Studies on the Silicone Resins Cured with Polymethylsilazanes at Ambient Temperature

Yuemei Zhang, Ying Huang, Xiangluan Liu, Yunzhao Yu

National Key Lab of Engineering Plastics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

ABSTRACT: Polymethylsilazanes (PMS) were synthesized and used to cure silicone resins at ambient temperature. The curing degree of the silicone resins depends on the structure of PMS and its concentration in the resin. Silicone resins of different structure and different silanol content can be cured to a satisfactory degree, if the concentration of the PMS is high enough. Silicone resins cured with PMS showed improved thermal stability in nitrogen, compared with that of the heat-cured counterparts. The mechanism of thermal decomposition of the silicone resins is discussed. The improvement of heat resistance using PMS as the curing agent is accounted for by diminished thermal rearrangement and degradation of the polysiloxane network initiated by silanol groups in the resins. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1702–1707, 2003

Key words: silicones; curing of polymers; thermal properties; polymethylsilazanes; resins

INTRODUCTION

Silicone resins are of excellent heat resistance and weather aging resistance. By virtue of their outstanding dielectric properties, corrosion resistance, and water repellency, they have acquired wide applications in industry as insulating binders, paints, varnishes, coatings, and adhesives. Usually a temperature of 200°C or above is necessary to cure the silicone resins. The high curing temperature creates problems in energy consumption and in equipment requirement for the processing. Moreover, in many cases, the properties of the products are negatively influenced.

Attempts have been made to reduce the curing temperature of silicone resins. Organic amines were used as additives in combination with soluble metal salts.[1] However, these catalyst combinations may impair the heat resistance of the silicone resin coatings to varying degrees. Polysilamines prepared from chlorosilanes and polyamine, such as ethylene diamine and polyethylene imines, were proposed as curing agents of silicone resins.[2] They enabled the silicone resins to cure at 150°C in 30 min and did not affect the thermal stability of the silicone resin. Nevertheless, the toxic by-products such as ethylene diamine were liberated during the curing process, which would also cause a decline in the dielectric properties. Polysilazanes have been successfully used as crosslinking agents for room-temperature vulcanization of silicone rubbers.

They significantly improved the heat resistance of the silicone rubber in nitrogen.[3]

The objective of the present work was to investigate the usefulness of polymethylsilazanes (PMS) for the curing of silicone resins. Three PMS were used for the curing of seven silicone resins with various structures. The thermal stability of the cured silicone resins was investigated by means of dynamic thermogravimetric analysis and gas chromatography–mass spectrometry (GC-MS) analysis of the thermal decomposition products.

EXPERIMENTAL

Materials

Methyltrichlorosilane and dimethyldichlorosilane were provided by Xin'an Huagong Synthetical Materials Co., Ltd. (Zhejiang, China). Phenyltrichlorosilane was from Huehe Chemical Factory (Anhui China). The chlorosilanes were all purified by distillation. 1,1,3,3,5,5-Hexamethylcyclotrisilazane (D_3^N, bp 187–189°C) was synthesized in this laboratory. Toluene and KOH were analytical reagents. Toluene used for the preparation of PDMS was dried by KOH and distilled.

Synthesis of silicone resins

Silicone resins were prepared by cohydrolysis of CH_3SiCl_3, $(CH_3)_2SiCl_2$, and $C_6H_5SiCl_3$ and subsequent condensation of the hydrolyzates. The structural parameters of seven silicon resins are listed in Table I. R/Si and Ph/(Me + Ph) were calculated using the ^{1}H-NMR and ^{29}Si-NMR data. The molecular weight of the silicone resins was determined using a Knauer

TABLE 1
Structural Parameters of Silicone Resins and the Gel Fractions of These Resins Cured
with 5 wt % SN-1 at Room Temperature for 72 h

Resin	R/Si	Ph/(Ph + Me)	Silanol content (wt %)	Molecular weight	Gel fraction (wt %)
SR-1	1.15	0.54	3.6	5500	81
SR-2	1.3	0.54	3.6	3750	87
SR-3	1.5	0.3	1.3	4980	86
SR-4	1.3	0.4	3.9	2720	87
SR-5	1.3	0.3	3.7	3620	85
SR-6	1.3	0.4	2.8	4073	91
SR-7	1.3	0.4	4.6	2310	84

vapor pressure osmometer (Model 11.00, Germany) with chloroform as a solvent. The content of silanol groups in the silicone resins was determined by the lithium aluminum hydride method with diglyme as solvent.[4]

Synthesis of PMS

The PMS were synthesized by coammonolysis of methyltrichlorosilane and dimethyldichlorosilane. For example, 119.6 g CH_3SiCl_3, 25.8 g $(CH_3)_2SiCl_2$, and 510 mL toluene were added to a round-bottom flask equipped with a mechanical stirrer, a reflux condenser, and a gas inlet. Dried ammonia was introduced under vigorous stirring, while the flask was cooled with ice water. As absorption of ammonia was saturated, the white precipitate was filtered and washed repeatedly with toluene. The concentration of the PMS in toluene was adjusted to 10 wt %. The nitrogen content in PMS was determined by the coulometric titration method.[5] Carbon and hydrogen contents were determined by elementary analysis. The results are listed in Table II.

Preparation of silicone resin films

A solution of silicone resin in toluene was mixed with a given amount of 10 wt % PMS solution in toluene. The mixture was cast into Teflon molds, and the solvent was evaporated. After curing at ambient temperature for 72 h, silicone resin films of thickness 200–300 μm were obtained. For the preparation of high temperature–cured silicone resin films, the curing agent

was omitted. After removal of the solvent, the curing was accomplished by heating in an oven at 260°C for 4 h.

Determination of the curing degree of silicone resin films

The curing degree of silicone resin films was characterized in terms of gel fraction, which was determined by extracting the cured resin film with toluene in a Soxhlet extractor for 72 h.

Thermogravimetric analysis

Thermogravimetric analysis was carried out on a Pyris 1 TGA thermogravimetric analyzer (USA) in the range of 50–700°C, under a nitrogen flow of 30 mL/min. The activation energies (E_a) for thermal degradation of silicone resins under nitrogen were obtained according to the first Kissinger technique[6] and the Flynn–Wall technique,[7] in which the data at heating rates of 5, 10, 20, and 40°C/min were employed. Thermostatic gravimetric analysis was run on the same apparatus at 420°C for 8 h under a nitrogen flow of 30 mL/min.

Analysis of thermal degradation products

For analysis of thermal degradation products, samples of about 1.5 g cured resin film were sealed in glass tubes under nitrogen. The sealed glass tubes (empty end down) were heated in a muffle furnace at 490°C for 48 h. After cooling, the viscous decomposition product located at the lower end of the tube was taken

TABLE II
Elementary Analysis for the Polymethylsilazanes

Sample	R/Si	N (wt %)		C (wt %)		H (wt %)	
		Calcd	Found	Calcd	Found	Calcd	Found
SN-1	1.2	27.90	27.97	23.06	25.17	7.75	7.77
SN-2	1.3	29.25	27.92	21.50	24.60	7.46	7.46
D_3^N	2.0	19.18		32.88		0.59	

TABLE III
Gel Fractions of the Silicone Resin SR-6 Cured with Polymethylsilazanes

Curing agent	R/Si of polymethylsilazane	Level of polymethylsilazane (wt %)	Gel fraction of the resin (wt %)
Heat-cured[a]	—	—	93
SN-1	1.2	2	77
SN-1	1.2	4	87
SN-1	1.2	5	91
SN-1	1.2	7.5	95
SN-2	1.3	5	92
D_3^N	2.0	5	95

[a] Heat-curing was carried out at 260°C for 4 h.

and analyzed using a gas chromatograph–mass spectrometer GC MS-QP5050A (Shimadzu Co., Japan).
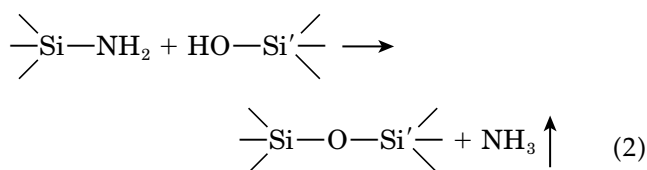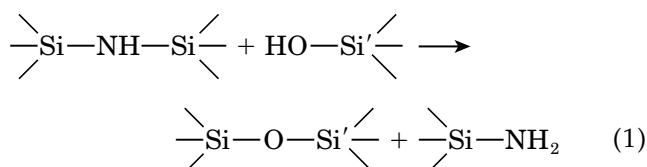
RESULTS AND DISCUSSION

PMS as the room-temperature curing agent for silicone resins

Silicone resins are low molecular weight prepolymers with an average number of organic groups, typically methyl groups and phenyl groups, on a silicon atom R/Si ranging from 1.1 to 1.7. Many silanol groups are in the molecule of silicon resins, as seen in Table I. The curing of the resin was accomplished through condensation of these groups.

The curing degree of thermosetting resins is usually characterized in terms of gel fraction. In the absence of catalysts, a high temperature is needed for the curing of silicone resins. For example, the gel fraction of the resin SR-6 after curing at 260°C for 4 h reached 93%, a percentage that is acceptable for most applications.

Polymethylsilazanes are polymers with –Si—NH—Si– units in the molecules. When PMS are introduced to the silicone resins, network formation through the following reactions becomes possible[8–10]:

$$-\overset{|}{\underset{|}{Si}}-NH-\overset{|}{\underset{|}{Si}}- + HO-\overset{|}{\underset{|}{Si'}}- \longrightarrow$$

$$-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si'}}- + -\overset{|}{\underset{|}{Si}}-NH_2 \quad (1)$$

$$-\overset{|}{\underset{|}{Si}}-NH_2 + HO-\overset{|}{\underset{|}{Si'}}- \longrightarrow$$

$$-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si'}}- + NH_3\uparrow \quad (2)$$

These reactions proceed smoothly at room temperature. Therefore, PMS are effective room-temperature curing agents for silicone resins. As indicated by the data in Table I, the gel fractions of the silicone resin films cured with 5 wt % (based on the weight of the resin) PMS SN-1 reached reasonably high values.
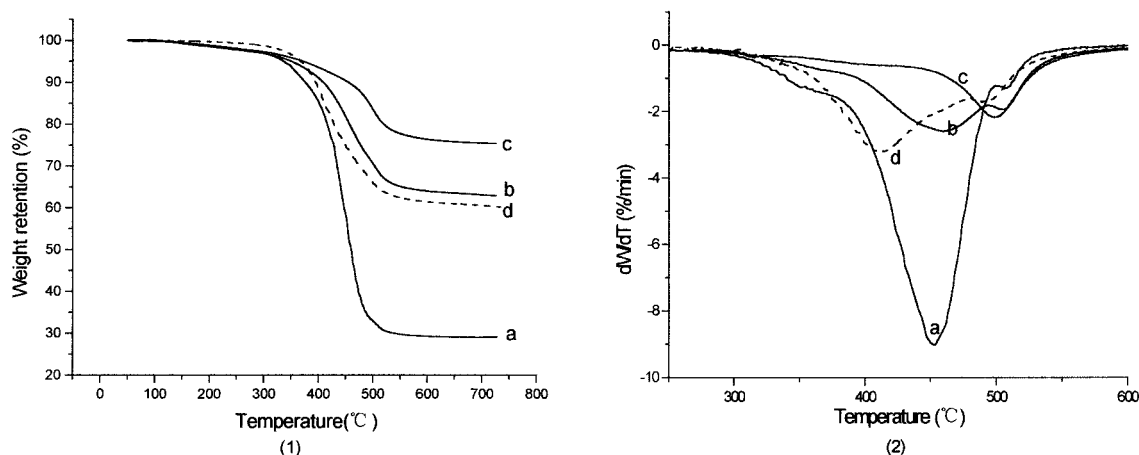

Figure 1 Dynamic thermogravimetric diagrams in nitrogen at a heating rate of 10°C/min: (1) weight retention curves; (2) derivative curves. The silicone resin SR-6 was cured with (a) 2 wt % SN-1, (b) 4 wt % SN-1, and (c) 5 wt % SN-1 at room temperature for 72 h, respectively. Curve (d) is for the silicone resin SR-6 cured at 260°C for 4 h.

TABLE IV
Thermal Properties of the Silicone Resin SR-6 Cured with the Curing Agent SN-1

Level of SN-1	Temperature (°C)			Weight retention at 700°C (%)
	For 5 wt % wt loss	For 10 wt % wt loss	At maximum decomposition rate	
0 (HTC)[a]	366	394	409	60
2%	334	375	453	29
4%	348	408	459	63
5%	370	453	498	75

[a] Heat-curing was carried out at 260°C for 4 h.

The concentration of the PMS curing agent is important. It is seen in Table III that 2 wt % SN-1 was not sufficient to effectively cure the silicone resin SR-6, whereas 5 wt % of SN-1 was sufficient to effect the cure of silicone resin at room temperature to a degree close to that for the resin cured at 260°C for 4 h.

The results in Table III also indicate that the number of methyl groups attached to the silicon atom in the PMS is of minor importance to the gel fraction of the cured resins. Hexamethylcyclotrisilazane, which consists of only the dimethylsilazane units, is as effective as SN-1 and SN-2 in curing silicone resins.

Thermal stability of the silicone resins cured with PMS

To study the thermal stability, the resin SR-6 was cured with different amounts of polysilazane SN-1 and a heat-cured film was prepared as well. Thermogravimetric analysis (TGA) was carried out to investigate the heat resistance of the silicone resins. Figure 1 shows the TGA diagrams and their derivative curves in nitrogen. The temperatures for 5% weight loss, 10% weight loss, and maximum decomposition rate as well as the weight retention at 700°C are summarized in Table IV.

It is seen that the heat resistance of the silicone resin was greatly improved by introduction of the polysilazane curing agent. The temperature for the maximum decomposition was improved for about 90°C by use of 5 wt % SN-1 as the curing agent, compared with the heat-cured counterpart.

The resin cured with 2 wt % SN-1 was less stable at high temperatures. Undercuring may be responsible for the inferior properties. The incompleteness of the curing is indicated by the low gel fraction of the resin (see Table III).

The superior thermal stability of the silicone resins cured with PMS was also demonstrated by thermostatic gravimetric tests (see Fig. 2).

The TGA data in Figures 3 and 4 at heating rates of 5, 10, 20, and 40°C/min were used for calculation of E_a for thermal decomposition according to the first Kissinger technique[6] and the Flynn–Wall technique.[7] The results are given in Table V.

It is seen that the E_a for decomposition is significantly influenced by the method of curing, although the two mathematical treatment methods give diverse results to some extent. The E_a of the thermal decomposition in nitrogen for the silicone resin cured with 5
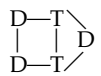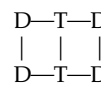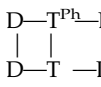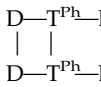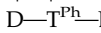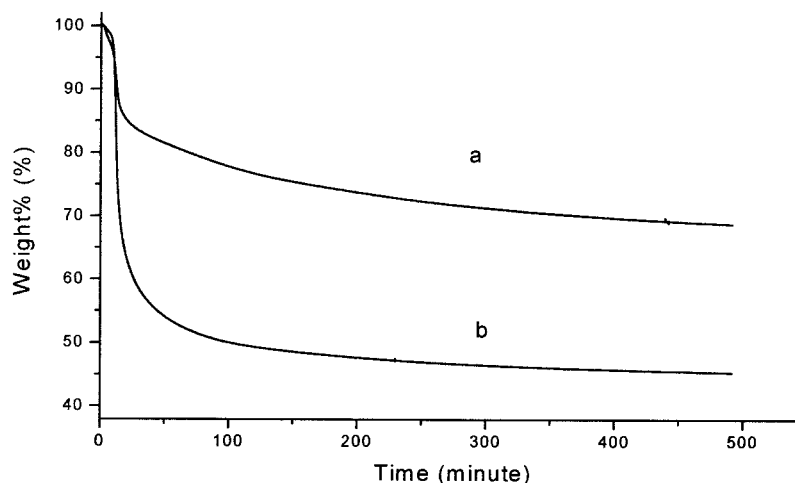

Figure 2 Thermostatic gravimetric diagram in nitrogen at 420°C for 8 h for the silicone resin SR-6: (a) cured with 5 wt % SN-1 at room temperature for 72 h and (b) cured at 260°C for 4 h.

Figure 3 TGA curves in nitrogen for the silicone resin SR-6 cured with 5% SN-1 at room temperature for 72 h, at heating rates of 5, 10, 20, and 40°C/min, respectively.

wt % SN-1 is 100 kJ/mol higher than that for the heat-cured counterpart.

Radhakrishman[12] reported an E_a of 170 kJ/mol for the thermal degradation of the hydroxyl-terminated polydimethylsiloxane; Kang et al.[13] reported an E_a of 334 kJ/mol for the thermal decomposition of trimethylsiloxy end-capped polydimethylsiloxane. It is quite interesting that the E_a for thermal decomposition of the heat-cured silicone resin is close to that for the hydroxyl-capped polydimethylsiloxane, whereas the E_a for the silicone resin cured with 5% SN-1 is very close to that for the trimethylsiloxy-capped polydimethylsiloxane.

Mechanism of thermal degradation

It is noteworthy that in the derivative curve of the TGA diagram for the heat-cured silicone resin, two

Figure 4 TGA curves in nitrogen for the silicone resin SR-6 cured at 260°C for 4 h, at heating rates of 5, 10, 20, and 40°C/min, respectively.

TABLE V
Activation Energies of Thermal Decomposition in Nitrogen for the Silicone Resin SR-6 Cured by Different Methods

Curing method	Activation energy (kJ/mol)	
	Kissinger technique	Flynn–Wall technique
260°C for 4 h	198	151
5 wt % SN-1, RT for 72 h	297	288

distinct peaks are very clear: a large peak located at about 400°C and a small peak located at about 500°C (Fig. 1, curve d). Therefore, two different mechanisms of thermal decomposition should be considered.

Similar to the thermal degradation of hydroxyl-terminated PMS,[11,12] the thermal decomposition at the lower temperature may be attributed to the rearrangement and degradation of polysiloxane chains initiated by the residual silanol groups, as shown in formula (3); and the thermal decomposition at about 500°C might proceed according to a random thermal redistribution and degradation mechanism,[13] as shown in formulas (4) and (5):

M = H, Metal···
R = Me, Ph

TABLE VI
Decomposition Products of the Silicone Resin Found by GC-MS

M/e	MW	mol %	Structure	M/e	MW	mol %	Structure[a]
91	92	14.2	$C_6H_5CH_3$	403	418	1.9	D—T | | D D—T/
153	154	28.9	$C_6H_5C_6H_5$	415	430	1.7	D—T—D | | | D—T—D
207	222	20.5	D_3	477	492	2.7	D—T^{Ph}—D | | | D—T —D
281	296	27.3	D_4	539	554	0.8	D—T^{Ph}—D | | | D—T^{Ph}—D
355	370	2.0	D_5				

[a] D, T, and T^{Ph} stand for the dimethylsiloxy unit, the methylsiloxy unit, and the phenylsiloxy unit, respectively.

$$(5)$$
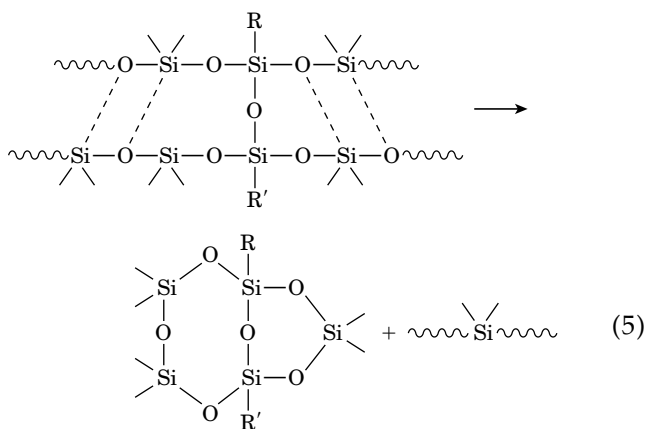
When 5 wt % SN-1 was used to cure the silicone resin, the peak at about 400°C disappeared; only one peak at about 500°C in the curve can be seen (Fig. 1, curve c). We suppose that in the cured resin, silanol groups are in general scavenged through reaction with the polysilazane.

The result of GC-MS analysis of the thermal degradation product of the silicone resin SR-6 cured with 5 wt % SN-1 is summarized in Table VI. The cured sample was sealed in a glass tube under nitrogen and then heated at 490°C for 48 h. As seen in Table VI, in the thermal decomposition product, toluene, biphenyl, and low molecular weight cyclic polysiloxanes consisting of dimethylsiloxy, methylsiloxy, and phenylsiloxy units were found. D_3 and D_4 were 20.5 and 27.3 mol %, respectively. The formation of cyclic polysiloxanes demonstrates the chain rearrangement, whereas the presence of toluene and biphenyl indi-cates the cleavage of the Si—C bonds at high temperatures.

CONCLUSIONS

Polymethylsilazanes can be used as curing agents for silicone resins to allow the resins to cure at ambient temperature. Silicone resins of different structure and different silanol content can be cured to a satisfactory degree, if the level of the curing agent is high enough. Because silanol groups in the cured resin are in general scavenged by the polysilazane-curing agent, the degradation initiated by this group is diminished, and thus the thermal stability of the resin in nitrogen is greatly improved.

References

1. Noll, W. Chemistry and Technology of Silicones; Academic Press: New York, 1968; p. 414.
2. Jpn. Kokai Tokkyo Koho, JP 39494, 1974.
3. Wang, Q.; Shi, T.; Xie, Z.; Sun, X.; Wang, J.; Li, G. Acta Polym Sinica 1994, 5, 573.
4. Barnes, G. H.; Daughenhaugh, N. F. Anal Chem 1963, 35, 1309.
5. Xie, Z.; Wang, Q.; Beng, L.; Zheng, J.; Yao, Y.; Li, G. Chin J Anal Chem 1993, 21, 206.
6. Li, X.; Huang, M. Polym Degrad Stab 1999, 64, 81.
7. Flynn, J. H.; Wall, L. A. J Polym Sci B, 1966, 4, 323.
8. Pike, R. M. J Org Chem 1961, 26, 232.
9. Pike, R. M. J Polym Sci 1961, 50, 151.
10. Wang, Q.; Xie, Z.; Shi, T.; Wang, J.; Li, G. Acta Polym Sinica 1996, 5, 596.
11. Thomas, T. H.; Kendrick, T. C. J Polym Sci A-2, 1969, 7, 537.
12. Radhakrishnan, T. S. J Appl Polym Sci 1999, 73, 441.
13. Kang, D. W.; Rajendran, G. P.; Zeldin, M. J Polym Sci Part A: Polym Chem 1986, 24, 1085.