

Synthesis and Effects of MDT Silicone Resin on PMPS-Based Ablative Composites

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ABSTRACT: A novel methylphenyl silicone resin, with M, D, and T units, was synthesized by cohydrolysis and cocondensation method from dimethyldimethoxysilane ($\text{Me}_2\text{Si}(\text{OMe})_2$), phenyltrimethoxysilane ($\text{PhSi}(\text{OMe})_3$), hexamethyldisiloxane, and 1,3-divinyl-1,1,3,3-tetramethyldisiloxane in toluene/water mixture catalyzed by hydrochloric acid and trifluoromethanesulfonic acid. The vinyl end-capped MDT silicone resins were chosen for reinforcement filler to enhance the mechanical properties of silicone-based ablative composites. The effects of resins with various R/Si ratios, vinyl content, and loadings on mechanical properties of PMPS rubbers were investigated. It was revealed that on the premise of good fluidity and processing performance, MDT resin showed excellent reinforcing effect and thermal stability compared with silica. MDT reinforced ablative composite showed satisfactory mechanical and antiablation properties. The linear ablation rate was 0.01 mm/s, which maybe associated with high yield of charred residue in thermogravimetric analysis results. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41571.

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INTRODUCTION

Polymethylphenylsiloxane (PMPS)-based silicone rubber has been widely used as antiablation polymer, such as inhibiting of solid rocket propellants and insulation layer of solid rocket motor or ramjet combustor,^{1–5} due to its excellent thermal stability and higher carbon residual yield.

At present, there are many manual procedures in construction of inhibiting or insulation layer for stick method when used high temperature vulcanization silicone rubber, such as rubber cutting and pasting, which is difficult to ensure the quality and the working efficiency is low. But for room temperature vulcanized (RTV) silicone rubber, casting, spraying, coating, or roller coating methods can be chosen. The advantage is that there are no joints and uneven thickness is much decreasing. Silica (SiO_2) as reinforcing filler has been used to date. But for RTV silicone rubber, too much SiO_2 increases the viscosity, which makes processing and application more difficult.⁶ It was found in previous study that adding 6 phr SiO_2 helped to form helmet in ablative layer surface, but with the increasing of SiO_2 the ablative resistance of composites would decreased. Line ablation rate of 6 and 20 phr silica filled polydimethylsiloxane are 0.11 and 0.34 mm/s, respectively.⁷ It can be concluded that silica is not ideal reinforcing filler for RTV silicone-based ablative composites. Now for silicone-based ablative composites, the research

focused on the fillers, properties, and mechanism of composites.^{8–15} In fact, how to solve the contradiction between properties and good fluidity, processing performance is also one of the key issues to be solved.

Silicone resin, containing $\text{Me}_3\text{SiO}_{1/2}$ units (i.e., M units) and $\text{SiO}_{4/2}$ units (i.e., Q units) is widely used as reinforcing materials for silicone rubber, which exhibits the same reinforcing effect produced by silica but has little influence on the viscosity of the silicone rubbers.^{16–19} However, there is no phenyl group for commercialized MQ silicone resin, which has poor compatibility with PMPS. Phenyl-modified MQ resins were often synthesized by end-capping agents containing the phenyl group, such as methylphenylethoxysilane or dimethylphenylethoxysilane, which are expensive, resulting in limitations to its wide application in preparing MQ silicone resins.^{20,21} So, some derivatives of MQ resins with more sophisticated structures, containing $\text{PhSiO}_{3/2}$ units (i.e., T units) and $\text{MePhSiO}_{2/2}$ units (i.e., D units), such as MDQ, MTQ, MDT, or even MDTQ, have been developed as reinforcing materials for silicone rubber. But few researches about effect of silicone resin on ablative properties were reported.^{13,22}

In this work, vinyl end-capped methylphenyl MDT silicone resins were synthesized as reinforcing filler for PMPS-based silicone rubber. The effects of MDT resins with various R/Si ratios,

Table I. Formulas of the Silicone Rubber Reinforced by MDT

Ingredients	Vinyl-polysiloxanes	Hydrogen-polysiloxanes	MDT resins	silica	Pt catalyst
Fractions	100	8-22	40-240	0	0.01-0.03
	100	5.7	0	20	0.01

Parts per hundred grams of vinyl-polysiloxanes (phr).

vinyl content, and loadings on mechanical properties of PMPS were investigated. Thermogravimetric analysis (TGA) were also investigated in contrast to PMPS reinforced by silica. Finally, the ablative composites reinforced by MDT resin and silica were prepared, and the processing performance, mechanical and ablative properties were studied.

EXPERIMENTAL

Materials and Methods

$\text{Me}_2\text{Si}(\text{OMe})_2$ and $\text{PhSi}(\text{OMe})_3$ were purchased from Xinan Chemicals (Zhejiang Province, China). 1, 3-divinyl-1, 1, 3, 3-tetramethyldisiloxane were supplied by Datian Chemical Auxiliaries Research Institute. Additive liquid PMPS silicone rubber was prepared from vinyl-poly methylphenylsiloxane, hydrogen-PMPS, and Pt catalyst (i.e., $\text{Pt}[(\text{ViMe}_2\text{Si})_2\text{O}]$) in our laboratory. The viscosity and functional group content of the two polysiloxanes are 2800 cp, 3.5 wt %, 150 cps, and 3 wt %, respectively.

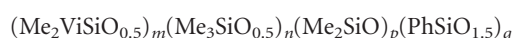
Mechanical tensile tests were performed on a universal testing machine (Shimadzu, AGS-J, capacity 10 kN), at 25°C and around 60% room humidity (RH). The dumbbell-shaped specimens were obtained from cured sheet, and an average of at least three measurements for each sample was recorded. Thermogravimetry was performed using Mettler-Toledo SDTA851e TGA at a heating rate of 10°C/min in an atmosphere of nitrogen. Ablation tests were conducted using oxyacetylene torch according to GJB-323A-96. The samples were compression molded with inner diameter of 2.0 mm.

Preparation of Vinyl End-Capped Methylphenyl MDT Resins

A typical process for preparation of MDT resins is as follows. An appropriate amount of hexamethyldisiloxane (MM), 1,3-divinyl-1,1,3,3-tetramethyldisiloxane (TMDVS), deionized water, toluene, and catalyst (mixture of hydrochloric acid and trifluoromethanesulfonic acid) were added to a four-necked flask and stirred. $\text{Me}_2\text{Si}(\text{OMe})_2$ and $\text{PhSi}(\text{OMe})_3$ were added dropwise to the above solution and the temperature must be held below 25°C in this procedure, and then the reaction mixture was heated to a backflow temperature for 3 h. The organic phase was washed to neutralize and dried. Then, the target resin was

obtained after condensation at 130°C for 5 h. After filtration and removing toluene or MM or TMDVS by evaporation, the vinyl end-capped methylphenyl MDT silicone resins were obtained. Following these procedures, a series of samples with different structures and properties were prepared by changing the composition of the raw materials.

Molecular formula of MDT is as follows,



Preparation of PMPS-Based Silicone Rubber Reinforced by MDT Resins and Silica

Vinyl and hydrogen polysiloxanes, MDT resins, and Pt catalyst were mixed using planetary mixer according to the desired Si-H/Si-Vi ratio. The mixtures were degassed in vacuum and then poured into a mold (120 × 40 × 2 mm³). The curing was conducted at room temperature for 24 h. To ensure the liquidity of gum, 20 phr silica was the upper limit for reinforcement using. Formulas of the silicone rubber reinforced by MDT are listed in Table I.

Preparation of PMPS-Based Ablative Composites

Formulas for PMPS-based ablative composite are shown in Table II.

The composites were prepared using kneading mixer or two-roll mill at room temperature. Polysiloxanes was added first and then relevant fillers were added in turn. The mixing process lasted 10 min. The mixture were molded and cured into flat sheets at room temperature for 48 h.

RESULTS AND DISCUSSION

Synthesis of MDT Resins

In this work, MDT resins were synthesized through cohydrolysis and cocondensation of alkylalkoxy silane as the basic raw materials. Hydrochloric acid and trifluoromethanesulfonic acid were used for hydrolysis catalysts. It is well known that the performance of silicone resin is closely related to R/Si, Ph/R, and functional group content. To investigate the effects of silicone resins, MDT resins with various R/Si ratios were first prepared by changing the molar ratio of the starting materials (listed in the

Table II. Formulas of PMPS-Based Ablative Composites

Ingredients	Vinyl-polysiloxanes	Hydrogen-polysiloxanes	MDT resins	Silica	Ablative fillers	Pt catalyst
1#	100	8-22	40-240	0	23	0.01-0.03
2#	100	5.7	0	20	23	0.01

Parts per hundred grams of vinyl-polysiloxanes (phr).

Ablative fillers were complex of carbon fiber, SiC, Al₂O₃, and ZnO according to the weight ratio of 5 : 7 : 7 : 4.

Table III. Various MDT Silicone Resins

Sample	M : n : p : q	Vi ^a (wt %)	R/Si (molar ratio)	Ph/R (molar ratio)
1	0.7 : 0.5 : 0 : 2.5	3.68	1.65	40.98
2	0.7 : 0.25 : 0.1 : 3.1	3.86	1.52	48.06
3	0.7 : 0.3 : 0.1 : 3.3	3.62	1.48	50.77
4	0.8 : 0.25 : 0 : 4.1	3.49	1.41	56.55
5	1 : 0.1 : 0.1 : 5.2	3.49	1.36	59.77

^aVi (wt %) were measured by chemical titration method.

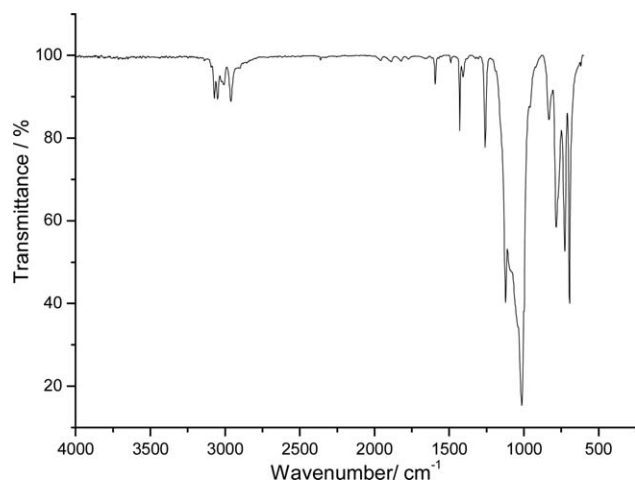
Table III). R/Si ratios varied from 1.65 to 1.36, and Ph/R increased from 40.98 to 59.77% according to the resin formulas of sample 1–5.

The fourier transform infra-red (FTIR) of silicone resin (Sample 3) is shown in Figure 1. The single band at 1429 cm^{-1} can be assigned to the characteristic peak of the Si-Ph group. The absorption peak at 1592 cm^{-1} can be attributed to the characteristic peak of the Si-Vi group. The absorptions at 1261 and 2965 cm^{-1} can be ascribed to the symmetric deformation vibration and stretching vibrations of the Si-Me. The results confirmed that the products obtained were vinyl end-capped methylphenyl MDT silicone resins.

Properties of PMPS-Based Silicone Rubber

Effects of R/Si Ratio. The addition of MDT resins in composites is maintained at 120 phr, and the unreinforced PMPS silicone rubber is taken as control for comparison. The effects of R/Si ratio of MDT resins on PMPS are well defined in Table IV.

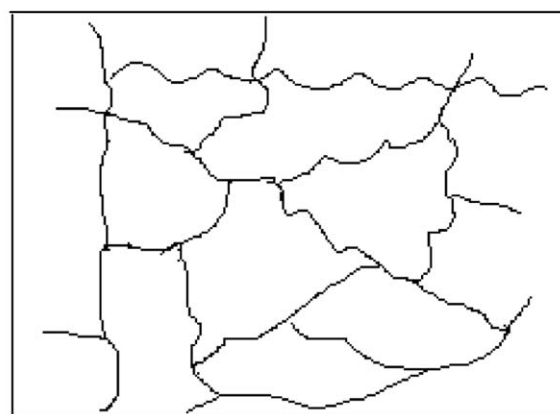
It is interesting to note that all MDT resin with various R/Si ratios show well reinforcing effect on PMPS. With the decreasing of R/Si ratio, the tensile strength and tearing strength increased, and the elongation at break decreased. In this work, vinyl end-capped methylphenyl MDT resin is branched three-dimensional (3D) crosslinked structure, and the crosslinked density increases with the decreasing of R/Si ratio. The end-capped vinyl groups of MDT introduced the crosslinked resins

**Figure 1.** FTIR spectra of MDT silicone resin Sample 3.**Table IV.** Effects of R/Si Ratio of MDT Resins on PMPS

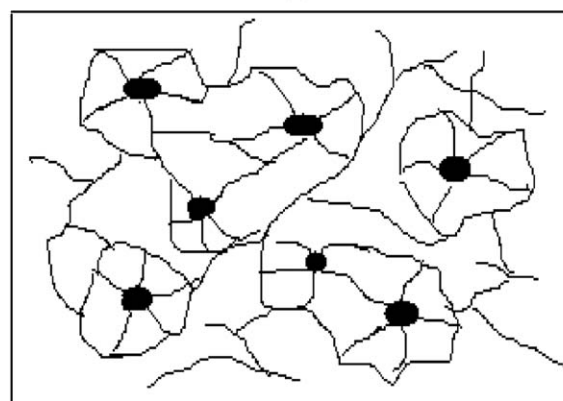
Samples	Viscosity at 25°C (cP)	Tensile strength (MPa)	Elongation at break (%)	Tearing strength (N/mm)
PMPS	2600	0.3	250	4.5
R/Si 1.65	2750	1.6	212	8.9
1.52	3200	2.8	195	10.2
1.48	3900	4.6	180	12.6
1.41	8600	5.4	126	12.2
1.36	10,200	6.2	78	10.4

into silicone rubber by curing reaction (hydrosilylation reaction), which is a kind of concentration crosslinking for PMPS, and the mechanical properties are improved by this way. The scheme of crosslinking in silicone rubber with vinyl end-capped methylphenyl MDT is shown in Figure 2.

It must be noted that with the decreasing of R/Si ratio, the viscosity of MDT resin increased. When the R/Si ratio reached 1.41, the viscosity was much too high for practical application when used as ablative matrix materials with poor liquidity and not easy to handle, which cannot be used for further study.



(a)



(b)

Figure 2. Scheme of crosslinking in silicone rubber. (a) PMPS and (b) PMPS reinforced by MDT resins.

Table V. Effects of Vinyl Content of MDT Resins on PMPS

M : n : p : q	Vi ^a wt %	Tensile strength (MPa)	Elongation at break (%)	Tearing strength (N/mm)
0.5 : 0.5 : 0.1 : 3.3	2.58	3.5	198	8.9
0.6 : 0.4 : 0.1 : 3.3	3.10	4.2	194	9.6
0.7 : 0.3 : 0.1 : 3.3	3.62	4.6	180	12.6
0.8 : 0.2 : 0.1 : 3.3	4.13	4.8	162	13.2
0.9 : 0.1 : 0.1 : 3.3	4.65	5.4	134	15.4
1 : 0 : 0.1 : 3.3	5.19	5.7	116	15.8

^a Vi (wt %) were measured by chemical titration method.

Effects of Vinyl Content. When R/Si ratio and MDT loading were maintained at 1.48 and 120 phr, respectively, vinyl content was adjusted from 2.58 to 5.19% by changing the molar ratio of MM/TMDVS. Table V summarizes the mechanical properties of reinforced silicone rubber as a function of MDT vinyl content. With the increasing of vinyl content, the concentration cross-linking pots increased, and the tensile strength and tearing strength increased, the elongation at break decreased.

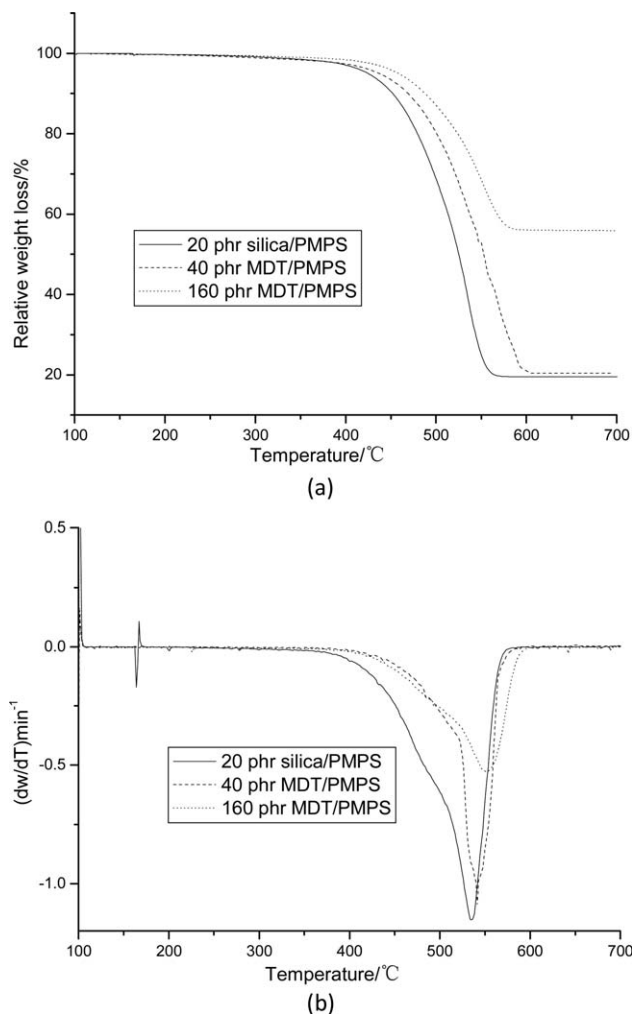
Effects of MDT Loading. It is the same principle for increasing the loading of MDT resins. When R/Si ratio and Vi wt % are maintained at 1.48 and 4.13, respectively, the effects of resin loading are listed in Table VI. With the increasing of MDT content, the crosslinking density increased and the mechanical properties improved. The tensile strength of composite is 5.6 MPa at 160 phr loading of MDT resins. When the loading of MDT is more than 160 phr, the elongation at break decreased greatly, and it is deadly for elastomers and has no useful value in this study. It can be found that 80 phr MDT resins has similar reinforcement effect as 20 phr silica, but MDT has less influence on viscosity of PMPS.

Thermogravimetric Analysis. To investigate the thermal stability of reinforced PMPS, 40 and 160 phr MDT silicone resin (R/Si ratio, 1.48; Vi wt %, 4.13) were chosen to compare with 20 phr silica. TGA [Figure 3(a)] and DTG [Figure 3(b)] curves for thermal degradation were shown below.

To compare their thermal stabilities clearly, three parameters were measured, that is, the onset temperature of thermal degradation (T_{onset} , the temperature at which weight loss is 5 mass %), the

Table VI. Effects of MDT Content on PMPS

Reinforcing filler	Viscosity at 25°C (cP)	Tensile strength (MPa)	Elongation at break (%)	Tearing strength (N/mm)	
Silica (phr)	20	7600	1.8	265	8.6
MDT (phr)	40	2950	1.1	246	9.5
	80	3200	1.8	198	10.2
	120	3850	4.8	162	13.2
	160	4500	5.6	148	12.6
	200	6600	6.4	98	14.8
	240	8900	8.9	76	12.8

**Figure 3.** TGA (a) and DTG (b) curves for PMPS reinforced by MDT and silica.

center temperature of thermal degradation (T_{max} , the temperature at which weight loss is the fastest), and the yield of charred residue at 700°C. The characteristic data are listed in Table VII.

The T_{onset} and T_{max} of the PMPS filled with MDT resins were higher than that of filled with silica. 40 phr MDT/PMPS and 20 phr silica/PMPS have similar residual mass, but T_{onset} and T_{max} of 40 phr MDT/PMPS was 436.4 and 541.6°C, 11.5 and 6.4°C higher than silica/PMPS. This fact confirms that MDT resins play more important role in improving the thermal stability of PMPS compared with silica. The main reason is that MDT resins are polymers with highly branched 3D structures, and the bulky MDT increased the crosslinking density by the chemical

Table VII. Characteristic Data of Thermal Degradation

Samples	T_{onset} (°C)	T_{max} (°C)	Residual mass (%)
Silica/PMPS	424.9	535.2	19.6
40 MDT/PMPS	436.4	541.6	20.47
160 MDT/PMPS	457.9	552.1	55.86

Table VIII. Properties of PMPS-Based Ablative Composites

Samples	Viscosity at 25°C (cP)	Tensile strength (MPa)	Elongation at break (%)	Tearing strength (N/mm)	Line ablation rate (mm/s)
Pristine PMPS	2600	0.3	116	10.4	0.28
PMPS/silica/ablative fillers	11,800	2.2	165	14.8	0.32
PMPS/MDT/ablative fillers	7200	3.58	108	18.2	0.01

linkage between the polysiloxane chain and MDT groups, which are in favor of thermal property.

From the effects analysis of MDT loading, it can be found that 160 phr MDT resin showed super strength, elongation at break and fluidity. The T_{onset} , T_{max} , and residual mass at 700°C of 160 phr MDT /PMPS are 457.9°C, 552.1°C, and 55.86%, respectively, which are all much higher than 40 phr MDT and 20 phr silica filled PMPS.

Performance of PMPS-Based Ablative Composites

PMPS-based ablative composites were reinforced by MDT and silica, respectively. Pristine PMPS was taken as control. Mechanical properties including tensile strength, elongation at break, tearing strength, and line ablation rate are illustrated in Table VIII.

The 160 phr addition of MDT resin (R/Si ratio, 1.48; Vi wt %, 4.13) in PMPS matrix elevated the tensile strength up to 62.7%, and tearing strength raised to 23% as compared with silica filled PMPS. This happens due to the extraordinary mechanical properties and well dispersion of MDT resins in the host matrix. While for silica filled PMPS, due to low addition, silica can not play the full advantage of reinforcement. After the ablation by oxyacetylene flame, line ablation rates of ablative composites were determined. PMPS filled with silica showed higher data compared with pristine PMPS, which illustrated that 20 phr silica showed the opposite role in ablation properties. Interestingly, similar change in phenomenon was observed in the case of silica-PDMS composites.⁷ The linear ablation rates of the ablative composites filled with MDT resin was 0.01 mm/s, indicating that the composite exhibits excellent antiablation properties. It also can be found from Table VIII that MDT filled composite showed lower viscosity, which was more favorable for processing.

CONCLUSIONS

Compared with silica, vinyl end-capped methylphenyl MDT resin was more suitable as reinforcement filler for PMPS-based silicone rubber. MDT resin can play the function of concentration crosslinking by end-capped vinyl groups, which was the most important reason for reinforcement role. T_{onset} , T_{max} , and yield of charred residue at 700°C of PMPS/MDT was 457.9°C,

552.1°C, and 55.86%, respectively, 33°C, 16.9°C, and 36.26% higher than silica reinforced silicone rubber. For PMPS-based ablative composites, MDT resin-filled composites showed excellent processing, mechanical, and antiablation properties compared with silica.

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