

Supercritical CO₂-assisted, silicone-modified wood for enhanced fire resistance

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Abstract A composite fabrication method is reported that incorporates silicones into bulk aspen substrates and subsequently crosslinks the additives in situ. This process utilizes supercritical CO₂, a non-toxic and easily recoverable solvent, as a transport and reaction medium resulting in aspen composites that have been uniformly infused with silicone. Flexure properties of aspen–silicone composites were determined to be indistinguishable from those of aspen. However, after thermal degradation, the residual flexure properties of the composite char were significantly improved compared to the virgin aspen char. Energy release rate, total energy released, and char yield of aspen and aspen–silicone composites were measured and a significant improvement in all three of these fire-resistance parameters was observed after the incorporation of silicone. Samples were also exposed to a controlled thermo-oxidative environment under an applied stress to measure lifetimes of each sample at given temperatures and stress levels. This data were subjected to an Arrhenius analysis and show a good linear correlation. Composite systems demonstrate significantly longer lifetimes than virgin aspen and the slopes of all lines are nearly identical, suggesting that no change in the chemical degradation mechanism has occurred.

Introduction

Wood is an amazing structural material having high specific strength and stiffness and low manufacturing cost, making it a useful and versatile material. Flammability, mechanical anisotropy, and degradability, however, are inherent problems that limit the range of wood's usefulness in many applications [1]. Several different composites, including pressure treated wood, plywood, and wood polymer composites (WPCs), have been fabricated to address the mechanical anisotropy and degradability of wood; however, relatively little effort has been made to address the problem of flammability. There are several methods employed to improve the fire resistance of natural materials. One method involves the incorporation of an inorganic phase into wood using sol–gel chemistry. This process involves infusing alkoxysilanes into wood and condensing them to form an inorganic network throughout the natural material. This network is also able to react with the hydroxyl groups of the cellulose to covalently attach the inorganic phase to the material [1, 2]. In addition to improved fire resistance, leaching of the additives is significantly reduced by creating a network within the cellulosic material and the hydrophobicity of the material is increased [2]. Other chemical modifications have also been employed to improve the fire resistance, which specifically target the modification of the hydroxyl groups of the cellulose. Chlorosilanes [2] and isocyanates in conjunction with organophosphorous compounds [3] have been successfully used to improve the fire resistance of wood; however, these chemical modifications are limited by diffusion of the additives into the wood. Typically, wood flour or small particles are used for these processes to reduce diffusion time. Others have fabricated WPCs and incorporated metal hydroxides into the composites to improve the fire resistance of these materials [4];

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however, the thermoplastics are the continuous phase and suffer from creep especially at high temperatures [5].

We have developed a composite fabrication method that allows for rapid incorporation of polymer precursors into bulk bamboo substrates and subsequent polymerization [6]. In research reported here, silicones were chosen to demonstrate the effectiveness of this fabrication method and, more importantly, to improve the fire resistance of wood. Silicones are ideally suited as fire-resistant additives in this process because they have appreciable solubility in SC CO₂ [7] and have been shown to improve fire resistance of various materials [2, 8–10]. The resulting aspen–silicone composites exhibit not only improved fire resistance, but a greater retention of mechanical properties after exposure to excessive thermo-oxidative conditions.

Experimental

Materials

Aspen samples (match sticks) were obtained from Diamond Brand matches. The match heads were removed and the samples were purified as described later. 1,3,5,7-Tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane (D₄V), 1,3,5,7-tetramethylcyclotetrasiloxane (D₄H), polymethylhydrosilane (PMHS), 1600 Mw, and Karstedt's catalyst were purchased from Gelest (Morrisville, PA). Ethanol was purchased from the Fisher Chemical Co. (Pittsburgh, PA) and laboratory grade compressed carbon dioxide and oxygen were purchased from Merriam Graves (West Springfield, MA). All solvents and reagents were used as received.

Synthesis of wood–silicone composites

The purification and fabrication procedures of silicone composites were established and discussed in previous work [6, 11, 12]. Briefly described, the aspen matchsticks, with dimensions of roughly 2 × 2 × 60 mm, were treated with a continuous supercritical CO₂ extraction assisted with ethanol as a co-solvent. The sample chamber was maintained at 70 °C and extraction was carried out for 4 h. A high-pressure CO₂ pump, set at 2500 psi, was combined with a second high-pressure pump to administer the ethanol co-solvent at a constant flow rate of 0.25 mL/min. A valve was left slightly open to allow the extractives to flow out of the system where they were collected by bubbling through ethanol. This process removes inorganic impurities as well as any free organics such as lignin [13, 14]. Two silicone mixtures were prepared for incorporation into the aspen samples: Mixture 1 was a mixture of D₄V and D₄H

(1:1 mol ratio of Si–H to Si–vinyl) and mixture 2 consisted of PMHS and D₄V (6:1 mol ratio of Si–H to Si–vinyl). Mixtures 1 and 2 were then used to make composites 1 and 2, respectively. The composites were fabricated by introducing the aspen samples into a high-pressure vessel and submersing them in the appropriate silicone mixture. The vessel was then sealed, pressurized to 2500 psi with CO₂, and allowed to equilibrate at 70 °C for 24 h. The vessel was then depressurized slowly and the platinum catalyst solution (50 μL of 20:1 D₄V: Karstedt's catalyst by volume) was introduced into the vessel. The reactor was sealed and placed on a vortex mixer to ensure good mixing of the catalyst into the silicone mixture. The vessel was filled to 60 psi with pure oxygen to promote the hydrosilation crosslinking reaction. The vessel was heated again to 70 °C, and pressurized to 2500 psi with CO₂. The reaction was allowed to proceed for 24 h, the vessel was depressurized slowly, and the samples were isolated. All samples were then dried under high vacuum at 70 °C and stored in a desiccator before analysis.

Density measurements

The mass of all samples was recorded before coating each sample with a thin layer of paraffin wax. The samples were then submerged in a 10 mL graduated cylinder filled to 7 mL with water and the volume displacement was recorded. The values shown in Table 1 are an average of five different sample densities.

The density of the crosslinked silicones was also measured using this technique. The pure silicones were prepared by curing each mixture without the presence of wood or supercritical CO₂. A total of 50 μL of platinum catalyst solution was added to 10 mL of each mixture and poured into a petri dish. The silicone mixtures were allowed to crosslink in an oven at 70 °C for 24 h and then cut into samples to be weighed. The volume was measured by recording the displacement of water in a graduated cylinder.

Table 1 Density and water uptake measurements

Sample	Mass uptake of silicone (%)	Density (g/cm ³)	Density of silicone additive (g/cm ³)	EMC ^a (%)
Aspen	–	0.48 ± 0.06	–	11.7
Composite 1	78	0.95 ± 0.04	1.06	5.7
Composite 2	91	0.85 ± 0.08	0.88	4.3

^a Calculated from the weight increase relative to the dry mass after 2 months

Water uptake

The mass of all samples was recorded at ambient conditions. The samples were then thoroughly dried at reduced pressure for 24 h at 70 °C and the mass was recorded again. Wood samples were then exposed to 76% relative humidity at 27 °C for 1 month before recording the mass uptake. The mass of each sample was recorded again at 2 months to ensure constant mass uptake. Humidity was controlled by placing 500 mL of a supersaturated sodium chloride solution into a sealed humidity chamber along with the samples.

Characterization techniques

Cross sections were taken from the middle of each sample and analyzed by optical microscopy, attenuated total reflectance infrared (ATR-IR), and X-ray photoelectron spectroscopy (XPS) to ensure that the silicone has been incorporated throughout each composite. ATR-IR spectroscopy was done on a Horiba Jobin Yvon HR800 spectrometer equipped with an ATR-IR lens. XPS was carried out using a Quantum 2000 Scanning ESCA microprobe (Physical Electronics, Chanhassen, MN). Optical microscopy was carried out using an Olympus BX51 optical microscope equipped with a QImaging Micropublisher CCD camera.

Fire-resistance properties

Total heat release, heat release rate, and char yield were measured using a pyrolysis combustion flow calorimeter (PCFC). This technique, developed by the Federal Aviation Administration (FAA), is equivalent to the cone calorimetry technique with the added advantage of requiring very little sample for the analysis (2–5 mg) [15]. The combustion chamber was set at 900 °C and the pyrolysis chamber was set at an initial temperature of 110 °C. Samples were cut into sections weighing approximately 5 mg, placed in the pyrolysis chamber, and were allowed to equilibrate for 2 min to remove any water in the samples. The samples were then pyrolyzed by ramping the pyrolysis chamber up to 800 °C at a constant rate of 1 °C/s.

Flexure properties

A three-point bend test was used to measure the flexural modulus and ultimate strength of all samples. The three-point bend apparatus was set to a span width of 40 mm (20:1 span width to sample height). The flexure properties were analyzed at room temperature using a crosshead speed of 1 mm/s.

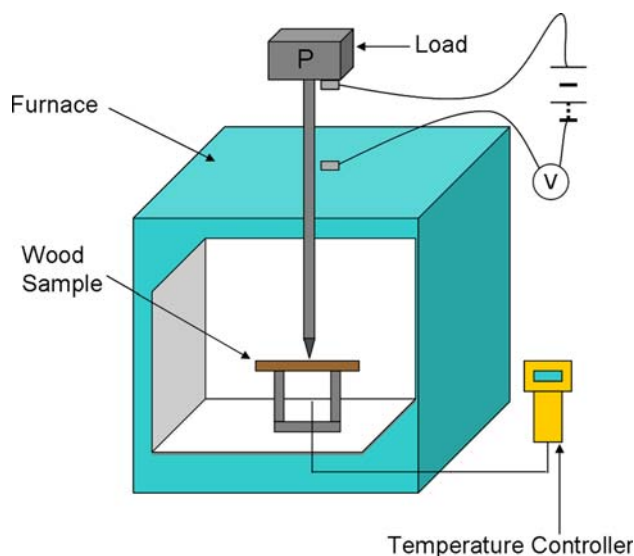


Fig. 1 Schematic of the instrument used to measure mechanical degradation kinetics of aspen samples and composites

Mechanical degradation kinetics under excessive thermo-oxidative exposure

An instrument was built to measure the time that it takes wood samples to fail under given temperature and applied stress conditions. A Fisher Scientific Isotemp muffle furnace was equipped with a three-point bend apparatus. A load basket was installed through the exhaust port and to the exterior of the furnace to control the applied load. The load was controlled by adding standardized weights to a load basket. Temperature was controlled using a Fisher Scientific thermocouple which was placed just under the sample. A simple switch was fitted to the apparatus and a custom written Labview program monitored the time and voltage. Figure 1 shows a schematic of the apparatus. All samples were dried in a desiccator before being analyzed. The furnace was equilibrated to the desired temperature and a specified load was added to the load basket. A sample was then placed quickly into the three-point bend apparatus to minimize the time that the furnace was open. The timer was started and the sample was allowed to thermally degrade. Failure of the sample triggers the switch, and the Labview program records the time of failure.

Results and discussion

Density and water uptake

As shown in Table 1, the incorporation of silicone increases the density of the composite materials. No measurable difference in the volume of the wood was observed after the composite fabrication process, but an appreciable

difference in density is measured. These observations suggest that very little or no swelling occurs throughout the fabrication process, rather the majority of the silicone is being incorporated within the aspen substrate. While it appears that composite 1 has a higher density than composite 2, the values are too similar to conclude which has the greater density given the experimental error of the technique used.

The equilibrium moisture content (EMC) of the aspen and the composites (Table 1) demonstrates that the EMC has been reduced by a factor of two, indicating that the hydrophobic silicone additives effectively inhibit water absorption. Significant reduction in the water absorption in wood samples may help to prevent the wood from warping and may lead to an increase in rot resistance [16, 17].

Characterization of composites

The ATR-IR spectra of sample cross sections shown in Figs. 2 and 3 indicate that the silicones are incorporated throughout the wood microstructure. Peaks at 2200 and 2950 cm^{-1} represent the Si–H and alkane–silicone, respectively, which can be seen in each of the composites. Table 2 summarizes the XPS analysis and indicates that there is some silicon present in the pure aspen; however, there is a significant increase in the amount of silicon in the composites. The silicon present in the pure aspen is attributed to inorganic impurities within the aspen that can be drawn up from the soil [18]. Figure 4a and b are optical images of the unmodified aspen morphology perpendicular to the grain showing a number of hollow vessels or pores in the cellular morphology. After incorporation and subsequent crosslinking of the silicone mixtures throughout

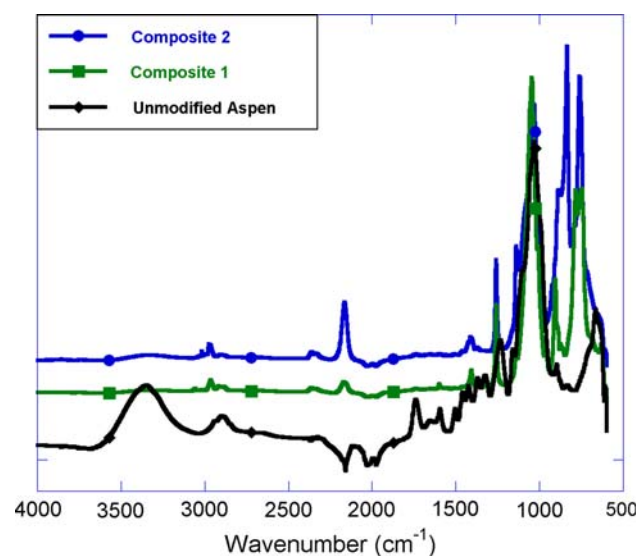


Fig. 2 ATR-IR spectra of aspen and aspen–silicone composites

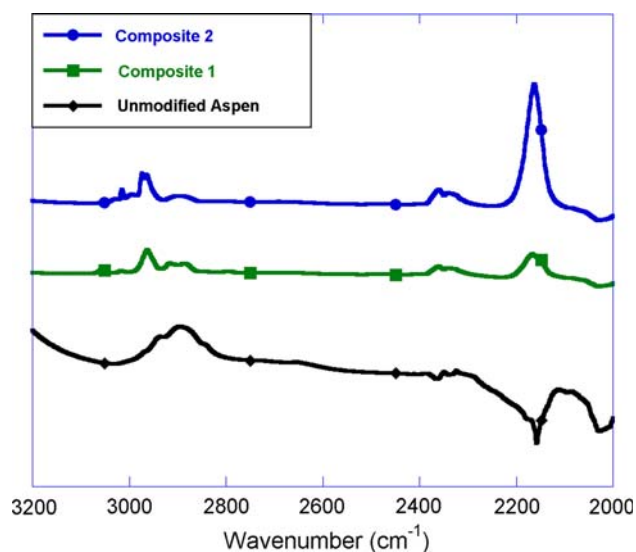


Fig. 3 A closer look at the ATR-IR spectra of aspen and aspen–silicone composites to demonstrate the differences in the composite IR spectra from the unmodified aspen spectrum

the aspen substrate, it is apparent from Fig. 4c and d that the vessels of the aspen have been completely filled with solid silicone.

Fire-resistance properties

It has been reported that silicones may decompose into an inorganic glass when exposed to extreme temperatures [9, 10]. To demonstrate this, each sample cross section was exposed to a propane torch to completely oxidize the sample. The unmodified aspen completely burns away, leaving only small amounts of ash and completely loses its microstructural registry. Both composites, however, form a solid char and retain some of the original aspen microstructural registry. Figure 5 shows the resulting morphology of composite 1 after exposure to the propane torch. The morphology seen in the charred cross section (Fig. 5a) is relatively uniform, which would be expected if the silicone was present within both the pores as well as the cells. The transverse section (Fig. 5b) shows a similar morphology seen in the undegraded transverse section (Fig. 5c) and demonstrates the retention of the microstructural registry of the aspen. The analysis of the char by XPS indicates that the char is primarily silicon and oxygen, confirming that the silicone has ceramified into silicon dioxide (Table 2).

The formation of a significant amount of char is one indication of improved fire resistance, but in order to quantify the fire-resistance properties of the aspen and the aspen–silicone composites, the samples were analyzed with a pyrolysis combustion flow calorimeter (PCFC). From this technique, energy release rate (J/g K), total energy released (kJ/g), and char yield can be calculated. A decrease in both

Table 2 Summary of the XPS data for all samples before and after thermal degradation

Element	Aspen	Composite 1	Composite 2	Aspen char	Composite 1 char	Composite 2 char
Carbon (%)	63	45	36	–	6	3
Oxygen (%)	31	30	25	–	67	67
Silicon (%)	6	25	29	–	28	30

Fig. 4 A cross section of unmodified aspen at 20× (a) and 40× (b) magnification depicting empty pores throughout the microstructure. A cross section of composite 1 at 20× (c) and 40× magnification (d) showing that silicone has completely filled the pores. Scale bars represent 200 μm

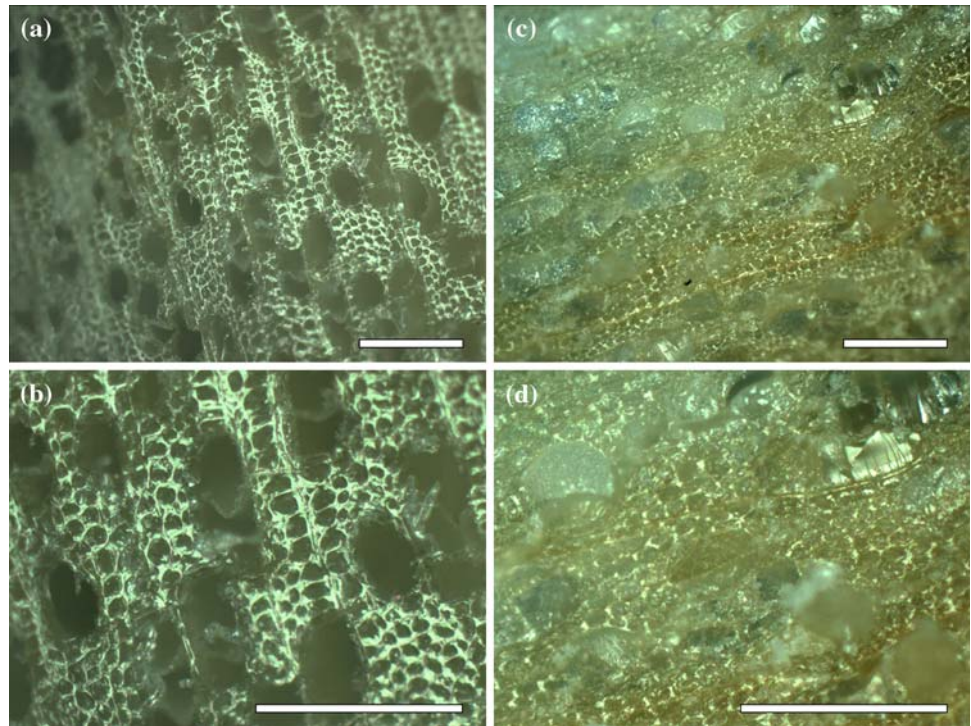
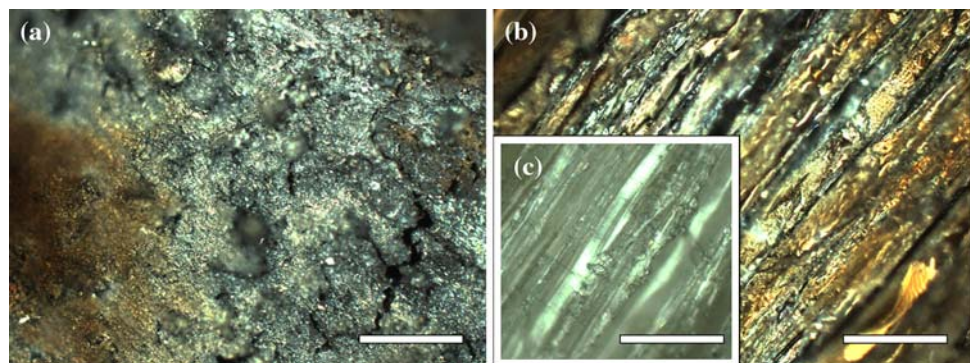


Fig. 5 Cross section (a) and transverse section (b) of composite 1 after exposure to a propane torch. A transverse section of undegraded, unmodified aspen is shown for comparison of retained microstructure (c). Scale bars represent 200 μm



the energy release rate and the total energy released in conjunction with an increase in char yield indicates an improvement in the fire resistance of a material. Figure 6 demonstrates that the composites show an improvement in all three fire-resistance parameters. In fact, both aspen–silicone composites qualify as ultra-fire resistant materials by FAA standards, having heat release rates of less than 100 J/g K [15].

Flexure properties

Table 3 illustrates the flexure properties of unmodified aspen and each of the aspen–silicone composites. The modulus of aspen is unaffected by the incorporation and crosslinking of the silicone additives. This is expected because the flexure modulus is dominated by the wood fibers and supercritical CO₂ cannot penetrate highly

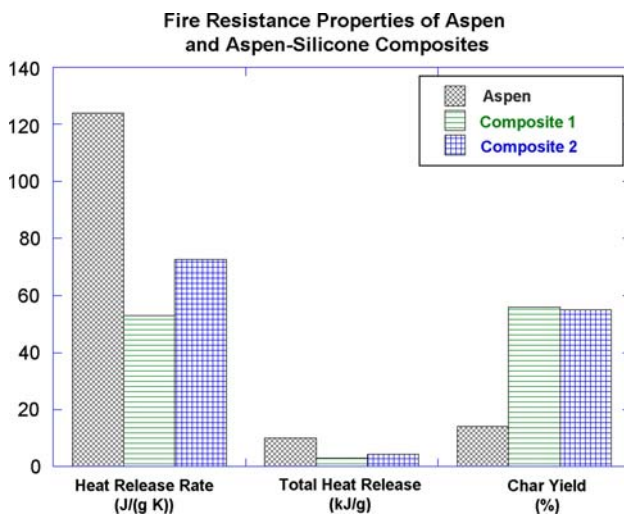


Fig. 6 Fire resistance of aspen and aspen–silicone composites

ordered domains such as fibers or crystals [19]. The ultimate stress has increased slightly. While the mechanical properties are nearly unaffected in their undegraded state, the formation of silicon dioxide char suggests that significant improvements could be seen when the samples are thermally degraded, therefore five sample specimens from each material were placed in an oven at a given temperature and allowed to thermally oxidize. Aspen and composite 1 were thermally degraded simultaneously in the same furnace at 285 °C for 3.5 h to ensure that the thermal history was exactly the same. Composite 2 was thermally oxidized separately at a slightly lower temperature (282 °C for 3.5 h). The samples were allowed to cool to room temperature and the flexure properties of the degraded samples were measured as described previously. Comparisons of the residual modulus and ultimate strength of aspen and the composites indicate a dramatic improvement in both quantities for the composite systems as seen in Table 3. It cannot be concluded which composite system shows better improvement since the thermal histories were slightly different; however, it can be concluded that both composites significantly outperform the unmodified aspen after exposure to a thermo-oxidative environment. This improvement of flexure properties after thermal

degradation is not surprising given the optical microscopy, PCFC, and XPS results shown previously and further supports that an inorganic glass is formed during thermal degradation. The composites' ability to retain both microstructural registry and residual flexural properties suggests that the composites are composed of a bicontinuous network of aspen and silicone. When the composites are thermally degraded, the organic material decomposes into volatile products whereas the silicone forms silicon dioxide and leaves a glass replica of the aspen microstructure.

Mechanical degradation kinetics under excessive thermo-oxidative exposure

Not only does the formation of an inorganic glass after thermal degradation lead to a retention of mechanical properties, but the glass may also slow the kinetics of mechanical degradation when subjected to an applied stress and defined thermo-oxidative environment. As described earlier, an instrument was built to measure the mechanical degradation kinetics of samples at given temperature and stress level conditions. Two different stress levels were chosen (230 and 610 kPa) to perform the analysis. Failure time of the samples, temperature, and applied stress were recorded for each trial. An Arrhenius analysis was applied to the data by plotting $\ln(\text{failure time})$ vs. $1/T$ for the unmodified aspen and the composites as shown in Figs. 7 and 8. All of the data sets result in linear correlations confirming an Arrhenius relationship. From this analysis, the activation energy of thermal degradation can be calculated from the slope of each line. The slopes of the composites compared with the unmodified aspen are nearly identical, which indicate that the activation energies are unchanged after incorporation of crosslinked silicone. This suggests that the degradation mechanism does not change even after adding a second chemistry to the material. The composite systems do, however, exhibit longer lifetimes at all temperatures as seen from the upward shift in the lines compared to the unmodified aspen. This increase in lifetime without changing the activation energy may be explained by a combination of two factors. First,

Table 3 Flexure properties of aspen and aspen–silicone composites before and after thermal degradation

Sample	Density (g/cm ³)	Modulus (GPa)	Ultimate stress (MPa)	Modulus after char (GPa)	Ultimate stress after char (MPa)
Aspen	0.48	10.0 ± 1.4	6.55	0.30 ± 0.02 ^a	0.35 ^a
Composite 1	0.95	9.3 ± 1.4	8.55	1.8 ± 0.1 ^a	1.4 ^a
Composite 2	0.85	9.2 ± 0.9	7.96	1.9 ± 0.1 ^b	1.9 ^b

^a Samples subjected to 285 °C for 3.5 h together in the same furnace

^b Samples subjected to 282 °C for 3.5 h

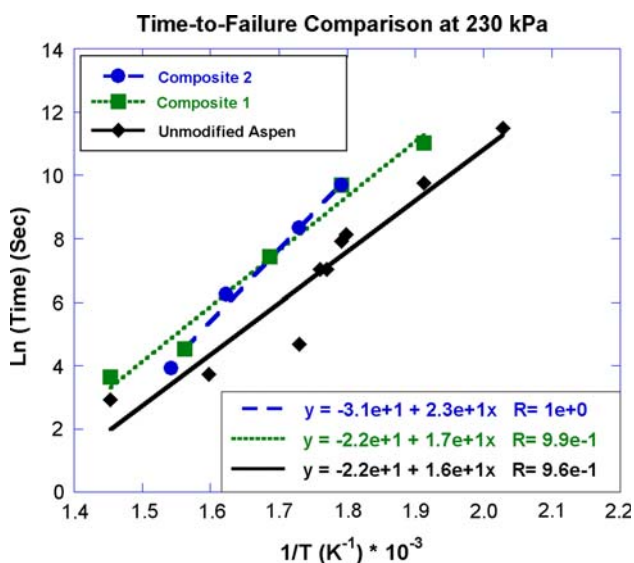


Fig. 7 Comparison of time-to-failure of all samples at 230 kPa

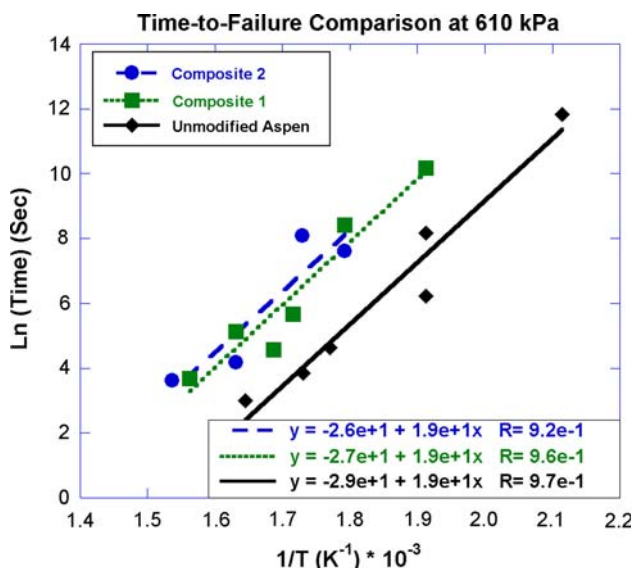


Fig. 8 Comparison of time-to-failure of all samples at 610 kPa

the formation of silicon dioxide from the silicone results in a greater retention in mechanical properties. Since the mechanical properties can be retained for longer times, the samples must be degraded to a greater extent before the sample fails. Second, a shielding effect created from the outer char of the material may also play a role in increasing the lifetime of the composites during thermal degradation. This shielding effect occurs as the outer layer of sample chars, leading to the formation of a protective coating. This may insulate the inner material from the heat and restrict the diffusion of volatiles from the sample, effectively slowing degradation [9].

It is also observed from Figs. 7 and 8 that changing the applied stress does not affect the activation energy of

thermal degradation. This is not surprising since applying a stress to the system does not affect the chemical degradation of the system. The only change seen is that by increasing the applied stress, the lifetime of the samples at all temperatures is significantly shorter. This is also expected since less material needs to degrade before the critical stress is achieved.

Conclusions

From procedures established for making bamboo–polymer composites, we have demonstrated that aspen can be used as a substrate for hydrosilation reactions. By incorporating low molecular weight silicones into bulk aspen substrates and crosslinking them in situ, composites consisting of a bicontinuous network of aspen and silicone were fabricated. The additives in these composites are physically trapped within the aspen substrate, resulting in long-term composites that will not exhibit any leaching of the additives over time. There were no detrimental effects to the mechanical properties of aspen after silicone incorporation, while significant improvements to a number of post-degradation properties were seen. Specifically, an improvement in fire resistance, residual mechanical properties, and mechanical degradation kinetics was observed for both composite systems. The formation of silicon dioxide char is the main factor contributing to these improvements. The silicone forms an inorganic glass upon thermal degradation, which reinforces the composite samples during degradation and may also act as an insulating layer to protect the inner material from degradation.

While this work demonstrates that the addition of silicone can improve the fire resistance and post-degradation properties of aspen, silicones are just one potential additive that can be added to natural substrates in order to improve specific properties of the material. By tuning the composition and the chemical nature of these additives and polymerizing them in situ, many of the inherent flaws associated with natural materials can be addressed while still maintaining their desirable properties.

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