Effect of Crosslinking on the Conductivity of Conductive Silicone Rubber

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ABSTRACT: We investigated the effect of polyvinylsilicone oil (C gum) as a crosslinker and 2,5-bis(*tert*-butyl peroxy)-2,5-dimethyl hexane (DBPMH) as a curing agent on the conductivity of conductive silicone rubber with two different kinds of conducting mechanisms. The experimental results show that the volume resistivity of conductive silicone rubber changed with its degree of crosslinking. When the carbon black loading was 25 parts per hundred rubber (phr) and a completely continuous conducting network had not formed, the volume resistivity of the vulcanizates decreased with increasing crosslink density. The volume resistivity of the vulcanizate with a suitable amount of C gum decreased to 53%, and the tensile strength increased by 0.8 MPa compared to the vulcanizate without C gum. When the carbon black loading was 40 phr and a completely continuous conducting network had formed, the crosslink density of vulcanizates changed as the amount of DBPMH changed. The volume resistivity of vulcanizates first decreased and then increased with increasing crosslink density. There was a valley value in the resistivity–crosslink density curve. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 3471–3475, 2003

Key words: silicones; rubber; crosslinking; modulus

INTRODUCTION

Silicone rubber is an insulator to which conductivity is imparted by the addition of conductive fillers such as carbon black, metallic powder, and carbon fiber. According to the concentrations of fillers, conductive silicone rubber can be formulated over a broad range of conductivity. It has been widely used in many fields[1] because of its ability to be fabricated by conventional techniques, its easy controlled volume resistivity, and its inherent silicone advantages, including excellent thermal stability and climate resistance. However, theoretical studies on conductive silicone rubber have often lagged behind its applications.

Ajayi and Hepburn[2] investigated the effect of the type and proportion of carbon black on the electrical resistivity of dicumyl-peroxide-cured conductive silicone rubber and derived a theory based on the probability of conducting chain formation in a filler/rubber composite. Princy et al.[3] reported the effect of different types of carbon black [e.g., acetylene black, lamp black, and ISAF (N-234) blacks], copper powder, and graphite on the conductivity and mechanical properties of silicone rubber compounds. A quantitative model relating electrical resistance with strain and time for carbon-black-filled silicone rubber was developed by Cost et al.[4] The effects of compressive strain and stress on conductive silicone rubber have also been investigated.[5–9] As a matrix of conductive composites, the structure of silicone rubber influences the formation of conducting networks; thus, it plays an important role in the conductivity of composites. Aneli and Koberidze[10] demonstrated the effect of vulcanization modes on the conductivity of conductive silicone rubber filled with carbon black. For silicone rubber vulcanized by the same mode, a different crosslinking state should lead to a different conductivity despite the same loading of carbon black. Furthermore, the influence of crosslinking on the conductivity of conductive silicone will be different when the conducting mechanisms are different. These variables were investigated in this study.

Generally, the crosslinking state of silicone rubber can be altered by the addition of a concentrative crosslinker[11,12] or by the variation of the amount of curing agent. In this study, polyvinylsilicone oil (C gum) was used as concentrative crosslinker, and 2,5-bis(*tert*-butyl peroxy)-2,5-dimethyl hexane (DBPMH) was used as curing agent.

EXPERIMENTAL

Materials

Silicone rubber (number-average molecular weight $= 5.8 \times 10^5$ and vinyl group content = 0.15 mol %), C

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TABLE I
Formulation of Conductive Silicone Rubber

Material	1	2	3	4
Silicone gum	100	100	100	100
Carbon black	5–40	25	40	40
C gum	—	0–3.0	0–3.0	—
DBPMH	1.5	1.5	2.0	2.0–3.2

All values are expressed as (phr) by weight.

gum (92.2 cp and vinyl group content = 8.45 mol %), DBPMH, and VXC-72 conductive carbon black were all industrial chemicals.

Preparation of conductive silicone rubber

Formulation

The formulation of the conductive silicone rubber is listed in Table I.

Processing

According to the literature,[13,14] materials were compounded and then vulcanized at 170°C under 9.8 MPa of pressure. The optimum cure times (the time for attaining 90% of the maximum torque) of the conductive silicone rubber were determined with a Monsanto rheometer (MDR2000E-1) and are listed in Table II. The samples were postcured at 190°C for 3 h.

Testing

The electrical resistance of samples with typical dimensions of 2.0 × 7.0 × 0.15 cm^3 were measured at room temperature with a QJ83 direct current bridge (Zhengyang Instruments, Ltd., Shanghai, China). Its measuring current range was from 25 μA to 100 mA, and the electrical power consumed within sample was less than 1 W.[15] The volume resistivity (ρ) of the samples was calculated according to the following equation:

$$\rho = RA/t \qquad (1)$$

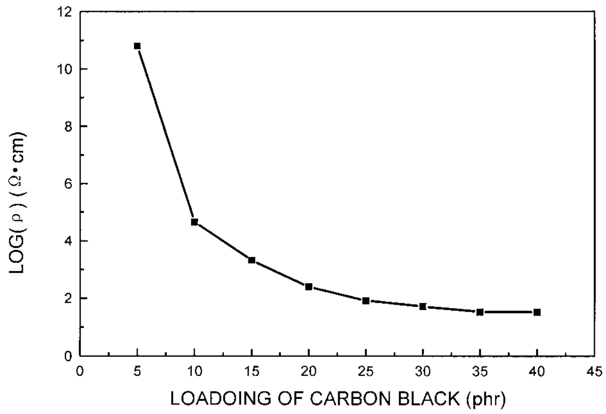

Figure 1 Logarithm of the resistivity versus the loading of carbon black.

where R is resistance, A is area, and t is thickness of samples. The data presented are the averages of five samples. The mechanical properties of the vulcanizates were measured as described in the literature.[13]

The density of vulcanizates were measured according to the literature.[16]

RESULTS AND DISCUSSION

Effect of carbon black loading on conductivity

Table II summarizes some of the physical properties of the conductive silicone rubber given by eq. (1). The conductivity, hardness, and tensile strength of conductive silicone rubber increased with increasing loading of carbon black. Elongation at break first increased and then decreased. The cure time increased with increasing loading of carbon black, which may have been due to the retarding effect of VXC-72 blacks on vulcanization.

Figure 1 illustrates the relation between the carbon black loading and the volume resistivity. At very low carbon black loading, the resistivity of the composite was very high. As the carbon black loading increased to 10 parts per hundred rubber (phr), the resistivity decreased by many orders of magnitude to a particular region, where the resistivity decrease was not so

TABLE II
Properties of Condutive Silicon Rubber Given by Eq. (1)

Sample	Carbon black loading	DBPMH content	Cure time (min)	Tensile strength (MPa)	Elongation at break (%)	Hardness (shore A)	ρ (Ω cm)
I-1	5	1.5	3.00	0.38	138.5	33	6.3×10^{10}
I-2	10	1.5	3.58	1.32	318.3	34	4.5×10^{4}
I-3	15	1.5	4.67	1.82	333.4	35	2.1×10^{3}
I-4	20	1.5	5.60	3.45	366.7	37	2.5×10^{2}
I-5	25	1.5	7.22	4.18	383.3	39	83.77
I-6	30	1.5	8.35	4.75	403.3	40	52.28
I-7	35	1.5	11.58	4.88	420.0	42	34.08
I-8	40	1.5	12.70	4.93	416.7	44	32.76

TABLE III
Properties of Conductive Silicon Rubber Given by Eq. (2)

Sample	C gum content	M_{100} extension (MPa)	Tensile strength (MPa)	Elongation at break (%)	Hardness (shore A)	υ	ρ (Ω cm)
2-1	0	0.74	4.18	383.3	39	υ_0	83.77
2-2	1.0	0.75	3.81	371.6	39	$1.01\upsilon_0$	101.91
2-3	1.5	0.70	4.28	405.9	37	$0.95\upsilon_0$	107.35
2-4	2.0	1.00	4.91	353.4	43	$1.35\upsilon_0$	44.62
2-5	2.5	0.95	3.70	313.3	42	$1.28\upsilon_0$	65.78
2-6	3.0	0.80	4.35	378.3	41	$1.10\upsilon_0$	75.77

rapid. It is generally accepted that the dominant conducting mechanism in this region is electron tunneling.[17] According to this mechanism, electrons may pass through thin, insulating films at field strengths experimentally encouraged in gaps between adjacent carbon black particles, aggregates, and agglomerates. In electron tunneling, the current is an exponential function of the gap width; thus, an obvious decrease in resistivity still existed as the carbon black loading increased. When the carbon black loading was above 35 phr, the resistivity ultimately saturated. Thereafter, a further increase in carbon black loading resulted in a slight difference in the resistivity of the conductive silicone rubber. This occurred because a completely continuous conducting network had formed, and then, the dominant conducting mechanism was general contact conduction.[18] So, we investigated the effect of crosslinking on the conductivity of conductive silicone rubber at two carbon black loading, 25 and 40 phr, which corresponded to two different conducting mechanisms.

Effect of crosslinking on the conductivity of conductive silicone rubber loaded with 25 phr carbon black and varying amounts of C gum

The toluene-swelling method is often used to determine the crosslink density (υ) of vulcanizates. However, it is unsuitable for vulcanizates loaded with carbon black because carbon black can prevent rubber from expanding.[19] It has been shown that the proportionality between the tensile modulus (M) and the crosslink density (υ), predicated by the statistical theory of rubber elasticity[20]

$$M = \upsilon RT(\lambda - \lambda^{-2}) \quad (2)$$

where R is the gas constant, T is the absolute temperature, and λ is the extension ratio, is valid for black-filled rubber only at strains near 100% with an ordinary tensile test.[21] With filled rubber, the expression for the modulus has to include the hydrodynamic term to account for the modulus amplification caused by the fillers. When the statistical theory and the function $f(\Phi_e)$ for the hydrodynamic effect are considered, one writes the expression for 100% modulus (M_{100}) by setting the extension ratio (λ) to 2 as[21]

$$M_{100} = 1.75\upsilon RTf(\phi_e) \quad (3)$$

Because $f(\Phi_e)$ would vary with both the effective volume fraction (Φ_e) of fillers and the degree of mixing,[22] we propose $f(\Phi_e)$ to be constant for a given recipe when Φ_e and the mixing conditions are strictly controlled to be the same.[23] In this study, we examined how the resistivity of conductive silicone rubber changed with varying crosslink density when the loading of carbon black was fixed; thus, the relative values of crosslink density of samples were enough. With all of this under consideration, the 100% modulus could be used to manifest the relative values of the crosslink density of conductive silicone rubber filled with the same amount of carbon black. In this study, we presumed the crosslink density of a certain sample as υ_0 and M as M_0; the crosslink densities of other samples were expressed as relative values calculated by the following equation:

$$\upsilon = (M/M_0)\upsilon_0 \quad (4)$$

which was derived from eq. (3).

The properties of conductive silicone rubber given by eq. (2) are listed in Table III. From the data in Table III, we found that C gum influenced both the mechanical properties and resistivity of the conductive silicone rubber. When 1.5 phr C gum was added, the crosslink density of the vulcanizate was lower, as shown by a low modulus and hardness and a high elongation. At the same time, its volume resistivity was at its largest. When 2.0 phr C gum was added, the crosslink density of the vulcanizate reached its biggest value. Meanwhile, the vulcanizate had the largest hardness and the lowest volume resistivity. Any further increase in C gum after this point eventually resulted in a decreased crosslink density and an increased volume resistivity. Because the addition of C gum made the curing reaction of the composites more complicated than that of the composites without C gum, we took the conductive silicone rubber with varying amounts of C gum as the object of study.

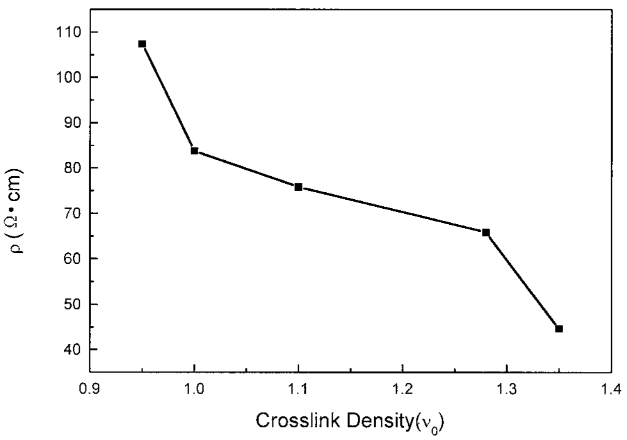

Figure 2 Resistivity versus the crosslink density of conductive silicone rubber loaded with 25 phr carbon black and varying amounts of C gum.

Figure 2 shows the effect of crosslink density on the resistivity of conductive silicone rubber loaded with 25 phr VXC-72 black and varying amounts of C gum.

As mentioned previously, when the carbon black loading was 25 phr, the dominant conducting mechanism was electron tunneling.[17] The current was an exponential function of the gap widths of adjacent carbon black particles, aggregates, and agglomerates. A higher crosslink density of composites resulted in a high density, which is shown by the hardness data in Tables III and IV and the density data in Table IV. A high density of composites meant a concentrated conducting network, which led to a decrease in the gap width and thus an obvious decrease in volume resistivity.

Effect of crosslinking on the conductivity of conductive silicone rubber loaded with 40 phr carbon black and varying amounts of DBPMH

As mentioned previously, conductive silicone rubber with different loadings of fillers obeys different conducting mechanisms. For this reason, we also investigated the effect of crosslinking on the conductivity of conductive silicone rubber with a carbon black loading of 40 phr, when a completely continuous conducting network had formed. The results are listed in Table V.

As shown by the data in Table IV, the addition of C gum did not play an effective role in changing the crosslink density of the conductive silicone rubber, as shown by the very small changes in hardness and modulus. This may have been due to two reasons. The first may have been the physical separation effect of carbon black. Because carbon black cannot combine strongly with silicone gum, the physical separation effect became distinct when the loading was as high as 40.0 phr, so C gum failed to change the crosslink density significantly. The second reason may have been carbon black's chemical reactivity. Because carbon black could take part in a free-radical reaction, a high loading of carbon blacks made the C gum's chemical reaction complicated. All in all, when the loading of carbon blacks was 40.0 phr, the addition of C gum could either increase or decrease the volume resistivity of the conductive silicone rubber, and the decreases in volume resistivity were not as much as in eq. (2). To study clearly the effect of crosslinking on the conductivity of conductive silicone rubber with a completely continuous conducting network, we changed the crosslink density of vulcanizates by varying the amounts of DBPMH according to eq. (4).

Table V summaries both the mechanical and electrical properties of silicone rubber given by eq. (4).

As the amount of DBPMH increased, the crosslink density of the vulcanizates increased distinctly, as shown by increases in hardness, modulus, and tensile strength, as well as a decrease in elongation. Meanwhile, the density of the vulcanizates increased with increasing crosslink density. When the amount of DBPMH changed from 2.0 to 2.5 phr, the volume resistivity of the vulcanizate reached its smallest value as the result of the concentrated conducting network. However, the decrease in volume resistivity was not very large. This was because a completely continuous conducting network had formed in the silicone rubber and the contact resistance of carbon black aggregates and agglomerates were not very sensitive to the change in the crosslinking state of the vulcanizates. When the amount of DBPMH increased further, the volume resistivity kept increasing.

Figure 3 shows the effect of crosslink density on the resistivity of conductive silicone rubber loaded with

TABLE IV
Properties of Conductive Silicone Rubber Given by Eq. (3)

Sample	C gum content	M_{100} (MPa)	Tensile strength (MPa)	Elongation at break (%)	Hardness (shore A)	ρ (Ω cm)
3-1	0	1.40	6.13	334.5	50	20.20
3-2	1.5	1.58	5.58	290.4	52	27.38
3-3	2.0	1.50	5.85	301.1	51	18.35
3-4	2.5	1.60	5.50	274.4	52	22.47
3-5	3.0	1.58	6.08	294.4	52	17.20

TABLE V
Properties of Conductive Silicone Rubber Given by Eq. (4)

Sample	DBPMH content	M_{100} (MPa)	Tensile strength (MPa)	Elogation at break (%)	Hardness (shore A)	υ	ρ (Ω cm)	Density (10^3kg/m^3)
4-1	2.0	1.40	6.13	334.5	50	υ_0	20.20	1.0895
4-2	2.5	1.57	6.20	305.5	52	$1.12\upsilon_0$	16.58	1.1323
4-3	2.7	1.68	6.25	283.6	53	$1.20\upsilon_0$	19.99	1.1399
4-4	3.0	1.78	6.30	268.9	54	$1.27\upsilon_0$	21.52	1.1423
4-5	3.2	1.87	5.33	228.0	56	$1.34\upsilon_0$	25.06	1.1500

40 phr VXC-72 black and varying amounts of DBPMH.

As we know, carbon black is the carrier of a great deal of free radicals. These free radicals are electric current carriers and make carbon black a conductor. Besides initiating a curing reaction, the excessive free radicals produced by additional DBPMH could also combine with these free radicals in carbon black under the curing reaction conditions. Thus, at the same time it increased the crosslink density of the vulcanizates, additional DBPMH also decreased the density of current carriers and, therefore, decreased the conductivity of silicone rubber. Moreover, a high degree of crosslinking may have had another influence on the conductivity of the conductive composites. In the course of processing conductive composites, some carbon black agglomerates were broken down. However, in the subsequent course of the curing reaction, those agglomerates had chances to reunite because of thermodynamic dispersion at high temperatures. A high degree of crosslinking of the composite may have led to a decreased dispersion speed of carbon black aggregates, which might have had a negative influence on the formation of the conducting network. In summary, the conductivity of the conductive silicone rubber given by eq. (4) may have been influenced by the three factors. The eventual results depended on which factor prevailed.

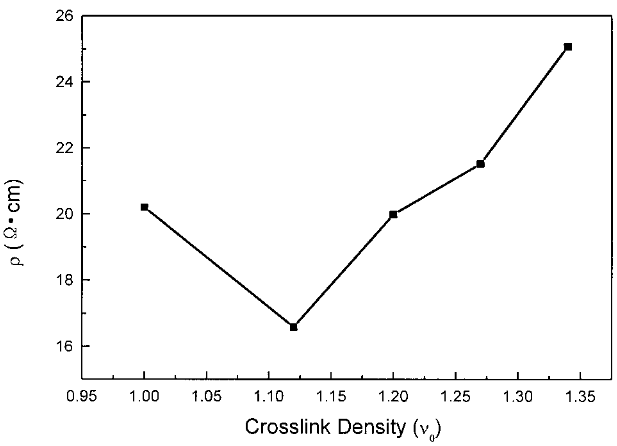

Figure 3 Resistivity versus the crosslink density of silicone rubber loaded with 40 phr carbon black and varying amounts of DBPMH.

CONCLUSIONS

The conductivity of conductive silicone rubber loaded with conductive carbon black was improved by an increase in degree of crosslinking when the loading of carbon blacks was low and a completely continuous conducting network had not formed. C gum, a kind of concentrative crosslinker, played a role in changing the degree of crosslinking of the conductive silicone rubber with a low loading of carbon black. For silicone rubber with a high loading of carbon black when a completely continuous conducting network had formed, DBPMH, a kind of curing agent, played a role in changing the degree of crosslinking of the conductive silicone rubber. Under these circumstances, the conductivity first increased and then decreased with increasing crosslink density of the vulcanizates. There was a valley value in the resistivity–crosslink density curve.

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