

Synergistic Effect of Coupling Agents on Polypropylene-Based Wood-Plastic Composites

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ABSTRACT: In this study, polypropylene grafted with maleic anhydride (PP-*g*-MA) and styrene ethylene-*co*-butylene styrene block copolymer grafted with maleic anhydride (SEBS-*g*-MA) were used as coupling agents for polypropylene-based wood-plastic composites containing 50 wt % wood flour. Adding up to 5 wt % PP-*g*-MA to the composite increased the tensile strength of the wood-plastic composite (WPC) by almost 100% and the reversed-notch Izod impact strength by more than 100%; the modulus remained essentially unchanged. By contrast, the same amount of SEBS-*g*-MA had a greater effect on the impact strength but a smaller influence on the tensile strength; in addition, the modulus was reduced. On using a combination of 2 wt % PP-*g*-MA and 1 wt % SEBS-*g*-MA, the impact strength of the composite could be increased significantly, but the tensile strength and modulus were not reduced to any appreciable extent relative to the use of PP-*g*-MA alone. Because WPCs are building products where minimizing costs is extremely important, this finding has important commercial implications. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Lumber used for residential applications such as decking is typically treated with chemicals like chromated copper arsenate (CCA) to prevent degradation. However, beginning in 2004, CCA-treated wood has been phased out of the building products market by the U.S.¹ Environmental Protection Agency. A replacement product is wood/plastic composite (WPC) made by dispersing about 50 wt % wood flour into a matrix of polypropylene (PP), polyethylene (PE), polystyrene (PS), poly vinyl chloride, or acrylonitrile-butadiene-styrene (ABS). Because the wood content in the polymer matrix is high, the appearance of WPCs is similar to natural wood, and the preferred processing method is either profile extrusion or injection molding. Because polymers like PP are nonpolar (hydrophobic), whereas wood particulates are polar (hydrophilic), obtaining good adhesion between wood and polymer can be a problem, and this shows up as low tensile and flexural strengths.² To improve the adhesion between wood and plastics, maleic anhydride-grafted polypropylene (PP-*g*-MA) is used as a coupling agent. On the one hand, it is compatible with the PP matrix. On the other hand, the anhydride groups on the coupling agent react with the hydroxyl groups on the surface of wood

flour. The result is that the filler particles get bound to the polymer. A schematic diagram of esterification of cellulose is shown in Figure 1, and the improved adhesion between the fiber and the matrix reveals itself as an increase in both the tensile and flexural strengths of the WPC.

The major application of WPCs in the U.S. is in decking, and here impact strength is a key property of interest. This is because it is common practice for children to jump or run on the deck. In this situation, inadequate impact strength can lead to failure of the composite, resulting in injuries. In Europe, on the other hand, natural fiber composites are replacing glass fiber-reinforced plastics in automotive applications³; this is due to ease of recycling. Here again, mechanical property requirements include impact strength, flexural modulus, and ultimate strength.³ In this study, we explore the possibility of using a combination of additives to increase the tensile strength and the impact strength of WPCs. Note that the impact strength of PP-based WPCs is very sensitive to the wood flour content. Also, as with most semicrystalline polymers, PP possesses pseudo-ductile characteristics,⁴ and in our case, it does not fracture during the unnotched Izod impact test at room temperature. Consequently,

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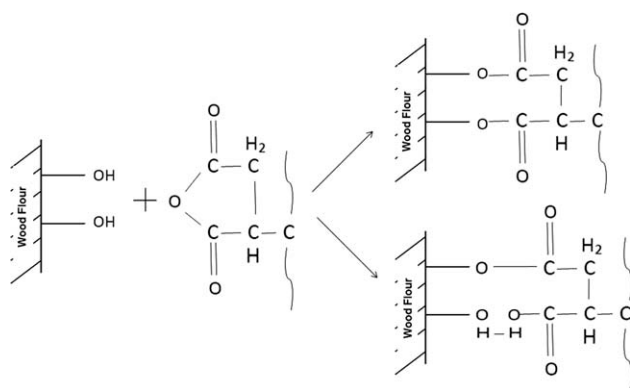


Figure 1. Schematic diagram showing how PP-g-MA helps to couple cellulose fibers to the PP matrix.

the reversed-notch Izod impact test is used, and the impact strength of PP-based WPCs is found to drop from 250 J/m to 80 J/m in this test when the wood content is increased from 10 to 50 wt %.⁵

Toughening of WPCs, using different additives, has been examined by Dalvåg et al. in the past.⁶ In their results, these authors found that the addition of an elastomer provides pronounced improvement in impact strength, but this happens at the expense of the modulus. This is an expected result which is observed when a low modulus material is added to composites. In this regard, SEBS-g-MA has been used as a compatibilizer and toughening agent for polymer blends containing glass fibers.^{7,8} In particular, it is compatible with PP, PE, and PS because it contains different moieties that make it miscible with these different polymers. Therefore, it is logical to use SEBS-g-MA as a coupling agent in PP-based WPCs. Indeed, Oksman et al studied the effect of adding SEBS-g-MA on the properties of PE- or PP-based WPCs.^{9–12} These and other researchers^{13–15} found that the addition of SEBS-g-MA not only improved the tensile strength of WPCs but also it improved impact strength; however, the modulus decreased. According to their results for PP-based WPCs made with 40 wt % pine flour, the use of 10 wt % SEBS-g-MA and 4 wt % PP-g-MA resulted in 107% better notched impact strength, but the modulus decreased by 35%. Given the expensive nature of polymer additives and the reduction in modulus of WPCs upon addition of SEBS-g-MA, it is of interest to vary the amount and nature of the different additives in order to obtain a better balance of WPC properties while using only limited amounts of elastomers and coupling agents. Note that, in the past, we have used additives to enhance the modulus of WPCs.¹⁶ Our current work, therefore, represents a continuation of this work.

EXPERIMENTAL PROCEDURE

Maple wood flour (Maple 8010), of 80-mesh size (about 177 μm), was provided by American Wood Fibers of Columbia, MD, USA, while the polymer used was BP Amoco's polypropylene homopolymer PP1246 (melt flow index = 20 g/10 min at 230°C and 2.16 kg, ASTM D1238). According to the manufacturer, wood flour was not pretreated or modified with chemi-

cals. PP-g-MA compatibilizer used was from Chemtura, Middlebury, CT, USA; it had a molecular weight of 120,000 (g/mol) with 1.0 wt % MA content. SEBS-g-MA was gifted by Kraton, Houston, TX, USA; it is a clear linear triblock copolymer based on styrene and ethylene/butylene, with a polystyrene content of 30% and maleic anhydride content of 2 wt %. An antioxidant, Anox BB011, was also used at the 0.1 wt % level to prevent polymer degradation during melt compounding. It is a blend of phenol and phosphite, and it was provided by Chemtura, Middlebury, CT, USA.

WPC samples were compounded using a Leistritz Micro-27 corotating twin-screw extruder with K-Tron powder and pellet loss-in-weight feeders. The screw geometry is shown in Figure 2. The L:D ratio of the screw is 40 : 1, and the extruder has 10 barrels. The kneading blocks are located at barrels 2, 3, 5, 6, and 8. This extrusion line is housed on the campus of West Virginia University. The PP-g-MA pellets, SEBS-g-MA pellets, or their combination were hand mixed with PP pellets in a bag before loading into the feeders. The wood flour used was predried in an oven at 100°C for 7 h before compounding, and the residual moisture content was less than 1 wt %. Using the thermogravimetric analysis technique at 100°C, it had been found that the moisture content of the as-received wood flour was about 7 wt % which is consistent with the data provided by the supplier. Rizvi and coworkers have done a detailed study about drying wood flour and using moisture as the blowing agent for WPC foaming. Their results indicated that for loosely packed wood flour, drying above 75°C seemed to remove most of the absorbed moisture content.¹⁷ The barrel temperature was controlled at 165–180°C from hopper to the die, while the screw rotation speed was fixed at 150 rpm. The total feeding rate was controlled at 4.8 kg/h, and all of the samples contained 50 wt % wood flour; the experimental matrix is listed in Table I.

The compounded WPC pellets were dried at 100°C and then injection molded using a Battenfeld model BA 1000/315 CDC injection molding machine to produce standard mechanical testing samples which can be used with ASTM D638 and D256 tests. The barrel temperature was controlled between 165 and 175°C, the injection pressure was fixed at 68.95 MPa (10000 psi) while the holding pressure was fixed at 27.58 MPa (4000 psi). The dog bone shaped and impact specimens were obtained in the same injection shot. The tensile and impact strength and stiffness properties of these samples were measured using an Instron 5869 universal testing machine and a SATEC™ BLI impact tester, Grove City, PA, USA. The tensile strength was analyzed according to ASTM D638 while the impact test refers to ASTM D256 (12.7 \times 63.5 \times 3.2 mm³). The cross sectional area of the tensile samples was 13 \times 3.2 mm², whereas the overall length of the samples was 165 mm (ASTM D638, Type I). Because WPCs generally showed relatively low impact strength in the standard Izod impact test, the reversed notch impact test method was applied to enhance the difference resulting from the presence of the coupling agents used. This technique is well accepted and has been used by other research groups to characterize the impact strength of wood and other natural fiber composites.^{18–21} Note that a minimum of five samples were tested in each case.



Figure 2. Screw geometry of the Leistritz Micro-27 extruder, L:D = 40 : 1.

The fracture surfaces of the WPCs obtained from tension tests were examined with a Hitachi S-4700 Field Emission Scanning Electron Microscope (FESEM) available in the Department of Chemical Engineering at West Virginia University. In addition, the polymer matrix was dissolved in boiling xylene and the wood flour analyzed. Wood flour extracted from WPCs and potassium bromide (KBr) were separately predried in an oven at 80°C to ensure that the moisture content was less than 1 wt %.

Table I. Composition of Various PP/Wood Flour Composites (Numbers Are Percentages)

Sample number	PP content (wt %)	PP-g-MA (wt %)	SEBS-g-MA (wt %)	Wood content (wt %)
1	50			50
2	49	1		50
3	48	2		50
4	45	5		50
5	49		1	50
6	48		2	50
7	45		5	50
8	47	2	1	50
9	46	2	2	50
10	43	2	5	50

Five milligrams of wood flour was mixed with KBr and compressed into disks and analyzed with the help of a Perkin Elmer Spectrum GX system FTIR. The xylene was purchased from J. T. Baker, while the KBr was purchased from Fluka.

Finally, the rate of water absorption of the WPCs was determined using a “blot and weigh” method. Three weighed samples were taken from WPCs having different amounts of SEBS-g-MA but a fixed amount of PP-g-MA to conduct this test. The typical injection-molded sample of $12.5 \times 64 \times 3.175 \text{ mm}^3$ was put on a tray of desiccants and dried in a vacuum oven at 80°C for 12 h. After that, each sample was immersed in a sealed container full of distilled water and was periodically removed and weighed. The results of the water absorption tests were represented as percentage weight gained versus time of immersion.

RESULTS AND DISCUSSION

Typical stress–strain curves of samples compounded with the two coupling agents and their combination are shown in Figure 3. This figure supports our contention that adding a small

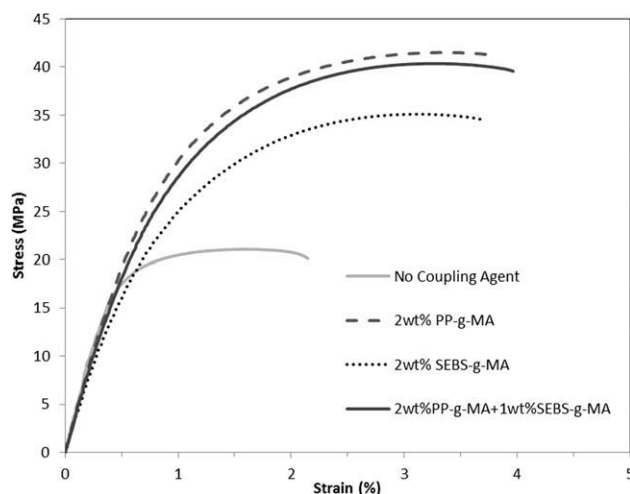


Figure 3. Stress–strain curve of WPC samples compounded with and without different coupling agents.

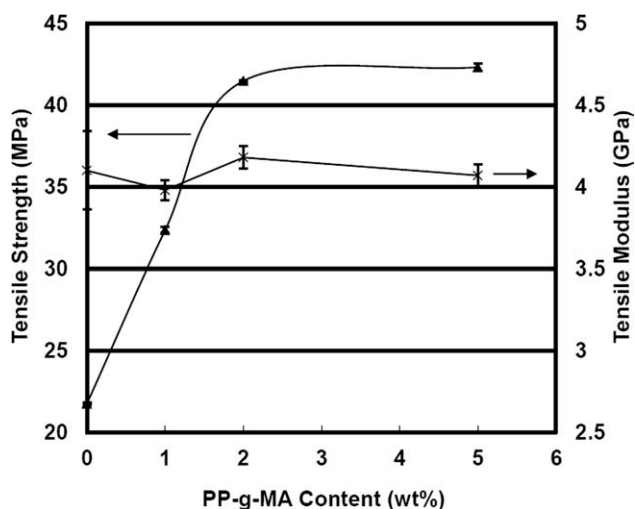


Figure 4. Tensile Strength and tensile modulus of WPCs formulated with PP-g-MA.

amount of a coupling agent can improve composite strength significantly. In addition, the use of 1 wt % of SEBS-g-MA together with 2 wt % of PP-g-MA results in a stress-strain curve similar to that obtained with 2 wt % PP-g-MA but with a slightly higher elongation at break. The tensile strength and tensile modulus of WPCs containing different amounts of either PP-g-MA or SEBS-g-MA are shown in Figures 4 and 5, respectively. As can be seen in Figure 4, the tensile strength of WPCs increased from 21.76 to 41.48 MPa when the PP-g-MA loading level increased from 0 to 2 wt %. However, there were diminishing returns on adding PP-g-MA beyond the 2 wt % level. For example, the tensile strength only increased by less than 1 MPa when the loading level of PP-g-MA was increased from 2 to 5 wt %. Thus, the addition of 2 wt % of PP-g-MA in WPCs would appear to be the optimum loading level of coupling agent necessary to provide good adhesion between PP and wood flour. The modulus of WPCs is clearly not a function of PP-g-MA content and remains essentially constant. This is because the modulus is a small strain property, and it should

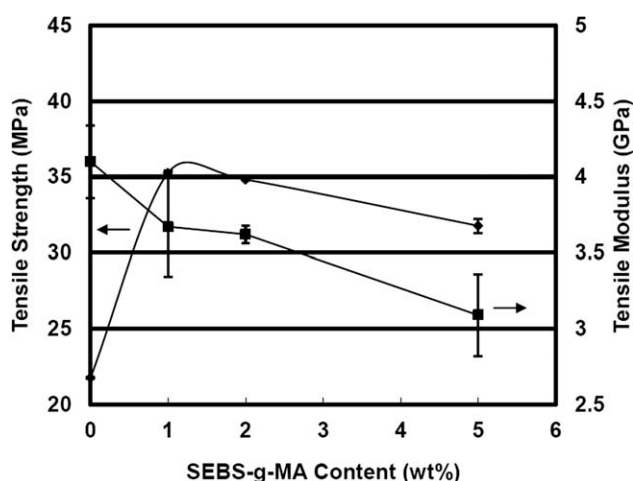


Figure 5. Tensile strength and tensile modulus of WPCs formulated with SEBS-g-MA.

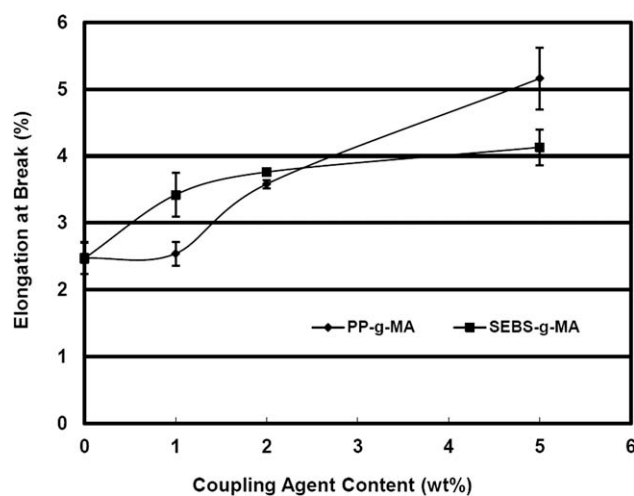


Figure 6. Elongation at break of WPCs formulated with PP-g-MA or SEBS-g-MA.

not depend on the coupling agent content provided that adhesion is maintained between the reinforcement and the matrix and provided that the presence of the coupling agent does not alter the properties of the matrix. In this case, the modulus of the PP-g-MA is very similar to the modulus of the PP itself, and this was verified by experiment. Different compositions of PP1246 and PP-g-MA were made by twin screw extrusion and followed by injection molding. Mechanical testing showed that PP1246, PP-g-MA, and their mixtures possessed similar modulus values.²² On the other hand, as can be seen from Figure 5, the strength of WPCs first increased when 1 wt % of SEBS-g-MA alone was added to the WPC, but then it decreased with SEBS-g-MA loading level. This is not surprising since it is known that when elastomers are used as impact modifiers in thermoplastics, the tensile strength decreases.¹⁰ In addition, the modulus of WPCs decreases progressively with SEBS-g-MA content, and this is undesirable because the design of WPCs is limited by modulus and not strength. The elongation at break of WPCs with added amounts of the two coupling agents is shown in Figure 6. As expected, the elongation at break of WPCs containing SEBS-g-MA first increased at the 1 wt % loading level and then leveled off at higher concentrations. The elongation at break increased with PP-g-MA loading level as well, especially when the PP-g-MA content exceeded 1 wt %. It should be noted that the elongation at break of WPCs does not increase at low PP-g-MA content. The reason for this needs to be further investigated. The impact strength of WPCs with different amounts of added PP-g-MA or SEBS-g-MA is shown in Figure 7. It is found that both PP-g-MA and SEBS-g-MA increase the reversed-notch impact strength, but SEBS-g-MA provides better impact resistance than PP-g-MA. In the case of SEBS-g-MA, 1 wt % of the additive led to a more than 100% increase in impact strength, whereas, in the case of PP-g-MA, 2 wt % of PP-g-MA gave the best enhancement in impact strength. The effect of combining the two coupling agents was studied next.

Because 2 wt % of PP-g-MA provides good tensile and impact strengths, the loading level of PP-g-MA was fixed at 2 wt %, and the SEBS-g-MA content was varied. The tensile properties

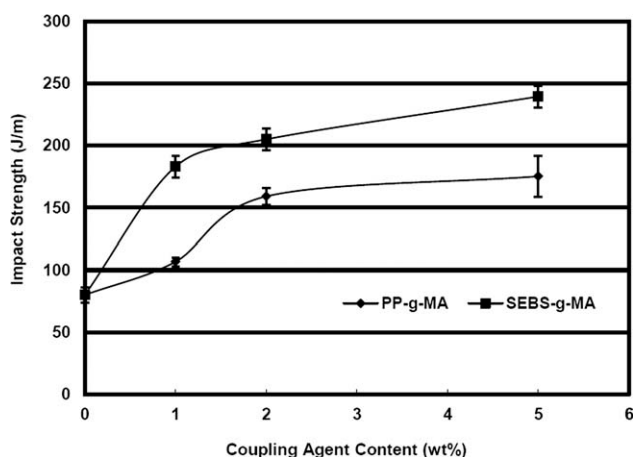


Figure 7. Reversed-notch Izod impact strength of WPCs formulated with PP-g-MA or SEBS-g-MA.

of WPCs containing 2 wt % PP-g-MA and different amounts of SEBS-g-MA are shown in Table II. Also shown in this Table are data for 3 wt % PP-g-MA alone and 3 wt % SEBS-g-MA alone, as obtained from Figures 4 and 5 by interpolation. Here, our logic is to show the synergistic effect of the two coupling agents. Based on this idea, we have compared the effect of the two coupling agents separately with the combination of coupling agents, all at a fixed loading level of 3 wt %. It is seen that although both the tensile modulus and the tensile strength decrease in the presence of SEBS-g-MA, the property reductions are marginal. With 1 wt % of added SEBS-g-MA, the tensile strength of WPCs formulated with 2 wt % PP-g-MA decreased by only 2.5%, whereas the tensile modulus decreased by only 4.5%. These minor reductions in strength and modulus, however, are more than compensated by large increases in the reversed-notch Izod impact strength and elongation at break as shown in Table II. By adding only 1 wt % SEBS-g-MA, the reversed-notch Izod impact strength increased from 153 to 206 J/m, an increase of 35%. For purposes of comparison, it should be noted that the reversed-notch impact strength of WPCs without any coupling agent is 80 J/m. In the presence of 2 wt % of PP-g-MA, this value increases to 153 J/m, and it further increases to only about 160 J/m when 3 wt % of PP-g-MA is added to the composite. Feng et al.²³ saw an identical increase in the un-notched impact strength on adding 3 wt % PP-g-MA to 50 wt % short kenaf fiber blends with PP. Thus, using 2 wt % PP-g-MA together with 1 wt % SEBS-g-MA would appear to give a better

balance of mechanical properties than using 2 wt % PP-g-MA alone or 3 wt % PP-g-MA alone. It should be noted that PP-g-MA and SEBS-g-MA cannot react with each other. They can only possibly compete with each other for the hydroxyl groups present in the wood flour, and the result is improved filler-polymer adhesion regardless of which coupling agent dominates. Because wood has a porous structure, most of the hydroxyl groups are actually present on interior surfaces. It is only the surface hydroxyl groups that participate in the esterification reaction. Given this fact and given the fact that the two coupling agents are added in small quantities, they appear to act independently of each other as far as improvement in adhesion is concerned. As a consequence, one observes characteristics of the coupling action of both materials, including the toughening action of SEBS-g-MA. However, the amount of added SEBS-g-MA is not such as to cause a significant reduction in modulus.

The results of the examination of the microstructure of WPCs with 1 wt % SEBS-g-MA only and 1 wt % SEBS-g-MA plus 2 wt % PP-g-MA are shown in Figures 8 and 9, respectively. The tensile fracture surface of the sample which contains 1 wt % SEBS-g-MA is shown in Figure 8. Ductile failure is observed through the entirety of the tensile fracture surface with only 1 wt % of added SEBS-g-MA. Similar behavior has been reported in reference 15 but at a much higher SEBS-g-MA content. On the other hand, a typical fracture surface of the sample containing 1 wt % SEBS-g-MA and 2 wt % PP-g-MA is shown in Figure 9. In this sample, almost no ductile failure was found on the fracture surface. This explains why a WPC sample containing a combination of 1 wt % SEBS-g-MA and 2 wt % PP-g-MA possesses a higher modulus (3.99 GPa) when compared with a sample containing 1 wt % SEBS-g-MA (3.67 GPa). Since previous studies have not reported such a large improvement of impact strength, it is useful to review the work of other researchers and compare the observed behavior of similar ternary composite systems. Indeed, SEBS-g-MA is commonly applied for toughening in many thermoplastic composites because of its excellent compatibility with different polymers. For example, it has been used to compatibilize and toughen nylon/PP/glass fiber,^{24,25} PP/glass fiber,^{8,26–32} and polyolefin/wood fiber^{9–12,14,15} systems. This is because glass fibers, nylon and wood fibers are known to have many hydroxyl groups either in the structure or on the surface of the fiber and thus would react with the maleic anhydride groups via esterification. This assumption was supported by observing the cryofractured surface of the composites where a thin layer of coated polymer was found on the surface of the glass fiber.^{8,26–32} In addition,

Table II. Mechanical Properties of WPCs Containing Different Amounts of Coupling Agents. The Numbers in the Parenthesis Are Standard Deviation

	Tensile strength (Mpa)	Young's modulus (Gpa)	Elongation at break (%)	Impact strength (J/m)
No coupling agent	21.76 (0.07)	4.1 (0.24)	2.47 (0.33)	80 (5.97)
2 wt % PP-gMA	41.48 (0.08)	4.18 (0.07)	3.58 (0.20)	153.24 (11.48)
2 wt % PP-g-MA + 1 wt % SEBS-g-MA	40.45 (0.77)	3.99 (0.15)	3.98 (0.21)	206.5 (9.8)
2 wt % PP-g-MA + 2 wt % SEBS-g-MA	38.92 (0.08)	3.77 (0.18)	4.28 (0.21)	214.82 (10)
2 wt % PP-g-MA + 5 wt % SEBS-g-MA	37.93 (1.68)	3.72 (0.17)	4.24 (0.19)	239.15 (15.75)
3 wt % SEBS-g-MA	33.79	3.44	3.88	216.48
3 wt % PP-g-MA	41.76	4.14	4.11	160.56



Figure 8. Tensile fracture surface of 50 wt % wood WPCs containing 1 wt % of SEBS-g-MA.

Oksman et al. further found that the thin layer coating on the wood fiber was SEBS-g-MA using transmission electronic microscopy.¹² These observations strongly suggested that adding SEBS-g-MA would improve the stress transfer between fiber and matrix, and it would lead to ductile failure around the wood fibers. In our case, we found that the ductile failure phenomenon was significantly reduced when another 2 wt % of PP-g-MA was added to the polymer matrix. It is possible that part of the hydroxyl groups on the surface of wood fibers were coupled with PP-g-MA and thus less SEBS-g-MA was attached to the fiber surface, but the SEBS rubber in the matrix still improved the impact strength of the material.

Water absorption by WPCs is an important concern due to the possibility of dimensional changes during use and the possibility of fungus attack. The results of water absorption are displayed in Figure 10. At the 2 wt % PP-g-MA content, the rate of water absorption decreases with increasing amounts of added SEBS-g-MA. Either coupling agent forms covalent bonds with the wood surface and is itself compatible with the polymer matrix. The presence of a coupling agent has multiple effects: the reaction

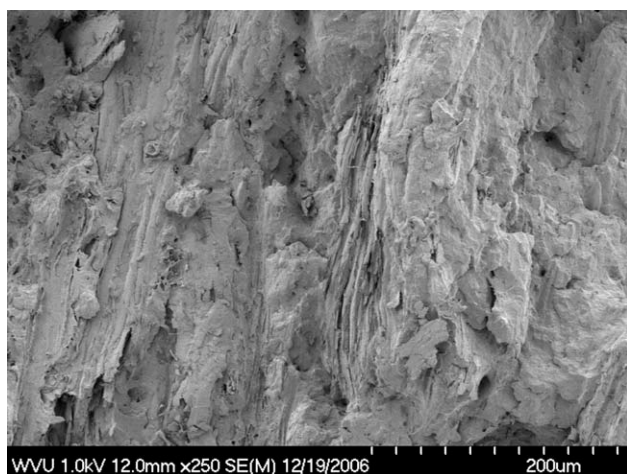


Figure 9. Tensile fracture surface of 50 wt % wood WPCs containing 1 wt % SEBS-g-MA and 2 wt % of PP-g-MA.

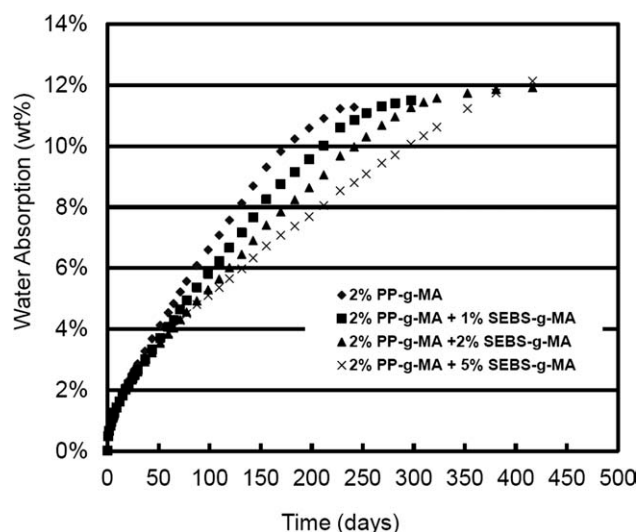


Figure 10. Rate of water absorption by WPCs containing 2 wt % of PP-g-MA and different amounts of SEBS-g-MA.

between the maleic anhydride groups in SEBS-g-MA and the hydroxyl groups on the surface of the wood flour serves to consume the hydrophilic hydroxyl groups via the esterification reaction shown in Figure 1; this reduces the driving force for diffusion of moisture into the composite. In addition, the coupling of the wood to the matrix acts to limit the swelling of the WPC, and it also acts as a mass transfer barrier around the wood particulates.³³ Figure 10 clearly shows that the rate of moisture absorption decreases progressively as additional amounts of SEBS-g-MA are added to the WPC. It, therefore, appears that the dominant influence of the added SEBS-g-MA is to act as an effective barrier to moisture trying to diffuse into the wood particulates. Thus, adding SEBS-g-MA together with PP-g-MA is beneficial as far as reducing the rate of water absorption of WPCs is concerned.

Because the addition of PP-g-MA and SEBS-g-MA decreases the rate of water absorption and the addition of SEBS-g-MA

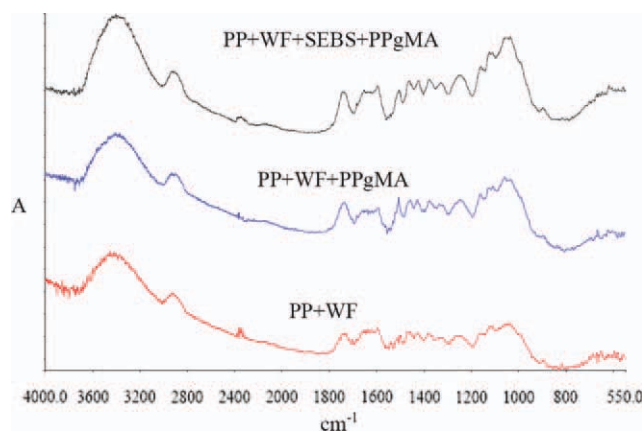


Figure 11. FTIR spectra of wood flours treated with and without coupling agent. Wood flours were extracted from WPC samples using hot xylene. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

increases the impact strength significantly, it is of interest to examine the infrared spectrum of wood flour with and without PP-g-MA after compounding. Typical FTIR spectra are shown in Figure 11. However, no real difference can be seen between the two IR spectra because wood flour itself contains ester groups. Thus, the esterification reaction between hydroxyl groups and maleic anhydride cannot be seen by FTIR.³⁴ Nevertheless, the broad absorption peak of free hydroxyl groups located between 3650 and 3200 cm^{-1} can be identified easily.³⁵ The spectrum showed that the peak of hydroxyl groups was lowered in the presence of PP-g-MA which is the indication of the esterification reaction. When SEBS-g-MA was added together with PP-g-MA, the characteristic peak corresponding to the hydroxyl group was further flattened. In other words, the FTIR spectrum showed that adding a coupling agent would lower the peak of hydroxyl group, and this indicates that the hydroxyl groups were consumed by reaction with the maleic anhydride groups.

SUMMARY

It is standard practice to add PP-g-MA as a coupling agent to PP-based WPCs to increase tensile and flexural strengths. The optimum loading level of the additive is about 2 wt % for WPCs containing 50 wt % wood flour because property levels tend to saturate beyond this value. Here, we show that simultaneously adding 1 wt % of SEBS-g-MA and 2 wt % of PP-g-MA as coupling agents can increase the reversed-notch impact strength of the WPCs by a factor of 2.5 relative to the situation without the use of a coupling agent. This impact strength is also significantly higher than that obtained with the use of either 2 wt % or 3 wt % PP-g-MA alone and demonstrates a synergistic effect with the use of a combination of coupling agents. This increase in impact strength is accompanied with only a very slight decrease in the tensile modulus and tensile strength of the WPC. At the same time, the rate of water absorption by the WPCs decreases slightly.

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