Eur. J. Wood Prod. (2014) 72:165–176
DOI 10.1007/s00107-013-0736-x

ORIGINALS ORIGINALARBEITEN

Dimensional stability of wood–plastic composites reinforced with potassium methyl siliconate modified fiber and sawdust made from beetle-killed trees

Cheng Piao · Zhiyong Cai · Nicole M. Stark · Charles J. Monlezun

Received: 12 October 2012 / Published online: 29 November 2013

Abstract Wood from two varieties of beetle-killed trees was used to fabricate wood–plastic composites. Loblolly pine and lodgepole pine beetle-killed trees were defibrated mechanically and thermomechanically, respectively, into fiber. Fiber and sawdust produced from the trees were modified with potassium methyl siliconate (PMS) and injection-molded into fiber/sawdust reinforced plastic composites. Modification of fiber and sawdust with PMS improved the compatibility between lignocellulosic materials and ethylene plastic in the composites, resulting in decreased water sorption, increased dimensional stability, and increased tolerance to morphological variations in the fiber and sawdust. Fiber-to-sawdust ratio and size of sawdust particles affected the time required for saturation with water, as well as dimensional stability.

Dimensionsstabilität von Holz-Kunststoff-Verbundwerkstoffen aus mit Kaliummethylsiliconat modifizierten Fasern und Sägespänen von durch Käferbefall abgetöteten Bäumen

Zusammenfassung Holz aus zwei verschiedenen durch Käferbefall abgetöteten Baumbeständen wurde zur Herstellung von Holz-Kunststoff-Verbundwerkstoffen verwendet. Durch Käferbefall abgetötete Weihrauchkiefer- und Küstenkieferbäume wurden mechanisch bzw. thermomechanisch zerfasert. Die so produzierten Fasern und Sägespäne wurden mit Kaliummethylsiliconat (PMS) behandelt und daraus wurden im Spritzgussverfahren Kunststoff-Verbundwerkstoffe hergestellt. Eine Behandlung der Fasern bzw. Sägespäne mit PMS verbesserte die Kompatibilität zwischen Lignocellulose und dem Ethylenkunststoff im Verbundwerkstoff, was eine geringere Wasseraufnahme, verbesserte Dimensionsstabilität sowie eine höhere Toleranz hinsichtlich morphologischer Variationen in den Fasern bzw. Sägespänen bewirkte. Das Faser-Sägespäne-Verhältnis und die Größe der Sägespäne hatten einen Einfluss auf die Wassersättigungsdauer sowie die Dimensionsstabilität.

C. Piao (✉)
Calhoun Research Station, Louisiana State University Agricultural Center, Calhoun, LA 71225, USA
e-mail: cpiao@agcenter.lsu.edu

Z. Cai (✉) · N. M. Stark
Engineered Composites Science Group, USDA Forest Service, Forest Products Laboratory, Madison, WI 53726, USA
e-mail: zcai@fs.fed.us

C. J. Monlezun
Department of Experimental Statistics, Louisiana State University, Baton Rouge, LA 70803, USA

1 Introduction

Each year from the southeast region to the northwest region of the United States, bark beetles (i.e. mountain pine beetles and loblolly pine beetles) kill millions of acres of pine trees in commercial and federal timberland. Periodic pine beetle outbreaks in these regions often cause catastrophic levels of mortality, creating large areas of standing dead and dying pine timber. Standing dry timber increases the risk of severe fires and poses a safety threat to the forest-urban interface. To stop the spread of forest pests such as bark beetles, several methods have been recommended, including chemical control, pile-and-burn, cut-and-leave, and salvage removal (Woodson 1983). Of these options, utilization of beetle-killed trees is currently the most economical because salvage removal not only helps control the spread of tree-killer beetles, but also provides a good management practice for increasing profits (Billings 1980).

Substantial amounts of water are lost almost immediately after a tree dies, although the amount of drying depends on both length of time since death and environmental conditions. Significant strength reduction occurs to the wood in beetle-attacked trees after the dead trees stand over 6 months in the forest (Goehring 1980). Reduction in strength makes any wood unsuitable for structural products such as dimensional lumber. Moreover, the wood in standing beetle-attacked trees often becomes heavily stained by blue-stain fungi carried by the pine beetle (Woodson 1983). The blue color makes the wood unsuitable for any application in which natural wood color is important. Beetle-attacked wood, however, is a good material for the production of pulp and wood-based composites, such as particleboard and medium density fiberboard (Woodson 1983). Studies have shown that pulp yield drops very little from beetle-killed pines dead up to 12 months in east Texas and up to 24 months in Virginia (Westbrook et al. 1981). Recently, beetle-killed tree wood has been used to make wood–plastic composites (Yadama et al. 2009, Chang et al. 2010) and ethanol biofuel (Zhu et al. 2011). The mechanical properties of wood–plastic composite reinforced with flour made from highly deteriorated beetle-killed wood have been shown to be comparable to the mechanical properties of wood–plastic composite reinforced with virgin wood flour (Yadama et al. 2009).

Wood flour has been the traditional organic filler in the fabrication of plastic composites (Woodhams et al. 1984). To increase mechanical performance, high aspect-ratio wood fibers (pulp fiber and medium density fiberboard fiber) have also been investigated as reinforcing materials (Woodhams et al. 1984; Kazayawoko et al. 1999; Mohanty et al. 2001; Bledzki and Faruk 2003; Winandy et al. 2008; Migneault et al. 2009; Gu et al. 2010). Compared to wood flour plastic composites, fiber reinforced plastic composites demonstrate higher flexural strength (Bledzki and Faruk 2003; Migneault et al. 2009) and lower water sorption rates (Bledzki and Faruk 2003); however, increasing fiber aspect ratios may result in greater water sorption and volumetric swell (Migneault et al. 2009).

In this report, fibers and sawdust made from beetle-killed loblolly pine trees and beetle-killed lodgepole pine trees were used to reinforce plastic composites. Prior to compounding with thermoplastic, fibers and sawdust were modified with potassium methyl siliconate (PMS) nanoparticles. The morphology and topography of PMS modified fibers and sawdust particles, as well as water sorption and dimensional stability of PMS modified fiber/sawdust reinforced plastic composites, are characterized.

2 Experimental procedure

PMS having solid content of ~40 % was obtained in an aqueous solution from ReUse Concrete Sealing Specialists, Overland Park, KS, and was used as received. The chemical structure of PMS is shown in Fig. 1.

Beetle-killed loblolly pine (*Pinus taeda*) trees were collected from Kisatchie National Forest in Winfield, Louisiana. Beetle-killed lodgepole pine (*Pinus contorta*) trees were collected from the Chequamegon-Nicolet National Forest in Rhinelander, Wisconsin. All trees used in this study stood over 2 years in their respective forests since death. Each sample tree was felled, debarked, and cut into slabs, which were then turned into wood chips. Sawdust produced during processing was collected for each species and used in the fabrication of wood–plastic composites. Loblolly pine wood chips were boiled in water at ambient pressure for 3 h and then mechanically defibrated in a Sprout-Waldron Model 105-A disc refiner with a 0.13 mm plate clearance. Lodgepole pine wood chips were both cooked and then defibrated thermomechanically in a Sprout-Bauer Model 1210P refiner with a refiner gap setting of 0.13 mm. After refining, both loblolly and lodgepole pine fibers were oven-dried and used in composite preparations.

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

A 2,200 ml aqueous solution containing 0.5 M PMS was prepared in a 3,000 ml glass beaker. Approximately 60 g (dry-equivalent) of fiber or sawdust were suspended in the solution. The system was vigorously stirred at room temperature while carbon dioxide was bubbled through the solution. When the pH of the solution was between 8.5 and 10.5, carbon dioxide bubbling was stopped and the system was stirred for an additional 4 to 6 h at room temperature. PMS treated particles (either fiber or sawdust) were then filtered from the solution and washed five times with deionized water to remove un-reacted chemicals. Fibers and fiber bundles were oven-dried at 100 °C for 6 h. Sawdust was oven-dried at 100 °C for 24 h. Dry fiber bundles were shredded into individual fibers using a Wiley mill with a 1.0 mm (18 mesh) screen. The fibers obtained were further screened using a 0.18 mm (80 mesh) sieve to remove short fibers and PMS nanoparticles that fell from

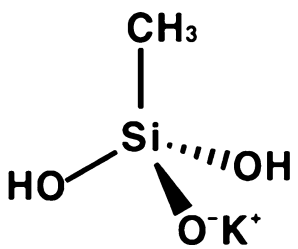

Fig. 1 Chemical structure of potassium methyl siliconate (PMS)
Abb. 1 Chemische Struktur von Kaliummethylsiliconat (PMS)

the fibers during milling. The fibers on the screen were stored and subsequently used for the fabrication of plastic composites.

The crystal structure and morphology of the prepared PMS nano film on the surfaces of fibers and sawdust particles were examined using a Fourier transform infrared spectroscope (FTIR) (VARIAN FTS 800) and a scanning electron microscope (SEM) (Hitachi TM-1000). The SEM images obtained from the analyses were also used to estimate the sizes of sawdust and milled fiber particles of the two species (lodgepole and loblolly) using image analysis software.

A 15 cc twin screw microcompounder (DSM Explore, Netherlands) was used to mix the components (polyethylene, sawdust, and/or fiber) of each plastic composite sample at 50 rpm and 190 °C in a batch process. Predetermined amounts of high-density polyethylene, fiber and/or sawdust were loaded in the chamber of the microcompounder. The compounding cycle for each sample took from 7 to 9 min, depending upon the amount of fiber in the sample. The mixed compound exiting the twin screw microcompounder was collected and immediately transferred to an injection molder 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. Nine samples were fabricated for each of twelve formulations of polyethylene, fiber and/or sawdust. After the nine duplicate samples of a particular formulation were fabricated, the twin screws were stopped and the compounder chamber was opened and cleaned for the fabrication of samples for the next formulation. The twelve formulations appear in Table 1, in the time order of sample preparation. By weight, all fiber/sawdust plastic composite samples consisted of 50 % polyethylene and 50 % fiber/sawdust. Two of the nine samples of each formulation were used in this study to evaluate dimensional stability.

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

The water sorption test of fiber/sawdust reinforced plastic composites was conducted according to American Society for Testing and Materials (ASTM) standard D 570-98 (ASTM 2006). Prior to water soaking, each sample was oven-dried at 50 °C for 24 h. After drying, each sample was weighed; this was the initial (dry-equivalent) weight of the sample. Three crosses were marked on one of the two 12.7 mm × 133 mm surfaces of each sample before it was soaked in water. The average of the thicknesses at these three locations was used as the initial thickness of the sample (i.e. the thickness prior to water soaking). Samples were then submerged in a container of distilled water maintained at 23 °C. At each predefined time interval (6, 12, 24, 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, 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.

Table 1 Weight compositions of fiber/sawdust plastic composites
Tab. 1 Gewichtsanteile der Kunststoff-Verbundwerkstoffe mit Fasern/Sägespänen

Composition#	Species	Treatment	Fiber (%)	Sawdust (%)	Plastic[a] (%)
1	Loblolly	PMS	0	50	50
2	Loblolly	PMS	15	35	50
3	Loblolly	PMS	30	20	50
4	Loblolly	Control	0	50	50
5	Loblolly	Control	15	35	50
6	Loblolly	Control	30	20	50
7	Lodgepole	PMS	0	50	50
8	Lodgepole	PMS	15	35	50
9	Lodgepole	PMS	30	20	50
10	Lodgepole	Control	0	50	50
11	Lodgepole	Control	15	35	50
12	Lodgepole	Control	30	20	50

[a] High-density polyethylene

3 Results and discussion

3.1 Morphology and topography of PMS modified fibers and sawdust

Figure 2 displays the morphologies of beetle-killed loblolly pine and beetle-killed lodgepole pine fibers that were defibrated mechanically and thermomechanically, respectively, and modified with PMS. The two defibration processes produced fibers of substantially different morphologies. As seen in Fig. 2a, b, loblolly pine wood chips were poorly defibrated by the mechanical process. Fiber bundles (consisting of two or more fibers) and fiber cell wall fractions accounted for a considerable portion of loblolly pine fiber after defibration. The cell wall fractions (Fig. 2b) were fractions of the cell walls of fibers that were broken during the defibration process. Diameters and lengths of loblolly pine cell wall fractions/fibers/fiber bundles varied from 1 to 300 μm and 10 μm to 1 mm, respectively. On the other hand, lodgepole pine wood chips were properly defibrated into fiber by the thermomechanical process. A few fiber bundles were present in lodgepole pine fibers, but, overall, lodgepole pine fibers came through

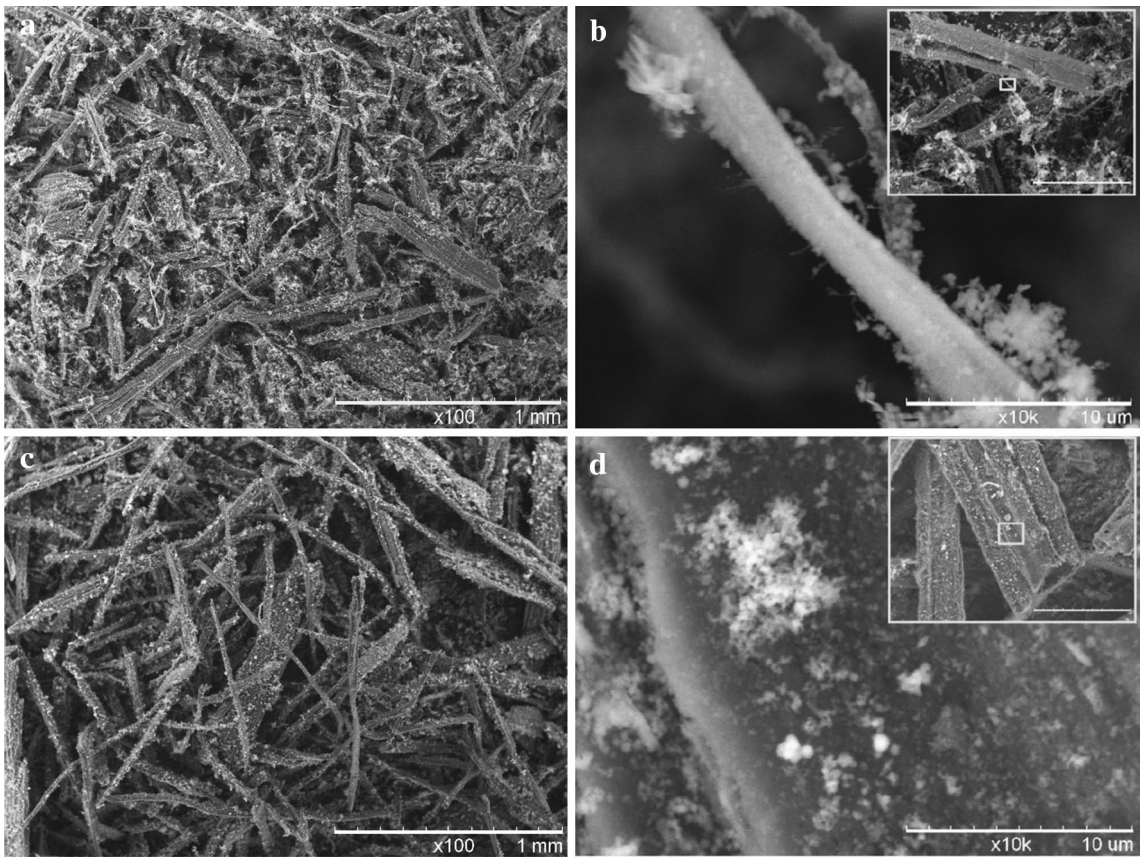

Fig. 2 SEM images of PMS modified wood fibers made from beetle-killed trees. **a** Loblolly pine fiber is a mixture of fibers, fiber bundles, and fiber cell wall fractions. **b** A cell wall fraction of a loblolly pine fiber (enlarged view). Micro and nano-scale PMS particles are identifiable on the surface of the cell wall fraction. **c** Lodgepole pine fiber consists of fibers and fiber bundles. **d** An enlarged view of the surface of a fiber in a lodgepole pine particle. The scale for the inset *bars* in (**b**) and (**d**) are 200 and 100 μm, respectively
Abb. 2 REM-Aufnahmen von mit PMS behandelten Holzfasern aus durch Käferbefall abgetöteten Bäumen. **a** Die Weihrauchkieferfaser ist eine Mischung aus Fasern, Faserbündeln und Faserzellwandfraktionen. **b** Zellwandfraktion einer Weihrauchkiefernfaser (vergrößerte Aufnahme). PMS-Partikel im Mikro- und Nanomaßstab sind auf der Oberfläche der Zellwandfraktion erkennbar. **c** Küstenkieferfaser bestehend aus Fasern und Faserbündel. **d** Vergrößerte Aufnahme einer Faseroberfläche in einem Küstenkiefernpartikel. Der Maßstab der Ausschnitte in (**b**) und (**d**) ist 200 bzw. 100 μm

Table 2 Wood particle size
Tab. 2 Abmessungen der Holzpartikel

Species/type	Diameter (mm)		Length (mm)	
	Average	Standard error	Average	Standard error
Loblolly pine sawdust	0.30	0.020	0.66	0.044
Lodgepole pine sawdust	0.29	0.025	1.07	0.088
Loblolly pine fiber (bundles)	0.001–0.3	–	0.01–1.0	–
Lodgepole pine fiber (bundles)	0.03–0.25	–	0.2–2.5	–

the defibration process in good condition (Fig. 2c). Diameters and lengths of lodgepole pine fibers/fiber bundles ranged from 30 to 250 μm and from 0.2 to 2.5 mm, respectively. This information, together with the corresponding summaries for the loblolly pine and lodgepole sawdust particles of this study, appears in Table 2.

After modification with PMS, oven-dried loblolly pine and lodgepole pine fiber mats were broken down into fibers using a Wiley mill. As shown in Fig. 2b, d, micro- and nano-scale PMS particles, ranging in size from less than 100 to 400 nm, covered the surfaces of fiber bundles, fibers, and fiber fractions. In a previous report (Piao et al.

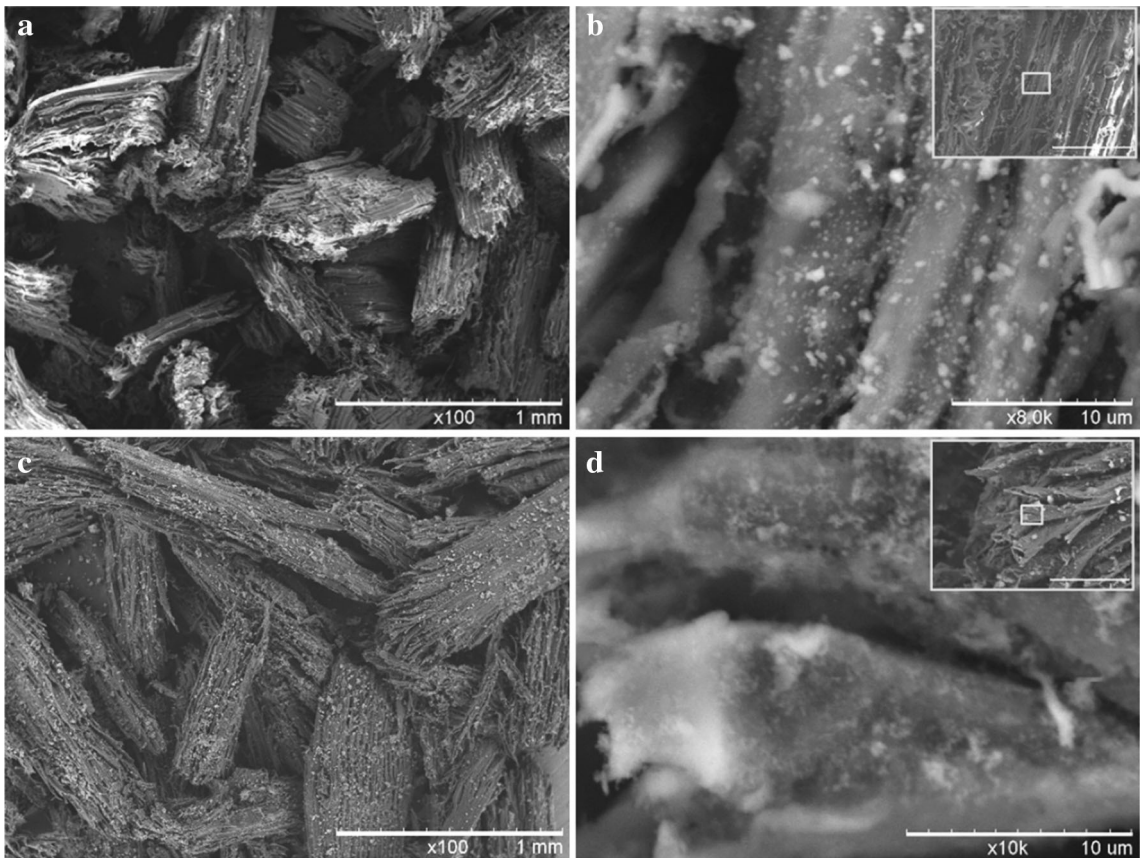

Fig. 3 SEM images of PMS modified sawdust made from beetle-killed trees. **a** Loblolly pine sawdust particles. **b** An enlarged view of the surface of a loblolly pine sawdust particle. **c** Lodgepole pine sawdust particles. **d** An enlarged view of a lodgepole pine sawdust particle. The scale for both inset bars in (**b**) and (**d**) is 100 μm

Abb. 3 REM-Aufnahmen von mit PMS behandelten Sägespänen aus durch Käferbefall abgetöteten Bäumen. **a** Weihrauchkieferpartikel. **b** Vergrößerte Aufnahme der Oberfläche eines Weihrauchkieferpartikels. **c** Küstenkieferpartikel. **d** Vergrößerte Aufnahme eines Küstenkieferpartikels. Der Maßstab beider Ausschnitte in (**b**) und (**d**) ist 100 μm

2012), PMS modified pulp fiber mats were broken down into individual fibers without damaging the PMS particles on the pulp fibers. This study further confirms that PMS modified fibers can be safely processed using a Wiley mill.

Figure 3 displays the morphologies of loblolly pine sawdust and lodgepole pine sawdust that were treated with PMS. As seen in Fig. 3a, c, and Table 2, loblolly pine sawdust particles were shorter than lodgepole pine sawdust particles. The ends of some lodgepole pine particles were defibrated during cutting and became furry (see the inset in Fig. 3d). Micro- and nano-scale PMS particle films were also observed on the surfaces of sawdust particles of both species and on the surfaces of fibers at the ends of lodgepole pine sawdust particles (Fig. 3b, d).

3.2 Surface characterization of nano fiber/sawdust plastic composites

In a previous study naked fibers were observed at the surface of composites having poor compatibility between the natural fiber and the plastic (Piao et al. 2012). When natural fibers were compatible with the plastic, however, most of the fibers were contained in thermoplastic and usually not identifiable using SEM. Therefore, using SEM to evaluate surface morphology of wood–plastic composites with similar wood content and manufacturing parameters can be the first step in the evaluation of the compatibility of phases in the wood–plastic composite.

Figure 4 displays SEM images of the surfaces of four plastic composite samples reinforced with 30 % fiber and 20 % sawdust. Fiber and sawdust came from loblolly pine trees in Fig. 4a, b, and from lodgepole pine trees in Fig. 4c, d. Fiber and sawdust were modified with PMS in Fig. 4a, c, and were untreated in Fig. 4b, d. Fibers were observed on the composite surfaces, as indicated by arrows in Fig. 4a, b, d. Fewer fibers were observed on composite surfaces reinforced with PMS modified fiber/sawdust than on those reinforced with untreated fiber/sawdust. Of all the composite samples fabricated for this study, those reinforced with PMS modified lodgepole pine fiber/sawdust exhibited the fewest surface fibers.

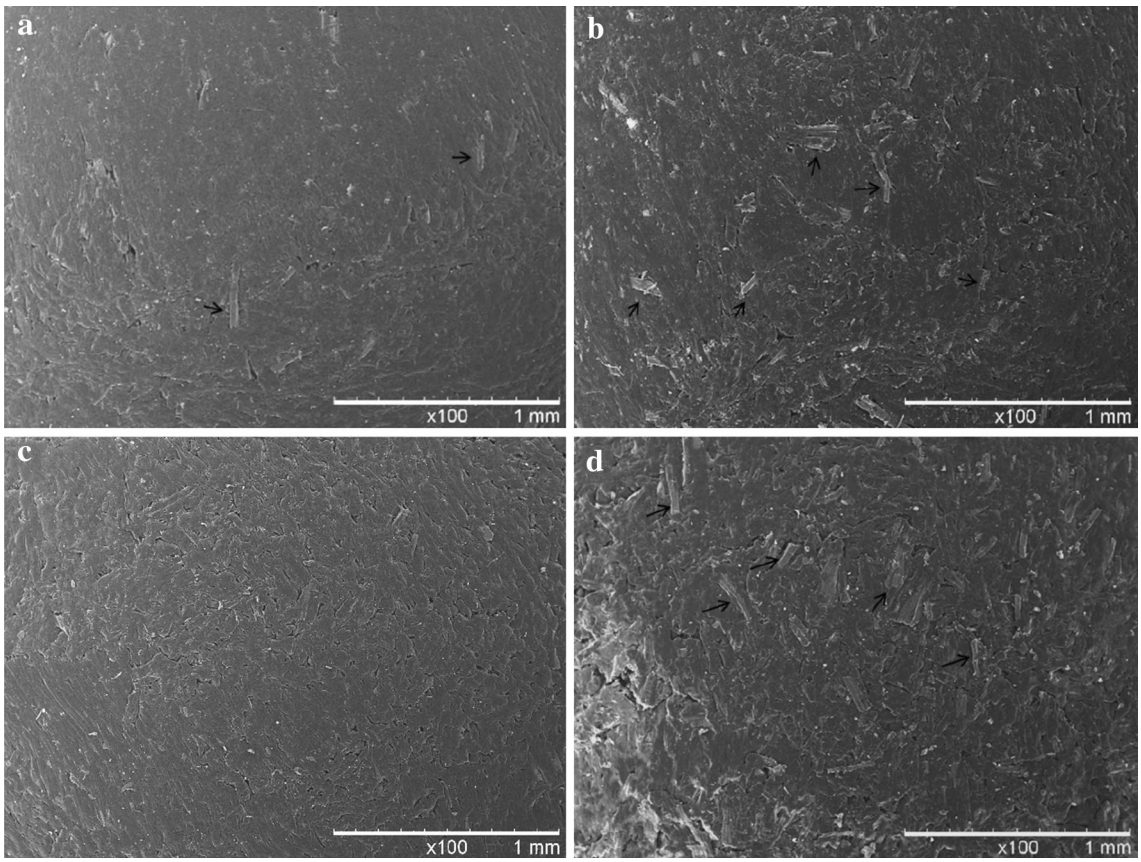

Fig. 4 SEM images of the surface of plastic composites reinforced with 30 % fiber and 20 % sawdust. **a** PMS modified beetle-killed loblolly pine fiber and PMS modified beetle-killed loblolly pine sawdust. **b** Untreated beetle-killed loblolly pine fiber and untreated beetle-killed loblolly pine sawdust. **c** PMS modified beetle-killed lodgepole pine fiber and PMS modified beetle-killed lodgepole pine sawdust. **d** Untreated beetle-killed lodgepole pine fiber and untreated beetle-killed lodgepole pine sawdust

Abb. 4 REM-Aufnahmen der Oberfläche von Kunststoff-Verbundwerkstoffen, die mit 30 % Fasern und 20 % Sägespänen aus durch Käferbefall abgetöteten Bäumen hergestellt wurden. **a** Mit PMS behandelte Weihrauchkieferfasern und Weihrauchkieferspäne. **b** unbehandelte Weihrauchkieferfasern und unbehandelte Weihrauchkieferspäne. **c** mit PMS behandelte Küstenkieferfasern und Küstenkieferspäne. **d** unbehandelte Küstenkieferfasern und Küstenkieferspäne

Figure 5 shows the FTIR absorbance spectra of three PMS modified lodgepole pine fiber and/or PMS modified lodgepole pine sawdust plastic composite samples, one for each of three fiber-to-sawdust ratios. Also shown in Fig. 5 are the spectra of untreated pure lodgepole pine fiber and pure PMS particles. The absorbance bands at 1,272, 1,030, and 1,116 cm^{-1} correspond to the stretching vibrations of $Si–CH_3$ bonds, the stretching vibrations of Si–O–Si bonds, and the asymmetric vibrations of the Si–O–C bonds formed between PMS and cellulosic fiber and between PMS and sawdust particles, respectively (Tzeng et al. 1981; Bogart et al. 1998; Tshabalala et al. 2003; Hacker et al. 2005). It can be seen in Fig. 5 that as the amount of PMS modified fiber in the samples increased, the absorbance intensity of these bonds increased. Therefore, as the amount of PMS modified fiber increased, the concentration of $Si–CH_3$, Si–O–Si, and in particular Si–O–C bonds increased, indicating that more chemical interaction occurred between PMS and fiber in fiber/sawdust composites. The methyl groups of the PMS polymer on the surfaces of fibers and sawdust particles orient toward the plastic polymer at the fiber/sawdust and plastic interface and are associated with polyethylene molecular chains through van der Waals forces. As a result, PMS modified fibers/sawdust were more compatible with polyethylene than untreated fibers/sawdust. In addition, due to the larger surface area of fibers compared with sawdust, increasing the fiber/sawdust ratio resulted in additional compatibility.

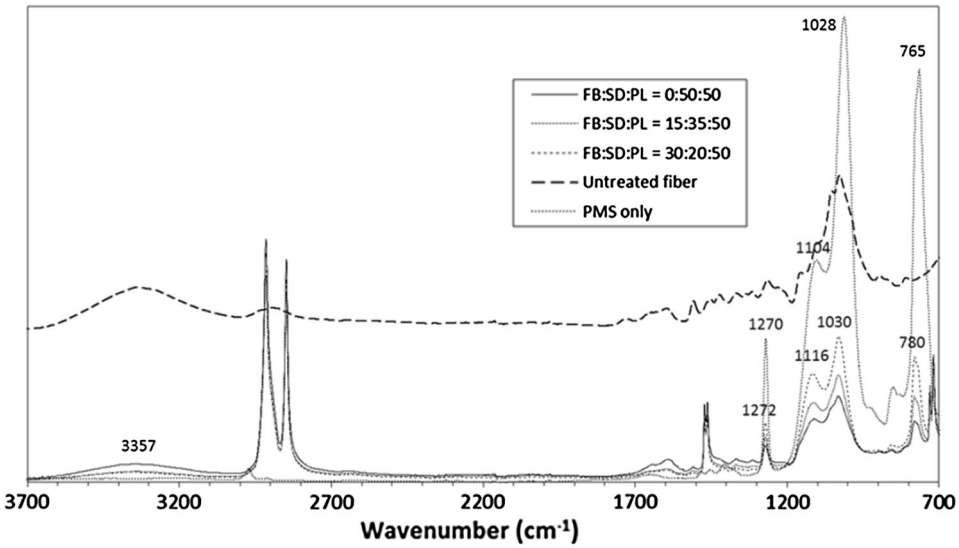

Fig. 5 FTIR spectra of three plastic composite samples reinforced with PMS modified sawdust and/or PMS modified fiber made from beetled-killed lodgepole pine trees, FTIR spectra of pure lodgepole pine fiber, and FTIR spectra of pure PMS. The unit of measurement for numbers in the legend is percentage (%) by weight: *FB* fiber, *SD* sawdust, and *PL* plastic (polyethylene)

Abb. 5 FTIR Spektren dreier Prüfkörper, die mit PMS behandelten Sägespänen und/oder PMS behandelten Fasern aus durch Käferbefall abgetöteten Küstenkiefern hergestellt wurden, FTIR Spektrum einer unbehandelten Küstenkieferfaser und FTIR Spektrum von reinem Kaliummethylsiliconat (PMS). Die Zahlen in der Legende sind in Masseprozent (%) angegeben: *FB* Faser, *SD* Sägespäne und *PL* Kunststoff (Polyethylen)

3.3 Water sorption and volumetric swell

Figure 6 displays water sorption and volumetric swell as a function of soaking time for plastic composite samples reinforced with loblolly pine fiber and/or sawdust. Figure 7 shows water sorption and volumetric swell as a function of soaking time for plastic composite samples reinforced with lodgepole pine fiber and/or sawdust. Each water sorption or volumetric swell curve shown in Figs. 6 and 7 consists of two phases, namely a fast growing phase and a saturating phase. Transition times between the two phases range from about 800 h (33 days) to 2,000 h (83 days), depending upon PMS treatment, fiber/sawdust ratio, and presence of fibers/sawdust at the composite surface.

Transition times for all composite samples reinforced with PMS treated loblolly pine fiber/sawdust are approximately the same for both water sorption and volumetric swell, regardless of fiber/sawdust composition (Fig. 6a, b). These samples absorbed water and swelled at the same rate during the initial soaking periods, and transitioned from the fast growing phase to the saturating phase at nearly the same time. Transition times for untreated loblolly pine fiber/sawdust composites decreased, however, as the fiber/sawdust ratio increased (Fig. 6c, d). Moreover, for any fixed value of soaking time, untreated loblolly pine fiber/sawdust composites absorbed more water and swelled more as the fiber/sawdust ratio increased, while for any fixed value of soaking time past the initial fast growing phase, PMS treated loblolly pine fiber/sawdust composites absorbed less water and swelled less as the fiber/sawdust ratio increased.

Composites reinforced with lodgepole pine fiber/sawdust behaved differently than those reinforced with loblolly pine fiber/sawdust. The transition times of PMS treated lodgepole pine fiber/sawdust plastic composites increased with an increase in fiber/sawdust ratio, while transition times of untreated lodgepole pine fiber/sawdust plastic composites were nearly the same, regardless of fiber/sawdust ratio. Furthermore, at any fixed value of soaking time during the saturating phase, untreated lodgepole pine fiber/sawdust plastic composites absorbed less water and swelled less as the fiber/sawdust ratio increased (Fig. 7c, d).

The water sorption and volumetric swell behaviors of healthy loblolly pine pulp fiber/flour plastic composites reported in a previous study (Piao et al. 2012) were similar to the water sorption and volumetric swell of plastic composites reinforced with beetle-killed lodgepole pine fiber/sawdust. In both cases PMS treatment resulted in increased transition times, less absorbed water, and less swelling as fiber content increased. Untreated fiber/sawdust and untreated fiber/flour plastic composites exhibited similar transition times regardless of fiber/sawdust or fiber/flour ratios, but also absorbed less water and swelled less as fiber content increased.

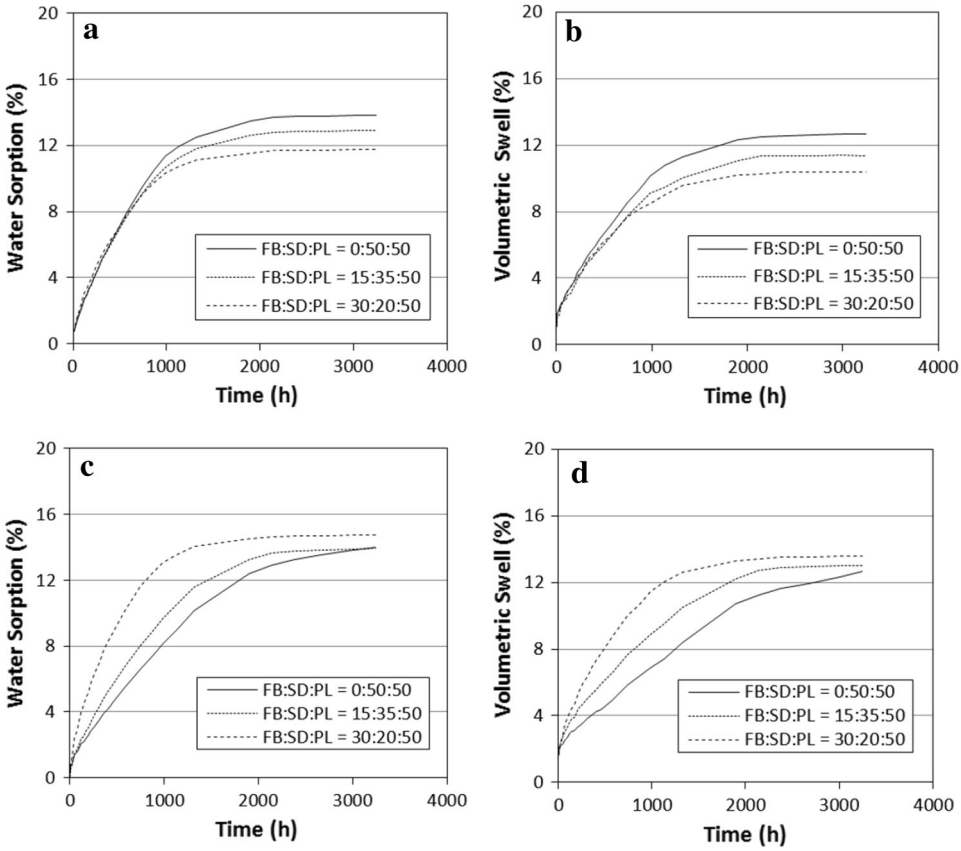

Fig. 6 Water sorption and volumetric swell of plastic composite samples reinforced with fiber and/or sawdust made from beetle-killed loblolly pine trees. **a**, **b** Samples reinforced with PMS modified fiber and/or PMS modified sawdust. **c**, **d** Samples reinforced with untreated fiber and/or untreated sawdust. The legend is identical to that of Fig. 5

Abb. 6 Wasseraufnahme und Volumenquellung der Kunststoff-Verbundwerkstoffprüfkörper mit Fasern und/oder Sägespänen aus durch Käferbefall abgetöteten Weihrauchkiefern. **a** und **b** sind Prüfkörper mit PMS behandelten Fasern und/oder Sägespänen. **c** und **d** sind Prüfkörper mit unbehandelten Fasern und/oder Sägespänen. Legende siehe Abb. 5

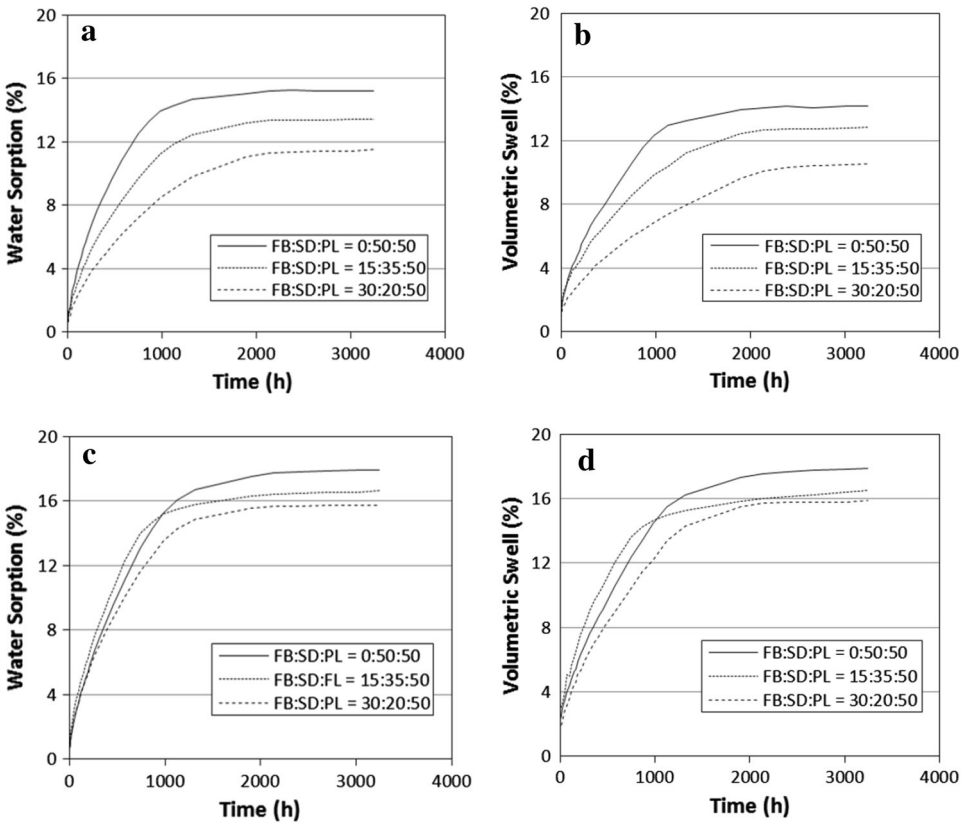

Fig. 7 Water sorption and volumetric swell for plastic composite samples reinforced with fiber and/or sawdust made from beetle-killed lodgepole pine trees. **a**, **b** Samples reinforced with PMS modified fiber and/or PMS modified sawdust. **c**, **d** Samples reinforced with untreated fiber and/or untreated sawdust. The legend is identical to that of Fig. 5

Abb. 7 Wasseraufnahme und Volumenquellung der Kunststoff-Verbundwerkstoffprüfkörper mit Fasern und/oder Sägespäne aus durch Käferbefall abgetöteten Küstenkiefern. **a** und **b** sind Prüfkörper mit PMS behandelten Fasern und/oder Sägespänen. **c** und **d** sind Prüfkörper mit unbehandelten Fasern und/oder Sägespänen. Legende siehe Abb. 5

The behavior of the sorption and swelling curves of untreated beetle-killed loblolly pine fiber/sawdust plastic composites (Fig. 6c, d), therefore, was very different from that of PMS treated beetle-killed loblolly pine fiber/sawdust plastic composites (Fig. 6a, b), healthy loblolly pine pulp fiber/flour plastic composites from a previous study, and beetle-killed lodgepole pine fiber/sawdust plastic composites (Fig. 7a–d). For (any) fixed soaking time, untreated beetle-killed loblolly pine fiber/sawdust plastic composites exhibited an increase in water sorption and swell as fiber content increased. The trend was reversed for those plastic composite samples of this study reinforced with either PMS treated beetle killed loblolly pine particles or beetle-killed lodgepole pine particles, as well as for the plastic composites of the previous study reinforced with healthy loblolly pine particles: for fixed soaking times beyond the initial quick soaking periods, samples absorbed less water and swelled less as fiber content increased.

The unexpected water soaking and swelling characteristics of composites reinforced with untreated beetle-killed loblolly pine particles (Fig. 6c, d) were attributed primarily to the size and morphology of particles made of beetle-killed loblolly pine wood. As shown in Fig. 2, beetle-killed loblolly pine fiber obtained from the mechanical (only) defibration process was different from lodgepole pine fiber obtained from the thermomechanical process. Fiber bundles and fiber fractions, instead of large aspect-ratio fibers, accounted for most of the fiber obtained from the mechanical defibration process (Fig. 2a). As a result, untreated beetle-killed loblolly pine fiber/sawdust composites absorbed more water and swelled more as fiber content increased.

There is no obvious explanation for the decrease in transition times for untreated beetle-killed loblolly pine fiber/sawdust composites as fiber ratio increased (Figs. 6c, d). One possible reason is that short, untreated loblolly pine sawdust particles had better distribution in the plastic matrix, resulting in more fiber/sawdust encapsulation. In addition, loblolly pine wood is denser than lodgepole pine wood. Therefore, there is less volume and less particles of loblolly pine sawdust relative to lodgepole pine sawdust for the same fiber-sawdust ratio. As a result (shorter particles, higher density), fewer gaps occurred at the beetle-killed loblolly pine fiber/sawdust and plastic interface than at the beetle-killed lodgepole pine fiber/sawdust and plastic interface, thereby hindering the penetration of water into the loblolly pine fiber/sawdust composites. Therefore, smaller, denser sawdust particles potentially hindered the penetration of water in the plastic composites.

Figure 8 summarizes the effects of PMS nano modification, species, and fiber/sawdust ratio on water sorption and volumetric swell of beetle-killed fiber/sawdust plastic composites after soaking in water for 3,247 h (135 days). Except for the samples that were reinforced with untreated beetle-killed loblolly pine fibers and untreated loblolly pine sawdust, water sorption and volumetric swell percentage averages decreased as fiber content increased, so that more fiber content resulted in lower water sorption and higher dimensional stability. For each species of pine, the lowest water sorption and volumetric swell percentage averages were observed for those composites consisting of 30 % PMS treated fiber and 20 % PMS treated sawdust.

For each of the two species, water sorption and volumetric swell of PMS treated fiber/sawdust plastic composites were

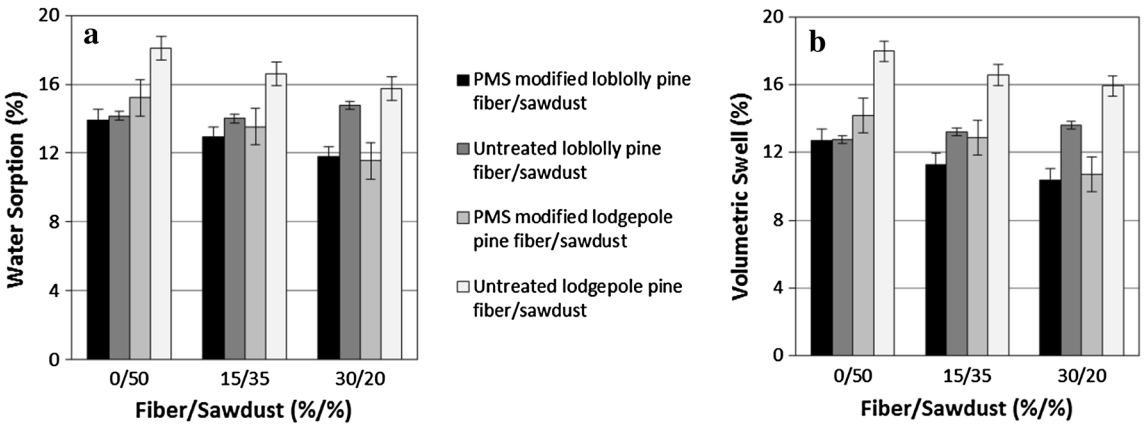

Fig. 8 Volumetric swell and water sorption percentage averages for plastic composite samples reinforced with either beetle-killed loblolly pine fiber and/or beetle-killed loblolly pine sawdust, or beetled-killed lodgepole pine fiber and/or beetle-killed lodgepole pine sawdust. For each of the four categories, both fiber and/or sawdust were modified with PMS, or neither fiber nor sawdust was modified with PMS

Abb. 8 Mittlere prozentuale Volumenquellung und Wasseraufnahme von Kunststoff-Verbundwerkstoffprüfkörpern mit Fasern und/oder Sägespänen aus durch Käferbefall abgetöteten Weihrauchkiefern oder mit Fasern und/oder Sägespänen aus durch Käferbefall abgetöteten Küstenkiefern. In beiden Fällen wurden die Fasern und/oder Sägespäne entweder mit PMS behandelt oder nicht (4 Kategorien)

significantly lower than the water sorption and volumetric swell of untreated fiber/sawdust reinforced plastic composites, respectively, regardless of fiber/sawdust ratio ($p < 0.0001$ for all comparisons). The covalent bonds (via Si–O–C bonds) between PMS and lignocellulosic materials, as well as the intimate contact between PMS and polyethylene chains (via van der Waals forces), reduced the permeation of water into fiber/sawdust–PMS and PMS–plastic interfaces, and, thus, into the cell walls of the fiber and sawdust in the composites. The superior compatibility of PMS modified fibers and PMS modified sawdust with polyethylene plastic contributed to the reduced water sorption and volumetric swell of composites containing PMS modified fiber and/or PMS modified sawdust.

As seen in Fig. 8, for each level of fiber content and each level of PMS modification (i.e. treated with PMS or untreated), composite samples reinforced with beetle-killed loblolly pine particles exhibited better water sorption and volumetric swell rates than samples reinforced with beetle-killed lodgepole pine particles, the lone exception being the 30/20 % fiber/sawdust category, where the water sorption rate for the beetle-killed loblolly pine samples was only slightly larger than that for the lodgepole pine samples. Average water sorption (13.0 %) and average volumetric swell (11.7 %) of composites reinforced with beetle-killed loblolly pine particles were significantly lower than average water sorption (15.0 %) and average volumetric swell (14.4 %) of composites reinforced with beetle-killed lodgepole pine particles, respectively ($p = 0.0032$ and 0.0011, respectively). This superiority was more pronounced for samples containing untreated fiber and/or sawdust than for samples containing PMS modified fiber and/or sawdust. In addition to the effects of wood density, the morphology of the fiber (in particular the morphology of the sawdust in the composites) affected the water sorption and dimensional stability of composite samples (Fig. 3a, c; and also Table 2). As mentioned previously, shorter sawdust particles contributed to the reduced water sorption and volumetric swell of beetle-killed loblolly pine fiber/sawdust plastic composites, especially those made of untreated fiber and untreated sawdust. Practically speaking, a reduction in the length of sawdust particles usually leads to a reduction in mechanical properties such as the bending strength (Stark and Berger 1997). However, the addition of fiber mitigates the degradation in mechanical properties due to the reduction in sawdust particle length. In this regard, shorter sawdust particles can be used as a generic filler material to produce more dimensionally stable and more economically viable fiber/sawdust plastic composites.

It should also be noted that although the morphology of beetle-killed loblolly pine fiber and sawdust was different from the morphology of lodgepole pine fiber and sawdust, respectively, the water sorption and volumetric swell of PMS modified loblolly pine fiber/sawdust plastic composites were not significantly different from the water sorption and volumetric swell of PMS modified beetle-killed lodgepole pine fiber/sawdust plastic composites ($p = 0.0785$ and 0.0556, respectively). Therefore, PMS treatment allowed the plastic composites to have some degree of morphological variation in the reinforcing fibers and sawdust particles without substantially affecting dimensional stability.

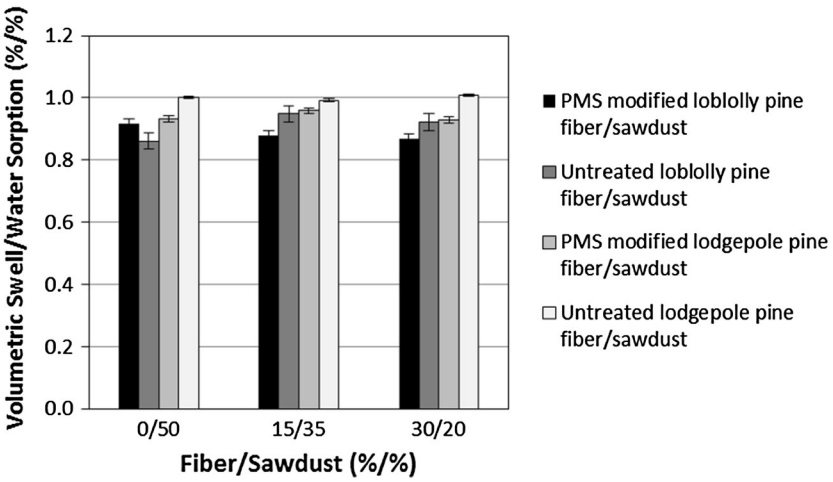

Fig. 9 Volumetric swell per percentage water sorption averages of plastic composite samples reinforced with either beetle killed loblolly pine fiber and/or beetle killed loblolly pine sawdust, or beetle killed lodgepole pine fiber and or beetle killed lodgepole pine sawdust. For each of the four categories, both fiber and/or sawdust were modified with PMS, or neither fiber nor sawdust was modified with PMS

Abb. 9 Mittlere Dickenquellung pro Prozent Wasseraufnahme von Kunststoff-Verbundwerkstoffprüfkörpern mit Fasern und/oder Sägespänen aus durch Käferbefall abgetöteten Weihrauchkiefern oder mit Fasern und/oder Sägespänen aus durch Käferbefall abgetöteten Küstenkiefern. In beiden Fällen wurden die Fasern und/oder Sägespäne entweder mit PMS behandelt oder nicht (4 Kategorien)

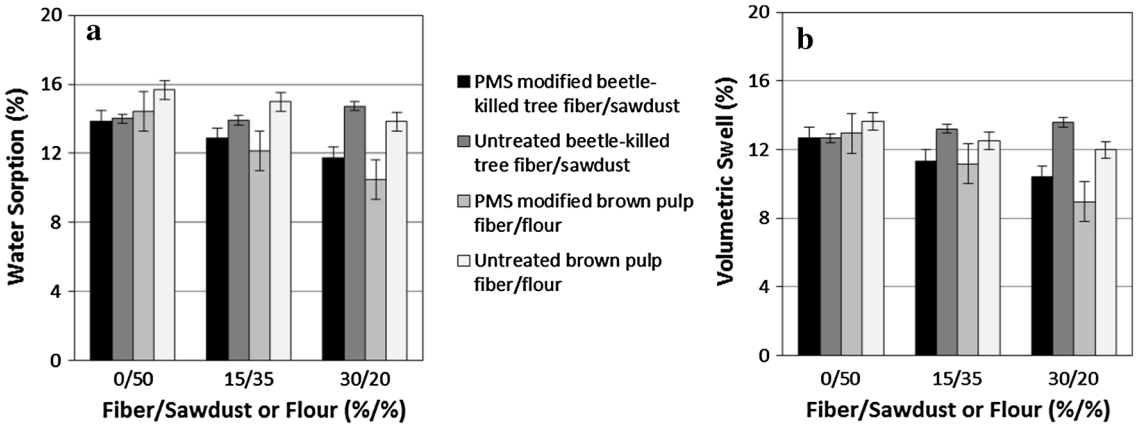

Fig. 10 Volumetric swell and water sorption percentage averages for plastic composite samples reinforced with either wood fiber/sawdust made from beetle killed loblolly pine trees (this study) or wood fiber and/or flour made from healthy loblolly pine trees (Piao et al. 2012). For each of the four categories, all wood particles were modified with PMS, or neither fiber nor sawdust was modified with PMS

Abb. 10 Mittlere prozentuale Volumenquellung und Wasseraufnahme von Kunststoff-Verbundwerkstoffprüfkörpern mit Fasern/Sägespänen aus durch Käferbefall abgetöteten Weihrauchkiefern (diese Studie) oder Holzfasern und/oder Holzmehl aus nicht befallenen Weihrauchkiefern (Piao et al. 2012). In beiden Fällen wurden alle Holzpartikel mit PMS behandelt oder nicht behandelt (4 Kategorien)

For natural fiber reinforced plastic composites, water sorption is always accompanied by volumetric swell. Figure 9 displays volumetric swell per percentage water sorption (or VS/WS) averages for the plastic composite samples fabricated for this study. All wood particles (made of beetle-killed wood) in each sample were modified with PMS, or all particles were untreated. As seen in Fig. 9, VS/WS was smaller for samples containing PMS treated beetle-killed lodgepole pine wood fiber and sawdust than for samples containing untreated beetle-killed lodgepole pine wood fiber and sawdust, regardless of fiber content. Except for those composites containing 50 % sawdust and no fiber, VS/WS was smaller for samples containing PMS treated beetle-killed loblolly pine wood particles than for samples containing untreated beetle-killed loblolly pine wood particles. Figure 9 also shows that VS/VW rates for beetle-killed lodgepole pine samples were higher than VS/VW rates for beetle-killed loblolly pine samples, regardless of fiber content. Except for the untreated lodgepole pine samples consisting of 30 % fiber, which had a VS/VW value slightly larger than 1 percent, all samples had VS/VW values <1 %. It has been reported that the moisture expansion of fiber is about 1 % for each percent increase in fiber moisture (Caulfield 1988). The fiber saturation point (70–80 %) of fiber is much greater than the fiber saturation point of wood (about 30 %). Therefore, some water permeated into the plastic composites did not participate in the swelling of wood particles in the composites.

Figure 10 displays graphically volumetric swell and water sorption percentage averages for some composites prepared for this study and some that were prepared for a previous study. The samples reinforced with fibers and/or sawdust from beetle killed trees came from this study, while the samples reinforced with brown pulp fiber and/or commercial wood flour came from a previous study (Piao et al. 2012). All wood particles in each sample were modified with PMS, or all particles were untreated. As seen in Fig. 10, volumetric swell and water sorption of composites containing PMS modified beetle-killed fiber and/or sawdust exceeded that of the samples containing PMS modified brown fiber and/or flour when the percentage of fiber in the samples was at least 15. The inequality was reversed for samples containing only PMS treated sawdust or PMS treated flour. Since fiber bundles were present in the beetle-killed fiber but not in the brown pulp fiber, it is conjectured that the morphological difference between the two lignocellulosic materials (fiber/sawdust and fiber/flour) caused the different volumetric swell and water sorption rates. A better defibration process may allow beetle-killed tree fiber to be used as a fibrous reinforcing material in the fabrication of wood–plastic composites, resulting in dimensional stability comparable with that of brown pulp fiber reinforced plastic composites.

4 Conclusion

Potassium methyl siliconate (PMS) modified cellulosic fibers and sawdust made from beetle-killed loblolly pine trees and beetle-killed lodgepole pine trees were investigated as natural fiber reinforcing materials for wood–plastic composites. The morphology and topography of PMS modified fibers and sawdust particles, and the water sorption and volumetric swell of PMS modified fiber and sawdust reinforced polyethylene composites were characterized. The morphology of beetle-

killed loblolly pine fiber obtained from the mechanical defibration process was substantially different from the morphology of beetle-killed lodgepole pine fiber obtained from the thermomechanical process. Fiber bundles and fiber fractions were the principal components of the mechanically produced loblolly pine fiber, while fiber bundles (to a lesser degree) and clean fiber were the principal components of the thermomechanically produced lodgepole pine fiber. After PMS treatment, micro- and nano-scale PMS particles were observed covering the surfaces of fiber bundles, fiber fractions, complete fibers, and sawdust. PMS treatment of fiber and sawdust improved the compatibility between the reinforcing lignocellulosic material and the polyethylene matrix, resulting in decreased water sorption and increased dimensional stability of fiber/sawdust ethylene plastic composites. Treatment with PMS also increased the tolerance of the molding process to morphological variations in the reinforcing lignocellulosic materials, producing comparably dimensionally stable wood–plastic composites reinforced by fiber/sawdust of different morphologies.

All fiber/sawdust reinforced plastic composites displayed a two-phase water sorption and volumetric swell profile after long-term soaking in water. Morphology of fiber and sawdust (specifically, the size of sawdust particles) and the fiber/sawdust ratio affected the transition time from the fast growing phase to the saturating phase during the soaking period.

The morphology of fiber and sawdust and the fiber/sawdust ratio also influenced composite water sorption and dimensional stability. Furthermore, composite samples containing PMS treated wood particles absorbed less water and swelled less than samples containing untreated wood particles.

When dimensional stability of wood–plastic composites is a primary consideration, beetle-killed loblolly pine and beetle-killed lodgepole pine trees can be used as reinforcing lignocellulosic materials in the fabrication of wood–plastic composites.

References

American Society for Testing Materials (ASTM) (2006) Standard test method for water absorption of plastics. ASTM D 570-98 (Reapproved 2005). In: Annual book of ASTM Standards 08.01, plastics (1). ASTM, West Conshohocken

Billings RF (1980) The southern pine beetle, Chapter 10: Direct control. In: Thatcher RC, Search JL, Coster JE , Hertel GD (eds) USDA, Expanded Southern pine beetle research and application program, Forestry Services, Science Education Admissions, Technnolgy Bullet 1631. http://www.barkbeetles.org/spb/spbbook/Chapt10.html. Accessed 6 July 2011

Bledzki AK, Faruk O (2003) Wood fibre reinforced polypropylene composites: effect of fibre geometry and coupling agent on physic-mechanical properties. Appl Compos Mater 10:365–379

Bogart KHA, Ramirez SK, Gonzales LA, Bogart GR, Fisher ER (1998) Deposition of SiO_2 films from novel alkoxysilane/O_2 plasmas. J Vac Sci Technol A 16:3175–3184

Caulfield DF (1988) Dimensional stability of paper: papermaking methods and stabilization of cell walls. In: Suchsland Otto (ed) Wood science seminar 1: stabilization of the wood cell wall. Michigan State University, East Lansing, p 12p

Chang FC, Lam F, Englund KR (2010) Feasibility of using mountain pine beetle attached wood to produce wood–plastic composites. Wood Fiber Sci 42:388–397

Goehring CB (1980) In-grade flexural properties of structural lumber harvested from a bark beetle infested southern pine forest. MS Thesis, Virginia Polytechnic Institute and State University, Blacksburg, VA

Gu R, Kokta BV, Michalkova D, Dimzoski B, Fortelny I, Slouf M, Krulis Z (2010) Characteristics of wood–plastic composites reinforced with organo-nanoclays. Reinf Plast Compos 29(24):3566–3586

Hacker CA, Anderson KA, Richter LJ, Richter CA (2005) Comparison of Si-O-C interfacial bonding of alcohols and aldehydes on Si(111) formed from dilute solution with ultraviolet irradiation. Langmuir 21:882–889

Kazayawoko M, Balatinecz JJ, Matuana LM (1999) Surface modification and adhesion mechanisms in wood fiber–polypropylene composites. J Mater Sci 34:6189–6199

Migneault S, Koubaa A, Erchiqui F, Chaala A, Englund K, Wolcott MP (2009) Effects of processing method and fiber size on the structure and properties of wood–plastic composites. Composites A 40:80–85

Mohanty AK, Misra M, Drzal LT (2001) Surface modifications of natural fibers and performance of the resulting biocomposites: an overview. Compos Interfaces 8(5):313–343

Piao C, Cai Z, Stark NM, Monlezun CJ (2012) Wood plastic composites reinforced with potassium methyl siliconate-synthesized pulp fibers: water sorption and dimensional stability. J Appl Polym Sci. http://onlinelibrary.wiley.com/doi/10.1002/app.38736/abstract. Accessed 24 Jan 2013

Stark N, Berger MJ (1997) Effect of species and particle size on properties of wood-flour-fillers for thermoplastics and thermosets. In: Proceedings functional fillers for thermoplastics and thermosets, Le Meridien at Coronado, San Diego

Tshabalala MA, Kinshott P, VanLandingham MR, Plackett D (2003) Surface chemistry and moisture sorption properties of wood coated with multifunctional alkoxysilanes by sol-gel process. J Appl Polym Sci 88:2828–2841

Tzeng D, Fong RH, Soysa HSD, Weber WPJ (1981) Evidence for the intermediacy of 1,1-dimethyl-2-phenyl-1-sila-1,3-butadiene in the photochemistry and pyrolysis of 1,1-dimethyl-2-phenyl-1-sila-2-cyclobutene. J Organomet Chem 219:153–161

Westbrook RF, Hertel GD, Searcy JL (1981) Wood products from beetle-killed wood. South Lumberm 241:8–9

Winandy JE, Stark NM, Horn E (2008) Wood–plastic composites using thermomechanical pulp made from oxalic acid-pretreated red pine chips. In: Proceedings of 7th global WPC and natural fiber composites congress and exhibition. Kassel, Germany, pp A16-1–A16-7

Woodhams RT, Thomas G, Rodgers DK (1984) Wood fibers as reinforcing fillers for polyolefins. Polymer Eng Sci 24(15):1166–1171

Woodson GE (1983) Utilization of beetle-killed southern pine. http://www.barkbeetles.org/spb/ubksp/UBKSPTC.html. Accessed 6 July 2011

Yadama V, Lowell EC, Petersen N, Nicholls D (2009) Wood–thermoplastic composites manufactured using beetle-killed spruce from Alaska. Polymer Eng Sci 49(1):129–136

Zhu JY, Luo X, Tian S, Gleisner R, Negrón J, Horn E (2011) Efficient ethanol production from beetle-killed lodgepole pine using SPORL technology and *Saccharomyces cerevisiae* without detoxification. TAPPI J 10(5):9–18