

Functionalization of Wood Particles through a Reactive Extrusion Process

Karana Carlborn, Laurent M. Matuana

Department of Forestry, Michigan State University, East Lansing, Michigan 48824

Received 25 April 2005; accepted 8 July 2005

DOI 10.1002/app.22577

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Wood particles were modified in a reactive extrusion process with maleated polyethylene (MAPE) and maleated polypropylene (MAPP) compounds. Contents of MAPE were varied to study the effect of material composition on grafting efficiency during reactive extrusion, while extruder barrel temperatures and rotational screw speeds were varied to evaluate the effects of processing conditions on the modification of wood particles. Polymer molecular weight effects were followed using MAPP, with different molecular weights. Efficiency of the modification was assessed using FTIR and XPS surface analysis techniques, along with a titrimetric analysis, to verify the esterification reaction between the wood particles and maleated polyolefins. The grafting of maleated polyolefins onto the surface of the wood particles through a reaction of the hydroxyl groups on the wood surface with the maleated groups of the

maleated polyolefins was confirmed, while the level of grafting of MAPE onto wood particles was determined to be a function of the MAPE concentration. However, there was no significant difference found in grafting efficiency at different extrusion processing conditions, rather all of the conditions resulted in adequate grafting. Similarly, there was no difference in grafting efficiency with the molecular weight of MAPP. Reactive extrusion was found to be a suitable technique for the modification of wood particles, with maleated polyolefins, for all of the material compositions and processing conditions studied. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 3131–3142, 2006

Key words: reactive extrusion; surface modification; wood particles; maleated polyolefins; esterification; FTIR; XPS; titration

INTRODUCTION

In response to the need for new adhesives for wood composite products, a formaldehyde-free binding system for wood particles, which used only maleated polyolefins to create direct wood particle to wood particle bonding, was developed in our prior work.^{1,2} Wood composite panels were manufactured from maleated polyolefin-modified wood particles, without using any additional adhesive. These panels met and in some cases even exceeded standard requirements for particleboard made with formaldehyde-based adhesive. However, the mechanism for the adhesive bonding was not fully developed.

Maleated polyolefins react with wood particles through an esterification reaction (Fig. 1). This reaction occurs between the maleated groups of the polyolefins and the hydroxyl groups on the wood surface, forming a monoester or a diester. This results in the grafting of a pendant polyolefin chain to the wood surface through the ester linkage. Several authors have stud-

ied this reaction with maleated compounds and wood particles (or other cellulosic materials).^{3–14} However, most of this previous work focused on fibers modified through a solvent-based process, where the maleated compounds were dissolved in heated xylene, toluene, *N,N*-dimethylformamide, or other organic solvents, and cellulosic particles were added.^{3–10,12–14} Cellulosic fibers have to be filtered and dried after modification, which makes this process both cost-ineffective and time consuming, and the often harmful organic solvents must be properly disposed off. To produce modified wood particles that could be used to make alternative composite panels, it is necessary to change from a solvent-based process to a dry process. A solvent-free process that has been reported by Kazayawoko and coworkers utilized a thermokinetic high-intensity mixer to graft maleated polypropylene (MAPP) onto wood fibers.^{11,12} However, the esterification reaction of wood particles and MAPP could not be confirmed through surface characterization techniques. An effective dry process for grafting maleated polyolefins onto the surface of wood particles is still needed to produce a large volume of modified wood particles required to manufacture formaldehyde-free wood composite panels.

Reactive extrusion is a technique that can be used for the chemical modification of compounds, usually polymers, which can melt during processing. Because

Correspondence to: L. M. Matuana (matuana@msu.edu).

Contract grant sponsor: USDA-CSREES Grant-Advanced Technology Applications; contract grant number: 2002–34158–11914.

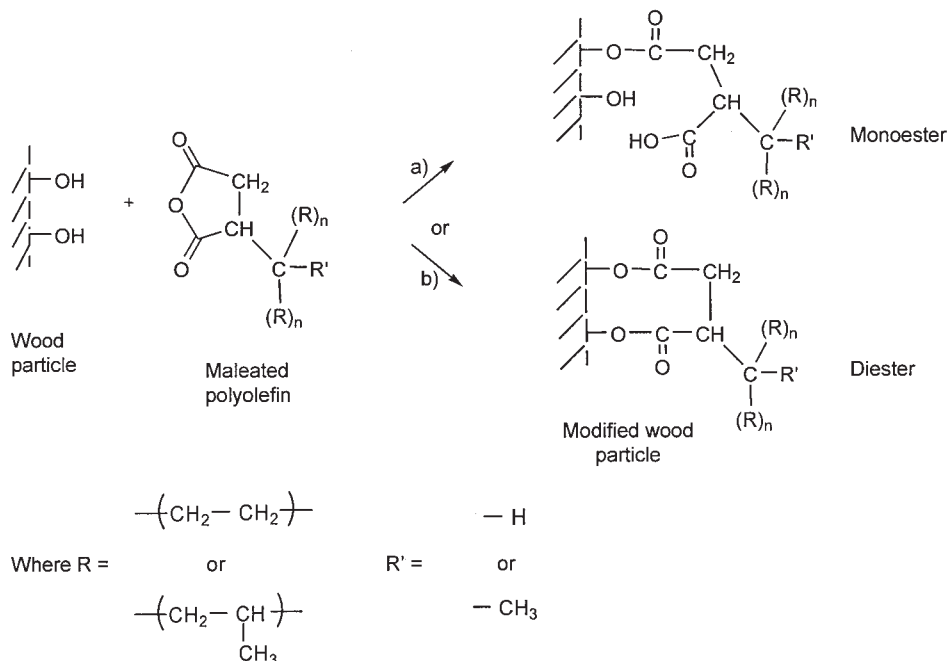


Figure 1 Modification scheme for esterification reaction between wood particles and maleated polyolefins: (a) monoester and (b) diester formation.

no solvent is involved during processing, reactive extrusion is an environmentally friendly technique for surface modification. It also allows for control of reaction times and temperatures through variation of rotational screw speeds and extruder barrel temperatures. Reactive extrusion offers the advantage of intensive mixing of components in a short time, especially in a twin-screw extruder, which ensures a more thorough reaction of components.¹⁵ This process also has the advantage of low retention times in the extruder, and so a series of different reaction conditions can be tested in a relatively short period of time. Reactive extrusion has only rarely been used for wood fiber surface modification,^{1,2} probably because the wood component does not melt and flow in the extruder. However, the ease of processing and control of reaction conditions makes this technique attractive for wood fiber surface modification.

In this study, reactive extrusion was employed to graft maleated polyethylene (MAPE) and MAPP compounds to wood particles, with an ultimate goal of determining optimum surface modification conditions. Particular emphasis was placed on examining the efficiency of grafting of the surface modification, as functions of material compositions (MAPE contents and molecular weights of MAPP compounds) and extrusion processing conditions (barrel temperatures and rotational screw speeds). X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) spectroscopy, and titrimetric analysis were used to monitor chemical changes on the surface of the wood

particles before and after reactive extrusion, with maleated polyolefins. XPS has an approximate sampling depth of 0.1–8 nm,¹⁶ which makes it even more surface-sensitive than FTIR. When used together, these techniques provide detailed information about the surface chemistry and bonding mechanism in modified wood fibers.

EXPERIMENTAL

Materials

Maple wood particles of 150- μm (100-mesh) size, used in this study, were supplied by American Wood Fibers (Schofield, WI). Hydrated zinc acetate, the catalyst, and xylene (99.9%, ACS Grade), the solvent used for Soxhlet extraction, were obtained from Baker Analytical Reagents (JT Baker Co., Phillipsburg, NJ). MAPE (G-2608) and several MAPPs (G-3216, G-3015, G-3003, and E-43) supplied by Eastman Chemical Co. (Kingsport, TN) were used as binding agents. Characteristics of these maleated polyolefins are listed in Table I. Hydrochloric acid (concentrated) was obtained from EM Science (Cherry Hill, NJ). Sodium hydroxide, methanol (absolute), pyridine (99.9%), toluene (100%), 1-butanol (99.6%), ethanol (190 proof), and acetic anhydride (100%), all obtained from Baker Analytical Reagents (JT Baker Co.), were used as titration reagents. Titration reagents were used as directed in Pure and Applied Chemistry methods.¹⁷ The wood particles were dried for 48 h at 105°C to a final mois-

TABLE I
Characteristics of Maleated Polyolefins

Properties	MAPE G-2608	MAPP ^a			
		E-43	G-3216	G-3015	G-3003
Maleic anhydride (wt %)	1.5	8	2.5	2.5	1.5
Melting point (°C)	122	155	142	155	156
Approximate weight average molecular weight M_w (g/mol)	51,700	11,200	39,000	47,000	52,000
Melt flow index at 190°C ^b	8	—	—	—	12.7
Viscosity at 190°C (Pa s)	—	0.3	20	25	60

^a G-3216 is a maleated PE/PP copolymer.

^b Melt flow index measured at 190°C and 2.16 kg, according to ASTM standard D 1238.

ture content of less than 1%, before processing. All other chemicals were used as received.

Surface modification of wood particles with maleated polyolefins in a reactive extrusion

A 10-L high intensity TGAHK20 mixer (Papenmeier, Germany) was used for dry-blending of the wood particles, binding agent, and catalyst. All ingredients were combined in the mixer and blended for 10 min at room temperature. Amounts of all components used in the formulation are listed in Table II. These mixtures were then fed into a 32-mm conical counter-rotating twin-screw extruder (C. W. Brabender Instruments, Inc., South Hackensack, NJ), with a length to diameter (L/D) ratio of 13 : 1. The extruder was driven by a 5.6 kW Intelli-Torque Plasti-Corder Torque Rheometer[®]. The extruder had three temperature zones on the barrel (Fig. 2) and an adjustable rotational screw speed. Various processing temperatures and rotational screw speeds were used to study the effects of processing conditions on the effectiveness of grafting maleated polyolefins to the surface of the wood particles. In all cases, a uniform barrel temperature was set for each test. For example, when the desired processing temperature was 130°C, all three zones were set at that temperature. This was done similarly for the other studied processing temperatures of 140, 160, and 180°C.

The effect of material composition on the grafting of MAPE onto wood particles in a reactive extrusion process was investigated by holding the extruder bar-

rel temperature and rotational screw speed constant at 160°C and 60 rpm, respectively. Whereas, the MAPE contents were varied from 5 to 20% of the total batch weight (Table II).

To determine the effects of processing conditions on grafting efficiency of modified wood particles, the MAPE concentration was fixed at 20%, and the extruder barrel temperatures and rotational screw speeds were varied. Barrel temperatures were limited to the range above the melting point of MAPE and below the degradation temperature of wood (130, 140, 160, and 180°C). The rotational speed of the screws was varied from 20 to 80 rpm, in 20-rpm increments, at each barrel temperature profile.

The influence of molecular weight on the efficiency of the grafting reaction was studied using four different MAPP compounds (Table I). Extrusion processing conditions were held constant, with the barrel temperature at 160°C and the rotational speed of the screws at 60 rpm.

Extraction of wood particles

Unmodified wood particles were Soxhlet-extracted with acetone for 24 h to remove impurities, air-dried for 60 h, and then oven-dried at 105°C to a constant weight, before using for further analysis. Modified wood particles were also Soxhlet-extracted with xylene for 24 h to remove any unreacted maleated polyolefins, which had not been linked to the wood particles, followed by air-drying for 60 h, and oven-drying to a constant weight at 105°C. These modified wood particles were then analyzed by FTIR. A second 24-h Soxhlet extraction was performed to ensure the removal of unreacted maleated polyolefin was complete from the surface of wood particles upon the first extraction. Following the second extraction, modified wood particles were again air-dried for 60 h, and then dried to a constant weight at 105°C, after which FTIR, XPS, and titrimetric analyses were performed.

TABLE II
Formulations Used for Modified Wood Particles

Maple particles (g)	MAPE or MAPP (g)	Hydrated zinc acetate (g)
94	5	1
89	10	1
84	15	1
79	20	1

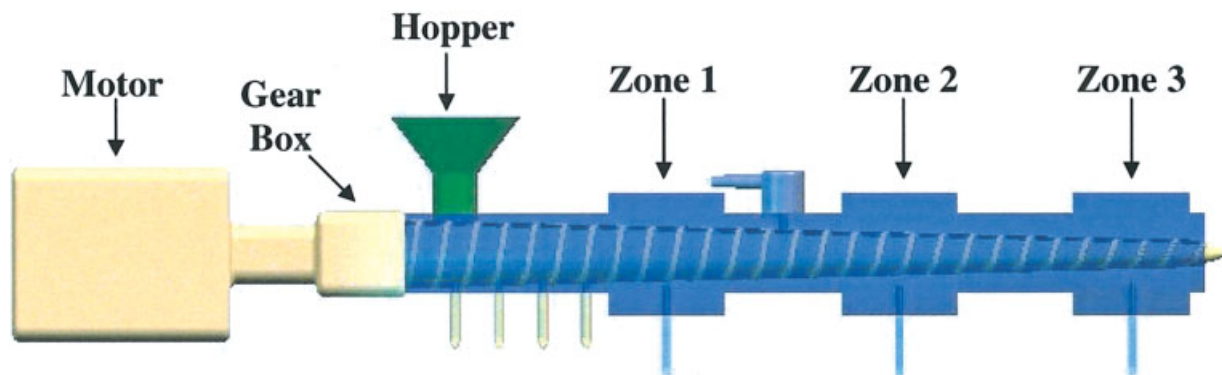


Figure 2 Diagram of the extruder showing the three heating zones. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Surface characterization of wood particles

FTIR spectra of both unmodified and modified wood particles were obtained using a Nicolet Protégé 460 FTIR spectrometer (Nicolet Instrument Co., Madison, WI), to determine the functional groups present at the surface of the samples before and after modification. Spectra were recorded in Kubelka–Munk units, in the range of $4000\text{--}400\text{ cm}^{-1}$, with a resolution of 4 cm^{-1} and a coaddition of 128 scans, for each spectrum. All spectra were collected using diffuse reflectance with FTIR for transfer of IR radiation. Pure powdered potassium bromide (KBr) was used as a reference substance. No dilution of the wood particles in KBr was required to obtain the spectra. Data analysis was performed using WinFIRST software from Thermo Nicolet (Madison, WI). No baseline modification was done before performing data analysis of the spectra.

On the basis of prior work,¹ the regions of interest in the FTIR spectra of wood particles modified with maleated polyolefins were the absorbance bands near 2900 and 1740 cm^{-1} , for CH stretching of aliphatic carbon chains and carbonyl group stretching, suggesting the formation of ester linkages, respectively. Using the integrated area under these peaks, a grafting index (GI) was calculated using the following equation:

$$GI_x = \frac{A_{x(\text{Modified})}}{A_{x(\text{Unmodified})}} \quad (1)$$

where x represents the absorbance band at either 2900 or 1740 cm^{-1} , $A_{x(\text{Modified})}$ represents the integrated area of the peak after modification, and $A_{x(\text{Unmodified})}$ represents the integrated peak area of the unmodified wood particles.

XPS analysis was carried out on a Physical Electronics Phi 5400 ESCA System, (Physical Electronics, Chanhassen, MN), using a nonmonochromatic Mg source and a takeoff angle of 45° relative to the detector. A low resolution scan from 0 to 1100 eV binding energy was used to determine the concentration of

each element present on the surface of the samples, along with the oxygen to carbon (O/C) atomic ratio, whereas a high resolution scan of the C_{1s} region from 280 to 300 eV was performed to further analyze the chemical bonding of the carbon atoms. Carbon component C1 arises from carbon atoms bonded only to carbon and hydrogen atoms (C–C/C–H), C2 from carbon atoms bonded to a single oxygen atom, other than a carbonyl oxygen (C–OH), C3 from carbon atoms bonded to two noncarbonyl oxygen atoms or to a single carbonyl oxygen atom (O–C–O, C=O), and C4 from carbon atoms, which are linked to a carbonyl and a noncarbonyl group (O–C=O).^{9,11,16} The procedure for XPS data collection and analysis was detailed in other articles.^{9,11}

As mentioned, the chemical reaction of maleated polyolefins and wood particles takes place between the maleate groups of the polyolefin and hydroxyl groups on the surface of wood. Since C2 component arises from atoms bonded to a single oxygen atom other than a carbonyl oxygen (C–OH), the change in the content of C2 component before and after modification can be used to monitor the occurrence of the esterification between the maleated polyolefins and the wood particles. To quantify this change, hydroxyl index (HI) was calculated from C2 component of C_{1s} data as follows:

$$HI = \frac{C2_{\text{Modified}}}{C2_{\text{Unmodified}}} \quad (2)$$

where $C2_{\text{Modified}}$ and $C2_{\text{Unmodified}}$ represent C2 after modification and in the unmodified wood particles, respectively.

A complimentary technique to FTIR and XPS analyses, titrimetric analysis, was also performed on unmodified and modified wood particles to provide additional proof of the esterification reaction, and to elucidate the mechanism of the chemical reaction between wood and MAPE. Titrations were carried out

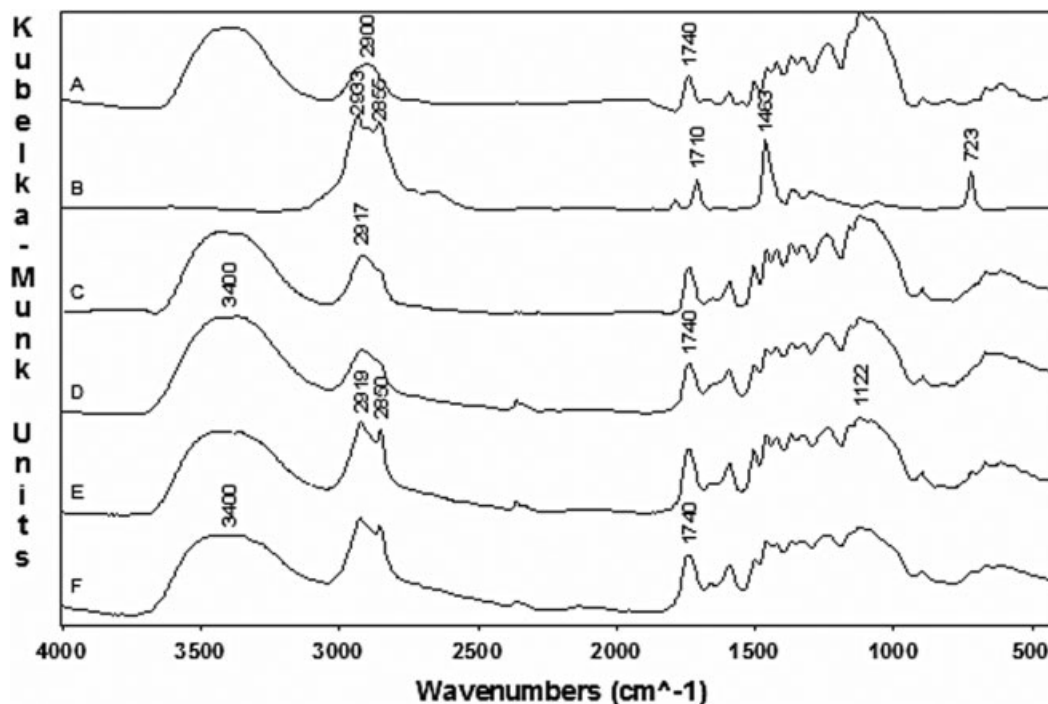


Figure 3 FTIR spectra of unmodified wood particles (spectrum A), pure MAPE (spectrum B), wood particles modified with 5% MAPE (spectrum C), 10% MAPE (spectrum D), 15% MAPE (spectrum E), and 20% MAPE (spectrum F) after a second 24-h Soxhlet extraction in the region 4000–400 cm^{-1} .

following a procedure described elsewhere,¹⁷ using an Oakton pH CON 510 pH meter. Accurate endpoints were difficult to determine when a visual indicator was used, because wood particles significantly darkened the solution color. To ensure greater accuracy, potentiometric titrations were used with a first derivative method for endpoint determination.¹⁸ Four samples each of unmodified and modified wood particles were analyzed for acid value (AV), saponification value (SV), and hydroxyl value (HV). AV accounts for the amount of free carboxylic acid groups present in the sample, while SV measures both acid and ester groups in the sample. HV quantifies the free and accessible hydroxyl groups present in the sample.¹⁷ These quantities were calculated using the following formulas:¹⁷

$$AV = 56.1 \frac{N}{p} \quad (3)$$

$$SV = 56.1(b - a) \frac{N}{p} \quad (4)$$

$$HV = [(b - a)N(56.1)] + AV \quad (5)$$

where N is the normality of potassium hydroxide (KOH), p is the amount in grams of wood particles, b is the volume of KOH needed to neutralize the blank (solvent only), and a is the volume of KOH required to

neutralize the sample. The factor 56.1 accounts for the molecular weight of KOH.

RESULTS AND DISCUSSION

Effect of MAPE content

FTIR spectroscopy was used to monitor and quantify changes that occurred on the surface of wood particles, after reactive extrusion with MAPE. Infrared spectra of unmodified wood particles, pure MAPE, and wood particles modified with various concentrations of MAPE are shown in Figure 3. Table III lists the wavenumbers of peaks found in these spectra, along with the assignments of corresponding functional groups. Regardless of the MAPE content, evidence of the grafting of MAPE compound to the surface of wood particles was apparent in the spectra of modified wood particles (spectra C–F). A distinct change was clearly seen near the absorption band at 2900 cm^{-1} , where a large band between 2920 and 2850 cm^{-1} , having two distinct peaks similar in appearance to pure MAPE (spectrum B) replaced the single peak in the unmodified wood particle (spectrum A). This change was most noticeable at MAPE concentrations above 10%, where the integrated area under the absorption band near 2900 cm^{-1} increased in the modified wood particles compared to the unmodified ones, implying the grafting of the pendant polyethylene

TABLE III
FTIR Absorption Bands and Assignments for Unmodified Wood Particles, Pure MAPE, Pure MAPP,
and Modified Wood Particles

wood (cm^{-1})	Pure MAPE (cm^{-1})	Pure MAPP (cm^{-1})	Wood particles modified with MAPE (cm^{-1})	Wood particles modified with MAPP (cm^{-1})	Peak assignments	References
3500–3100	—	—	3500–3100	3500–3100	OH stretching	10,14,19
2900	2933–2855	2960–2839	2925–2852	2951–2840	CH stretching of CH_2 , CH_3	10,14,19
—	1775	1775	—	—	Anhydride $\text{C}=\text{O}$ stretching	10,19
1740	—	—	1740	1740	$\text{C}=\text{O}$ stretching (ester carbonyl)	6,9,10,13,19
—	1710	1713	—	—	$\text{C}=\text{O}$ stretching (acid carbonyl)	6,9,10,13,19
1590–1400	—	—	1590–1400	1590–1400	Aromatic ring stretching	10,19
1480–1435	1463	1456	1461–1462	1460–1462	CH_2 deformation	19
1400–1300	—	1376	—	1376	CH_2 deformation	19
1240, 1122	—	1164–1166	1240, 1122	1240, 1122–1128	$\text{C}-\text{O}$ and $\text{C}-\text{O}-\text{C}$ stretching,	10,13,19
—	—	997–809	—	—	OH deformation	19
—	723	—	—	—	CH rocking vibration	19
					$(\text{CH}_2)_n$ rocking vibration ($n > 3$)	19

chain of MAPE to the surface of wood particles. Similarly, the integrated area under the absorption band near 1740 cm^{-1} has significantly increased for wood particles extruded with MAPE compound. Several authors have correlated the increased integrated area or peak height of this band with the esterification reaction between wood particles and maleated compounds, since absorbance in the range of $1725\text{--}1750 \text{ cm}^{-1}$ is characteristic of ester carbonyl stretching.^{5–10,12–14,19}

The grafting efficiency of wood particles with various MAPE contents through a reactive extrusion process was quantified, by calculating the GI (eq. (1)) from the integrated area under the peaks near 2900 and 1740 cm^{-1} for unmodified and modified wood particles. Figure 4 clearly illustrates that GI increased with the MAPE content up to 15%, independent of the absorption peak used. There appeared to be some leveling off between 15 and 20% MAPE concentration, which may indicate that a level of maximum grafting efficiency has been reached. These results suggest that the esterification reaction was a function of the MAPE concentration used.

XPS and titrimetric data listed in Tables IV and V, respectively, corroborated the conclusions drawn from FTIR analysis. As expected, reactive extrusion of wood particles with MAPE caused an increase in the concentration of unoxidized carbon atoms (C1 component) and decreased the contents of oxidized carbon atoms (C2–C4 components). Consequently, a significant decrease of the O/C atomic ratios was observed, because of the presence of aliphatic carbons of polyethylene chains of MAPE. Furthermore, both the HI (in Table IV) and the free and accessible hydroxyl groups (HV in Table V) have significantly decreased after modification with MAPE compounds through a reactive extrusion process. The decrease in both HI and free and accessible hydroxyl groups after modification implied that esterification reaction took place

through the hydroxyl groups on the surface of the wood particles.

Unlike FTIR, which clearly showed an increase in ester carbonyl as a function of MAPE content, C3 component (carbonyl groups) showed a decreasing trend as MAPE content increased, while C4 component (ester groups) was not detected at all on the surface of the modified wood particles. This apparent difference can be explained by the higher surface sensitivity of XPS, which has a probing depth of only a few nanometers.^{11,16} Unoxidized carbon from the pendant polyolefin chain of MAPE was concentrated on the wood particle surface, as evidenced by the high content of C1 component (Table IV), and may have

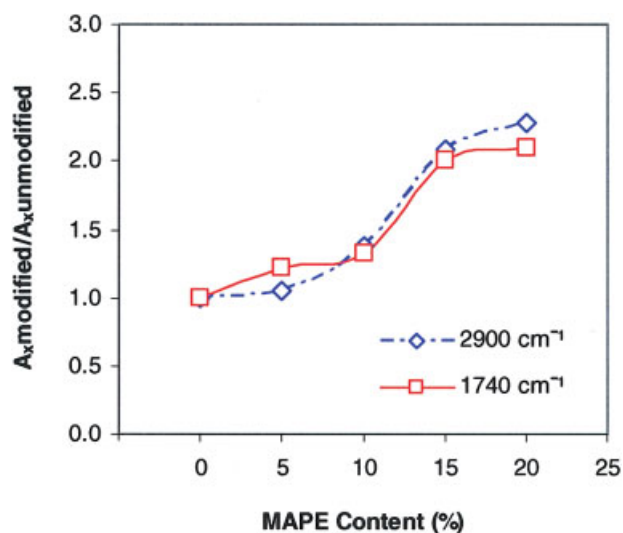


Figure 4 GI for FTIR absorbance bands near 2900 and 1740 cm^{-1} for unmodified wood particles and wood particles modified with 5–20% MAPE. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE IV
Elemental Surface Compositions and High-Resolution C_{1s} Peaks of Wood Particles, Determined by XPS

Materials ^a	Elemental compositions (%)			O/C atomic ratios	Analysis of C _{1s} peaks (%)				OH index (HI) ^c
	O	C	Zn ^b		C1	C2	C3	C4	
Unmodified wood particles	31.85	68.15	0.00	0.47	39.75	51.20	8.46	0.58	1.00
Pure MAPE	10.09	89.91	0.00	0.11	87.13	7.71	5.16	0.00	0.15
Wood particles modified with 5% MAPE	15.44	83.69	0.87	0.18	82.22	13.30	4.48	0.00	0.26
Wood particles modified with 10% MAPE	11.97	87.39	0.64	0.14	85.32	10.97	3.71	0.00	0.21
Wood particles modified with 15% MAPE	6.37	93.39	0.24	0.07	92.80	5.29	1.91	0.00	0.10
Wood particles modified with 20% MAPE	2.97	97.03	0.00	0.03	95.08	4.34	0.58	0.00	0.08

^a Unmodified and modified wood particles used were those obtained after a second 24-h Soxhlet extraction.

^b Zn from the esterification catalyst was detected in some samples.

^c OH index calculated from eq. (2).

obstructed the detection of C3 and C4 components during XPS analysis.

As shown in Figure 1, two possible reactions could occur between MAPE and wood particles in a reactive extrusion process: a single site reaction, which led to the formation of a monoester with carboxylic acid pendant groups (Fig. 1(a)) or a diester formation without carboxylic acid pendant groups (Fig. 1(b)).^{9,13} AV and SV determined by titrimetric analysis (Table V) were used to elucidate, which reaction had occurred. The AV, which accounts for the free carboxylic acid group content in the system, slightly increased in the samples after modification (Table V). However, this increase was not significant compared to the unmodified wood particles. Thus, there was a negligible amount of free carboxylic acid groups in the system. By contrast, the SV, which accounts for both ester and acid groups, increased significantly after modification (Table V). Since there was a negligible amount of free carboxylic acid groups on the surface of the modified wood particles, the increased SV originated mainly from the formation of maleate ester with OH groups on the wood particle surface. This result suggests that most of the MAPE was attached to the wood particle

surface via two acid groups from the cyclic anhydride of the MAPE, i.e., through diesterification reaction (Fig. 1(b)). Moreover, FTIR spectra, shown in Figure 3, support this mechanism. Two distinct peaks in the range of 1700–1750 cm⁻¹ should have been detected if the esterification reaction had occurred through monoester reaction.^{6,9,13} The first peak at around 1705–1710 cm⁻¹ is associated with the nonreacted carboxylic acid (monoester formation), whereas the second one near 1725–1750 cm⁻¹ is caused by the ester carbonyl absorption of the reacted MAPE with the OH groups of wood (diester formation).^{6,9,13} As seen in Figure 3, all the spectra of modified wood particles showed only one peak at 1740 cm⁻¹, which is characteristic of ester carbonyl, and the absence of bands at 1705–1710 cm⁻¹ in these spectra clearly proved that there were no free carboxylic acid groups in the samples, thus confirming diester formation.

The relatively high temperature (160°C), used to modify the wood particles in the reactive extrusion process, may also explain why the diester form was predominant in this system. Other authors have reported higher monoester formation in the reaction of maleated compounds with wood particles in solvents

TABLE V
Hydroxyl Value, Acid Value, and Saponification Value, Determined by Titrimetric Analysis

Wood particles ^a	Titration values ^b (eq/kg)		
	Hydroxyl value (HV)	Acid value (AV)	Saponification value (SV)
Unmodified	268 ± 4	3.15 ± 0.11	64 ± 6
Modified with 5% MAPE	233 ± 8	3.37 ± 0.23	65 ± 4
Modified with 10% MAPE	233 ± 26	3.53 ± 0.12	79 ± 8
Modified with 15% MAPE	217 ± 11	3.87 ± 0.20	132 ± 10
Modified with 20% MAPE	215 ± 3	4.00 ± 0.24	131 ± 8

^a Unmodified and modified wood particles used were those obtained after a second 24-h Soxhlet extraction.

^b Titration values represent an average of four samples.

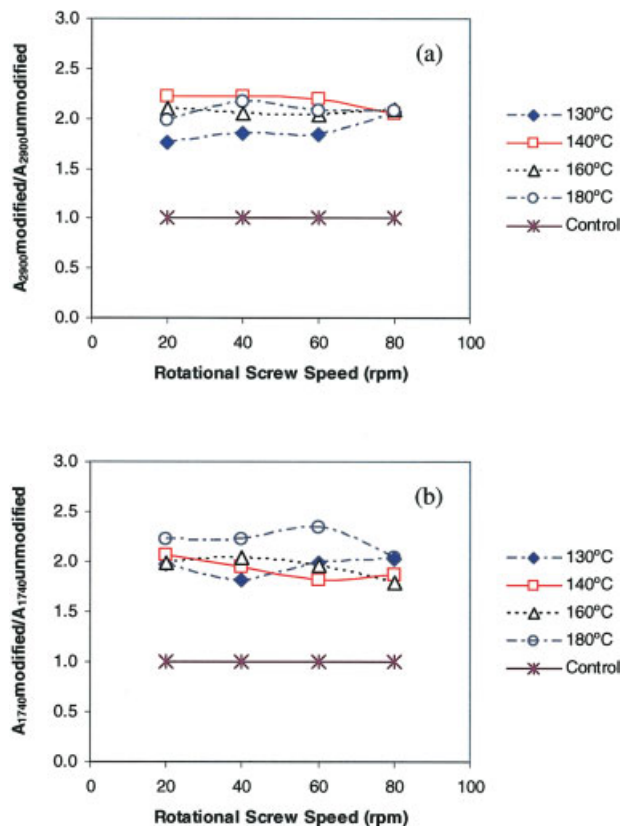


Figure 5 Effect of processing conditions on GI for unmodified and modified wood particles over the range of extruder barrel temperature and rotational screw speed combinations: (a) band near 2900 cm^{-1} and (b) band near 1740 cm^{-1} . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

at room temperature.^{3–8} Additional heat was required to cause the second acid group of the maleated compound to react with wood particles, forming the diester.^{4,6} Hon and Xing determined that diesters began to increase in their system at temperatures above 140°C .⁴ Similarly, Felix and Gatenholm found more diester content than monoester in cellulosic particles modified with MAPP at 100°C .¹³ Since the temperature used for reactive extrusion of wood particles in this study was even higher than those reported by

other authors, it was likely sufficient to cause the reaction of both acid groups in the MAPE, with hydroxyl groups on the wood particle surface, resulting in diester as the primary ester form.

Although AV and SV were calculated, it was not possible to quantify the total ester content in these samples, because calculation of monoester, diester, and total ester content require sample weight gain after modification.^{3,4} During reactive extrusion process, waste material is produced at the beginning and end of the run, so not all modified sample can be collected. Even without this information, evidence of the grafting reaction suggests that reactive extrusion is an efficient process for modifying wood particles with binding agents, such as MAPE compounds.

Effect of extrusion processing conditions

In a prior part of this study, wood particles were modified at a constant extrusion temperature profile (160°C) and rotational screw speed (60 rpm). Since the chemical reaction between wood particles and maleated polyolefins can be affected by both temperature and residence time in the extruder, it was important to understand how these extrusion processing conditions would affect the grafting efficiency of wood particles modified through reactive extrusion.

Figure 5 shows the GIs for the absorption bands near 2900 cm^{-1} (Fig. 5(a)) and 1740 cm^{-1} (Fig. 5(b)) plotted for each extruder barrel temperature, over the range of rotational screw speeds investigated. There was a clear indication that the GIs increased after modification, irrespective of the extrusion temperature profile and rotational screw speed used. The increased GI values indicated that more CH_2 and $\text{C}=\text{O}$ groups had been attached to the wood particle surface, which implied that the esterification reaction had occurred between the wood particles and MAPE. However, surface modification was not a function of processing conditions used, since no trend in GI was observed with increasing the extruder's temperature profile or increasing rotational screw speed for either absorbance band.

TABLE VI
Effect of Extruder's Rotational Screw Speed on Surface Chemistry of Wood Particles, Modified with 20% MAPE at 160°C

Extruder's rotational screw speed (rpm)	Elemental compositions (%)		O/C atomic ratios	Analysis of C_{1s} peaks (%)				OH index (HI)
	O	C		C1	C2	C3	C4	
Unextruded (control)	31.85	68.15	0.47	39.75	51.20	8.46	0.58	1.00
20	5.61	94.39	0.06	92.62	5.12	2.26	0.00	0.10
40	3.72	96.28	0.04	95.80	3.40	0.80	0.00	0.07
60	2.39	97.61	0.02	96.90	3.10	0.00	0.00	0.06
80	2.97	97.03	0.03	95.08	4.34	0.58	0.00	0.08

TABLE VII
Effect of Extruder's Barrel Temperature on Surface Chemistry of Wood Particles, Modified with 20% MAPE at 60 rpm

Extruder's barrel temperature (°C)	Elemental compositions (%)		O/C atomic ratios	Analysis of C _{1s} peaks (%)				OH index (HI)
	O	C		C1	C2	C3	C4	
Unextruded (control)	31.85	68.15	0.47	39.75	51.20	8.46	0.58	1.00
130	3.36	96.64	0.03	95.27	3.04	1.69	0.00	0.06
140	5.47	94.53	0.06	92.61	5.26	2.12	0.00	0.10
160	2.39	97.61	0.02	96.90	3.10	0.00	0.00	0.06
180	5.05	94.95	0.05	95.24	4.76	0.00	0.00	0.09

XPS results agreed with the aforementioned conclusions, obtained from the infrared spectroscopy (Tables VI and VII). Changing the extruder's rotational screw speeds while maintaining a constant temperature profile (Table VI) or vice versa (Table VII) did not affect the grafting efficiency. In both cases, it was apparent that the surfaces of modified wood particles had been chemically changed from the unmodified wood particles, as evidenced by the large increase in the concentration of unoxidized carbon atoms (C1 component) coupled with a significant reduction in both the O/C atomic ratios and HIs, under all processing conditions. However, no trend was observed in C1, HI, or the O/C atomic ratio, as the extruder's rotational screw speed or barrel temperature was increased.

Effect of MAPP molecular weight

Maleated polyolefins with a wide variety of molecular weights are available in the market. Four different

MAPP compounds were used (Table I) to determine how different molecular weights (from a low of 11,200 to a high of 52,000 g/mol) affect the surface modification of wood particles in reactive extrusion process. To achieve this objective, the MAPP content was held constant at 20%, while the extrusion temperature profile and rotational speed of the screws were set at 160°C and 60 rpm, respectively.

Figures 6 and 7 illustrate the FTIR spectra of pure MAPP compounds, with various molecular weights and wood particles modified with these MAPPs, respectively. The peak assignments for these spectra are also listed in Table III. Evidence of the grafting of MAPP to the wood particles through esterification is apparent in the modified wood spectra (Fig. 7, spectra B–E), because the single absorption band near 2900 cm⁻¹ in the spectrum of unmodified wood particles has been replaced by a large band between 2955 and 2840 cm⁻¹, having distinct peaks similar in appear-

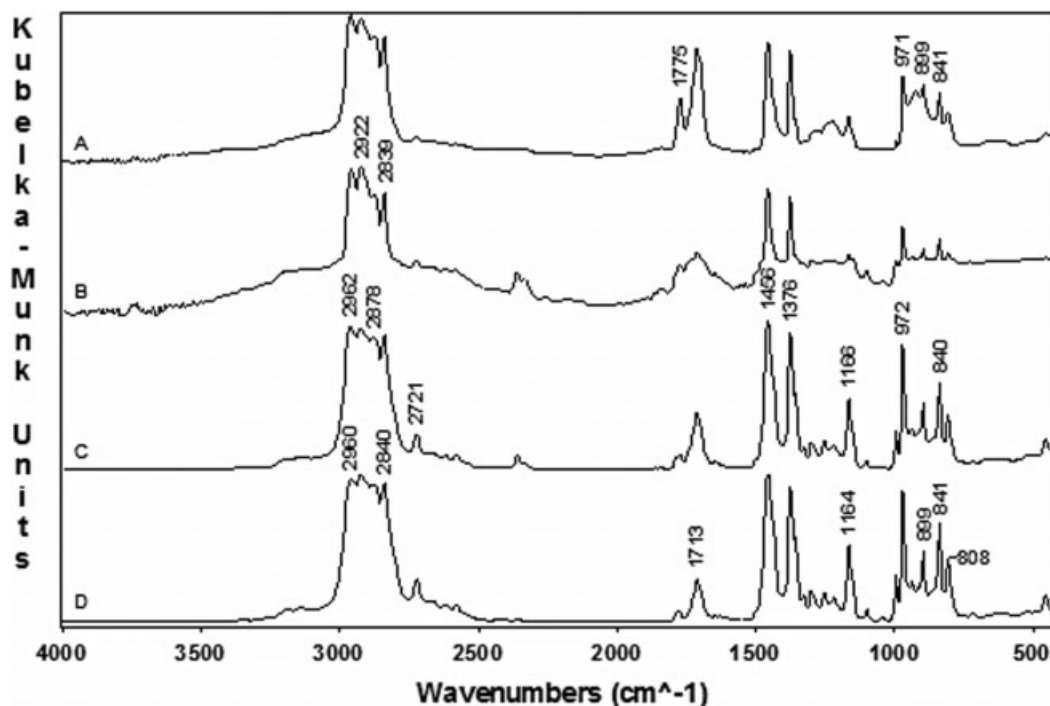


Figure 6 FTIR spectra of pure MAPP compounds with various molecular weights: 11,200 g/mol or E-43 (spectrum A), 39,000 g/mol or G-3216 (spectrum B), 47,000 g/mol or G-3015 (spectrum C), and 52,000 g/mol or G-3003 (spectrum D) in the region 4000–400 cm⁻¹.

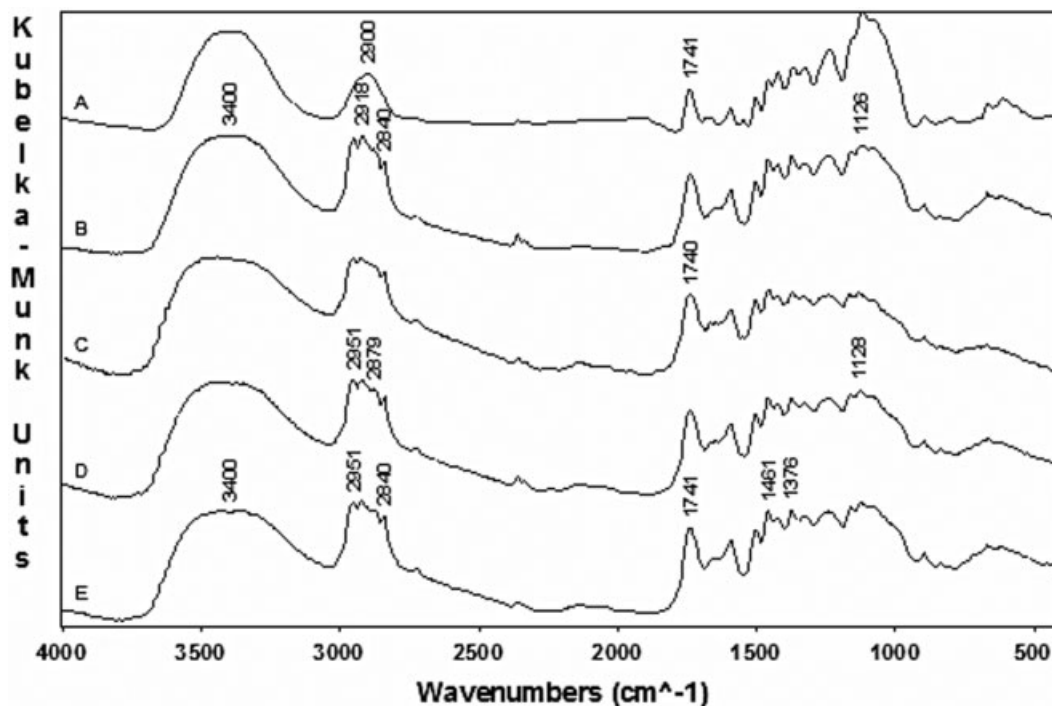


Figure 7 FTIR spectra of unmodified wood particles (spectrum A), wood particles modified with MAPP compounds of various molecular weights: 11,200 g/mol or E-43 (spectrum B), 39,000 g/mol or G-3216 (spectrum C), 47,000 g/mol or G-3015 (spectrum D), and 52,000 g/mol or G-3003 (spectrum E) in the region 4000–400 cm^{-1} .

ance to the pure MAPP counterparts. Another indication of grafting of the maleated polyolefin was an increased area of the absorption band at around 1740 cm^{-1} , from C=O groups attached to the wood surface, likely from the esterification reaction.^{5–10,12–14} Although not clearly seen in Figure 7 due to stacking of five spectra in one figure, the individual spectra of modified wood particles showed an increased intensity in the bands at 1462 and 1376 cm^{-1} , which also indicated that the grafting reaction had occurred and added more C—H to the surface of the modified samples.^{10,12,14}

Moreover, all four MAPP compounds had significantly increased GIs, when compared to unmodified wood particles (Fig. 8). However, no significant difference in GI was observed between the four types of MAPP-modified wood particles. These results were in agreement with those obtained from the XPS analysis (Table VIII). As expected, the surface of the modified wood particles resulted in an increased C1 content and a significant decrease in both O/C atomic ratio and HI, all of which provided evidence of the surface modification through esterification reaction.

However, no distinct trend was observed between molecular weight of MAPP and grafting efficiency, through a reactive extrusion process. Since both FTIR and XPS results confirmed that there was no significant differences in grafting of MAPP with various molecular weights, the molecular weight range stud-

ied (11,200–52,000 g/mol) may not have been large enough to observe differences in reactivity. Another possibility could be that at 20% MAPP content, the maximum level of grafting had already been achieved with each compound, regardless of its molecular

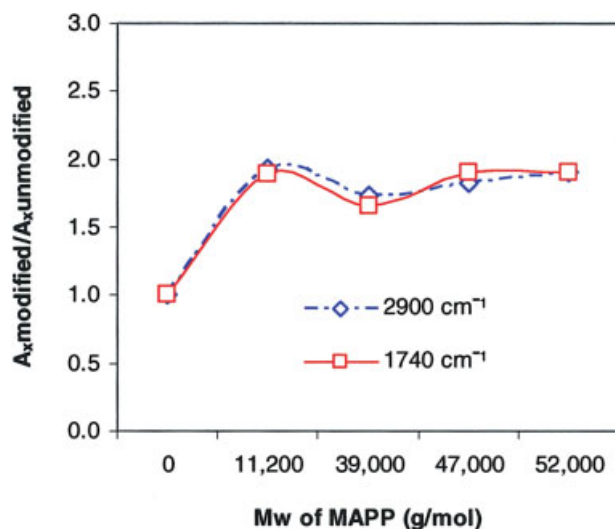


Figure 8 Effect of molecular weight on GI for unmodified wood particles and wood particles modified with 20% MAPP compounds. [Color figure can be viewed in the on-line issue, which is available at www.interscience.wiley.com.]

TABLE VIII
Elemental Surface Compositions and High-Resolution C_{1s} Peaks of MAPP, Wood Particles, and Wood Particles Modified with MAPP, Determined by XPS

Materials	Elemental compositions (%)		O/C atomic ratios	Analysis of C _{1s} peaks (%)				OH index (HI)
	O	C		C1	C2	C3	C4	
E-43 ($M_w = 11,200$)	4.89	95.11	0.05	94.92	4.35	0.74	0	0.08
G-3216 ($M_w = 39,000$)	3.86	96.14	0.04	95.85	3.24	0.91	0	0.06
G-3015 ($M_w = 47,000$)	3.77	96.23	0.04	96.01	2.62	1.37	0	0.05
G-3003 ($M_w = 52,000$)	3.28	96.72	0.03	96.58	2.57	0.84	0	0.05
Unmodified Wood	31.85	68.15	0.47	39.75	51.20	8.46	0.58	1.00
Wood-E-43	7.22	92.78	0.08	93.39	4.75	1.86	0	0.09
Wood-G-3216	3.60	96.40	0.04	94.86	4.17	0.97	0	0.08
Wood-G-3015	3.36	96.64	0.04	95.38	4.20	0.42	0	0.08
Wood-G-3003	5.87	94.13	0.06	90.99	6.19	2.83	0	0.12

weight. Thus, the differences in the grafting efficiency were not detected. Moreover, Figure 4 clearly illustrates that the GI leveled off between 15 and 20% maleated polyolefin content, which may indicate that a level of maximum grafting efficiency had been reached. Perhaps another study at lower MAPP concentrations would elucidate differences of MAPP molecular weight on the efficiency of the grafting reaction.

CONCLUSIONS

This study examined the chemical reactions between maleated polyolefins and wood particles in a reactive extrusion process. The effects of MAPE content, extrusion processing conditions (barrel temperature and rotational screw speed), and molecular weight of MAPP were studied, with the goal of determining the effects of each set of conditions on the grafting efficiency of modified wood particles in a reactive extrusion process. Efficiency of the modification was evaluated using FTIR, XPS, and titrimetric analysis. From the experimental results, the following conclusions can be drawn:

1. The esterification reaction between wood particles and MAPE was a function of the MAPE concentration, used to modify the wood particles. The grafting reaction produced mostly the diester form of the modified wood particle during reactive extrusion.
2. No significant difference was found in grafting efficiency of the modified wood particles at different extrusion processing conditions. Changing extruder's barrel temperature profile (130–180°C) or its rotational screw speed (20–80 rpm) resulted in adequate grafting, which indicated that the esterification reaction was not a function of processing conditions.
3. Regardless of MAPP molecular weight (from a low of 11,200 to a high of 52,000 g/mol), all investigated MAPP compounds were effective in changing the surface of wood particles after modification, compared to unmodified wood particles. However, no distinct trend was observed between molecular weight of MAPP and grafting efficiency through a reactive extrusion process. Regardless of molecular weight, it is believed that the high content of MAPP (20%) used in this study prevented the detection of differences in the grafting efficiency, because the level of maximum grafting reaction had already occurred with each compound at 20% MAPP content.
4. The reactive extrusion process was found to be a suitable way to modify wood particles with maleated polyolefins, as it worked quickly and without the use of solvents. This process would be industrially friendly, and in the light of our prior success, bonding the modified fibers together in a hot press would allow large quantities of modified wood particles to be produced, for the manufacture of a formaldehyde-free wood composite product.

The authors gratefully acknowledge Dr. Richard K. Stuart, Jr. and Mr. Travis J. Keener of Eastman Chemical Co. (Kingsport, TN) and Mr. Michael J. Piszcor of American Wood Fibers (Schofield, WI) for the kind donation of supplies.

References

1. Carlborn, K.; Matuana, L. M. *Polym Compos* 2005, 26, 534.
2. Matuana, L. M.; Carlborn, K. U.S. Provisional Pat. 60/592,918 (2004).
3. Matsuda, H. *Wood Sci Technol* 1987, 21, 75.

4. Hon, D. N.-S.; Xing, L.-M. In *Viscoelasticity of Biomaterials*; Glasser, W. G., Hatakeyama, H., Eds.; American Chemical Society: Washington, DC, 1992; p 118.
5. Marcovich, N. E.; Reboledo, M. M.; Aranguren, M. I. *Holz Roh Werkst* 1996, 54, 189.
6. Aranguren, M. I.; Marcovich, N. E.; Reboledo, M. M. In *Recent Advances in Biotechnology for Tree Conservation and Management*, Proceeding of an IFS Workshop, Brazil, 1998; International Foundation for Science (IFS): Stockholm, 1998; p 180.
7. Timar, M. C.; Mihai, M. D.; Maher, K.; Irle, M. *Holzforchung* 2000, 54, 71.
8. Timar, M. C.; Maher, K.; Irle, M.; Mihai, M. D. *Holzforchung* 2000, 54, 77.
9. Matuana, L. M.; Balatinecz, J. J.; Sodhi, R. N. S.; Park, C. B. *Wood Sci Technol* 2001, 35, 191.
10. Kazayawoko, M.; Balatinecz, J. J.; Woodhams, R. T. *J Appl Polym Sci* 1997, 66, 1163.
11. Kazayawoko, M.; Balatinecz, J. J.; Sodhi, R. N. S. *Wood Sci Technol* 1999, 33, 359.
12. Kazayawoko, M.; Balatinecz, J. J.; Matuana, L. M. *J Mater Sci* 1999, 34, 6189.
13. Felix, J. M.; Gatenholm, P. *J Appl Polym Sci* 1991, 42, 609.
14. Li, Q.; Matuana, L. M. *J Appl Polym Sci* 2003, 88, 278.
15. Cheremisinoff, N. *Guidebook to Extrusion Technology*; Prentice-Hall: Englewood Cliffs, NJ, 1993; Chapter 5.
16. Ratner, B. D.; Castner, D. G. In *Surface Analysis, The Principal Techniques*; Vickerman, J. C., Ed.; Wiley: New York, 1997; Chapter 3.
17. Anonymous. *Pure Appl Chem* 1973, 33, 417.
18. Harris, D. C. *Qualitative Chemical Analysis*, 4th ed.; W.H. Freeman: New York, 1995; Chapter 12.
19. Socrates, G. *Infrared Characteristic Group Frequencies, Tables and Charts*, 2nd ed.; Wiley: New York, 1994.