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NEW MATERIALS FROM CELLULOSE FIBERS. A CONTRIBUTION TO THE IMPLEMENTATION OF THE INTEGRATED BIOREFINERY CONCEPT

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ABSTRACT

In recent years we have been studying the preparation of new materials based on cellulose, using different strategies. One of the strategies involves the heterogeneous chemical modification of fibers, aiming at producing in the one hand new materials with surface hydrophobic properties by the modification with fatty acids that can be applied as reinforcing agents in composites with polyolefin matrices and, on other hand, at producing derivatives with superhydrophobic/omniphobic properties by the surface modification with perfluorinated and/or silane reagents. A different strategy involves the combination of cellulose fibers with other polysaccharides possessing unique properties, like chitosan and other emerging natural materials such as bacterial cellulose and nanofibrillated cellulose, which also opened wide perspectives on the preparations of papers with original features, as well as a wide range of promising functional materials. A general overview of the preparation, characterization and properties of these novel materials will be presented in this communication.

INTRODUCTION

In recent years, with the predicted dwindling of fossil resources, there has been an increasing interest in the search for renewable and sustainable alternatives that might replace petroleum as a source of chemicals, materials and fuels. In this perspective well established industrial sectors, such as the pulp and paper industry, are seen nowadays as the basis for the refineries of the future, the so called biorefineries, where lignocellulosic materials will be processed to produce platform chemicals, materials fuels and energy to fulfil society needs in a sustainable way.

Among the lignocellulosic components, cellulose is considered as the most promising alternative to fossil resources, mostly because of its natural abundance, ubiquity and renewable nature, and also due to its unique properties. Therefore, although paper is still the main and most valuable final product of the pulp industry, it is essential to search for new and more valuable applications of cellulose fibers, which could be an important contribution to the valorisation of this raw material.

In addition to "conventional" vegetal cellulose fibers, other forms of cellulose have attracted the attention of the scientific community in the last few years, namely, nanofibrillated cellulose (NFC) and bacterial cellulose (BC) (**Figure 1**).

Nanofibrillated cellulose can be obtained from cellulose fibers by different methods in the form of aqueous suspensions of nanoscale fibers with high aspect ratio (10-20 nm diameter and lengths in the micrometer range), and specific surface areas combined with remarkable strength and flexibility (Dufresne, 2008; Nakagaito and Yano, 2004). Bacterial cellulose is an extracellular polysaccharide produced by several bacteria (e.g. of the *Gluconacetobacter* genus). BC is generated as a three-dimensional network of nano- and microfibrils of cellulose with 10–100 nm diameter, which possesses unique physical and mechanical properties. In comparison with cellulose from plants, BC has a higher water holding capacity, crystallinity, tensile strength and Young modulus (Pecoraro *et al.*, 2008).

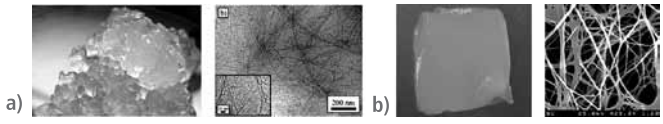

Figure 1. Visual and SEM micrographs of a) nanofibrillated cellulose (Innventia, 2011; Pääkko *et al.*, 2007) and b) bacterial cellulose

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The use of cellulose fibers as reinforcing agents in composite materials is one of the domains which have attracted more attention of researchers in the last few years. This application 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, however, to well known products such as carboxymethylcellulose or cellulose acetates (Hienze and Petzold, 2008, Klemm *et al.*, 2005) - is not suitable, and the more recent approach of controlled heterogeneous modification of cellulose fibers has to be considered (Belgacem and Gandini, 2008). 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 these 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.

A different approach involves the use of cellulose as reinforcing agent for matrices of other polysaccharides that bear promising functional properties, but poor mechanical performance. In this case, due to the structural similarity of both cellulose fibers and polysaccharide matrices, the former can be used as reinforcing elements without any chemical modification.

One of the most interesting examples of polysaccharides matrices in which various cellulose forms can play an interesting role as reinforcing agent is chitosan (**Figure 2**). Chitosan ((poli-[β-(1-4)–*N*-*D*-glucosamine])) can be obtained by deacetylation of chitin, the main component of the exoskeleton of crustaceans and considered as the second most abundant natural polymer on earth (Peniche *et al.*, 2008).

Chitosan 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, pharmaceutics, biomedicine, packaging, wastewater treatment, cosmetics, and food science, among others (Peniche *et al.*, 2008). However, despite the numerous advantages and unique properties, its films displayed poor mechanical performance, which limits their applications. One way to improve the mechanical properties (and other functionalities) of chitosan films, is to prepare blends with other polymers. In this perspective, chitosan–cellulose blends are of particular interest due to the mentioned structural similarity of the two biopolymers, resulting in materials that combine the physicochemical properties of chitosan with the excellent mechanical properties of natural fibers. Of particular interest is also the use of bacterial and nanofibrilated cellulose, as, in these cases, their nanofibrilar structure allow the preparation of materials with superior mechanical properties and transparency.

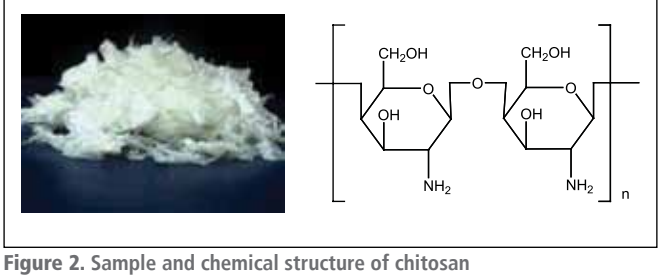

Figure 2. Sample and chemical structure of chitosan

In the last years we have been studying the development of new materials from cellulose fibers, together with other polysaccharides and synthetic polymers following some of the approaches mentioned above. This communication is intended to give a general overview of our most interesting achievements in this field.

RESULTS AND DISCUSSION

Controlled heterogeneous modification of cellulose fibers

As mentioned above, the controlled heterogeneous modification of cellulose fibers is gaining growing attention. Within this topic we have been studying the controlled heterogeneous modification of cellulose fibers with several precursors, such as fatty (Freire *et al.*, 2005, 2006a, 2006b) and perfluorinated acids (Cunha *et al.*, 2006, 2007a, 2007b, 2007c). Those studies were carried out using mainly *E. globulus* ECF bleached kraft pulp. As a general procedure for fibers modification, the appropriate acyl chloride was added to the fibers suspended in a solvent (toluene, to limit the reaction to the fiber surface, and *N,N*-dimethylformamide (DMF) to promote fibers swelling and allow the reaction to go deeper into the structure), in the presence of pyridine, keeping the [acyl chloride]/ [total cellulose OH] ratio constant, but varying reaction time and temperature.

The modified fibers were characterized by several techniques (FTIR, ^{13}C NMR, XRD, XPS, ToF-SIMS and SEM), allowing to get information about the extent of reaction, the preservation of fibers bulk structure, and their surface properties.

Controlled heterogeneous modification of cellulose fibers with fatty acids

The modification of fibers with fatty acids of various chain lengths (C6, C12, C18 and C22) in toluene and in DMF allowed to obtain esterified cellulose fibers with DS values ranging from 0.008 to 1.28, depending on the reaction time, fatty acid chain length and on the solvent used (Freire *et al.*, 2006a). As the percentage of OH groups at fibers surface is of around 4% (DS 0.12), when higher DS values were obtained the reaction must have involved hydroxyl groups of the inner layers of the fibers.

In general, the extent of esterification in toluene increased appreciably with reaction time and, for the same reaction time, decreased considerably with the fatty acid chain length, particularly for the C18 and C22 derivatives. For short reaction times, the DS values

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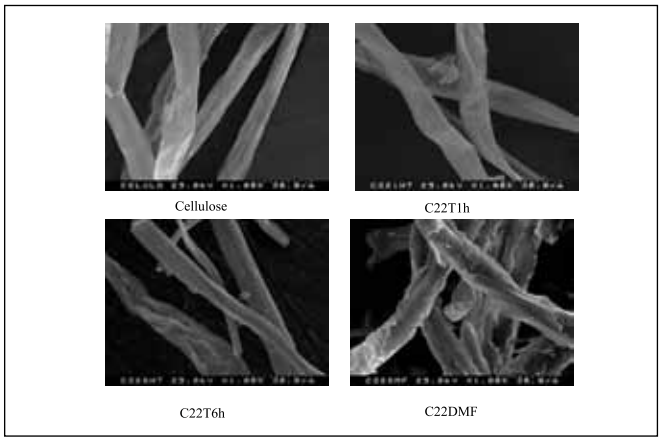

Figure 3. SEM micrograph of cellulose fibers before and after esterification with C22 acid chloride for 1 and 6 h in toluene and 6 h in DMF (reprinted from Freire *et al.*, 2006a)

were in general lower than 0.5, suggesting that the modification was limited to the surface or to the outmost layers of the fiber cell wall, as discussed later. As expected, the DS values of the fibers esterified in DMF were considerably higher than those obtained in toluene under similar conditions, particularly for the C18 and C22 derivatives, due to the fibers swelling.

The X-ray diffraction analysis of the esterified cellulose fibers shows that for reactions carried out in toluene the modification was limited to the outmost or amorphous regions of the cell walls, without substantially affecting the ultrastructure of the fiber, whereas for reactions carried out in DMF an extensive decline in the crystalline order of the fibers was observed, confirming that the reaction went deeper into the structure of the fiber. This effect on fibers ultrastructure can be easily observed in the SEM analysis of cellulose fibers after esterification with C22 acid chloride in toluene and in DMF (**Figure 3**).

The surface energy of the esterified cellulose fibers decreased substantially after esterification (**Figure 4**) essentially due to the reduction in its polar component, because of the replacement of the surface hydroxyl groups by the non-polar aliphatic chains. Furthermore, increasing DS values only slightly affect the surface

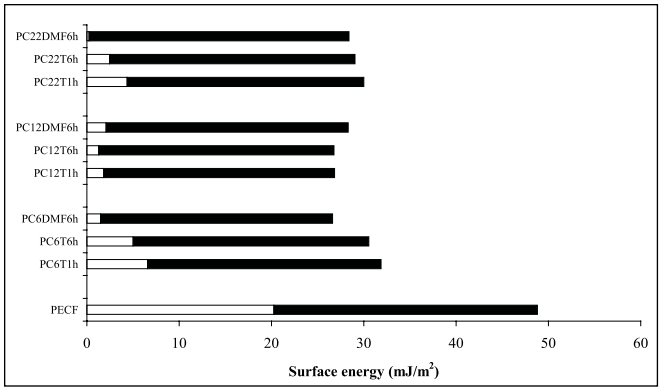

Figure 4. Polar □ and dispersive ■ components of the surface energy of pristine and esterified fibers

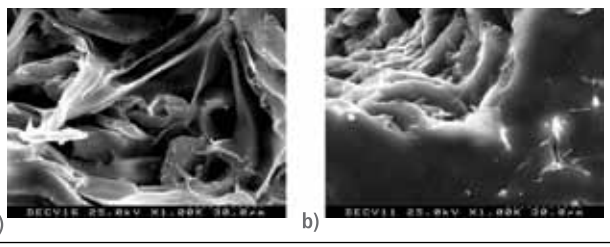

Figure 5. SEM micrographs of (a) the fracture zone of a polyethylene/modified cellulose fibers (with low DS) composite and of (b) a film formed by hot-pressing of modified fibers with high DS

energy values, which is in agreement with the coverage results as determined by XPS.

The results obtained show that these esterified fibers might have two distinct applications: i) the fibers modified in toluene with short reaction times and modification limited to the outmost layers surface, while preserving the fiber ultrastructure, will be appropriated for reinforcing composite materials with non polar polymeric matrices (**Figure 5a**); ii) the fibers with higher DS obtained in DMF, where the modification occurs also in the inner parts of the cell wall, are not suitable for reinforcing materials, but may present thermoplastic properties and could be used in the preparation of co-continuous composites, yielding transparent films by hot-pressing, (**Figure 5b**).

In this context, these modified fibers were then used to prepare composites with low density polyethylene, LDPE (Freire *et al.*, 2006.a). In all cases, the modification with fatty acids promoted a strong interfacial adhesion between fibers and PE and a good dispersion of the fiber in the matrix, as opposed to the poor adhesion observed with the pristine fibers, leading to composites with improved mechanical properties as shown for Young modulus (**Figure 6a**). The water uptake of the composites was also substantially reduced with fibers modification (**Figure 6b**).

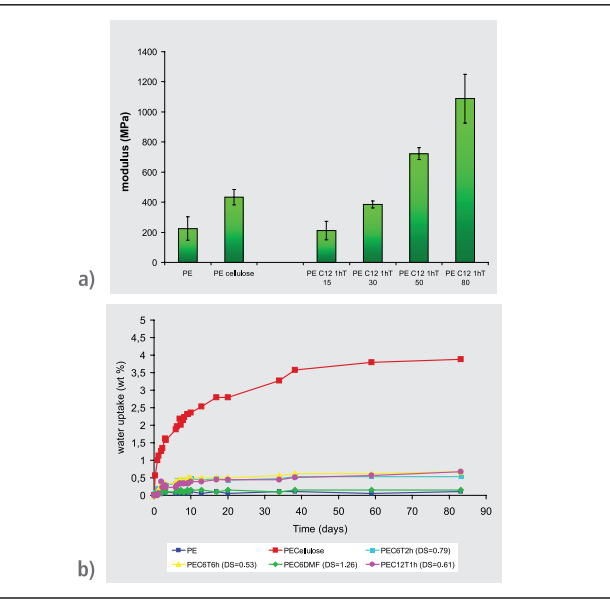

Figure 6. Variation of Young modulus a) and water uptake b) of PE composites reinforced with modified cellulose fibers

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Table 1. DS contact angles ranges (with water and diiodomethane) and surface energy values for the perfluoroacetylated fibers studied

Sample	DS	Contact angle		γ
		Water	CH_2I_2	(mJ/m²)
Pristine Fiber	-	56	37	~50
TFA-Fiber	0.04 - 0.3	119 - 126	94 - 104	6.7 - 11.7
PFB-Fiber	0.0014 - 0.39	120 - 128	71 - 82	~20
TFP-Fiber	<0.006 - 0.30	113 - 122	84 - 91	~15

Controlled heterogeneous modification of cellulose fibers with fluorinated reagents

The functionalization of organic molecules with fluorine atoms or fluorinated moieties leads to remarkable changes in their chemical and physical properties, namely enhanced hydrophobicity/lipophobicity, low surface energy, high thermal and oxidative stability among others (Pagliaro and Ciriminna, 2005). Furthermore, when this project was started only a few publications dealing with cellulose modification with fluorine-containing compounds were found, e.g. (Fabbri *et al.*, 2004; Glasser *et al.*, 2000, Navarro *et al.*, 2003), most of them dealing with modification under homogeneous conditions. In this perspective, the study of controlled heterogeneous modification of cellulose with fluorine containing compounds seemed to have an important potential for the development of innovative functional biopolymeric materials.

The modification studies started with trifluoroacetic anhydride, followed by pentafluorobenzoyl chloride and 3,3,3-trifluoropropanoyl chloride. Modified fibers with DS values in the range of 0.0014 to 0.39 (**Table 1**) were obtained and fully characterized (Cunha *et al.*, 2006, 2007a, 2007b, 2007c). The contact angles measurements for the perfluoroacylated samples have shown remarkably high θ values with water and diiodomethane (Table 1), evidencing simultaneously high hydrophobic and lipophobic character.

The high θ values and the phobic nature of the perfluoroacylated fibers are related with their very low surface energies (Table 1), in deep contrast with the corresponding typical values for cellulose.

A relevant feature of the studied materials is the fact that this bi-phobic behaviour (expressed by the high θ values and low surface energies) is observed even at very low DS values and (particularly for PFB and TFP fibers) is not significantly affected by increasing DS values (Cunha *et al.*, 2007a, 2007c).

The ester moieties of perfluoroacylated fibers have shown quite different hydrolytic stabilities, with TFA fibers showing a high lability (Cunha *et al.*, 2006, 2007b), whereas PFB (Cunha *et al.*, 2007a) and TFP fibers (Cunha *et al.*, 2007c) where shown to be considerably stable towards hydrolysis. The different hydrolytic stability of the perfluoroacyl groups could be exploited for the preparation of bi-phobic materials that require different hydrolytic stability profiles. TFA fibers might be useful for applications where the hydrophobic character is required for a short period of time. However, when long term stability of the modified fibers in contact with moisture is required, PFB and TFP fibers could be used. Nevertheless, in every case, at the end of their useful life, these perfluoroacylated materials will always be readily recycled/degraded by restoring the characteristic hydrophilic behaviour of pristine cellulose fibers through alkaline hydrolysis.

Controlled heterogeneous modification of cellulose fibers with siloxanes

The preparation of organic-inorganic hybrid materials by the heterogeneous chemical modification of cellulose fibers with (3-isocyanatopropyl)triethoxysilane (ICPTEOS), followed by the acid hydrolysis (and condensation) of the appended siloxane moieties as such, and in the presence of either tetraethoxysilane or 1H,1H,2H,2H-perfluorodecyltriethoxysilane (**Figure 7**) was also studied (Cunha *et al.*, 2010).

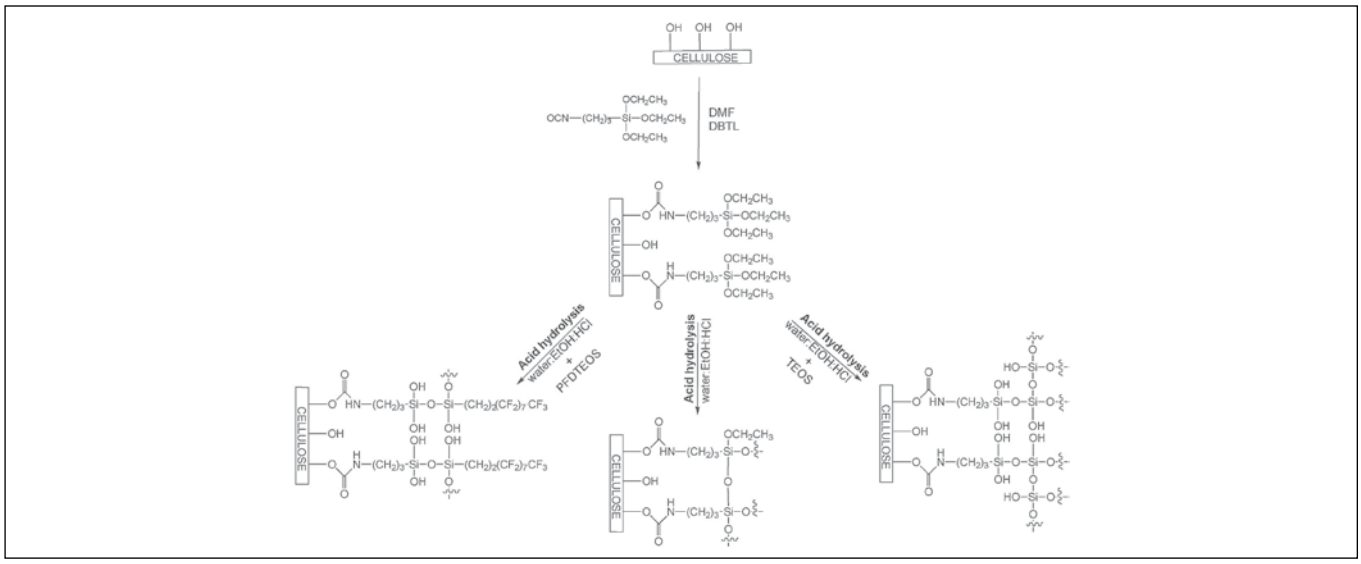

Figure 7. Scheme of the chemical modification of the cellulose fibers with ICPTEOS and of the acid hydrolysis treatments of the modified cellulose fibers (reprinted from Cunha *et al.*, 2010)

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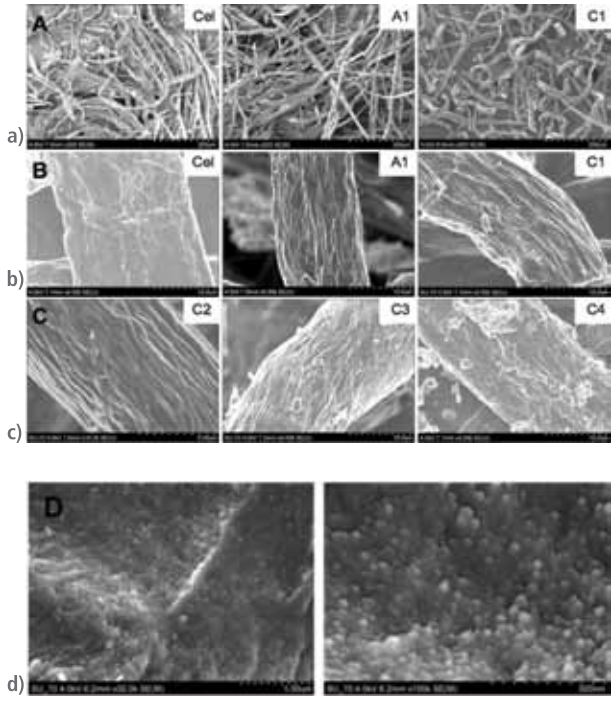

Figure 8. SEM micrographs of unmodified fibers and of fibers modified with ICPTEOS at x 200 (A) and x 4 000 (B) magnifications and for some hydrolyzed samples (C), (adapted from *Cunha et al.*, 2010)

These modifications produced an inorganic "coating" around the fibers, while preserving their ultrastructure (**Figures 8A-C**); additionally, these surface coatings also showed a quite interesting nanometric spherical rugosity (**Figure 8D**).

The hybrids obtained by hydrolysis in the presence of 1H,1H,2H,2H-perfluorodecyltriethoxysilane displayed a very pronounced hydrophobic and lipophobic character (reaching contact angles with water and diiodomethane as high as 140º and 134º, respectively) due to the presence of the perfluorinated moieties and most certainly to the nanometric rugosity referred to above. This omniphobic character opens perspectives for the application of these modified fibers in applications such as self-cleaning materials.

Chitosan nanocomposites with nanofibrillated cellulose and bacterial cellulose

The preparation and characterization of nanocomposite films based on different chitosan matrices and bacterial cellulose (Fernandes *et al.*, 2009) or nanofibrillated cellulose (Fernandes *et al.*, 2010) aimed at preparing chitosan films with improved mechanical properties, while keeping their transparency properties and thermal stability, was also investigated.

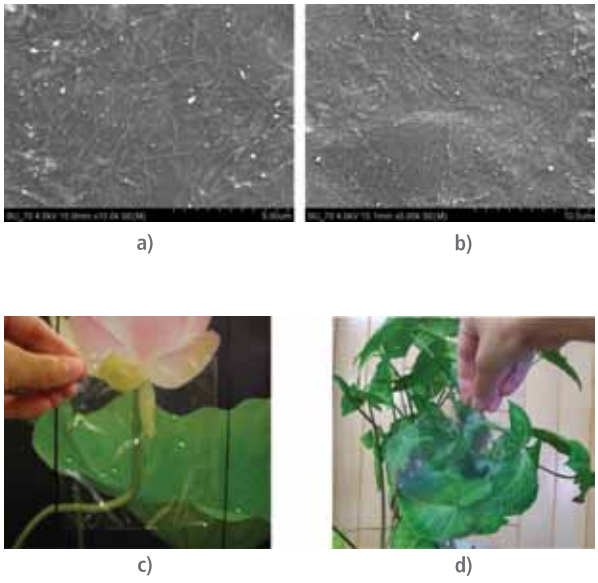

Figure 9. SEM micrographs of chitosan nanocomposites with bacterial (a) and nanofibrillated (b) cellulose and images of the corresponding (c and d) transparent films (adapted from Fernandes *et al.*, 2009, 2010)

The nanocomposite films were prepared by a simple and green procedure of casting a water-based suspension 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 9**).

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

CONCLUSIONS

The development of new polymeric materials based on cellulose and other polysaccharides is one of most interesting and promising strategies within the context of new sustainable and environmental friendly materials. As exemplified in this brief communication, the chemical modification and the intelligent combination of different natural polymers could be exploited for the development of new functional materials with improved and tailored properties, and therefore with applications in several fields. In this context, the exploitation of this renewable resource is certainly an important contribution to the implementation of the biorefinery concept in the pulp industry. ■

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