

Comparative Spectroscopic Study of the Modification of Cellulosic Materials with Different Coupling Agents

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Received 13 January 1999; accepted 22 March 1999

ABSTRACT: The reactions of two cellulosic materials (an industrial cellulosic by-product from a Kraft pulp mill facility and a reference material) with three coupling agents, used to improve compatibility between cellulosic reinforcements and thermoplastic matrices, were studied by diffuse reflectance Fourier-transform infrared (DRIFT) spectroscopy and diffuse reflectance ultraviolet-visible spectroscopy. A maleated polypropylene wax (Epolene E-43TM) and two silanes (*N*-2-aminoethyl-3-aminopropyltrimethoxysilane and methyltrimethoxysilane) were used as coupling agents. The two cellulosic materials reacted in a similar way and the three coupling agents were covalently bonded to the cellulose. For the aminosilane, a reaction with cellulose involving a fraction of the amino groups was detected. A simple method, based on the analysis of the oxidation kinetics of treated and untreated materials, was developed to compare the degree of cellulose modification achieved by each coupling agent. The analysis revealed that a reduced fraction of the cellulose reactive groups was converted by esterification with the maleated polypropylene. However, when applied in the appropriate conditions, the two silanes converted most of such cellulose reactive groups. Finally, the reaction of cellulose with mixtures of coupling agents was studied. The aminosilane-treated cellulose reacted with the maleated polypropylene with formation of amide links. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 256–266, 2000

Key words: cellulose; maleated polypropylene; silane coupling agents; FTIR spectroscopy; composite interfaces

INTRODUCTION

The use of cellulosic materials as reinforcements for thermoplastic polymers offers a number of well-known advantages.^{1–10} These include low

cost, availability of renewable natural resources, biodegradability, low density, limited damage to the equipment (due to the nonabrasive character of the cellulosic materials), no health hazard, and, finally, some good mechanical properties derived, at first, from an aspect ratio over the critical value necessary for reinforcement. Unfortunately, there are also some disadvantages which may lead to composites of poor final properties. Mainly, they are that

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Journal of Applied Polymer Science, Vol. 75, 256–266 (2000)

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CCC 0021-8995/00/020256-11

- Cellulosic materials have rather poor thermal stability. Substantial degradation may occur during the processing of thermoplastic matrix composites.
- Cellulosic materials are polar and hydrophilic, whereas thermoplastics are nonpolar and hydrophobic. This lack of compatibility leads to a difficult dispersion of the cellulosic material in the thermoplastic melt and causes a poor adhesion between fillers and matrices, both factors which determine to a large extent the final performance of the composites.

During the past two decades, several methods have been tested to enhance adhesion between lignocellulosic fillers and thermoplastic matrices. In general, these methods involve fiber or/and polymer modification by physical or chemical methods. Physical methods, such as corona or plasma discharges, are known to be useful for polymer matrices like polypropylene or polystyrene.^{5,8,11} In chemical methods, several coupling agents have been used to modify the chemical nature of the surfaces.

Among these coupling agents, maleic anhydride and graft copolymers of polypropylene and maleic anhydride (maleated polypropylenes) have been widely studied in recent years.^{1-3,5-10,12-14} In general, the mechanical properties improved when these coupling agents were used. Both maleic anhydride and maleated polypropylenes may be covalently bonded to cellulose through an esterification process,^{6,13,14} thus improving the wettability and the adhesion to thermoplastic matrices. The polypropylene chains in maleated polypropylenes play an important role in promoting adhesion, favoring the cohesive coupling of the polar cellulose with the nonpolar thermoplastic matrix; however, the long polypropylene chains appear to limit the esterification to the surface layer of the cellulose, due to steric hindrance.^{6,15} The esterification process also depends on the nature of the lignocellulosic material. Recently, Kazayawoko et al.¹³ reported that, while a maleated polypropylene wax chemically reacted with a bleached Kraft cellulose, no direct evidence of chemical reaction was obtained when a thermomechanical pulp was treated with the same coupling agent. However, both cellulosic materials reacted with maleic anhydride.

Other coupling agents like isocyanates^{12,16,17} and silanes¹⁷⁻²² have also been widely used. Silane coupling agents are compounds of the gen-

eral formula RSiX_3 , where X is an easily hydrolyzable group and R is an organic group that provides the desired organic functionality to the modified substrate. Several silane coupling agents have been used. Maldas et al.¹⁷ reported that good results were obtained in wood fiber-polystyrene composites when an aminosilane (3-aminopropyltriethoxysilane, APS) was used in conjunction with maleic anhydride. Significant improvements in interfacial adhesion have also been obtained from 3-methacryloxypropyltrimethoxysilane treatments.^{18,21} Coutinho et al.²² reported a significant increase in the mechanical properties of wood fiber-polypropylene composites when a vinylsilane was used.

The reaction between cellulosic materials and silanes is not simple. It is known that silane coupling agents react with cellulose moisture (or additional water) to form silanol (Si—OH) groups. After hydrolysis, the coupling agent can develop either covalent or hydrogen bonds with cellulose hydroxyl groups, but the degree of conversion of such hydroxyls is not well known. The modification process with silanes may be affected by the presence of free-radical sources such as organic peroxides. Xanthos¹⁸ reported that the presence of free-radical sources resulted in improvement of the performance of a methacryloxysilane used as a coupling agent. Beshay and Hoa¹⁹ pointed out that organic peroxides are necessary to form covalent bonds between silane coupling agents and cellulose.

The effect of coupling agents on the properties of cellulose-reinforced composites depends on both the chemical nature of the cellulose modification and the degree of cellulose modification achieved in these treatments. Hence, the understanding of the nature and the knowledge of the extension of the modification processes is of special importance for making progress in the improvement of the properties of the cellulose-reinforced composites made by melt blending of their components. However, to the present, little attention has been paid to evaluate and compare the extent of the reaction between cellulose and coupling agents. Another scarcely studied matter has been the modification of cellulosic materials with mixtures of coupling agents.

In this work, we studied the reaction of two cellulosic materials (Cel A and Cel B) with three coupling agents. Cel A is a by-product obtained in the manufacture of Kraft cellulose pulp, mostly consisting of unbleached cellulose. Knowledge of the reactions between Cel A and coupling agents

is relevant in order to evaluate the suitability of the by-product as a reinforcement for thermoplastic–matrix composites. Cel B is an almost pure cellulose (Whatman no. 42 filter paper) and was used as a reference material. A maleated polypropylene wax and two silanes [*N*-2-aminoethyl-3-aminopropyltrimethoxysilane (AAPS) and methyltrimethoxysilane (MS)] were chosen for this purpose. AAPS is a diaminosilane primarily used in glass fiber-reinforced composites.^{23–25} It has been reported^{23,24} that diaminosilanes may provide better results in some cases than will aminosilanes like APS due to the longer flexible organic chain and to the increased reactivity. MS is primarily used to make inorganic surfaces hydrophobic. Maleated polypropylenes have been previously used for modifying the nonpolar surface of polyolefins (such as polypropylene) in composites made from those matrices and some wood-based materials.^{9,10}

Three goals were taken into account in this work: The first was to obtain information about the suitability of those agents for modifying the by-product (Cel A) and improving its compatibility with thermoplastic matrices in composites. The second goal was to compare the degrees of cellulose modification achieved in the treatments with the three coupling agents. A new and simple method was developed for this purpose, based on the analysis of the oxidation kinetics of treated and untreated cellulose. Finally, the third goal was to study the modification of cellulosic materials with mixtures of coupling agents, in order to investigate new ways to achieve the desired degrees of interaction between modified cellulosic reinforcements and thermoplastic matrices.

Diffuse reflectance Fourier-transform infrared (DRIFT) spectroscopy and diffuse reflectance ultraviolet-visible (UV-vis) spectroscopy were used to characterize the nature of the chemical modifications. DRIFT was used to compare the degrees of conversion of cellulose reactive groups achieved in our treatments.

EXPERIMENTAL

Cellulosic Materials

Two cellulosic materials were used in this work. Cel A was obtained from CEASA, a Kraft pulp mill located in Navia, Asturias (Spain). It was a by-product obtained in the manufacture of Kraft cellulose pulp, consisting of unbleached cellulose.

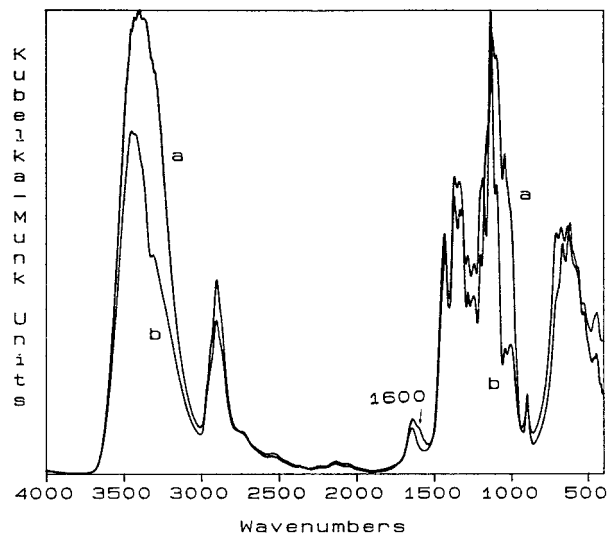


Figure 1 DRIFT spectra of (a) cellulosic by-product (Cel A) and (b) Whatman no. 42 paper (Cel B).

Its cellulose content is higher than 95%, most of the rest being unreacted wood. The material was used almost as received. After eliminating the large fragments of unreacted wood, the only pre-treatments were washing with water and drying in air at 65°C for 18 h. The powder was ground and sieved in order to isolate a fraction of $-0.5 + 0.25$ mm that was used in all experiments. Cel B, used as a reference material, was a Whatman no. 42 ashless filter paper, consisting of >99% cellulose, and was also dried in air at 65°C for 18 h.

The starting cellulosic materials were characterized using DRIFT spectroscopy (Fig. 1) and diffuse reflectance UV spectroscopy (Fig. 2). Both materials present the infrared absorption bands expected for cellulosic materials.^{26–30} The main difference is a weak band at 1600 cm^{-1} appearing in the infrared spectrum of Cel A. This band may be due to the presence in this material of a low amount of lignin (C—C aromatic stretching vibration at 1600 cm^{-1}),³⁰ but also may indicate the presence of low amounts of some unsaturated compounds. Figure 2 reveals that Cel A is less reflecting than is Cel B in the UV region of the spectrum. As no specific absorption bands appear for Cel A in this region, this difference appears to be due mainly to the different textures of the samples (powder form for Cel A and sheet form, more reflecting, for Cel B).

Coupling Agents

A commercially available maleic anhydride–polypropylene copolymer, Epolene E-43™ (East-

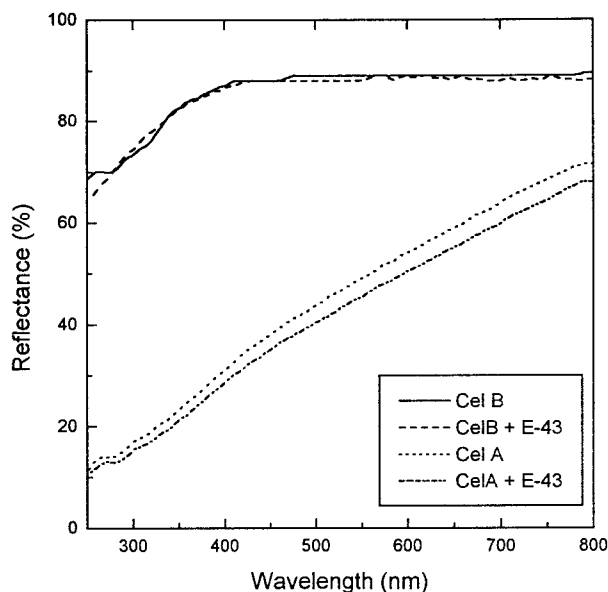


Figure 2 Diffuse reflectance UV-vis spectra of untreated and E-43-treated materials.

man Chemical Products, Inc., Kingsport, TN), was used for the treatment of the cellulosic materials. The acid number is 47. M_n and M_w are 3900 and 9100, respectively. AAPS [(CH₃O)₃Si—CH₂—CH₂—CH₂—NH—CH₂—CH₂—NH₂, Z-6020] and MS [(CH₃O)₃SiCH₃, Z-6070] were kindly supplied by Dow Corning Iberica S.A. (Barcelona, Spain) and were used as received.

Other Reagents and Solvents

Benzoyl peroxide (Merck, Darmstadt, Germany) and acetone and xylene (Fluka, Madrid, Spain) were used without further purification. Toluene (Fluka) was dried over CaCl₂.

Treatment with Silanes

One gram of cellulosic material was added to 20 mL of silane solutions in acetone/water (95/5; v/v). Additional water was used in the reaction because Schneider and Brebner²⁰ reported that, although cellulosic materials contain bound moisture, water must be added to the silane in the cellulose in order to achieve a complete hydrolysis of the silane. Silane concentration varied from 0.5 to 10% (based on the cellulose weight). The silane coupling agents were used in conjunction with 0.3% (based on the cellulose weight) of benzoyl peroxide as a free-radical source. The reaction mixture was kept under a nitrogen atmosphere at 60°C for 2 h. After washing with the solvent,

treated materials were oven-dried at 65°C for 18 h.

Treatment with Maleated Polypropylene

The method described by Felix and Gatenholm⁶ was used to treat the original cellulosic materials and some silane-treated materials with Epolene E-43. The reaction was carried out in refluxing toluene for 5 min. The concentration of E-43 was 5% (based on the cellulose weight). Before use, the maleated polypropylene was activated by heating at 160°C for 5 min. After washing with toluene, the treated materials were oven-dried at 65°C for 18 h. Some samples were Soxhlet-extracted with xylene for 8 h to remove all components not covalently bonded to the cellulosic material.

Diffuse Reflectance Spectroscopy

DRIFT spectra of cellulosic materials before and after treatment were obtained with a Mattson 3020 FTIR spectrometer, using a Specac diffuse reflectance accessory. Each spectrum was recorded at a resolution of 4 cm⁻¹, with a total of 90 scans. Background scans were obtained using KBr powder. All DRIFT spectra were plotted according to the Kubelka–Munk function.³¹ The diffuse reflectance UV-vis spectra were obtained with a Shimadzu 2401 PC spectrophotometer, using a Shimadzu diffuse reflectance accessory, at 200 nm min⁻¹.

RESULTS AND DISCUSSION

Treatment with E-43

We studied the reaction in toluene of our cellulosic materials with E-43, a low molecular weight maleated polypropylene which has been frequently used as a coupling agent in the development of wood fiber–polypropylene composites. The coupling agent was previously heated at 160°C for 5 min in order to remove water and regenerate the more reactive anhydride groups through condensation of the carboxylic groups existing in E-43. Figure 2 shows the diffuse reflectance UV-vis spectra of samples treated with E-43, after curing at 110°C for 1 h, in order to improve condensation between the anhydride groups of E-43 and the cellulose hydroxyl groups. The treatment with E-43 slightly reduced the spectral reflectance of the two cellulosic materi-

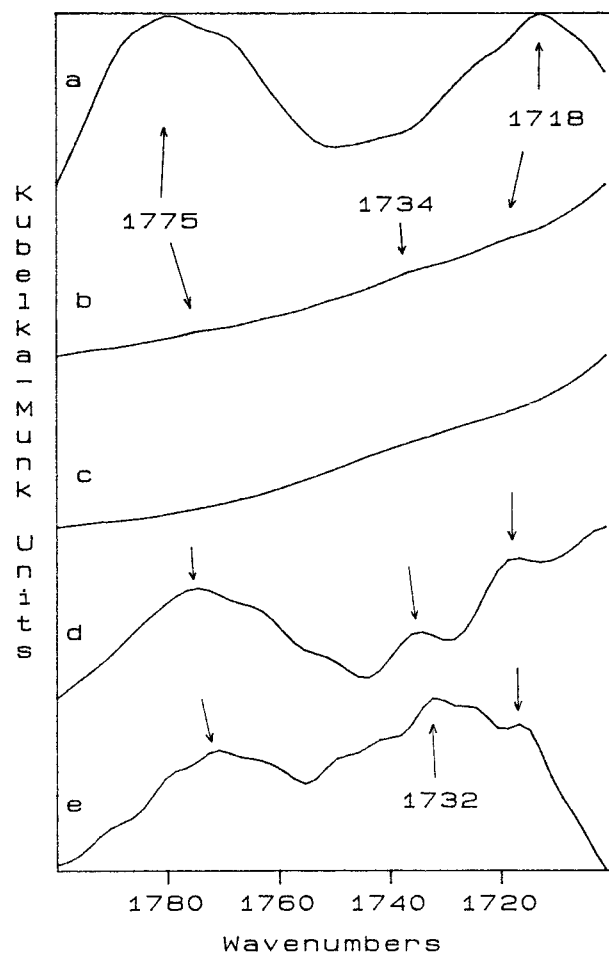


Figure 3 DRIFT spectra of (a) activated E-43, (b) Cel A treated with E-43, and (c) untreated Cel A. (d) Difference spectrum of (b) and (c). (e) Difference spectrum for Cel B treated with E-43.

als, but no new absorption bands appeared as a consequence of treatment.

Figure 3 shows the main results obtained in the comparative infrared study of the reaction. The most interesting absorption bands of the activated E-43 are presented in Figure 3(a). The band centered at 1775 cm^{-1} is associated with an anhydride carbonyl ($\text{C}=\text{O}$) stretching vibration.^{6,13} The band at 1718 cm^{-1} may be assigned to a carbonyl stretching vibration of carboxyl groups present in E-43 even after activation. Figure 3(b) shows the DRIFT spectrum of Cel A treated with activated E-43, after curing at 110°C for 1 h. Two weak absorption bands at 1718 and 1775 cm^{-1} show the presence of E-43 in the treated cellulose. Also appearing is a very weak new band centered at 1734 cm^{-1} , which is clearly seen in the difference spectrum obtained by digi-

tal subtraction [Fig. 3(d)]. This band is important as it may be explained as an ester carbonyl absorption. Felix and Gatenholm⁶ showed that the esterification of cellulose fibers with maleated polypropylene waxes may be detected by the appearance, in the FTIR spectra of treated celluloses, of two new carbonyl bands at 1739 and 1746 cm^{-1} . Kazayawoko et al.¹³ assigned a new band at 1722 cm^{-1} to the esterification of a bleached Kraft cellulose with E-43. An ester carbonyl band was also reported at 1730 cm^{-1} .¹⁴ Figure 3 also shows the corresponding difference spectrum for the treatment of Cel B with activated E-43 [curve (e)]. In this case, the ester band appears at 1732 cm^{-1} .

Thus, these results reveal a chemical reaction of both Cel A and Cel B with the maleated polypropylene. However, the very low absorbance at 1734 cm^{-1} indicates a reduced esterification of the cellulosic materials. Other authors have reported similar results. Joly et al.¹⁵ reported that the treatment of cellulosic fibers with a maleated polypropylene shows no measurable effect on water uptake. Kazayawoko et al.¹³ studied the esterification of a thermomechanical pulp with E-43 and with maleic anhydride. The pulp reacted with maleic anhydride with the formation of ester links, but no direct evidence of esterification was observed with E-43. These results were explained by considering that the relatively long polypropylene chains in maleated polypropylenes may inhibit the access to the hydroxyl groups for reaction, thus limiting the esterification to the extreme surface layers of cellulose fibers.

Treatment with Silanes

The two cellulosic materials were treated with AAPS and MS in the presence of benzoyl peroxide as free-radical source. The DRIFT spectra of the by-product (Cel A) samples treated with 0.3% benzoyl peroxide and AAPS are shown in Figure 4(b–d). These figures show how the amount of deposited silane depends on the concentration of the treating solution. Figure 4 also shows the DRIFT spectrum of Cel B samples treated with 5% AAPS [curve (e)].

The presence of AAPS in treated materials may be deduced from the absorption at 1599 cm^{-1} , which may be explained as an amine deformation band.²³ The band at 1550 cm^{-1} also corresponds to the silane treatment. Another characteristic absorption is the weak 930 cm^{-1} band, which has been assigned to unreacted silanol

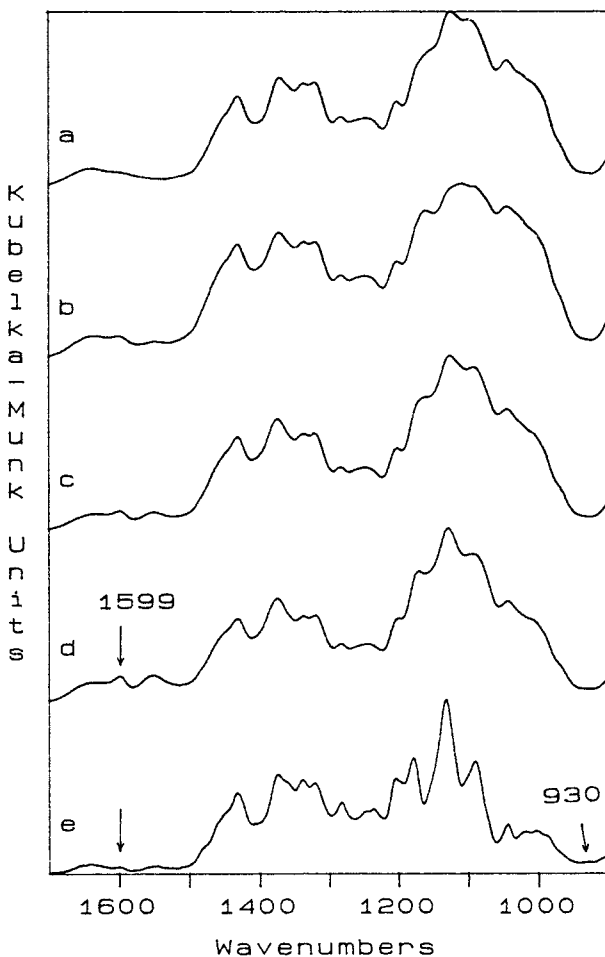


Figure 4 DRIFT spectra of (a) untreated Cel A and Cel A samples treated with 0.3% benzoyl peroxide and (b) 1%, (c) 2.5%, or (d) 10% AAPS. (e) DRIFT spectrum of Cel B treated with 0.3% benzoyl peroxide and 5% AAPS (all percentages based on the cellulose weight).

groups (Si—O stretching) produced in the silane hydrolysis.^{23,32} The strong absorption of the two substrates in the 1060–1260 cm^{-1} region precludes the complete assignment of silane bands in this spectral region, including the Si—O—C_{cel} and the polysiloxane bands. A weak band also appeared at 2940 cm^{-1} (not shown in Fig. 4), due to CH₂ groups of AAPS.

The diffuse reflectance UV-vis spectra of the cellulosic materials after treatment with the two silane coupling agents are presented in Figure 5. The main result of the modification with AAPS was the appearance of a new absorption band centered at about 340 nm. As this new band does not appear in the spectra of cellulosic samples modified with the methylsilane, we can conclude that the 340 nm band cannot be explained by the

general mechanism of cellulose modification with silanes, that is, the condensation between silanol groups produced in the hydrolysis of the silane and hydroxyl groups of the cellulose. This new absorption band reveals a second cellulose modification process, existing when AAPS is used as coupling agent, which involves a reaction between the amino groups of AAPS and some reactive groups of the cellulose.

In this case, this new band has been assigned to imines (C=N) produced in the reaction with celluloses of the amino groups of AAPS. It is well known that amines react easily with carbonylic compounds, such as some carbohydrates, to form imines. Some carbonylic compounds may exist in the untreated celluloses, and additional carbonyls may be generated during the treatments with the silane at 60°C. It is known that imines present a weak ($n-\pi^*$) absorption band centered at about 300 nm, although this maximum strongly depends on the substituents of the imine group.³³ Thus, the diffuse reflectance UV-vis spectroscopy reveals that certain silane coupling agents, like AAPS, can modify the cellulose materials by two parallel mechanisms. As the infrared spectra of AAPS-treated celluloses clearly show the amine characteristic bands, we can conclude that only a fraction of the amino groups deposited onto the cellulose are involved in the formation of the new chromophore, when the reaction is carried out in the presence of organic peroxides at 60°C.

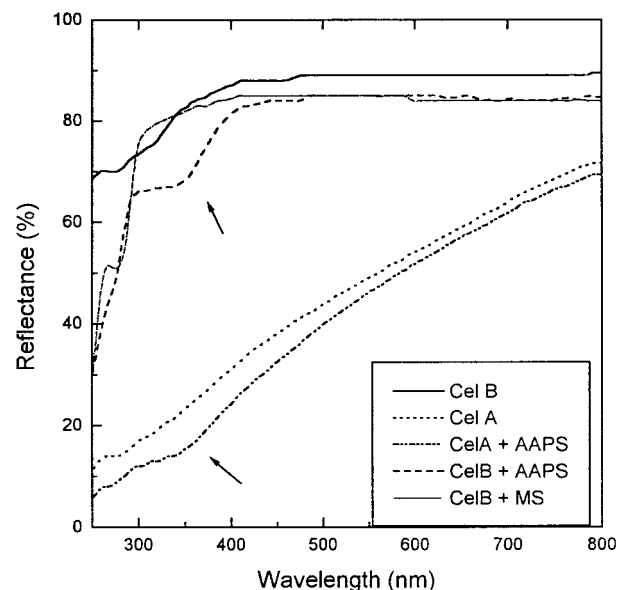


Figure 5 Diffuse reflectance UV-vis spectra of untreated and silane-treated materials.

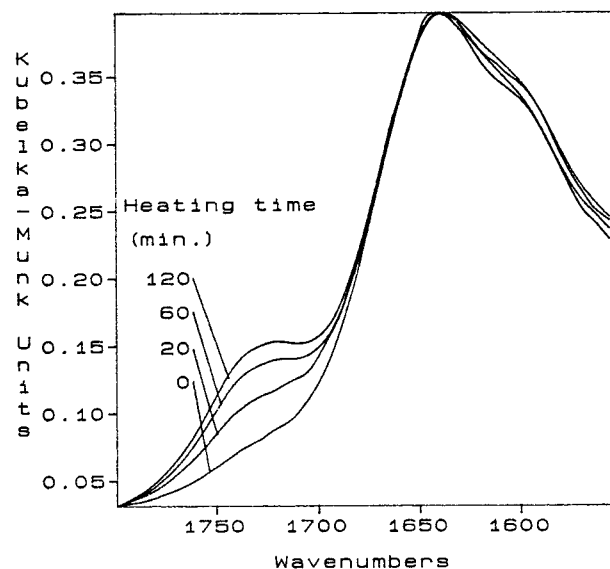


Figure 6 DRIFT spectra of cellulosic by-product before and after heating in air at 180°C.

Comparative Analysis of the Cellulose Modification with E-43 and Silane Coupling Agents

When coupling agents are used in treatments of reinforcements for composite materials, it is interesting to know the nature of the involved modification processes, as well as the degree of conversion by the coupling agent of the reactive groups of the reinforcement. This degree of conversion determines the chemical nature of the interfaces and thus some properties of the composite materials such as modulus, tensile strength, and elongation. Cellulosic materials have many reactive groups, the more reactive of them being the primary alcohol ($-\text{CH}_2\text{OH}$) groups. We have compared the conversion of the cellulose reactive groups achieved in the treatments with E-43 and silanes. A new and simple method was developed for this purpose, based on comparison of the oxidation kinetics of treated and untreated celluloses.

The untreated cellulosic materials and the chemically modified samples were oxidized in air at 180°C, and the oxidation kinetics was measured by using DRIFT spectroscopy. Figure 6 shows the evolution of the infrared absorbance of the by-product during the oxidation process. An absorption band at 1730 cm^{-1} appears in the first stages of the oxidation. This absorption may be assigned to the carbonyl stretching vibration of carbonyl and carboxyl groups produced in the easy oxidation of the cellulose alcohol groups.²⁶⁻²⁸

Forziati et al.²⁷ assigned an absorption band at 1730 cm^{-1} in oxidized cellulose to carboxyl groups and reported that the intensity of this band in such materials is a good measure of their carboxyl content even in the presence of appreciable amounts of noncarboxylic carbonyls.

We used the band at 1730 cm^{-1} to follow the oxidation of the cellulose alcohol groups. The medium band at 900 cm^{-1} , assigned to the β -glucosidic linkages,^{30,34,35} remains unchanged during the first stages of the oxidation and was used as an internal standard in order to normalize the results. The normalized peak area at 1730 (A_{1730}/A_{900}) was also corrected by subtracting the value before the reaction [i.e., $(A_{1730}/A_{900})_{t=0}$]. This correction allows one to eliminate the contribution of other bands to the absorbance at 1730 cm^{-1} , as, for example, the contribution of the ester carbonyl band in samples treated with maleated polypropylene.

Figure 7 gives plots of the normalized peak area at 1730 cm^{-1} versus the oxidation time for as-received Cel A samples and samples treated with E-43 or AAPS. It may be seen that the oxidation kinetics clearly depends on the treatments. The main effect of AAPS treatment is the inhibition of the oxidation process at low heating times. As the 1730 cm^{-1} band appearing at low heating times may be assigned to the oxidation of cellulose reactive groups, this inhibition effect ap-

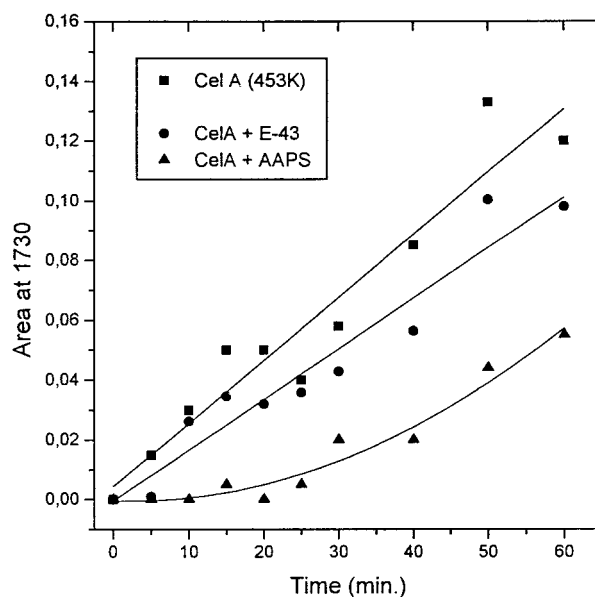


Figure 7 Oxidation plots (normalized peak area at 1730 cm^{-1} versus heating time) for Cel A before and after treatment with E-43 or AAPS.

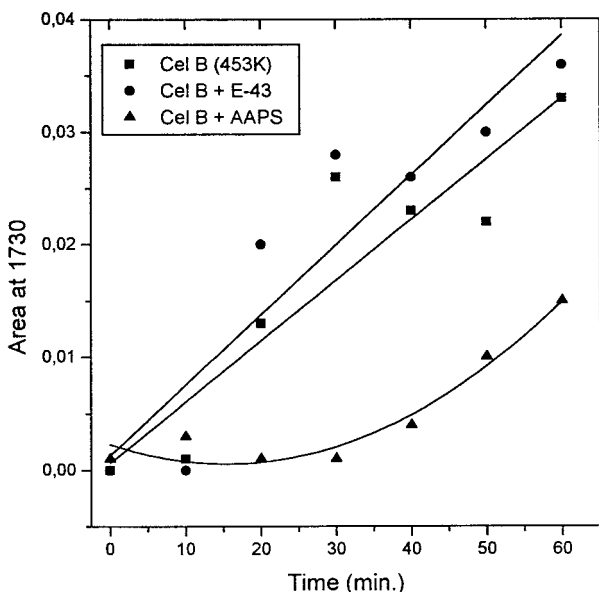


Figure 8 Oxidation plots for Cel B before and after treatment with E-43 or AAPS.

pears to indicate that the diaminosilane effectively reacts with most of such cellulose reactive groups.

Figure 7 also shows an oxidation plot for a sample treated with E-43. The ester bonds' contribution to the increasing peak area at 1730 cm^{-1} was considered negligible due to the very low absorbance of the ester band at 1734 cm^{-1} (see Fig. 3). The treatment with E-43 scarcely affects the oxidation rate of the material and does not appear to have the inhibition effect observed in silane-treated samples. We can conclude that the maleated polypropylene converts only a reduced fraction of the cellulose reactive groups. This result confirms that only a reduced esterification of our cellulosic material was achieved when E-43 was used as a coupling agent.

The same behavior was observed for the oxidation of treated and untreated samples of Cel B (Fig. 8). Again, the oxidation plots were clearly dependent on the coupling agent used in the cellulose treatments, and the treatment with AAPS produced a clear inhibition effect.

We also studied the effect on the cellulose oxidation of other silane treatments. The cellulosic by-product was treated in the presence of benzoyl peroxide, with methyltrimethoxysilane, a silane with a nonreactive organofunctional group. Figure 9 shows that this treatment also produced an inhibition effect on the oxidation at low heating times. This silane can modify the cellulosic sub-

strate only by condensation between silanol groups and cellulose hydroxyl groups. These results reveal the importance of this mechanism in the processes of cellulose modification with silanes, that is, we can expect that all commercial silane coupling agents, when applied in the appropriate reaction conditions, may convert most of the reactive groups of cellulosic materials.

The differences observed in the inhibition effects produced by different silane coupling agents may be explained as a consequence of their different chemical nature. In this case, the differences observed in the treatments with MS and AAPS (see Figs. 7 and 9) were explained as a consequence of the second mechanism of cellulose modification existing for AAPS and not for MS, involving the reaction with celluloses of a fraction of the amino groups of AAPS.

Treatment with Mixtures of Coupling Agents

We studied the reaction of celluloses Cel A and Cel B with mixtures of the coupling agents used in this work. In general, the use of mixtures is a possible way for achieving the desired functionalization of the substrate. In our case, the understanding of the interaction between silanized cellulose and maleated polypropylene is significant in order to evaluate the suitability of silanized celluloses as reinforcements for polymeric matrices which have been previously modified with

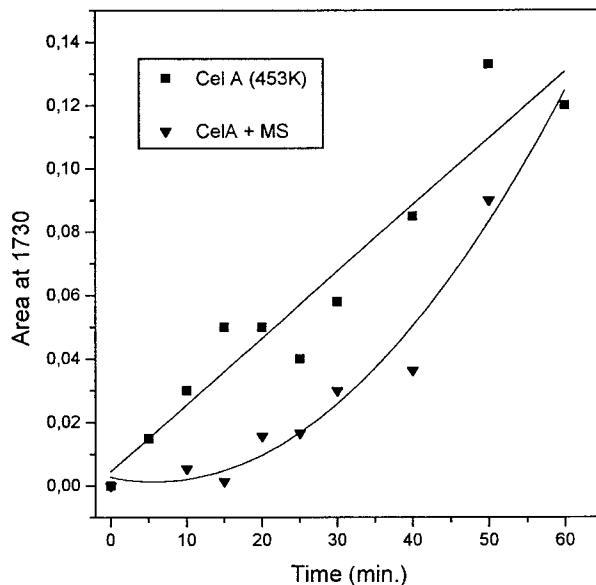


Figure 9 Oxidation plots for as-received Cel A before and after treatment with MS.

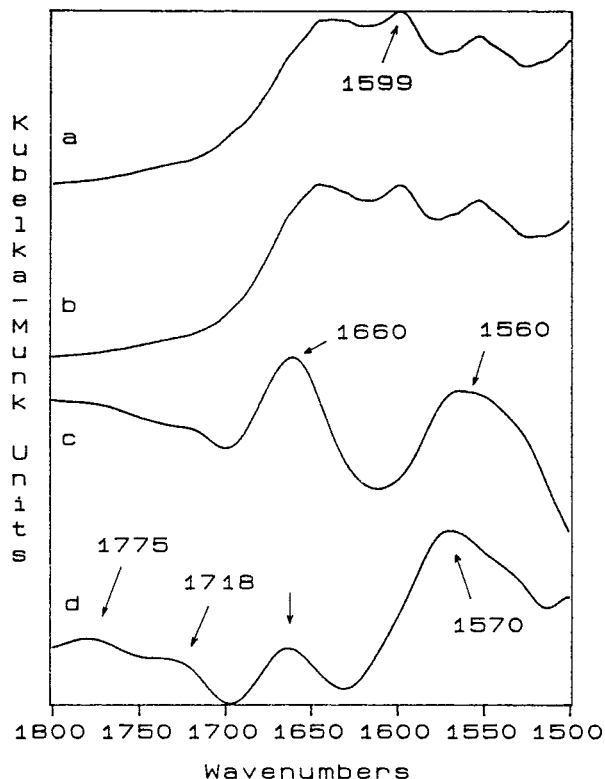


Figure 10 DRIFT spectra of a Cel A sample treated with AAPS (0% by weight) and benzoyl peroxide (0.3%) (a) before and (b) after treatment with E-43 (5% by weight) in refluxing toluene and Soxhlet extraction. (c) Difference spectrum of (b) and (a). (e) Difference spectrum for the treatment of AAPS-treated Cel B with E-43.

maleated polypropylene waxes or maleic anhydride. As amines have more nucleophilic groups than have alcohols, we can expect that celluloses treated with AAPS will react with maleated polypropylene faster than with unmodified celluloses.

The reaction of silane-treated celluloses with E-43 was carried out in refluxing toluene. After drying, a portion of the treated material was Soxhlet-extracted with xylene for 8 h. As expected, no specific chemical reaction was observed between MS-treated celluloses and E-43. However, infrared analysis revealed a chemical reaction between AAPS-treated celluloses and E-43. Figure 10 shows the DRIFT spectrum of the original AAPS-treated Cel A [Fig. 10(a)], as well as the spectrum recorded after treatment with E-43 and Soxhlet extraction [Fig. 10(b)]. The difference spectrum of (b) and (a) is shown in (c). The corresponding difference spectrum for Cel B is shown in (d).

The appearance in spectrum 10(b) of the characteristic absorptions of silane, such as the amine deformation band at 1599 cm^{-1} , shows that silane remains on the cellulosic by-product after Soxhlet extraction. This result confirms that the silane is covalently bonded to the cellulose when applied in the presence of organic peroxides. The amine bands in Figure 10(b) also indicate that a significant portion of the reactive amino groups of silanized cellulose remained unmodified by the treatment with maleated polypropylene.

Although Soxhlet extraction partially removed the maleated polypropylene deposited on the cellulose, the appearance of two weak bands at 1718 and 1775 cm^{-1} in the difference spectra shows the presence of E-43 covalently bonded to the cellulose. However, no absorption band at 1734 cm^{-1} appears in Figure 10(c) or (d), revealing that no ester linkages were formed in the treatment of silanized celluloses with E-43. This additional evidence confirms that the treatment with AAPS converts most of the primary alcohol groups of the cellulose, thus preventing the esterification with E-43. The absorption bands at 1718 and 1775 cm^{-1} may be attributed to maleated polypropylene units attached to the cellulose by other chemical bonds.

The nature of these chemical bonds may be deduced from the two bands at 1660 and 1560 cm^{-1} , which may be clearly seen in the difference spectrum corresponding to Cel A (1660 and 1570 cm^{-1} for Cel B). The chemical reaction of a diaminosilane, like AAPS, with E-43 may produce a secondary amide or a cyclic imide. Both structures are illustrated in Figure 11. The formation of a tertiary amide must be unlikely due to the steric hindrance of the secondary amine groups in AAPS. The two bands at 1660 and $1560\text{--}1570\text{ cm}^{-1}$ correspond to a secondary amide.³⁶ The 1660-cm^{-1} absorption (amide I) is attributed mainly to an amide carbonyl stretching vibration, and the $1560\text{--}1570\text{ cm}^{-1}$ band (amide II) is assigned mainly to a deformation mode of the amide N—H groups. The absence of a band at 1740 cm^{-1} , which would be expected for the cyclic imide structure,³⁷ reveals that no cyclic imide was formed under our reaction conditions.

The evidence of amide bond formation in this reaction indicates that a strong interaction may be achieved between an aminosilane-treated cellulosic filler and a polymer matrix, like polypropylene, which has been previously modified with maleic anhydride units. These results can thus explain the good properties reported by Maldas et

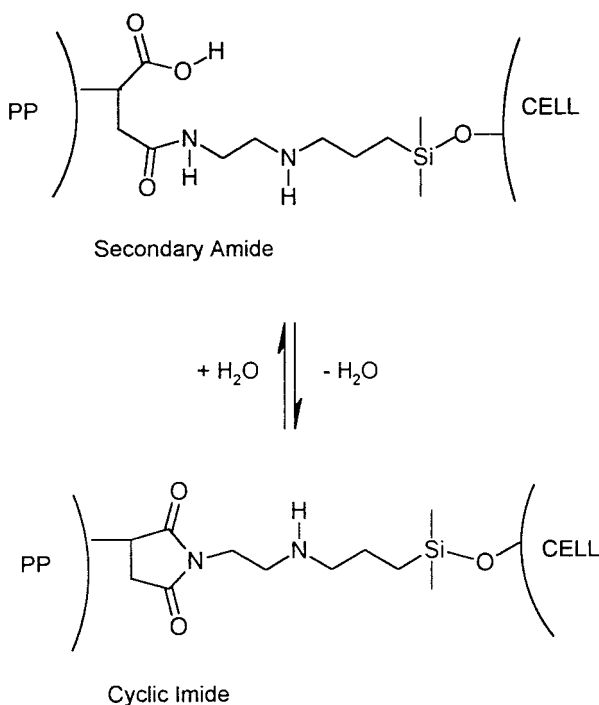


Figure 11 Possible products for the reaction between AAPS-treated cellulose and E-43 (PP, polypropylene; CELL, cellulose).

al.¹⁷ for polystyrene–wood fiber composites when APS and maleic anhydride were used as coupling agents. Our results also agree with the report of Chun and Woodhams³⁸ on the effects of APS and E-43 on the mechanical properties of mica–polypropylene composites. These authors reported that the ultimate strength obtained when both APS and E-43 were used was higher than that obtained when only one coupling agent was used.

CONCLUSIONS

- The same behavior was observed for the two cellulosic materials (an industrial cellulosic by-product and a reference material) in the reactions with coupling agents. Both materials can be chemically modified by treatment with the studied coupling agents in order to improve their compatibility with thermoplastic matrices.
- The degree of cellulose modification strongly depends on the nature of the coupling agent. A reduced fraction of the cellulose reactive

groups was converted by esterification with the maleated polypropylene. However, the treatment with silanes in the appropriate reaction conditions converted most of the cellulose reactive groups.

- A reaction between the amino groups of AAPS and cellulose was detected by diffuse reflectance UV-vis spectroscopy.
- The aminosilane-treated celluloses may be linked by strong amide bonds to maleated polypropylenes and other maleic anhydride-modified thermoplastics.

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