The Effects of Different Silane Crosslinking Approaches on Composites of Polyethylene Blends and Wood Flour

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ABSTRACT: Though silane chemistry has been used to crosslink unfilled polyethylene for many years, such crosslinking has only been recently applied to wood plastic composites to improve properties such as creep resistance. However, the presence of wood significantly changes the silane chemistry and a greater understanding is necessary for optimal processing and performance. We investigated three different approaches of adding silane and peroxide during reactive extrusion of wood-plastic composites were investigated and compared to their unfilled counterparts. Up to 2 grams of a 20:1 solution of vinyltrimethoxysilane and dicumyl peroxide by weight were added per 100 grams of plastic. Low density polyethylene, high density polyethylene, and a blend of the two were investigated as matrices in composites containing approximately 25% wood flour. The unfilled plastics crosslinked efficiently and little premature crosslinking occurred during processing. Though only modest improvements in tensile strengths were found in unfilled plastics, the notched Izod impact energy of unfilled HDPE improved nearly 600% when crosslinked. Unlike the unfilled plastics, most of the crosslinking of the composites occurred during processing. This resulted in high viscosities and processing difficulties, negating some of the advantages of a separate crosslinking step and limiting the amount of crosslinking possible. Some reinforcement of the plastics by the wood flour was achieved when sufficient crosslinking solution was added. Adding crosslinking solution also and greatly increased reverse-notched impact energies. The differences between the approaches for preparing the crosslinked composites appeared to largely be a matter of efficiency in terms of the amount of crosslinking solution required to affect processing and performance. The most efficient approach was a two-step procedure where the silane was first grafted to the plastic and then wood flour was compounded with the grafted silane in a second step. Published 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 2292–2303, 2011

Key words: polyethylene; silane; reactive extrusion; crosslinking; composites

INTRODUCTION

Wood–plastic composites (WPCs) are a major outlet for recycled polyethylene (PE) film[1] and may also represent a potential outlet for some mixed recycled plastics that are technically difficult or uneconomical to separate. WPCs are used in applications such as automotive paneling, furniture, and consumer products.[2] However, the largest use of WPCs is in the construction industry.[3] 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.[3] There has been considerable interest lately in new applications such as signs, furniture, siding, and roofing, as well as using WPCs in a variety of applications requiring increased structural performance.[4]

Recently silane crosslinking technologies have been shown to improve strength, toughness, and creep resistance of WPCs[5–11] made with high-density PE (HDPE) or low-density PE (LDPE) and may offer potential for mixed PEs as well. Much of this recent work has been based on a two-step crosslinking process for PE where free radicals are used to graft silane onto PE in a first step. The grafted PE is then exposed to moisture in a second step leading to hydrolysis and condensation of the silane and resulting in crosslink formation.[12]

Silane crosslinking has several potential advantages with respect to its use in WPCs. Because WPCs typically have high filler contents, they also have high viscosities. Crosslinking after extrusion by exposure to moisture prevents additional viscosity

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increases that could result in processing difficulties, limit wood content, and limit the types of plastics used to only those with low viscosity. Also, adding wood improves moisture penetration, which may be useful during the crosslinking step.

However, the interaction between wood, silane, peroxide, and plastics is complex. In addition to crosslinking of the plastic via free-radical grafting, hydrolysis, and condensation reactions, the silane can also react with the wood as well, via free-radical grafting or reaction between the silanol and hydroxyl groups of the wood, for example. Because of its ability to react with wood, silanes have been used to treat wood to improve adhesion with plastics, and small amounts of silane-grafted plastics have been used as coupling agents.[13–15] Additional complexities also arise. Wood, if not entirely dry, can provide moisture to hydrolyze silane-grafted plastic and lead to premature crosslinking in the extruder, for example.

Silane crosslinking of WPCs still faces a number of challenges. For example, premature crosslinking during extrusion results in viscosity increases that negate some of the advantages of a separate crosslinking step. More efficient crosslinking is also desired because gel contents for WPCs are often not as high as those for unfilled PE.[16] Greater understanding and control of the silane chemistry is necessary for optimal processing and performance of moisture crosslinked WPCs.

In the following investigation, we evaluated the effects of three different approaches of adding silane and peroxide during extrusion of WPCs on processing and performance. HDPE, LDPE, and a blend of the two were investigated as matrices to determine the differences between them and the potential for each.

EXPERIMENTAL

The 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, Housto, TX). The LDPE was a homopolymer with a melt flow index of 3 g/10 min (Muehlstein and Co., Norwalk, CT). The wood filler was a nominal 40 mesh (420 μm) western pine wood flour (WF) from American Wood Fibers (Schofield, WI). The silane and peroxide used were vinyltrimethoxysilane (VTMS) and dicumyl peroxide (DCPO) 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. For the reactive extrusion of the unfilled plastics and blends, the DCPO was first dissolved in VTMS in a 1 : 20 weight ratio, and then the solution was metered into the main feed throat of the extruder along with the plastic.

For the WF-filled plastics and blends, three different reactive extrusion approaches were investigated (Fig. 1). In the first approach, the crosslinking solution (i.e., the VTMS and DCPO solution) and plastic were added similarly to the unfilled plastics and blends. After mixing these components in the first part of the extruder, dried WF was added in the fifth of 10 zones using a twin-screw side feeder. In the second approach, no WF was added to the extruder allowing the reaction of the crosslinking solution with the plastics only. The resulting pellets were then fed back into the extruder along with dried WF. In the third approach, the plastic and wood were compounded in the first pass of the extruder. Then, the compounded material was fed back into the extruder along with the crosslinking solution. The different formulations for the investigation are summarized in Table I.

For all of the compounding, a reverse temperature profile was used with a temperature of 193°C at the feed throat and 182°C at the die. The extrusion speed was 80 rpm, and the overall feed rate was held constant at 5.4 kg/h. The molten strands exiting the extruder die were air-cooled to minimize any hydrolysis of the silane and then were pelletized. Injection molding was used to prepare specimens for mechanical testing to avoid the need for additional additives such as lubricants that are necessary in the more conventional extrusion profiling of WPCs. The compounded materials were injection molded into 2-mm-thick circular disks with a 10 cm diameter and into standard Izod impact specimens.[17] Barrel temperatures were set at 193°C for all three zones and the nozzle. A mold temperature of 49°C was used, and the injection speed was 25.4 cm/s.

Half of the disks were placed in a humidity chamber at 90% relative humidity and 85°C for 3 days to allow the silane to crosslink and then dried for 3 h at 105°C. Three days was determined to be the amount of time required for essentially complete crosslinking to occur (i.e., gel contents of samples were not observed to increase beyond the level obtained after 3 days in the humidity oven).[18] The other half were tested without this exposure to humidity at elevated temperature. Type V tensile test specimens were punched from the disks and tested according to ASTM D638-03.[19] The Izod impact specimens were tested according to ASTM D256-07.[17] The degree of crosslinking was determined by gel content according to ASTM D2765-01[20] 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. At least two replicates were performed for each condition, and additional replicates were tested for conditions with greater than expected variability in gel contents. Gels were air-dried overnight, and then oven-dried for 24 h at 105°C.

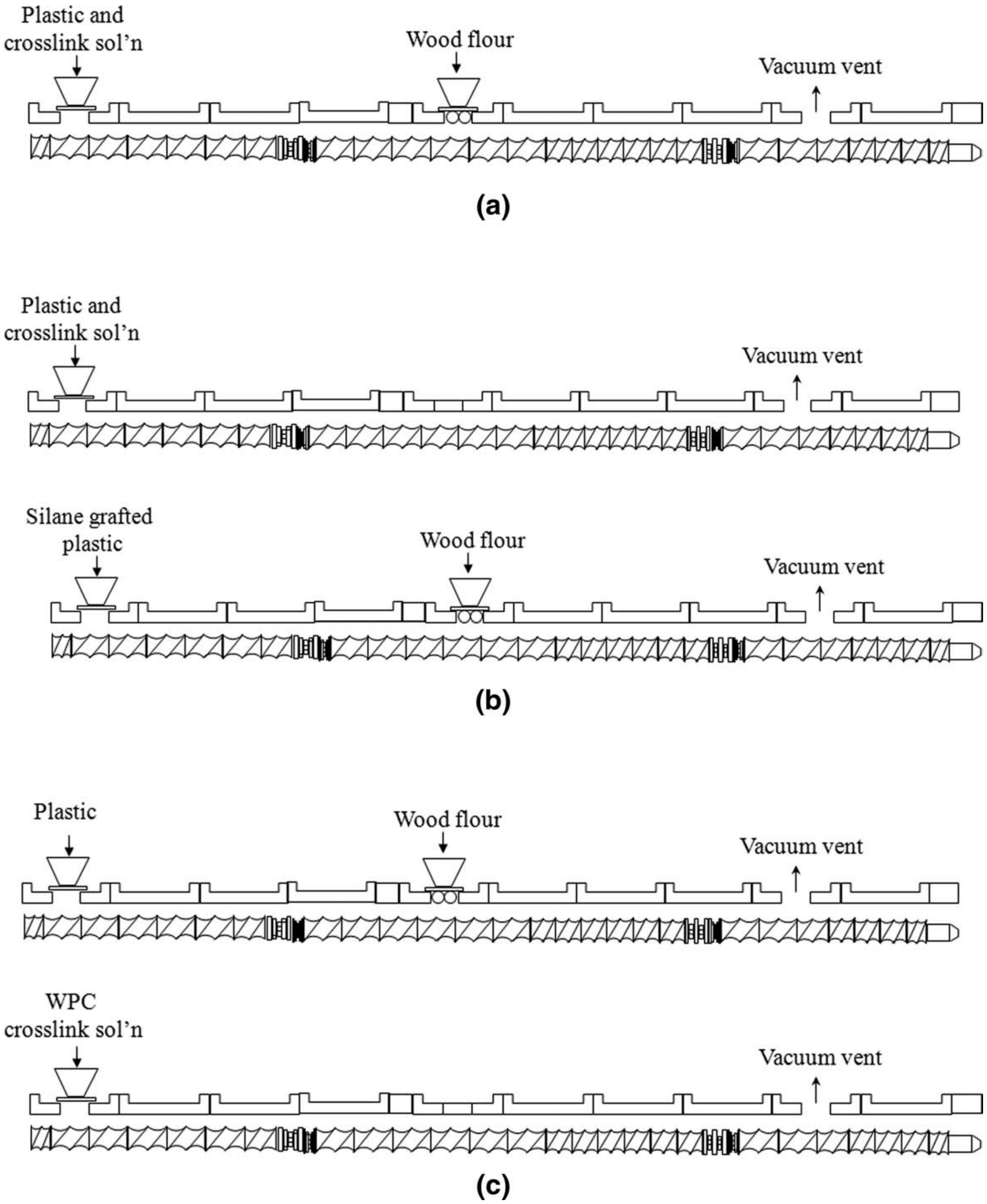

Figure 1 Schematic of the three approaches for reactive extrusion of WPCs.

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 determining the area under the melting peak and dividing by the weight of polymer in the sample. The percent crystallinity (χ) of the polymer was then calculated by dividing the specific heat by 293 J/g, the heat of fusion for 100% crystalline PE according to Ref. 21.

A Mattson Galaxy 5000 Fourier transform infrared (FTIR) spectrometer equipped with a Harrick DRA-2CN diffuse reflectance attachment was used to obtain diffuse reflectance Fourier transform spectra, scanning 4000–450 cm^{-1} with 4 cm^{-1} resolution. The spectra were obtained from the average of 512 scans and processed with no baseline modification. Extruded samples were prepared by manually

TABLE I
Blend Compositions and Gel Contents

Matrix and blend no.	Approach (1, 2, 3)	HDPE : LDPE weight ratio	Plastic : WF : crosslink solution weight ratio			Gel content before humidity chamber (%)		Gel content after humidity chamber (%)		χ^a (%)
						Average	Standard error	Average	Standard error	
HDPE										
1	1	100 : 0	100	0	0	2.5	0.0	–	–	63.7
2	1	100 : 0	100	0	0.5	1.8	1.1	7.2	2.4	62.3
3	1	100 : 0	100	0	1	4.6	1.2	73.1	2.2	61.8
4	1	100 : 0	100	0	2	14.1	7.3	85.1	1.4	58.9
5	1	100 : 0	100	33	0	−3.3	0.6	−3.6	2.2	69.9
6	1	100 : 0	100	33	0.5	−0.3	6.3	−3.2	1.4	67.8
7	1	100 : 0	100	33	1	20.1	3.2	25.1	1.5	60.5
8	1	100 : 0	100	33	2	–[b]	–	–	–	–
9	2	100 : 0	100	33	0.5	11.3	4.5	15.2	2.4	65.8
10	3	100 : 0	100	33	0.5	−6.6	2.9	−11.5	1.7	63.7
11	3	100 : 0	100	33	1	10.1	0.5	13.4	1.1	67.5
12	3	100 : 0	100	33	2	33.7	5.3	45.7	0.1	55.6
LDPE										
13	1	0 : 100	100	0	0	1.7	0.6	1.1	0.6	44.3
14	1	0 : 100	100	0	0.5	1.7	0.9	37.1	0.8	45.6
15	1	0 : 100	100	0	1	5.3	4.2	60.6	1.0	44.7
16	1	0 : 100	100	0	2	15.9	15.1	74.3	0.3	41.6
17	1	0 : 100	100	33	0	0.7	4.3	−3.6	2.2	44.3
18	1	0 : 100	100	33	0.5	0.5	2.5	−3.2	0.8	38.5
19	1	0 : 100	100	33	1	26.6	1.9	38.7	0.8	37.4
20	1	0 : 100	100	33	2	–	–	–	–	–
21	2	0 : 100	100	33	0.5	34.7	2.2	44.0	0.3	40.5
22	3	0 : 100	100	33	0.5	−2.3	3.8	−5.4	1.7	35.0
23	3	0 : 100	100	33	1	4.8	9.1	19.5	3.3	34.3
24	3	0 : 100	100	33	2	35.7	6.8	54.2	0.1	34.3
Blends										
25	1	50 : 50	100	0	0	4.4	1.8	2.7	0.7	55.2
26	1	50 : 50	100	0	0.5	3.8	1.7	22.8	0.3	51.1
27	1	50 : 50	100	0	1	4.1	2.0	60.8	0.9	48.3
28	1	50 : 50	100	0	2	10.0	2.7	82.6	0.3	47.1
29	1	50 : 50	100	33	0	−3.7	0.9	−4.8	0.5	49.7
30	1	50 : 50	100	33	0.5	−3.7	0.9	4.2	0.0	45.2
31	1	50 : 50	100	33	1	41.0	0.4	45.3	0.2	46.2
32	1	50 : 50	100	33	2	–	–	–	–	–
33	2	50 : 50	100	33	0.5	33.0	3.6	44.2	1.1	46.2
34	3	50 : 50	100	33	0.5	−5.1	4.6	−7.4	0.2	48.5
35	3	50 : 50	100	33	1	−6.3	0.5	−4.6	2.5	47.2
36	3	50 : 50	100	33	2	29.6	2.4	48.4	1.9	45.8

[a] χ is the polyethylene crystallinity.
[b] Gel content not measured.

roughing the surface with a razor so as to minimize specular contributions, apparent by derivative-shaped peaks, and to obtain a flat baseline. Homo-crosslinked VTMS was finely ground and dispersed in KBr to obtain the diffuse reflectance Fourier transform spectrum. Liquid VTMS samples were run neat between KBr plates and acquired in absorbance mode. Homo-crosslinked VTMS was prepared simply by leaving liquid VTMS in a humidity oven at 90% relative humidity and 85°C for 10 days, after which it was a crosslinked solid. Scanning electron microscopy on both the solid wood and WPC composites after coating with a gold-palladium alloy were performed using a Zeiss EVO40 scanning electron microscope (Carl Zeiss SMT, Thornwood, NY).

RESULTS AND DISCUSSION

Compositions of the blends and their composites are summarized in Table I. A constant 20 : 1 weight ratio of silane to peroxide was used as the crosslinking solution. A weight of 0–2 g of crosslinking solution per 100 g of plastic was added during extrusion of unfilled plastics or wood-filled plastics using three different approaches summarized in Figure 1.

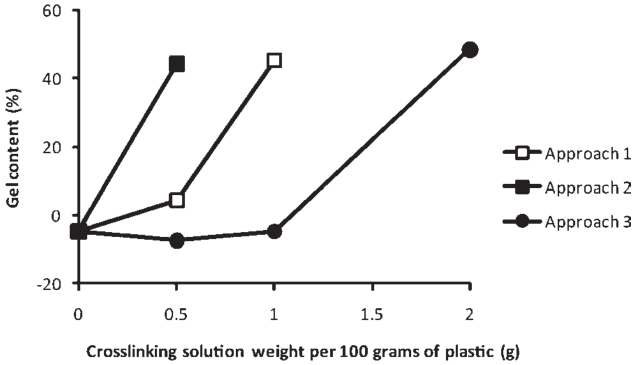

Figure 2 Comparison of different approaches of crosslinking WPCs with HDPE-LDPE blends as matrices.

In the first approach, the crosslinking solution and plastic were added in the first part of the extruder, and dried WF was added downstream. This is the easiest and likely the most economical approach, which has been commonly used in prior investigations.[7,8] However, this approach may be the most difficult in which to control the chemistry. The peroxide, silane, and plastic have little time to react before addition of the WF, and many reactions are possible once all of the components (i.e., plastic, silane, peroxide, wood, and possibly some residual moisture from the wood) are mixed.

In the second approach, the silane can graft to the plastic in the first pass through the extruder, and the resulting grafted plastic is then compounded with dried WF in the second pass. The grafting of the silane onto the plastic is more easily accomplished with fewer competing reactions, but there is an additional heat history because of the two extrusion steps. Also, as with the first approach, any residual moisture in the wood could lead to premature hydrolysis of the silane and crosslinking.

In the third approach, the wood and the plastics are compounded in the first pass, and then the silane solution is added to the compound in the second pass. Because the wood is at least partially encapsulated in the plastic, this approach may limit access of the crosslinking solution to the WF. Previous work has suggested that much of the silane may impregnate the wood, at least at high silane content,[7] and this approach might minimize this effect. It also provides the best opportunity to keep the WF dry and hopefully avoid moisture-induced crosslinking in the extruder.

Die pressures during compounding of the composites increased considerably with addition of crosslinking solution. This pressure increase limited the maximum the amount of crosslinking solution possible for approaches 1 and 2 (Table I). The die pressure increases for approach 3 were the lowest, and preparation of composites at all crosslinking levels was possible. Similar viscosity increases have been found by others and has been attributed to premature crosslinking.[7] Additionally, high viscosities prevented injection molding of disks (for tensile and high speed puncture tests) and Izod impact specimens for blends 8, 20, and 32 as well as the disks for blend 31.

Gel contents before and after exposure to high humidity are shown in Table I. The negative values were determined to be largely due to fine wood particles that were generated during processing and that were able to pass through the wire mesh used in the gel contents procedure after the polymer was dissolved. WF that had not been extruded did not pass through the mesh, and similar extraction of unextruded WF alone resulted in no loss in weight of the WF (i.e., the negative gel contents were not due to extractives). Furthermore, a sample (blend 10) that resulted in a negative gel content (−6.6% ± 2.9%) as determined by ASTM D2765-01[20] using a wire mesh yielded statistically zero (−2% ± 4%) gel contents when the extractions were carried out in a Soxhlet thimble and extraction apparatus. The unfilled plastics and blend behaved well, generally showing little premature crosslinking and final gel contents (i.e., after exposure to high humidity and temperature) of about 75–85% at the highest concentrations of crosslinking solution.

Comparing the gel contents of the composite before and after exposure to high humidity and temperature shows that considerable premature crosslinking occurs during processing. Gel contents of the unfilled plastic after processing but before moisture exposure were at most 20% of the final gel contents, and those for the composites were 60–90% of the final gel contents. This premature crosslinking resulted in the high die pressures found during extrusion, and Table I shows that the maximum gel content where the composites could still be processed was about 40%.

In unfilled PEs, premature crosslinking, sometimes called "scorch," is controlled through the use of proprietary, scorch-retardant additives, for example.[22] However, no work has been performed yet on using additives to control the chemistry in silane crosslinking of WPCs. Before such research can be undertaken, the reaction chemistry needs to be better understood so that appropriate methods can be identified to mitigate undesirable reactions during extrusion yet not impair potentially favorable reactions such as those improving the wood–plastic adhesion, for example.

Figure 2 shows the effect of crosslinking solution on final gel content for the composites containing the HDPE-LDPE blend as matrices. Similar trends were found for the composites with unblended HDPE or LDPE matrices. Approach 2 was the most efficient in crosslinking the composites in terms of the crosslinking solution required. This is perhaps not surprising because this approach provides the best opportunity

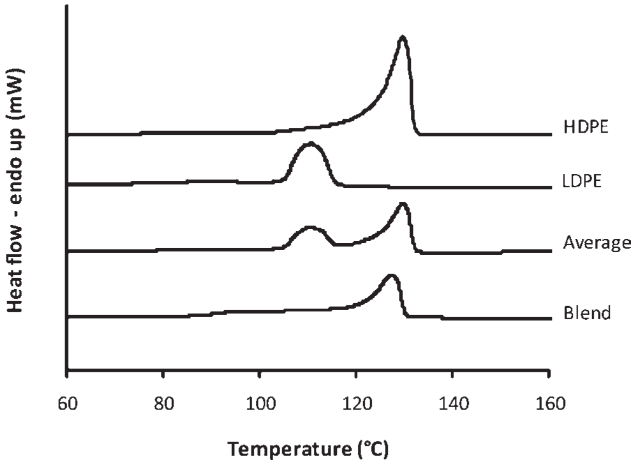

Figure 3 First heating scans for individual plastics and a blend of the two (equal parts by weight). Also included is a scan obtained when the HDPE and LDPE scans are averaged.

for silane grafting of the plastic and minimizes the opportunity for the silane to be absorbed by the WF, which might reduce the crosslinking of the plastic. Additionally, this approach provides the longest reaction times for the silane and peroxide because of its two passes through the extruder.

Approach 1 seemed to be more efficient in crosslinking the composite than approach 3 in terms of crosslinking solution. This was unexpected because we expected that approach 3 would limit the access of the crosslinking solution to the WF by at least partially encapsulating it in plastic. Perhaps, if the reaction between the crosslinking solution and the plastic was fast enough, it would largely occur in the first part of the extruder. If this is true, approach 1 might be more efficient because no wood is present to absorb the VTMS crosslinking solution when it is introduced, leaving more of the silane available for grafting to the PE in approach 1 than approach 3. To help clarify the situation, we tried to determine the distribution of silane in the composite using X-ray imaging to locate the silicon atoms (and therefore the silane) in our scanning electron microscope. However, because of the low silane concentrations used, it was not possible to image the silane in our composites. The composites with HDPE as matrices consistently yielded the lowest gel contents at the high crosslinking solutions levels. Perhaps somewhat surprisingly, the blended and LDPE matrices yielded roughly similar gel contents.

Table I also summarizes the crystallinity of the PE from the first heating scans of the differential scanning calorimetry analysis on the plastics and composites after exposure to humidity at elevated temperature. The crystallinity of the HDPE was higher than that of the LDPE, and the crystallinity was somewhat suppressed when WF was added to LDPE or the blend. Generally, HDPE and LDPE tend to crystallize separately when blended, but the specific crystallization behavior depends on the number, length, and distribution of branches in the LDPE component.[23] In our blends, the HDPE and LDPE melting peaks were both distinguishable, but the HDPE melted at a lower temperature and the LDPE crystallinity was greatly reduced when the two plastics were blended and exists more as a shoulder to the HDPE peak (Fig. 3). Similar results have been found by others.[24]

The peak melt temperature of the plastics and composites changed little with addition of crosslinking solution. However, the crystallinity decreased by as much as 23% in some cases (e.g., compare blends 17 and 24 in Table I). This reduction in crystallinity has been attributed to the reduced molecular mobility of the crosslinked plastic inhibiting crystal formation.[8] Figure 4 compares differential scanning calorimetry scans for a composite processed without any crosslinking solution (blend 29) to one with the most crosslinking solution (blend 36) and its gel. The second heating scan for all samples was used for the comparison in this case because the extraction process likely would have affected crystallinity. Both LDPE and HDPE are present in the gel, indicating that at least a portion of both have been crosslinked. The crystalline melting points (T_m) for both LDPE and HDPE are lower in the gel, suggesting a less perfect or finer crystal structure in it. This shift in melting point in the crosslinked plastic helps explain the broadening of the HDPE peak of the composite due to crosslinking. The overall crystallinity of the gel was about 38% lower than in the same specimen before extraction. This is not surprising given the reduction of the molecular mobility in the gel. The crystallization behavior in composites produced using the different crosslinking approaches were similar.

Figure 5 shows scanning electron micrographs of the fracture surfaces of notched Izod impact

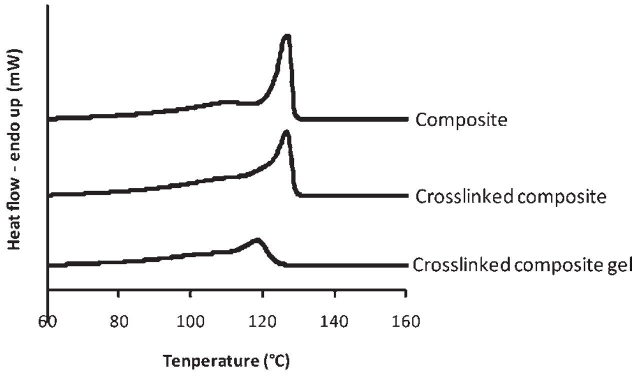

Figure 4 Second heating scans for the composite processed without crosslinking solution (blend 29) as well as a crosslinked composite (blend 36) and its gel.

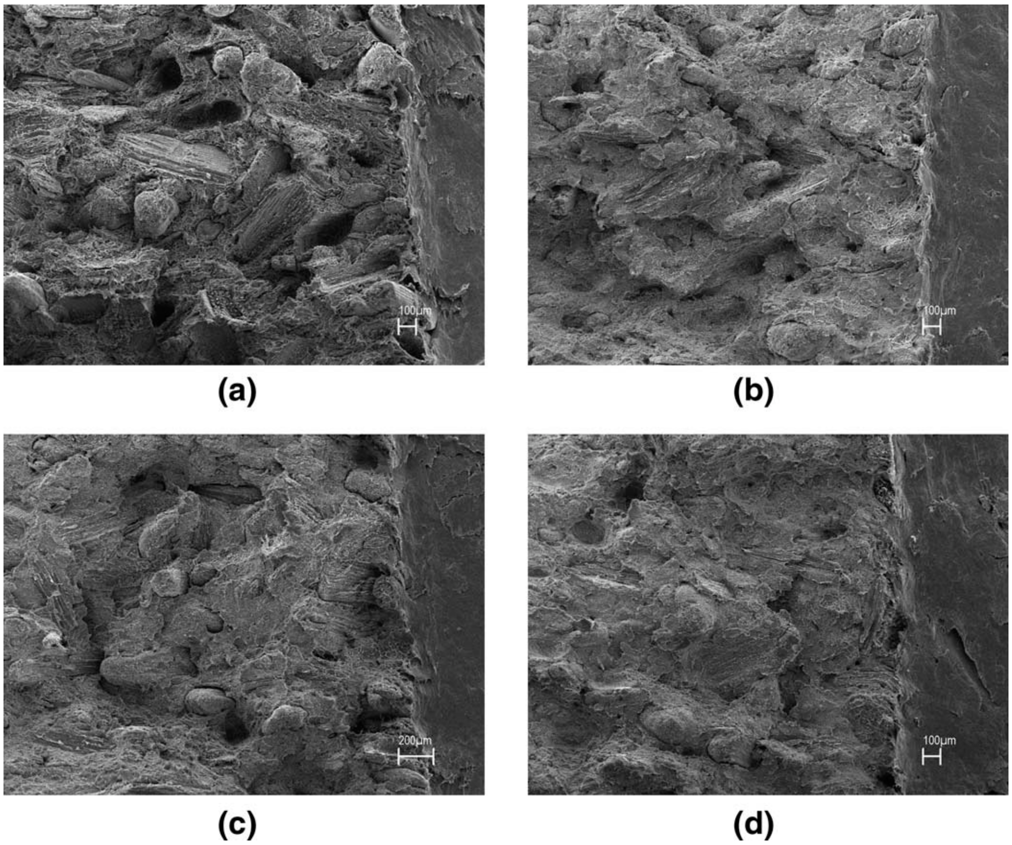

Figure 5 Scanning electron micrographs of the fracture surfaces of notched Izod impact specimens. Composites shown have HDPE-LDPE blend as the matrix material and no crosslinking solution (a), approach 1 with 1% crosslinking solution (b), approach 2 with 0.5% crosslinking solution (c), and approach 3 with 2% crosslinking solution (d). The notch is at the right edge of each micrograph.

specimens. Shown are the composites that have the HDPE-LDPE blend as the matrix material and no crosslinking solution (a) and the highest levels of crosslinking solution added using approaches 1 (b), 2 (c), and 3 (d). Poor adhesion between the WF particles and plastic is apparent in the composite containing no crosslinking solution [Fig. 5(a)]. The WF particles have pulled out of the matrix and gaps can be seen at the wood–plastic interface. In the crosslinked composites, the WF particles are not as easily found because many are coated with plastic. Adhesion between WF and the plastic matrix seems much improved in the crosslinked composites but not perfect because some gaps are still seen at the interfaces. There were no obvious differences in adhesion between the different approaches despite the large differences in crosslinking solution levels (i.e., 1, 0.5, and 2% for approaches 1, 2, and 3, respectively).

FTIR spectroscopy confirms that the VTMS is crosslinked and likely grafted to the PE blend. Because peak assignments for silane-grafted and crosslinked polymers and composites are often not clearly defined throughout the literature, a FTIR spectral analysis of homo-crosslinked VTMS is provided here. Figure 6 shows the FTIR spectra of VTMS neat liquid (top) and VTMS homo-crosslinked solid (i.e., only neat VTMS crosslinked at elevated humidity and temperature) (middle). Because of the simplicity of the VTMS structure (Fig. 7), most of spectral peaks can be assigned. The region of about 3030–2920 cm^{-1} is broadly attributed to C-H stretches and to asymmetric stretches of CH_3 and is not particularly diagnostic. However, the symmetric CH_3 stretch is sharp and occurs at about 2880–2815 cm^{-1}. In Figure 6, the neat VTMS exhibits a strong, sharp peak at 2842 cm^{-1}, which is clearly absent in the homo-crosslinked VTMS and, thus, indicates the complete hydrolysis of the silane ether linkages to CH_3. This is consistent with the disappearances on crosslinking of the following: broad 1458 — (asymmetric and symmetric CH_3 deformations), strong 1193 cm^{-1} (CH_3 rock), very strong 1093 cm^{-1} (asymmetric stretch of $Si{-}O{-}CH_3$), and medium 815 cm^{-1} peaks (symmetric stretch of $Si{-}O{-}CH_3$).[25] Also note that homo-crosslinked VTMS exhibits very broad peaks at about 3730–3200 cm^{-1} and 915–860 cm^{-1}, representing a condensed phase broad OH stretch and a strong Si—O stretch of the Si—OH group, respectively.[25] These peaks associated with the OH group are expected for single linkage Si—O—Si

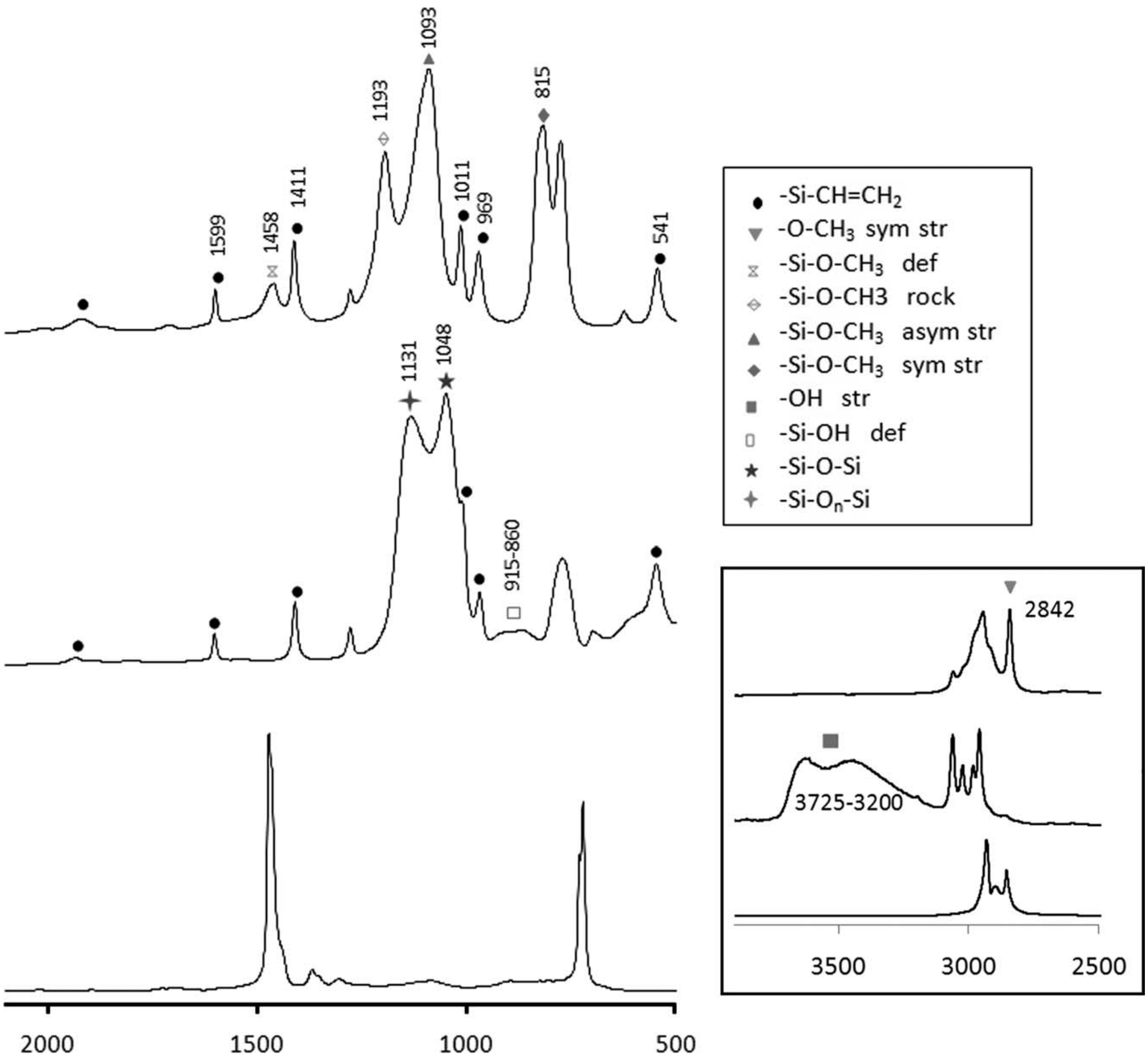

Figure 6 FTIR spectra of neat VTMS liquid (top), homo-crosslinked VTMS solid (middle), and neat HDPE : LDPE blend (blend 25) (bottom). Horizontal axis represents wavenumbers in cm^{-1}.

crosslinking. Examination of the vinylic peaks in Figure 6 provides very strong evidence that crosslinking occurs via hydrolysis and condensation to form Si—O—Si bonds rather than via a polymerization reaction of the vinyl groups. Characteristic frequencies of Si—CH=CH$_2$ are shown in Table II. Note that all of these peaks are present and unshifted in both the neat and homo-crosslinked VTMS. The homo-crosslinked VTMS in Figure 6 exhibits new very strong peaks at 1048 and 1131 cm^{-1}. The former is attributed to small, linear linkage[25] and the latter to multiple linkages[26] of Si—O$_n$—Si. The unassigned peaks at 772 and 769 cm^{-1} in the neat and homo-crosslinked VTMS, respectively, are attributed to skeletal vibrations. Because many strong peaks (1599, 1193, 1093, and 815 cm^{-1} of neat VTMS and 1138 and 1048 cm^{-1} of homo-crosslinked VTMS) are absent in the PE blend (bottom spectra of Fig. 6), they were considered good candidates for the analysis of the silane-containing blends.

Figure 8 shows the FTIR spectra for the unfilled polymer blend containing 2% VTMS solution before (a) and after (b) conditioning in humidity for over 3

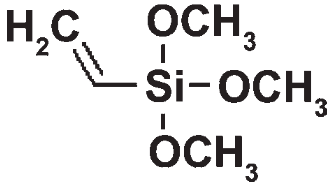

Figure 7 Chemical structure of vinyltrimethoxysilane (VTMS).

TABLE II
Characteristic Frequencies of Si-CH=CH$_2$[25]

Peak position (cm^{-1}), intensity	Vibration	Observed (cm^{-1})
1925, weak	Overtone	1924
1615–1590, medium	C=C stretch	1599
1410–1390, medium	CH$_2$ in-plane deformation	1411
1020–1000, medium	Trans CH wag	1011
980–940, medium	CH$_2$ wag	969
540–410, very strong	Skeletal C=C	541

days. Notably, the 1599 cm^{-1} peak representing the vinyl stretches is absent, suggesting that the VTMS is grafted to the PE.[27] Because only 2% VTMS was added to the sample, the absence of the peak may be due to the low concentration of silane. However, the increased viscosity of the melt and high gel content (82.6%) of the crosslinked polymer blend demonstrate that the VTMS is grafted to the polymer. Figure 8(b) shows the humidity-conditioned blend has markedly decreased intensity at 1193 and 1093 cm^{-1} and has developed shoulders in the regions of 1131 and 1048 cm^{-1}, indicating hydrolysis of the methyl ether linkage and condensation to form Si—O—Si bonds.[7,15,26] The shoulder at 1131 cm^{-1} is less prominent than the 1048 cm^{-1} shoulder, indicating a lesser degree of multiple linkage than was observed in the homo-crosslinked VTMS in Figure 6(b). A decrease in the intensity of the 1193 cm^{-1} peak, as shown in Figure 8, has previously been reported on the hydrolysis of VTMS.[26] Figure 8(b) also shows a very marked decrease in 815 cm^{-1} Si—O—CH$_3$ symmetric stretch, as would be expected. Although spectroscopy supports the expectation that VTMS grafts to PE via free radical-initiated reaction of the vinyl groups and crosslinks via hydrolysis and condensation reaction, the spectral analysis of the wood-filled composites was inconclusive because of the severely overlapping peaks from WF.

The tensile properties of all of the blends and composites are summarized in Table III. Little difference was seen in the tensile properties before and after exposure to moisture at elevated temperature. Modulus was slightly increased in the unfilled HDPE and LDPE but is likely due to annealing effects because increases were also found in the plastics made without crosslinking solution. Crosslinking the unfilled plastics tended to increase the yield strengths but decreased the moduli, most likely because of the reduction in crystallinity. The elongation at yield was unaffected in the unfilled HDPE and LDPE. However, the low elongations were improved in the unfilled blend, possibly as the result of some crosslinking between the HDPE and LDPE.

Not surprisingly, adding WF without crosslinking solution increased moduli but decreased yield strength and elongation at yield. The effect of adding crosslinking solution on the modulus of the composites was variable, but it improved strengths by up to 62%. These increases offset and, in some cases, exceeded that of the unfilled plastic, indicating reinforcement and increased stress transfer between the plastic and WF. Reinforcement of the plastic was likely limited by the low aspect ratio of the WF, which is well below 10. Elongation at yield generally decreased with addition of crosslinking solution except for the very low elongations in the composites with the HDPE-LDPE blend as matrix, which were improved. Increases in tensile yield strength seemed to be largely a function of gel content, and different amounts of crosslinking solution for the approaches are required to achieve a particular gel content.

The Izod impact performance was the most improved mechanical property of those measured and are shown in Table IV. The notched Izod impact energy of unfilled HDPE improved remarkably when crosslinked, increasing nearly sixfold over uncrosslinked HDPE at the highest gel content. Adding even small amounts of crosslinking solution to the unfilled HDPE-LDPE blends prevented fracture in notched Izod tests. None of the unfilled samples fractured during the reverse-notch tests.

Adding WF greatly reduced both notched and reverse-notched impact tests. The WF particles act as stress concentrators, reducing the energy required to initiate cracking. Also, weak interfaces, particularly in composites where no crosslinking solution was used, make it easier to propagate cracks once initiated. Adding crosslink solution during composite preparation did not result in the remarkable improvement in the notched impact seen in the

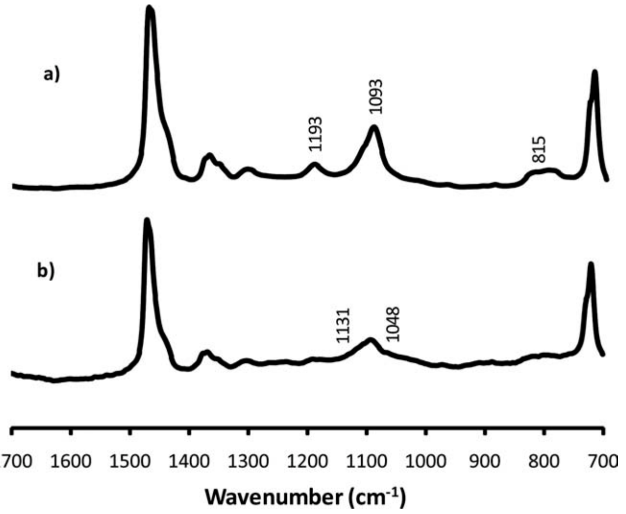

Figure 8 FTIR spectra of HDPE : LDPE blend with 2% VTMS crosslinking solution (a) before and (b) after exposure to high humidity at elevated temperature. Horizontal axis represents wavenumbers in cm^{-1}.

TABLE III
Tensile Test Result Summary

	Before humidity chamber						After humidity chamber					
Matrix and blend no.	Tensile modulus (GPa)	SD[a]	Tensile yield strength (MPa)	SD	Tensile elongation at yield (%)	SD	Tensile modulus (GPa)	SD	Tensile yield strength (MPa)	SD	Tensile elongation at yield (%)	SD
HDPE												
1	0.76	0.06	20.5	0.3	40.8	0.1	0.81	0.05	21.7	0.4	40.8	0.0
2	0.73	0.04	21.2	0.3	40.9	0.1	0.85	0.03	23.3	0.2	40.8	0.2
3	0.72	0.03	22.5	0.2	40.9	0.0	0.80	0.05	24.3	0.3	40.7	0.2
4	0.65	0.03	24.8	0.6	40.8	0.1	0.71	0.02	27.2	0.7	40.7	0.1
5	1.63	0.12	18.6	0.7	18.2	7.3	1.51	0.16	19.1	0.4	14.5	0.8
6	1.77	0.29	23.0	0.7	11.7	5.8	1.69	0.06	23.6	0.9	9.6	2.5
7	1.46	0.10	31.8	1.7	8.9	3.3	1.60	0.19	29.2	1.7	8.0	2.7
8	–[b]	–	–	–	–	–	–	–	–	–	–	–
9	1.56	0.10	28.7	1.0	8.1	1.3	1.70	0.39	25.5	1.1	6.9	3.1
10	1.75	0.19	23.6	0.4	10.8	2.0	1.78	0.19	21.8	0.4	15.2	2.8
11	1.42	0.09	32.0	0.9	10.5	1.1	1.51	0.12	29.7	1.0	9.5	1.5
12	1.42	0.11	31.8	1.1	10.0	1.3	1.57	0.09	31.0	1.1	7.1	0.5
LDPE												
13	0.13	0.00	15.9	0.3	40.6	0.1	0.15	0.01	15.0	1.0	40.5	0.1
14	0.12	0.01	16.6	1.1	40.5	0.0	0.16	0.01	16.6	0.6	40.7	0.1
15	0.13	0.00	18.0	0.9	40.5	0.1	0.15	0.01	17.8	0.4	40.6	0.1
16	0.12	0.01	16.9	1.0	40.5	0.1	0.14	0.01	17.1	0.2	40.6	0.1
17	0.38	0.06	12.0	0.7	22.9	5.5	0.40	0.04	11.7	0.5	20.9	4.9
18	0.38	0.02	14.8	1.2	20.5	5.0	0.41	0.01	13.7	0.8	18.7	2.3
19	0.40	0.02	15.5	0.4	16.2	3.5	0.52	0.13	15.1	0.5	13.0	4.5
20	–	–	–	–	–	–	–	–	–	–	–	–
21	0.37	0.04	13.6	0.7	16.0	4.0	0.42	0.05	12.2	0.2	17.4	3.1
22	0.42	0.01	15.2	0.3	20.9	1.8	0.58	0.07	14.0	0.6	15.6	1.5
23	0.43	0.06	15.9	1.5	15.6	4.2	0.49	0.06	15.5	1.0	16.9	4.2
24	0.41	0.03	15.8	0.8	16.5	3.3	0.45	0.03	15.7	0.5	17.4	3.1
Blends												
25	0.47	0.05	16.3	0.2	12.6	1.4	0.49	0.05	17.2	0.3	12.8	0.8
26	0.36	0.05	14.6	0.2	13.6	1.0	0.37	0.05	15.7	0.2	14.3	1.0
27	0.33	0.06	15.2	0.5	19.1	10.4	0.32	0.06	16.0	0.3	18.2	3.0
28	0.27	0.03	14.5	0.3	17.0	1.3	0.28	0.05	15.7	0.2	21.6	9.3
29	0.75	0.06	13.1	0.2	4.9	1.0	0.75	0.05	13.0	0.4	5.9	1.2
30	0.72	0.05	17.6	1.2	7.3	3.2	0.72	0.05	17.6	0.4	6.6	2.0
31	–	–	–	–	–	–	–	–	–	–	–	–
32	–	–	–	–	–	–	–	–	–	–	–	–
33	0.69	0.07	20.3	1.4	9.5	3.4	0.71	0.04	20.7	2.1	9.5	2.5
34	0.78	0.02	14.8	0.3	5.1	0.4	0.80	0.05	14.4	0.4	5.2	1.0
35	0.78	0.03	17.8	0.5	6.2	0.9	0.75	0.06	18.7	1.5	7.7	2.2
36	0.74	0.06	21.9	2.5	10.5	3.0	0.75	0.06	20.5	0.4	8.4	0.7

Blend compositions are listed in Table I.
[a] Values are one standard deviation.
[b] Not measured because the blend could not be injection molded.

unfilled plastics, increasing impact energies at most 32%. However, adding crosslinking solution greatly increased reverse-notched impact energies, generally resulting in 50–100% increases, though these were still well below those of the unfilled plastics. Figure 9 shows the increases in reverse-notched impact energy as a function of gel content. As with the tensile yield strengths, little differences were seen between the different approaches for the HDPE and LDPE composites when their gel contents are considered, and an approximately linear relationship was found. Interestingly, for the composites made with the HDPE-LDPE blend, the approaches yielded very different impact energies at low gel contents but were very similar at high gel contents. This might suggest better efficiency in improving wood polymer adhesion in the different approaches. However, further investigation is necessary to verify this improvement in efficiency.

SUMMARY AND CONCLUSIONS

Three different approaches of adding silane and peroxide during extrusion of WPCs were investigated. HDPE, LDPE, or a blend of the two were compared as

TABLE IV
Izod Impact Result Summary

Matrix and blend no.	Notched Izod impact (J/m)	SD[a] (J/m)	Reverse notched Izod impact (J/m)	SD (mm)
HDPE				
1	95	4	NB	–
2	147	9	NB	–
3	233	11	NB	–
4	692	27	NB	–
5	52	4	81	12
6	54	3	106	10
7	67	7	121	14
8	–[b]	–	–	–
9	65	8	105	16
10	51	2	94	6
11	51	5	146	11
12	56	2	158	16
LDPE				
13	NB	–	NB	–
14	NB	–	NB	–
15	NB	–	NB	–
16	NB	–	NB	–
17	115	19	149	19
18	111	8	166	10
19	143	9	247	26
20	–	–	–	–
21	142	8	264	36
22	84	5	146	7
23	125	9	228	17
24	152	13	283	36
Blends				
25	151	8	NB	–
26	NB	–	NB	–
27	NB	–	NB	–
28	NB	–	NB	–
29	81	3	148	4
30	84	8	214	25
31	95	5	258	33
32	–	–	–	–
33	100	6	215	27
34	67	2	152	10
35	73	4	210	40
36	80	5	291	23

Blend compositions are listed in Table 1.
[a] Values are one standard deviation.
[b] Not measured because the blend could not be injection molded.
NB, did not break.

matrices. The unfilled plastics crosslinked efficiently, with little premature crosslinking occurring during processing. Portions of both LDPE and HDPE were crosslinked, but reduced molecular mobility impeded crystal formation somewhat, which likely accounted for the reductions in tensile moduli. Although only modest improvements in tensile strengths were found in unfilled plastics, the notched Izod impact energy of unfilled HDPE improved remarkably when crosslinked, increasing approximately 600% over uncrosslinked HDPE at the highest gel contents. Additionally, adding even small amounts to unfilled HDPE-LDPE blends prevented fracture during the notched impact tests.

Unlike the unfilled plastics, most of the crosslinking of the composites occurred during processing. This resulted in high viscosities, negating some of the advantages of a separate crosslinking step and limited the composites that could be processed to those with gel contents of about 40% at most. Better protecting the WF from moisture sorption did not seem to mitigate these viscosity increases, perhaps suggesting that WF is reacting directly with the crosslinking solution rather than simply providing water that leads to moisture-induced crosslinking of the plastic during processing. Further work needs to be performed to precisely determine and control the reaction chemistry during processing.

Some reinforcement of the plastics by the WF was achieved when sufficient crosslinking solution was added. This reinforcement was likely limited by the low aspect ratio of the WF and likely would be more

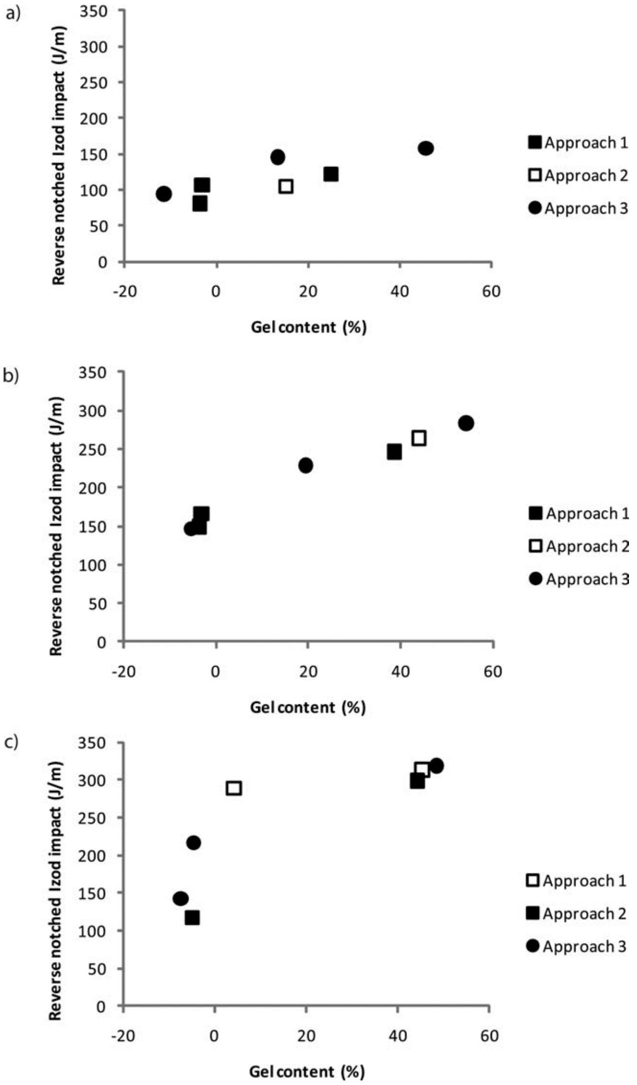

Figure 9 Effects of different crosslinking approaches on the reversed-notched impact energies of composites with HDPE (a), LDPE (b), or HDPE-LDPE blend (c) matrix.

pronounced if higher aspect ratio wood or pulp fibers were used. Adding crosslinking solution also improved the low elongations in the composites with the HDPE-LDPE blend as matrix. Adding crosslink solution during composite preparation resulted in modest improvements in notched impact energies but greatly increased reverse-notched impact energies in the composites with the highest levels of crosslinking solution.

The differences between the approaches for preparing the crosslinked composites seemed to largely be a matter of efficiency in terms of the amount of crosslinking solution required to affect processing and performance. The most efficient approach was a two-step procedure where the silane was first grafted to the plastic and then WF was compounded with the grafted silane in a second step. The least efficient was a two-step process where the wood and plastics were first compounded and then crosslinking solution was added in a second step. A procedure where all materials were compounded in a single step was of intermediate efficiency but is likely the most economical approach.

Improvement and a useful balance for properties were found for composites made with HDPE-LDPE blends with the crosslinking upgrading some performance attributes such as strength, elongation at yield, and reverse-notch Izod impact energies. Further advances in processing and performance require that the reaction chemistry be better understood, controlled, and optimized and is an on-going area of research.

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