

Bamboo is a Suitable Template for Polymerizations

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ABSTRACT: *In situ* hydrosilation reactions and ring-opening metathesis polymerizations were demonstrated to occur in bulk samples of bamboo. Bamboo was infused with silicone precursors or cyclodiene monomers with the assistance of supercritical CO₂ and subsequently crosslinked or polymerized, respectively. Bending stiffness, energy release rate, and specific fire resistance properties of the bamboo-polymer composites were measured and compared with unmodified

bamboo. Bamboo-silicone composites showed an increase in fire resistance and a slight increase in mechanical properties. The bamboo-poly(alkenamer) composites showed significant increases in mechanical properties. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3961–3967, 2008

Key words: composites; flame resistance; polybutadiene; renewable resources; silicones

INTRODUCTION

The wood composite industry has boomed to over \$1 billion in the last decade due to the demand for new materials that not only have improved mechanical properties and reduced maintenance costs, but also meet the environmental regulations set on these materials.¹ Increased strength, dimensional stability, durability, fire-resistance, and rot resistance are just a few of the desired attributes needed to improve these already versatile and renewable resources.² To address one or more of these needs, natural materials are usually doped with different chemical additives or chopped into particles of various sizes and blended with an assortment of polymers and additives.^{3,4} While each approach has its distinct advantages, neither process is without flaw.

Typically, water-soluble additives are forced into wood by simply diffusing the water/additive solution into wood under pressure. There are two inherent disadvantages to this process. First, if the additives can diffuse into the wood, they will surely diffuse out over time. Second, since these additives are water-soluble, the additives can leach out when the wood products are exposed to environmental conditions.³ In addition, many additives currently used such as chromated copper arsenate (CCA) and alkaline copper quaternary (ACQ) compound are either harmful to the environment or caustic to metal fixtures making them poor additive choices.⁵ Blending natural fibers with different polymers is another method to attaining specific improvements in mate-

rial properties. These composites, however, are typically susceptible to both creep and fire.⁶ These wood-plastic composites (WPCs) are not ideally suited to meet the demands for an improved, durable natural composite material and do not satisfy the environmental and safety issues that are vital to using these materials in the real world.

It is possible to create novel WPCs by utilizing supercritical CO₂ as a solvent and transport medium. There have been several efforts describing the process to make novel polymer-polymer blends by impregnating and subsequently polymerizing different monomers into various polymers. The first and most notable efforts by Watkins have demonstrated the ability to incorporate styrene monomer and a radical initiator into bulk polyethylene and polychlorotrifluoroethylene samples using supercritical CO₂. These samples were then heated to initiate and polymerize the styrene inside of the polymer.⁷ Utilizing this unique method, we incorporate silicones and cyclodiene monomers into a bamboo template to improve the mechanical and fire resistance properties of bamboo.

EXPERIMENTAL

Materials

Bamboo was purchased at from a local garden center. 1,3,5,7-Tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane (D₄V), 1,3,5,7-tetramethyl cyclotetra-siloxane (D₄H), polymethylhydrosilane, 1800 *M_w* (PMHS), vinyl-terminated polydimethylsiloxane, 28,000 *M_w* (PDMS-V), and Karstedt's catalyst (2.1–2.4% in xylene) were purchased from Gelest and used without further purification. Cyclooctadiene (COD) and dicy-

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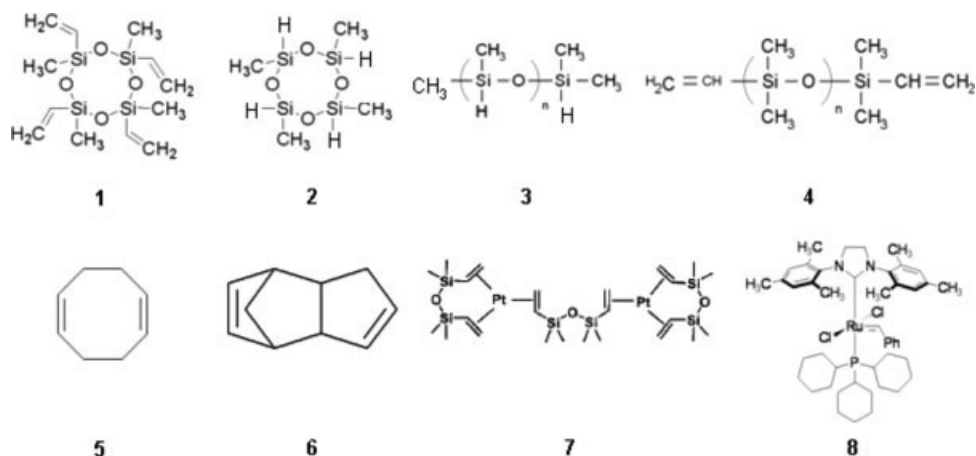


Figure 1 Reagents and catalysts used to fabricate of bamboo composites. 1) 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane (D_4V), 2) 1,3,5,7-tetramethyl cyclotetra-siloxane (D_4H), 3) PMHS, 4) PDMS-V, 5) COD, 6) DCPD, 7) Karstedt's catalyst, 8) Grubb's generation two catalyst.

clopentadiene (DCPD) were purchased from Aldrich, dried over sodium and distilled at reduced pressure before use. Methylene chloride was purchased from Aldrich, dried over Calcium hydride and distilled at reduced pressure before use. Grubbs second generation catalyst was purchased from Aldrich and used as received. Ethanol was purchased from the Fisher Chemical Co. and used as received. Compressed carbon dioxide and oxygen were purchased from Merriam Graves and were used as received. Refer to Figure 1 for chemical structures of the additives and catalysts used.

Instrumentation

Samples were purified using a high pressure CO_2 pump from Thar Designs and a model 260D syringe pump combined with an Isco Series D pump controller for the ethanol cosolvent. X-ray photoelectron spectroscopy (XPS) was carried out using a Quantum 2000 Scanning ESCA microprobe (Physical Electronics). Infrared spectra were recorded on a Horiba Jobin Yvon HR800 spectrometer equipped with an ATR-IR lens. Mechanical analysis was performed on an Instron 4411. Thermographic analysis (TGA) was performed on a TGA 2950 Thermographic Analyzer from TA Instruments. Pyrolysis data was collected using a pyrolysis combustion flow calorimeter (PCFC) certified by the FAA.

Bamboo sample preparation

The large bamboo culm (stalk), having an inner and outer diameter of approximately 8 and 10 cm, respectively, was cut into 4 cm long cylindrical cross sections. These cylindrical cross sections were segmented into the samples which would be appropriate

for our supercritical fluid reactor, approximately $1 \times 1 \times 4 \text{ cm}^3$ sections. Figure 2 depicts the typical morphology of bamboo as well as some typical bamboo templates used to fabricate and analyze our composites.

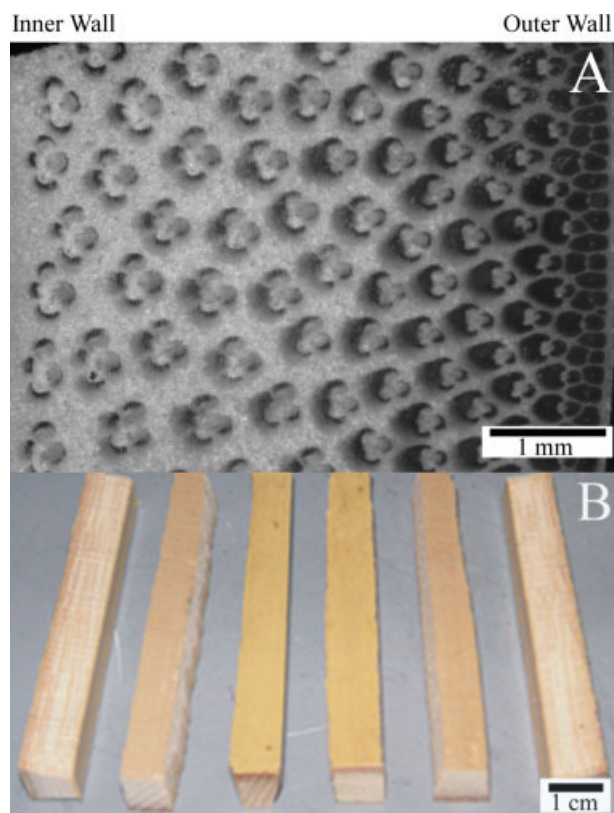


Figure 2 Optical images of bamboo samples. A) Cross section of bamboo showing the increase in fiber density from the inner periphery to the outer periphery.⁸ B) Image showing typical sample size. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
Preparation of Silicone Mixtures

Silicone mixture	Component 1	Component 2	Si-H : Vinyl ratio
a	D ₄ H	D ₄ V	1 : 1
b	PMHS	D ₄ V	5 : 1
c	PMHS	PDMS-V	5 : 1

Purification of bamboo

Bamboo samples were weighed, placed in a high pressure vessel, and purified by a continuous supercritical CO₂ extraction process assisted with ethanol. Similar extractions have been reported to extract certain organic compounds from natural materials.^{9,10} The extraction apparatus was designed with two pumps, a Thar Designs master pump to control the pressure of CO₂ and a second Isco D260 syringe pump to control the flow rate of ethanol. The flow rate out of the system was set to a constant rate and controlled by a flow regulator. The pressure of CO₂ was maintained at a constant pressure of 2500 psi and the ethanol cosolvent was set to a constant flow rate of 0.25 mL/min. The solvent mixture was allowed to flow through the sample holder which was maintained at 70°C for 3 h. The extractant was allowed to bubble through a trap filled with ethanol. After the extraction was completed, the samples were dried at reduced pressure overnight and weighed again. Samples were kept in a desiccator until they were needed.

Preparation of bamboo-silicone composites

A 20 : 1 mixture, by volume, of (D₄V) with Karstedt's catalyst was used for the catalyst solution. Supercritical fluid-extracted bamboo samples were weighed and placed in a high pressure reactor. Composite **A** was prepared by adding enough of mixture **a** (see Table I) into the reactor to entirely cover the bamboo samples (~ 6 mL). The reactor was then sealed and heated to 50°C. The vessel was then pressurized with CO₂ at 2500 psi and equilibrated for 24 h. The vessel was then slowly depressurized to atmospheric pressure over 4 h. The vessel was opened and three drops of Karstedt's catalyst solution were added. The vessel was sealed again and was shaken vigorously to ensure good mixing of the catalyst into mixture **a**. After mixing, 60 psi pure oxygen was added to the vessel. The reaction vessel was heated to 70°C and carbon dioxide was then added to the vessel to bring the pressure to 2500 psi.

The hydrosilation reaction was allowed to proceed overnight. After this time, the vessel was depressurized over a period of 4 h. The samples were cleaned of residual crosslinked silicone, dried at reduced

pressure, and weighed. Composites **B** and **C** were prepared in much the same way except that the initial infusion of the mixtures into the bamboo was not administered because the mixtures were too viscous for rapid dissolution of the catalyst solution. Three drops of catalyst solution were added to mixtures **b** and **c** and stirred vigorously before introducing them into the reaction vessel. The vessel was then sealed, oxygen and CO₂ were added and the mixtures were equilibrated for 24 h at 50°C. The temperature was then increased to 70°C and the reaction was allowed to proceed for another 24 h to fully crosslink the reagents.

Preparation of bamboo-poly(alkenamer) composites

Composites **D** and **E** were made by *in situ* ring opening metathesis polymerization of COD and DCPD respectively. Composites **D** and **E** were prepared by similar methods as described above. Bamboo samples were placed in a high pressure vessel and purified monomer was added to fully cover the samples. The vessel was then sealed, heated to 50°C, and filled with CO₂ to a pressure of 2500 psi. The monomer was allowed to soak for 24 h after which time the vessel was depressurized and catalyst was added. The catalyst was prepared by dissolving Grubb's second generation catalyst in methylene chloride (1 mg in 1 mL MeCl₂). The vessel was pressurized again to 2500 psi and heated to 70°C for a period of 24 h to allow the polymerization to occur. All samples were dried under high-vacuum after being removed from the reaction vessel.

Density measurements

At least three bamboo samples from each composite were weighed. The samples were coated with a thin layer of paraffin wax to prevent water uptake into the bamboo samples. Each sample was then submerged in a graduated cylinder and the volume displacement was recorded. The density measurements from each composite were averaged to give the reported values seen in Table II.

Spectroscopic techniques

Cross sections of each sample were cut through the center of the specimen. These sections were then analyzed by ATR-IR and XPS.

Thermographic analysis

Samples were analyzed under a nitrogen atmosphere to determine the onset of degradation as well as

TABLE II
Comparison of Mass Uptake, Density, and Silicon Content between Unmodified Bamboo and Bamboo-Polymer Composites

Sample	Mass uptake (%)	Density (g/cm ³)	Silicon (%) [*]	Expected silicon content (%) [†]
Bamboo	0	0.71	5	5
A	41.0	0.93	28	25
B	11.3	0.78	30	30
C	11.1	0.79	23	25
D	18.5	0.84	6	5
E	9.8	0.77	5	5

^{*} Silicon % was determined by XPS analysis of sample cross-sections.

[†] Silicon % calculated from elemental composition of silicone mixtures.

identify characteristic degradation fingerprints of the additives in each composite.

Three point bend test

All samples were measured, accounting for the trapezoidal shape of the sample specimens, and the samples were placed in the three point bend apparatus so that the inner periphery of the bamboo sample was under tension [see Fig. 2(a)].

Wedge opened double cantilever beam test

Samples were held vertically with a fixed clamp on the bottom of the specimen. A razor blade was affixed to the mobile, upper clamp and forced into the center of the length of the bamboo. Crack lengths were determined by imaging the crack at different displacements using a Panasonic GP-KR222 industrial color CCD camera.

Pyrolysis combustion flow calorimetry

All samples were prepared by cutting a 3 mm cross section out of the middle of sample. The edges of each cross section were removed to assure that no residual polymer from the outer part of the sample was included in the analysis. The cross sections were cut into 2–5mg samples and analyzed in an FAA certified PCFC.

RESULTS AND DISCUSSION

Bamboo-silicone composite characterization

To improve fire resistance performance of bamboo, we chose to incorporate silicone precursors into bamboo and subsequently crosslink them *in situ*. There are several advantages to choosing silicones for our additive reagents. First, silicones are known to dissolve readily in SC CO₂ making CO₂ an excel-

lent solvent and transport medium for these reagents. Second, silicones have been demonstrated to improve fire resistance in certain composite systems.^{11,12} Lastly, leaching of these water insoluble, environmentally benign materials should be negligible since the crosslinking will immobilize the additives inside the bamboo template.

The incorporation of silicone was determined by mass uptake, IR, XPS, and TGA. To assure complete incorporation of silicone throughout the entire sample, cross sections were cut from the middle of each sample and analyzed by IR and XPS. Figure 3 shows the IR spectra of cross sections of each composite. Peaks at 2200 and 2950 cm⁻¹ are representative of the Si-H and alkane-silicone respectively, which can be seen in each of the composites **A** and **B**. Composite **C** shows a peak at 2950 cm⁻¹ however the peak at 2200 cm⁻¹ is nearly absent due to the nature of the silicone mixture. The population of alkane-silicone moieties is significantly higher than Si-H moieties which results in a relatively low Si-H signal. Both of these peaks are absent in the unmodified bamboo suggesting that there is complete incorporation of silicone throughout the modified bamboo samples. Figure 4 shows an elemental map of a cross section of unmodified bamboo and composite **A**, showing the distribution of silicon in a specific area. It is common to see about 3–5% silicon impurity in these natural materials, but it is clear that the silicon concentration of the modified bamboo is significantly higher than 3–5%. It is apparent by mass uptake (shown in Table II) that lower molecular weight silicones diffuse into the bamboo more readily. Even though SC CO₂ is a

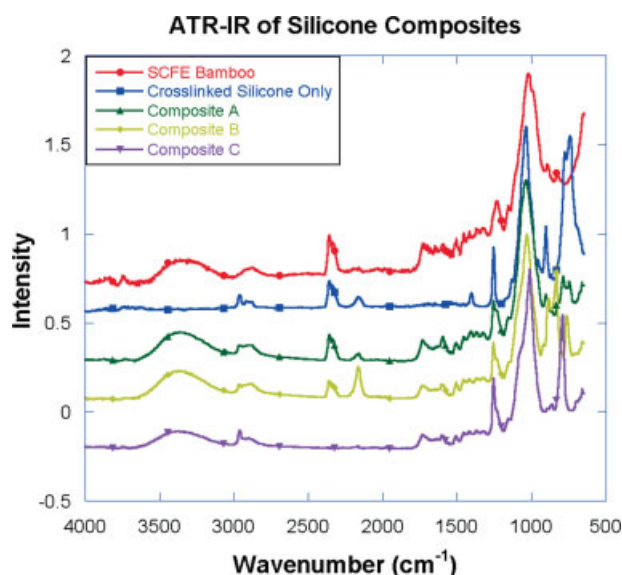


Figure 3 ATR-IR spectra of bamboo-silicone composites and each of their components. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

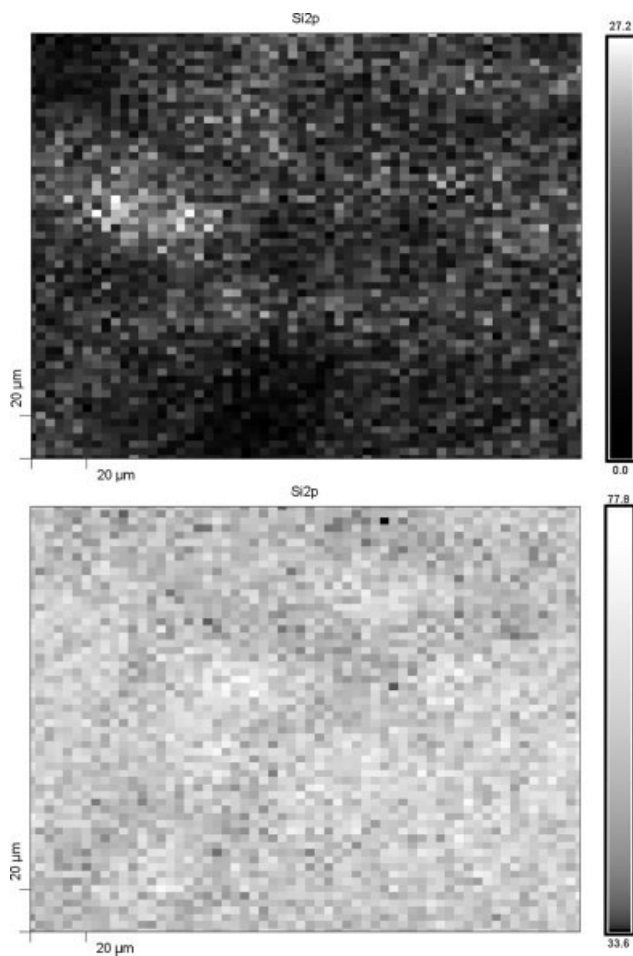


Figure 4 XPS map of silicon of unmodified bamboo (Left) and composite A (Right). Scale bars indicate the amount of silicon present for each map. Note that the scales are not the same.

good solvent for silicones, diffusion of higher molecular weight silicones through the bamboo is hindered due to molecular size. Increasing the diffusion time before crosslinking, the silicones should improve the mass of silicone incorporated into the bamboo.

TGA shows further evidence of silicone incorporation by assessing the degradation trends of each of the composites compared with the unmodified bam-

TABLE III
Summary of TGA Data for all Composites

Sample	Initial onset (°C)	Peak decomposition (°C)	Third decomposition onset (°C)	Char (wt %)
Bamboo	252	338	n/a	24
A	273	338	541	56
B	269	364	n/a	23
C	271	361	n/a	22
D	251	354	441	22
E	262	362	n/a	22

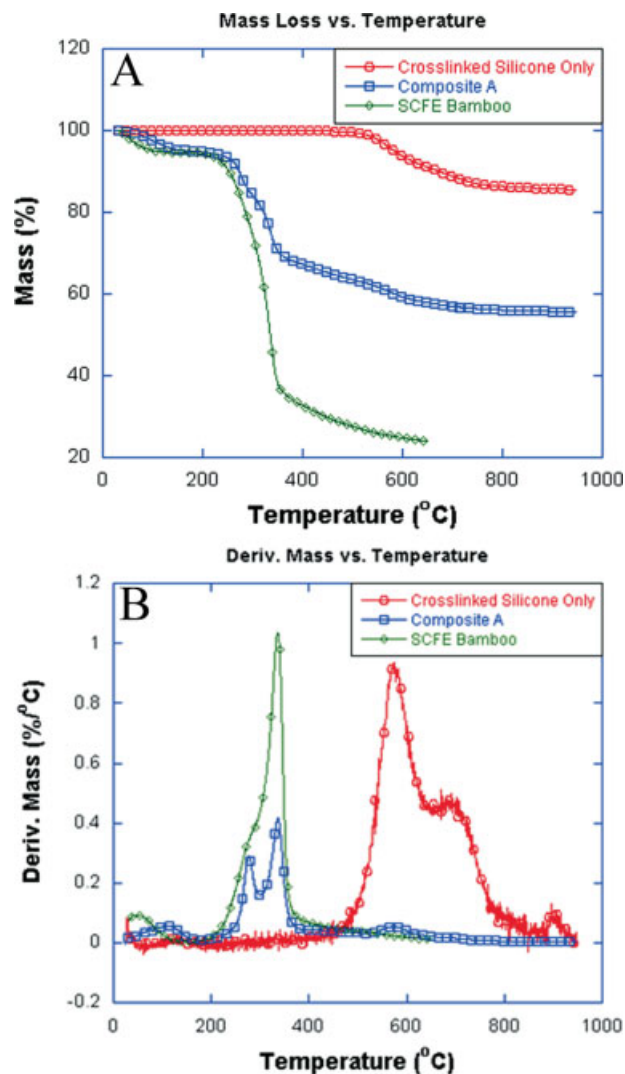


Figure 5 Determination of silicone incorporation into bamboo. A) Mass loss versus temperature. B) Derivative of mass loss versus temperature. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

boo. Table III summarizes the TGA data for each composite. In all cases, it is apparent that the onset of degradation and the peak degradation are shifted to higher temperatures with the addition of silicone to the bamboo. With the incorporation of over 18% silicone (by weight) a third degradation peak is seen around 550°C which is indicative of the presence of silicone as shown in Figure 5. The greatest improvement in char yield is seen in composite A due to the greater total incorporation of silicone and the high crosslink density of the silicone. Composites B and C actually show a slight decrease in char yield. This can be explained by a difference in the decomposition mechanism of silicones with different crosslink densities. Linear silicones are known to degrade to cyclic trimers, tetramers, and pentamers upon heat-

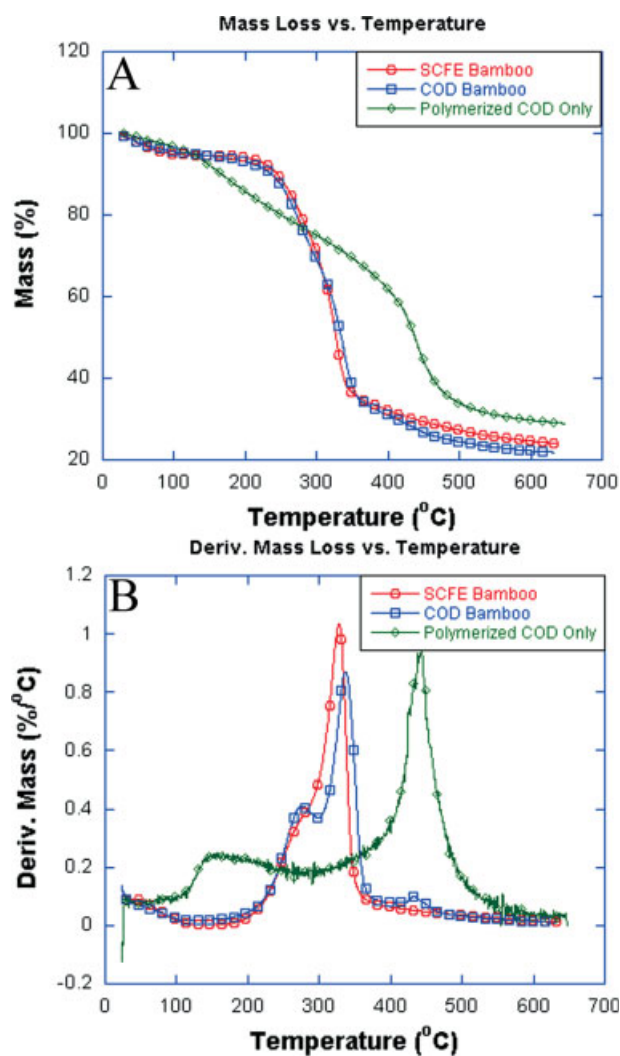


Figure 6 Determination of poly(alkenamer) incorporation into bamboo. A) Mass loss versus temperature. B) Derivative of mass loss versus temperature. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ing.^{13,14} Unlike the cyclic tetramers that were crosslinked in composite A, composites B, and C are comprised of linear reagents which can undergo such depolymerization. The resulting cyclic siloxanes would then evaporate from the system leaving a less char than even the unmodified bamboo.

Bamboo-poly(alkenamer) composite characterization

Analysis of the incorporation of poly(alkenamer) into bamboo was more difficult than for the silicone composites since there is no distinct characteristic that would stand out in either IR or XPS analysis. A slight increase in mass, as seen in Table II, after thoroughly drying the composites, suggests that polymer is present inside the bamboo. To verify the incorpo-

TABLE IV
Summary of Mechanical Properties of Unmodified Bamboo and Bamboo-Polymer Composites

Sample	Modulus (GPa)	G1c (kJ/m ²)
Bamboo	7.0	0.6
A	7.0	0.7
B	7.6	1.4
C	8.6	1.7
D	9.8	1.7
E	9.1	2.0

ration of polymer, TGA was done on each of the samples and distinct differences in the decomposition characteristics were observed (Fig. 6). It can be seen that the total mass lost is greater for the poly(alkenamer) composite. This is expected since there is more combustible material in the composites compared to the unmodified bamboo. It is also apparent in Figure 6 that the decomposition temperature and peak decomposition has shifted slightly to higher temperature and that a third peak around 450 °C is present. This suggests that incorporation of poly(alkenamer) has occurred and contributes to the combustion of the composite samples. Complete details of the degradation trends for each bamboo-poly(alkenamer) composite can be seen in Table III.

Mechanical properties of composites

Modulus and energy release rate of each composite were analyzed and compared with the unmodified bamboo. Table IV illustrates the mechanical properties of each composite. In all cases, the composite mechanical properties were improved or unchanged. Composites B–E show an improvement in both energy release rate and modulus compared to the purified bamboo. We note that composite A, which has the highest incorporation of polymer as well as the highest crosslinking density shows no improvement to mechanical properties. Rubbery additive materials such as the poly(alkenamers) and the lightly crosslinked silicones significantly increase both modulus and toughness.

TABLE V
Summary of Fire Resistance Properties of Each Composite Determined by PCFC

Sample	Mass uptake (%)	HR capacity (J/(g*K))	Total HR (kJ/g)	Char yield (%)
Bamboo	0	110	6.2	23
A	41.0	52	3.5	47
B	11.3	110	6.4	24
C	11.1	94	5.5	27
D	18.5	100	7.4	19
E	9.8	110	7.8	19

Pyrolysis combustion flow calorimetry

It is expected that the incorporation of silicone into bamboo will improve fire resistant properties by increasing char yield and lowering the total energy evolved during combustion. Poly(alkenamers)-bamboo composites should not be improved over the fire resistance of bamboo and may even lower resistance. Table V summarizes the pyrolysis data of each composite. Composite **A** shows the greatest improvement in fire resistant properties, whereas the other silicone composites show slight improvement. This is most likely due to the high percent of silicone incorporation in composite **A** compared with the other silicone composites. As described above, the decomposition of composites **B** and **C**, which contain linear silicone precursors may result in volatile cyclic silicones giving rise to the lower fire resistance and char yields for these composites.¹⁴ As expected, composites **D** and **E** exhibited no improvement in fire resistance.

CONCLUSIONS

We have demonstrated a method to incorporate monomers into bamboo and subsequently polymerize them. We have determined that incorporation is throughout samples and have shown that mechanical properties as well as its fire resistance can be improved. By incorporating monomers into a bulk substrates and polymerizing after, better composites

can be prepared that will not leach out the additives that give them the intended improvements. When silicones are added to bamboo, they improve both the mechanical and fire resistant properties. Other advantages that may be obtained using silicone additives include water repellency and possibly rot resistance. These new WPCs should not have the problems of creep or flammability as typically seen in the WPCs today and seem like promising, environmentally friendly, light-weight alternatives to additives such as chromated copper arsenate.

References

1. McGrawand, D. F.; Smith, P. M. *Forest Products J* 2007, 57, 76.
2. Donath, S.; Militz, H.; Mai, C. *Wood Sci Technol* 2004, 38, 555.
3. Lebow, S.; Foster, D.; Lebow, P. *Forest Products J* 2004, 54, 81.
4. Khan, M. A.; Ali, K. M. I. *J Appl Polym Sci* 1993, 49, 1989.
5. Baker, A. J. *Forest Products J* 1992, 42, 39.
6. Xu, B.; Simonsen, J.; Rochefort, W. E. *J Appl Polym Sci* 2001, 79, 418.
7. Watkins, J. J.; McCarthy, T. J. *Macromolecules* 1994, 27, 4845.
8. Ray, A. K.; Mondal, S.; Dasand, S. K.; Ramachandrarao, P. *J Mater Sci* 2005, 40, 5249.
9. Dean, J. R.; Liu, B. *Phytochem Anal* 2000, 11, 1.
10. Salgin, S.; Salgin, U. *Eur J Lipid Sci Technol* 2006, 108, 577.
11. Mai, C.; Militz, H. *Wood Sci Technol* 2004, 37, 453.
12. Hshieh, F. Y. *Fire Mater* 1998, 22, 69.
13. Zhang, J.; Fengand, S. Y.; Ma, Q. Y. *J Appl Polym Sci* 2003, 89, 1548.
14. Hayashida, K.; Tsugeand, S.; Ohtani, H. *Polymer* 2003, 44, 5611.