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Interaction of Silane Coupling Agents with Cellulose

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The adsorption of several prehydrolyzed alkoxysilanes onto the surface of cellulosic fibers in ethanol/water mixtures has been studied quantitatively. The corresponding isotherms show the formation of a monolayer followed by further adsorption. The nature of the fourth substituent on the silane plays a specific role on the features of this association. Whereas at room temperature only dispersive and polar attractive interactions occur, heating above 100 °C produces condensation reactions resulting in covalent bonding between the substrate and the silane forming the monolayer. As a result of this investigation, the possibility of calling upon this surface modification in order to compatibilize cellulosic fibers with polyolefinic matrixes for the elaboration of composite materials seems to be a promising strategy.

Introduction

Cellulosic fibers constitute an interesting alternative to the inorganic counterparts used as reinforcing agents in the preparation of composite materials^{1–5} because of their good mechanical properties, low cost, ubiquitous availability in a variety of forms, and recyclability. These advantages, however, are counteracted by the marked hydrophilic character of these macromolecules which, on one hand, limits their compatibility with widely used hydrophobic polymeric matrixes such as polyolefins and, on the other hand, can reduce the mechanical properties of the composite if moisture is absorbed as they age. The consequences of the former drawback are (i) a bad adhesion between the fiber and the matrix, which reduces the load transfer efficiency from the matrix to the fibers,⁶ and (ii) an uneven dispersion of the fibers within the matrix. It is therefore necessary to modify the surface properties of cellulosic fibers to minimize these problems. Several approaches have been explored, such as physical treatments by corona⁴ or plasma,⁷ and chemical grafting with molecules and macromolecules which display a good compatibility with the matrix and introduce surface hydrophobicity.^{8–14}

The chemical modification by coupling agents susceptible to react with the fibers and the matrix constitutes a particularly astute way of controlling the quantity and the nature of the groups present at their surface. Moreover, it creates covalent bridges between the fibers and the matrix which ensure the best mechanical properties for the composite. Several types of reagents have been studied in this context, among which anhydrides and isocyanates^{9–10} or organosilanes^{13,14} are the most representative. To the best of our knowledge, only two studies on the interaction between silane-based reagents and cellulose and the incidence of this treatment on the mechanical properties of the ensuing composites have been published to date.^{13,14} Because these investigations concentrated mostly on the end result and did not focus on the actual interactions between cellulose and the only silane used, we decided to undertake a more thorough study aimed at unraveling these features.

The silanes considered here bear the general formula R–Si–(X)₃, where X is an oxyalkyl group and R an organic moiety, which is chosen as a function of the nature of the matrix. The industrial development of these products is mostly due to their application as coupling agent between glass fibers and polymer matrixes¹⁵ and has led to a wide diversity of structures and properties. It seemed therefore appropriate to test them on cellulosic fibers, which bear the same potentially reactive groups, i.e., OH functions.

Materials and Methods

The fibers used in this work were commercial microcrystalline cellulose (TECHNOCEL-150DM). Their average length was about 50 μm, and their specific surface, measured by the BET technique using nitrogen as the adsorbed gas, was found to be 2.5 m²/g. Inverse gas chromatography analysis of this substrate provided the following information regarding its surface properties: the dispersive component of the surface energy was found to be 38 ± 1 mJ/m² at 50 °C and the acceptor–donor number ratio was 3.0 ± 0.2, i.e., the typical acidic character of most cellulose fibers. The presence of negative moieties was confirmed

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Table 1. The Silane Coupling Agents Used in This Work

Silane	Formula
MPS	$\text{CH}_2=\underset{\text{CH}_3}{\text{CH}}-\text{COO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Si}(\text{OCH}_3)_3$
APS	$\text{NH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Si}(\text{OC}_2\text{H}_5)_3$
PAPS	$\text{C}_6\text{H}_5-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Si}(\text{OC}_2\text{H}_5)_3$
TAS	$\text{NH}_2-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Si}(\text{OC}_2\text{H}_5)_3$
MRPS	$\text{HS}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Si}(\text{OC}_2\text{H}_5)_3$

by ζ potential measurements which gave 10 ± 2 mV at room temperature.

The five silane coupling agents chosen for this study were kindly provided by OSI-WITCO. Their structures are given in Table 1. Since the only methoxy derivative, viz., MPS, was submitted, like all the other silanes, to a prehydrolysis treatment in an ethanol/water mixture (see below), most of the methoxy moieties were converted to ethoxy counterparts by exchange reaction with the excess of alcohol. It follows that all the hydrolyzed silane oligomers adsorbed on cellulose bore ethoxy functions.

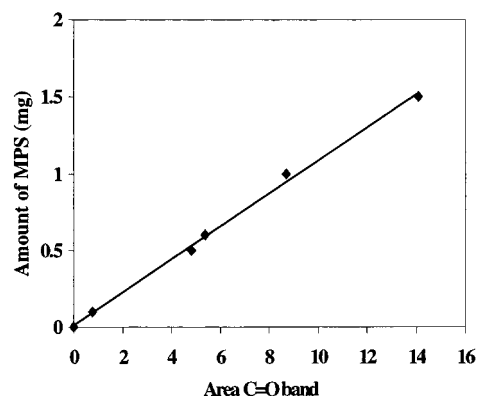
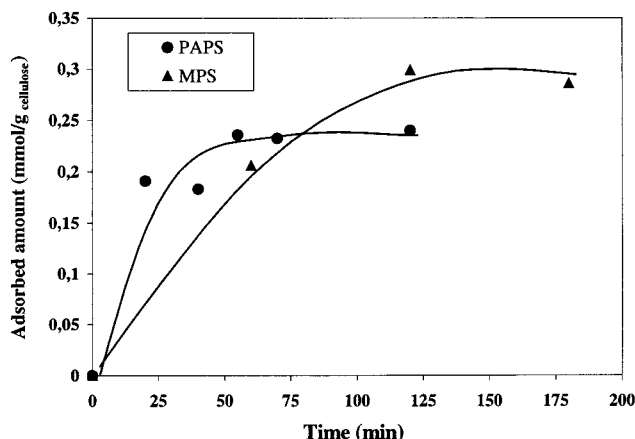
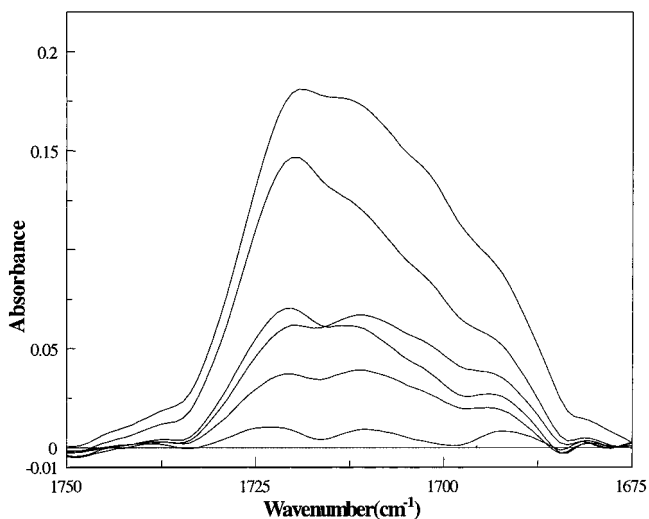
All other reagents and solvents were commercial products of the highest purity available.

The adsorption isotherms were established by adding different amounts of the given silane (prehydrolyzed for 2 h at room temperature) to a 5% w/w cellulose suspension in a mixture of 80/20 v/v ethanol/water and by stirring for 2 h. The cellulosic fibers were then centrifuged at 2500 rpm for 20 mn. Different techniques were used in order to determine the quantity of adsorbed coupling agent depending on the actual silane used. For MPS, it was assessed by FTIR spectroscopy through the area of the C=O peak. For this purpose, KBr pellets containing 10 mg of modified cellulose and 200 mg of KBr were prepared and their FTIR spectra recorded. For PAPS, it was determined by measuring the optical density at 250 nm of the UV spectrum of the silane remaining in solution, after having adjusted the pH to 8–9 by adding a small volume of a NaOH concentrated solution, to avoid the protonation of the amine function. In the case of APS and TAS, the residual silane was determined on the filtrate by colorimetry according to the following procedure:¹⁶ An excess of salicylic aldehyde solution was added to the filtrate to induce its conversion of the amino groups borne by the silane agent into the corresponding imine functions, which were quantified after an hour by UV spectroscopy at 404 nm. Each technique was accompanied by the establishment of a calibration curve.

Special attention was paid to ensure the validity of the procedures used to determine the extent of adsorption of each silane. For all the spectroscopic methods the domains of concentration studied remained within the applicability of Lambert–Beer law, as shown in the example of Figure 1. Moreover, since the adsorption isotherms must be assessed when equilibrium is reached, the adsorption kinetics of each silane were investigated. For PAPS and MPS it was found that 1 and 2 h, respectively, were needed to reach equilibrium (Figure 2). Therefore, in all the experiments described in this paper the reaction medium (cellulose + solvent + coupling agent) was kept under stirring for 2 h before measuring the extent of adsorption.

Results and Discussion

The FTIR spectra of cellulose treated with MPS showed a gradual increase in the C=O peak area as a function of the initial concentration of added silane. Figure 3 shows

**Figure 1.** Calibration curve giving the amount of MPS, as a function of the area of its C=O peak.**Figure 2.** Time evolution of the adsorbed quantities of MPS and PAPS from solutions with 0.08 mol/L initial concentration.**Figure 3.** Typical evolution of the C=O peak of a cellulose sample treated with different concentrations of MPS.

a typical example of this behavior. These areas were used to establish the adsorption isotherms presented in Figure 4, which indicated that the amount of adsorbed MPS increased with increasing initial concentration C_0 and reached a plateau situated at about 0.24×10^{-3} mol of adsorbed MPS per gram of cellulose. After a C_0 value of about 0.1 mol/L, the adsorption started to increase and the isotherm form suggested the formation of multilayers.^{17,18} It is also worth noting that MPS displays a low adsorption affinity toward the cellulose substrate, as witnessed by the large deviation between the theoretical

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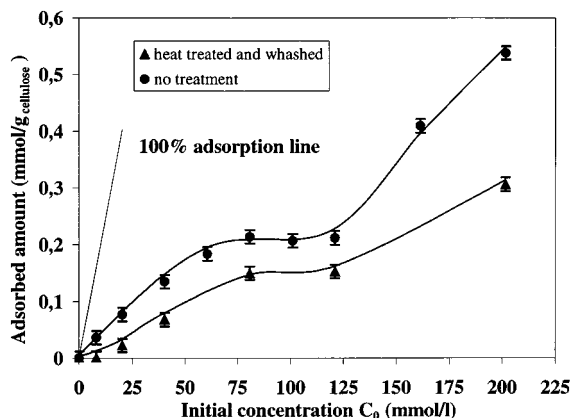


Figure 4. Adsorption isotherms of MPS onto the cellulose surface before and after heat treatment at 110 °C, followed by Soxhlet extraction with ethanol.

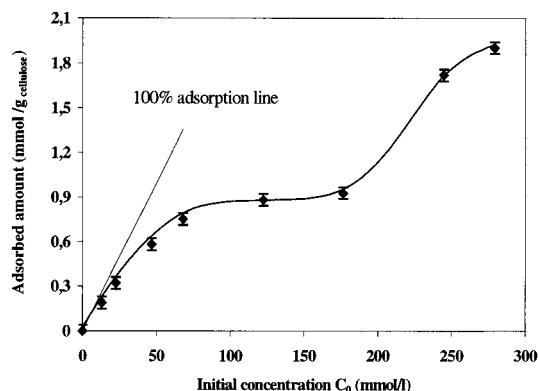


Figure 5. Adsorption isotherm of APS onto the cellulose surface.

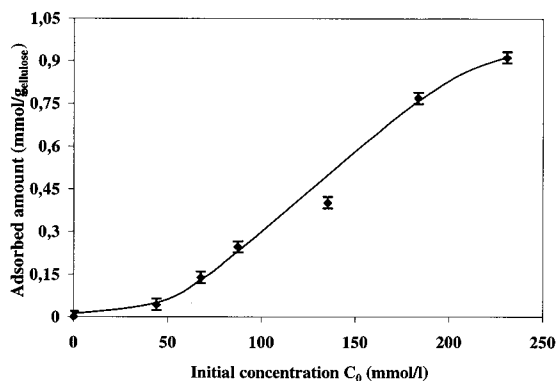


Figure 6. Adsorption isotherm of PAPS onto the cellulose surface

line corresponding to 100% adsorption and the experimental curve.

The adsorption isotherms of amine-based silanes are presented in Figures 5, 6, and 7. APS and TAS were found to show the same trend as that observed with MPS, except for the fact that in the low C_0 range, the adsorption of these two agents was closer to the 100% line, which indicates a higher affinity of these coupling agents with the cellulose substrate. In the case of PAPS a different behavior was observed. Indeed, for a C_0 value lower than 0.03 mol/L, practically no absorption was detected, after

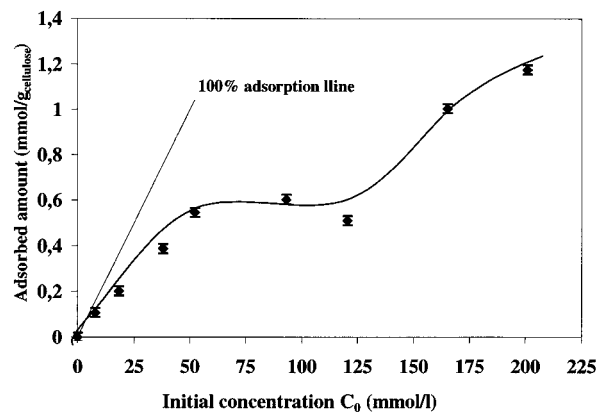


Figure 7. Adsorption isotherm of TAS on cellulose surface.

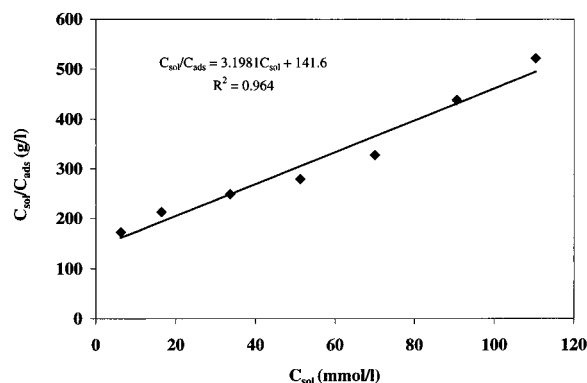
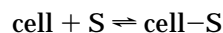


Figure 8. Application of the Langmuir approach to the cellulose samples treated with MPS.

which the adsorption increased in a nearly linear fashion. This feature will be discussed later.

The adsorption data of MPS, APS, and TAS were fitted according to a Langmuir model.¹⁹ Thus, the reaction between cellulose and the silane coupling agent can be written as follows:



It follows that

$$C_{\text{ads}} = \frac{KC_{\text{max}}C_{\text{sol}}}{1 + KC_{\text{sol}}}$$

$$\frac{C_{\text{sol}}}{C_{\text{ads}}} = \frac{1}{C_{\text{max}}} C_{\text{sol}} + \frac{1}{KC_{\text{max}}}$$

where C_{ads} is the concentration of adsorbed molecules at the cellulose surface, K the adsorption equilibrium constant, C_{sol} the residual concentration of the silane in the solution, and C_{max} the maximum concentration of adsorbed molecules at the cellulose surface,

Plotting $C_{\text{sol}}/C_{\text{ads}}$ vs C_{sol} gives a clear-cut idea about the validity of this model, in the present context. The linearity of the plots for MPS, APS, and TAS, shown in Figures 8, 9, and 10, respectively, confirmed that the Langmuir model was an adequate choice. It should be specified that only the first region of the adsorption isotherms was taken into account, since the model applies to monolayer formation. The adsorption equilibrium constant K , as well as the maximum concentration of adsorbed molecules at

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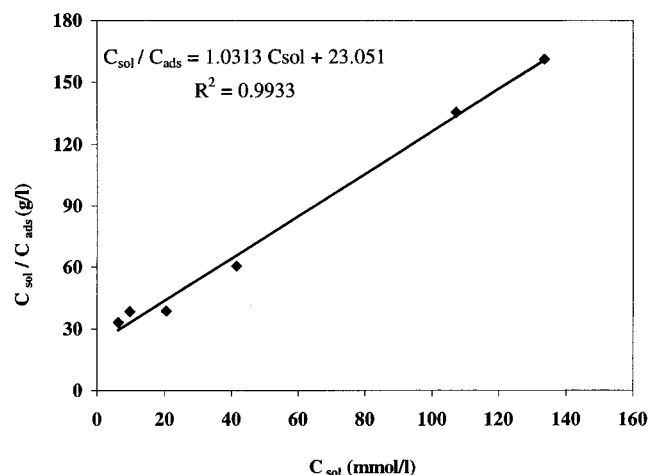


Figure 9. Application of the Langmuir approach to the cellulose samples treated with APS.

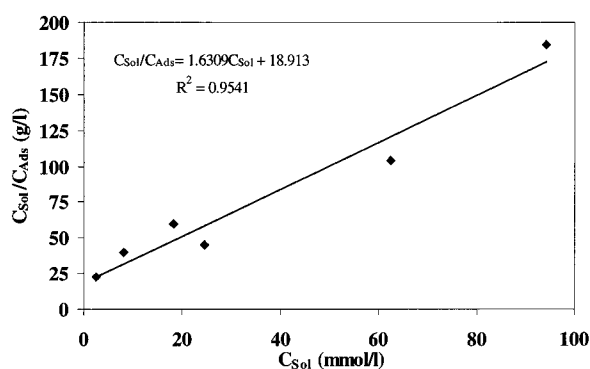


Figure 10. Application of the Langmuir approach to the cellulose samples treated with TAS.

Table 2. Results Related to the Adsorption of Three Silanes on Cellulose

silane	C_{\max}^a (mmol/g of cellulose)	C_{\max}^b (mmol/g cellulose)	K_{ads} (g/mol)	ΔG_{ads}^0 (kJ/mol)
MPS	0.23	0.31	22	-7.50
APS	0.91	1.01	42	-9.40
TAS	0.60	0.61	86	-11.04

^a Determined from adsorption isotherms. ^b Determined from the Langmuir model.

the cellulose surface, C_{\max} , were calculated, as summarized in Table 2. These results suggest the following remarks:

(i) The C_{\max} values deduced graphically were close to those observed at the plateau in the adsorption isotherms curves, which confirms the validity of the model proposed.

(ii) The adsorption equilibrium constants increased in the order MPS > APS > TAS, which is in tune with the increasing affinity of these three agents toward the cellulose surface. This was also confirmed by the progressive decrease in the values of the adsorption free energy ΔG_{ads}^0 . This trend can be attributed to the presence of the NH_2 group in APS and the three NH groups in TAS, which favored the interaction between the coupling agents and the cellulose substrate, thanks to the establishment of hydrogen bonds.

(iii) The surface area of the cellulose substrate can be calculated from the quantity of adsorbed silane corresponding to the formation of a monolayer, as obtained from the plateau and calculated C_{\max} values. In fact, if it is assumed that the adsorbed molecules are oriented perpendicularly to the cellulosic fibers²⁰ and that the surface which is covered by one molecule of silane is about 50 \AA^2 , the surface area of cellulose substrate could be

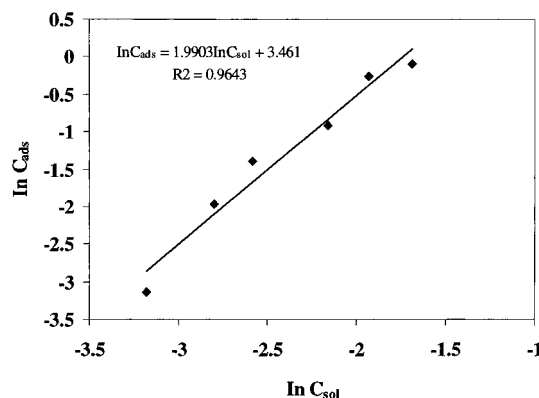


Figure 11. Application of the Freundlich approach to PAPS-treated cellulose samples.

estimated at about $90 \text{ m}^2/\text{g}$, which is much higher than the $2.5 \text{ m}^2/\text{g}$ obtained from BET measurements. This apparent discrepancy can be rationalized by considering that the use of an aqueous swelling medium favored the diffusion of the coupling agents into the pores of the cellulose substrate and consequently increased the available interaction area. The fact that the C_{\max} value for TAS is lower than that for APS suggests that the former adsorbed molecule was not perpendicular to the cellulose surface but tended instead to lie on it because of the three amino moieties placed along the silane structure.

In the case of PAPS, the linearity of the logarithmic plot between C_{ads} and C_{sol} (Figure 11) suggested that the adsorption mechanism followed a Freundlich-type model,¹⁹ viz.

$$C_{\text{ads}} = K C_{\text{sol}}^{1/n}$$

From the plot in Figure 11, we calculated $K = 32$ and $n = 0.5$. The much lower affinity of PAPS for the cellulose surface, compared to that of the other three silanes, can be explained by the steric hindrance introduced by the aromatic ring.

To examine the nature of the interaction mechanisms between the silanes and the cellulose surface, the treated fibers were submitted to (i) a Soxhlet extraction with ethanol for 15 h or (ii) a thermal treatment at 110°C under vacuum (about 2 mmHg) for 2 h followed by a Soxhlet extraction with ethanol for 15 h. After each treatment, the quantity of silane remaining on the fibers was determined.

The first treatment showed a total desorption of the silane agents which indicated that they were only physically adsorbed onto cellulose surface. This adsorption was probably driven by the hydrogen bonds between cellulose and the silanes, except for MPS which could only establish acid-base interactions between its ester group and the surface cellulosic OH groups. The latter hypothesis was confirmed by the observation of two peaks, respectively at 1720 cm^{-1} (the only peak in the FTIR spectrum of MPS alone), corresponding to the $\nu_{\text{C=O-free}}$ vibration and around 1710 cm^{-1} attributed to the $\nu_{\text{C=O-OH}}$ mode (see Figure 12).

The thermal treatment at 110°C , followed by Soxhlet extraction with ethanol, showed that an important proportion of silane (about 75% with MPS, close to 100% with APS and TAS) remained at the cellulose surface, as shown in Figure 4 for MPS. This indicated that a chemical grafting of MPS onto the surface of cellulose had indeed occurred. In fact, it is well-known from the chemistry of

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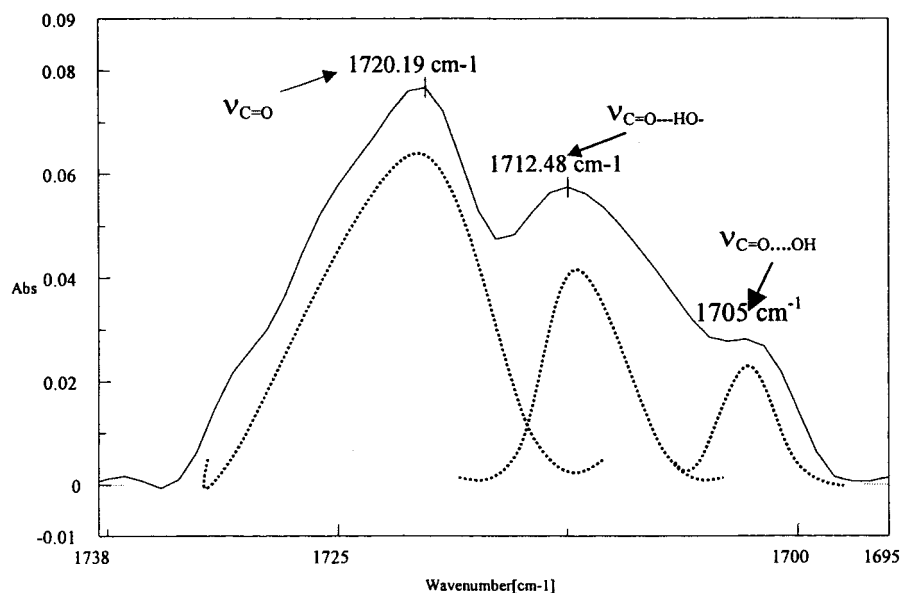


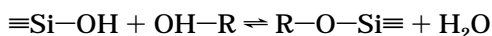
Figure 12. Deconvolution of the C=O peak of a cellulose sample treated with 3% MPS.

Table 3. Elemental Analyses and Surface Silane Contents of Cellulosic Fibers before and after Treatment

sample	composition (%)						silane (mmol/g)
	C	H	O	N	Si	S	
cellulose	44.44	6.17	49.38				calcd
	43.1	6.55	50.57				measd
cellulose-MPS	43.80	6.3.5	47.5		1.54		calcd
	42.25	6.38	47.		1.93		measd
cellulose-MPS ^a	42	6.32	46.68		1.29		measd
cellulose-MRPS	40.65	6.08			1.54	1.4	measd
cellulose-APS	45.62	6.34	44.02	1.31	2.62		calcd
	42.6	6.61	45.97	0.85	2.01		measd

^a Thermal treatment at 110 °C followed by Soxhlet extraction with ethanol. ^b Calculated from the adsorption isotherms.

silane on glass fibers¹⁵ that the silane OH groups formed by hydrolysis condense with the OH moieties present on the glass surface:



A similar reaction can be postulated in the present context when the hydrolyzed silane adsorbed onto the cellulose fibers is heated for 2 h at 110 °C. These results are in agreement with those observed in the case of the interactions between glass fibers and silane coupling agents.¹⁵

After the plateau corresponding to the formation of a monolayer was reached, more silane remained attached to the fibers, albeit about one-half of the amount originally adsorbed (Figure 4). The only reasonable explanation of this observation calls upon the temperature-driven self-condensation between the OH groups borne by the hydrolyzed silane molecules.

Table 3 presents the results of elemental analyses of cellulose samples treated with a 5% solution of silane, except for APS which was used as a 3% solution. The experimental values for untreated cellulose were very close to those calculated from its structure. For treated fibers, the presence of silicon was systematically detected as well as that of sulfur and nitrogen, when these elements were present in the initial structure of the modifying agent. The persistence of about 70% of the silicon adsorbed in the elemental analyses of the heat-treated MPS sample confirmed the observation that a large proportion of the silane had indeed remained bound to the cellulose surface.

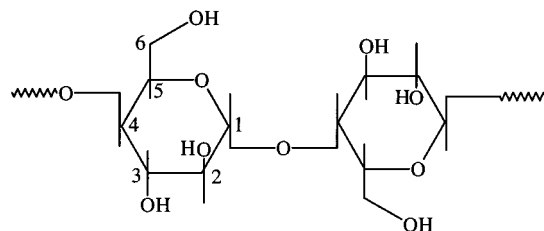
ESCA analyses were also carried out in order to ascertain more precisely the chemical composition of the

Table 4. ESCA Analysis Data before and after Surface Silane Treatment

	rel carbon composition (%)			
	O/C	C ₁ C-C 285 eV ^a	C ₂ C-O 286.7 eV ^a	C ₃ O-C-O 288.3 eV ^a
pure cellulose	0.83	0	83.3	16.7
cellulose	0.71	19.0	64.8	16.2
cellulose-MPS	0.53	48.0	40.7	11.3
cellulose-MRPS	0.58			

^a Binding energy.

surface, since the depth of penetration associated with this technique is a few nanometers (Table 4). The cellulose structure, as well as its numbered carbon atoms, are represented in the following scheme:



The ESCA spectrum of untreated cellulose is given in Figure 13. Its detailed features have already been examined.²¹ The spectrum of the MPS-modified cellulose

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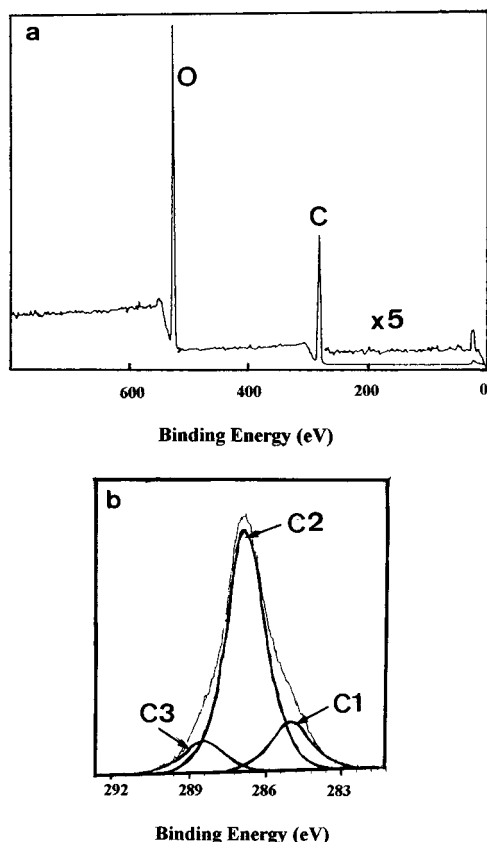


Figure 13. ESCA spectrum of untreated cellulose (a) and deconvolution of its C_{1s} peak (b).

is shown in Figure 14a. The first two peaks at 288 and 535 eV correspond to the carbon and oxygen atoms, respectively, whereas the double peak at 102 and 150 eV indicates the presence of silicon atoms, thus confirming the attachment of MPS on the cellulose fibers.

The ESCA spectrum of MRPS-treated cellulose is presented in Figure 15, in which the presence of both silicon and sulfur atoms is witnessed by the corresponding peaks at 102 + 150 and 160 eV, respectively, confirming the interaction of MRPS with the cellulose surface. Moreover, the surface O/C ratio with respect to untreated cellulose (Table 4) decreased from 0.71 to 0.58, corroborating the presence of the grafted MRPS.

The deconvolution of the peak corresponding to carbon atoms in the ESCA spectrum of the MPS-treated cellulose (Figure 14b) revealed a major difference related to the C1 peak, when compared with that of untreated cellulose (Figure 13b), viz., a large increase, from 19 to 48% (Table 4), which was attributed to the methylene groups from MPS. This large variation was corroborated by the corresponding decrease in the surface O/C ratio which went from 0.71 to 0.53, as expected by the carbon-rich silane coverage.

Conclusion

This study has clearly shown that one should distinguish adsorption phenomena from actual chemical grafting when considering the interactions of silanes with the

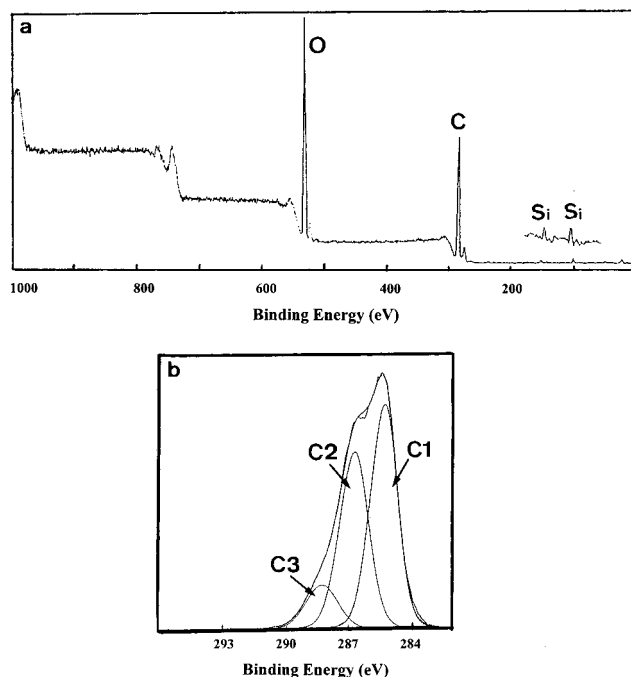


Figure 14. ESCA spectrum of MPS-treated cellulose (a) and deconvolution of its C_{1s} peak (b).

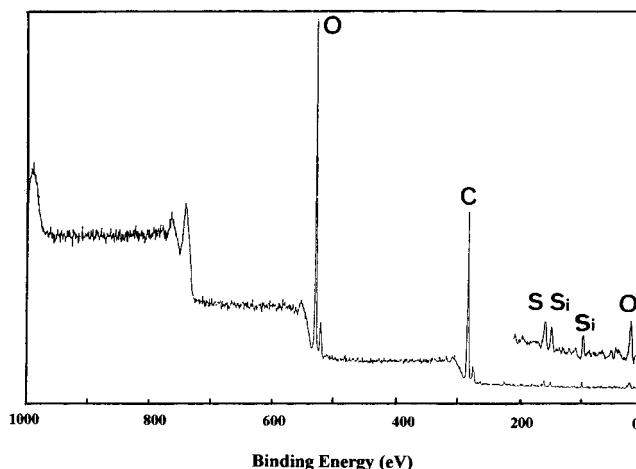


Figure 15. ESCA spectrum of MRPS-treated cellulose.

surface of cellulose. The quantitative assessment of the physicochemical equilibria for several silanes indicated that the adsorption of a monolayer and multiple layers of prehydrolyzed silanes is readily achieved but that a simple extraction with ethanol removes entirely these molecules. Only a heat treatment can induce a condensation between the OH groups of the hydrolyzed silanes and those present at the surface of cellulose, giving rise to a real chemical modification. The investigation of the surface properties of these modified fibers and of their inclusion into polymeric matrixes is in progress.

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