Wood-polymer bonding in extruded and nonwoven web composite panels

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Abstract

The effectiveness of a maleated polypropylene (MAPP) as a coupling agent in extruded wood flour / polypropylene composites and nonwoven web wood fiber / polypropylene composites are compared. In the extruded system the MAPP was incorporated by dry blending prior to extrusion; in the nonwoven web system, the MAPP was incorporated by spraying an emulsified form on the wood fibers. At levels of 3 percent or less, MAPP increased cantilever beam strength and modulus in both systems, although the effects were more pronounced in the nonwoven web system. Similarly, MAPP increased unnotched impact energy, particularly in the nonwoven web system. MAPP also led to small improvements in water resistance for nonwoven web composites containing 85 percent wood fiber. The greater effectiveness of MAPP in the nonwoven web composite is believed to be a result of more efficient incorporation of MAPP at the wood / polypropylene interface and the greater aspect ratio of the wood fiber.

Introduction

Promising technology is evolving for using waste or low grade wood blended with polyolefin plastics to make an array of high-performance reinforced composite products. This technology provides a strategy for producing advanced materials that take advantage of the enhanced properties of both wood and plastic. Advantages associated with these composite products include light weight and improved acoustic, impact, and heat reformability properties. The research program outlined here focused on extrusion and nonwoven web technology.

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Extrusion technology

Extrusion is an inherently low-cost, high production rate process. The incorporation of wood flour and wood fibers in thermoplastic composites using extrusion technology offers several advantages, which include economy on a cost per unit volume basis, desirable aspect ratios, flexibility (less fiber breakage), and low abrasiveness to equipment. Composite panels can be produced containing up to 50 weight percent wood fiber and are low cost, thermoformable, and relatively insensitive to moisture.

Nonwoven web technology

A wide variety of wood fibers and synthetic fibers can be assembled into a random web or mat using air-forming or nonwoven web technology. The fibers are initially held together by mechanical interlacing. The web can then be fused or thermoformed into panels with a variety of shapes. Alternatively, a thermosetting resin can be incorporated in the web to provide additional bonding of the fibers. Nonwoven web systems can be made with up to 95 weight percent wood fibers. Compared to products made by extrusion, nonwoven web composites have the potential for better mechanical properties, greater biodegradability, and greater flexibility for manufacture into products with intricate shapes.

The increased processing flexibility inherent in both extrusion and nonwoven web technologies gives rise to a host of new natural or synthetic fiber products. These products can be produced in various thicknesses-from a material only a few millimeters thick to structural panels up to several centimeters thick. A great variety of applications are possible because of the many alternative configurations of the products. Potential Products include

- storage bins for crops or other commodities
- temporary housing structures
- furniture components, including both flat and curved surfaces
- automobile and truck components
- paneling for interior wall sections, partitions, and door systems
- floor, wall, and roof systems for light-frame construction
- packaging applications, including containers, cartons, and pallets

Extrusion and nonwoven web technologies provide options for balancing performance properties and costs, depending upon the application under consideration. However, poor attraction and low interracial bonding between the hydrophilic wood and hydrophobic polyolefin limit the reinforcement imparted to the plastic matrix by the wood component. This reinforcement could be enhanced if the polar nature of the cellulosic surface were modified so that the wood surface characteristics were more compatible with the nonpolar nature of the polymer matrix. One approach to developing greater compatibility is to use a coupling agent that possesses a dual functionality abling it to interact or react with both components.

The purpose of the research reported here was to determine if a maleated polypropylene coupling agent (MAPP-1 for the extruded system and MAPP-2 for the nonwoven web system) could improve the properties of wood / polypropylene composites made by extrusion and nonwoven web technologies.

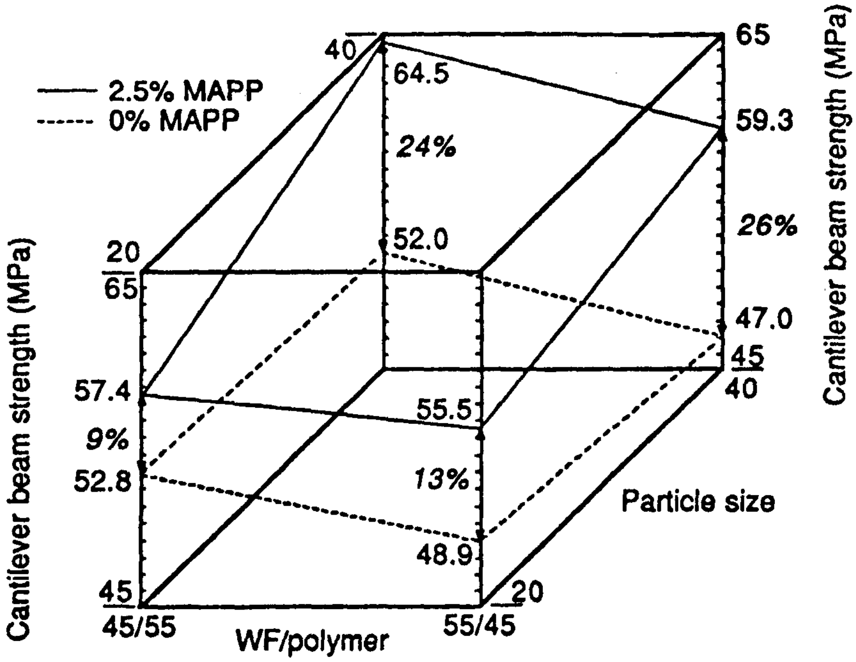

Figure 1. — Maximum cantilever beam strength of extruded composite as a function of wood flour to total polymer weight ratio, wood flour particle size, and MAPP-1 level. (All data points are the average of results for one and three extrusions, MAPP levels are weight percentages of total system.)

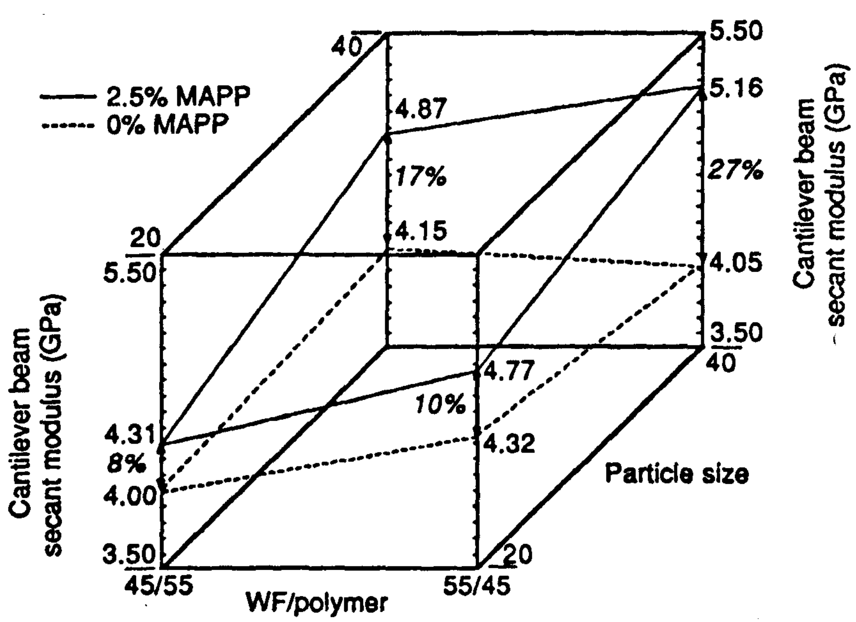

Figure 2. — Cantilever beam secant (9°) modulus of extruded composite as a function of wood flour to total polymer weight ratio, wood flour particle size, and MAPP-1 level. (All data points are the average of results for one and three extrusions. MAPP levels are weight percentages of total system.)

Extruded system

Experimental design and analysis

The experiment involved the following four-variable, two-level matrix: 1) ratio of wood flour to total polymer — 45 / 55 and 55 / 45 by weight (total polymer - polypropylene + MAPP-1); 2) wood flour particle size — nominal 20 and 40 mesh; 3) MAPP-1 level -0 and 2.5 weight percent of total system; and 4) number of extrusions — 1 and 3. The matrix was replicated and experiments were performed in random order. The data were analyzed by standard statistical procedures for the main effects of the variables and the interactions between variables (4).

Materials

The wood flours were American Wood Fibers, Inc. (Schofield, Wis.) no. 402, nominal 40-mesh pine — predominantly ponderosa *(Pinus ponderosa)*, jeffrey *(Pinus jeffreyi)*, and lodgepole *(Pinus contorta)* pine — and no. 202, nominal 20-mesh loblolly pine *(Pinus taeda). The* polypropylene was Soltex Fortilene 9101 homopolymer spheres with a density of 0.900 g / ml and a melt flow index of 2.5 g / 10 min. (230°C / 2160 g). Stabilizers and processing aids were added to the polymer prior to processing: 0.10 percent Irganox-1010 (a tertiary butylhydroxyhydrocinnamate) from McKesson chemical (Houston, Tex.), 0.20 percent Ionol (a butylated hydroxy toluene) from Ciba-Geigy Corporation (Hawthorne, N.Y.), 0.10 percent GMS (mono- and diglycerides of fatty acids) from ICI United States, Inc. (Wilmington, Del.), and 0.20 percent distearyl thiodipropionate (DSTP) from Witco Chemical (New York, N.Y.). The maleated polypropylene was Epolene E-43 powder (MAPP-1) from Eastman Chemical Products, Inc. (Kingsport, Tenn.), with density of 0.934 g / ml, acid number of 47, approximate molecular weight of 4,500, and approximately three anhydride groups per molecule.

Processing

Wood flour was vacuum dried at 50°C to 60°C for 24 hours to a moisture content of 1 to 2 percent and then stored over desiccant in sealed containers. All other ingredients were added to the dried flour and dry blended. Trials were extruded in random order with a Brabender 2503 P1asti-Corder 19-mm, single- screw extruder (3 mm in diameter, 58 mm long die) at 200°C (barrel and die temperature), with a residence time of about 2 minutes (note that MAPP-1 was also incorporated at this time by dry blending the powder with the polypropylene and wood flour and subsequently extruding). The extruded rod was pelletized and either stored dry immediately or re-extruded and repelletized two additional times. Test specimens were prepared in the same random order as the extrusions, using a Frohring Mini-Jector model SP50 plunger injection molding machine at 215°C with an average residence time of 1 to 2 minutes, ram pressure of 8.9 MPa, and mold temperature of 25° to 30°C. After molding, the specimens were stored over desiccant at 23°C for at least 3 days before testing at that temperature. Densities of the injection molded specimens were close to the theoretical values, varying from about 1.06 g/ml at 45/55 wood flour/polypropylene to about 1.11 g/ml at 55/45 wood flour/polypropylene.

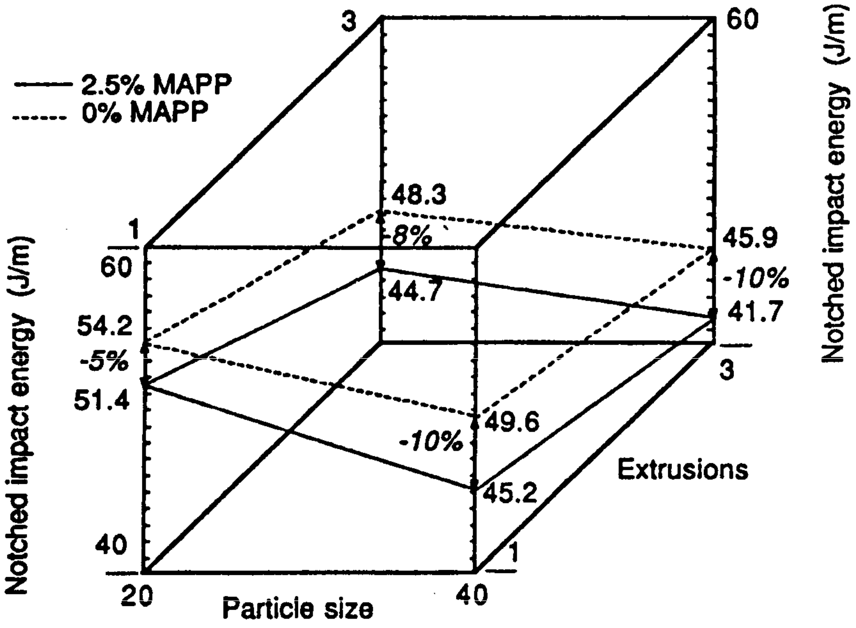

Figure 3. — Notched impact energy of extruded composite as a function of wood flour particle size, number of extrusions, and MAPP-1 level. (All data points are the average of results for one and three extrusions. MAPP levels are weight percentages of total system.)

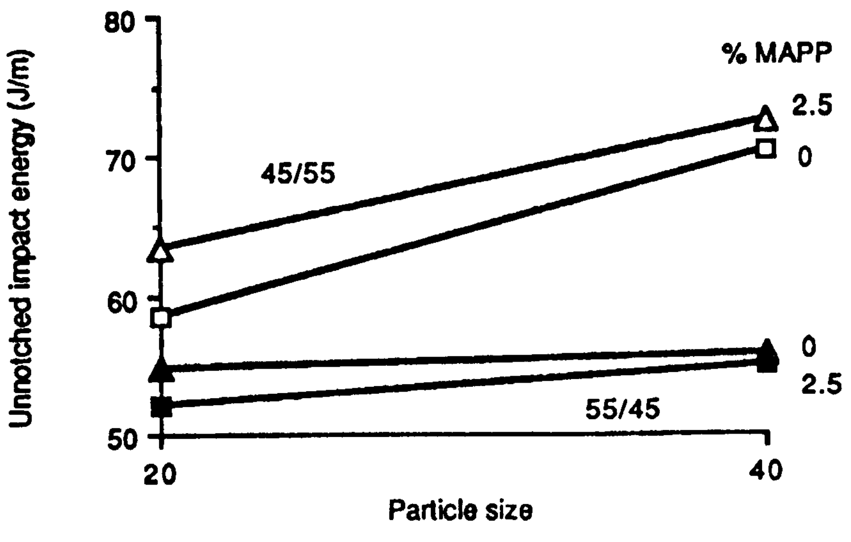

Figure 4. — Unnotched impact energy of extruded composite as a function of wood flour particle size, wood flour to total polymer weight ratio, and MAPP level.

Testing

All testing was performed at 23°C on injection molded specimens taken directly from desiccant storage with minimal exposure to ambient humidity. Maximum cantilever bending strength and 9° secant modulus were measured on a Tinius Olsen tester in conformance with ASTM D 747 (2), using specimens 127 by 12.7 by 3.2 mm and a loading rate of about 60°/min. Notched and unnotched impact energy specimens were 64 by 12.7 by 6.4 mm and were tested in conformance with ASTM D 256-84 (1) using an Izod impact tester. Except for unnotched impact energy ten specimens were tested from each trial of the replicate matrices. The unnotched impact energy test was performed on specimens from only partial experimental matrices, and those data were not analyzed statistically.

Results

Figures 1 to 4 provide a qualitative or semiquantitative presentation of the results. A more statistically quantitative presentation of the results is shown in Table 1.

The addition of MAPP-1 to the composite increased cantilever bending strength (Table 1 and Fig. 1) approximately 16 percent, averaged over the other three variables. Smaller wood flour particles had a further positive effect on strength in the presence of MAPP-1, where the increase was about 25 percent averaged over the remaining two variables. Effects on cantilever bending modulus were similar (Table 1 and Fig. 2), with the exception of a small increase with the higher number of extrusions and the expected increase from 45/55 to 55/45 wood flour/polypropylene. In contrast to the cantilever bending properties, notched impact energy was decreased to a small degree by incorporation of

Table 1. — *Main effects and interactions of variables on extruded composites* [a]

Effect	Variable[b]	Cantilever beam Strength	Cantilever beam Modulus	Notched impact energy
		(MPa)	(GPa)	(J/m)
Overall mean		54.4	4.45	47.5
Main effects	WF/Pol	-3.6	0.24	
	Mesh	1.2	0.22	-4.2
	MAPP-1	7.4	0.64	-3.6
	Extrusions		0.21	-4.8
Interactions	WF//Pol × Mesh	(-1.0)	(-0.15)	
	WF/Pol × MAPP		-0.13	
	Mesh × MAPP	2.3	0.26	
	Mesh × Ext		0.15	
	MAPP × Ext	1.6		
	Mesh × MAPP × Ext	(1.1)		

[a] Values without parentheses are at 95 percent confidence limit; values in parentheses are at 90 percent confidence limit. Values show change in property resulting from the particular variable, averaged over all other variables.

[b] WF = wood flour; Pol = polypropylene + MAPP; WF/Pol = weight ratio; Mesh = wood flour particle size; MAPP-1 = powdered Epolene E-43; Ext = number of extrusions. X × Y interaction is half the average effect of X at first level of Y minus the average effect of X at second level of Y. X × Y × Z interaction is half the difference between the X × Y interactions at the two levels of Z (4).

Table 2. — *Treatment combinations for testing of nonwoven web system.*

Set	Wood fiber	Polypropylene	MAPP-2
	(%)		
1	85	12	3
2	85	14	1
3	85	15	0

Table 3. — *Experimental design for tests on nonwoven web composite panels.*

Specimen variable	Mechanical properties: Impact energy	Mechanical properties: Cantilever bending strength and modulus	Dimensional stability[a]: 2-hour water boil	Dimensional stability[a]: 24-hour water boil
Specimens per set	3	4	2	3
Specimen size (mm)	254 by 254	127 by 25.4	51 by 51	51 by 51

[a] Thickness swell.

MAPP-1, smaller particle size, and greater extrusion time (Fig. 3 and Table 1). However, the less complete unnotched impact energy testing indicated that this impact behavior may be enhanced by smaller particle size and the presence of MAPP-1 (Fig. 4).

Nonwoven web system

Experimental design and analysis

The experiment was a full factorial testing of two levels of wood fiber to total polymer (polypropylene plus MAPP-2) ratio and three levels of maleated polypropylene (MAPP-2) to yield six treatment combinations (Table 2).

Each treatment combination was considered a replicated set, consisting of 10 individual panels, for a total of 60 panels. Three panels in each set were tested for impact energy. The remaining seven panels in each set were tested for other mechanical properties and dimensional stability (Table 3).

The data were analyzed by standard statistical procedures for the main effects of the variables and the interactions between variables (4). Because of the significant interaction between amount of wood fiber and amount of MAPP-2, we were required to examine the effect of different MAPP-2 levels separately for each level of wood fiber.

Materials

Western hemlock *(Tsuga heterophylla)* wood fibers, obtained from Canfor, Ltd. (Vancouver, B.C.), were produced from 100 percent pulp grade chips, steamed for 2 minutes at 7.59 MPa, disk refined, and flash dried at 160°C in a tube dryer. The fibers were then hammermilled using a 12.7-mm screen. The polypropylene fibers, obtained from Hercules, Inc. (Norcross, Ga.), were 2.2 denier, 37-mm long, and crimped. They had a density of 0.910 g/ml and a melting point of 162°C. The maleated polypropylene coupling agent (MAPP-2) was an anionic emulsion of Epolene E-43, from Eastman Chemical Products, Inc. (Kingsport, Tenn.).

Processing

The hemlock fibers had an initial moisture content of 5 percent. They were sprayed with 40 percent solids content MAPP-2 anionic emulsion, to give 1 and 3 percent (dry weight basis) coupling agent contents. The hemlock fibers used for the control boards were not sprayed with MAPP-2.

The wood and polypropylene fibers were air mixed, transferred via an air stream to a moving support bed, and subsequently formed into a continuous, low density, 305-mm-wide web of intertwined fibers, ranging in length from 12.2 to 18.3 m, depending upon the density of the formed web, Each roll of the web was trimmed to 305-mm square sheets. Six to eight sheets were selected according to their weight and stacked to maintain the same machine direction orientation and the same weight for each stack.

A manually controlled, steam-heated press was used to press the panels at a temperature of 213°C for 6 minutes at a maximum pressure of 2.95 MPa. The panels were then cooled in the press for an additional 6 minutes until they reached a final temperature of 38°C. All panels were trimmed to 254 mm square, with a density of 1.0 g/cm^3 and thickness of 3.2 mm.

Testing

In previous work with composites made from similar materials, the coefficient of variation for MOR and MOE was about 10 percent. Based upon this information, we estimated that with 20 tests per property per set, we would be able to detect a 10 percent difference resulting from the amount of MAPP-2 80 percent of the time.

The conditioned (65% relative humidity, 20°C specimens for determination of mechanical properties were tested at room temperature (about 23°C, with minimal exposure to ambient humidity. Maximum cantilever beam flexural strength and secant modulus at 9° were determined on cantilever beam specimens in conformance with ASTM D 747 (2) using a Tinius Olsen tester with a loading rate of about 60°/min. Impact energy was measured in conformance with TAPPI standard T803 om-88 (10) with a General Electric impact tester.

Thickness swell was measured after a 24-hour water soak at ambient temperature and after a 2-hour water boil; these tests were performed in conformance with ASTM D 1037 (3) and CAN3-0188.0-M78 (5), respectively,

Results

The results are presented in Figures 5 to 9 as bar charts; solid horizontal lines above the bars indicate statistical significance. Bars that are connected by a solid line are not significantly different at the 95 percent confidence level.

Dimensional stability properties. - Depending upon the end use of the product, dimensional stability in water, especially in the thickness direction, can be a great problem in composites made from high percentages of wood fibers. The composites undergo not only normal (reversible) swelling but also swelling caused by the release of residual compressive stresses imparted to the product during pressing. A 24-hour water soak test and 2-hour boil test were used to measure thickness swell properties of the panels.

Although thickness swell after the 2-hour water boil was approximately twice the thickness swell that occurred after the 24-hour water soak, the effects of MAPP-2 were similar for both tests (Figs. 5 and 6). Thickness swell of the 70 percent wood fiber system was increased by incorporating 3 percent MAPP-2 (increase of approximately 20% and 23% for 24-hour and 2-hour tests, respectively). However, for the 85 percent wood fiber treatment combinations, both 1 and 3 percent MAPP-2 decreased thickness swell (decrease of approximately 21% and 14% for 24-hour and 2-hour tests, respectively).

Perhaps the most noteworthy observation from the thickness swell experiments is that doubling the amount of polypropylene (85 to 70% wood fiber) approximately halved the thickness swell.

Mechanical properties. - At the 70 percent wood fiber level, 1 percent MAPP-2 did not significantly influence impact energy (Fig. 7); however, 3 percent MAPP-2 increased impact energy by 45 percent. At the 85 percent wood fiber level, impact energy of both the 1 and 3 percent MAPP-containing panels was increased by about 60 percent.

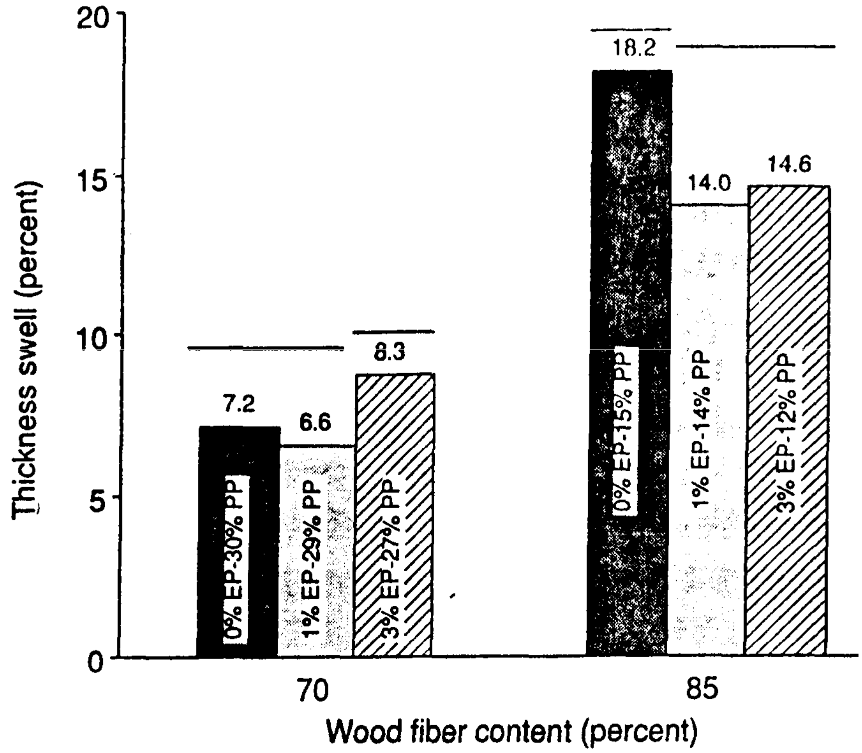

Figure 5. — 24-hour water-soak thickness swell of nonwoven web composite as a function of wood fiber content and MAPP-2 level. (EP is MAPP-2; PP is polypropylene; percentages are weight percent of total system. Bars connected by a solid line are not significantly different at the 95% confidence level.)

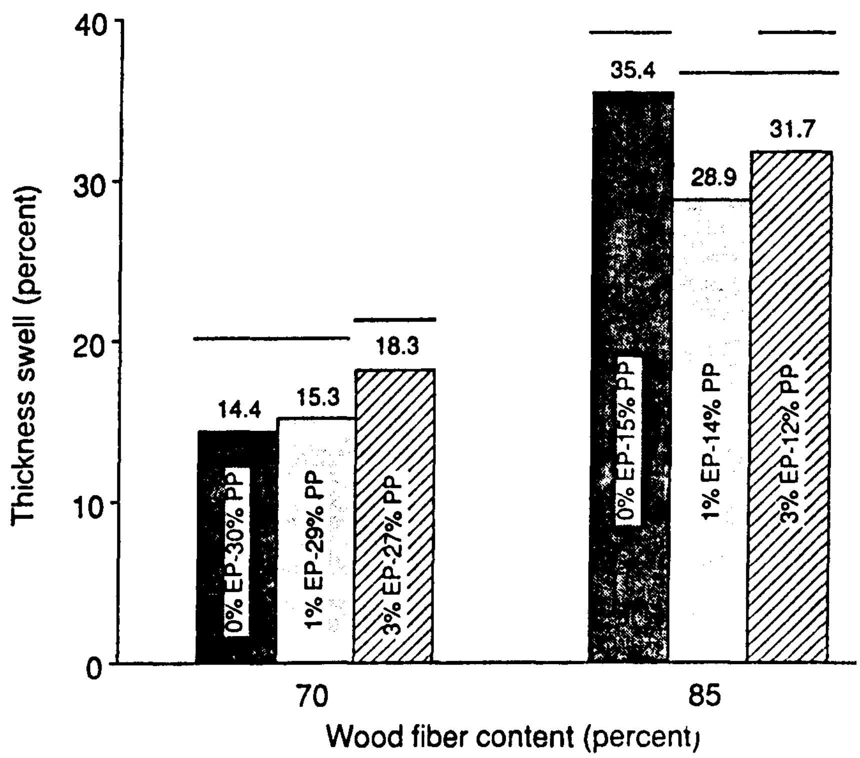

Figure 6, — 2-hour water-boil thickness swell of nonwoven web composite as a function of wood fiber content and MAPP-2 level. (EP is MAPP-2; PP is polypropylene; percentages are weight percent of total system. Bars connected by a solid line are not significantly different at the 95% confidence level.)

At both wood fiber levels, MAPP-2 increased maximum cantilever beam flexural strength from 42 to 58 percent (Fig. 8). For secant modulus, the increases were somewhat smaller, from 29 to 42 percent (Fig. 9). For either property, additional benefits obtained from increasing MAPP-2 content from 1 to 3 percent were small.

Discussion

The increase in strength and modulus for both extruded and nonwoven web systems after incorporation of MAPP indicates that MAPP does indeed provide some degree of coupling between the wood fiber and polypropylene. We presume that the greater effectiveness of MAPP for strength and modulus in the nonwoven web system is the consequence of two factors: 1) MAPP is used more efficiently in the nonwoven web system because of its direct application to the wood interface, in contrast to the extruded system where MAPP needs to migrate to the interface during the melt processing; and 2) in the nonwoven web, bonding polypropylene to wood fibers provides greater potential for reinforcement because the fibers possess a larger aspect ratio than does the wood flour.

Three different impact measurements were used in our study. The TAPPI standard impact test used for the nonwoven web system is probably the best impact test for conditions that automotive panels are likely to be sub jetted to. Both this test and the unnotched impact energy test on injected molded specimens emphasize the initiation step of impact fracture and hence the influence of stress concentrations at existing defects. On the other hand, the notched impact energy test emphasizes the fracture propagation process initiated at the predominating stress concentration at the crack tip. Therefore, the lack of correlation between the effects of MAPP observed from the notched impact energy test and those from the other two tests is not surprising (compare Fig. 3 with Figs. 4 and 7). At this time, we can only speculate about the reasons for the small negative influence of MAPP on notched impact energy and the positive effects observed for the other tests, particularly for the nonwoven webs. For example, the positive influence of MAPP on impact

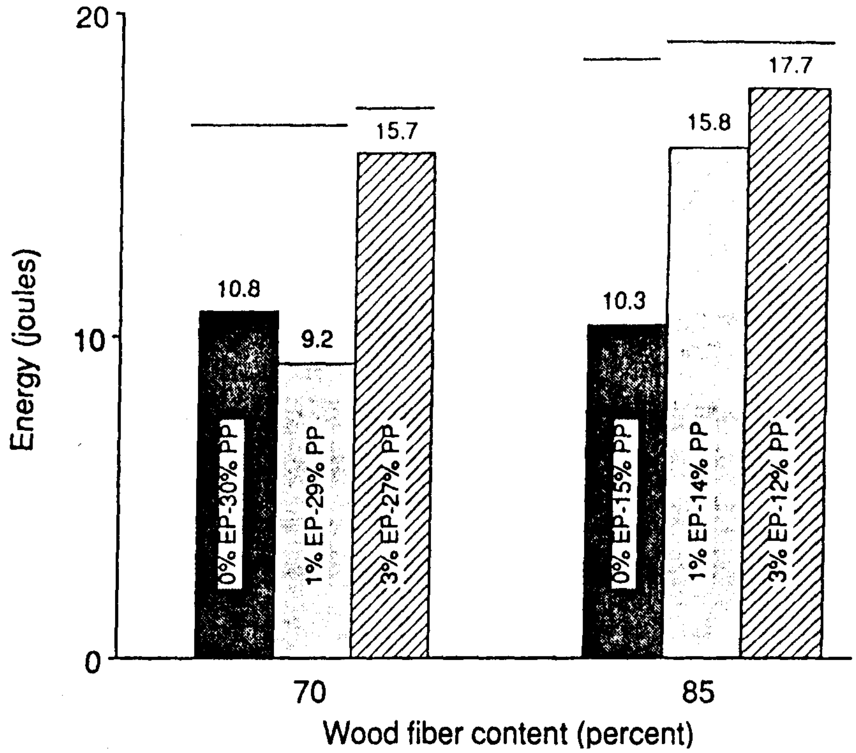

Figure 7. — Impact energy of nonwoven web composite as a function of wood fiber content and MAPP-2 level. (EP is MAPP-2; PP is polypropylene; percentages are weight percent of total system. Bars connected by a solid line are not significantly different at the 95% confidence level.)

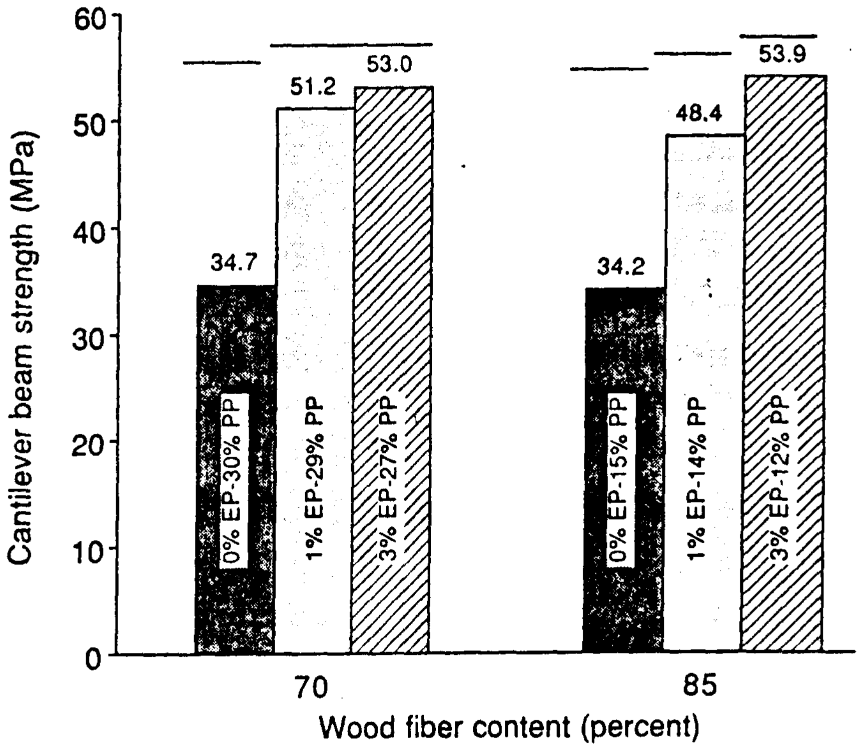

Figure 8. — Maximum cantilever beam strength of nonwoven web composite as a function of wood fiber content and MAPP-2 level. (EP is MAPP-2; PP is polypropylene; percentages are weight percent of total system. Bars connected by a solid line are not significantly different at the 95% confidence level.)

fracture initiation (Fig. 7) may reflect the improved bonding and wetting between wood and polymer and a consequent reduction in number and size of fracture-initiating defects. However, the small loss in notched impact energy with MAPP (Fig. 3) may reflect some loss in polymer mobility and energy absorbing ability caused by increased bonding between wood and polymer.

The absence of large, consistent improvements in water resistance of the nonwoven webs after incorporating MAPP-2 (Figs. 5 and 6) is disappointing and contradicts the findings by others for extruded wood / polypropylene systems (7,9). However, the extruded systems contain much lower quantities of wood. Therefore, interfacial bonding and wood fragment encapsulation should be much more influential in reducing water uptake in extruded systems compared to nonwoven web systems, which have very high wood fiber contents.

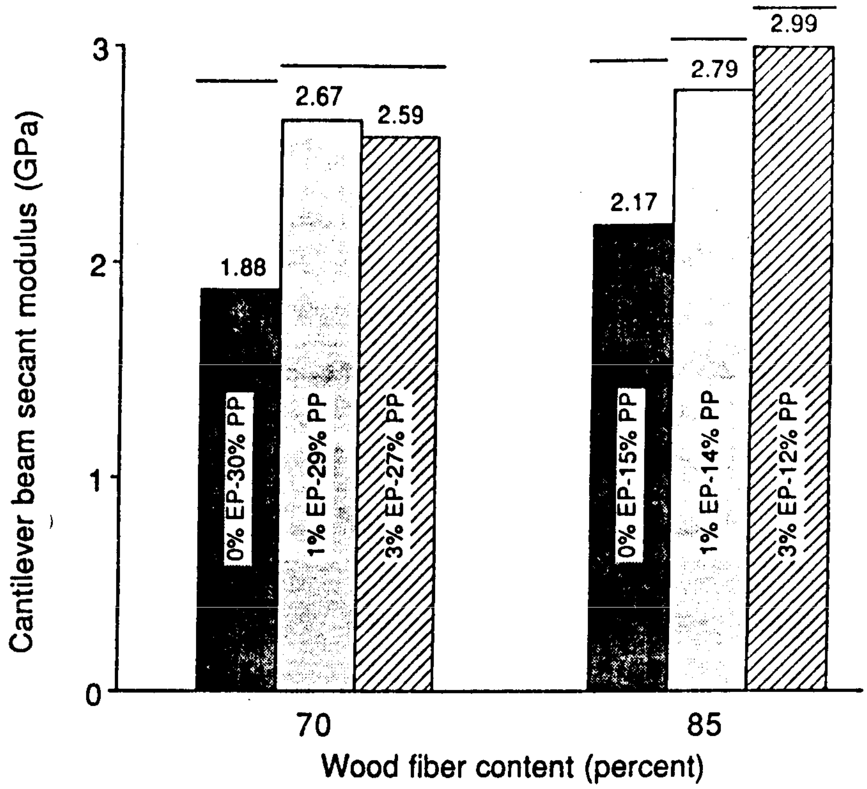

Figure 9.— Cantilever beam secant (9°) modulus of nonwoven web composite as a function of wood fiber content and MAPP-2 level. (EP is MAPP-2; PP is polypropylene; percentages are weight percent of total system. Bars connected by a solid line are not significantly different at the 95% confidence level.)

Concluding remarks

We examined the influence of small quantities of a maleated polypropylene on the properties of thermoformable composites prepared by extruding wood flour / polypropylene mixtures or by using nonwoven web technology with wood and polypropylene fibers. The maleated polypropylene was incorporated into the extruded system by dry blending a powdered form (MAPP-1) prior to extrusion, and it was incorporated into the nonwoven web system by spraying the wood fiber with an emulsified form (MAPP-2) prior to the air-laying process.

The major findings of our study were as follows:

1. MAPP increased cantilever beam strength and modulus in both the extruded and nonwoven web systems, but to a greater extent in the nonwoven web system.
2. In the nonwoven web system, MAPP-2 increased impact energy.
3. MAPP-2 improved water resistance of the nonwoven web system at 85 percent wood fiber content but not at 70 percent wood fiber content.

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