Effects of Polymethylvinylsilicone Oil with Side Tetraphenylphenyl Groups on the Radiation Resistance of Addition-Type Silicone Rubber

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ABSTRACT: Polymethylvinylsilicone oil with side tetraphenylphenyl groups (called C_2 gum for short) as a low molecular additive was used in two kinds of addition-type silicone rubber, polymethylvinyl silicone rubber and poly(dimethyl-diphenyl) silicone rubber, and the radiation resistance of silicone rubbers obtained was investigated by γ-rays radiation with the dose rate of 117 Gy/min at doses up to 350, 500, and 850 kGy, respectively. Moreover, the average molecular weight between crosslinks and mechanical properties of silicone rubbers after irradiated in air and N_2 were determined by toluene-swelling method and on a XLS-A rubber test instrument, respectively. The results show that C_2 gum can effectively improve the radiation resistance of silicone rubber. When C_2 gum is used in poly(dimethyl-diphenyl) silicone rubber, phenyl groups and tetraphenylphenyl groups may have synergistic effect, and the radiation resistance is improved greatly. The suitable amount of C_2 gum used in silicone rubber is 10–14 phr. The crosslinking density of vulcanizates irradiated in N_2 is higher than that of vulcanizates irradiated in air because of the oxidative degradation. The radiation protection mechanism of C_2 gum was also discussed. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 4144–4148, 2007

Key words: radiation resistance; silicone rubber; tetraphenylphenyl groups; hydrosilylation

INTRODUCTION

Silicone rubber belongs to an important class of special-purpose synthetic rubbers, which are partly inorganic and partly organic.[1] With fine electric insulation, good thermostability, excellent resistance to oxygen, ozone, and sunlight, low toxicity, and chemical reactivity, silicone rubber has been applied in aviation, nuclear power plants, military weapons, and so on. Therefore, its radiation resistance is especially important.

In our previous work,[2,3] such aromatic compounds as biphenyl, naphthalene, and phenanthrene can be used to improve silicone rubber's radiation resistance, in which the aromatic compounds are mixed physically with silicone rubber and the radiation protection effects are called external protection.[2,4] It is found that acenaphthenyl groups on the side chain of polysiloxane have better radiation protection effects toward peroxide heat-curable silicone rubber.[3] But in the peroxide heat-curable rubber system, acenaphthenyl groups have stabilization on radicals forming during decomposition of peroxide and thus inhibit the cure of vulcanizates, making the vulcanizates be in a state of "lack-of-cure."[5] Vulcanizates with better vulcanization characteristics could be obtained only by increasing the amount of peroxide used. At the same time, the by-products from decomposition of peroxide during the cure also increase with an increase of peroxide used, which will affect the application of silicone rubber in electronic field.

In this article, polymethylvinylsilicone oil with side big conjugated tetraphenylphenyl groups was synthesized, and used as an antirays of polymethylvinyl silicone rubber, which is cured by hydrosilylation. It is well known that polymethylphenyl silicone rubber has better radiation resistance than polymethylvinyl one. To obtain high radiation resistant silicone rubber, the effects of polymethylvinylsilicone oil with side tetraphenylphenyl groups on the radiation resistance of poly(dimethyl-diphenyl) silicone rubber are also studied.

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EXPERIMENTAL

Materials

Benzil and 1,3-diphenylacetone were from Shanghai Chemical Reagent Company. Hydrogen-containing

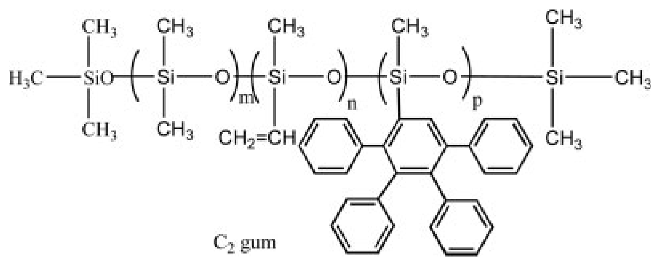

Figure 1 Schematic structure of C_2 gum.

silicone oil (H-oil; H content, 1.4 wt %), polymethylvinyl silicone gum (M_n, 5.0 × 10^5; vinyl group content, 0.15 mol %), 4# fumed silica (specific surface area, 176 m^2/g), and octamethylcyclotetrasilazane (D_4^N) were from Jinan Chemical Plant. Polymethylvinylsilicone oil (vinyl group content, 15.0 mol %; viscosity, 190 mPa.s) was synthesized according to the method reported in the literature.[6] Poly(dimethyl-diphenyl) silicone rubber (M_n, 6.5 × 10^5; phenyl group content, 10.0 mol %; vinyl group content, 0.15 mol %) was obtained from Shanghai Resin Plant. The catalyst (Pt-cat) was prepared by dissolving 1 g chloroplatinic acid in 60 mL isopropanol.

Preparation of polymethylvinylsilicone oil with side tetraphenylphenyl groups

Polymethylvinylsilicone oil with side tetraphenylphenyl groups (C_2 gum, Fig. 1) was synthesized by Diels–Alder reaction of polymethylvinylsilicone oil and tetraphenylcyclopentadienone.[6,7] The content of vinyl and tetraphenylphenyl groups in C_2 gum, 1.2 mol % and 13.0 mol % chain unit, respectively, was calculated by ^{1}HNMR analysis according to the integral value of various H atoms.[6]

Preparation of silicone rubber

Formula

The formula of silicone rubber is listed in Table I.

Processing

Referring to the literature,[8,9] materials were compounded and then vulcanized at 150°C for 30 min under 10 MPa, and post cured at 190°C for 2 h under ambient pressure to obtain vulcanizates.

Radiation

The silicone rubber samples were irradiated with γ-rays from a Co-60 source in air and pure N_2 (99.99%). The total dose was chosen as 350, 500, and 850 kGy, respectively. The dose rate was 117 Gy/min.

Measurements and testing

The mechanical properties of vulcanizates were measured on a XLS-A rubber test instrument. The average molecular weight between crosslinks (M_c) is determined by the toluene-swelling method.[3,10,11]

RESULTS AND DISCUSSION

Effects of C_2 gum on the M_c of vulcanizates before and after radiation

The average molecular weight between crosslinks (M_c) is an important structural parameter, which can indicate the degree of crosslinking of rubber system. It is the total reflection of physical and chemical action of additives with additives, main links with main links, and each other.[5] In the previous work, when vulcanizate with 14 phr C_1 gum is cured by peroxide, the vulcanizate is in a state of ''lack-of-cure'' and the M_c is 5102.[3] But vulcanizates with good vulcanization characteristics can be obtained by hydrosilylation. It can be found from the data in Table II that when 14 phr C_2 gum is used, the M_c of polymethylvinyl silicone rubber is 3411, which is close to the value of rubber without C_2 gum (3112). Similar results can be found in the vulcanizates of poly(dimethyl-diphenyl) silicone rubber (see Table III). This is attributed to the special curing mechanism of addition-type silicone rubber. The addition reaction between Si-H and vinyl group is not affected by the content of phenyl groups or tetraphenylphenyl groups during curing.

Both crosslinking and scission reactions of silicone molecular chains occur simultaneously at different rates when silicone rubber is exposed to high-energy radiation. Many researchers have reported that crosslinking reactions predominate over scission reactions under γ-rays radiation.[12–16] So, silicone rubber belongs to ''crosslinking polymer.'' From the data in Table II, it can be found that the M_c of all samples decreases after radiation, indicating the increase of crosslinking density and being in agreement with the reported results. When the radiation dose is 500 kGy, the M_c of vulcanizate without C_2 gum is 1306 (in air) and 1204 (in N_2), respectively; while the M_c of sample containing 10 phr C_2 gum is 1600 (in air) and 1516 (in N_2), respectively, illustrating that C_2 gum has obvious radiation protection effects on radiation of polymethylvinyl silicone rub-

TABLE I
The Formula of Silicone Rubber

Polymethylvinyl silicone gum	100	–
Poly(dimethyl-diphenyl) silicone gum	–	100
4# fume silica	50	50
D_4^N	8	8
C_2 gum	0–22	0–22
H-oil	1	1
Pt-cat	0.2	0.2

All values are expressed as (phr) by weight.

TABLE II
M_c of Polymethylvinyl Silicone Rubber Before and After Radiation under Different Atmospheres

Amount of C_2 gum used/phr	Before radiation	350-kGy radiation in air	350-kGy radiation in N_2	500-kGy radiation in air	500-kGy radiation in N_2
0	3112	1844	1641	1306	1204
2	3100	2039	1889	1433	1309
4	3123	2107	1914	1504	1399
6	3191	2131	1954	1550	1467
8	3190	2163	1978	1589	1495
10	3200	2178	2001	1600	1516
12	3246	2209	2046	1624	1527
14	3301	2259	2098	1648	1529
16	3337	2299	2102	1692	1572
18	3358	2398	2178	1716	1605
20	3407	2408	2221	1758	1627
22	3411	2491	2288	1816	1704

ber and reduces the crosslinking efficiency remarkably. Similar results can be found in poly(dimethyl-diphenyl) silicone rubber system (see Table III).

The radiation resistance of silicone rubber depends on many factors, such as the molecular structure, the formulation, and the radiation environmental conditions. From the data in Tables II and III, it can be found that the M_c of samples irradiated in N_2 is smaller than that of samples in air at the same radiation dose, respectively. In air, oxygen takes part in the radiation-induced reactions, so the rubber suffers more or less oxidative degradation, which decreases the degree of crosslinking.[17] It is consistent with the results reported in literatures.[12–16]

Effects of C_2 gum on the mechanical properties of silicone rubber before and after radiation

Figures 2 and 3 illustrate the effects of C_2 gum on the mechanical properties of two kinds of silicone rubbers after radiation. It is clear that the hardness increases with increasing radiation dose, as a result of the higher crosslinking density induced by radiation. In addition, the hardness of samples containing C_2 gum is lower than that of samples without C_2 gum at the same radiation dose, indicating the radiation protection effects of C_2 gum. When samples are irradiated in N_2, the hardness is higher than that of samples irradiated in air because of the oxidative degradation during radiation. This can be also supported by data in Table IV. The modulus at 100% of silicone rubber increases obviously after radiation, reflecting the increase of crosslinking density. Similarly, the modulus increment of samples containing C_2 gum is less than that of samples without C_2 gum on account of the radiation protection effects of C_2 gum.

The tensile strength of two kinds of silicone rubbers shows a reduction after radiation [see Figs. 2(b) and 3(b)]. For polymethylvinyl silicone rubber without C_2 gum, the tensile strength is 5.7 MPa (350 kGy in N_2), 3.2 MPa (500 kGy in N_2), and 2.0 MPa (850 kGy in N_2); when 10 phr C_2 gum is used, the tensile strength is 6.7 MPa, 4.5 MPa, and 2.6 MPa, respectively. So, the radiation protection effects of C_2 gum are obvious. When 10 phr C_2 gum is used in poly(dimethyl-diphenyl) silicone rubber, the tensile strength is 8.7 MPa, 5.7 MPa, and 3.5 MPa, respectively, showing obviously that the radiation

TABLE III
M_c of Poly(Dimethyl-Diphenyl) Silicone Rubber Before and After Radiation under Different Atmospheres

Amount of C_2 gum used/phr	Before radiation	350-kGy radiation in air	350-kGy radiation in N_2	500-kGy radiation in air	500-kGy radiation in N_2
0	5608	2361	2251	2122	2054
2	5614	2947	2748	2535	2394
4	5624	3008	2820	2585	2457
6	5628	3340	3099	2602	2516
8	5647	3486	3286	2704	2634
10	5669	3538	3451	2739	2685
12	5681	3596	3501	2770	2707
14	5697	3600	3587	2798	2736
16	5704	3704	3598	2804	2768
18	5734	3791	3607	2818	2789
20	5743	3842	3816	2839	2794
22	5806	4055	3918	2867	2801

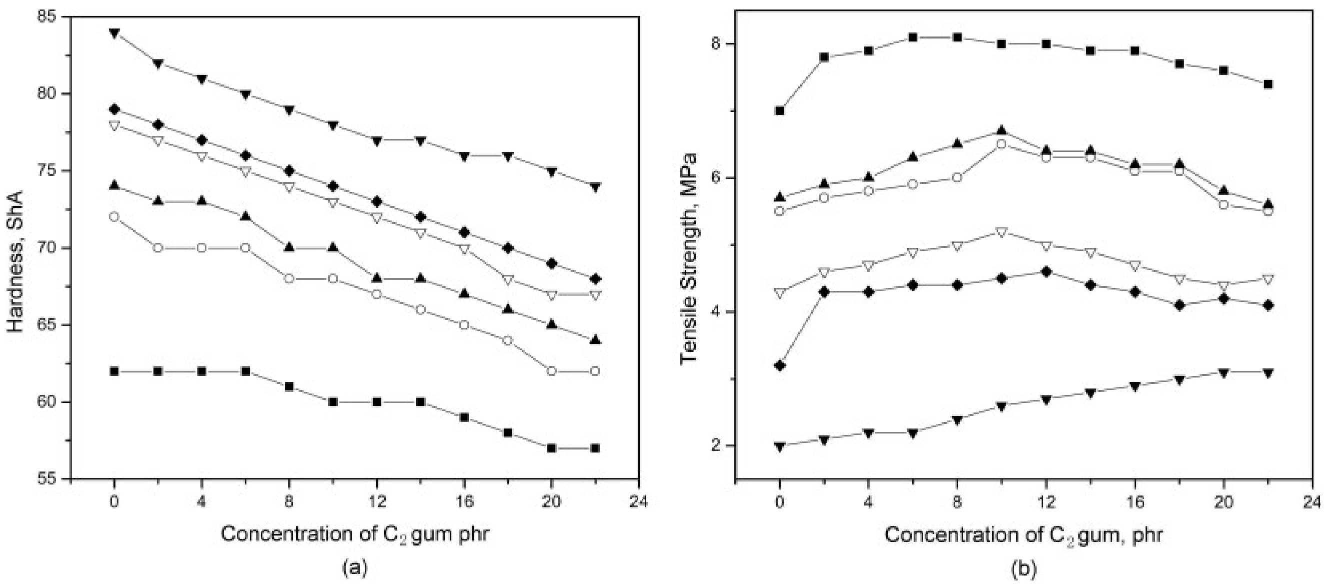

Figure 2 Effects of C_2 gum on the mechanical properties of polymethylvinyl silicone rubber before and after radiation, (a) the changes of hardness, (b) the changes of tensile strength: (■) before radiation; (○) 350 kGy in air; (▲) 350 kGy in N_2; (▽) 500 kGy in air; (◆) 500 kGy in N_2; (▼) 850 kGy in N_2.

resistance of poly(dimethyl-diphenyl) silicone rubber is much better than that of polymethylvinyl silicone rubber with the same amount of C_2 gum used. It is attributed to the phenyl substitution on silicon atoms, which offers partial protection to dimethyl siloxane units.[18] In addition, when a mass of phenyl and tetraphenylphenyl groups exist in the same rubber system, they may have synergistic effect, which leads to the great improvement of radiation resistance.

It can be seen that the mechanical properties of vulcnaizates containing C_2 gum are better than those of vulcanizates without C_2 gum after radiation. The higher the concentration of C_2 gum, the better the mechanical properties are. But when the amount of C_2 gum used exceeds 14 phr, the general mechanical properties decrease because the relative concentration of SiO_2 in the rubber system decreases with the increase of C_2 gum used. So, the suitable amount of C_2 gum used in silicone rubber is 10–14 phr.

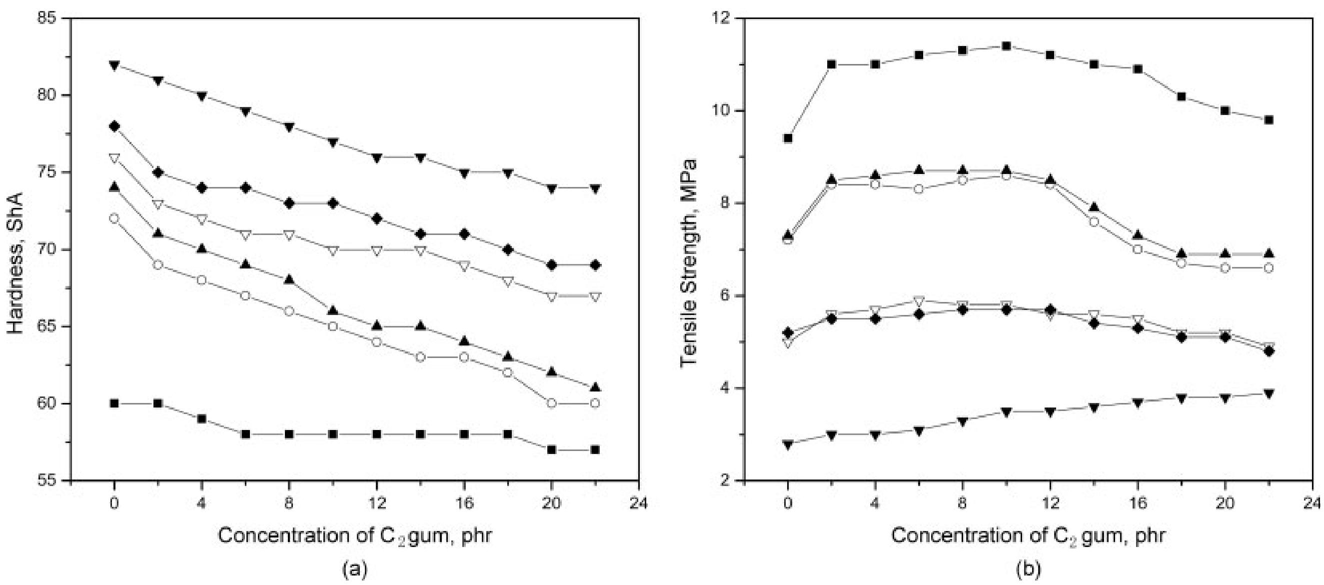

Figure 3 Effects of C_2 gum on the mechanical properties of poly(dimethyl-diphenyl) silicone rubber before and after radiation, (a) the changes of hardness, (b) the changes of tensile strength: (■) before radiation; (○) 350 kGy in air; (▲) 350 kGy in N_2; (▽) 500 kGy in air; (◆) 500 kGy in N_2; (▼) 850 kGy in N_2.

TABLE IV
Effects of C_2 Gum on the Modulus at 100% of Silicone Rubber Before and After Radiation

Amount of C_2 gum used/phr	Before radiation/MPa		350-kGy radiation in air/MPa		350-kGy radiation in N_2/MPa		500-kGy radiation in air/MPa		500-kGy radiation in N_2/MPa	
	I	II	I	II	I	II	I	II	I	II
0	2.1	1.5	4.6	3.6	4.9	5.9	—	—	—	—
2	2.1	1.3	4.4	3.1	4.6	3.9	—	4.3	—	5.0
4	2.1	1.2	4.3	2.9	4.3	3.3	—	4.2	—	4.8
6	2.0	1.2	4.0	2.5	4.1	2.8	—	4.0	—	4.5
8	2.0	1.2	3.8	2.4	4.0	2.6	—	3.8	—	4.4
10	2.0	1.2	3.6	2.2	3.7	2.4	—	3.7	—	4.2
12	1.9	1.2	3.3	2.0	3.6	2.3	—	3.6	—	4.0
14	1.8	1.2	3.0	1.9	3.3	2.1	—	3.5	—	3.7
16	1.6	1.1	2.9	1.9	3.0	2.0	—	3.5	—	3.8
18	1.5	1.1	2.6	1.9	2.9	1.9	—	3.6	—	3.7
20	1.5	1.1	2.5	1.7	2.7	1.9	—	3.4	—	3.5
22	1.4	1.1	2.3	1.6	2.4	1.8	—	3.3	—	3.4

I, polymethylvinyl silicone rubber; II, poly(dimethyl-diphenyl) silicone rubber.

The radiation protection mechanism of C_2 gum

During the curing of addition-type silicone rubber, tetraphenylphenyl groups could be introduced into the molecular network of silicone rubber by the addition reaction between vinyl groups on C_2 gum and silicone gum and Si-H groups on H-oil. So, the radiation protection effects of C_2 gum could be characterized as internal protection in contrast to the external protection of aromatic compounds. When samples are irradiated, the absorbed energy could dissipate in the large conjugated structure of tetraphenylphenyl groups before bond rupture occurs. When C_2 gum is used in poly(dimethyl-diphenyl) silicone rubber, both the tetraphenylphenyl groups and phenyl groups could provide radiation protection effects to silicone rubber with synergistic effect as they are in the same rubber system.

CONCLUSIONS

When polymethylvinylsilicone oil with side tetraphenylphenyl groups (C_2 gum) is used in addition-type silicone rubber, samples with good vulcanization characteristics can be obtained. As a low molecular additive of addition type silicone rubber, C_2 gum can effectively improve the radiation resistance of silicone rubbers. Especially when C_2 gum is used in poly(dimethyl-diphenyl) silicone rubber, phenyl and tetraphenylphenyl groups may have synergistic effect and vulcanizates with better radiation resistance can be obtained. In addition, the suitable amount of C_2 gum used is 10–14 phr.

The crosslinking density of vulcanizates irradiated in N_2 is higher than that of vulcanizates irradiated in air because oxygen takes part in the radiation-induced reactions and the rubber molecules suffer more or less oxidative degradation, which decreases the crosslinking of the vulcanizates.

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