

**Flame retardant lignin-based silicone composites**

Journal:	<i>RSC Advances</i>
Manuscript ID	RA-ART-11-2015-024093
Article Type:	Paper
Date Submitted by the Author:	14-Oct-2015
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Subject area & keyword:	Organic materials < Materials



ARTICLE

Flame retardant lignin-based silicone composites

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Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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The use of lignin as a filler for polymers to give composites provides both economic advantages and, in some cases, improved mechanical performance. The presence of lignin can also introduce certain advanced properties, including biodegradability, antimicrobial and antioxidant activity. Here we demonstrate that improved thermal insulation, thermal stability, and flame retardancy result when lignin is compounded with hydride-functionalized silicones to give elastomers and foams. In the absence of any additional inorganic flame retardant agent, the V-1 rating (UL-94) could be reached after chemical post-treatment of the materials with NH₃ vapor to remove excess SiH groups (which were identified as a culprit for excessive flammability). The fire resistance was further improved to the V-0 rating (UL-94) by applying additional thermal post-treatment at 220 °C in air. These foams also demonstrated low thermal conductivity, which were comparable with pure silicone foams of similar density. The improved thermal stability is attributed to flame retardant silica char, lignin repolymerization and char and the ability of lignin to scavenge radicals.

Introduction

Global resource shortages are driving scientists to better explore the use of sustainable and renewable materials.¹ Lignin, a constituent comprising more than 25 weight% in some plants, is still underutilized in commerce; lignin is mostly used as a low-value fuel. However, a promising future for this material is developing as both a feedstock for monomeric aromatics, following depolymerization²⁻⁵ or a substrate to be used in bio-composite fabrication.⁵⁻⁸ Lignin is particularly useful in the latter capacity as it has a high concentration of surface functional groups.⁸ For example, lignin has been incorporated into both thermoplastic (e.g., polylactic acid) and thermoset (e.g., polyurethane) polymers as fillers and/or reinforcing agents.⁹⁻¹²

Enhancing the utility of lignin beyond its use as a low cost fuel⁵ requires a better understanding of its properties within a synthetic polymer matrix. Previously, it has been demonstrated that the biodegradability of lignin leads ultimately to eco-friendly composites. At the same time, lignin

has both antimicrobial and antioxidant activities that can stabilize polymer matrices from radical degradation.⁶ Further such paradoxes exist with this material.

Lignin can be used as flame retardant agent in materials, which is ironic given its high caloric content and broad use as a fuel. Due to the abundance of aromatic structures of which it is comprised, lignin yields a high char content upon heating.¹³⁻¹⁵ The lignin char is able to provide a barrier to both heat and oxygen diffusion, consequently suppressing further combustion.^{16,17} Instead of using lignin alone, it has been used as synergistic agent with other traditional flame retardant agents for improved flame retardancy.^{15,18-21} For example, by physically blending lignin and ammonium polyphosphate into polylactic acid, a V-0 rating could be achieved in the UL-94 test. Lignin shows better performance in this test than other organic carbon sources.¹⁹

Flame retardant agents have also been chemically grafted onto lignin to improve fire resistance.¹⁸ Enhanced thermal stability and high yield of char (~50 wt% more than lignin alone) were achieved by covalently modifying lignin with phosphorous and/or nitrogen-based flame retardant agents:^{15,20-22} the addition of certain metal compounds at small loadings (~2%) led to even better performance.²³ The modification of lignin with these agents improved the miscibility of lignin in the polymer matrix and resulted in a more homogeneous mixture.^{17,18}

Silicones and silane derivatives have also been employed as flame retardant agents. Unlike carbon-based polymers, silicones produce inorganic silica upon combustion.²⁴ Silica residues act as a “firewall,” inhibiting rates of heat and mass transfer and, therefore, prevent fires from spreading.²⁴ More importantly, the combustion of silicones does not produce any toxic emissions.²⁴ As a consequence, silicone foams are of interest in transportation applications. Silicone derivatives

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† Electronic Supplementary Information (ESI) available: experimental setup for chemical post-treatment using NH₃ vapor; experimental setup and procedure for production of elastomer-foam-elastomer “sandwich” composites; an illustration of the instrument for thermal conductivity tests; images of aqueous dispersions of unmodified lignin and PMDS-modified lignin; DRIFT-IR spectra of lignin and PHMS-modified lignin; images showing dripping during combustion of lignin-silicone composites; photos of residue from lignin-silicone composites after combustion tests, an image of silica char coating around a sample; images of lignin-silicone composites showing differences in flexibility before and after combustion tests; ATR-FTIR spectra of lignin-silicone elastomer showing residual Si-H groups at the interface. See DOI: 10.1039/x0xx00000x

with branched structures or bearing aromatic rings exhibit enhanced preference for flame retardancy.²⁵ Hydroxyl-terminated silicone oil has been used as a synergistic agent with ammonium polyphosphate in composites for intumescent flame retardants.²⁶

In a previous study, we described a simple and effective route to prepare lignin-based silicone elastomers and foams.^{27, 28} The lignin acts both as a filler and a crosslinker in the silicone network. These composites demonstrated very good mechanical performance, and solvent and thermal resistance, even at high lignin contents (~40 wt%). In this paper, we describe the excellent fire resistance, thermal stability, and low thermal conductivity of these composites even in the absence of additional flame retarding agents.

Experimental

Materials

Vi-PMDS (vinyl-terminated dimethylsilicone, DMS-V35, MW = ~49500 g/mol), hydride-functional siloxanes/silicones, including PMDS (pentamethyldisiloxane), H-PDMS-H (hydride-terminated PDMS, DMS-H31, MW = 28000 g/mol), and PHMS (poly(hydromethylsiloxane), HMS-992, MW = 1800 ~ 2100 g/mol), and D₅ (decamethylcyclopentasiloxane) were purchased from Gelest. The catalyst B(C₆F₅)₃ (BCF) was purchased from Sigma-Aldrich, and dissolved in anhydrous toluene to give a stock solution (40.0 mg/ml, 78.13 mM). All solvents, and KOH (potassium hydroxide) were purchased from Sigma-Aldrich and used without purification. Ammonium hydroxide (containing 28 to 30% NH₃) was purchased from Caledon Laboratories and used directly. Softwood lignin was provided by Weyerhaeuser, and used as received, without the use of additional drying or milling processes.

Cast and cure for lignin-silicone elastomer and silicone foam

An optimized method to produce lignin-silicone elastomers was reported previously.²⁷ A brief overview of the method to prepare an elastomer containing 41% of lignin is provided here (Table 1). Lignin (3.2 g, 41 wt%) was first blended with hydride-terminated PDMS (DMS-H31, 4.0 g, 51 wt%) and D₅ (4.0 ml). Then, catalyst B(C₆F₅)₃, (38 μl, 307 ppm) and PHMS (0.76 g) were added with mixing until a homogeneous dispersion was obtained. The elastomer precursor mixture was poured into a Petri dish, and placed in a vacuum oven (685 mm Hg vacuum, VWR 1415M) at 40 °C; after 12 h, the temperature was raised to 90 °C for an additional 12 h cure.

The silicone foam (unfilled) was made from Vi-PDMS (7 g) and PHMS (0.68 g), catalyzed by Pt (Karstedt's catalyst, 20 μL, 50 ppm). The mixture was mixed vigorously to introduce air bubbles. Then, the foam precursor was cured rapidly at 120 °C.

Extrusion and compression molding for lignin-silicone foams

The process for production of lignin-silicone foam was slightly different than that used for the lignin-silicone elastomer, as it utilized a combination of extrusion and

molding processes.²⁸ The process for the foam requires no additional solvent to facilitate the dispersion of lignin in the silicone matrix. All the raw materials, including lignin, H-PDMS-H, PHMS, and catalyst solution were fed into a microextruder (DMS Micro 15 cc Twin-screw Compounds, 100 rpm); the mixed precursor was allowed to circulate for 3 min before being transferring to a volume-confined mold (the mass/volume ratio was kept to ~0.7). The curing process was allowed to proceed at 90 °C for 5 min in a compression-molding instrument (TECHMO, clamping force = 2 tons), after which post-treatments at elevated temperatures or/and in NH₃ vapor were applied. Details of the formulations and post-treatment conditions for lignin-silicone foams are listed in Table 1.

"Elastomer-foam-elastomer sandwiches"

A "sandwich"-structured composite, in which the foam was protected by elastomer layers, was produced by combining a preformed lignin-silicone elastomer in the molding process. Pieces of lignin-silicone elastomer were used to cover the top and bottom walls, respectively, of the mold. The foam precursor from the extruder was used to fill the space between the elastomer films (ESI⁺). The molding process used the same conditions as other samples (5 min at 90 °C).

Post-treatment of lignin-silicone composite thermally or/and using NH₃

After molding, post-treatments were applied to the composites to develop enhanced mechanical performance, flame retardancy and thermal stability. Thermal post-treatments were carried out using a regular oven in ambient air for 12 h. The temperatures were chosen to be lower than the thermal degradation temperatures of lignin and silicone (220 and 300 °C, respectively). Chemical post-treatment using NH₃ vapor was utilized to eliminate residual "Si-H" without damaging the lignin-silicone composite. The foam (3 mm thick) was immersed in NH₃ vapor (see ESI⁺ for details) for 24 h, and then placed in a vacuum oven (50 °C) for 12 h.

Quantification of residual Si-H groups

Residual Si-H groups on the surfaces of elastomer or foam could be detected qualitatively using ATR-FTIR. In order to measure quantitatively the residual Si-H throughout the composites, the Si-H groups were hydrolyzed, producing measureable volumes of hydrogen gas.²⁸ The composite (~ 400 mg) was cut into slices (0.5 mm × 5 mm × 10 mm) that were suspended in 15 ml 1-butanol, and warmed in an oil bath (30 °C). Gas production started once a KOH solution (2 ml, saturated solution in 1-butanol) was added to the suspension. The volume of gas produced from hydrolysis was read after 30 min. The residual Si-H concentration (i.e., the SiH groups that remained after elastomer/foam had completed cure) was calculated using the following equation:

$$Residual_{Si-H} \% = \frac{Volume_{collected\ gas}}{Mass_{foam\ layer} \times wt\%_{PHMS} \times 37.42} \times 100\%$$

where the $V_{\text{collected gas}}$ is the gas produced from hydrolysis of Si-H, the $M_{\text{Si-H foam layer}}$ is the weight of composite dispersed in 1-butanol, the $\text{wt\%}_{\text{PHMS}}$ for is the weight ratio of PHMS in formulation, which can be found in Table 1.

Characterization

ATR-FTIR (attenuated total reflectance infrared spectroscopy, Thermo Scientific Nicolet iS10) and DRIFTS (diffuse reflectance infrared Fourier transform mode, Thermo Nicolet 6700) were used to characterize the surface modification of lignin and residual Si-H groups on the elastomer surface. The morphologies of foam cross-sections were imaged using a digital single-lens reflex camera using macro view mode (Canon T3). Thermogravimetric analysis (TGA, TA instruments Q500 or Q50) was employed for testing the thermal stability of lignin, silicone, and lignin-silicone composites. The samples were gradually heated from 50 - 800 °C (10 °C/min) in flowing air (100 ml/min). The initial sample weight was chosen to be ~20 mg for these tests.

A flame retardancy test was performed according to the UL-94 flammability test.²⁹ Briefly, the sample was placed vertically, and a flame was applied to the bottom of sample for 10 s; a flame may optionally be applied for second 10 s as soon as the sample flame “self-extinguished”. The process was timed, and the weights of the sample before and after the tests were also recorded. The dimensions of the sample for this test were 100 mm x 10 mm x 3 mm.

Thermal conductivity of the composite was also measured. The composites were made in square sheets (40 mm x 40 mm x 3 mm). The square sample was placed in tight contact with the two blocks; the heat (Q) transferred from hot block (~80 °C) to cold block (~18 °C), as well as the real-time temperatures of the blocks, were measured and used for thermal conductivity calculation (see ESI† for instrument and equation for thermal conductivity calculation). These tests were performed in open atmosphere at room temperature.

Table 1. Formulations and post-treatment conditions for silicone foam, and lignin-silicone elastomers/foams.

Sample code ^a	Lignin (wt%)	PHMS (wt%)	H-PDMS-H (wt%)	B(C ₆ F ₅) ₃ (ppm)	Solvent (ml/g)	Thermal post-treatment		NH ₃ vapor post-treatment (h)	Residual Si-H (%) ^b
						Temperature (°C)	Time (h)		
SF	- ^c	- ^c	- ^c	- ^c	- ^c	- ^d	- ^d	No	66
E-41	41	8	51	307	0.5	- ^d	- ^d	No	64
F-25	25	5	70	2050	- ^e	- ^d	- ^d	No	36
F-41A	41	8	51	2050	- ^e	- ^d	- ^d	No	57
F-41B	41	8	51	2050	- ^e	- ^d	- ^d	24	~0 ^f
F-41C	41	8	51	2050	- ^e	220	12	No	23
F-41D	41	8	51	2050	- ^e	220	12	24	~0 ^f
F-41E	41	8	51	2050	- ^e	300	12	No	21
F-55	55	10	35	2050	- ^e	- ^d	- ^d	No	59

^a Sample code: SF = silicone foam, E = lignin-silicone elastomer, F = lignin-silicone foam; the number in the label refers to the weight ratio of lignin in the formulation. ^b Residual Si-H % after cure was obtained based on the volume of gas hydrolyzed from Si-H by base. ^c Silicone foam was cured using a Pt catalyst; neither lignin nor BCF was used in this formulation. ^d No thermal/NH₃ post-treatment was applied. ^e No solvent was used in this formulation. ^f No gas was detected in these two samples.

Results

The abundant ether linkages and hydroxyl groups found in lignin can be efficiently reduced and converted to labile hydrophobic alkyl and silyl ether groups using PMDS or PHMS, respectively, in the presence of B(C₆F₅)₃.^{27, 28, 30} Just a few hundred to thousand ppm of catalyst were required to surface modify lignin particles with silyl groups that act to compatibilize the lignin in lignin-filled elastomers or foams.^{27,28} foams are generated by methane and hydrogen produced during the process (Figure 1, ESI†). Before reduction, lignin particles could be readily dispersed in water. By contrast, after reaction with hydrosiloxanes, the lignin particles aggregated, forming an immiscible layer on the surface of water (ESI†), but were readily dispersed in organic solvents, including hexane.³⁰

In formulas for lignin-silicone elastomers or foams, lignin (as a multifunctional crosslinker), PHMS (co-crosslinker), and hydride-terminated PDMS were mixed together with B(C₆F₅)₃ to create polymeric networks. For foam production, the same reagents were mixed using an extruder; and then cured in a volume-confined mold. Taking the advantage of gaseous byproducts, this formula and processing require no additional blowing agents. The process is essentially solvent-free, using only a small portion of solvent (less than 3 wt% in the entire formula) to dissolve the catalyst. By contrast, the production of elastomers required more solvent, both to slow the reaction rate and lower viscosity, which facilitated loss of gaseous by-products from the elastomer.

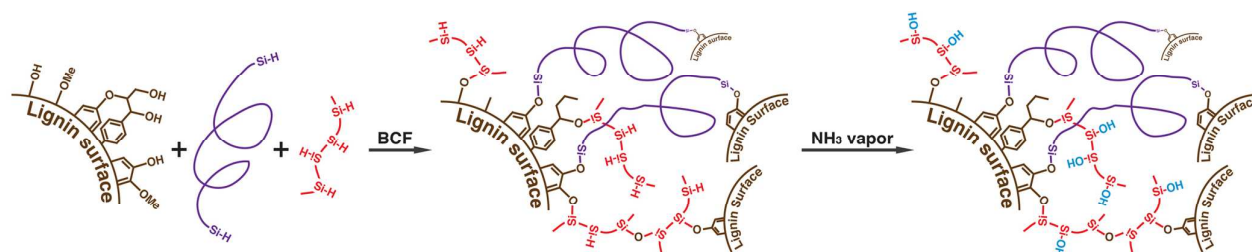


Figure 1. Illustration of lignin crosslinked silicone network, the functional groups at interface were silylated for covalent bonding.

It was necessary to incorporate excess amounts of hydride-functionalized silicones in the formulation of lignin-based composites to achieve an optimized crosslinking density.²⁷ As a consequence, residual Si-H groups were found in the composites even after compression molding (see below). We examined a variety of strategies to remove the excess Si-H, including thermal or/and chemical post-treatments, and correlated the thermal stability of the composites as a function of SiH concentration.

The concentrations of SiH groups before and after these treatments were established using a titration method based on hydrolysis in basic solution. Residual Si-H in the composite could be fully hydrolyzed using a basic 1-butanol solution ($R_3SiH \rightarrow R_3SiOH$ (or R_3SiOBu) + H_2). Each Si-H group produces one molecule of H_2 per reaction. Thus, it is possible to quantitate the residual Si-H groups in the matrix through gas evolution (Table 1): depending on the formulation about 60% of the initially available Si-H groups remained after curing to form the composite, (e.g., F-25, F-41A, and F-55 in Table 1).

Two different strategies were utilized to consume the SiH groups: thermal oxidation, and base-catalyzed hydrolysis/oxidation in the gas phase. In both cases, the SiH groups are converted to SiOH groups that, in turn, can condense to form disiloxanes SiOSi (Figure 1).²⁸

Thermal post-treatment at 220 °C for 12 hours (F-41C in Table 1) led to the loss of Si-H groups in the composite, from

about 60% to 20%. Further increases in temperature (e.g., to 300 °C) had no significant effect on reducing the SiH concentration (which changed only from ~23% to 21%, F-41E in Table 1).

NH_3 vapor, as with moisture, readily penetrates silicone elastomers.^{31, 32} This was used as an alternative and more effective means to eliminate Si-H groups from the composite. Exposure of the lignin-silicone composite to vapor produced by ammonium hydroxide led to complete reduction of Si-H groups to ~0% after 24 hours of exposure (F-41B and D in Table 1). Complete loss of SiH was confirmed by IR and by the absence of reaction with the samples were exposed to basic 1-butanol.

The flammability of lignin composites was established. As a control, pure silicone foam (unfilled) produced by the hydrosilylation of vinyl-terminated PDMS with PHMS (PHMS in excess at the same ratio as it in formulation of lignin-silicone composite, F-41A, ~9 wt%) was shown to ignite within 10 seconds of exposure to a flame, after which the flame propagated slowly across the whole sample (Figure 2A). A layer of ash separated from the sample during combustion; dripping was sometimes observed (ESI⁺), however, the drips did not ignite a layer of cotton wool underneath, which was used as a secondary flammability assay. The combustion lasted for ~110 seconds, leaving about 68% ash by weight (Table 2).

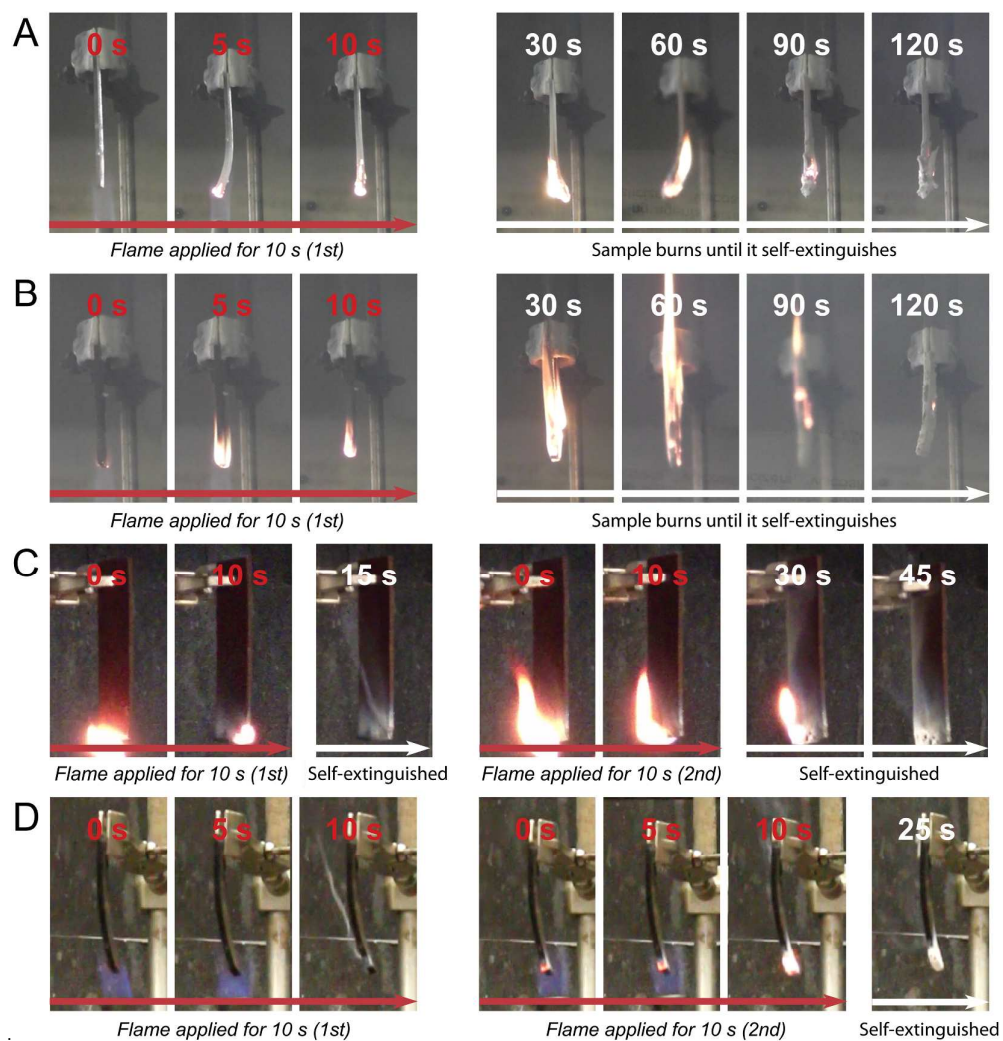


Figure 2. Combustion of silicone foam (A), and lignin-silicone foam (B: F-41A; C: F-41B; and D: F-41D). For (A) and (B), no obvious combustion was observed after applying the 2nd 10-second flame; the 10-second flame was applied twice for C: F-41B and D: F-41D.



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Table 2. Flammability test of silicone foam, lignin, and lignin-silicone elastomer/foams.

Sample code	Dripped ^a		Ranking	Residue after burning (%)	Combustion time (s) ^b		Residue ^c
	1 st	2 nd			1 st	2 nd	
SF	Y	N	NC ^d	68	110	0	Brittle
E-41	Y	N	NC ^d	50	75	0	Brittle
F-41A	Y	N	NC ^d	59	120	0	Brittle
F-41B	N	N	V-1	94	5	35	Flexible
F-41C	Y	N	NC ^d	60	80	0	Brittle
F-41D	N	N	V-0	96	0	15	Flexible
F-41E	N	Y	NC ^d	61	15	140	Brittle

^a Dripping in all cases refers to burned residue falling from the sample, see ESI† for examples. Drips from samples during flame tests did not ignite the cotton wool underneath; ^b numbers in columns of "1st" and "2nd" indicate the combustion time after the 1st and 2nd 10-second exposures to flame, respectively. ^c Description of "brittle" and "flexible" for residual samples refer as to a "loss" or "maintenance" of the original elasticity, respectively. ^d NC = Not classified.

Silicone/lignin-based foams with excess Si-H groups (PHMS was also ~9 wt% in the formulation as with F-41) were found to be much more flammable than simple silicones. Using the same flame test (without any post-treatment) a vigorous fire was generated after ignition and dripping was more significant (F-41A Figure 2B). This difference could be attributed to the presence of SiH groups rather than the lignin. After combustion of lignin-silicone foam, the initially flexible brown sample was converted to a brittle, black char coated with a layer of white silica (ESI†). The sample twisted during the combustion process due to stress from mass loss (also see Table 1, ESI†).

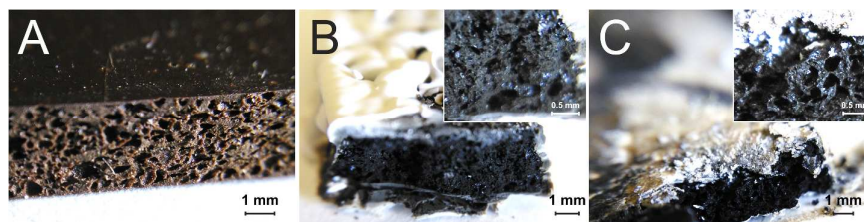
Thermal post-treatment of the composites reduced the Si-H content from ~60% to ~20%. Enhanced flame retardancy was one consequence of this change. As shown in the combustion photos (ESI†), only a small fire (F-41C, thermal post-treated at 220 °C, ESI†) was induced, which quickly quenched. Note that the residual SiH concentration was essentially the same after treatment at 300 °C (F-41E, thermally post-treated at 300 °C), but the sample exhibited

lower flammability, which is due to other effects (see below). The samples self-extinguished after 80 s and 15 s, respectively, and only glowed upon applying the 2nd 10-second flame exposure (Table 2, ESI†). Even so, the whole sample smoldered until it had completely burned leaving same amount char residual as that of untreated F-41A (Figure 2B, Table 2).

Attempted combustion of the analogous composite from which all SiH groups had been effectively removed (F-41B, Figure 2C) by treatment with NH₃ vapor led to very different results. The flame retardancy was improved from NC (no classification) to V-1 rating (UL-94 test). The fire self-extinguished in ~5 s and ~35 s after application of the 1st and 2nd 10-second flame, respectively. The flame was confined to the bottom of sample, yielding ~94% of sample that was not burned).

A combination of thermal and chemical post-treatments led to further enhancements in fire resistance: the flame retardancy improved to a V-0 rating (UL-94, Table 2). As shown in Figure 2D, the sample (F-41D) did not ignite after applying the 1st 10-second flame, generating only a wisp of smoke. Then, the 2nd 10-second flame was applied immediately; the sample smoldered instead of burning, glowing for only ~15 s. No dripping was observed during the test. About ~96% of sample remained unburned). The sample was still as soft and flexible as it was before this test (ESI†).

One final observation is noteworthy. In the case of foams, the porous morphology could be preserved in the more fire resistant formulations after both oxidative and thermal treatment. Such porous structures are efficient insulating layers that further improve thermal stability and resistance to flame. As shown in Figure 3B and C, F-41A, which had not been oxidatively treated, lost the porous morphology during combustion and appears to be a "melt." By contrast, the oxidized and thermally treated F-41E exhibited preserved foam morphology after surface combustion.

Figure 3. Cross-sectional morphologies of (A) F-41A, (B) residue of F-41A after flame exposure, and (C) F-41E (post-treatment at 220 °C and in NH₃ vapor) after flame exposure.

Sandwich Composites

Foams do not always possess sufficient mechanical strength for certain applications. The utilization of elastomer sheets on the top and bottom of the foam can help alleviate this problem. Although residual Si-H groups can be problematic for flammability, as noted above, they provide useful anchors to adhere the elastomer/foam interface. A “sandwich” structured composite could be made by utilizing the residual Si-H groups on the surface of the lignin-silicone elastomer (see ESI† for ATR-FTIR), which participated in reactive foaming process. As shown in Figure 4A, peel tests demonstrated that the resulting elastomer/foam interface was stronger than the foam, which underwent cohesive failure (Figure 4B and C). Any residual SiH groups in this composite with complex 3-D structure could still be removed using heat and ammonia after formation of the sandwich.

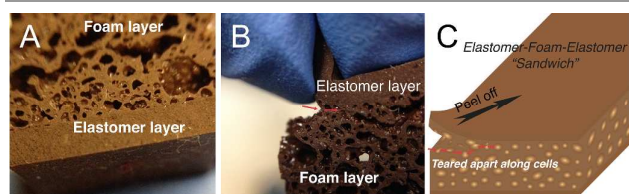


Figure 4. A “elastomer-foam-elastomer sandwich” composite (A) cross-section of the “sandwich structure”, (B) and (C) “Elastomer layer” being peeled from the “foam layer” showing cohesive failure of the foam.

Thermal conductivity was also affected by the presence of lignin in silicone composites. As shown in Table 3, the thermal conductivity of lignin-silicone elastomers or foams were less ($0.15\text{--}0.18\text{ W m}^{-1}\text{K}^{-1}$) than silicone rubber ($\sim 0.25\text{ W m}^{-1}\text{K}^{-1}$).³³ Lower thermal conductivity was also observed for lignin-silicone elastomer that had not been treated by either heat or ammonia (E-41, Table 3). As with the treated materials, lower conductivity may be attributed to the interfacial thermal resistance of lignin with silicone matrix.³⁴ The thermal conductivity of lignin-silicone foams was lower than elastomer due to the porous morphology.

Table 3. Thermal conductivity of silicone foam, and lignin-silicone elastomer/foams

Sample code	Lignin content (%)	Density (g/cm^3)	Thermal conductivity ($\text{W}/(\text{m}\cdot\text{K})$)
SF	0	0.81	0.181
E-41	41	1.13	0.175
F-25	25	0.65	0.166
F-41A	41	0.60	0.148

Discussion

Flammability

There are three key requirements for combustion: heat, oxygen and fuel.³⁵ During this test, heat and oxygen were provided by the environment. The fuel in these composites included residual Si-H groups > lignin > methylsiloxanes, sorted by reactivity in descending order. We consider each in turn.

Hydrosilanes are very sensitive to oxidation. Thermodynamics favor the cleavage of a relatively weak SiH bond to form a strong SiO bond (net difference, about 200 kJ mol^{-1}).³⁶ Undesired and explosive oxidation of SiH compounds in industry has been reported with hydrogen-rich silicones and, more dramatically, silane gas.³⁷ It is, therefore, not surprising that the concentration of SiH groups is the key parameter associated with the high flammability of silicone-lignin composites. However, as SiH groups were partially removed by thermolytic oxidation or more effectively with base (F-41B and D, Figure 2), the thermal stability of the composites dramatically increased to a level that exceeds both pure silicone and lignin (Figure 5).

Dimethylsilicones are thermally stable even above $300\text{ }^\circ\text{C}$. At higher temperatures, silicone equilibration (and depolymerization, Figure 5) begins and at yet higher conditions, the methyl groups in silicone elastomers undergo oxidation to give silanols.²⁴ In the case of an elastomer, flames typically spread along the air interface converting methylsiloxanes into a silica layer on the surface. That is, the surface is intumescent and forms intact silica chars following exposure to a flame, with an increase in volume. The char acts to effectively shield heat and mass transfer (see ESI†).³⁸

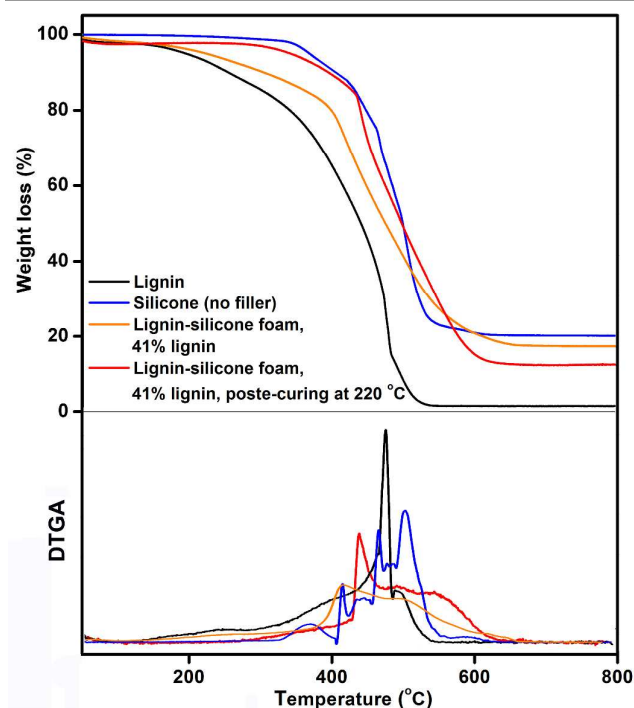


Figure 5. TGA and DTG curves of lignin, silicone (no filler), and lignin-silicone composites performed in an air environment.

The char yield of lignin is normally around 80 wt% and a decrease in flammability is noted once the material is thermally treated beyond its degradation temperature to facilitate forming of char coating.

Thermal Stability

The data in Table 1 and Figure 5 show a synergy in the behaviour of silicones and lignin in producing composites with enhanced thermal stability. The presence of lignin in the silicone *increased* the temperature of decomposition of the composite (Figure 5). This is a consequence of changes in lignin inside the composite during heating. The lignin-silicone foam lost about 20% by weight from 200 to 350 °C, consistent with the char yield of lignin, which is normally around 80 wt%. The enhanced thermal stability of the composite after thermal post-treatment at 220 °C for 12 h (Figure 5), close to that of pure silicone, is a consequence of repolymerization of lignin which results in a more thermally stable structure.^{39, 40} Moreover, the lignin char reduces the diffusion of oxygen and led to a slower oxidative degradation rate.¹⁷

Lignin also slowed down the decomposition rate of composites in the temperature range between 450 to 600 °C (Figure 5). With an increase of temperature, free radicals will be generated from homolytic scission of Si-CH₃ and C-H bonds, which normally accelerates the decomposition of silicones.²⁴ However, as a phenolic antioxidant lignin can capture these radicals, protecting silicone from radical degradation.¹³

Silicone elastomers and foams have been widely used as thermal insulation materials, due to their unique properties, including thermal stability, low thermal conductivity, and elasticity etc. However, silicones are also more expensive than carbon-based polymers, which is a disincentive in commerce. Incorporating much less expensive lignin into silicones provides an economic benefit. What was more surprising is that this filler, once treated properly, led to composites with significantly enhanced thermal stability and flame retardancy.

Frequently, the use of renewable materials is seen as a trade off between the benefits of “green” technology against a loss of desirable properties. Lignin, a naturally occurring, renewable, biodegradable amorphous polyphenol polymer shows that no compromise is necessary in this application. The presence of lignin in silicone elastomers or foams reduces thermal conductivity, reduces flame spreading, and increases thermal stability and, not least, reduces the cost when compared to pure silicones.

Conclusions

Lignin can be integrated using a simple and effective method into silicone elastomer matrices. The resulting composites have properties that are readily controlled by varying formulation and processing conditions. If untreated, the composites were very flammable, due to residual Si-H groups. The fire resistance was improved to a V-1 rating of the UL-94 test once the residual Si-Hs were removed using NH₃ vapor. Enhanced flame retardancy, the V-0 rating, could be obtained following an additional thermal post-treatment beyond the critical temperature for lignin decomposition. In spite of the high energy content of the lignin, the composites were surprisingly thermally stable, to a degree comparable to pure silicone elastomers or foams, provided they were post treated. The lignin-silicone composites also had low thermal conductivities that were comparable to pure silicone foams.

Acknowledgements

We acknowledge with gratitude the financial support of the Natural Sciences and Engineering Research Council of Canada (NSERC) and Sentinel: NSERC Research Network on Bioactive Paper. We thank Weyerhaeuser for the gift of softwood lignin, and the FIBRE network for providing a travel grant to JZ to permit collaborative work in France. We also thank Dr. James Cotton, Ahmed Ali Mahmoud Ahmed, Mustafa Morsy, and Loic Riggenbach in Department of Mechanical Engineering, McMaster University for thermal conductivity measurements.

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