

Diffuse Reflectance Fourier Transform Infrared Spectra of Wood Fibers Treated with Maleated Polypropylenes

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ABSTRACT: The esterification reaction between wood fibers and maleated polypropylenes was investigated. The reaction was conducted in a reactor in the presence of xylene used as a solvent and sodium hypophosphite as catalyst. The reaction between wood fibers and pure maleic anhydride was also investigated. The appearance of an infrared absorption band near 1730 cm^{-1} indicated that maleated polypropylene chemically reacted by esterification with bleached Kraft cellulose. However, no direct evidence of an esterification reaction was obtained between thermomechanical pulp and maleated polypropylene. The Fourier transform infrared (FTIR) studies showed also that both bleached Kraft cellulose and thermomechanical pulp reacted with maleic anhydride with the formation of ester links. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1163–1173, 1997

Key words: diffuse reflectance; wood fiber; cellulose; maleated polypropylene; esterification; chemical modification; polymer composites

INTRODUCTION

Maleated polypropylene waxes have been used as coupling agents in the development of wood-fiber-reinforced polypropylene.^{1–3} The surface modification of wood fibers with maleated polypropylene prior to compounding with polypropylene resin is known to be effective for increasing the tensile and flexural strengths of the wood fiber–polypropylene composites. The beneficial effects of maleated polypropylene on the strength properties of wood fiber–polypropylene composites have been attributed to the esterification reaction between wood fiber hydroxyl groups and anhydride functionality of maleated polypropylene, as illustrated

in Figure 1. Kishi et al.⁴ have investigated the esterification of maleated polypropylene with refined pulp in a kneader at 160°C . Infrared absorption bands at 1860 and 1780 cm^{-1} of the extracted pulp were attributed to the formation of ester bonds between maleated polypropylene and wood fiber. Recently, Felix and Gatenholm⁵ have carried out esterification of cellulose fiber with maleated polypropylene. Using Fourier transform infrared spectroscopy (FTIR), they observed new absorption bands of the extracted cellulose fiber. One absorption band occurred at 1739 cm^{-1} when cellulose fiber was treated with nonactivated maleated polypropylene, and another at 1746 cm^{-1} when cellulose fiber was treated with an activated maleated polypropylene. The absorption band at 1739 cm^{-1} was assigned to the monomeric form of the dicarboxylic acid, while the peak at 1746 cm^{-1} was assigned to ester bonds between the ma-

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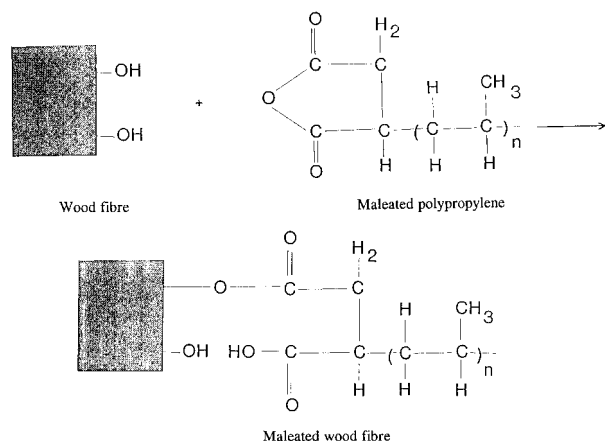


Figure 1 Hypothetical model of esterification reaction in wood fiber-polypropylene composites.

leated polypropylene and cellulosic hydroxyl groups. The discrepancy between the work of Kishi and coworkers and that of Felix and coworkers in the assignment of infrared (IR) band absorption related to ester bonds, and the lack of substantial evidence that these bonds exist, indicate that there is a need for more research to obtain evidence of chemical bonding between maleated polypropylene and wood fiber. Although maleated polypropylene has anhydride groups that may react to hydroxyl groups of wood fiber, the presence of long polypropylene chains may lead to a rigid molecule that may inhibit its ability to access the hydroxyl groups for reaction. Besides the effect of the presence of long polypropylene chains on the reactivity of anhydride groups towards hydroxyl groups of the wood fiber, the nature or type of wood fiber may also influence the extent of reaction between maleated polypropylene and wood fiber. The present study investigated the esterification reaction between wood fibers and maleated polypropylenes using diffuse reflectance FTIR spectroscopy. The esterification between wood fibers and maleic anhydride was also studied in order to determine the effect of the long polypropylene substituents on the formation of ester bonds.

EXPERIMENTAL

Materials

Bleached Kraft cellulose and unbleached thermomechanical pulp were used. These wood fibers

were obtained from Abitibi-Price Inc. (Ontario, Canada). The pulps were fibrillated in a Wiley Mill (Thomas-Wiley Laboratory Mill Model 4) into small uniform fibers and sieved to 250 μm . The thermomechanical pulp and bleached Kraft cellulose materials possess different surface chemistries. Thermomechanical pulps are derived from wood chips by a mechanical refining process. The thermomechanical pulp surface is largely residual lignin. This is due to the fact that the zone of failure during the refining process at high temperature and pressure occurs in the lignin-rich middle lamella. Unlike thermomechanical pulp, bleached Kraft cellulose consists of chemical fibers obtained from wood chips by dissolving and extracting the lignin and most of the hemicelluloses of wood. Thus, bleached Kraft cellulose surface is made up mainly of exposed cellulose molecules, which comprise a number of reactive hydroxyl groups.

The two polymeric reagents were maleated polypropylenes with commercial trade names Epolene E-43 and Epolene G-3002 (both manufactured by Eastman Chemical Products Inc., Kingsport, TN). These two maleated polyolefins were chosen because they possess different acid numbers and molecular weights. Table I summarizes some of the physical properties of these maleated polypropylenes (Epolene E-43 and Epolene G-3002). Other chemical reagents included maleic anhydride, sodium hypophosphite hydrate, and xylene purchased from Aldrich Chemical Company, Inc. The physical properties of maleic anhydride are also summarized in Table I. It is believed that the polypropylene substituents reduce molecular mobility and reduce the reactivity of the anhydride ring through steric hindrance. Sodium hypophosphite hydrate was used as an esterification catalyst in xylene.

Surface Modification of Wood Fiber

The modification of wood fibers was conducted in a reactor in the presence of a solvent. The reaction procedure used for modifying wood fiber was as follows. 250 mL of solvent (xylene) was placed in a 500 mL reactor and stirred to 130–140°C. After reaching this temperature, 67–70 g of maleic anhydride or 6–7 g of maleated polypropylenes (Epolene E-43 and Epolene G-3002), 3 g of wood fiber, and 1 g of catalyst were placed in the reactor. The reaction was carried out for 2 h at 130–140°C. After the reaction, the mixture was filtered to isolate the reacted wood fiber, subjected to Soxh-

Table I Typical Properties of Two Maleated Polypropylene and Maleic Anhydride

Properties	Epolene E-43	Epolene G-3002	Maleic Anhydride
Acid number (mg KOH g) ^a	47	60	—
Density (g cm ³)	0.934	0.959	1.48
Viscosity (cps)	400 (190°C)	15,000 (225°C)	—
M_w	9100	60,000	98.06
M_n	3900	20,000	—
Maleic anhydride units	1.6	10.7	—

Sources: Eastman Chemical Company Publication AP-40 (1995) and *The Merck Index* (1968).

^a Acid number is the number of milligrams of KOH to neutralize 1 g of epolene sample.

let extraction with xylene for 24 h to remove the unreacted anhydride, and oven-dried at 70°C for 24 h. The reaction product thus obtained was used for diffuse reflectance FTIR spectroscopy analysis.

Diffuse Reflectance FTIR Spectroscopy

FTIR spectroscopy was used to confirm whether an esterification reaction occurred between wood fibers and maleated polypropylenes.

The IR spectroscopy is based on the irradiation of a sample by a source of IR radiation and analysis of the absorbance spectrum. IR radiation can be absorbed if a molecule has a vibrational frequency identical to the frequency of the incident radiation. The vibrational frequency of a molecule depends on the mass of its atoms, the geometry of the molecule, and the strength of chemical bonds.⁶ The analyzed IR energy is processed by a computer to generate a spectra of radiation intensities as a function of wavelength.

FTIR spectra of wood fiber before and after treatment were obtained with a Bruker FTIR unit, Model IFS 85. All the IR spectra of wood fibers were recorded in absorbance units ($-\log R/R_0$) in 4000–1000 cm⁻¹ range, with a resolution of 4 cm⁻¹; and there were 100 scans for each spectrum. Pure powdered potassium bromide (KBr) was used as a reference substance. No dilution of the powdered wood sample in powdered KBr was required to obtain a spectrum. Finely powdered wood fiber samples were transferred to a 4 mm diameter cups with slight compression and then levelled using a spatula. Finely powdered samples were required in order to obtain high-quality spectra. In addition to the quality of the spectra, the bandwidths and relative intensity may also be affected by the particle size.⁷ The optical configuration of the diffuse reflection attachment used in

this work is shown in Figure 2. The system consisted of two ellipsoidal mirrors, M3 and M4. These two ellipsoids were arranged with a common focal point, S (sample). Mirrors M1 and M2 transfer the spectrometer (FTIR) IR radiation or beam to the sample, S. The second ellipsoid collects the radiation diffusely reflected from the sample. This IR radiation is then directed by mirrors M5 and M6 to the detector. A digital absorbance subtraction method was used to isolate molecular changes and interactions. According to Koenig,⁸ when chemical changes produce new functional groups, new absorbance bands appear, which may be weak and overlapped by bands arising from similar chemical types present in the original sample; or if changes in the absorptivity of the bands occur, different absorbance frequencies may appear and eliminate any interference of the original sample.

RESULTS AND DISCUSSION

FTIR Spectra of Maleated Polypropylene and Maleic Anhydride

For reference, Figure 3 shows the absorption spectra of maleated polypropylene and maleic anhydride in the 4000–1000 cm⁻¹ region. The major FTIR absorption bands and assignments of absorption bands for maleated polypropylene and maleic anhydride are presented in Table II.

In the FTIR spectra of maleated polypropylene (Epolene E-43), the bands in the region 3100–2600 cm⁻¹ are characteristics of the CH stretching vibrations of CH₂ and CH₃ in polypropylene chains of maleated polypropylene.⁹ The bands in the region 1870–1770 cm⁻¹ are associated with the anhydride carbonyl (C=O) symmetric and

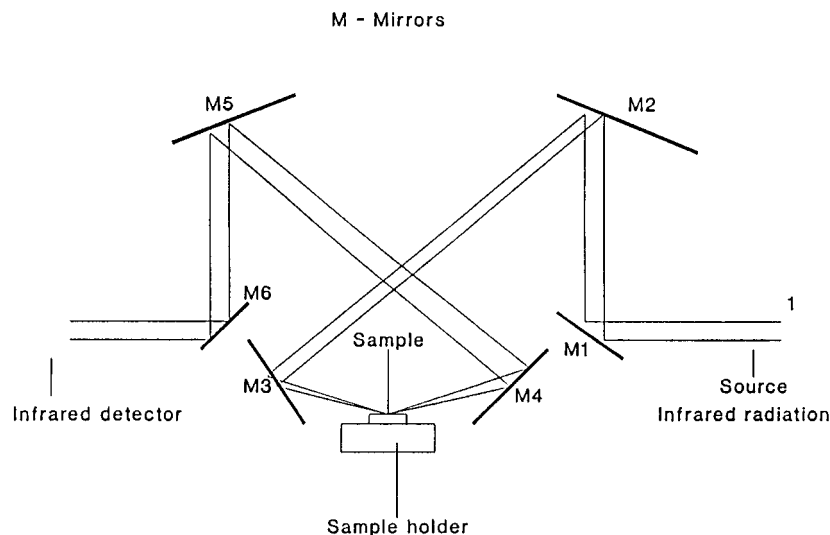


Figure 2 Optical diagram of the diffuse reflection attachment for transfer of IR radiation to the sample and for direction of IR radiation to the detector.

asymmetric stretching vibrations.⁹⁻¹¹ The bands near 1710 cm^{-1} may be attributed to carbonyl stretching vibrations of carboxyl groups present in maleated polypropylene. The bands appearing in the $1400\text{--}1300\text{ cm}^{-1}$ region are due to the CH deformation vibrations of CH_2 and CH_3 ,⁹ while those in the $1200\text{--}1000\text{ cm}^{-1}$ region may be attributed to the CH rocking vibrations of CH_2 and CH_3 ⁹ and also to C—C stretching vibrations.¹²

The FTIR spectra of pure maleic anhydride shown in Figure 3 is different from that of maleated polypropylene. Maleic anhydride contains a large number of bands. The appearance of bands in the $3100\text{--}2600\text{ cm}^{-1}$ region are due to the CH stretching vibrations of CH_2 . The anhydride carbonyl symmetric and asymmetric stretching vibrations are characterized by absorption bands in the $1870\text{--}1770\text{ cm}^{-1}$ region. The bands near 1710 cm^{-1} may be ascribed to carboxyl groups present in maleic anhydride. The bands in the $1400\text{--}1300\text{ cm}^{-1}$ region are due to the CH deformation vibrations of CH_2 , while the bands in the $1200\text{--}1000\text{ cm}^{-1}$ region may possibly be due to the CH rocking vibrations of CH_2 , and also to C—C stretching vibrations.

FTIR Spectra of Untreated Wood Fibers

Figure 4 shows the absorption spectra of untreated wood fibers (thermomechanical pulp and bleached Kraft cellulose) in the $4000\text{--}1000\text{ cm}^{-1}$ region. The major FTIR absorption bands and as-

signments of absorption bands for lignocellulosic materials are summarized in Table III.

The absorption bands in the $3500\text{--}3100\text{ cm}^{-1}$ region for both wood fibers may be due to various hydroxyl (OH) stretching vibrations. The OH compounds may include absorbed water, aliphatic primary and secondary alcohols found in cellulose, hemicelluloses, lignin, extractives; aromatic primary and secondary alcohol in lignin and extractives; and carboxylic acids in extractives.¹³⁻¹⁵ The shoulder near the OH stretching vibrations may be associated to CH stretching vibrations. The aliphatic CH stretching vibrations of methyl and methylene groups in wood,¹² aromatic CH stretching vibrations,^{16,17} and aliphatic aldehydes CH stretching vibrations¹⁸ absorb in this region.

The differences between thermomechanical pulp and bleached Kraft cellulose can be seen in the $1750\text{--}1700\text{ cm}^{-1}$ region. In the spectra of thermomechanical pulp, there is a presence of absorption bands near 1730 cm^{-1} , which may be associated to carbonyl (C=O) stretching of acetyl groups in hemicelluloses; carbonyl aldehyde in lignin and extractives and/or to carbonyl (C=O) stretching vibrations of carboxyl groups in hemicelluloses, lignin, and extractives; and also to esters in lignin and extractives.^{12-14,19-21} This absorption band is absent in the FTIR spectra of bleached Kraft cellulose. The FTIR spectra of bleached Kraft cellulose did not show any detectable absorption bands in the $1750\text{--}1700\text{ cm}^{-1}$ region. The observed absorption band at 1645 cm^{-1} was associated to the double band (C=C).⁹ How-

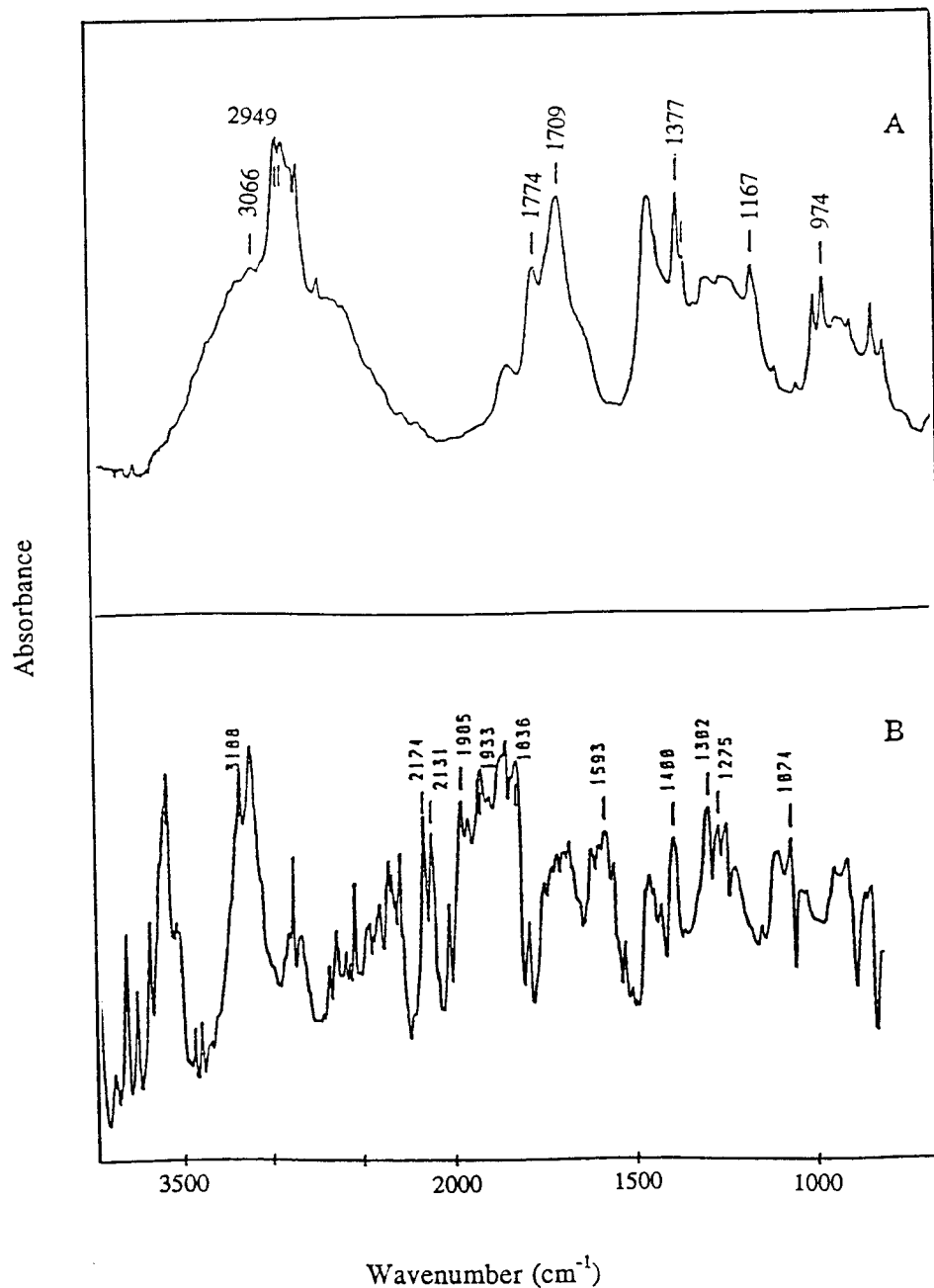


Figure 3 FTIR spectra of (A) maleated polypropylene and (B) maleic anhydride.

ever, Kolboe and Ellefsen¹⁴ suggested that the bands in this region for cellulose may be attributed to C=O stretching vibration of the alpha-keto carbonyl. Tsuboi²² assigned the band at 1645 cm⁻¹ to absorbed water. The absence of absorption bands in the 1750–1700 cm⁻¹ region in the spectra of bleached Kraft cellulose may be explained to the fact that the compounds rich in carbonyl (C=O), lignin, hemicelluloses, and extractives

are dissolved during the production of bleached Kraft cellulose.

The absorption bands in the 1600–1400 cm⁻¹ region in the spectra of thermomechanical pulp may be attributed to the presence of aromatic or benzene rings in lignin.¹⁴ The weak vibrations near 1400–1300 cm⁻¹ may be attributed to the aliphatic and aromatic (C–H) in the plan deformation vibrations of methyl, methylene, and me-

Table II FTIR Absorption Bands and Assignments of Bands of Maleated Polypropylene (Epolene E-43) and Maleic Anhydride

Maleated Polypropylene (cm ⁻¹)	Maleic Anhydride (cm ⁻¹)	Assignments	References
3100–2600	3100–2600	CH stretching of CH ₂ and/or CH ₃	9
1870–1770	1870–1770	C=H symmetric and asymmetric stretching	9–11
1740–1710	1740–1710	C=O stretching of carboxyl groups	11
1400–1300	1400–1000	CH deformation of CH ₂ and/or CH ₃	9

thoxy groups in wood.^{9,13} For bleached Kraft cellulose, the bands from 1400–1300 cm⁻¹ are associated with CH in the plane deformation of CH₂ groups.¹⁴

The bands in the region 1300–1000 cm⁻¹ involve the C—O stretching vibrations of aliphatic primary and secondary alcohols in cellulose, hemicelluloses, lignin, and extractives; and aromatic primary and secondary alcohols in lignin and extractives.^{13,14} Aliphatic ethers in cellulose

and lignin^{23,24} and aromatic ethers in lignin^{25,26} absorb also in this region. The 1300–1000 cm⁻¹ region may also be associated to the OH deformation of vibrations of carbohydrates.^{27,28}

FTIR Spectra of Maleated Polypropylenes Treated Wood Fibers

Since the ester functional groups absorb in the 1750–1720 cm⁻¹ region, our discussion will focus

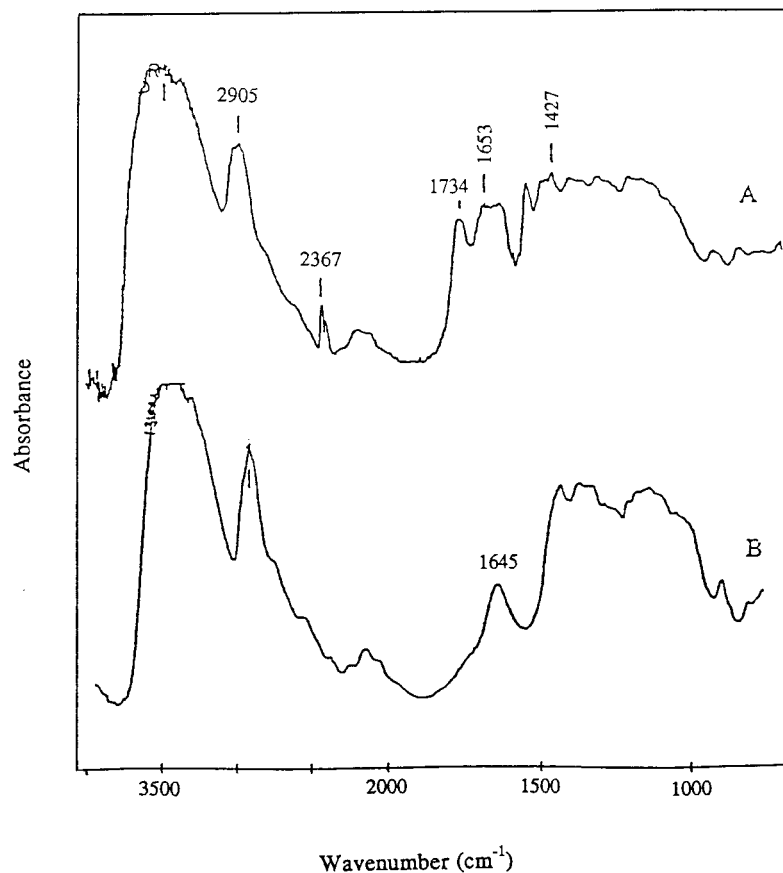


Figure 4 FTIR spectra of untreated (A) thermomechanical pulp and (B) bleached Kraft cellulose.

Table III FTIR Absorption Bands and Assignments of Bands of Untreated Lignocellulosic Materials

TMP (cm ⁻¹)	BKCELL (cm ⁻¹)	Assignments	References
3500–3100	3500–3100	OH stretching	13–15
3100–2600	3100–2600	CH stretching of CH ₂ and CH ₃	12, 16–18
1750–1700	—	C=O stretching	12–14, 19–21
—	1645	C=O stretching	14
—	1645	Absorbed water	22
1600–1400	—	Aromatic ring stretching	13, 14
1400–1300	1400–1300	CH deformation of CH ₂ , CH ₃ , OCH ₃	9, 13, 14
1300–1000	1300–1000	C—O stretching	13, 14
1300–1000	1300–1000	C—O—C stretching	23, 25, 26
1300–1000	1300–1000	OH deformation	27

TMP, thermomechanical pulp; BKCELL, bleached Kraft cellulose.

on that region. Furthermore, since thermomechanical pulps already have ester groups that absorb near 1730 cm⁻¹, the confirmation of esterification between thermomechanical pulp and maleated polypropylene may only be indicated by an increase in the intensity of the absorption bands near 1730 cm⁻¹.

Figure 5 shows the FTIR spectra of untreated thermomechanical pulps and treated with maleated polypropylenes (Epolene E-43 and Epolene G-3002). As may be seen from a comparison of the FTIR spectra of untreated thermomechanical pulp [Fig. 5(A)] and that of maleated polypropylenes treated thermomechanical pulps [Fig. 5(B,C)], there is no visible change in the spectra of treated thermomechanical pulps in the absorption bands and in their relative intensities. The absorption bands near 1730 cm⁻¹ did not show any significant change in intensity upon treatment. The digital subtraction spectra [Fig. 5(D,E)] obtained did not indicate the presence of any distinct absorption bands near 1730 cm⁻¹ that may be associated to ester links between hydroxyl groups of wood fibers and anhydride groups of maleated polypropylenes. The observed sharp and strong absorption bands at 1778 cm⁻¹ in the digital subtraction spectra may be due to anhydride carbonyl symmetric and asymmetric stretching vibrations in maleated polypropylene, while the absorption band at 1711 cm⁻¹ may possibly be due to the carbonyl stretching of carboxyl groups in maleated polypropylene. It is probable that the extraction in xylene removed some of the maleated polypropylene, while some of them remained attached to the thermomechanical pulp surface.

The failure of thermomechanical pulp to react chemically with maleated polypropylene by esterification reaction is probably due to the predominance of lignin on the thermomechanical pulp surface. Unlike cellulose molecules (Fig. 6), which are linear homopolysaccharides with high concentrations of reactive hydroxyl groups, lignin is a phenolic and highly branched heteropolymer formed by condensation of phenylpropane units, as illustrated in Figure 7. Because of the complex lignin chemical structure, lignin is not sufficiently reactive since most of the phenolic hydroxyl groups are not readily accessible for reaction. In addition to the chemical structure of the lignin, the presence of long polypropylene chains or high molecular weight of maleated polypropylene may also restrict the esterification through the inability of maleated polypropylene molecules to access the few phenolic hydroxyl groups.

Figure 8 shows the FTIR spectra of untreated bleached Kraft cellulose and maleated-polypropylene-treated bleached Kraft cellulose. The FTIR spectra of untreated bleached Kraft cellulose did not show the presence of ester absorption bands near 1730 cm⁻¹. If esterification had occurred, then new bands near 1730 cm⁻¹ should have appeared. It may be noted that there are some differences between the FTIR spectra of untreated bleached Kraft cellulose [Fig. 8(A)] and maleated polypropylenes (Epolene E-43 and Epolene G-3002) [Fig. 8(B,C)]. There is an appearance of small and weak shoulder in the higher frequency of absorption band at 1645 cm⁻¹. In addition, the absorption band at 1645 cm⁻¹ decreased in intensity. The digital subtraction of the FTIR spectra

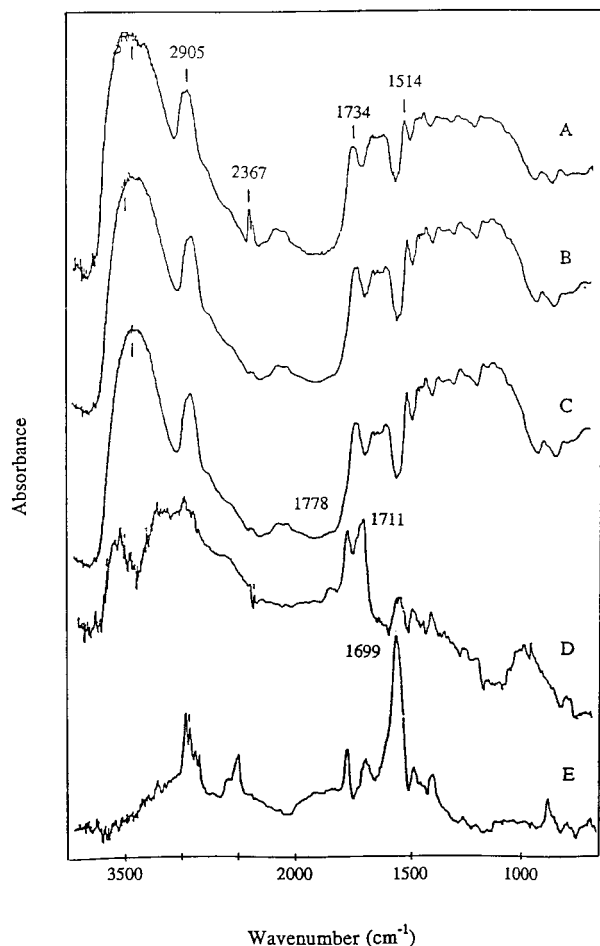


Figure 5 FTIR spectra of untreated and maleated polypropylenes treated thermomechanical pulp in solution in xylene (A) untreated thermomechanical pulp, (B) Epolene E-43 treated thermomechanical pulp, (C) Epolene G-3002 treated thermomechanical pulp, (D) digital subtraction (B - A), and (E) digital subtraction (C - A).

of untreated bleached Kraft cellulose from that of treated bleached Kraft cellulose [Fig. 8(D) and (E)] confirms the appearance of a weak absorption band at 1722 cm^{-1} . The observed changes

may be related to the occurrence of ester functional groups formed by reaction between hydroxyl groups of bleached Kraft cellulose and anhydride groups of maleated polypropylene.

FTIR Spectra of Maleic Anhydride Treated Wood Fibers

The esterification of wood fibers (thermomechanical pulps and bleached Kraft cellulose) with maleic anhydride was studied in order to compare with that of maleated polypropylenes.

Figure 9 shows the FTIR spectra of untreated thermomechanical pulp and maleic anhydride treated thermomechanical pulps in the presence and absence of sodium hypophosphite catalyst. As may be seen from the comparison of the FTIR spectra of untreated thermomechanical pulp and treated thermomechanical pulp, there is a great change in the relative intensities of absorption bands near 1730 cm^{-1} . The absorption bands near 1730 cm^{-1} increased strongly in intensity following thermomechanical pulp treatment. However, in the lower frequency region near 1730 cm^{-1} , absorption bands decreased in intensity. The digital subtraction of untreated thermomechanical pulp spectra from that of treated thermomechanical pulp shows the presence of strong, sharp, and well-defined absorption bands near 1730 cm^{-1} . The presence of this band is attributed to the esterification reaction between hydroxyl groups of thermomechanical pulp and anhydride groups of maleic anhydride. This conclusion is in agreement with previous studies reported by Matsuda.²⁹

The FTIR spectra of untreated bleached Kraft cellulose and maleic anhydride treated bleached Kraft cellulose in the presence or absence of sodium hypophosphite are presented in Figure 10. A comparison of the FTIR spectra of untreated bleached Kraft cellulose and treated bleached Kraft cellulose shows the emergence of a new, strong, sharp and well-defined absorption band on the low frequency side of the 1645 cm^{-1} . In

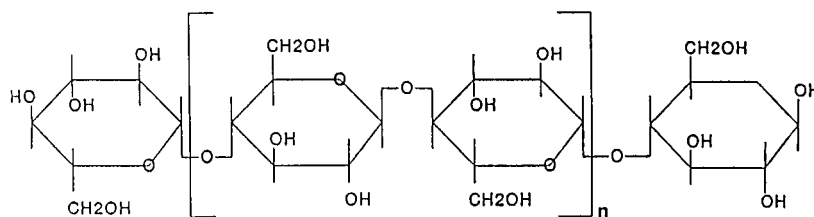


Figure 6 A segment of a cellulose molecule showing its linear and unbranched structure of glucose units.

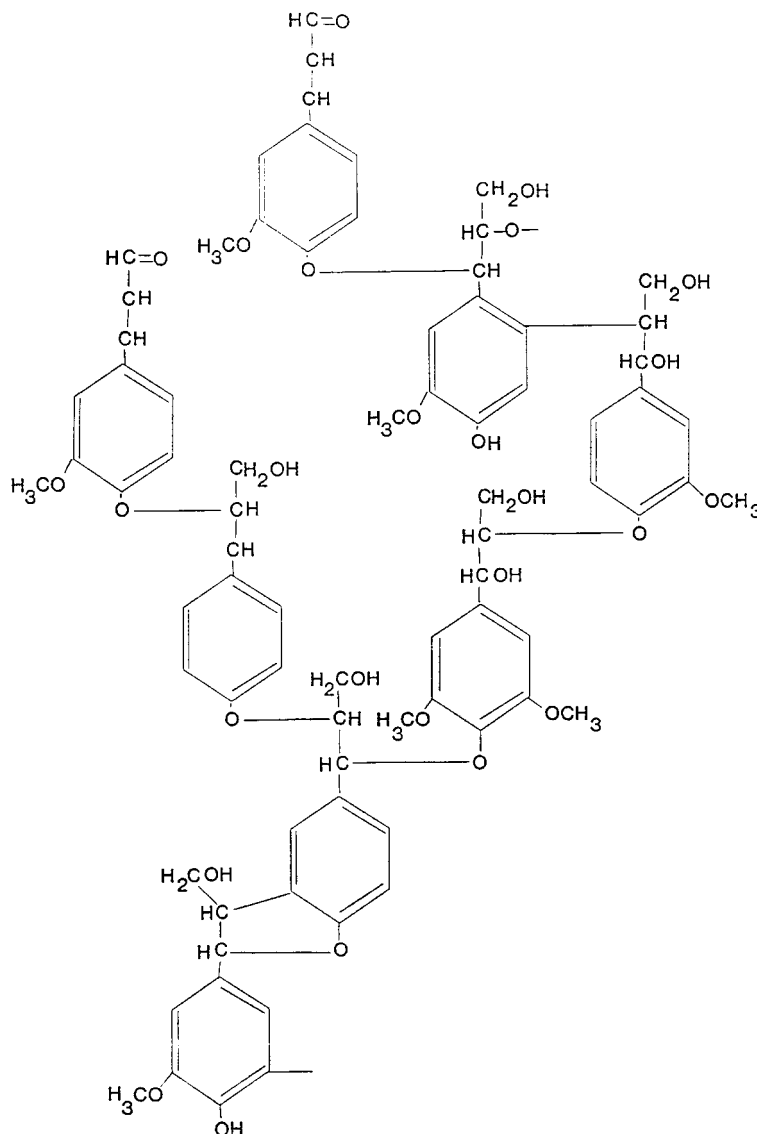


Figure 7 Chemical structure of a typical softwood lignin (Alder 1977).

addition, the absorption band at 1645 cm^{-1} decreased in intensity. These changes, which are well illustrated in the digital subtraction spectra may be attributed to ester functional groups formed by esterification reaction between the hydroxyl groups of bleached Kraft cellulose and anhydride groups of maleic anhydride. Unlike in the case of thermomechanical pulp, the presence of sodium hypophosphite appears to catalyze the esterification reaction. The absorption band near 1730 cm^{-1} become stronger, sharper, and well defined in the presence of sodium hypophosphite. Similar observations were reported by Yang.¹¹ Yang observed that the presence of a catalyst (so-

dium hypophosphite) was necessary in order to catalyze the esterification reaction between cellulose (cotton) and maleic anhydride. The absorption bands in the $1728\text{--}1721\text{ cm}^{-1}$ region were ascribed to ester links formed by the esterification reaction.

CONCLUSIONS

The specific objectives of this research work were to confirm the esterification reaction between anhydride groups of maleated polypropylenes and hydroxyl groups of wood fibers and to determine

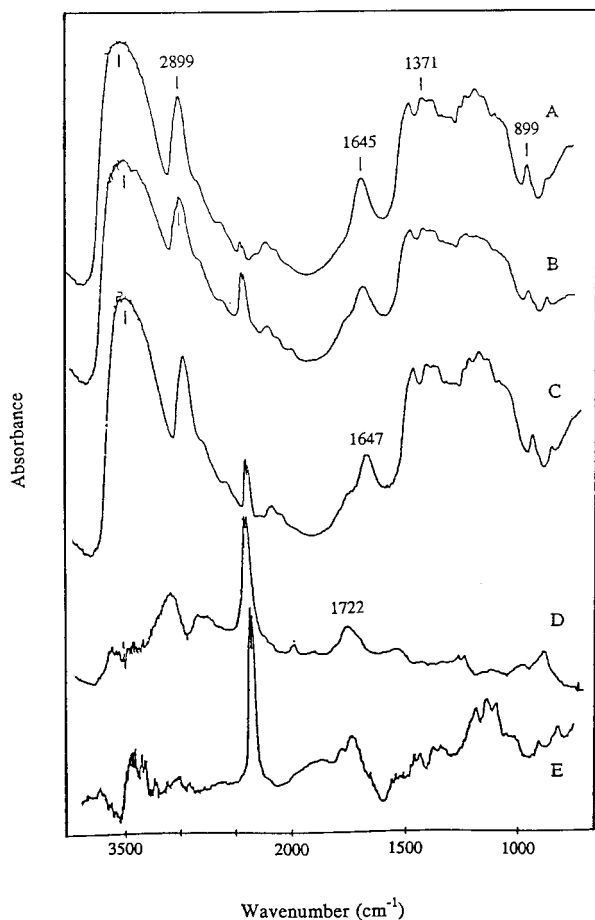


Figure 8 FTIR spectra of untreated and maleated polypropylenes treated bleached Kraft cellulose in solution in xylene (A) untreated bleached Kraft cellulose, (B) Epolene E-43 treated bleached Kraft cellulose, (C) Epolene G-3002 treated bleached Kraft cellulose, (D) digital subtraction (B - A), and (E) digital subtraction (C - A).

the effect of wood fiber type and the presence of long polypropylene chains on the esterification reaction. In summarizing the FTIR results, the following conclusions may be drawn.

1. The FTIR results demonstrated that bleached Kraft cellulose surface chemistry differs from that of thermomechanical pulps.
2. The FTIR results confirmed that esterification between bleached Kraft cellulose and maleated polypropylene had occurred. The appearance of a weak absorption band near 1730 cm^{-1} on the FTIR spectrum of maleated polypropylene treated bleached Kraft cellulose was attributed to the formation of an es-

ter groups. The presence of sodium hypophosphite catalyst had no effect on the extent of esterification.

3. The FTIR studies were unable to confirm any evidence of esterification between thermomechanical pulp and maleated polypropylenes (Epolene E-43 and Epolene G-3002) either in the presence or the absence of sodium hypophosphite.
4. The FTIR studies showed that both bleached Kraft cellulose and thermomechanical pulps did chemically react with maleic anhydride with formation of ester bonds.
5. The wood fiber type and the presence of poly-

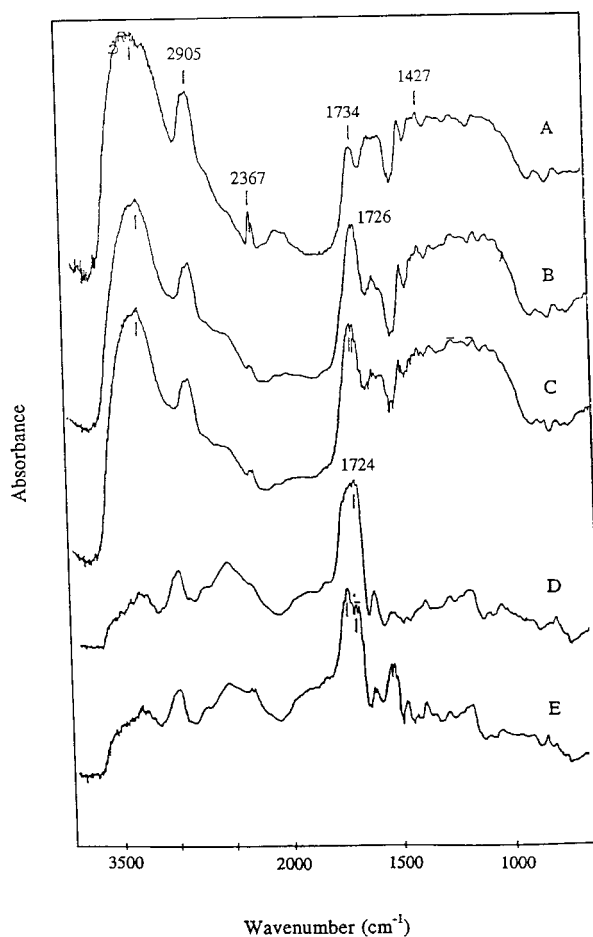


Figure 9 FTIR spectra of untreated and maleic anhydride treated thermomechanical pulp in solution in xylene (A) untreated thermomechanical pulp, (B) maleic anhydride treated thermomechanical pulp, (C) maleic anhydride treated thermomechanical pulp (catalyst), (D) digital subtraction (B - A), and (E) digital subtraction (C - A).

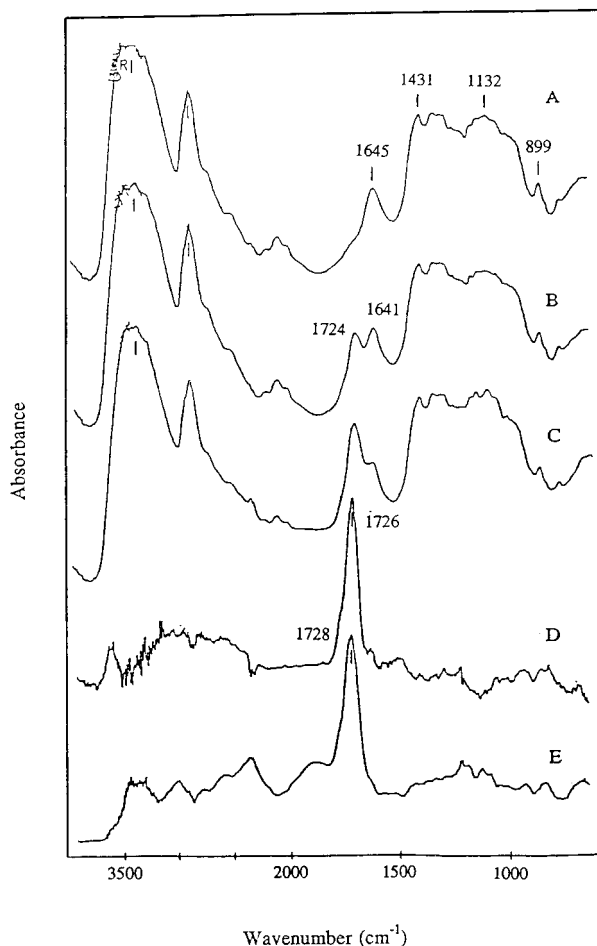


Figure 10 FTIR spectra of untreated and maleic anhydride treated bleached Kraft cellulose in solution in xylene (A) untreated bleached Kraft cellulose, (B) maleic anhydride treated bleached Kraft cellulose, (C) maleic anhydride treated bleached Kraft cellulose (catalyst), (D) digital subtraction (B - A), and (E) digital subtraction (C - A).

propylene substituents on the maleic anhydride moiety had a significant influence on the formation of ester links.

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