Hydrogen-Containing Silicone Resin As the Crosslinking Agent of Heat-Curable Silicone Rubber

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ABSTRACT: The hydrosilation-cured vulcanizates (HCV) of silicone rubber were prepared by using hydrogen-containing silicone resin (HSR) as the crosslinking agent. The influences of both the amount and structure of HSR on hydrosilation-curing silicone rubber (HCSR) were discussed. The results indicate that HSR is a good crosslinking agent for HCSR. The tensile strength, tearing strength, elongation at break, and hardness of the vulcanizates can reach 9.6 MPa, 37.8 kN/m, 870% and 56 SHA, respectively. The aging stability of the vulcanizates can be improved greatly. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 3066–3069, 2003

Key words: crosslinking; silicone; mechanical properties; ageing

INTRODUCTION

Compared to peroxide-curing silicone rubber, hydrosilation-curing silicone rubber (HCSR) is of higher tearing strength, less amount of catalyst, lower toxicity, etc.[1] However, it is of low strength compared to organic rubbers. Considerable efforts have been directed at improving the mechanical properties of silicone rubber, such as replacing parts of methyl groups of polydimethylsiloxane with vinyl groups,[2] using vinyl-terminated methylvinylpolysiloxane as gum, adding methyllene[3] or phenylene[4] to the main chains, using mixed silicone gum with long and short macromolecular chains,[5] and so forth. In addition, the crosslinking agent used impacts the properties of vulcanizates greatly. Choosing a novel crosslinking system is one of the main ways to improve the mechanical properties of vulcanizates.[6] For example, compounds or polymers that contain multiple Si—H groups are all good crosslinking agents[7,8] of HCSR because they can cause concentrative crosslinking, which can distribute stress well in vulcanizates.

Theoretically, hydrogen-containing silicone resin (HSR) has multiple Si—H groups and should therefore be a concentrative crosslinking agent of silicone rubber. In this study we report the results of testing several kinds of HSRs with different structures as the crosslinking agent of HCSR. The mechanical properties of the vulcanizates both before and after aging were measured.

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EXPERIMENTAL

Materials

Silicone gum (Mn, 5.5×10^5 and vinyl group content, 0.15 mol %); octamethylcyclotetrasilazane (D_4^N); C gum (vinyl group content, 10.20 mol %); H-oil (H content 1.23 wt %); and 4# fumed silica (specific surface area of 176 m^2/g) are all industrial products. 1,1,3,3-tetramethyl-1,3-divinyldisiloxane-Pt complex (Pt-cat) was prepared in our laboratory.

Formulation of HSRs

HSRs were prepared by cohydrolysis[9] of varied silanes, the monomer ratios of which are listed in Table I. The ten HSRs are marked Ha, Hb, Hc, Hd, He, Hf, Hg, Hh, Hi, and Hg, respectively. Si—H contents of HSRs were measured according to eudiometer.[10]

Preparation of HCSR

The mixture of hydrogen-containing silicone oil (H-oil) and multivinyl silicone oil (C gum) is the usual crosslinking agent of HCSR. In accordance with the formula for high strength silicone rubber (Table II), HCSR was prepared using HSRs instead of the mixture of H-oil and C gum as crosslinking agents. Referring to the related literature,[11] stocks were compounded and vulcanized. The first stage of cure was at 160°C for 30 min under a pressure of 29.4 MPa; the second stage of cure was 180°C for 2 h in hot air.

TABLE I
Details of HSR Formulation (mole ratios)

Monomers	Ha	Hb	Hc	Hd	He	Hf	Hg	Hh	Hi	Hj
Me_3SiCl	1	1	1	1	1	1	1	1	2	3
Me_2SiCl_2	0	1	1	1	1	0	1	1	1	1
$MeHSiCl_2$	7	7	7	5	5	7	7	7	7	7
$MeSi(OEt)_3$	2	2	3	3	5	0	0	0	0	0
$PhSi(OEt)_3$	0	0	0	0	0	2	2	3	3	3
H content (wt %)	1.01	0.94	0.78	0.66	0.70	0.61	0.83	0.60	0.59	0.53

Aging of the vulcanizates

The vulcanizates were placed in an oven and aged in hot air at 250°C for 24 h.

Measurement of mechanical properties of vulcanizates

The mechanical properties of vulcanizates and aged samples were measured on a XLD-A rubber test instrument.

RESULTS AND DISCUSSION

Effects of amount of HSR on mechanical properties of HCSR

To explore the feasibility of HSR as a crosslinking agent of HCSR, various amounts of HSR were added to samples of HCSR. We used Hc to show the effects of different amounts of HSR on the mechanical properties of HCSR; the related results are listed in Table III. HC1–HC5 are the vulcanizates cured with different amounts of Hc.

From the data in Table III, we could see that good mechanical properties of vulcanizates have been achieved by using a suitable amount of Hc as a crosslinking agent of HCSR. With increasing Hc, both tensile strength and tearing strength of vulcanizates reach optimum values, surpassing those of H-0. When 1.8 parts of Hc are used, the crosslink density of vulcanizate is too low because the strength and hardness are low and elongation is large. Increasing the amount of Hc used produces greater strength in the vulcanizates. However, when the amount of Hc used surpasses 4.0 parts, the vulcanizates are overcured because their strength decreases with the increase of hardness and modulus. That is because curing is one of the important factors affecting the mechanical properties of rubber. With increasing amounts of crosslinking agent, the crosslink density will increase and there will be more crosslinked chains to disperse the stress in vulcanizates, so the mechanical properties could also be increased. However, excessive amounts of crosslinking agent cause the formation of too many cross bonds to distribute force well, so the network cannot disperse external force evenly, which leads to stress concentration as well as a decrease in strength. This study suggests that 2.5 parts of Hc are optimal because both the tensile strength and the tearing strength of HC3 are higher than that of H-0.

TABLE II
Formulation of HCSR

Materials	Silicone gum	$4*SiO_2$	HSR^a	H-oil	C gum	D^N_4	Pt-cat
Weight part	100	55	0–4.2	1.0 or 0	2.0 or 0	8.0	1.0

[a] Without H-oil and C gum, HSR is 1.0–4.2; otherwise HSR is 0.

TABLE III
Effects of Hc on Mechanical Properties of HCSR

Sample No.	Amount of HSR (wt. part)	Hardness (SHA)	Tensile strength (MPa)	Tearing strength (kN/m)	Modulus at 100% (MPa)	Modulus at 300% (MPa)	Elongation at break (%)
H-0	[a]	62	9.4	36.2	1.4	3.4	737
HC1	1.3	53	8.4	27.0	0.8	1.7	975
HC2	1.8	55	9.5	28.8	0.9	2.3	890
HC3	2.5	56	9.6	37.8	1.0	2.3	870
HC4	3.0	58	9.9	30.7	1.1	2.8	800
HC5	4.0	60	8.4	30.5	1.2	2.4	730

[a] 1.0 part H-oil and 2.0 parts C gum.

TABLE IV
Suitable Amounts of HSR (in 100 parts of silicone gum)

HSR	Ha	Hb	Hc	Hd	He	Hf	Hg	Hh	Hi	Hj
Wt.parts	1.2	2.5	2.5	3.0	5.0–6.0	4.0	3.0	5.0	6.0	6.0
Tensile strength (MPa)	9.6	8.1	9.6	9.0	9.6–11.5	10.4	9.4	9.4	10.1	11.6
Tearing strength (kN/m)	34.9	33.5	37.8	27.8	39.2–28.7	31.2	28.8	26.3	25.2	29.5

The influences of the amounts of other HSRs (from Ha to Hj) on the mechanical properties of HCSR are similar to that of Hc, although their suitable amounts are different (see Table IV).

Effects of HSR with different structures on mechanical properties of HCSR

The effects of the ten HSRs on the mechanical properties of HCSR differ because of their different molecular structures. The applicable data are shown in Table V. HA–HJ are the vulcanizates, respectively, using Ha–Hj as the crosslinking agents.

To show the effect of concentrative crosslinking on the mechanical properties of silicone rubber, the vulcanizates, H-1 and H-0, which respectively used H-oil and H-oil with C gum as the crosslinking agents, were prepared. The data in Table V show that the difference in tensile strength between H-1 and H-0 is small, while that of tearing strength is large. That is because different concentrative crosslinking networks have been formed in the two vulcanizates. C gum in H-0 may form more effective concentrative crosslinking than in H-1, which can enhance the mechanical properties of silicone rubber, especially the tearing strength.

When HSR is used as the crosslinking agent of HCSR, the tensile strength of every vulcanizate is higher than that of H-0, and the tearing strength of some vulcanizates using the proper amounts of HSR surpass that of H-0. Therefore, the HSR with the appropriate structure is a good crosslinking agent of HCSR. This is because the HSRs were prepared by the cohydrolysis of multifunctional silanes, which generated more regular micro-crosslinked structures in the HSRs than those of H-oil with C gum in H-0. Our study indicates that HSR could form even more effective concentrative crosslinking in vulcanizates than form when H-oil with C gum is used as the crosslinking agent in H-0. In the event of external force, the concentrative crosslinked network of vulcanizates using HSR as a crosslinking agent can disperse stress to crosslinked bonds evenly and display higher strength than H-0.

Tearing strength

In the tearing test of vulcanizates, we found parts of samples splitting up towards two sides of the crack, so the tearing of the sample changed with the tension of it. We thought this may be the typical phenomenon resulting from the concentrative crosslinking. It is natural that the tearing strength of this kind of vulcanizate will be higher than that of the typical tearing pattern. For example, the tearing strength of one piece of three samples using 1.3 parts of Hc can reach 52.8 kN/m, which is not listed in Table III because the data from the other two pieces had a larger deviation, and we will investigate it later. In addition, the vulcanizate with highest tearing strength is HE3, which used He, the HSR with the most $SiO_{1.5}$ unit ratios, as the crosslinking agent. This is also the result of concentra-

TABLE V
Effects of Different HSRs on Mechanical Properties of HCSR

Sample No.	Amount of HSR (wt. part)	Hardness (SHA)	Tensile strength (MPa)	Tearing strength (kN/m)	Modulus at 100% (MPa)	Modulus at 300% (MPa)	Elongation at break (%)
H-1	[a]	56	8.8	27.6	1.0	2.5	760
H-0	[b]	62	9.4	36.2	1.4	3.4	737
HC3	2.5	56	9.6	37.8	1.0	2.3	870
HC4	3.0	58	9.9	30.7	1.1	2.8	800
HE3	5.0	56	9.6	39.2	1.0	2.5	850
HE4	6.0	57	11.5	28.7	1.1	2.6	760
HF1	3.0	57	9.6	33.6	0.9	2.5	750
HF2	4.0	58	10.4	31.2	1.0	2.9	720
HJ2	5.0	52	10.8	26.8	0.6	1.3	965
HJ3	6.0	52	11.6	29.5	0.7	1.5	910

[a] 1.0 part H-oil.
[b] 1.0 part H-oil and 2.0 parts C gum.

TABLE VI
The Mechanical Properties of Aged HCSR Before and After Aging

Sample No.	Amount of HSR (wt. part)	Hardness (SHA)		Tensile strength (MPa)		Tearing strength (kN/m)		Modulus at 100% (MPa)		Modulus at 300% (MPa)		Elongation at break (%)	
		before	after	before	after	before	after	before	after	before	after	before	after
H-0	a	62	86	9.4	2.4	36.2	3.7	1.4	-	3.4	-	737	47
HA2	1.2	51	72	9.6	4.8	34.9	21.0	0.7	1.7	1.6	-	975	290
HB4	2.5	57	86	8.1	2.7	33.5	2.9	1.0	-	1.9	-	1010	40
HC3	2.5	56	84	9.6	3.4	37.8	4.6	1.0	-	2.3	-	870	80
HD4	3.8	55	74	9.6	4.7	26.0	16.5	1.0	2.3	2.4	-	843	210
HE4	6.0	57	86	11.5	3.0	28.7	4.9	1.1	-	2.6	-	760	30
HF2	4.0	58	73	9.4	6.6	31.6	25.7	1.2	1.7	3.9	5.7	620	340
HG3	3.0	54	72	9.4	6.9	28.8	23.4	0.8	1.5	2.2	5.1	800	360
HH3	5.0	54	72	9.4	7.5	26.3	24.5	0.7	1.7	1.6	5.1	890	400
HI4	6.0	52	72	10.1	4.9	25.2	21.9	0.7	1.9	1.6	4.9	890	300
HJ1	4.0	49	72	8.8	6.6	36.1	23.9	0.5	1.6	1.3	4.9	975	450

a 1.0 part H-oil and 2.0 parts C gum.

tive crosslinking in vulcanizates. When there are more $SiO_{1.5}$ units in HSR, there will be more Si—O bonds to disperse the stress in vulcanizates. From these results, we conclude that more $SiO_{1.5}$ units in HSR contribute to the higher tearing strength of HCSR.

Aging stability of the vulcanizates

The mechanical properties of the vulcanizates heated at 250°C for 24 h in hot air are shown in Table VI.

It is known that siloxane undergoes stepwise degradation of the backbone and oxidation of the methyl groups when aged in air above 200°C. Although the Si—C bond is thermodynamically less stable than the Si—O bond, thermal degradation of siloxane occurs by depolymerization through the Si—O bonds' rearrangement[10] below 400°C via kinetically favored paths, leading to the production of cyclic oligomers. The HSRs are branched molecules, which may destroy the helical coiling structure of siloxane. Both the branched structure of HSRs and their capacity to destroy helical coiling structures prevent the rearrangement of Si—O bonds in siloxane. As HSRs blocked the formation of the cyclic oligomers, the rate of thermal degradation decreased, too. Thus HSRs could enhance the thermal stability of siloxane rubber. The data in Table VI show that the mechanical properties of almost every kind of vulcanizate that uses HSR as a crosslinking agent are superior to those that use the mixture of H-oil and C gum, especially when the HSR contains phenyl groups. Phenyl groups in the HSR could stabilize the siloxane radicals created in hot air. Thus HSRs can slow the oxidative crosslinking reaction of siloxane and improve the thermal aging stabilities of vulcanizates. For example, the tensile strength of H-0 before aging is 9.4 MPa (see Table VI), but the sample only retains 25.6% of that strength after aging (2.4 MPa). The tearing strength of aged vulcanizate is

3.7 kN/m, 10.1% of the tearing strength before aging (36.2 kN/m). For the aged vulcanizates using HSR as the crosslinking agents, the tensile strength, tearing strength, and elongation at break could retain more than 70% of their values before aging in some cases.

CONCLUSIONS

By using HSR as the crosslinking agent of addition-cured heat curable silicone rubber, the mechanical properties of vulcanizates surpass those that result from using H-oil and/or C gum, especially the tearing strength because of the effective concentrative crosslinking. More $SiO_{1.5}$ units in HSR enhance the tearing strength of vulcanizates. HSR could increase the thermal aging stability of silicone rubber greatly, especially when the HSR contains phenyl groups.

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