

Effects of Some Phenylethynylsilicon Compounds on Heat-Curable Silicone Rubber. I. 1,3-Bis(methylphenylethynylvinyl)disiloxane

SHENGYU FENG* and ZUODONG DU

Institute of New Materials, Shandong University, Jinan, Shandong, People's Republic of China

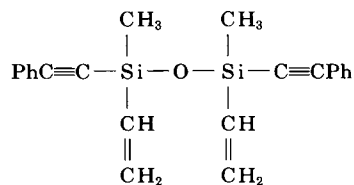
SYNOPSIS

We have investigated the effects of 1,3-bis(methylphenylethynylvinyl)disiloxane (BMPVDS) as crosslinker on heat-curable silicone rubber and measured sol fractions and crosslink density of vulcanizates by benzene-extract and toluene-swelling methods, respectively. The experimental results show that, adding suitable amounts of BMPVDS, the vulcanizates exhibited rather fine mechanical properties. The tear strength of some vulcanizates could reach as high as 60.31 kN/m, the tensile strength 13.46 MPa, and the modulus at 100% extension 2.45 MPa, and the permanent deformation is rather low. BMPVDS is also a good curing retarder of hydrosilation curing silicone rubber. When adding 0.08 part of BMPVDS or more, the stocks can store at $20 \pm 1^\circ\text{C}$ more than 50 days without curing.

INTRODUCTION

Since methylsilicone vulcanizates were obtained by peroxide curing of methylsilicone gum, the theoretical and applied research of silicone rubber has been widely developed. To improve the mechanical properties of vulcanizates, a lot of work has been done by research workers.¹⁻⁹ From their work it has been found that high strength vulcanizates can be obtained by introducing a few vinyl units into main links of methylsilicone gum and using polyvinylsilicone oil (C gum) or polyvinylsilicon compounds as cross linkers. Still adding suitable hydric silicone oil (H-oil) will gain high strength hydrosilation curing vulcanizates (HCV).^{8,10} The main reasons that the mechanical properties of vulcanizates can be improved are that adding H-oil and/or C gum to methylvinylsilicone gum can cause "concentrative crosslinking" in curing.^{4,9} Theoretically, using polyfunctional alkynylsilicon compounds as crosslinkers of silicone rubber will be more favorable to "concentrative crosslinking" and more effective in im-

proving properties of vulcanizates than using C gum because of the higher unsaturated degree of the former. However, to our knowledge, there have been no reports on alkynylsilicon compounds as crosslinkers of silicone rubber until now. Moreover, we once reported that phenylacetylene and propiolic alcohol could be used as curing retarders of hydrosilation curing silicone rubber to improve its processing property.¹¹ For the above-mentioned reasons, we used 1,3-bis(methylphenylethynylvinyl)disiloxane (BMPVDS),



as crosslinker of silicone rubber to determine whether it could play roles of both "concentrative crosslinker" and retarder. The experimental results agreed well with theoretical inferences. The mechanical strength of vulcanizates could be effectively enhanced by adding suitable amounts of BMPVDS. Tensile strength, tear strength, and modulus at 100% extension of some vulcanizates reached as high

* To whom correspondence should be addressed.

as 13.46 MPa, 60.31 kN/m, and 2.45 MPa, respectively. At the same time, the HCV stocks containing BMPVDS could store a long time at room temperature. To observe curing state of vulcanizates, their sol fraction (S) and crosslink density (shown by average molecular weight \bar{M}_c of effective units) were measured.

EXPERIMENTAL

Materials

Silicone gum (\bar{M}_n , 6.5×10^5 and V_i , 0.15 mol %), octamethylcyclotetrasilazane (D_4^N), C gum (92.2 cp and V_i , 9.0 mol %), 4[#] SiO₂ (specific surface area, 176 m²/g) and H-oil (H , 1.23 wt %) are all industrial chemicals. 1,1,3,3-Tetramethyl-1,3-divinylsiloxane-Pt complex (Pt-cat) was prepared by us. BMPVDS was prepared according to the previously reported method.¹²

Preparation of Heat Curable Silicone Rubber (HCSR)

Formulation. The formulation of HCSR is listed in Table I.

Processing. Referring to the literature,^{7,8} materials were compounded and then vulcanized at 170°C for 30 min under 29.4 MPa, and postcured at 200°C for 3 h to obtain vulcanizates.

Mechanical Measure of Vulcanizates

The mechanical properties of vulcanizates were measured as described in the literature.⁷ Their S

and \bar{M}_c were determined by benzene-extract and toluene-swelling methods,¹³ respectively. The HCV stocks compounded stored at $20 \pm 1^\circ\text{C}$ to observe the cure retardation of BMPVDS.

RESULTS AND DISCUSSION

Effects of BMPVDS on Mechanical Properties of HCSR

To prepare high strength silicone rubber, C gum is generally used as a crosslinker, causing "concentrative crosslinking" when stocks cure. However, BMPVDS is an organosilicon compound which has polyfunctional groups. We thought that using it as a crosslinker of silicone rubber would be conducive to "concentrative crosslinking." For that reason we chose BMPVDS as crosslinker to observe its effects on both peroxide curing and hydrosilation curing silicone rubber. As a contrast we used the suitable amount of C gum as crosslinker to test correspondingly (I-0, II-0). The experimental results are shown in Table II.

From the data in Table II we can find that the comprehensive mechanical properties of both PCV and HCV containing certain amounts of BMPVDS as crosslinker all rise distinctly, surpassing those of I-0 and II-0, using C gum as crosslinker. Moreover, they reach an optimum with the increase of used amounts of BMPVDS. If the used amounts of BMPVDS keep increasing, the properties will reduce again.

For the PCV, when adding 0.04 part of BMPVDS, its crosslink density is higher, shown concretely by low tear strength and elongation as well as high modulus and hardness. With increase of the amounts of BMPVDS used, because of distinct stabilization of phenyl group on radical to stabilize radicals produced by catalyst decomposition, excessive crosslinking caused by relative increase of phenylethynyl and vinyl groups can be inhibited to make elongation rise and hardness reduce. When adding 0.16 part of BMPVDS, the degree of crosslinking is in an ideal state, so that the properties of vulcanizates reach an optimum. For example, tensile strength, tear strength, and modulus at 100% extension of I-4 are 13.46 MPa, 61.31 kN/m, and 2.45 MPa, respectively, and much better than I-0. When amounts of BMPVDS used increase further the addition of the phenyl group largely inhibits the activity of the catalyst, making the vulcanizates to be in the state of "lack of cure." On the contrary, the properties of vulcanizates become poor.

Table I Formulation of HCSR

Materials	PCV ^a (wt parts)	HCV (wt parts)
Silicone gum	100	100
4 [#] SiO ₂	57	57
D ₄ ^N	8	8
C gum ^b	2 or 0	2.1 or 0
H-oil	—	1.15
BMPVDS	0–2.4	0–2.4
Pt-cat	—	0.2
DCBP	1	—

^a PCV = peroxide-curing vulcanizate.

^b When used amount of BMPVDS is 0, that of C gum is 2; if not, that of C gum is 0.

Table II Effects of BMPVDS on HCSR

Type	Sample No.	Used Amounts of BMPVDS (wt parts)	Tensile Strength (MPa)	Tear Strength (kN/m)	Modulus at 100% Extension (MPa)	Elongation at Break (%)	Hardness Shore A	Permanent Deformation (%)
PCV	I-0	0	10.80	59.80	2.30	542	59	6.0
	I-1	0.04	11.42	23.91	3.07	327	60	3.6
	I-2	0.08	10.17	42.52	2.45	442	58	3.6
	I-3	0.12	10.75	41.48	2.07	452	57	5.0
	I-4	0.16	13.46	61.31	2.45	520	57	5.6
	I-5	0.20	10.38	36.86	1.97	596	56	6.0
	I-6	0.24	9.93	36.74	1.86	675	54	6.4
HCV	II-0	0	12.50	22.50	4.10	356	64	3.2
	II-1	0.04	9.59	26.19	6.66	200	68	2.2
	II-2	0.08	13.50	26.84	5.69	282	67	3.2
	II-3	0.12	14.21	55.79	5.09	340	66	3.2
	II-4	0.16	12.42	30.34	4.14	362	66	4.0
	II-5	0.24	12.36	25.88	3.95	386	66	4.0

The situation of HCV is similar to PCV. When adding 0.04 part of BMPVDS, the degree of crosslinking of vulcanizates is also higher, shown by higher modulus and hardness as well as lower tear strength and elongation. Phenylethynyl groups have cure retardation to HCV stocks.¹¹ With addition of used amounts of BMPVDS, distinct cure retardation of phenylethynyl groups limit the excessive crosslinking of vulcanizates caused by added BMPVDS. When the amount of BMPVDS used is 0.12 part, the degree of crosslinking of HCV is in an ideal state and their properties reach an optimum; tensile strength, tear strength, and modulus at 100% extension are 14.21 MPa, 55.79 kN/m, and 5.09 MPa, respectively, surpassing those of II-0. However, if the amounts of BMPVDS used keep increasing, too strong a cure retardation of a lot of phenylethynyl groups will make vulcanizates be in a state of "lack of cure" and their properties become poor.

From the data in Table II we can also find that modulus and elasticity of HCV are higher and lower than those of PCV, respectively. This is because the former uses H-oil as crosslinker. At the same time, the higher the modulus, the lower the tear strength, findings also reported by Du and Yu.⁹

S and \bar{M}_c of Vulcanizates

To observe and study the crosslinking state of various vulcanizates, we measured their S and \bar{M}_c . Add a definite amount of vulcanizate of constant weight in a Soxhlet extractor and extract it with benzene for 36 h, and then weigh it after vacuum drying. Calculate its S by the following formula:

$$S = \frac{W_0 - W_1}{W_0} \times 100\% \quad (1)$$

where W_0 is the weight of unextracted vulcanizate and W_1 is that of extracted vulcanizate.

\bar{M}_c is determined by the toluene-swelling method and is calculated by the formula

$$\ln(1 - \phi_2) + \phi_2 + X_1\phi_2^2 + \frac{\rho\bar{V}_0}{\bar{M}_c}\phi_2^{1/3} = 0 \quad (2)$$

where ϕ_2 is the volume fraction of vulcanizate in the swelling body, X_1 , the macromolecule-solvent interaction efficiency, here 0.465, ρ , the density of vulcanizate, and \bar{V}_0 , the mole volume of the solvent. S and \bar{M}_c of vulcanizates are listed in Table III. From the data in Table III we can find that the amounts of BMPVDS used have no large effects on S , but S of PCV is larger than HCV. This is because peroxide-curing crosslinking is not so even as hydrosilation

Table III S and \bar{M}_c of Vulcanizates

Sample No.	S (%)	\bar{M}_c	Sample No.	S (%)	\bar{M}_c
I-0	2.22	5981	II-0	1.90	3551
I-1	2.09	5056	II-1	1.80	2972
I-2	2.39	7225	II-2	1.85	3033
I-3	2.65	7872	II-3	1.83	3739
I-4	2.50	8079	II-4	1.82	4033
I-5	2.40	8256	II-5	1.94	4086
I-6	2.77	10902			

curing in the solid state so that a small part of un-crosslinking molecules "slipping through the net" always exists. Generally speaking, the low S shows that the cure state of vulcanizates obtained is fairly good.

The average molecular weight \bar{M}_c of effective units means the degree of crosslinking of vulcanizates. It is the total reflection of physical and chemical action of additives with additives, main links with main links and each other. From the data in Table III it can be found that the \bar{M}_c 's of PCV are larger than those of HCV, agreeing with high elasticity and low hardness of PCV and low elasticity and high hardness of HCV. Except "lack of cure," to sum up, if \bar{M}_c is small, tear strength is low and vice versa (also see Table II), that is, to enhance tear strength of vulcanizates, their crosslinking density must be reduced to a certain range.¹⁴

Summarizing the results in Tables II and III, it can also be found that influences of BMPVDS on \bar{M}_c 's of vulcanizates agree with those on tensile strength, tear strength, modulus, elongation, and hardness.

Cure Retardation of BMPVDS to Hydrosilation Curing Silicone Rubber

The poor shelf stability of HCV stocks at room temperature (RT) is a difficult problem in production processing. To solve it, some curing retarders are needed. From our experimental results it was found that BMPVDS could be taken not only as crosslinker of HCV but also as curing retarder of HCV, as shown in Table IV. II-0 not containing BMPVDS began to cure after being stored at $20 \pm 1^\circ\text{C}$ for 16 h, with losing processing property. However, the stocks containing more than 0.08 part of BMPVDS can be stored at $20 \pm 1^\circ\text{C}$ for 50 days without curing, solving the above difficult problem. This is favorable for industrial production of HCV. Thus it can be said that BMPVDS is a good curing retarder of hydrosilation curing silicone rubber.

Table IV Cure Retardation of BMPVDS to Hydrosilation Curing Silicone Rubber ($20 \pm 1^\circ\text{C}$)

Sample No.	Shelf Time (days)	Sample No.	Shelf Time (days)
II-0	0.7	II-3	> 50
II-1	21	II-4	> 50
II-2	> 50	II-5	> 50

On "Concentrative Crosslinking"

Du et al.^{4,9} thought that C gum, or similarities, as crosslinker of HCSR could effectively improve mechanical properties of HCSR by producing "concentrative crosslinking" in curing. Theoretically, BMPVDS as crosslinker is more favorable to "concentrative crosslinking" than C gum, as our results demonstrate (see Tables II and III). \bar{M}_c 's of I-4 and II-3 are larger than those of I-0 and II-0, respectively, and comprehensive properties of I-4 and II-3 are also better than I-0 and II-0, respectively. This agrees with both Du's viewpoint and our theoretical inferences.

CONCLUSION

BMPVDS is a good cure crosslinker of HCSR, which is more conducive to "concentrative crosslinking" than C gum. Adding certain amounts of BMPVDS in the stocks, the comprehensive properties of vulcanizates can be largely improved. At the same time, BMPVDS is also a good curing retarder of hydrosilation cure silicone rubber.

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