

Further Investigation of Polyaminoamide-Epichlorohydrin/Stearic Anhydride Compatibilizer System for Wood-Polyethylene Composites

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ABSTRACT: The combination of a polyaminoamide-epichlorohydrin (PAE) resin (a paper wet strength agent) and stearic anhydride was recently reported as an effective compatibilizer system for wood-polyethylene composites. Further investigation of this new compatibilizer system revealed that the pH value of a PAE solution, dosages of PAE and stearic anhydride, and the weight ratio of PAE to stearic anhydride had significant impacts on the compatibilization effects of the compatibilizer system. Adjusting the pH value of the PAE solution from 5.0 to 10.4 increased the strength of the resulting wood-polyethylene composites. The highest strength of the resulting wood-polyethylene composites was obtained at 3 wt % PAE and 3 wt % stearic anhydride. At 4 wt % or 6 wt % of a compatibilizer, this PAE-stearic anhydride system was superior to maleic anhydride-grafted

polyethylene (MAPE), one of the most effective compatibilizers, in terms of enhancing the strength of the resulting wood-polyethylene composites. Fourier transform infrared spectroscopy (FTIR) analysis revealed that PAE and stearic anhydride formed covalent bonding with wood flour. The compatibilization mechanisms of this PAE-stearic anhydride compatibilizer system were investigated in detail. Water-resistance tests indicated that the PAE-stearic anhydride compatibilizer system increased the water-resistance of the resulting composites. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 712–718, 2006

Key words: compatibilizer; paper wet-strength agent; polyaminoamide-epichlorohydrin; polyethylene; stearic anhydride; wood; wood-plastic composites

INTRODUCTION

Wood as a filler for strengthening thermoplastics, such as polyethylene (PE), has many advantages over commonly used inorganic fillers, such as glass fibers. For example, wood is inexpensive and renewable. Wood-filled thermoplastics products can be burned after their useful lives, thus leaving much less solid waste than inorganic-based materials-filled thermoplastics. In the past several years, wood-filled thermoplastics, commonly called wood-plastic composites (WPCs), have become one of the fastest growing composite materials in the wood composites industry. More than 700 million pounds of WPCs were produced in 2002. However, the amount of WPCs sold in 2002 was only about 5% of penetrable markets.¹ One of the obstacles preventing WPCs from gaining a bigger market share is that the strength of WPCs is still not high enough to meet strength requirements of many applications.

Wood is hydrophilic and thermoplastics are hydrophobic. Wood and thermoplastics are thus not compatible, that is, the interphase between wood and plastics is typically weak, failing to transfer stress. A cou-

pling agent, commonly called a compatibilizer, is normally added in the production of WPCs for improving the interfacial adhesion. At present, maleic anhydride-grafted PE (MAPE) and maleic anhydride-grafted polypropylene (MAPP) are commonly used compatibilizers for WPCs. However, the compatibilization effect of MAPE or MAPP is still much lower than what is potentially achievable. Moreover, the choice of compatibilizers for WPCs is still limited. In an effort to gain a better understanding of the interfacial chemistry of WPCs, we recently discovered a new compatibilizer system consisting of a polyaminoamide-epichlorohydrin (PAE) resin (a paper wet strength agent) and stearic anhydride.² In this study, this new compatibilizer system was further investigated for improvement of its compatibilization effect on wood-PE composites.

EXPERIMENTAL

Materials

Wood flour (pine flour, 0.425 mm, moisture content, 2.04%) was donated by American Wood Fibers (Schofield, WI). High density polyethylene (PE) (melt flow index, 0.55 g/10 min) was donated by BP Solvay Polyethylene North America (Houston, TX). Stearic

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TABLE I
The Composition of Wood-PE Composites

Mixing procedure	Composite	Wood flour (wt %)	MAPE (wt %)	PAE (wt %)	Stearic anhydride (wt %)	HDPE (wt %)
A	Control	40	—	—	—	60
B	MAPE2	40	2	—	—	58
	MAPE4	40	4	—	—	56
	MAPE6	40	6	—	—	54
	PAE1S1	40	—	1	1	58
C	PAE2S1	40	—	2	1	57
	PAE3S1	40	—	3	1	56
	PAE5S1	40	—	5	1	54
	PAE3S2	40	—	3	2	55
	PAE3S3	40	—	3	3	54
	PAE3S4	40	—	3	4	53
	PAE3S5	40	—	3	5	52
	PAE2S2	40	—	2	2	56

anhydride was purchased from Aldrich (Milwaukee, WI). MAPE (maleic anhydride grafted polyethylene, A-C OptiPak™ 210) was a gift from Honeywell International, Inc. (Morristown, NJ). The PAE resin used in this study was Kymene® 557H (12.5% aqueous solution) that was donated by Hercules Inc. (Wilmington, DE).

Preparation of wood-PE composites

Wood-PE composites were prepared by mixing wood flour and PE powder in the presence or absence of a compatibilizer in a Brabender Plasticorder with roller blade mixing bowl attached (C. W. Brabender Instruments, Inc., South Hackensack, NJ), followed by compression molding of the mixed material in a stainless steel mold. Mixing procedures varied with the compatibilizer used. The composition of wood-PE composites and the mixing procedure are listed in Table I. *Mixing procedure a.* Mixing procedure A was mixing wood flour and PE without a compatibilizer. The bowl of the Brabender Plasticorder was preheated to 120°C and the speed of the rotors in the bowl set to 100 rpm. Wood flour (17.96 g) was added and blended for 10 min. The bowl temperature was then raised to 170°C and HDPE (26.40 g) was added and blended for 5 min. The contents were then removed from the Brabender and stored for compression molding.

Mixing procedure b. Mixing procedure B was mixing wood flour, PE, and MAPE. The Brabender bowl was preheated to 120°C and the rotor speed was set to 100 rpm. Wood flour (17.96 g) was then added to the bowl. After the bowl temperature was returned to 120°C, MAPE was added and mixed for 10 min. The bowl temperature was then raised to 170°C and PE was added and mixed for 5 min. The contents were then removed from the Brabender and stored for compression molding.

Mixing procedure c. Mixing procedure C was used for preparing wood-PE composites with a PAE-stearic anhydride compatibilizer. The following is an example of the mixing procedure for preparing wood-PE composites with wood/PAE/stearic anhydride/PE weight ratio of 40/2/1/57. The PAE solution (7.04 mL, 0.88 g dry weight) was diluted with de-ionized water (36.96 mL). The diluted PAE solution was adjusted to the predetermined pH value by adding 1.5M aqueous sodium hydroxide solution. Then, wood flour (17.96 g) was added to the diluted PAE solution and mixed well by mechanical stirring. The resulting wood-PAE mixture was dried at 104°C for about 20 h. The oven-dry wood-PAE mixture was added to the preheated Brabender bowl at 120°C. After the bowl temperature was returned to 120°C, stearic anhydride was added and mixed for 10 min. The bowl temperature was then raised to 170°C and PE was added and mixed for 5 min. The contents were then removed from the Brabender and stored for compression molding.

*Press procedure.*² A stainless steel mold with dimensions of 101.6 × 101.6 × 2 mm was used to compression mold the wood-PE composites into boards. The platens of an automatic benchtop press (Carver, Inc., Wabash, IN) were preheated to 185°C. The mold was filled with the well-mixed wood-PE sample, placed on the lower platen of the Carver press, and preheated for 10 min. The press was closed slowly, allowing the wood-plastic to flow into the mold shape. The press pressure was raised from 34.5 to 344.8 kPa in two min, and the mold was pressed at 344.8 kPa for an additional 10 min. The mold was then removed from the hot press and cooled under clamps at ambient conditions. The resulting wood-PE sample was cut into 10 small test specimens. Each specimen had dimensions of 52.46–56.46 mm of length, 10.70–14.28 mm of width, and 2.10–3.10 mm of thickness.

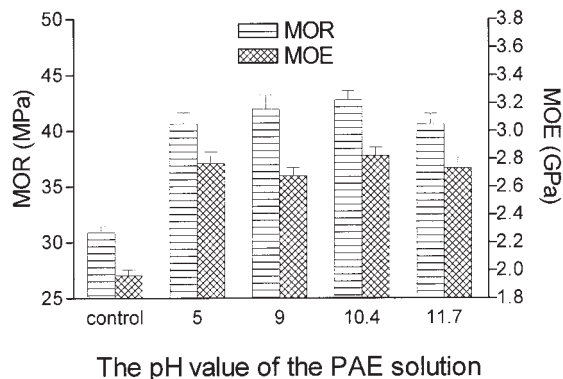


Figure 1 Effect of pH value of the PAE solution on MOR and MOE of wood-PE composites. Control: wood/PE weight ratio = 40/60; the weight ratio in other wood-PE composites: wood/PAE/stearic anhydride/PE = 40/2/1/57. Data are the mean of at least ten replicates, and the error bars represent one standard error of the mean.

Determination of the strength and stiffness of the wood-PE composites

This test method was basically the same as described in our previous article.² The small specimens were tested on a Sintech machine (MTS Systems Corp., Enumclaw, WA) and the load-deflection curves determined. The support span was 43 mm and the cross-head speed was 1.0 mm/min. At least 10 specimens were tested for each wood-PE composite, in accordance with ASTM D790-02. All specimens showed a yielding fracture mode. The modulus of rupture (MOR) and modulus of elasticity (MOE) were calculated from the load-deflection data. The MOR was defined as the first point on the load-deflection curve to show a slope of zero. The MOE was determined from the slope in the initial elastic region of the load-deflection curve.

Water-Resistance test

Five specimens of each wood-PE composite were used for the water-resistance test. All specimens were pre-weighed and then soaked in water at room temperature. The specimens were taken out of water, wiped with tissue paper, weighed once every 24 h for the first five days, and then weighed at a longer time interval until day 65. The water uptake percentage was determined from the weight gain divided by the dry weight of the specimens.

Removal of PE from wood-PE composites

Four wood-PE composites were investigated in this set of experiments: (1) the composite without any compatibilizer, (2) the composite with 3 wt % PAE at pH 10.4, (3) the composite with 3 wt % stearic anhy-

dride, and (4) the composite with 3 wt % stearic anhydride and 3 wt % PAE at pH 10.4. The wood-PE composites were cut into small pieces by a fodder chopper, and wrapped in filter paper. The wrapped wood-PE composite specimens were extracted with *p*-xylene in a modified Soxhlet extractor for 48 h. The thimble holder of the Soxhlet extractor was wrapped with heating tape and heated to maintain the temperature of the solution in the thimble at about 120°C. The extracted wood residue was dried and characterized with FTIR.

RESULTS

The effect of the pH value of the PAE solution on the MOR and MOE of the resulting wood-PE was investigated at the 40/2/1/57 wood/PAE/stearic anhydride/PE weight ratio (Fig. 1). At all pH values studied, both MOR and MOE were higher than those of the control, that is, without the PAE-stearic anhydride compatibilizer. There were no statistically significant changes in either MOR or MOE of the resulting composites when the pH value of the PAE solution was adjusted from 5.0 (the original pH value of the PAE solution) to 9.0 (Fig. 1). When the pH value was further increased to 10.4, the MOR at pH 10.4 was significantly higher than that at pH 5.0, whereas the MOE at pH 10.4 was still statistically the same as that at pH 5.0 (Fig. 1). However, both MOR and MOE decreased with a further increase in the pH value from 10.4 to 11.7 (Fig. 1). pH 10.4 thus appeared to be the optimal pH value for the compatibilization effect.

With a pH 10.4 PAE solution and a loading of 1.0 wt % stearic anhydride (the weight percentage based on the wood-PE composite), both MOR and MOE gradually increased with increasing PAE dosage from 1 wt % to 3 wt % (Fig. 2). When the PAE dosage was further

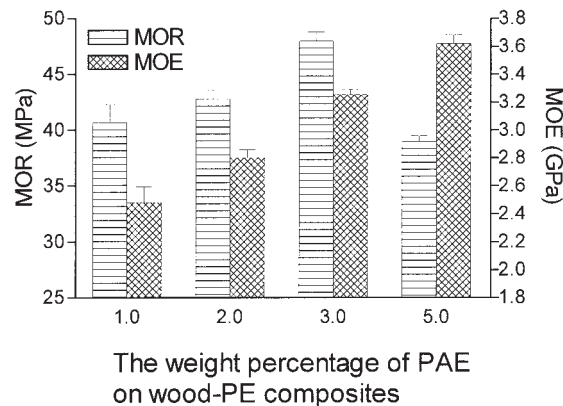


Figure 2 Effect of PAE dosage on MOR and MOE of wood-PE composites. Wood/PAE/stearic anhydride/PE weight ratio = 40/X/1/Y (X + Y = 59). Data are the mean of at least ten replicates, and the error bars represent one standard error of the mean.

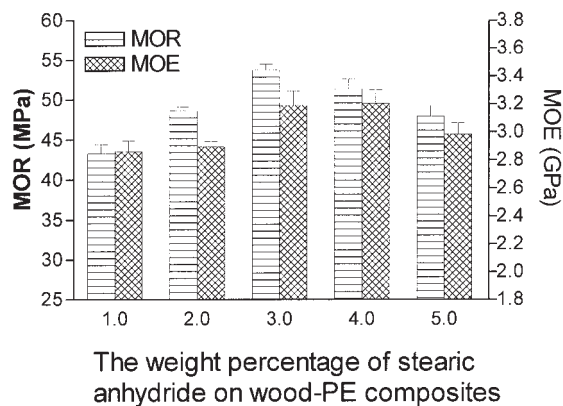


Figure 3 Effect of stearic anhydride dosage on MOR and MOE of wood-PE composites. Wood/PAE/stearic anhydride/PE weight ratio = 40/3/X/Y ($X + Y = 57$). Data are the mean of at least ten replicates, and the error bars represent one standard error of the mean.

increased from 3 wt % to 5 wt %, the MOE further increased, but the MOR significantly decreased (Fig. 2). Therefore, 3 wt % PAE was determined to be the optimal dosage of PAE, given that adding 5 wt % PAE reduced the MOR (Fig. 2).

For the wood-PE composites containing 3 wt % PAE, the MOR gradually increased with increasing stearic anhydride dosage from 1.0 wt % to 3.0 wt % (Fig. 3). The MOE at 1.0 wt % stearic anhydride was basically the same as that at 2.0 wt % stearic anhydride, and the MOE at 3.0 wt % stearic anhydride was higher than that at 1 wt % or 2 wt % (Fig. 3). However, the MOR of the wood-PE composites gradually decreased when the stearic anhydride dosage further increased from 3 wt % to 5 wt %. The MOE values at 3 wt % and 4 wt % stearic anhydride were statistically the same and were slightly higher than those at 5 wt %. Therefore, the PAE-stearic anhydride compatibilizer with 3 wt % PAE and 3 wt % stearic anhydride resulted in the highest MOR and MOE (Fig. 3).

The PAE-stearic anhydride compatibilizer system was compared with MAPE for its compatibilization effects on wood-PE composites (Fig. 4). At a 2 wt % level, that is, 1 wt % PAE plus 1 wt % stearic anhydride versus 2 wt % MAPE, MAPE resulted in higher MOR and MOE than the PAE-stearic anhydride system (Fig. 4). However, at the 4 wt % level, that is, 2 wt % PAE plus 2 wt % stearic anhydride versus 4 wt % MAPE, the MOR with the PAE-stearic anhydride system was higher than that with MAPE, and the MOE values were statistically the same (Fig. 4). The MOR value of the PAE-stearic anhydride sample was much higher than that of MAPE when the two compatibilizers were compared at the 6 wt % level (Fig. 4). The MOR and MOE were much higher at 4 wt % MAPE than those at 2 wt % or 6 wt % MAPE. The MOR and MOE at 2 wt % PAE and 2% stearic anhydride were

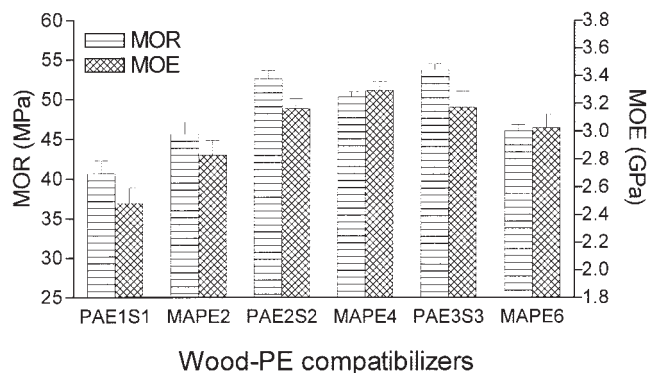


Figure 4 Comparison of the PAE-stearic anhydride compatibilizer system with MAPE. Data are the mean of at least ten replicates, and the error bars represent one standard error of the mean.

comparable to those at 3 wt % PAE and 3 wt % stearic anhydride (Fig. 4).

The water uptake of all the samples increased with increasing soaking time (Fig. 5). The wood-PE composites with 3 wt % PAE had the highest water-uptake percentages among all wood-PE composites studied (Fig. 5). However, a combination of PAE and stearic anhydride dramatically reduced the water-uptake percentages when compared with PAE alone. The wood-PE composites with the stearic anhydride and PAE-stearic anhydride compatibilizer system had similar water-uptake percentages and were more water-resistant than the control, that is, the composites without any compatibilizer. MAPE resulted in the lowest water-uptake percentages.

The HDPE used in this study was completely soluble in *p*-xylene above 100°C. The modified Soxhlet extractor efficiently removed the PE in the wood-PE composites. Extensive studies revealed that the extraction for 48 h completely removed nonchemically bonded PE and stearic anhydride-related products (stearic anhydride, stearic acid, and stearic acid esters

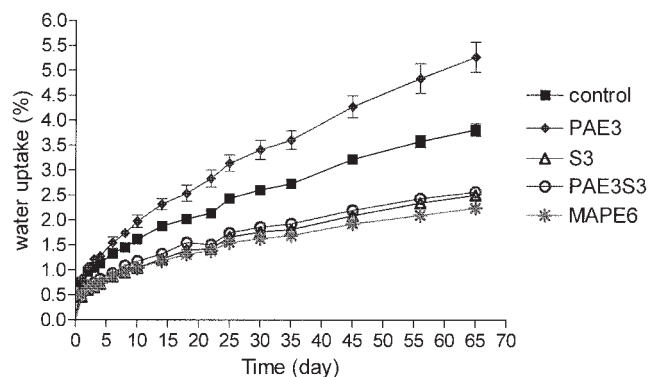


Figure 5 Water-resistance test. Data are the mean of five duplicates, and the error bars present one standard error of the mean.

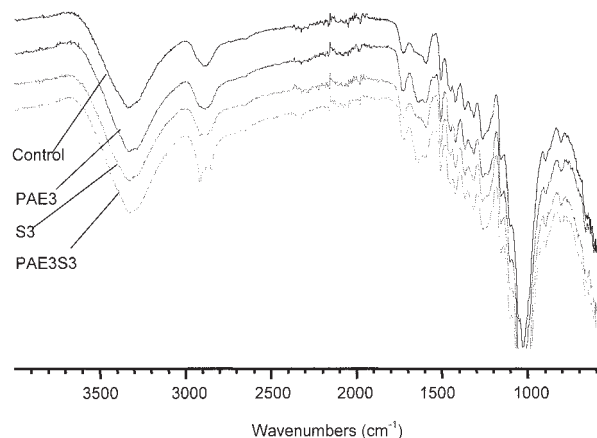


Figure 6 FTIR spectra of extracted samples.

with low molecular weights) from the wood-PE composites. FTIR spectra of the extracted wood residues are shown in Figure 6. The effects of compatibilizers on the properties of the extracted wood residues were better understood from subtracted FTIR spectra (Fig. 7). After subtracting the control, the FTIR spectrum of the residues with 3 wt % PAE (PAE3-control spectrum in Fig. 7) had weak absorbance peaks at 2920 cm^{-1} and 2850 cm^{-1} . The absorbance peaks at 2920 cm^{-1} and 2850 cm^{-1} in the S3-control FTIR spectrum were stronger than those in the PAE3-control FTIR spectrum (Fig. 7). The PAE3S3-control FTIR spectrum had stronger absorbance peaks at 2920 cm^{-1} and 2850 cm^{-1} than the S3-control spectrum and the PAE3-control spectrum (Fig. 7). The expanded spectra between 1500 cm^{-1} and 1800 cm^{-1} from Figure 7 are shown in Figure 8. All three spectra (PAE3-control, S3-control, and PAE3S3-control) had weak absorbance peaks for the carbonyl group (C=O) of esters (Fig. 8). The S3-control spectrum lacked an absorbance peak for the carbonyl group (C=O) of amides. The absorbance peak of the amide C=O for the PAE3S3-control spectrum was stronger than that for the PAE3-control spectrum (Fig. 8).

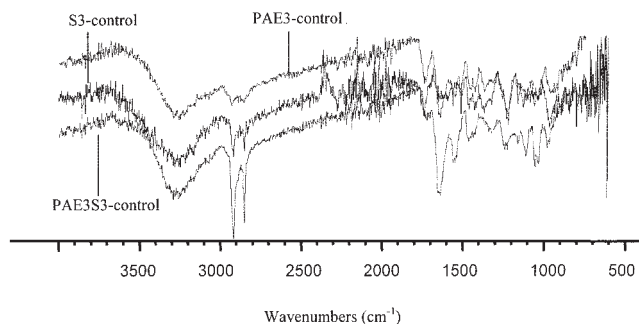


Figure 7 FTIR spectra of extracted samples with control spectrum subtracted.

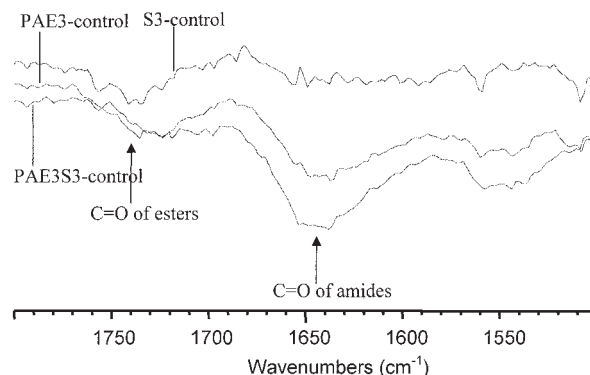


Figure 8 Expanded FTIR spectra of extracted samples with control spectrum subtracted.

DISCUSSION

As proposed in our previous study, the ability of the PAE-stearic anhydride system to improve the interfacial adhesion between wood and PE results from the following actions: (1) The PAE resin strengthens and stiffens wood fibers and serves as a wood-bonding domain; (2) The hydrocarbon chain of stearic anhydride forms entanglements or cocrystallizes with the matrix, serving as a PE-bonding domain; and (3) The anhydride functional group of stearic anhydride reacts with PAE-bonded wood, thus linking the two domains together.²

When compared to the control, the *p*-xylene-extracted wood residues containing PAE as a compatibilizer had an additional relatively strong absorbance peak at $1600\text{--}1650\text{ cm}^{-1}$, representing the C=O group of the amide linkages in the PAE resin, and additional weak absorbance peaks at 2920 cm^{-1} and 2850 cm^{-1} , representing hydrocarbon (CH_2) groups from PAE resins (Figs. 7 and 8).³ These results indicated that PAE resins indeed bonded to wood, which is also consistent with results from the application of PAE as a paper wet-strength agent.^{4,5} The extracted wood residues with stearic anhydride as a compatibilizer had additional absorbance peaks at 2920 cm^{-1} and 2850 cm^{-1} from the hydrocarbon groups of stearic anhydride and an additional absorbance peak of the carbonyl group of esters. This implies that stearic anhydride formed ester linkages with wood (see S3-control spectra in Figs. 7 and 8). The PAE3S3-control spectrum had stronger absorbance peaks for hydrocarbon at 2920 cm^{-1} and 2850 cm^{-1} and stronger absorbance peaks for the C=O group of amides than the S3-control spectrum, which demonstrated that the extracted wood residues with PAE3S3 as a compatibilizer contained a higher amount of covalently bonded stearic-anhydride-based products than those with S3 as a compatibilizer. The stronger absorbance of the carbonyl group of amides in the PAE3S3 FTIR spectrum suggested that amide linkages were likely

formed from the reactions between stearic anhydride and PAE-bonded wood. All these results support the previously proposed compatibilization mechanism, except that there was no direct evidence of entanglement/cocrystallization between the hydrocarbon chain of stearic anhydride and the HDPE matrix.

In our previous study, the PAE solution was directly mixed with wood flour without adjusting its pH value. Our results in this study indeed showed that the resulting wood-PE composites had the highest strength at pH 10.4 (Fig. 1), which was consistent with results that the highest paper wet strength for the PAE resins develops around pH 10.^{4,5} As proposed in our previous study, the PAE resin evidently strengthens and stiffens the wood fibers through homo-polymerization and covalent linkages with wood, thereby increasing the strength of the resulting composites. The hydroxy-azetidium (the cationic four-membered ring structure) is the key functional group for wet strength development in paper.⁴⁻⁶ The characteristic four-membered azetidium structure is fairly stable under acidic conditions at room temperature, but can react with various nucleophiles at elevated temperatures to form various ring-opening structures. When the pH value is increased, the nucleophilicity of some nucleophiles also increases, resulting in faster reactions between the azetidium structure and the nucleophiles. However, the rate of the undesirable reaction between the azetidium structure and the hydroxyl group of sodium hydroxide would also increase with increasing pH values, which may explain the lower MOR and MOE at pH 11.7 when compared with those at pH 10.4.

According to the previously proposed compatibilization mechanism, the dosage of the PAE resin and stearic anhydride would have a significant impact on the strength of the wood-PE composites. The amount of wood fibers being strengthened and stiffened would increase with increasing PAE dosage, which may explain why the strength (MOR) and the stiffness (MOE) of the wood-PE composites increased with increasing PAE dosage (Fig. 2). However, if too much PAE resin is added, the excess PAE resin might remain on the wood flour surface and become a weak interphase between wood and PE, resulting in lower strength. The results from Figure 2 suggested that 3 wt % of PAE was optimal for strength.

The quantity of covalent linkages between stearic anhydride and the PAE-bonded wood should increase with increasing stearic anhydride dosage, thus increasing the interfacial strength, which may explain why the MOR and MOE increased when the stearic anhydride dosage increased from 1 wt % to 3 wt %. However, if too much stearic anhydride is added, the excess stearic anhydride may serve as a plasticizer for the PE matrix or concentrate in and weaken the interphase between the PAE-bonded wood and PE, thus

lowering the strength and stiffness of the wood-PE composites. That both MOR and MOE significantly decreased with increasing the stearic anhydride dosage appears to be in accord with this explanation (Fig. 3). It has generally been observed in our work on composites containing 40% wood filler that the loading becomes optimal somewhere in the range of 2 to 4%. Our hypothesis for this effect is that somewhere in this range the surface of the wood becomes saturated with the compatibilizer. The behavior of PAE and stearic anhydride conform to this general hypothesis. Both PAE and stearic anhydride show improved performance up to 3% when added independently (Figs. 2 and 3). Yet the combination of 3% PAE plus 3% stearic anhydride does not show a significant improvement over the 2% PAE + 2% stearic anhydride compatibilizer system. That both show improvement independently suggests that they are interacting with the wood surface up to this loading. However, the 3% PAE + 3% stearic anhydride system is higher than the optimum loading generally observed for compatibilizers. This suggests that both the PAE and SA are competing for sites on the wood surface, in addition to reacting with each other, and that the 3% PAE + 3% stearic anhydride system is "overloaded" in this sense.

PAE resin is a water-soluble polymer. It is plausible that the surface of PAE-bonded wood became more hydrophilic than wood, thus being able to adsorb more water than wood, which might explain why the water-uptake percentage for the wood-PE composites with PAE was higher than the control. Stearic anhydride was able to react with the hydroxyl groups and amino groups on the surface of the PAE-bonded wood, thus greatly reducing the water-uptake of the resulting wood-PE composites. The wood-PE composites with PAE3S3 indeed had much lower water-uptake percentages than the control and the composites with PAE3.

CONCLUSIONS

Adjustment of the pH value of the PAE solution from 5.0 to 10.4 increased the MOR of the resulting wood-PE composites. Optimization of the PAE and stearic anhydride dosages revealed that the MOR and MOE of the resulting wood-PE composites were the highest at 3 wt % PAE and 3 wt % stearic anhydride. At a low dosage level, that is, 2 wt %, MAPE was superior to the PAE-stearic anhydride system. At the 4 wt % or 6 wt % levels, the PAE-stearic anhydride system resulted in higher strengths for the resulting wood-PE composites. The MOR and MOE were higher at 4 wt % MAPE than those at 2 wt % or 6 wt % MAPE. An extraction method was successfully developed to remove PE from the wood-PE composites. Characterization of the *p*-xylene-extracted wood-PE composites demonstrated that stearic anhydride covalently bonded to wood and the PAE-bonded

wood. The PAE-stearic anhydride compatibilizer system increased the water-resistance of the resulting composites. However, this compatibilizer system was still slightly less effective than MAPE in increasing the water-resistance.

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