

Modification of Cellulose Fibers with Functionalized Silanes: Effect of the Fiber Treatment on the Mechanical Performances of Cellulose–Thermoset Composites

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ABSTRACT: Unsaturated polyester and epoxy resin matrices were filled with silane-treated cellulose fibers and the ensuing composites were tested in terms of mechanical properties before and after accelerated aging consisting of their immersion into water. The coupling agents used were γ -aminopropyltriethoxysilane (APS), γ -methacrylopropyltrimethoxysilane (MPS), hexadecyltrimethoxysilane, and γ -mercaptopropyltrimethoxysilane (MRPS) and those containing reactive functions capable of reacting at one end with the fibers and at the other with the matrix, namely, APS, MPS, and MRPS, were more efficient in improving the mechanical properties of the composites. The immersion into

water induced a drastic loss of mechanical properties of the materials. The water uptake of the composites was also studied and showed that the silane treatment was poorly efficient in preventing cellulose from water absorption. The fracture surfaces were inspected by scanning electron microscopy, which confirmed the quality of the interface. These observations were in agreement with the results obtained from the dynamic mechanical characterization. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 974–984, 2005

Key words: polymer composites materials; polymer science; cellulose-fiber-based composites

INTRODUCTION

The use of cellulose fibers as reinforcing agents in composite materials based on polymeric matrices has recently attracted a growing interest, as shown by the large number of articles and reviews published during the past decade.^{1–11} The main driving force of this tendency resides in the potential of these fibers as serious substitutes to conventional glass fibers in many applications, including composites for the automotive and building sectors.^{12,13} Compared to glass, cellulose offers a number of advantages, namely (i) its lower density, which gives rise to lighter material, (ii) its renewable and ubiquitous character, (iii) its non-abrasive nature, giving less wear of the mixing and moulding equipment, (iv) its higher flexibility, which reduces the risk of fragmentation during processing and, last, but not least, (v) its low cost.^{14–17}

Despite their overall excellent properties, the development of composites based on cellulosic fibers is limited by their hydrophilic character, which arises from the presence of hydroxy groups in the cellulose

structure.¹⁸ Moreover, the notable difference in the surface properties compared with hydrophobic polymer matrices impedes intimate intermolecular contact between the fiber and the matrix, leading to inadequate adhesion between the two phases.^{1,7,19} Thus, the efficiency of the stress transfer across the fiber–matrix interface is poor and the resulting composite materials display low strength properties.^{5,7,20,21} Also, the swelling of the fibers induced by moisture uptake can lead to the failure of the interface zone and consequently to the total deterioration of the mechanical properties of the composite materials.²² The surface modification of cellulose fibers appears therefore a necessity to reduce the polar contribution of their surface energy and their hydrophilic character and thus improve the quality of the fiber–matrix interface.^{22–26}

In a previous study, we established the optimal reaction conditions of the treatment of cellulose fibers with trialkoxysilanes and showed that this approach was an effective means to modify their surface properties. Spectroscopic analyses such as FTIR and ESCA gave clear evidence of the occurrence of a chemical reaction between the silane and the cellulose surface OH groups. The grafting of the coupling agent was performed through a preliminary physical adsorption of the hydrolyzed silane, followed by a curing process at 120 °C in an inert atmosphere.²⁷ Contact angle and

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IGC measurements showed that this treatment strongly reduced the polar contribution of the surface energy and brought about a hydrophobic character whose extent depended of course on the specific silane structure used.²⁸

The aim of the present investigation was to assess the mechanical properties of cellulose-based thermoset composites as a function of the surface modification and the fiber content. The quality of the fiber-matrix adhesion was also examined by scanning electron microscopy. The innovative character of this work resides in the fact that only a few studies were devoted to the preparation of cellulose-based composites using thermosetting matrices. Moreover, the use of silane-coupling agents is a quite recent and promising field, since it calls upon the use of common, industrial, and relatively cheap chemicals. In this work different silane-coupling agents were tested and showed that treated fibers had a beneficial effect on the mechanical properties of the ensuing composite materials.

MATERIALS AND METHODS

Materials

The cellulose fibers used in this study were a bleached soda pulp from the Tunisian annual plant esparto (*Alfa tenassissima*). They were highly porous and had a specific surface of 3 m²/g. Their morphology (length and width distribution) was determined by measuring 7380 fibers with optical microscopy.

The four grafting agents were γ -aminopropyltriethoxysilane (APS), γ -methacrylopropyltrimethoxysilane (MPS), hexadecyltrimethoxysilane (HDS), and γ -mercaptopropyltrimethoxysilane (MRPS), kindly provided by OSI-WITCO. All other reagents and solvents were high-purity commercial products.

Two thermosetting liquid resins were employed in this study, viz. a standard unsaturated glycerophthalic polyester resin (60% (w/w) in styrene) (UP) and an epoxy resin (EP) (Epon 862). The UP resin used was a commercial product based on a 60% w/w solution of unsaturated glycerophthalic polyester in styrene. Its hydroxy (I_{OH}) and acid (I_{COOH}) indexes were determined according to standard procedures NFT 51-513 and NFT 51-511, respectively. They were 160 and 18, respectively. The molecular weight of the starting prepolymer was about 600. The EP resin used was based on bis-phenol diglycedylether with an epoxy index of 5.5, which corresponds to 170 g/equivalent of epoxy functions. Its molecular weight was around 340. The crosslinking reactions were achieved with isophorone diamine (DA) using a molar stoichiometry of EP/DA = 1/1.8).

Fiber treatment

Before the surface treatment, handmade sheets from the cellulose fibers were Soxhlet-extracted with etha-

nol for 24 h to remove contaminants and air-dried to constant weight. The treatment of these sheets with 3% (w/w) of the chosen silane was carried out in a 80/20 v/v ethanol/water medium for 2 h. Then, the fibers were dried at room temperature for 2 days and heat-treated at 120 °C under a nitrogen atmosphere for 2 h in order to promote the actual chemical coupling.

Morphological characterization

The average fiber morphology was determined using an optical microscope equipped with a CCD camera and image analysis software. These measurements gave the fiber length and width distribution, as well as the curl index.

Composite and specimen preparation

The handmade cellulose sheets were impregnated with the chosen liquid resin. When the UP resin was used as the matrix, benzoyl peroxide (1.5 wt %) was added as the free-radical initiator. The formulation used in the preparation of epoxy-based composites consisted of mixing 66.6 parts of EP resin and 33.4 parts of isophorone diamine as hardener. The resin mixtures were degassed before the sheet impregnation. In order to favor the complete wetting of the mat and to remove the air from within the fibers, the systems were kept under a vacuum of 10 mm Hg for 15 min. The composites were then cured at 80 °C for 1.5 h under a pressure of 2.5 MPa. The postcuring was accomplished at 100 °C for 24 h with the UP matrix and at 140 °C for 24 h with the epoxy one.

Characterization of the obtained composites

Flexure tests

The composites prepared were characterized by tensile flexure tests (standard NFT 51-001) using an Instron 4501 working at a cross-head speed of 10 mm/min. The specimen was a thin rectangular strip (10 × 40 × 1.5 mm in width, length, and thickness, respectively).

Dynamic mechanical analysis

Dynamic mechanical tests were carried out with a RSA2 spectrometer from Rheometrics working in the tensile mode. The value of 0.05% for the strain magnitude was chosen in order to fall into the linear domain of viscoelasticity of the material. The samples were thin rectangular strips with dimensions of about 30 × 5 × 0.5 mm³. Measurements were performed in isochronal conditions at 1 Hz, and the temperature was varied between 200 and 500 K at a rate of 3 K/min. This setup measured the complex tensile modulus E^* , i.e., the storage component E' and the loss

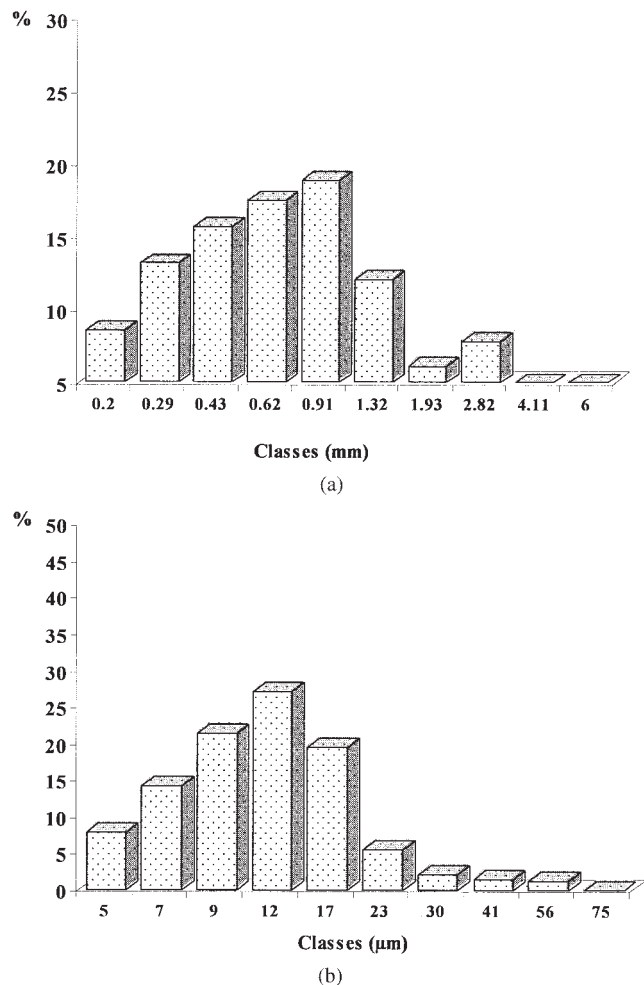


Figure 1 Length (a) and width (b) distribution of cellulose fibers used in this work.

component E'' , as well as the ratio between these two components (E''/E'), i.e., $\tan\delta$.

Scanning electron microscopy

The tensile fracture surfaces of the composites, containing 15% (v/v) of long viscose fibers, were examined with a scanning electron microscope (ABT-55) operated at 7 kV.

Water absorption tests

The effect of water absorption of unmodified and silane-modified fibers was determined on composites containing 40% (v/v) of fibers. The samples were immersed into water at room temperature. The percentage of water absorption and the percentage increase in thickness were calculated using eq. (1) and (2), respectively,

$$W = \frac{W_w - W_0}{W_0} \times 100\%, \tag{1}$$

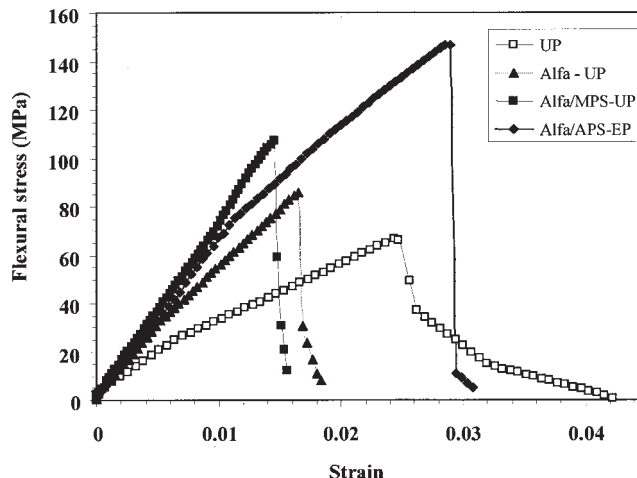


Figure 2 Typical stress versus strain curves for cellulose-based composites.

$$e = \frac{e_w - e_0}{e_0} \times 100\%, \tag{2}$$

where W_w and e_w are, respectively, the weight and the thickness of the sample after immersion into water for a given period, and W_0 and e_0 are the corresponding weight and thickness of the dry sample.

The water uptake was measured regularly at different immersion times. The average scatter around the mean value was $\pm 0.1\%$.

RESULTS AND DISCUSSION

From Figure 1, the mean fiber length and width were found to be 0.75 mm and 14.2 μm , respectively, corresponding to an aspect ratio of 52.

For both matrices, the cellulose-based composite materials displayed linear elastic behavior up to the fracture, as illustrated in Figure 2. The effect of fiber loading

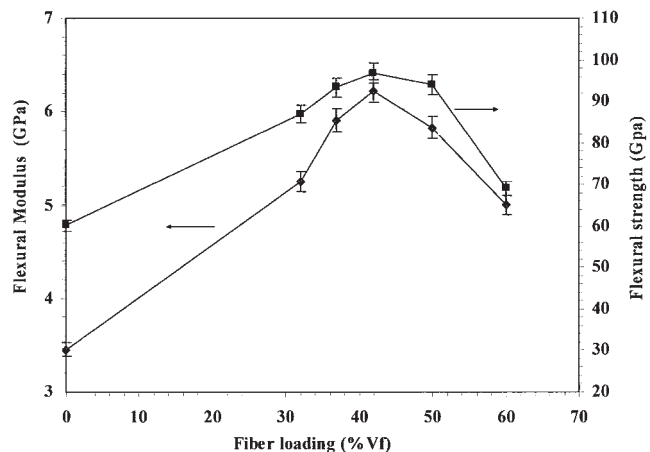


Figure 3 Flexural modulus and flexural strength versus fiber loading ($\%V_f$) of a composite material based on a polyester matrix and untreated cellulose fibers.

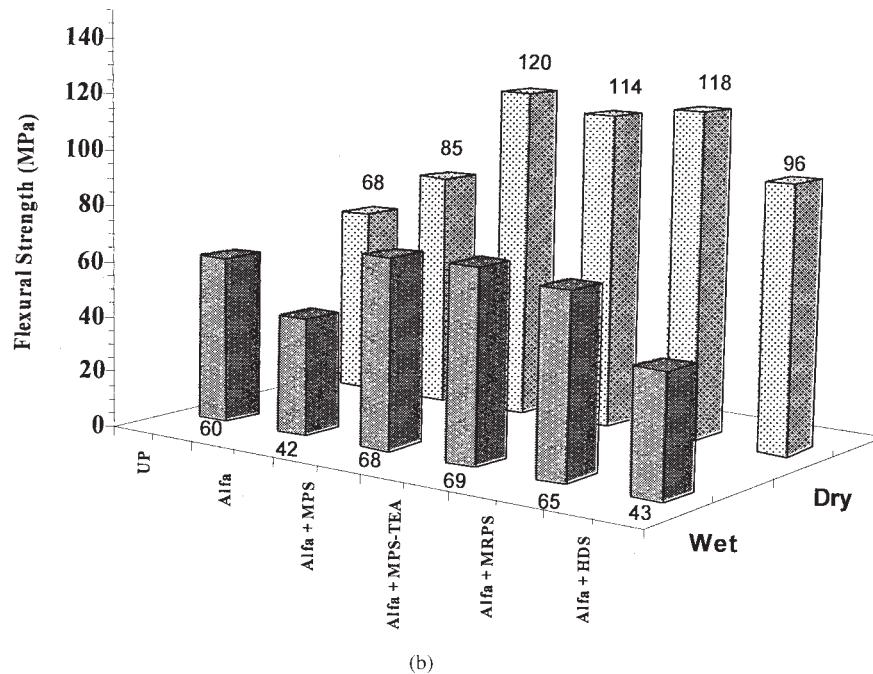
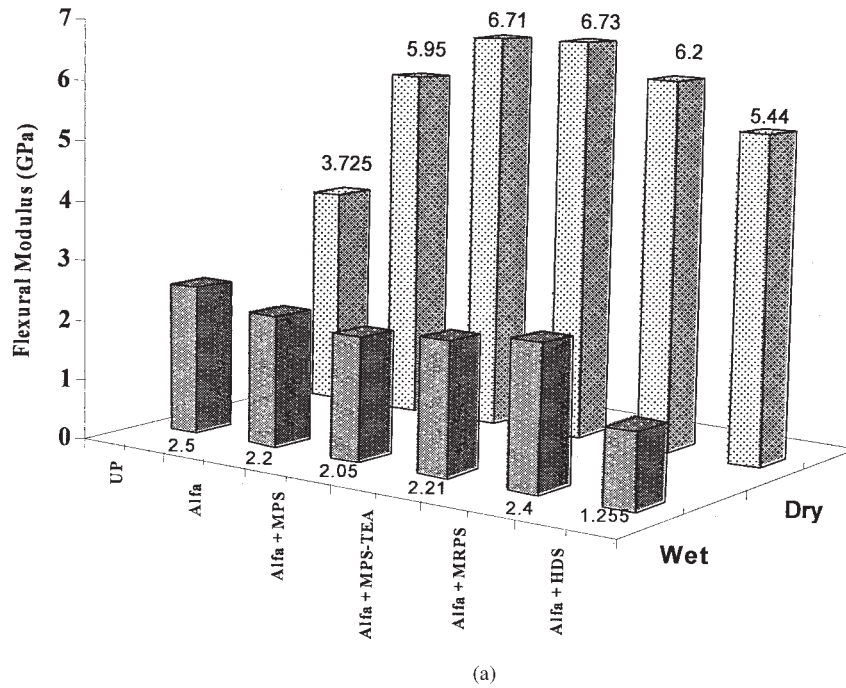


Figure 4 The effect of fiber treatment on the tensile flexural modulus (a) and the tensile flexural strength (b) of cellulose-polyester composites under dry and wet conditions.

on both flexural modulus and strength for polyester with untreated fibers was also studied and showed an increase of the mechanical performance for composites containing reinforcing fibers in the range of 0 to 45% (v/v), as shown in Figure 3. Thus, the incorporation of cellulose fibers into this thermoset matrix gave rise to a progressive increase of the flexural modulus from 3.5 to 6.5 GPa, reflecting the reinforcement effect of the fibers, as reported previously.^{22,29,30} For higher fiber contents, the modulus

decreased most probably because of the insufficient wetting of the fibers by the resin, as confirmed by optical microscopy. Indeed, at these high levels of fiber filling, the amount of resin available for surface coverage was inadequate, also because some of it was used up in capillary adsorption by the porous fibers.

The effect of the surface modification on the mechanical properties of the composite materials was investigated with composites containing 40% fibers.

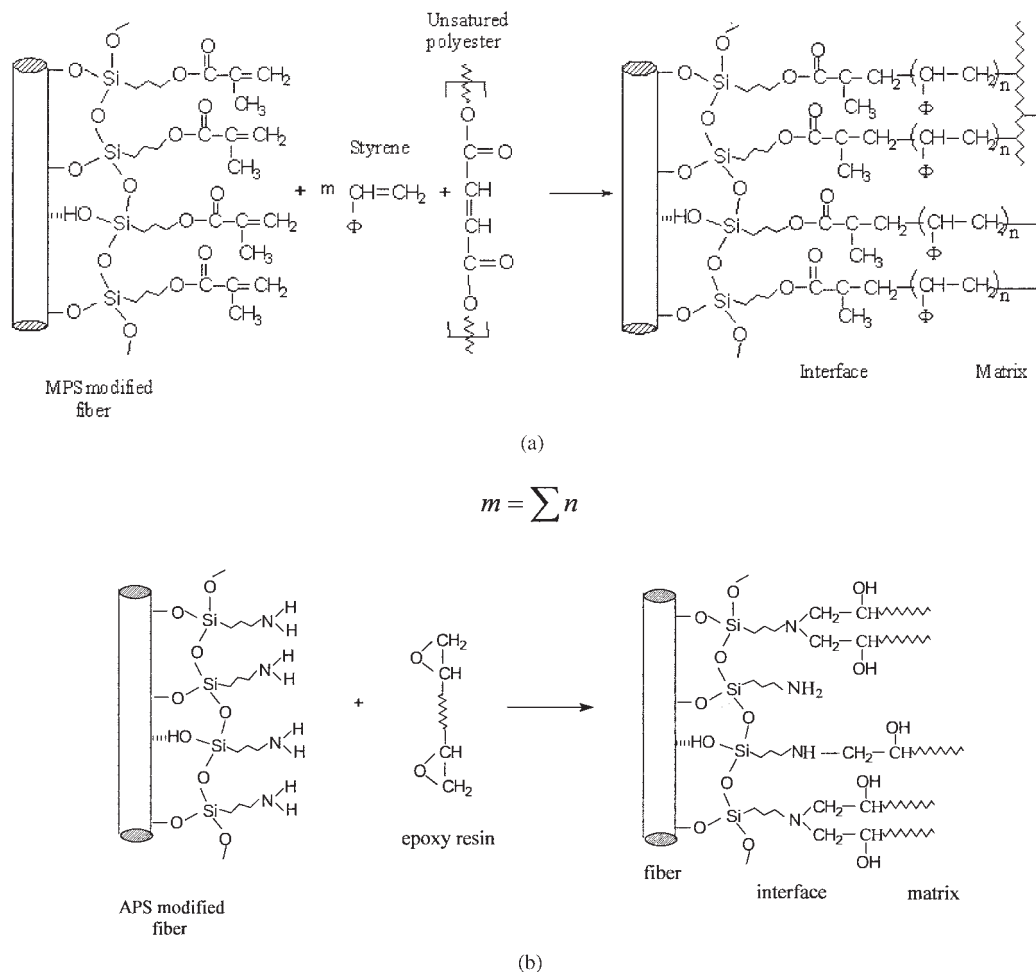


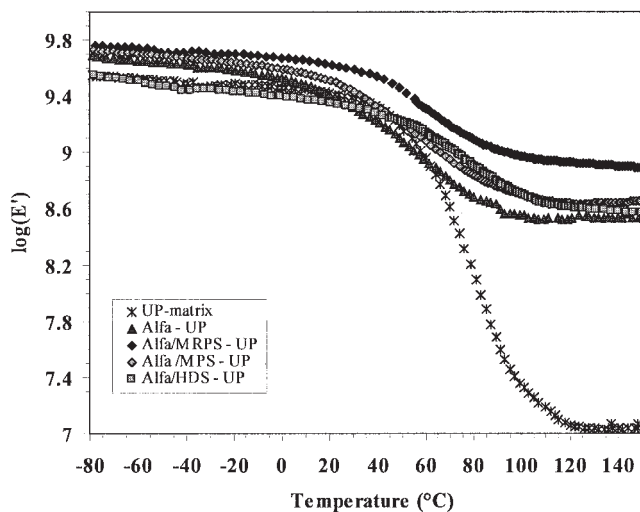
Figure 5 Schematic illustration of the interfacial zone of composites containing modified cellulose fibers: (a) unsaturated polyester matrix in contact with with MPS-modified fibers; (b) epoxy matrix in contact with APS-modified fibers. Note that the relative size of the fibers and of the chemical species are not on scale.

Figure 4 shows the effect of different silane coupling agents on the flexural modulus and strength of the UP-based composites both in the dry state and after immersion in water for 10 days. These results revealed that the fiber treatment with the different silanes did not bring about a significant modification of the flexural modulus. For composites based on the UP matrix, the modulus was about 6 GPa for untreated fibers and reached 6.7 and 5.4 GPa for MPS- and HDS-treated fibres, respectively. Since we have already shown that triethylamine (TEA) increases the amount of adsorbed silanes, we decided to prepare composites based on treated fibers in the presence of TEA. Unfortunately, no improvement was detected in this system, as illustrated in Figure 4. With the epoxy matrix, the flexural modulus attained 6.7 GPa for composites based on untreated fibers and remained practically unchanged after the fiber treatments (results not shown).

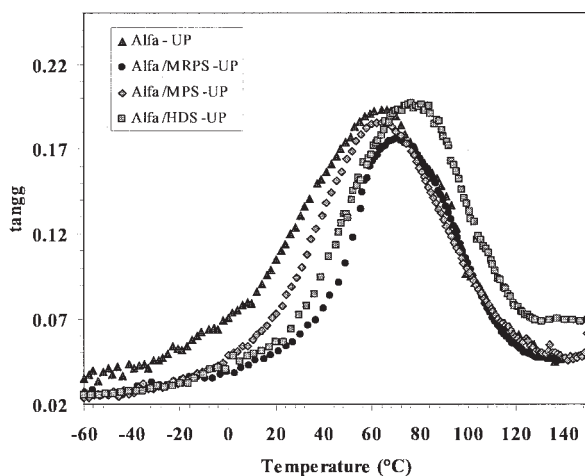
These results could be explained by the fact that the modulus is determined from the slope of the stress versus strain curves at very low deformation level, where the fiber–matrix interface is not yet

subjected to important shear deformation. On the contrary, the flexural strength was greatly affected by the silane treatment, as shown in Figure 4 for the UP-based composites. The effect was highly dependent on the silane structure used. The strength increased from 85 MPa for untreated fibers up to 120, 118, and 95 MPa for composites prepared with MPS-, MRPS-, and HDS-treated fibers, respectively. The improved mechanical properties in the presence of the reactive MPS and MRPS was attributed to the ability of these coupling agents to give rise to a covalent bond continuity between the fibers and the polyester matrix, which enhanced the interfacial bonding between the two phases and increased the efficiency of stress transfer between the matrix and the fibers.^{22,29,30}

In the case of MPS, the methacrylic double bond participated in the free radical polymerization involving styrene and the resin's unsaturations in what became a terpolymerization system, whereas with MRPS the covalent bonds with the matrix were established through the transfer reaction between the growing



(a)



(b)

Figure 6 Temperature dependence of the logarithm of the storage tensile modulus E' (a) and $\tan\delta$ at 1 Hz (b) for UP composites based on silane-treated cellulose fibers (40% v/v).

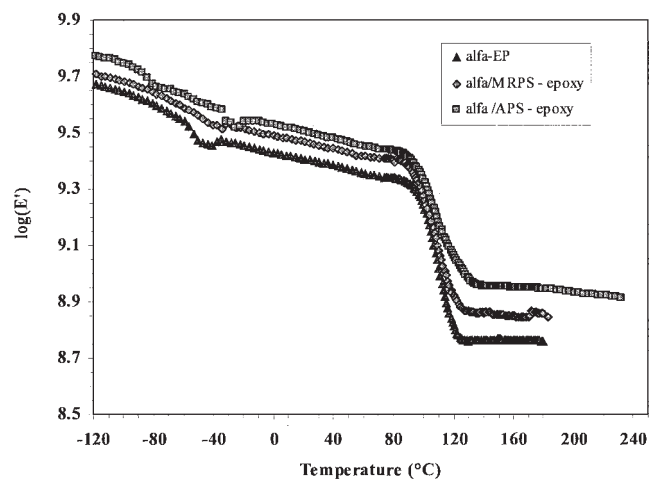
radical and the mercapto groups. The ability of the silane-modified fibers to undergo chemical reaction with monomers had in fact been confirmed previously.²⁸ In the case of HDS, the small effect on the strength properties was probably due to the fact that only van der Waals type interactions could be established with the polymer matrix, leading to a modest enhancement of adhesion between the fibers and the polyester matrix. Figure 5 gives a schematic representation of the possible chemical reactions between the grafted silane and both matrices.

For epoxy-based materials, even though the modulus (3.9 GPa) of the composite was twice as high as that of the unfilled matrix (6.7 GPa), the fiber incorporation at 40% (v/v) did not lead to any evolution in flexural strength. This may be due to the effect of stress concentration induced by the presence of the fibers, which initiated the rupture prematurely.

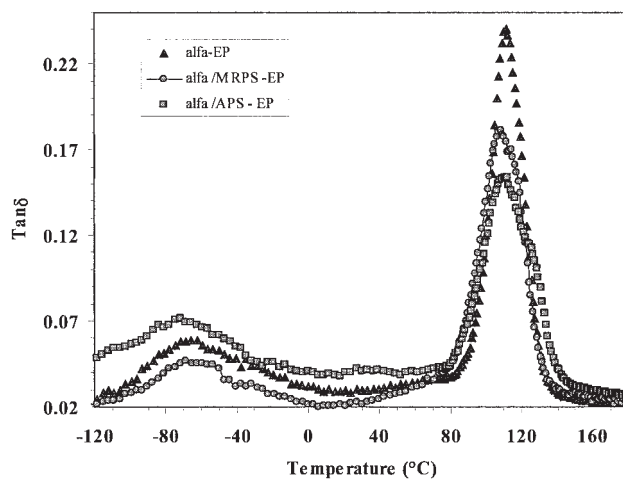
Dynamic mechanical analysis

The dynamic mechanical analysis of composites is one of the most suitable methods to provide clear-cut evidence on the effect of the fiber treatments on the properties of the ensuing materials.^{7,31} The evolution of the logarithm of the storage modulus E' as a function of the temperature is reported in Figure 6(a) for polyester-based composites containing 40% (v/v) fibers. A plateau is observed up to 30 °C, followed by a drastic decrease associated with the main α relaxation, which corresponds to the glass transition temperature of the crosslinked polyester matrix. This relaxation process corresponds to an energy dissipation phenomenon, as shown by the maximum in the $\tan\delta$ versus temperature plot [Fig. 6(b)].

The storage glassy modulus E' was only modestly affected by the introduction of silane-treated fibers into the matrix, as shown in Figure 6(a). Thus, E' at 20

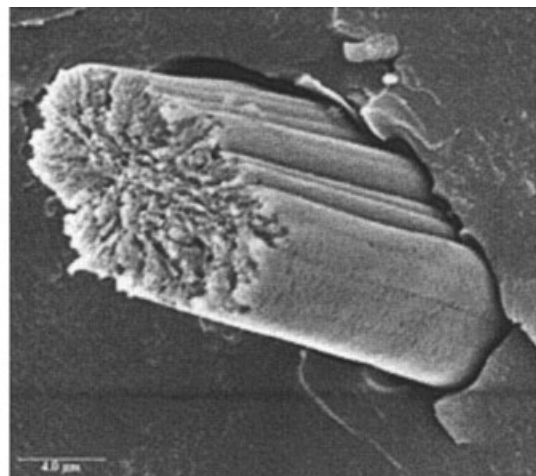
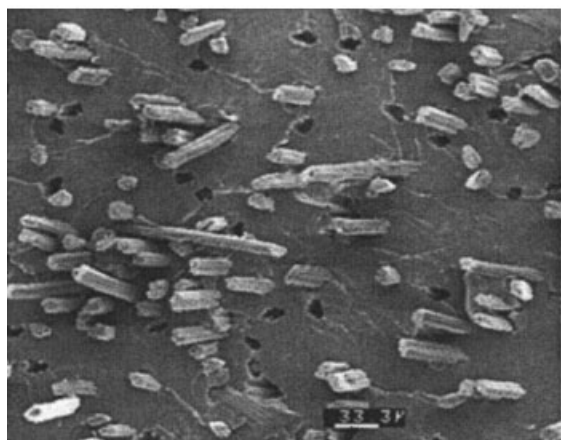


(a)

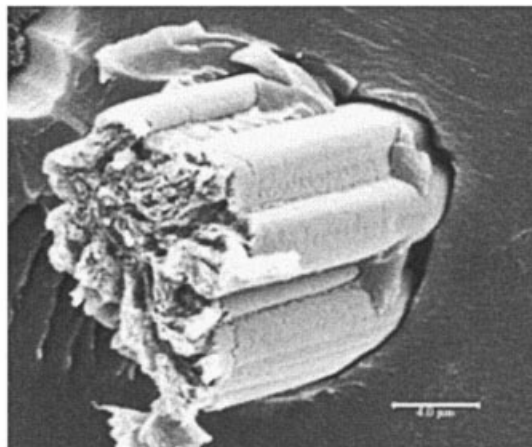
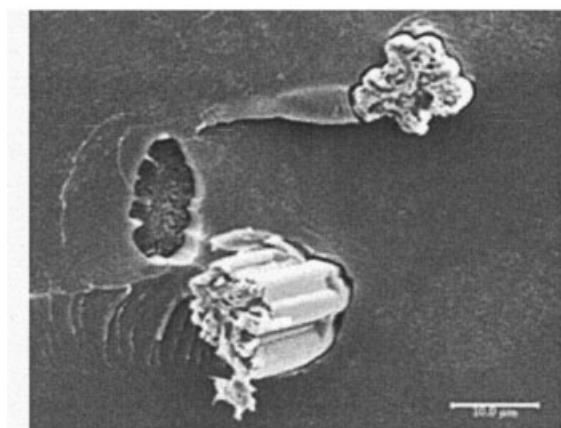


(b)

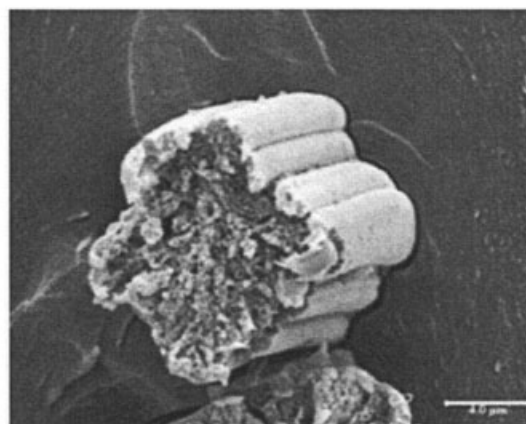
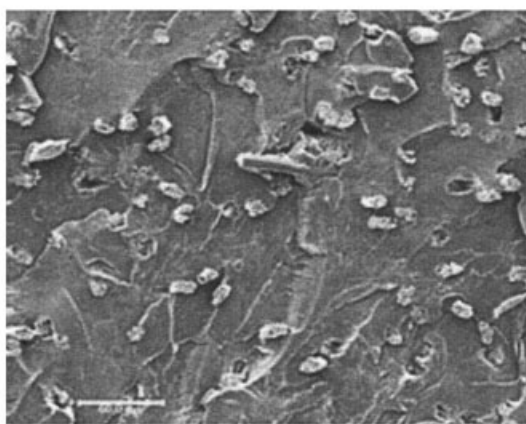
Figure 7 Temperature dependence of the logarithm of the storage tensile modulus E' (a) and $\tan\delta$ at 1 Hz (b) for epoxy composites based on silane-treated cellulose fibers (40% v/v).



(a)



(b)



(c)

Figure 8 SEM of freshly fractured surfaces of polyester composites based on long viscose fibers: before treatment (a) and after treatment with MPS (b), MRPS (c), and HDS (d).

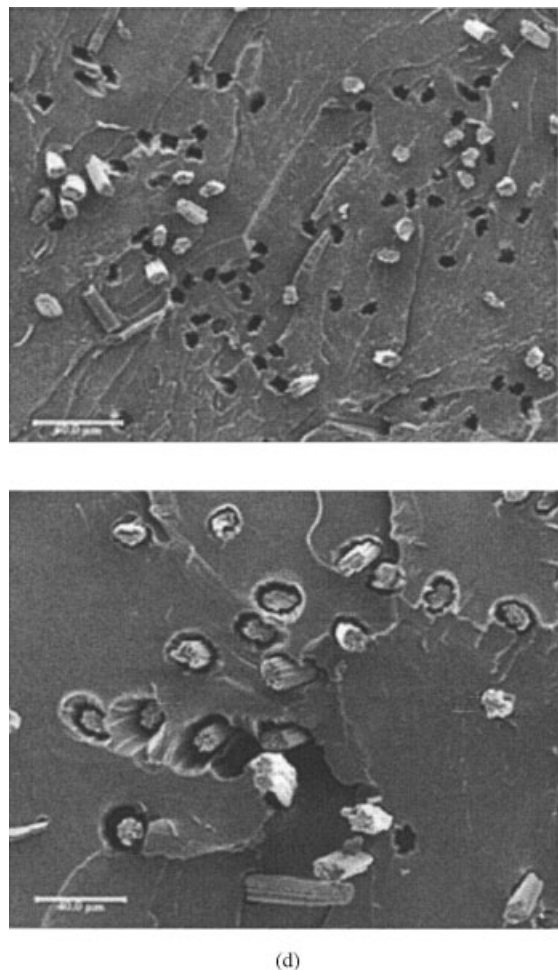


Figure 8 (Continued from the previous page.)

°C varied from 2.8 GPa, for the untreated-fiber-reinforced composite, to 3.25, 4.2, and 2.25 GPa, respectively, when MPS-, MRPS-, and HDS-treated fibers were used. The increase in E' values when MPS and MRPS were used as coupling agents was certainly due to the ability of these reagents to establish covalent bonds with the matrix, which induced an increase of the interfacial work of adhesion between the fiber and the matrix, as discussed above. In the case of HDS, the modulus decreased, probably because of the inert chemical character of the long aliphatic chain borne by HDS. However, the exact determination of the modulus depends on the precise knowledge of the sample dimensions and since the variations reported for the glassy modulus were small, some uncertainty remains about the significance of the observed variations.

The sensitivity of the modulus with respect to both the fiber content and the fiber treatment was much more pronounced at temperatures higher than the T_g of the matrix. As indicated in Figure 6(a), the storage rubbery modulus, taken as the E' value at 120 °C, increased from 10 MPa for the unfilled UP matrix to 0.33 GPa for the composite containing 40% (v/v) untreated fibers and then, respectively, to 0.44, 0.85, and

0.46 GPa for the MPS-, MRPS-, and HDS-treated counterparts. This drastic increase gave a better visibility of the fiber reinforcing effect and also showed clearly the positive effect of the fiber silane treatment on the quality of the interface between them and the matrix, particularly with MRPS.

For epoxy-based composites, the evolution of E' as a function of the temperature showed the presence of a glassy plateau up to 85 °C, followed by a drastic decrease in the modulus, associated with the glass transition, at ≈ 100 °C [Fig. 7(a)]. As in the case of the polyester-based composites, the fiber treatment by silane coupling agents bearing functions capable of reacting with the epoxy groups of the matrix induced an increase in the modulus of the composite, both in its glassy and in its rubbery states, but again, the variations were more pronounced in rubbery region. Thus, at 20 °C, the modulus increased from 2.55 GPa, for composites with untreated fibers, to 2.93 and 3.2 GPa, respectively, for composites made with MRPS- and APS-treated fibers and at 150 °C, a temperature higher than the T_g of the epoxy matrix, the corresponding moduli increased from 0.58 to 0.72 and 0.90 GPa, respectively. The stronger reinforcing effect of the APS-treated fibers can be rationalized in terms of the higher reactivity of the NH_2 functions toward the epoxy moieties of the matrix compared with that of the mercapto (SH) groups.

The evolution of the loss angle as a function of temperature [Fig. 7(b)] showed a secondary β relaxation around -70 °C ascribed to the free rotating hydroxypropylether groups of the main chain of the polymer.³³ The α relaxation associated with the glass transition of the matrix was detected at ≈ 110 °C. With the silane-treated fibers, the α relaxation displayed a shoulder on the high temperature side of the main relaxation process, located around 115 and 130 °C, for composites made with MRPS- and APS-treated fibers, respectively. This feature suggests that a better interfacial adhesion had occurred in the composites based on fibers treated with coupling agents bearing functions capable of reacting with the matrix, as discussed above. The presence of this high temperature shoulder could be ascribed to a decrease of the epoxy chain mobility in the vicinity of the fiber surface. This trend was confirmed by a decrease in the surface area of the $\text{tg}\delta$ peak for silane-treated fibers, as shown in Figure 6.

Scanning electron microscopy analysis

SEM is generally a good tool for assessing the wetting of the fibers by the matrix, especially when one can observe the freshly fractured surface.^{22,32} In order to get better evidence, these observations were made on composites prepared with 10% (v/v) long fibers, obtained from regenerated cellulose. Figures 8 and 9 show the SEM micrographs related to UP- and EP-based composites, respectively. For the materials pre-

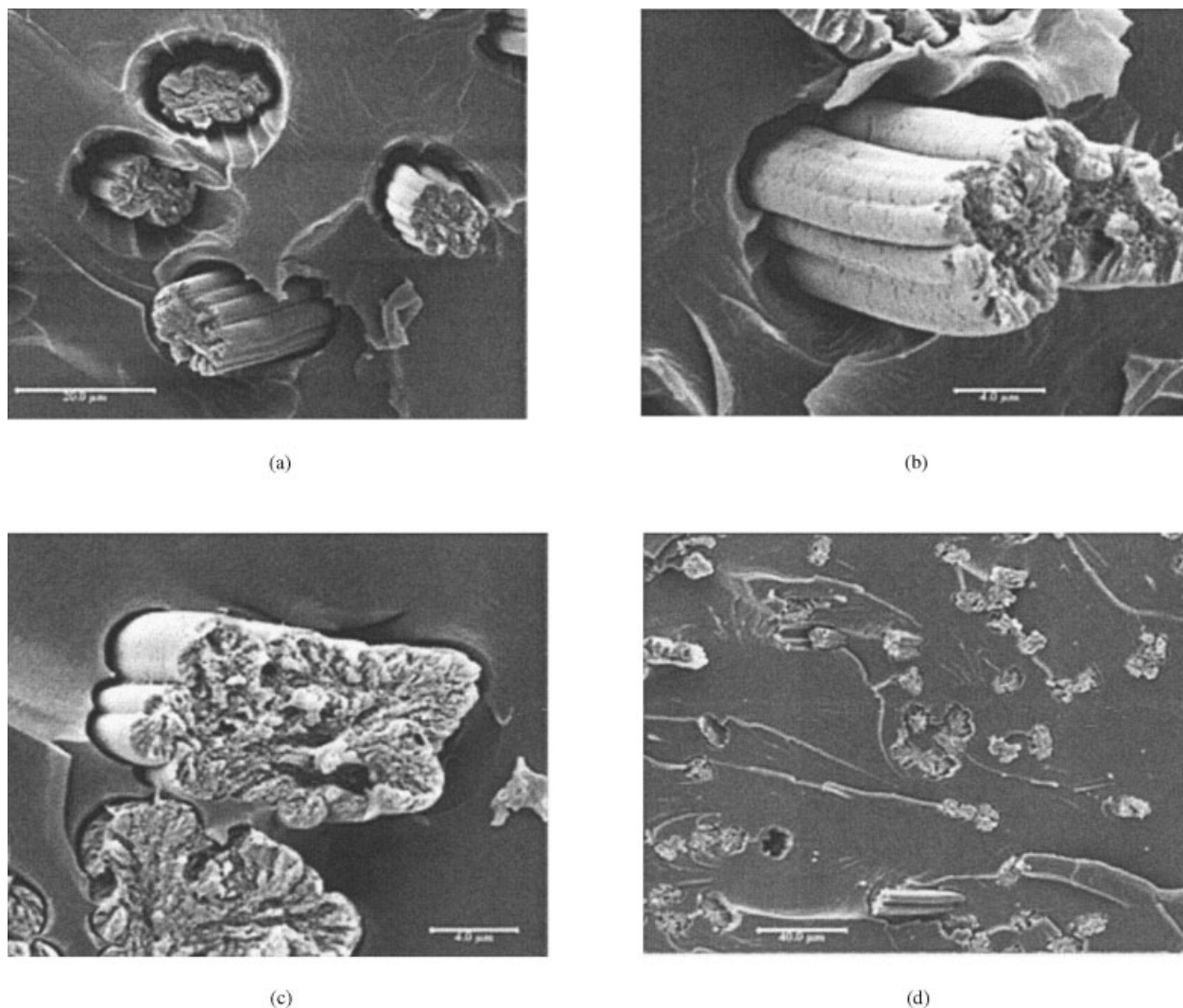


Figure 9 SEM of freshly fracture surfaces of epoxy composites based on long viscose fibers: before treatment (a) and after coupling with APS (b).

pared with untreated fibers [Figs. 8(a) and 9(a)], the rupture was accompanied by a clean withdrawal of the fibers, leaving holes, which indicates a very poor adhesion between the fibers and the matrix, as emphasized by the magnification of this zone in Figures 8(a) and 9(a). For composites containing MRPS-treated fibers, a significant improvement of the fiber–matrix interface was observed, as suggested by the absence of holes and the breaking of the fibers [Fig. 8(c)].

The treatment of the fibers with MPS, HDS, or APS and their incorporation into a polyester or an epoxy matrix showed intermediate results [Figs. 8(b), 8(d), and 9(b)] in that the adhesion quality was somewhat better than with untreated fibers, but not as good as that observed for MRPS-treated fibers. In the case of the UP-based composites containing HDS-treated fibers, the adhesion quality worsened, because of the perturbation brought about, as already pointed out, by the inert character of the long aliphatic chain borne by this silane [Fig. 9(d)].

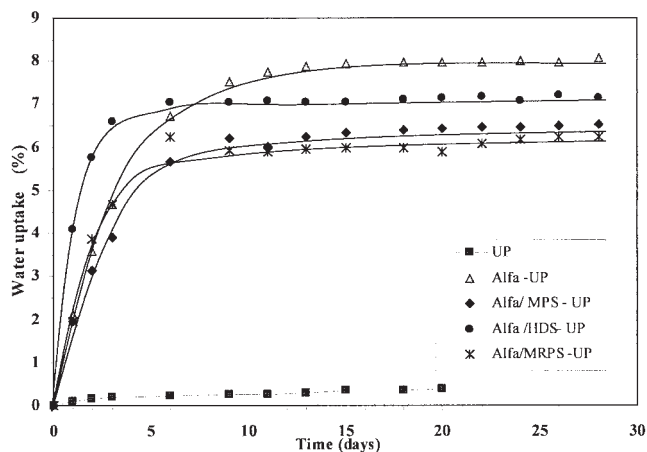


Figure 10 Percentage water uptake versus immersion time at 25 °C for polyester composites containing 40% (v/v) Alfa fibers.

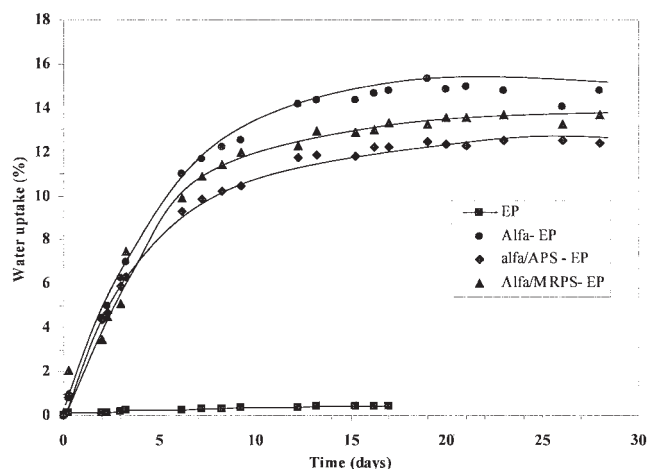


Figure 11 Percentage water uptake versus immersion time at 25 °C for epoxy composites containing 40% (v/v) Alfa fibers.

On the whole, the SEM observations on these materials corroborated the results obtained by studying their mechanical properties and the interpretations given in that context.

Water absorption properties

The most serious handicap related to the use of cellulose fibers in composite materials is their extreme sensitivity to water, which reduces dramatically their mechanical properties in a damp atmosphere. The evolution of water absorption as a function of the immersion time is shown in Figures 10 and 11 for UP- and EP-based composites, respectively. For all composites, the water absorption increased with immersion time and reached a plateau after about 8 days. The equilibrium water uptake depended on the treatment of the fibers. Thus, the UP composites containing untreated fibers absorbed 8% of the water, whereas the composites based on HDS-, MPS-, and MRPS-treated fibers absorbed 7, 6.5, and 6% of the water, respectively. The same trend was observed for epoxy-based composites (Fig. 11). Surprisingly, the treatment of the fibers with HDS was not efficient as a water barrier, despite the marked hydrophobic character of the modified fiber surface.

The mechanical properties of the composites after their immersion into water for 10 days are shown in Figure 4. A drastic decrease of the mechanical performances and the total loss of the reinforcing effect of the cellulose fibers were observed, for both pristine and treated fibers and whatever the nature of the silane coupling agent. The silane coupling was inefficient in preventing water absorption compared with the untreated fibers.

The SEM micrographs of the rupture surface after immersion into water showed a significant increase of

the hole number (not shown), which indicated a total debonding between the fibers and the matrix.

This poor moisture barrier effect provided by the silanes could be rationalized by (i) an incomplete fiber surface coverage by the coupled silanes, (ii) the very low thickness of the grafted silane layer, and (iii) the diffusion of water molecules through the fiber lumen or its migration to the interfacial zone and consequently the induction of the hydrolysis of Si-O-C functions. These results were also observed when using short fibers of Technocel fibers.

CONCLUSION

Composite materials based on cellulose fibers and thermoset matrices showed that the incorporation of up to 40% (v/v) of fibers can be achieved. Their reinforcing effect proved to be promising, especially with some silane-treated fibers, namely those bearing functions capable of reacting with the polyester or the epoxy matrix. Thus, this improvement was especially true for an amino silane in contact with an epoxy matrix and for a methacrylic silane in contact with an unsaturated polyester resin. The improved interface quality was confirmed by microscopic observations. However, these silane coupling agents were inefficient in preventing water absorption by their surface-modified cellulose fibers.

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