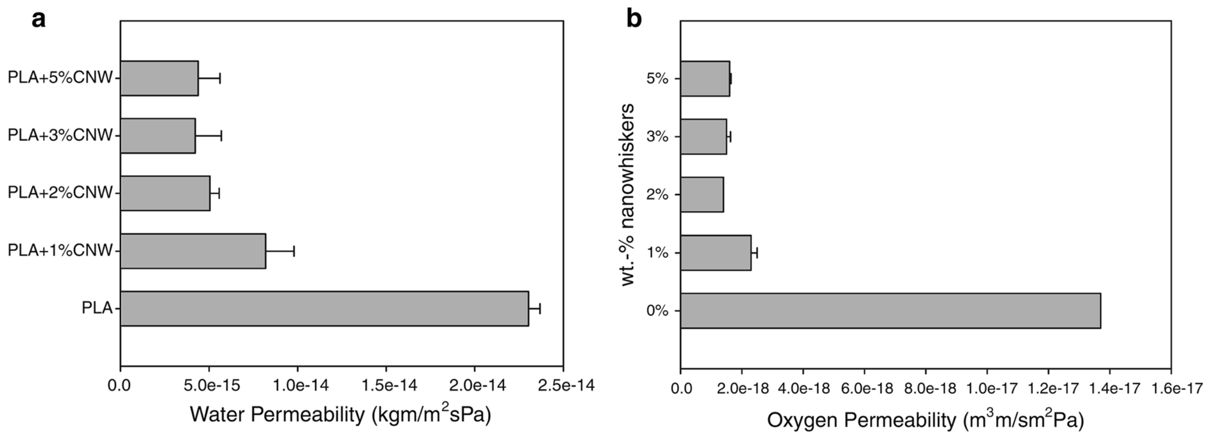

Fig. 5 Barrier properties of neat PLA and PLA/CNWs nanocomposites with 1, 2, 3 and 5 wt% of CNWs: water permeability (**a**) and oxygen permeability (**b**). With kind permission from Springer Science + Business Media: (Sanchez-Garcia and Lagaron 2010)

and water, see Figs. 5a, b (Sanchez-Garcia and Lagaron 2010; Martínez-Sanz et al. 2012). Moreover, hydrophobic nanocellulose can act as a barrier agent even at lower filler content. Functionalization of CNWs with n-octadecyl isocyanate determines a drastic reduction of the water vapour permeability of PLA with respect to untreated CNWs (Espino-Pérez et al. 2013), whereas the permeability to oxygen remained practically constant. Song et al. (2014) fabricated CNF/PLA coatings for lowering water vapor transmission rate of paper, observing excellent improvement with an addition of 1% of modified CNF. Trifol et al. (2016a) compared CNF, CNC and nanoclay as fillers for PLA, demonstrating that CNF and CNC determined the highest barrier properties. Moreover, the same authors reported that either CNFs and CNCs synergistically interact with nanoclays for the improvement of thermomechanical and especially barrier properties towards O_2 of PLA films (Trifol et al. 2016b).

Biodegradation behavior Several works report on the disintegrability in compost and enzymatic degradation of PLA nanocomposites reinforced with cellulose nanocrystals extracted from biomass and agro-waste (such as *Posidonia Oceanica, Phormium tenax* leaves) (Fortunati et al. 2014, 2015; Luzi et al. 2015; Shi et al. 2012; Arjmandi et al. 2015). The disintegrability in compost conditions put into evidence that PLA-CNC nanocomposites degraded in less than 14 days, in addition it has been proved that CNCs modified with surfactant promote the disintegration behavior. These findings suggest the potential application for short-term food packaging with low environmental impact, thus opening scenarios for an innovative reuse of coastal plant (Fortunati et al. 2014, 2015; Luzi et al. 2015). The in vitro degradation tests carried out on electrospun bio-nanocomposite mats made by PLA and CNCs, highlighted that the sample containing CNC degraded more rapidly than neat PLA in phosphate-buffered saline solution, especially at high CNC-loadings (Shi et al. 2012).

It has been also pointed out that partial replacement of montmorillonite with CNW improves the biodegradability of PLA-nanocomposites, which was assessed using soil burial method (Arjmandi et al. 2015).

Optical properties Many studies report on the effect of CNC on the optical properties of PLA and PLA/PHB blends, highlighting a slight decrease in optical transparency in the visible range and a stronger decrease of the transmittance in the UV region (below 400 nm), thus making these materials amenable for applications where UV protection is needed, such as food packaging and agricultural bags (Arrieta et al. 2014b, 2015; Herrera et al. 2015b).

Chitin-containing nanocomposites

Preparation routes

Since ChNCs exhibit many hydroxyl groups on their surface, they regularly self-aggregate and subsequently, micrometer scale agglomerates can be found when filled in a hydrophobic polymer matrix. This shortcoming was avoided by Zhang et al., which acetylated ChCNs before the incorporation into PLA matrix by solvent casting technique. This method enhanced the nanofiller dispersion and adhesion with PLA. The acetylated-ChNCs (AChNCs), obtained with anhydrous pyridine and acetic anhydride, were then incorporated in PLA previously dissolved in CH_2Cl_2 with different weight ratio (up to 10 wt%). Results highlighted that the acetylation ensured a better dispersion of ChNCs both in CH_2Cl_2 and in PLA solution (Zhang et al. 2014).

Herrera et al., developed a plasticized PLA nanocomposites based on CNC and ChNCs mixed with the triethyl citrate (TEC), chosen as plasticizer. The liquid feed, presenting a final composition of 2.6 wt% nanocrystals, 52 wt% TEC, 22.7 wt% H_2O and 22.7 wt% ethanol, was fed in a co-rotating twin-screw extruder with a peristaltic pump in order to obtain a final nanocomposites composed by 79 wt% of PLA, 20 wt% of TEC and 1 wt% of nanocrystals. The nanocomposites morphology showed several micro-sized particles with a flake shape and some agglomeration (Herrera et al. 2015b).

In another work, the same authors fabricated films in PLA filled by ChCNs by using film blowing technology. The nanocomposite was prepared as masterbatch that was then diluted with PLA and mixed with talc to obtain a final nanocomposite compound filled with 1 wt% ChNCs. The process was carried out using a laboratory film blowing extruder operating with a temperature profile from 160 to 180 °C (Herrera et al. 2016).

Guan and Naguib prepared PLA and blends of PLA with polyhydroxybutyrate-*co*-valerate (PHBV) by melt. A co-rotating twin screw microcompounder was used to prepare the blends and nanocomposites in various mixtures containing fixed ratio of 15 wt% PHBV and 85 wt% PLA varying the filler contents. Furthermore, the described materials were also CO_2 foamed by sealing molded samples in high-pressure, CO_2 saturated, chambers. After the gas release, the samples were soaked with water at 90 °C for 10 s and then quenched in cold water after the designated foaming time. This step is needed to freeze the cell morphology and prevent further changes (Guan and Naguib 2014).

Recently, Li et al. (2016) prepared by solution casting a series of PLA/ChNCs films. In order to improve the reinforcing effect of the polysaccharide nanocrystals, ChNCs were surface modified with L-lactide to obtain g-ChNCs.

The same surface modification was carried out by Liu et al. The authors prepared electrospun composite nanofibrous membrane of PLA and ChNCs surface modified with L-lactide in order to improve mechanical properties and cytocompatibility. In order to improve the dispersion, the nanocrystals were dispersed in the solvent systems by ultrasonic treatment before adding PLA. The authors used a conventional electrospinning setup (Liu et al. 2016b).

Zou et al. prepared by injection molding PLA/MgO/ChNCs and PLA/g-MgO/g-ChNCs ternary composites with different filler contents. Both ChNC and MgO were surface modified with L-lactide in order to improve the dispersion in the polymer matrix (Zou et al. 2016).

Main properties

Mechanical properties Table 4 summarizes the main results in terms of mechanical properties registered for various types of PLA/ChNCs systems. The table highlights that the improvements are affected by the filler content, the technique used for the preparation of nanocomposites and by surface treatments, able to improve both interfacial adhesion and dispersibility.

The mechanical properties of PLA filled with Acetylated-ChNCs (AChNCs) were studied, by Zhang et al., as a function of the weight fraction (see Fig. 6). TS and E reached the maximum values of 36.3 and 1573.8 MPa, respectively, when AChNCs concentration was 4 wt%, with an increase of 45 and 37%, in comparison with the neat PLA film. When AChNCs exceeded that values (6, 8, and 10 wt%), a decrease in tensile stress at break and elastic modulus was observed since the original PLA structure was slightly damaged (Zhang et al. 2014).

A similar result was found by Guan and Naguib studying the effect of ChNCs content in melt mixed PLA in presence of N,N-Dimethyl acetamide (DMAc). Adding small amounts of ChNCs (<2 wt%) improved both TS and E while EB was reduced. The addition of ChNCs affects two competing effects: the improvement of the strength and stiffness of the composite and the matrix degradation induced by the DMAc that reduces all mechanical

Table 4 Main achievements in terms of mechanical properties registered for PLA/chitin and PLA/starch nanocomposites

Content (wt%)	Filler modification	Other components	Preparation method	Main results	References
ChNCs up to 10%	Acetylation	–	Solvent casting	E = + 37% TS = +45%	Zhang et al. (2014)
ChNCs 1%	–	TEC	Extrusion	E = +67% TS = +28%	Herrera et al. (2015b)
ChNCs 1%	–	Glycerol triacetate, polybutylene adipate-co-terephthalate, talc	Film blowing	E = +75% TS = +65%	Herrera et al. (2016)
ChNCs up to 5%	–	PHBV, DMAC	CO_2 Foaming	TS = +133%	Guan and Naguib (2014)
ChNCs up to 10%	L-Lactide	–	Solvent casting	E = +133% TS = +63%	Li et al. (2016)
ChNCs up to 10%	L-Lactide	–	Electrospinning	E = +143% TS = +49%	Liu et al. (2016a, b)
ChNCs up to 5%	L-Lactide	MgO	Injection molding	E = +18% TS = +33%	Zou et al. (2016)
SNCs 3.2%	PLA	–	Grafting reaction	Successful grafting of PLA onto SNCs	García et al. (2012)
SNCs up to 8%	Cross-linking	–	Solvent casting	E = +35% TS = +12%	Yin et al. (2015)
SNCs up to 30%	PCL	–	Solvent casting	TS = +132% ε_b = +400%	Yu et al. (2008)
SNCs up to 2%	Ozone-mediated styrene grafting	–	Solvent casting	WVP up to - 52%, DTG_{peak} up to +130 °C	Espino-Pérez et al. (2016)

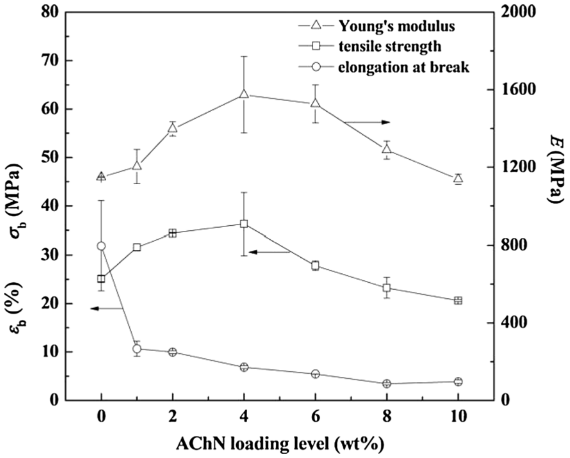

Fig. 6 Young's modulus (*E*), tensile strength (σ_b), and elongation at break (ε_b) for the PLA/AChN nanocomposite films as a function of the AChN loading. Reprinted from (Zhang et al. 2014), Copyright (2013), with permission from John Wiley and Sons

properties. By considering these two effects, an optimal working point was found for the ultimate TS at low ChNCs content (0.5 wt%) while the stiffness was maximized whereas at 1 wt% content. The induced solvolitic degradation become dominant at higher ChNCs contents, particularly at 5 wt% (20 wt% DMAc), causing the worst performance.

The inclusion of ChNCs on foamed PLA dramatically improved the specific tensile strength (nearly 60–100% for ChNCs content in the range 0.5–5 wt%), with the highest increase 0.5 wt% (Guan and Naguib 2014).

Another interesting study was focused on the effect of the load of 1 wt% of ChNCs on PLA by using TEC as plasticizer. When the blend was rapidly cooled the yield strength and E values were improved by 478% (from 3.7 to 21.4 MPa) and by 300% (from 0.3 to 1.2 GPa), respectively. In the case of the slow cooled plasticized PLA, TS significantly increased by 28%

(from 15.8 to 20.3 MPa) while E increased significantly by 67% (from 0.6 to 1.0 GPa) (Herrera et al. 2015b).

Nanocomposite blown films based on PLA showed that by adding 1 wt% of ChNCs the tensile modulus and strength are increased from 0.4 to 0.7 GPa (74%) and from 17 to 28 MPa (64%), respectively if compared with neat PLA films. It seems that the presence of ChNCs restricts the movement of the polymer chains during the film blowing process, resulting in more isotropic nanocomposite films (Herrera et al. 2016).

The successful functionalization of ChNCs with L-lactide presented by Li et al., resulted in excellent tensile properties of the PLA/g-ChNCs nanocomposites. In particular, the nanocomposites filled with 5 wt% of ChNCs and g-ChNCs showed the highest mechanical performance exhibiting and increase of E value from 600 MPa (neat PLA) to 1.2 GPa (ChNCs) and 1.4 GPa (g-ChNCs). The authors ascribed these results to the improved the dispersion and interfacial adhesion between the g-ChNCs and PLA (Li et al. 2016).

Liu et al., demonstrated that the functionalization of ChNCs with L-lactide successfully improved mechanical properties of electrospun nanofibrous membranes. In particular, the presence of 5 wt% of g-ChNCs induced the best tensile performance with an increase of E value from 0.83 to 2.02 GPa even higher than that of the PLA/ChNCs composites. The better dispersion induced by the PLLA grafted chains on the ChNCs are the reason of this significant increment in E value (Liu et al. 2016b).

Zou et al., evaluated the synergistic effect of MgO nanoparticles and ChNCs on the mechanical behavior of PLA. By adding the neat and the surface-grafted with L-lactide MgO and ChNCs into the PLA matrix, the tensile strength and especially the fracture energy of the resulting composites increased as compared to those of pure PLA. Moreover, the author demonstrated that the mechanical properties of the ternary composites is higher if compared with the composites with only one filler. Finally the surface grafting with L-lactide further enhanced the tensile performance of the ternary composites because the functionalization lead to a better fillers dispersion (Zou et al. 2016).

Thermal properties ChNCs affects the thermal properties of the PLA based nanocomposites including T_g, T_m and melt enthalpy (ΔH_m). Zhang et al. (2014) observed that T_g of nanocomposites decreases since the ChNCs affect the interactions between the amorphous and crystalline PLA domains. The T_m of the PLA/ChNCs nanocomposites were lower than those of the neat PLA film thus indicating that the ChNCs change the size of the crystalline domains of PLA matrix. Furthermore, the crystallinity is higher for the nanocomposite than for the neat PLA. This phenomenon was attributed to the nucleation function of ChNCs (Zhang et al. 2014).

Shinyama et al. (2012) also showed that the presence of ChNCs leads to an increase of PLA crystallinity. Furthermore, they demonstrated that the crystallization speed of PLA can be substantially increased by adding chitin and then performing heat treatment (see Fig. 7). Moreover they showed that the crystallization peak temperature of PLA chitin nanocomposites is higher than that of the neat PLA, thus indicating that the chitin facilitated the PLA crystallization process, acting as a nucleating agent.

DSC tests carried out of film blown samples indicate that the addition of 1 wt% of ChNCs slightly improved the thermal stability and interaction between the components in the nanocomposite, thus hindering

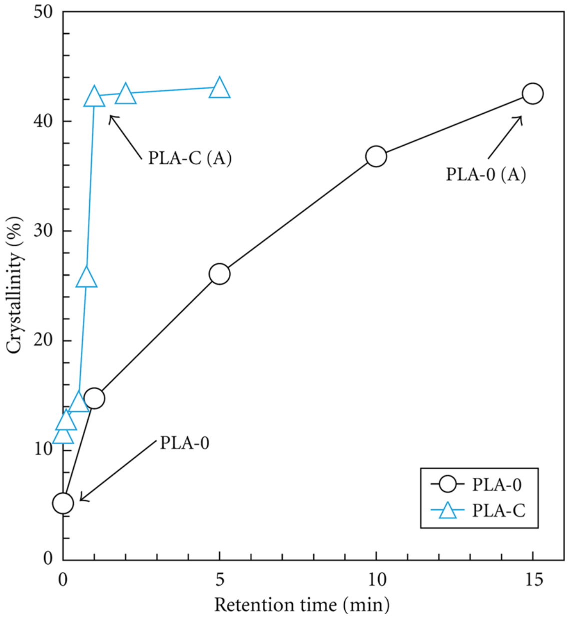

Fig. 7 Effect of heat treatment at 100 °C on crystallinity of neat PLA (PLA-0) and PLA containing 1.0 wt% of chitin nanocrystals (PLA-C). Reproduced from (Shinyama et al. 2012)

polymer chain mobility (Herrera et al. 2016). The degree of crystallinity (X_c) of the nanocomposite films was slightly higher (56%) if compared with that of neat PLA films (52%) (Herrera et al. 2016).

Guan and Naguib carried out DSC analysis on PLA/ChNCs and PLA/PHBV ChNCs nanocomposites focusing on the effect of filler and consequently DMAc (in which ChNCs were suspended) concentration on PLA. The DSC analysis of PLA/ChNCs/DMAc showed a lowering in the characteristic transition temperatures of PLA, i.e. glass transition, cold crystallization and melting temperatures. The authors attributed this phenomenon to the solvolytic degradation caused by the DMAc rather than to the CNCs content. Furthermore, the ChNCs/DMAc presence in PLA, transformed the characteristic double melting peaks of the polymer into a single melting peak. TGA showed that ChNCs decomposed as a single phase with the PLA matrix at 382 °C, in fact, PLA and chitin degrade in the same temperature range. However, the decomposition temperature slightly decreased to 357 °C, probably because the DMAc induced the solvolytic degradation of PLA (Guan and Naguib 2014).

The effects of the ChNCs and ChNCs surface modified with oligo (L-lactide) (g-ChNCs) on the crystallization rate and crystal size of the PLLA matrix were investigated by Li et al. (2016). The authors determined that ChNCs acted as nucleating agents inducing a higher number of small spherulites in the PLA matrix. The presence of g-ChNCs induced a higher crystallization rate because both the ChNCs itself and the grafted chains acted as a nucleating agents.

Zou et al., evaluated the crystallinity and the thermal stability of PLA/MgO/ChNCs and PLA/g-MgO/g-ChNCs ternary composites with different filler contents. Results showed that the crystallization ability was improved by loading ChNCs. As regards the thermal stability, evaluated by TGA, a new stage was observed within the range 200–285 °C. This peak can be attributed to the dehydroxylation from MgOH and decarboxylation from Mg–CO_3H formed on the surfaces of the MgO whiskers (MgO-Ws) and also to the thermal degradation of grafted PLA chains on the surfaces of g-MgO-Ws.

Antistatic behavior Herrera et al. demonstrated that the ChNCs act as an antistatic agent. PLA is characterized by high density of polar linkages, which can result in electrostatic forces. The presence of amine groups on ChNCs surface can interact with bind water molecules and moisture thus decreasing the electrostatic interactions. As matter of fact the nanocomposite films filled with ChNCs are easily opened if compare to that of neat PLA (Herrera et al. 2016).

As a matter of fact, it was found that ChNCs act as a multifunctional additive of PLA: modified its melt strength as well as enhanced the thermal stability and the crystallinity of the PLA composites thus reinforcing the polymer from a mechanical point of view. Moreover, the chitin nanocrystals were found to act as an antistatic additive, facilitating the opening of the films, and an antifungal agent, decreasing the fungal activity against A. Niger.

Other properties ChNCs were found to provide PLA with interesting optical properties. Herrera et al. evaluated the light transmittance for PLA films filled with ChNCs and produced by film blowing. The light transmittance of the nanocomposite materials was very similar to that of the reference material thus indicating that ChNCs were well dispersed in the PLA matrix and did not decrease the transparency of the films. Furthermore, a slight decrease was found in the region below 400 nm that corresponds to the radiations that can damage photosensitive nutrients present in foods (Herrera et al. 2016).

The barrier properties of PLA/ChNCs nanocomposite films were studied by Herrera et al. The results demonstrated that the addition of ChNCs did not significantly affect the vapor transmission rate and oxygen permeability of the films (Herrera et al. 2016).

Herrera et al. tested the antifungal activity of PLA films filled with ChNCs. The incorporation of even a small amount of ChNCs (as 1 wt%) considerably increased the antifungal activity of the film showing a fungal growth inhibition of approximately 70% with respect to the reference film (Herrera et al. 2016). The results demonstrated the potential use of the nanocomposite films as fungal inhibitors for packaging applications.

Liu et al., studied the cytocompatibility of electrospun PLA filled with ChNCs and ChNCs surface modified with oligo (L-lactide) (g-ChNCs). Cell culture results revealed that g-ChNCs/PLA nanofiber membrane was more suitable for cell adhesion, spreading and proliferation than the PLA and ChNCs/PLA nanofiber membranes. The authors related these results to presence of surface hydrophilic groups that often improve the cytocompatibility of the materials (Liu et al. 2016b).

Starch-containing nanocomposites

Preparation routes

Garcia et al. grafted PLA onto starch nanoparticles using a novel and exacting synthetic strategy which involves three reaction steps. In the first reaction, PLA hydroxyl groups were protected by benzoylation to obtain benzoylated PLA (PLABz). The second reaction aimed to activate PLABz carboxyl groups using thionyl chloride. In the third reaction path, the resulting modified PLA chains were grafted onto the starch nanoparticles surface (PLASTARCH). The content of SNCs in the PLASTARCH was estimated as 3.2 wt% (García et al. 2012).

In order to prepare different additive amounts (1, 3, 5, and 8 wt%) of cross-linked starch nanocrystals (CSNCs)/PLA nanocomposites, Yin et al. mixed CSNCs and PLA, wherein the simple cross-linking modification reaction of SNCs significantly improve the dispersive stability and interface compatibility in polymer matrix. Under stirring, chloroform suspensions of different dry weight of CSNCs were separately added to chloroform solution which contained PLA, and the chloroform was recycled by gradual distillation. Then, the resulting products were dried in a vacuum and different formulation of CSNCs/PLA nanocomposites were obtained. Subsequently, they were compression molded to fabricate films with thickness in the range 0.1–0.3 mm (Yin et al. 2015).

In another study, Yu et al. manufactured completely biodegradable nanocomposites with enhanced mechanical properties by grafting poly(ε-caprolactone) (PCL) to the surface of starch nanocrystals via ROP under microwave irradiation. Six different weight percentages of the resulting nanoparticles SNCs-g-PCL, with weight ratio of SNC:ε-caprolactone equal to 1:10, were introduced into a PLA matrix by solvent casting method (Yu et al. 2008).

Main properties

Certainly, the nature of the polymeric matrix, the amount and the surface chemistry of nanoparticles, and the fabrication method, greatly influence the structure and the final properties of nanocomposites manufactured (Yu et al. 2008).

Mechanical properties Table 4 summarizes the main results in terms of mechanical properties registered for various types of PLA starch nanocrystals systems. Yin et al. showed that TS and toughness of CSNCs/PLA nanocomposites are improved, in agreement with the microstructures of tensile fracture surface which demonstrate that CSNCs were uniformly dispersed in PLA matrix. Figure 8 shows the variation of the mechanical properties of CSNCs/PLA nanocomposites as a function of filler content. It can be observed that the mechanical properties increase up to a certain loading (3 wt%), thereafter they were found to level off or to decrease, due to CSNCs aggregation, which has obvious repercussions on interphase volume and filler-matrix adhesion (Yin et al. 2015).

Yu et al. improved the mechanical performance of PLA/SNCs nanocomposites by forming a miscible interfacial layer mediated with grafted long chains of PCL onto starch nanocrystals. The grafted PCL chains improved the interaction of the SNCs with the PLA matrix and facilitated their reinforcing function owing to the formation of an interfacial layer able to transfer the stresses.

Unlike the study of Yin et al., in this case, the addition of SNCs-g-PCL resulted in the enhancement of elongation at break at the expense of Young's modulus, due to the presence of the rubbery PCL. The

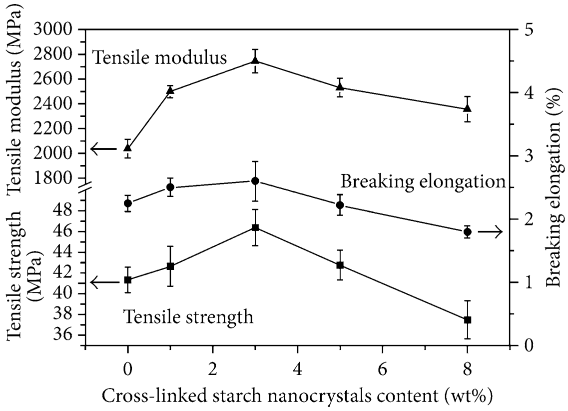

Fig. 8 Tensile modulus, tensile strength and breaking elongation of cross-linked starch nanocrystals/PLA nanocomposites as function of the starch nanocrystals content. Reproduced from (Yin et al. 2015)

optimal loading level of SNCs-g-PCL is 5 wt%, leading to a simultaneous enhancement in strength and elongation. With increasing the loading-level, SNCs-g-PCL self-aggregated as microparticles and agglomerates and, consequently, inhibited improvement of mechanical properties and, especially, EB (Yu et al. 2008).

Thermal properties García et al. analyzed the effect of neat and PLA-grafted SNCs (PLASTARCH) on the thermal properties of PLA-based nanocomposites. DSC results clearly indicated that SNCs acts in a different way depending on whether they are chemically linked to PLA or not (García et al. 2012). In fact, adding SNCs leads to a slight increase of melting temperature, likely due to physical interactions. In PLASTARCH, instead, two contrary effects act simultaneously: (1) a free volume increment induced by the presence of benzoyl groups and (2) a confinement of the polymer chains, caused by the grafting onto SNCs. As a consequence, the T_g of PLASTARCH is comparable to that of PLA.

The capacity for crystallizing of PLA is different in the presence of the benzoyl groups. This mechanism is strongly affected by SNCs that act as a nucleating agent only whether these are chemically attached to PLA chains (García et al. 2012).

Furthermore, the same authors studied the thermogravimetric behavior of the PLA/SNCs systems. They showed that the materials containing neat SNCs display lower thermal stability than PLA, since the onset of degradation begins at lower temperature even if the residual char was found to be higher than that of neat polymer. On the contrary, the materials containing PLASTARCH, owing to the covalent functionalization, show an onset closer to that of unmodified PLA and the highest residual char amount (García et al. 2012).

Yin et al. found that the addition of CSNCs significantly lowers the softening temperature of PLA nanocomposites (from 62 to 53 °C) without affecting its melting temperature. The reason of this reduction was ascribed to the lubricating effect of nanoscale CSNCs between PLA molecules (Yin et al. 2015).

In the work by Yu et al., after adding SNCs-g-PCL the T_g assigned to PLA downshifted of about 10 °C for 5 wt% amount of SNCs-g-PCL, and was even absent under higher loading-levels of SNCs-g-PCL (i.e., higher than 15 wt%). This was attributed to the plasticizing effect of PCL, which increased the motion of PLA chains (Yu et al. 2008).

Water vapor permeability (WVP) Experimental tests demonstrated that the incorporation of CSNCs in PLA matrix reduces the water vapor permeability of PLA nanocomposite films. This can be explained considering that CSNCs have good hydrophilicity which get stronger the interaction forces with water molecules. Moreover, the high crystallinity of CSNCs inhibits the penetration of water molecules, which are found to move along the surface of CSNCs lamellae Furthermore, the uniform dispersion of CSNCs within a PLA matrix was found to decrease the water permeation rate (Yin et al. 2015).

Espino-Pérez et al. showed that ozone-mediated grafting is a promising approach for the surface functionalization of CSNCs, particularly useful to produce PLA based nanocomposite films with improved water vapor barrier properties. In particular, the WVP of PLA incorporating 2 wt% of functionalized SNCs decreased by 52%, if compared with that of neat PLA. The improved barrier properties were attributed to the platelet-like shape of the grafted SNCs that develop a tortuous permeation pathway (Espino-Pérez et al. 2016).

Main applications of PLA/PNs nanocomposites

The excellent properties displayed by PLA/PNs nanocomposites, as well as the renewability, the biodegradability and the relatively low cost of both matrix and filler, make them suitable for different application fields, such as packaging and biomedicine.

In particular, due to their cytocompatibility and biodegradability, cellulose nanoparticles are suitable nanofillers to fabricate PLA-based biomedical devices with enhanced mechanical performance. Blaker et al. (2010) used ice-microsphere templating to prepare PLA-based highly porous scaffolds with pores selectively lined by bacterial CNW. This technique, exploiting hydrophilic–hydrophobic interactions between the polar ice spheres, hydrophilic bacterial CNW and hydrophobic PLA and solvent mixture, allows producing scaffolds of controlled porosities up to 97% with spherical interconnected pore walls lined by bacterial CNW, thus ensuring the direct interaction of CNW with cultured cells.

Cho et al. reported that PLA-CNF foams with different cellular structures could be achieved for various biomedical applications, by simply controlling the nanometric filler size and processing conditions (Cho et al. 2012). PLA-CNC fibers for tissue engineering can be prepared by electrospinning. In this case, the breaking properties of the fibers can be enhanced only at low filler contents. The results demonstrated that unmodified CNCs can be conveniently added only up to 3 wt% (Pirani et al., 2013), whereas PEG-grafted CNCs enhance the mechanical performance of electrospun fibers until a loading level of 5% (Zhang et al. 2015).

Ternary systems containing PLA, CNC and silver nanoparticles exhibited strong antibacterial activity against *S. aureus* and *E. coli* cells, thus offering good perspectives for active food packaging applications (Fortunati et al. 2012a, b, 2014; Yu et al. 2016). Herrera et al., prepared blown films of PLA/ChNCs nanocomposites finding a potential use in packaging application. Puncture and tear strength were found to increase in the presence of ChNCs without affecting the transparency of the film. Moreover, ChNCs were found to act as an antistatic additive, thus facilitating the films' opening, and as an antifungal agent, decreasing the fungal activity against *A.Niger* (Herrera et al. 2016).

Electrospun PLA-CNC mats were also tested for the release of pesticides against whiteflies for green house applications, giving excellent results (Xiang et al. 2013).

The incorporation of functionalized starch nanocrystals into PLA led to nanocomposites with improved barrier properties making them suitable for food packaging applications (Espino-Pérez et al. 2016).

Future perspectives

Recently, Xu et al. (2016) explored the possibility to increase the compatibility between PLA and microsized starch by adding an extremely low amount of GO (0.03%). The authors observed a strong enhancement of mechanical, thermal and barrier properties, due to the formation of strong nanointerfaces. This route could be extended to CSNCs and, of course, to the other PNs in order to avoid long-time consuming derivatization routes.

However, as regards functionalization routes, one successful strategy might be represented by fluorination. In this context, perfluorocarbon moieties could be easily introduced onto PNs surface by substituting –OH moieties via an aromatic nucleophilic substitution mechanism, thus providing PNS with hydrophobicity and additional properties, suitable for biomedical applications (Maio et al. 2016b).

Furthermore, the incorporation of PNs bi-filler in a PLA matrix might lead to a synergistic effect on mechanical, thermomechanical and barrier properties. Indeed, the combination of 1D (e.g. CNW) and 2D (e.g. SNCs) PNs was successfully used by Wang et al. (2010) to reinforce a waterborne polyurethane. The authors demonstrated that the simultaneous addition of these two fillers in the host polymer leads to a lowering of rheological and mechanical percolation thresholds, thus reducing the filler content necessary to enhance some ultimate properties of nanocomposites, such as the stiffness in the rubbery region and the barrier properties. In this perspective, using a combination of chitin and cellulose nanofillers might gather the mechanical and antimicrobial properties of the two nanofillers, thus opening to the possibility to fabricate totally renewable antimicrobial materials, whereas this property is currently achieved by incorporating silver nanoparticles together with CNCs (Fortunati et al. 2012b).

On the other hand, the type of fabrication technique was found to strongly affect the ultimate performance of PLA-PNs nanocomposites, having direct repercussions on filler dispersion and/or polymer degradation. The analysis of recent trends in nanotechnologies show the proliferation of hybrid techniques combining different approaches, often borrowed from other fields, to prepare high performance materials. To this end, the implementation of novel strategies may solve some challenges still affecting PLA-PNs materials.

Conclusions

The use of polysaccharide nanocrystals as nanofillers is an attractive and powerful way to extend and to improve the properties of PLA by allowing the preparation of high-performance PLA-based nanocomposites without compromising the biological and the environmental advantages of the polymeric matrix, i.e. biodegradability, cytocompatibility, compostability and renewability. Indeed, the combination of these highly rigid crystals with PLA has been shown to provide excellent mechanical, thermal, and barrier properties making PLA/PNs nanocomposites suitable for different applications, particularly for packaging and biomedical applications.

However, the key issue is to enhance the interfacial interaction between the nanocrystals and the polymer matrix. In this context, new directions could involve the use of solid amphiphilic nanointerfaces, already adopted for similar systems, or other functionalization routes, such as fluorination, in order to provide nanocrystals not only with hydrophobicity but even with additional properties, suitable for biomedical uses.

Another possible future scenario might be represented by the fabrication of bi-filler polymer nanocomposites, aiming at exploring the possibility to achieve eventual synergistic effects in mechanical and thermomechanical properties by using, a combination of 1D and 2D PNs, analogously to the current trend observed in the case of polymer nanocomposites containing both graphene and CNTs.

The properties of nanocomposites based on PLA and natural organic fillers were directly affected by the source and extraction technique of the nanocrystals and by the preparation techniques of the nanocomposites. In this perspective, the development of novel nanotechnologies for the fabrication of PLA-PNs nanocomposites could further enhance the ultimate performance of this intriguing class of bionanomaterials.

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