

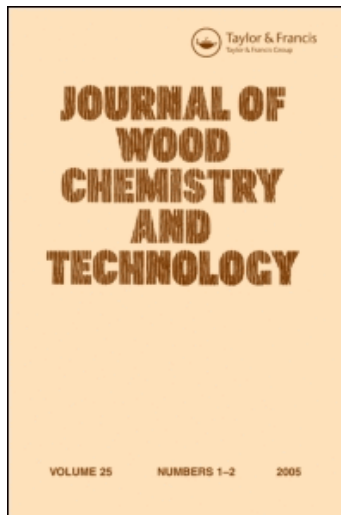
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X-Ray Photoelectron Spectroscopy of Lignocellulosic Materials Treated with Malea Ted Polypropylenes

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X-RAY PHOTOELECTRON SPECTROSCOPY OF LIGNOCELLULOSIC MATERIALS TREATED WITH MALEATED POLYPROPYLENES

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ABSTRACT

The esterification reaction between lignocellulosic materials (ALCELL lignin and Bleached kraft cellulose) and maleated polypropylenes (graft copolymerization of maleic anhydride into polypropylene chains) was investigated.

The reaction was conducted in a reactor in the presence of xylene used as a solvent and sodium hypophosphite as a catalyst. The reaction between lignocellulosic materials and pure maleic anhydride was also conducted to determine the effect of the long polypropylene chains on the formation of ester bonds. The XPS studies of maleated bleached kraft cellulose showed the emergence of C4 carbon type on high resolution spectra, which was related to ester carbonyl functionality formed by esterification reaction. No evidence of esterification was observed between ALCELL lignin and maleated polypropylenes.

The XPS studies demonstrated that both ALCELL lignin and bleached kraft cellulose chemically react with maleic anhydride with the formation of ester bonds.

INTRODUCTION

Over the past years there has been widespread interest in the development of wood fiber filled polymers. Typical polymers are polypropylene (PP), polyethylene (PE), polystyrene (PS) and polyvinyl chloride (PVC). A common property of these polymers is that they can be processed below the decomposition temperature of wood fibers which is about 220°C. Wood fibers are of particular interest as fillers and/or reinforcement agents in polymer composites because wood fibers are abundant, renewable, recyclable and biodegradable; they have high specific strength and stiffness; they cause less equipment wear; and they are generally low cost.¹⁻⁴ The problem, however, is that after compounding wood fiber with a polymer (polypropylene) it often leads to poor strength properties of the composites (particularly tensile strength, impact strengths, and elongation at break). The poor strength properties of wood fiber-polypropylene composites has been attributed to: (1) poor compatibility between the polar hydrophilic wood fiber and the nonpolar hydrophobic polypropylene, with weak interfacial adhesion between wood fiber and polypropylene matrix,⁵⁻⁷ and (2) poor dispersion of wood fiber in the polypropylene matrix due to the strong fiber-fiber interactions resulting from strong intermolecular hydrogen bonding.⁸⁻¹⁰

Several physical and chemical approaches have been used to overcome these problems, including heat treatment,^{11,12} hydrolytic modification,¹³ acetylation,⁹ and use of adhesion promoters or coupling agents.^{2,6} Maleated polypropylene as a coupling agent has received attention because of its effectiveness in improving the mechanical properties (tensile and flexural strengths) of wood fiber-polypropylene

composites^{2,8,14,15,16} and relative low cost. Many theories have been advanced to account for the improvement brought about by the use of maleated polypropylene and maleated polyolefins in general. One of these theories is the esterification theory^{14,15} which suggests that maleated polypropylene chemically bonds to wood fiber by reaction between the anhydride groups of maleated polypropylene and hydroxyl groups of wood fiber. The hypothetical esterification mechanism between maleated polypropylene and wood fiber is illustrated in Figure 1. Although maleated polypropylene has anhydride groups which may react with hydroxyl groups of wood fiber, the presence of long polypropylene chains may introduce steric interference that may reduce its ability to access the surface hydroxyl groups of wood fiber for reaction. Besides the steric effect of polypropylene substituents on the reactivity of anhydride groups with hydroxyl groups of wood fiber, the nature of lignocellulosic material may also influence the reaction. The present study proposes to employ X-ray photoelectron spectroscopy to obtain information on the surface chemistry of different lignocellulosic materials before and after treatment with maleated polypropylenes, and thereby elucidate the esterification reaction between the anhydride groups of maleated polypropylene and hydroxyl groups of lignocellulosic material.

EXPERIMENTAL

Materials

Bleached kraft cellulose and ALCELL lignin were selected for this investigation. Bleached kraft cellulose was obtained from Abitibi-Price Inc.

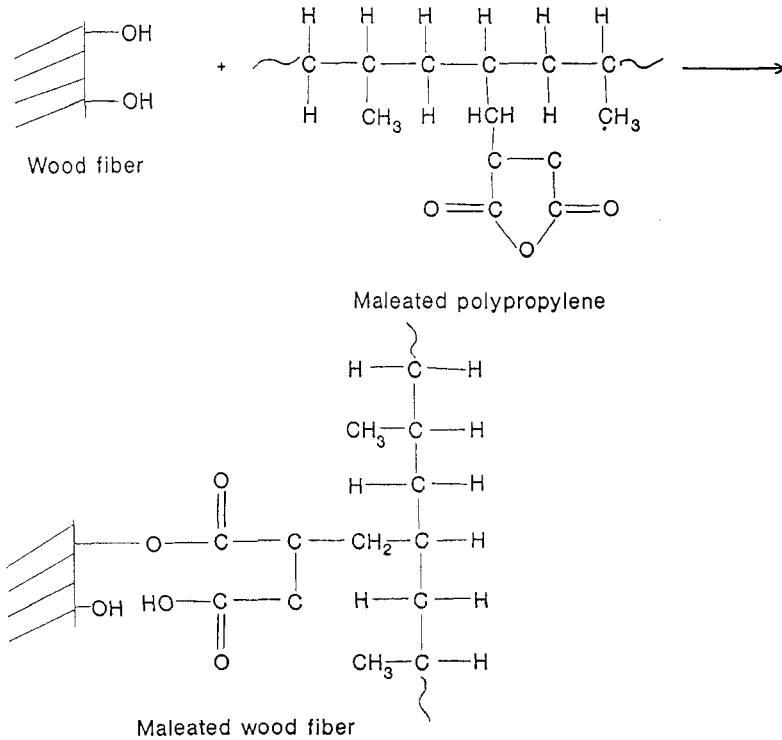


FIGURE 1: Hypothetical model of esterification reaction between wood fiber and maleated polypropylene.

(Mississauga, Ontario, Canada). The pulp was defibrillated in a wiley mill (Thomas-Wiley Laboratory Mill Model 4) into small uniform fiber, and sieved to 250 μm . ALCELL lignin powder (organosolv lignin) was obtained from Repap Technologies Inc. (Montreal, Canada). Bleached kraft cellulose was obtained through a kraft pulping process from black spruce wood chips by dissolving the lignin, extractives, and most of the hemicelluloses. The ALCELL lignin was recovered from an organosolv pulping process from hardwood chips by extraction with an aqueous ethanol liquor.¹⁷ In the

TABLE 1

Typical Properties of two Maleated Polypropylene and Maleic Anhydride

Properties	Epolene E-43 ¹⁸	Epolene G-3002 ¹⁸	Maleic anhydride ¹⁹
*Acid number (mg KOH/g)	47	60	-
Density, g/cm ³	0.934	0.959	1.48
Viscosity, cps	400(190°C)	15,000(225°C)	-
M _w	9,100	60,000	98.06
M _n	3,900	20,000	-
Maleic anhydride units	1.6	10.7	-

*Acid number is the number of milligrams of KOH to neutralize one gram of Epolene sample

extraction process, hemicelluloses and other various components of wood were extracted from the chips to form a black liquor. The ALCELL lignin is recovered by precipitation, centrifugation, and drying.

Two different reagents were used to modify the wood fiber surface. The two polyolefins compounds were derived from maleated polypropylenes designated as Epolene E-43 and Epolene G-3002 (manufactured by Eastman Chemical Products Inc.). These anhydride polyolefins possess different acid numbers and molecular weights. Table1 summarizes the physical properties of maleated polypropylenes (Epolene E-43 and Epolene G-3002).

Other chemicals used included maleic anhydride, sodium hypophosphite hydrate, and xylene (all from Aldrich Chemical Company, Inc.). Maleic anhydride was chosen to compare its reactivity with that of the maleated polyolefins. It is believed that the polypropylene substituent reduces molecular mobility and reduces reactivity by forming a steric barrier between the reacting groups. Sodium hypophosphite hydrate was used as a catalyst to accelerate the esterification reaction. Xylene was used as the reaction medium.

Surface Modification of Lignocellulosic Materials.

The treatment of bleached kraft cellulose and ALCELL lignin was conducted in a reactor. The reaction procedure used for modifying lignocellulosic material 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 lignocellulosic material, and 1 g of catalyst were placed in the reactor. The reaction was carried out for two hours at 130-140°C. After completion of the reaction, the mixture was filtered to isolate the reacted lignocellulosic material, subjected to soxhlet 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 X-ray photoelectron spectroscopy analysis.

X-ray Photoelectron Spectroscopy.

X-ray photoelectron spectroscopy (XPS) was used to characterize the surface chemical composition of untreated and treated lignocellulosic material. XPS provides a means of obtaining detailed characterization of the surface. It gives a quantitative elemental composition and functional groups of the surface to depth of about 1-10 Å.^{20,21} The ability of XPS to provides quantitative elemental composition and chemical functional groups on the surface before and after treatment allows to estimate the effectiveness of surface treatment, and aid in elucidating the extent of esterification between lignocellulosic materials and maleated polypropylenes.

The untreated and treated specimens are irradiated in a high vacuum with X-ray photons. Figure 2 illustrates the X-ray photoelectron spectroscopy apparatus. The X-ray photons interact with the atomic and molecular orbital electrons in the sample. If the energy of the X-ray photons is greater than that required to remove the electrons from the sample, the excess energy is imparted to the electron as a kinetic energy according to the following equation:

$$E_k = h\nu - E_b + \emptyset \quad (1)$$

where E_k is the kinetic energy, $h\nu$ is the X-ray photon energy, E_b is the binding energy, and \emptyset is the work function of the spectrometer. The emitted electrons from the sample are then analyzed for the number of electrons having different kinetic energies. The

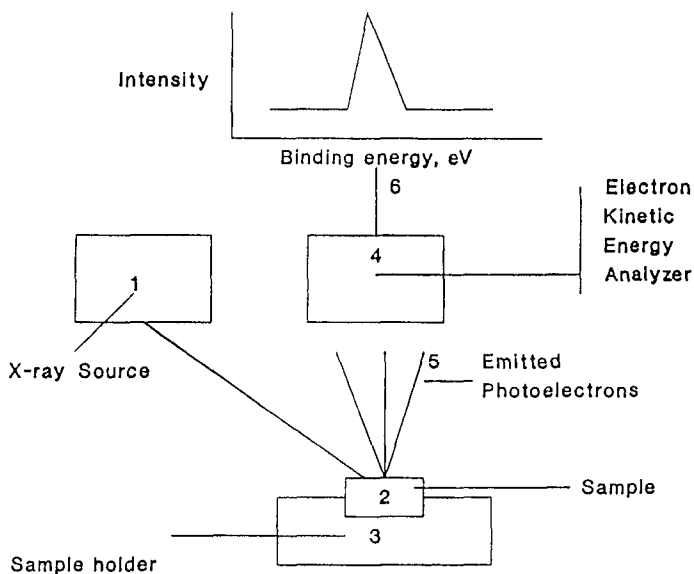


FIGURE 2: Schematic diagram of the principle of X-ray photoelectron spectroscopy.

information is processed by a computer to produce a spectrum of photoelectron intensities as a function of binding energies. The binding energy position of peaks allows elemental identification to be made. The quantity or concentration of element is obtained by measuring the peak area and applying appropriate corrections and sensitivity factors.

The XPS spectra were recorded by using a Leybold Max 200 X-ray photoelectron spectrometer (Leybold, Cologne, Germany) with an unmonochromated magnesium K_{α} source with an excitation energy of 1253.6 eV. The sample was mounted onto a holder with double sided adhesive tape, and placed in a vacuum in the range of 10^{-8} - 10^{-7} torr. The analyzed area was 4x7 mm. The XPS spectra were

recorded with a photoelectron takeoff angle of 90° relative to the surface. Atomic percentages of the elements present were derived from spectra run in a low-resolution mode (pass energy = 192 eV). The sensitivity factors used ($O1s = 0.78$, and $C1s = 0.34$) were empirically derived by Leybold for spectra normalized to unit transmission of the electron spectrometer.²² For more information on the nature of the surface to be obtained, the spectra regions of interest were also run in a high-resolution mode (pass energy = 48 eV). Binding energy and peak areas were obtained by use of the routines provided with the spectrometer. The energy scale of the spectrometer was calibrated to the $Ag\ 3d_{5/2}$ and $Cu\ 2p_{3/2}$ peaks at 368.3 and 932.7 eV, respectively,²¹ and the binding energy scale was then shifted to place the $C1s$ feature present at 285.0 eV.

RESULTS AND DISCUSSION

X-ray Photoelectron Spectroscopy of Untreated Lignocellulosic Materials

Due to the similarities of the $O1s$ chemical shifts, and hence difficulties in estimating their relative intensities,²³⁻²⁵ the discussion in this section will be focused on the $C1s$ chemical shifts.

Figure 3 shows the survey spectra of bleached kraft cellulose and ALCELL lignin. It shows the number of electrons recorded versus the binding energy in electron volts (eV) from 1000 eV to 0 eV. The spectra consists of $1s$ electrons from carbon ($C1s$) and $1s$ electrons from oxygen ($O1s$) as well as the associated Auger electron peaks. The survey spectra of bleached kraft cellulose is different from that of ALCELL

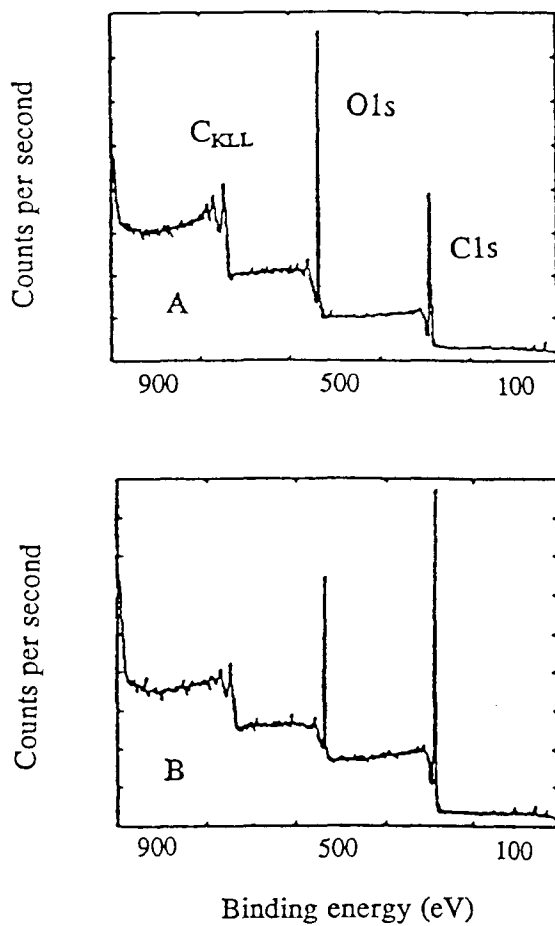


FIGURE 3: X-ray photoelectron spectroscopy survey spectra of untreated Lignocellulosic materials: (A) bleached kraft cellulose, and (B) ALCELL lignin.

lignin. The survey spectra of bleached kraft cellulose shows higher intensity of oxygen atoms compared to carbon atoms, whereas the spectra of ALCELL lignin shows a higher intensity of carbon atoms compared to oxygen atoms. The greater intensity of oxygen atoms as observed by XPS on bleached kraft cellulose is consistent with the chemical structure of cellulose molecules. Cellulose molecules are highly oriented homopolysaccharide forms of β -D-glucose units, and largely composed of oxygen atoms. Most of the oxygen atoms in the cellulose molecules are from primary and secondary alcohols, and glycosidic bonds that link β -D-glucose units. The chemical structure of lignin differs completely from that of cellulose. In contrast to cellulose, lignin is a phenolic and highly branched three dimensional heteropolymer formed by polymerization of phenylpropane units. The higher intensity of carbon atoms observed on the ALCELL lignin surface is a consequence of its aromatic structure.

The elemental composition and oxygen-carbon ratio of bleached kraft cellulose and ALCELL lignin as obtained from the XPS survey spectra are shown in Table 2. Relative atomic percents were obtained from peak areas of the various emissions corrected for intensity by appropriate sensitivity factor. It is clear that bleached kraft cellulose show higher oxygen-carbon ratio than ALCELL lignin. However, the ratio is less compared to the actual composition of 0.83 from the cellulose molecule $(C_6H_{12}O_5)_n$. Such low oxygen-carbon ratios have also been observed by Mjoberg.²⁶ It was indicated that strong absorption of impurities on the cellulose surface or the presence of extractives, terpenes and terpenoides, fats, waxes and phenolic compounds might lower the oxygen-carbon ratio since they have fewer hydroxyl groups, and are rich in aliphatic and aromatic carbons.

TABLE 2

Elemental Composition and Oxygen-carbon Ratio of Untreated Lignocellulosic Materials as Obtained by X-ray Photoelectron Spectroscopy Survey Spectra

Wood fibers	C (%)	O (%)	O/C (%) (XPS)	O/C (%) (Theoretical)
ALIGN	81.6	18.5	22.5	34.7 ²⁷
BKCELL	63.9	36.1	56.7	83.0 ²⁸

ALIGN-ALCELL lignin, BKCELL-bleached kraft cellulose

ALCELL lignin shows a higher proportion of carbon atoms than bleached kraft cellulose as may be seen in Table 2. This is due to the fact that lignin is mainly made up of aliphatic and aromatic carbons (C-H/C-C) with very few carbonyl, carboxyl or hydroxyl groups. The oxygen-carbon ratio of ALCELL lignin is lower than the theoretical oxygen-carbon ratio of ALCELL lignin obtained by chemical analysis of ALCELL lignin.²⁷ This discrepancy may indicate a difference between the surface composition sensed by XPS and the true chemical formula (C₉H_{8.53}O_{2.45} (OCH₃)_{1.04}) obtained by chemical analysis of ALCELL lignin. The observed oxygen-carbon ratio for ALCELL lignin is also lower than the oxygen-carbon ratio reported in the literature for lignin. Oxygen-carbon ratios of 0.25, 0.38, and 0.39 were reported by Ahmed et al.²⁹ for Iotech lignin, thioglignin, and milled wood lignin, respectively. Hon²³ observed an oxygen-carbon ratio of 0.34 for milled wood lignin. Oxygen-carbon ratio in the range of 0.31-0.36 were found by Dorris and Gray²⁸ for dioxane lignin.

The C1s high resolution spectra fitting of untreated bleached kraft cellulose (Figure 4A) and ALCELL lignin (Figure 5A) show three different carbon atoms, C1, C2, C3 or C4 corresponding to carbon atoms bonded with other carbon atoms and/or carbon atoms bonded to hydrogen atoms (C-C/C-H), carbon atoms bonded to a non-carbonyl oxygen atoms (C-O), carbon atoms bonded to carbonyl oxygen atoms and/or carbon atoms bonded to two non-carbonyl oxygen atoms (C=O/O-C-O) or carbon atoms bonded to carbonyl oxygen atoms and non-carbonyl oxygen atoms (O-C=O), respectively.^{28,30} The binding energies which correspond to these different bonding after shifting the binding energy scale to place C1 feature at 285.0 eV are summarized in Table 3. Most of the C1 carbons in these lignocellulosic materials may be attributed to aliphatic carbons in cellulose, and to aliphatic and aromatic carbons in lignin; C2 carbon to primary and secondary alcohol in cellulose and lignin; C3 carbon to aliphatic ethers in cellulose; and C4 carbon may be related to esters and carboxylic acids in lignin. As can be observed, the C1s high resolution spectra fitting of bleached kraft cellulose is different from that of ALCELL lignin.

The C1s high resolution of bleached kraft cellulose is fitted with three components, C1, C2, and C3, however there is absence of C4 carbon in bleached kraft cellulose which may be attributed to the dissolution of hemicelluloses, lignin, and extractives during bleached kraft cellulose production. These components, particularly extractives (fatty acids) are known to be rich in esters and carboxylic groups.

Like bleached kraft cellulose, the C1s high resolution spectra of ALCELL lignin is also fitted with three components, C1, C2, and C4. There is absence of C3 component in ALCELL lignin, which may be explained by the cleavage of ether links

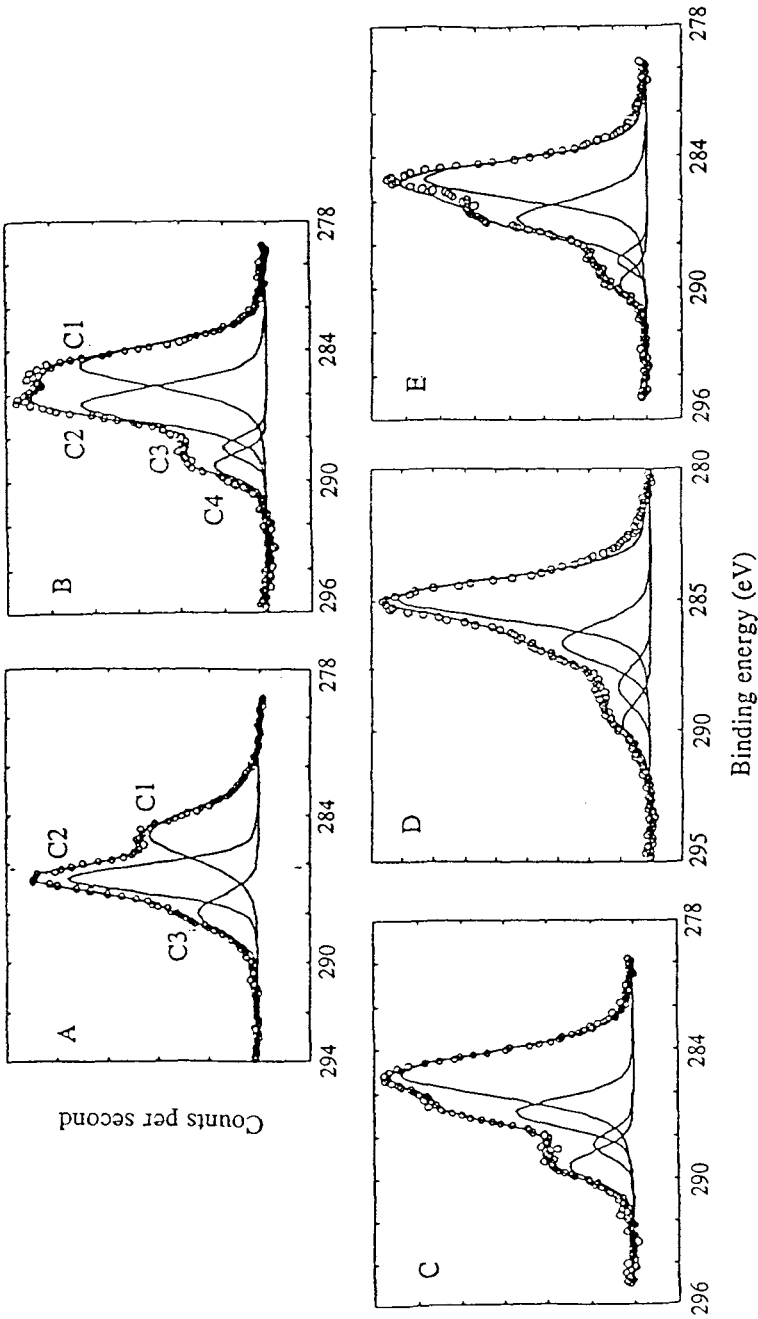


FIGURE 4: Curve fitting of C1s high resolution spectra of untreated and treated bleached kraft cellulose by X-ray photoelectron spectroscopy. (A) untreated bleached kraft cellulose, (B) maleic anhydride treated bleached kraft cellulose, (C) maleic anhydride treated bleached kraft cellulose (catalyst), (D) Epolene E-43 treated bleached kraft cellulose, and (E) Epolene G-3002 treated bleached kraft cellulose.

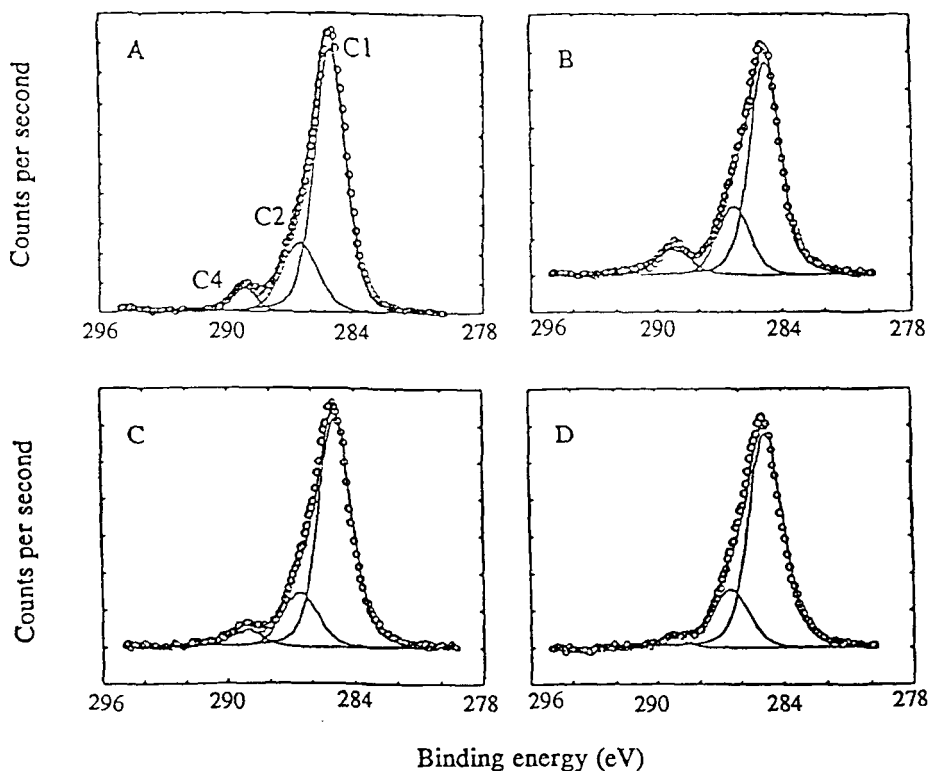


FIGURE 5: Curve fitting of C1s high resolution spectra of untreated and treated ALCELL lignin by X-ray photoelectron spectroscopy (A) untreated ALCELL lignin, (B) maleic anhydride treated ALCELL lignin, (C) Epolene E-43 treated ALCELL lignin, and (D) Epolene G-3002 treated ALCELL lignin.

during the production of ALCELL lignin. The C4 carbon in ALCELL lignin may be attributed to some carboxylic or esters components.

X-ray Photoelectron Spectroscopy of Maleated Lignocellulosic Materials

The results of the C1s high resolution spectra fitting of maleic anhydride, maleated polypropylene, treated bleached kraft cellulose, and treated ALCELL lignin

TABLE 3

Binding Energies of Different Oxidation States of Carbon Atom from the X-ray Photoelectron Spectroscopy High Resolution of C1s Spectra of Lignocellulosic Materials.

Carbons types	Bonding	Binding energy (eV)
C1	C-C/C-H	285.0 ± 0.4
C2	C-O	285.6 ± 0.4
C3	C=O/O-C-O	288.0 ± 0.4
C4	O-C=O	289.5 ± 0.4

are shown in Table 4. The curves fitting of untreated and treated lignocellulose materials are illustrated in Figures 4 and 5.

The modification of bleached kraft cellulose with maleated polypropylenes (Epolene E-43 and Epolene G-3002) demonstrates a change in the shape of the spectra as well as in the nature of the surface chemical groups. The C1s high resolution spectra fitting (Figure 4) shows a surface enriched in aliphatic carbon (C-C/C-H), indicating a substantial retention of maleated polypropylenes. This is also confirmed by the reduction of oxygen-carbon ratio of bleached kraft cellulose after maleated polypropylenes treatment (Table 4). It appears that the soxhlet extraction washed away some of the untreated maleated polypropylene, while some remained to form a hydrocarbon rich layer on bleached kraft cellulose. The examination of the C1s high resolution spectra fitting of maleated polypropylenes as presented in Figure 6, demonstrates that maleated polypropylenes contain mainly carbon atoms. Most of the

TABLE 4

Results of the C1s High Resolution Spectra Fitting, and Oxygen-carbon Ratio of Maleic Anhydride, and Untreated and Treated Wood Fibers by X-ray Photoelectron Spectroscopy

Treated wood fibers	C1 (%)	C2 (%)	C3 (%)	C4 (%)	O/C (%)
MA	74.6	16.6	-	8.8	29.4
ALIGN-0	72.9	22.1	-	5.0	22.5
ALIGN-MA**	68.2	22.7	-	9.1	30.5
ALIGN-E43**	75.7	19.1	-	5.3	24.0
ALIGN-G3002**	76.8	21.3	-	1.8	22.7
BKCELL-0	47.4	35.4	17.3	-	56.0
BKCELL-MA*	45.8	40.6	6.0	7.7	53.4
BKCELL-MA**	60.6	21.2	6.5	11.8	54.5
BKCELL-E43**	75.4	14.3	7.6	2.7	22.5
BKCELL-G3002**	61.8	25.8	8.0	4.4	38.9

MA: maleic anhydride

ALIGN-0: untreated ALCELL lignin

ALIGN-MA**: maleic anhydride treated ALCELL lignin with catalyst

BKCELL-MA*: maleic anhydride treated bleached kraft cellulose without catalyst

carbons atoms sensed on the maleated polypropylene surfaces by XPS are those from aliphatic carbons of polypropylene chains. The signals of carbonyl (C=O) groups are hardly detected by the XPS. Therefore, the observed increase in aliphatic carbons (C-C/H) on maleated polypropylenes treated bleached kraft cellulose is due to aliphatic carbons brought about by the maleated polypropylenes. The C-O, and C=O/O-C-O

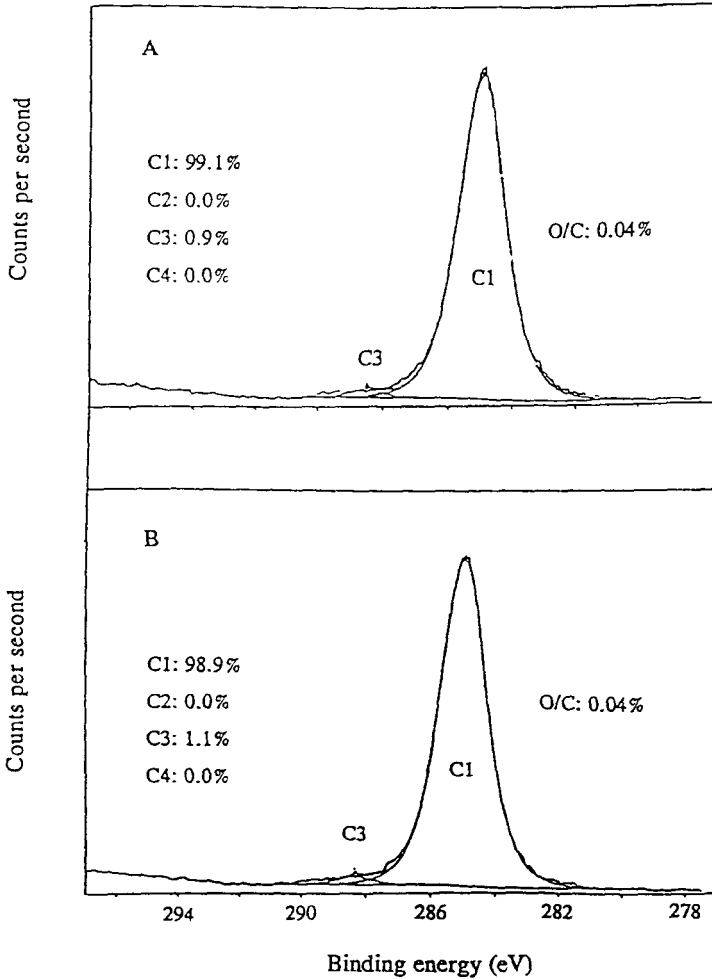


FIGURE 6: C1s high resolution spectra of maleated polypropylene by X-ray photoelectron spectroscopy (A) Epolene E-43, and (B) Epolene G-3002

portions are reduced following treatment of bleached kraft cellulose with maleated polypropylenes. It is interesting to note that the treatment of bleached kraft cellulose with maleated polypropylenes in the presence or absence of sodium hypophosphite shows the emergence of C4 Carbon type (O-C=O). The appearance of the C4 carbon type may indicate that the esterification reaction between hydroxyl groups of bleached kraft cellulose and anhydride groups of maleated polypropylenes may have taken place.

The C4 carbon type (O-C=O) increased from 0 to 2.7% when bleached kraft cellulose was treated with Epolene E-43, while an increase from 0 to 4.4% was observed when bleached kraft cellulose was treated with Epolene G-3002. The observed difference in the extent of esterification reaction of bleached kraft cellulose with maleated polypropylenes (Epolene E-43 and Epolene G-3002) may be explained by the difference in acid number of maleated polypropylenes as shown in Table 1. Olsen³¹, Sanadi et al.¹⁶ reported that the larger the acid number of maleated polypropylene, the greater the concentration of anhydride groups available for reaction with hydroxyl groups of wood fiber.

The modification of ALCELL lignin (Figure 5 (C and D)) with maleated polypropylenes (Epolene E-43 and Epolene G-3002) results in little change in different oxidation states of carbon atom. The aliphatic portion (C-C/C-H) shows an increase of 3.8%, and 5.3% when ALCELL lignin was treated with Epolene E-43 and Epolene G-3002, respectively. The C4 carbon type (O-C=O) shows an increase of 6.0% when ALCELL lignin was treated with Epolene E-43, and a decrease of 64.0% with Epolene G-3002. The absence of any remarkable increase in C4 carbon type (O-C=O) when ALCELL lignin are treated with maleated polypropylenes may suggest that the

esterification reaction between ALCELL lignin and maleated polypropylenes may have not taken place under the experimental conditions used in this study. Further, the use of sodium hypophosphite catalyst has no effect on the esterification reaction between ALCELL lignin and maleated polypropylenes. The failure of ALCELL lignin to chemically react by esterification reaction with maleated polypropylenes may be attributed to the low concentration of reactive hydroxyl groups on ALCELL lignin surface, and/or to high molecular weight of maleated polypropylenes, which reduce the ability of maleated polypropylenes to access the few reactive hydroxyl sites in the lignin structure.

X-ray Photoelectron Spectroscopy of Maleic Anhydride Treated

Lignocellulosic Materials

For reference, the XPS survey spectra and curve fitting of the C1s high resolution spectra of maleic anhydride are shown in Figure 7. From the XPS survey spectra, it can be seen that maleic anhydride shows higher intensity of carbon atoms than oxygen atoms. The C1s high resolution spectra fitting of maleic anhydride shows three components, C1, C2, and C3. The C1 component is related to C-C/C-H links, C2 carbon to C-O links, and C3 carbon to C=O links.

The treatment of bleached kraft cellulose (Figure 4 (B and C)) with maleic anhydride shows a significant change in the shape of the spectra and nature of the surface chemical groups. Compared to untreated bleached kraft cellulose, the C1s high resolution spectra of maleic anhydride treated bleached kraft cellulose in the presence

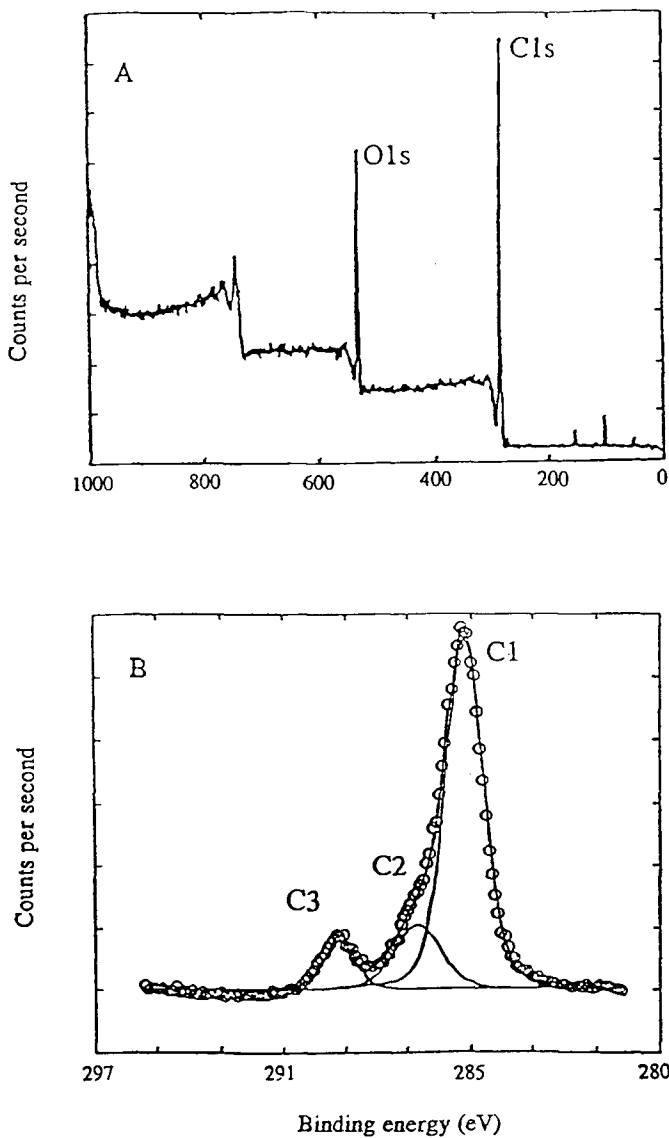


FIGURE 7: X-ray photoelectron spectroscopy survey spectra, and C1s high resolution spectra fitting of maleic anhydride by X-ray photoelectron spectroscopy.

or absence of sodium hypophosphite is fitted with four components, C1 (C-C/C-H), C2 (C-O), C3 (C=O/O-C-O), and C4 (O-C=O). However, as shown in Table 4, in the absence of sodium hypophosphite, the C-C/C-H portion decreased by 3.3%, C-O portion increased by 14.6%, and C=O portion decreased by 65.3%. The highest oxidation state of carbon (O-C=O) component emerged with a relative proportion of 7.7%. In the presence of sodium hypophosphite, the C-C/C-H portion increased to 27.8%, C-O portion decreased by 40.1%, and C=O/O-C-O decreased by 62.4%. The relative proportion of the highest oxidation state of carbon increases from 0 to 11.8%. The emergence of C4 carbon type (O-C=O) on bleached kraft cellulose upon treatment with maleic anhydride in the presence or absence of sodium hypophosphite is a clear indication that the esterification between hydroxyl groups of bleached kraft cellulose and anhydride groups of maleic anhydride has taken place. The higher proportion of C4 (O-C=O) observed on treated bleached kraft cellulose in the presence of sodium hypophosphite is an indication that sodium hypophosphite catalysed the esterification reaction between hydroxyl groups of bleached kraft cellulose and anhydride groups of maleic anhydride.

The modification of ALCELL lignin (Figure 5B) with maleic anhydride in the presence of sodium hypophosphite used as a catalyst shows little change in the shape of the spectra. The aliphatic carbons (C-C/C-H) decreased of 6.4%, practically no change is observed in C2 carbon type (C-O), and a substantial increase of 82.0% in C4 carbon type (O-C=O). The observed increase in C4 carbon type after treatment of ALCELL lignin with maleic anhydride may indicate the formation of ester bonds by esterification

reaction between hydroxyl groups of ALCELL lignin and anhydride groups of maleic anhydride.

CONCLUSIONS

The specific objectives of the present study were to characterize the surface chemistry of two different lignocellulosic materials (bleached kraft cellulose and ALCELL lignin) before and after treatment, and confirm the esterification reaction between these lignocellulosic materials and maleated polypropylenes. In summarizing the results, the following conclusions were drawn:

(1) The XPS results indicate that Bleached kraft cellulose surface chemistry (elemental composition and oxygen-carbon ratio) differ from that of ALCELL lignin.

(2) The XPS demonstrates that the esterification reaction of both bleached kraft cellulose and ALCELL lignin in pure maleic anhydride/xylene solution in the absence or presence of sodium hypophosphite used as a catalyst has occurred. The XPS analysis shows the emergence of C4 carbon type on high resolution C1s spectra of treated bleached kraft cellulose, which may be related to ester carbonyl functionality formed by esterification reaction between bleached kraft cellulose and maleic anhydride. The substantial increase in intensity of C4 carbon type on high resolution C1s spectra of maleic anhydride treated ALCELL lignin may also be related to ester bonds formed by esterification reaction.

(3) The XPS studies confirmed that esterification of bleached kraft cellulose in maleated polypropylenes/xylene solution in the absence or presence of sodium

hypophosphite catalyst has occurred. Evidence for this is observed in the emergence of C4 carbon type on high resolution C1s spectra of maleated polypropylene treated bleached kraft cellulose surface. However, no evidence of esterification is observed between ALCELL lignin and maleated polypropylenes.

(4) Both the lignocellulosic material and presence of long polypropylene on the short maleic anhydride chain have an effect on the esterification reaction.

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