

# Effect of Silane Coupling Agents on the Properties of Pine Fibers/Polypropylene Composites

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**ABSTRACT:** In the present work, PP-based composites, reinforced with surface modified pine fibers, have been prepared. The surface of the fibers has been treated with several silane derivatives bearing specific functionalities.  $-NH_2$ ,  $-SH$ , long aliphatic chain, and methacrylic group were chosen as functionalities of the silane derivatives for evaluating the compatibility with the polymer matrix. Mechanical analysis, contact angle and XPS spectra, SEM microscopy, and water uptake measurements were used as characterization techniques for evaluating the nature of composites. XPS as well as contact angle measurements demon-

strated that pine fibers and silane derivatives were effectively coupled. The mechanical analysis showed an increase in Young's and flexural moduli, by 12% and 130% respectively, and nonsignificant changes in the ultimate tensile strength were noted after surface modification. Water uptake measurements revealed a low water absorption by the materials, always lower than 2 wt %. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3706–3717, 2007

**Key words:** composite; cellulose fibers; silane; interface; fibers treatment; PP

## INTRODUCTION

The recourse of lignocellulosic fibers as a reinforcing element in composite materials still attracts much interest at both the academic and industrial level.<sup>1–5</sup> Since 1990 composites based on natural fibers, namely those associated with thermoplastic matrices, find application in the automotive and construction industry and are more and more used as a substitute of fiberglass composites.<sup>6</sup> Besides environmental and economic concerns, many important factors are now driving the use of lignocellulosic fibers, such as weight saving, good acoustic and thermal insulation, nonabrasive effect, and good availability.

The potential use of plant fibers as a reinforcement of polymer matrices is greatly harmed by their hydrophilic character, high capacity of moisture absorption (7 to 9 wt % at 50% humidity), and poor adhesion between them and the matrix. Indeed, the presence of an adsorbed layer of molecular water on the surface hinders any possible contact or interaction at a molecular level between both phases and prevents fiber wetting by the polymer. Likewise, the high density of

hydroxyl groups on the surface ensures a high cohesion within the fiber network through hydrogen bonding, which is difficult to break up and to bring about efficient and homogenous dispersion of the fiber aggregates on the organic matrix. As a result, a considerable effort is currently being directed toward improving the quality of the interfacial bonding between the polymer and fibers, by surface modification of lignocellulosic fibers.<sup>7–10</sup>

Different approaches have been investigated to improve the compatibility between cellulosic fibers and polymeric matrices, i.e., chemical modification,<sup>11,12</sup> polymer grafting on the surface of the fibers,<sup>13</sup> incorporation of compatibilizer, such as maleated polymer<sup>13,14</sup> or treatment with coupling agents.<sup>9,10,15–17</sup> The former approach is one of the most adopted and studied because of the high density of hydroxyl groups on the surface of the fiber, on which a wide variety of reactions could be undertaken. By means of these reactions, the substitution of this function by the other target group can be carried out to modify the surface structure and bring about better compatibility between both components of the composite.

Among the different coupling agents, organo-silane ( $R-Si-(OR')_3$ ) is the most effective, commercially available, and low cost product and is widely used for modifying surface properties of inorganic substrates such as fiberglass or oxide filler. Silane coupling chemicals bear alkoxy-silane groups, which after hydrolysis are capable of reacting with OH-rich surfaces. Furthermore, there is a wide range of avail-

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able functionalities for the R group. This R group is responsible for improving the compatibilization between the reinforcing element and the polymer matrix or even establishing covalent bonds between them. Even though the beneficial effect on the adhesion between the fiber and the matrix is well established with fiberglass and inorganic fillers,<sup>18</sup> their effects on the properties of lignocellulosic fibers reinforced composites are not formally established and still receive considerable attention.<sup>9,10,15–17,19–23</sup>

Using different coupling agents, Demir et al.<sup>15</sup> showed that treatments of luffa fibers with  $\gamma$ -aminopropyltrimethoxysilane and  $\gamma$ -mercaptopropyltrimethoxysilane improved both tensile strength and Young's modulus by more than 40%, compared with untreated fibers. Colom et al.<sup>10</sup> modified the surface of aspen wood fibers with  $\gamma$ -methacryloxypropyltrimethoxysilane for enhancing interface adhesion. An increase by 37.5% in tensile strength (20 wt %) was reported. However, most of these works were in agreement with regard to a gain in mechanical properties and elastic moduli provided by the silane treated fibers, while a discrepancy appeared regarding the evolution of the tensile strength.

In a previous work, we have showed that trialkoxysilane could be effectively anchored on cellulosic fibers through a preliminary physical adsorption from diluted solution followed by a thermal treatment.<sup>19,20</sup> Different spectroscopic techniques have been used to prove the presence of silane, to quantify its amount on the substrate, and to elucidate the structure of the anchored siloxane network on the fiber's surface. For thermoset-based composites, it has been clearly established that the reinforcing effect of the fibers could be significantly improved by their treatment with a silane bearing functional group that is able to react with the matrix.<sup>21</sup> Conversely, in a recent work an analogue result was shown, where in the presence of LDPE matrix, the treatment of fibers with a reactive silane coupling agent was performed, obtaining an improvement in both the tensile modulus and the tensile strength, and a drop by more than 35% in the composite water uptake.<sup>22</sup>

The encouraging results obtained for thermoset-based and LDPE composites<sup>21,22</sup> motivated the present study, in which the effect of silane-treated pine fibers, on the properties of polypropylene matrix, was investigated.

## MATERIALS AND EXPERIMENTAL PROCEDURES

### Cellulose fibers

Bleached softwood (pine) fibers with an arithmetic average length of about 1.1 mm were used as reinforcement.

### Silane coupling agents

R-trialkoxysilanes with different R functionalization: methacryloxypropyl-(MPS), hexadecyl-(HDS), aminopropyl-(APS) and mercaptopropyl-(MRPS) (Table I) were kindly provided by Degussa and were used without prior treatment.

### Polymer matrix

Poly(propylene) (PP; Isplen 070, Repsol-YPF) was used as polymer matrix. This polymer has a melting temperature of 169°C and a degree of crystallinity around 45%, as determined by differential scanning calorimetry (DSC), with a heating rate of 10°C/min. Its density at room temperature was 0.905 g/cm<sup>3</sup>. The melt flow index of this polymer matrix was 12 g/10 min, measured at 230°C and using a load of 2.16 kg.

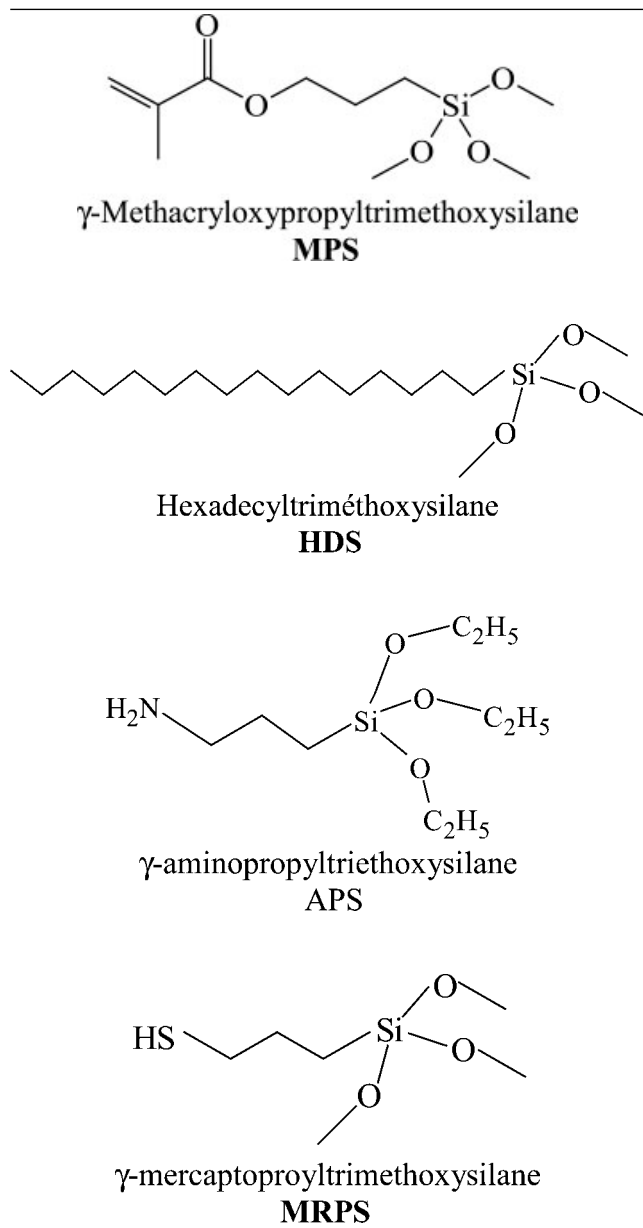
### Fiber treatment

The procedure followed for the fiber treatment with silane was optimized to obtain maximum amount of silane coupling agent anchored on the fiber surface. Different steps were preliminary investigated and the following procedure was adopted: in an ethanol/water (80/20 v/v) solution, chosen silane (1.5 wt %) was added and the pH was adjusted to 4.5–5 by addition of acetic acid (exception made of AMPS because of its auto-catalytic nature), and was kept under stirring for 1 h to ensure complete silane hydrolysis. Then, the hydrolyzed silane solution was added on an ethanol/water (80/20) pine fiber suspension (5 wt %) and was kept under mechanical stirring for 2 h to reach an effective fiber soaking. After this process, obtained fibers were filtered, dried at room temperature for 2 days and heated at 110°C under a nitrogen atmosphere for 2 h, to promote actual chemical coupling.

### Preparation of the composites

PP and pine fibers (treated and untreated) were mixed at 70/30 ratio (PP/fibers) in a two-roll mill (IQAP LAB) at (190 ± 5)°C for 10 min to obtain a well-dispersed material. The mill is equipped with two parallel rolls, turning at two different speeds of 23 and 29 rpm. Obtained blends were cut down to pellets with a particle size in the range of 10 mm, using a pelletizer equipped with a set of knives and different grids. Pellets were dried and stored at 80°C during 24 h. After drying, the pelletized material was injected by an injection-molding machine (Meteor-40, Mateu and Solé). Processing temperature of heated areas of the injector machine was 175°C, 175 and 190°C being the highest corresponding to the nozzle. First and second injection pressures were 120 and 25 kgf cm<sup>-2</sup>, respectively. By means of this

**TABLE I**  
The Silane Coupling Agents Used in this Work



procedure, specimens for tensile and flexural tests were obtained with a shape according to ASTM D638 and ASTM D790 standard specifications, respectively.

#### Chemical analysis of the surface of the materials

XPS spectra were recorded in an XSAM800 (KRATOS) apparatus, operated in the fixed analyzer transmission mode, with a pass energy of 10 eV and nonmonochromatic MgK $\alpha$  and AlK $\alpha$  X-radiations ( $h\nu = 1253.7$  eV and 1486.7 eV, respectively). A current of 10 mA and a voltage of 13 kV were used. Samples were analyzed in an ultrahigh-vacuum chamber

( $\sim 10^{-7}$  Pa) at room temperature, using 60° analysis angles relative to the surface's normal. Samples were transferred from the last rinsing solution inside the introduction chamber under argon atmosphere. Spectra were recorded by a Sun SPARC Station 4 with Vision software (Kratos) using a step of 0.1 eV. A Shirley background was subtracted and curve fitting for component peaks was carried out using Voigt profiles.

#### Contact angle measurements

Dynamic contact angle (CA) measurements were performed using a Dataphysics OCA 20 apparatus. Surfaces were prepared by mild pressing of fibers to form film-like materials suitable for CA measurements. A calibrated droplet of water was deposited on the surfaces and the evolution of CA with time was recorded using a CCD camera with an automatic acquisition of 50 images per second.

#### Fiber morphology evaluation

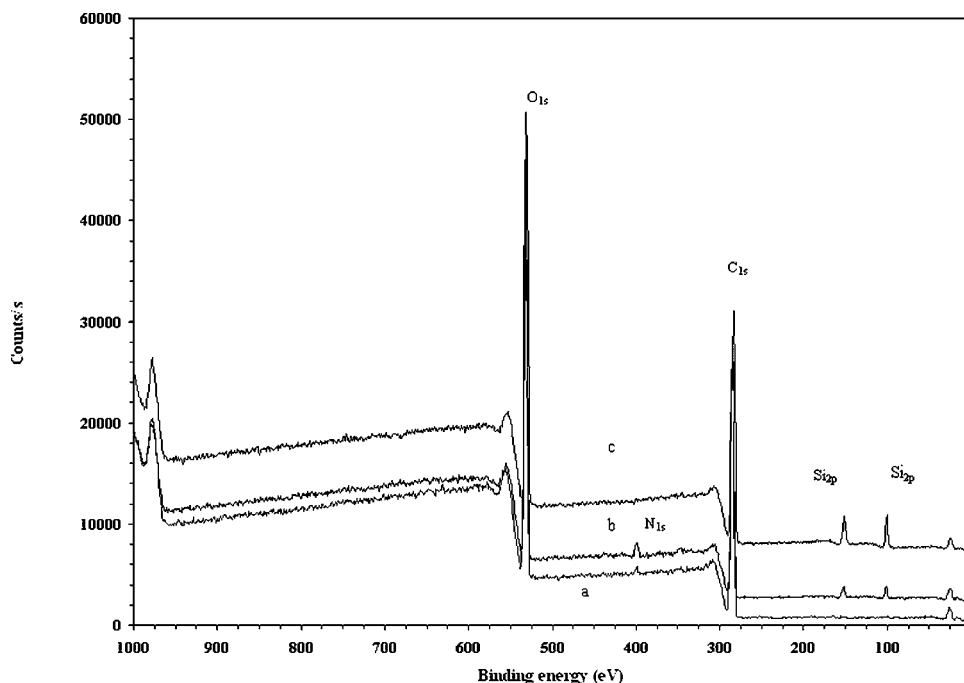
Average fiber morphology was determined using an optical microscope equipped with a CCD camera and image analysis software. These measurements gave the fiber length and particle diameter distribution.

#### Thermal analysis

DSC was performed with a Perkin-Elmer thermal analysis DSC 8230-B equipment fitted with a cooler system using liquid nitrogen. Samples, around 10 mg, were placed in pressure-tight DSC cells and at least two individual measurements were collected. Each sample was heated from 0 to +230 °C at a heating rate of 10°C/min, held at 230°C for 5 min and finally cooled at the same cooling rate. Melting temperature ( $T_m$ ) and crystallization temperature ( $T_c$ ) was taken as the peak temperature of the melting endotherm and crystallization exotherm.

#### Mechanical analysis

Tensile and flexural tests were performed using a Universal Testing Machine (Instron 1122 according to ASTM D638 and ASTM D790 standard specifications, respectively). Before use, samples were stored at 23°C and 50% of relative humidity for 48 h, according to ASTM D618 standard specifications. A minimum of five specimens were used for obtaining each value at room temperature and 50% of relative humidity. Ultimate tensile strength ( $\sigma_t$ , UTS), elastic modulus or Young modulus ( $E_t$ ), flexural strength ( $\sigma_f$ ) and flexural modulus ( $E_f$ ) were studied.



**Figure 1** XPS survey spectra for (a) virgin pine fibers, (b) APS, and (c) MPS treated pine fibers.

### Evaluation of the fracture surface

Surface fractured areas of tensile specimens were observed by scanning electron microscopy (SEM) (Zeiss DMS 960). By means of this technique, it was possible to determine qualitatively adhesion degree between the matrix and reinforcement.

### Water absorption measurements

Sample dimensions for water absorption experiments were 1 cm × 1 cm × 0.5 mm. A minimum of two samples were tested for each material. Samples were weighted and then soaked in distilled water at room temperature. Samples were removed at specific time intervals, blotted to remove the excess of water on the surface, and were immediately weighed. The difference between the mass after a given time of immersion and initial mass compared with initial mass led to determine water absorption.

## RESULTS AND DISCUSSION

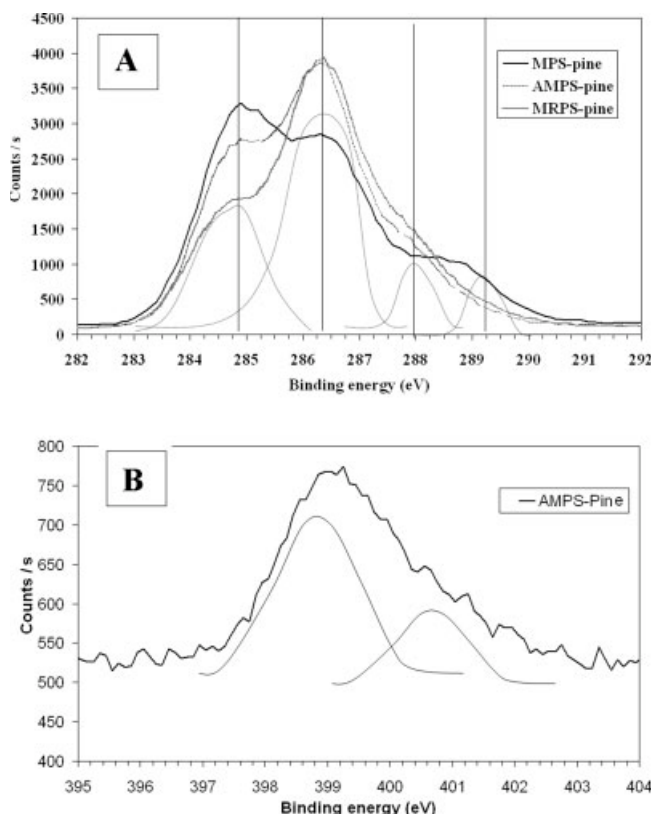
To bring about the surface modification, fibers were kept in contact with the silane solution for 2 h followed by a curing process at 110°C for 1 h after solvent removal. During the first stage of the treatment, silanes were physically adsorbed on the surface of the fibers through hydrogen bonding interaction between cellulose hydroxyl groups and silanol groups (Si—OH) of the silanes. The silanol groups are generated by acid hydrolysis of the triethoxy groups. As reported previously, subsequent heat treatments ensured an

efficient and irreversible chemical bonding of the silane on the cellulose surface through condensation reaction of  $\equiv\text{Si—OH}$  with cellulose hydroxyl groups and self-condensation, giving rise to polysiloxane bridges.

XPS analyses were carried out to give evidence of silane presence and quantify its amount on the fiber surface. Because of the low amount of silane held on the fiber surface, this technique is the most adapted to provide both qualitative and quantitative information, regarding the different elements present on the surface and their chemical environment. Figure 1 depicts XPS survey spectra of electron intensity as a function of binding energy for virgin fibers, MPS-, and AMPS-treated fibers. As expected, virgin fibers displayed only two peaks at about 533 and 285 eV attributed to  $\text{O}_{1s}$  and  $\text{C}_{1s}$ , respectively. On the other hand, silane treated fibers revealed that, in addition to the peaks associated with oxygen and carbon, emission peaks at 103 and 150 eV characteristic of

**TABLE II**  
XPS Chemical Quantitative Analysis for Treated and Untreated Cellulose Fibers

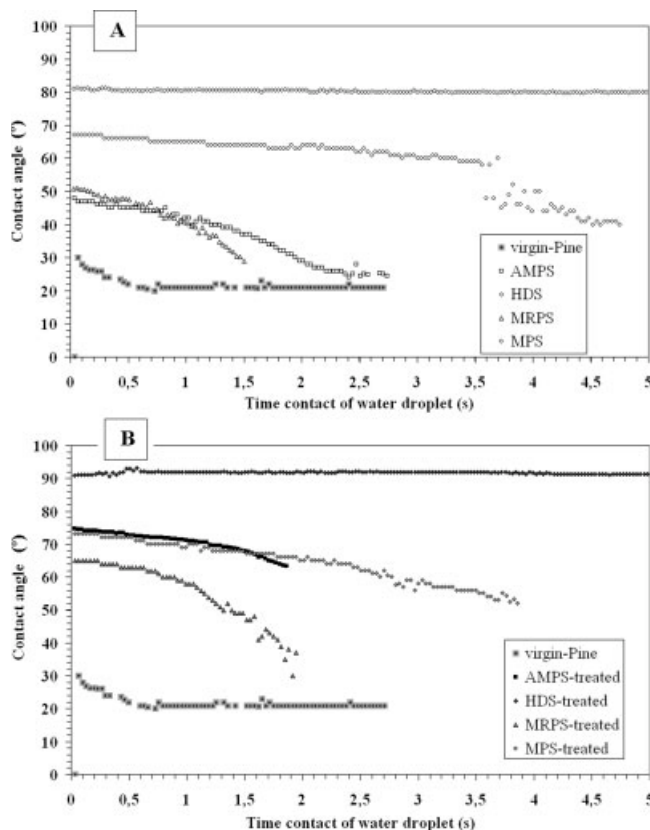
Sample	Element and the corresponding binding energy (eV)				
	C(1s) 285	O(1s) 533	Si(2p) 103	N(1s) 398	S(2p) 165
Virgin pine	54.76	44.8	0.24	0.2	0.0
Pine-MRPS	59.74	37.17	1.54	0.3	1.25
Pine-MPS	46.67	33.96	18.36	1.01	0.0
Pine-AMPS	52.37	35.28	6.77	5.24	0.34



**Figure 2** XPS spectra of (A) C1s carbon peaks for virgin and MPS, MRPS, and AMPS pine fibers; (B) N1s peaks for AMPS pine fibers.

$\text{Si}_{2s}$  and  $\text{Si}_{2p}$ , respectively, were found. The presence of these peaks confirms the attachment of the silane on cellulose fibers. Elemental composition on the surface layer, determined from the area of each peak normalized with sensitivity factors, for different silane modified fibers are summarized in Table II. It is worth noting that the amount of sulfur and nitrogen is close to that of silicon in MRPS and AMPS, respectively, which gives further confirmation of the accuracy of the quantitative analysis. Likewise, the amount of anchored silane varied from 1.5 up to 18%, according to the silane structure. The highest level is observed for MPS-treated fibers, followed by AMPS and MRPS. Better information regarding chemical environment of different elements detected on the surface of fibers could be emerged through an amplification of  $\text{C}_{1s}$ ,  $\text{N}_{1s}$ , and  $\text{Si}_{2p}$  peaks related to different fibers [Fig. 2(A)].  $\text{C}_{1s}$  peak was deconvoluted in four different carbon types fitted at 284.8, 286.5, 288, and 289.3 eV and attributed to C1 (C—C/C—H/C—Si), C2 (C—O/C—OH), C3 (O—C—O), and C4 (O—C=O), respectively. C4 peak appeared only in the presence of MPS. The increase in C1 contribution after treatment is in agreement with silane anchoring on cellulose surface, since its presence brings three aliphatic carbons per anchored silane coupling agent. With more amount of bonded sili-

con, more was the contribution of the C1 peak. The amino N1s peak could be deconvoluted in two peaks at 399.0 and 400.8 eV corresponding to amino groups ( $-\text{NH}_2$ ) and to their protonated form ( $-\text{NH}_3^+$ ), respectively [Fig. 2(B)]. The higher contribution of the former suggests that the major part of amino groups in adsorbed AMPS is in their unprotonated form. The evolution of the fibers surface properties was investigated by CA measurements with water as liquid probe. Figure 3 depicts dynamic CA versus time for virgin and silane treated fibers after curing treatment and after several weeks of aging. Before treatment, CA did not exceed  $30^\circ$  and dropped rapidly with time, as a result of the high hydrophilic character of cellulose. Silane treatment brings about an increase in CA which depends on the silane structure; the highest effect was observed with HDS, followed by MPS, MRPS, and AMPS. High CA in the presence of HDS and MPS could be ascribed to their relatively high amount on the surface and to their hydrophobic character. On the other hand, the presence of amino groups on AMPS silane may explain the persistence of the hydrophilic character after treatment. However, the possible interference of  $\equiv\text{Si}-\text{OH}$  groups on the surface character should be taken into account. Indeed, when fibers were sub-



**Figure 3** Water contact angles change for virgin and treated pine fibers (A) after heat treatment at atmospheric pressure and (B) after heat treatment at partial vacuum.

mitted to a further heat treatment at 110°C for 1 h under partial vacuum ( $5 \times 10^{-2}$  mmHg), a significant raise in CA was noted as shown in Figure 3. This result was imputed to further condensation between  $\equiv\text{Si}-\text{OH}$  groups, which gives rise to a bidimensional polysiloxane network that hinders more efficiently hydroxyl groups on the surface of the fibers. Therefore, for obtaining an efficient anchoring of the silane coupling agent on cellulose substrate, it is advisable to carry out a heat treatment under partial vacuum to ensure a high level of surface modification. It is worth noting that treated fibers used for this work in composite preparation were only subjected to heat treatment at 110°C at atmospheric pressure, without recourse to vacuum. Indeed, it was difficult to carry out this procedure efficiently for a relatively high amount of fibers.

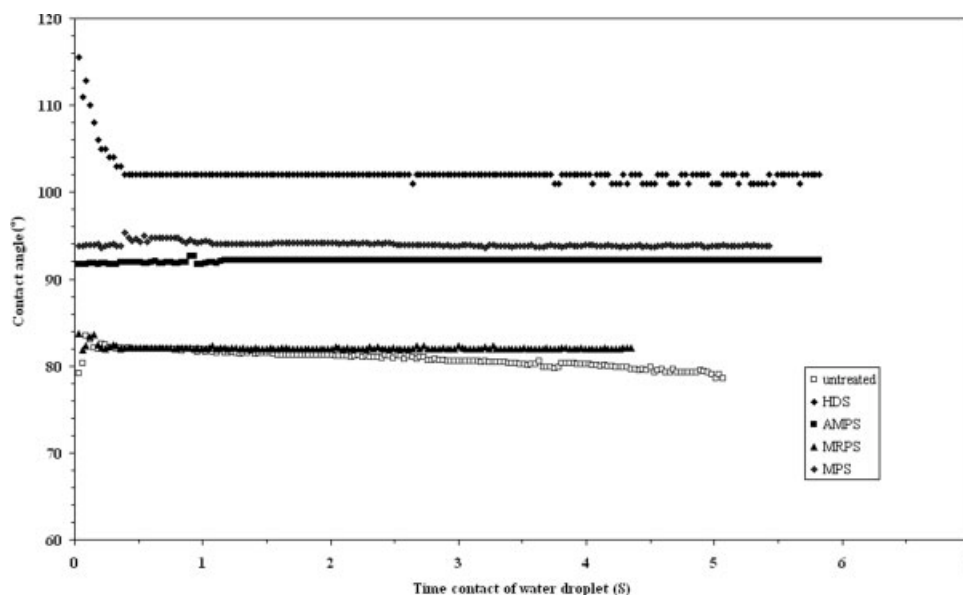
CA measurements have also been carried out on fibers recovered from composites after complete removal of polypropylene matrix by soxhlet extraction with xylene. Results reported on Figure 4 revealed that ensued fibers exhibited a higher hydrophobic character, with a CA exceeding 80°, which did not evolve after repeated soxhlet extraction for a longer time. The more the CA of silane treated fibers before their blend with matrix, the more the hydrophobic character of extracted fibers. This phenomenon is probably imputed to the presence of residual polypropylene chains confined inside the pores of the fibers. Likewise, a chemical linkage between the surface of the fiber and polypropylene can be considered, through a transfer reaction followed by radical combination or an addition reaction between radical species and methacrylic group of MPS. The transfer site is a

reactive function within the radical silane moiety such as mercapto, amine or alkyl groups. The radical species may be generated through peroxide decomposition which arises from the thermal oxidation likely to occur during the processing of the composite.

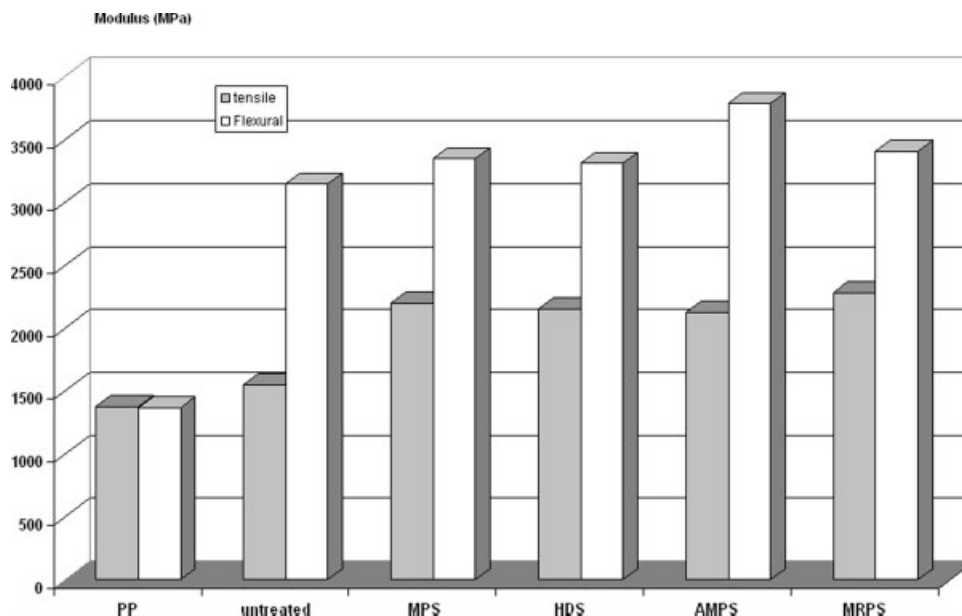
### Mechanical properties

Mechanical properties of composites have been investigated using tensile and flexural test carried out on composite samples with 30 wt % of pine fibers loading. The incorporation of cellulose fibers avoided yielding and reduced plastic deformation, compared with that of the unfilled matrix. The effects of fiber addition and fiber treatment on modulus and strength (tensile and flexural) are shown in Figures 5 and 6, and Table III, from which the following remarks could be pointed out:

- Tensile modulus increased only by 12% after incorporation of untreated fibers to PP matrix.
- Treatment with silane led to a significant rise (about 60% compared with that of unfilled matrix) in tensile modulus. A higher effect was noted for MRPS, followed by MPS, HDS, and AMPS,
- Flexural modulus was amplified by 130% with fiber addition and modestly enhanced after silane treatment. Compared with that of untreated fibers, flexural modulus was raised by 6, 5, 20, and 8% in the presence of MPS, HDS, AMPS, and MRPS, respectively.
- A slight increase in ultimate tensile strength was observed when the polymer matrix was reinforced with surface modified fibers. The highest value



**Figure 4** Water contact angles change for fibers, both untreated and silane treated, after PP extraction by soxhlet washing with xylene.



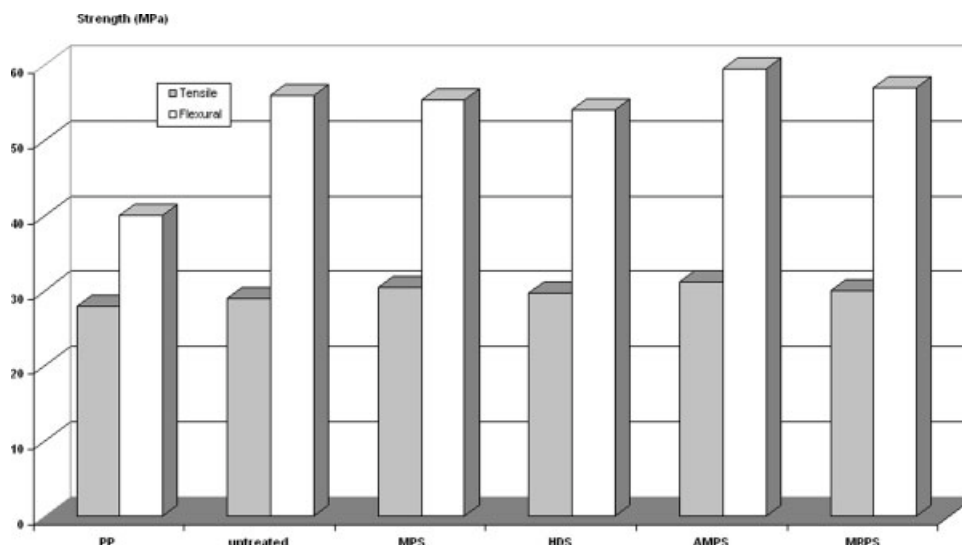
**Figure 5** Young's and flexural modulus of PP-based composites reinforced with 30 wt % pine fibers subjected to different silane treatments.

corresponded to the material reinforced with AMPS, giving rise to an increase of 11%, compared with that of pure PP.

Flexural strength was enhanced by about 40% after fiber addition and it is equally not affected by silane treatment. A great decrease in elongation at break was noted because of fiber incorporation. Its value fell from 20% for pure PP matrix until below 4% for the filled one. Fiber treatment led to a decrease in elongation at break by 20–30% compared with that of untreated fibers. Similar trends were observed in flexural elongation.

In comparison with the work carried out on LDPE, similar trends regarding modulus and elongation are noted. However, as opposed to PP-based composites, a significant rise in tensile strength was observed after treatment of fibers with MPS, MRPS, and APS silane coupling agents, when LDPE was used as matrix.<sup>23</sup> It is worth noting that numerous studies using other lignocellulosic fibers treated with diverse silane coupling agents have noted a continuous fall in tensile strength after fiber addition to PE or PP matrix.<sup>15,17</sup>

It is well known that the mechanical behavior of heterogeneous materials depends on four main parameters: (i) modulus of each component, (ii) volume fraction of each component, (iii) morphology



**Figure 6** Tensile and flexural strength of PP-based composites reinforced with 30 wt % pine fibers subjected to different silane treatments.

**TABLE III**  
**Tensile and Flexural Properties of Unfilled PP and PP-Based Composites Reinforced with 30 wt % of Pine Subjected to Different Silane Treatments**

	Tensile properties			Flexural properties			D <sup>a</sup> (mm)
	$\sigma_t$ (MPa)	$\varepsilon_{\text{break}}$ (%)	$E_t$ (GPa)	$E_f$ (GPa)	$\sigma_f$ (MPa)	$\varepsilon_{\text{break}}$ (%)	
PP	28.0 [0.2]	>20	1.40 [0.04]	1.37 [0.05]	40 [0.8]	–	–
Untreated	29.0 [0.9]	4.5 [0.4]	1.50 [0.12]	3.14 [0.14]	56 [0.4]	6.2 [0.4]	0.40
MPS	30.5 [0.7]	3.4 [0.3]	2.20 [0.13]	3.34 [0.18]	55 [1.1]	5.3 [0.2]	0.29
HDS	29.7 [0.8]	3.5 [0.3]	2.15 [0.04]	3.32 [0.08]	54 [1.0]	5.6 [1.6]	0.24
AMPS	31.2 [0.4]	3.5 [0.2]	2.13 [0.10]	3.88 [0.14]	59.5 [2.6]	5.3 [0.3]	0.33
MRPS	30.0 [0.8]	3.1 [0.4]	2.28 [0.13]	3.41 [0.10]	57 [0.8]	4.6 [1.2]	0.27

Values in brackets refer to 95% confidence interval.

<sup>a</sup> Arithmetic average fibres' length (in mm) after extraction of PP matrix.

and aspect ratio of the filler, length distribution, and orientation of fibers in the composite, and (iv) interface properties due to its liability in load transfer. The latter parameter depends mainly on the degree of interaction between phases, i.e., fiber treatment for fiber-filled composites. In this work, as the main topic to study is the influence of the coupling agent, only three of these factors (i.e., i, ii, and iv) have been investigated using different characterization techniques.

The degree of crystallinity ( $X_c$ ) of pine/PP composites, calculated using the heat of melting per gram of matrix in the composite (normalized value) and the melting temperature as determined by DSC measurements, are reported in Table IV for both unfilled PP and reinforced composites with 30 wt % of pine, having undergone the same processing procedure, i.e., extrusion and injection molding. All the samples displayed only a single melting endothermic peak which slightly decreased from 169 to 165°C after the fibers addition and to 163°C in presence of the silane coupling agent [Fig. 7(A)]. The crystallization temperature ( $T_c$ ), determined after a cooling

process from 230°C to room temperature, followed the opposite trend and was increased from 114°C for neat PP up to 122°C for the different composite [Fig. 7(B)]. Conversely, the crystallinity degree was raised from 30% up to 56% by the fiber incorporation within the PP matrix, which could be imputed to the nucleating effect of the fibers for the crystallization of the PP matrix. On the other hand, within the experimental accuracy, the crystallization level does not seem to evolve significantly after the treatment of the fibers by the different silane coupling agents used.

Because of their extremely finite size and their higher modulus, the crystalline regions behave as filler particles and improve the composite modulus. However, since the silane treatment does not bring about a significant raise in the crystallization degree, this later could not account for the notable improvement, by more than 40%, in the tensile modulus after the fiber treatment with silane.

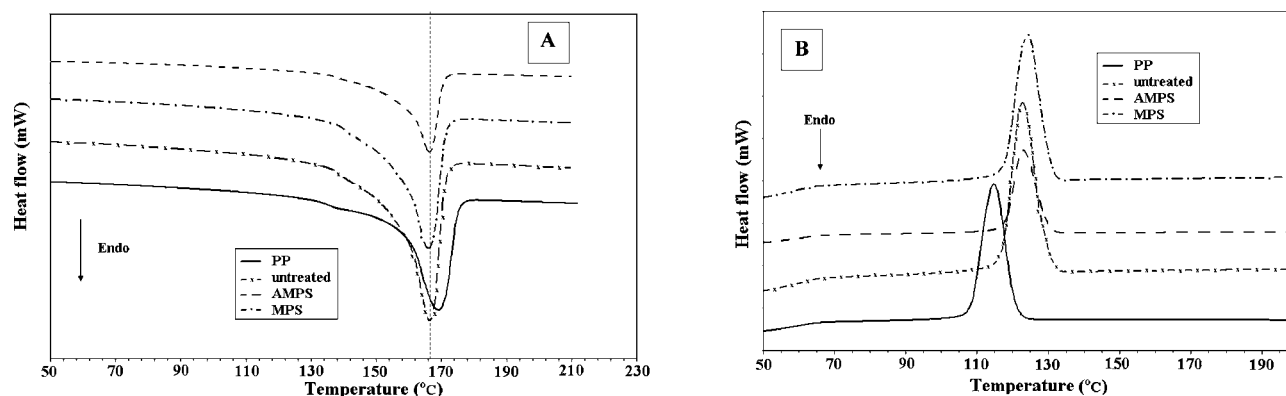
The second factor that has been investigated is the fiber average length after processing. Indeed processing techniques such as extrusion and injection are known to induce fiber break-up owing to the strong

**TABLE IV**  
**Normalized Melting Enthalpy ( $\Delta H_m$ ), Degree of Crystallinity ( $X_c$ ), Melting ( $T_m$ ) and Crystallization Temperature ( $T_c$ ) of PP-Pine Composites Reinforced with Different Silane-Treated Fibers at 30 wt %**

		$\Delta H_m$ or $\Delta H_c$ (J/g)	$T_m$ or $T_c$ (°C)	$X_c$ (%)	$T_m - T_c$ (°C)
PP	Heating	50.4	169.2	29.5	54.5
	Cooling	108.0	114.7	61.0	
Composite with 70 wt % PP					
Untreated	Heating	96.0	165.0	56.5	42.2
	Cooling	115.0	122.8	68.0	
MRPS	Heating	100.5	163.8	59.0	39.8
	Cooling	112.0	124.0	66.0	
MPS	Heating	101.5	166.0	60.0	41.8
	Cooling	120.8	124.2	71.0	
HDS	Heating	101.0	162.3	59.4	37.9
	Cooling	107.9	124.4	63.0	
AMPS	Heating	98.6	163.5	58.0	40.5
	Cooling	108.5	123.0	63.8	

$X_c = \Delta H_m / W_F \cdot \Delta H_m^0$ , where  $\Delta H_m^0 = 170 \text{ J g}^{-1}$  is the melting enthalpy for 100% crystalline PP and  $w_F$  is the weight fraction of polymeric matrix material in the composite.

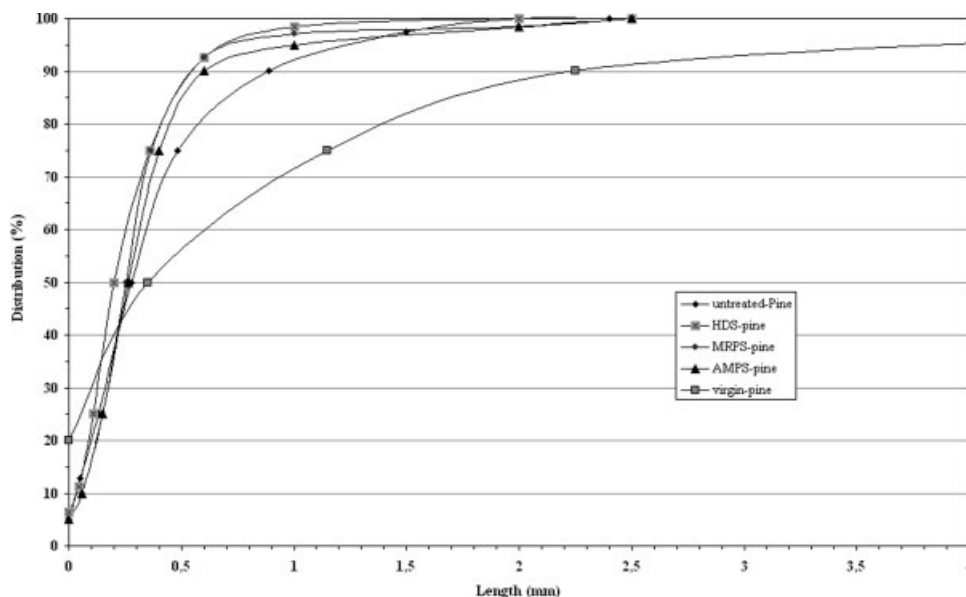




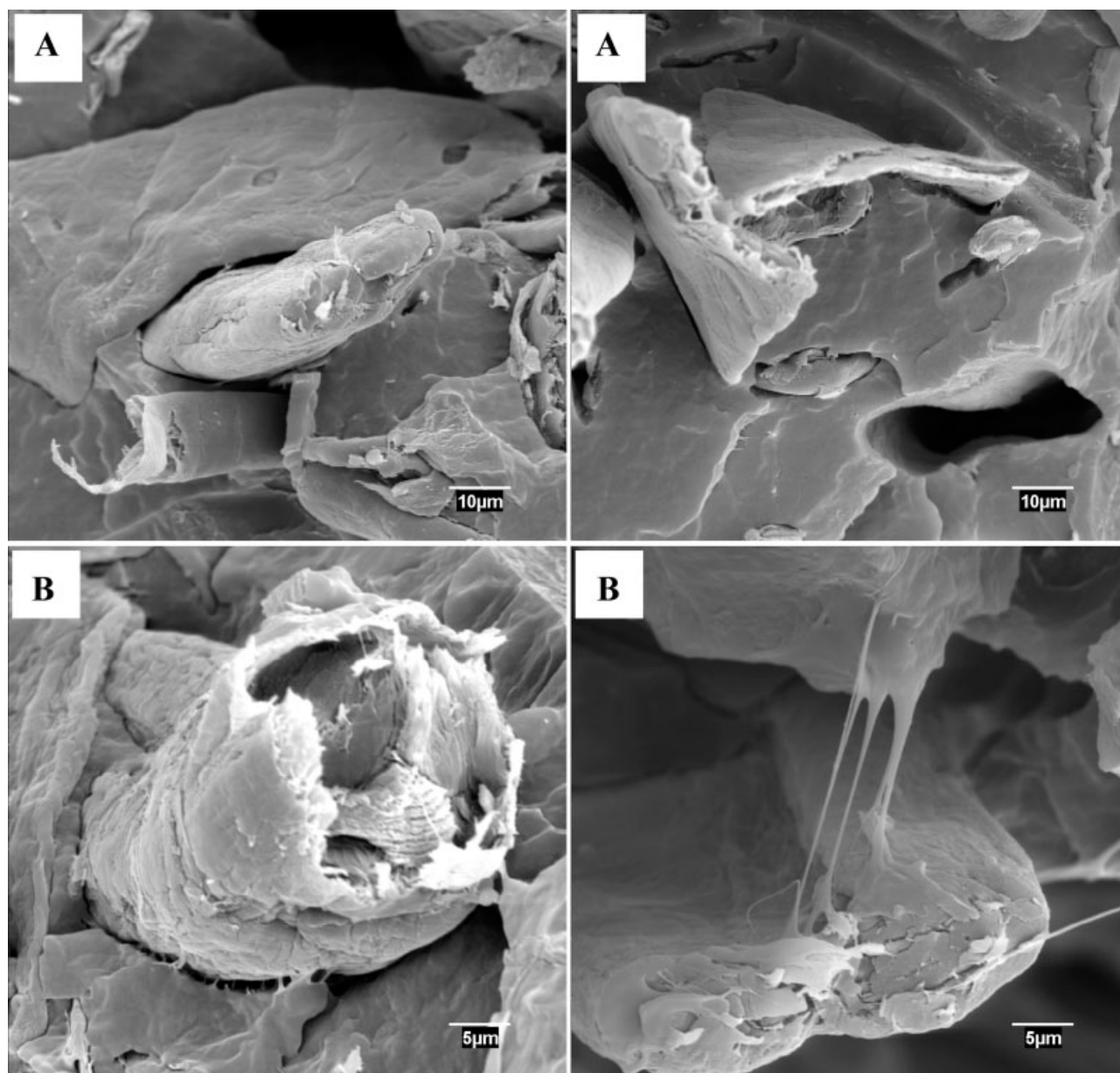
**Figure 7** DSC curves of heating (A) and cooling (B) PP-based composites reinforced with 30 wt % pine fibers subjected to different silane treatments.

shear stress acting in viscous molten polymer. The length distribution after the mixing process followed by injection molding for untreated and silane modified fibers are presented in Figure 8 and the corresponding arithmetic average is reported in Table III. Fiber dimension measurements carried out after soxhlet extraction of PP matrix by xylene is based on an image analysis technique using a CCD camera and a polarized light source. Both, untreated and treated fibers were subjected to a severe decrease in fiber size after mixing and injection. The arithmetic average length fell down from 1.1 mm for virgin fibers to 0.4 mm for untreated fibers and attained 0.29, 0.24, 0.33, and 0.27 mm for AMPS, MRPS, MPS, and HDS silane, respectively. The higher shortening effect observed for treated fibers may be related to a better compatibility with the matrix, generated by the presence of silane on its surface which in turn

reduces the lubrication effect during shearing and further increase in fiber–fiber and fiber–matrix friction. The severe breaking effect that occurred after composite processing may explain the low effectiveness of both fiber incorporation and their treatment with silane coupling agents on tensile strength. Indeed, according to the Cox approach, reinforcement efficiency increases with aspect ratio reaching a maximum in continuous composite.<sup>23</sup> Conversely, there is a minimum critical fiber length ( $l_c$ ) under which the stress transfer from matrix to fibers is not enough to reach fiber failure strength. For practical purposes, it can be considered that the fiber diameter remained constant (as has been confirmed by SEM observations), and hence a great proportion of fibers in the composite may be shorter than  $l_c$  and therefore are not fully loaded. This hypothesis is corroborated by SEM observation (Fig. 9) which clearly



**Figure 8** Distribution of fibers' length for virgin fibers and fibers extracted from the composite.



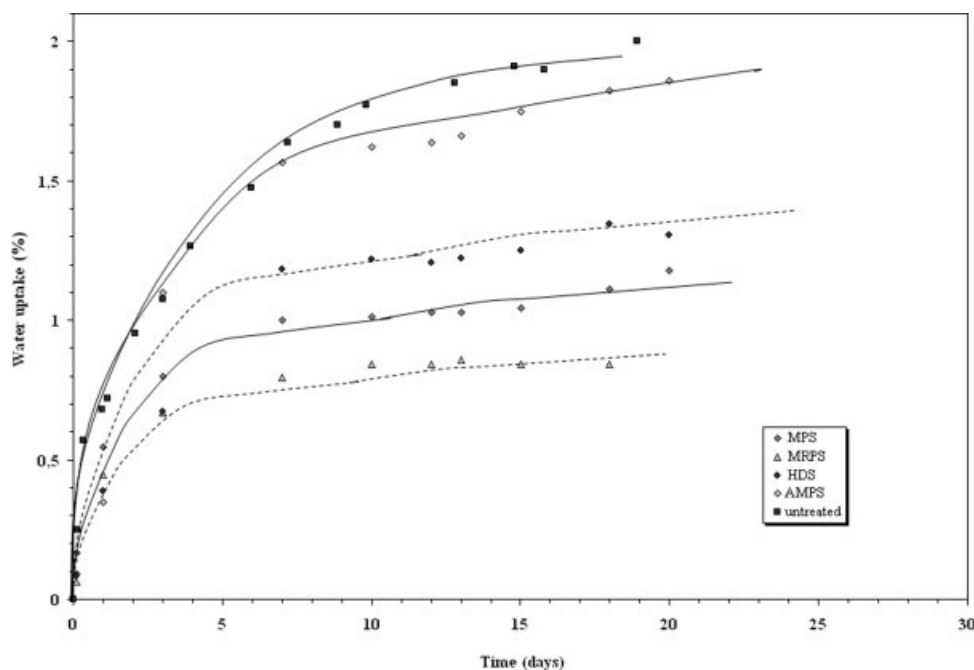
**Figure 9** SEM micrographs of freshly fractured surfaces of PP-based composites reinforced with 30 wt % pine fibers; (A) untreated, (B) APS-treated fibers.

indicated that a high fraction of fibers on the fractured surface seems to be pulled out from the matrix giving rise to holes, whereas others are broken off near the surface. The former corresponds to fibers shorter than  $l_c$ , for which the strength cannot reach the fiber's failure stress, and so they are not broken and they merely slipped through the interface.

Given the fact that the crystallization degree of the PP matrix did not evolve significantly after the silane treatment of the fibers, and despite the decrease in the fiber's length after their treatment, we could infer that the significant enhancement of the tensile modulus after silane treatment could be attributed to the improvement in the fiber–matrix adhesion through

(i) a possible chemical reaction between the reactive groups linked to the silane coupling agent and the PP matrix, (ii) and also physical interaction that improves fiber wetting, enhancing the compatibility between the two phases. The resulting better interface bonding quality yields to a higher deformation restriction of the matrix within the elastic zone increasing tensile modulus.

If we consider MPS, MRPS, or APS, the improvement in the interfacial adhesion between the fibers and the PP matrix could be related to interfacial chemical bridging between the two phases. Indeed, based on their structure, these silanes contain functional groups which can react with radical species to



**Figure 10** Water uptake versus immersion time at 25°C for PP-based composites reinforced with 30 wt % pine. The lines serve to guide the eye.

generate a covalent bond; either by an addition reaction with the  $\pi$ -bond (for MPS) or through a transfer reaction with the mercapto moiety or amino groups. The radical species may be generated through peroxide decomposition which arises from the thermal oxidation likely to occur during the processing of the composite. Likewise, the evolution of the surface properties after silane treatment i.e., surface energy lowering, namely with relatively hydrophobic silane is likely to contribute also to the improvement of the fiber–matrix compatibility by better wetting of the melted matrix to the surface filler.

### Water absorption properties

The most serious handicap related to the use of lignocellulosic fibers in composite materials is their relative sensitivity to water, which reduces dramatically their mechanical performances in a damp atmosphere. Therefore, besides the improvement in the interfacial adhesion, the coupling agent must reduce the water uptake of lignocellulosic composite.

The evolution of water absorption as a function of immersion time is shown in Figure 10 for PP-based composites reinforced with 30 wt % pine fibers subjected to different fiber surface treatments. For all composites, water absorption was found to increase with immersion time, reaching a plateau after about 10–15 days. For unfilled PP, water absorption was very low because of the nonpolar nature of this polymer. With the incorporation of hydrophilic lignocellulosic fibers water molecules are able to diffuse inside

the composite and to accumulate within the fibers leading to some expansion of the material. For composites, the equilibrium water uptake was found to depend on the treatment of the fibers. Thus, PP composites containing untreated fibers exhibited 2% of water absorption at plateau, whereas composites based on HDS-, MPS-, MRPS- and AMPS-treated fibers absorbed 1.3, 1.2, 0.82, and 1.85% of water, respectively. The reduction in water uptake after silane treatment may be associated on one hand to the ability of these coupling agents to bring about some hydrophobic character to fibers which decreases their potential interaction with water molecules, and on the other hand to their capability to enhance fibers–matrix adhesion.

### CONCLUSIONS

Composites materials based on pine cellulose fibers, treated with different silane coupling agents, and PP matrix were prepared and characterized, in terms of mechanical performances, thermal properties, and water absorbance behavior have been elaborated. The surface modification has been accomplished satisfactorily, since a C–Si/C–C linkage contribution has been obtained in XPS spectra. It means that there is some interaction between natural fibers and silane derivatives. The addition of silanes on the surface produced an increase in CA due to a change in the polarity on the surface. This change produces an increase in Young's and flexural moduli giving rise to a material with an enhanced stiffness. A very slightly increase was appreciated regarding ultimate

tensile strength. Water uptake of the samples of composites was in all of the cases lower than 2 wt %, which indicates a controlled dimensional stability. With all of these results, it is possible to conclude that surface modification of pine fibers, using silane coupling agents give rise to materials useful for increasing the stiffness of polymer matrices to obtain reinforced composites.

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