

PAPER • OPEN ACCESS

Synthesis of phenolic resin modified silicone rubber utilizing for ablation thermal protection materials

To cite this article: B Q Li *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **504** 012043

View the [article online](#) for updates and enhancements.

Synthesis of phenolic resin modified silicone rubber utilizing for ablation thermal protection materials

B Q Li¹, C He², W Lu³ and J S Wang⁴

¹ Aerospace Research Institute of Materials & Processing Technology, Beijing, 100076, P. R. China

² Aerospace Research Institute of Materials & Processing Technology, Beijing, 100076, P. R. China

³ Aerospace Research Institute of Materials & Processing Technology, Beijing, 100076, P. R. China

⁴ Aerospace Research Institute of Materials & Processing Technology, Beijing, 100076, P. R. China

Corresponding author and e-mail: C He, wewewenn@163.com

Abstract. Phenolic resin modified silicone rubber (PMS) was synthesized via hydrosilation reaction between novolak with allyl group and silicone rubber containing Si-H groups. The chemical structure of PMS was characterized by FT-IR, ¹H NMR and GPC. The thermal stability of PMS was characterized through TGA and compared with traditional single phenyl silicone rubber (PSR). Ablation properties was measured through muffle furnace ablation test. Compared with PSR, the PMS has better thermal stability and wider pyrolysis temperature range. The carbon yield after ablation was promoted greatly and stable ablation layer was obtained.

1. Introduction

Ablative materials are at the base of entire aerospace industry. Polymer based ablative materials represent the largest and most versatile class of thermal protection materials. [1] Silicone based ablation matrix including silicone rubber was always adopted in ablative thermal protection materials. [2]

Silicone rubber has good thermal stability and toughness, however, most of the ablative applications of silicone rubber involve low to moderate heat fluxes and shear forces, because of its low ablation layer strength. [3-4] Under aerodynamic heating, silicone rubber pulverizes seriously and mainly realizes thermal protection through thermal barrier mechanism. [5-7] These defects limit the application of silicone rubber greatly. [8]

Many researchers tried to increase ablation efficiency and ablation layer strength of silicone rubber. Several decades ago phenyl siloxane rubber was invented to increase the thermal stability of silicone rubber. [9-10] But the introduction of phenyl group was limited by the synthetic method. Furthermore, many functional fillers were adopted, including carbon fibers, montmorillonite and so on. [11-15] These functional fillers could increase the ablation layer strength of silicone rubber significantly, however, insulation, which has very low thermal protection efficiency, was still the main way for silicone rubber to realize thermal protection. Phenolic resin has high ablation thermal protection efficiency. Compared to other charring matrices, it yields one of the higher amount of char at



hyperthermal environment. [1] Thus it is ideal for increasing ablation layer strength and efficiency of silicone rubber.

In our study, well defined silicone rubber with Si-H groups was synthesized and modified with phenolic resin containing allyl groups. The PMS realized uniform mixing macroscopically. TGA and muffle ablation test showed that the residue weight of PMS was much higher than single phenyl silicone rubber (PSR). The pyrolysis rates were reduced obviously and the pyrolysis temperature range was broadened. The porous carbon layer formed after ablation could induce heat blocking effect, heat radiation at hyperthermal environment. The synthesized PMS could increase the ablation thermal protection efficiency of silicone rubber greatly.

2. Experimental

2.1. Materials

Phenol, oxalic acid, formaldehyde solution and toluene were obtained from Sinopharm Chemical Reagent Co., Ltd. Tetrahydrofuran and acetone were obtained from Tianjin Kemiou Chemical Reagent Co., Ltd. Allyl bromide and potassium carbonate were obtained from J&K Scientific. Octamethylcyclotetrasiloxane and tetramethylcyclotetrasiloxane were obtained from Energy Chemical. Trifluoromethanesulfonic acid and Karstedt catalyst were obtained from Acros Organics. Tetraethyl orthosilicate and hexamethylenetetramine (HMTA) were obtained from Energy Chemical.

2.2. Synthesis of novolac resin.

Phenol (94g) and oxalic acid (5g) was added into round bottom flask. The temperature was raised to 50 °C. When the phenol melted adequately, formaldehyde solution (70g) was added into the flask dropwise and the temperature was raised to 100 °C slowly. After the formaldehyde solution was added completely, the temperature was maintained for another two hours. The crude product was purified via vacuum distillation under 150 °C to obtain the colorless transparent solid novolac resin.

2.3. Allylation of novolac resin

The synthesized novolac resin was dissolved in acetone. Allyl bromide and potassium carbonate was added into round bottom flask. The temperature was raised to 70°C and maintained for 48 hours. Potassium carbonate was removed via filtration and the filtrate was purified through vacuum distillation under 100 °C for 6 hours to obtain the light yellow transparent oily liquid product.

2.4. Synthesis of silicone rubber containing Si-H groups

Certain proportions of octamethylcyclotetrasiloxane and tetramethylcyclotetrasiloxane was added into the round bottom flask and toluene was added equal mass. Under the protection of nitrogen, triflic acid was added slowly, and the temperature was raised to 70 °C and maintained for 5 hours. The solution was precipitated in anhydrous ethanol and the solvents was removed through vacuum extraction to obtain the colorless transparent oily liquid product.

2.5. Synthesis of PMS

Certain proportions of silicone rubber containing Si-H groups and novolac resin with allyl groups were added into round bottom flask and THF was added equal mass. Under the protection of nitrogen, the temperature was raised to 60 °C. Karstedt catalyst was added slowly. The temperature was maintained for another 5 hours to obtain the light yellow transparent solution.

2.6. Curing of PMS

Certain amount of tetraethyl orthosilicate and HMTA was added into the synthesized PMS. The mixture was mixed uniformly and heated to 150 °C with reduced pressure for 2 hours to obtain the transparent light yellow blocks.

2.7. Characterization and measurements

Composition, Component and Microstructure Analysis. The fingerprints and functional groups in the PMS were investigated with FT-IR spectroscopy on a Varian 640. The FT-IR spectra of the pristine silicone rubber and PMS were recorded and compared with respect to the appearing functional groups. The gel permeation chromatography (GPC) instruments used for the evaluation of the molecular weight of silicone rubber and PMS were a SHIMADZU RID-20A refractive index detector, a SHIMADZU LC-20AT high performance liquid chromatography (HPLC) pump, and Styragel HR3, HR4 tetrahydrofuran column. NMR measurements were performed on an Avance 600MHz NMR spectrometer (Bruker) to obtain ^1H NMR spectra. The samples were dissolved in Chloroform-d.

Thermal and Ablation Characterization. TGA was performed to follow the trends of the thermal decomposition process and the thermal stability of the PMS as they were burned in a nitrogen environment on a simultaneous thermal analyzer (STA 449F3). The samples were heated in a platinum crucible from RT to 800 °C in nitrogen atmosphere at a heating rate of 10 °C /min. Muffle furnace ablation test was performed according to HB-5240.

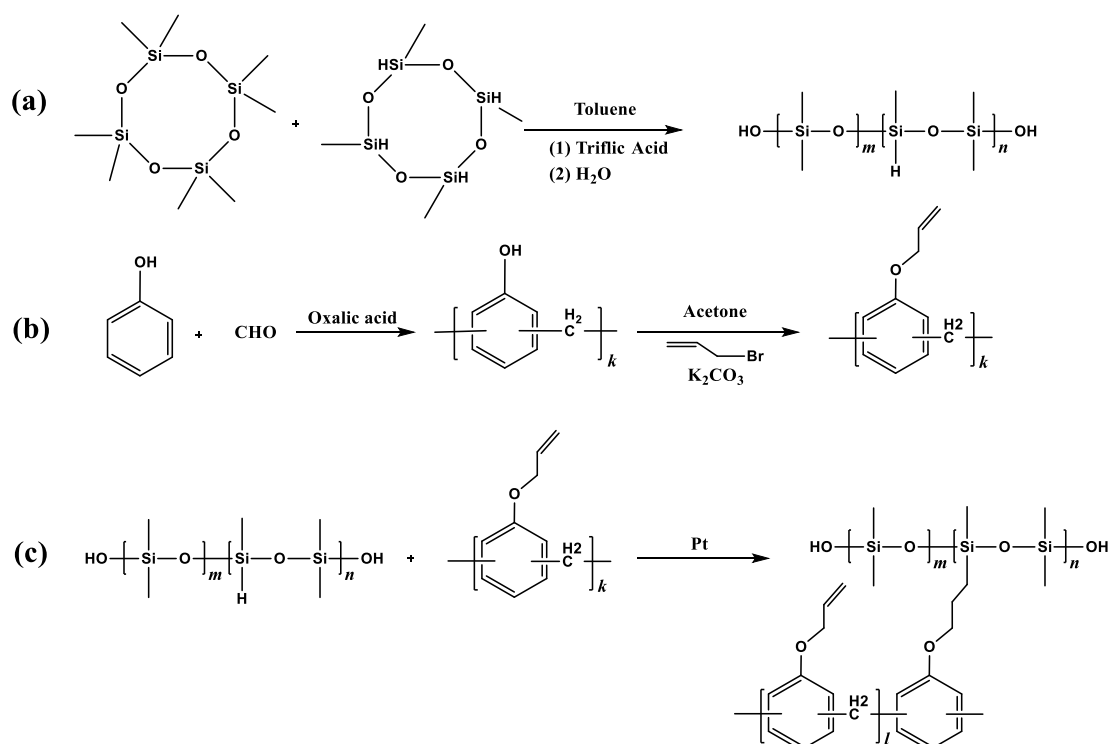


Figure 1. Synthesis route of PMS: (a) synthesis of silicone rubber with Si-H; (b) synthesis of modified phenolic resin; (c) synthesis of PMS.

3. Results and discussion

3.1. Synthesis of PMS.

Table 1. PMS with different phenolic resin content (weight %).

	Silicone Rubber	Phenolic Resin
PMS-1	100	30
PMS-2	100	60
PMS-3	100	90

PMS with different phenolic resin contents were labeled PMS-1 to PMS-3 (Table 1). The chemical structure of the synthesized PMS was characterized by FT-IR (Figure 2A) and GPC (Figure 2B). For

the FT-IR spectra of PMS from PMS-1 to PMS-3, the absorption at 2100 cm^{-1} almost disappeared completely, which was attributed to the stretching vibration of the Si-H bond in the FT-IR spectra of silicone rubber. This was caused by the reaction between Si-H groups of silicone rubber and allyl groups of modified phenolic resin. The absorptions at 1261 and 800 cm^{-1} were attributed to the stretching and rocking vibrations of Si-C. The broad absorption from 1090 to 1020 cm^{-1} was attributed to the stretching vibration of Si-O. The absorption peaks at 3076 cm^{-1} were attributed to the stretching vibration of C-H on the phenylene. All of these absorptions indicated that the modified phenolic resin combined with the silicone rubber.

Compared with the GPC curves of the silicone rubber and the synthesized PMS, the peaks of PMS-1 to PMS-3 moved forward obviously, indicating that the modified phenolic resin was successfully grafted onto silicone rubber. With the increase of modified phenolic resin contents, the allyl groups contents was much more than the Si-H contents, which reduced the reaction trends between the freshly synthesized PMS and silicone rubber containing Si-H. Thus, the molecular weight was decreased with the increase of modified phenolic resin contents.

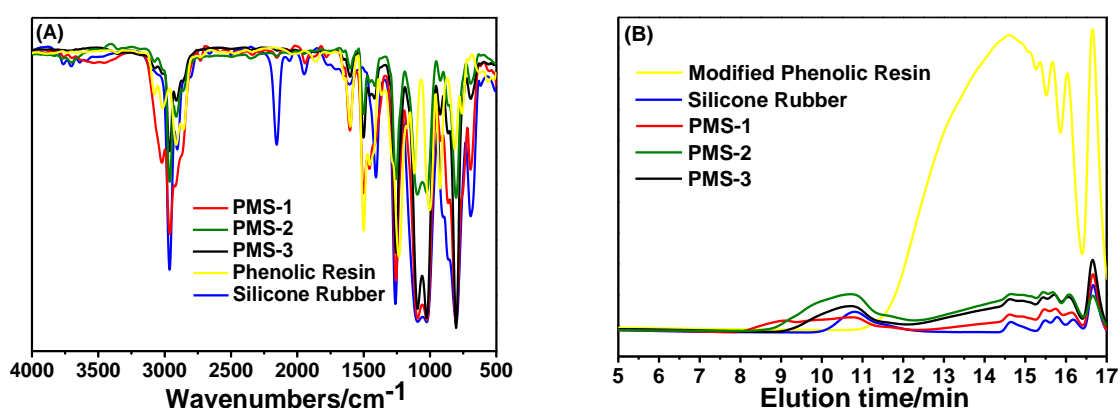


Figure 2. IR spectrum (A) and GPC curves (B) of PMS.

Figure 3 shows the chemical structure and $^1\text{H-NMR}$ spectra of silicone rubber with Si-H and the synthesized PMS. The peak at 0.05 ppm was the signal of hydrogen on the Si-CH₃ (peak a). The peak at 4.7 ppm was the signal of hydrogen on the Si-H (peak b). The peaks at 6.67 to 7.08 ppm were the signals of hydrogen on the phenylene of phenolic resin (peaks d-f). The peaks from 4.3 ppm to 6.1 ppm were the signals of excess allyl groups. The $^1\text{H-NMR}$ spectrum of HBPSE revealed that the peak of Si-H disappeared after reacting with allyl modified phenolic resin, indicating that the phenolic resin had grafted onto silicone rubber successfully.

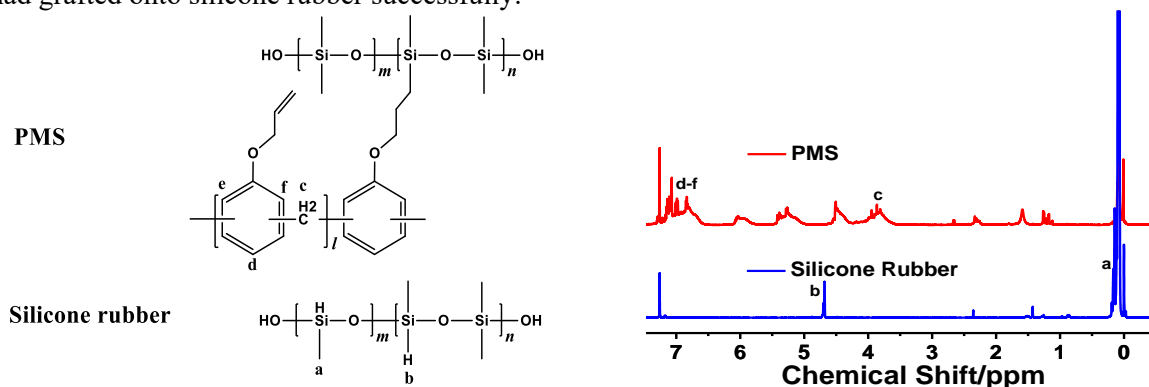


Figure 3. Chemical structure and $^1\text{H-NMR}$ spectra of silicone rubber and PMS.

3.2. Properties of the PMS

Thermal stability of PMS. The TG and DTG curves of PMS from PMS-1 to PMS-3 are shown in Figure 4. The TG curves (Figure 4A) showed that the main mass reduction of PSR and PMS occurred from 300 °C to 600 °C. At the temperature higher than 600 °C, the residual weight of PSR was only 2%, while the residual mass of PMS-1, PMS-2 and PMS-3 were 51%, 60% and 69%, respectively. The residual mass of PMS increased as the modified phenolic resin contents increased, because the rigid molecular chain of phenolic resin could restrain the fraction reaction of siloxane chain, reducing the mass loss of resin matrix effectively.

According to the DTG curves (Figure 4B), two pyrolysis reaction ratio peaks can be found in the temperature range from 300 °C to 450 °C and from 450 °C to 600 °C, in the curves of PSR. However, the pyrolysis reaction ratio peaks of PMS was in the temperature range from 360 °C to 540 °C and from 540 °C to 650 °C. Both the thermal stability and pyrolysis temperature range were enhanced compared with PSR. The pyrolysis ratio of PSR was 1.3%/min, while the pyrolysis ratios of PMS-1 to PMS-3 were 0.32%/min, 0.21%/min and 0.18%/min respectively, which can also be attributed to the high contents of phenolic resin restrained the fraction reaction of the main chain of silicone rubber.

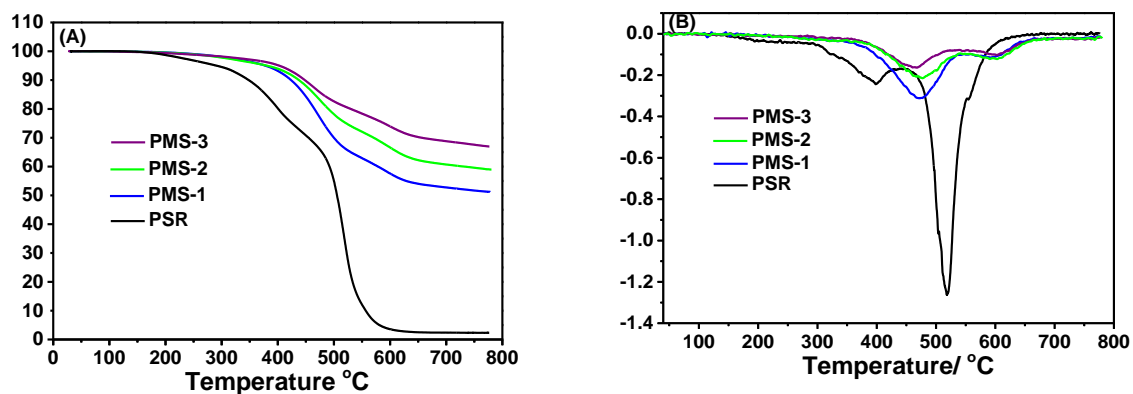


Figure 4. TG (A) and DTG curves (B) of PSR and PMS.

Muffle furnace ablation properties of PMS. Figure 5 shows the muffle furnace ablation test results of PSR and PMS with different phenolic resin contents at 400 °C for 300s. The PMS before ablation was transparent light yellow blocks. The surface of PMS-1 to PMS-3 after ablation was smooth, while the surface of silicone rubber after ablation was rough.

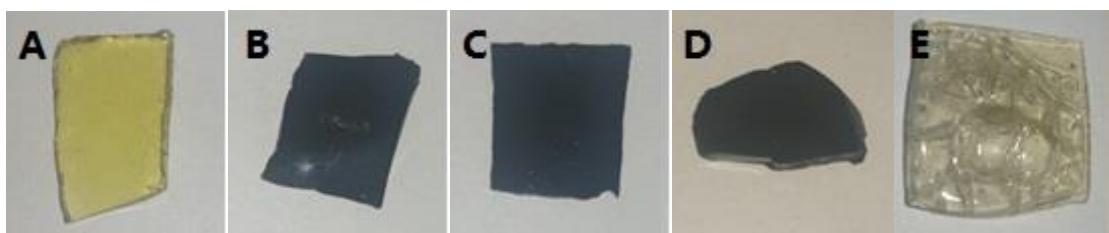


Figure 5. Different phenolic resin contents PMS ablated at 400 °C for 300s (A-before ablation; B-PMS-1; C-PMS-2; D-PMS-3; E-PSR).

Figure 6 shows the muffle furnace ablation test results of PSR and PMS with different phenolic resin contents at 600 °C for 300s. Compared with the ablation results at 400 °C, the surface of PMS-1 to PMS-3 was not smooth and the pure silicone rubber pulverized seriously. PMS-2 had better surface state, while PMS-3 crazed after ablation. This could be attributed to the high contents of phenolic resin, which decreased the toughness of resin before and after ablation.

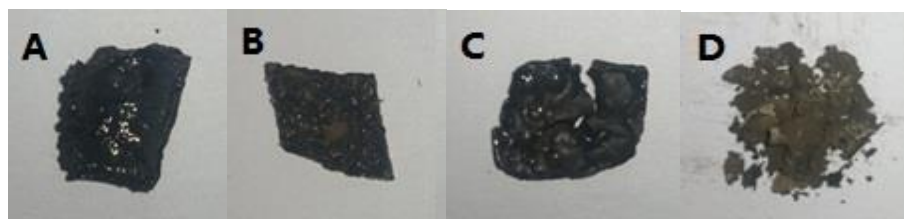


Figure 6. Different phenolic resin contents PMS ablated at 600 °C for 300s (A-PMS-1; B-PMS-2; C-PMS-3; D-PSR).

Table 2 shows the muffle furnace ablation residue results of PMS. At 400 °C, the weight loss of PMS was not obvious. At 600 °C, the residue weight of PMS-1 to PMS-3 was 23%, 44% and 45%, respectively. This phenomenon was conformed to the TGA curves, which indicated the main mass loss of PMS occurred from 400 °C to 600 °C. With the increase of phenolic resin content, the residue after ablation at 600 °C increased obviously, however PMS-2 and PMS-3 nearly have the same residue weight. This could be attributed to the poor compatibility between phenolic resin and silicone rubber when the phenolic resin content was too high, which may decrease the thermal stability of PMS.

Table 2. Muffle furnace ablation residue weight of the PMS.

Temperature °C	400	600
PMS-1	90%	23%
PMS-2	96%	44%
PMS-3	97%	45%

4. Conclusions

In this work, PMS was successfully synthesized by grafting allyl modified phenolic resin onto silicone rubber with Si-H groups. The pyrolysis ratio of PMS was much lower than the PSR. The pyrolysis temperature of PMS ranged from 360 °C to 650 °C and the residue weight was more than 50% at 800 °C. With the increase of phenolic resin content, the residue weight of PMS raised obviously. Muffle furnace ablation test showed that the PMS could form stable carbon layer after ablation at 600 °C for 300s. However, too much phenolic resin content would result in the cracking of resin after ablation, therefore, 100/60 could be a more appropriate reaction proportion of PMS.

References

- [1] Natali M, J M Kenny, and L Torre 2016 *J. Progress in Materials Science*. **84** 192-275.
- [2] Ahmad S et al 2005 *J. Progress in Organic Coatings*,. **54(3)** 248-255.
- [3] Grassie N and I G Macfarlane 1978 *J. European Polymer Journal*. **14(11)** 875-884.
- [4] Oyumi Y 2015 *J. Journal of Polymer Science Part A Polymer Chemistry*. **36(2)** 233-239.
- [5] Shit S C 2013 *J. National Academy Science Letters*. **36(4)** 355-365.
- [6] Thomas M 2012 *J. Journal of Macromolecular Science: Part A - Chemistry*. **3(4)** 585-612.
- [7] Whipple C L and J A Thorne 1966 *J. Rubber Chemistry & Technology*. 1247-1257.
- [8] George K et al 2017 *J. Polymers for Advanced Technologies*. (11).
- [9] Grassie N, K F Francey, and I G Macfarlane 1980 *J. Polymer Degradation & Stability*. **2(1)** 67-83.
- [10] Grassie N, I G Macfarlane, and K F Francey 1979 *J. European Polymer Journal*. **15(5)** 415-422.
- [11] Le H H et al 2008 *J. Plastics Rubber & Composites*. **37(8)** 367-375.
- [12] Torre L, J M Kenny, and A M Maffezzoli 1998 *J. Journal of Materials Science*. **33(12)** 3137-3143.
- [13] Wang J et al 2015 *J. Polymer Degradation & Stability*. **121(3)** 149-156.
- [14] Yang D et al 2013 *J. Composites Part A Applied Science & Manufacturing*. **44(1)** 70-77.
- [15] Zhang J, S Feng, and Q Ma 2010 *J. Journal of Applied Polymer Science*. **89(6)** 1548-1554.