# The Nature of Adhesion in Composites of Modified Cellulose Fibers and Polypropylene

JOHAN M. FELIX and PAUL GATENHOLM*

Department of Polymer Technology, Chalmers University of Technology, S-412 96 Göteborg, Sweden

## SYNOPSIS

Cellulose fibers were surface modified with polypropylene–maleic anhydride copolymer. The physical properties of such fibers were characterized by contact angle measurements, and the chemical structure was identified with ESCA and FTIR. ESCA showed that the modifying agent was localized at the surface of the fibers. The modified fibers were compounded with polypropylene, and composites with various amount of fibers were manufactured by injection molding. All mechanical properties were improved when treated fibers were used. SEM showed improved dispersion, wetting of fibers, and adhesion. The nature of adhesion was studied using FTIR. It was found that the surface modifying agent is covalently bonded to the fibers through esterification. The degree of esterification is enhanced by activating the modifying agent before fiber treatment. This study has shown the effects of treatment conditions on activation of reactive species and chemical reaction between fiber and modifying agent. Moreover, a better understanding has been achieved of the nature of adhesion for the system.

## INTRODUCTION

The use of thermoplastics and composites thereof has increased tremendously in recent years. As a result, considerable efforts have been made to find suitable reinforcing fillers. Using a reinforcing filler can reduce material costs at the same time as certain properties are improved.[1] Among organic fillers, wood and cellulose fibers are attractive alternatives for reinforcing thermoplastics.[2-5] Composites based on cellulose fibers offer a number of benefits. These include: high specific stiffness and strength, desirable fiber aspect ratio, flexibility during processing with no harm to the equipment, low density, biogradability, and, finally, low cost per unit volume basis.[6]

Despite the advantages mentioned above, use of cellulose fibers in thermoplastics in general, and in polypropylene (PP) in particular, has not been extensive. Possible reasons, all of which contribute to unsatisfactory final properties of the composite, include: limited thermal stability during processing, poor dispersion characteristics in the thermoplastic melt, and limited compatibility with the matrix.[7,8]

Coupling or compatibilizing agents have been tested in order to improve dispersion, adhesion, and compatibility for a system containing hydrophilic cellulose and a hydrophobic matrix. These agents can modify the interface by interacting with both the fiber and the matrix, thus forming a link between the components.[9]

For example, chlorotriazines were successfully used as coupling agents in cellulose fiber–polyester composites, increasing the wet strength by 60%.[5] Kokta et al. investigated in a number of studies the effect of such coupling agents as isocyanates and silanes on the mechanical properties of composites of wood cellulose fiber and various thermoplastics.[10-13] Especially the isocyanates remarkably improved the performance of the composites. In another study, an alkylketene dimer sizing agent improved the performance of a wood-filled polypropylene[14] and similarity methacryloxysilane and m-phenylenedimaleimide (PDM) showed promising results for wood flour/polypropylene composites, especially in the presence of a free-radical source.[15] This was believed to be due to the formation of a

graft copolymer, for example of PDM and PP, at the interface. This copolymer would link the components together, improving adhesion and hence mechanical properties. For the same reason, graft copolymers of the nonpolar matrix polymer and a polar monomer have been tested as coupling agents. Graft copolymers of PP and maleic anhydride (MAH–PP) have shown to be very effective additives for wood cellulose/PP composites.[16-20] This is said to be due to the fact that the similarity of the additive and the matrix structures permits the occurance of segmental crystallization, which is desirable for cohesive coupling between the copolymer and the PP matrix, while the carboxylic groups provide polar or covalent bonding to the surfaces of cellulosic fibers.[17,19] Contrary to the case of silanes, relatively little attention has been paid to examining the adhesion mechanism for these graft copolymers.

In this study, cellulose fibers were treated with an MAH–PP copolymer that in earlier studies[16,20] performed well as coupling agent. In order to determine the functioning of the coupling agent on the molecular level, surface analysis techniques such as ESCA and contact angle measurements were used. Moreover, the nature of adhesion for the system was investigated using FTIR.

## EXPERIMENTAL

### Materials

#### Polypropylene (PP)

The matrix material used for the preparation of composites was commercially available polypropylene, GY 621 M (ICI), density 0.905 g/cm$^3$, MFI$_{230/2.16}$-value 13, broad MW-distribution with $\bar{M}_n$ 6500 and $\bar{M}_w$ 83,600.

#### Maleic Anhydride–Polypropylene Copolymer (MAH–PP)

A commercially available MAH–PP, Hercoprime G (Hercules Inc.), was used for fiber treatment. $\bar{M}_n$ and $\bar{M}_w$ are 5000 and 39,000, respectively, and the acid value is 59, which corresponds to 6 wt % MAH.

#### Cellulose Fibers

Filter paper, Whatman no. 41, consisting of > 99% cellulose, 0.01% ash, and a neglible amount of lignin, was used for surface studies. α-Cellulose (Nymölla AB), obtained from 60% beechwood and 40% birchwood, was used for the preparation of composites. The fibers consist of > 99% cellulose (86% α-cel-

lulose), 0.3% ash, and a neglible amount of lignin. The pH of a 5% aqueous suspension is 5.9 for both types.

### Solvent

Toluene of reagent grade was used without further purification.

### Methods

#### Fiber Treatment

Cellulose fibers used for the surface studies were, before treatment, Sohxlet-extracted with toluene for 24 h and dried at 70°C in an oven with circulating air for 24 h. The fibers were then immersed in a solution of MAH–PP copolymer in hot toluene (100°C) for 5 min. The concentration of copolymer in solution was 5 wt % on the fibers. After treatment, the fibers were Sohxlet-extracted with toluene for 48 h to remove all components not covalently bonded to the fibers. Finally, the fibers were dried as described above until constant weight was achieved. As the treatment temperature was far below the processing temperature for PP composites, fibers treated with copolymer that had been preheated to 180°C for 5 min were also studied.

Both Sohxlet extraction steps were excluded for the cellulose fibers used in the composites. However, after treatment, the fibers were immersed in hot toluene for 12 h to remove copolymer which had not reacted with the fibers.

#### Contact Angle Measurements

The contact angle for treated fibers was measured with a Zeiss microscope equipped with a Goniometerocular. The contact liquid used was distilled water. The volume of the droplet was 10 μL, and the contact angle given is the average value of 10 measurements.

#### Electron Spectroscopy for Chemical Analysis (ESCA)

The surface chemistry of the cellulose fibers was investigated with ESCA. An AEI ES200 Spectrometer with an Al(K$_\alpha$) X-ray source, at 14 kV and 20 mA, was used. The energy scale was chosen so that the binding energy of C 1s in aliphatic hydrocarbons was 285 eV. A Tektronix 4051 graphics terminal was used for background subtraction, peak separation, and peak area measurements. The C 1s spectrum was resolved under the assumption of Gaussian distribution. Two parameters, the full width at half-

maximum and the peak position, were varied until rough correspondence to the observed spectrum was obtained. The surface composition in mole fractions was calculated using a relative yield factor that was obtained by analyzing a poly-HEMA standard.

### Infrared Spectroscopy (IR)

Transmission spectra were obtained with the KBr technique, using a Nicolet DX-10 FTIR spectrophotometer at a resolution of 2 cm$^{-1}$ with the co-addition of 32 scans.

### Titrimetric Analyses

Free acid, saponification, and free hydroxyl values were determined according to methods described elsewhere.[21]

### Manufacturing of Composite Samples

The filler, the additive, and the matrix polymer were mixed and homogenized in a mixing extruder (Buss-Kneader PR 46, diameter $D = 46$ mm, $D/L = 11$) using a 15-mm exit die. The average residence time was on the order of 100 s and the temperature 180°C. After granulating, the mixes were injection moulded at 180°C with a conventional injection molding machine (Arburg 221E/170R) into tensile test bars (DIN 53455, effective length 75 mm, cross section $10 \times 3.4$ mm$^2$).

### Mechanical Testing

The mechanical properties of the samples (tensile modulus and tensile strength at yield) were measured with an instron tensile tester (Instron 1193, extensometer G51-15MA). The strain rate was 1.1 $\times 10^{-3}$ s$^{-1}$ and the temperature 23 ± 0.5°C. All results given are the average values of five measurements.

### Scanning Electron Microscopy (SEM)

The tensile fracture surfaces of the composite samples were studied with a Jeol JSM-U3 scanning electron microscope, operated at 25 keV.

## RESULTS AND DISCUSSION

### Surface Properties of Treated Fibers

When the fibers had been treated, they were characterized by means of contact angle measurements, ESCA, FTIR, and titrimetric analyses.

### Physical Properties

Contact angle measurements on treated cellulose fibers showed that the fibers had become totally hydrophobic. Figure 1 illustrates the fact that contact
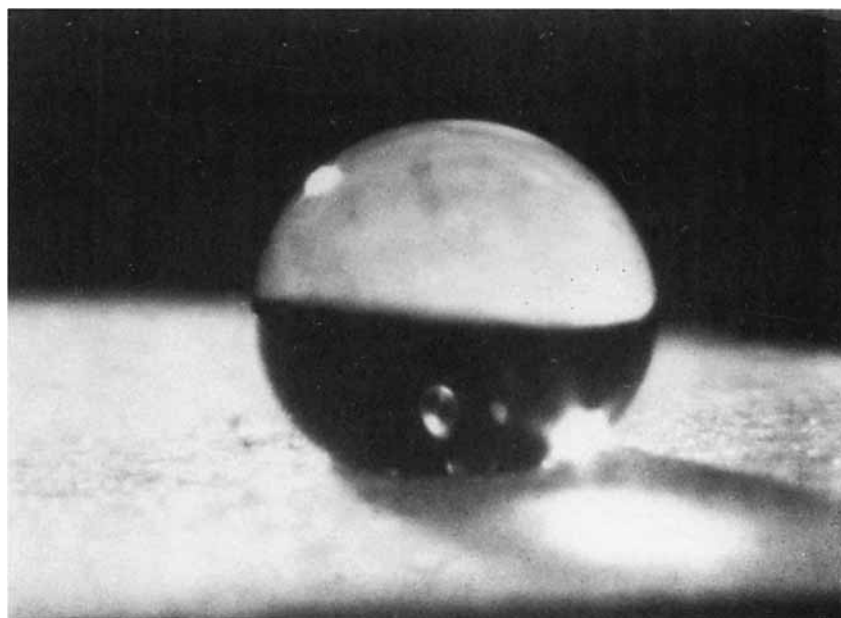


**Figure 1**   Photomicrograph of a water droplet on surface-modified cellulose (26×). Contact angle = 140°.

**Table I  Contact Angle Measurements on Surface Treated Cellulose Fibers**

| Sohxlet-Extracted with | Contact Angle | |
| --- | --- | --- |
| | MAH–PP (As Received) | MAH–PP (Preheated) |
| 1. — | 138° | 142° |
| 2. Toluene | 132° | 135° |
| 3. As 2 but also with toluene–DMF | 132° | 134° |
| 4. As 3 but also with water | 110° | 115° |
| 5. As 4 but also with 0.1 $M$ NaOH | 67° | 70° |

angles around 140° were observed. The results of contact angle measurements on treated cellulose are listed in Table I. As can be seen, there is no significant difference between the contact angles for fibers treated with MAH–PP copolymer as received and fibers treated with preheated copolymer. According to the results of the gravimetric and titrimetric analyses presented in Table II, this could be due to the fact that almost the same amount of MAH–PP copolymer was bonded to the fiber surfaces. Moreover, titrimetric analyses indicate that the difference between the two kinds of treated fibers in the number of free accessible hydroxyl groups, determined to be 8%, is probably too small to affect the contact angle significantly.

Sohxlet extraction with different solvents was carried out in order to confirm whether the modifying agent was attached to the fibers by hydrogen or covalent bonding. Dimethylformamide (DMF) is known to effectively release hydrogen bonding and was therefore used in the second extraction step. However, no significant decrease of contact angle was measured after this extraction step.

To determine the sensibility to moisture of the bonding between the modifying agent and the fibers, treated fibers were also Sohxlet-extracted with distilled water, which caused a 17% decrease in the contact angle. Furthermore, after extraction with 0.1 $M$ NaOH, the contact angle decreased by a further 39%. These findings are most likely due to a partial hydrolysis of the ester bonds linking the modifying agent to the fibers. This was also confirmed by the titrimetric analyses of extracted fibers which, particularly for the NaOH-extracted fibers, showed significantly lower saponification values and a greater number of free accessible hydroxyl groups.

## Chemical Properties

ESCA was used for the characterization of modified fibers. Figure 2 shows the spectra of untreated fibers and that of fibers treated with MAH–PP copolymer as received. In the latter, the peak at 285 eV characteristic for C—C has increased dramatically. Moreover, the O/C ratio and the O/(O—C=O) ratio have decreased by 40 and 50%, respectively. However, the gravimetric analyses show that the decrease of the O/C ratio of the fiber bulk is only 6%. This indicates that the MAH–PP copolymer is concentrated on the surfaces of the treated fibers, thus explaining their hydrophobic properties.

Table II presents the results of gravimetric and titrimetric analyses of fibers before and after treatment, as well as after Sohxlet extraction with solvents affecting the contact angle. The increase in weight due to treatment was almost the same for fibers treated with unheated copolymer as for those treated with a preheated one. This indicates that the same amount of copolymer was bonded to the fibers. However, titrimetric analyses showed that the number of free accessible hydroxyl groups, as well as the free acid value, were larger for fibers treated

**Table II  Titrimetric and Gravimetric Analyses of Cellulose Fibers**

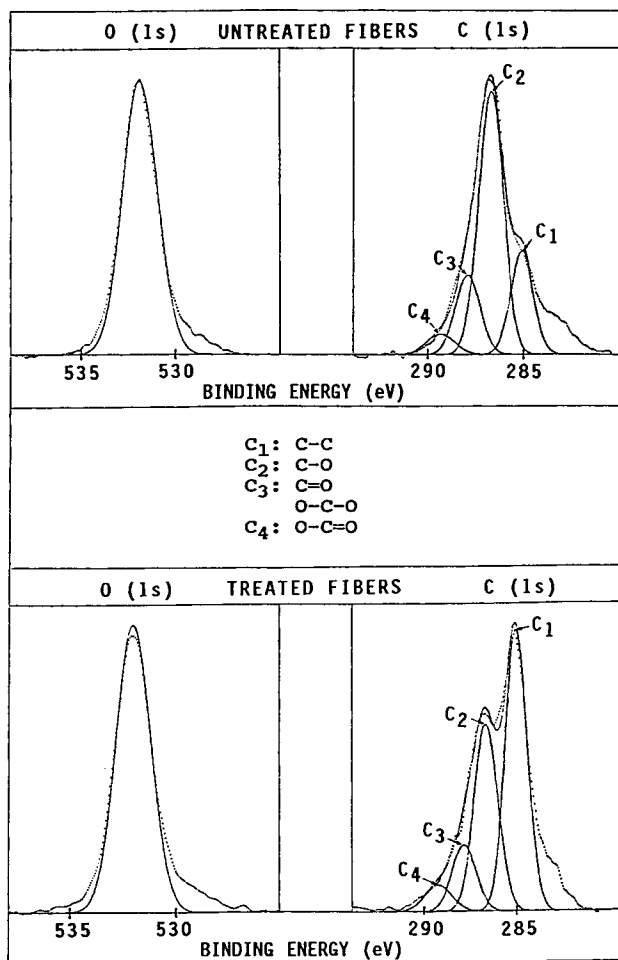| Treatment | Sohxlet-Extracted with | Weight Gain (g) | Free Hydroxyl Groups (mmol/g) | Saponification Value (mmol/g) | Free Acid Value (mmol/g) |
| --- | --- | --- | --- | --- | --- |
| 1. — | Toluene | — | 1.72 | 0 | 0 |
| 2. MAH–PP (preheated) | Toluene | +0.337 | 1.41 | 0.373 | 0.058 |
| 3. MAH–PP (as received) | Toluene | +0.323 | 1.53 | 0.354 | 0.152 |
| 4. MAH–PP (as received) | As 3 but also with water | −0.085 | 1.61 | 0.252 | 0.159 |
| 5. MAH–PP (as received) | As 4 but also with 0.1 $M$ NaOH | −0.158 | 1.68 | 0.112 | 0.077 |

**Figure 2** ESCA spectra of untreated and treated cellulose fibers. Untreated fibers: $C_1$ electron intensity = 281 counts/s; 0 electron intensity = 722 counts/s. Treated fibers: $C_1$ electron intensity = 656 counts/s; 0 electron intensity = 408 counts/s.



**Figure 3** Tensile stress–strain curves for a composite containing (A) 40% treated fibers, (B) 40% untreated fibers, (C) 10% treated fibers, (D) 10% untreated fibers.



**Figure 4** The effect of fiber content on the tensile strength of cellulose fiber/PP composites.



**Figure 5** The effect of fiber content on the tensile modulus of cellulose fiber/PP composites.

with unheated copolymer, while the saponification value (amount of free and hydrolyzable acid) for treated fibers was almost the same for in both cases. All the above results indicate that the esterification was more extensive for fibers treated with preheated copolymer, thus giving a higher diester content. Still, the same amount of copolymer was bonded to the fiber surfaces.

Titrimetric and gravimetric analyses were also carried out for the cellulose fibers, which showed a decrease in the contact angle after Sohxlet extraction with distilled water and 0.1 $M$ NaOH. For fibers extracted with water, the decrease in weight was measured to be 26%, whereas the saponification value decreased by 29%. For fibers extracted further with NaOH, the decrease of weight and saponification value for this extraction step were both 56%.
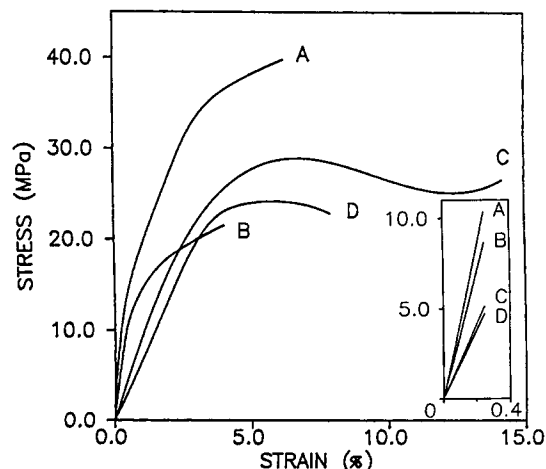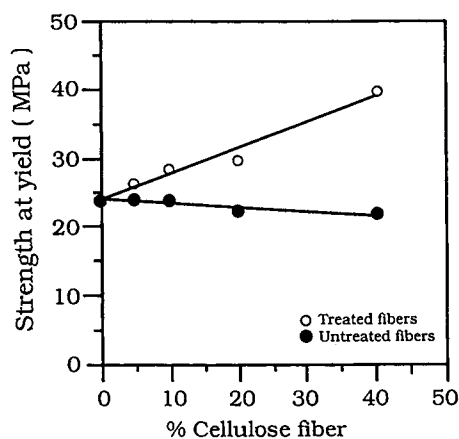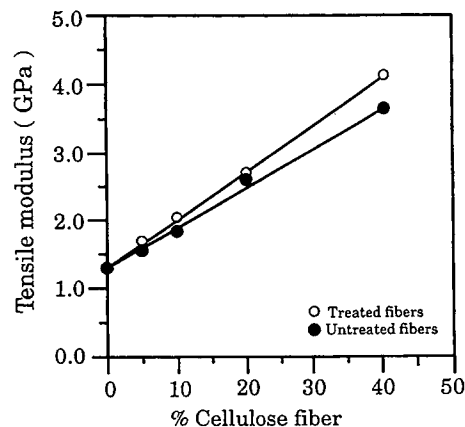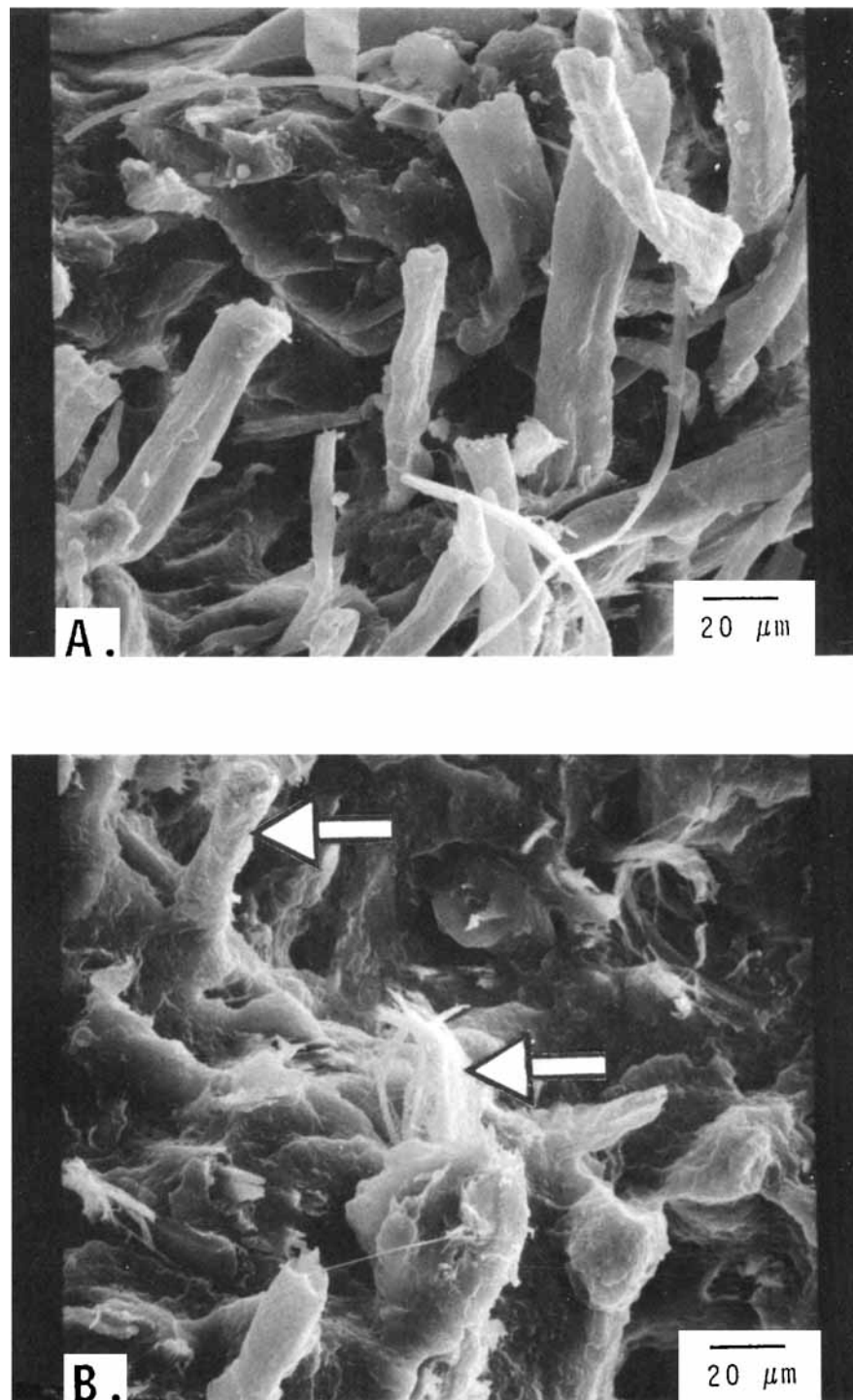
**Figure 6** Scanning electron micrographs of tensile fracture surfaces of 20% cellulose fiber/PP composites. Magnification: (A) 500×; (B) 500×; (C) 2000×; (D) 2000×; (E) 2000×. (A and C) untreated fibers; (B, D, and E) treated fibers.

No significant difference in this behavior was detected between the fibers treated with unheated copolymer and a preheated one. These findings explain the decreases in contact angle due to extraction that were presented under physical properties.

**Properties of Composites**

PP composites were manufactured to investigate the effect of the MAH–PP copolymer on the mechanical and interfacial properties.
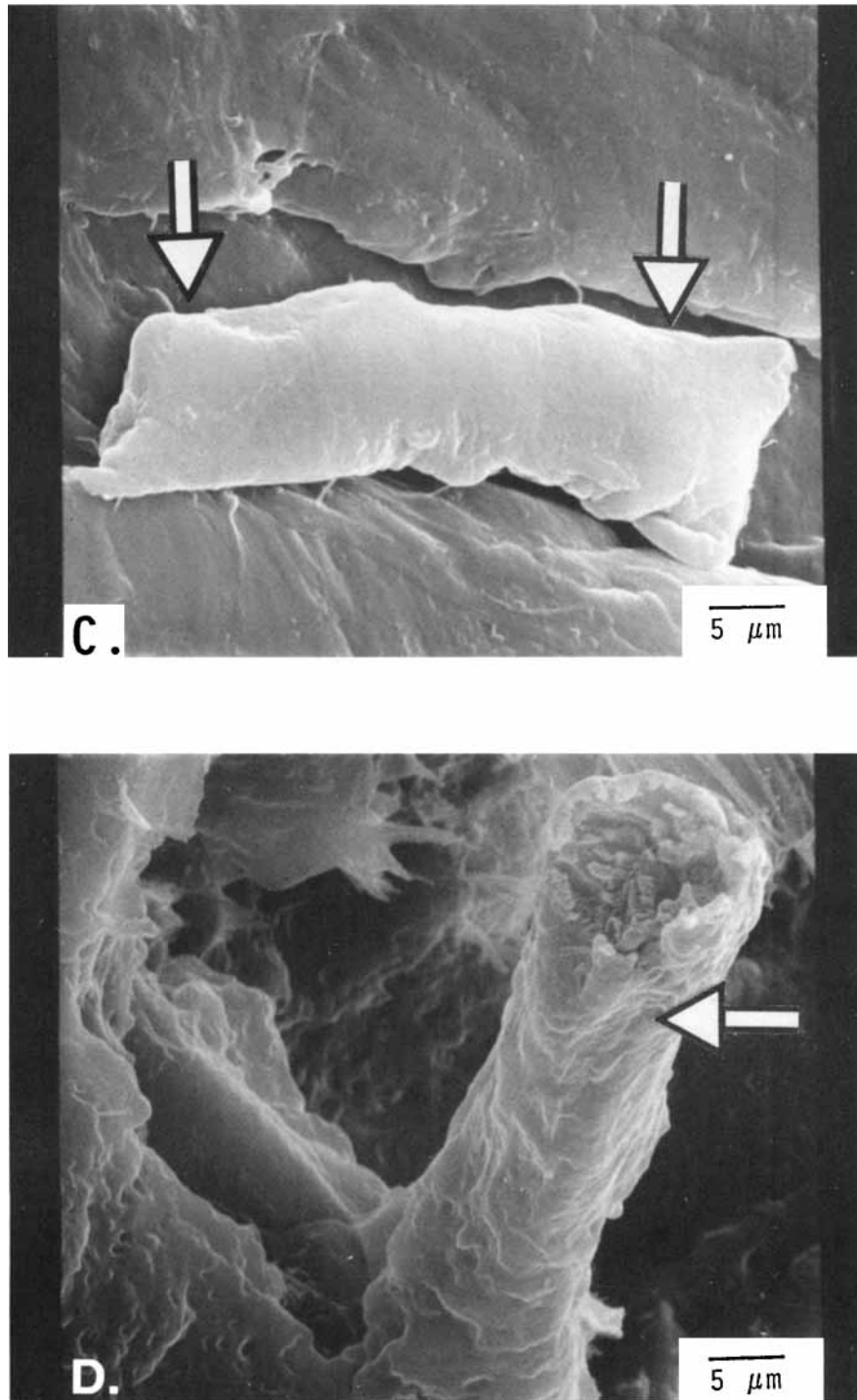
**Figure 6**    (*continued from the previous page*)

## Mechanical Properties

Mechanical properties were evaluated for composites based on PP/untreated cellulose fibers and PP/cellulose fibers treated with MAH–PP copolymer as received. The stress–strain behavior for composites containing various amount of fibers was examined.

Figure 3 shows the stress–strain behavior at two fiber contents, 10 and 40%. The curves, extending into the nonlinear region in all cases, indicate that fiber treatment improves interfacial adhesion, yielding a stronger and more ductile material. As shown in Figure 4, the effect of treatment becomes more pronounced with an increased fiber content.
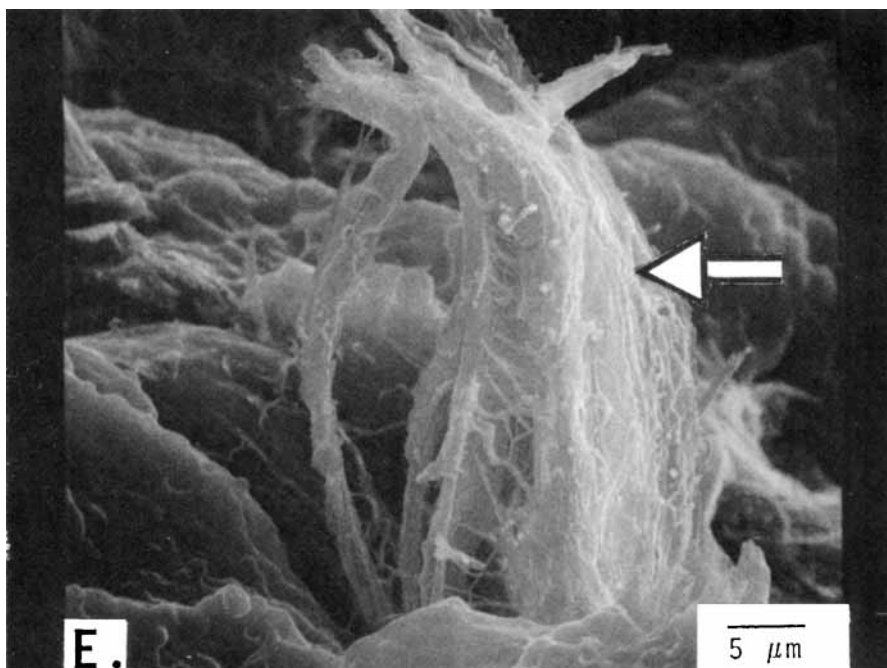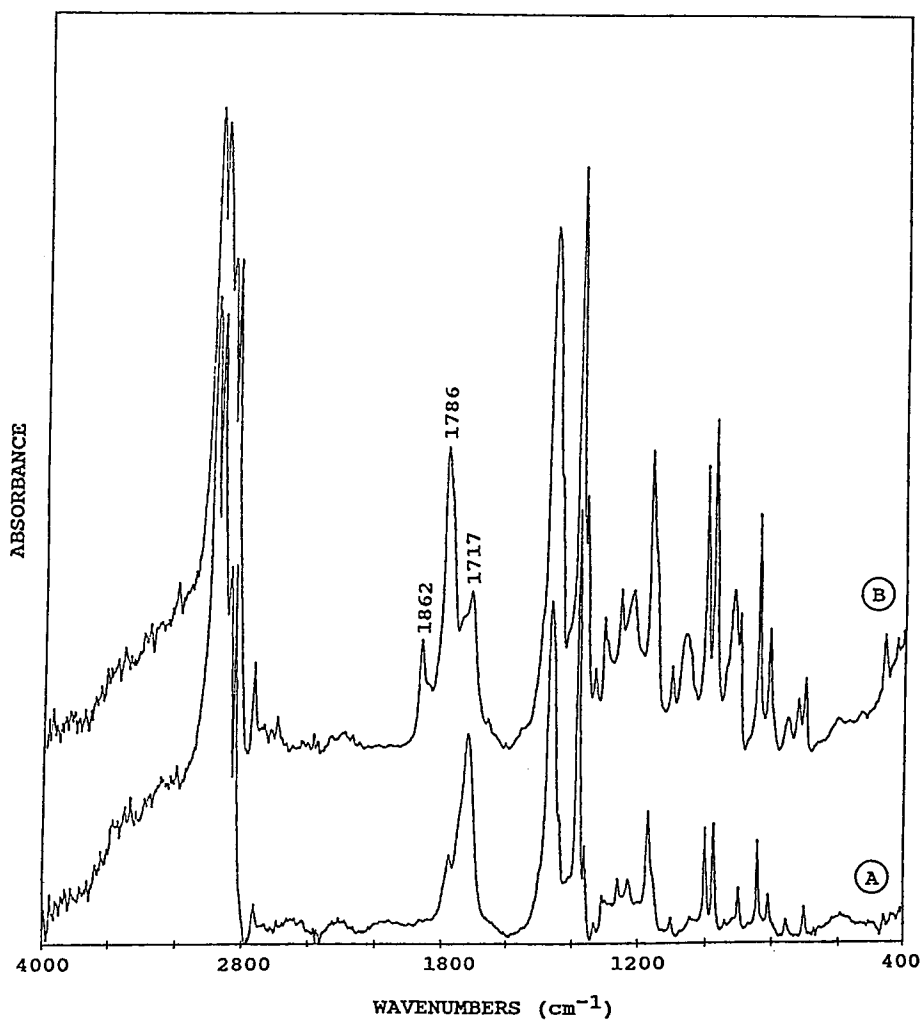
**Figure 6** (*continued from the previous page*)



**Figure 7** FTIR spectra of: (A) MAH–PP copolymer as received; (B) activated MAH–PP copolymer (180°, 5 min).

At a fiber loading of 40%, the strength and the elongation at yield increased by 80 and 30%, respectively. In the case of a 10% fiber content, the corresponding values were 20 and 17%, respectively. However, in the latter case, the elongation at break increased by more than 50%. Furthermore, Figure 4 shows that contrary to the case of treated fibers, where tensile strength increased with increased fiber loading, tensile strength decreased when the loading of untreated fibers increased.

In both Figures 3 and 5, increasing the filler content results in an improvement in stiffness as expected. However, improved adhesion does not affect the initial tensile modulus to a great extent. Fiber treatment causes only a 14% increase at 40% fiber loading.

### Interfacial Properties

Scanning electron microscopy (SEM) was used to study the tensile fracture surfaces of composite samples based on 20% untreated fibers and treated fibers. SEM micrographs of the fracture surfaces are shown in Figures 6(A)-(E).

In order to obtain composite materials with satisfactory mechanical properties, good dispersion of fibers in the matrix, effective wetting of fibers by matrix, and strong interfacial adhesion are required. This is not the case however, when untreated fibers are used in PP.

Due to hydrogen bonds formed between untreated fibers and the wide difference in character between untreated fibers and the matrix, the fibers tend to agglomerate into bundles and become unevenly distributed throughout the matrix. This is shown in Figure 6(A). Treatment of the fibers prevents hydrogen bonds from being formed and causes the properties of the fiber surfaces and the matrix to become more similar. As shown in Figure 6(B), a better dispersion is obtained in this case. [The spots pointed out by the markers are enlarged and shown in Figs. 6(D) and (E).]

The markers in Figure 6(C) show the poor wetting of a fiber when untreated fibers were used. The reason for this is the large difference in surface energy between fibers and matrix.[1] By treating the fibers, their surface energy is lowered to a level much closer to the surface energy of the matrix. Thus better wetting is obtained, as is shown in Figure 6(D) [enlargement of the spot pointed out by the upper marker in Figure 6(B)]. It can be seen, that the entire fiber is covered by layers of the matrix material that have been pulled out together with the fiber.

Without effective wetting of the fiber strong interfacial adhesion cannot exist. Lack of interfacial

interactions leads to a material response that, at least for small strains, will be the same as though the matrix contained holes of a shape identical to that of the filler.[1] The left marker in Figure 6C shows insufficient adhesion between the untreated fiber and matrix, causing fiber pullout. Improved adhesion decreases the critical aspect ratio, so that fibers with a lower aspect ratio become sufficiently long to bear the load.[5] Treatment of the fibers with MAH–PP copolymer provides covalent bonds across the interface, permitting segmental crystallization and thus cohesive coupling between fiber and matrix.[19] Figure 6(E) [enlargement of the spot pointed out by the lower marker in Fig. 6(B)] shows how improved adhesion causes fiber breakage with separation of the fibrils of the cellulose fiber.

### Nature of Adhesion

FTIR was used extensively to investigate the nature of adhesion. The MAH–PP copolymer was first characterized. Figure 7 shows the spectrum of the copolymer (the lower one). The peak at $1717 \text{ cm}^{-1}$ is characteristic for the dimeric form of a dicarboxylic acid, whereas the relatively small peak at $1786$ $\text{cm}^{-1}$ and the hardly detectable one at $1862 \text{ cm}^{-1}$
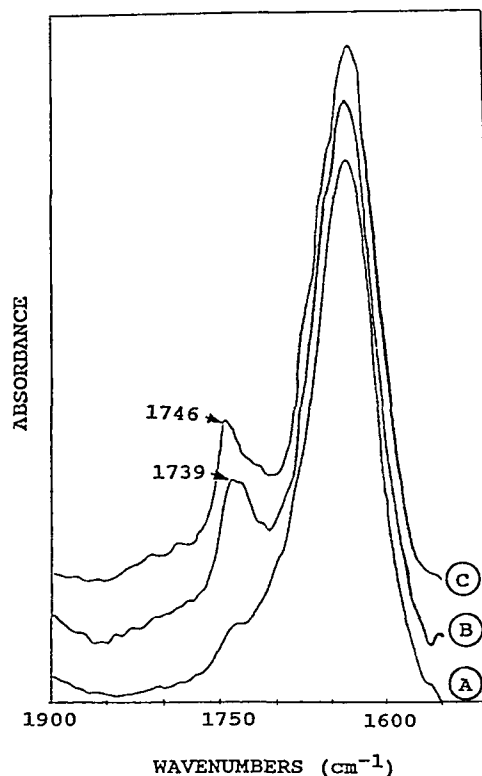


**Figure 8** FTIR spectra of: (A) untreated cellulose fibers; (B) cellulose fibers treated with MAH–PP as received; (C) cellulose fibers treated with activated MAH–PP.
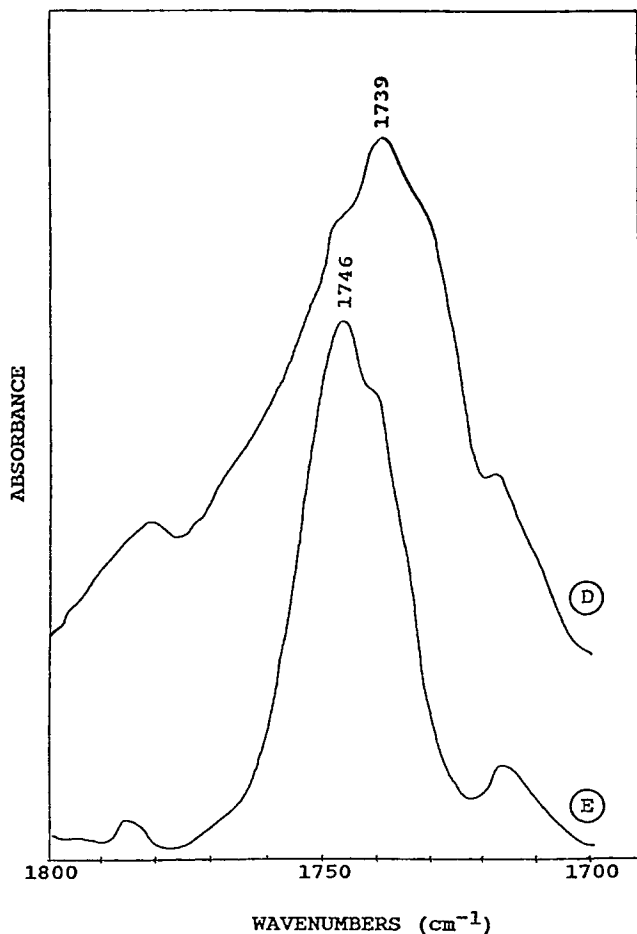
**Figure 9**    Difference spectra between: (D) the spectrum of cellulose fibers treated with MAH–PP as received and that of untreated fibers; (E) the spectrum of cellulose fibers treated with activated MAH–PP and that of untreated fibers.

are characteristic for a cyclic anhydride. Furthermore, the spectrum proves that the MAH–PP under normal conditions mainly exists in its hydrolyzed form, i.e., as maleic acid–PP copolymer. However, by heating the less reactive dicarboxylic acid form to processing temperatures for PP composites, the MAH–PP copolymer condenses to the more reactive anhydride form. This is confirmed by the upper spectrum in Figure 7, which shows the MAH–PP after "activation" (180°C, 5 min).

In order to investigate the effect of the difference in reactivity, fibers were treated with activated and nonactivated copolymer. FTIR spectras of the fibers were recorded, after treatment and Sohxlet extraction. Figure 8 shows an enlargement of the interesting region of the spectra of treated fibers. Due to the treatment, a peak located at 1739 cm$^{-1}$ is observed for fibers treated with nonactivated copolymer, whereas a peak at 1746 cm$^{-1}$ is observed for

fibers treated with an activated one. By subtracting the spectrum of untreated fibers from the spectra of treated fibers, the difference spectra shown in Figure 9 are obtained. These spectra further confirm the position of the peaks just mentioned, and also indicate the appearance of smaller peaks at 1746 cm$^{-1}$ in the former difference spectrum and at 1739 cm$^{-1}$ in the latter. This suggests the appearance of the same species on the two kinds of treated fibers. However, fibers treated with activated MAH–PP copolymer have a larger amount of the compound, causing the peak at 1746 cm$^{-1}$, than fibers treated with nonactivated.

The possibility that one of the peaks could arise from the monomeric form of the dicarboxylic acid, hydrogen bonded to the fibers, led us to investigate diluted solutions of the MAH–PP copolymer in $n$-butanol. Figure 10 shows a spectrum of the diluted copolymer at a concentration of 1.0 g/L. The peak at 1739 cm$^{-1}$ grows larger during dilution, while the peak at 1717 cm$^{-1}$ decreases. This phenomenon is
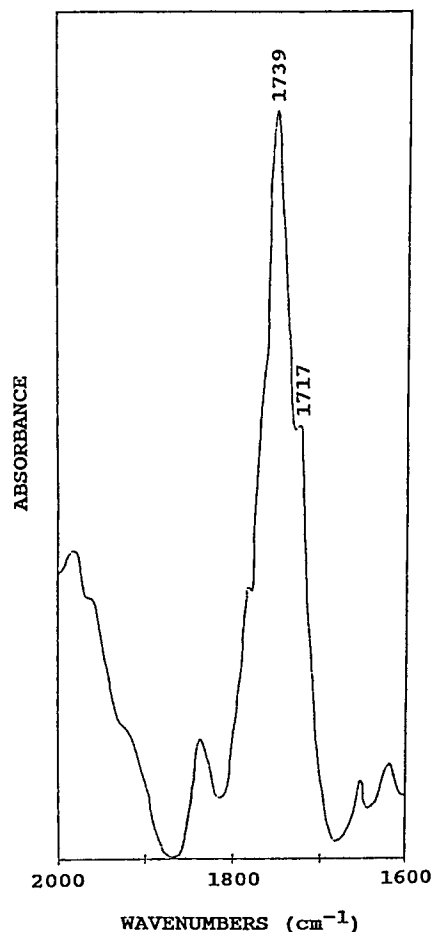


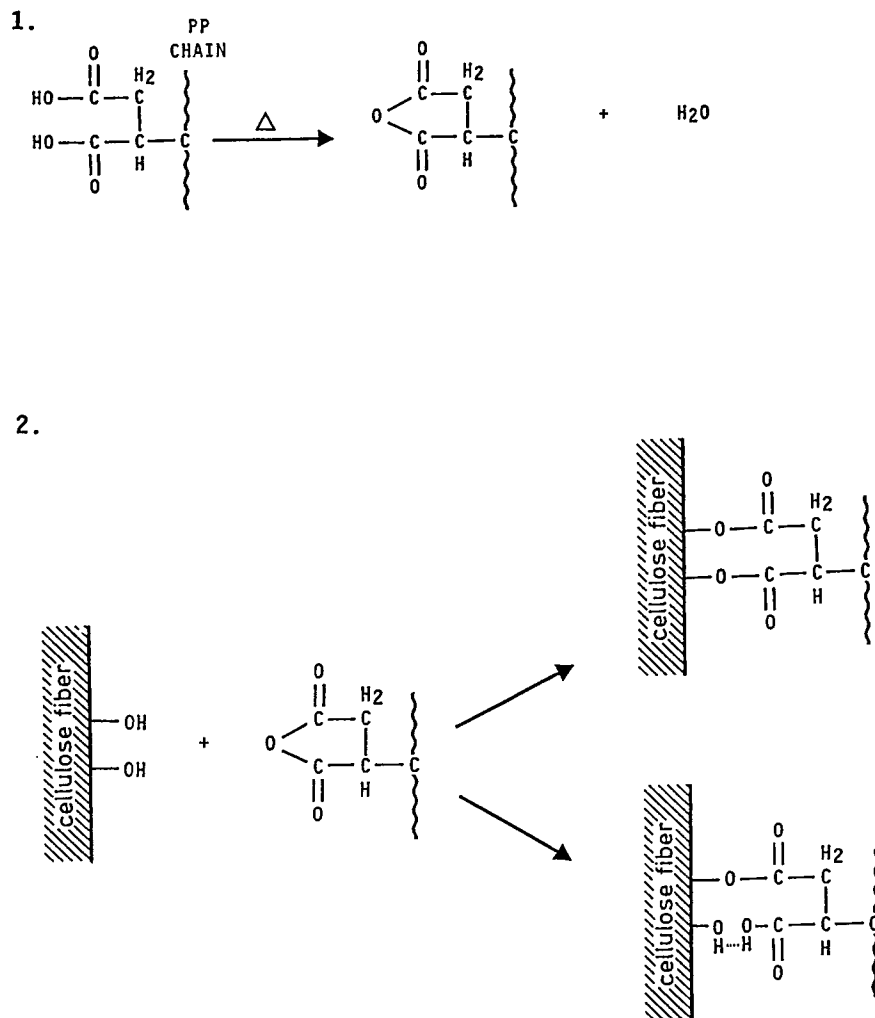**Figure 10**    FTIR spectrum of MAH–PP in $n$-butanol (1.0 g/L).

**Figure 11** Reactions as cellulose fibers are surface treated with MAH–PP.

probably caused by the increasing influence of the monomeric form through dilution. It is therefore most likely that the peak at 1739 cm$^{-1}$ in the difference spectra arises from the monomeric form of the dicarboxylic acid, whereas the peak at 1746 cm$^{-1}$ arises from ester bonds between the copolymer and the fibers. Thus, when activated copolymer is used, the amount of ester bonds is larger than in the case of nonactivated. This was further confirmed by the results of titrimetric and gravimetric analyses. When activated copolymer is used, a greater number of hydroxyl groups reacts per gram cellulose fibers than in the case of nonactivated. The saponification values of the fibers also indicate that the diester content is higher in the former case. The reaction between cellulose and copolymer can thus be divided into two main steps, according to Figure 11. In the first step, the copolymer is converted into the more reactive anhydride form; esterification of the cellulose fibers takes place in the second place.

As no swelling agents are used, the capillary system of pores and cracks of the cellulose are closed throughout the reaction. This makes it impossible for the relatively large MAH–PP molecules to penetrate into the cellulose fibers, hence limiting the esterification to the surface layer.[22] Furthermore, steric hindrance will most probably make the copolymer react preferentially with the primary hydroxyl groups in the surface layer.

## CONCLUSIONS

Surface studies of cellulose fibers treated with a maleic anhydride–polypropylene copolymer were carried out in order to investigate the nature of adhesion between cellulose fibers and the copolymer.

Contact angle measurements showed that cellulose fibers treated with the copolymer turned totally

hydrophobic and according to ESCA this was due to the fact that a considerable amount of copolymer was concentrated on the fiber surfaces.

FTIR and titrimetric analyses showed that the copolymer was bonded to the fibers by ester linkages and hydrogen bonds. The degree of esterification was increased by heating the copolymer to 170°C before fiber treatment.

The mechanical properties, tensile modulus, and tensile strength at yield, for cellulose fiber/PP composites, were improved when treated instead of untreated fibers were used. The reason for this improvement was detected by SEM studies of the tensile fracture surfaces. Composites containing treated fibers showed better dispersion of fibers in the matrix, a more effective wetting of fibers by the matrix and a better adhesion between the two phases.

The findings made in this study can be summarized as follows: The compatibility with polypropylene is radically improved by pretreating cellulose fibers with an MAH–PP copolymer. Such strong interfacial interactions as covalent and hydrogen bonds are formed across the interface between the two components and account for the adhesion in the system. The amount of covalent bonds are increased by activating the copolymer before treatment. The formation of covalent bonds can be divided into two steps: activation of the copolymer and esterification of the fibers.

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