

Effect of Tetraphenylphenyl-Modified Fumed Silica on Silicone Rubber Radiation Resistance

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ABSTRACT: Two kinds of treated fumed silica were prepared by treatment with either tetraphenylphenyltriethoxysilane (TPHTS) or both tetraphenylphenyltriethoxysilane and hexamethyldisilazane (TPHMTS), and were used as reinforcing filler for silicone rubber. The resistance to irradiation of the silicone rubber obtained was investigated by gamma ray of dose 500 kGy in air. The mechanical properties and the average molecular weight between crosslinking points (Mc) of the silicone rubber were determined before and after irradiation. The results show that the fumed silica treated by tetraphenyl-

phenyltriethoxysilane (TPHPHS) can effectively improve the radiation resistance of silicone rubber while the fumed silica treated by both tetraphenylphenyltriethoxysilane and hexamethyldisilazane (MM^N) cannot only effectively improve the radiation resistance of silicone rubber but also has excellent reinforcing effect on silicone rubber. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2440–2447, 2011

Key words: radiation resistance; silicone rubber; tetraphenylphenyltriethoxysilane; fumed silica

INTRODUCTION

Silicone rubber is one of the main organic silicone products. It exhibits unique properties, including biocompatibility, superior temperature and chemical resistance, good electrical insulation properties, and so on.¹ Silicone rubber has been extensively used in various fields. In such application fields as aviation, electron, sterilization of instruments, nuclear power plants, and military weapons where high dose of radiation is existed; the radiation resistance of silicone rubber is especially significant.

According to the previous reports,^{2–11} there are mainly two methods to improve the radiation resistance of silicone rubber, that is, addition of radiation-resistant additives in silicone rubber or using the polysiloxane containing radiation resistant groups as base

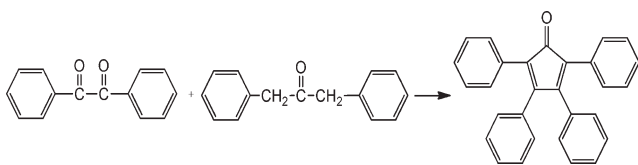
gum. Some additives such as plumbous, tungsten, and aromatic compounds can improve the radiation resistance of material. But as the additives are mixed physically with the material, their radiation protection effects are characterized as external protection and the mechanical properties of the material are damaged with the increase of the additives because of the poor compatibility between organic phase and inorganic phase. It has been reported that the radiation resistance of polymethyl phenyl silicone rubber is better than that of polymethyl vinyl silicone rubber due to the conjugated structures of phenyl groups. In our previous work,^{12,13} the condensed aromatics were induced onto the main chain of polyvinylsilicone oil, and then the obtained polysiloxanes with condensed aromatic groups were used as the additives to silicone rubber for investigating its effects on the radiation resistance. It was found that this kind of polysiloxanes offer good protection against radiation to silicone rubber. Here, the conjugated groups are parts of the main chains of silicone gum, and their radiation protection effects are characterized as internal protection.¹⁴ And the higher concentration of conjugated groups, the better the radiation resistance is. But if such polyvinylsilicone oil is used too much, the mechanical properties of silicone rubber obtained will decrease because of the relative excess crosslinking in rubber system. Therefore, both

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Scheme 1 Synthesis route of tetraphenylcyclopentadienone.

of the two methods have disadvantages to some extent. It is worth attention to find new methods to improve the radiation resistance of silicone rubber.

In preparing silicone rubber, fumed silica is generally used as the reinforcing filler.^{15–17} Silica can bond to polysiloxane chains via Van der Waals' forces, hydrogen bonds, and chemical bonds. Polysiloxane chains are connected to each other through silica. However, the fumed silica must be surface-treated with treating agents before blending into silicone gum to avoid the phenomena of crepe hardening. If such conjugated groups as phenyl groups are grafted onto the silica during surface-treatment, maybe radiation resistance of silicone rubber is improved with the treated silica as reinforcing filler. If so, the radiation protection effects can also be characterized as internal protection. However, no such research, to our best knowledge, has been reported yet.

In this article, silane coupling agent with tetraphenylphenyl group was synthesized by Diels–Alder reaction and was used to treat silica. And then the treated silica was used as the reinforcing filler to silicone rubber for investigating its effects on the radiation resistance. The mechanical properties and the average molecular weight between crosslinking points (M_c) of the silicone rubber before and after irradiation were studied. The treating process has two significant effects, that is, on one hand the tetraphenylphenyl groups were grafted onto the silica surface to improve the radiation resistance, on the other hand the excrescent hydroxyls on the surface of silica were treated off to avoid the phenomena of crepe hardening. It is found that this is an easy and effective method to improve the radiation resistance of silicone rubber.

EXPERIMENTAL

Materials

Benzil and dibenzyl ketone were obtained from Sino-pharm Chemical Reagent (China). Vinyltriethoxysilane was obtained from the Jinan Haohua Industry (China). Polymethyl vinyl silicone gum (M_n , 6.3×10^5 ; vinyl group content, 0.04 mol %) was purchased from Zhejiang Huasheng Chemical (China). The treated fumed silica (TS-530) and untreated fumed silica (M-5) were purchased from Cobot (USA).

Both 2, 5-bis (*tert*-butylperoxy) -2, 5-dimethylhexane (DBPMH) and hexamethyldisilazane (MM^N) were industrial products, and used as obtained.

Preparation of silane coupling agent TPHPHS

Synthesis of tetraphenylcyclopentadienone (TPHCPD)

TPHCPD was synthesized according to the literature (Scheme 1).^{18,19} About 21.0 g benzyl (0.1 mol) and 21.0 g dibenzyl ketone (0.1 mol) were dissolved in 200 mL ethanol, and the mixture was heated to 78°C. And then a solution of 3.0 g KOH in 15 mL ethanol was added in the reactor slowly drop by drop. The reaction mixture was stirred at 78°C for 15 min. Then the mixture was cooled to room temperature. The solid product was filtrated and washed three times with ethanol. And then the product was obtained. The yield was about 91%, mp. 218°C (literature: mp. 220°C).

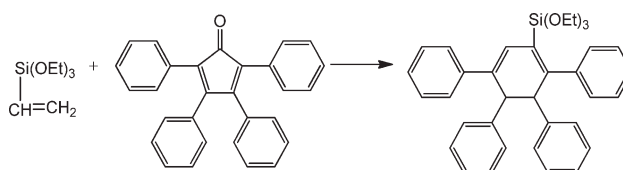
Synthesis of TPHPHS

TPHPHS was prepared by Diels–Alder reaction of TPHCPD with vinyltriethoxysilane (Scheme 2).²⁰ TPHCPD (19.2 g, 0.05 mol) and vinyltriethoxysilane (11.4 g, 0.06 mol) were dissolved in 60 mL toluene in a sealed stainless steel reactor, and the reaction was carried out for 24 h at 220°C under a nitrogen atmosphere. Then the toluene was removed and TPHPHS was purified with silica gel column chromatography. The yield was about 82%.

¹H NMR ($CDCl_3$): $\delta = 0.8–1.2$ (t, $-CH_3$, 9H), $\delta = 3.5–3.8$ (m, $-CH_2-$, 6H), $\delta = 6.5–8.0$ (m, condensed aromatics, 21H).

Surface-treatment of silica

The silica was surface-treated by TPHPHS in dry toluene.^{21–25} For example, about 100 g of fumed silica was dispersed in 1000 mL dry toluene and stirred for a few minutes at room temperature, then TPHPHS (25.1 g, 0.045 mol) was added to the suspension and refluxed for 12 h. After slow cooling to room temperature, the solids were filtered and washed with toluene, and dried at 120°C for 12 h. Then the treated silica was obtained, which was abbreviated TPHTS.



Scheme 2 Synthesis route of tetraphenylphenyltriethoxy silane.

TABLE I
Composition of the Silicone Rubber

| Sample no. | TS530 | TPHTS | TPHMTS |
|------------|-------|-------|--------|
| 1 | 50 | 0 | 0 |
| 2 | 40 | 10 | 0 |
| 3 | 30 | 20 | 0 |
| 4 | 20 | 30 | 0 |
| 5 | 10 | 40 | 0 |
| 6 | 0 | 50 | 0 |
| 7 | 60 | 0 | 0 |
| 8 | 50 | 0 | 10 |
| 9 | 40 | 0 | 20 |
| 10 | 30 | 0 | 30 |
| 11 | 20 | 0 | 40 |
| 12 | 10 | 0 | 50 |
| 13 | 0 | 0 | 60 |

All values are expressed as (phr) by weight. Silicone gum, 100 phr; DBPMH, 1.5 phr.

TPHTS was sequentially treated by MM^N without any solvent. For example, TPHTS (100 g) and MM^N (10 g) were mixed and refluxed for 12 h. And then the product was dried at 120°C for 12 h. The material obtained was abbreviated TPHMTS.

Fumed silica characterization

TPHPHS was characterized by ¹H NMR. ¹H NMR was recorded using CDCl₃ as a solvent on a Bruker AVANCE-300 spectrometer without interference.

Treated and untreated silica were characterized by various techniques. N₂ adsorption–desorption data were measured on a QuadraSorb SI apparatus at liquid N₂ temperature ($T = -196^\circ\text{C}$). The surface areas were determined by the BET (Brunauer-Emmett-Teller) method. The size distribution and volume of the mesopores were calculated by the BJH (Barrett-Joyner-Halenda) theory. The contents of silanol groups on silica surface were determined by acid-base titration of the silica against aqueous sodium hydroxide.^{26,27} Fourier transform infrared (FTIR) spectra were measured within the 4000–400 cm⁻¹ region with the aid of a Bruker TENSOR27 infrared spectrophotometer, by reflection on a KBr powder containing the treated and untreated silica.

Vulcanization of silicone rubber

Composition

The composition of silicone rubber is listed in Table I.

Processing

Materials were milled on a two-roll mill. Base gum was encapsulated onto rollers. Then treated fumed silica was added step by step.^{28,29} After being milled

uniformly, DBPMH was added. Then the materials were cured in a stainless steel mold at 170°C under a pressure of 10 MPa, and postcured at 180°C for 2 h under ambient pressure to obtain vulcanizates.

Gamma ray irradiation

The silicone rubber samples were irradiated with γ -ray from a Co-60 source in air. The total dose was 500 kGy, and the dose rate was 50 Gy min⁻¹.

Measurements of silicone rubber

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.

The silicone rubber's swelling degree was determined with the toluene-swelling method according to literatures.^{12,13,30–32} The average molecular weight between two crosslinking points (Mc) can be calculated by the following formula:

$$Mc = -\rho_2 V_0 \phi^{1/3} / [\ln(1 - \phi) + \phi + \chi_1 \phi^2] \quad (1)$$

where Mc is the average molecular weight between two crosslinking points; ρ_2 is the density of silicone rubber before swelling; V_0 is the mol volume of the solvent; ϕ is the volume percent of silicone rubber in the swollen rubber; and χ_1 is Flory-Huggins interaction parameter between polymer and solvent, here 0.465.

Whereby,

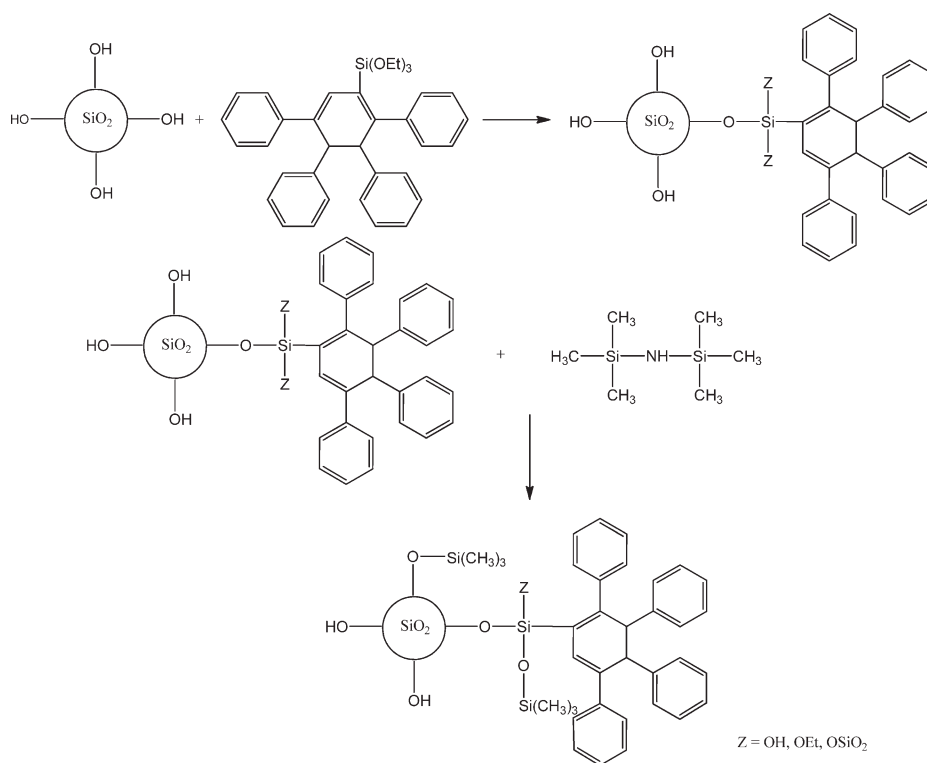
$$\phi = (W_1 / \rho_2) / [(W_2 - W_1) / \rho_1 + W_1 / \rho_2] \quad (2)$$

where W_1 is the initial weight of vulcanizate; W_2 is the weight of swollen vulcanizate; ρ_1 is the density of toluene (25°C).

RESULTS AND DISCUSSION

Characterization of silica

The procedure used for the chemical treatment of silica is referred to the surface hydroxyl groups of silica (silanol groups) reacting with the silane coupling agents. It is schematically represented in Scheme 3. The silanol groups on the silica surface can react with the ethoxy groups of TPHPHS, liberating ethanol in the medium. Moreover, absorbed water on the silica surface has a great effect on the treatment of silica because it can induce the hydrolysis of the ethoxy groups of TPHPHS and can also increase the extent of condensation between the neighboring silane coupling agents and generate polymerization of the treating agent with itself.²³



Scheme 3 Schematic representation of the silica surface treatment by tetraphenylphenyltriethoxysilane and hexamethyl disilazane.

Figure 1 shows the diffuse reflectance FT-IR of dried untreated and treated silica powders. As observed the band at 3400 cm^{-1} (—OH) of untreated silica is strong while that of TPHTS is a little weaker, it can be concluded that hydroxyl groups on the surface of silica are replaced by tetraphenylphenyl groups after treatment. Table II shows the surface area and pore diameter before and after treatment. Both the surface area and pore diameter become smaller after treatment. The reason is that the tetraphenylphenyl

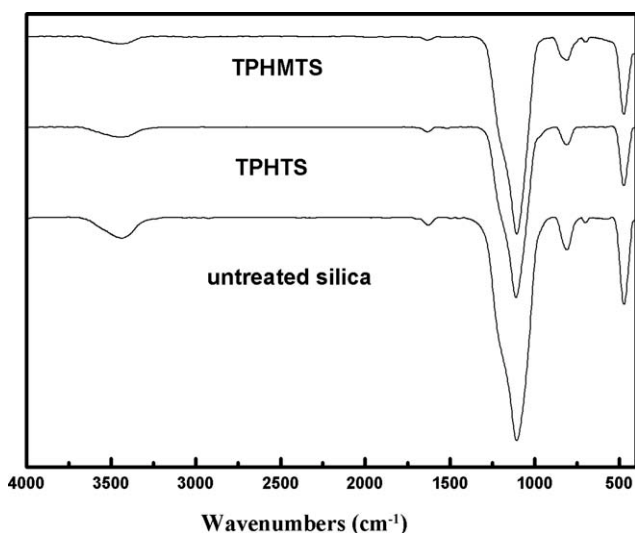


Figure 1 FT-IR of the treated and untreated silica.

groups are modified on the silica after treated. The titration revealed a silanol group density of about $3.30\text{ SiOH per nm}^2$ before treatment. And TPHTS has a silanol group density of about $2.43\text{ SiOH per nm}^2$. Such result indicates only a little part of TPHTS can react with the silanol group on the silica surface because of the large steric hindrance of tetraphenylphenyl group. So there are still too many silanol groups on the surface of TPHTS. To avoid the phenomena of crepe hardening, MM^{N} was used to treat TPHTS sequentially to react with the residual silanol groups.

Compared to TPHTS, on the diffuse reflectance FT-IR of TPHMTS the band at 3400 cm^{-1} (—OH) is much weaker. And the results of N_2 adsorption-desorption show the surface area and pore diameter of TPHMTS are also smaller than before treatment. The TPHMTS has a silanol group density of about $1.86\text{ SiOH per nm}^2$, which seems to be a good estimation

TABLE II
Surface Area and Pore Diameter of Untreated and Treated Silica

| | Surface area ($\text{m}^2\text{ g}^{-1}$) | Pore diameter (nm) |
|------------------|--|-----------------------|
| Untreated silica | 216 | 15.6 |
| TPHTS | 150 | 3.1 |
| TPHMTS | 162 | 2.9 |

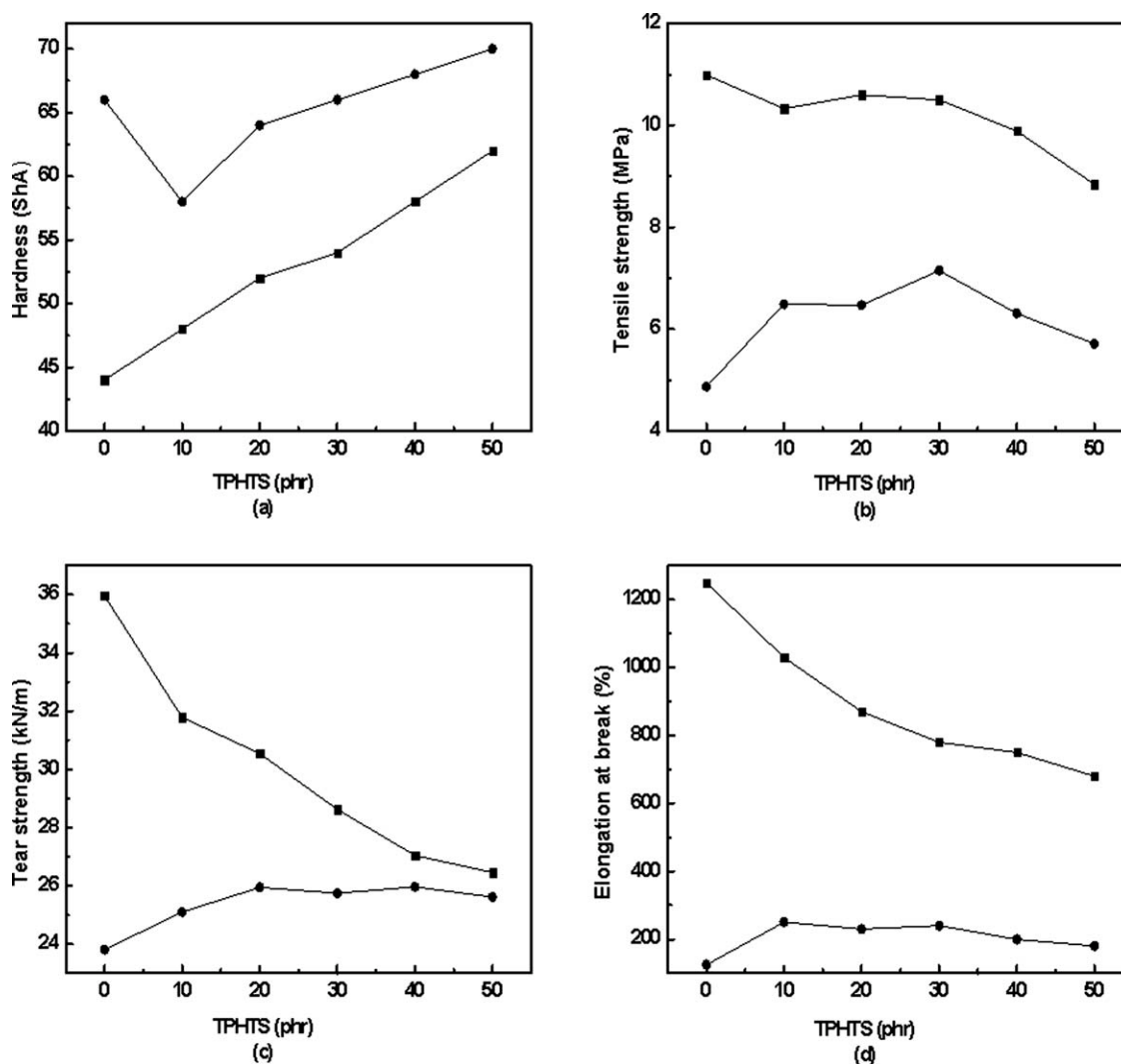


Figure 2 Effect of TPHTS on the mechanical properties of silicone rubber before and after irradiation of 500 kGy: (■) before irradiation; (●) after irradiation.

of the content of chemically reactive and available surface silanol groups on fumed silica.²³ So it can be concluded that TPHTS is well treated and can be used as reinforcing filler for silicone rubber.

Mechanical properties of silicone rubber before and after irradiation

Figure 2 shows the effects of TPHTS on the mechanical properties of silicone rubber before and after irradiation. As shown in Figure 2(a) the hardness increases after radiation, relative to that before irradiation. This is mainly due to the higher crosslinking density induced by radiation. For Sample 1 reinforced by 50 phr TS530 the hardness increases from 44 to 66 while for Sample 5 reinforced by 40 phr TPHTS the hardness increases from 58 to 68. The radiation change of the vulcanizates reinforced by TPHTS is lower than that reinforced only by TS-530. Figure 2(b) shows the tensile strength decreases after

irradiation. For example, the tensile strength of Sample 1 reinforced by 50 phr TS530 decreases from 10.99 to 4.87 MPa after irradiation. For Sample 4 reinforced by 30 phr TPHTS the tensile strength decreases from 10.50 to 7.15 MPa after irradiation. For Sample 6 reinforced by 50 phr TPHTS the tensile strength decreases from 8.84 to 5.71 MPa after irradiation. The similar results can be found on the changes of the tear strength [Fig. 2(c)] and the elongation at break decrease [Fig. 2(d)]. After irradiation the radiation resistance of silicone rubber reinforced by TPHTS is better than without TPHTS. The more TPHTS is used the better the radiation protection exhibited by silicone rubbers. However, it can also be found that the reinforcing effect of TPHTS is poorer. The reason is that there are too many silanol groups on the surface of TPHTS, which is also enhancing the crosslinking density when exposure to radiation.³³ The phenomena of crepe hardening would also occur if too much TPHTS was used. So TPHTS is an effective

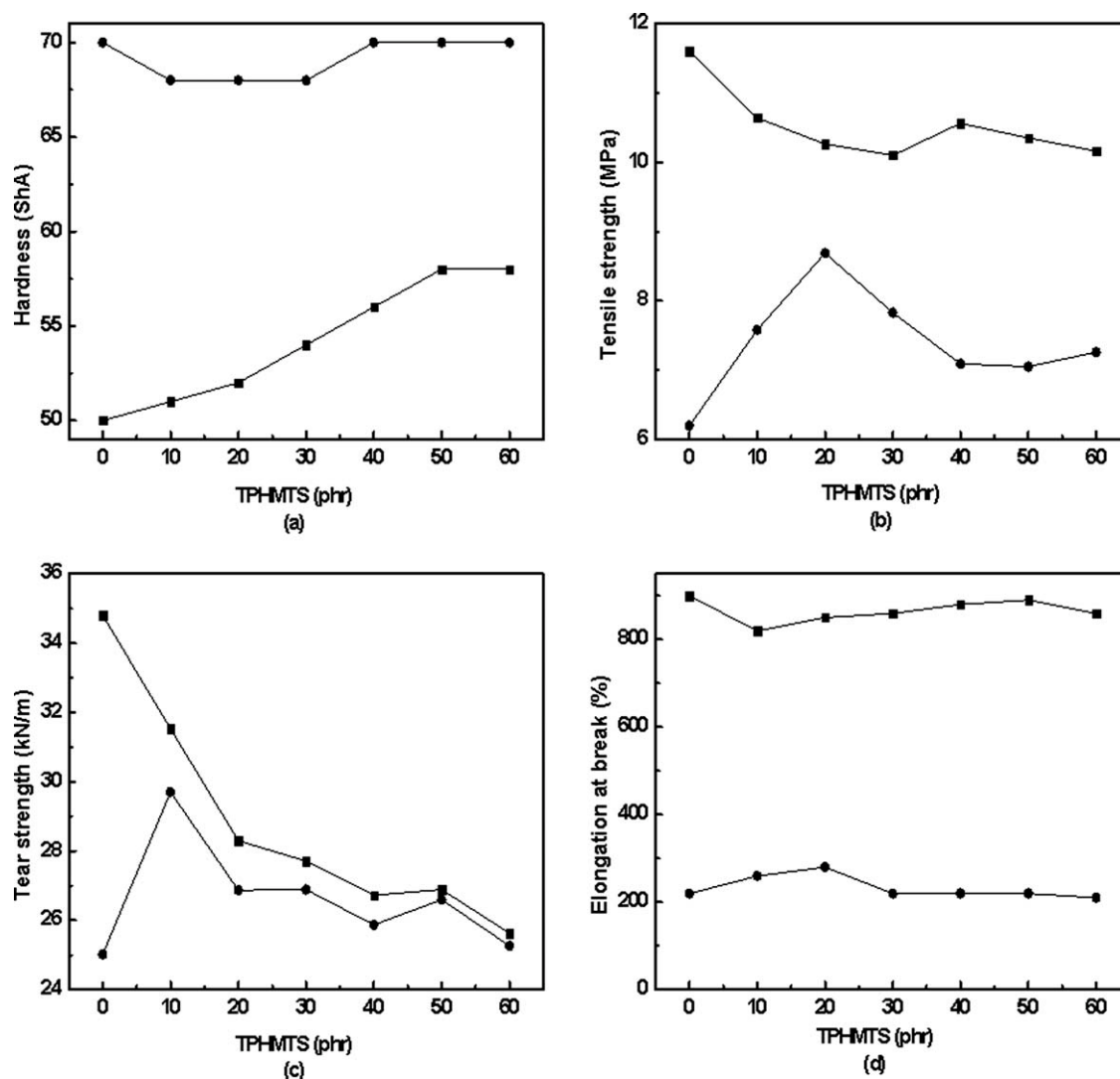


Figure 3 Effect of TPHMTS on the mechanical properties of silicone rubber before and after irradiation of 500 kGy: (■) before irradiation; (●) after irradiation.

antiradiation additive for silicone rubber while its reinforcing effect is not so good.

Figure 3 show the effects of TPHMTS on the mechanical properties of silicone rubber before and after irradiation. Compared to TPHTS, the mechanical properties of silicone rubber reinforced by TPHMTS are as excellent as those reinforced by only TS530 before irradiation. For example, for Sample 7 reinforced by 60 phr TS530 the hardness is 50 and the tensile strength is 11.60 MPa; for Sample 10 reinforced by 30 phr TPHMTS the hardness is 54 and the tensile strength is 10.10 MPa; for Sample 13 reinforced by 60 phr TPHMTS the hardness is 58 and the tensile strength is 10.16 MPa. This is probably because in TPHMTS which is treated sequentially by MM^N the silanol group density is appropriate to bond the polysiloxane chains to each other, and does not cause too much crosslinking in the vulcanizate. So the reinforcing effect of TPHMTS is better

than that of TPHTS. On exposure to radiation, for Sample 7 reinforced by 60 phr TS530 the hardness increases from 50 to 70 and the tensile strength decreases from 11.60 to 6.20 MPa while for Sample 13 reinforced by 60 phr TPHMTS the hardness increases from 58 to 70 and the tensile strength decreases from 10.16 MPa to 7.26 MPa. The radiation change of the vulcanizates reinforced by TPHMTS is lower than that reinforced only by TS-530 or TPHTS, which is mainly attributed to the effect of tetraphenylphenyl groups and the appropriate silanol group density. Additionally, the tear strength [Fig. 3(c)] of samples with TPHMTS before and after irradiation changes lower than that with only TS530. These results fully illustrate that TPHMTS has obvious protection effects on radiation of silicone rubber. It can be concluded that TPHMTS is not only fine reinforcing filler but also an effective antiradiation additive for silicone rubber.

TABLE III
Effect of TPHMT, DA, and C₁ Gum at Same Molar Concentration on the Mechanical Properties Before and After Irradiation of 500 kGy

| | Tensile strength (MPa) | | Tear strength (kN m ⁻¹) | | Elongation at break (%) | | Hardness (ShA) | |
|----------------------------------|------------------------|-------------------|-------------------------------------|-------------------|-------------------------|-------------------|--------------------|-------------------|
| | Before irradiation | After irradiation | Before irradiation | After irradiation | Before irradiation | After irradiation | Before irradiation | After irradiation |
| TPHMT | 10.35 | 7.05 | 26.89 | 26.60 | 890 | 220 | 58 | 70 |
| DA ¹⁵ | 8.30 | 4.10 | 18.90 | 6.80 | 372 | 60 | 56 | 79 |
| C ₁ gum ¹⁵ | 7.70 | 6.30 | 23.40 | 14.10 | 507 | 143 | 50 | 69 |

TPHMT, 50 phr; DA, 4.17 phr; C₁ gum, 14 phr.

In our previous work,¹² the radiation resistance of 9,10-diphenylanthracene (DA) which is defined as external protection and polyvinylsilicone oil with condensed aromatics (C₁ gum) which is defined as internal protection is compared. In this article we also compared the radiation protection effects of TPHMTS with DA and C₁ gum, for which 50 phr TPHMTS was added to ensure the condensed aromatics groups was the same as the molar concentration of DA and the condensed aromatics groups in C₁ gum. The experimental results show that the sample with TPHMTS exhibits both the best mechanical properties and the best radiation protection effects, as shown in Table III. With the respect to radiation protection of silicone rubber TPHMTS is better than DA, which can be attributed to the difference of external protection and internal protection, and TPHMTS is better than C₁ gum because of the wide decentralization of the condensed aromatics groups. The radiation protection of both TPHMTS and C₁ gum can be regarded as internal protection. The difference is that in the sample with TPHMTS the large conjugated groups are widely dispersed while in the sample with C₁ gum the large conjugated groups are relatively concentrated. Moreover the residual vinyl groups in C₁ gum induce crosslinking reaction more easily upon exposure to radiation.

TABLE IV
Mc of Silicone Rubber Reinforced by TPHTS Before and After Irradiation of 500 kGy

| TPHTS | TS-530 | Mc | |
|-------|--------|--------------------|-------------------|
| | | Before irradiation | After irradiation |
| 0 | 50 | 8367 | 1737 |
| 10 | 40 | 6429 | 1917 |
| 20 | 30 | 6877 | 1739 |
| 30 | 20 | 4884 | 2145 |
| 40 | 10 | 5013 | 1878 |
| 50 | 0 | 4468 | 2083 |

Mc of silicone rubber before and after irradiation

The average molecular weight between two crosslinking points (Mc) is an important structural parameter which can indicate the degree of crosslinking of vulcanizates. The higher the crosslinking density is, the smaller the Mc is. It is the total result of the physical and chemical interaction among fillers, silicone polymer chains and between fillers and the silicone polymer chains.³⁴ When silicone rubber is irradiated by gamma rays, both crosslinking and degradation reactions of polymer chains occur simultaneously with different rates.^{35,36} The data given in Tables IV and V show that Mc of silicone rubbers decrease after irradiation, which proves that the crosslinking density increases and the crosslinking reaction is more predominant than the degradation.

From the data in Table IV, it can be found that Mc of vulcanizates reinforced by TPHTS decreases before irradiation with the increase of TPHTS. For example, when 10 phr TPHTS was used, the Mc of silicone rubber is 6429. When 50 phr TPHTS was used, the Mc of silicone rubber is 4468. The high silanol group density results in such phenomena. With the further increase of TPHTS the crepe hardening occurs and the vulcanizates are excessively crosslinked, which also shows that TPHTS should be treated sequentially by MM^N. On the other hand the change of silicone rubber's Mc reinforced by TPHTS

TABLE V
Mc of Silicone Rubber Reinforced by TPHMTS Before and After Irradiation of 500 kGy

| TPHMTS | TS-530 | Mc | |
|--------|--------|--------------------|-------------------|
| | | Before irradiation | After irradiation |
| 0 | 60 | 6169 | 2104 |
| 10 | 50 | 4630 | 1865 |
| 20 | 40 | 5821 | 3114 |
| 30 | 30 | 5473 | 2156 |
| 40 | 20 | 5116 | 2474 |
| 50 | 10 | 5233 | 2226 |
| 60 | 0 | 5547 | 2492 |

is lower than that reinforced only by TS-530. The Mc of silicone rubber reinforced by 50 phr TS530 decreases from 8367 to 1737 after irradiation while the Mc of silicone rubber reinforced by 50 phr TPHTS decreases from 4468 to 2083, indicating that TPHTS has fine radiation resistant effect for silicone rubber and reduces the crosslinking reactions.

From the data in Table V it can be found that Mc of vulcanizates reinforced by 20 phr and 60 phr TPHMTS are 5821 and 5547, respectively. The corresponding change is lower than that of TPHTS, indicating that TPHMTS is well treated. Compared to TS-530, the Mc of silicone rubber reinforced by 60 phr TPHMTS decreases from 5547 to 2492 after irradiation, and the change of Mc is lower. Accordingly, TPHMTS is not only good reinforcing filler but also an effective antiradiation additive for silicone rubber to reduce the radiation crosslinking reactions.

CONCLUSIONS

Two new kinds of silica (TPHTS and TPHMTS) were prepared by treating fumed silica with either TPHPHS or with both TPHPHS and MM^N , and they can effectively inhibit the crosslinking reactions induced by gamma radiation as reinforcing filler for silicone rubber. The fine radiation protection effects of TPHTS and TPHMTS can be attributed to the tetraphenylphenyl groups on the surface of silica, which dissipate the absorbed radiant energy in the large conjugated structure before bond rupture occurs. TPHTS, which is not well treated because of the large steric hindrance of tetraphenylphenyl group, is good filler for silicone rubber to improve the radiation resistance but the reinforcing effect is poor while TPHMTS is an effective reinforcing filler to improve as well radiation resistance. Using TPHMTS as reinforcing filler is a novel effective method to improve the radiation resistance of silicone rubber.

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