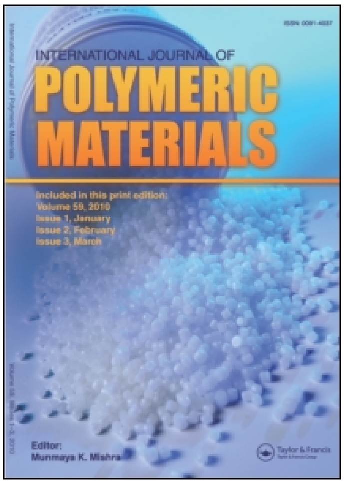

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The main objectives of the present study was to investigate the surface chemistry of different wood fibers, and evaluate its relative importance with respect to mechanical properties of wood fiber-polypropylene composites, and ascertain other factors of wood fibers that may affect the mechanical properties. Wood fiber surface chemistry had no direct influence on the mechanical properties of wood fiber-polypropylene composites. However, the surface chemistry was found to be an important factor which determines the wettability of wood fibers by the polypropylene matrix. Morphological features of wood fibers (fluffy, fibrous, curled, and twisted nature), and bulk density of wood fibers had a significant influence in determining the mechanical properties of wood fiber-polypropylene composites as they affect the dispersion of wood fibers in polypropylene matrix and the interlocking of wood fibers into the polypropylene matrix.

Keywords: Injection molding; wood chemistry; polypropylene; wood composites; ESCA; FT-IR

INTRODUCTION

Wood fibers have been used as reinforcement agents and/or fillers in thermoplastic industry to reduce the manufacturing cost and enhance the strength performance of the resulting composites [1–4]. Methods of pulping wood give rise to various types of wood fibers, according to the method of recovery (chemical and/or mechanical). The most common wood fibers are bleached cellulose fibers, thermomechanical pulp and wood flour. Cellulose fibers, for example bleached Kraft cellulose fibers (BKCELL) are chemical fibers obtained from wood chips by dissolving and extracting lignin, most of the hemicelluloses, and extractives. Cellulose fibers are nearly pure cellulose and are strong, fibrous and have a high concentration of hydroxyl groups. Thermomechanical pulp (TMP) consists of fibers produced from wood chips by mechanical refining process at high temperatures using steam. The resulting fibers are slender, fluffier, fibrous, and retain a lignin-like surface. Wood flour (WF) consists of particles produced by grinding solid wood. The methods of grinding include use of attrition mills, disk mills or hammermills. The product obtained is usually a mixture of broken fibers, poorly fibrillated fibers, and fiber bundles. Wood flours are generally rough, rigid and have a greater bulk density than pulp fibers. Depending on the manufacturing process used, wood flour may present three distinct types of surface [5]: (1) the highly polar cellulose and hemicellulose rich secondary wall. This surface is obtained by intercellular fracture of the cell during manufacturing; (2) the residue coated lumen wall; and (3) the lignin rich compound middle lamella. This latter is produced by intrawall fracture of the cell during grinding.

Several workers have shown that wood fiber surface chemistry is the essential factor which determines the mechanical properties of wood fiber-polypropylene composites. Lightsey *et al.* [6–7] have demonstrated that wood fiber with primary non-polar, hydrophobic, lignin-like surface produced composites with higher strength properties than wood fiber having primarily polar, hydrophilic, cellulose-like surface. This was explained by relatively better compatibility between the lignin-like surface of wood fibers with the non-polar polymer matrix. The contribution of the concentration of hydroxyl groups on the wood fibers surface to the mechanical properties has been investigated by Han *et al.* [8]. They observed that wood fiber surface with relatively low concentration of hydroxyl groups produced relatively high performance composites when used as a reinforcing filler in nonpolar polymers. However, since the change in wood fiber surface chemistry is often accompanied by a change in wood fiber morphology and physical characteristics, we understand that a direct relationship between wood fiber surface chemistry and mechanical properties of the composites may be partial.

Because of the importance of understanding the surface properties of wood fiber in the design of wood fiber-polypropylene composites, the present work is aimed at investigating the surface chemistry of different wood fibers and assessing the relative importance of the wood fiber surface chemistry on the mechanical properties of the resulting composites, and to ascertain other attributes of wood fiber that may affect the mechanical properties. To achieve these objectives, various experimental methods were employed including, X-ray Photoelectron Spectroscopy (XPS), Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electron Microscopy (SEM) and mechanical properties of wood fiber-polypropylene composites. The practical value of this work may help in the selection of wood fibers for use in reinforced composites (i.e. important wood fiber properties to be considered), modification techniques and selection of appropriate processing aids and enhancing agents.

EXPERIMENTAL

Materials

Polypropylene (PP), Profax 6301 homopolymer from Himont Canada Inc. was selected as a typical polymer matrix. The density of PP was 0.960 g/cm^3, and the melt flow of PP was 10 dg/min. Polypropylene was selected as the matrix because it is one of the major commodity plastics which may be readily processed below the atmospheric decomposition temperature of wood fiber (about 220 °C).

Unbleached thermomechanical pulp, bleached Kraft cellulose, inked recycled newsprint, and wood flour were chosen for evaluation. Black pruce thermomechanical pulp and bleached Kraft cellulose were obtained from Abitibi-Price Inc. (Mississauga, Ontario, Canada). The pulp were defibrillated in a Wiley Mill (Thomas-Wiley Laboratory Mill Model 4) into small uniform fibers, and sieved to 250 μm. The fraction of softwood flour (spruce and pine) passing 45 mesh and retained on 60 mesh sieve (−45/60) was collected for examination.

X-ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) was used to characterize the surface chemical composition of wood fibers. XPS provides a means of obtaining detailed characterization of the surface. It gives a quantitative elemental composition and identify certain functional groups on the surface to depth of about 1–10 A° [9–10].

The XPS spectra were recorded 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 on a holder using double sided adhesive tape, and placed in a vacuum in the range of 10^{-8}–10^{-7} torr. The analyzed area was 4 × 7 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 normalised to unit transmission of the electron spectrometer [11]. For more information on the nature of the surface, 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 [10], and the binding energy scale was then shifted to place the C1s feature present at 285.0 eV.

Diffuse Reflectance Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FT-IR) was used as a complementary tool to XPS to obtain further details on the surface characteristics of wood fibers.

FT-IR spectra of wood fiber were obtained with a Bruker FT-IR unit, Model IFS 85. All the infrared spectra of wood fiber were recorded in absorbance units ($-\log R/R_0$) in range 4000–1000 cm^{-1} 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. Diffuse reflectance was used with the FT-IR for transfer of infrared radiation.

Bulk Density Measurements of Wood Fibers

The bulk density of wood fibers (thermomechanical pulp, recycled newsprint, and wood flour) was obtained as a ratio of the weight of packed wood fibers in a chromatographic column and the internal volume of the column. Wood fibers were packed under vacuum with a vibrator into a copper column (inner diameter 4 mm, length 1.2 m), which the end was plugged with glass wool.

MECHANICAL PROPERTIES OF THE COMPOSITES

Compounding and Injection Molding

Wood fibers were compounded with polypropylene in a high intensity thermokinetic mixer (Werner and Pfleiderer Gelimat Model 456441G1) at 3300 rpm. and discharged at 180 °C. The proportion of wood fiber to polypropylene matrix was maintained constant at 30 percent by weight. After compounding, the molten discharge was allowed to cool to room temperature and then granulated into fine particles using a Brabender granulator (Model S-10-9). The compounds were injection molded using an Engel ES-28 machine equipped with a standard ASTM test specimen mold. The injection molding conditions are shown in Table I.

Mechanical Properties Testing

The tensile and flexural tests were conducted according to ASTM-D-638 and ASTM-D-790 respectively. These tests were performed on a standard computerised testing machine (Sintech, Model 20) with a crosshead speed of 12.5 mm/min. The tensile and flexural properties were calculated through the computing software (Testwork program, Ver. 2.10, Sintech Inc. U.S.A). Six specimens were tested to obtain an average value.

TABLE I Injection molding conditions

Parameters	*Values*
Injection pressure, MPa	4.83
Clamp pressure, MPa	11.72
Heating zone temperature, °C	
Zone 1	204
Zone 2	204
Zone 3	204
Nozzle, %	60
Injection time, sec.	9.5
Cooling time, sec.	25
Mold opening time, sec.	2

Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) was used to qualitatively examine the dispersion of wood fibers and morphological structure in the injection molded composites.

Polished surfaces of injection molded wood fiber-polypropylene composites were examined with a Hitachi Scanning Electron Microscope, Model S-2500. The polishing was done by embedding the samples in Epoxy for 24 hours, and polishing with a Buehler Metaserv Grinder Polisher with silicon carbide wet abrasive papers (60/CWT/1A-3; 240/CWT/NR9; 400/CWT/TE3; and 1200 grit/400P/372E). The standard quality alumina paste was used to provide a final polish of 0.25 μm. The polished samples were washed with water and air-dried. The dry samples were then coated with thin layer of carbon before microscopic observation in order to increase the conductivity of the samples and reduce the charging effects.

RESULTS AND DISCUSSION

X-ray Photoelectron Spectroscopy Wood Fibers

Due to the similarities of the O1s chemical shifts, and difficulties in estimating their relative intensities [12–14], the discussion in this section will be focused on the C1s chemical shifts.

Figure 1 shows the survey spectra of thermomechanical pulp, recycled newsprint, wood flour, and bleached Kraft cellulose. It shows

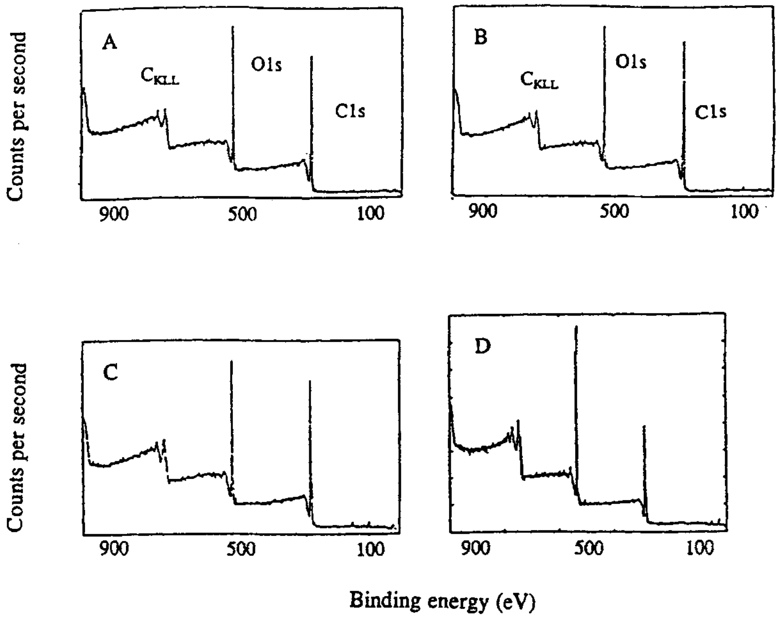

FIGURE 1 X-ray Photoelectron Spectroscopy survey spectra of untreated wood fibers (A) thermomechanical pulp, (B) recycled newsprint, (C) wood flour, (D) bleached Kraft cellulose.

the number of electrons counted 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 (C_{KLL}). As can be seen the survey spectra of the thermomechanical pulp, recycled newsprint, and wood flour are similar, which shows slightly greater intensity for oxygen atoms compared to carbon atoms. This is different from the survey spectra of bleached Kraft cellulose which indicates greater intensity of oxygen atoms compared to carbon atoms.

The elemental composition and oxygen-carbon ratio of different wood fibers are shown in Table II. Relative atomic percents were obtained from peak areas of the various emissions corrected for intensity with an appropriate sensitivity factor. Thermomechanical pulp, recycled newsprint, and wood flour show a higher proportion of carbon as compared to bleached Kraft cellulose. The higher proportion of carbon in these wood fibers may be attributed to the presence of lignin and other cell compounds on the surface (fatty acids, proteins resins).

TABLE II 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)*
TMP	74.7	25.2	33.8	–
RNWP	73.7	26.3	35.6	–
WF	74.6	25.4	34.0	–
BKCELL	63.9	36.1	56.7	83.0[a]

[a] Dorris and Gray 1978.

TMP thermomechanical pulp, RNWP – recycled newsprint, WF - wood flour, BKCELL bleached Kraft cellulose.

The oxygen-carbon ratios of different wood fibers (thermomechanical pulp, recycled newsprint, and wood flour) appear to be similar and are consistent with the oxygen-carbon ratios reported in the literature for lignin, indicating that the surface of these wood fibers is a more lignin-like surface. Oxygen-carbon ratios of 0.25, 0.38, and 0.39 were reported by Ahmed *et al.* [15] for Iotech lignin, thiolignin, and milled wood lignin, respectively. Hon [12] observed an oxygen-carbon ratio of 0.34 for milled wood lignin. Oxygen-carbon ratios in the range of 0.31–0.36 were found by Dorris and Gray [16] for dioxane lignin. The lignin-like surface of thermomechanical pulp may be explained by the fact that during the production of thermomechanical pulp, the zone of failure in the defibration process at high temperature in the presence of steam is located more in the lignin rich middle lamella. The high oxygen-carbon ratio of recycled newsprint may suggest the presence of chemical pulp rich in carbohydrates. This may be due to the fact that the recycled newsprint is generally produced from a mixture of mechanical (or thermomechanical pulp) and chemical pulp. Although wood flour was described in the literature as having a polar or cellulose-like surface [6], it appears from the oxygen-carbon ratio (0.34) that the surface of wood flour is less polar and lignin-like. This discrepancy may be due to the surface sensitivity of XPS or to a preferential splitting of the lignin-rich middle lamella in the wood flour as compared to wood flour samples analyzed by Lightsey *et al.* [6].

Bleached Kraft cellulose shows the highest oxygen-carbon ratio. However, the value is less than the ratio of 0.83 from the cellulose atomic formula $(C_6H_{12}O_5)_n$. Such low oxygen-carbon ratio has also been observed by Mjoberg[17]. It was indicated that strong absorption of impurities on cellulose or the presence of extractives, terpenes and terpenoides, fats, waxes and phenolic compounds might reduce the oxygen-carbon ratio since they have fewer hydroxyl groups, and are rich in aliphatic and aromatic carbons.

Figure 2 illustrates the XPS high resolution spectra of C1s peaks of wood fibers (thermomechanical pulp, recycled newsprint, wood flour, and bleached Kraft cellulose).

The C1s high resolution spectra fitting of wood fibers, thermomechanical pulp, recycled newsprint, and wood flour show four different carbon atoms, C1, C2, C3 and C4 corresponding with carbon atoms bonded to 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

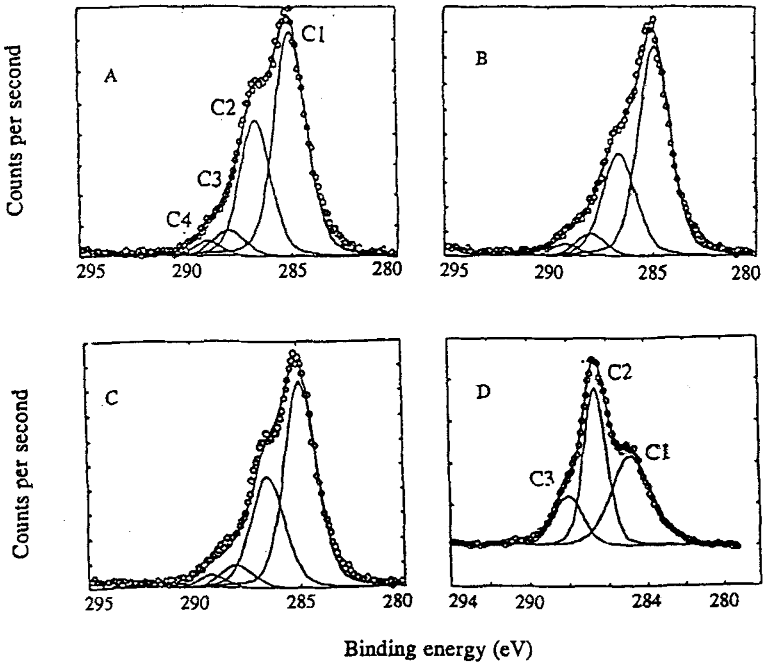

FIGURE 2 C1s high resolution spectra fitting of untreated wood fibers (A) thermomechanical pulp, (B) recycled newsprint, (C) wood flour, (D) bleached Kraft cellulose by X-ray Photoelectron Spectroscopy.

atoms (C=O / O—C—O) and carbon atoms bonded to carbonyl oxygen atoms and non-carbonyl oxygen atoms (O—C=O), respectively [18–20]. The binding energies which correspond to these different carbons bonding after shifting the binding energy scale to place C1 feature at 285.0 eV are summarized in Table III. Most of the C1 carbon in these wood fibers may be attributed to aliphatic carbons in lignin and extractives, and to aromatic carbons in lignin and extractives, C2 carbon to primary and secondary alcohol in lignin and extractives, C3 carbon to aliphatic and aromatic ethers in lignin and extractives, and carbonyl esters, carbonyl aldehydes, carbonyl ketones, or carbonyl carboxylics in lignin and extractives (fatty acids), and C4 carbon may be related to esters and carboxylic acids in lignin and extractives.

The C1s high resolution spectra fitting of bleached Kraft cellulose is different from those of thermomechanical pulp, recycled newsprint, and wood flour. The C1s high resolution of bleached Kraft cellulose is fitted with three components, C1, C2 and C3, and there is an absence of C4 carbon in bleached Kraft cellulose which may be attributed to the selective extraction of hemicelluloses, lignin, and other extractives during bleached Kraft cellulose production. These components, particularly extractives (fatty acids) are known to be rich in esters and carboxylic groups.

The results of the C1s high resolution spectra fitting for thermomechanical pulp, recycled newsprint, wood flour, and bleached Kraft cellulose are summarized in Table IV. It can be seen that the proportion of carbon in different binding environments of wood fibers (thermomechanical pulp, recycled newsprint and wood flour) are similar, in view of the typical experimental error (≈ 10%) for X-ray Photoelectron Spectroscopy measurements [20, 21]. The proportion of C1 component for thermomechanical pulp is 70.3%, 74.9% for recycled

TABLE III Binding energies of different oxidation states of carbon atom from the X-ray Photoelectron Spectroscopy high resolution of C1s spectra of lignocellulosic materials [18–20]

Carbon 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

TABLE IV Results of the C1s high resolution spectra fitting of untreated lignocellulosic materials by X-ray Photoelectron Spectroscopy

Wood fibers	C1 (C—C/C—H)	C2 (C—O)	C3 (C=O/O—C—O)	C4 (O—C=O)
TMP	70.3	20.2	6.3	3.2
RNWP	74.9	15.8	5.9	3.4
WF	69.9	19.6	5.3	5.2
BKCELL	40.3	44.8	14.9	–

TMP–thermomechanical pulp, RNWP–recycled newsprint, WF–wood flour, BKCELL–bleached Kraft cellulose.

newsprint and 69.9% for wood flour. The proportion of C2 component for thermomechanical pulp 20.2%, 15.8% for recycled newsprint, and 19.6% for wood flour. Almost the same pattern is observed for C3 and C4 components.

The results of C1s high resolution spectra fitting for bleached Kraft cellulose are different from those for thermomechanical pulp, recycled newsprint and wood flour. The contribution of C—C/C—H bonds are lower, C—O / O—C—O bonds are more pronounced, and there is no indication of the presence of O=C—O groups.

Fourier Transform Infrared Spectra of Wood Fibers

Figure 3 shows the FT-IR spectra of wood fibers (thermomechanical pulp, wood flour and bleached Kraft cellulose) in the region from 4000 to 1000 cm^{-1}.

The absorption bands in the region from 3500–3100 cm^{-1} for all 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 [22–24]. The shoulder near the OH stretching vibrations may be associated with CH stretching vibrations. The aliphatic CH stretching vibrations of methyl and methylene groups in wood [25], aromatic CH stretching vibrations [26, 27] and aliphatic aldehydes CH stretching vibration [28] also absorb in this region.

The differences between the different wood fiber samples can be seen in the region 1750–1700 cm^{-1}. In the spectra of thermomechani-

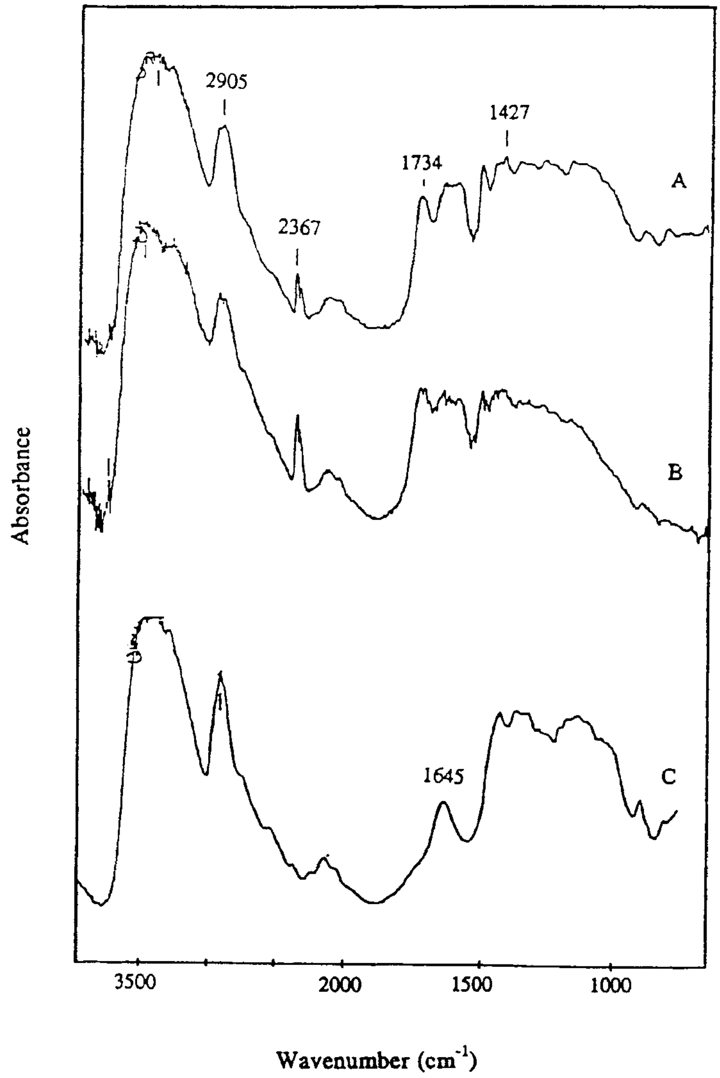

FIGURE 3 FT-IR spectra of untreated wood fibers (A) thermomechanical pulp, (B) wood flour, (C) bleached Kraft cellulose.

cal pulp and wood flour, there are absorption bands near 1730 cm^{-1} which may be associated with 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 also of esters in lignin and various extractives [22, 23, 25, 29–31].

The spectra of bleached Kraft cellulose does not show any detectable absorption bands in the region 1750–1700 cm^{-1}. The observed absorption band at 1645 cm^{-1} was associated with the double band (C=C) [32]. However, Kolboe and Ellefsen [23] suggested that the bands in this region for cellulose may be attributed to C=O stretching vibrations of the alpha-keto carbonyl. Tsuboi [33] assigned the band at 1645 cm^{-1} to absorbed water. The absence of absorption bands in the region 1750–1700 cm^{-1} in the spectra of bleached Kraft cellulose may be due to the fact that the compounds rich in carbonyl (C=O), lignin, hemicelluloses and extractives are removed during the production of bleached Kraft cellulose.

The absorption bands in the region 1600–1400 cm^{-1} in the spectra of thermomechanical pulp, and wood flour may be attributed to the presence of aromatic structures in lignin [23]. The weak vibrations near 1400–1300 cm^{-1} in the spectra of these wood fibers may be attributed to the aliphatic and aromatic (C—H) in the plane deformation vibrations of methyl, methylene and methoxy groups [22, 32]. For bleached Kraft cellulose, the bands at 1400–1300 cm^{-1} are associated with CH in the plane deformation of CH_2 groups [23].

The bands in the region 1300–1000 cm^{-1} involve the C—O stretching vibrations of aliphatic primary and secondary alcohols in cellulose, hemicelluloses, and lignin and extractives, and aromatic primary and secondary alcohols in lignin and extractives [22, 23]. Aliphatic ethers in cellulose and lignin [33, 35], and aromatic ethers in lignin [36, 37] absorb also in this region. The 1300–1000 cm^{-1} region may also be associated with OH vibrations in carbohydrates [38, 39].

MECHANICAL PROPERTIES OF WOOD FIBER-POLYPROPYLENE COMPOSITES

Mechanical Properties

Tensile Properties

The tensile strength, tensile modulus, and elongation at break of wood fiber-polypropylene composites are shown in Table V. The tensile

TABLE V Effect of untreated wood fiber addition in polypropylene on the mechanical properties of injection molded wood fiber-polypropylene composites (compound ratio 30% wood fiber-70% polypropylene)

Properties	*Wood fiber-polypropylene composites*				
	PP	*TMP-PP*	*RNWP-PP*	*WF-PP*	*BKCELL-PP*
Tensile strength, MPa	30.67	34.59	34.18	27.97	32.51
Tensile modulus, GPa	0.99	2.45	2.32	1.97	2.19
Elongation at break, %	–	3.68	4.14	4.47	4.18
Flexural strength, MPa	46.83	65.60	66.22	54.31	59.45
Flexural modulus, GPa	1.33	3.45	3.26	3.19	2.77

PP–neat polypropylene.
TMP-PP–thermomechanical pulp-polypropylene composites.
RNWP-PP–recycled newsprint-polypropylene composites.
WF-PP–wood flour-polypropylene composites.
BKCELL-PP–bleached Kraft cellulose-polypropylene composites.

strength and tensile modulus of unfilled polypropylene is also shown for reference. The elongation at break for polypropylene was not recorded because of the extreme ductility. Polypropylene did not fracture, but continued to yield.

Except for wood flour, the addition of wood fiber in polypropylene slightly increased the tensile strength of the composites. The addition of thermomechanical pulp in polypropylene increased the tensile strength by 13%, 11% for recycled newsprint, 6% for bleached Kraft cellulose. The addition of wood flour decreased the tensile strength by 9%.

In contrast to the tensile strength, the addition of wood fiber in polypropylene substantially increased the tensile modulus. The improvement in tensile modulus with the addition of thermomechanical pulp is about 147%, 134% for recycled newsprint, 99% for wood flour, and 121% for bleached Kraft cellulose.

The observed slight improvement in tensile strength of the composites as compared to tensile modulus following the addition of wood fiber may be attributed to the poor adhesion between wood fibers and polypropylene matrix, and poor dispersion of wood fibers in polypropylene matrix [40]. The poor dispersion of wood fibers in polypropylene may be explained by the presence of strong wood fiber-wood fiber polar interactions. The substantial increase in tensile modulus with wood fiber addition in polypropylene is due to the greater stiffness of wood fibers [2].

The effect of the addition of different wood fibers in polypropylene may be also seen in Figure 4 which illustrates the stress-strain curves in tensile testing for injection molded wood fiber-polypropylene composites. The stress-strain curve indicates three zones, the elastic zone, plastic deformation zone, and breaking or failure zone. The elastic zone is illustrated by the straight-line portion of the curve where the strain induced in the composites is proportional to the applied stress. The steepness of the slope of this straight-line is a measure of the tensile modulus. The plastic deformation starts at the end of the linear zone. In this portion of the curve the stress increases monotonically up to a maximum value, called the ultimate stress. In the breaking or failure zone the stress decreases monotonically until final failure occurs.

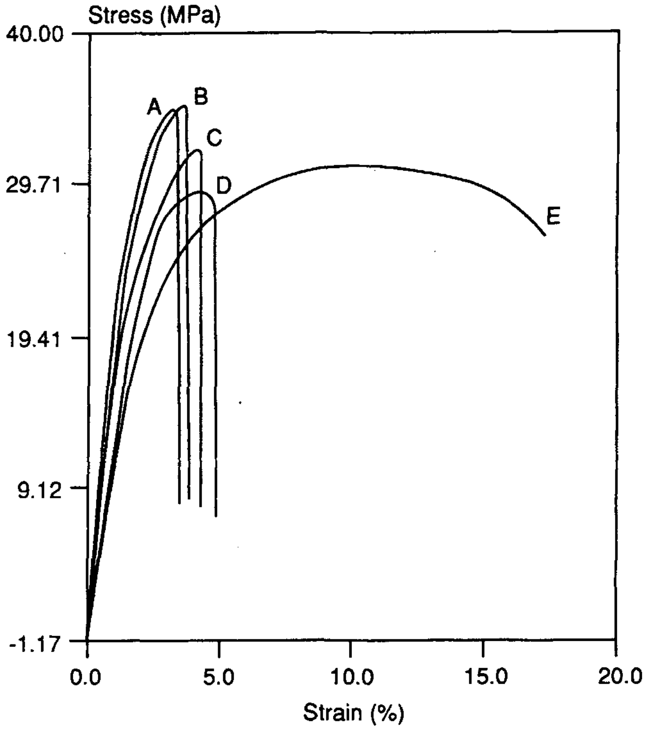

FIGURE 4 Stress-strain curves of injection molded untreated wood fiber-polypropylene composites in tensile testing (compound ratio 30% wood fiber-70% polypropylene). (A) thermomechanical pulp-polypropylene, (B) recycled newsprint-polypropylene, (C) bleached Kraft cellulose-polypropylene, (D) wood flour-polypropylene composites, and (E) polypropylene.

The series of curves A, B, C and D are experimental stress-strain curves of wood fiber-polypropylene composites. The curve E is the experimental stress-strain curve of polypropylene. The examination of these series of curves demonstrates that the addition of wood fibers in polypropylene increased the maximum applied stress and the tensile modulus. The increase in the tensile modulus is well illustrated by the steepness of the slope in the elastic zone. The fracture for most of the wood fiber-polypropylene composites occurs in the range of 25–35 MPa at a strain of less than 5.00%. The Stress-strain curves for wood fiber-polypropylene composites show that there is almost no plastic deformation or yielding before fracture. The composites break abruptly with relatively no plastic yielding. On the other hand, although the failure of polypropylene also occurs in the range of 25–35 MPa, the plastic deformation zone is pronounced, indicating large plastic deformation or yielding before failure.

The significance of these series of curves is that they show the embrittlement of polypropylene with wood fiber addition. There is a change in the mode of failure, from ductile behaviour to brittle fracture. The brittle fracture of wood fiber filled polypropylene is likely due to a lack of sufficient adhesion between wood fibers and polypropylene matrix. This is supported by the scanning electron micrographs of a polished cross-section perpendicular to the flow direction of an injection molded wood fiber-polypropylene composite (Fig. 5). The dark and light regions correspond to polypropylene and wood fibers respectively. It can be seen that there is a gap between the wood fiber and polypropylene matrix. The presence of the gap at the wood fiber-polypropylene interface may indicate a low degree of adhesion between wood fibers and polypropylene matrix.

Flexural Properties

The flexural strength and flexural modulus of wood fiber-polypropylene composites are also shown in Table V.

The flexural strength of polypropylene increased substantially following the addition of wood fibers. The addition of thermomechanical pulp in polypropylene increased the flexural strength by 40%. Almost the same performance was observed with recycled newsprint as filler. The flexural strength increased by 16% with the addition of wood

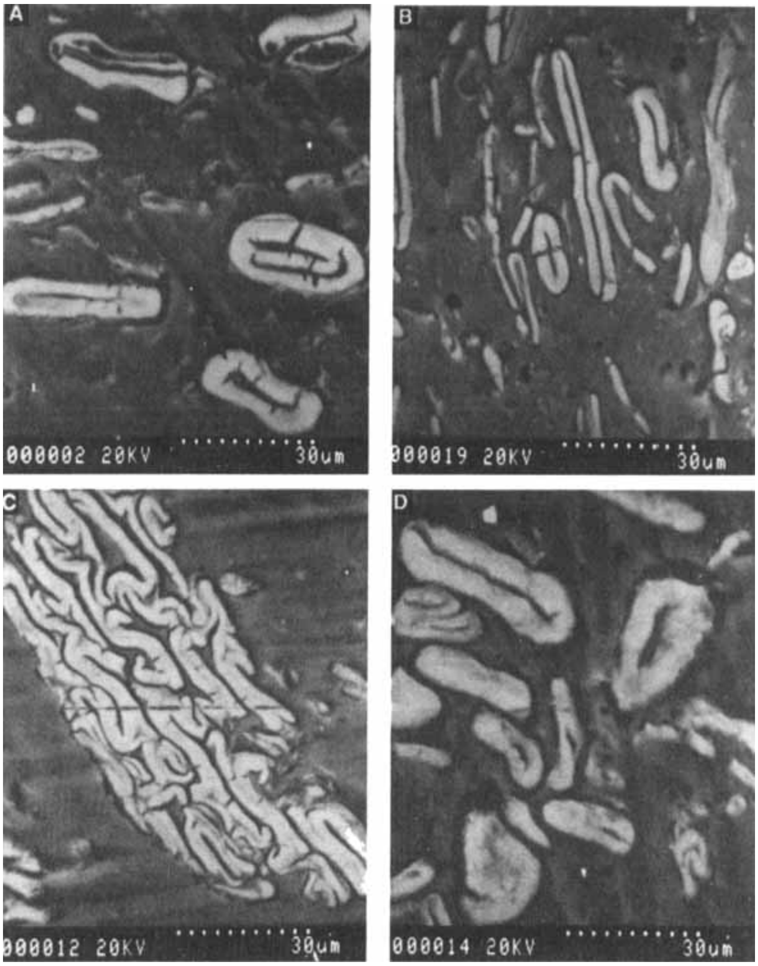

FIGURE 5 Scanning electron micrographs of polished cross-section specimens of injection molded untreated wood fiber-polypropylene composites (A) untreated thermomechanical pulp-polypropylene, (B), untreated recycled newsprint-polypropylene, (C) untreated wood flour-polypropylene, and (D) untreated bleached Kraft cellulose-polypropylene composites.

flour, and 27% with the addition of bleached Kraft cellulose. The increase in flexural strength with the addition of wood fiber was attributed to the high modulus of wood fibers which reinforces the much weaker polypropylene.

The flexural modulus of wood fiber-polypropylene was greater than that of polypropylene. In all cases, an increase of over 100% in flexural modulus was observed compared to unfilled polypropylene.

STATISTICAL ANALYSIS OF THE EFFECT OF DIFFERENT WOOD FIBERS ADDITION

A one-way analysis of variance on a completely randomized design was conducted to test the effect of different wood fibers addition in polypropylene with respect to the mechanical properties of the composites (i.e. tensile strength, tensile modulus, elongation at break, flexural strength, and flexural modulus).

Five experimental groups representing four different wood fibers and polypropylene (as control) were used. The F test obtained by analysis of variance of the effect of different wood fibers addition on the mechanical properties demonstrates that the five groups differ significantly from one another, in view of the critical value of 5%. This test indicates that the wood fiber-polypropylene composites differ significantly from polypropylene, and the effect of wood fiber addition on the mechanical properties of the composites also depends on the wood fiber type.

The test of significance for differences between means using Turkey's Studentized Range Test was also conducted for tensile strength, tensile modulus, flexural strength, and flexural modulus. The purpose of this test was to test all possible paired comparisons of five groups of composites (included injection molded polypropylene).

Table VI shows the test of significance for differences between tensile strength means, and tensile modulus means of five groups of composites. Table VII indicates the test of significance for differences between flexural strength means, and flexural modulus means. These Tables VI–VII summarize the means, Minimum Significant Difference (MSD), level of probability (α), and difference means. A pair of means is significantly different if their difference equals or exceeds the Minimum Significant Difference at the 5% level of probability and is indicated by an asterisk. For example, the mean 34.59 MPa for the tensile strength of thermomechanical pulp-polypropylene composites differs significantly at the 5% level from the mean 27.97 MPa for the

TABLE VI Differences between tensile properties means of wood fiber-polypropylene composites due to the addition of different wood fibers in polypropylene

A. Tensile Strength (MSD = 0.784, $\alpha = 5\%$)

Composites	*Means*	*Composites*			
		RNWP-PP	*WF-PP*	*BKCELL-PP*	*PP*
TMP-PP	34.59	0.41	6.61*	2.08*	3.92*
RNWP-PP	34.18	–	6.21*	1.67*	3.51*
WF-PP	27.97	–	–	4.54*	2.70*
BKCELL-PP	32.51	–	–	–	1.84*
PP	30.67	–	–	–	–

B. Tensile modulus (MSD = 0.352, $\alpha = 5\%$)

Composites	*Means*	*Composites*			
		RNWP-PP	*WF-PP*	*BKCELL-PP*	*PP*
TMP-PP	2.45	0.13	0.48*	0.26	1.46*
RNWP-PP	2.32	–	0.35*	0.13	1.33*
WF-PP	1.97	–	–	0.22	0.98*
BKCELL-PP	2.19	–	–	–	1.20*
PP	0.99	–	–	–	–

*Significantly different.

tensile strength of wood flour-polypropylene composites. This is true because the difference in absolute value (6.62) is greater than the Minimum Significant Difference (MSD) of 0.784.

Tables VI–VII show also that the effect of the addition of different wood fibers differs for each mechanical property considered. Thus, it can be observed that wood fiber type has a more pronounced effect on the tensile and flexural strengths of the composites than the tensile and flexural modulus. This may be due to the fact that the strength properties of the composites are more sensitive to the interfacial adhesion between wood fibers and polypropylene matrix [7, 41, 42], and morphological characteristics of the wood fibers, while modulus properties are more dependent on the wood fiber modulus which does not vary significantly between wood fiber samples.

A comparison of wood fiber-polypropylene composites from Tables VI–VII reveals that thermomechanical pulp-polypropylene composites differ significantly from wood flour-polypropylene composites. Lightsey *et al.* [7] attributed the higher strength properties of

TABLE VII Differences between flexural properties means of wood fiber-polypropylene composites due to the addition of different wood fibers in polypropylene.

A. Flexural strength (MSD = 2.450, $\alpha = 5\%$)

Composites	*Means*	*Composites*			
		RNWP-PP	*WF-PP*	*BKCELL-PP*	*PP*
TMP-PP	65.60	0.60	11.29*	6.15*	18.77*
RNWP-PP	66.22	–	11.91*	6.77*	19.89*
WF-PP	54.31	–	–	5.14*	7.48*
BKCELL-PP	59.45	–	–	–	12.62*
PP	46.83	–	–	–	–

B. Flexural modulus (MSD = 0.134, $\alpha = 5\%$)

Composites	*Means*	*Composites*			
		RNWP-PP	*WF-PP*	*BKCELL-PP*	*PP*
TMP-PP	3.45	0.19*	0.26*	0.67*	2.12*
RNWP-PP	3.26	–	0.07	0.47*	1.93*
WF-PP	3.19	–	–	0.40*	1.86*
BKCELL-PP	2.77	–	–	–	1.45*
PP	1.33	–	–	–	–

*Significantly different.

thermomechanical pulp-polypropylene composites to hydrophobic or non-polar character of the lignin-like surface, which makes them more compatible with a polypropylene matrix. However, Sanschagrin *et al.* [4] suspected that the wood fiber aspect ratio may play an important role in influencing the strength properties of the composites. Thus, it was suggested that the higher aspect ratio of thermomechanical pulp compared to that of wood flour may explain the higher strength properties of thermomechanical pulp-polypropylene composites.

As previously demonstrated, the XPS and FT-IR studies of wood fibers (thermomechanical pulp and wood flour) has indicated that the surface chemistry of these two wood fiber types possess lignin-like surfaces. The differences observed in oxygen-carbon ratio (thermomechanical pulp-0.33, and wood flour-34.0%) are so small that these may be practically without influence on the interfacial adhesion between these different wood fibers and polypropylene, and likewise to the mechanical properties of their respective composites. Thus, the observed differences in strength between thermomechanical pulp-polypropylene and wood flour-polypropylene composites may be attributed to factors other than the wood fiber surface chemistry. It is expected that the fluffy, fibrous, curled and twisted nature and bulk density of wood fibers may account for these differences. Table VIII gives the bulk density values for thermomechanical pulp, recycled newsprint, and wood flour.

The fluffy, fibrous, curled, and twisted nature of wood fiber may affect the strength of the composites because of their flexibility within the polymer network, which may enhance the mechanical interlocking of fibers with polymer matrix. In addition, because composites are made up to a given weight of wood fibers, thus if the bulk density of wood fiber is the only variable of wood fibers, composites made from wood fibers with high bulk density will contain fewer fibers for the same weight of composite made from wood fibers with low bulk density. As a consequence, there will be less opportunity for interfacial contact between wood fibers with high bulk density and polymer matrix than between wood fibers with low bulk density wood fiber and polymer matrix. Large interfacial contact between fibers and polymer matrix is necessary to promote high degree of transfer of load from the matrix to the fibers. Further, high bulk density fibers tend to form coherent agglomerates throughout the polymer matrix, thus limiting the uniform load transfer from the polymer matrix to the fibers.

Figure 6 shows the scanning electron micrographs of polished cross-section perpendicular to the flow direction for injection molded wood fiber-polypropylene composites. The dark and bright regions correspond to polypropylene and wood fibers respectively. It can be seen that the poorly fibrillated, rigid and high bulk density wood flour

TABLE VIII Bulk density of wood fibers as determined from chromatographic column (inner diameter 4 mm, length 1.2 m)

Wood fibers	*Weight* (*g*)	**Bulk density* (g/cm^3)
TMP	2.4217	0.160
RNWP	6.1150	0.406
WF	12.4200	0.824

*The bulk density is obtained as the ratio of the weight of packed material divided by the internal volume of the column.

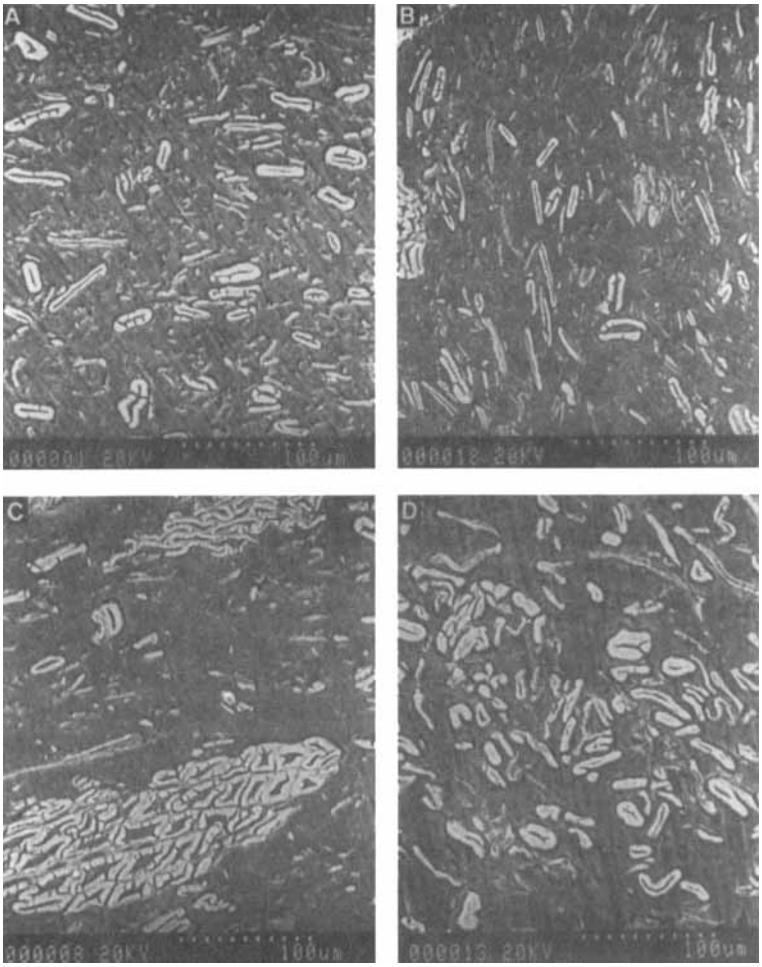

FIGURE 6 Scanning electron micrographs of polished cross-section specimens of injection molded untreated wood fiber-polypropylene composites (A) thermomechanical pulp-polypropylene, (B) recycled newsprint-polypropylene, (C) wood flour-polypropylene, (D) bleached Kraft cellulose-polypropylene composites.

disperses poorly in the polypropylene matrix, and tends to form agglomerates. This behaviour tends to limit the uniform transfer of load from the matrix to fibers. In contrast, the fibrous, fluffy, and low bulk density thermomechanical pulp disperses more uniformly. The uniform dispersion of thermomechanical pulp in polypropylene matrix promotes more efficient stress transfer with resultant increase in composite strengths.

Therefore, the higher values in strength properties of thermomechanical pulp-polypropylene composites compared to those observed for wood flour-polypropylene composites is probably due to the fluffy, curled, twisted and fibrous nature of themomechanical pulp, and its low bulk density.

The significant difference observed in strength properties between thermomechanical-polypropylene and bleached Kraft cellulose-polypropylene composites may be partly attributed to the difference in surface chemistry as demonstrated by XPS and FT-IR analysis. Bleached Kraft cellulose with a cellulose-like surface is less compatible with polypropylene, does not readily disperse in polypropylene (Fig. 6).

The tests of significance in Tables VI – VII confirm that bleached Kraft cellulose-polypropylene and wood flour-polypropylene composites differ in strength. The higher strength values of bleached Kraft cellulose-polypropylene composites as compared to those of wood flour-polypropylene composites is attributed to the lower aspect ratio of the wood flour particles as well as incomplete dispersion (Fig. 6). The poor dispersion of wood flour is most likely due to its physical or morphological characteristics (less fibrous, rigid, and fiber bundles). Although, the wood fiber surface chemistry may play a role in determining its compatibility to polypropylene matrix, may not be relevant to explain the observed differences between bleached Kraft cellulose-polypropylene and wood flour-polypropylene composites.

CONCLUSIONS

The specific objectives of this work was to analyze the surface chemistry of different wood fibers and evaluate its relative importance with respect to the mechanical properties of their composites, and to ascertain other factors of wood fiber that may affect the mechanical properties. In summarizing the results, the following conclusions may be drawn:

(1) The XPS results indicate that thermomechanical pulp, recycled newsprint, and wood flour are similar in terms of the surface chemistry (elemental composition and oxygen-carbon ratio), and

their surfaces are comparable to that of lignin. The similarities in surface chemistries of these wood fibers are also confirmed by the FT-IR spectra. The XPS and FT-IR results demonstrate that bleached Kraft cellulose surface chemistry differs from that of thermomechanical pulp, recycled newsprint, and wood flour.

(2) The addition of wood fiber in polypropylene has a significant effect on the tensile and flexural properties of polypropylene. However, the effects of different wood fiber addition in polypropylene have different significance according to the mechanical properties.

(3) The comparison between surface analysis of wood fibers and mechanical properties of their composites indicates that the wood fiber surface chemistry has no direct influence on the mechanical properties of wood fiber-polypropylene composites.

(4) The observed differences between different composites are likely due to the differences in wood fiber morphological and physical properties than in wood fiber surface chemistries.

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References

[1] Czarnecki, L. and White, J. L. (1980). *J. Appl. Polym. Sci.*, **25**, 1217.
[2] Dalvag, H., Klason, C. and Stromvall, H. E. (1985). *Int. J. Polym. Mater.*, **11**, 9.
[3] Michell, A. J. (1986). *Appita*, **39** (3), 223.
[4] Sanschagrin, B. S., Sean, T. and Kokta, B. V. (1988). *J. Thermoplast. Compos. Mater.*, **1**, 184.
[5] River, B. H., Gillespie, R. H. and Vick, C. B. (1991). Wood as an Adherend. In *Treatise on Adhesion and Adhesives Series* (Marcel Dekker Inc., New York), 1–229.
[6] Lightsey, G. R., Mann, L. and Short, P. H. (1978). *Plast. Rubber Mater. Appl.*, 69.
[7] Lightsey, G. R., Short, P. H., Kalasinsky, K. S. and Mann, L. (1979). *J. Mississippi Academ. Sci.*, **24**, 76.
[8] Han, G. and Shiraishi, N. (1990). *Mokuzai Gakkaishi.*, **36** (11), 976.
[9] Andrade, J. D. (1985). X-ray Photoelectron Spectroscopy (XPS). In *Surface and Interfacial Aspects of Biomedical Polymers* (Plenum Press, New York), J. D. Andrade (ed.), **I**, 105–163.
[10] Briggs, D. and Seah, M. P. (1985). *Practical Surface Analysis* (John Wiley and Sons, Chichester, England), D. Briggs and M. P. Seah (eds.), **I**, 2nd ed., 7–17.

[11] Berreshein, K. M., Mattern-Klossom, M. and Wilmers, M. (1991). *J. Anal. Chem.*, **341**, 121.
[12] Hon, D. N. -S. (1984). *J. Appl. Polym. Sci.*, **29**, 2777.
[13] Ahmed, A., Adnot, A. and Kaliaguine, S. (1988). *J. Appl. Polym. Sci.*, **35**, 1909.
[14] Siggel, M. R. F. and Thomas, T. D. (1989). *J. Elect. Spectrosc.*, **48**, 101.
[15] Ahmed, A., Adnot, A. and Kaliaguine, S. (1987). *J. Appl. Polym. Sci.*, **34**, 359.
[16] Dorris, G. M. and Gray, D. G. (1978). *Cell. Chem. Technol.*, **12**, 9.
[17] Mjoberg, P. J. (1981). *Cell. Chem. Technol.*, **15**, 481.
[18] Clark, D. T., Cromarty, B. J. and Dilks, A. (1978). *J. Polym. Sci., Polym. Chem.* Ed., **16**, 3173.
[19] Kamdem, P. D., Riedl, B., Adnot, A. and Kaliaguine, S. (1991). *J. Appl. Polym. Sci.*, **43**, 1901.
[20] Dorris, G. M. and Gray, D. G. (1978). *Cell. Chem. Technol.*, **12**, 721.
[21] Lopez, G. P., Castner, D. G. and Ratner, B. D. (1991). *Surf. Interface Anal.*, **17**, 267.
[22] Mubarak, A. K., Idriss Ali, K. M. and Basu, S. C. (1993). *J. Appl. Polym. Sci.*, **49**, 1547.
[23] Kolboe, S. and Ellefsen, O. (1962). *Tappi.*, **45** (2), 163.
[24] Bellamy, L. J. (1958). *The Infrared Spectra of Complex Molecules* (Methuen, London), 2nd ed.
[25] Stoil, K. D. and Koenig, J. L. (1979). *Appl. Spectrosc.*, **33** (6), 555.
[26] Lebas, J. M., Carrigou-Lagrange, C. and Josien, M. L. (1959). *Spectrochim. Acta.*, **15**, 225.
[27] Wiberley, S. E., Bunce, S. C. and Bauer, W. H. (1960). *Anal. Chem.*, **32** (2), 217.
[28] Pinchas, S. (1957). *Anal. Chem.*, **29**, 334.
[29] Rao, C. N. R., Goldman, G. K. and Lurie, C. (1959). *J. Phys. Chem.*, **63**, 1311.
[30] Hartwell, E. J., Richards, R. E. and Thompson, H. W. (1948). *J. Chem. Soc., London*, 1436.
[31] Liang, C. Y., Basset, K. H., Mcginnes, E. A. and Marchessault, R. H. (1962). *Tappi.*, **43** (12), 1017.
[32] Szymanski, H. A. and Alpert, N. L. (1964). *IR Theory and Practice of Infrared Spectroscopy*, (Plenum Press, New York).
[33] Tsuboi, M. (1957). *J. Polym. Sci.*, **25**, 159.
[34] Snyder, R. G. and Zerbi, G. (1967). *Spectrochim. Acta.*, **A 23**, 391.
[35] Barry, A. O., Kamdem, P. D. and Riedl, B. (1989). *J. Wood Chem. Technol.*, **9** (3), 341.
[36] Katritzky, A. R. and Coats, N. A. (1959). *J. Chem. Soc., London*, 2062.
[37] Sax, K. J., Saari, W. S., Mahoney, C. L. and Gordon, J. M. (1960). *J. Org. Chem.*, **25**, 1590.
[38] Kuhn, L. P. (1950). *Anal. Chem.*, **22** (2), 276.
[39] Liang, C. Y. and Marchessault, N. G. (1959). *J. Polym. Sci.*, **39**, 269.
[40] Klason, C., Kubat, J. and Stromvall, H-E. (1984). *Int. J. Polym. Mater.*, **10**, 159.
[41] Han, G., Ichinose, H., Takase, S. and Shiraishi, N. (1989). *Mokuzai Gakkaishi.*, **35** (12), 1100.
[42] Riley, A. W., Paynter, C. D., Mcgenity, P. M. and Adams, J. M. (1990). *Plast. Rubber Proc. Appl.*, **14** (2), 85.