



Surface modification of cellulosic fibres for multi-purpose TiO₂ based nanocomposites

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ABSTRACT

Vegetable cellulose fibres have been surface modified using the hydrolysis of tetraethoxysilane (TEOS), octyltrimethoxysilane (OTMS) or phenyltrimethoxysilane (PTMS), followed by the layer-by-layer deposition of previously synthesized TiO₂ nanoparticles. Raman, FTIR and ²⁹Si Solid State NMR spectroscopies, and SEM were used to characterize the resulting nanocomposites. Water contact angle measurements were performed and the results indicate a quite distinct behaviour depending on the employed surface modification procedure. We anticipate that some of the cellulose-based composite materials have potential to be used in self-cleaning surfaces and reinforcing agents in polymer matrices, namely due to their hydrophobic surface and photostability when exposed to solar radiation.

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1. Introduction

Cellulose is the most abundant and widespread biopolymer on Earth. Owing to its abundance, biodegradability, and specific properties, cellulose is a very important renewable resource for the development of environment friendly, biocompatible, and functional materials, quite apart from its traditional and massive use in papermaking and cotton textiles. The remarkable properties of cellulose and its derivatives have been exploited by humankind for millennia and new potential applications for this ubiquitous renewable resource are still being sought [1].

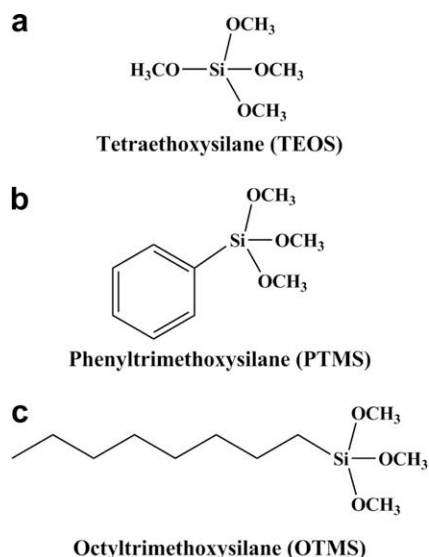
Cellulose fibres present a polar surface associated to the hydroxylated nature of the constituting anhydroglucose units. Such feature is responsible for the high hydrophilicity of cellulose, enabling the establishment of strong hydrogen bonding between fibres and the formation of three dimensional fibre-based structures, as in the production of paper-based products [2,3]. On the other hand, the presence of these hydrophilic groups can promote the nucleation and growth of inorganic phases, such as TiO₂, at the cellulose fibre surfaces and thus allowing to produce nanocomposites [4,5].

TiO₂ pigments have been used in paper products usually to improve opacity and brightness. However, its high cost, compared to clay and calcium carbonate, limits conventional TiO₂ usage to high-value-added printing papers [6]. Nanocrystalline TiO₂ parti-

cles have been particularly investigated because of their specifically size related properties, such as band gap tuning, and high specific surface area. However, nanosized TiO₂ pigments, mechanically mixed with fibres, are poorly retained in the fibre materials, unless agglomeration is promoted by means of polyelectrolytes or other retention aids [2,3], thus decreasing the optical efficiency of the pigment. Recently we have reported the deposition of this pigment in the fibre cell walls by generating TiO₂ *in situ* (in the presence of the cellulose fibres) [5]. There was evidence from those studies that in certain experimental conditions, the cellulose fibres promote the nucleation and growth of TiO₂ particles, yielding a TiO₂/cellulose nanocomposite containing up to 46% TiO₂. However, the intimate contact between TiO₂, which is a photoactive semiconductor, and the organic substrate (cellulose) may limit the applications of such materials for long periods of time [6]. In fact it is well known that, under UV irradiation and in the presence of H₂O and O₂, TiO₂ generates active radical oxygen species such as O₂⁻, HO₂[•] and HO. These radical species may lead to the oxidative degradation of cellulose and successive cleavage polymer chain [6]. Our own studies [5] revealed that permanent light exposure of TiO₂/cellulose nanocomposites result in the degradation of the cellulose fibres, which was clearly noticeable by an uncharacteristic yellowish colour.

Having these limitations in mind, we have carried out the present work to optimize the TiO₂/cellulose composites properties. In order to attenuate detrimental effects of the cellulose fibres due to the photoactivity of deposited TiO₂, two surface modification procedures were investigated here:

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Scheme 1. Chemical structure of tetraethoxysilane (TEOS) (a), phenyltrimethoxysilane (PTMS) (b), and octyltrimethoxysilane (OTMS) (c).

- (1) Cellulose surface coating with amorphous SiO_2 layers prepared from the hydrolysis of tetraethoxysilane (TEOS – Scheme 1a), followed by the layer-by-layer (LbL) deposition of previously synthesized TiO_2 nanoparticles;
- (2) The use of trialkoxysilanes (OTMS: octyltrimethoxysilane) and (PTMS: phenyltrimethoxysilane) as interface coupling agents between the cellulose fibres and the deposited TiO_2 nanoparticles (Scheme 1b and c) [7].

We believe that these procedures contribute to the development of TiO_2 /cellulose nanocomposites that show improved chemical resistance to the inherent photoactivity of TiO_2 .

2. Experimental

2.1. Materials and instrumentation

All chemicals, except cellulose fibres, were supplied by Aldrich and used as received. Wood cellulose fibres (*Eucalyptus globulus*), ECF bleached kraft pulp, composed essentially of cellulose (~85%) and glucuronoxytan (~15%) supplied by Portucel (Portugal) was disintegrated and washed with distilled water before use.

Scanning electron microscopy (SEM) images were obtained using a FEG-SEM Hitachi S4100 microscope operating at 25 kV. Raman spectra were recorded using a Bruker RFS100/S FT-Raman spectrometer (Nd:YAG laser, 1064 nm excitation). The FTIR spectra for solid samples were recorded with a BRUKER IFS-55 FTIR spectrometer equipped with a single horizontal golden gate ATR cell with resolution 8 and 128 interferograms. In order to quantify the TiO_2 retained in the fibres, about 0.1 g of nanocomposite material were submitted to acid digestion (3 mL HCl + 1 mL HNO_3 + 0.5 mL HF), using 25 mL Teflon reactors, in a microwave oven. The resulting solution was diluted to 100 mL and analysed for its titanium content by Inductively Coupled Plasma (ICP), using a Jobin Yvon 70 Plus equipment. The thermogravimetric (TG) assays were carried out with a Shimadzu TGA 50 analyser equipped with a platinum cell. Samples were heated at a constant rate of $10^\circ\text{C}/\text{min}$ from room temperature up to 800°C in static air. Contact angles were measured with a “Surface Energy Evaluation System” commercialized by Brno University (Czech Republic). Each θ value was the average of four determinations. Zeta potential of inorganic nanoparticles was measured using Zetasizer Nano-ZS (red badge)

model ZEN3600. Solid-state magic-angle-spinning (MAS) NMR spectra were recorded at 79.49 MHz for ^{29}Si on Bruker Avance 400/500 spectrometers. ^{29}Si MAS NMR spectra were recorded with 40° pulses, spinning rates of 5.0–5.5 kHz and 60 s recycle delays.

2.2. Methods

The methodologies used to prepare the new materials described are summarized in Fig. 1. The experimental conditions for the preparation of the different materials are described below.

2.3.1. TiO_2 nanoparticles synthesis

TiO_2 nanoparticles were prepared by the controlled hydrolysis of titanium tetraethoxide ($\text{Ti}(\text{EtO})_4$) in ethanol following a methodology described by Eiden-Assmann et al. [8]. A volume of $400\ \mu\text{L}$ of $0.1\ \text{mol dm}^{-3}$ KCl aqueous solution was mixed with 100 mL of absolute ethanol in a closed vessel under nitrogen atmosphere. The temperature was controlled by a water circulation bath at 20°C . After temperature stabilization, 1.7 mL of titanium tetraethoxide was added with constant stirring. The suspension was left under stirring during 24 h and the solid was then collected by centrifugation and intensively washed with ethanol and water. In order to remove organic residues and obtain higher crystalline particles, the solids were calcined at 500°C , during 4 h.

2.3.2. Surface treatment of fibres with TEOS (SiO_2 /cellulose)

Cellulose fibres were coated with SiO_2 following method by Pinto et al. [9]. Typically, cellulosic fibres were added to a mixture of ethanol, H_2O and NH_3 under moderate stirring. The consistency ($(\text{g}(\text{fibres})/\text{ml}(\text{suspension})) \times 100$) of the mixture being 1%, followed by addition of TEOS. This mixture was then kept under constant stirring at room temperature for 24 h. The final fibres were collected by filtering, thoroughly washed with distilled water, and finally dried at 50°C .

2.3.3. LbL deposition of TiO_2 particles on SiO_2 /cellulose fibres ($\text{TiO}_2//\text{SiO}_2$ /cellulose)

Aqueous suspensions of previously synthesised TiO_2 nanoparticles were first submitted to sonication to promote a good dispersion of the particles. The following aqueous solutions of polyelectrolytes have been previously prepared: 1% (wt/v) of poly(diallyldimethylammonium chloride) (poly(DADMAC)) in NaCl $0.5\ \text{mol dm}^{-3}$, 1% (wt/v) of poly(sodium 4-styrenesulfonate) (PSS) in NaCl $0.5\ \text{mol dm}^{-3}$. The LbL technique was used to coat the fibres by alternate dipping of the fibres in poly(DADMAC), PSS and again in the poly(DADMAC) solutions. After each immersion step (10 min), the fibres were rinsed with deionised water to remove the excess of polyelectrolyte. Finally, these surface-treated cellulose

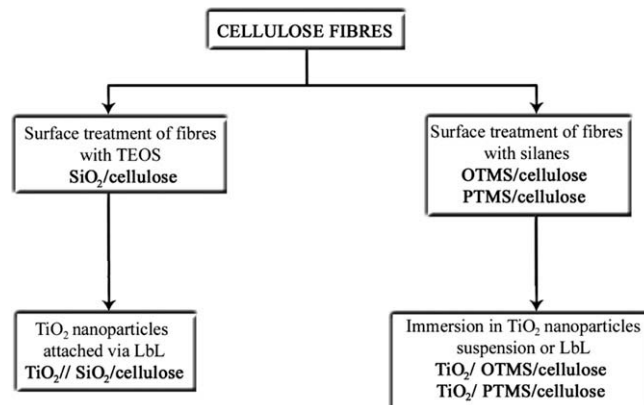


Fig. 1. Schematic representation of the methodology used to prepare the different nanocomposites.

losic fibres were immersed in the TiO_2 suspension, stirred during 30 min and finally the resulting composites were washed with distilled water and dried overnight at 50 °C.

2.3.4. Surface treatment of cellulose fibres with trialkoxysilanes (OTMS/cellulose and PTMS/cellulose)

0.5 g of cellulose fibres were added to a mixture containing 2.0 mL of silane reagent, 1.9 mL of NH_4OH , 5.4 mL of H_2O and 44.6 mL of ethanol under vigorous stirring. This mixture was left under stirring during 6 h at room temperature. Subsequently, the silane-treated cellulose fibres were filtered and thoroughly washed with distilled water and ethanol to remove the excess of silane. Then, the fibres were heated at 110 °C, overnight.

2.3.5. Deposition of TiO_2 nanoparticles on trialkoxysilane coated cellulose fibres ($\text{TiO}_2/\text{OTMS}/\text{cellulose}$ and $\text{TiO}_2/\text{PTMS}/\text{cellulose}$)

The hydrophobic nature of the OTMS and PTMS coated fibres precluded the TiO_2 deposition by using the procedures described above for the $\text{SiO}_2/\text{cellulose}$ fibres. However, it was found that the TiO_2 nanoparticles adsorbed to these silane-coated fibres just by immersing them in an aqueous suspension of TiO_2 nanoparticles and subjecting to vigorous stirring during 30 min at room temperature. At the end, the fibres were washed and dried as described above.

3. Results and discussion

3.1. TiO_2 deposition at $\text{SiO}_2/\text{cellulose}$ fibres by LbL deposition

First, the cellulose fibres were coated with amorphous silica through the controlled hydrolysis of TEOS in the presence of the cellulose fibres, using a methodology recently reported [9]. The amount of SiO_2 in the final composite was controlled by varying the concentration of TEOS during the synthesis. In the present work we have used 0.2 mol dm^{-3} of TEOS, leading to fibres with 25% (w/w) of SiO_2 as determined by thermogravimetric analysis. These fibres were then used as substrates in the LbL deposition of previously prepared TiO_2 (anatase) nanoparticles. Anatase spherical particles with average diameter 175 ± 25 nm were used and then attached to the $\text{SiO}_2/\text{cellulose}$ fibres via adsorption of oppositely charged polyelectrolytes. The Raman spectrum of the $\text{TiO}_2/\text{SiO}_2/\text{cellulose}$ composite showed an intense band at 143 cm^{-1} characteristic of the anatase phase (Fig. 2). A SEM image of a typical $\text{TiO}_2/\text{SiO}_2/\text{cellulose}$ is shown in Fig. 3. SEM analysis shows a homogeneous distribution of TiO_2 nanoparticles at the surface of the silica modified cellulose fibres.

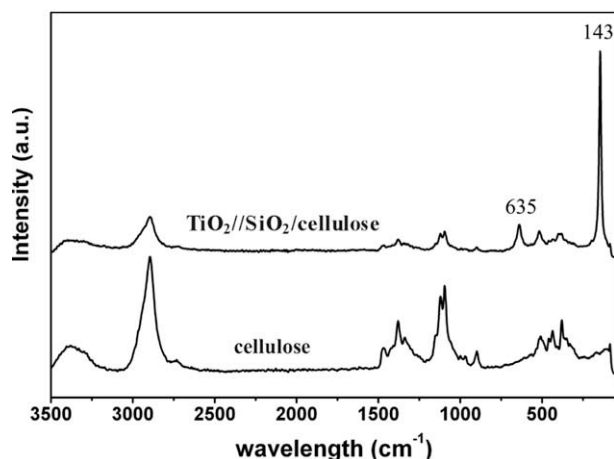


Fig. 2. Raman spectrum of $\text{TiO}_2/\text{SiO}_2/\text{cellulose}$ and blank cellulose fibres.

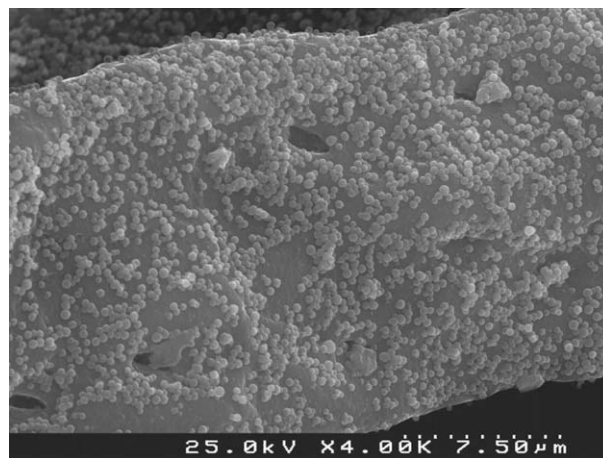


Fig. 3. SEM image of $\text{TiO}_2/\text{SiO}_2/\text{cellulose}$.

These composites contain about 11% (w/w) of TiO_2 and the TiO_2 content did not change significantly when dispersions of the composites have been submitted to vigorous mechanical stirring in water. This means that the TiO_2 nanoparticles became strongly attached to the cellulosic fibres because of strong electrostatic interactions between the negatively charged TiO_2 nanoparticles and the positively charged polyelectrolyte layer previously attached to the $\text{SiO}_2/\text{cellulose}$ fibres. It is well known that amorphous silica particles in contact with neutral aqueous solutions are negatively charged. The zeta potential of aqueous suspensions of SiO_2 (prepared from TEOS hydrolysis) and TiO_2 particles measured at the working pH (6.2) was respectively -29 mV and -22 mV. Therefore the deposition of the TiO_2 nanoparticles on the silica coated cellulosic fibres is in this case mediated through a positive polyelectrolyte top layer which result from the alternate deposition of the modified cellulosic fibres in aqueous solutions of poly(DADMAC) (+), PSS (-) and finally in the poly(DADMAC)(+) solution. The final value of zeta potential of these polyelectrolyte treated fibres was $+12$ mV. This procedure promotes charge and morphological homogeneity of the fibres for subsequent deposition steps.

3.2. Surface treatment of cellulose fibres with trialkoxysilanes

The interaction between silane-based reagents and cellulose is well documented [10–13]. Briefly, the silanes dissolved in a water–ethanol solution hydrolyse giving the corresponding silanol derivative $\text{R-Si}(\text{OH})_3$ (totally or partially hydrolysed); the resulting hydroxyl groups establish hydrogen bonds with their analogues of cellulose [10]. Chemical condensation is promoted during solvent evaporation, leading to siloxane bridges between silanol moieties and, depending on reaction conditions, with the cellulose OH groups, thus forming a polysiloxane network at the cellulose surface [12,13]. Further condensation reactions lead to gel-like networks, which precipitate in the form of colloidal particles.

At the micro-scale, the surface of the OTMS and PTMS treated cellulose fibres appear with a continuous coating as exemplified in Fig. 4 for the OTMS case. The FTIR spectra confirmed this silanes coating at the cellulose surfaces. Fig. 5a and b shows respectively the spectra of OTMS and PTMS coated cellulose fibres, together with the spectra of blank cellulose fibres for comparison. An increase of the relative intensity of the bands at $\sim 1100\text{--}1040 \text{ cm}^{-1}$ is observed in the spectra of silanes treated fibres, when compared to untreated cellulose. Such increase may be assigned to the Si–O–Si and Si–O–C asymmetric stretching vibration [14,15]. With respect to the FTIR spectra of OTMS treated fibres (Fig. 5a), the bands at ~ 2920 , 2850 cm^{-1} ($\nu(\text{CH}_2)$), and $\sim 1460 \text{ cm}^{-1}$ ($\delta(\text{CH}_2)$)

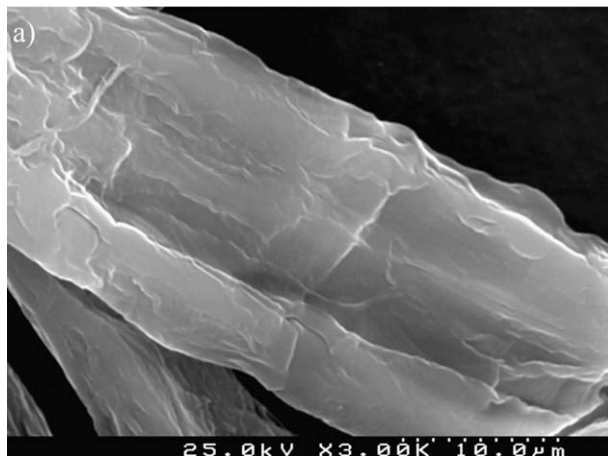


Fig. 4. SEM images of OTMS/cellulose.

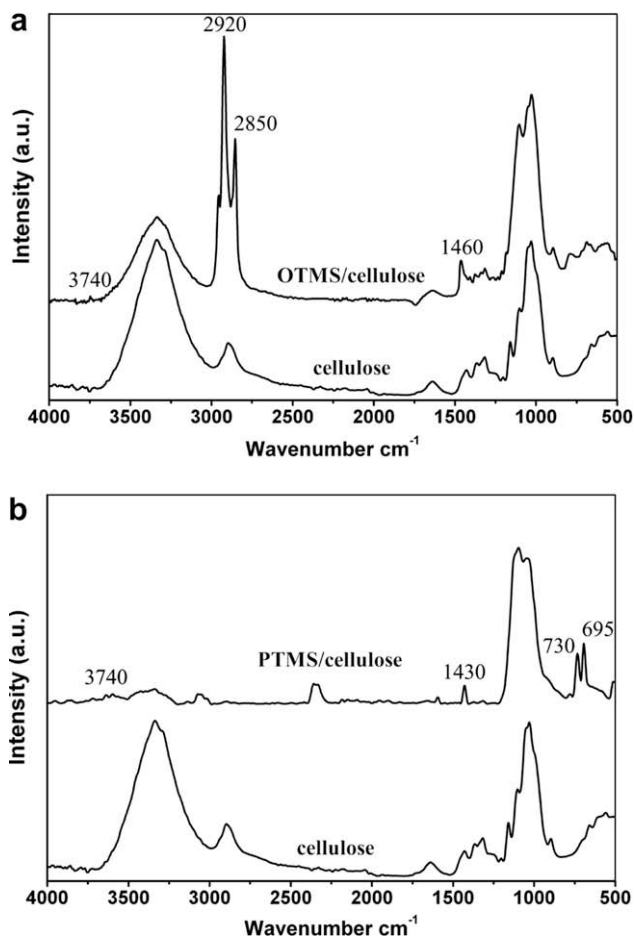


Fig. 5. FTIR spectra of OTMS/cellulose (a) and PTMS/cellulose (b) and corresponding untreated cellulose.

are consistent with the presence of alkyl groups [14]. In the PTMS treated fibres spectra (Fig. 5b) the presence of the aromatic ring is detected at 1430, 730 and 695 cm^{-1} . The planar ring vibration with some Si–C stretching character appears at 1125–1000 cm^{-1} superimposing again with the cellulose bands [15]. Note that both spectra show a less intense band at 3740 cm^{-1} attributed to non-hydrolysed residual Si–O–CH₃ groups.

Further evidence for the OTMS and PTMS coating of the cellulose fibres was acquired by ²⁹Si NMR spectroscopy. The chemical shift of silicon is determined by the chemical nature of its neigh-

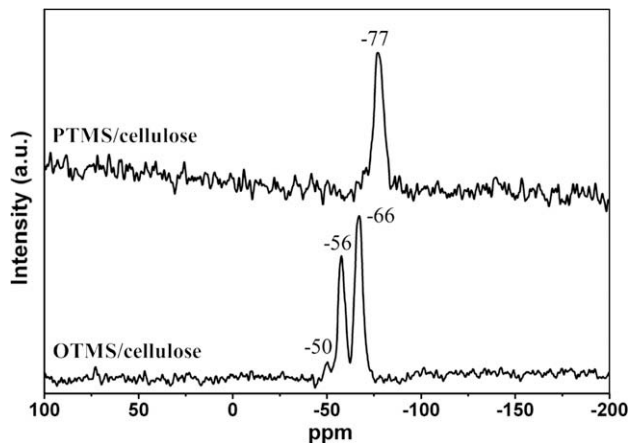


Fig. 6. ²⁹Si solid NMR of OTMS/cellulose (a) and PTMS/cellulose (b).

bour, namely, the number of siloxane bridges attached to a silicon atom; M, D, T and Q structures are the commonly used notation corresponding to one, two, three, and four Si–O bridges, respectively [11]. The ²⁹Si NMR spectra of OTMS and PTMS coated fibres are shown in Fig. 6. Chemical shifts at –56 and –66 ppm are present in the OTMS/cellulose ²⁹Si NMR spectrum. These shifts are in accordance with the presence of T² and T³ structures, respectively. The T² structure is consistent with the chemical structure R–Si–(OSi)₂–OR, where the silicon atom in analysis is surrounded by two –OSi groups and one –OR group. In the case of T³, the chemical structure is described by R–Si–(OSi)₃, the Si atom being surrounded by three O–Si groups [11,16]. The presence of the small peak at –50 ppm corresponds to a T¹ structure (R–Si–OSi–(OCH₃)) that is probably related to the non-hydrolyzed –Si–O–CH₃ groups, as previously noticed by FTIR spectroscopy. The chemical shift at –77 ppm in the PTMS/cellulose spectrum is somehow difficult to attribute. Relatively to the most likely T³ structure, there is a shift of 10 ppm from the theoretic value. According to Casserly and Gleason [16] T groups can be shifted approximately 10 ppm downfield from the calculated shift if the T groups are strained due to the formation of –SiO– rings between the silanes.

The change of the cellulose surface properties after the modification with alkoxisilanes was ascertained by water contact angle measurements. Measures of contact angles are ideally made on smooth, flat, surfaces, because contact angles are significantly influenced by surface roughness, chemical heterogeneities and are known to dramatically change between the wet and dry states of a material [17,18]. Because of this, the fibres were previously conditioned in an excicator and then were pressed in a mould to obtain pellets with flat surfaces. Water contact angles were measured on these substrate surfaces and the results are summarized in Fig. 7. From the results obtained, and bearing in mind that cellulose is a highly hydrophilic substrate (water contact angles around 50°), it is evident that the present modifications with alkoxisilanes reversed this behaviour, leading to hydrophobic surfaces. In fact, surface modified cellulose fibres following the hydrolysis of OTMS and PTMS showed contact angles of 110° and 98°, respectively. These water contact angle values are maintained over several minutes, thus indicating stable siloxane coatings.

3.3. TiO₂ deposition at silane-treated fibres

Unlike the silica modified fibres using the TEOS hydrolysis, the hydrophobic nature of the OTMS and PTMS/cellulose fibres precluded the use of a similar strategy to deposit TiO₂ nanoparticles via polyelectrolytes adsorption in water. Fortunately, it was observed that the simple immersion of the silane-treated fibres in

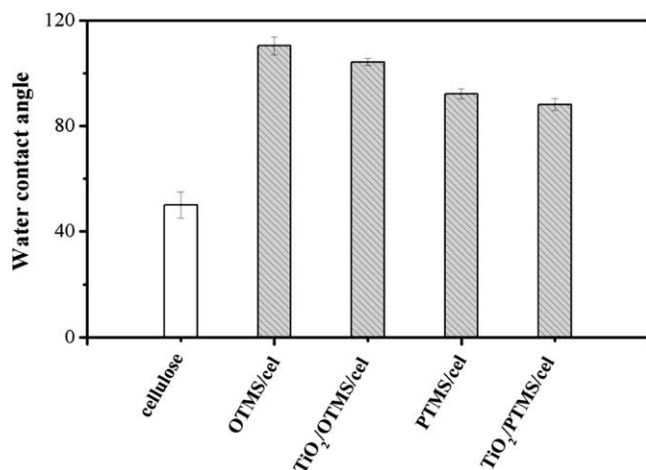


Fig. 7. Water contact angles of the nanocomposites.

an aqueous suspension of TiO₂ nanoparticles led to their attachment to the fibres surfaces. Fig. 8 show the SEM image of the resulting nanocomposites. As can be observed in these images the TiO₂ nanoparticles are hold at the silane modified cellulose surfaces. The TiO₂ load of these materials determined by ICP analysis was around of 6% (w/w). Water contact angles of these TiO₂ coated fibres were also measured (Fig. 7) showing a small decrease in their values when compared with uncoated ones, as expected due to the TiO₂ hydrophilicity. These materials when subjected to mechanical stirring in aqueous medium did not show a lower TiO₂ content. Although we can not give a definite explanation for the type of interaction between the TiO₂ nanoparticles and the silane-coated fibres, it is suggested that probably non-hydrolysed Si–O–CH₃ groups have the ability to react with surface Ti–OH groups of the anatase particles, eliminating methanol. In fact, this type of condensation reaction is used in the synthesis of silane-coated TiO₂ particles using silanes as surface modifiers though in distinct experimental conditions [19].

4. Conclusions

In this work, novel TiO₂/cellulose composites with interfacial silica and siloxane barriers were prepared and characterized. Distinct properties were achieved for the cellulosic nanocomposites depending on the nature of the interlayer. While hydrophilic

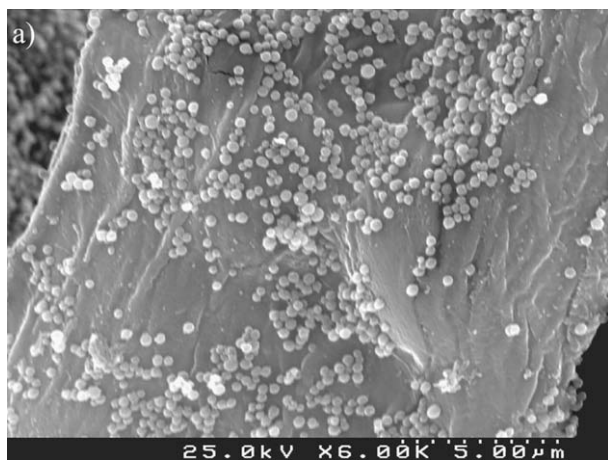


Fig. 8. SEM images of TiO₂/silane-coated cellulose fibres.

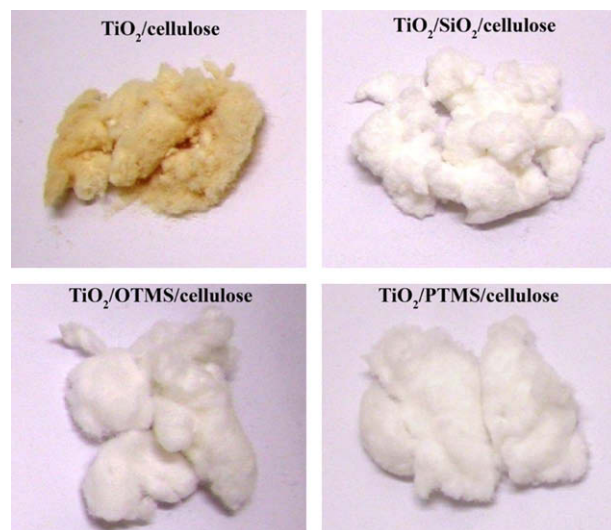


Fig. 9. Photographic pictures of nanocomposites after direct sunlight exposure.

TiO₂/SiO₂/cellulose composites were obtained by hydrolysis of TEOS, the OTMS and PTMS treated fibres (TiO₂/OTMS/cellulose and TiO₂/PTMS/cellulose) showed hydrophobic characteristics. These nanocomposites can be investigated as starting materials in the fabrication of cellulosic based products (TiO₂/silane/cellulose). For example, in a first attempt to evaluate the photostability of the TiO₂ – surface modified cellulose nanocomposites, these materials were exposed to sunlight, together with a sample of TiO₂ directly attached to the cellulose fibres (10% w/w). The latter was used for sake of comparison and was prepared as described previously [5]. After sunlight irradiation, the nanocomposite containing untreated fibres (TiO₂/cellulose) acquired a yellow colour denoting partial degradation of the cellulose fibres (Fig. 9). Conversely, all the surface modified TiO₂ cellulose nanocomposites remained colourless even after several weeks of exposition to sunlight. The improved photostability of these TiO₂/cellulose nanocomposites, together with their compatibility with synthetic polymer matrices (hydrophobic or hydrophilic), opens up new perspectives for the development of new polymer based materials for several applications, including self-cleaning materials and air purification filters.

Acknowledgments

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