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Review

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Novel cellulose-based composites based on nanofibrillated plant and bacterial cellulose: recent advances at the University of Aveiro – a review

Abstract: The development of (nano)materials based on the renewable cellulose is a challenge. The present article provides a brief overview of the recent research efforts carried out at the CICECO Laboratory of the University of Aveiro on the development of novel composites based on nanofibrillated plant and bacterial cellulose embedded in natural and synthetic polymeric matrices such as poly(lactic acid), chitosan, starch, and pullulan. These materials have high potential for applications in packaging, paper coating, organic electronics, and biomedical products and devices.

Keywords: bacterial cellulose (BC), biopolymers, nanocomposites, nanofibers, nanofibrillated cellulose (NFC), plant cellulose, polysaccharides, renewable resources, transparent films

Introduction

The finiteness of fossil raw materials led in the last decades to intense research activities toward a more sophisticated utilization of renewable materials, such as plant biomass (lignocellulosic feedstock), which are subsumed as "biorefinery" (Fernando et al. 2006; Kamm et al. 2006). The biorefinery concept is analogous to the traditional petroleum refinery, which means that biomass conversion processes should be improved so that more value-added chemicals can be produced aside from heat and power. The biorefinery concept is frequently developed in the context of the well-established pulping industry, with pulp (cellulose and hemicelluloses) as its main product and lignin as its byproduct. Also, the University of Aveiro met this rewarding challenge and dedicated intense research efforts to many aspects of wood chemistry, pulping, and bleaching technologies. Frequently, *Eucalyptus globulus* is in focus, a tree of large importance for pulp production in Portugal. Since the last decade, the biorefinery concept is an integrated part of the research efforts aiming at better utilization of important forest species of Portugal.

Concerning *E. globulus*, the research has been mainly devoted to high-value components from bark residues (Freire et al. 2002; Domingues et al. 2010; Santos et al. 2011) and to new applications of cellulose fibers (Freire et al. 2005, 2006a,b, 2008; Cunha et al. 2007a,b, 2010; Fernandes et al. 2011a; Tomé et al. 2011a).

The outstanding properties of cellulose fibers (Figure 1a and b) are well documented (Fengel and Wegener 1989; Klemm et al. 1998, 2005) in terms of mechanical strength, chemical behavior, biocompatibility, biodegradability, nontoxicity, absorption properties, and low density. These properties are the basis for novel applications beyond the well-established utilization in paper and textile products (Klemm et al. 2005).

Esterification, etherification, urethane formation, and cross-linking or graft copolymerization enlarge the application possibilities of cellulose (Klemm et al. 1998; Gandini 2008; Heinze and Petzold 2008; Yu and Chen 2009). A peculiarity is the controlled heterogeneous modification of cellulose fibers, where the reaction is limited to the most accessible regions of the fibers while its bulk mechanical properties are preserved. This is one of the strategies for utilization of cellulose as reinforcing elements in composites (Bledzki and Gassan 1999; Schurz

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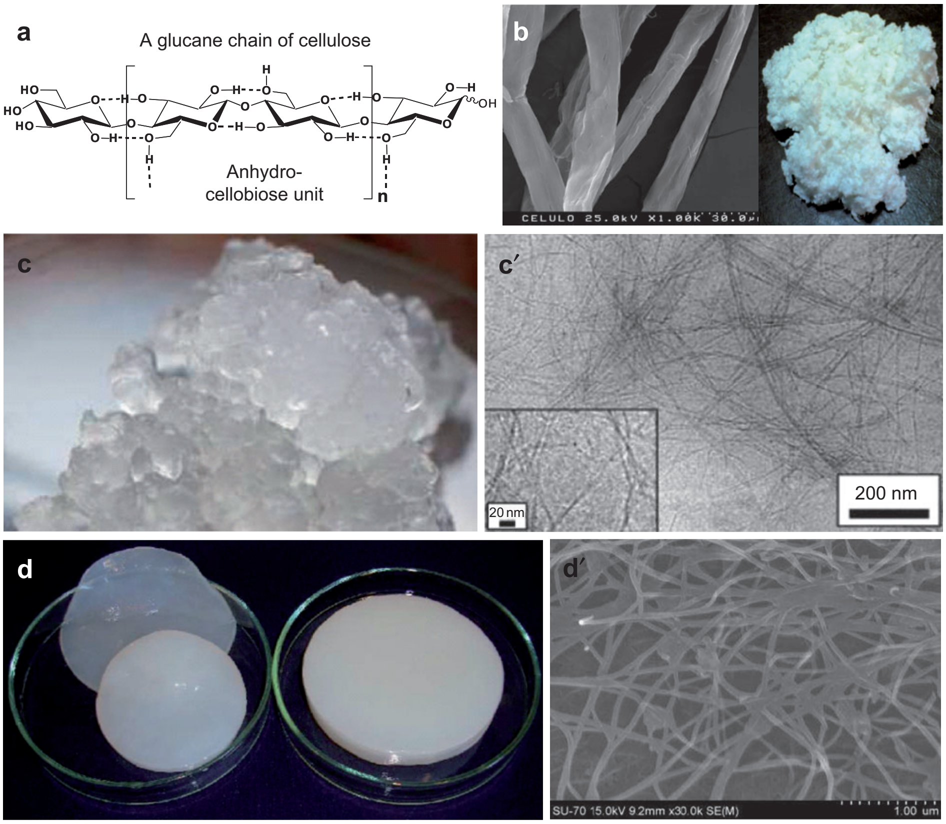

Figure 1 Images of cellulose.
(a) A glucan chain of cellulose with repeating anhydrocellobiose units. (b) Macroscopic and SEM images of conventional pulp fibers. (c and c′) Macroscopic and SEM images of NFC. (d) Image of BC. (d′) SEM image of BC.

1999; Mohanty et al. 2001; Belgacem and Gandini 2005; Samir et al. 2005; Freire and Gandini 2006; Teeri et al. 2007; Dufresne 2008). Here, cellulose replaces inorganic (mineral)-based fibers (Wang and Zhang 2009). Automotive, construction, and packaging are among the largest segments for these materials with an exponential growth in recent years.

More recently, polymer-based nanocomposites (multiphase materials) consisting of a polymer matrix and a nanofiller, gained particular attention and interest. They have very special properties in comparison with conventional polymer composites (Bordes et al. 2009), for example, improved mechanical, thermal, and barrier properties and transparency (Zimmermann et al. 2004; Hubbe et al. 2008; Nogi and Yano 2008; Azeredo 2009; Fukuzumi et al. 2009; Kim et al. 2009). The nanocomposites of this category, in which the micro- and nanofibrillated cellulose (MFC and NFC, respectively), cellulose whiskers, and bacterial cellulose (BC) play an essential role, have a wide range of application domain (Nakagaito and Yano 2004, 2005; Nakagaito et al. 2005; Shimazaki et al. 2007; Jung et al. 2008; Nogi et al. 2009). The preparation, properties, modification, and application of NFC were reviewed extensively (Zimmermann et al. 2004; Samir et al. 2005; Hubbe et al. 2008; Chinga-Carrasco 2011; Klemm et al. 2011; Petersen and Gatenholm 2011; Siqueira et al. 2011).

The first production of MFC from wood fibers was reported by Turbak et al. (1983). Meanwhile, the term NFC is more frequently applied. The disintegration of cellulose fibrils to nanocellulose is realized by high-pressure homogenizers combined with chemical or enzymatic treatments (Preston 1974; Sjöström 1981; Klemm et al. 1998; Teeri et al. 2007). The obtained NFC suspensions (Figure 1c and c′) bear the appearance of highly viscous shear-thinning transparent gels and have high aspect ratios and specific surface areas combined with remarkable strength and flexibility, low thermal expansion, high optical transparency, and specific barrier properties. MFC and NFC can be incorporated in different matrices such as hydroxypropylcellulose (Zimmermann et al. 2004), chitosan (CH; Nordqvist et al. 2007), viscous polysaccharide matrices in the form of 50/50 amylopectin-glycerol blends (Svagan et al. 2007), poly(lactic acid) (PLA; Iwatake et al. 2008; Suryanegara et al. 2009), polyvinyl alcohol (Zimmermann et al. 2004), and polyurethanes (Seydibeyoglu and Oksman 2008). The NFC-based nanocomposites are used for the production of transparent materials (Yano et al. 2005; Fukuzumi et al. 2009) and gas barrier films (Fukuzumi et al. 2009).

BC, also known as microbial cellulose, is produced by different bacteria genera, such as *Gluconacetobacter*, *Sarcina*, and *Agrobacterium*, but *Gluconacetobacter xylinus* is probably the most commonly referred strain in this context (Budhiono et al. 1999; Shoda and Sugano 2005; Pecoraro et al. 2008). Recently, it was reported by our group that *G. sacchari* also produces BC in very high yields (Trovatti et al. 2011). These bacteria are Gram-negative aerobic and nonphotosynthetic bacteria usually found in fruits, vegetables, vinegar, and alcoholic beverages. They are capable of converting several substrates into cellulose within a few days. Studied substrates comprise glucose, glycerol, and other organic materials, including residues from agroforest industries (Chawla et al. 2009; Carreira et al. 2011). BC can be produced as a highly swollen hydrogel and, depending on the static or agitated nature of the culture media, as a membrane (Figure 1d and d′) or in the form of small beads. BC consists of ribbons of microfibrils generated at the surface of the bacterial cell. The bacteria first segregate a structurally homogeneous slimy substance, and after a short time, the cellulose nanofibers are formed (Chawla et al. 2009). More precisely, BC is a three-dimensional network consisting of nano- and microfibrils with the dimensions of 3–4 nm thickness and 70–80 nm length (Figure 1d′), that is, the fibrils are approximately 1000 times thinner than typical plant cellulose fibrils. These dimensions explain the unique properties of BC. Additionally, BC is free of lignin, hemicelluloses, and other natural components usually associated with cellulose isolated from the cell wall of plants. BC has a high degree of polymerization and crystallinity, extremely high water holding capacity, high tensile strength, and high surface area (George et al. 2005a,b). BC is well suited as a reinforcing element in nanocomposites in several polymeric matrices, namely, cellulose acetate butyrate (Gindl and Keckes 2004), acrylic thermosetting resins (Yano et al. 2005; Ifuku et al. 2007), phenolic resins (Nakagaito et al. 2005), poly(ethylene oxide) (Brown and Laborie 2008), plasticized starch (Wan et al. 2009), PLA (Kim et al. 2009), and epoxidized soybean oil matrix (Retegi et al. 2012), just to mention a few examples.

Recent advances of nanocomposite research with NFC and BC as reinforcing elements achieved at the University of Aveiro will be reported in the next chapter.

Research on cellulose nanocomposites at the University of Aveiro

Different strategies were applied to obtain nanocomposites, namely, heterogeneous chemical modification, compounding with synthetic polymers matrices such as PLA, and blending with other natural polymers such as CH, starch, and pullulan. Polysaccharide matrices are compatible with cellulose because of their structural similarity. This is the reason why simple “green procedures” such as casting of water-based suspensions or melting-mixing can be applied for the production of composites with polysaccharides and nanocellulose fibers. The next paragraphs will present some examples of these approaches.

BC-PLA nanocomposites

PLA is a versatile and biodegradable thermoplastic polyester (Figure 2a), which is produced entirely from renewable resources, specifically from starch-enriched raw materials such as sugar beet, corn, and wheat (Averous 2008). The properties of PLA such as high mechanical strength and stiffness, UV stability, and gloss open a large field of applications in the automotive industry, packaging, and medicine.

Nanocomposites with improved properties based on PLA matrix and BC were described by Tomé et al. (2011b), who prepared such materials by heterogeneous acetylation of BC followed by simple melting-mixing with PLA. The acetylation increases substantially the hydrophobicity of nanofibers and therefore their compatibility and adhesion with the PLA matrix. The compatibility was evidenced by scanning electron microscopy (SEM) images (Figure 2b′).

PLA-BC nanocomposites have considerably improved mechanical properties as evidenced by the significant increase both in the storage modulus (E′/Pa; Figure 3a) as well as Young’s modulus and in the tensile strength (Tomé et al. 2011b). The increments were approximately 100%, 40%, and 25% for elastic modulus, Young’s modulus, and tensile strength, respectively, even when the level of nanofiller loadings (up to 6%) was low.

The incorporation of both unmodified and acetylated BC nanofibers in the PLA matrix also resulted in a considerable increase in the thermal properties of the corresponding nanocomposites (Figure 3b) and particularly those with acetylated BC fillers (PLA-BCAc), observed by the increment in both initial and maximum degradation temperatures, which reflect their excellent interfacial

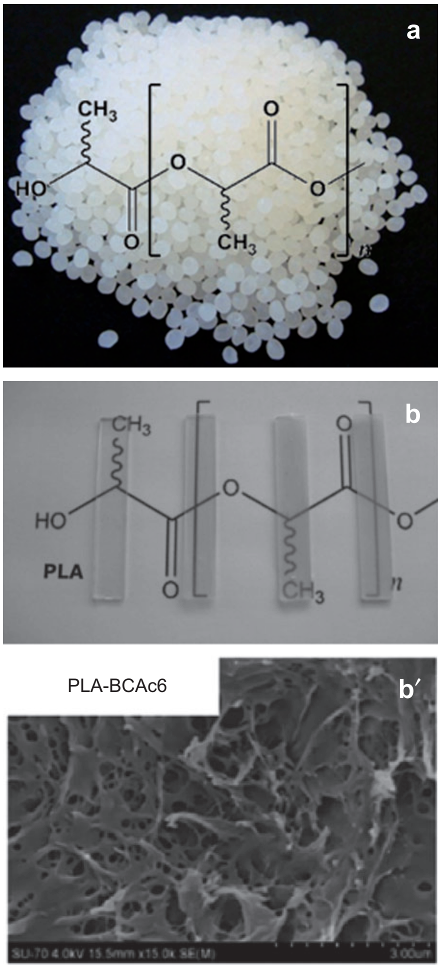

Figure 2 Images of PLA.
(a) Visual aspect of PLA pellets. (b and b′) Optical and SEM images of PLA and PLA-BC nanocomposites (PLA-BC).

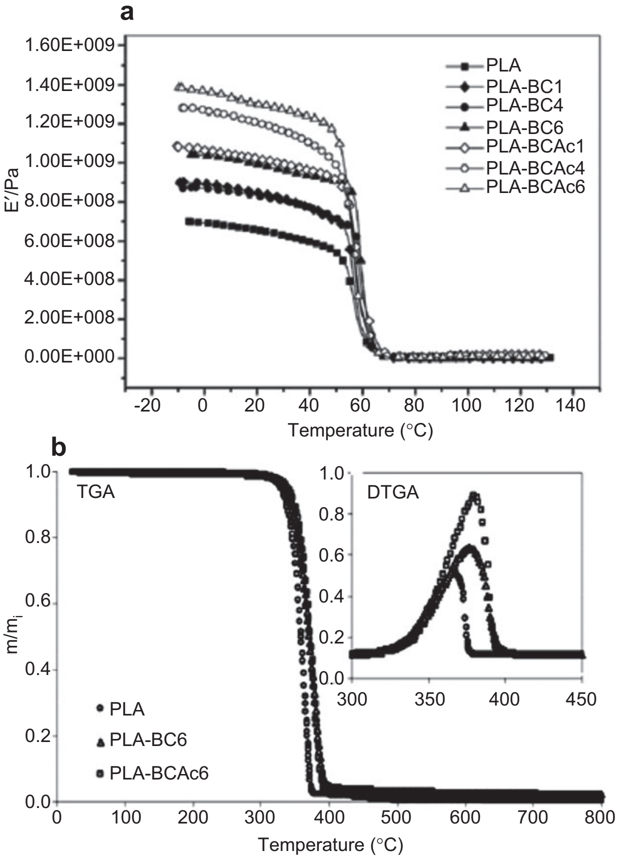

Figure 3 Properties of PLA and PLA-BC composites.
(a) Storage modulus of PLA and PLA-BC and PLA-BCAc acetylated (PLA-BCAc). (b) Thermogravimetric analysis and differential thermogravimetric analysis of PLA, PLA-BC, and PLA-BCAc.

compatibility. For example, the incorporation of 6% of acetylated BC (PLA-BCAc6) elevated the initial and maximum degradation temperatures by 15°C and 14°C, respectively.

Moreover, these nanocomposites also have a low hygroscopicity and considerable transparency (Figure 1b). For example, their transmittance (measured for specimens with a thickness of ~1 mm) at 580 nm was approximately 80% for PLA, 70% for the nanocomposites prepared with PLA and 1% of acetylated BC (PLA-BCAc1), and 60% with 4% and 6% of acetylated BC (PLA-BCAc4 and PLA-BCAc6).

CH-nanocellulose transparent nanocomposites

CH (Figure 4a), obtained from deacetylation of chitin, which is the main component of crustacean shells and insects' exoskeletons, is unique concerning biocompatibility, antimicrobial activity, biodegradability, and excellent film-forming ability (Rinaudo 2006; Peniche et al. 2008), which have attracted scientific and industrial interest in biotechnology, pharmaceutics, biomedicine, packaging, and wastewater treatment, among many other application fields. CH behaves in aqueous acidic media as a polycation contrasting with the other polysaccharides, which are usually neutral or anionic (Rinaudo 2006; Peniche et al. 2008).

The preparation and characterization of nanocomposite films (Figure 4b and c) were described based on different matrices of CH and BC (Fernandes et al. 2009, 2011b) or NFC (Fernandes et al. 2010, 2011b). The goal is the preparation of CH films with improved mechanical properties while keeping their transparency and thermal stability. The preparation was carried out by casting NFC or BC suspensions in aqueous CH (or chemically modified CH). The components are perfectly compatible; moreover, CH solutions are an efficient media for stable suspensions of NFC or BC. As a result, the BC (as well as NFC) is very homogeneously distributed in the matrix (Figure 4b

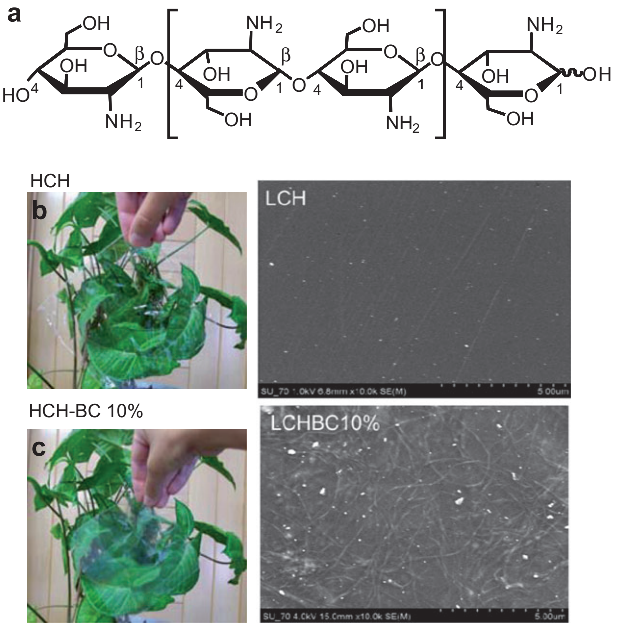

Figure 4 Images to CH and CH-based composites.
(a) Chemical structure of a CH chain. (b) Illustration of the transparency of a CH film (HCH; left) and the SEM image of LCH. (c) Illustration of the transparency of a CH-BC nanocomposite (HCH-BC 10%; left) and the SEM image of LCH-BC 10%.

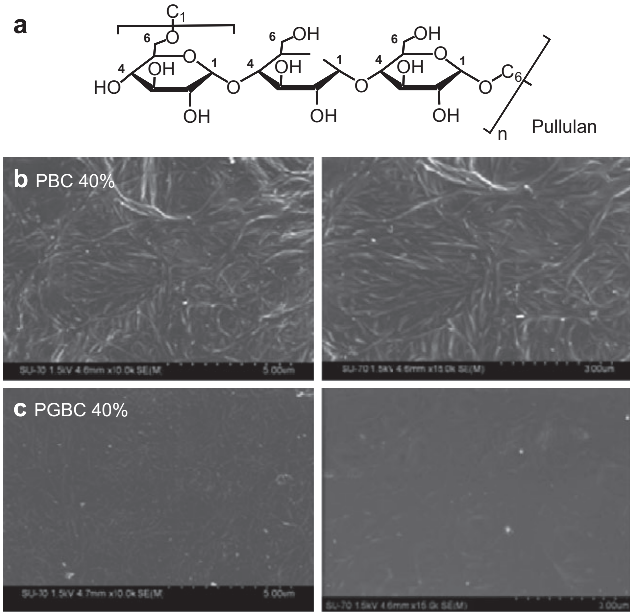

Figure 5 Images to pullulan and pullulan-based composites.
(a) Chemical structure of pullulan. Pullulan is a polysaccharide consisting of maltotriose units also known as α-1,4-;α-1,6-glucan.
(b) SEM image of a PBC-based nacocomposite (PBC 40%). (c) SEM image of a PBC-glycerol-based nanocomposite (PGBC 40%).

and c). The same figure demonstrates that the films are highly transparent and flexible. The mechanical properties of the films are manifested by excellent Young's modulus (that can go up to 320% improvement for some formulations) and tensile strength, and the thermal stability of the films is better compared with pure CH films.

These films are well suited for the development of transparent electronic devices, namely, organic field-effect transistors (Pereira et al. 2011). Finally, CH- and BC-based aqueous formulations can be used successfully as surface coating of paper with substantially improved properties concerning the surface and printing quality and mechanical strength (Fernandes et al. 2011c).

Pullulan-nanocellulose nanocomposites

Pullulan is a linear water-soluble homopolysaccharide of glucose (Leathers 2003) consisting of maltotriose units that are integrated in the polymers by α-(1–6) linkages (Figure 5a). Pullulan is produced aerobically by certain strains of the polymorphic fungus *Aureobasidium pullulans*. It is able to form films that show high oxygen impermeability, nontoxicity, edibility, biodegradability, and compatibility to humans and the environment and have good mechanical properties (Krochta and DeMulder 1997). These films are normally used as coating or packaging materials for dried foods as well as in the pharmaceutical industry.

Novel pullulan-BC (PBC) nanocomposite films were prepared by Trovatti et al. (2012a) and the material was filled with 5%, 10%, 20%, 40%, and 60% (w/w) BC and with glycerol as plasticizer. The procedure is similar to that described above for the CH nanocomposite films. The morphology of the nanocomposites was studied by SEM, aiming at the assessment of the dispersion of the BC nanofibrils into the pullulan matrix and the interfacial adhesion between the two components (Figure 5b and c). As visible, the BC is well dispersed in the pullulan matrix, without forming considerable aggregates, even for high fiber contents (up to 40%).

Figure 6 displays the stress-strain curves of nanocomposites made of pullulan, pullulan-glycerol (PG) films, PBC, and PG-BC. The incorporation of BC into the pullulan matrix improves considerably both Young's modulus and tensile strength, with increments of up to 100% and 50% for films without glycerol and up to 8000% and 7000% for films plasticized with glycerol. Glycerol as plasticizer increases the flexibility of the films, which is an important parameter in many applications.

The thermal stability of all PBC nanocomposites is considerably improved as a function of the BC content as evidenced by an increment in the degradation temperatures.

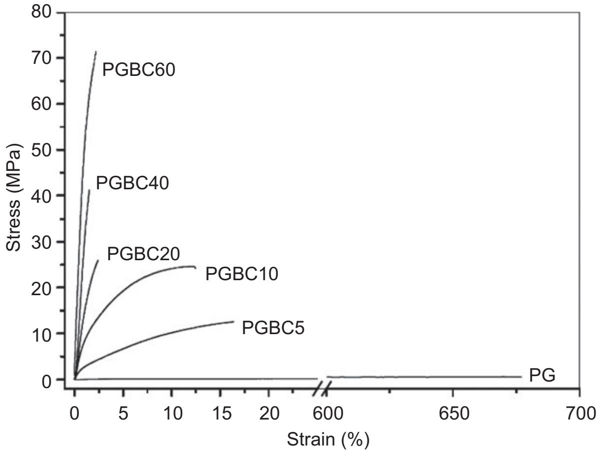

Figure 6 Stress-strain curves of PG and PG-BC nanocomposites (PGBC).
The numbers indicate the BC concentration in %.

For instance, for PBC nanocomposites, the incorporation of 5% BC resulted in an increase of approximately 3°C and 7°C in the initial and maximum degradation temperatures, respectively, whereas the incorporation of 20% BC resulted in an increment of 9°C and 17°C of the initial and maximum degradation temperatures, respectively (Trovatti et al. 2012a).

Similar nanocomposites were also developed based on NFC as reinforcing element (Trovatti et al. 2012b). As in the case of the materials prepared with BC, all pullulan-NFC nanocomposites show a good homogeneity (atomic force microscopy images in Figure 7a and a′) and a high translucency as evidenced by the optical image of nanocomposite specimens against a printed background (Figure 7b). The image in the corner of Figure 7b demonstrates the considerable flexibility of the films. Pullulan-NFC nanocomposites also showed considerable improvements in thermal stability, which means increments of up to 20°C in the degradation temperature (Trovatti et al. 2012b); finally, pullulan-NFC nanocomposites showed increments in mechanical properties of up to 5500% and 8000% in the Young's modulus and tensile strength, respectively, for films plasticized with glycerol when compared with the unfilled pullulan films (Trovatti et al. 2012b).

Thermoplastic starch-cellulose nanocomposites

Starch (Figure 8a) is one of the most abundant and available natural polysaccharides, which is well investigated as part of novel biocomposites. The disruption of the molecular chain interactions in starch granules (Figure 8b) leads to a thermoplastic material [thermoplastic starch (TPS)] under specific conditions and in the presence of a plasticizer, such as water or glycerol.

Figure 7 Images of nanocomposites based on pullulan and NFC (PNFC 40%).
(a and a′) Atomic force microscopy images of PNFC 40% with different enlargements. (b) Optical images to illustrate the transparency of films made of PG, PGNFC 20%, and PGNFC 40%. For abbreviations, see also Figure 5.

TPS composites are prepared in a single step with cornstarch by adding glycerol/water as plasticizer and BC (1% and 5%, w/w) as reinforcing agent (Martins et al. 2009). The BC is well dispersed in the matrix and there is a strong adhesion between BC and TPS (Figure 8c).

Plant NFC and especially BC proved to be efficient reinforcement agents even in low quantities. At 5% BC loading, the Young's modulus and the tensile strength of the composite are elevated considerably (Figure 9a and b). The good performance of BC in comparison with plant NFC has to be emphasized (Figure 9a and b). This is probably due to the high aspect ratio and three-dimensional network of the BC.

In principle, these materials are promising in applications of food packaging and biodegradable materials. Then again, TPS-based materials are sensitive to humidity. The moisture sorption maximum was slightly reduced by the incorporation of BC. The interpretation is that starch is more hydrophilic than cellulose and nanofibers absorb

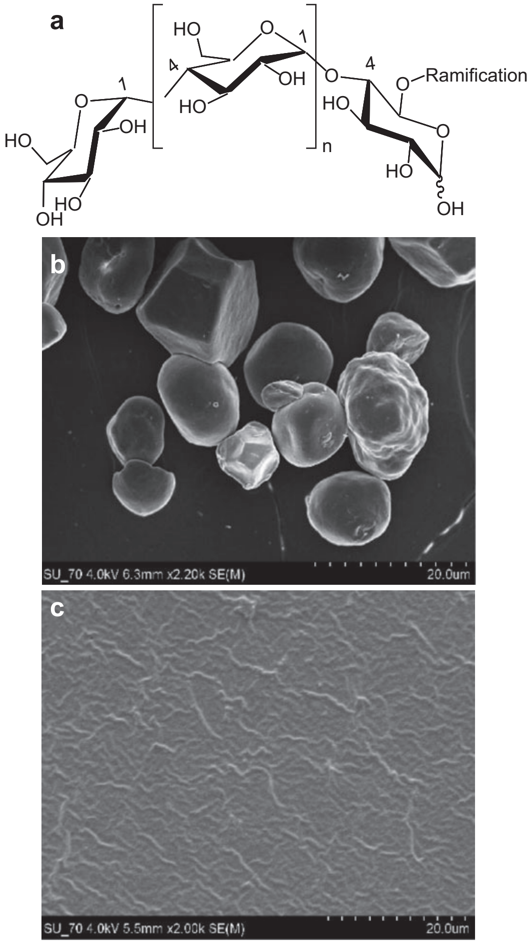

Figure 8 Starch and composites of starch.
(a) Segment of the chemical structure of a starch helix. (b) Starch granulates. (c) TPS film.

a part of the glycerol that will be not available to absorb humidity (Curvelo et al. 2001).

Conclusions

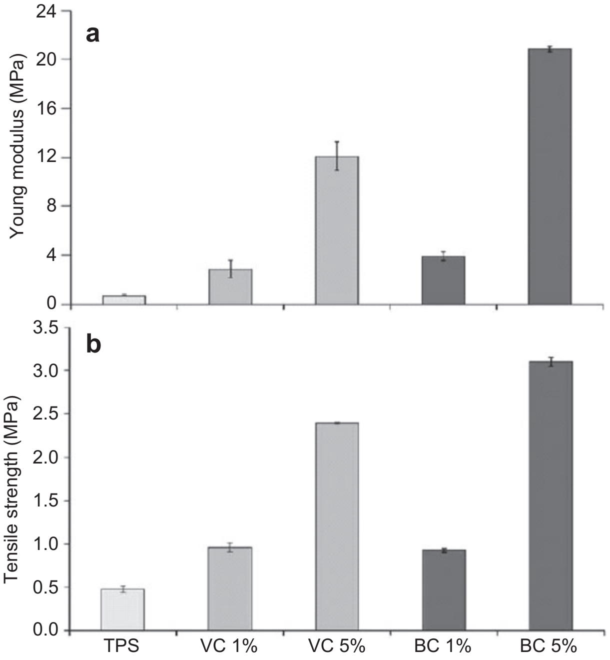

Figure 9 Properties of TPS and composites made of TPS reinforced with 1% and 5% BC and plant cellulose (VC).
(a) Tensile strength. (b) Young's modulus.

Novel composites based on nanofibrillated plant cellulose and BC embedded in natural and synthetic polymeric matrices such as PLA, CH, starch, and pullulan are promising because of the high compatibility of the enforcement and the matrix. The physical and thermal properties of these materials are unique, which predestine them for applications in packaging, electronic devices, and biomedicine. The family of these materials can be substantially widened by the combination with inorganic nanophases, a topic that has also been addressed by our group (Gonçalves et al. 2008, 2009; Pinto et al. 2008, 2009, 2012; Vilela et al. 2010). The development of cellulose-based nanocomposites is still a rewarding research field.

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