

Vinyl-Containing Silicone Resin as the Crosslinking Agent of Heat-Curable Silicone Rubber

SHIGUI ZHAO, SHENGYU FENG

Institute of New Materials, Shandong University, Jinan 250100, China

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ABSTRACT: Heat-curable silicone rubber (HCSR) was prepared by using vinyl-containing silicone resin (VSR) as the crosslinking agent instead of polyvinylsilicone oil (C gum). Mechanical properties and crosslink density of the vulcanizates were measured. The results indicate that VSR is a good crosslinking agent for HCSR. The tensile strength, tearing strength, elongation at break, and hardness of the vulcanizate can reach 10.2 MPa, 29.1 kN/m, 720%, and 58 SHA, respectively. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 3123–3127, 2002; DOI 10.1002/app.10054

Key words: silicone rubber; crosslinking agent; vinyl-containing silicone resin

INTRODUCTION

Silicone rubber has been widely used in many areas because of its unusual merits. However, it is of low strength compared with that of organic rubbers because of the weaker interaction between polysiloxane macromolecules. 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,^{1,2} using vinyl-terminated methylvinylpolysiloxane as gum,³ adding methylene⁴ or phenylene^{5,6} to the main chains, using mixed silicone gum with long and short macromolecular chains,^{7,8} and so forth.

Given the distinct influence of the crosslinking agent on the properties of vulcanizates, the choice of a novel crosslinking system is one of the main ways to improve the mechanical properties of vulcanizates. Polyvinylsilicone oil (C gum),⁹ silicon compounds or polymers that containing multivinyl¹⁰ or multiethynyl^{11–15} are all good crosslink-

ing agents of HCSR because they can cause *concentrative* crosslinking in cured silicone rubber.

Theoretically, polyvinyl silicone resin has many vinyl groups that can cause concentrative crosslinking and should be used as the crosslinking agent of silicone rubber, too. To date there have been few reports on vinyl-containing silicone resin (VSR) as crosslinking agent of HCSR and no reports on either the curing mechanism or the properties of vulcanizates. In this study we report the results of several kinds of VSRs with different structures used as the crosslinking agents of peroxide-cured HCSR and the measurements of both mechanical properties and crosslink density (shown by average molecular weight M_c of effective chains) of the vulcanizates.

EXPERIMENTAL

Materials

Silicone gum (M_n , 5.5×10^5 and vinyl group content, 0.15 mol %), C gum (vinyl group content, 10.2 mol %), octamethylcyclotetrasilazane (D_4^N), 4[#] fumed silica (specific surface area, 176 m²/g),

Correspondence to: S. Zhao.

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Table I Details of VSR Formulation (mol ratios of monomers)

Monomer	Va	Vb	Vc	Vd	Ve	Vf	Vg
Me ₃ SiCl	1	1	1	1	1	1	1
Me ₂ SiCl ₂	5	5	5	4	8	5	5
ViSi(OEt) ₃	1	1	2	1	1	1	2
PhSiCl ₃	1	1	0	0	0	0	0
Ph ₂ SiCl ₂	0	1	1	2	0	0	0
Vinyl contents ^a	1.45	1.55	1.73	1.44	1.40	1.65	2.00

^a The unit of vinyl group content in VSR is mmol Vi/g resin.

and 2,5-bis(*tert*-butyl peroxy)-2,5-dimethyl hexane (DBPMH) are all industrial products.

Formulation of VSRs

VSRs were prepared by cohydrolysis of varied silanes,¹⁶ the monomer ratios of which are listed in Table I. The seven VSRs are marked Va, Vb, Vc, Vd, Ve, Vf, and Vg, respectively. Vinyl group contents were measured according to iodimetry.¹⁷

Preparation of HCSR

Following the formula of high-strength silicone rubber, HCSRs were prepared using VSR or C gum as crosslinking agent. The formulation of HCSR is given in Table II. Referring to the related literature,⁹ stocks were compounded and vulcanized. The first stage of cure was 160°C for 30 min under a pressure of 29.4 MPa; the second stage of cure (postcure) was 180°C for 2 h in hot air.

Measurement of Mechanical Properties of Vulcanizates

The mechanical properties of the vulcanizates were measured¹⁸ on an XLD-A rubber test instrument. The M_c was determined by the toluene-swelling method.¹⁹

RESULTS AND DISCUSSION

Effects of Amount of VSR on Mechanical Properties of HCSR

C gum is generally used as the crosslinking agent of high-strength silicone rubber and the conven-

tionally used amount is 2.0 wt parts.¹⁶ The initial amounts of VSR were designed to contain the same amount of vinyl groups as in 2.0 parts of C gum. To explore the feasibility of VSR as a crosslinking agent of HCSR, various amounts of VSR were added. We used Va to show the effects of amounts of VSR on the mechanical properties of HCSR, the results of which are listed in Table III. VA1–VA5 are the vulcanizates cured with different amounts of Va, respectively.

From the data in Table III, we can see that rather good mechanical properties of vulcanizate could be achieved by using a suitable amount of Va as crosslinking agent of HCSR. With increasing Va, both tensile strength and tearing strength of vulcanizates reach optimum values surpassing those of V-0. Additional amounts of Va result in a decline of both tensile strength and tearing strength with the increase of hardness and modulus at 100 or 300% as a result of overcure. 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 that could disperse the stress in vulcanizates, so the mechanical properties could also be increased. However, when excessive amounts of crosslinking agent are used, the crosslinking density of vulcanizates is too high (overcured) to distribute well, and thus the stress concentration is easy to form. The tensile strength of vulcanizates using 2.5–3.6 parts of Va is higher than that of V-0, so Va should be a good crosslinker of HCSR. We think that 2.5–2.9

Table II Formulation of HCSR

Material	Silicone Gum	4 [#] SiO ₂	D ₄ ^N	C Gum ^a	VSR ^b	DBPMH
Wt parts	100	55	8	2or0	0–4.2	1.0

^a Vinyl group content in C gum is 1.35 mmol Vi/g C gum.

^b Without VSR, C gum is 2.0; otherwise, C gum is 0.

Table III Effects of Va on Mechanical Properties of HCSR

Sample No.	Amounts of Va (wt parts)	Hardness (SHA)	Tensile Strength ^b (MPa)	Tearing Strength ^b (kN/m)	Modulus at 100% ^b (MPa)	Modulus at 300% ^b (MPa)	Elongation at Break (%)
V-0 ^a	0	56	9.4 ± 0.3	25.1 ± 0.9	0.9 ± 0.1	2.3 ± 0.2	760
VA1	1.6	52	8.2 ± 0.2	23.0 ± 0.9	0.8 ± 0.1	1.7 ± 0.3	800
VA2	2.5	55	10.0 ± 0.2	27.0 ± 0.8	0.9 ± 0.1	1.9 ± 0.3	760
VA3	2.9	57	10.9 ± 0.2	25.9 ± 0.8	0.8 ± 0.1	1.4 ± 0.1	760
VA4	3.2	60	10.6 ± 0.3	24.8 ± 0.7	1.0 ± 0.1	2.3 ± 0.2	750
VA5	3.6	61	10.0 ± 0.4	24.4 ± 0.9	1.0 ± 0.1	2.7 ± 0.2	720

^a V-0 is the vulcanizates using 2.0 parts of C gum as crosslinking agent.

^b Plus/minus values represent standard deviations.

parts of Va are suitable because both tensile strength and tearing strength of VA2 and VA3 are higher than that of V-0.

The influence of the amount of other VSRs (from Vb to Vg) is similar to that of Va on the mechanical properties of HCSR, although their suitable amounts are different (see Table IV).

Effects of VSR with Different Structures on Mechanical Properties of HCSR

The effects of seven VSRs on mechanical properties of vulcanizates differ from each other because of their different molecular structures. The applicable data are shown in Table V. VA, VB, VC, VD,

VE, VF, and VG are the vulcanizates, respectively, using Va, Vb, Vc, Vd, Ve, Vf, and Vg as the crosslinking agent.

From the data in Table V, we find that the concentrative crosslinking formed in the vulcanizate can improve the mechanical properties of silicone rubber, especially the tearing strength. The tensile strengths of V-0 and V-1 are almost the same (9.4 and 9.3 MPa), but the tearing strengths are different (25.1 and 23.2 kN/m). Failure in tension occurred at the minimum of cross-sectional area; failure in tearing, on the other hand, is the result of expansion of the crack. On the macromolecular chains of silicone gum there are fewer vinyl groups (0.15 mol %) and the net-

Table IV Suitable Amounts of VSR in HCSR

VSR	Va	Vb	Vc	Vd	Ve	Vf	Vg
Wt parts	2.5–2.9	3.8–4.2	1.6–2.0	1.9	2.3	1.9	1.6

Table V Effects of Various VSRs on Mechanical Properties of HCSR

Sample No.	Amounts of VSR (wt parts)	Hardness (SHA)	Tensile Strength (MPa)	Tearing Strength (kN/m)	Modulus at 100% (MPa)	Modulus at 300% (MPa)	Elongation at Break (%)
V-1 ^a	0	56	9.3 ± 0.3	23.2 ± 0.5	0.8 ± 0.1	1.9 ± 0.1	780
V-0 ^b	0	56	9.4 ± 0.3	25.1 ± 0.9	0.9 ± 0.1	2.3 ± 0.2	760
VA	2.5	55	10.0 ± 0.2	27.0 ± 0.8	0.9 ± 0.1	1.9 ± 0.3	760
VB	3.8	56	10.6 ± 0.2	21.4 ± 0.8	1.0 ± 0.1	2.2 ± 0.2	760
VC	2.0	56	9.8 ± 0.3	27.8 ± 0.8	0.9 ± 0.0	2.3 ± 0.1	730
VD	1.9	55	10.2 ± 0.3	26.6 ± 1.1	0.9 ± 0.1	2.2 ± 0.2	780
VE	2.3	58	10.5 ± 0.2	27.4 ± 0.8	1.0 ± 0.1	2.4 ± 0.0	780
VF	1.9	57	10.5 ± 0.3	28.1 ± 0.8	0.8 ± 0.0	1.8 ± 0.0	890
VG	1.6	58	10.2 ± 0.1	29.1 ± 1.0	1.0 ± 0.1	2.7 ± 0.3	730

^a V-1 is the vulcanizate without C gum or VSR.

^b V-0 is the vulcanizate using 2.0 parts of C gum as crosslinking agent.

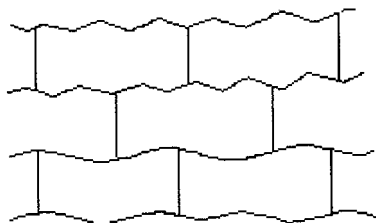


Figure 1 Network of dispersive crosslinking.

work of *dispersive* crosslinking (see Fig. 1) formed in the vulcanizate without C gum was easy to break, so the tearing strength is poor. There are more vinyl groups in C gum (10.2 mol %) than in silicone gum. When using C gum as a crosslinking agent, the concentrative crosslinked network (see Fig. 2) could be formed and it can distribute the stress near the crack to many crosslinked bonds, and so the tearing strength of vulcanizates is higher.

VSR is a microcrosslinked polymer (see Fig. 3) whose structure is different from the lineal structure of C gum (see Fig. 4). When VSR is used as the crosslinking agent of HCSR, it could form a more favorable concentrative crosslinking network than C gum because of its net structure with crosslinkable vinyl groups in all directions. This kind of network in a vulcanizate could disperse stress to even more crosslinked bonds than that of C gum, and so the vulcanizate should display further higher mechanical properties. Our experimental results coincide with this view. Data in Table V show that the mechanical properties of vulcanizates using VSR surpass that of using C gum. Thus VSR is a good crosslinking agent of HCSR.

In addition, the influence of the structure of VSR on tearing strength is apparent. The tearing strength increases when $\text{SiO}_{1.5}$ units in VSR increase. For example, with the increasing of $\text{SiO}_{1.5}$ units in Ve, Vf, and Vg (see monomer ratios in Table I), the optimum values of the tensile

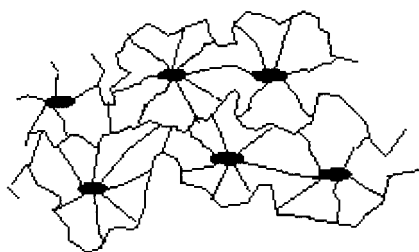


Figure 2 Network of concentrative crosslinking.

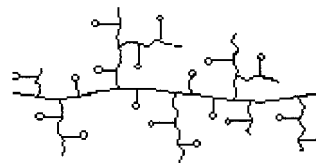


Figure 3 Structure of VSR, where \circ represents vinyl group.

strength of VE, VF, and VG are 10.5 ± 0.2 , 10.5 ± 0.3 , and 10.2 ± 0.1 MPa, surpassing that of V-0 by about 12.1, 11.4, and 8.6%, respectively. The tearing strength values are 27.4 ± 0.8 , 28.1 ± 0.8 , and 29.1 ± 1.0 kN/m, surpassing that of V-0 by about 9.3, 12.0, and 16.1%, respectively. Thus more $\text{SiO}_{1.5}$ units in VSR are favorable to the tearing strength of vulcanizates.

Average Molecular Weight of Effective Chains

The average molecular weight (M_c) of effective chains is an important structural parameter that indicates the crosslinking degree of vulcanizates. It is the total reflection of physical and chemical actions of additives with additives, main links with main links, and additives with main links. M_c is determined by the toluene-swelling method¹⁹ and is calculated by the formula

$$M_c = -\rho_2 V_1 \phi_2 / [\ln(1 - \phi_2) + \phi_2 + \chi_1 \phi_2]$$

where ϕ_2 is the volume fraction of vulcanizates in the swelling body; χ_1 is the macromolecule-solvent interaction efficiency, here 0.465; ρ_2 is the density of vulcanizates; and V_1 is the molar volume of solvent, here 107 mL/mol. From the data in Table VI, we find that the values of M_c of the vulcanizates using VSRs as crosslinking agents are higher than that of V-0, using C gum ($M_c = 5375$). It indicates that to reach or surpass the mechanical properties of vulcanizates using C

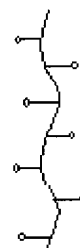


Figure 4 Structure of C gum, where \circ represents vinyl group.

Table VI M_c of Vulcanizates

Sample No.	M_c	Sample No.	M_c
V-0	5357	VB	5688
VA1	6011	VC	6110
VA2	5526	VD	5747
VA3	5475	VE	6242
VA4	5788	VF	5519
VA5	5747	VG	4762

gum as crosslinking agent, the crosslink density of vulcanizate using VSR is lower, which is what we wish to achieve by using concentrative crosslinking. The results not only show that concentrative crosslinking has been formed in curing of stocks but also demonstrate the view, again, that concentrative crosslinking can improve the mechanical properties of silicone rubber.^{10,20}

CONCLUSIONS

VSR is a good crosslinking agent of HCSR, which is more favorable than C gum to concentrative crosslinking. By adding appropriate amounts of VSR in the stocks, the strength of vulcanizate can be improved, especially the tearing strength. The more $\text{SiO}_{1.5}$ units in the VSR, the higher the strength of the vulcanizates will be. To reach or surpass the mechanical properties of vulcanizates using C gum as crosslinking agent, the vulcanizates using VSR must have lower crosslink density.

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