

Preparation of Aminopropyl Polysiloxane-Based Heat-Curable Silicone Rubber

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ABSTRACT: By using polysiloxane containing aminopropyl groups as a base gum and polysiloxane containing epoxy groups as a crosslinker, we prepared a new type of addition-curable silicone rubber and investigated in detail the effect of various factors on the silicone rubber. Better technical conditions were determined and the vulcanizates with fine mechanical properties were obtained. The tensile strength, tear strength, elongation at break, and hardness of the vulcanizates reach 8.1 MPa, 19.4 kN/m, 420%, and 64 ShA, respectively. To analyze the crosslinking statue, we measured their crosslinking density by toluene-swelling methods. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2341–2346, 2001

Key words: preparation; aminopropyl groups; heat-curable; silicone; rubber

INTRODUCTION

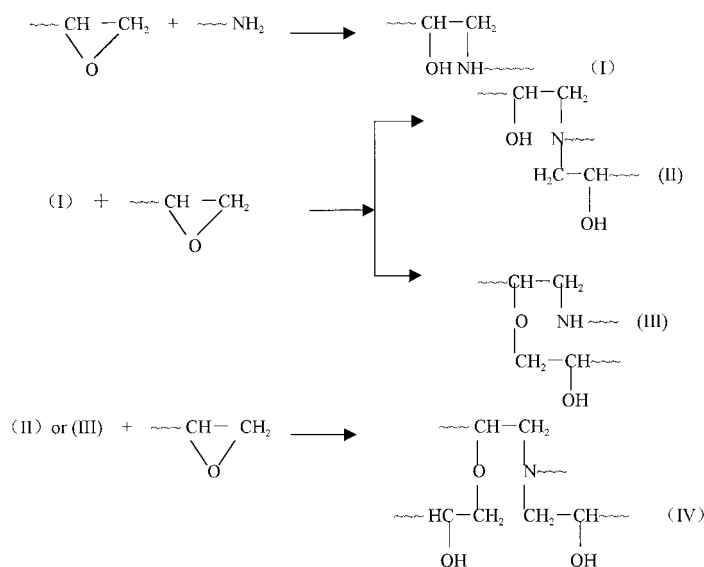
Silicone rubber is one of the four kinds of the main organic silicone products. It exhibits unique performance properties and has been widely used in many fields such as aviation, electrical, medical treatment, and automobile manufacturing.¹ Vulcanization of silicone rubber can be carried out by a variety of methods at both elevated and ambient temperatures, that is, high-temperature vulcanization (HTV) and room-temperature vulcanization (RTV).² In RTV reactions, the silicone polymers are mainly hydroxyl-terminated polysiloxanes. The crosslinking condensation reactions normally involve silanol chain ends and polyfunctional silicon compounds. Vinyl-terminated silicone polymers are also used in RTV products. By

using low molecular weight silicone oil having Si—H groups in molecule chains as crosslinkers and chloroplatinic acid as a catalyst, room-temperature crosslinking can be accomplished through a hydrosilation reaction in which a Si—H group was added to a vinyl group. The silicone polymers used in HTV production are principally siloxanes with less than 0.5 mol % of methyl groups replaced by vinyl groups. They can be cured at elevated temperatures either by free-radical crosslinking reactions using peroxides as a catalyst or by hydrosilation reactions using Si—H-containing silicone oil as crosslinkers and chloroplatinic acid as a catalyst. However, no reports on polysiloxanes containing aminoalkyl groups as silicone polymers to prepare silicone rubber have been presented up to now. Because of the high activity of aminoalkyl groups, it should be possible to use polysiloxane containing aminoalkyl groups as base gums to prepare silicone rubber. One of the research directions related to silicone rubber is to develop a new curing system to improve its properties. At present, by using the polysiloxanes containing aminopropyl groups syn-

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Scheme 1 Mechanism of the reaction between APPS and EPS.

thesized in our lab as base gums and the polysiloxanes containing epoxy groups as curing agents, we prepared a new type of addition-curable silicone rubber. Through initial practice, we found that the silicone rubber prepared by such a way has a fine mechanical strength.

EXPERIMENTAL

Materials

Polysiloxanes containing aminopropyl groups (APPS)^{3,4} ($[\eta]_{\text{toluene}, 25^\circ\text{C}} = 148 \text{ mL/g}$) and polysiloxanes containing epoxy (EPS, 2000 g/mol, the epoxy value was 0.196 mol/100 g)⁵ were synthesized in our laboratory following the published procedure. 4[#] fumed silica was obtained from the Shenyang Chemical Factory (China) and was modified with octamethylcyclotetrasiloxane (D₄) and hexamethyldisilazane (MM^N).^{6,7}

Preparation of Silicone Rubber

Composition

APPS	100 parts ^a
Modified 4 [#] fumed silica	35–60 parts ^a
EPS	1 : 1–4 : 1 (mol/mol) ^b

^a This is a basic composition; we take the mass part as a unit, that is, the mass of the base gum is 100 parts and the used amount of other compounds is shown by the mass parts, correspondingly.

^b The amount of EPS used is shown by the ratio of the epoxy groups in EPS to the aminopropyl groups in APPS.

Processing

Materials were milled on a two-roll mill. First, APPS was encapsulated onto rollers and then modified 4[#] fumed silica was added step by step. By being milled uniformly, EPS was then milled into eight to 10 passes. After being milled batch-off, the materials were cured in a mold under pressure to obtain vulcanizates.

Measure of Vulcanizates

The mechanical properties of vulcanizates were measured using an XLD-A electronic rubber tension tester made in the Second Experimental Machine Factory of Changchun, China. Their degree of swelling was determined with the toluene-swelling method according to ref. 8. The average molecular weight (M_c) of the effective units showing the crosslinking density of the vulcanizates was further calculated from the degree of swelling.

RESULTS AND DISCUSSION

Preparing silicone rubber using APPS as the base gum and EPS as the crosslinker relies mainly on the reactivity of amino and epoxy groups. (The mechanism of the reaction is shown in Scheme 1.) There exist active hydroxyl groups in the three-dimensional network structure (IV), as shown in Scheme 1. They could further react with epoxy groups.

Table I Effect of the Amounts of EPS Used

Properties	Epoxy/Amino (mol/mol)			
	1 : 1	2 : 1	3 : 1	4 : 1
Hardness (ShA)	41	53	64	74
Tensile strength (MPa)	2.1	4.1	8.1	8.1
Elongation at break (%)	60	132	420	96
Tear strength (kN/m)	7.6	10.1	19.4	19.7

APPS, 100 parts (content of aminopropyl groups is 0.2%); modified 4[#] fumed silica, 50 parts; first stage: 160°C × 2 h, 29.4 MPa; postcure: 180°C × 10 h.

From refs. 9–11, the nitrogen atoms in the aminopropyl groups of APPS can form $d\pi-p\pi$ coordinate bonds with silicon atoms in the chains of polysiloxane, because there are lone-pair electrons in the nitrogen atoms and an empty d -orbital in the silicon atoms, making self-vulcanization phenomena in the base gum occur. This can be confirmed by a N→Si special model in the IR spectrum. Only when the nitrogen and silicon atoms are separated can amino groups react with epoxy groups and a cured network be obtained. So, in the curing process, heating to high temperature is necessary to destroy the $d\pi-p\pi$ of nitrogen-to-silicon atoms.

The properties of silicone rubber depend on both the chemical structures of the base gum and the amounts of fillers and crosslinkers used. The curing temperature and time also have an important effect on the properties of silicone rubber. We discuss below how the properties of silicone rubber are affected by these aspects.

Amount of EPS Used

Uncured polysiloxane exhibits a high degree of tackiness. When these polymers react with the crosslinkers, a three-dimensional elastic structure is formed and permanent elasticity can be obtained. The amounts of the crosslinkers used can affect the degree of crosslinking of the elastomer. In maintaining other conditions and changing the amount of EPS used, we obtained the experimental results shown in Table I.

Table I shows that silicone rubber presents optimal properties when the ratio of epoxy-to-amino groups is 3 to 1 (mol/mol). From the above, we know that the hydroxyl groups produced in the curing reaction of silicone rubber have active reactivity and can also react with the epoxy groups. When small amounts of EPS (e.g., 1/1 and 2/1) are

added, some base gums cure incompletely. So, the properties of the vulcanizates are poor. On the contrary, if too much EPS is added, the degree of curing is excessive; then, the properties of the vulcanizates are also poor.

Contents of Aminopropyl Groups in Base Gums

The properties of silicone rubber are closely related to the number of the crosslinking points, which depends on the contents of the functional group crosslinking in base gums.¹² In maintaining other conditions and changing the contents of aminopropyl groups in the base gums, we obtained the experimental results shown in Table II.

Table II shows that the properties of silicone rubber are superior when the content of aminopropyl groups is 0.2%. The properties of silicone rubber are related to its crosslinking density while it could be controlled through adjusting the contents of the aminopropyl groups. When the content of the aminopropyl groups is little, the mechanical properties of the vulcanizates are poor, which is indicated by their low hardness and tensile and tear strength and high elongation. But too many aminopropyl groups may cause some properties of the vulcanizates to decrease because of the forming of excessive crosslinking points.

Amount of Fillers Used

Silicone polymers are amorphous and the attractive forces between molecular chains are small. Unfilled cured silicone polymers exhibit low tensile strength; hence, reinforcing fillers are re-

Table II Effect of the Contents of Aminopropyl Groups

Properties	CAG ^a (%)			
	0.1	0.2	0.3	0.4
Hardness (ShA)	56	64	70	74
Tensile strength (MPa)	6.0	8.1	8.2	8.2
Elongation at break (%)	460	420	360	280
Tear strength (kN/m)	14.8	19.4	19.7	20.3

APPS, 100 parts; modified 4[#] fumed silica, 50 parts; the ratio of epoxy-to-amino groups is 3 to 1 (mol/mol); first stage: 160°C × 2 h, 29.4 MPa; postcure: 180°C × 10 h.

^a CAG is the content of aminopropyl groups that is shown with the percent of the chain units of aminopropyl groups in the base gums.

Table III Effect of the Used Amount of Silica

Properties	4 [#] Silica (Parts)			
	30	40	50	60
Hardness (ShA)	47	58	64	74
Tensile strength (MPa)	4.8	6.6	8.1	8.1
Elongation at break (%)	420	440	420	240
Tear strength (kN/m)	10	15.9	19.4	11

APPS, 100 parts (based on weight) (content of aminopropyl groups is 0.2%); the ratio of epoxy-to-amino groups is 3 to 1 (mol/mol); first stage: 160°C × 2 h, 29.4 MPa; postcure: 180°C × 10 h.

quired to improve the mechanical properties of vulcanizates.¹³ Silica is a good and common reinforcing filler for silicone rubber.¹⁴ In maintaining other conditions and changing the amount of silica used, we obtained the experimental results shown in Table III.

It can be found from the data in Table III that silicone rubber has optimal properties when the amount of silica used is 50 parts. As a reinforcing filler, silica can improve the resistance of silicone rubber against deformation and destruction. Silica can bond to silicone polymers via van der Waals forces, hydrogen bonds, and chemical bonds. Silicone chains are connected to each other through silica; thus, a network with a certain strength is formed. When the base gums are cured, high-strength silicone rubber can be obtained. With a certain amount of silica used, the interacting forces among silica and silicone chains can improve the mechanical strength of silicone rubber. But small amounts of silica cannot reinforce silicone rubber distinctly, while too much silica may cause some properties of silicone rubber to decrease because of the insulating of silica to silicone chains, which will affect the crosslinking of the base gums.

Curing Temperature

From the curing mechanism mentioned above, we can see that the nitrogen atoms of aminopropyl groups in silicone gums can form $d\pi-p\pi$ bonds with silicon atoms in silicone chains. To make amino groups react with epoxy groups, heating is necessary to destroy the $d\pi-p\pi$ bonds.

First-stage Temperature

In the first stage under certain pressure, it is necessary to keep the fixed form of silicone rubber

stable. In maintaining other conditions, we carried out the experiments at different temperatures. The results are shown in Table IV.

Table IV shows that the vulcanizates prepared at 160°C have a certain of strength and fixed form and can be peeled off easily from the mold. At too low a temperature such as 140°C, the ring-opening reaction of amino-to-epoxy groups is difficult. So, in this case, the vulcanizates have not only low strength but also no fixed forms. But at a slightly higher temperature such as 180°C, the vulcanizate became yellow through an easy ring-opening reaction, and the vulcanizate also has a fixed form. So, 160°C is suitable for the first-stage temperature.

Postcure Temperature

The destination of the postcure is to make the ring-opening reaction of amino-to-epoxy groups complete, so that the vulcanizates can exhibit optimal properties. We investigated the effect of the postcure temperature. The results are shown in Table V.

Table V shows that the silicone rubber cured at 180°C has an optimal appearance and performance characters, and that cured at 160°C has only low strength because of the low crosslinking degree. Compared to 180°C, the performance characters of the silicone rubber cured at 200°C are improved only slightly but it becomes brown. The silicone rubber cured at 250°C becomes black and opaque, and its performance characters becomes poorer, apparently being caused by the cyclizing degradation of silicone chains and aging at high temperature. So, 180°C is chosen as the postcure temperature.

Curing Time

Here, the curing time means the postcure time. At a certain high temperature, the functional groups

Table IV Effect of the First-stage Temperature

Properties	Temperature (°C)		
	140	160	180
Hardness (ShA)	40	48	50
Tensile strength (MPa)	1.8	2.5	2.7
Elongation at break (%)	50	80	85
Tear strength (kN/m)	5.7	7.1	7.3
Appearance	Colorless	Colorless	Yellow

APPS, 100 parts (content of aminopropyl groups is 0.2%); modified 4[#] fumed silica, 50 parts; ratio of epoxy-to-amino groups is 3 to 1 (mol/mol).

Table V Effect of the Postcure Temperature

Properties	Temperature (°C)			
	160	180	200	250
Hardness (ShA)	60	64	72	74
Tensile strength (MPa)	7.7	8.1	8.1	4.1
Elongation at break (%)	390	420	320	80
Tear strength (kN/m)	17.4	19.4	20.2	7.1
Appearance	Colorless, clear	Yellow, clear	Brown, clear	Black, opaque

APPS, 100 parts (content of aminopropyl groups is 0.2%); modified 4[#] fumed silica, 50 parts; ratio of epoxy-to-amino groups is 3 to 1 (mol/mol); first stage: 160°C × 2 h, 29.4 MPa.

may react completely but only when reacted for a long enough time. By putting the vulcanizate sheet obtained from the first stage into a hot-air oven at 180°C and observing the effect of the curing time on the strengths of silicone rubber, we obtained the results shown in Table VI.

Table VI shows that silicone rubber cured for 10 h exhibits optimal mechanical properties. A longer time does not help the improvement of the performance characters. On the contrary, by curing for too long a time, the properties of silicone rubber will become poorer because of its aging.

Crosslinking Density of the Silicone Rubber

With different crosslinking densities, silicon rubber exhibits different properties. The lower the crosslinking density is, the larger the elasticity the silicone rubber exhibits. A too high crosslinking density may result in loss of the elasticity of the silicone rubber. The crosslinking density is shown with the average molecular weight of effective units (M_c) between crosslink points. The higher the crosslinking density is, the smaller the

M_c is. M_c can be calculated by the following formula⁸:

$$M_c = -\rho_2 V_1 \phi_2^{1/3} / [\ln(1 - \phi_2) + \phi_2 + \chi_1 \phi_2^2]$$

where ρ_2 is the density of the silicone rubber before swelling; V_1 , the mol volume of the solvent; ϕ_2 , the volume percent of silicone rubber in the swelling rubber; and χ_1 , the interaction parameter between silicone rubber and the solvent. The results of the experiments are shown in Table VII.

M_c shows the degree of crosslinking of silicone rubber. It is the total result of the physical and chemical interaction among fillers, silicone polymer chains and fillers, and the silicone polymer chains. Table VII shows that M_c decreases as the ratio of epoxy-to-amino groups increases while maintaining other conditions. This is consistent with the results in Table I, in which the hardness of the silicone rubber increases with increasing of the ratio of epoxy-to-amino groups. M_c decreases with increasing of the temperature of the posture while maintaining the ratio of the epoxy-to-amino

Table VI Effect of the Postcure Time

Properties	Time (h)			
	5	10	15	20
Hardness (ShA)	58	64	65	62
Tensile strength (MPa)	6.1	8.1	8.1	8.0
Elongation at break (%)	330	420	424	405
Tear strength (kN/m)	13.2	19.4	19.9	18.4
Appearance	Colorless, clear	Yellow, clear	Brown, clear	Dark brown, opaque

APPS, 100 parts (content of aminopropyl groups is 0.2%); modified 4[#] fumed silica, 50 parts; ratio of epoxy-to-amino groups is 3 to 1 (mol/mol); first stage: 160°C × 2 h, 29.4 MPa; postcure: 180°C.

Table VII M_c of the Silicone Rubber

	Samples No.					
	1	2	3	4	5	6
Epoxy/amino (mol/mol)	1 : 1	2 : 1	4 : 1	3 : 1	3 : 1	3 : 1
Postcure temperature (°C)	180	180	180	160	180	200
(M_c) (g/mol)	3737	3256	2332	2605	2539	2437

APPS, 100 parts (content of aminopropyl groups is 0.2%); modified 4[#] fumed silica, 50 parts; ratio of epoxy-to-amino groups is 3 to 1 (mol/mol); first stage: 160°C × 2 h, 29.4 MPa; postcure: 180°C × 10 h.

groups, such as 3 to 1. This is also consistent with the results in Table V, in which the hardness of the silicone rubber increases with increasing of the postcure temperature. Analyzing the experimental results, it can be concluded that silicone rubber exhibits fine properties when M_c is about 2500.

CONCLUSIONS

These results of our experiments have proved that the optimal conditions to produce the silicone rubber using polysiloxanes containing aminopropyl groups as base gums is as follows:

1. The content of the aminopropyl groups in APPS is 0.2% (chain block).
2. The amount of EPS used is that of an epoxy-to-amino group ratio of 3 to 1 (mol/mol).
3. The amount of the modified 4[#] fumed silica used is 50 parts (base gums 100 parts).
4. The first stage: 160°C × 2 h, 29.4 MPa.
5. The postcure: 180°C × 10 h.

Under these conditions, we can obtain silicone rubber with optimal performance properties.

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