

Mechanical Properties of Wood Flake–Polyethylene Composites. II. Interface Modification

P. W. BALASURIYA,¹ L. YE,¹ Y.-W. MAI,¹ J. WU²

¹ Centre for Advanced Materials Technology, School of Aerospace, Mechanical and Mechatronic Engineering, University of Sydney, NSW 2006, Australia

² Department of Mechanical Engineering, Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong

Received 16 November 2000; accepted 3 April 2001

ABSTRACT: This article discusses the methods of interface modification of composites based on raw wood flakes and high-density polyethylene (HDPE) and the effects of these modifications on composite properties. An HDPE matrix was modified by a reaction with maleic anhydride (MA) in a twin-screw extruder and then compounded with wood flakes to produce wood–polyethylene composites. Wood flakes were modified by a reaction with a silane coupling agent in an aqueous medium before being compounded with HDPE to produce silane-modified WPCs. Differential scanning calorimetry and Fourier transform infrared spectroscopy data provide evidence for the existence of a polyethylene (PE)–silane-grafted wood structure, which acts as a compatibilizer for wood flakes and PE. The results of MA-modified composites indicate that some maleated HDPE is reacting with wood through esterification to form a compatibilizer for wood flakes and HDPE. Significant improvements in tensile strength, ductility, and Izod impact strength were obtained. Scanning electron micrographs provide evidence for strong interactions between the wood flakes and the matrix agent. The results indicate that 1–2 wt % MA modification on HDPE and 1–3 wt % silane treatment on wood flakes provide WPCs with the optimum properties. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2505–2521, 2002

Key words: wood–polyethylene composites; interface modification; silane coupling agent; compatibilizer; maleated polyethylene

INTRODUCTION

During the last decade, wood fibers and wood flour were successfully used as reinforcing fillers in plastics to produce wood–plastic composites (WPCs) with acceptable mechanical properties.¹ Recent studies have revealed that raw wood flakes can be used instead of wood fibers or flour to produce WPCs. Unlike wood fibers, wood flakes

consist of many wood fibers, which are present as fiber bundles, and so the wood flake wetting and flake distribution need to be optimized to obtain WPCs with good mechanical properties.²

As discussed in a previous article,² one of the advantages of using wood flakes in place of wood fiber is possible high-density polyethylene (HDPE) penetration into wood fiber lumens, which provides additional reinforcement via mechanical interlocking. In addition, because the raw wood flakes do not require additional fiber separation or pretreatment, they are claimed to be industrially attractive. Major limitations of us-

Correspondence to: L. Ye (ye@mech.eng.usyd.edu.au).

Journal of Applied Polymer Science, Vol. 83, 2505–2521 (2002)
© 2002 John Wiley & Sons, Inc.
DOI 10.1002/app.10189

ing wood flakes as reinforcing fillers include the difficulties of mixing wood flakes and plastics³ and poor interfacial adhesion between polar, hydrophilic wood fibers and nonpolar, hydrophobic plastics.⁴ The twin-screw extrusion compounding technique, which uses high shear mixing and fast conveying sections, has been successfully employed to optimize the distribution and wetting of wood flakes.² The optimization of interfacial adhesion between cellulose-based fillers and thermoplastics has been the focus of a large amount of research conducted during the past 2 decades. Several techniques, ranging from grafting short-chain molecules onto fiber surfaces to using coupling/adhesion-promoting agents, have been reported.^{3–6} Maleic anhydride (MA)-grafted polypropylene (PP) and MA-grafted styrene–ethylene–butylene–styrene (MA-*g*-SEBS) triblock copolymers have shown a strong compatibilizing effect between wood flour and PP or polyethylene (PE).^{5,6} In addition, some of the research work has shown that the silane coupling agent is effective in improving the interfacial adhesion between wood and plastics.^{7,8} However, there are very few articles that describe the compatibility of wood flakes with HDPE.

In this work, both the matrix agent and wood flake interface were modified, and the effect of the modification on the mechanical properties was studied. To minimize the effect of polymer penetration through wood lumens, we selected HDPE with a very low melt flow index (MFI). The mechanical properties of the low-MFI HDPE composites were compared with those of WPCs based on high-MFI HDPE. Two composite systems, one based on MA-modified PE (MAPE)–pure wood flakes and the other based on virgin HDPE–silane-treated wood flakes, were evaluated.

EXPERIMENTAL

Materials

Two HDPE grades, labeled *medium melt flow index* (MMFI) and *low melt flow index* (LMFI), from Kemcor Australia Pty, Ltd., were used for the study. The MFIs at 190°C/2.16 kg for these two HDPEs were 7 and 0.15 g/10 min, respectively. The HDPE densities were 0.957 and 0.949 g/cm³, respectively. Commercially prepared radiata pine flakes with average length distributions of 1–4 mm and flake breadths of 0.1–2 mm were obtained from CSR, Ltd.² MA, dicumyl peroxide

(DCP), and other analytical-grade chemical reagents such as methanol were obtained from Aldrich Chemical Co. (Australia). The Z6032 silane used to modify wood flakes was obtained from Dow Corning (United States) and contained 40 wt % *N*-(4-vinylbenzyl)-*N'*-(3-trimethoxysilylpropyl-ethyl)enediamine, hydrochloride (CVBS) in methanol.

Modification of HDPE with MA

The modification of HDPE with MA was carried out according to Mohanakrishnan et al.⁹ in the presence of DCP with a 30-mm corotating intermeshing twin-screw extruder (ZSK 30 Werner and Pfleiderer) with a length of 900 mm (i.e., the length was equal to 30 times the diameter of the screw and was written as 30D). The screw configuration was designed with a melting zone of 11D and a mixing zone of 9D. The rest of the configuration consisted of conveying elements to facilitate fast conveying of the reacted material. MA and DCP, first preblended at a weight ratio of 1 to 0.35, were mixed with some HDPE powder to make a mix containing 10 wt % MA, which was fed into the extruder hopper with a volumetric feeder. HDPE pellets were fed into the same hopper with a gravimetric feeder to produce five different MAPE containing 0.5, 1, 2, 3, and 5% MA with respect to the weight of HDPE. The temperature profile of all the sections in the extruder was 180°C, and the screw speed was 200 rpm. The extrudate was passed through a water bath and pelletized to obtain MAPE pellets. These pellets were dried at 70°C for 15 h before being compounded with wood flakes.

Pretreatment of Wood Flakes with Silane Coupling Agents

Wood flakes were pretreated with aqueous solutions of CVBS coupling agents in the presence of DCP. DCP was dissolved in methanol, and the rate of DCP addition was 0.35 g/g of CVBS.^{10,11} To prepare an aqueous solution of the active silane CVBS, we mixed and stirred 100 parts of Z-6032, 5 parts of glacial acetic acid, and 28 parts of water for an hour until Z-6032 became completely soluble. The solution was considered equivalent to 30 wt % CVBS and was further diluted with water to obtain the silane solutions of a certain amount of CVBS. The following procedure was used for pretreatment: 100 g of wood flakes were mixed with 200 mL of the aqueous CVBS solution with con-

tinuous stirring to obtain 0.5, 1, 2, 3, and 4% treatments with respect to the weight of the wood flakes. The resultant slurry was mixed with a high shear mixer at 55°C for 45 min. These treated flakes were initially dried at 80°C *in vacuo* for 24 h, dried at 100°C for another 2 h, and used for twin-screw compounding as described later.

Preparation of the Composite Blends

A ZSK-30 extruder with two feed ports was used to compound wood flakes with HDPE. HDPE or MAPE was fed from the first port, and the wood flakes or CVBS-modified wood flakes were fed from the second port to produce 50/50 w/w wood flake-HDPE composites. The details of the screw configuration and temperature profile are described in a previous work.² The temperature of the mixing zone was 200°C, and the screw speed was 200 rpm. Two different series of composites based on LMFI PE were prepared. One series was based on the unmodified wood flakes and MAPE with 0.5, 1, 2, 3, and 5 wt % MA, and the other series was based on the virgin LMFI PE and CVBS-modified wood flakes with 0.5, 1, 2, 3, and 4 wt % CVBS. To evaluate the effect of the melt flow behavior of PE on the mechanical properties of the interface-modified WPC, we modified both MMFI and LMFI PE with 2 wt % MA and mixed them with unmodified wood flakes in 80/20, 60/40, 50/50, and 40/60 w/w ratios to produce eight different composites. Furthermore, virgin MMFI PE and LMFI PE were mixed with 2 wt % CVBS-modified wood flakes in the same ratios to produce eight more composites. For comparison, we mixed virgin MMFI and LMFI PE and unmodified wood flakes in a 50/50 w/w ratio to produce two base composites. All the extruded strands were pelletized and dried *in vacuo* at 60°C for 12 h and compression-molded into sheets as described in a previous study.²

Mechanical Testing

The tensile and flexural properties of all the composites were measured with an Instron 5567 machine according to ASTM Standard D 638M with a crosshead speed of 5 mm/min and according to ASTM Standard D 790M with a crosshead rate of 2.6 mm/min, respectively. At least five specimens were tested to obtain the strength and modulus of the elasticity of the composites. The Izod impact strength was measured with a Radmana IRT-

2000 impact tester according to ASTM Standard D 256M with notched samples. At least 10 test specimens of every composite were tested to obtain the impact strength.

Differential Scanning Calorimetry (DSC)

The thermal properties of the wood flake-LMFI MAPE composites and CVBS-modified wood flake-LMFI PE composites were studied with modulated DSC (TA instruments, DSC 2920) at a heating and cooling rate of 5°C/min. In addition, the grafting reaction of CVBS onto HDPE was studied dynamically with a 50/50 w/w mix of modified wood flakes and HDPE powder (no screw compounding was carried out).

Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectra of MAPE, 50/50 w/w MAPE-wood flake composites, and 50/50 w/w HDPE-CVBS-modified wood flake composites were acquired with a Bruker IFS66v FTIR spectrometer. Samples were measured in the form of thin films, which were prepared by the compression molding of powdered composite pellets. For each spectrum, 128 consecutive scans with 4-cm⁻¹ resolution were co-added.

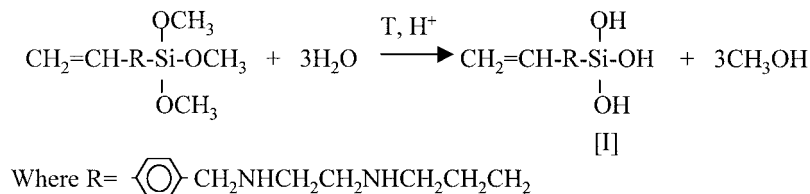
Scanning Electron Microscopy (SEM)

The fractured surfaces from Izod impact test specimens were examined with a Philips SEM 505 at an acceleration voltage of 20 kV. All the specimens were sputter-coated with gold before examination.

RESULTS AND DISCUSSION

Reactivity of Silane with Wood Flakes

The silane modification described here does not involve refluxing with solvents as reported in the literature^{10,11} and can be conducted during the processing of composites. The CVBS used for the study has three reactive functional groups. Methoxy functionality shows inorganic reactivity, whereas vinyl and amino functionality shows organic reactivity. Several researchers^{7,8,11,12} have suggested possible coupling mechanisms of silane and wood. It is known that the methoxy groups (OCH₃) in the silane can be hydrolyzed to produce silanol [-Si(OH)₃; see Scheme 1, structure I]. During the fiber pretreatment process, these sila-



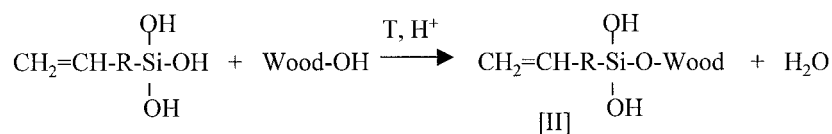
Scheme 1

nol groups (structure I) can either develop covalent siloxane bonds (Scheme 2, structure II) or form hydrogen bonds with OH groups of wood. Wu et al.¹² suggested that the hydrolysis and subsequent reaction with cellulose, that is, dehydration, be carried out in an acid environment because the rate and degree of these two chemical reactions are low under neutral conditions. At the other end of CVBS, the vinyl and amino groups have relatively high miscibility with PE. Thus, during the screw compounding of modified wood flakes and HDPE, the reaction of these functional groups with HDPE may be established. In addition, PE grafting may be initiated in the presence of silane.¹³

The results of the DSC analysis of the HDPE–CVBS-modified wood flake mix before twin-screw compounding are shown in Figure 1. DSC traces of dried wood flakes show glass-transition temperatures (T_g 's) around 116 and 186°C, which correspond to T_g 's of lignin and hemicellulose, respectively.¹⁴ Furthermore, T_g of cellulose, which is hindered by the thermal decomposition of lignin, occurs around 223°C. Unlike T_g of hemicellulose, which is largely influenced by the moisture content, T_g of lignin reaches an equilibrium state, that is, 115°C, at a fairly low moisture content, after which it remains unchanged by a further increase in moisture.¹⁴ The melting endotherm of the CVBS-modified wood flake–HDPE mix (not compounded), given in Figure 1, remains unchanged with a change in the CVBS content, and it is similar to that of the virgin HDPE, that is, 129.9°C. The α transition of HDPE corresponding to chain rotation,¹⁵ which occurs around 30°C for the virgin HDPE [Fig. 1(A,F)], shifts toward a higher temperature with an increase in the wood

content in the composites but still occurs around 40–50°C [Fig. 1(B–E)]. However, T_g of wood now shifts from 116°C to a lower temperature. For example, 1, 2, 3, and 4 wt % CVBS-treated wood flakes show T_g 's at 67.3, 72.2, 73.4, and 65.1°C, respectively. The shifting in T_g indicates that CVBS is reacting with wood. According to Timar et al.,¹⁶ T_g of modified wood (e.g., oligoesterified wood) may be as low as 50–60°C.

Furthermore, a close examination of the DSC traces of these composites from 140 to 200°C shows a very small exothermic peak between 150 and 190°C (Fig. 2), which is relevant to the grafting of silane onto PE induced by DCP or the grafting of PE in the presence of DCP. Also, this peak disappeared during the second heating of the mix, indicating completion of the grafting reaction after the first heating. The DSC trace of HDPE mixed with 0.7 wt % DCP, equivalent to the amount of DCP in the WPC (50/50 w/w composite) treated with 4 wt % CVBS, given in Figures 1 and 2, confirms that the exotherm between 150 and 190°C is due to the grafting of PE in the presence of DCP. The heat of the grafting reaction, given in Figure 2, suggests that the WPC mix containing CVBS and DCP generates more exothermic heat than the HDPE–DCP mix. For example, WPC containing 0.7 wt % DCP and 2 wt % CVBS (an equivalent amount of CVBS in the 50/50 w/w WPC with the 4 wt % CVBS treatment) produces 4.42 J/g of reaction heat, compared with 2.18 J/g for HDPE containing 0.7 wt % DCP. These results are in agreement with previously published data by Shieh and Tsai.¹³ The DSC traces of twin-screw compounded WPC composites, given in Figure 3, still show shifting in T_g of wood to lower temperature ranges with an in-



Scheme 2

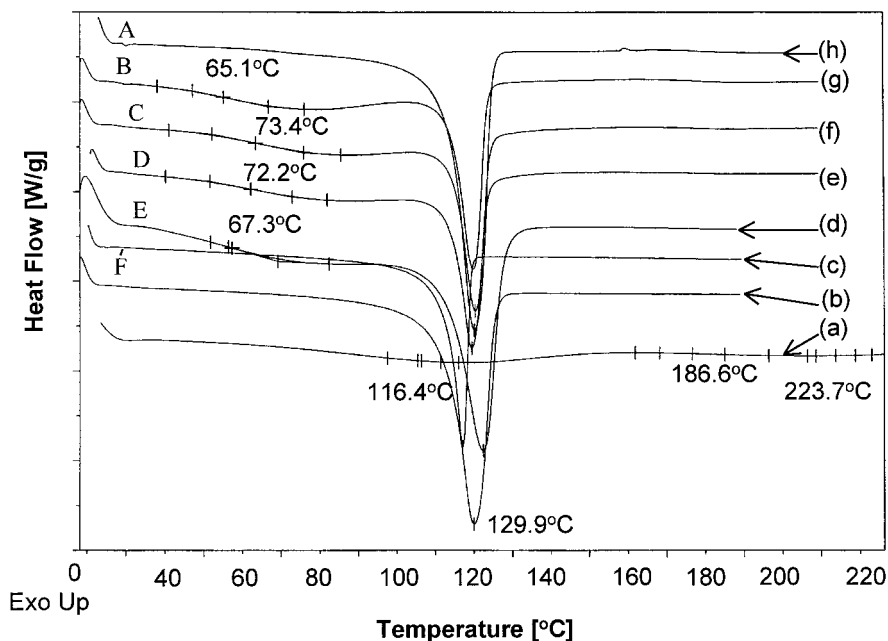


Figure 1 DSC traces of an HDPE-CVBS-modified wood flake mix before twin-screw compounding (first heating): (a) wood flakes, (b) HDPE, (c) HDPE-wood flakes, (d) 1 wt % CVBS, (e) 2 wt % CVBS, (f) 3 wt % CVBS, (g) 4 wt % CVBS, and (h) HDPE with 0.7 wt % DCP only (all the graphs are drawn to the same Y-axis scale but offset for clarity).

creasing CVBS content in the composite. In addition, composites containing 1 and 2 wt % CVBS show an exothermic peak between 140 and 190°C,

indicating that the grafting reaction keeps taking place after screw compounding. The reaction is incomplete during the screw compounding for the

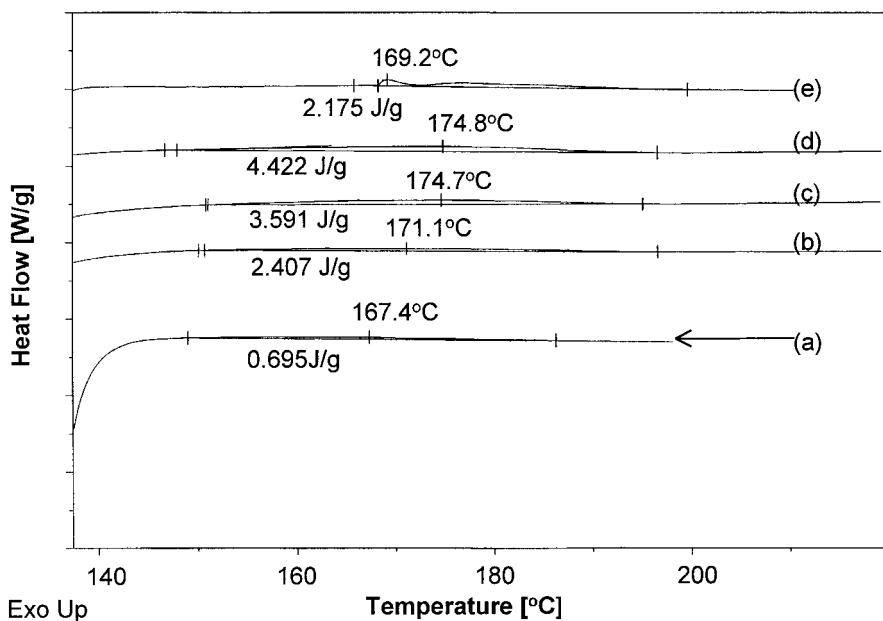


Figure 2 DSC traces of an HDPE-CVBS-modified wood flake mix before twin-screw compounding from 140 to 200°C: (a) 1 wt % CVBS, (b) 2 wt % CVBS, (c) 3 wt % CVBS, (d) 4 wt % CVBS, and (e) HDPE with 0.7 wt % DCP only (all the graphs are drawn to the same Y-axis scale but offset for clarity).

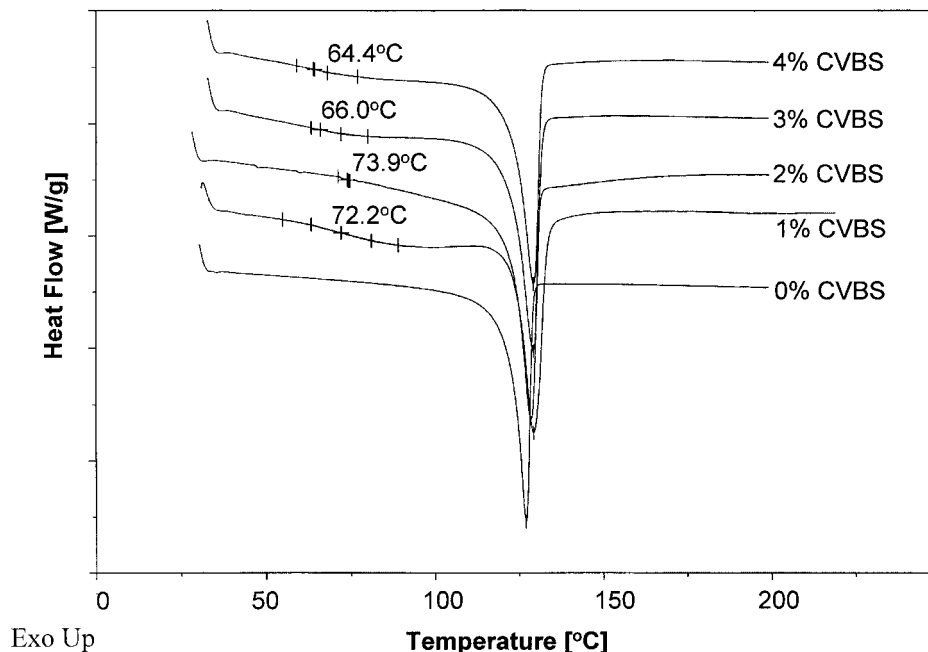


Figure 3 DSC traces of WPCs based on CVBS-modified wood flakes after twin-screw compounding (all the graphs are offset for clarity).

composites containing small quantities of DCP because of the short resident time of the material in the extruder, and this reaction may be completed in the subsequent processing of WPC.

FTIR analysis was used to study the reactivity of CVBS. PE shows a characteristic doublet in the

spectral range of $3000\text{--}2600\text{ cm}^{-1}$ and has been assigned for the C—H stretching vibration [Fig. 4(1-B), $2938\text{--}2884\text{ cm}^{-1}$, and Fig. 4(C), $2858\text{--}2844\text{ cm}^{-1}$]. The absorption band of the 50/50 w/w WPC composite, which occurs in the range of $2960\text{--}2834\text{ cm}^{-1}$ as a single band [Fig. 4(4)], is

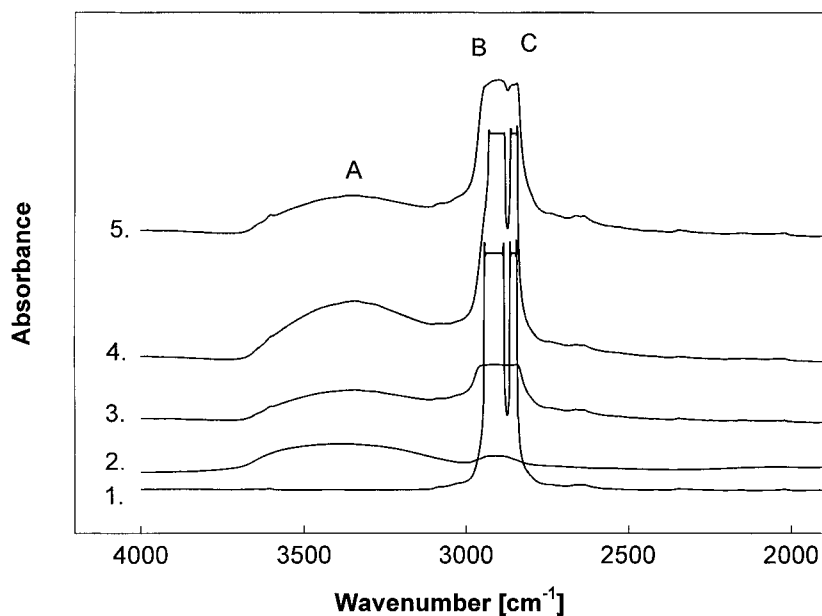


Figure 4 FTIR spectra of wood-PE composites containing CVBS in the range of $4000\text{--}1800\text{ cm}^{-1}$: (1) HDPE, (2) wood, (3) 0% CVBS, (4) 2% CVBS, and (5) 4% CVBS.

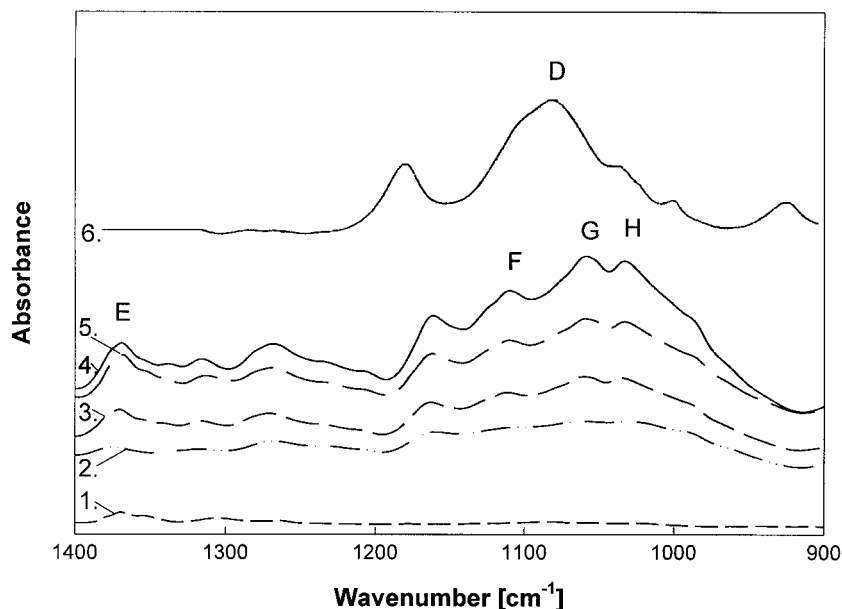


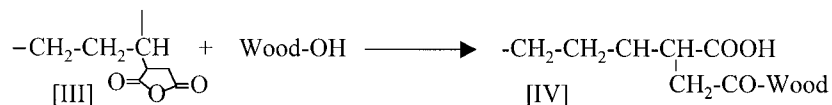
Figure 5 FTIR spectra of wood-PE composites containing CVBS in the range of 1400–900 cm^{-1} : (1) HDPE, (2) wood, (3) 0% CVBS, (4) 2% CVBS, (5) 4% CVBS, and (6) pure CVBS.

mainly due to the C—H stretching vibration of PE and wood.^{17,18} The sum of the spectra of the constituents, that is, HDPE and wood, shows a similar spectrum to that of the compounded WPC. The FTIR spectra of CVBS-modified wood composites (Fig. 4) show a doublet in the same spectral range. However, the peaks are now shifted to 2926–2883 and 2859–2843 cm^{-1} for the 2 wt % CVBS composite and to 2919–2882 and 2861–2839 cm^{-1} for the 4 wt % CVBS composite, respectively. The shifting in the C—H stretching vibration to a lower range indicates that some chains of HDPE are interacting with another polymer, CVBS, or modified wood. Furthermore, the intensity of the bending vibration of C—CH₃ groups [Fig. 5(4,5-E), 1370 cm^{-1}] increases with an increase in the CVBS content in the composites, which provides evidence of the branched structure of HDPE.^{14,16,19} These changes confirm that HDPE is interacting with another polymer, and more chain branching may be present in WPCs containing CVBS.

CVBS shows three characteristic bands in the range of 1800–1500 cm^{-1} , given in Figure 6, and has been assigned for the stretching vibration of the Ar—C=C group (I, 1628 cm^{-1}), aromatic ring (J 1600 cm^{-1}), and deformation vibration of the NH₂⁺ group (K, 1538 cm^{-1}).^{19,20} However, in the 2 and 4 wt % CVBS-modified WPCs, these bands disappear, and three new absorption bands ap-

pear, suggesting that the vinyl and amino groups of CVBS interact with HDPE or wood in the mix. The 2 wt % CVBS-modified WPC shows a band at 1718 cm^{-1} [Fig. 6(3-L)], and this band shifts to a lower range for the 4 wt % CVBS-modified WPC. In comparison with the spectrum of wood (spectrum 1), where absorption occurs at 1746 cm^{-1} , the occurrence of the new band indicates the reactivity of PE in the presence of DCP. Demjen et al.²⁰ suggested that this band is due to a carbonyl vibration and is the result of oxidation of polymer chains. The absorption band at 1656 cm^{-1} (spectra 3 and 4, M), which is assigned for the amide-I vibration of a tertiary amide,²⁰ indicates that the NH groups in CVBS are reacting with PE to form a tertiary amide. The absorption band at 1605 cm^{-1} (spectra 3 and 4, N), which is assigned for the skeletal vibration of the aromatic ring with additional interaction,²⁰ further confirms that CVBS is interacting with PE.

CVBS has another characteristic band in the range of 1400–1000 cm^{-1} ,^{19,20} in Figure 5(6), assigned for the trimethoxy-silyl group (D, 1084 cm^{-1}). This band completely disappeared in the CVBS-modified WPC [Fig. 5(4,5)]. The modified composites show appreciable spectral shifts, with the same features of unmodified composites present in the spectra, but the intensity has changed by more than 30%. In particular, the increase in the intensity of the absorption band at



Scheme 4

study the reactivity of wood flakes and HDPE. The IR spectrum of MAPE containing 2 wt % MA, given in Figure 7, shows several additional absorption bands compared with that of HDPE. The absorption bands at 1865 [Fig. 7(A)], 1786 [Fig. 7(B)], 1795–1775 cm^{-1}], 1305 [Fig. 7(F)], and 1220 cm^{-1} [Fig. 7(G)] are characteristic of the C—O stretching vibration of cyclic anhydride.¹⁷ The absorption at 1865 cm^{-1} suggests that the anhydride in the mix is not a conjugated anhydride and provides possible evidence for the existence of structure III in MAPE. The absorption band at 1710 cm^{-1} [Fig. 7(C)], which is due to maleic acid carbonyl,¹⁶ suggests that the maleic acid may be present in the mix as an intermediate product. The band at 917 cm^{-1} [Fig. 7(I)] is assigned for peroxide.¹⁷ Most importantly, a significant increase in the intensity of the absorption band at 1375 cm^{-1} [Fig. 7(E)] due to the bending vibration of C—CH₃ groups,^{14,17} which provides evidence of the branched structure of HDPE, clearly indicates that the MA grafting reaction is taking place.

For WPC based on MA-modified HDPE (Fig. 8), the absorption bands at 917, 1865, 1786, and 1305 cm^{-1} completely disappear, and the intensity of

the band at 1220 cm^{-1} is reduced dramatically. These data indicate that there is no cyclic anhydride left in the composites. The band at 1714 cm^{-1} [Fig. 8(J)], assigned for the C—O stretching vibration of carboxylic acid,¹⁷ is believed to be relevant to the carboxylic acid functionality of structure IV. Both the unmodified and MA-modified WPCs show characteristic broad bands for hydrogen-bonded OH in the range of 3500–3100 cm^{-1} . However, the increase in the intensity of the band for the MA-modified WPC provides evidence for the presence of additional carboxylic acid functionality as in structure IV.

DSC traces of composites based on MAPE and wood flakes, shown in Figure 9, indicate that T_g of wood has shifted to a lower temperature with an increase in the MA content in the composites. For example, 50/50 w/w WPCs containing 0.5, 1, 2, 3, and 5 wt % MAPE have T_g 's at 99.7, 93.8, 93.3, 91.4, and 88.8°C, respectively. The shifting in T_g is mainly due to esterified wood, as suggested by Timar et al.,^{16,25} who reported $T_g = 80\text{--}100^\circ\text{C}$ for oligoesterified wood. Both IR and DSC results provide evidence for the existence of esterified wood in WPCs (structure IV). With these results,

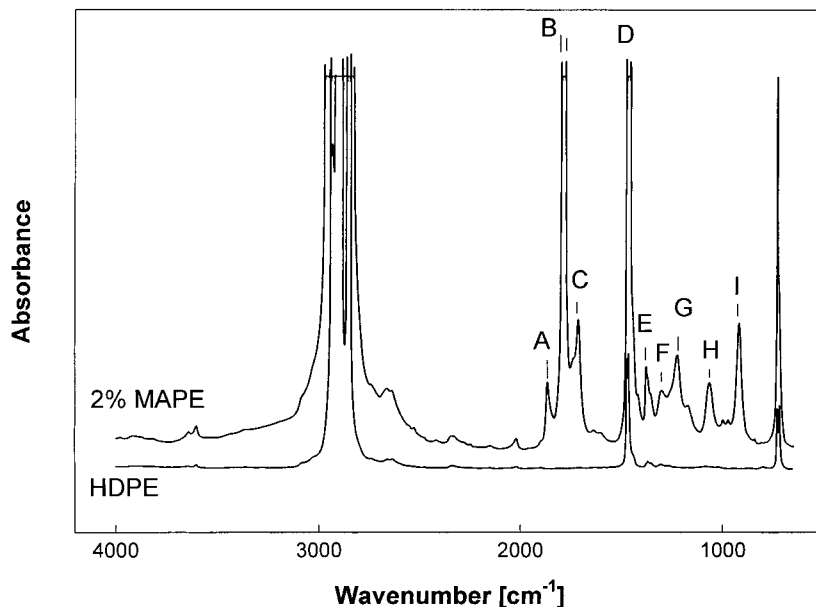


Figure 7 FTIR spectra of 2 wt % MAPE and HDPE.

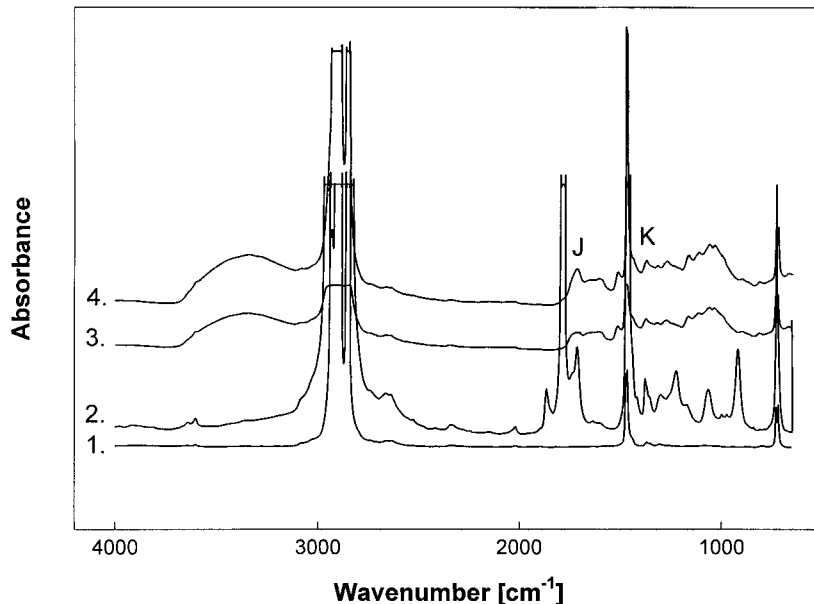


Figure 8 FTIR spectra of wood-PE composites containing MA: (1) HDPE only, (2) 2% MAPE only, (3) WPC with 0% MA, and (4) WPC with 2% MA.

one can suggest that MAPE reacts with wood through esterification to form a compatibilizer. This compatibilizer may further interact with wood through hydrogen bonding to form a strong interface.

Mechanical Properties of the Interface-Modified WPC Based on LMFI PE

MA-modified composites and CVBS-modified composites show similar trends in flexural prop-

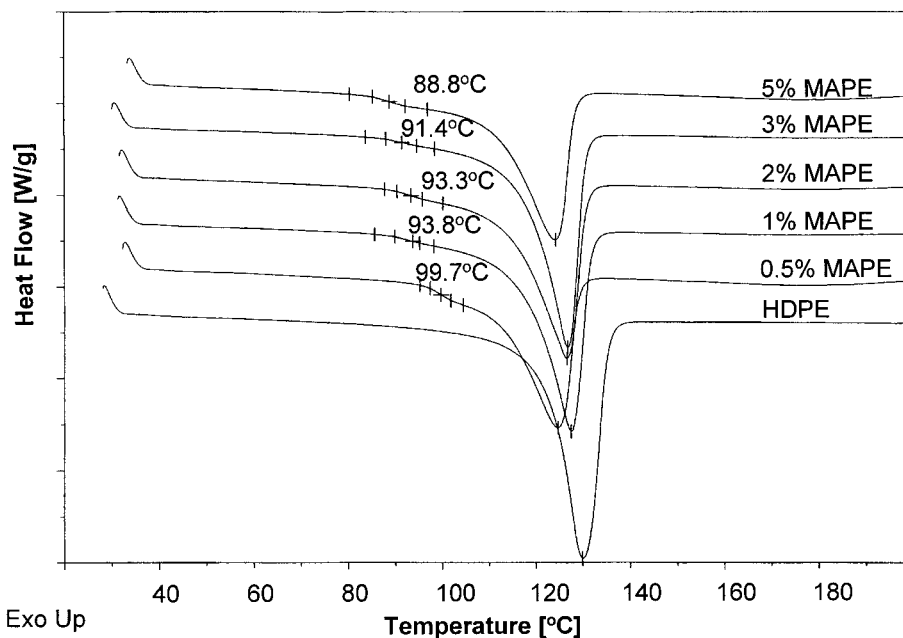


Figure 9 DSC traces of WPCs based on MAPE after twin-screw compounding (all the graphs are offset for clarity).

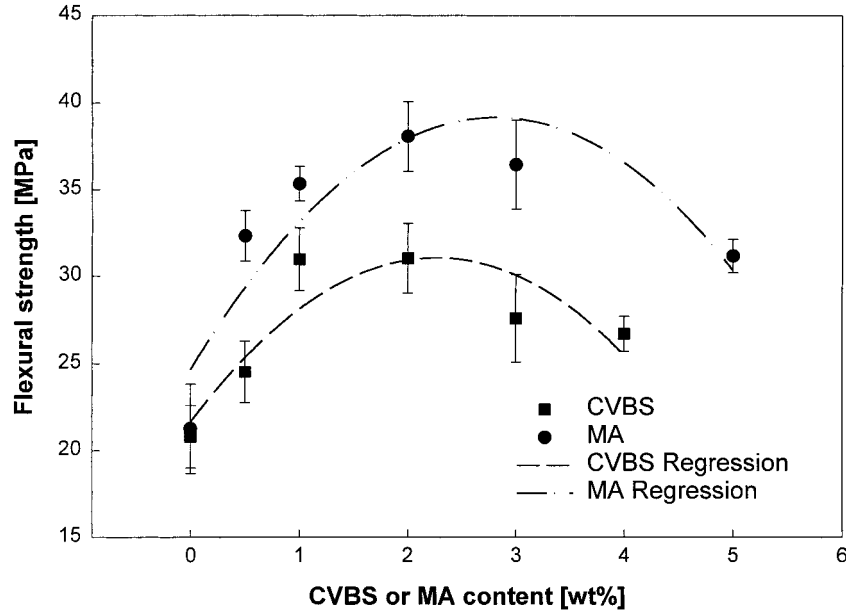


Figure 10 Comparison of the flexural strengths of 50/50 w/w MAPE-wood flake and HDPE-CVBS-modified wood flake composites.

erties with the amount of compatibilizer (Fig. 10). The flexural strength of both composites increases with an increase in MA or CVBS content to a maximum at 1–2 wt % of the compatibilizer and then gradually decreases with a further increase in the compatibilizer. The flexural strength

of 2 wt % MA-modified composites is twice as high as that of the unmodified composite. However, the flexural strength of the CVBS-modified composite with the same amount of CVBS is lower than that of the MA-modified WPCs. The tensile strength of WPCs based on MA and CVBS compatibilizers,

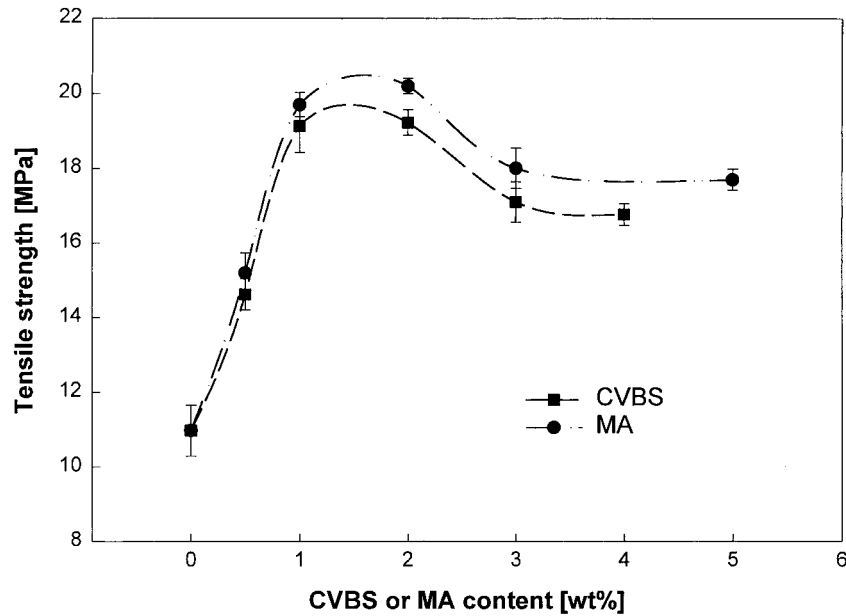


Figure 11 Comparison of the tensile strengths of 50/50 w/w MAPE-wood flake and HDPE-CVBS-modified wood flake composites.

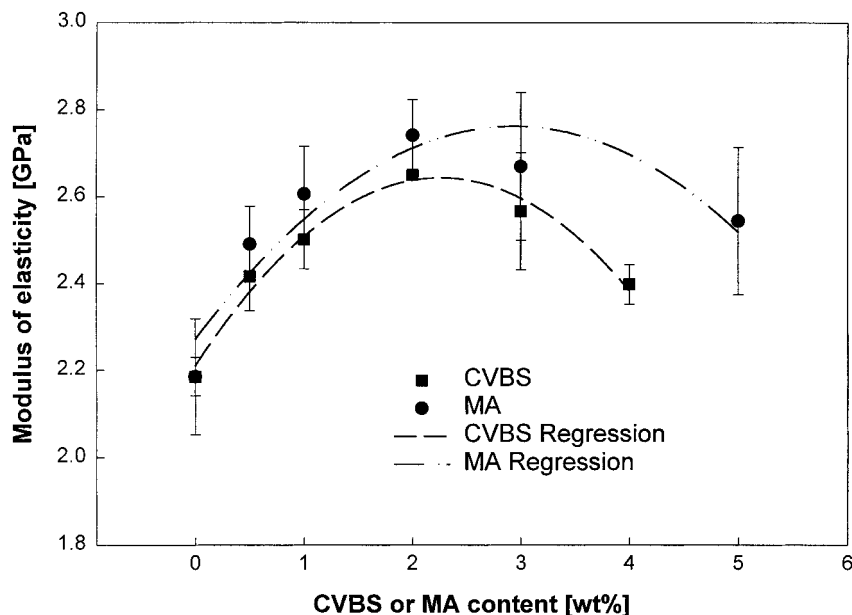


Figure 12 Comparison of the modulus of elasticity of 50/50 w/w MAPE–wood flake and HDPE–CVBS-modified wood flake composites.

shown in Figure 11, is significantly dependent on the MA or CVBS content. However, the strength is reduced considerably when the MA or CVBS content in the composites exceeds 3 wt %. The increase in the tensile strength for the modified composites (Fig. 11) can be attributed to the improved interfacial adhesion resulting from the presence of a compatibilizer, that is, MA or CVBS (structures II and IV). Lower flexural and tensile strength values for WPCs containing more than 3 wt % MA are mainly due to the excessive mal- eation of the base matrix, that is, HDPE. However, the reduction in the strength properties of WPCs containing more than 3 wt % CVBS is believed to be attributed to the reduction in wood flake properties during interface modification or interaction of PE with CVBS. However, the tensile strength of WPCs containing more than 3 wt % MA or CVBS is still higher than that of the unmodified WPCs, suggesting that interface interactions are present in these composites.

The variation in the modulus of elasticity, shown in Figure 12, of WPCs containing CVBS-modified wood shows a considerable reduction in the modulus for WPCs containing more than 3 wt % CVBS. In general, both MA- and CVBS-modified WPCs show an increase in modulus with a moderate compatibilizer content, indicating that the modulus is influenced by the interfacial adhesion or improved surface wetting.

Both the MA and CVBS modifications provide similar improvements in impact strength (Fig. 13), suggesting that either the matrix or the wood flake can be modified to improve the impact performance of the composite. The impact strength of WPCs containing 2–3 wt % CVBS is slightly higher than that of WPCs with the same amount of MA. The percentage elongation at break in Figure 14 indicates that the interface modification provides an increase in toughness or ductility to WPCs. Furthermore, the composites containing CVBS show higher values of elongation at break than MA-modified composites. The comparatively high ductility of the CVBS-modified composite is attributed to the nature of the compatibilizer at the composite interface. For example, if the vinyl groups in CVBS interact with HDPE, the number of carbon atoms in the compatibilizer chain, that is, wood to HDPE linkage, will be more than 10, compared with 2 in the MA compatibilizer linkage. The long-chain structure can be expected to introduce high ductility to the WPCs.

The significant improvement in mechanical properties with the CVBS modification indicates that CVBS is also a potential interface modifier for wood, and the optimum level of CVBS modification for wood is in the range of 1–3 wt %. The optimum MA modification level for HDPE is in the range of 1–2 wt %, and these results are in agreement with the published data based on wood flour or fiber.^{3–6}

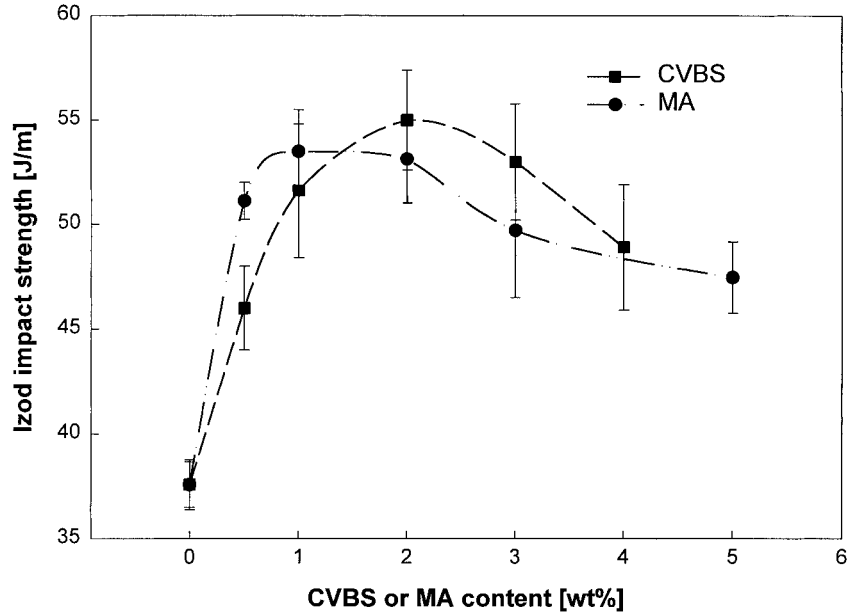


Figure 13 Comparison of the Izod impact strength of 50/50 w/w MAPE-wood flake and HDPE-CVBS-modified wood flake composites.

Morphology of WPCs Based on LMFI

SEM micrographs of the fracture surfaces of MA-modified 50/50 w/w HDPE-wood flake composites containing 1, 2, and 5 wt % MA were compared with the surfaces of unmodified composites (Fig. 15). Unmodified composites show some fiber pull-

out and some clean flake surfaces,² whereas the MA-modified composites show torn matrix with a considerable amount of matrix remaining on the wood flakes, which indicates improved interface interaction. Furthermore, the fracture surface of the composite containing 5 wt % MA (Fig. 16)

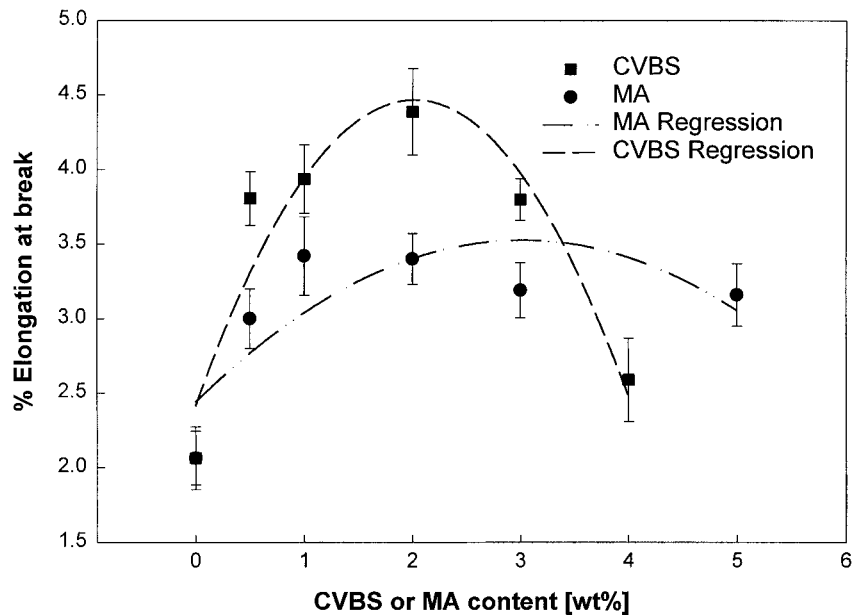


Figure 14 Comparison of the elongation at break of 50/50 w/w MAPE-wood flake and HDPE-CVBS-modified wood flake composites.

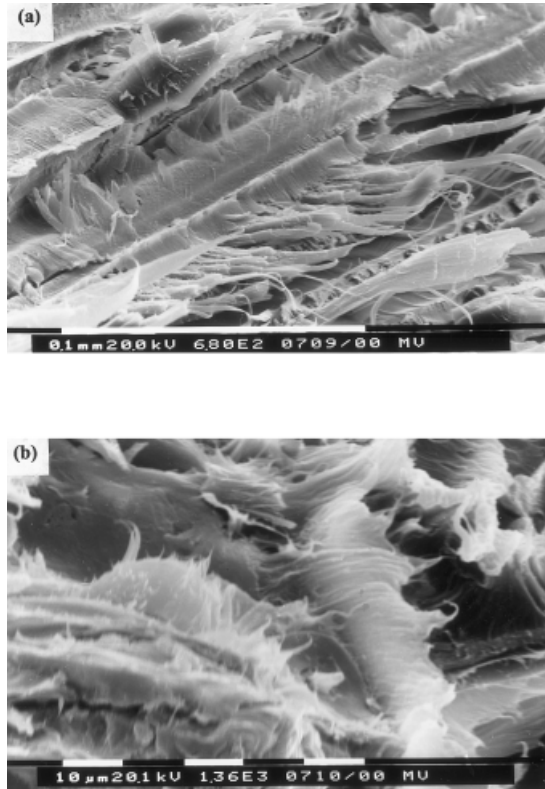


Figure 15 SEM micrographs of the fracture surfaces of MA-modified 50/50 w/w WPCs: (a) 1 wt % MA and (b) 2 wt % MA.

shows a very limited amount of torn matrix, suggesting that the matrix is more brittle than those in composites containing 1–2 wt % MA. As discussed before, this phenomenon is mainly due to the excessive modification of the base polymer. However, the matrix seems to have adhered to the wood flake very well, indicating that the interface interaction in the WPCs is adequate.

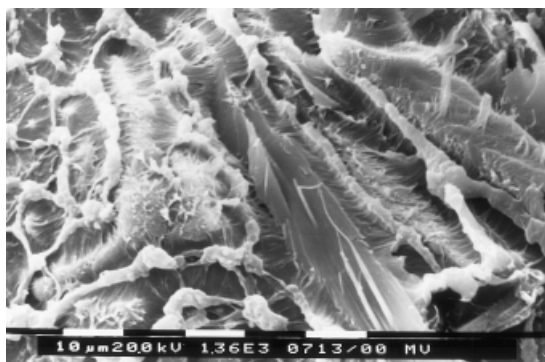


Figure 16 SEM micrograph of the fracture surface of a 5 wt % MAPE-wood flake composite.

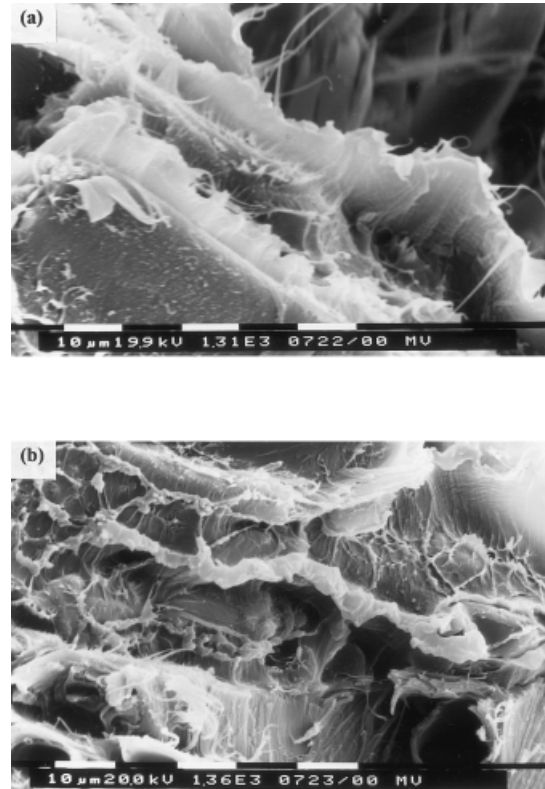


Figure 17 SEM micrographs of the fracture surfaces of CVBS-modified 50/50 w/w WPCs: (a) 2 wt % CVBS and (b) 4 wt % CVBS.

SEM micrographs of the fracture surfaces of CVBS-modified wood flake–HDPE composites (Fig. 17) also show torn matrix and a considerable amount of matrix remaining on the wood flakes in comparison with the surface of the unmodified composite.² HDPE stretching or tearing in the composites containing 2 wt % CVBS is significant, indicating that there is improved interaction between the wood flake and the matrix. Although some matrix tearing is present in the composites containing 4 wt % CVBS [Fig. 17(b)], the microstructure of the composite is somewhat similar to that of the 5 wt % MA-modified composite. The brittle morphology of the matrix polymer in WPCs containing 4 wt % CVBS indicates that the high silane content in the composites could also modify HDPE excessively, thus resulting in lower mechanical properties.

Comparison of the Mechanical Properties of Modified WPC Based on LMFI and MMFI PE

The effect of HDPE melt flow behavior on the mechanical properties of modified WPCs was

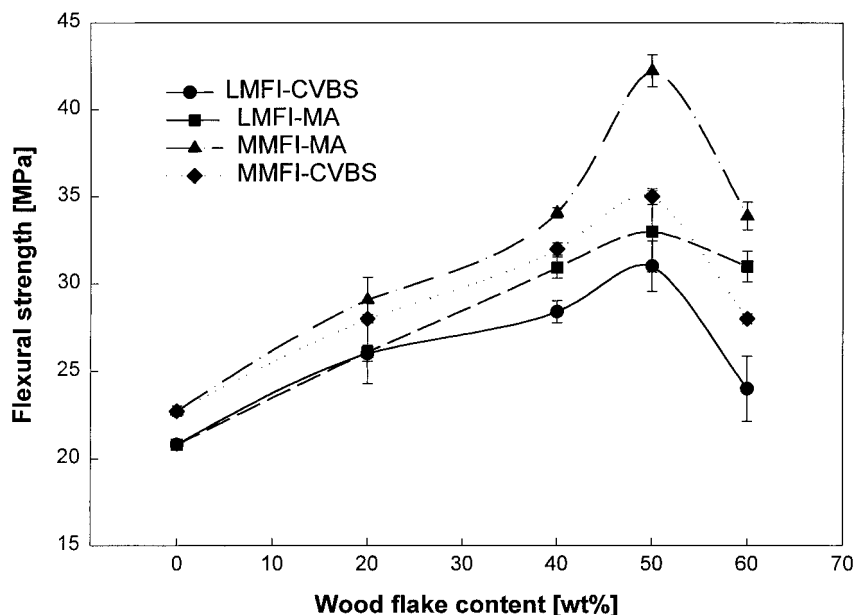


Figure 18 Effect of the matrix melt flow behavior on the flexural strength of WPCs based on 2 wt % MA or CVBS.

studied with HDPE of LMFI and MMFI, respectively. The modification with 2 wt % MA or CVBS was selected to study the variation of flexural and tensile properties with wood flake content in WPCs. Both CVBS- and MA-modified composites based on low-viscosity PE, that is, MMFI, show higher values of flexural strength than those of high-viscosity PE, that is, LMFI (Fig. 18). In addition, 50/50 w/w composites based on MMFI, particularly the MA-modified composites, have considerably higher flexural strengths. Although the flexural strength of the modified WPC is considerably higher than that of the unmodified composite,² the trend of variation with the flake content noticed here is similar to that of the unmodified WPC. It is believed that this phenomenon is attributable to flake wetting and distribution, as explained elsewhere.² The tensile strengths of the different composites based on LMFI, shown in Figure 19, indicate that the tensile strength of the composite is equal to or higher than that of the bulk HDPE. However, the tensile strength of the unmodified WPC (Fig. 11) is well below the value, indicating that there is a strong interface interaction between HDPE and wood flakes in the modified WPC. The tensile strength of the composites based on MMFI, shown in Figure 19, significantly increases with an increase in wood flake content and is always higher than that of the bulk matrix. This phenomenon is attributed

to the interface interaction and PE penetration, as discussed elsewhere.² However, the low strength values for WPC containing more than 60 wt % wood flake are attributed to the poor distribution of wood flakes, which is caused by strong interactions between wood flakes at a high flake content.²

The results for WPCs based on the MMFI and LMFI PE indicate that the matrix melt flow behavior greatly influences the mechanical properties of the WPCs. However, the improved interfacial adhesion with a compatibilizer could significantly enhance the properties of WPCs based on high-viscosity HDPE.

CONCLUSION

The results indicate that the properties of wood flake-HDPE composites can be improved through modification of the matrix polymer with MA or the wood flake surface with a CVBS coupling agent. DSC results of the CVBS-modified composites, showing considerable shifting in T_g of wood to a low range of temperatures with an increase in CVBS content, indicate that wood is reacting with the CVBS coupling agent. In the subsequent processing stage of the modified wood-HDPE composites, some HDPE is grafted onto the CVBS-modified wood, as confirmed by FTIR data, which

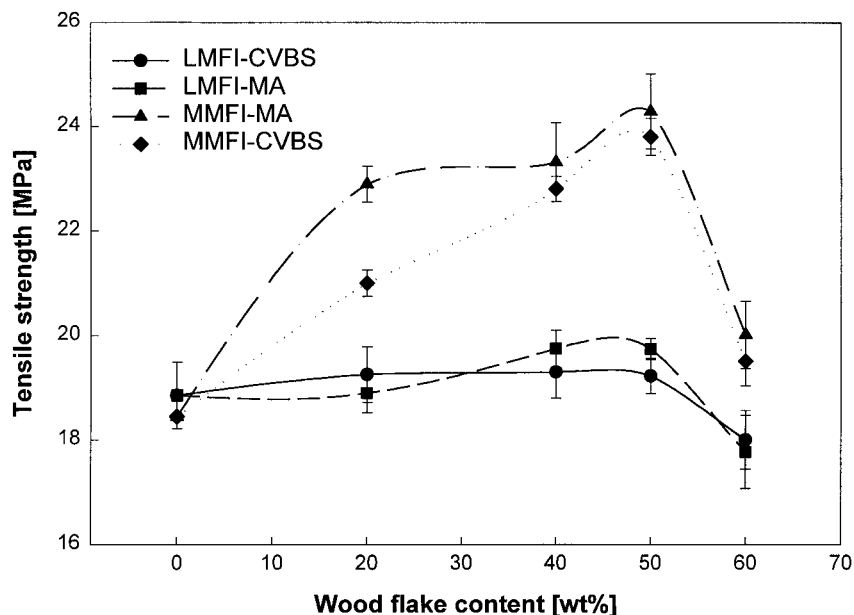


Figure 19 Effect of the matrix melt flow behavior on the tensile strength of WPCs based on 2 wt % MA or CVBS.

indicate appreciable spectral changes in the modified WPCs. DSC data also show an exotherm relevant to silane grafting. Furthermore, these data provide evidence for the existence of the PE–silane-grafted wood compatibilizer. DSC and FTIR results based on MA-modified WPCs indicate that some MAPE is reacting with wood flakes through esterification to form a compatibilizer for wood flake–PE composites. These results for the MA-modified composites are in agreement with the previously reported data based on wood flour or wood fiber.

Both the CVBS-modified wood flake–HDPE and MAPE–wood flake composites show a significant increase in strength properties with respect to the unmodified composites. The results indicate that 1–2 wt % MA modification on HDPE and 1–3 wt % CVBS treatment on wood flakes provide WPCs with optimum properties. The significant improvement in tensile strength and elongation at break, which shows an increase in the ductility of the WPCs, is attributed to the improved interfacial adhesion resulting from the presence of a compatibilizer, as confirmed by SEM micrographs. Furthermore, a slight increase in modulus was observed for the modified WPC.

The results based on HDPE of high or low viscosity confirm again that the matrix melt flow behavior greatly influences the mechanical properties of WPCs. Also, these data suggest that the influence of limited flake wetting and distribution

associated with high-viscosity PE, which results in low mechanical properties, can be minimized with an interface modifier.

REFERENCES

1. Simonsen, J. Proceedings of Woodfiber–Plastic Composites Conference No. 7293, Forest Product Society, Madison, WI, May 1995; p 47.
2. Balasuriya, P. W.; Ye, L.; Mai, Y.-W. *Compos A* 2001, 32, 619.
3. Yam, K. L.; Gogoi, B. K.; Lai, C. C.; Selke, S. K. *Polym Eng Sci* 1990, 30, 693.
4. Raj, R. G.; Kokta, B. V. In *Emerging Technologies for Materials and Chemicals from Biomass*; Rowell, R. M.; Schuler, T. P.; Narayn, R., Eds.; ACS Symposium Series 476; American Chemical Society: Washington, DC, 1992; p 76.
5. Raj, R. G.; Kokta, B. V.; Grouleau, G.; Daneault, C. *Polym-Plast Technol Eng* 1990, 29, 339.
6. Liao, B.; Huang, Y.; Cong, G. *J Appl Polym Sci* 1997, 66, 1561.
7. Maldas, D.; Kokta, B. V.; Raj, R. G.; Daneault, C. *Polymer* 1988, 29, 1255.
8. Karnani, R.; Krishnan, M.; Narayan, R. *Polym Eng Sci* 1997, 37, 476.
9. Mohanakrishnan, C. K.; Narayan, R.; Nizio, J. D. Proceedings of Woodfiber–Plastic Composites Conference No. 7292, Forest Product Society, Madison, WI, 1994; p 57.

10. Coutinho, F. M. B.; Costa, T. H. S.; Carvalho, D. L. *J Appl Polym Sci* 1997, 65, 1227.
11. Raj, R. G.; Kokta, B. V. In *High-Tech Fibrous Materials*; Vigo, T. L.; Turbak, A. F., Eds.; ACS Symposium Series 457; American Chemical Society: Washington, DC, 1991; p 102.
12. Wu, J.; Yu, D.; Chan, C.-M.; Kim, J. K.; Mai, Y.-W. *J Appl Polym Sci* 2000, 76, 1000.
13. Shieh, Y. T.; Tsai, T. H. *J Appl Polym Sci* 1998, 69, 255.
14. Back, E. L.; Salmen, N. L. *Tappi* 1982, 65, 107.
15. Saini, D. R.; Shenoy, A. V. *Polym Commun* 1985, 26, 50.
16. Timar, M. C.; Mihai, M. D.; Maher, K.; Irle, M. *Holzforschung* 2000, 54(1), 71.
17. Grasselli, J. G. *CRC Atlas of Spectral Data and Physical Constants for Organic Compounds*; CRC: OH, 1973.
18. Garton, A. *Infrared Spectroscopy of Polymer Blends, Composites and Surfaces*; Hanser: Munich, 1992; p 201.
19. Socrates, G. *Infrared Characteristic Group Frequencies*; Wiley: Chichester, England, 1980.
20. Demjen, Z.; Pukanszky, B.; Nagy, J., Jr. *Polymer* 1999, 40, 1763.
21. Brown, J. F., Jr.; Vogt, L. H., Jr.; Prescott, P. I. *J Am Chem Soc* 1964, 86, 1120.
22. Ishida, H.; Miller, D. J. *J Polym Sci Polym Phys Ed* 1985, 23, 2227.
23. Oksman, K.; Lindberg, H.; Holmgren, A. *J Appl Polym Sci* 1998, 69, 201.
24. Xanthos, M. *Reactive Extrusion: Principles and Practice*; Hanser: Munich, 1992.
25. Timar, M. C.; Maher, K.; Irle, M.; Mihai, M. D. *Holzforschung* 2000, 54(1), 77.