

FLAMMABILITY STUDIES OF SILICONE AND PHENOLIC RESINS AND THEIR COMPOSITE LAMINATES

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ABSTRACT

The fire performance of neat silicone and phenolic resins and their composite laminates was evaluated by testing in a cone calorimeter under an incident heat flux of 50 kW/m². For neat resins, the addition cure silicone resin had peak heat release rate of 130 kW/m² while the phenolic resins had peak heat release rates of 400 kW/m². The neat condensation cure phenyl silicone resin had peak heat release rate of 100 kW/m² while the methyl silicone resin had peak heat release rate of 20 kW/m². For composite laminates using approximately 60 volume percent of E-glass fabric, the addition cure silicone resin had a peak heat release rate of 70 kW/m² while the phenolic resin composite had a peak heat release rate of 60 kW/m². The condensation cure methyl silicone resin composites were essentially non-burning and had peak heat release rates less than 10 kW/m². No fire retardant additives were used in fabricating silicone resin composites. These results indicate that silicone resins have low flammability compared to that of phenolic resins. However, the flexural strengths of the silicone resin composites were weaker than the phenolic resin composites.

1. INTRODUCTION

Silicone resins are known for their high thermal stability and low flammability, among other unique properties [1,2]. They are good candidates as matrices for fabricating fiber reinforced polymer matrix composites [3]. These composite materials have the potential to be used in structural applications with stringent fire requirements such as the interiors of airplanes, offshore oil platforms, automobiles, trains, etc.

In 1995 a project funded by the Federal Aviation Administration (FAA) was initiated to study the flammability of silicone resin composites and nanocomposites for potential use in the next-generation aircraft interiors. In this study, both addition and condensation cure silicone resins were investigated. By incorporating fillers, a variety of compositions were formulated. These materials were burned in the cone calorimeter to determine the impact of filler morphology and structure on flammability. In addition, mechanical properties of these composites were measured. Two papers have been published based on the flammability studies of these composite materials [1,2]. Another paper will be submitted for publication based on the nanocomposites work [4].

In the first paper in this series [1] we reported the flammability of silicone resins with the general formula, (PhSiO_{1.5})_x(MeSiO_{1.5})_{0.75-x}(ViMe₂SiO_{0.5})_{0.25} (x=0, 0.25, 0.5, 0.75), cured by hydrosilylation. Within this series, the peak heat release rates varied between 100 and 150

kW/m² at an incident heat flux of 50 kW/m². Higher phenyl content resins had higher heat release rates, CO and smoke yields. Fillers such as chopped fibers greatly improved the char integrity of the filled resins after fire testing. In the second paper of this series [2], the flammability of methyl resins cured by a Si-OH/Si-OH condensation were studied. When cured, the methyl resins had very low heat release rates. Composite laminates prepared from the resins using either Nicalon[®] fabric or E-glass fabric were ignition-resistant and produced very little CO or smoke.

Phenolic resin composites are currently used in many aircraft interiors. However, phenolic resins are difficult to process and the evolution of formaldehyde during cure remains a health and safety concern for workers handling the resins. [5]. The present paper describes the cone calorimetry data of silicone and phenolic resins and their composite laminates. In addition, the mechanical strengths of these materials are presented.

2. EXPERIMENTAL

2.1 Materials. The addition cure silicone resin (PhSiO_{1.5})_{0.75}(ViMe₂SiO_{0.5})_{0.25} and the condensation cure methyl silicone resin were obtained from Dow Corning Corp [1,2]. The condensation cure phenyl silicone resin was purchased from Gelest Inc., Tullytown, PA. The 6070 phenolic resin was purchased from CytecFiberite, Inc., Orange, CA. The RPMS 307T35 phenolic resin was obtained from Georgia-Pacific Resins, Inc., Ukiah, CA. The MXB 6070/7781 phenolic resin/E-glass prepreg was purchased from CytecFiberite, Inc., Orange, CA. The heat-treated Style 7781 E-glass fabric was obtained from Clark-Schwebel, Anderson, SC. All other reagents were commercially available.

2.2 Measurements. Thermal gravimetric analyses were recorded on a DuPont 592 TGA analyzer. During the TGA analysis a heating rate of 10 °C/min over a temperature range of 25-1000 °C was used. The flow rate was 150 cm³/min of helium or air. Heat release rates were measured on a cone calorimeter (Custom Scientific Instrument) under an incident heat flux of 50 kW/m².

2.3 Fabrication of Neat Silicone Resin Plaques. Only the addition cure silicone resin was used to make plaques. In a typical experiment, toluene was removed from the resin solution by rotary evaporation. The solid resin was melted in a glass beaker at 100 °C in an oven. The beaker was removed from the oven and a measured amount of a crosslinker was stirred in (SiH/Vi=1.0). The mixture was allowed to cool down to about 55 °C and then a catalyst-inhibitor mix was stirred in. The amount of Pt in the resin mix was 2-4 ppm based on the weight of resin and crosslinker. The mix was degassed in a vacuum oven and then poured into a preheated aluminum mold. The mold was placed in the curing oven at 60 °C and the temperature was slowly increased to 150 °C. The temperature was held at 150 °C for 1 hour and then the oven was allowed to cool down. The cured resin plaque was removed from the mold and postcured at 180 °C for 5 hours.

2.4 Fabrication of Neat Phenolic Resin Plaques. In order to make void free plaques of phenolic resins, a slow cure method lasting several days was developed. The resin was degassed in a vacuum oven at room temperature to remove some solvent. The resin was then poured into an aluminum mold and curing was started in an air circulating oven at 60 °C. The temperature was raised 5 °C every 24 hours. After 72 hours, the gelled resin plaque was carefully removed from the mold and placed between two steel plates. Pieces of a teflon coated porous glass fabric were placed between the steel plates and the resin plaque. Further cure was started in an air circulating oven at 70 °C and the temperature was raised 5 °C every 24 hours. After the temperature reached 100 °C, it was increased 5 °C every 10 hours. The maximum cure temperatures were 145 °C and 160 °C for the CytecFiberite resin and the Georgia-Pacific resin, respectively.

2.5 Fabrication of Silicone Resin Composite Laminate. The procedures for fabricating condensation cure methyl silicone resin composites have been previously described [2]. Similar procedures were used for the addition cure silicone resin. Approximately 1 m² piece of E-glass fabric was placed on corrugated aluminum foil supported by a metal screen. A toluene solution of the resin, catalyst and inhibitor was sprayed onto the fabric. After drying overnight in a fume hood, the dry prepreg was cut into sixteen 9" squares which were stacked, all warps parallel, and placed inside a vacuum bag. The layup was cured in an autoclave using a combined debulk and cure cycle. The laminates were then postcured in an air circulating oven. The corresponding temperatures were 150 °C and 180 °C. The fiber contents of the laminates have been reported along with mechanical properties.

2.6 Fabrication of Phenolic Resin Composite Laminates. One roll of commercial prepreg was procured from CytecFiberite. The same type of prepreg is also utilized by Boeing in aircraft interiors. The 9" square sections were cut from the prepreg roll and stacked with all warps parallel. The prepreg stack containing 16 plies was cured in a heated press using the conditions recommended by CytecFiberite. Laminates were also fabricated using a vacuum bag/autoclave cure according to the recommendations from CytecFiberite.

2.7 Three-Point Flexure Testing. Neat resin and composite specimens were evaluated by three-point flexure testing in accordance with ASTM D790. The neat resin specimens were 2" long, 0.5" wide and nominally 0.125" thick. The span to thickness ratio for the neat resin specimens was 16. The specimens were tested in an Instron test frame using a crosshead speed of 0.1"/min. The composite specimens were 4" long, 0.5" wide and nominally 0.125" thick. The span to thickness ratio for the composite specimens was 32. The composite specimens were also tested at a crosshead speed of 0.1"/min.

2.8 Cone Calorimetry Fire Testing. Neat resins and composite specimens were tested in a cone calorimeter under a radiant heat flux of 50 kW/m². Both sets of samplers were 4" squares and nominally 0.25" thick. The bottom and edges of the specimens were wrapped with aluminum foil. The specimens were then placed into a sample holder and covered with a wire grid. This was done to prevent loss of material after it was observed that some resin specimens fractured and popped out during test. The surface area exposed to the radiant

flux was approximately 0.007136 m². The sample holder and the wire grid would act as heat sinks during the test and might have influenced the test results. The neat condensation cure silicone resins were cured at 200 °C for 16 hours and crushed to powder form for fire testing. No wire grid was used when the condensation cure silicone resin composite was burned.

4. RESULTS AND DISCUSSION

3.1 Neat Addition Cure Silicone Resin and Phenolic Resins. The heat release rates, CO and smoke yields are listed in Table I. The peak heat release rates measured by cone calorimetry studies have been used to determine the flammability of materials [6]. Both phenolic resins had markedly higher peak heat release rates (350-400 kW/m²) than the silicone resin (140 kW/m²). In addition, the phenolic resins had higher CO and smoke yields. These results are significant because no reinforcing fibers or other additives were used during the fabrication. As a result, the values reflect the inherent flammability of the two sets of materials. The plots of heat release rates, CO and smoke yields are shown in Figures 1-3.

Table I. Cone calorimetry data of neat silicone resin (PhSiO_{1.5})_{0.75}(ViMe₂SiO_{0.5})_{0.25} and phenolic resins.

Resin	Peak Heat Release Rate (kW/m ²)	Average CO Yield (kg/kg)	Average Specific Extinction Area (m ² /kg)
CytecFiberite Phenolic	414	0.0106	229
GP Phenolic	358	0.0167	230
Silicone Resin	143	0.0002	147

The 3-point flexure testing data (measured at ambient conditions) of neat resins are shown in Table II. All the neat resin specimens exhibited brittle failure during flexural testing. The presence of voids in the phenolic resin plaques significantly reduced flexural strength. Besides voids, microcracks were also visible in the phenolic plaques. As void and microcrack contents decreased, the flexural properties of the resin improved significantly (Table III). The best properties were observed in the void and microcrack free plaques fabricated by the slow cure method.

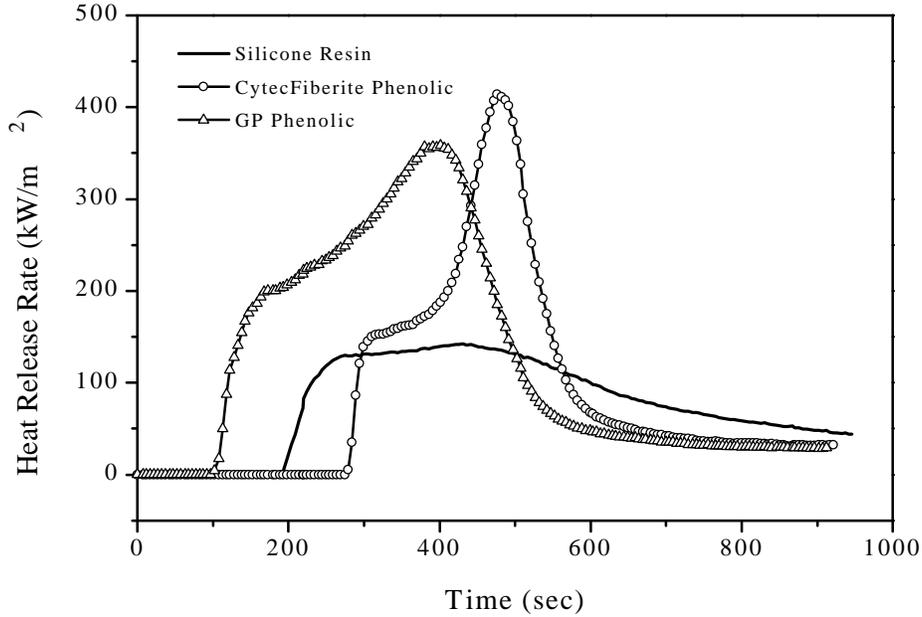


Figure 1. Comparison of the heat release rates of an addition cure silicone resin, $(\text{PhSiO}_{1.5})_{0.75}(\text{ViMe}_2\text{SiO}_{0.5})_{0.25}$, and two commercial phenolic resins.

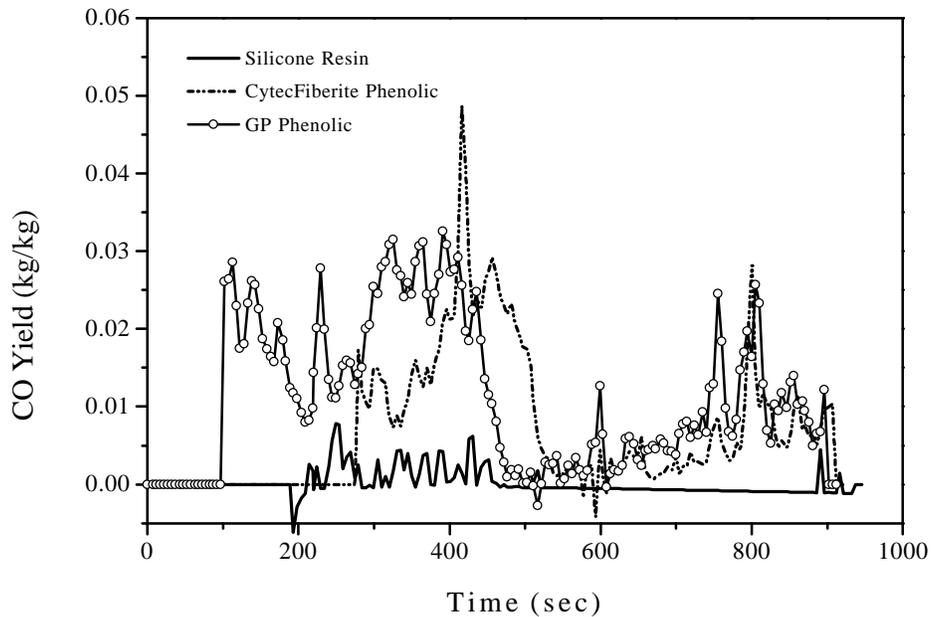


Figure 2. Comparative CO yields from a neat silicone resin, $(\text{PhSiO}_{1.5})_{0.75}(\text{ViMe}_2\text{SiO}_{0.5})_{0.25}$, and two commercially available phenolic resins burned in a cone calorimeter at an incident heat flux of 50 kW/m^2 .

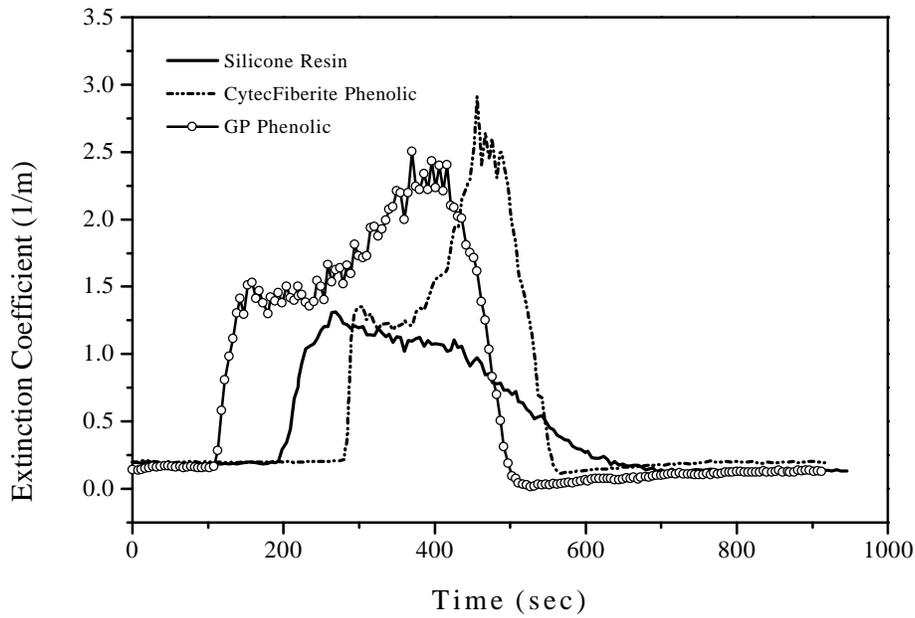


Figure 3. Comparison of the extinction coefficients of an addition cure silicone resin, $(\text{PhSiO}_{1.5})_{0.75}(\text{ViMe}_2\text{SiO}_{0.5})_{0.25}$, and two commercial phenolic resins.

Compared to the phenolic resins, the flexural properties of the silicone resin were poor, regardless of the void content in the phenolic resin. However, all these resins are brittle in nature.

Table II. Three-point flexure testing data of neat silicone resin $(\text{PhSiO}_{1.5})_{0.75}(\text{ViMe}_2\text{SiO}_{0.5})_{0.25}$ and phenolic resins.

Resin	Strength (ksi)	Modulus (ksi)	Strain (%)
CytecFiberite Phenolic	24.3	737.7	3.38
GP Phenolic	24.8	714.7	3.66
Silicone Resin	4.1	153.4	4.72

Table III. Effect of voids and microcracks on three-point flexure testing data of neat CytecFiberite phenolic resins.

Content of Voids and Microcracks	Strength (ksi)	Modulus (ksi)	Strain (%)
More	5.9	645.4	0.93
Less	13.9	722.9	1.92
None	24.3	737.7	3.38

Thermogravimetric analysis (TGA) in a Helium atmosphere was also utilized to compare the thermal stability of addition cure silicone resin and phenolic resins (Figure 4). Cured resin samples were obtained from the neat resin plaques fabricated for the fire and mechanical tests. A weight loss of approximately 1.2% was observed at about 200 °C for the silicone resin. It is speculated that the loss of unreacted crosslinkers may be responsible for the weight loss even though the resin plaque was postcured at 180 °C for 5 hours.

Both phenolic resins started losing weight below 100 °C. The 5% weight loss temperatures for both phenolic resins were significantly lower than the addition cure silicone resin. The phenolic resin plaques were cured using a very slow cure cycle lasting over several days, with maximum cure temperatures of 145 and 160 °C, respectively. It appears that the plaques were not fully cured and therefore, further curing occurred during TGA experiments with a loss of cure by-products. However, it is not fully understood why weight loss occurred below 100 °C when the final cure temperatures were higher. The total weight loss after heating to 1000 °C was significantly higher for the phenolic resins compared to the silicone resin.

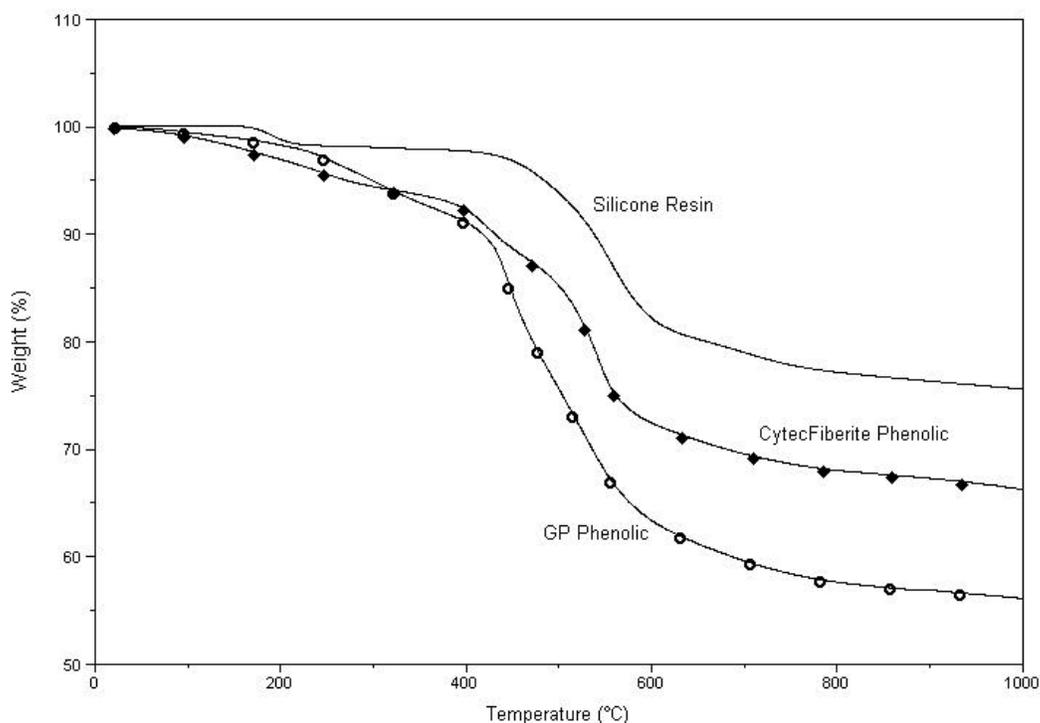


Figure 4. TGA (Helium atmosphere) of silicone resin $(\text{PhSiO}_{1.5})_{0.75}(\text{ViMe}_2\text{SiO}_{0.5})_{0.25}$ and phenolic resins.

The TGA results of the resins in air are shown in Figure 5. The thermal stability of the addition cure silicone resin was slightly lower in the air atmosphere compared to those in helium. The weight loss after heating to 1000 °C was approximately 47%. The thermal stability of both phenolic resins in air was substantially lower than the silicone resin. The

5% weight loss temperatures were just above 300 °C, slightly higher than the values measured in helium. The weight loss at the lower temperatures is probably due to further curing and loss of by-products as well as loss of previously trapped volatiles from initial cure. Since the experiments in air were conducted approximately one month after those in helium, it is possible that the time delay influenced the equilibrium of the trapped volatiles in the resin samples. More volatiles might have escaped during storage resulting in reduced weight loss during early stages of TGA experiments in air. Both phenolic resins exhibited complete weight loss at approximately 600 °C. A summary of the TGA data is shown in Table IV.

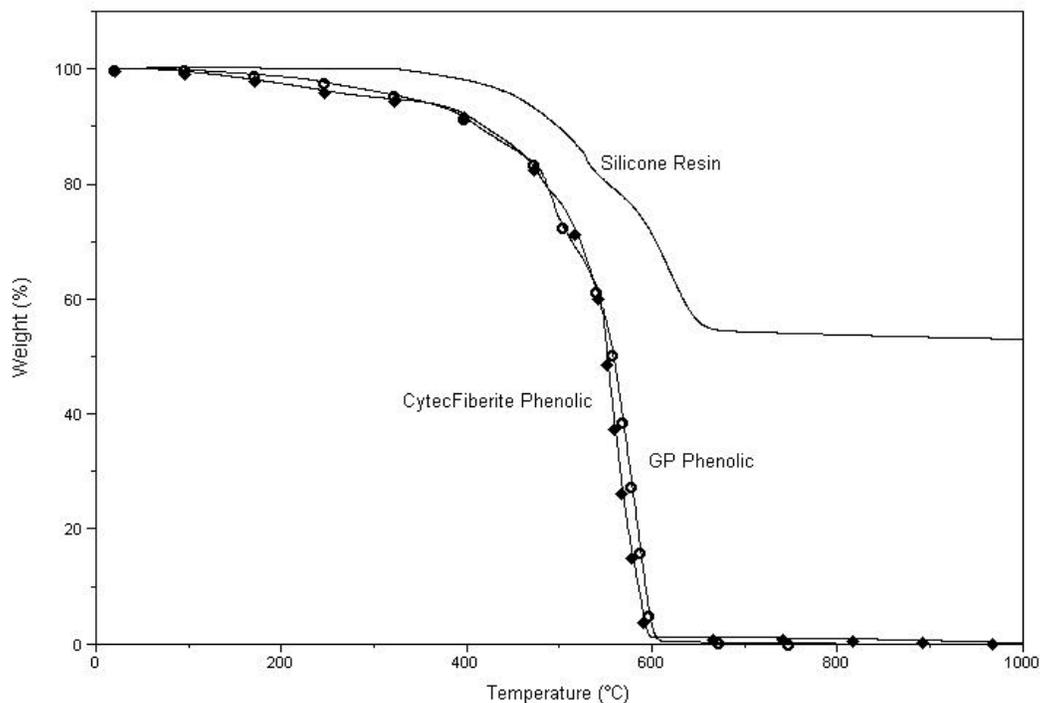


Figure 5. TGA (in air) of silicone resin $(\text{PhSiO}_{1.5})_{0.75}(\text{ViMe}_2\text{SiO}_{0.5})_{0.25}$ and phenolic resins.

Table IV. Thermal properties of silicone and phenolic resins.

Resin	Helium		Air	
	T_{d5} (°C) ^a	W_{1000} (%) ^b	T_{d5} (°C) ^a	W_{1000} (%) ^b
CytecFiberite Phenolic	272	66	308	0.05
GP Phenolic	299	56	335	0.05
Silicone Resin	484	76	456	53

^a 5% weight loss temperature. ^b Weight percentage of the residue after heating to 1000 °C.

3.2 Composite Laminates of Addition Cure Silicone Resin and Phenolic Resin. The heat release rates, CO and smoke yields are listed in Table V. It should be noted that the phenolic resin composite had a lower heat release rate, CO and smoke yields compared to the neat resin. Based on the appearance of the charred residue (the phenolic resin composite had white powder deposition), it is speculated that fire retardants were used in the commercial phenolic resin prepreg. However, no fire retardant additives were used in the silicone resin composite. The plot of heat release rates is shown in Figure 6.

Table V. Cone calorimetry data of E-glass fabric reinforced silicone resin ($(\text{PhSiO}_{1.5})_{0.75}(\text{ViMe}_2\text{SiO}_{0.5})_{0.25}$) and phenolic resin composite laminates.

Resin	Fiber Volume (%)	Peak Heat Release Rate (kW/m^2)	Average CO Yield (kg/kg)	Average Specific Extinction Area (m^2/kg)
Fiberite Phenolic	59.7	59	0.021	55
Silicone Resin	61.7	72	0.009	102

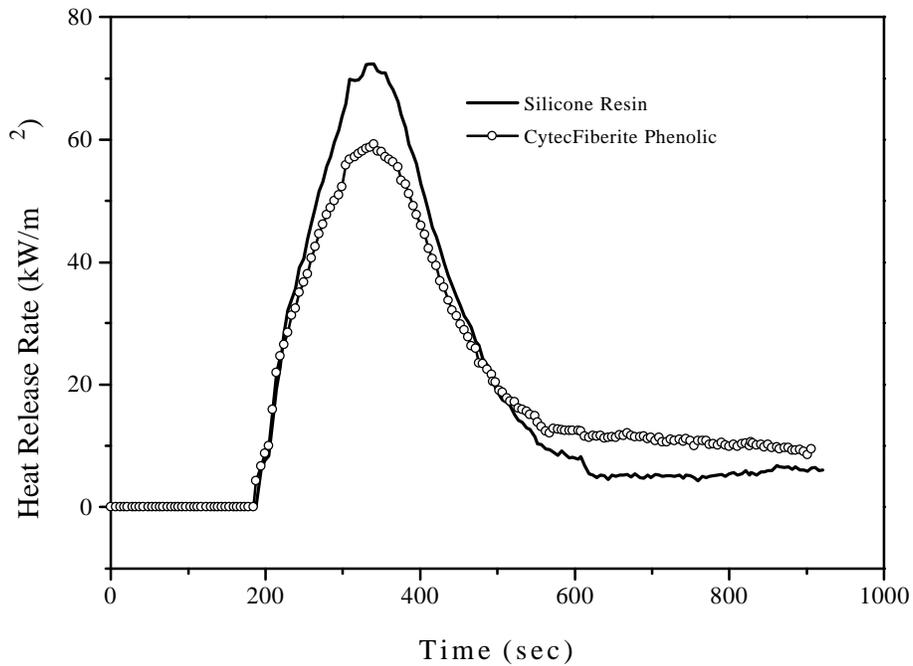


Figure 6. Heat release rate of silicone resin ($(\text{PhSiO}_{1.5})_{0.75}(\text{ViMe}_2\text{SiO}_{0.5})_{0.25}$) and phenolic resin composite laminates.

The results from the 3-point flexure testing of the silicone and phenolic resin composite laminates are shown in Table VI. All the composite specimens exhibited compressive failure at the top surface during flexural testing. Overall, the phenolic resin composite performed better than the silicone resin composites. Both the flexural modulus, strain to

break and strength of the phenolic resin composite was higher than the silicone resin composites. However, the silicone resin composites were fabricated from heat treated glass fibers without any sizing to enhance fiber-matrix interface. No attempts were made to screen different coupling agents or optimize the processing conditions used to fabricate the composite. As such, the values obtained for the silicone resin composite are unoptimized and represent minima which can be further improved upon. In contrast, the values for the commercially available phenolic resin composite may have fibers with proprietary sizings to improve interfacial adhesion.

Table VI. Three-point flexure testing data of E-glass fabric reinforced silicone resin ($(\text{PhSiO}_{1.5})_{0.75}(\text{ViMe}_2\text{SiO}_{0.5})_{0.25}$) and phenolic resin composite laminates.

Resin	Fiber Volume (%)	Strength (ksi)	Modulus (Msi)	Strain (%)
CytecFiberite Phenolic	59.7	67.7	3.7	2.00
Silicone Resin	61.7	38.8	3.2	1.28

3.3 Neat Condensation Cure Methyl and Phenyl Silicone Resin and Phenolic Resins.

These silicone resins are known as silsesquioxanes [7], which can be represented with the general formula $(\text{RSiO}_{1.5})_n$, where R = Me or Ph. The heat release rates of the uncured and cured methyl silicone resin have been reported earlier [1]. The peak heat release rate of the methyl resin was 65 kW/m^2 before curing and 10 kW/m^2 after curing. The uncured phenyl resin had a peak heat release rate of 130 kW/m^2 and it decreased to 100 kW/m^2 after curing. For comparison, the TGA and heat release rates of both resins after curing are shown in Figures 7 and 8. From this data, it is clear that the methyl silicone resin has better thermal and flammability properties than the phenyl resin. However, both silicone resins have lower heat release rates than phenolic resins (cf. Figure 1).

3.4 Composite Laminates of Condensation Cure Methyl Silicone Resin and Phenolic Resins.

The methyl silicone resin was fabricated into laminates using Nicalon[®] fabric and E-glass fabric [2]. In both cases, the peak heat release rates were below 10 kW/m^2 at an incident heat flux of 50 kW/m^2 . Even with continuous sparking, neither of the composites ignited during the course of the test (20 minutes). A comparison of heat release rate data obtained for the methyl and phenolic resin composites is shown in Figure 9. The tensile strengths of Nicalon[®] and E-glass fabric composite laminates were 41.3 and 28.0 ksi, respectively [2]. The flexural strength was not measured. The composites retained their shape after fire testing and delamination was hardly seen. The burned samples retained up to 78% of their initial tensile strengths.

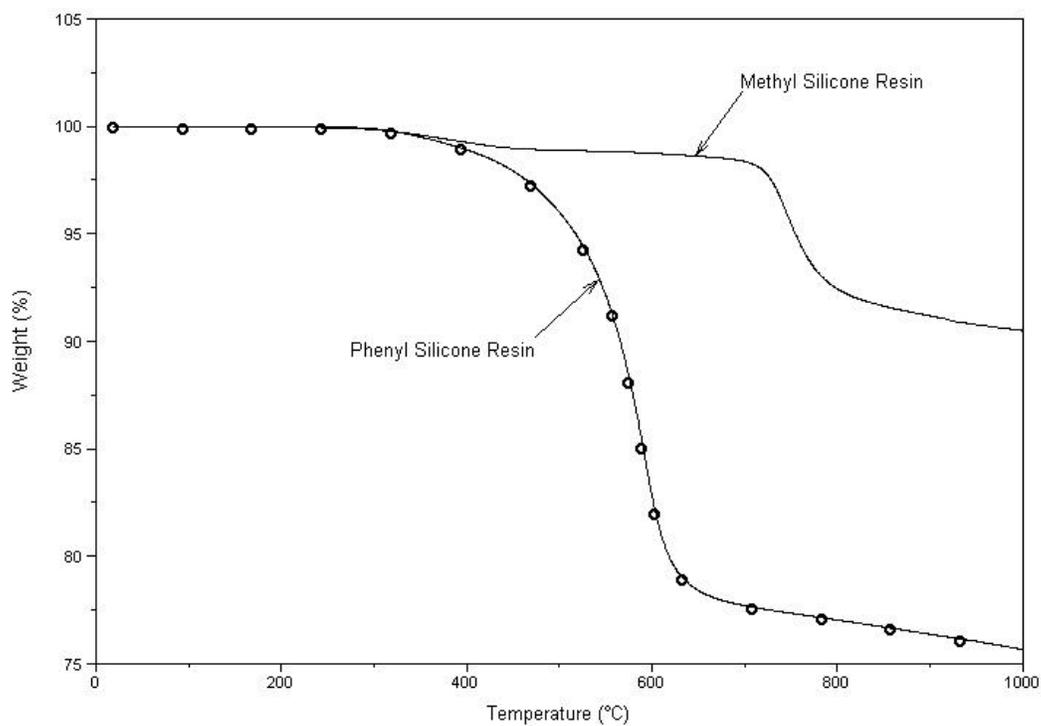


Figure 7. TGA (Helium atmosphere) of condensation cure methyl and phenyl silicone resins.

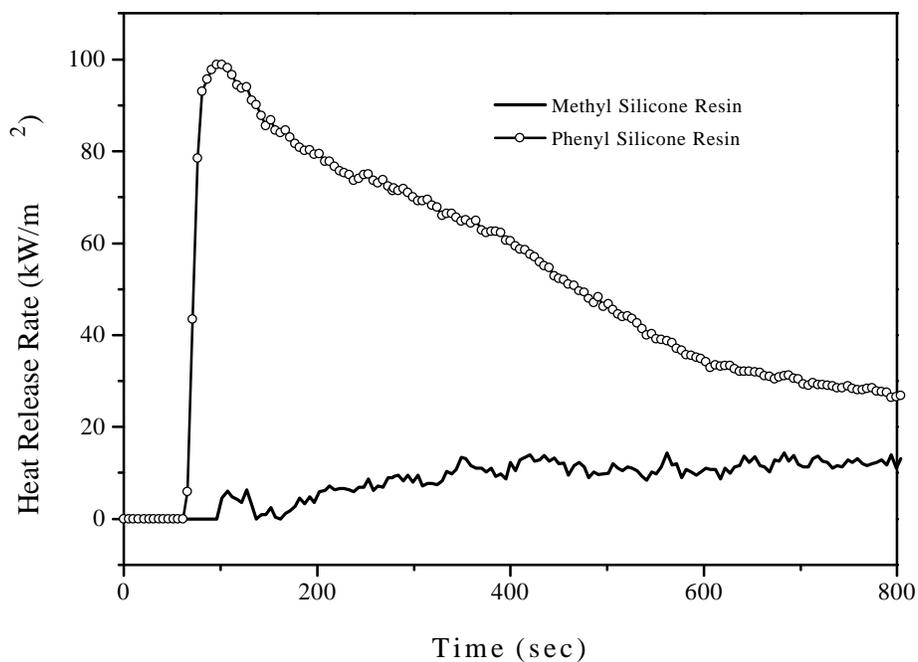


Figure 8. Heat release rates of condensation cure methyl and phenyl silicone resins.

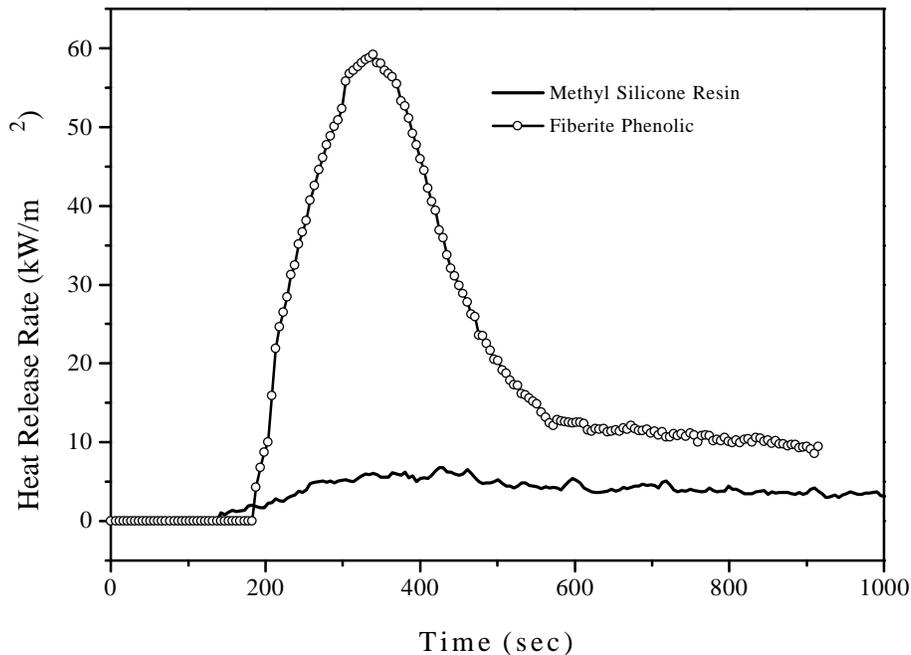


Figure 9. Heat release rates of condensation cure methyl silicone resin and phenolic resin composites.

4. CONCLUSIONS

All silicone resins had lower peak heat release rates, CO and smoke yields than phenolic resins. Composite laminates of the addition cure silicone resin had similar peak heat release rate compared to composites of the phenolic resin. The condensation cure methyl silicone resin composites were essentially non-burning. The mechanical strengths of silicone resins were lower than those of phenolic resins. No fire retardant additives were used in fabricating silicone resin composites. This study demonstrates that silicone resin composites are good candidates for fire resistant materials, although further improvements in their mechanical properties are still needed.

5. ACKNOWLEDGMENTS

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