

Surface of Cellulosic Materials Modified with Functionalized Polyethylene Coupling Agents

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ABSTRACT: The interfacial adhesion between a wood fiber and a plastic matrix strongly influences the performance of wood-fiber-reinforced thermoplastic composites. Fiber surface modification with coupling agents is generally needed to induce bond formation between the fiber and polymer matrix. This study investigated the chemical reactions between cellulosic materials and functionalized polyethylene coupling agents. Both wood flour and cotton cellulose powder were treated with acrylic acid-functionalized polyethylene and maleic anhydride-functionalized polyethylene (maleated polyethylene) for surface modifications, and chemical changes resulting from these treatments were followed by a study of the Fourier transform infrared and

X-ray photoelectron spectroscopy spectra. Variations in the band intensities, oxygen-to-carbon ratios, and concentrations of unoxidized carbon atoms were related to changes that occurred on the surfaces of modified cellulosic materials. The experimental results indicated that chemical bonds between the hydroxyl groups of the cellulosic materials and the functional groups of the coupling agents occurred through esterification reactions. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 278–286, 2003

Key words: plastics; fibers; composites; FT-IR; surfaces; modification; XPS

INTRODUCTION

Plastic/wood-fiber composites constitute a rapidly growing industry in the United States. These composites are being used in a large number of applications, including decks and docks, window frames, and molded panel components for automotive interiors. It has been reported that 460 million pounds of plastic/wood-fiber composites were produced in 1999.¹ Recent statistics show that the production of these composites in 2001 increased to 700 million pounds.^{1,2} Commodity thermoplastics such as polyethylene (PE),^{3,4} polypropylene (PP),^{5–8} poly(vinyl chloride) (PVC),^{9–12} and polystyrene¹³ are the polymer matrices mostly used in the manufacture of plastic/wood-fiber composites. Among these thermoplastics, PE represents the largest portion of the plastic/wood-fiber composites produced in North America, accounting for almost 70% of the polymeric matrices used in the manufacture of these composites.¹

Plastic/wood-fiber composites make use of wood fibers as fillers and/or reinforcing agents in the plastic matrix. These composites have a lower material cost

and a higher stiffness than neat plastics.^{5–12} Despite these advantages, the strength properties (e.g., tensile and flexural strengths) of these composites are usually inferior to those of the neat plastics because of the poor stress transfer from the polymer matrix to the load-bearing fibers due to the weak adhesion between them.^{5–10} This weak adhesion results from the incompatibility between the hydrophilic wood fibers and the hydrophobic plastics and the difficult dispersion of wood fibers in the plastic matrix because of the intermolecular fiber–fiber hydrogen bonding.^{5–10} The surface modification of wood fibers by coupling agents is an effective approach for promoting the affinity between wood fibers and plastics by facilitating the fiber dispersion into the polymer matrix and inducing the bond formation between the fibers and plastic matrix.^{5–11} When the fibers are properly treated, the stress transfer from the polymer matrix to the load-bearing fibers takes place, and as a result, the strength properties of the composites are enhanced.

In the past few years, maleated polypropylene (MAPP) as a coupling agent has received substantial attention because of its ability to enhance the tensile and flexural strengths of PP/wood-fiber composites.^{5–8} The improvement in the strength properties of PP/wood-fiber composites has been attributed to the formation of ester bonds between the anhydride carbonyl groups of MAPP and the hydroxyl groups of the wood fibers^{14–17} coupled with the diffusion of the PP backbone of MAPP

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TABLE I
Characteristics of Coupling Agents Based on High-Density PE

| Coupling agents | Functional monomer | Melt-flow rate ^a (g/10 min) | Melting point (°C) | Percentage functionality |
|---|--------------------|--|--------------------|--------------------------|
| PE acrylic acid copolymer (Polybond 1009) | Acrylic acid | 6 | 135 | 6.0 |
| PE maleic anhydride copolymer (Polybond 3009) | Maleic anhydride | 5 | 127 | 1.0 |

^a Melt-flow rate measured at 190°C and 2.16 kg according to ASTM D1238.

introduced to the surface of treated wood fibers into the PP matrix phase during manufacturing.⁵⁻⁸ In other words, MAPP is able to attach to both of the major composite components during processing, creating good interfacial adhesion between the wood-fiber reinforcement and the PP matrix.

However, MAPP appeared less effective when polymer matrices other than PP were used in the composites (e.g., in PE/wood-flour or PVC/wood-flour composites) because of the incompatibility between the PP backbone of MAPP and the PE or PVC matrix in the composites.^{4,9,10,18,19} By contrast, functionalized PE coupling agents such as maleated PE have been reported to be effective in significantly improving the strength properties of PE/wood-fiber composites.^{4,18} Despite these promising results, the mechanisms by which this improvement occurs have not been extensively investigated. It is believed that an understanding of the fundamental mechanism by which functionalized PE coupling agents bond to cellulosic fibers would be necessary for the prediction of the strength properties of PE/wood-fiber composites. Therefore, the objective of this work was to investigate the surfaces of cellulosic materials before and after treatments with functionalized PE coupling agents to elucidate the mechanisms by which these compatibilizing agents react with cellulosic materials. The effectiveness of the modifications made on the surfaces of cellulosic materials was monitored with spectroscopic techniques such as Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS). FTIR spectroscopy is a valuable technique for elucidating functional groups and linkages in any chemical structure analysis, whereas XPS is useful for analyzing the surface elemental compositions of cellulosic materials before and after treatment.^{5,10,14-17,20}

EXPERIMENTAL

Materials

Wood flour from hardwood maple (100-mesh size; American Wood Fibers, Schofield, WI) and cotton cellulose powder (CF11; Whatman, Ltd., Springfield Mill Maid Stone Kent, England) were used as cellulosic

materials. Acrylic acid-functionalized PE (Polybond 1009) and maleated PE (Polybond 3009), supplied by Uniroyal Chemicals (Middlebury, CT), were used as coupling agents for surface modification. Detailed information on these coupling agents is summarized in Table I. Xylene (certified American Chemical Society-grade; Fisher Scientific, Hanover Park, IL) and acetone (Guaranteed Reagent, (GR)-grade; EM Science, Cincinnati, OH) were used as solvents.

Treatment of cellulosic materials with coupling agents

Before surface modification, wood flour and cotton cellulose powder were extracted in a Soxhlet-extraction apparatus with acetone for 24 h, air-dried for 60 h, and then oven-dried at 100°C until a constant weight was achieved.

The surface treatment of the extracted cellulosic materials with coupling agents was carried out in a flask by the immersion of the cellulosic materials in 100 mL of a xylene solution containing 30% of a coupling agent (based on the oven-dried weight of the cellulosic materials), unless stated otherwise. The reaction mixtures were stirred at 138°C for 2 h. After the reactions, the mixtures were filtered for the removal of the solvent. The treated cellulosic materials were air-dried for 60 h and then oven-dried at 100°C until a constant weight was achieved.

The dried and treated cellulosic materials were again extracted in a Soxhlet-extraction apparatus with xylene for 24 h for the removal of the unreacted coupling agents. The extracted cellulosic materials were air-dried for 60 h and oven-dried at 100°C until a constant weight was achieved. FTIR spectra were collected on these extracted cellulosic materials. A second 24-h Soxhlet extraction with xylene was performed on the treated cellulosic materials so that the unreacted coupling agents would completely be removed from the surfaces of the cellulosic materials upon the first extraction. This second extraction was also followed by air-drying of the cellulosic materials for 60 h and oven-drying at 100°C until a constant weight was

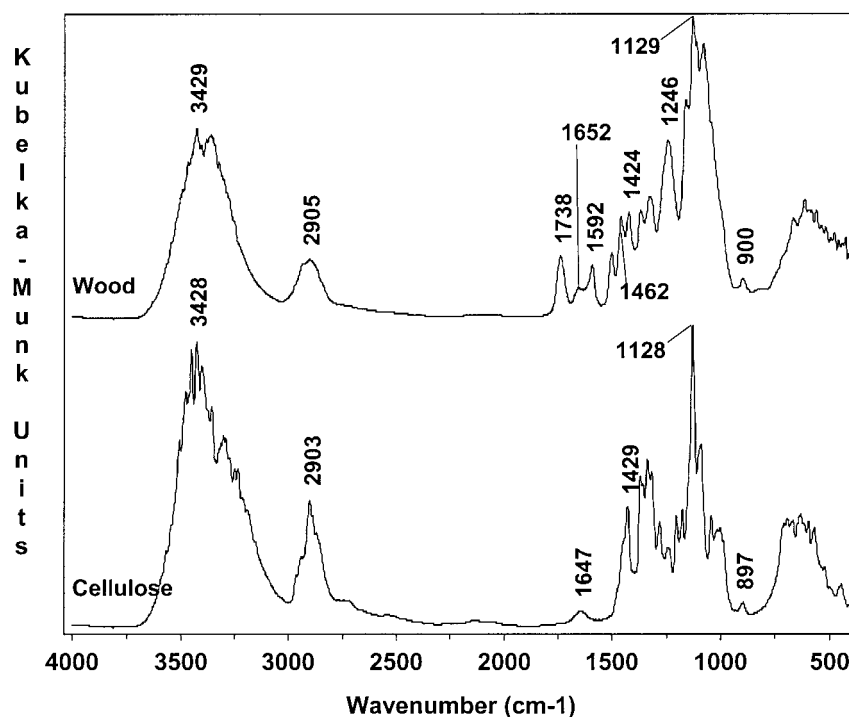


Figure 1 FTIR spectra of untreated wood flour and cotton cellulose powder.

achieved. The IR spectra were collected for comparison with those collected after the first 24-h extraction.

FTIR spectroscopy and XPS measurements

FTIR spectra of untreated and treated cellulosic materials were obtained on a Genesis II FTIR spectrophotometer (Mattson Instruments, Madison, WI) at a resolution of 4 cm^{-1} with a coaddition of 100 scans for each spectrum.¹⁴ All of the IR spectra were recorded in Kubelka–Munk units in the $4000\text{--}500\text{ cm}^{-1}$ range. Pure powdered potassium bromide (KBr) was used as a reference substance, whereas no dilution of powdered cellulosic materials in KBr was required to obtain a spectrum. Diffuse reflectance was used with FTIR for the transfer of IR radiation. Data analysis, including spectra normalization, peak smoothing (cubic smooth method with 10 smooth points), and spectral subtraction, was performed with WinFIRST software from Thermo Nicolet (Madison, WI). No baseline correction was used during spectral analysis.

XPS spectra of unmodified and modified cotton cellulose powders were recorded with an X-ray photoelectron spectrometer (Leybold Max 200, Cologne, Germany) with an unmonochromated Mg $K\alpha$ source (1253.6 eV). The samples were analyzed at a takeoff angle of 90° relative to the electron detector, and this gave an approximate sampling depth of 50 \AA . The procedure for XPS data collection and analysis has been described in previous articles.^{10,14,20}

RESULTS AND DISCUSSION

FTIR spectra of untreated cellulosic materials

FTIR spectra of untreated cellulosic materials are shown in Figure 1. Obviously, there are many similarities and differences between the cellulosic materials. Both wood flour and cotton cellulose have absorption bands around 3428 cm^{-1} associated with hydroxyl group (OH) stretching vibrations, around 2905 cm^{-1} due to the C—H stretching vibrations, and around $1647\text{--}1652\text{ cm}^{-1}$ that might be due to the absorbed water in cellulosic materials, and most of the bands at 1375 and $1280\text{--}1202\text{ cm}^{-1}$ are related to CH_2 , CH, and OH deformation vibrations of cellulosic materials.^{21,22}

The major differences between the FTIR spectra of the two cellulosic materials are seen at 1738 , 1592 , 1462 , 1429 , and 1128 cm^{-1} . The FTIR spectrum of wood flour has absorption bands at 1738 and $1592\text{--}1462\text{ cm}^{-1}$ that are due to the carbonyl (C=O) stretching vibrations and benzene stretching in the lignin, respectively.²³ By contrast, as expected, the spectrum of cotton cellulose does not show any absorption bands at 1738 or 1592 cm^{-1} associated with carbonyl (C=O) stretching vibrations and benzene stretching in lignin. Instead, the peak intensity of absorption bands at 1429 (CH_2 stretching)^{21,24} and 1128 cm^{-1} (C—O stretching vibrations of alcohols and C—C stretching)²¹ has significantly increased, implying that the surface is rich in cellulose.

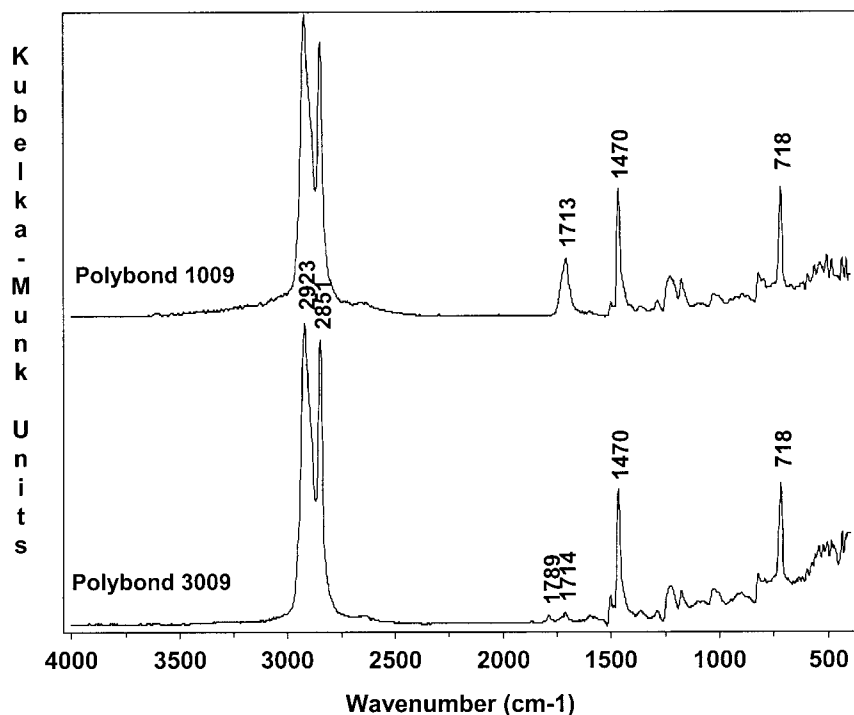


Figure 2 FTIR spectra of acrylic acid-functionalized PE (Polybond 1009) and maleated PE (Polybond 3009).

The differences in the FTIR spectra of wood flour and cotton cellulose are relevant for the confirmation of the presence of the ester groups formed by the esterification reaction between cellulosic materials and functionalized PEs. The absorption bands characteristic of ester carbonyl groups merge around $1765\text{--}1710\text{ cm}^{-1}$.²⁵ Because wood flour already contains carbonyl groups (Fig. 1), the increase in the relative intensity of the $\text{C}=\text{O}$ stretching bands in the $1710\text{--}1765\text{ cm}^{-1}$ region will provide good evidence of the esterification of wood flour.¹⁴ However, there is also a possibility that the carbonyl peak of wood flour may obscure the detection of bands characteristic of the ester carbonyl stretching groups on the FTIR spectra of treated wood flour if the esterification reaction takes place.^{5,16} Conversely, cotton cellulose does not show any absorption bands in the $1765\text{--}1720\text{ cm}^{-1}$ region; therefore, it may provide a better identification of the ester link between cellulosic materials and coupling agents.

FTIR spectra of functionalized PEs

Figure 2 shows the FTIR spectra of acrylic acid-functionalized PE (Polybond 1009) and maleated PE (Polybond 3009). The chemical structures of these coupling agents are shown in Figure 3.

Both spectra show a pair of very strong absorption bands at 2851 and 2923 cm^{-1} due to the symmetrical and asymmetrical CH_2 stretching vibrations of the aliphatic carbons of the coupling agents.^{25–29} Addi-

tional absorption bands at 1470 and 718 cm^{-1} are attributed to CH_2 deformation vibrations and $\text{—}(\text{CH}_2)_4\text{—}$ skeletal vibrations, respectively.²⁵ These absorption bands are all associated with the aliphatic carbons of PE chains of the coupling agents (Fig. 3).

Despite the aforementioned similarities, the IR spectra of the coupling agents are also very distinctive (Fig. 2). Two distinct characteristics are seen in the carbonyl stretching bands located in the $1800\text{--}1700\text{ cm}^{-1}$ frequency range. The IR spectrum of acrylic acid-functionalized PE (Polybond 1009) shows a single absorption band at 1713 cm^{-1} due to the stretching mode of the carboxyl carbonyl (ketone carbonyl) groups in the Polybond 1009 molecules.^{25–28} However, the IR spectrum of maleated PE (Polybond 3009) shows two distinct peaks at 1789 and 1714 cm^{-1} that are likely due to the asymmetrical stretching of the anhydride carbonyl

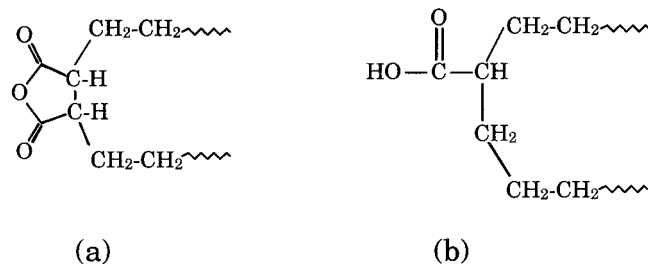


Figure 3 Chemical structures of (a) maleated PE (Polybond 3009) and (b) acrylic acid-functionalized PE (Polybond 1009).

(ester carbonyl) and the carboxyl groups present in maleated PE, respectively.^{25–28} The intensity of the absorption bands of the carbonyl groups in Polybond 3009 is much weaker than that of the absorption band of the carbonyl groups in acrylic acid-functionalized PE (Polybond 1009).

The C—H stretching vibrations of the functionalized PEs (Fig. 2) have distinct features compared with those of cellulosic materials (Fig. 1). It can be seen in Figure 2 that the C—H stretching absorption bands of functionalized PEs are sharp, with a pair of very strong absorption peaks (2923 and 2851 cm^{-1}). Although absorption in this wave-number region is also found in cellulosic materials (2903 cm^{-1}), it is weak in intensity and single-banded (Fig. 1).

Surface characterization of cellulosic materials treated with functionalized PE coupling agents

In Figure 4(a), the FTIR spectra of untreated cellulose (spectrum A), cellulose treated with 30% maleated PE (spectra B and C), and cellulose treated with 30% acrylic acid-functionalized PE (spectra D and E) are illustrated, whereas Figure 4(b) shows the FTIR spectra of wood-flour counterparts. For the interpretation of IR spectra, it is important that all unreacted coupling agents are removed in the 24 h Soxhlet extraction with a solvent. The IR spectra of the treated cellulosic materials from the second 24 h Soxhlet extraction (spectra C and E) are similar to those obtained after the first 24 h Soxhlet extraction (spectra B and D). This result suggests that most of the unreacted coupling agents have been successfully removed from the surface of the treated cellulose after the first 24 h Soxhlet extraction.

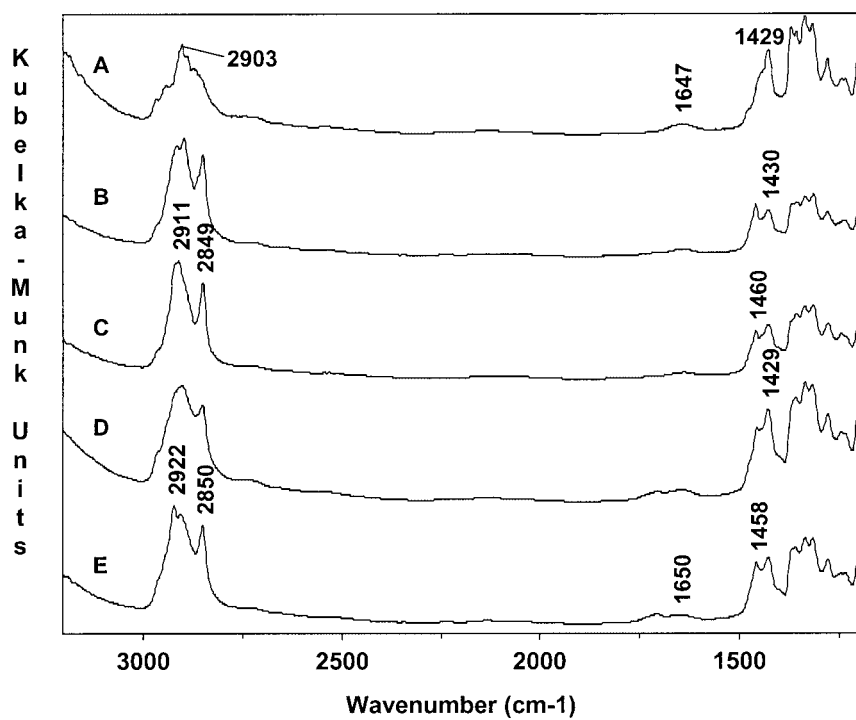
Comparisons of the FTIR spectra of untreated cellulosic materials (spectrum A) and those treated with maleated PE (spectra B and C) and acrylic acid-functionalized PE (spectra D and E) provide clear evidence that the surfaces of the cellulosic materials are changed after treatments with coupling agents. Both coupling agents were chemically attached to the surfaces of the cellulosic materials, as evidenced by the appearance of three new absorption bands on the surfaces of the treated cellulosic materials (spectra B, C, D, and E). These new bands, characteristic of the maleated and acrylic acid-functionalized PE coupling agents, appeared around 2922, 2849, and 1462 cm^{-1} and are attributed to different CH_2 vibrational modes characteristic of the aliphatic hydrocarbon chain of the coupling agents.^{25–29}

The evidence supporting the chemical bonding of both Polybond 3009 and acrylic acid-functionalized PE (Polybond 1009) to the surfaces of cellulosic materials obtained by IR results was confirmed by the XPS results listed in Table II. The treatments of cotton

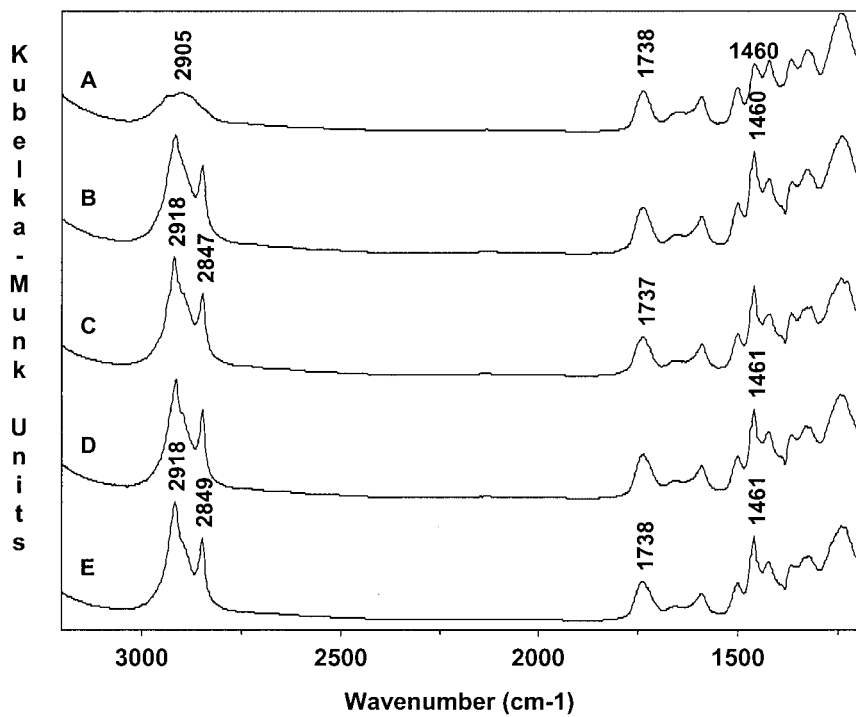
cellulose powder with both coupling agents caused a significant increase in the concentration of unoxidized carbon (C1), that is, carbon atoms bonded only to carbon and/or hydrogen atoms (C—C/C—H),^{10,14,20} while reducing the contents of oxidized carbon atoms (C2, C3, and C4) and, consequently, resulting in a significant decrease in the oxygen-to-carbon (O/C) atomic ratios, as expected from compounds rich in carbon-containing groups. As previously mentioned, the increased content of unoxidized carbon (C1) must have originated from the aliphatic carbons of PE chains and from the carbons of the monomer of the coupling agents (e.g., carbon atoms from acrylic acid and five-member rings for Polybond 1009 and Polybond 3009, respectively).

Although the proof of chemical surface modification of cellulosic materials was obtained by the IR spectra shown in Figure 4(a,b), it is important to notice that absorption peaks associated with ketone and ester carbonyls (around 1715–1765 cm^{-1})²⁵ were not detected in the spectra illustrated in these figures, probably because of the very strong intensity of new peaks appearing in the 2923–2849- and 1462 cm^{-1} frequency range. The lack of detection for these absorption bands related to the formation of ester links may prevent elucidating the mechanisms by which the coupling agents were attached to the surfaces of the cellulosic materials. It was believed that the intensities of the peaks associated with the ester links in the spectra of the treated cellulosic materials were very weak and that digital spectral subtraction was necessary for their visualization.

Figure 5 shows the FTIR spectra of treated cellulosic materials after the subtraction of the spectra of untreated specimens in the 1900–1600 cm^{-1} region. The results for cotton cellulose and wood flour are shown in Figure 5(a,b), respectively. Contrary to the belief that the carbonyl peak already present in the spectra of untreated wood flour may obscure the identification of the ester link between wood flour and coupling agents, our experimental results show that esterification was not dependent on the types of cellulosic materials used. Regardless of the cellulosic material types, absorption bands associated with ester carbonyl stretching are clearly detected in the spectra of treated cellulosic materials, and this indicates that esterification occurred when cellulosic materials were treated with coupling agents. Two new absorption bands emerged around 1785 and 1710 cm^{-1} , as clearly seen in the subtraction spectrum of cellulosic materials treated with maleated PE (spectrum D). These two peaks are associated with the ester carbonyl group and carboxyl carbonyl groups, respectively. However, the subtraction spectrum of cellulosic materials treated with acrylic acid-functionalized PE (Polybond 1009) shows a single absorption band [spectrum E in Fig. 5(a)] around 1714 cm^{-1} attributed to the carbonyl



(a)



(b)

Figure 4 FTIR spectra of untreated cellulosic materials (spectrum A), cellulosic materials treated with 30% maleated PE (spectra B and C), and cellulosic materials treated with 30% acrylic acid-functionalized PE (spectra D and E): (a) FTIR spectra for cotton cellulose and (b) FTIR spectra for wood flour. The IR spectra B and D are the spectra obtained after the first 24-h Soxhlet extraction of the treated cellulosic materials, whereas spectra C and E are from the second 24-h Soxhlet extraction.

TABLE II
Elemental Surface Compositions, Oxygen-to-Carbon Ratios, and C_{1s} High-Resolution Spectra Fitting of Cotton Cellulose Powder (Before and After Treatments) Determined by XPS

| Cotton cellulose powder | Analysis of C_{1s} peaks (%) ^a | | | | Elemental composition (%) | | O/C ratio |
|---|---|------|------|-----|---------------------------|------|-----------|
| | C1 | C2 | C3 | C4 | O | C | |
| Untreated | 27.1 | 55.6 | 11.4 | 5.8 | 37.5 | 62.5 | 0.60 |
| Treated with 5% acrylic acid-functionalized PE (Polybond 1009) | 60.9 | 28.3 | 7.8 | 3.0 | 20.7 | 79.3 | 0.26 |
| Treated with 5% maleic-anhydride-functionalized PE (Polybond 3009) | 79.7 | 15.3 | 3.0 | 1.9 | 12.4 | 87.6 | 0.14 |
| Treated with 30% maleic-anhydride-functionalized PE (Polybond 3009) | 78.1 | 15.5 | 6.4 | 0.0 | 8.5 | 91.5 | 0.09 |

^a Carbon component C1 arose from carbon atoms bonded only to a carbon atom and/or a hydrogen atom (C-C/C-H), C2 [carbon atoms bonded to a single oxygen atom, other than a carbonyl oxygen (C-OH)], C3 [carbon atoms bonded to two noncarbonyl oxygen atoms or to a single carbonyl oxygen atom (O-C-O, C=O)], and C4 carbon type arose from carbon atoms that were linked to a carbonyl and a noncarbonyl group (O-C=O).

group absorption. This absorption band shifted to a higher wave number ($1737\text{--}1726\text{ cm}^{-1}$) in the spectra of treated wood flour [spectrum E in Fig. 5(b)]. The occurrence of these new absorption bands on the subtraction spectra indicate that cellulosic materials were esterified by both acrylic acid-functionalized PE (Polybond 1009) and maleic anhydride-functionalized PE (Polybond 3009). These coupling agents are believed to be attached to the surfaces of cellulosic materials via ester links be-

tween the hydroxyl groups of cellulosic materials and the anhydride group^{5,14,16} (Polybond 3009) or carboxylic group (Polybond 1009) of the coupling agents. The proposed reaction schemes for the esterification reaction between cellulosic materials with coupling agents are shown in Figure 6.

The ester links formed between the cellulose and coupling agents were not detected by XPS spectroscopy. In fact, the treatments of cotton cellulose powder

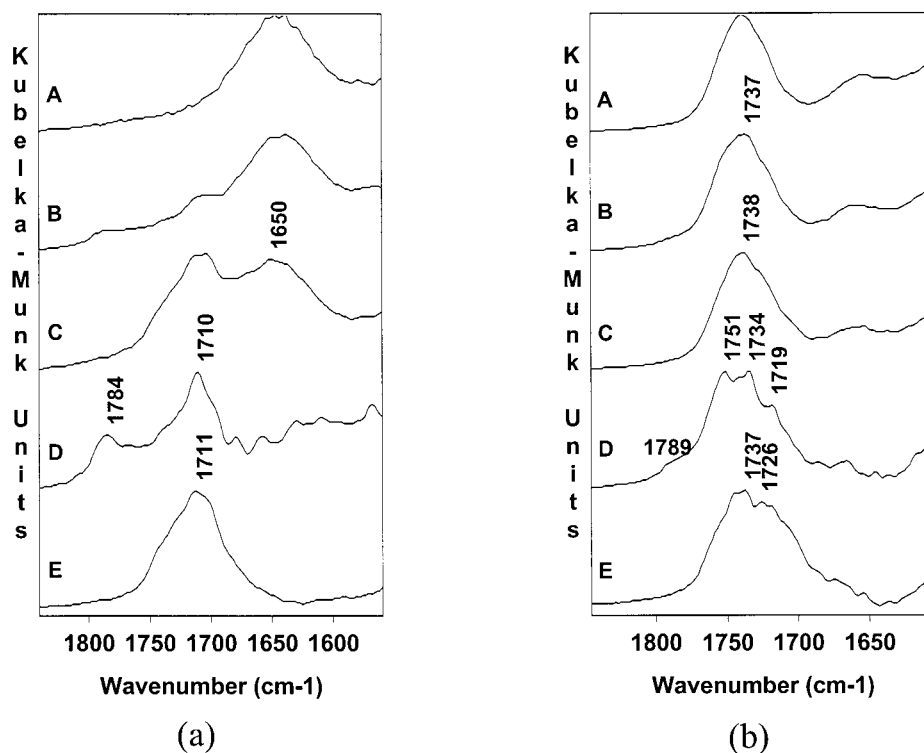


Figure 5 Different spectra of untreated cellulosic materials subtracted from the treated specimens in the $1900\text{--}1650\text{ cm}^{-1}$ region: (a) FTIR spectra for cotton cellulose and (b) FTIR spectra for wood flour. Spectrum A is the spectrum of untreated cellulosic materials, and spectra B and C are the spectra of cellulosic materials treated with 30% maleated PE and 30% acrylic acid-functionalized PE, respectively. Spectra D (B - A) and E (C - A) are the digital subtraction spectra.

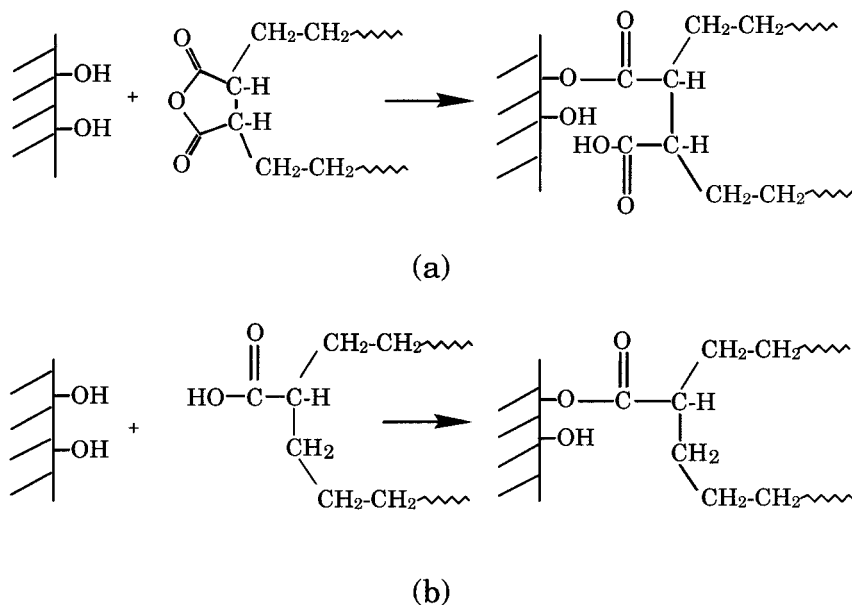


Figure 6 Proposed reaction schemes for the esterification reaction between cellulosic materials and coupling agents: (a) cellulosic materials treated with maleated PE and (b) cellulosic material treated with acrylic acid-functionalized PE.

with only 5% coupling agents caused a significant decrease in the concentration of C4 carbon atoms (Table II) associated with some ester and/or carboxylic groups.¹⁴ Notice that this carbon component C4 was not detected on the surface of cellulose when the coupling agent content increased from 5 to 30%. The decreased content of the C4 carbon type on the surface of treated cellulose is attributed to the high concentration of hydrocarbons of the coupling agent accumulated on the surface of treated cellulose powder, which may have hindered the detection of the C4 atom by XPS, which is a more surface-sensitive technique (probing depth $< 100 \text{ \AA}$) than FTIR spectroscopy.¹⁴

CONCLUSIONS

This study investigated the chemical reactions between cellulosic materials and functionalized PE coupling agents. Both wood flour and cotton cellulose powder were treated with acrylic acid-functionalized PE and maleic anhydride-functionalized PE (maleated PE) for the surface modification of the cellulosic materials. The chemical changes resulting from these treatments were followed by the study of the FTIR and XPS spectra. Variations in the band intensities, oxygen-to-carbon ratios, and concentrations of unoxidized carbon atoms were related to changes that occurred on the surfaces of the modified cellulosic materials. The following conclusions may be drawn from the experimental results:

1. Both FTIR spectroscopy and XPS results provided clear evidence that the surfaces of the cellulosic materials were changed after treatments with coupling agents. The observation of the surfaces of treated cellulosic materials showed three new bands characteristics of pure maleated and acrylic acid-functionalized PE coupling agents around 2922 , 2849 , and 1462 cm^{-1} . These peaks were attributed to different CH_2 vibrational modes characteristic of the aliphatic hydrocarbon chain of the coupling agents.
2. The attachment of both maleated PE (Polybond 3009) and acrylic acid-functionalized PE (Polybond 1009) to the surfaces of cellulosic materials was shown with IR spectroscopy and was further supported by the XPS results. The treatments of cotton cellulose powder with both coupling agents caused a significant increase in the concentration of unoxidized carbon (C1) while reducing the contents of oxidized carbon atoms (C2, C3, and C4); consequently, a significant decrease in the oxygen-to-carbon (O/C) atomic ratios was found, as expected from compounds rich in carbon-containing groups.
3. FTIR spectra showed that chemical bonds between the hydroxyl groups of the cellulosic materials and functional groups of the coupling agents occurred in esterification. However, XPS spectroscopy did not detect the existence of ester links.

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