Applied Polymer

Green Composites Using Switchgrass as a Reinforcement for a Conjugated Linseed Oil-Based Resin

Daniel P. Pfister, Richard C. Larock

Department of Chemistry, Iowa State University, Ames, Iowa 50011 Correspondence to: R. C. Larock (E-mail: larock@iastate.edu)

ABSTRACT: Switchgrass (SWG) has been used as a filler to produce conjugated linseed oil-based green composites. The effect of the amount of the SWG; the matrix crosslink density; and the incorporation of a compatibilizer, maleic anhydride (MA), on the structure, water absorption, and thermal and mechanical properties of the composites has been investigated. The thermal stability of the composites is primarily dependent on the amount of the SWG fibers, which are far less thermally stable than the linseed oil-based resin. For the most part, improvements in the mechanical properties can be achieved by increasing the amount of SWG (up to 70 wt %), increasing the amount of the crosslinker, and adding MA to increase the filler–matrix interaction. The uptake of water in the composites is mostly influenced by the loading of the SWG fibers. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: renewable resources; composites; mechanical properties; vegetable oil; natural fibers

Received 4 March 2011; accepted 22 February 2012; published online **DOI: 10.1002/app.37536**

INTRODUCTION

With the recent push toward the use of environmentally friendly materials, much attention has been given to the use of natural fibers as a replacement for synthetic fibers in the preparation of composites. Natural fibers have the main advantage of being biorenewable and biodegradable, but are also light in weight, have high strength, and stiffness, and can be obtained at a very low cost.

"Green composites" is the term often given to composites prepared from both natural fibers and a bio-based matrix. Of the bio-based matrices often employed in the preparation of green composites, natural oil-based resins are among the most common, because natural oils are available in large quantities and are relatively inexpensive. These natural oils typically contain multiple functional groups per molecule leading to highly crosslinked thermosetting resins with very good thermal and mechanical properties.

Of all the work on the preparation of natural oil-based green composites, most have focused on the use of functionalized natural oils. Early work in this area, conducted by Wool and coworkers, prepared high performance composite materials using flax, hemp, cellulose, and pulp to reinforce an acrylated epoxidized soybean oil-based resin.^{1,2} Aranguren and coworkers employed a linseed oil monoglyceride maleates-based resin and wood flour in order to produce green composites.³ Several groups have utilized resins containing epoxidized vegetable oils

to prepare green composites. Epoxide-functionalized soybean and linseed oils, and their derivatives have been used to prepare bio-based matrices reinforced with various natural fillers, including hemp, flax, and kenaf fibers and soy proteins.^{4–7} More recently, acrylated epoxidized soybean oil has been used in the preparation of biofoam and structural composites with sisal, flax, hemp, and pulp as the natural fibers.^{8,9}

Unfunctionalized natural oil-based green composites have been studied to a lesser extent. Composites prepared by Silva et al. and Mohanty and coworkers utilized polyurethane resins based on castor oil and coconut and sisal fibers¹⁰ and distillers dried grains with solubles, the coproduct of dry mill ethanol production,¹¹ as a reinforcement. Work in our group has focused on agricultural coproducts and residues produced here in the Midwest to reinforce unfunctionalized regular and conjugated natural oils. Spent germ,¹² the coproduct of wet mill ethanol production, soybean hulls,¹³ corn stover,¹⁴ wheat straw,¹⁵ and rice hulls^{16,17} have been used, along with tung, conjugated soybean, and conjugated linseed oil (CLIN)-based resins to prepare green composites. With natural fiber contents as high as 90 wt %, all the aforementioned natural oil-based green composites contain a significant amount of biorenewable materials and most have properties suitable for applications in the automotive, construction, and furniture industries.

The present work focuses on the use of switchgrass (SWG) to reinforce a CLIN-based resin. Linseed oil is a highly unsaturated

© 2012 Wiley Periodicals, Inc.



WWW.MATERIALSVIEWS.COM

triglyceride oil containing approximately six C—C double bonds per triglyceride. It consists of 57% linolenic acid (C18 : 3), 15% linoleic acid (C18 : 2), 19% oleic acid (C18 : 1), and 4% stearic acid (C18 : 0) and is typically used as a drying oil for surface coatings.¹⁸

SWG is a perennial warm-season grass native to North America. A lot of attention has been given to the use of SWG as a bioethanol feedstock, because it can be easily integrated into existing farming operations, is highly productive, is suitable for marginal lands, and has low water and nutritional requirements.¹⁹ But there is also potential for the use of SWG as a reinforcement in the preparation of composite materials and research in this area has been conducted. Kuo et al. produced wood/agricultural fiberboard, which utilized a soy protein-based adhesive to bond wood and SWG fibers,²⁰ and in another study, Van den Oever et al. prepared petroleum-based thermoplastic composites containing polypropylene and SWG.²¹ To our knowledge, research on the use of SWG as a reinforcement in natural oil-based green composites has not been reported.

EXPERIMENTAL

Materials

The linseed oil was supplied by Archer Daniels Midland (Decatur, IL) and was conjugated to produce CLIN according to our previously published procedure.²² The extent of conjugation was calculated to be approximately 100%. The divinylbenzene (DVB, technical grade; assay 80% by gas chromatography, 20% ethylvinylbenzene), maleic anhydride (MA), and *t*-butyl peroxide (TBPO) were purchased from Sigma-Aldrich Corporation (St. Louis, MO) and used as received. *n*-Butyl methacrylate (BMA) was purchased from Alfa Aesar (Ward Hill, MA) and used as received. The release film, Wrightlon[®] 5200, was supplied by Airtech International (Huntington Beach, CA). The SWG was supplied by Chariton Valley Resource Conservation and Development (southern Iowa) and was ground to pass through a 2 mm screen using a Wiley mill.

Preparation of Conjugated Linseed Oil/Switchgrass Composites

The composites were prepared using a compression molding process. The designated amounts of 100% CLIN, BMA, and DVB were mixed and stirred. Five weight percent of the total resin weight of the TBPO initiator was then added. The following nomenclature is used: CLIN represents conjugated linseed oil and BMA, DVB, and MA represent the *n*-butyl methacrylate, divinylbenzene, and maleic anhydride comonomers, respectively. For example, CLIN50-BMA30-DVB15-MA05 corresponds to a resin prepared from 50 wt % CLIN, 30 wt % BMA, 15 wt % DVB, and 5 wt % MA and 5 wt % of this total weight was the amount of TBPO initiator used. The resin mixture was added to the SWG, which was dried in a vacuum oven at 70°C for approximately 18 h prior to use. This mixture was stirred until all of the SWG was wet and was then placed in the cavity of the preheated (140°C) steel mold lined with the release film. The mold was closed and cured at 140°C for 3 h, followed by 160°C for 3 h, under a pressure of 400 psi. The mold was then placed in an oven and cured under atmospheric pressure at 180°C for 2 h. Once the mold cooled to room temperature, the composite

Applied Polymer

was removed and postcured at 180°C for 1 h. The reported amounts of SWG are based on the initial amounts of SWG and resin used. For example, for the composite containing 60 wt % SWG, 40 g of resin was added to 60 g of SWG. The standard composition used for preparing the composites was CLIN50-BMA35-DVB15 and 70 wt % SWG. When one variable was changed, the rest were held constant. In all cases, the matrix composition was CLIN50-(BMA + DVB + MA)50. For example, a composite designated CLIN-DVB05-70 refers to a composite prepared using CLIN50-BMA45-DVB05 as the resin and 70 wt % SWG as the filler. It is assumed that the remaining undesignated comonomer is BMA.

It should be noted that in our previous work, we have prepared unreinforced, free-radically cured natural oil-based resins, but because of shrinking and cracking problems, these resins were cured for much longer time periods (3 days) and at lower temperatures. Since we are using higher cure temperatures and much shorter times, we were unable to produce the unreinforced resin, because of the previously mentioned problems. If the cure temperature was reduced and the time increased in order to produce a viable unreinforced resin, it would be inaccurate to compare the pure resin to the composites. For these reasons, we are unable to obtain the thermal and mechanical properties of the pure resin.

Characterization

Soxhlet extraction was used to determine the amount of soluble materials in the composites and to characterize the structure of the resulting composites. A 4.5 g composite sample was extracted for 24 h with 110 mL of refluxing methylene chloride using a Soxhlet extractor. After extraction, the resulting solution was concentrated on a rotary evaporator and both the soluble and insoluble materials were dried in a vacuum oven at 70°C overnight before weighing. ¹H-NMR spectroscopic analysis of the soluble substances was carried out in CDCl₃ using a Varian Unity spectrometer (Varian Associates, Palo Alto, CA) at 400 MHz.

A Q50 thermogravimetric analyzer (TGA) (TA Instruments, New Castle, DE) was used to measure the weight loss of the samples under an air atmosphere. The samples were heated from room temperature to 650° C at a heating rate of 20 °C/min. Generally, a 10–12 mg sample was used for the thermogravimetric analysis.

The dynamic mechanical properties of the composites were obtained on a TA Instruments Q800 dynamic mechanical analyzer (DMA) in tension mode. A rectangular specimen of about 22 mm \times 8.5 mm \times 1.5 mm (length \times width \times thickness) was cut from the samples. Each specimen was cooled to -120° C and then heated under air at 3 °C/min to 200°C at a frequency of 1 Hz.

The tensile tests were conducted at 25°C according to ASTM D638 using an Instron universal testing machine (model 4502) at a crosshead speed of 10 mm/min. The dogbone-shaped test specimen (type I specimen in ASTM D638M) had a gauge section with a length of 57 mm, a width of 12.7 mm, and a thickness of about 4.5 mm.

The water uptake of the composites was measured according to ASTM D570-98. The test specimens were conditioned by drying

Applied Polymer

in an oven at 50° C for 24 h, cooled in a desiccator, and weighed. The specimens were then immersed in distilled water for 4 weeks. At specific time intervals, the specimens were removed from the water, quickly wiped dry with a paper towel, weighed, and placed back in the water. The water uptake was calculated as:

Water uptake ,
$$\% = \frac{\text{Wet weight} - \text{conditioned weight}}{\text{conditioned weight}} \times 100$$

At the end of the 4 week period, the specimens were reconditioned by drying in an oven at 50°C for 24 h, cooled in a desiccator, and weighed to determine the amount of soluble matter lost during immersion. The soluble matter was calculated as:

Soluble matter, %

$$=\frac{\text{conditioned weight} - \text{reconditioned weight}}{\text{conditioned weight}} \times 100$$

RESULTS AND DISCUSSION

Soxhlet Extraction Analysis

The % soluble materials for the SWG and all of the composites are given in Table I. The 2 mm SWG (entry 1) used in this work contains approximately 3% soluble materials. Based on the ¹H-NMR spectrum [Figure 1(a)], the SWG extract seems to consist mainly of a fatty substance. There appears to be very little triglyceride oil. The extract appears to be a mixture of fatty acids and derivatives.

Changing the amount of the SWG (entries 2–6); the crosslinker, DVB (entries 7–10); or the compatibilizer, MA (entries 11–14);

Table	I.	Extraction	Data	and	Thermal	Properties	of	the	Switchgrass	and
Comp	os	ites								

		Soxhlet extraction	TGA	
Entry	Sample	% Soluble	T10 (°C)	T ₅₀ (°C)
1	SWG ^a	3	292	348
2	CLIN-DVB15-50	3	311	425
3	CLIN-DVB15-60	3	305	407
4	CLIN-DVB15-70 ^b	4	302	394
5	CLIN-DVB15-80	3	298	375
6	CLIN-DVB15-90	3	293	351
7	CLIN-DVB05-70	3	302	386
8	CLIN-DVB25-70	3	301	406
9	CLIN-DVB35-70	3	305	423
10	CLIN-DVB45-70	3	306	434
11	CLIN-DVB15-MA05-70	4	300	403
12	CLIN-DVB15-MA15-70	3	298	408
13	CLIN-DVB10-MA05-70	3	300	391
14	CLIN-DVB00-MA15-70	4	296	389

^a2 mm SWG, ^bStandard composition: CLIN50-BMA35-DVB15-MA00, 70 wt % SWG.



Figure 1. ¹H-NMR spectra of (a) extract of 2 mm SWG, (b) extract of the CLIN-DVB15-70 composite, and (c) CLIN.

has little effect on the % soluble materials obtained from the composites. All of the composites, regardless of the composition, have 3 or 4% soluble materials. Figure 1(b) shows that the extract is mostly composed of unreacted CLIN or low molecular weight oligomers containing CLIN. This ¹H-NMR spectrum is representative of all of the composite extracts. The small range of chemical shifts in the vinylic region (5.2-5.5 ppm) of the spectrum and the absence of a peak at 2.8 ppm indicate that the extracted oil is not conjugated and contains no bisallylic protons. It may be that the unreacted oil contains significant amounts of saturated or monounsaturated (oleic acid) fatty acid side chains. It is also possible that the oil was incorporated into an oligomer through one of the carbon-carbon double bonds of a polyunsaturated fatty acid side chain, which would result in a loss of conjugation and eliminate the possibility for bisallylic protons. The presence of a small peak in the aromatic region (\sim 7.1 ppm) also indicates a small amount of DVB, which is most likely part of an oligomer.

Thermogravimetric Analysis

The temperatures at 10% (T_{10}) and 50% (T_{50}) weight loss and the TGA curves for the SWG and all of the composites are given in Table I and Figure 2, respectively. From the TGA curves, it is seen that the SWG and resulting composites essentially degrade in three stages. The first stage corresponds mainly to the loss of water in the temperature range of 100–150°C. In the final two stages, the fiber components (cellulose, hemicellulose, and lignin) of the SWG and the resin degrade. Because the degradation of the fiber components, when in an oxidative atmosphere, is very complex, it is not possible to determine when each degrades.²³

The TGA curves and data show that the SWG is far less thermally stable than the CLIN-based resin. T_{10} and T_{50} decrease from 311 to 293°C and 425 to 351°C respectively, when the amount of SWG is increased from 50 to 90 wt %. When looking at the TGA curves given in Figure 2 for the composites prepared with differing amounts of DVB, it is seen that the resin most likely begins to degrade at around 375°C. It is at this point where a large difference in the TGA curves is observed. Since the resin does not begin to degrade until about 375°C, varying the amount of DVB does not have much of an effect



Figure 2. TGA curves for the (a) SWG and composites prepared from differing amounts of SWG, (b) composites prepared from differing amounts of DVB, and (c) composites prepared from differing amounts of MA.

on the T_{10} values, but T_{50} increases from 386 to 434°C as the amount of DVB is increased from 5 to 45 wt %. Increasing the amount of DVB should significantly increase the crosslink density of the resin, resulting in an improvement in the thermal stability. Again, changing the resin composition, this time by incorporating a compatibilizer, MA, has little effect on the initial thermal stability of the composites. Replacing BMA (entries 11 and 12) and DVB (entries 13 and 14) with 5 and 15 wt % MA has little or no effect on T_{10} , but does have more of an effect on T_{50} . If 15 wt % MA is used to replace BMA, an increase in T_{50} from 394 to 408°C is observed, but it appears that the crosslinker, DVB, is more important than the compati-

Applied Polymer

bilizer with regards to the thermal stability of the composites. As all of the DVB is replaced by MA, T_{50} slightly decreases from 394 to 389°C.

Dynamic mechanical Analysis

The rubbery plateau storage moduli (E') and glass transition temperatures (T_{q}) for the composites are given in Table II. The T_{gs} were obtained from the peak of the tan δ vs. temperature curves, which are given in Figure 4 along with the storage modulus vs. temperature curves. From the DMA data and curves, it is observed that the SWG acts as an effective reinforcement to increase the stiffness of the composites. E' increases from 557 to 1002 MPa as the amount of SWG is increased from 50 to 80 wt % (entries 1-4). But increasing the SWG loading further to 90 wt % (entry 5) results in a dramatic decrease in E'. Adding too much SWG leads to a weaker material because an insufficient amount of resin is available to wet the fibers and effectively bind them together. As expected, increasing the amount of DVB, and therefore the crosslink density of the resin, results in significant increases in E', which increases from 677 to 1690 MPa as the amount of DVB is increased from 5 to 45 wt % (entries 6–9).

MA is used as a compatibilizer to increase the interaction between the CLIN-based resin and the SWG fibers. It is expected that MA can be incorporated into the matrix through the C–C double bond and also chemically bind to the fibers through ring opening of the anhydride by the hydroxyl groups present on the lignocellulosic fibers (shown schematically in Figure 3). Seeing that E' increases from 1001 to 1231 MPa when 15 wt % MA is used to replace BMA (entries 10 and 11), it can be concluded that MA is a useful compatibilizer. But the improvements in E' gained by the use of MA are not enough to compensate for the removal of DVB. Replacing the crosslinker with either 5 or 15 wt % MA results in a reduction in E'(entries 12 and 13).

From the tan δ vs. temperature curves given in Figure 4, it is observed that two peaks (T_{es}) are present for most of the composites indicating a phase separated matrix. The reactivity of the vegetable oil and the comonomers used in the matrix are very different. Initially, the more reactive DVB polymerizes resulting in a homopolymerization or copolymerization with BMA to form a "DVB-rich" phase. As the concentration of DVB monomer decreases, more CLIN is incorporated into the polymer to form an "oil-rich" phase. Each of these two phases have their own separate T_g s: the "oil-rich" phase with a T_g of ~ 15°C and the "DVB-rich" phase with a T_g of ~ 85°C. Similar results have been observed in previous work.12 When the amount of SWG is increased from 50 to 80 wt %, both Tes tend to increase. Based on the shoulder peak at approximately -60°C that becomes more evident as the amount of SWG is increased, the increase in the T_{es} may be the result of a more phase separated matrix. As the amount of SWG is increased, the mobility of the larger oil molecule may decline, limiting its ability to be incorporated into the polymer. This could lead to another phase in the matrix that is even more "rich" in CLIN. If more oil is incorporated into this phase and not in the other two phases, that would explain the observed increase in the T_{g} s.

Applied Polymer

		DMA		Tensile pr	Tensile properties			
Entry	Sample	E′ (MPa) ^a	Τ _g (°C)	E (MPa)	σ (MPa)			
1	CLIN-DVB15-50	557	12, 77	986 ± 23	7.1 ± 0.5			
2	CLIN-DVB15-60	868	15, 80	1190 ± 49	7.2 ± 0.6			
3	CLIN-DVB15-70 ^b	1001	18, 76	1247 ± 43	7.6 ± 0.6			
4	CLIN-DVB15-80	1002	22, 83	1077 ± 64	4.4 ± 0.6			
5	CLIN-DVB15-90	421	72	385 ± 91	0.9 ± 0.4			
6	CLIN-DVB05-70	677	25	937 ± 51	5.9 ± 0.5			
7	CLIN-DVB25-70	1379	-8, 87	1525 ± 124	9.9 ± 1.2			
8	CLIN-DVB35-70	1487	-21, 87	1652 ± 28	9.3 ± 0.7			
9	CLIN-DVB45-70	1690	-24, 89	1639 ± 49	9.2 ± 1.0			
10	CLIN-DVB15-MA05-70	1103	9, 85	1283 ± 51	8.5 ± 0.5			
11	CLIN-DVB15-MA15-70	1231	4, 85	1523 ± 75	10.4 ± 2.1			
12	CLIN-DVB10-MA05-70	673	28, 75	1235 ± 62	8.5 ± 0.9			
13	CLIN-DVB00-MA15-70	781	39	1070 ± 73	6.6 ± 0.4			

Table II. Thermomechanical Properties of the Composites

^aStorage modulus at 150°C, ^bStandard composition: CLIN50-BMA35-DVB15-MA00, 70 wt % SWG.

Increasing the amount of DVB in the matrix causes a dramatic outward shift in the T_g s, resulting from a more phase separated matrix. If only 5 wt % DVB is used, a homogeneous matrix results with a T_g of 25°C, but as the amount of DVB is increased from 15 to 45 wt %, the T_g s shift from 18 and 76°C to -24 and 89°C respectively.

Adding MA at the expense of BMA tends to make the resin more phase separated. The lower temperature T_g decreases from 18 to 4°C and the higher temperature T_g increases from 76 to 85°C as BMA is replaced by 15 wt % MA. But, as might be expected, replacing the highly reactive DVB with 5 wt % MA causes the two T_gs to shift toward one another, indicating a more homogeneous matrix. If all of the DVB is replaced with MA, a homogeneous resin is obtained with a T_g of 39°C.



Figure 3. Potential chemical link between the resin and the SWG fibers.

Tensile Properties

The Young's moduli (*E*) and tensile strengths (σ) for the composites are given in Table II. As the amount of SWG is initially increased from 50 to 70 wt %, *E* and σ increase from 986 to 1247 MPa and 7.1 to 7.6 MPa, respectively, but, because of an insufficient amount of resin to bind the fibers together, increasing the amount of SWG further to 90 wt % results in a significant decrease in both *E* and σ .

Increasing the crosslink density of the matrix, by increasing the amount of DVB, tends to improve the mechanical properties. *E* increases from 937 to 1652 MPa as the amount of DVB is increased from 5 to 35 wt % and stays relatively constant when further increasing to 45 wt %. However, σ peaks at 25 wt % DVB and decreases slightly when more DVB is added. The tensile strength increases from 5.5 to 9.9 MPa when the amount of DVB is changed from 5 to 25 wt % and decreases to 9.2 MPa at 45 wt % DVB. The drop in σ above 25 wt % DVB is most likely a result of a more brittle matrix caused by too much crosslinking.¹⁴

Significant improvements in *E* and σ can be obtained by using a small amount of a compatibilizer, MA, in place of BMA. As a compatibilizer, the MA increases the filler–matrix interaction by chemically binding the SWG fibers to the resin. Approximately 22% and 37% increases in *E* and σ respectively were observed by replacing 15 wt % BMA with MA.

DVB is used as an effective crosslinker to improve the thermal and mechanical properties of the composites, but it is also quite expensive. Limiting its use in the resin will make the composites more economically advantageous, when finding applications in industry. When 5 wt % DVB is substituted with MA, the mechanical properties of the composites are retained. *E* decreases very little from 1247 to 1235 MPa and σ improves



Figure 4. E' and tan δ curves for composites prepared with (a) differing amounts of SWG, (b) differing amounts of DVB, and (c) differing amounts of MA.

from 7.6 to 8.5 MPa, but replacing all of the DVB with MA results in a reduction in both the strength and stiffness.

Water Uptake

The saturation water content, soluble matter lost, and total water absorbed and the water uptake vs. square root of time curves are given in Table III and Figure 5, respectively, for selected composites. As expected and seen in the data and the curves, the hydrophilic lignocellulosic SWG fibers have the largest influence on the water uptake of the composites. The total water absorbed increases from 33 to 45% when increasing the amount of SWG from 50 to 70 wt % (entries 1 and 2), but

Applied Polymer

more than doubles to 100% when further increasing the fiber loading to 90 wt % (entry 3). The diffusion constant of water in the composite, which is proportional to the initial slope of the water uptake vs. square root of time curve, and soluble matter also increase significantly as the amount of SWG is increased. Since all of the monomers are quite hydrophobic and immiscible in water, it is expected that the soluble matter is extracted from the SWG fibers. Changing the composition of the resin, by either varying the amount of the crosslinker or incorporating a compatibilizer, has a much lower effect on the water uptake of the composites. Increasing the amount of DVB tends to result in slight decreases in the soluble matter, water absorbed, and the diffusion constant of the water (entries 4-6). Whether MA replaces 15 wt % BMA or DVB (entries 7 and 8), decreases in the water absorbed and diffusion constant of the water are obtained. This is likely the result of the increased filler-matrix interaction and, therefore, "shielding" of the fibers by the resin caused by the use of MA.

CONCLUSIONS

Green composites have been prepared using SWG as a reinforcing filler for a bio-based resin containing CLIN. The composites, with a biorenewable content of 75–95 wt %, have thermal stabilities up to 300°C and Young's moduli and tensile strengths ranging from 385 to 1652 MPa and 0.9 to 10.4 MPa, respectively. Increasing the amount of SWG up to 70 wt % leads to improved mechanical properties, but because of the low thermal stability of the fibers, increasing the amount of SWG also results in composites with a lower thermal stability. DVB is used as an effective crosslinker and the thermal and mechanical properties are enhanced by increasing its concentration. By incorporating a compatibilizer, MA, to increase the filler–matrix interaction, an improvement in the mechanical properties can be obtained.

Water uptake in the composites is primarily influenced by the amount of the hydrophilic SWG fibers. Dramatic increases in the water absorbed results from an increase in the amount of

Table III. Water Uptake Data for the Composites

Entry	Sample	Saturation water content ^a (%)	Soluble matter ^b (%)	Water absorbed ^c (%)
1	CLIN-DVB15-50	31	2.1	33
2	CLIN-DVB15-70 ^d	42	3.1	45
3	CLIN-DVB15-90	94	5.8	100
4	CLIN-DVB05-70	46	3.5	50
5	CLIN-DVB25-70	40	3.1	43
6	CLIN-DVB45-70	41	2.9	44
7	CLIN-DVB15-MA15-70	37	2.8	40
8	CLIN-DVB00-MA15-70	40	3.4	43

^aSaturation water content was taken from the plateau of the water uptake vs. square root of time curve, ^bSoluble matter is the percent mass lost during immersion, ^cWater absorbed is the sum of the saturation water content and the soluble matter lost, ^dStandard composition: CLIN50-BMA35-DVB15-MA00, 70 wt % SWG.



Figure 5. Water uptake vs. the square root of time for composites prepared with (a) differing amounts of SWG, (b) differing amounts of DVB, and (c) differing amounts of MA.

the SWG, although slight decreases in the water absorbed can be obtained by increasing the amount of DVB or incorporating MA. A high water uptake of the composites could be good or bad depending on the intended application of the material. The water will likely compromise the mechanical properties of the composites, but should also accelerate the biodegradation of the SWG fibers. If the mechanical properties are crucial to the application, it may be necessary to coat or seal the composite to deter the absorption of water.

Polyethylene-, polypropylene-, and poly(vinyl chloride)-based wood-plastic composites (WPCs) have found many applications in the automotive and construction industries. Although slightly weaker than traditionally used WPCs, the green composites produced here have the advantage of having a high annually renewable content and should find nonstructural applications as automotive panels, wall panels, ceiling tiles, furniture, windows, and doors.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support of the Recycling and Reuse Technology Transfer Center of the University of Northern Iowa, the Grow Iowa Values Fund, the Consortium for Plant Biotechnology Research, and the U.S. Department of Education for a GAANN Fellowship. They would like to thank Judy Brayton and Chariton Valley Resource Conservation and Development Inc. for the supply of switchgrass. They also thank Dr. Michael Kessler from the Department of Materials Science and Engineering, Dr. Jay-Lin Jane from the Department of Food Science and Human Nutrition, and Dr. Douglas Stokke and the Department of Natural Resource Ecology and Management at Iowa State University for the use of their facilities.

REFERENCES

- 1. Williams, G. I.; Wool, R. P. Appl. Compos. Mater 2000, 7, 421.
- O'Donnell, A.; Dweib, M. A.; Wool, R. P. Compos. Sci. Technol. 2004, 64, 1135.
- 3. Mosiewicki, M.; Borrajo, J.; Aranguren, M. I. *Polym. Int.* **2005,** *54*, 829.
- 4. Boquillon, N. J. Appl. Polym. Sci. 2006, 101, 4037.
- Liu, Z. S.; Erhan, S. Z.; Akin, D. E.; Barton, F. E. J. Agric. Food Chem. 2006, 54, 2134.
- 6. Tran, P.; Graiver, D.; Narayan, R. J. Appl. Polym. Sci. 2006, 102, 69.
- Haq, M.; Burgueno, R.; Mohanty, A. K.; Misra, M. Compos. Sci. Technol. 2008, 68, 3344.
- Åkesson, D.; Skrifvars, M.; Walkenström, P. J. Appl. Polym. Sci. 2009, 114, 2502.
- Wu, S. P.; Qiu, J. F.; Rong, M. Z.; Zhang, M. Q.; Zhang, L. Y. Polym. Int. 2009, 58, 403.
- Silva, R. V.; Spinelli, D.; Bose, W. W.; Neto, S. C.; Chierice, G. O.; Tarpani, J. R. *Compos. Sci. Technol.* 2006, 66, 1328.
- 11. Wu, Q. X.; Mohanty, A. K. J. Biobased Mater. Biol. 2007, 1, 257.
- Pfister, D. P.; Baker, J. R.; Henna, P. H.; Lu, Y.; Larock, R. C. J. Appl. Polym. Sci. 2008, 108, 3618.
- 13. Quirino, R. L.; Larock, R. C. J. Appl. Polym. Sci. 2009, 112, 2033.
- 14. Pfister, D. P.; Larock, R. C. Bioresource Technol. 2010, 101, 6200.

- 15. Pfister, D. P.; Larock, R. C. Compos. A 2010, 41, 1279.
- 16. Quirino, R. L.; Larock, R. C. J. Appl. Polym. Sci. 2011, 121, 2039.
- 17. Quirino, R. L.; Larock, R. C. J. Appl. Polym. Sci. 2011, 121, 2050.
- Henna, P. H.; Andjelkovic, D. D.; Kundu, P. P.; Larock, R. C. J. Appl. Polym. Sci. 2007, 104, 979.
- Keshwani, D. R.; Cheng, J. J. Bioresource Technol. 2009, 100, 1515.
- 20. Kuo, M. L.; Adams, D.; Myers, D.; Curry, D.; Heemstra, H.; Smith, J. L.; Bian, Y. *Forest Prod. J.* **1998**, *48*, 71.
- Van denOever, M. J. A.; Elbersen, H. W.; Keijsers, E. R. P.; Gosselink, R. J. A.; De Klerk-Engels, B. *J. Mater. Sci.* 2003, 38, 3697.
- 22. Larock, R. C.; Dong, X. Y.; Chung, S.; Reddy, C. K.; Ehlers, L. E. J. Am. Oil Chem. Soc. 2001, 78, 447.
- 23. Tomczak, F.; Sydenstricker, T. H. D.; Satyanarayana, K. G. *Compos. A* **2007**, *38*, 1710.