Surface modification and adhesion mechanisms in woodfiber-polypropylene composites

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The interfacial adhesion between wood fiber and thermoplastic matrix polymer plays an important role in determining the performance of wood-polymer composites. The objectives of this research were to elucidate the interaction between the anhydride groups of maleated polypropylene (MAPP) and hydroxyl groups of wood fiber, and to clarify the mechanisms responsible for the interfacial adhesion between wood fiber and polypropylene matrix. The modification techniques used were bulk treatment in a thermokinetic reactive processor and solution coating in xylene. FT-IR was used to identify the nature of bonds between wood fiber and MAPP. IGC and wood veneer pull-out test was used to estimate the interfacial adhesion. Mechanical properties of injection molded woodfiber-polypropylene composites were also determined and compared with the results of esterification reaction and interfacial adhesion tests. Confocal Microscopy was employed to observe the morphology at the wood fiber-polypropylene interface, and the dispersion and orientation of wood fiber in the polypropylene matrix, respectively. The effectiveness of MAPP to improve the mechanical properties (particularly the tensile strength) of the composites was attributed to the compatibilization effect which is accomplished by reducing the total wood fiber surface free energy, improving the polymer matrix impregnation, improving fiber dispersion, improving fiber orientation, and enhancing the interfacial adhesion through mechanical interlocking. There was no conclusive evidence of the effects of ester links on the mechanical properties of the composites. © 1999 Kluwer Academic Publishers

1. Introduction

Much interest has been shown over the last few years in the development of wood fiber reinforced polymers due to low cost, renewability, biodegradability, low specific gravity, abundancy and high specific strength and stiffness of wood fiber [1–4]. The problem, however, is that the compounding of wood fiber with a polymer matrix (such as polypropylene) often leads to poor mechanical properties of the composites (particularly tensile, impact strengths and elongation at break). The poor mechanical properties of wood fiber reinforced polypropylene composites has been attributed to: (1) poor compatibility between the polar hydrophilic wood fiber and the non-polar hydrophobic polypropylene, with weak interfacial adhesion between wood fiber and polypropylene matrix [5] and (2) poor dispersion of wood fiber in the polypropylene matrix due to strong fiber-fiber interactions resulting from hydrogen bonding [6]. Several physical and chemical means have been used to overcome these problems [5, 7]. Maleated polypropylene (MAPP) 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 [6, 8]. The effectiveness of MAPP has been attributed to its ability to wet and disperse the wood fiber efficiently. More specifically, two types of mechanisms have been postulated for this effect. The first is the formation of ester bonds between the hydroxyl groups of wood fiber and the anhydride carbonyl groups of MAPP [9, 10]. The second suggests the formation of an adhesive bridge between treated wood fiber and polypropylene matrix, thereby increasing the interfacial adhesion between wood fiber and polypropylene matrix [10].

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Although the mechanical properties of the wood fiber-polypropylene composites have been extensively studied, little study has been done to understand the esterification mechanism of MAPP with wood fiber and how it is related to the mechanical properties of the woodfiber-polypropylene composites. In addition, the adhesion mechanism between wood fiber and polypropylene and how it is related to the mechanical properties of the composites is not well understood. Therefore, the main objective of this study was to gain an in-depth understanding of the mechanisms governing the interfacial adhesion between wood fiber and polypropylene matrix. The specific objectives were: (1) to investigate the esterification reaction between the anhydride groups of MAPP and the hydroxyl groups of wood fiber, and evaluate its potential role in the mechanical properties of composites, and (2) to estimate the interfacial adhesion between wood fiber and polypropylene matrix as well as to identify the fundamental mechanisms responsible for the interfacial adhesion.

Diffuse Reflectance Fourier Transform Infrared Spectroscopy (FT-IR) was used to provide detailed chemical information on untreated and treated wood fiber, and to elucidate the presence of ester bonds between wood fiber and MAPP. Inverse Gas Chromatography (IGC) and pull-out test were used to estimate the interfacial adhesion between wood fiber and polypropylene matrix. Confocal Microscopy was used to examine dispersion and orientation of wood fiber in the polypropylene matrix. Mechanical properties of injection molded composites were also determined.

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

Bleached Kraft pulp (BKP) and unbleached thermomechanical pulp (TMP) were used. These pulps were obtained from Abitibi-Price Inc. (Ontario, Canada). The pulps were defiberized in a Wiley Mill (Thomas-Wiley Laboratory Mill Model 4) into small uniform fiber, and sieved to 250 μm. TMP is rich in lignin whereas BKP is nearly pure cellulose.

Balsam poplar (Populus balsamifera L.) and red oak (Quercus rubra L.) wood veneers of 76.2 × 25.4 × 6 mm size with a moisture content of about 8% were used for the pull-out tests.

Two different types of MAPP were used as polymeric reagents: Epolene E-43 and Epolene G-3002 (both manufactured by Eastman Chemical Products Inc.). These two maleated polyolefins possess different acid numbers, and molecular weights. Table I summarizes some of their properties. Other chemicals used in this study were: maleic anhydride, sodium hypophosphite hydrate, and xylene, all purchased from Aldrich Chemical Company, Inc. The physical properties of maleic

TABLE I Typical properties of two MAPP and maleic anhydride (Eastman Chemical Company, Publication AP-40, 1995, and Merck Index, 1968)

Properties	Epolene E-43	Epolene G-3002	Maleic anhydride
^{a}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	—

^{a}Acid number is the number of milligrams of KOH to neutralize one gram of Epolene sample.

anhydride are also summarized in Table I. Sodium hypophosphite hydrate was used as an esterification catalyst in xylene.

2.2. Surface modification of wood fiber in the thermokinetic mixer
Prior to mixing wood fiber with polypropylene, wood fibers (TMP and BKP) were mechanically treated with MAPP in a high intensity thermokinetic mixer (Werner and Pfleiderer Gelimat Model # 456441G1). TMP (750 g) was compounded with 1 to 3% of surface modifying agent (relative to weight of wood fibers) at 180 °C for 10 min. Only one level of treatment was used for BKP (3% of coupling agent relative to the weight of BKP). The mixing was performed at different speeds to reach the discharge temperature of 180 °C in 10 min.

2.3. Surface modification of wood fiber in a solvent
The modification of wood fiber 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 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 MAPP (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 two hours at 130–140 °C. After the reaction, the mixture was filtered to isolate the reacted wood fiber. The treated fiber was soxhlet extracted with xylene for 24 h to remove the unreacted anhydride, and then oven-dried at 70 °C for 24 h. This treated fiber was used for FT-IR analysis.

2.4. Surface treatment of wood veneer
Different wood veneer surfaces were investigated, sawn wood veneer, roughened wood veneer, and MAPP treated wood veneer. The roughening of the wood veneer surface was done by combing with a wire brush. This approach was used to evaluate the role of the surface roughness on the interfacial shear strength. It is well established that the surface roughness of materials may affect the shear joint strength through mechanical interlocking. The treatment of wood veneer with MAPP

was done by applying first the melted epolene directly on the wood veneer surface. The coated wood veneer was then placed in an oven, set at 185 °C for 5 min, which melted the MAPP. Excess MAPP was removed by using a tissue to ensure a very fine layer of epolene on the wood veneer surface.

2.5. Diffuse Reflectance Fourier Transform Infrared Spectroscopy

FT-IR spectra of wood fiber before and after treatment 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 2000–1500 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.

2.6. Inverse gas chromatography
2.6.1. Data treatment

IGC was used to estimate the wood fiber-polypropylene interfacial adhesion from the work of adhesion between wood fiber and polypropylene. According to Fowkes and Maruchi [11], the work of adhesion, W_{SL} arises from two types of forces, the physical, Lifshitz-van der Waals forces (W_{SL}^d), and polar forces arising from hydrogen, ionic, and covalent bonds (W_{SL}^p). The work of adhesion can thus be written:

$$W_{SL} = W_{SL}^d + W_{SL}^p \tag{1}$$

In terms of surface free energy, the above work of adhesion becomes:

$$W_{SL} = 2\left(\gamma_S^d \gamma_L^d\right)^{1/2} + 2\left(\gamma_S^p \gamma_L^p\right)^{1/2} \tag{2}$$

Where γ_S^d is the London dispersive component of the surface free energy of a solid, γ_L^d is the London dispersive component of the surface free energy of a liquid, γ_S^p is the polar component of the surface free energy of a solid, and γ_L^p is the polar component of the surface free energy of a liquid.

The work of adhesion between a neutral material which is only able to interact through dispersion interactions with another material is determined according to Fowkes and co-workers by the work of adhesion due to physical interactions as expressed in Equation 3. According to this equation, the work of adhesion between a neutral material and another material would be expected to change with the London dispersive component of the surface free energy of one of the materials involved.

$$W_{SL} = W_{SL}^d = 2\left(\gamma_S^d \gamma_L^d\right)^{1/2} \tag{3}$$

The present study has been conducted to estimate the work of adhesion between wood fiber and polypropylene, a neutral component. While the London dispersive component of the surface free energy of polypropylene can be measured directly by conventional technique, the London dispersive component of the surface free energy of wood fiber was derived from the relationship between the Gibbs free energy change upon adsorption per methylene group of n-alkanes ($\Delta G_a^\circ(-CH_2-)$) and the work of adhesion [12] by the following equation:

$$\gamma_S^d = \frac{\left(\Delta G_a^\circ(-CH_2-)\right)^2}{4N^2 a(-CH_2-)^2 \gamma(-CH_2-)} \tag{4}$$

where N is the Avogadro's number (6.023×10^{23}), $a(-CH_2-)$ is the area occupied by a methylene group on the surface (0.06 nm^2), and $\gamma(-CH_2-)$ is the surface free energy of a methylene group (mN/m). The variation of $\gamma(-CH_2-)$ with temperature [13] is given by:

$$\frac{d\gamma(-CH_2-)}{dT_C} = 35.6 + 0.058(293.15 - T_C) \tag{5}$$

The Gibbs free energy of adsorption per methylene segment of n-alkanes is obtained as the slope of the variation of the Gibbs free energy of adsorption (ΔG_a°) or ($RT_C \ln V_N$) as a function of the number of carbon atoms in the n-alkane probes. R is the universal gas constant, T_C is the column temperature, and V_N is the retention volume.

2.6.2. Chromatographic measurements

TMP used for IGC analysis was treated as described in Section 2.2. Fiber was packed under vacuum with a vibrator into a copper column (inner diameter 4 mm, length 1.2 m), which end was plugged with glass wool. Prior to use, the columns were maintained overnight at 105 °C in nitrogen stream to remove moisture and other volatiles from wood fiber before each experiment.

Chromatograms were obtained with a Hewlett Packard 5890 programmable Gas Chromatography. Peak maxima method was used to determine the retention time. Each retention time was obtained from the average of 3 to 4 thermograms. Data was recorded in various column temperatures: 50, 60, 70, 80 and 90 °C, with injector and detector temperature at 200 °C. Probes (n-heptane to n-decane) were manually injected in the column through the injection port in the form of vapour at very low concentration with a 0.5 μl Hamilton syringe.

2.7. Wood veneer pull-out test

Wood veneer pull-out specimens were prepared using an aluminium dish (diameter 65 mm, length 35 mm). The procedure was as follows: (1) two pins were first inserted in the tangential sections of wood veneer to exactly 27 mm along the longitudinal direction, and 3 mm along the tangential direction. This allowed the wood veneer to be suspended in the polymer without touching the bottom of the dish, (2) polypropylene (about 58 g) was poured in the dish, (3) wood veneer was placed in the centre of the dish, which is supported by the pins rested on the dish lateral wall. To obtain an alignment of wood veneer normal to the polymer surface, a thick aluminium sheet of 67 by 67 mm with a slight slightly larger than the cross-section of wood veneer was placed through the wood veneer, then two

wood blocks of 25.4 × 25.4 × 25.4 mm were placed on each radial section of wood veneer, and slightly tightened to wood veneer with an aluminium wire to hold the two wood blocks and keep wood veneer normal to the polymer surface during melting.

The specimens thus prepared were placed in a vacuum oven, set at 200 °C for 60 min, which melted the polypropylene around the wood veneer. After 60 min, the oven was opened and the specimens were placed in another oven, set at 60 °C for 60 min, allowing the specimens to cool slowly. After these 60 min, the specimens were allowed to cool at room temperature, separated from the dish, and sanded to flatten the polymer surface normal to wood veneer. At least 10 specimens were tested for each surface condition to obtain an average interfacial shear strength between wood veneer and polypropylene.

Testing apparatus for the pull-out tests is illustrated in Fig. 1. The average interfacial shear strength, τ_A was calculated by:

$$\tau_A = \frac{F_B}{3wt + 4L_e} \quad (6)$$

where F_B is the load to debond the wood veneer from the polypropylene matrix, w is wood veneer width, t is wood veneer thickness, and L_e is the embedded wood veneer length. The embedded lengths of the wood veneers were estimated before the test and measured after being pulled out from polypropylene.

2.8. Manufacturing and property testing of the composites

After the modification of wood fiber (Section 2.2.), untreated and treated wood fibers were subsequently compounded with polypropylene in a high intensity thermokinetic mixer operating at 3300 rpm and then discharged at 180 °C. The proportion of wood fiber to polypropylene matrix was maintained constant at 30%. After compounding, the melted compounds were allowed to cool to room temperature and then granulated in a Brabender granulator (Model S-10-9). The resulting compounds were injection molded using an Engel ES-28 machine equipped with a standard ASTM test specimen mold (ASTM 638). The injection molding conditions were: injection pressure-4.83 MPa, clamp pressure-11.72 MPa, injection temperature-204 °C, injection time-9.5 s, cooling time-25 s, and mold opening time-2 s.

The tensile and flexural tests were conducted according to ASTM D-638, and ASTM D-790, respectively. These tests were performed on a standard computerized 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 provided (Testwork program, Ver. 2.10, Sintech Inc. U.S.A). Six specimens were tested to obtain an average value.

2.9. Confocal imaging system

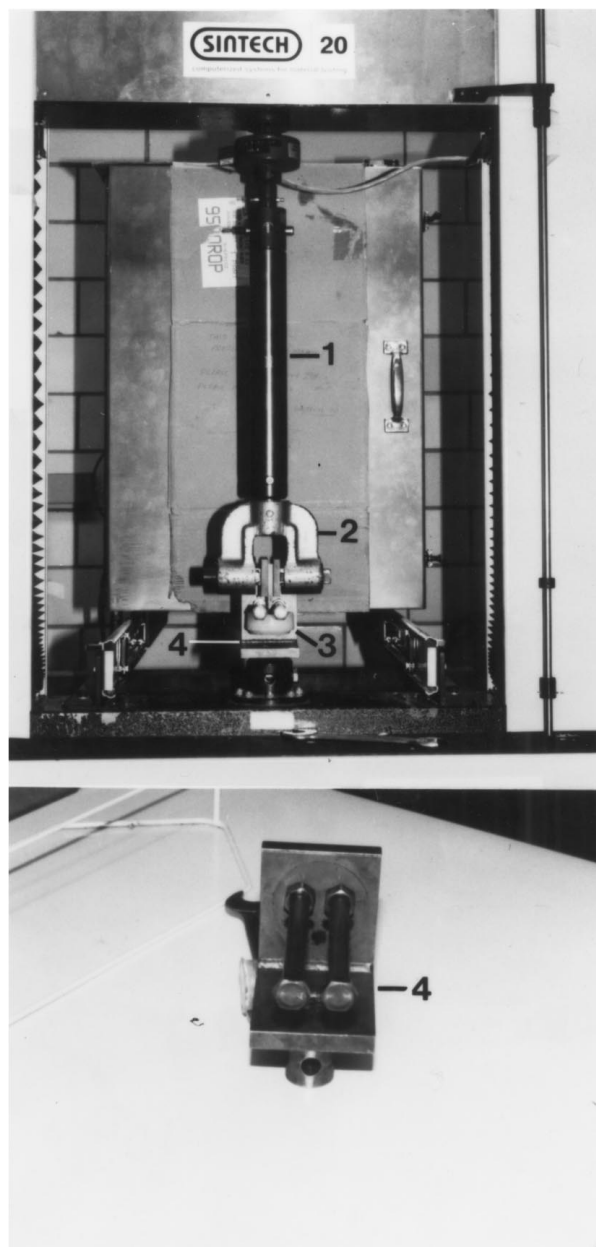The MRC-600 confocal microscope was used to assess the dispersion and orientation of wood fiber in

Figure 1 Optical photograph of wood veneer pull-out apparatus (1) loading extension, (2) wood veneer clamp, (3) wood veneer pull-out specimen, and (4) specimen holder.

polypropylene matrix. The confocal microscope builds an image by scanning a low-power laser beam over the sample surface and taking periodic intensity reading of the reflected light. The image formation depends on the reflecting behaviour of the dispersed and continuous phases. The analysis was performed on a 20 μm cross-section perpendicular and parallel to the flow direction for injection molded woodfiber-polypropylene composites. The samples were stained with 1% aniline safranine to increase the contrast between wood fiber and polypropylene.

3. Results and discussion
3.1. FT-IR spectra of untreated wood fibers
Figs 2A and 3A show the absorption spectra of untreated TMP and BKP, respectively, in the 2000 to 1500 cm^{-1} region. The differences between TMP and
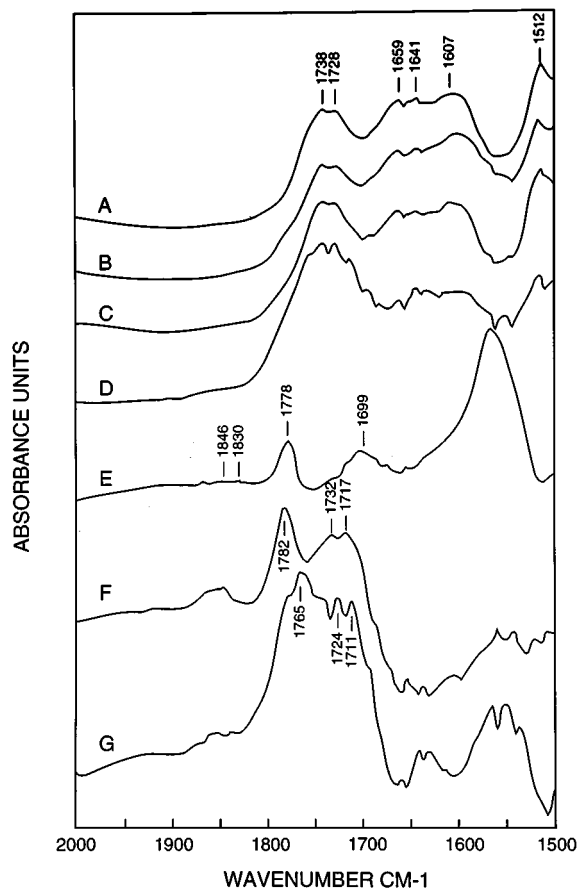
Figure 2 FT-IR spectra of untreated and treated thermomechanical pulp (TMP). (A) Untreated TMP, (B) Epolene E-43 treated TMP, (C) Epolene G-3002 treated TMP, (D) maleic anhydride treated TMP, (E) digital subtraction ((B) − (A)), (F) digital subtraction ((C) − (A)), and (G) digital subtraction ((D) − (A)).
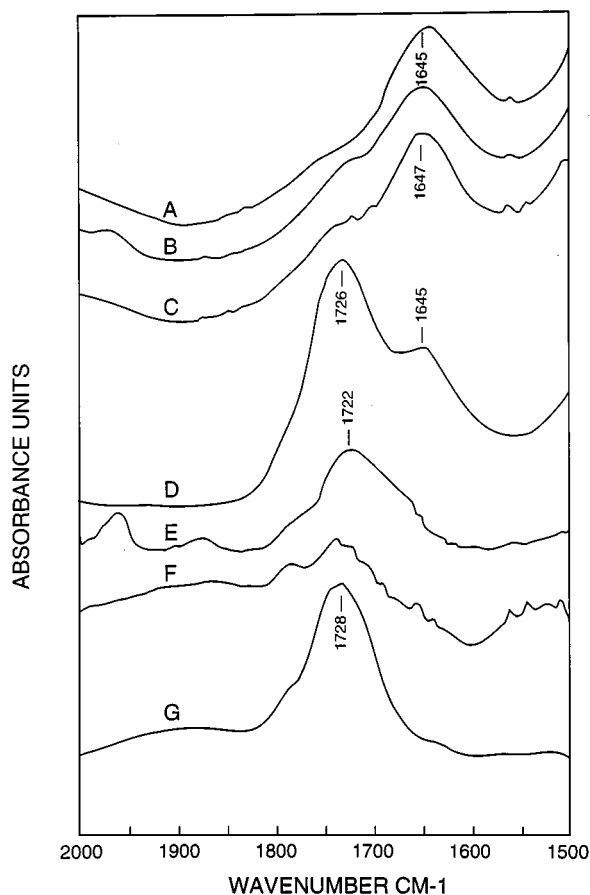

Figure 3 FT-IR spectra of untreated and treated bleached Kraft cellulose (BKP). (A) Untreated BKP, (B) Epolene E-43 treated BKP, (C) Epolene G-3002 treated BKP, (D) maleic anhydride treated BKP, (E) digital subtraction ((B) − (A)), (F) digital subtraction ((C) − (A)), and (G) digital subtraction ((D) − (A)).

BKP can clearly be seen in the 1750–1700 cm^{-1} region of the absorption spectra. The absorption bands near 1730 cm^{-1} in the spectrum of TMP 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 extractives [14–16].

The spectrum of BKP does not show any detectable absorption bands in the 1750–1700 cm^{-1} region. The observed absorption band at 1645 cm^{-1} was attributed to C=O stretching vibrations of the alpha-keto carbonyl by Kolboe and Ellefsen [15]. Tsuboi [17] assigned the band at 1645 cm^{-1} to absorbed water. The absence of absorption bands in the 1750–1700 cm^{-1} region in the spectrum of BKP may be due to the fact that the compounds rich in carbonyl (C=O), lignin, hemicelluloses, and extractives are dissolved during the production of the pulp.

3.2. FT-IR spectra of MAPP treated wood fiber

The FT-IR spectra of MAPP (Epolene E-43 and Epolene G-3002) treated TMP are shown in Fig. 2B and C. Since untreated TMP has already some ester groups which absorb near 1730 cm^{-1}, the confirmation of ester links formation may be indicated by an increase in the intensity of the absorption bands near 1730 cm^{-1}. However, it is observed that the general feature of the FT-IR spectrum of untreated TMP (Fig. 2A) is similar to that of MAPP treated TMP. The absorption bands near 1730 cm^{-1} do not show any significant change in intensity upon treatment. These results imply that the esterification reaction between hydroxyl groups of fiber and anhydride groups of MAPP may not occur. The digital subtraction spectra (Fig. 2E and F) obtained do not indicate the presence of any distinct absorption bands near 1730 cm^{-1} which may be associated to ester links between hydroxyl groups of wood fiber and anhydride groups of MAPP. The absence of esterification between TMP and MAPP may be due to the presence of lignin on the fiber surface, and also of the long polypropylene chains attached to the short anhydride ring.

The FT-IR spectra of MAPP (Epolene E-43 and Epolene G-3002) treated BKP are shown in Fig. 3B and C. A comparison of the FT-IR spectrum of untreated BKP (Fig. 3A) and treated BKP (Fig. 3B and C) indicates the emergence of a weak shoulder on the low wavenumber side of the 1645 cm^{-1} absorption band. The appearance of this shoulder, which is confirmed by the broad absorption band at 1722 cm^{-1} in the digital subtraction (Fig. 3E and F) may suggest that the esterification reaction between hydroxyl groups of BKP and anhydride groups of MAPP may have occured.

3.3. FT-IR spectra of maleic anhydride treated wood fibers

The reaction of pure maleic anhydride with wood fiber was also studied to assess the reactivity of the anhydride rings with and without polypropylene chains. It is believed that the polypropylene substituents may reduce the reactivity of the anhydride ring through steric hindrance.

Fig. 2D shows the FT-IR spectrum of maleic anhydride treated TMP. A comparison of the FT-IR spectra of untreated TMP (2A) and treated TMP provides direct evidence that the treatment of TMP results in a change in absorption bands near 1730 cm^{-1}. The absorption bands near 1730 cm^{-1} increase following TMP treatment. The digital subtraction (2G) of untreated TMP spectrum from that of treated TMP shows the presence of a well defined absorption band at 1724 cm^{-1}. The presence of this band may be attributed to the esterification reaction between hydroxyl groups of TMP and anhydride groups of maleic anhydride. These results are in agreement with previous works reported by Matsuda [18].

The FT-IR spectrum of maleic anhydride treated BKP is presented in Fig. 3D. A comparison of the FT-IR spectra of untreated BKP (Fig. 3A) and maleic anhydride treated BKP also shows the emergence of a new, strong, sharp and well defined absorption band on the low frequency side of the 1645 cm^{-1} absorption band. The emergence of this new band may be attributed to ester links between the hydroxyl groups of BKP and anhydride groups of maleic anhydride. Similar observations were also reported by Yang [19]. The absorption bands in the 1728–1721 cm^{-1} region were ascribed to ester links formed by esterification reaction between hydroxyl groups of cellulose (cotton) and anhydride groups of maleic anhydride.

3.4. London dispersive component of the surface free energy

Table II shows the London dispersive component of the surface free energy of untreated and treated TMP. The London dispersive component of the surface free energy of polypropylene and MAPP as determined by Felix *et al*. [7] are also shown for reference. The London dispersive component of the surface free energy of TMP (untreated and treated) decreased slightly with

TABLE II London dispersive component of the surface free energy of untreated and MAPP (Epolene E-43) treated TMP by IGC

Wood fibers	γ_S^d (mJ/m^2)				
	50 °C	60 °C	70 °C	80 °C	90 °C
TMP-0	36.3	35.9	34.8	25.6	36.9
TMP-1E43	36.2	34.8	32.2	32.4	33.7
TMP-2E43	35.8	34.6	33.3	32.0	30.8
TMP-3E43	36.8	36.2	33.7	31.8	30.8
Polypropylene			31.7[a]		
Epolene E-43			31.6[a]		

TMP-0: Untreated thermomechanical pulp.
TMP-XE43: TMP treated with x% of Epolene E-43.
[a]Reference [16].

increasing temperature. However, the modification of TMP with MAPP did not result in change in the London dispersive component of the surface free energy. Since MAPP has a London dispersive component of the surface free energy comparable to that of untreated TMP, it is obvious that the modification of TMP with MAPP would not be expected to alter the London dispersive component of the surface free energy of TMP and thus the work of adhesion due to Lifshitz-van der Waals forces between TMP and polymer matrix.

3.5. Interfacial shear strength in pull-out test

Wood veneer pull-out test was performed to evaluate the interfacial adhesion of both untreated and treated wood veneer bonded with polypropylene.

Fig. 4 illustrates an example of the load-extension curve for poplar wood veneer/polypropylene system in pull-out test. This figure illustrates a well defined behaviour as often observed in single-fiber pull-out test [20]. The load increases monotonically up to a maximum value where debonding is initiated and quickly propagates along the interface. This is illustrated by the instantaneous load drop in the load-extension curve. After debonding of the wood veneer, the load increased slowly until wood veneer was completely pulled-out from the polypropylene matrix. The observed increase in load after debonding may be due to some residual forces induced at the interface by shrinkage of polypropylene on cooling from its melting point to room temperature.

The interfacial shear strength values obtained in wood veneer pull-out test are presented in Fig. 5 for different wood veneer surface conditions. For combed wood veneer (rough surface), the interfacial shear strength was higher than that for untreated wood veneer. The higher interfacial shear strength for combed wood veneer may be attributed to the greater
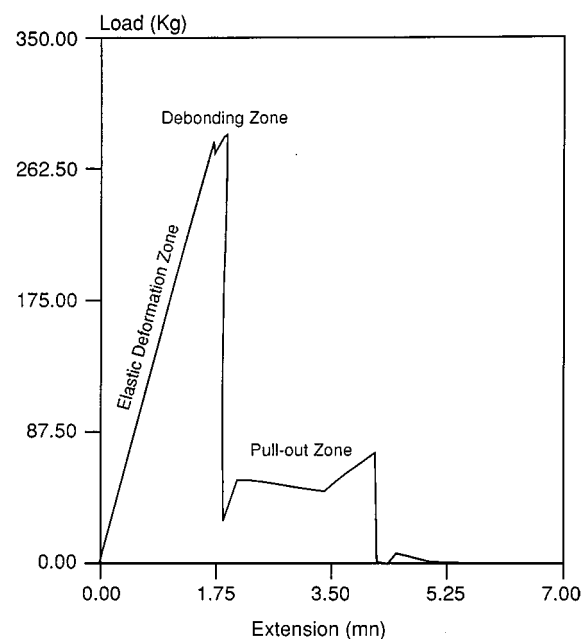

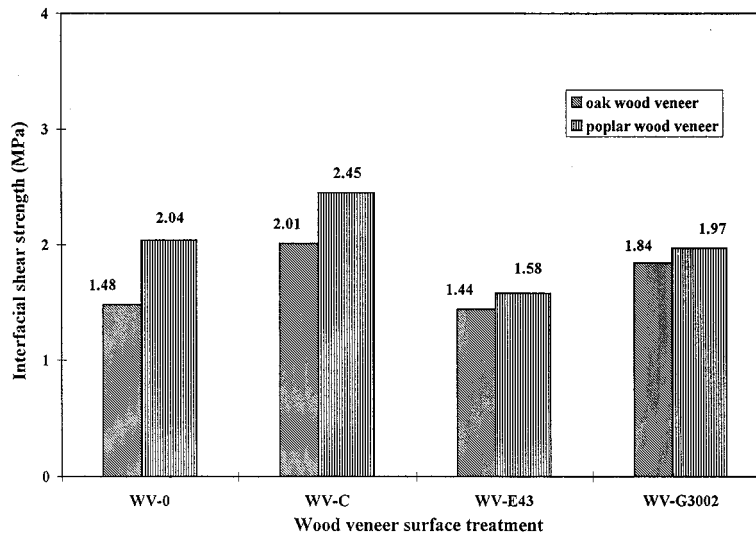*Figure 4* Load-extension curve of wood veneer pull-out specimen.

Figure 5 Interfacial shear strength between wood veneer and polypropylene in wood veneer pull-out test. WV-0: Untreated wood veneer, WV-C: Combed wood veneer, WV-E43: Epolene E-43 treated wood veneer, and WV-G3002: Epolene G-3002 treated wood veneer.

mechanical interlocking between combed wood veneer and polypropylene. The roughening of the wood veneer surface promotes more surface area, more possibility for mechanical interfacial bonds, and lock and key effect at the interface.

It is interesting to note that for both oak wood veneer and poplar wood veneer, the treatment of wood veneer with Epolene E-43 decreased the interfacial shear strength. Compared to the interfacial shear strength of untreated wood veneer, a decrease of 3% was observed when oak wood veneer was treated with Epolene E-43, while a decrease of 23% was observed for poplar wood veneer. The observed decrease in interfacial shear strength may be explained by the reduction in surface roughness of wood veneer following MAPP treatment. MAPP treatment might have covered the pores, crevices and irregularities on the wood veneer surface, and thus reduced the mechanical interlocking between wood veneer and polypropylene. For wood veneer treated with Epolene G-3002, the interfacial shear strength decreased by 3% for poplar wood veneer, and increased by 24% for oak wood veneer.

The interfacial shear strength for wood veneer treated with Epolene G-3002 was higher than that with Epolene E-43, regardless of wood species. There is an increase of 28% in interfacial shear strength when oak wood veneer was used while an increase of 25% was observed in the case of poplar wood veneer. The higher interfacial shear strength with higher molecular weight Epolene G-3002 was attributed to greater interdiffusion and interchain entanglements of grafted chains of Epolene G3002 with the polypropylene matrix at the interface [7]. The longer the parent hydrocarbon chains of MAPP, the greater the opportunity for the hydrocarbon chains to diffuse deeper into the polypropylene matrix, and thus become fully involved in interchain entanglements, thereby contributing to the mechanical contiguity of the system. The role of interdiffusion of polypropylene molecules at the interface on the interfacial shear strength of this system is not convincing. The observed differences in the interfacial shear strength be-

tween the two types of coupling agents may be due to their mechanical properties (strength or modulus).

3.6. Mechanical properties of injection molded woodfiber-polypropylene composites
3.6.1. Tensile properties
The results of the effect of MAPP treated TMP and BKP on the mechanical properties of injection molded composites are listed in Tables III and IV, respectively.

TABLE III Effect of MAPP (Epolene E-43 and Epolene G-3002) treated TMP on the mechanical properties of the composites (compound ratio 30% wood fiber-70% polypropylene)

| Properties | TMP-polypropylene composites | | |
	TMP	TMP-3E43	TMP-3G3002
Tensile strength, MPa	34.59	44.11	48.32
Tensile modulus, GPa	2.45	2.46	2.41
Elongation at break, (%)	3.68	4.67	5.38
Flexural strength, MPa	65.6	78.17	85.59
Flexural modulus, GPa	3.45	3.40	3.39

TMP: Untreated thermomechanical pulp.
TMP-3E43: TMP treated with 3% of Epolene E-43.
TMP-3G3002: TMP treated with 3% of Epolene G3002.

TABLE IV Effect of MAPP (Epolene E-43 and Epolene G-3002) treated BKP on the mechanical properties of the composites (compound ratio 30% wood fiber-70% polypropylene)

| Properties | BKP-polypropylene composites | | |
	BKP	BKP-3E43	BKP-3G3002
Tensile strength, MPa	32.51	40.86	43.24
Tensile modulus, GPa	2.19	2.44	2.33
Elongation at break, %	4.18	3.51	4.32
Flexural strength, MPa	59.45	75.21	76.45
Flexural modulus, GPa	2.77	3.10	2.85

BKP: Untreated bleached Kraft pulp.
BKP-3E43: BKP treated with 3% of Epolene E-43.
BKP-3G3002: BKP treated with 3% of Epolene G3002.

The surface treatment of both wood fibers with MAPP increased the tensile strength of the composites. As shown in Tables III and IV, at 3% of Epolene E-43, the tensile strength of TMP-polypropylene composites increased by 28%, and 27% for BKP-polypropylene composites. The greater improvement in tensile strength of the composites was observed using Epolene G-3002. At a concentration of 3% of Epolene G-3002, the tensile strength of TMP-polypropylene composites increased by 40%, and 29% for BKP-polypropylene composites. Olsen [21] suggested that the higher efficiency of MAPP using Epolene G-3002 was due to more available anhydride groups for reaction with hydroxyl groups of wood fiber, and to longer hydrocarbon chains that cocrystalize more effectively with the polypropylene matrix. The fact that there is no conclusive evidence of ester links between TMP and MAPP, there is no reason to assume that the anhydride groups on MAPP may have played a role on the composite properties. The tensile modulus remained unaffected with wood fiber treatment.

The elongation at break of the composites increased with wood fiber treatment. At 3% Epolene E-43, the elongation at break for TMP-polypropylene composites increased by 27%, and 16% decrease for BKP-polypropylene composites. At 3% Epolene G-3002, the elongation at break for TMP-polypropylene composites increased by 46%, and 3% for BKP-polypropylene composites.

3.6.2. Flexural properties

The surface treatment of wood fiber with MAPP increased the flexural strength of the composites. As in the case of tensile strength, the treatment of wood fiber with Epolene G-3002 gave the larger increase in flexural strength. For example, 3% Epolene E-43 increased the flexural strength of TMP-polypropylene composites by 19%, and 28% for BKP-polypropylene composites. An increase of 30% for TMP-polypropylene, and 29% for BKP-polypropylene composites were observed when wood fibers were treated with 3% of Epolene G-3002. The flexural modulus did not vary with wood fiber treatment.

3.6.3. Phenomena for improved strength properties

The observed increase in the strength properties of woodfiber-polypropylene composites following the treatment of wood fiber with MAPP is in agreement with previous works [6, 10]. The effectiveness of MAPP in increasing the strength of the composites may be explained by greater wettability of wood fiber by the polypropylene matrix, and improved dispersion and orientation of wood fibers in the polypropylene matrix. Fig. 6 shows the confocal micrographs of the microtomed cross-section perpendicular to flow direction for injection molded BKP-polypropylene composites. The black and white regions represent polypropylene matrix and BKP, respectively. It is apparent that the surface treatment of BKP with MAPP reduced the formation of agglomerates, and fibers are dispersed more uniformly.
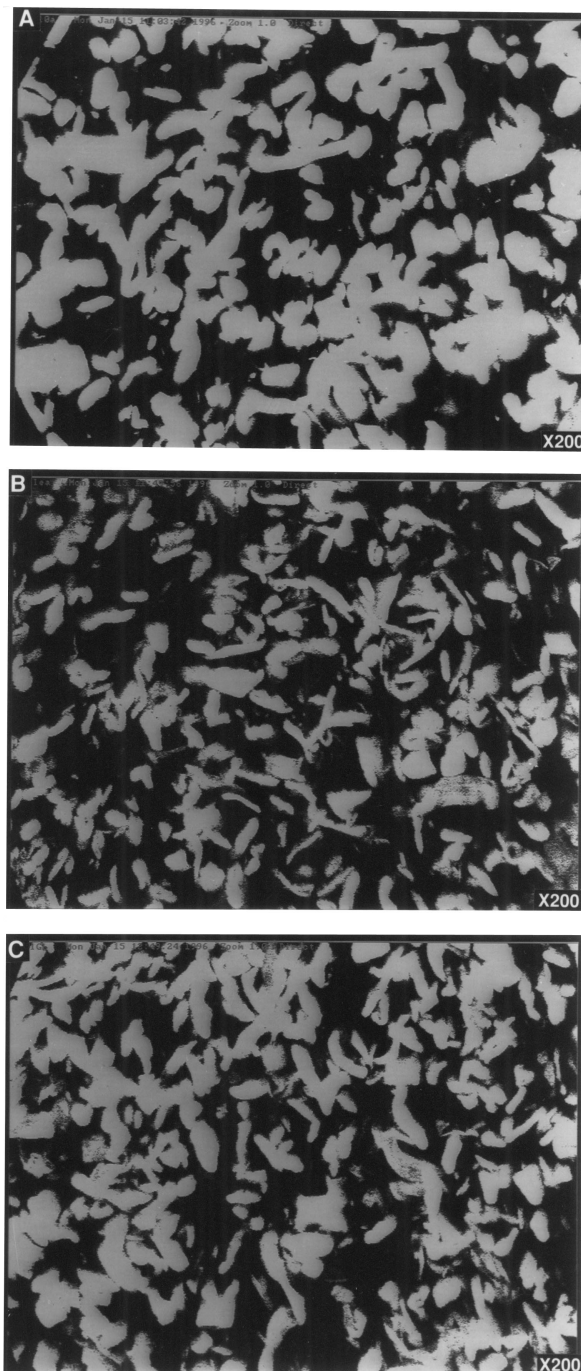

Figure 6 Confocal micrographs of microtomed cross-section perpendicular to flow direction for injection molded untreated and treated BKP-polypropylene composites (A) untreated BKP-polypropylene, (B) 3% Epolene E-43 treated BKP-polypropylene, and (C) 3% Epolene G-3002 treated BKP-polypropylene composites.

The improvement in orientation of fibers after treatment may be seen in Fig. 7 which shows the confocal micrographs of a cross-section parallel to flow direction for injection molded BKP-polypropylene composites. The different morphological structures are easily distinguishable. In the outer layers of the injection molded composites, fibers are well oriented in the flow direction for injection molding. This is due to flow orientation of the fibers in the cavity during filling of the mold. In the inner layers of the injection molded composites, different patterns are observed. As can be seen from Fig. 7A, the fibers in the inner layer of the untreated BKP-polypropylene composites are not as well oriented
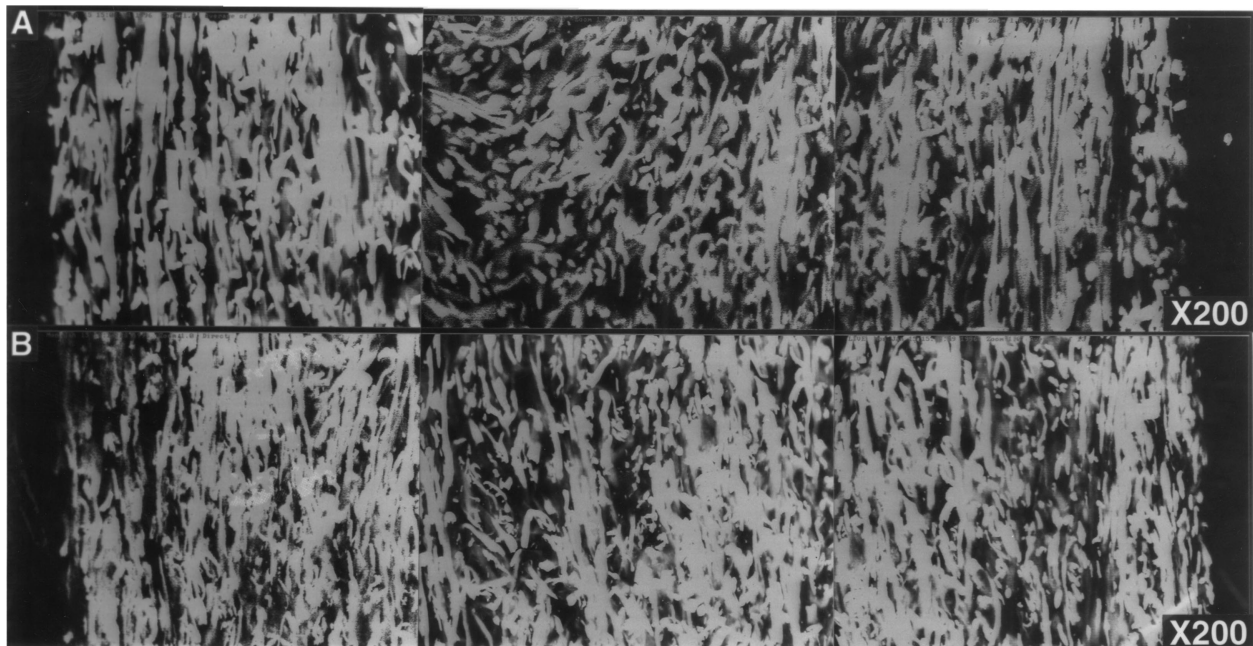
Figure 7 Confocal micrographs of microtomed cross-section parallel to flow direction for injection molded untreated and treated BKP-polypropylene composites (A) untreated BKP-polypropylene, and (B) 3% Epolene E-43 treated BKP-polypropylene composites.

as those in the outer layers. The fibers in this central part are more randomly oriented. However, the surface treatment of BKP changes the orientation of fibers in the inner layers of the composites (Fig. 7B). The fibers in the core layer of treated BKP-polypropylene composites are almost oriented in the flow direction as those in the outer layers.

3.7. Effect of ester links on tensile strength properties of the composites

Table V shows the results of the esterification reaction as obtained by the application of FT-IR and the tensile strength of woodfiber-polypropylene composites (before and after treatment with MAPP).

A comparison of the tensile strength of the composites and the esterification results suggests that there is no conclusive or direct evidence of the effect of ester links on the tensile strength of the composites. The fact that TMP which did not reveal any indication of ester-

ification reaction with MAPP showed higher strength properties than BKP which showed some evidence to chemically react with MAPP, implies that the ester links may not play a direct or significant role in determining the strength of the composites. The accompanied increase in strength of the composites with MAPP treatment may be explained by mechanisms other than the esterification mechanism.

The observed difference in strength properties between TMP-polypropylene composites and BKP-polypropylene composites may partly be attributed to the difference in surface chemistry of TMP and BKP [22]. Hydrophilic BKP with strong intermolecular hydrogen bonding is more likely to poorly disperse in the polypropylene than the more hydrophobic TMP.

3.8. Comparison between the London dispersive component of the surface free energy of wood fiber and tensile strength of the composites

Table VI compares the tensile strength of woodfiber-polypropylene composites and interfacial adhesion

TABLE V Dependence of the tensile strength of wood fiber-polypropylene composites on ester links (compound ratio 30% wood fiber-70% polypropylene)

Esterification reaction				Tensile strength (MPA)
Wood fibers	Modifying agents	Evidence of ester links	Composites	
TMP	—	—	TMP-PP	34.59
	Epolene E-43	No	TMP-3E43-PP	44.11
	Epolene G-3002	No	TMP-3G3002-PP	48.32
BKP	—	—	BKP-PP	32.51
	Epolene E-43	Yes	BKP-3E43-PP	40.86
	Epolene G-3002	Yes	BKP-3G3002-PP	43.24

TMP-PP: Thermomechanical pulp-polypropylene composites.
TMP-*x*E43-PP: *x*% Epolene E-43 treated TMP-PP composites.
TMP-*x*G3002-PP: *x*% Epolene G-3002 treated TMP-PP composites.
BKP-*x*MAPP-PP: *x*% MAPP treated BKP-PP composites.

TABLE VI Tensile strength of wood fiber-polypropylene composites dependence to London dispersive component of the surface free energy of wood fiber.

Wood fibers	$^a\gamma_S^d$ (mJ/m^2)	Composites	Tensile strength (MPa)
TMP-0	36.3	TMP-PP	34.59
TMP-1E43	36.7	TMP-1E43-PP	41.23
TMP-2E43	35.8	TMP-2E43-PP	44.40
TMP-3E43	36.8	TMP-3E43-PP	44.11

TMP-0: Untreated thermomechanical pulp.
TMP-XE43: *x*% Epolene E-43 treated TMP.
[a] At column temperature of 50 °C.

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between wood fiber and polypropylene as expressed by the London dispersive component of the surface free energy of wood fiber.

As can be seen, while the tensile strength of the composites increased with wood fiber treatment, the London dispersive component of the surface free energy of wood fiber remained unaffected with wood fiber modification. The fact that the modification of wood fiber with MAPP did not change the London dispersive component of the surface free energy of wood fiber, it can be assumed that the thermodynamic work of adhesion due to physical forces may not be relevant in explaining the improvement in the tensile strength of the composites. Thus, the effectiveness of MAPP in enhancing the tensile strength of the composites may be attributed to mechanisms other than the thermodynamic work of adhesion. However, it is worthwhile to note that, although the Lifshitz-van der Waals forces are not of direct significance in determining the strength properties of the composites, they are required forces for achieving a meaningful interfacial bond strength between wood fiber and polypropylene matrix.

3.9. Comparison between interfacial shear strength and tensile strength of the composites

Table VII shows the wood veneer-polypropylene interfacial shear strength as obtained from wood veneer pull-out test, and tensile strength of TMP-polypropylene composites.

A comparison between wood veneer-polypropylene interfacial shear strength and tensile strength of wood fiber-polypropylene composites demonstrates a very interesting point. As can be seen, while the wood veneer-polypropylene interfacial shear strength decreased with MAPP treatment, the tensile strength of wood fiber-polypropylene composites increased with MAPP treatment. This contrast which may be due to the difference in the configuration of the two systems, implies the role of wood fiber dispersion and orientation in polypropylene matrix, and also of the mechanical interlocking in woodfiber-polypropylene system. The fact that wood fibers are curved, twisted, and porous, there is reason to believe that the observed increase in tensile strength of woodfiber-polypropylene composites is not only due to the dispersion and orientation of wood fiber in polypropylene matrix, but also due to the accompa-

nied increase in interlocking between wood fiber and the polypropylene matrix.

Further, the interfacial shear strength of wood veneer-polypropylene, and tensile strength of woodfiber-polypropylene composites are influenced by the MAPP types. The higher the molecular weight of Epolene G-3002, the higher the interfacial shear strength of wood veneer-polypropylene, and tensile strength of wood fiber-polypropylene composites. Although the efficiency of the higher molecular weight MAPP was explained by greater interdiffusion and interchain entanglements of polypropylene molecules at the interface, mechanical properties of this MAPP may explain its effectiveness in providing better strength properties.

4. Conclusions
In summarising the results, the following conclusions were drawn:

1. FT-IR confirmed the presence of ester links between MAPP and BKP. No ester links were detected between MAPP and TMP.

2. Ester links are not the key determinants of mechanical properties in woodfiber-polypropylene composites.

3. MAPP which may attach to wood fibers either by chemical or physical means, improves the strength properties of the composites through compatibilization effect. The compatibilization effect is accomplished by reducing the total wood fiber surface free energy, lowering the attractive forces among fibers, improving the polymer matrix impregnation, improving fiber dispersion, improving fiber orientation, and enhancing the interfacial adhesion through mechanical interlocking. The thermodynamic work of adhesion due Lifshitz-van der waals forces does not play a direct role in the strength properties of woodfiber-polypropylene composites.

TABLE VII Tensile strength of wood fiber-polypropylene composites dependence to wood veneer-polypropylene interfacial shear strength

Poplar wood veneer surface treatment	τ_A (MPa)	Composites	Tensile strength (MPa)
WV-0	2.04	TMP-PP	34.59
WV-C	2.45		
WV-E43	1.58	TMP-3E43-PP	44.11
WV-G3002	1.97	TMP-3G3002-PP	48.32

WV-0: Untreated wood veneer.
WV-C: Combed wood veneer.
WV-E43: Epolene E-43 treated wood veneer.
WV-G3002: Epolene G-3002 treated wood veneer.

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