

NANOCELLULOSE FIBERS AND OTHER NATURAL POLYMERS AS UNIQUE PIECES FOR THE DEVELOPMENT OF SUSTAINABLE COMPOSITES: A CONTRIBUTION@UA.PT

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Abstract

In recent years we have been engaged on the development of novel (nano)composite materials based on nanocellulose forms and other natural polymers, following different strategies, including heterogeneous chemical modification and compounding with thermoplastic matrices, combination with other natural polymers like chitosan and starch and blending with other materials. A global overview of the research activities developed in these domains in our group will be presented and discussed in this communication.

1 Introduction

In recent years there has been an increasing interest in the search for renewable sources of novel composite materials for application in several fields such as in packaging and automotive industry. Polysaccharides and especially cellulose, due to its abundance and mechanical properties are among the most important resources for the development of sustainable composite materials [1]. More recently, nanocellulose forms like bacterial cellulose and nanofibrillated cellulose gained particular attention on this context because of their unique features (Figure 1). Bacterial cellulose (BC) is generated, by several bacteria, as a tridimensional network of nano- and micro-fibrills and has higher purity, water holding capacity, crystallinity, tensile strength and Young modulus than vegetable cellulose fibers [1,2]. Nanofibrillated cellulose (NFC) is obtained by disintegration of common cellulose fibers, like wood pulp, using high-pressure homogenizers [1,3]. The obtained cellulose fibril suspensions 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.

The use of cellulose fibers (or nanofibers) as reinforcing agents in polymer–matrix based composite materials (4) requires that on the one hand fibers are made compatible with the polymeric matrix, and, on the other hand, their bulk mechanical properties are preserved. To achieve such properties of the modified fibers, the classical and well established homogeneous chemical modification approach, where the reactions occur

indiscriminately along the fiber cell wall, leading to well known products such as carboxymethylcellulose or cellulose acetates [5,6], is not suitable, and the more recent approach of controlled heterogeneous modification of cellulose fibers has to be considered [7]. This last strategy has been gaining growing attention, as modifications can be limited to the groups present in the most accessible regions of the fibers. Under this conditions surface fibers properties can be dramatically changed, while their key bulk physical properties are preserved, allowing the new materials to be used as reinforcing agents in composite materials with common polymeric matrices.

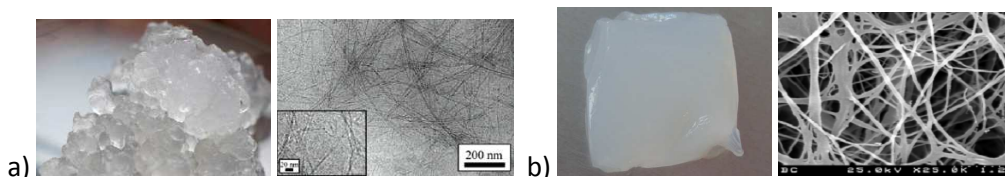


Figure 1. Visual and SEM micrographs of a) nanofibrillated cellulose (*www.innventia.com*, Pääkköet al,(2007) *Biomacromolecules*, 8(6), 1934-1941) and b) bacterial cellulose

A different approach involves the use of cellulose as reinforcing agent for matrices of other polysaccharides e.g. chitosan, starch (Figure 2) and pullulan (Figure 3, Results and Discussion section) that bear promising functional properties, but which exploitation is limited by poor mechanical performances. In this case due to the structural similarity of both cellulose fibers and the polysaccharide matrices, the former can be used as reinforcing elements without any chemical modification.

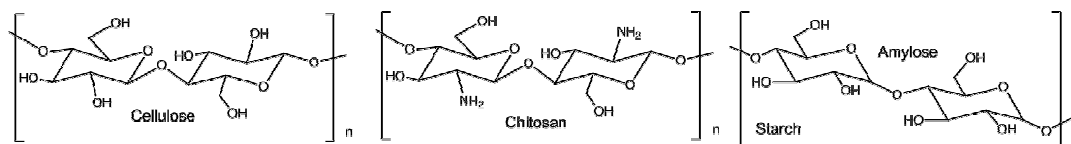


Figure 2 - Chemical structure of cellulose, chitosan, amylose (one of the two components of starch).

2 Results and Discussion

2.1 Chitosan nanocomposites with nanofibrillated cellulose and bacterial cellulose

Chitosan (Figure 2) exhibits unique physicochemical properties like biocompatibility, antimicrobial activity, biodegradability and excellent film-forming ability, which have attracted scientific and industrial interest in fields such as biotechnology, pharmaceuticals, biomedicine, packaging, wastewater treatment, cosmetics, and food science, among others [8]. However, despite the numerous advantages and unique properties, chitosan films display poor mechanical performance, which limits considerably their

applications. One way to improve the mechanical properties (among other functionalities) of chitosan films, is to prepare blends with other polymers. In this way, the preparation and characterization of nanocomposite films based on different chitosan matrices and bacterial cellulose [9] or nanofibrillated cellulose [10] aimed at preparing chitosan films with improved mechanical properties, while keeping their transparency properties and thermal stability was investigated.

The nanocomposite films were prepared by a simple and green procedure of casting water-based suspensions of chitosan (or chemically modified chitosan) samples and NFC or BC. Due to their structural similarity chitosan and NFC or BC are perfectly compatible, and on the other hand, chitosan solutions were shown to be an efficient media to prepare stable suspensions of NFC or BC, and to produce films with a very homogeneous distribution of BC and NFC (Figure 3).

The films obtained were shown to be highly transparent (Figure 3) and flexible; simultaneously they have shown considerably improved mechanical properties with substantial increments in the Young's modulus (that can go up to 320% for some formulations) and in the thermal stability of the films.

The excellent optical transparency of these films together with their improved mechanical properties and thermal stability, open very promising perspectives for the application of these new materials in packaging or electronic organic applications.

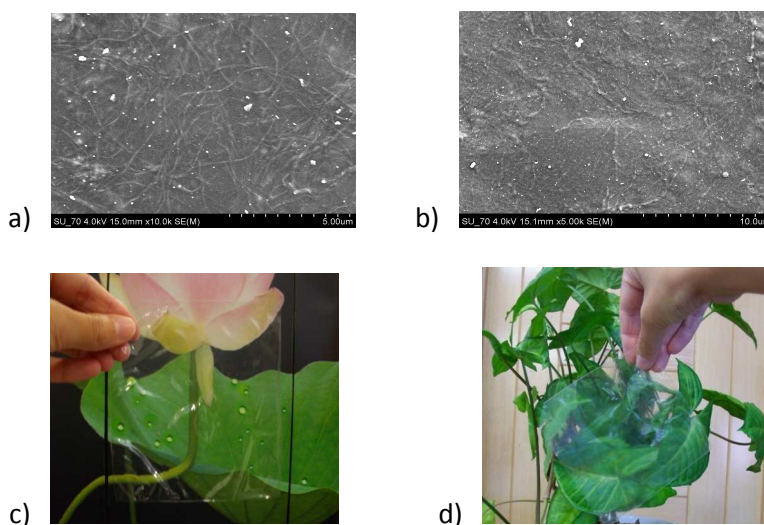


Figure 3. SEM micrographs of chitosan nanocomposites with bacterial (a) and nanofibrillated (b) cellulose; and images of the corresponding (c and d) transparent films (adapted from 9-11).

2.2 Pullulan-nanocellulose nanocomposites matrix reinforced with BC and NFC

Pullulan is a water soluble polysaccharide, produced aerobically by certain strains of the polymorphic fungus *Aureobasidium pullulans*. This polysaccharide is able to form films that are highly oxygen-impermeable, non-toxic, edible, biodegradable, compatible to human and environment and that also present good mechanical properties [11]; allowing their use in areas such as food and pharmaceutical industries, as coating or packaging materials for dried foods.

Regarding the potentialities of this biopolymer, we prepared novel pullulan-BC translucent nanocomposite films (Figure 4) filled with 5, 10, 20, 40 and 60% w/w of BC), using glycerol as plasticizer [12]. The morphology of the nanocomposites was studied by SEM, aiming to assess the dispersion of the BC nanofibrills into the pullulan matrix and the interfacial adhesion between the two components. The SEM images of BC-pullulan nanocomposites (Figure 4) demonstrated the good dispersion of the BC nanofibrills on the pullulan matrix, without considerable aggregates formation, even for high BC contents (up to 40%).

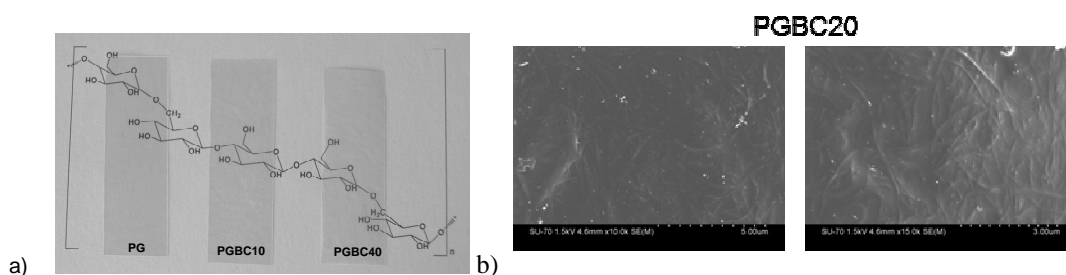


Figure 4. Images pullulan and nanocomposite films with 10 and 40% of BC (a) and SEM images of the pullulan PGBC20 (b).

The incorporation of BC into the pullulan matrix increased considerably the mechanical performance, compared to the unfilled pullulan films. On both Young's modulus and tensile strength, increments of up to 100 and 50%, were observed for films without glycerol and up to 8000 and 7000% for those plasticized with glycerol. The use of glycerol as plasticizer increases the flexibility of the films which is an important parameter in many applications. Figure 5 displays the stress-strain curves for pullulan-glycerol (PG) films and pullulan-glycerol-bacterial cellulose (PGBC) nanocomposites.

All BC-pullulan nanocomposites exhibited also considerable improvements in thermal stability as a function of the BC content, evidenced by the significant increase in the degradation temperature (up to 40 °C) (Figure 5). The TGA tracing of pullulan-BC (PBC) and pullulan-glycerol-BC (PGBC) nanocomposites with 5, 10 and 20% of BC contents is quite similar to that of unfilled P and PG matrices, however increments on the initial (T_{di}) and maximum (T_{max1}) degradation temperatures were observed. For nanocomposites prepared with 40 and 60% of BC the T_{di} was also displaced for higher temperatures but a second step (T_{max1}) (Figure 5) of degradation was observed probably due to the degradation of the BC enriched fractions.

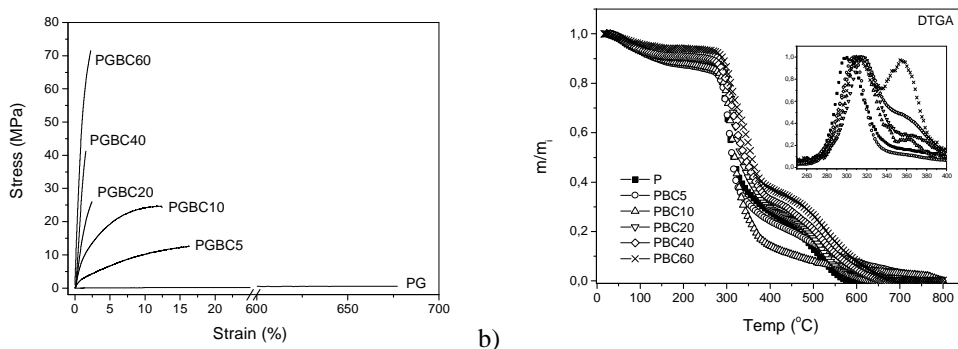


Figure 5. Stres-strain curves of PGBC nanocomposites (a) Thermograms of all PBC nanocomposites.

In the same manner, similar pullulan nanocomposites were also developed but using nanofibrillated cellulose (NFC) instead of BC [13]. As in the case of the nanocomposites prepared with BC, all bionanocomposites showed good homogeneity, high translucency, and considerable improvements in thermal stability (increments of up to 20°C in the degradation temperature) and mechanical properties (increments of up to 5500 and 8000% in the Young's modulus and tensile strength, respectively, for films plasticised with glycerol) when compared to the unfilled pullulan films.

2.3 Thermoplastic starch-bacterial cellulose nanocomposites

Starch is one of the most abundant natural polymers and is known as a promising resource for the development of novel materials, including biocomposites [14]. It can be converted into a thermoplastic material, known as thermoplastic starch (TPS), through the disruption of the molecular chain interactions under specific conditions, in the presence of a plasticizer. Water and glycerol are the most widely used plasticizers in the production of TPS.

In this context, BC nanocomposites with corn starch were prepared in a single step by adding glycerol/water as the plasticizer and bacterial cellulose (1% and 5% w/w) as the reinforcing agent [15]. All nanocomposites showed good dispersion of the nanofibers and a strong adhesion between the nanofibers and the matrix (Figure 6).

Bacterial cellulose acts efficiently as starch matrix reinforcement (Figure 6), even in relatively low quantities, e.g., a 5% BC load produced a significant increase in both modulus and tensile strength. These materials are promising candidates in applications like food packaging and biodegradable artifacts. However, the ensuing composites displayed a strong sensitivity to high relative humidity, even if the moisture sorption maximum was slightly reduced by the incorporation of bacterial cellulose, which is

ascribed to the facts that, on the one hand, starch is more hydrophilic than cellulose and that, on the other hand, the nanofibers absorb part of the glycerol (16).

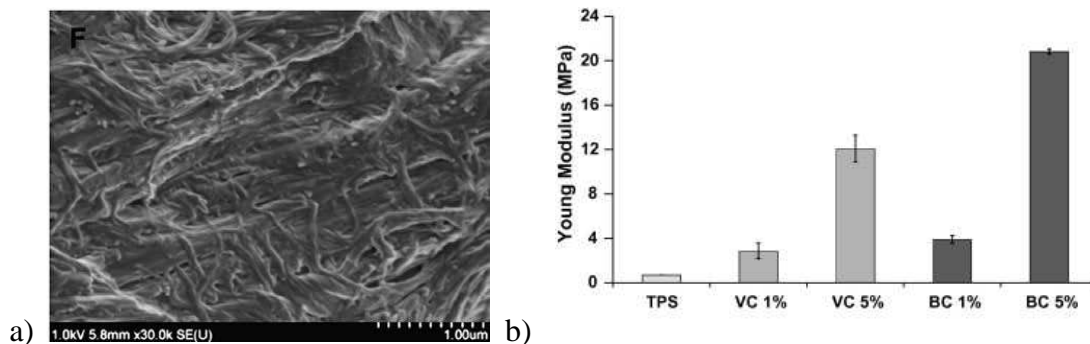


Figure 6. SEM image of TPS nanocomposite with 6% of BC (a) Young modulus of TPS-BC and VC composites.

2.4 BC-Poly(lactic acid) nanocomposites

Poly(lactic acid) (PLA) is a versatile biodegradable thermoplastic polyester entirely produced from renewable resources, such as starch enriched products like sugar beet, corn and wheat. This thermoplastic biopolymer presents interesting properties like high mechanical strength and stiffness, UV stability and gloss, and has, thus, gained increasing attention and interest in several fields of application, such as the automotive industry, packaging and medicine.

Bionanocomposites with improved properties based on PLA and bacterial cellulose (1, 4 and 6% of nanofibres), in its pristine form or after heterogeneous acetylation, were recently prepared [17], through the simple and green melting mixing. Here, the main objective of the BC nanofibers acetylation step was to increase substantially their hydrophobicity and to decrease polarity, and therefore their compatibility/adhesion with the PLA matrix. This compatibility was evaluated and evidenced by SEM images (Figure 7). PLA-BC bionanocomposites were particularly interesting, given the considerable improvement in mechanical properties (Figure 7), as evidenced by the significant increase in both elastic and Young's modulus, and in the tensile strength. The increments were of about 100, 40 and 25%, for elastic and Young's modulus and tensile strength, respectively; at very low nanofiller loadings (up to 6%). 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, particularly those with acetylated BC fillers, observed by the increment in both the initial and maximum degradation temperatures, which reflects their excellent interfacial compatibility. For example, the incorporation of 6% of acetylated BC resulted in an increase of 15 and 14 °C, respectively, in the initial and maximum degradation temperatures.

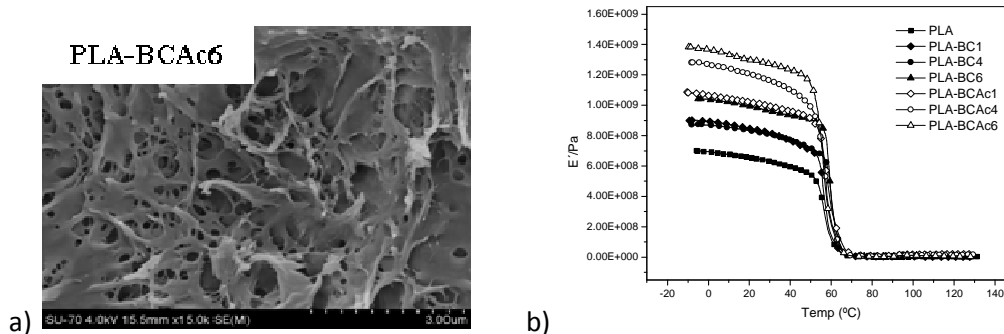


Figure 7. SEM image of PLA nanocomposite with 6% of acetylated BC (a) and storage modulus E' vs temperature (at 4 Hz) of all BC PLA composites.

Moreover, these nanocomposites also showed low hygroscopicity and considerable transparency (Figure 8). For example, the transmittance of these materials (measured for specimens with a thickness of approximately 1 mm) at 580 nm was about 80% for PLA, 70% for the nanocomposites prepared with PLA and 1% of acetylated BC, and 60% with 4 and 6% of acetylated BC.

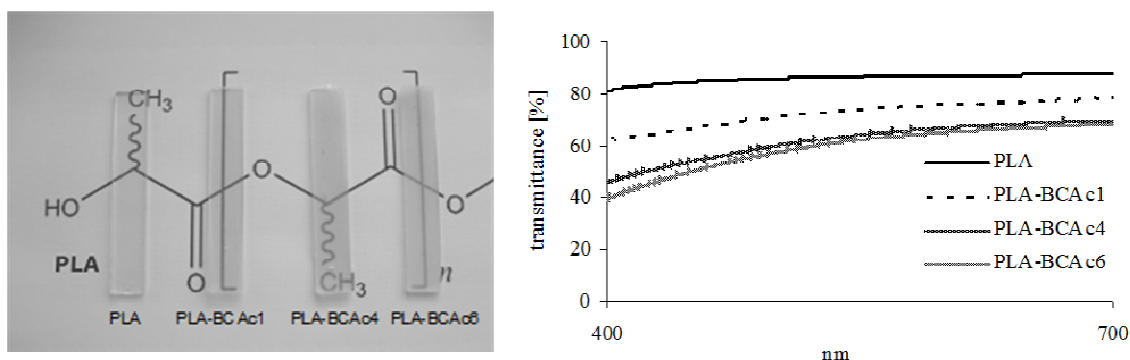


Figure 8. Images of PLA/BCAc nanocomposite films and their corresponding transmittances.

3. Conclusions

The studies revisited here clearly demonstrated the high potential of nanocellulose forms as reinforcing elements in nanocomposites. The possibility of developing such nanocomposites entirely based in natural or biobased polymers, and especially when due to their structural similarity no harsh chemical modifications are required to ensure compatibility and enhanced properties opens a wide area of future research for the development of fully renewable materials.

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