

Effects of Silane on the Properties of Wood-Plastic Composites with Polyethylene-Polypropylene Blends as Matrices

Craig M. Clemons,¹ Ronald C. Sabo,¹ Michael L. Kaland,² Kolby C. Hirth³

¹Engineered Composites Science group, USDA Forest Service, Forest Products Laboratory, Madison, Wisconsin 53726

²Department of Mechanical Engineering, University of Wisconsin-Madison, Madison, Wisconsin 53706

³Analytical Chemistry and Microscopy Laboratory group, USDA Forest Service, Forest Products Laboratory, Madison, Wisconsin 53726

Received 6 January 2010; accepted 2 April 2010

DOI 10.1002/app.32566

Published online 18 August 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The influence of 3-(trimethoxysilyl)propyl methacrylate and benzoyl peroxide on gel content, crystallinity, and mechanical performance of unfilled PP-PE blends, and their composites with wood was investigated. All materials were compounded in a twin screw extruder and then injection molded. Specimens were then exposed to high-humidity and elevated temperature in a humidity chamber to cross-link any unhydrolyzed silane.

Adding wood to the PE-PP blends, increased premature cross-linking but also increased gel contents. However, the gel contents of the composites were still low. The PP component did not appear to cross-link well and our gels were almost entirely HDPE. Fourier Transfer Infrared (FTIR) spectra provided additional evidence that TMSPM is grafted and cross-linked in unfilled PE-PP blends.

Unfortunately, the spectra of wood composites proved difficult to interpret because of the complexity and overlap of the FTIR spectra of the wood. The HDPE component annealed when exposed to high-humidity and elevated temperature, although less so in samples with high-gel contents, presumably because of the decreased mobility. Annealing influenced mechanical performance, especially increasing moduli. Adding peroxide and silane appeared to improve adhesion between the wood flour and matrix in the composites but had little effect on energy absorbed during high-speed puncture tests. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 1398–1409, 2011

Key words: polypropylene; polyethylene; reactive extrusion; cross-linking; composites

INTRODUCTION

Polymers are routinely combined to provide blends that better meet performance requirements or extend performance into new applications. Not surprisingly, there are many examples of polymer blends and reviews on the subject are readily available.^{1–3} However, from a recycling perspective, the motivations are often different. It is often technically difficult or uneconomical to separate certain combinations of plastics. For example, blends of polypropylene (PP) and poly-

ethylene (PE) often remain after various separation strategies have been applied to a plastics waste stream. The performance of these blends is often well-below those of the individual components due, in part, to the incompatibility of the plastics in the blends.

Wood-plastic composites (WPCs) may represent a potential outlet for these PE-PP blends as they are already a major outlet for recycled PE film.⁴ WPCs are used in applications such as automotive paneling, furniture, and consumer products.⁵ However, the largest and fastest growing use of WPCs is in the construction industry.⁶ Over half of the WPCs produced in North America are used in decking applications, and the great majority of WPCs are in exterior building products such as deck boards, railings, and window and door profiles (Morton and Rossi 2003). There has been considerable interest lately in other applications as well such as signs, furniture, siding, and roofing, as well as using WPCs in a variety of marine and construction applications requiring greater structural performance than demanded by current products.⁷

Although WPCs may provide an outlet for PE-PP blends, a number of technical hurdles need to be overcome. Also, performance benefits as well as favorable

The Forest Products Laboratory is maintained in cooperation with the University of Wisconsin. This article was written and prepared by U.S. Government employees on official time and is therefore in the public domain and not subject to copyright. The use of trade or firm names in this publication is for reader information and does not imply endorsement by the U.S. Department of Agriculture of any product or service.

Correspondence to: C. M. Clemons (cclemons@fs.fed.us).

Contract grant sponsor: Department of Agriculture, through Louisiana State University Agricultural Center; contract grant number: 68-3A75-6-508.

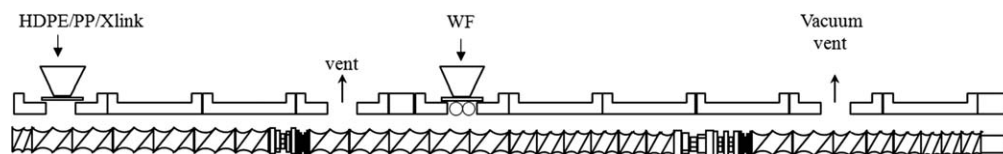


Figure 1 Setup for compounding of WPCs. "Xlink" refers to the cross-link solution containing the solution of BPO and TMSPM.

economics need to be demonstrated if PE-PP blends are to be widely used as a matrix material. A primary technical consideration is the compatibilization of the PE and PP to improve performance. Because of their importance in recycling, various strategies of compatibilizing PE and PP have been investigated,⁸ which generally fall into two categories: (1) the use of additives and (2) reactive compatibilization.⁹

In the additive approach, appropriate elastomeric block or random copolymers or terpolymers such as ethylene-propylene or ethylene-propylene-diene elastomers are synthesized and incorporated into the polymer blend. The miscible or at least compatible segments of the copolymer molecules help to tie the phases together. The resulting blend has a finer and more stable morphology and a useful balance of properties can be obtained in some circumstances.¹⁰ However, although elastomers have been investigated for use in WPCs, the resulting loss in stiffness and added cost have largely prevented their use commercially.

A number of reactive blending strategies of compatibilizing PE-PP blends have also been investigated.¹¹⁻¹⁴ Many use free radical initiators such as organic peroxides to generate macroradicals during processing that hopefully recombine to form PE-PP copolymers that can compatibilize the blend. To minimize unwanted side reactions, especially chain scission of PP, coreactants have been investigated to try and stabilize the macroradicals or act as vector fluids, carrying the reactive ingredients to the interface where compatibilizing copolymers can be formed.⁹⁻¹¹

One approach of possible interest to PE-PP blends in WPCs is the use of peroxides and silanes. Peroxide/silane chemistry has traditionally been used to cross-link polyolefins for use in wire and cable insulation, for example. The reactions often take place in two steps: (1) the grafting of silane onto the polyolefin followed by (2) moisture cross-linking of the silane-modified polyolefin.¹⁵ Unlike PE, PP cross-linking has not yet had much commercial success but progress continues to be made.^{16,17}

Silanes have also been investigated both as coupling¹⁸⁻²⁰ and cross-linking²¹⁻²⁷ agents for WPCs and similar composites to improve performance such as strength, toughness, and creep resistance. When added with peroxides, vinyl silanes can bond with polyolefins or wood flour or both, offering the opportunity for coupling the wood and plastic. Additionally, silanes can cross-link one or more of the plastic components.

Undesired side reactions resulting in molecular weight degradation, for example, are also possible. The wide range of possible reactions adds complexity but also offers opportunities to tailor performance.

This research is an initial, exploratory investigation combining reactive silane extrusion of WPCs²³ and silane grafting/cross-linking chemistries for PP²⁰ to prepare WPCs with PE-PP blends as matrices. Influences on gel content, crystallinity, and mechanical performance were investigated.

EXPERIMENTAL

The high-density PE (HDPE) used for this portion of the project was HD 6605, a HDPE homopolymer with a melt flow index of 5 g/10 min (ExxonMobil Chemical, Houston, TX). The PP was Certene PHM-20AN, a homopolymer with a melt flow index of 20 g/10 min. (Muehlstein and Co., Norwalk, CT). The wood filler was a nominal 40 mesh (420 μm) western pine wood flour from American Wood Fibers (Schofield, WI). The silane and peroxide used were 3-(trimethoxysilyl)propyl methacrylate (TMSPM) and benzoyl peroxide (BPO) from Sigma Aldrich (Milwaukee, WI).

A 32-mm, twin screw extruder (D-TEX extruder, Davis Standard, Pawcatuck, CT) and related gravimetric feed system (Accurate, Whitewater, WI) were used to compound the materials and carry out the grafting reactions. A schematic of the processing setup and screw design are shown in Figure 1. BPO was dissolved in TMSPM in either a 1 : 10 or 1 : 20 weight ratio, before extrusion. A peristaltic pump was used to meter the TMSPM/BPO solution into the main feed throat, where the PE and PP were also added. After mixing these components in the first part of the extruder, dried wood flour (WF) was added in the fifth zone using a twin screw side feeder. Atmospheric and vacuum vents at zones 4 and 9 were used to remove any volatiles during extrusion.

The molten strands exiting the extruder die were air-cooled, pelletized, and then injection molded into 2 mm thick circular plates with a 5 cm diameter. Cross-linking was performed in a humidity chamber at 90% RH and 85°C for 32 h. Specimens were then dried, before further testing. Degree of cross-linking was determined by gel content according to ASTM D2765-01²⁸ except that the xylene extractions were carried out in a 3 L reaction vessel for 24 h to accommodate the large number of samples tested in

this study. The extracted samples were also first air dried overnight. At least two replicates were performed for each condition, and additional replicates were tested for conditions with greater than expected variability in gel contents. High-speed puncture impact tests were performed on the cross-linked plates according to ASTM D3793.²⁹ Type V tensile specimens were cut from the cross-linked plates and tested according to ASTM D638-03.³⁰

The crystalline behavior of the injection molded samples and the composition of residual material from the gel content determinations were investigated using a differential scanning calorimeter (Perkin Elmer DSC 7). Samples of about 9.5–10 mg were heated at 10°C/min in a nitrogen environment. The specific heat of melting (ΔH_m) was calculated by integrating the appropriate melting peak (128°C and 162°C for HDPE and PP, respectively) and using eq. (1) to account for the amount of the relevant polymer phase (PP or HDPE) within the blend:

$$\Delta H_m = \frac{\Delta h_m}{xw} \quad (1)$$

where Δh_m is the integrated peak area, x is the weight fraction of polymer in the sample, and w is the weight of the sample. The percent crystallinity (χ) of each polymer phase was calculated by dividing the appropriate specific heat by the heat of fusion for pure crystalline material (ΔH_m^0).

$$\chi_{HDPE} = \frac{\Delta H_{m,HDPE}}{\Delta H_{m,HDPE}^0} \times 100 \quad (2)$$

$$\chi_{PP} = \frac{\Delta H_{m,PP}}{\Delta H_{m,PP}^0} \times 100 \quad (3)$$

There are numerous values for the heats of fusion of pure crystalline HDPE and PP depending upon the specific mode of crystallization. Heats of fusion for the pure crystalline of 293 J/g and 209 J/g were used for HDPE and PP, respectively.³¹

A Mattson Galaxy 5000 FTIR spectrometer equipped with a Harrick DRA-2CN diffuse reflectance attachment was used to obtain diffuse reflectance infrared fourier transform (DRIFT) spectra, scanning 4000–450 cm^{-1} with 4 cm^{-1} resolution. The spectra obtained were from the average of 512 scans and were manually baseline corrected. Solid samples were finely ground with a ball mill and dispersed in KBr to obtain DRIFT spectra. Liquid TMSPM was scanned in absorbance mode. Homo cross-linked TMSPM was prepared simply by leaving liquid TMSPM in a humidity oven at 90% RH and 85°C for 10 days, after which it was a cross-linked solid.

Scanning electron microscopy on both the solid wood and WPC composites were performed using a

Zeiss EVO40 scanning electron microscope (Carl Zeiss SMT, Thornwood, NY). Either secondary electrons or a combination of secondary and backscattered electrons were used in imaging specimens.

RESULTS AND DISCUSSION

Grafting onto PP using free radical initiators can be difficult because of unwanted side reactions such as chain scission and disproportionation.¹⁶ Recently, researchers have grafted TMSPM to PP using a free radical initiator to produce a coupling agent for viscose fiber/PP composites.²⁰ Additionally, several researchers have used TMSPM to cross-link PP as well.^{17,32} Therefore, we chose to investigate a TMSPM and BPO system with our blends and composites.

Compositions of the blends and their composites are summarized in Table I. To prevent an excessive number of formulations, we focused on a PE : PP weight ratio of 75 : 25. Several peroxide:silane weight ratios were investigated as well as two levels of cross-linking solution (i.e., solution of peroxide and silane) for both the unfilled blends and blends filled with 33% wood flour by weight. The wood flour content was kept low to ensure that thin specimens could be injection molded. Additionally, several other formulations with unblended PP or HDPE were included for comparative purposes.

Gel contents before placement in the humidity chamber are shown in Table I and plotted in Figures 2, 3. All unfilled blends yielded gel contents, even those without peroxide and silane. This suggests that even longer extraction times might be warranted, although most of these gel contents were less than 5% except those blends containing high-silane or peroxide contents or both. Furthermore, no visibly recoverable material remained in the mesh pouch for those specimens having gel contents less than about 5%, so gel contents lower than this were generally regarded as insignificant. The presence of significant gels before exposure to high-moisture levels and elevated temperature in the humidity chamber is evidence of undesired or premature cross-linking during processing. Although this premature cross-linking appeared minimal for the unfilled blends, the largest gel content was only about 16%, which is considerably below those found by Liu et al.¹⁷ for unfilled PP. However, the processing by Liu et al. was quite different as PP was cross-linked in a batch mixer at cooler temperatures and over a 9 minute time period. Such long residence times are not practical for reactive extrusion. The residence times for our extruder were only about 2 minutes.

The gel contents of the composites showed more premature cross-linking than the unfilled blends but had higher gel contents. The reason for the increases in gel content with the addition of wood in the TMSPM/

TABLE I
Compositions and Gel Contents for Unfilled PE:PP Blends and Composites

Blend	HDPE/PP wt. ratio	Plastic:WF: Xlink sol'n weight ratio		TMSPM:BPO wt. ratio in Xlink sol'n	Gel content before chamber (%)	Standard error (%)	Gel content after chamber (%)	Standard error (%)	Transfer pressure (MPa)	
Unfilled blends:										
0-00	75/25	100	0	0	NA	3.8	0.9	3.0	0.1	7.5
2-00	75/25	100	0	2	TMSPM only	2.8	1.3	3.7	0.0	7.1
2-05	75/25	100	0	2	20/1	4.4	0.6	3.6	0.1	7.0
2-10	75/25	100	0	2	10/1	3.8	1.0	7.2	0.3	7.1
4-00	75/25	100	0	4	TMSPM only	5.4	2.3	4.7	1.1	6.7
4-05	75/25	100	0	4	20/1	4.5	0.7	11.6	0.9	6.8
4-10	75/25	100	0	4	10/1	4.6	1.4	16.4	0.5	7.0
Composites:										
0-00-C	75/25	100	50	0	NA	2.3	1.3	1.3	2.2	10.9
2-00-C	75/25	100	50	2	TMSPM only	0.3	2.5	7.4	0.2	11.0
2-05-C	75/25	100	50	2	20/1	1.9	0.3	5.7	2.1	11.0
2-10-C	75/25	100	50	2	10/1	4.7	1.7	17.0	1.9	11.7
4-00-C	75/25	100	50	4	TMSPM only	0.5	0.2	4.0	2.8	10.0
4-05-C	75/25	100	50	4	20/1	8.1	0.3	15.0	3.0	9.8
4-10-C	75/25	100	50	4	10/1	14.3	0.6	22.9	1.8	10.9
Additional:										
PE	100/0	100	0	0	NA	—	—	—	—	10.1
Xlink PE	100/0	100	0	2	20/1	3.4	0.3	3.1	1.1	10.1
Xlink PE-C	100/0	100	50	2	20/1	-4.5	3.2	-1.5	0.2	15.3
PP	0/100	100	0	0	NA	—	—	—	—	5.3
Xlink PP	0/100	100	0	2	20/1	3.5	0.5	3.7	0.3	3.9
Xlink PP-C	0/100	100	50	2	20/1	2.8	2.3	7.0	0.1	6.5

BPO system is not immediately clear. Perhaps some small amount of moisture provided by the wood leads to premature cross-linking via the hydrolysis and condensation of the resulting silanol groups that prevents undesired volatilization of the silane before grafting. However, far more investigation is required to determine an actual mechanism.

Figure 4 shows scanning electron micrographs of the composite with high-silane and peroxide con-

tents before and after extraction in xylenes. Before extraction [Fig. 4(a)], wood flour particles are either collapsed or their lumens are filled with polymer, which results in an increase in density when wood is added. Some separation at the wood-polymer interface is seen but this may be an artifact of the specimen preparation. Because of the low-silane concentrations used, it was not possible to use X-ray imaging to locate the silicon atoms (and therefore

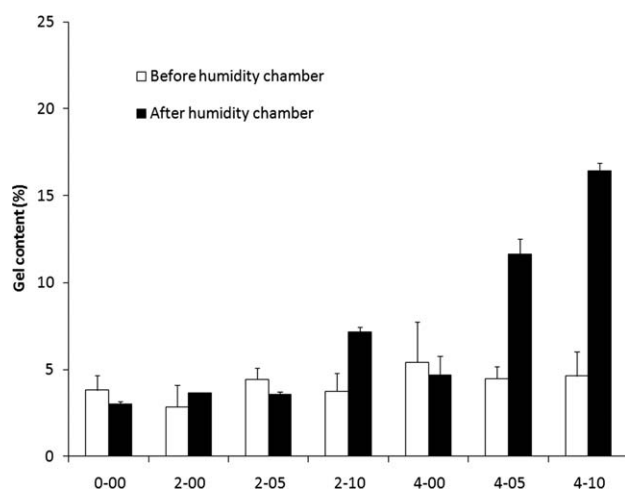


Figure 2 Gel contents for BPO-TMSPM grafted polymer blends before and after conditioning in a humidity chamber at 90% RH and 85°C for 32 h. Compositions are listed in Table I. Error bars represent the standard error of each blend.

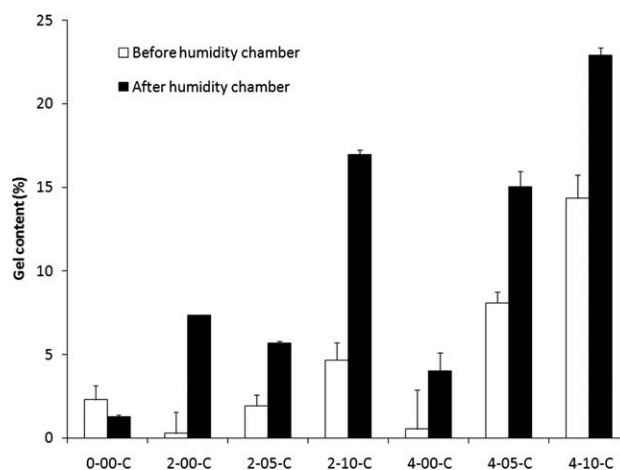


Figure 3 Gel contents for BPO-TMSPM grafted composite blends before and after conditioning in a humidity chamber at 90% RH and 85°C for 32 h. Compositions are listed in Table I. Error bars represent the standard error of each blend.

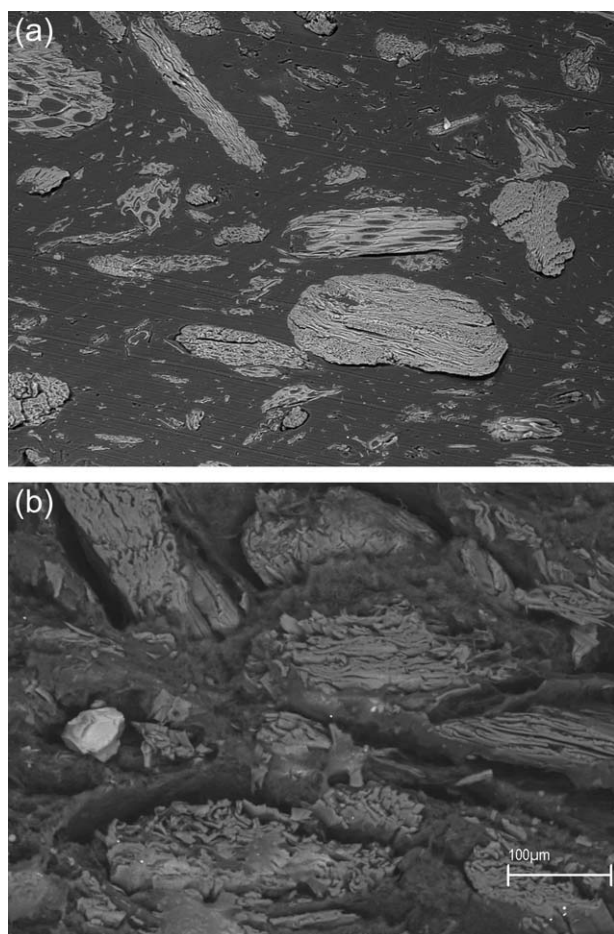


Figure 4 Cross section of specimen 4–10 before (a) and after (b) extraction in boiling xylenes.

the silane) except for several, very small concentrations of silicon suggesting that all of the silane was not well-dispersed. Alternatively, we examined the residual gel after the composite was extracted in xylenes [Fig. 4(b)]. The bulk matrix appears to have cross-linked but there is no clear and consistent indication of whether the gel forms solely in the bulk matrix or if the matrix cross-links with the wood flour.

FTIR analysis of the polymer blend suggests that the TMSPM is grafted to the polymer and cross-linked in the case of high-silane and peroxide content (i.e., sample 4–10). Figure 5 shows the FTIR spectra of TMSPM liquid (a) and homo cross-linked gel (b). The peak at 1638 cm^{-1} is because of the double bond in the silane, and the peak at 1722 cm^{-1} is because of the carbonyl stretching of the TMSPM,²⁰ whose chemical structure is shown in Figure 6. The carbonyl peak (1722 cm^{-1}) is considerably broadened for the cross-linked TMSPM compared with the peak for the neat TMSPM liquid, indicating chemical bonding of the silane molecules. Furthermore, the peaks in the $1,200\text{--}1,000\text{ cm}^{-1}$ range are broadened and more prominent for the cross-linked silane. The exact nature of the peaks is difficult to

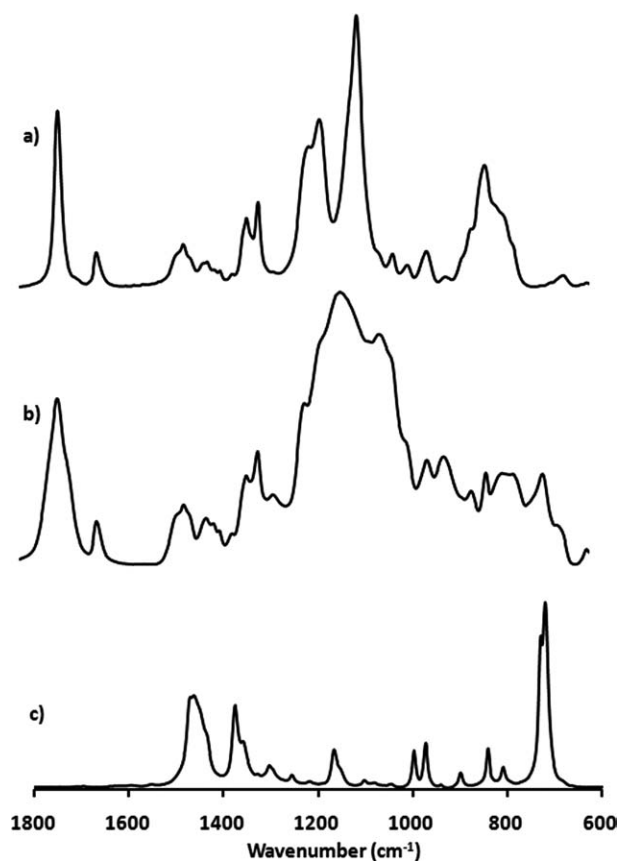


Figure 5 FTIR spectra of (a) neat TMSPM liquid, (b) homo cross-linked TMSPM, and (c) HDPE-PP blend (sample 0–00).

determine, but peaks in this region are often associated with various silane bonds including the Si—O—Si bonds expected in cross-linked silane.^{23,33} Also, the spectra shown in Figure 5(c) for the polymer blend has no peaks in the $1,800\text{--}1,600\text{ cm}^{-1}$ range and only a few, relatively weak peaks in the $1,200\text{--}1,000\text{ cm}^{-1}$ range, which are the regions of interest for the silane reactions. FTIR spectra for the silane-grafted polymer blend (sample 4–10) are shown in Figure 7. Here, the silane C=C peak at 1638 cm^{-1} is notably absent, indicating that the TMSPM is likely grafted to the polymer. No discernible difference was seen in the spectra of the silane-grafted blend prior to [Fig. 7(a)] and after [Fig. 7(b)] treatment in the humidity chamber, which may indicate premature cross-linking or a lack of sensitivity in our spectral analysis. Finally, the spectrum of the gel [Fig. 7(c)] shows that the gel consists of both polymer and cross-linked TMSPM. The region of

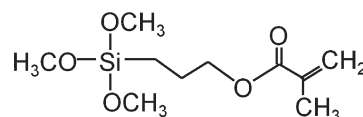


Figure 6 Chemical structure of TMSPM.

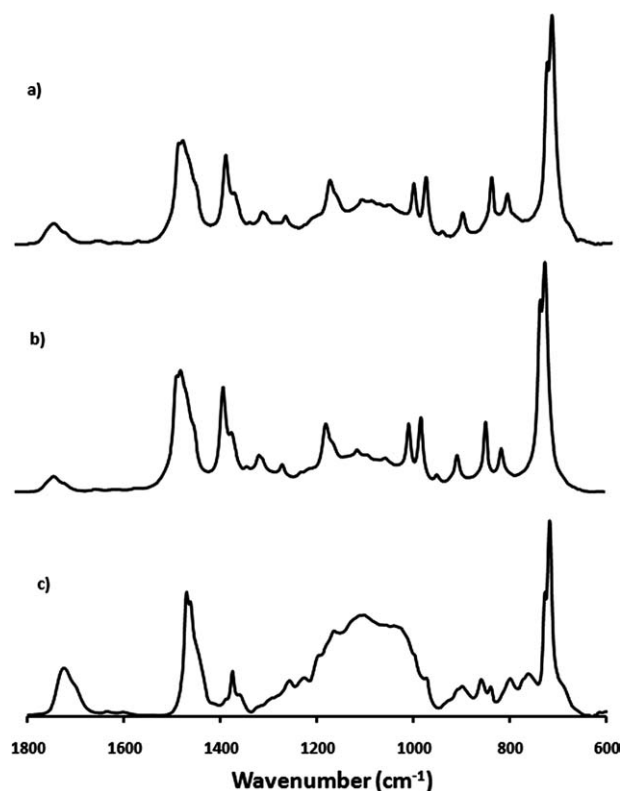


Figure 7 FTIR spectra of HDPE-PP polymer blend (sample 4–10) (a) after injection molding (b) after 32 h in a humidity chamber at 90% RH and 85°C, and (c) gel of the sample after the humidity chamber.

1200–1000 cm^{-1} appears similar to that of the homo cross-linked TMSPPM [Fig. 5(b)] and the peak at 718 cm^{-1} comes from the polymer blend, as shown in Figure 5(c). Unfortunately, our spectral analysis of the wood-filled composites was inconclusive due to the severely overlapping peaks from the wood flour.

Injection molding parameters were adjusted to minimize the residence time of the material (e.g., minimal shot size and cycle time). The transfer pressures for the blends and composites are listed in Table I. The transfer pressure is the hydraulic pressure required to inject the molten material into the mold at the specified speed. It is measured at the transfer point of the injection cycle when the mold is nearly filled. The higher the melt viscosity, the higher the transfer pressure required. Not surprisingly, the transfer pressure increased considerably when wood flour was added. However, the transfer pressure did not appear to change much with silane and peroxide content indicating that, at the high-shear rates typical in injection molding, the overall viscosities did not change much. This resulted in little difficulty in molding even the thin plates. By contrast, transfer pressure was reduced when peroxide and silane were added to pure PP suggesting polymer cleavage and molecular weight reduction during processing (compare PP and Xlink PP in Table I). This radical-

induced chain scission of PP often dominates at processing temperatures typical of PP and is one of the reported reasons limiting commercialization of cross-linked PP.¹⁶

The relative melting and crystallinity characteristics of PP and PE blend components were obtained by DSC and are summarized in Tables II and III and Figures 8,9. There was no apparent effect of silane or peroxide content on the degree of crystallinity of either HDPE or PP for the unfilled blends (Fig. 8). However, the relative crystallinity of the HDPE component increased after exposure to high-humidity and temperature in the humidity chamber [Fig. 8(a)]. The crystallinity increased even in the absence of silane, suggesting that the HDPE component was annealed at the elevated temperature (90°C) in the humidity chamber. Annealing was not apparent in the PP component, which is not surprising when considering its lower mobility at 90°C.

As with the unfilled blends, the HDPE component of the composite blends was also annealed in the humidity chamber [Fig. 9(a)]. However, the increase in HDPE crystallinity was reduced at high-silane contents suggesting that annealing was inhibited by the reduced mobility, because of cross-linking. This mobility effect on annealing was not as evident in the unfilled polymer blends but their gel contents were not as large either. As with the unfilled blends, exposure to high-humidity and elevated temperature did not change the relative crystallinity of the PP component of the composite blends. However, the degree of crystallinity increased with an increase of the cross-linking solution [Fig. 9(b)]. Since this increase even occurs when no peroxide is added, this is not likely to be because of an increase in mobility or because of chain scission, for example. The results might suggest that the silane is somehow nucleating the PP but unfilled PP did not bear this out (Tables II and III). However, it is not clear why this would happen and further work is necessary to investigate the increase in crystallinity.

DSC tests on the gels demonstrated that crystalline PP was nearly nonexistent. Considerable peak area, because of crystalline HDPE remained after extraction in xylenes; whereas the PP peak nearly disappears (Fig. 10). While others have found slight suppression in crystallinity, because of premature cross-linking,^{23,24} large reductions in peak area because of immobilization caused by cross-linking is not supported in the literature. Consequently, it is more likely that the PP component simply did not cross-link much. Similar behavior was found in all blends and composites regardless of silane or peroxide content.

Tables IV and V summarize the tensile testing results of the samples before and after cross-linking in the humidity chamber. The moduli of many of

TABLE II
DSC Results for Unfilled Blends and Composites Before Exposure to High-Humidity and Elevated Temperature

Sample	$T_{m,HDPE}$ (°C)	$\Delta H_{m,HDPE}$ (J/g)	X_{HDPE} (%)	$T_{m,PP}$ (°C)	$\Delta H_{m,PP}$ (J/g)	X_{PP} (%)
Unfilled blends:						
0-00	128.8	149.1	50.9	162.4	76.0	36.3
2-00	128.6	158.7	54.2	162.6	70.3	33.6
2-05	128.1	149.4	51.0	162.0	73.5	35.2
2-10	128.5	148.7	50.7	162.1	77.3	37.0
4-00	128.2	135.1	46.1	162.2	76.6	36.7
4-05	128.1	141.9	48.4	162.1	66.8	32.0
4-10	127.7	139.2	47.5	162.0	81.0	38.8
Composites:						
0-00-C	128.2	140.5	48.0	162.4	75.4	36.1
2-00-C	128.4	144.0	49.1	162.4	76.8	36.7
2-05-C	128.2	138.6	47.3	162.1	78.7	37.7
2-10-C	128.0	145.0	49.5	161.2	68.8	32.9
4-00-C	128.4	136.8	46.7	161.4	92.7	44.4
4-05-C	127.5	135.0	46.1	160.8	89.8	42.9
4-10-C	128.0	128.7	43.9	160.4	97.6	46.7
Additional						
PE	129.2	152.8	52.1	–	–	–
Xlink PE	129.0	148.9	50.8	–	–	–
Xlink PE-C	128.7	137.9	47.1	–	–	–
PP	–	–	–	163.1	76.1	36.4
Xlink PP	–	–	–	163.0	78.0	37.3
Xlink PP-C	–	–	–	162.5	64.9	31.0

See Table I for compositions.

the blends and composites increased after exposure to high-humidity and elevated temperature in the humidity chamber. This is presumably because of the increases found in the PE crystallinity, which constitutes the majority of the polymer matrix.

Aside from this annealing effect, gel content also appeared to affect modulus, especially in the composites (Fig. 11), as the two composites with the highest silane content with peroxide also had the highest moduli.

TABLE III
DSC Results for Unfilled Blends and Composites After Exposure to High-Humidity and Elevated Temperature

Sample	$T_{m,HDPE}$ (°C)	$\Delta H_{m,HDPE}$ (J/g)	X_{HDPE} (%)	$T_{m,PP}$ (°C)	$\Delta H_{m,PP}$ (J/g)	X_{PP} (%)
Unfilled blends						
0-00	128.7	174.3	59.5	161.9	74.9	35.8
2-00	128.6	173.6	59.3	161.6	73.8	35.3
2-05	128.8	173.9	59.4	160.6	67.8	32.4
2-10	128.6	174.0	59.4	160.2	72.4	34.6
4-00	128.7	177.3	60.5	161.7	81.8	39.1
4-05	128.0	168.2	57.4	160.2	78.6	37.6
4-10	129.2	165.7	56.5	160.9	85.0	40.7
Composites:						
0-00-C	128.3	178.5	60.9	160.3	68.9	33.0
2-00-C	128.6	174.9	59.7	160.3	71.3	34.1
2-05-C	128.3	174.4	59.5	160.0	70.5	33.7
2-10-C	128.2	164.3	56.1	159.7	72.4	34.6
4-00-C	128.2	155.7	53.1	159.8	94.8	45.4
4-05-C	127.8	153.2	52.3	160.0	99.9	47.8
4-10-C	129.0	143.1	48.8	160.8	94.6	45.3
Additional:						
PE	–	–	–	–	–	–
Xlink PE	129.6	179.9	61.4	–	–	–
Xlink PE-C	129.1	167.2	57.1	–	–	–
PP	–	–	–	–	–	–
Xlink PP	–	–	–	162.1	74.4	35.6
Xlink PP-C	–	–	–	160.7	75.9	36.3

See Table I for compositions.

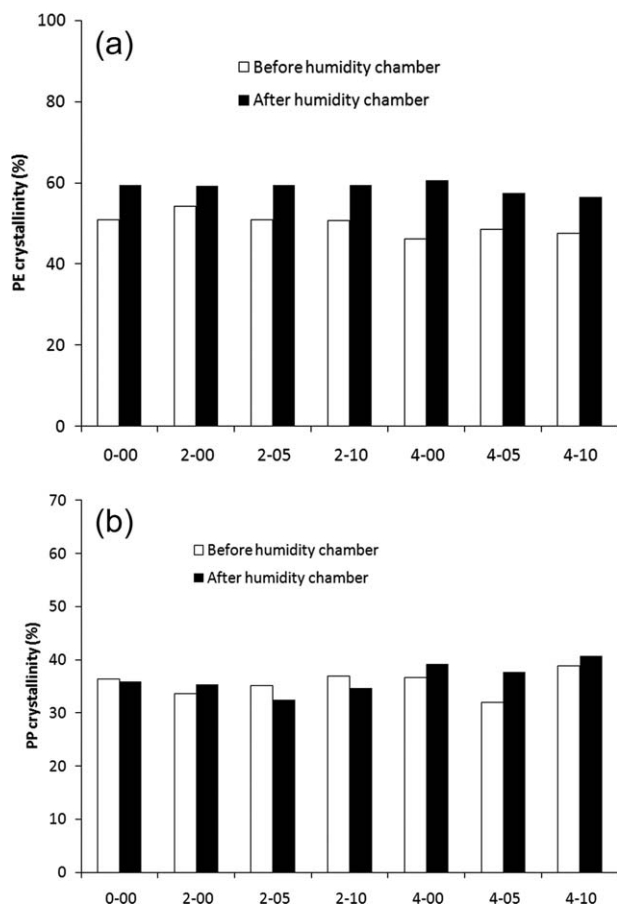


Figure 8 Crystallinity of HDPE (a) and PP (b) components in unfilled polymer blends.

The yield stresses for the unfilled blends showed slight increases after the humidity chamber but exhibited little other change (Fig. 12). Adding wood flour to the blends slightly decreased the yield strength but the combination of silane and peroxide resulted in a slight reinforcing effect suggesting that the adhesion between the wood flour and the matrix was improved in these blends (Fig. 13). This effect was similar for all composites containing silane and peroxide, regardless of the amounts added.

Scanning electron microscopy also yielded evidence of improved adhesion between the wood flour and polymer blend. Figure 14 show scanning electron micrographs of fracture surfaces composite samples with (0-00-C) and without (4-10-C) silane. Wood flour particles were more difficult to identify in the composite with silane, presumably because of fracture occurring through the matrix material rather than along the interfaces. Also, more evidence of particles being pulled out of the matrix and more fiber-matrix separation were evident in composites without silane.

The total energy absorbed by the blends and composites during high-speed puncture tests are plotted in Figures 15, 16, respectively. There is a severe

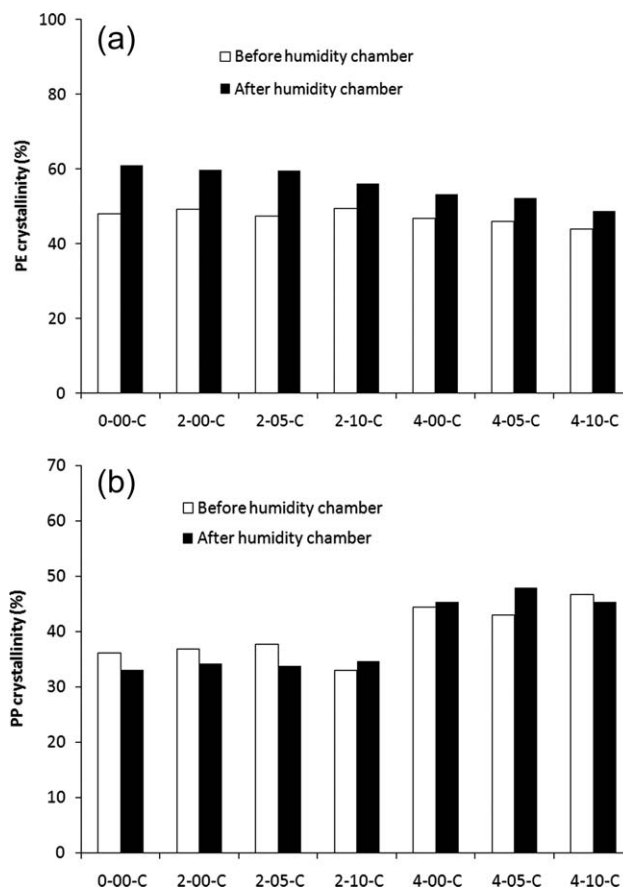


Figure 9 Crystallinity of HDPE (a) and PP (b) components in composites.

reduction in absorbed energy as peroxide and silane are added. The largest decreases resulted from a change in failure mechanism (Fig. 17). Specimens yielded before failing in blends without peroxide or silane, resulting in large energy absorption. However, little energy was required to initiate radial cracks in the blends with high peroxide and silane content, severely limiting energy absorption.

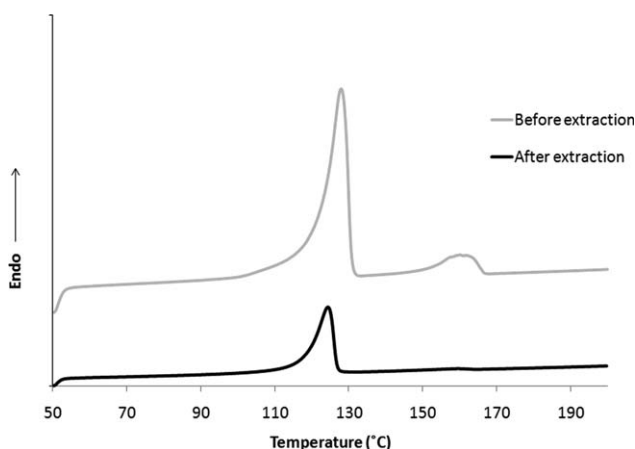


Figure 10 DSC heating curves for sample 4-05 before (top) and after (bottom) extraction in xylenes.

TABLE IV
Summary of Tensile Test Results for Specimens Before Cross-linking in a Humidity Chamber at 90% RH and 85°C for 32 h

Blend	Tensile modulus (GPa)	SD	Tensile yield strength (MPa)	SD	Tensile elongation at yield (%)	SD
Unfilled blends:						
0-00	0.91	0.06	25.7	0.6	4.2	0.2
2-00	0.71	0.02	24.5	0.4	5.2	0.1
2-05	0.79	0.03	25.3	0.3	4.7	0.2
2-10	0.68	0.02	25.3	0.2	5.5	0.1
4-00	0.56	0.02	23.4	0.2	5.8	0.2
4-05	0.62	0.01	24.6	0.2	5.6	0.1
4-10	0.78	0.02	26.4	0.3	5.2	0.1
Composites:						
0-00-C	1.89	0.13	21.9	0.5	1.4	0.1
2-00-C	1.76	0.08	21.0	0.3	1.4	0.1
2-05-C	2.01	0.12	28.2	0.7	1.3	0.1
2-10-C	2.12	0.04	29.5	0.2	1.3	0.1
4-00-C	1.85	0.28	21.4	0.1	1.4	0.2
4-05-C	2.29	0.15	28.1	0.7	1.1	0.1
4-10-C	2.31	0.38	27.1	1.0	0.9	0.2
Additional:						
PE	0.54	0.01	20.1	0.2	4.5	0.1
Xlink PE	0.54	0.04	21.4	0.1	4.9	0.1
Xlink PE-C	1.74	0.07	31.5	0.7	2.0	0.2
PP	1.67	0.09	37.4	0.1	3.1	0.1
Xlink PP	1.44	0.04	35.2	0.5	3.7	0.0
Xlink PP-C	3.39	0.22	39.1	1.1	1.0	0.1

See Table I for compositions.

TABLE V
Summary of Tensile Test Results for Specimens after Cross-linking in a Humidity Chamber at 90% RH and 85°C for 32 h

Blend	Tensile modulus (GPa)	SD	Tensile yield strength (MPa)	SD	Tensile elongation at yield (%)	SD
Unfilled blends:						
0-0-00	0.82	0.06	27.3	0.6	4.5	0.1
0-2-00	0.81	0.01	26.6	0.2	4.6	0.1
0-2-05	0.81	0.01	27.2	0.2	4.5	0.1
0-2-10	0.89	0.03	27.4	0.3	4.7	0.2
0-4-00	1.00	0.03	27.1	0.4	4.2	0.1
0-4-05	0.91	0.07	27.4	0.3	4.4	0.1
0-4-10	1.01	0.08	28.6	0.4	4.0	0.1
Composites:						
0-0-00-C	2.32	0.18	23.0	0.4	1.4	0.1
0-2-00-C	2.38	0.22	22.4	0.3	1.2	0.2
0-2-05-C	2.69	0.24	30.9	0.6	1.1	0.1
0-2-10-C	2.47	0.21	29.7	0.8	1.2	0.1
0-4-00-C	2.44	0.20	22.9	0.4	1.2	0.1
0-4-05-C	2.81	0.19	28.3	1.6	0.9	0.1
0-4-10-C	3.10	0.41	26.5	1.6	0.7	0.1
Additional blends/composites						
PE	–	–	–	–	–	–
Xlink PE	0.66	0.04	24.3	0.2	4.7	0.1
Xlink PE-C	2.22	0.14	35.1	0.9	1.9	0.1
PP	–	–	–	–	–	–
Xlink PP	1.72	0.07	38.2	0.3	2.8	0.1
Xlink PP-C	3.84	0.33	40.3	2.1	0.9	0.1

See Table I for compositions.

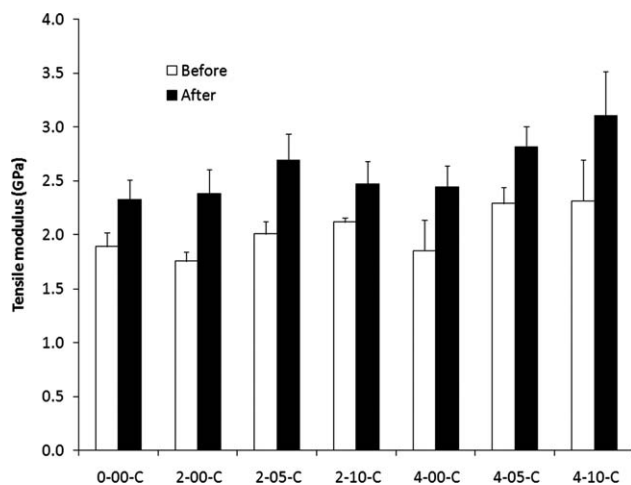


Figure 11 Tensile moduli of composite specimens before and after conditioning in a humidity chamber at 90% RH and 85°C for 32 h. Compositions are listed in Table I.

Exposure to high-humidity and temperature had little effect on the total energy absorbed for the unfilled blends. For the composites, the total energies were much lower than the unfilled blends and peroxide, silane, and exposure to high-humidity and temperature had little effect.

SUMMARY AND CONCLUSIONS

The influence of silane and peroxide on gel content, crystallinity, and mechanical performance of unfilled PP-PE blends and their composites with wood was investigated. The silane and peroxide, TMSPM and BPO, were chosen because of past success in avoiding unwanted side reactions (e.g., chain scission) with PP. All materials were compounded in a twin screw extruder and then injection molded. Specimens

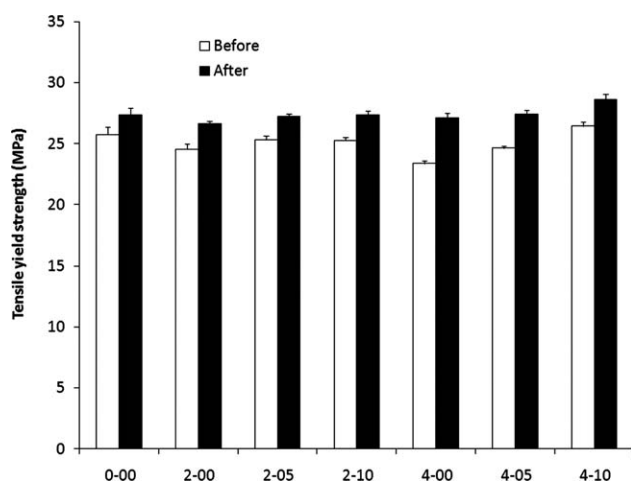


Figure 12 Tensile yield strengths for BPO-TMSPM grafted polymer blends before and after conditioning in a humidity chamber at 90% RH and 85°C for 32 h. Compositions are listed in Table I.

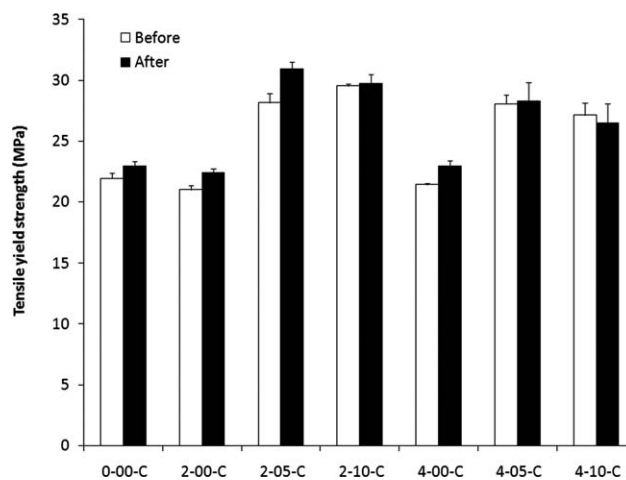


Figure 13 Tensile yield strengths for BPO-TMSPM grafted composite blends before and after conditioning in a humidity chamber at 90% RH and 85°C for 32 h. Compositions are listed in Table I.

were then exposed to high-humidity and elevated temperature in a humidity chamber to cross-link any unhydrolyzed silane.

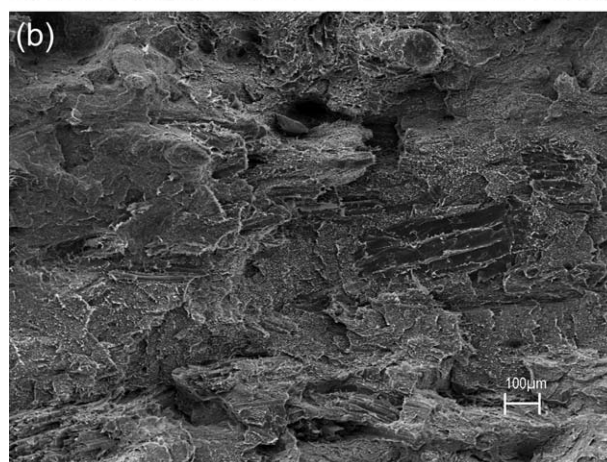
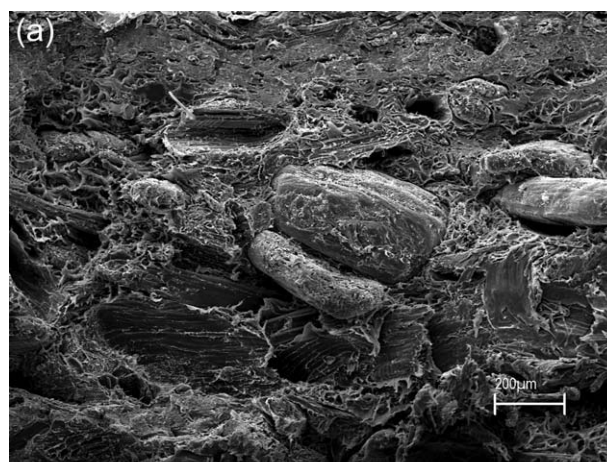


Figure 14 Scanning electron micrographs of fracture surfaces of composites without (a) and with silane (b). Micrographs are of samples 0-00-C (a) and 4-10-C (b).

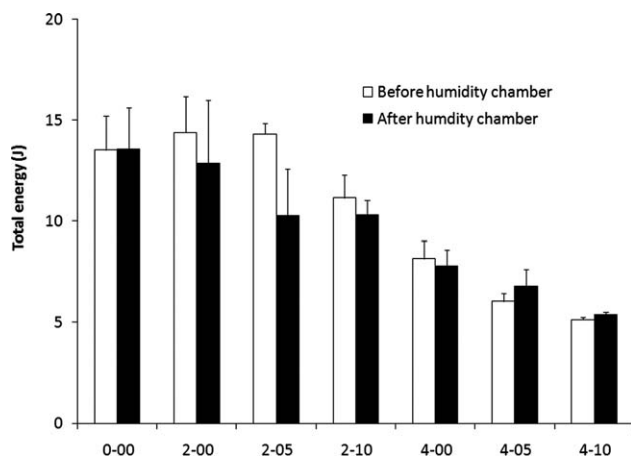


Figure 15 Total energy absorbed during high-speed puncture tests on BPO-TMSPM grafted blends before and after conditioning in a humidity chamber at 90% RH and 85°C for 32 h. Compositions are listed in Table I.

Final gel contents were at most 16% for the unfilled PE-PP blends. Adding wood to the PE-PP blends, led to an increase in premature cross-linking but also higher gel contents. However, the gel contents of the composites were still well-below those found by other researchers who cross-linked pure PP using batch preparation methods and long residence times. The PP component did not appear to cross-link well and our gels were almost entirely HDPE. Additionally, transfer pressures during injection molding suggested that the PP molecular weight was reduced during processing.

FTIR spectra provided additional evidence that TMSPM is grafted and cross-linked in unfilled PE-PP blends. Unfortunately, the spectra of wood composites proved difficult to interpret because of the complexity and overlap of the FTIR spectra of the wood.

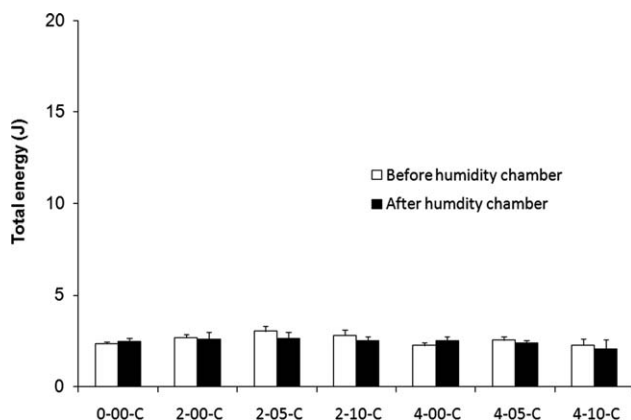


Figure 16 Total energy absorbed during high-speed puncture tests on BPO-TMSPM grafted composite blends before and after conditioning in a humidity chamber at 90% RH and 85°C for 32 h. Compositions are listed in Table I.

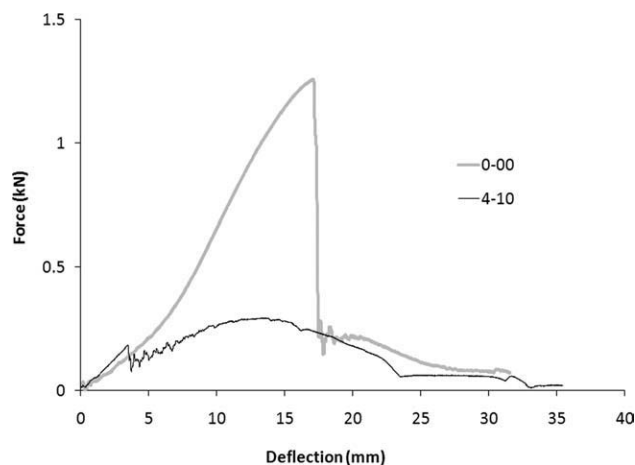


Figure 17 High-speed puncture curves for unfilled blend without peroxide or silane (0-00) and with silane and peroxide (4-10).

The HDPE component annealed when exposed to high-humidity and elevated temperature in a humidity chamber, although less so in samples with high-gel contents, presumably because of decreased mobility. Annealing influenced mechanical performance, especially increasing moduli. Adding peroxide and silane hardly affected yield strength of unfilled blends but appeared to improve adhesion between the wood flour and matrix in the composites. Adding silane and peroxide severely reduced the total energy absorbed by the unfilled blends during high-speed puncture tests and made it easier to initiate radial cracks. For the composites, the total energies were much lower than the unfilled blends and peroxide, silane, and exposure to high-humidity and temperature had little effect.

Overall, the results are disappointing because the composites did not cross-link well and considerable PP molecular weight reduction likely occurred. These two hurdles need to be overcome before this practical approach can be used to produce cross-linked WPCs from these materials.

The authors would like to acknowledge American Wood Fibers (Schofield, WI) for supplying the wood flour and the following personnel at the following FPL employees: Tom Kuster for the scanning electron microscopy and the Engineering Mechanics Laboratory personnel for the tensile testing. The opinions expressed herein are those of the authors and do not necessarily reflect the view of the U.S. Department of Agriculture or Louisiana State University Agricultural Center.

References

1. Utracki, L. A. *Commercial Polymer Blends*; Chapman and Hall: London, 1998.
2. Baker, W. E.; Scott, C. E.; Hu, G.-H. *Reactive Polymer Blending*; Carl Hanser Verlag: Munich, 2001.
3. Utracki, L. A. *Polymer Blends Handbook*; Kluwer Academic Publishers: Norwell, MA, 2002.

4. Moore Recycling Associates Inc., 2007 National Post-Consumer Recycled Plastic Bag & Film Report, 2009 American Chemistry Council, Inc., Arlington, VA, 2009, 1–31.
5. Clemons, C. M. *Forest Prod J* 2002, 52, 10.
6. Morton, J.; Rossi, L. Proc. 7th International Conference on Woodfiber-Plastic Composites; Forest Products Society: Madison, WI, 2003.
7. Smith, P. M.; Wolcott, M. P. *Forest Prod J* 2006, 56, 4.
8. Utracki, L. A. In *Polymer Blends Handbook*, Utracki, L. A., Ed.; Kluwer Academic Publishers: Norwell, MA, 2002; Chapter 16.
9. Kruliš, Z.; Kokta, B. V.; Horák, Z.; Michálková, D.; Fortelný, I. *Macromol Mater Eng* 2001, 286, 156.
10. Chodak, I. *Polym Plast Technol* 2004, 43, 1769.
11. Sun, Y.-J.; Baker, W. E. *Reactive Polymer Blending*; Carl Hanser Verlag: Munich, 2001.
12. Uboinnut, L.; Thongyai, S.; Praserttham, P. *J Appl Polym Sci* 2007, 104, 3766.
13. Colbeaux, A.; Fenouillot, F.; Gérard, J.-F.; Taha, M.; Wautier, H. *J Appl Polym Sci* 2005, 312, 95.
14. Monte, S. J. *Proceedings of the Global Plastics Environmental Conference (GPEC) 2005*; Atlanta, Georgia, 2005, 1–31.
15. Munteanu, D. *Reactive Modifiers for Polymers*, Al-Malaika, Ed.; Chapman and Hall: London, 1997, 196–265; Chapter 5.
16. Hoght, A. H.; Meijer, J.; Jelenič, J. *Reactive Modifiers for Polymers*, Al-Malaika, Ed.; Chapman and Hall: London, 1997, 84–132; Chapter 2.
17. Liu, N. C.; Yao, G. P.; Huang, H. *Polymer* 2000, 41, 4537.
18. Lu, J. Z.; Wu, Q.; Mcnabb, H. S. Jr., *Wood Fiber Sci* 2000, 32, 88.
19. Matuana, L. M.; Balatinecz, J. J.; Park, C. B.; Sodhi, R. N. S. *Wood Sci Technol* 1999, 259, 33.
20. Paunikallio, T.; Suvanto, M.; Pakkanen, T. T. *React Funct Polym* 2008, 797, 68.
21. Bengtsson, M. *Silane Crosslinked Wood-Thermoplastic Composites*, Doctoral thesis, Norwegian University of Science and Technology, 2005.
22. Bengtsson, M.; Gatenholm, P.; Oksman, K. *Compos Sci Technol* 2005, 65, 1468.
23. Bengtsson, M.; Oksman, K. *Compos Part A-Appl S* 2006, 37, 752.
24. Bengtsson, M.; Oksman, K. *Compos Sci Technol* 2006, 66, 2177.
25. Bengtsson, M.; Oksman, K.; Stark, N. M. *Polym Compos* 2006, 27, 184.
26. Bengtsson, M.; Oksman, K. *Compos Sci Technol* 2007, 67, 2738.
27. Kuan, C.-F.; Kuan, H.-C.; Ma, C.-C. M.; Huang, C.-M. *Compos Part A-Appl S* 2006, 37, 1696.
28. ASTM D2765-01, *Annual Book of ASTM Standards*, ASTM International: West Conshohockon, PA, 2008.
29. ASTM D3763-06, *Annual Book of ASTM Standards*, ASTM International: West Conshohockon, PA, 2007.
30. ASTM D638-03, *Annual Book of ASTM Standards*, ASTM International: West Conshohockon, PA, 2007.
31. Doroudiani, S.; Park, C. B.; Kortschot, M. *Polym Eng Sci* 1998, 38, 1205.
32. Yang, S.; Song, G.; Zhao, T.; Tang, C.; She, X. *Polym Eng Sci* 2007, 47, 1004.
33. Gazel, A.; Lemaire, J. *Makromol Chem Rapid Commun* 1985, 235, 6.