Carbohydrate Polymers 80 (2010) 1048–1056

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Preparation and characterization of novel highly omniphobic cellulose fibers organic–inorganic hybrid materials

Ana G. Cunha, Carmen S.R. Freire, Armando J.D. Silvestre *, Carlos Pascoal Neto, Alessandro Gandini

CICECO and Department of Chemistry, University of Aveiro, Aveiro, Portugal

ARTICLE INFO

Article history:
Received 11 September 2009
Received in revised form 8 January 2010
Accepted 11 January 2010
Available online 15 January 2010

Keywords:
Heterogeneous cellulose fiber modification
(3-Isocyanatopropyl)triethoxysilane
Siloxanes
Tetraethoxysilane
1*H*,1*H*,2*H*,2*H*-Perfluorodecyltriethoxysilane
Organic–inorganic hybrids
Hydrophobicity
Lipophobicity
Omniphobicity

ABSTRACT

This paper reports the preparation of class-II organic–inorganic hybrid materials by the heterogeneous chemical modification of cellulose fibers with (3-isocyanatopropyl)triethoxysilane, followed by the acid hydrolysis (and condensation) of the appended siloxane moieties as such, and in the presence of either tetraethoxysilane or 1*H*,1*H*,2*H*,2*H*-perfluorodecyltriethoxysilane. These modifications produced an inorganic "coating" around the fibers, while preserving their ultrastructure, as confirmed by XRD and SEM. The detailed characterization of these new hybrid materials by FTIR and ^{29}Si NMR showed that, upon hydrolysis of the ethoxy groups, condensation reactions took place leading mainly to Si–O–Si linear sequences, followed by a smaller contribution of more branched moieties, and that a significant amount of OH groups were also formed, which gave rise to hydrophilic surfaces. The hybrids obtained by hydrolysis in the presence of 1*H*,1*H*,2*H*,2*H*-perfluorodecyltriethoxysilane displayed a very pronounced hydrophobic and lipophobic character (reaching contact angles with water and diiodomethane as high as 140° and 134°, respectively), due to the presence of the perfluorinated moieties.

1. Introduction

The possibility of combining the properties of organic and inorganic substances for materials design and processing, is a very old challenge that started in prehistoric times, e.g. with the well-known cave frescos (Sanchez, Julián, Belleville, & Popall, 2005). Nowadays, functional hybrids have become a razor-edge realm because of the possibility to develop innovative advanced materials from the combination of organic macromolecules and inorganic compounds (Gómez-Romero & Sanchez, 2003, chap. 1).

These organic–inorganic hybrids do not merely consist of physical mixtures, but are instead well-designed composites, including nanocomposites, in which the organic and inorganic components share an intimate interface in terms of its low energy. The nature of the interface is indeed a crucial factor, which divides these materials into two distinct classes (Gómez-Romero & Sanchez, 2003). If the organic and inorganic components are linked only by physicochemical interactions, namely dispersive van der Waals contributions, polar attractions and/or hydrogen or ionic bonds, the materials are said to belong to class-I. In contrast, if the two phases are linked through covalent bonds, they pertain to class-II (Gómez-Romero & Sanchez, 2003, chap. 1).

It should be emphasized that the relevant hybrid materials do not simply reflect the mere sum of the features of their precursors, but rather display broad synergy effects resulting from specific morphological interactions between the two phases at the micro- or nano-scale. In general, however, the most important features of each phase are preserved, or even improved, in the ensuing hybrid materials, while new properties are generated by the synergy effects (Sanchez et al., 2005).

Organic–inorganic hybrid materials are not only academic alternatives to more traditional counterparts, since, instead, their original properties lead frequently to the development of innovative industrial applications. Such fields as electronics, optics, medicine, sensors, smart coatings and polymer composites are some examples of promising application areas where these types of materials have been successfully applied (Sanchez et al., 2005).

In this study, we used cellulose fibers as the organic component. Cellulose is an extraordinary renewable polysaccharide with unique properties (Klemm, Heublein, Fink, & Bohn, 2005). Because of its abundance, biodegradability, and remarkable properties, it has been widely exploited as a source of materials, either close to its native form (e.g. cotton and paper) or after appropriate chemical modifications (e.g. cellulose acetate and carboxymethyl cellulose). The recent surge of activities related to the chemical modification of cellulose, stems from the growing interest in the development of a variety of value-added, environment friendly, biocompatible functional materials (Edgar et al., 2001; Gandini &

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* Corresponding author. Tel.: +351 234 370 711; fax: +351 234 370 084.
E-mail address: armsil@ua.pt (A.J.D. Silvestre).

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doi:10.1016/j.carbpol.2010.01.023

Belgacem, 2008, chap. 1; Klemm et al., 2005; Nishio, 2006; Teeri, Brumer, Daniel, & Gatenholm, 2007; Yu & Chen, 2009, chap. 1) based on this ubiquitous renewable resource.

The preparation of organic–inorganic hybrid materials combining polysaccharides such as chitosan and cellulose with silicon compounds, has only been reported within the last decade (Barud et al., 2008; Fuentes, Retuert, Ubilla, Fernandez, & Gonzalez, 2000; Maeda, Nakajima, Hagiwara, Sawaguchi, & Yano, 2006; O'Kelly et al., 1997; Retuert, Quijada, Arias, & Pedram, 2003; Sequeira, Evtuguin, Portugal, & Esculcas, 2007; Silva et al., 2005; Tanaka & Kozuka, 2004; Yano, Iwata, & Kurita, 1998), and mostly concentrating on class-I combinations. To the best of our knowledge, only one study related to class-II organic–inorganic hybrid materials incorporating cellulose fibers and silicon compounds has been published before the present investigation (Hou, Shi, & Yu, 2009). That study called upon a third element, *viz.* a crosslinking agent, which served as a bridge between the cellulose fibers and the silicon compound.

Pursuing our interest in the chemical modification of cellulose fibers (Cunha, Freire, Silvestre, Neto, & Gandini, 2006; Cunha et al., 2007a, 2007b, 2007c; Freire, Silvestre, Neto, Belgacem, & Gandini, 2006; Freire, Silvestre, Neto, Gandini, et al., 2006; Freire et al., 2008; Freire, Silvestre, Neto, & Rocha, 2005; Gonçalves, Marques, Pinto, Trindade, & Neto, 2009; Gonçalves, Marques, Trindade, Neto, & Gandini, 2008; Marques, Trindade, & Neto, 2006; Pinto, Marques, Barros-Timmons, Trindade, & Neto, 2008; Pinto, Marques, Martins, Neto, & Trindade, 2007; Sequeira et al., 2007) aimed at producing materials with new functional properties, particularly those showing an omniphobic character (*i.e.* simultaneous lipophobicity and hydrophobicity) (Cunha et al., 2006, 2007a, 2007b, 2007c), as well as on the preparation of cellulose-derived hybrid materials, which so far has been focused on class-I hybrids (Gonçalves et al., 2008, 2009; Marques et al., 2006; Pinto et al., 2007, 2008), we now report the preparation of new cellulose fibers class-II organic–inorganic hybrid materials. The system investigated called upon the modification of cellulose fibers with a silane coupling agent, *viz.* (3-isocyanatopropyl)triethoxysilane (ICPTEOS) (Fig. 1) followed by an acid hydrolysis of the ethoxy groups of the siloxane moieties, in some cases in the presence of other siloxanes bearing specific side chains (Fig. 1). This last step was intended, on the one hand, to generate the adequate surface morphology of the siloxanes, and, on the other, to promote the insertion of specific side chains, allowing to tailor the final properties of the hybrid materials in terms of the desired applications. Thus, the hydrolysis in the presence of tetraethoxysilane (TEOS) was aimed at building a three-dimensional inorganic coating onto the fibers, based on the formation of additional multiple Si–O–Si bonds. Alternatively, the hydrolysis in the presence of 1*H*,1*H*,2*H*,2*H*-perfluorodecyltriethoxysilane (PFDTEOS) was intended to induce an omniphobic character at the surface of the ensuing materials, based on the well-known features associated with perfluorinated moieties (Pagliaro & Ciriminna, 2005).

2. Experimental

2.1. Materials

ECF (Elemental Chlorine Free) *Eucalyptus globulus* industrial bleached kraft pulp fibers, composed essentially of cellulose (~85%) and glucuronoxylan (~15%) and minor amounts of lipophilic extractives (~0.4%) (Gonçalves et al., 2008, 2009; Neto et al., 2004), were kindly provided by a Portuguese pulp mill and used as the cellulose fiber source. They were vacuum-dried at 60 °C in the presence of phosphorous pentoxide prior to their use. (3-Isocyanatopropyl)triethoxysilane (ICPTEOS), tetraethoxysilane (TEOS), anhydrous *N*,*N*-dimethylformamide (DMF) and dibutyltin dilaurate (DBTL) were supplied by Sigma–Aldrich and 1*H*,1*H*,2*H*,2*H*-perfluorodecyltriethoxysilane (PFDTEOS) was purchased from Fluorochem. Ethanol (EtOH) and hydrochloric acid were p.a. grade products, supplied by Riedel-de Haën. All the reagents and solvents were used as received.

2.2. Cellulose fiber modification

0.4, 0.6 or 1 equiv. (relative to the total cellulose + glucuronoxylan OH functions) of ICPTEOS were placed in a 100 mL round-bot-

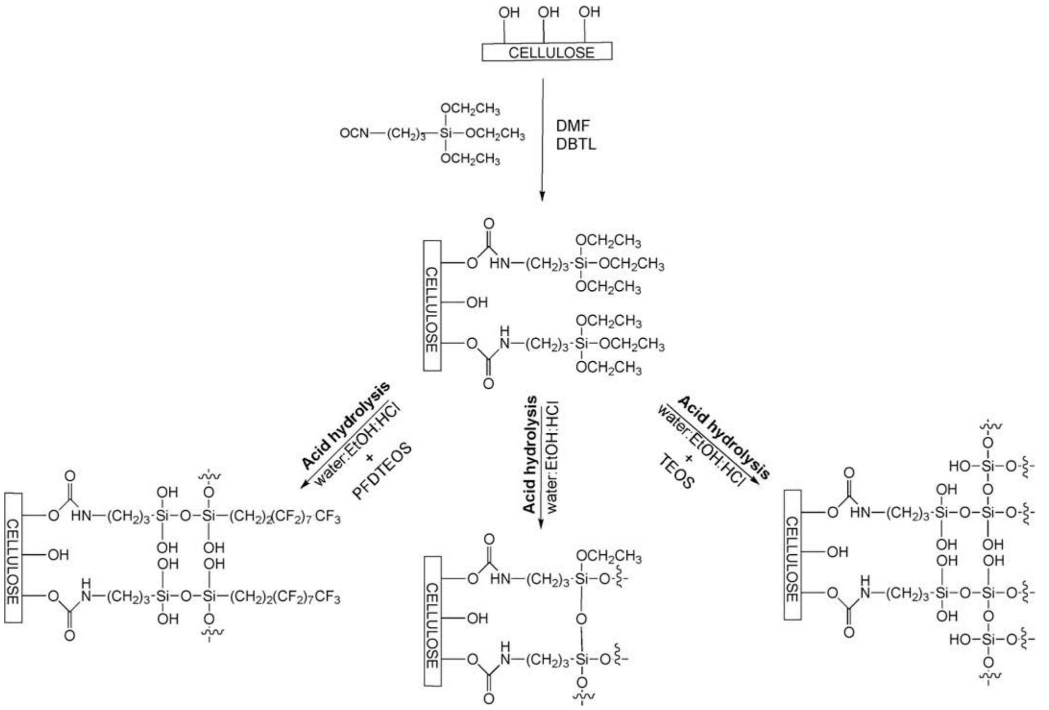

Fig. 1. Scheme of the chemical modification of the cellulose fibers with ICPTEOS and of the acid hydrolysis treatments of the modified cellulose fibers.

Table 1
Identification of the samples obtained in this study.

Sample name	[OH]:[ICPTEOS] ratio (reaction time)	Subsequent treatment
Cel	–	–
A1	1:0.4 (5 h)	–
A2		Acid hydrolysis
A3		Acid hydrolysis in the presence of TEOS
A4		Acid hydrolysis in the presence of PFDTEOS
B1	1:0.6 (5 h)	–
B2		Acid hydrolysis
B3		Acid hydrolysis in the presence of TEOS
B4		Acid hydrolysis in the presence of PFDTEOS
C1	1:1 (24 h)	–
C2		Acid hydrolysis
C3		Acid hydrolysis in the presence of TEOS
C4		Acid hydrolysis in the presence of PFDTEOS

tom flask, to which anhydrous DMF (70 mL), DBTL (0.05 equiv.) and the dried cellulose fibers (~3 g) were added while the system was kept under a nitrogen atmosphere. Reactions were conducted under magnetic stirring at 60 °C, for 5 h, when 0.4 or 0.6 equiv. of ICPTEOS were used, or for 24 h, with 1 equiv. of ICPTEOS. The latter reaction gave rise to a gel, which was dispersed in 1.5 L of acetone with continuous stirring for 30 min, before leaving the ensuing suspension to rest overnight in order to enable the modified fibers to sediment. After the subsequent filtration, the fibers were sequentially washed with acetone and ethanol, and then dried at 40 °C for 24 h.

2.3. Acid hydrolysis

The modified cellulose fibers (~0.5 g) were suspended in 35 mL of a 1/3.2/0.13 (v/v) water/EtOH/HCl mixture, in a 50 mL round-bottom flask and stirred for 24 h at room temperature. Two other samples were submitted to a similar treatment, but in the presence of TEOS (840 μL) or PFDTEOS (840 μL). The samples thus obtained are identified in Table 1.

2.4. Hybrid characterization

The FTIR-ATR spectra were recorded by placing a small amount of the powdered material above the detecting crystal of a Perkin Elmer FTIR BX spectrophotometer equipped with a single horizontal Golden Gate ATR cell.

For the X-ray diffraction (XRD) measurements, the hybrid samples (with the exception of those obtained with 1 equiv. of ICPTEOS, which were tested as obtained) were pressed into small pellets using a laboratory press and analyzed with a Philips X'pert MPD diffractometer using Cu Kα radiation.

The thermogravimetric assays (TGA) were carried out with a Shimadzu TGA 50 analyzer equipped with a platinum cell. Samples were heated in air at a constant rate of 10 °C/min from room temperature to ~900 °C.

Static contact angles with water and diiodomethane were measured 5 s after the deposition of the droplet (to ensure the attainment of equilibrium) using a "Surface Energy Evaluation System" commercialized by Brno University (Czech Republic). Each reported value (θ) was the average of five determinations. For this analysis, the pristine fibers and the hybrids were pressed (6 tons) into small pellets (10 mm diameter and 1 mm thick) using a laboratory press, in order to work on flat surfaces, which were insured by the polished steal surfaces of the press.

^{29}Si solid-state cross-polarized magic-angle spinning nuclear magnetic resonance (^{29}Si CP-MAS NMR) spectra were recorded on a Bruker Avance 400 spectrometer. The samples were packed into a zirconia rotor sealed with Kel-F caps and spun at 5 kHz. The acquisition parameters were: 4 μs 90° pulse width, 37 ms contact time, and 5 s dead-time delay.

Scanning electron microscopy (SEM) images were obtained with a Hitachi SU-70, operating at 4 kV. Air dried samples were deposited on an aluminium plate and coated with a carbon layer, approximately 15–50 nm thick, by evaporation of carbon rods (outgas time: 30 s, evaporating time: 1000 ms).

3. Results and discussion

3.1. FTIR-ATR spectroscopy

The progress of the reaction of the cellulose fibers with ICPTEOS, as well as the subsequent hydrolysis of the siloxane groups, were followed by FTIR-ATR spectroscopy. The success of the modification with ICPTEOS was clearly confirmed, mainly on the basis of the appearance of a new band at *ca.* 1700 cm^{-1} (Fig. 2A), attributed to the free C=O stretching mode of the urethane moieties. Moreover, in the case of the sample obtained after modification with a 1:1 ratio and 24 h reaction time (Table 1), another band appeared at 1650 cm^{-1}, which is typical of the hydrogen-bonded C=O stretching mode of urethanes (Bellamy, 1975) (Fig. 2A). The emergence of a new peak at ~1530 cm^{-1}, associated with the C–N vibrations, corroborated the success of these reactions.

Furthermore, the emergence of a new peak around 2960 cm^{-1}, typical of C–H bond stretching vibrations in CH_3 indicated the presence of methyl groups from the ethoxysilane moieties. Additionally, the occurrence of new absorptions at 1250 and 760 cm^{-1}, typical of methylene symmetric deformation and rocking vibrations from the Si–CH_2 groups, respectively, gave further confirmation of the presence of silane-containing moieties.

The results presented in Fig. 2A also showed that the extent of the modification increased with increasing amounts of ICPTEOS (from sample A1 to sample B1) as well as with the simultaneous increase in the amount of ICPTEOS and in the reaction time (from sample B1 to sample C1), as monitored by the peak at *ca.* 1700 cm^{-1}.

The reaction with ICPTEOS should obviously have involved cellulose and glucuronoxylan. However, even considering that glucuronoxylan is more abundant at the fibers surface (Lisboa, Evtuguin, & Neto, 2009) and predictably as reactive as the amorphous zones of cellulose, due to its equally amorphous character, the amount of reagent relative to the total number of OH was systematically high, and, in this perspective the reaction would always involve both polysaccharides. However, their individual contributions were not assessed in this work.

Finally, although ICPTEOS could also have reacted with pulp extractives, the overall impact of this fraction, both in the consumption of ICPTEOS and in the properties of the final materials, should be negligible: on the one hand because of their low abundance (Neto et al., 2004) and low concentration of reactive groups (this fraction is mainly composed by sterols and long chain fatty acids and alcohols); on the other hand, a considerable part of this fraction, or their ICPTEOS derivatives would be readily dissolved in the reaction media.

After the acid hydrolysis, it was observed that, for the samples prepared by the reaction with the 1:1 ratio and 24 h reaction time, the doublet of the urethane bands in the C1 FTIR-ATR spectrum had converged into a single peak at ~1700 cm^{-1}, revealing that

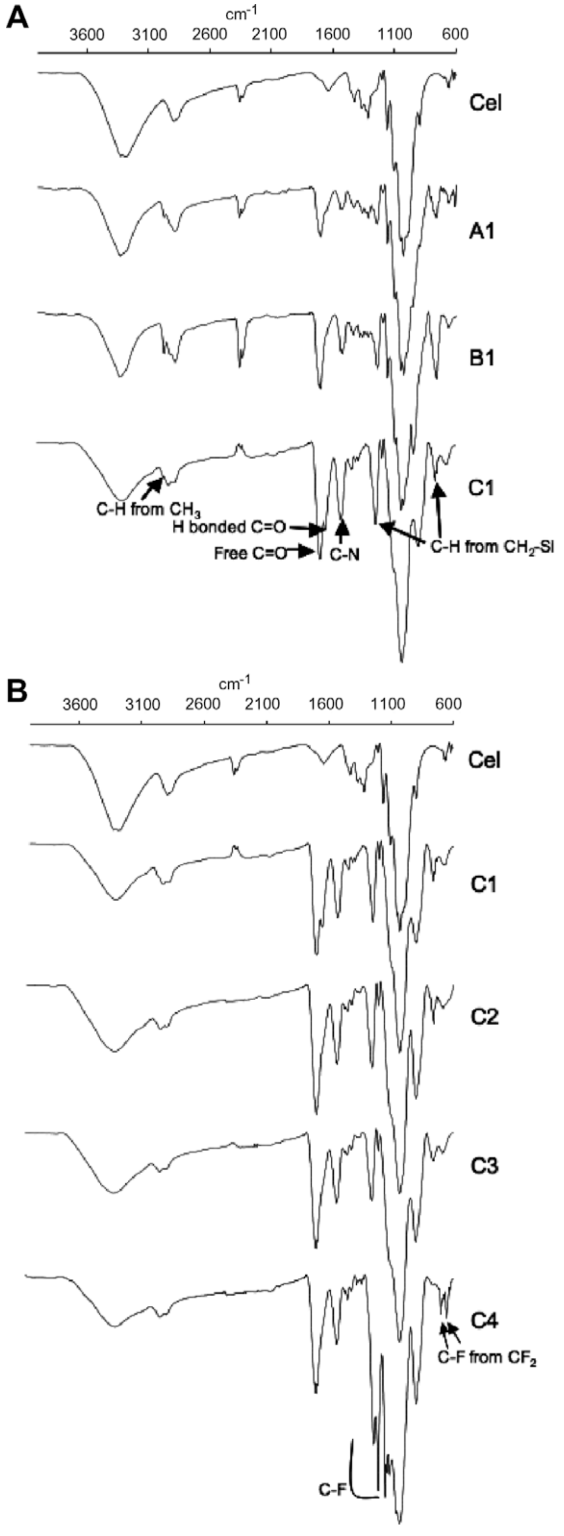

Fig. 2. FTIR-ATR spectra of cellulose fibers before and after modification with ICPTEOS at different ratios (A) and of cellulose fibers before and after modification with 1 equiv. of ICPTEOS and subsequent acid hydrolysis treatments (B).

this treatment had "broken" the hydrogen bonds established by the C=O of some urethane groups (Fig. 2B), possibly because of the formation of new Si–O–Si bridges. This treatment also induced the complete loss of the peak related to the CH_3 groups, which indicated its effectiveness, *i.e.* the near-complete hydrolysis of the ethoxysilane groups. These observations are in agreement with the evolution of the ^{29}Si NMR results discussed below, which clearly demonstrated the increase in the content of Si–O–Si bridges, with the corresponding decrease in Si–OEt linkages.

The presence of Si–OH or Si–O–Si bridges is not easily detected by FTIR, since the typical vibration frequencies of these groups around 950 and 1100 cm^{-1}, respectively, are masked by the large and intense cellulose C–O stretching band centered at 1026 cm^{-1} (Fig. 2B).

The FTIR-ATR spectra of the samples obtained after acid hydrolysis in the presence of TEOS (A3, B3 and C3) (Fig. 2B) were identical to those of the samples obtained by the simple acid hydrolysis, and thus no further information could be retrieved.

The spectra of the samples obtained after acid hydrolysis in the presence of PFDTEOS (A4, B4 and C4 samples) showed the presence of new intense absorptions at 1100–1235 cm^{-1} (Fig. 2B), characteristic of C–F stretching modes (Bellamy, 1975). Moreover, two new peaks at ~650 and ~705 cm^{-1} were also present in these spectra, which are attributed to the combination of CF_2 group rocking and wagging modes (Tingting, Hui, Shiyuan, & Pank, 2005). These observations clearly demonstrated the insertion of perfluorinated moieties into the inorganic network at the fiber surface.

3.2. Solid-state ^{29}Si NMR spectroscopy

This technique is particularly suitable for the inspection of the structure of silicon-type hybrid materials (Takayama, 1998, chap. 17). Fig. 3 illustrates the spectra of the cellulose fibers modified with 1 equiv. of ICPTEOS and subsequent acid hydrolysis treatments. The silicon sites were labeled according to the conventional T^n notation, corresponding to silicon moieties of the type $CH_2Si(OSi)_n(OEt)_{a-n'}(OH)_{b-n''}$ (where $n = 1–3$, $n' + n'' = n$ and $a + b = 3$). After modification of the cellulose fibers with different proportions of ICPTEOS, the spectra of the ensuing derivatives exhibited signals in four different regions, *viz. ca.* −45 (only for the B1 sample), −49, −57 to −58 and −67 ppm (only for the C1 sample), assigned to T^0, T^1, T^2 and T^3 environments, respectively

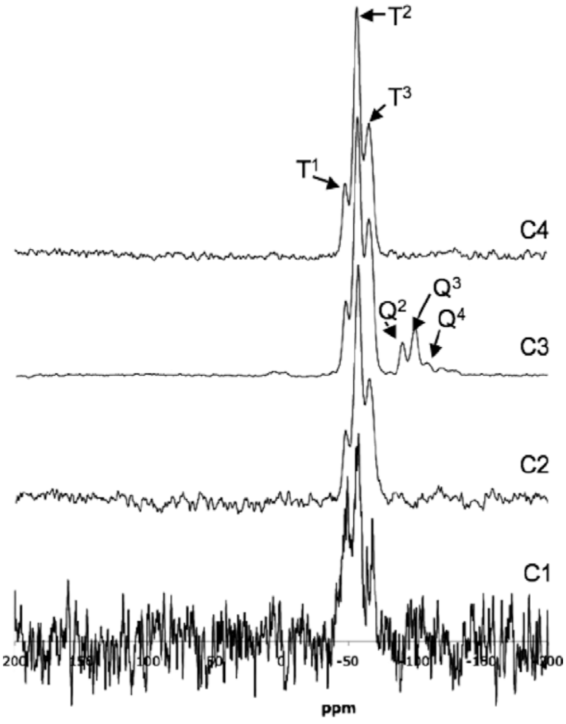

Fig. 3. ^{29}Si CP-MAS NMR spectra of cellulose fibers after modification with 1 equiv. of ICPTEOS and subsequent acid hydrolysis treatments.

(Silva et al., 2005). For the derivatives obtained with just 0.4 equiv. of ICPTEOS, it was difficult to detect any signal due to the background noise, which suggested that in these hybrids the amount of Si present was very small. The presence of T^1 and T^2 peaks in the B1 sample and of an additional T^3 signal in the C1 sample, indicated that the residual moisture present in the system had already started the hydrolysis of some ethoxysilane groups, leading to the formation of Si–O–Si or Si–OH moieties, a deduction that is in agreement with the previously discussed low intensity of the CH_3 peaks in the FTIR spectra of C1 samples. In these samples, T^2 peaks were predominant, followed by T^1 signals, suggesting that partial condensation favored the formation of linear segments and “dimeric” structures rather than more branched architectures associated with T^3 peaks.

The samples obtained after acid hydrolysis with or without PFDTEOS, exhibited the same T^1, T^2 and T^3 signals, but with an increase in the relative intensities of T^2 and particularly of T^3 signals when compared to T^1. This observation confirms a dominance of linear and branched silicon based structures.

After acid hydrolysis in the presence of TEOS, in addition to the three T^n environments, peaks at *ca.* −92, −101 and −112 ppm were also detected in the spectra of the cellulose fiber hybrids, namely in the B3 and C3 (Fig. 3) samples. These new signals were labeled according to the Q^n notation, corresponding to silicon moieties of the type $Si(OSi)_n(OEt)_{a-n'}(OH)_{b-n''}$ (where $n = 1–4$, $n' + n'' = n$ and $a + b = 4$), and assigned to Q^2, Q^3 and Q^4 structures, respectively. These new Si environments resulted from the hydrolysis of the TEOS ethoxy groups and the consequent formation of novel Si–O–Si or Si–OH moieties. As can be observed in Fig. 3, the Q^3 sites were predominant in the C3 sample, and the same was observed for B3, which indicates that the presence of TEOS favors the formation of three-dimensional silicon constructs, although, as can be seen in Fig. 3, these Q^n domains are still minoritary when compared to the T^n counterparts.

In the case of the hybrids obtained after hydrolysis with or without PFDTEOS, no Q^n moieties were observed, since in these cases all Si moieties bore a $Si–CH_2$ linkage.

It can be concluded that in all the hybrids studied in this investigation, the cellulose fibers were surrounded by an inorganic layer involving predominantly linear Si–O–Si networks together with smaller contributions from more branched networks as well as “dimeric” structures.

The predominantly linear structure of this layer, in conjunction with the absence of the characteristic CH_3 vibrations from the ethoxy groups, indicated that upon hydrolysis, in addition to the formation of Si–O–Si bridges, part of the Si–OEt groups were also converted into Si–OH groups, which will inevitably influence the surface properties of the corresponding hybrids. In the case of the hydrolysis in the presence of PFDTEOS, the perfluorinated moieties introduced additional peculiarities to the properties of the ensuing hybrids.

3.3. XRD analysis

The unmodified cellulose fiber diffractograms (Fig. 4A) exhibited the typical XRD pattern of cellulose I (Meshitsuka & Isogai, 1996, chap. 2), with the most important diffraction signals at 2θ values of 14.9°, 16.3°, 22.5° and 34.6°, assigned to the 1 0 1, 1 0 $\bar{1}$, 0 0 2 and 0 4 0 diffraction planes, respectively (Fengel & Wegener, 1989).

For the samples obtained after the reaction for 5 h with 1:0.4 and 1:0.6 ratios and further treatments, this pattern was maintained (Fig. 4), which indicated that the modification had not affected to a great extent the crystalline regions of the inner layers of the cellulose fibers. The samples obtained after acid hydrolysis in the presence of PFDTEOS exhibited three new diffraction signals at 2θ values of 6°, 9° and 18° (Fig. 4B), which were attributed to the self-assembly of the perfluorinated aliphatic chains grafted onto the fibers (Pagliaro & Ciriminna, 2005).

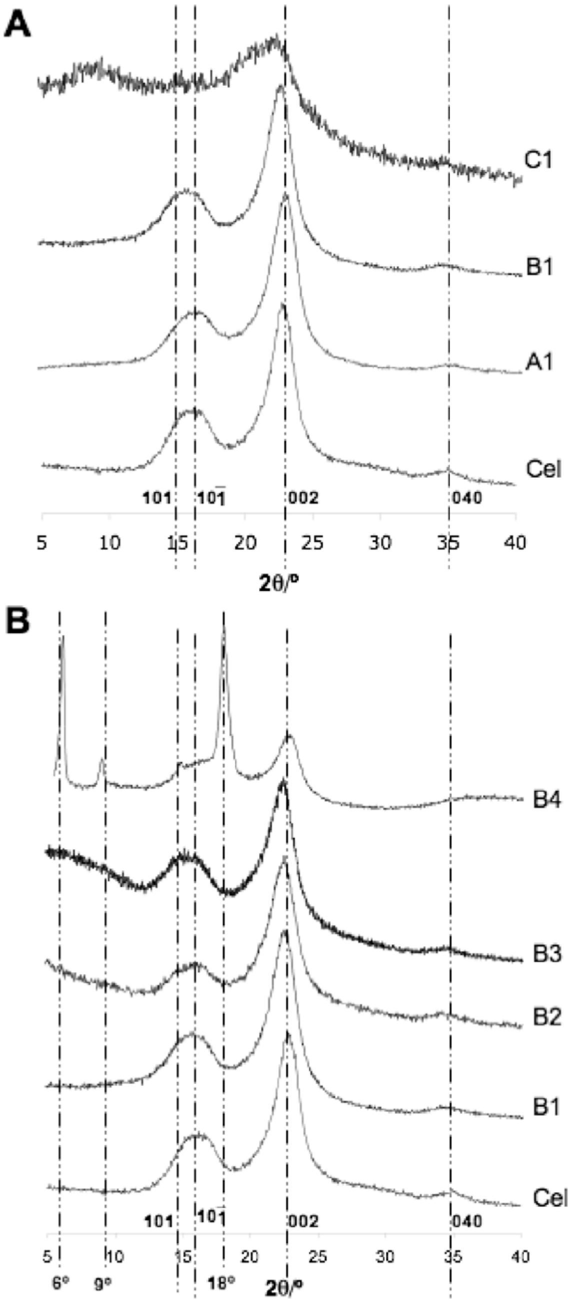

Fig. 4. XRD diffractograms of cellulose fibers before and after modification with ICPTEOS at different ratios (A) and of cellulose fibers before and after modification with 0.6 equiv. of ICPTEOS for 5 h and subsequent treatments (B).

Conversely, the cellulose pattern vanished in the XRD patterns of the samples obtained after a 1:1 ratio for 24 h modification (Fig. 4A) and subsequent treatments, suggesting that the crystalline structure of the fibers has been affected as a consequence of a deeper modification. This was probably due to the fact that the reaction was carried out in a cellulose fiber swelling solvent (DMF) which, associated to the severity of the treatment in terms of both the amount of reagent and the reaction time, facilitated the interaction between the ICPTEOS molecules and the hydroxyl groups from the inner crystalline layers of the fibers and leading also to some cellulose depolymerization. This feature could explain

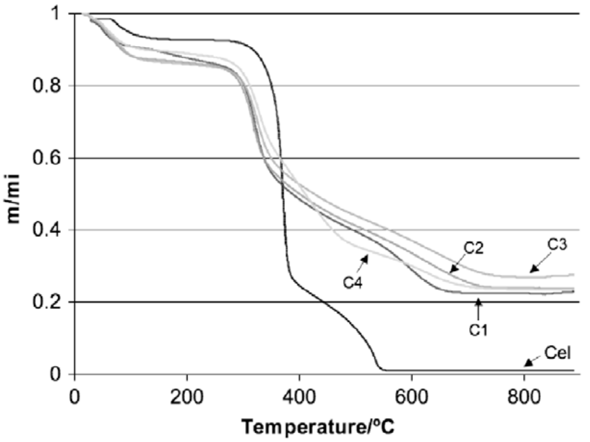

Fig. 5. TGA tracings of cellulose fibers before and after modification with ICPTEOS with a 1:1 ratio for 24 h and subsequent hydrolysis treatments.

the difference in morphology exhibited by the differently modified fibers, as discussed below, since the milder treatments left their appearance virtually unchanged, whereas with the 1:1 ratio, they acquired a powdery consistence.

3.4. TGA

Fig. 5 shows that the unmodified fibers exhibited the typical thermal degradation behaviour of native cellulose fibers, with the double weight loss and a maximum decomposition rate around 340 °C.

The hybrid cellulose fiber derivatives were shown to be slightly less stable, as they started degrading at lower temperatures, although with a less abrupt decay, certainly assigned to the lower heat transfer to cellulose due to the presence of the inorganic phase around the fiber, and with additional degradation steps than those shown by the pristine fibers, as illustrated for the samples prepared by the reaction with the 1:1 ratio and 24 h reaction time (Fig. 5). Finally, the absence of total weight loss at ~900 °C, corroborated the presence of an inorganic environment around the cellulose fibers. As expected, samples obtained after acid hydrolysis in the presence of TEOS, exhibited a higher final residue at 900 °C, indicating the presence of a correspondingly higher amount of inorganic components.

The derivatives obtained after acid hydrolysis in the presence of PFDTEOS showed a more pronounced degradation step with a maximum decomposition rate around 420 °C, which was tentatively attributed to the degradation of the perfluorinated aliphatic chains. The lower proportion of inorganic residue was here the consequence of the higher initial fraction organic structures associated with these long chains.

The thermal degradation behaviour of the samples prepared by reaction with 0.4 and 0.6 equiv. of ICPTEOS during 5 h showed quite similar profiles but with a much lower final residue, in agreement with the results discussed above.

3.5. SEM

All the materials were also analyzed by SEM in order to assess the effect of the modifications on their surface morphology.

The SEM micrographs of the cellulose fibers before and after modification with different amounts of ICPTEOS (Fig. 6A), indicated that for ratios [OH]:[ICPTEOS] of 0.4 and 0.6 and 5 h reaction time (illustrated only for fibers modified with a ratio of 0.4), the fiber structure was largely preserved, whereas with a ratio of 1 and 24 h of reaction time, the fibers were seriously fragmented. These observations are in agreement with the XRD results discussed

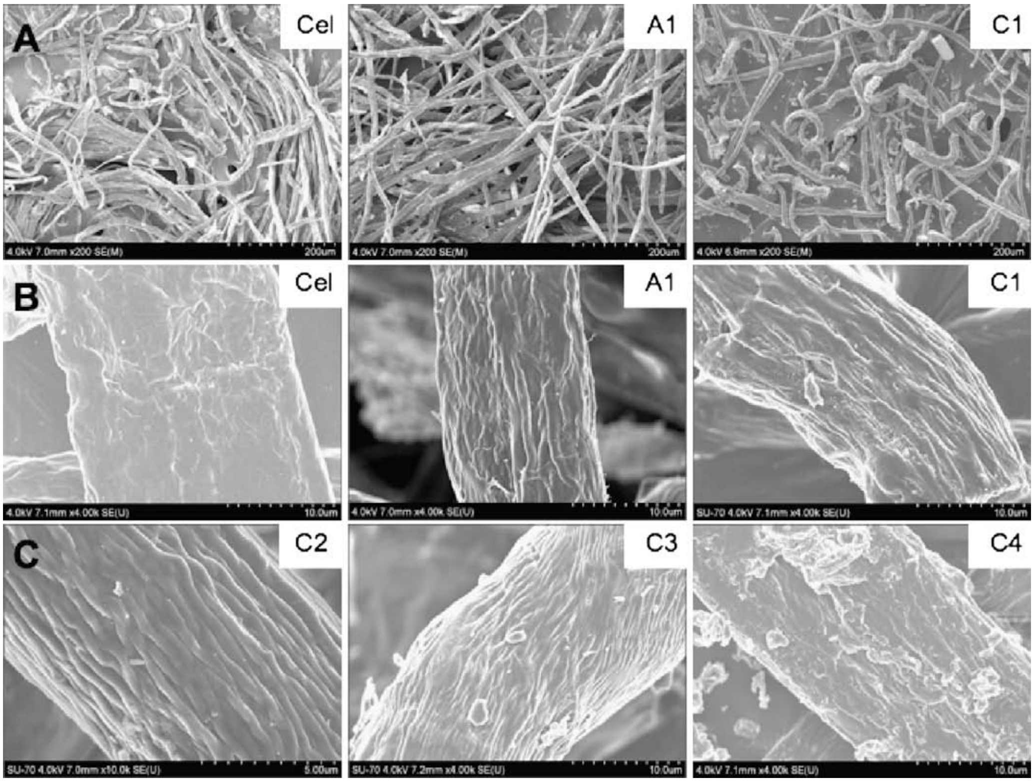

Fig. 6. Scanning electron micrographs of unmodified fibers and of fibers modified with 0.4 and 1 equiv. of ICPTEOS at 200× (A) and 4000× (B) magnifications and for some hydrolyzed samples (C).

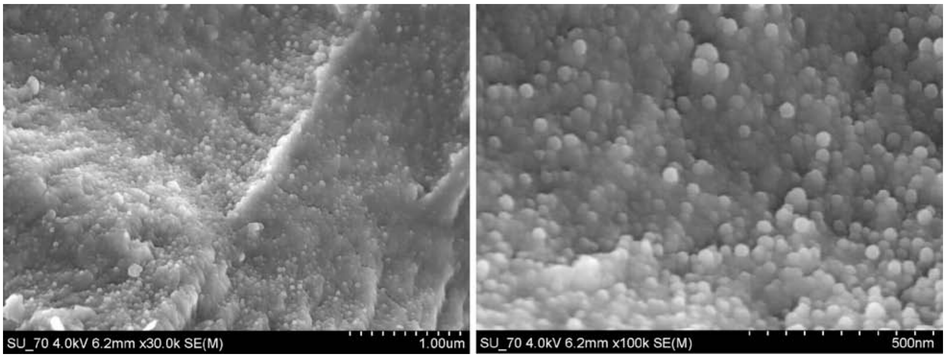

Fig. 7. Scanning electron micrographs of sample C4 at 30,000× and 100,000× of magnification.

above, and are related, not only to the decrease in crystallinity, but probably also to some depolymerization of cellulose.

With an increased magnification, a coating around the fibers became apparent, as shown in Fig. 6B, probably arising from the formation of the Si–O–Si bridges, as clearly indicated by the predominance of T^2 sites in the ^{29}Si NMR spectra discussed above.

This "sleeve" appeared to have arisen as a consequence of the increasing [OH]:[ICPTEOS] ratio, which can be associated to the formation of an increasing number of surface Si–O–Si bridges. Similar morphologies were observed in the SEM images of the hybrids obtained after simple acid hydrolysis (Fig. 6C). Furthermore, in the samples obtained after acid hydrolysis in the presence of PFDTEOS, a second coating seemed to have built up, which was much more heterogeneous and in the shape of irregular flakes (Fig. 6C). With an even higher magnification (Fig. 7), it was possible to observe that the inorganic surface was coated with nanospheres. Both the latter nano-morphologies are in principle conducive of the reduced wettability of the corresponding surfaces.

Globally, one can conclude that for samples treated with 0.4 or 0.6 equiv. of ICPTEOS for 5 h, the reaction should have been limited to the amorphous and outmost regions of the fibers since on the one hand ^{29}Si could hardly be detected by solid-state NMR and the final residue in the TGA was quite small, and on the other hand, XRD and SEM confirmed the preservation of the crystallinity and morphology of the fibers. On the contrary, in the case of the samples treated with 1 equiv. of ICPTEOS for 24 h, both solid-state NMR and the TGA confirmed that, in addition to the increasing "sleeve" effect, in this case the reaction also went deeply into the fiber structure, affecting its crystallinity and morphology, as shown by XRD and SEM, respectively.

3.6. Contact angles

The contact angles measured are shown in Table 2. All measurable contact angles did not vary appreciably with time over 30 min (the same values where measured also months after the preparation of the materials), irrespective of the liquid used. This suggests that the omniphobic character displayed by the modified surfaces was a permanent feature. As can be observed in Table 2, the modification of cellulose fibers with ICPTEOS changed their surface properties, since the contact angle with water increase by 40–60°, depending on the conditions. This feature is probably due to the presence of small amounts of $-OCH_2CH_3$ moieties at the surface of the cellulose fibers (in agreement with the FTIR results and with the dominant T^2, followed by T^1 domains, in the ^{29}Si NMR spectra), which are known to confer water-repellency to polar substrates, by lowering their surface free energy (Bogdan & Kulmala, 2006).

Table 2
Contact angles with water and diiodomethane on cellulose fiber pellets before and after modification.

Sample	θ_{water} (°)	$\theta_{diiodomethane}$ (°)
Cel	64	37
A1	112	–[a]
B1	103	–[a]
C1	129	–[a]
A4	137	111
B4	132	114
C4	140	134

[a] Droplet was absorbed within 2 s.

It was interesting to verify that even for the fibers modified with a 1:0.4 ratio, for which the extent of reaction was modest, a significant increase in hydrophobicity was however detected, which implies that it was not necessary to push the modification to a large extent in order to reach high contact angles. We had already observed a similar behaviour in other studies, in which perfluorinated reagents were used to modify the surface of cellulose fibers (Cunha et al., 2006, 2007a, 2007b, 2007c). The surface of these modified materials showed a high affinity with diiodomethane, as indicated in Table 2.

After the acid hydrolysis of the ethoxy groups present on the surface of the modified fibers, the ensuing silanol groups (SiOH) and Si–O–Si bridges formed by their self-condensation, increased the surface energy of these hybrid materials through their polar contributions, and the contact angles on the surface of the A2, B2 and C2 samples were impossible to measure, as the water drops spread immediately and were absorbed within a couple of seconds. A similar behaviour was observed with the samples obtained after acid hydrolysis in the presence of TEOS, since SiOH groups and Si–O–Si bridges were also formed after this treatment. No conclusive indications were obtained with diiodomethane, as the droplets were also readily absorbed by the surfaces.

As expected, after the hydrolysis in the presence of PFDTEOS, the fibers, on the contrary, became even more hydrophobic and simultaneously lipophobic, as the contact angles reached 140° and 134° with water and diiodomethane, respectively (Table 2). These results are intimately related to the properties of the perfluorinated compounds, which are known to display remarkable hydrophobic–lipophobic features, depending on the nature of the fluorine-containing moiety and its fluorine content (Pagliaro & Ciriminna, 2005). Furthermore, this highly omniphobic character was displayed even though some OH groups, resulting from ethoxy groups hydrolysis, must also have been present at the surface. This observation is in agreement with our previous work (Cunha et al., 2006, 2007a, 2007b, 2007c) where, even at very low levels of surface functionalization of cellulose fibers with perfluorinated reagents, hence, with most of the OH groups untouched, the materials became nevertheless highly omniphobic.

As expected, the high contact angles observed were not affected by the [OH]:[ICPTEOS] ratio/reaction time. Therefore, if the aim of the transformation is the modification of the surface properties of the fibers, preserving their morphology and mechanical properties, the less severe reaction conditions should be used.

It is important to emphasize that these contact angles were higher than those obtained in our previous studies related to surface modification of cellulose fibers with perfluorinated reagents, which only reached, at best, 130° and 100° with water and diiodomethane, respectively (Cunha et al., 2006, 2007a, 2007b, 2007c). Likewise, albeit less efficiently, Jeong, Kim, Lee, Kwon, and Kadono (2001), measured water contact angles up to 118° after coating cellulose fibers with different proportions of PFDTEOS and TEOS. However, in another of our recent studies on this topic on class-I hybrids (Gonçalves et al., 2008), the combination of surface roughness induced by the deposition of silica nanospheres on the surface and the presence of perfluoro moieties using a layer-by-layer assembling approach, gave rise to contact angles as high as those measured in the present investigation. These results corroborate the notion that a very high hydrophobicity as well as lipophobicity is better achieved by combining the presence of well-selected fluorinated moieties with a rough surface morphology, preferably at the nano-scale level (Roach, Shirtcliffe, & Newton, 2008).

4. Conclusions

The modification of cellulose fibers with (3-isocyanatopropyl)triethoxysilane showed to be a promising strategy for preparing new cellulose-based class-II hybrid materials. Thereafter, depending on the nature of the functionalities appended to the alkoxysilanes added during the hydrolysis/condensation step, new materials with a broad range of properties and, therefore, potential applications could be designed, notably with omiphobic surface properties. Furthermore, these new surface properties of the fibers can be attained with a limited extension of the modification, thus preserving their morphology and mechanical properties.

Work is in progress to extend the scope of this approach to other reactions, including the use of other inorganic reagents.

Acknowledgment

A.G. Cunha thanks the FCT (Fundação para a Ciência e a Tecnologia) for a Ph.D. grant (SFRH/BD/31134/2006). The authors also thank FCT for the funding within the scope of the “National Program for Scientific re-equipment”, Rede/1509/RME/2005 and REEQ/515/CTM/2005.

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