

Effects of a New Compatibilizer System on the Flexural Properties of Wood–Polyethylene Composites

Y. Geng, K. Li, J. Simonsen

Department of Wood Science and Engineering, Oregon State University, Corvallis, Oregon 97331

Received 2 June 2003; accepted 12 October 2003

ABSTRACT: A novel wood–plastic compatibilizer system containing a paper wet-strength agent as a wood-binding domain and stearic anhydride as a polyethylene (PE) binding domain was investigated. Treatment of wood flour with a commercial paper wet-strength agent Kymene[®] 557H (simply called Kymene) before the mixing of PE and the wood flour increased the modulus of rupture (MOR) and the modulus of elasticity (MOE) of the resulting wood–PE composites. Addition of stearic acid in the mixing of PE and the wood–Kymene mixture further increased the MOR and MOE. Stearic anhydride was even more effective than stearic acid in the increase of the MOR and MOE. Compared to wood–PE composites without a compatibilizer, the stearic anhydride–Kymene compatibilizer system increased the MOR by about 33% and the MOE by about 40%. The stearic

anhydride–Kymene compatibilizer system gave a slightly lower MOR, but higher MOE than those of the commercially used compatibilizer (maleic anhydride-grafted polypropylene). The compatibilization mechanisms were proposed as follows: Kymene not only bound to wood fibers, but also strengthened and stiffened the wood fibers. Stearic anhydride formed covalent linkages such as ester and amide with the Kymene-consolidated wood fibers and the long hydrocarbon chain of the stearic anhydride bonded to the PE matrix through entanglements and/or cocrystallization. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3667–3672, 2004

Key words: compatibilizer; Kymene; stearic anhydride; paper wet-strength agent; wood–plastic composites

INTRODUCTION

Over the past 50 years, plastics have become a regular part of our daily lives. From containers to car parts, plastics can be shaped and made into almost anything. Fillers are often added to the plastic as a means of lowering costs and increasing the strength and stiffness of the resulting material.^{1,2} Wood has been used by the plastics industry as an inexpensive filler for thermoplastics.² These wood-filled thermoplastics, commonly called wood–plastic composites (WPCs), have many property advantages over those of composites with wood or plastics alone.² However, WPCs also have some disadvantages compared to pure plastics, including water absorption and thickness swell.^{1,2} The bond between the wood filler and the thermoplastic matrix is very limited, allowing wood fibers to slip and pull out from the thermoplastic when stressed.³

The inability of wood fibers to produce effective bonds with thermoplastics is a major impediment to the continued development of WPCs. Wood fibers and particles are not compatible with thermoplastics because wood is hydrophilic and the plastic is hydrophobic. One approach to overcome this problem is to

add a coupling agent (commonly called a compatibilizer) to improve the interfacial adhesion between the wood fibers and the plastic, thereby increasing the strength properties of the resulting WPC.

Polyethylene (PE) is one of the most commonly used thermoplastics for WPCs. At present, the choice of an effective compatibilizer for wood–PE composites is limited. In this study, we developed and characterized a novel compatibilizer system that contained a paper wet-strength agent as a wood-binding domain and stearic anhydride as a PE-binding domain. The compatibilization mechanism of this new compatibilizer system was discussed in detail.

EXPERIMENTAL

Materials

Wood flour (pine flour, 0.425 mm, moisture content, 2.04%) was donated by American Wood Fibers (Schofield, WI). High-density polyethylene (HDPE; melt flow index, 0.55 g/10 min) was donated by BP Solvey Polyethylene North America (Houston, TX). Stearic acid was purchased from Acros (Morris Plains, NJ). Stearic anhydride was purchased from Aldrich (Milwaukee, WI). Maleic anhydride-grafted polypropylene (MAPP; A-C OptiPak[™] 210) was a gift from Honeywell International (Morristown, NJ). Kymene[®] 557H (12.5% aqueous solution) was provided by Hercules, Inc. (Wilmington, DE).

Correspondence to: K. Li (kaichang.li@oregonstate.edu).
Contract grant sponsor: U.S. Department of Agriculture.

TABLE I
Components and Their Ratio of Wood-PE Composites

Labels of wood-PE composites	Components of wood-PE composites	Weight ratio of the components	Blending procedure
Control	Wood/HDPE	40/60	A
MAPP	Wood/MAPP/HDPE	40/2/58	B
SA	Wood/stearic acid/HDPE	40/1/59	B
SAN	Wood/stearic anhydride/HDPE	40/1/59	B
K-1	Wood/Kymene/HDPE	40/2/58	C
K-2	Wood/Kymene/HDPE	40/2/58	D
K-3	Wood/Kymene/HDPE	40/2/58	E
K + SA	Wood/Kymene/stearic acid/HDPE	40/2/1/57	F
K + SAN	Wood/Kymene/stearic anhydride/HDPE	40/2/1/57	F

Preparation of wood-PE composites

Wood flour, HDPE powder, and the compatibilizer were mixed in a Brabender Plasticorder with roller blade mixing bowl attached (C. W. Brabender Instruments, South Hackensack, NJ). The weight ratio of the components and the blending procedure used are listed in Table I.

Blending procedures for wood-PE composites

Procedure A

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.

Procedure B

As described in procedure A, the 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 returned to 120°C, one of the following materials, stearic acid (0.44 g), stearic anhydride (0.44 g), or MAPP (0.88 g), was added and mixed for 10 min. The bowl temperature was then raised to 170°C and HDPE (25.96 g for stearic acid and stearic anhydride, 25.52 g for MAPP) was added and mixed for 5 min. The contents were then removed from the Brabender and stored for compression molding.

Procedure C

As described in procedure A, the 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 returned to 120°C, Kymene (7.04 g, 0.88 g dry solids) was added and mixed for 10 min. The bowl temperature was then raised to 170°C, and

HDPE (25.52 g) was added and mixed for 5 min. The contents were then removed from the Brabender and stored for compression molding.

Procedure D

Kymene (7.04 g, 0.88 g oven-dried solids) was diluted with deionized water (36.96 mL) to form a 2% aqueous solution. Wood flour (17.96 g) was added to the diluted Kymene solution (44 mL) and mixed well by mechanical stirring. The resulting wood-Kymene mixture was dried at 104°C for about 20 h. The oven-dried wood-Kymene mixture (18.48 g) was added to the preheated Brabender bowl at 120°C and 100 rpm, and mixed for 10 min. The bowl temperature was then raised to 170°C and HDPE (25.52 g) was added and mixed for 5 min. The contents were then removed from the Brabender and stored for compression molding.

Procedure E

Kymene (7.04 g, 0.88 g oven-dried solids) was added dropwise to wood flour (17.96 g) in a 400-mL beaker with mechanical stirring and mixed well. The wood-Kymene mixture was added to the preheated Brabender bowl at 120°C and 100 rpm and mixed for 10 min. The bowl temperature was then raised to 170°C, and HDPE (25.52 g) was added and mixed for 5 min. The contents were then removed from the Brabender and stored for compression molding.

Procedure F

The Brabender bowl was preheated to 120°C and the rotor speed was set to 100 rpm. The oven-dried wood-Kymene mixture (18.48 g) as prepared in procedure D was added. After the bowl temperature returned to 120°C, stearic acid (0.44 g) or stearic anhydride (0.44 g) was added and mixed for 10 min. The bowl temperature was then raised to 170°C and HDPE (25.08 g) was added and mixed for 5 min. The contents were then

removed from the Brabender and stored for compression molding.

Press procedure

A steel mold (dimensions: $101.6 \times 101.6 \times 2$ mm) was used to compression mold the wood-PE WPC into stock test samples. 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, thus allowing the wood-plastic to flow into the mold shape. The press pressure was raised from 34.5 to 344.8 kPa in 2 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 pressure at ambient conditions. The resulting wood-PE sample was cut into 10 small test specimens. Each specimen had dimensions of 52.46–55.16 mm of length, 10.70–14.28 mm of width, and 2.32–3.10 mm of thickness.

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

The small specimens were tested on a Sintech machine (MTS Systems Corp., Enumclaw, WA) and the load-deflection curve was determined. The support span was 43 mm and the crosshead speed was 1.0 mm/min. At least 10 specimens were tested for each wood-PE composite in accordance with ASTM D790-86. 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.

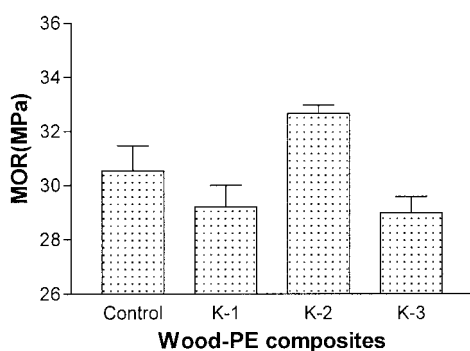


Figure 1 Effects of blending procedures on MOR of wood-Kymene-PE composites. Data are the means of at least 10 replicates and the error bars represent 1SD.

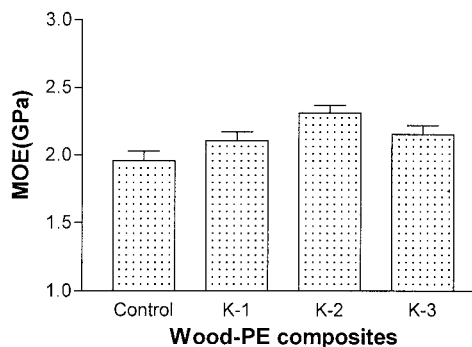


Figure 2 Effects of blending procedures on MOE of wood-Kymene-PE composites. Data are the means of at least 10 replicates and the error bars represent 1SD.

RESULTS AND DISCUSSION

When a Kymene solution was added directly to wood flour in the preheated Brabender bowl (blending procedure C), the resulting wood-PE composites had a lower MOR than that of the control (i.e., wood-PE composite without a compatibilizer) (Fig. 1). When wood flour was premixed with a diluted Kymene solution and dried in an oven (blending procedure D), the resulting composite had a higher MOR than that of the control (Fig. 1). Mixing of PE and wet wood-Kymene mixture in the preheated Brabender (blending procedure E) resulted in a composite with a lower MOR than that of the control (Fig. 1).

Compared with the control, addition of Kymene, regardless of the blending procedures, increased the MOE of the resulting wood-PE composites (Fig. 2). Mixing of PE with the oven-dried wood-Kymene mixture gave the highest MOE (Fig. 2).

Compared to the control, stearic acid had little effect on the MOR of the resulting wood-PE composites (Fig. 3). However, when both Kymene and stearic acid were present, the MOR of the wood-PE composites was much higher than that of the control and the composites containing either Kymene or stearic acid

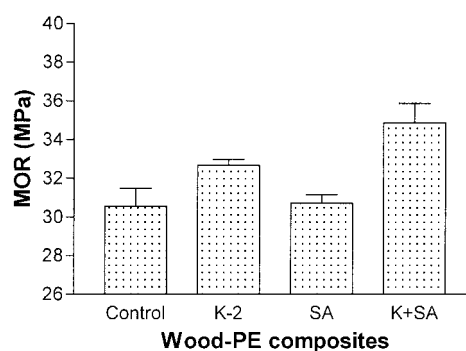


Figure 3 Effects of stearic acid and a combination of stearic acid and Kymene on MOR. Data are the means of at least 10 replicates and the error bars represent 1SD.

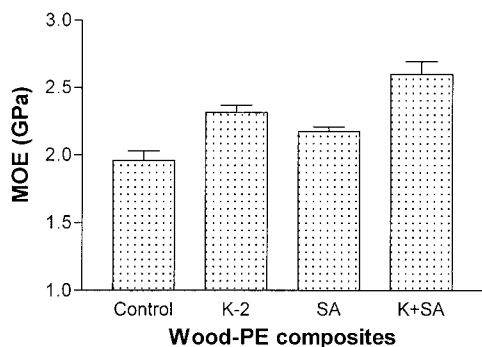


Figure 4 Effects of stearic acid and a combination of stearic acid and Kymene on MOE. Data are the means of at least 10 replicates and the error bars represent 1SD.

only (Fig. 3). Addition of Kymene and stearic acid increased the MOR by about 14% compared to that of the control. In contrast to the negligible effect of stearic acid on the MOR, the presence of stearic acid slightly increased the MOE of the composites compared to that of the control (Fig. 4). The MOE of the composites containing both Kymene and stearic acid was about 33% higher than that of the control and about 12% higher than that of the composites containing only Kymene (Fig. 4).

Stearic anhydride increased the MOR by about 12% compared to that of the control (Fig. 5). A combination of stearic anhydride and Kymene had a much greater compatibilization effect than stearic anhydride or Kymene alone. The wood-PE composites containing both stearic anhydride and Kymene had about 33% higher MOR than that of the control (Fig. 5). However, a combination of stearic anhydride and Kymene gave a slightly lower MOR than that of MAPP (Fig. 5).

The MOE of the wood-PE composites containing stearic anhydride as a compatibilizer was higher than that of the control. A combination of stearic anhydride and Kymene further increased the MOE, compared to stearic anhydride alone (Fig. 6). When both stearic

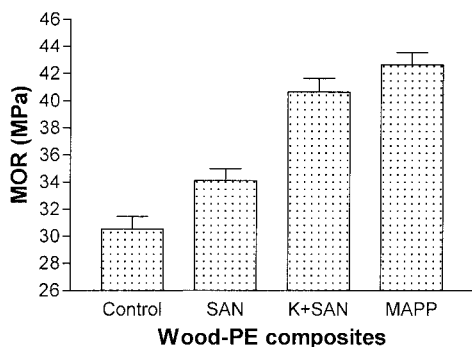


Figure 5 Effects of stearic anhydride, a combination of stearic acid and Kymene, and MAPP on MOR. Data are the means of at least 10 replicates and the error bars represent 1SD.

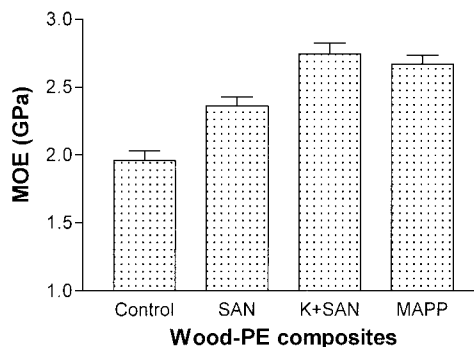
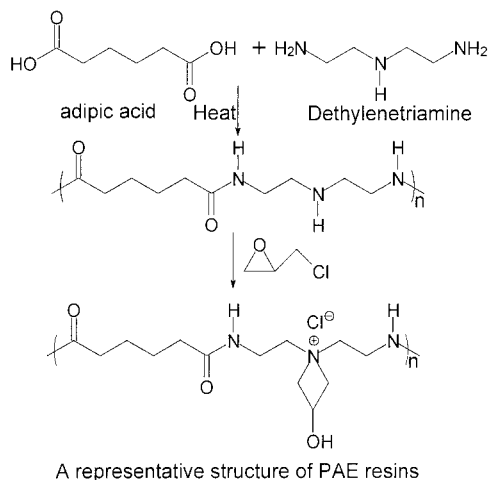


Figure 6 Effects of stearic anhydride, a combination of stearic acid and Kymene, and MAPP on MOE. Data are the means of at least 10 replicates and the error bars represent 1SD.

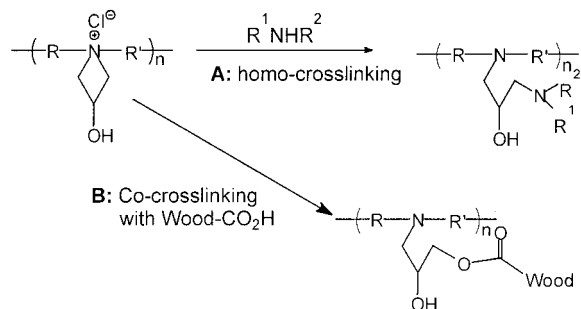
anhydride and Kymene were used together, the MOE was about 40% higher than that of the control. Interestingly, a combination of stearic anhydride and Kymene resulted in a higher MOE than that of MAPP (Fig. 6).

The Kymene[®] 557 (simply called Kymene) is the most widely used paper wet-strength agent. Kymene is a polyaminoamide-epichlorohydrin (PAE) adduct whose representative structure is shown in Scheme 1.^{4,5} It has been well established that hydroxy-azetidinium (the cationic four-membered ring structure) is the key functional group for wet-strength development in paper.^{6,7} The characteristic four-membered azetidinium structure is fairly stable in water at room temperature. However, the azetidinium undergoes various reactions at elevated temperatures. The chemistry and wet-strength mechanisms of PAE resins have been extensively studied and reviewed.⁶⁻¹⁰

Based on these studies in paper, we speculate that the key reactions between Kymene and wood flour are similar to those shown in Scheme 2.



Scheme 1 A synthetic scheme for industrial production of PAE resins.



Scheme 2 Proposed key reactions in the binding of Kymene to wood flour.

When wood flour is added to a diluted Kymene solution and mixed well, the PAE polymers are readily absorbed to the wood fibers because of the positive charges in the PAE polymers. Because of their low molecular weight, the PAE polymers may even diffuse into the cell walls of the wood fibers. Upon drying, the PAE polymers react with themselves, as shown in reaction A in Scheme 2, to form a highly crosslinked insoluble network around and through the fibers. One effect of this reaction is that the highly crosslinked network could consolidate fine and loose fibers on the wood flour surfaces. The PAE polymers could also form covalent linkages between fibers (as in reaction B in Scheme 2), thus reinforcing the natural hydrogen bonding in the wood flour. Therefore, treatment of wood flour with Kymene is expected to strengthen and stiffen the wood fibers. The results in Figure 2 indeed show that Kymene increased the MOE values. When wood flour was stirred in a diluted Kymene solution and then dried, the PAE polymers are expected to be well absorbed and well distributed in the wood fibers, resulting in significant strengthening and stiffening of the wood flour. This would explain why blending procedure D (thoroughly mixing the wood flour in a diluted Kymene solution following by oven-drying the mixture) gave rise to higher MOR and MOE than blending procedure C (mixing wood flour and Kymene in the Brabender bowl) or E (mixing wood flour and concentrated Kymene).

Extensive studies suggest that effective wood-plastic compatibilizers contain two domains with one domain able to bind to wood and the other able to bind to plastic.^{3,11–25} This study suggests that Kymene is a good wood-binding domain. It appears not only to bind strongly to wood flour, but also seems to strengthen and stiffen the wood flour. For effective compatibilization, a plastic-binding domain bonded to the wood-binding domain is still needed. Stearic acid was first investigated as a PE-binding domain, hoping that the long hydrocarbon chain of stearic acid would form entanglements or cocrystallization with the PE matrix, and the carboxylic acid group would form ester or amide linkages with the wood-Kymene mix-

ture at the high mixing temperature (170°C). The data in Figures 3 and 4 indeed show that addition of stearic acid in the mixing of PE and the oven-dried wood-Kymene mixture greatly increased the MOR and MOE. At the high mixing temperature (170°C) ester or amide linkages between the carboxylic acid and the wood-Kymene mixture would be expected, but the formation rate might be slow. Therefore, we investigated the more reactive stearic anhydride to see whether it could further increase the compatibilization effects. As expected, stearic anhydride gave a higher MOR and MOE than did stearic acid, and a combination of stearic anhydride and Kymene was superior to a combination of stearic acid and Kymene in terms of MOR and MOE (Figs. 5 and 6). That wood/stearic anhydride/Kymene/PE composites had higher MOE values than those of wood/MAPP/PE composites suggests that a combination of an acid anhydride with a long hydrocarbon chain and Kymene is a promising compatibilizer system for wood-PE composites.

CONCLUSIONS

Treatment of wood fibers with Kymene increased the MOR and MOE of the resulting wood-PE composites. The combination of stearic acid and wood flour pretreated with Kymene yielded a higher MOR and MOE than either stearic acid or Kymene alone. The combination of stearic anhydride and Kymene-pretreated wood flour had superior compatibilization effects, in terms of mechanical properties, compared to the combination of stearic acid and the Kymene-pretreated wood flour. A paper wet-strength agent could serve as an effective wood-binding domain of a wood-plastic compatibilizer system. The combination of Kymene and carboxylic anhydride was a superior compatibilizer system for wood-plastic composites. This compatibilizer system is particularly attractive for reactive extrusion of WPCs.

The authors thank American Wood Fibers (Schofield, WI), BP Solvay Polyethylene North America (Houston, TX), and Hercules Inc. (Wilmington, DE) for donating wood flour, high-density polyethylene, and Kymene[®] 557H wet-strength resin, respectively. This research was supported by a grant from the national research initiative competitive grants program of the U.S. Department of Agriculture (Grant no. 2003-35103-13864).

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