

# Investigation of Polysiloxanes Containing Phenylethynyl Groups as Cross-Linkers of Heat-Curable Silicone Rubber

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**ABSTRACT:** Hydrosilation-curing vulcanizates (HCV) and peroxide-curing vulcanizates (PCV) were prepared respectively by using polysiloxanes containing phenylethynyl groups (PE-PDMS) as cross-linkers. The mechanical properties and average molecular weights of effective units ( $\bar{M}_c$ ) of HCV and PCV were measured. The experimental results show that PE-PDMS can be used as cross-linkers of heat-curable silicone rubber instead of C gum, and when adding suitable amounts of PE-PDMS, the vulcanizates exhibited good mechanical properties. The tear strength of some vulcanizates reached 30.0 kN/m, the tensile strength 11.7 MPa, the modulus at 100% extension 3.3 MPa, and the permanent deformation is low. PE-PDMS also has cure retardation to hydrosilation-cure silicone rubber and thus can prolong the shelf time of stocks. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1554–1557, 2000

## INTRODUCTION

In 1940s, methylsilicone vulcanizates were obtained by peroxide curing of methyl silicone gum. Since then, both theoretical and applied researches about silicone rubber have been widely developed. To improve the mechanical properties of vulcanizates and broaden their use range, a lot of work has been done over the past 50 years.<sup>1–7</sup> By introducing a few vinyl groups into main chains of methylsilicone gum as side groups and using “concentrative cross-linkers,” such as polyvinylsilicone oil (C gum), polyvinylsilicon compounds, phenylethynylsilicon compounds, and so on, high-strength peroxide-curing vulcanizates (PCV) can be obtained. For hydrosilation-curing vulcanizates (HCV), hydric silicone oil (H-oil) is a suitable cross-linker. The main reasons that the mechanical properties of vulcanizates can be improved are that H-oil and/or C gum in compositions can cause “concentrative cross-linking” in curing. When an external force acts on materials

(vulcanizates), it can be dispersed on many chains via “concentrative cross-linking point,” therefore the ability for the materials to resist destruction caused by the external force is enhanced. About the theory of “concentrative cross-linking,” we did some of work<sup>8,9</sup> in which compounds containing phenylethynyl groups were used as cross-linkers of silicone rubber instead of C gum, and had a good effect. However, all the used compounds containing phenylethynyl groups were low-molecular-weight silanes or disiloxanes. Using higher molecular weight polysiloxanes containing phenylethynyl groups (PE-PDMS) as cross-linkers instead of C gum has not been reported yet. Theoretically, PE-PDMS as cross-linkers of silicone rubber will be more favorable to “concentrative cross-linking.” For this reason, we did an investigation on PE-PDMS as cross-linkers of heat-curable silicone rubber.

## EXPERIMENTAL

### Materials

Octamethylcyclotetrasilazane ( $D_4^N$ ), C gum (viscosity, 90 MPa.s and vinyl, 9.0 mol %), 4<sup>#</sup> SiO<sub>2</sub>

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**Table I Composition of HCSR (wt parts)**

Materials	PCV	HCV
Silicone gum	100	100
4 <sup>#</sup> SiO <sub>2</sub>	57	57
D <sub>4</sub> <sup>N</sup>	8	8
C gum <sup>a</sup>	2 or 0	2.1 or 0
H-oil	0	1.15
PE-PDMS	0–3.0	0–3.0
Pt-cat	0	0.2
DBPMH <sup>b</sup>	1	0

<sup>a</sup> When used amount of PE-PDMS is 0, that of C gum is 2; if not, that of C gum is 0.

<sup>b</sup> DBPMH is 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane.

(specific surface area, 176m<sup>2</sup>/g), H-oil (H, 1.3 wt %) and silicone gum ( $M_n$ ,  $5.5 \times 10^5$  and vinyl, 0.15 mol %) are all industrial chemicals. 1,1,3,3-tetramethyl-1,3-divinyl-disiloxane-Pt complex (Pt-cat)<sup>10</sup> and polysiloxanes containing phenylethynyl groups (PE-PDMS)<sup>11</sup> were prepared according to the literatures, respectively.

### Preparation of Heat-Curable Silicone Rubber

#### Composition

The composition of heat-curable silicone rubber (HCSR) is listed in Table I.

#### Processing

Referring to the literature,<sup>12</sup> materials were compounded and then vulcanized at 170°C for 30min under 9.4 MPa, and postcured at 200°C for 2 h under ambient pressure to obtain vulcanizates.

#### Measurement of Mechanical Properties of Vulcanizates

The mechanical properties of vulcanizates were measured as described in the literature.<sup>12</sup> Their average molecular weight of effective units ( $\bar{M}_c$ ) was determined by toluene-swelling method.

#### Cure Retardation of PE-PDMS to Hydrosilation-Curing Silicone Rubber

To observe the cure retardation of PE-PDMS to hydrosilation-curing silicone rubber, some stocks of HCV were stored at 25±1°C and their shelf time were recorded, seeing Table II.

## RESULTS AND DISCUSSION

### Effects of PE-PDMS on Mechanical Properties of Vulcanizates

In order to obtain high-strength silicone rubber, concentrative cross-linkers are usually intro-

duced into composition. The most frequently used cross-linker was C gum. From the “concentrative cross-linking” point of view, using PE-PDMS as cross-linkers of silicone rubber should be more effective in improving properties of vulcanizates than using C gum because of the higher unsaturated degree of the phenylethynyl than vinyl groups. On the above consideration, we used PE-PDMS as cross-linker to do experiments. The results are given in Table III.

From the data in Table III, we can find the comprehensive mechanical properties of HCV samples using PE-PDMS as cross-linker surpass the sample 01, which only uses H-oil as cross-linker, and reach the level of H0 using C gum as cross-linker. When adding 0.5 part of PE-PDMS, the cross-linking degree of vulcanizates already surpasses sample 01, which can be shown from the contrast of their modulus, hardness, and elongation. Phenylethynyl groups have cure retardation to HCV. With increase of used amounts of PE-PDMS, cure retardation of phenylethynyl groups limits the “excessive cross-linking” of vulcanizates caused by added PE-PDMS. When the amount of PE-PDMS used is 2.5 parts, the cross-linking degree of HCV (H5) is in an ideal state and its properties reach an optimum, for example, tensile strength, tear strength, and modulus at 100% extension of H5 are 11.7 MPa, 30.0 kN/m, and 3.3 MPa, respectively.

The data in Table III also show that the comprehensive mechanical properties of all PCV samples (P1-P6) using PE-PDMS as cross-linker are good. When adding 0.5 parts of PE-PDMS, the cross-linking degree of vulcanizate (P1) already reaches sample P0. Phenyl groups have stabilization on radicals from decomposition of catalyst. With the increase of the used amount of PE-PDMS, excessive cross-linking caused by relative increase of phenylethynyl groups can be inhibited

**Table II Cure Retardation of PE-PDMS to HCV<sup>a</sup>**

Sample No.	C Gum (wt parts)	PE-PDMS (wt parts)	Shelf Time (h)
1	2	0	4
2	0	1.3	>24
3	0	1.9	>24
4	0	2.5	>24

<sup>a</sup> Silicone gum 100, 4<sup>#</sup>SiO<sub>2</sub> 57, H oil 1.15, and D<sub>4</sub><sup>N</sup> 8 parts are the same in the composition.

**Table III Effects of PE-PDMS on HCSR**

Type	Sample No.	Used Amounts of PE-PDMS (wt parts)	Tensile Strength (Mpa)	Tear Strength (kN/m)	Modulus at 100% Extension (Mpa)	Elongation at Break (%)	Hardness (Shore A)	Permanent Deformation (%)
HCV <sup>a</sup>	O1	0	10.1	26.0	2.8	429	63	5.0
	H0	0	12.4	28.3	3.3	400	66	4.1
	H1	0.5	11.5	26.2	3.6	370	66	3.3
	H2	1.3	10.6	29.7	3.5	415	66	3.3
	H3	1.6	10.8	29.3	3.4	430	68	3.3
	H4	1.9	11.2	29.5	3.4	460	68	3.3
	H5	2.5	11.7	30.0	3.3	483	66	3.3
	H6	3.0	10.8	28.9	2.3	496	66	4.1
PCV <sup>a</sup>	P0	0	11.0	21.0	1.9	420	57	7.6
	P1	0.5	10.5	20.7	1.8	433	58	6.0
	P2	1.3	10.2	20.4	1.7	447	58	6.1
	P3	1.6	10.4	20.4	1.8	457	57	6.0
	P4	1.9	11.0	20.7	1.9	486	57	6.3
	P5	2.5	11.4	21.4	2.3	494	57	6.5
	P6	3.0	10.4	20.3	2.1	543	56	6.9

<sup>a</sup> For sample O1, used amount of C gum and PE-PDMS is 0.

by the stabilization of phenyl groups on radicals, shown concretely by rise of elongation and slight drop of hardness. When the amounts of PE-PDMS used is 2.5 parts, the cross-linking degree of vulcanizate (P5) is in an ideal state and its properties reach an optimum. For example, the tensile strength, tear strength, and modulus at 100% extension of P5 are 11.4 MPa, 21.4 kN/m, and 2.3 MPa, respectively, surpassing sample P0 using C gum as cross-linker. But when the amounts of PE-PDMS used increase further, the relative increase of phenyl groups inhibits the activity of the catalyst, causing the vulcanizates to be in a state of "lack of cure," and causing low strength and modulus, an increase in elasticity and permanent deformation, and causing the comprehensive properties of vulcanizates to become worse.

### $\bar{M}_c$ of Vulcanizates

For cross-linking polymers,  $\bar{M}_c$  is an important structural parameter, which has a great effect on physical mechanical properties of the polymers. To observe and study cross-linking state of vulcanizates, we measured their  $\bar{M}_c$  (see Table IV) using toluene-swelling method, which were calculated by the formula,

$$\ln(1 - \Phi_2) + \Phi_2 + x_1\Phi_2^2 + \frac{\rho\bar{v}_0}{\bar{M}_c}\Phi_2^{1/3} = 0$$

where  $\Phi_2$  is the volume fraction of vulcanizates in the swelling body;  $x_1$  is the macromolecule-solvent interaction efficiency, here 0.465;  $\rho$  is the density of vulcanizates, and  $\bar{v}_0$  is the mole volume of the solvent.

$\bar{M}_c$ , which reflects the cross-linking degree of vulcanizates, is the total reflection of physical and chemical action of additives with additives, main chains with main chains, and main chains with additives. From the data in Table IV, we can find that the  $\bar{M}_c$ 's values of PCV are larger than those of HCV, which agrees with high elasticity and low hardness of PCV and low elasticity and high hardness of HCV. In addition,  $\bar{M}_c$ 's values of vulcanizates using PE-PDMS as cross-linker are close to those using C gum as cross-linker, which further shows that PE-PDMS can be used as cross-linkers of heat-curable silicone rubber.

**Table IV  $\bar{M}_c$  of Vulcanizates**

Sample No.	$\bar{M}_c$	Sample No.	$\bar{M}_c$
P0	2765	H0	1909
P2	2794	H2	1655
P3	2854	H3	1838
P4	2945	H4	1861
P5	2976	H5	1958

### Cure Retardation of PE-PDMS to Hydrosilation-Curing Silicone Rubber

HCV stocks will slowly cure to lose processing property when stored at room temperature. To solve it, some curing retarders are usually needed.<sup>13</sup> The experimental results (see Table II) show that PE-PDMS not only can be used as cross-linkers of HCV but also has cure retardation to HCV. Sample 1 not using PE-PDMS began to cure after being stored at  $25\pm 1^\circ\text{C}$  for 4 h to lose processing property. However, samples 2–4 containing PE-PDMS can be stored at  $25\pm 1^\circ\text{C}$  over 24 h without curing.

### CONCLUSION

PE-PDMS can be used as cross-linkers of heat-curable silicone rubber instead of C gum. When adding certain amounts of PE-PDMS in the stocks, the vulcanizates having fine comprehensive properties can be obtained. At the same time, PE-PDMS also has cure retardation to hydrosilation-cure silicone rubber and thus the shelf time of stocks can be prolonged.

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