

Potassium Methyl Siliconate-Treated Pulp Fibers and Their Effects on Wood Plastic Composites: Water Sorption and Dimensional Stability

Cheng Piao,¹ Zhiyong Cai,² Nicole M. Stark,² Charles J. Monlezun³

¹Calhoun Research Station, Louisiana State University Agricultural Center, Calhoun, Louisiana 71225

²Engineered Composites Science Group, USDA Forest Service, Forest Products Laboratory, Madison, Wisconsin 53726

³Department of Experimental Statistics, Louisiana State University, Baton Rouge, Louisiana 70803

Correspondence to: Z. Cai (E-mail: zcai@fs.fed.us)

ABSTRACT: Potassium methyl siliconate (PMS) was investigated as a new nano modifier of wood fiber and wood flour to improve the compatibility between the fiber/flour and the plastic matrix in fiber reinforced plastic composites. Before injection molding, bleached and brown pulp fibers and mixed species wood flour were pretreated in PMS solutions. The morphology of the treated and untreated fiber and flour, the compatibility of PMS-treated fiber and flour with polyethylene (PE), and the water sorption and volumetric swell of PMS-treated fiber/flour plastic composites in a long-term soaking test were evaluated. Fiber and flour treated with PMS increased the compatibility between the fiber/flour and the PE matrix. The increased compatibility of PMS-treated fiber and flour with the matrix contributed to the reduction of water sorption and, thus, increased dimensional stability. For all composites, water sorption and volumetric swell of fiber/flour plastic composites decreased as the ratio of fiber to flour increased.

© 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 193–201, 2013

KEYWORDS: biopolymers and renewable polymers; cellulose and other wood products; polyolefins; composites; fibers

Received 17 July 2012; accepted 16 October 2012; published online 4 November 2012

DOI: 10.1002/app.38736

INTRODUCTION

The chemistry at fiber-plastic interfaces influences both mechanical performance and dimensional stability of natural fiber reinforced plastic composites. Poor compatibility between hydrophilic lignocellulosic fibers and hydrophobic thermoplastic usually leads to strength reduction and unsatisfactory dimensional stability. As a result, the compatibility of all phases in natural fiber reinforced plastic composites has attracted a great deal of research interest, especially in the last two decades. To increase compatibility, a common approach is to use coupling agents, which are compounds designed to interact with or chemically link the lignocellulosic fibers or particles with the thermoplastic.¹ The organic group of the coupling agent either reacts with or is compatible with molecular chains of the plastic, whereas the polar end of the coupling agent adsorbs and reacts with sites on lignocellulosic fibers. The resulting chemical bonds or links are coherent and impermeable to water penetration.

Traditionally, various organosilanes have often been used as coupling agents. The organosilanes that have recently been investigated include trimethoxysilyl propyl methacrylate,² triethoxyvinylsilane,^{3–6} aminopropyltriethoxysilane,^{7–9} and dichloro-

diethylsilane.^{8,9} Some of the nonsilane coupling agents that have also been studied include maleic anhydride modified polypropylene or polyethylene (PE),^{10–14} grafting copolymers, fiber acetylation and etherification,¹⁵ nanoclay,^{13,16} and oxalic acid.¹⁷ These chemicals are either mixed directly with fibers and plastics or used to modify the fibers before molding, resulting in increased tensile strength,^{4,7,8} increased tensile modulus,² and/or reduced water sorption.^{3,11} When compared with the direct mixing approach, modification of fibers before molding allows chemicals to locate only in the fiber-plastic interface, thereby reducing undesired side reactions, such as chain scission caused by free radicals going astray in the plastic.²

Wood flour particles have been the traditional organic fillers in the fabrication of plastic composites.¹⁷ To increase mechanical performance, high aspect-ratio pulp fibers have been investigated as reinforcing materials.^{10,14,16–19} When compared with wood flour plastic composites, pulp fiber reinforced composites demonstrate higher flexural strength^{11,19} and lower water sorption rates¹¹; however, increasing fiber aspect ratios may result in greater water sorption and volumetric swell.¹⁹

In this study, potassium methyl siliconate (PMS) was investigated as a new fiber nano modifier to improve the compatibility

This article (2012-255-6088) is published with the approval of the Director of the Louisiana Agricultural Experiment Station.

© 2012 Wiley Periodicals, Inc.

of cellulosic fibers with thermoplastic. PMS is used commercially as a hydrophobic sealant for cement protection and has also been used to create superhydrophobic surfaces on fabric substrates.²⁰ In this report, the topography of PMS-treated fibers as well as the water sorption and dimensional stability of PMS-treated fiber/flour plastic composites are characterized.

EXPERIMENTAL

Materials

PMS having solid content of about 40% was obtained in an aqueous solution from ReUse Concrete Sealing Specialists, Overland Park, KS, and was used as received.

Bleached and brown Kraft pulp fibers were obtained from International Paper in Texarkana, TX. The wet pulp fibers were made from loblolly pine using a mechanical and chemical pulping process. Mixed pine species 0.42 mm (40 mesh) wood flour was obtained from American Wood Fibers, Schofield, WI.

The plastic used in this study was high-density PE with a melt flow index of 33 g/10 min (ExxonMobil Chemical, HD-6733, Houston, TX).

Synthesis and Characterization of Nano PMS

Fibers and Flour

A PMS aqueous solution was prepared in a 3000 mL glass beaker containing 0.5 mol L⁻¹ PMS. Approximately 60 g (dry-equivalent) of pulp fiber (bleached or brown, but not both) or 60 g (dry equivalent) of flour was suspended in the solution. The system was vigorously stirred at room temperature, whereas carbon dioxide was bubbled through the solution. When the pH of the solution was somewhere between 9.5 and 10.5, carbon dioxide bubbling was stopped and the system was stirred for an additional 4–6 h at room temperature. After synthesis, the PMS-treated fibers and flour were washed five times with deionized water to remove unreacted chemicals from the fibers, which were then filtered from the solution and oven-dried at 100°C for 6 h. Dry fiber bundles were shredded into individual fibers using a Wiley mill with a 1.0 mm (18 mesh) screen. After Wiley milling, fibers were further screened using a 0.18 mm (80 mesh) sieve to remove short fibers and PMS nanoparticles that fell from the fibers during milling. The dry, treated flour mats were manually broken into flour without screening. The treated fiber and flour were stored separately and subsequently used for the fabrication of plastic composites.

The prepared PMS nano film on the surfaces of pulp fibers and flour particles were characterized using a Fourier transform infrared spectroscopy (FTIR) (VARIAN FTS 800) and a scanning electron microscope (SEM) (Hitachi TM-1000).

Injection Molding and Characterization of Fiber/Flour Plastic Composites

A 15 cc twin screw microcompounder (DSM Explore, Netherlands) was used to mix PE plastic with PMS-treated or -untreated wood components (flour and/or bleached or brown fibers) of each plastic composite sample in a batch process at 50 rpm and 190°C. To achieve an uniform distribution of flour and/or fibers in the plastic, each component was fed into the barrel separately in the following order. For each sample, PE

was manually fed into the mold first, followed by fiber, and then flour. Each compounding cycle took 7–9 min, depending on the amount of fiber in the sample. Because fibers had a larger volume and surface area than flour, higher fiber content usually led to a longer feeding and mixing time in the microcompounder.

The mixed compound exiting the twin screw microcompounder was collected and immediately transferred to an injection mold where the mold temperature was 40°C. Finally, a 12.7-mm wide, 3.2-mm thick, and 133-mm long sample was obtained from each injection molding cycle. All fiber/flour plastic composite samples consisted of 50% PE and 50% fiber and/or flour by weight. The flour and fiber contents in each sample were (by weight) either (a) 50% flour only, (b) 35% flour and 15% pulp fiber, (c) 20% flour and 30% pulp fiber, or (d) 50% pulp fiber only. No sample contained both brown fiber and bleached fiber. In each sample, either all wood particles were treated with PMS or none was treated with PMS.

Fiber and flour distribution in the plastic matrix and chemical crosslinking of PMS with lignocellulosic materials and plastic were characterized using an SEM (Hitachi TM-1000) and an FTIR (VARIAN FTS 800).

Water Sorption and Volumetric Swell

The water sorption test of fiber/flour plastic composites was conducted according to American Society for Testing and Materials standard D 570-98.²¹ Before water soaking, each sample was oven-dried at 50°C for 24 h. After drying, the weight of each sample was measured and was used as the initial weight of the sample in the long-term water soaking test. Three crosses were marked on a flat surface along the length of each sample before it was soaked in water. The average of the thicknesses at the three locations was used as the initial thickness of each (i.e., the thickness before the soaking test). Samples were then submerged in a container of distilled water maintained at 23°C. At each predefined time interval (6 h, 12 h, 24 h, 48 h, etc.), samples were removed from the water one at a time. Surface water was removed with a paper towel. Each sample was weighed and measured for thickness at the three marked locations, and then replaced in water. Water sorption and volumetric swell of each sample were calculated based on the weight and thickness of the sample before soaking and at predefined time intervals during soaking.

RESULTS AND DISCUSSION

Reactions of PMS with Cellulosic Fibers

In a typical reaction between PMS and cellulosic fibers, PMS is dissolved in a highly alkaline aqueous solution. When the pH is reduced, PMS is hydrolyzed to form silanols. Condensation among silanols leads to formation of a mixture of PMS monomers, silanols, and oligomers of polysilanols. At about 8.5–10.5 pH, a mixture of monomers, silanols, and oligomers gradually forms a three-dimensional network containing a liquid and a solid phase. The solid phase precipitates from the solution. Hydrogen bonds formed between polysilanols and hydroxyls on fibers permit the polysilanol network to be anchored to the fibers.²²

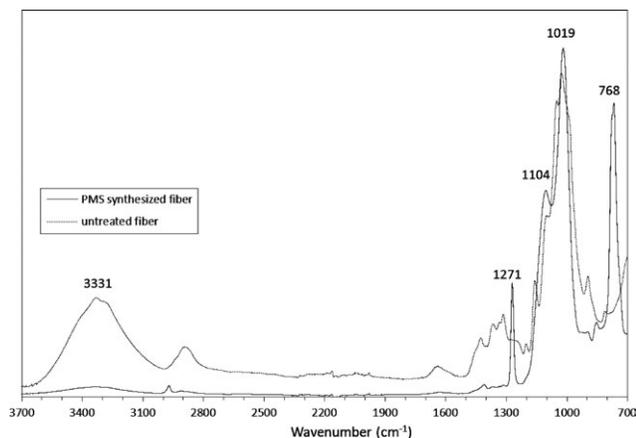


Figure 1. FTIR spectra of PMS-treated bleached pulp fiber and -untreated bleached pulp fiber.

Figure 1 exhibits the FTIR spectra of both PMS-treated and -untreated bleached pulp fiber. The absorbance peaks at 1271, 1104, 1019, and 768 cm^{-1} correspond to the molecular vibrations of siloxane components on the PMS-treated fibers. The peak at 1271 cm^{-1} of the PMS-treated fibers resulted from stretching vibrations of the Si—CH₃ bonds,^{20,22,23} whereas the peak at 768 cm^{-1} corresponds to the vibrations of a collection of bonds, including Si—O, Si—C, and/or Si—O—C.^{22,24} The

peak at 1019 cm^{-1} is typically attributed to stretching of Si—O—Si bonds^{23,25} developed among the silanols. The sharp peak at 1104 cm^{-1} is due to asymmetric vibrations of the Si—O—C bonds,^{26,27} which emerge when silanols and polysilanols are anchored chemically to cellulosic fibers. These results confirm the existence of PMS on the cellulosic fibers as well as the PMS covalent bonds to these fibers. In addition, the peak at 3331 cm^{-1} , due to O—H stretch of free hydroxyls, was substantially reduced in intensity for PMS-treated fibers because some of the hydroxyls on the fibers were replaced by O—Si bonds. These O—Si bonds connect the siloxane monomers and chains to the fibers. The FTIR spectra of PMS-treated brown fiber were similar to the FTIR spectra of PMS-treated bleached fiber shown in Figure 1.

Characterization of PMS-Treated Fibers and Flour

Figure 2 displays the SEM images of bleached pulp fiber and wood flour that were treated with PMS. Figure 2(a,b) shows the morphologies of PMS-treated bleached cellulosic fiber (the morphology of PMS-treated brown cellulosic fiber was virtually identical to that of PMS-treated bleached cellulosic fiber), and Figure 2(c,d) gives the morphologies of PMS-treated wood flour. PMS particles grew on the surfaces of both cellulosic fiber and wood flour. PMS particle sizes ranged from less than 100 nm to 800 nm. A number of larger PMS particles usually assembled into blocks, floating on the surfaces of the fibers and

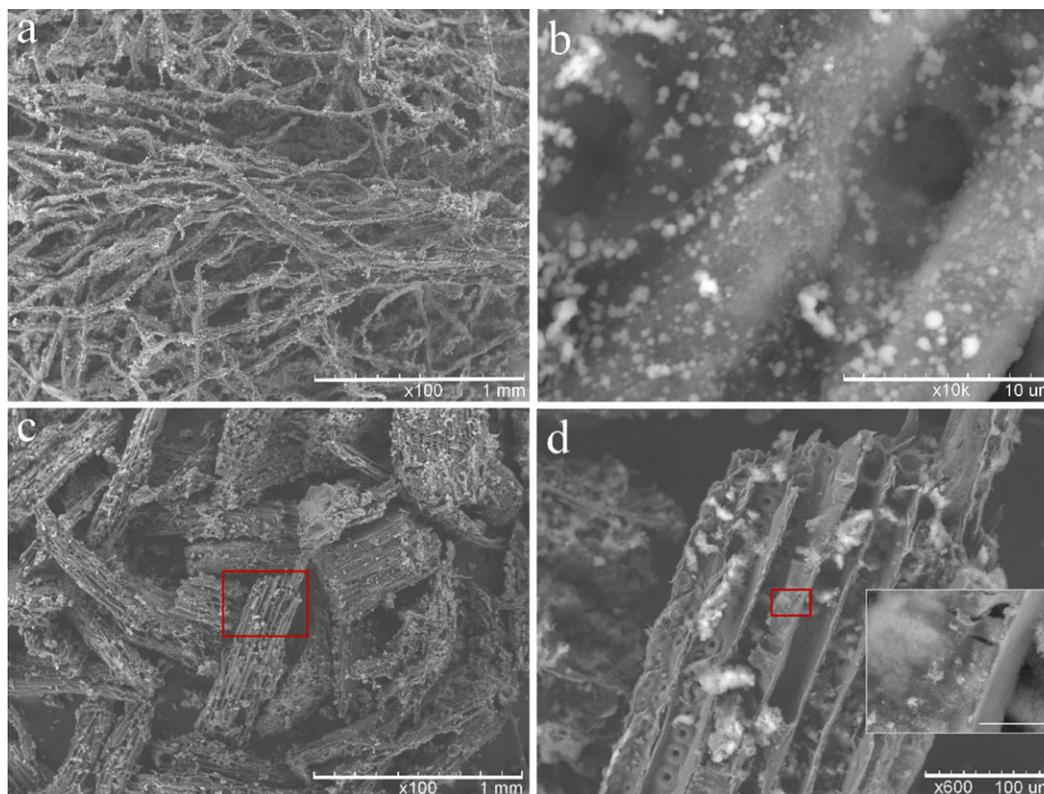


Figure 2. SEM images of PMS-treated bleached pulp fiber and PMS-treated wood flour. (a) Bleached fibers after PMS synthesis. (b) Bleached fiber surface covered by micro and nano PMS particles. (c) Wood flour after PMS treatment. (d) Cell lumens and cell walls of wood flour covered by micro and nano PMS particles. The scale for the inset bar in (d) is 10 μm . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

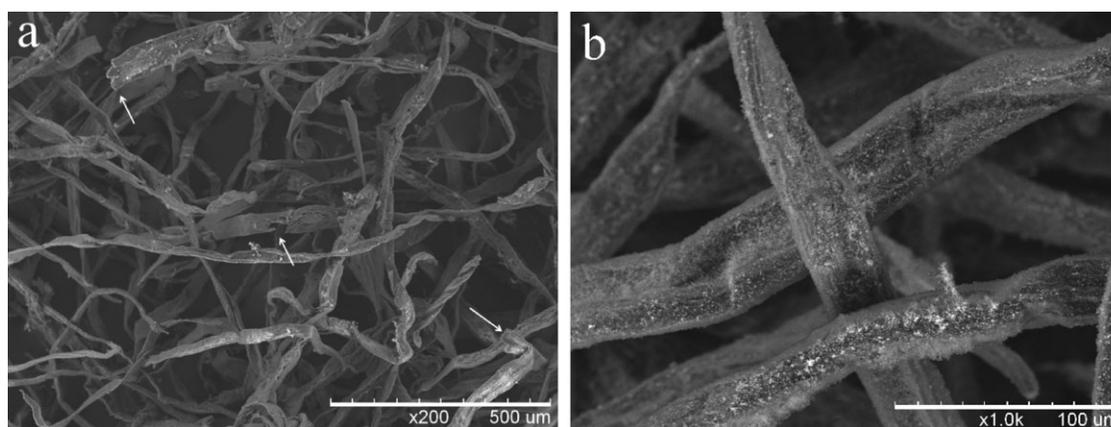


Figure 3. SEM images of PMS-treated bleached pulp fibers after milling using a Wiley mill. (a) After milling. (b) An enlarged view after milling.

flour particles. Beside the larger particles and blocks of particles were smaller particles (less than 100–300 nm in size) that grew on the surfaces of the fiber and flour.

After drying, treated and untreated fiber mats formed hard blocks of fibers. To distribute the fiber uniformly in the plastic matrix, these blocks of fibers had to be broken down into individual fibers. Before injection molding, both PMS-treated and -untreated fiber mats were processed into individual fibers using a Wiley mill. Figure 3 shows the morphology of PMS-treated bleached fibers after milling. As shown in Figure 3(a), fibers were cleaner after milling than before milling [Figure 2(a)]. Damage due to milling was observed on some of the fibers (pointed out by arrows), but most fibers came through the milling process in good condition. Figure 3(b) shows that after milling, treated fibers were still coated with small PMS particles. The PMS particle blocks on the surfaces of treated fibers were removed during milling and subsequent screening. Removal is necessary in order to prevent free PMS particles from entering the plastic matrix during compounding.

Characterization of PMS-Treated Fiber/Flour Plastic Composites

Figure 4 displays SEM images of plastic composite samples reinforced with 15% bleached fiber and 35% flour. Figure 4(a,b) shows the surface of a composite sample reinforced with PMS-treated pulp fibers, and Figure 4(c,d) shows the surface of a composite sample reinforced with untreated pulp fibers. As pointed out by the arrows in the figure, naked fibers were found on the surface of the sample in Figure 4(c), whereas the fibers in Figure 4(a) were embedded in the plastic matrix. Part of a fiber in Figure 4(b) was merged with PE plastic, leading to a disappearing interface between plastic and fiber on the left side of the fiber. A horizontal bruise across the fiber and plastic at the lower part of Figure 4(b) demonstrates that the fiber was covered by ethylene plastic. In contrast with merged fiber-plastic interface shown in Figure 4(b), all edges of the fiber shown in Figure 4(d) were clearly identifiable. Therefore, the fibers treated with PMS appeared to be more compatible with PE than untreated virgin fibers. Micro-scale holes and gaps were found on the surfaces of both types of composites. These defects usually occurred at the fiber/flour-plastic interfaces.

Figure 5 contains the FTIR absorbance spectra of PMS-treated and -untreated bleached fiber/flour plastic composite samples as a function of fiber/flour content in the samples. For comparison purposes, the FTIR spectrum of untreated virgin bleached pulp fiber sample (denoted by “Cellulosic fiber”) containing no PE is also shown in the figure. All spectra were normalized based on the absorbance intensity of the peaks at 1030 cm^{-1} . As mentioned previously, the absorbance peaks at 1271 , 1104 , and 1019 cm^{-1} in Figure 1 correspond to stretching vibration of Si—CH₃ bonds, asymmetric vibrations of the Si—O—C bonds, and stretching of Si—O—Si bonds formed between PMS and cellulosic fibers and flour particles, respectively, whereas the absorbance peak at 768 cm^{-1} represents the vibrations of a collection of bonds (Si—O, Si—C, and/or Si—O—C). After PMS-treated cellulosic fibers and flour particles were compounded with PE, the absorbance peaks at 1271 cm^{-1} (Si—CH₃) in Figure 1 remained the same in Figure 5, whereas the absorbance peaks at 1104 cm^{-1} (Si—O—C) and 1019 cm^{-1} (Si—O—Si) in Figure 1 shifted to 1114 and 1029 cm^{-1} in Figure 5, respectively, and the absorbance peak at 768 cm^{-1} shifted to 780 cm^{-1} . It can be seen in Figure 5 that as PMS-treated fiber content increased in the composites, the absorbance intensity of some of these bonds increased. According to Beer’s law, absorbance is proportional to the concentration of the bonds. Therefore, as the PMS-treated fiber content in the composites increased, the concentration of Si—CH₃, Si—O—Si, and/or Si—O—C bonds increased.

As shown in Figure 5, the typical absorption peaks at 1271 , 1114 , 1029 , and 780 cm^{-1} of PMS-treated bleached fiber/flour composites are missing from the FTIR spectra of untreated bleached fiber/flour plastic composites due to the absence of PMS coupling nanoparticles in the latter. The FTIR spectra of the plastic composites containing untreated fiber/flour are similar to the FTIR spectrum of the pure fiber sample, except for the adsorption peaks at 1462 and 718 cm^{-1} , which, as mentioned earlier, are characteristic absorption peaks of PE plastic.²⁸

Figure 6 displays the FTIR absorbance spectra between wavenumbers 3600 to 3000 cm^{-1} for the same samples of Figure 5. Absorption peaks for samples occur at 3331 cm^{-1} . As revealed in Figure 6, the hydroxyls of the plastic composites were substantially reduced after the fiber/flour was modified with PMS.

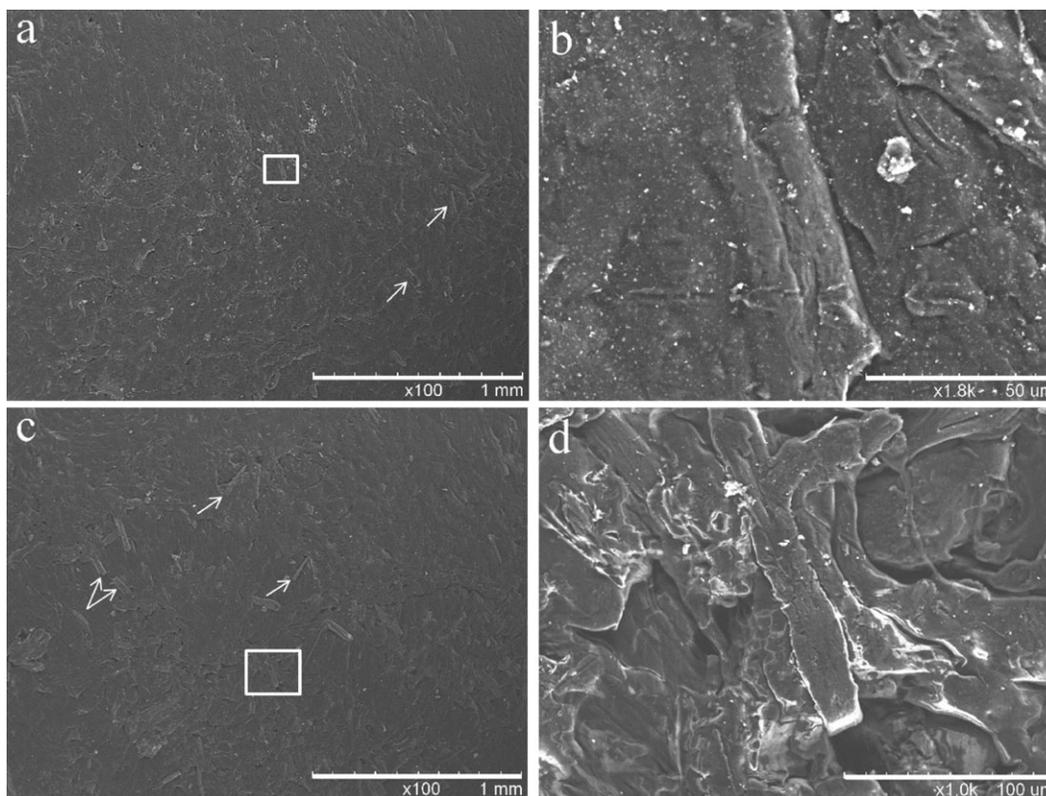


Figure 4. SEM images of plastic composites reinforced with 15% bleached fiber and 35% flour. (a) A sample reinforced with PMS-treated bleached fiber and PMS-treated flour. (b) An enlarged view of the area shown in the box of (a). (c) A sample reinforced with untreated bleached fiber and untreated flour. (d) An enlarged view of the area highlighted in the box of (c).

The FTIR absorbance spectra of plastic composite samples containing brown fiber were similar to the FTIR spectra of plastic composite samples containing bleached fiber, regardless of whether or not the fibers were treated with PMS.

Figure 7 depicts the association between cellulosic fibers, PMS, and PE chains in fiber reinforced plastic composite samples. The polar functional groups of PMS are connected to each

other through Si—O—Si bonds and to cellulosic fibers through Si—O—C covalent bonds, whereas the nonpolar functional groups (—CH₃) are associated with PE through van der Waals forces. Therefore, PMS-treated fibers and flour were more compatible with PE than untreated fibers and flour. In addition, due to the increase in surface area the fibers exhibited compared with flour, increasing the fiber-to-flour ratio may result in additional compatibility.

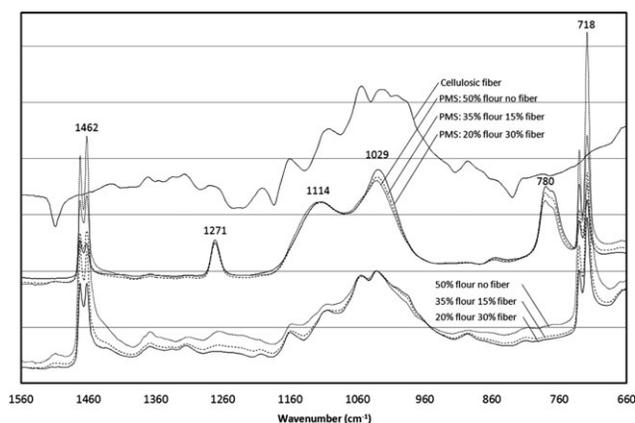


Figure 5. FTIR spectra of fiber/flour polyethylene composites, three of which contain PMS-treated fiber and flour. The spectrum denoted by “Cellulosic fiber” was obtained from a sample consisting of 100% untreated bleached cellulosic fibers and no polyethylene.

Water Sorption and Volumetric Swell

As shown in Figure 4, micro-scale holes and gaps formed in the plastic composite samples at the interface between fiber/flour and plastic. Holes and gaps were the gateways for water to penetrate the composites, exposing fiber and flour in the interior to water, causing volumetric swell. Figure 8 displays water sorption and volumetric swell as a function of soaking time for four PMS-treated bleached fiber/flour plastic composite samples. Figure 9 displays the same properties for three untreated bleached fiber/flour plastic composite samples. The corresponding curves for brown fiber/flour plastic composite samples were very similar to those of Figures 8 and 9. Each sorption or swell curve can be divided into two phases, i.e., a fast growing phase and a saturating phase. In Figure 8, the transition points between the two phases varied from 1 month (720 h) to 3 months (2160 h), depending upon fiber/flour content. Higher PMS-treated fiber to flour ratios led to longer fast growing phases for both water sorption and volumetric swell. In contrast to the transition

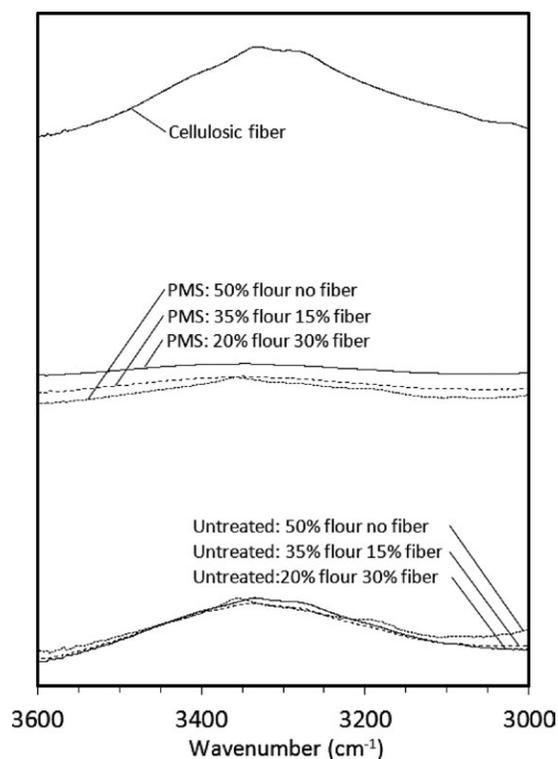


Figure 6. FTIR spectra for the samples of Figure 5 between the wavenumbers 3600 and 3000 cm^{-1} .

points for the PMS-treated fiber/flour plastic composites (Figure 8), the transition points for the untreated fiber/flour plastic composites (Figure 9) were much closer together. All untreated fiber/flour plastic composites transitioned from the fast growing phase to the saturating phase for both water sorption and volumetric swell after ~ 1 month (720 h) of soaking, regardless fiber to flour ratio. Plastic composites reinforced with PMS-treated fiber/flour took longer to be saturated by water than plastic composites reinforced with untreated fiber/flour or with PMS treated flour only. Furthermore, for plastic composite samples

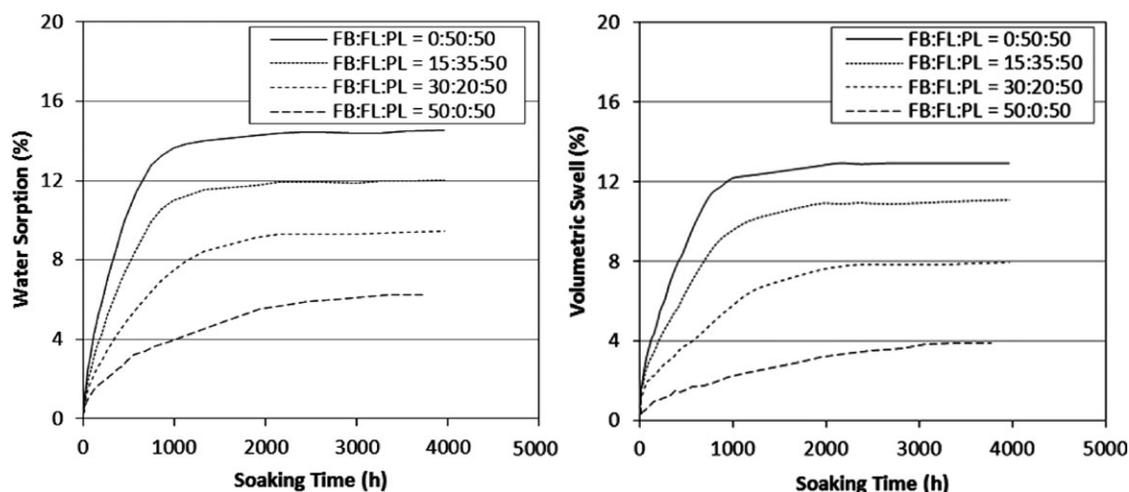


Figure 8. Water sorption and volumetric swell of PMS-treated fiber/flour polyethylene composites. In the legend (% by weight): FB, fiber; FL, wood flour; and PL, plastic (polyethylene).

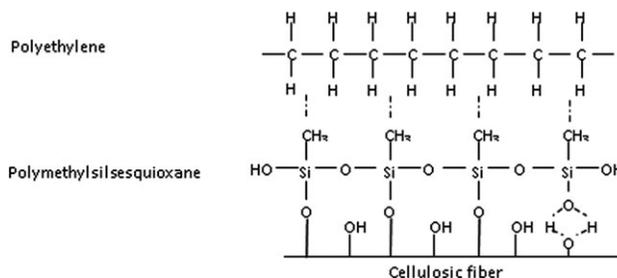


Figure 7. Schematic diagram of the formation of bonds between polyethylene chain, polymethylsilsesquioxane, and cellulosic fiber.

containing PMS-treated fiber and/or flour, water sorption and volumetric swell decreased as fiber content increased, regardless of soaking time (Figure 8). This decrease in water sorption and volumetric swell was present, but not nearly as dramatic for plastic composite samples containing untreated fiber and/or flour (Figure 9).

PE is hydrophobic; it does not adsorb water and does not swell. Therefore, the dimensional instability of fiber/flour plastic composites in humid environments or in contact with water is due solely to the dimensional instability of the fiber (whether brown or bleached) and flour in the composites. Surface fibers and flour, such as those shown in Figure 4, would swell, roughening the surface and reducing the esthetic values of fiber/flour plastic composite products. The swell of fiber, and especially flour in the composites, may disintegrate the connections between plastic and lignocellulosic materials, causing more water sorption and volumetric swell.

Figure 10 summarizes the effects of PMS nano treatment, fiber type (bleached or brown pulp fibers), and fiber content on water sorption and volumetric swell of fiber/flour plastic composites. Each average depicted in Figure 10 is an average over two composite samples. As expected, water sorption and volumetric swell decreased as fiber content increased, regardless of whether the fibers were treated with PMS or not. For each of the three fiber contents, PMS-treated bleached pulp fiber performed at least as

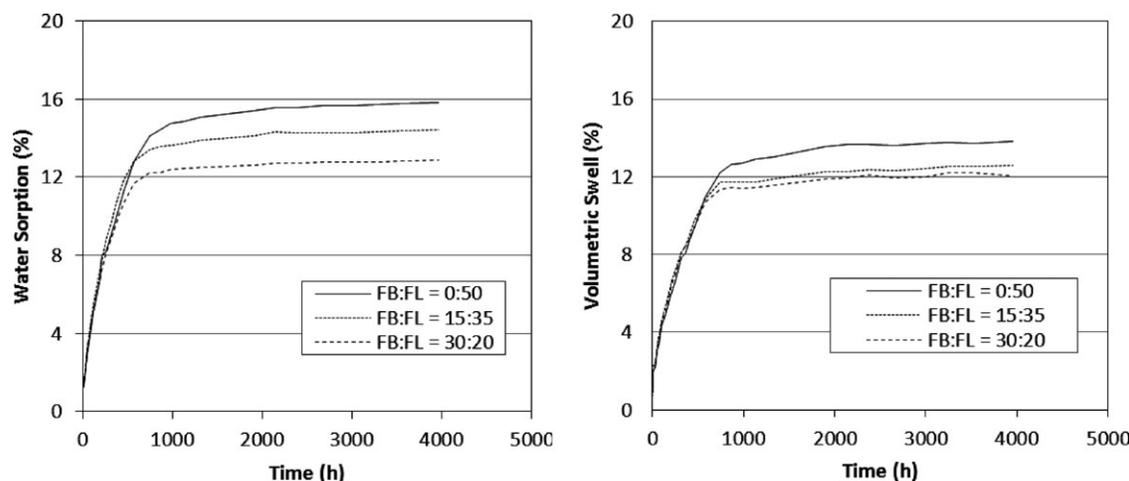


Figure 9. Water sorption and volumetric swell of untreated fiber/flour polyethylene composites. The legend is the same as that of Figure 8.

well and usually better than PMS-treated brown pulp fibers in reducing water sorption and volumetric swell.

The compatibility of PMS-treated fibers and flour with PE may have contributed to the reduced water sorption and volumetric swell of the PMS fiber/flour plastic composites compared with untreated fiber/flour composites. The covalent bonds (via Si—O—C bonds) between PMS and lignocellulosic materials, as well as the intimate contact between PMS and PE chains (via van der Waals forces), reduced the permeation of water into fiber/flour-PMS and PMS-plastic interfaces and, thus, into the cell walls of the fiber and flour in the composites. Increasing compatibility between thermoplastic and reinforcing fiber reduced volumetric swell and thus reduced the damaging stress incurred by the swelling flour particles.

As confirmed in Figure 6, there were fewer hydroxyls in PMS-treated fiber/flour plastic composites than in the pure cellulosic fiber sample or the untreated fiber/flour plastic composites. Hydroxyls on the surfaces of PMS treated cellulosic fibers and flour particles were replaced by siloxane groups in the PMS synthesis, where PMS nanoparticles adhered to the surfaces of both pulp fibers and flour particles [Figure 2(b,d)]. Thus, the water sorption groups (—OH) of both PMS-treated fiber and flour

were reduced before the fiber and flour were injection molded into composites. Moreover, because pulp fiber has a higher aspect ratio and a larger surface area than flour, more hydroxyls were replaced by siloxane groups on pulp fibers than on flour because of the limited penetration of PMS molecules into flour. Therefore, PMS-treated fiber plastic composites would have less free hydroxyls, adsorb less water, and swell less than PMS-treated wood flour plastic composites.

During PMS synthesis, some PMS molecules permeated into amorphous regions of the cell walls, where they grew into nanoparticles, blocking water molecules out of the cell walls. It would be easier for PMS molecules to permeate the cell walls of bleached fibers (more void spaces) than to penetrate the cell walls of either brown fibers or flour particles. Therefore, the PMS polymer surface coverage would be higher on bleached pulp fibers than on brown fibers, and especially higher than on flour particles. This partially explains why PMS-treated bleached fiber with PMS-treated flour plastic composites adsorbed less water and swelled less than did PMS-treated brown fiber with PMS-treated flour plastic composites.

For fiber/flour plastic composites, water sorption is always accompanied by volumetric swell. However, for a given amount

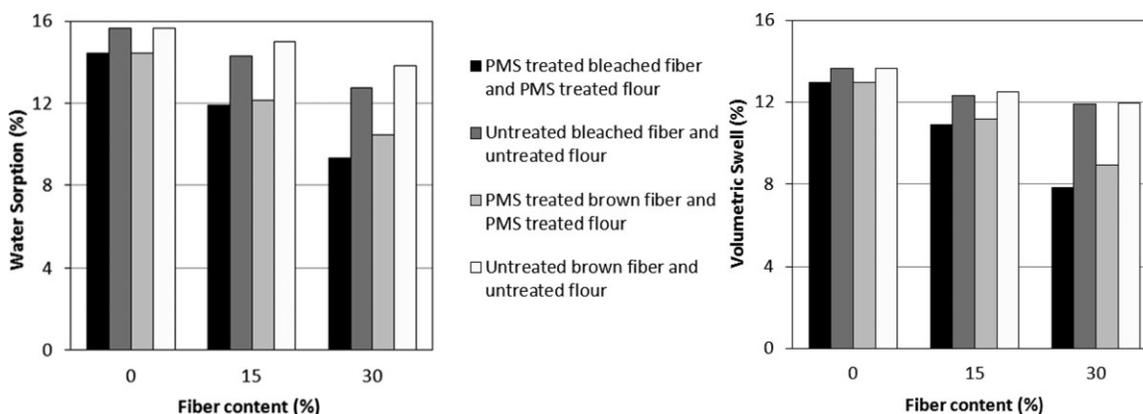


Figure 10. Volumetric swell and water sorption of fiber/flour polyethylene composites.

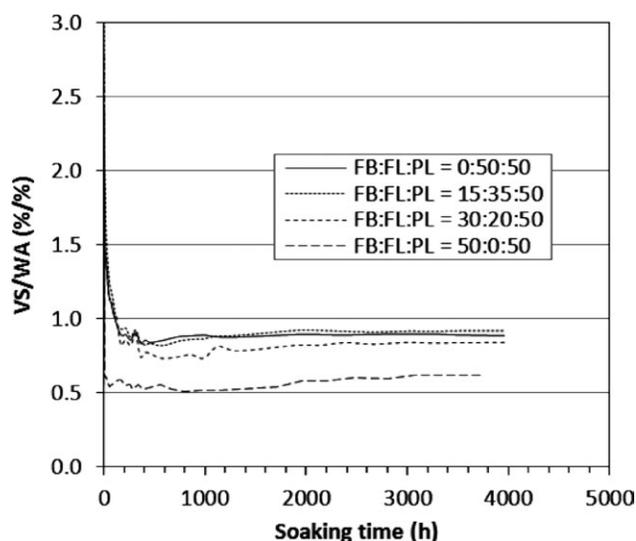


Figure 11. Volumetric swell per percentage of water sorption for PMS-treated bleached pulp fiber/flour polyethylene composites. The legend is the same as that of Figure 8.

of fiber in the composite, volumetric swell rates per percentage water sorption were different for different soaking times, and for a given soaking time, volumetric swell rates per percentage water sorption were different for different amounts of fiber in the composites. Figure 11 displays the swell rate per percentage water sorption as a function of soaking time for four PMS-treated bleached fiber/flour composites, each containing a different amount of fiber. Corresponding curves for brown fiber/flour composites were very similar to those of Figure 11. As can be seen in Figure 11, volumetric swell rates per percentage water sorption initially decreased with soaking time, and then increased slightly before leveling off. The initial soaking in water caused immediate swell of the fibers and/or flour particles at the surface layer. Swell rates per percentage water sorption decreased thereafter and leveled after about 2 weeks in water. The swell rates slowly increased again after 3 weeks, and afterward leveled off. This may be due to swelling stress resulting from the swell of interior fibers and flour particles near holes or gaps in the composites. The final volumetric swell rates per percentage water sorption were less than 1% for all the fiber/flour plastic composites investigated in this study. Some water drawn by the composites may have filled the void spaces inside the composites without penetrating and swelling the fibers or flour particles. In addition, the swell rates per percentage water sorption decreased as the fiber content in the composites increased. This indicates that as the ratio of PMS-treated fiber to PMS-treated flour increased, more water stayed in void spaces than penetrated the fibers. Less swell of the composites was the result.

CONCLUSIONS

The morphology of PMS-treated pulp fiber and flour, the chemical linkage between PMS and cellulosic fiber and flour, and the water sorption and volumetric swell of PMS-treated fiber/flour plastic composites were investigated. Micro-scale and nano-scale

PMS particles were found on the surfaces of bleached and brown Kraft pulp fiber and wood flour. FTIR analysis confirmed the existence of PMS on cellulosic fiber, and the covalent bonding of PMS to cellulosic fiber and flour. Milling with a Wiley mill caused little damage to the smaller PMS particles grown on cellulosic fiber. Therefore, PMS-treated pulp fiber can be safely milled without affecting the nano-scale PMS particles on cellulosic fiber.

PMS-treated pulp fiber and PMS-treated flour were more compatible with PE plastic than untreated pulp fiber and untreated flour. As the fiber to flour ratio of the composites increased, compatibility between plastic and reinforcing lignocellulosic materials (fiber and flour) increased. The increased compatibility of all phases contributed to the reduction of water sorption and thus to the increased dimensional stability of PMS-treated fiber/flour plastic composites relative to untreated virgin fiber/flour plastic composites.

All fiber/flour plastic composites in this study displayed a two-phase water sorption and volumetric swell profile after long-term soaking. Composites containing only PMS-treated fiber took more time to be saturated with water, absorbed less water, and swelled less than composites reinforced with untreated fiber/flour or composites reinforced with at least 20% PMS-treated flour. For the same fiber/flour loadings, lower swell and sorption rates were observed for PMS-treated fiber/flour plastic composites than for untreated fiber/flour plastic composites. Water sorption and volumetric swell decreased with an increase in fiber to flour ratio for both treated and untreated fibers. Volumetric swelling rates per percent water sorption initially decreased with soaking time and eventually stabilized to less than 1% for all samples produced for this study.

ACKNOWLEDGMENTS

The authors thank Dr. Cran Lucas, Department of Biological Sciences, Louisiana State University in Shreveport, LA and Dr. Todd Shupe, School of Renewable Natural Resources, Louisiana State University, Baton Rouge, LA for their support to this research. They also thank Mr. Xinan Zhang, School of Renewable Natural Resources, Louisiana State University, Baton Rouge, LA, Dr. Yao Chen, USDA Forest Service, Forest Products Laboratory, Madison, WI, and Mr. Neal Hickman, Calhoun Research Station, Louisiana State University Agricultural Center, Calhoun, LA for their assistance in this study. This research was funded by USDA Forest Service, Forest Products Laboratory (GR NO 11-JV-1111124-130).

REFERENCES

- Zisman, W. A. *Ind. Eng. Chem. Prod. Res. Dev.* **1969**, *8*, 98.
- Clemons, C. M.; Sabo, R. C.; Kaland, M. L.; Hirth, K. C. *J. Appl. Polym. Sci.* **2011**, *119*, 1398.
- Gwon, J. G.; Lee, S. Y.; Chun, S. J.; Doh, G. H.; Kim, J. H. *Compos. A* **2010**, *41*, 1491.
- Bengtsson, M.; Oksman, K. *Compos. Sci. Technol.* **2006**, *66*, 2177.
- Valadez-González, A.; Cervantes-Uc, J. M.; Olayo, R.; Herrera-Franco, P. J. *Compos. B* **1998**, *30*, 321.

6. Geng, Y.; Laborie, M. P. G. *Polym. Compos.* **2010**, *31*, 897.
7. Huda, M. S.; Drzal, L. T.; Mohanty, A. K.; Misra, M. *Compos. Sci. Technol.* **2008**, *68*, 424.
8. Pickering, K. L.; Abdalla, A. *Compos. A* **2003**, *34*, 915.
9. Matuana, L. M.; Balatinecz, J. J.; Park, C. B.; Sodhi, R. N. S. *Wood Sci. Technol.* **1999**, *33*, 259.
10. Mohanty, A. K.; Misra, M.; Drzal, L. T. *Compos. Interface* **2001**, *8*, 313.
11. Bledzki, A. K.; Faruk, O. *Appl. Compos. Mater.* **2003**, *10*, 365.
12. Rowell, R. M.; Lange, S. E.; Jacobson, R. E. *Mol. Cryst. Liq. Cryst.* **2000**, *353*, 85.
13. Faruk, O.; Matuana, L. M. *Compos. Sci. Technol.* **2008**, *68*, 2073.
14. Kazayawoko, M.; Balatinecz, J. J.; Matuana, L. M. *J. Mater. Sci.* **1999**, *34*, 6189.
15. Cui, Y.; Lee, S.; Noruziaan, B.; Cheung, M.; Tao, J. *Compos. A* **2008**, *39*, 655.
16. Gu, R.; Kokta, B. V.; Michalkova, D.; Dimzoski, B.; Fortelny, I.; Slouf, M.; Krulis, Z. *Reinf. Plast. Compos.* **2010**, *29*, 3566.
17. Winandy, J. E.; Stark, N. M.; Horn, E. In Proceedings of the 7th Global WPC and Natural Fiber Composites Congress and Exhibition, Kassel, Germany, **2008**.
18. Woodhams, R. T.; Thomas, G.; Rodgers, D. K. *Polym. Eng. Sci.* **1984**, *24*, 1166.
19. Migneault, S.; Koubaa, A.; Erchiqui, F.; Chaala, A.; Englund, K.; Wolcott, M. P. *Compos. A* **2009**, *40*, 80.
20. Li, S.; Zhang, S.; Wang, X. *Langmuir* **2008**, *24*, 5585.
21. ASTM. American Society for Testing Materials (ASTM) D 570-98, Annual Book of ASTM Standards 08.01, Plastics (1); **2006**, ASTM: West Conshohocken, PA.
22. Tshabalala, M. A.; Kinshott, P.; VanLandingham, M. R.; Plackett, D. *J. Appl. Polym. Sci.* **2003**, *88*, 2828.
23. Gwon, J. G.; Lee, S. Y.; Doh, G. H.; Kim, J. H. *J. Appl. Polym. Sci.* **2010**, *116*, 3212.
24. Bogart, K. H. A.; Ramirez, S. K.; Gonzales, L. A.; Bogart, G. R.; Fisher, E. R. *J. Vac. Sci. Technol. A* **1998**, *16*, 3175.
25. Homma, H.; Kuroyagi, T.; Izumi, K. *IEEE Trans. Dielect. Electr. Insul.* **1999**, *6*, 370.
26. Hacker, C. A.; Anderson, K. A.; Richter, L. J.; Richter, C. A. *Langmuir* **2005**, *21*, 882.
27. Tzeng, D.; Fong, R. H.; Soysa, H. S. D.; Weber, W. P. *J. Organomet. Chem.* **1981**, *219*, 153.
28. Matuana, L. M.; Jin, S.; Stark, N. M. *Polym. Degrad. Stab.* **2011**, *96*, 97.

Potassium Methyl Siliconate-Treated Pulp Fibers and Their Effects on Wood Plastic Composites: Water Sorption and Dimensional Stability, C. Piao, Z. Cai, N.M. Stark, C.J. Monlezun, *Journal of Applied Polymer Science*, 129(1): 193-201, 2013.