

# Effects of Polyvinylsilicone Oil with Condensed Aromatics on the Radiation Resistance of Heat-Curable Silicone Rubber

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Received 3 December 2005; accepted 2 March 2006

DOI 10.1002/app.24487

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Polyvinylsilicone oil with condensed aromatics (called C<sub>1</sub> gum) was synthesized by Diels-Alder reaction of polyvinylsilicone oil and acenaphthenecyclone, and was used as an additive in heat-curable silicone rubber. The resistance to irradiation of the silicone rubber obtained was investigated by  $\gamma$ -rays at doses up to 300, 500, and 1000 kGy in vacuum. The dose rate was 150 kGy/min. After irradiation, the average molecular weight between crosslinks ( $M_c$ ) and mechanical properties of the silicone rubber were determined. The results show that C<sub>1</sub> gum can effectively

improve the radiation resistance of silicone rubber. When the amount of C<sub>1</sub> gum used in silicone rubber changes from 2 to 14 parts per hundred silicone gum, the radiation protection effects increase with increasing amount of C<sub>1</sub> gum. The radiation protection mechanism of C<sub>1</sub> gum was also discussed. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1937–1942, 2006

**Key words:** polysiloxanes; radiation; rubber; Diels-Alder reaction; condensed aromatics

## INTRODUCTION

Silicone rubber, because of its excellent properties, has been applied in aviation, nuclear power plants, and military weapons, etc, in which, however, the radiation resistance of silicone rubber is especially important. Approaches to improve the radiation resistance of silicone rubber include addition of additives in it and use of polysiloxane containing radiation resistant groups as gum. It is well known that the addition of some aromatic compounds, such as biphenyl, naphthalene, phenanthrene, can improve material's radiation resistance.<sup>1,2</sup> In these cases, since the aromatic additives are mixed physically with the material, their radiation protection effects are characterized as external protection.<sup>3</sup> It has been reported that the radiation resistance of polymethyl phenyl silicone rubber is better than that of polymethyl vinyl silicone rubber because of the conjugated structures of phenyl groups.<sup>4–6</sup> The phenyl groups, which offer the protec-

tion against radiation, are parts of molecular structures of silicone gum, and their radiation protection effects are characterized as internal protection.<sup>7</sup> Condensed aromatics may have better radiation protection effects because of their larger conjugated structure. If they were grafted onto the main chain of silicone gum, the radiation resistance of silicone rubber that obtained may be greatly improved. However, to our knowledge, no such research has been reported. In this article, we induced the condensed aromatics onto the main chain of polyvinylsilicone oil (called C gum) by Diels-Alder reaction to obtain polyvinylsilicone oil with condensed aromatics (C<sub>1</sub> gum) and used C<sub>1</sub> gum as an additive to silicone rubber for investigating its effects on the radiation resistance. The aromatic compound with large conjugated structure, 9,10-diphenylanthracene (DA), was also used as an additive in silicone rubber to compare the radiation protection effects of DA and C<sub>1</sub> gum on the same molar concentration. The average molecular weight between crosslinks ( $M_c$ ) and mechanical properties of silicone rubber before and after radiation by  $\gamma$ -rays were studied. This work aims to find an effective way to improve silicone rubber's radiation resistance.

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Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 29974016.

Contract grant sponsor: National Science Foundation of Shandong Province of China; contract grant number: Y2003B01.

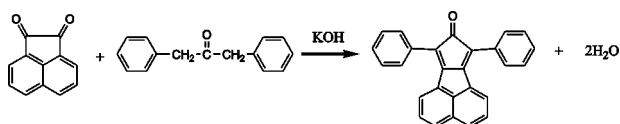
Contract grant sponsor: Foundation for University Key Teacher by the Ministry of Education of China; contract grant number: 2000(65)-24.

*Journal of Applied Polymer Science*, Vol. 102, 1937–1942 (2006)  
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## EXPERIMENTAL

### Materials

Acenaphthenequinone, 1,3-diphenylacetone, and 9,10-diphenylanthracene were obtained from Shanghai Chemical Reagent Company. Polymethyl vinyl silicone



Scheme 1 Synthesis of acenaphthenecyclone.

gum ( $M_n$ ,  $5.0 \times 10^5$ ; vinyl group content, 0.15 mol %), No. 4 fumed silica (specific surface area,  $176 \text{ m}^2/\text{g}$ ), otamethylcyclotetrasilazane ( $\text{D}_4^{\text{N}}$ ), and 2,5-bis(*tert*-butyl peroxy)-2,5-dimethyl hexane (DBPMH) are all industrial products, and were used as obtained.

### Preparation of $\text{C}_1$ gum

#### Synthesis of acenaphthenecyclone

Acenaphthenecyclone was synthesized according to the literature (Scheme 1).<sup>8</sup> About 10.9 g acenaphthenequinone (0.06 mol) and 12.6 g 1,3-diphenylacetone (0.06 mol) were dissolved in 120 mL ethanol, and the mixture was heated to  $78^\circ\text{C}$ . A solution of 1.6 g KOH in 8 mL ethanol was added slowly to the mixture. The reaction mixture was stirred at  $78^\circ\text{C}$  for 15 min, and then cooled to  $0^\circ\text{C}$  to stop the reaction. Solid product was filtrated and washed three times with ethanol. After drying, acenaphthenecyclone was obtained. The total yield was 89.5%, mp  $289^\circ\text{C}$  (lit. mp  $290^\circ\text{C}$ ).<sup>8</sup>

#### Synthesis of C gum and $\text{C}_1$ gum

C gum (vinyl group content, 15.0 mol %; viscosity, 190 mPa s) was synthesized according to the method reported in the literature.<sup>9</sup>

$\text{C}_1$  gum was prepared by Diels-Alder reaction of acenaphthenecyclone with C gum (Scheme 2).<sup>10</sup> Nine grams of acenaphthenecyclone and 12.8 g C gum were dissolved in 60 mL xylene in a sealed stainless steel reactor, and the reaction was run for 70 h at  $230^\circ\text{C}$  under a nitrogen atmosphere. Then xylene was removed under reduced pressure.  $\text{C}_1$  gum was purified with silica gel column chromatography. The change of  $^1\text{H}$  NMR spectra of polysiloxanes from Figure 1 before and after reaction can indicate that the condensed aromatics are grafted onto the main chain of C gum successfully:  $\delta$  0.0–0.15 (Si—CH<sub>3</sub>), 5.7–6.0 (—CH=CH<sub>2</sub>), 7.0–8.0 (condensed aromatics). The content of vinyl groups and condensed aromatics in

$\text{C}_1$  gum was calculated by  $^1\text{H}$  NMR analysis according to the integral value of various H atoms.<sup>9</sup> The content of vinyl groups in  $\text{C}_1$  gum was 4.50 mol % and the content of condensed aromatics was 9.69 mol %.

### Preparation of silicone rubber

#### Formula

The formula of silicone rubber is listed in Table I. It has been reported that phenyl groups have stabilization on radicals forming during decomposition of initiator (DBPMH) and inhibit the crosslinking reactions of silicone rubber.<sup>11,12</sup> With the increase of amount of  $\text{C}_1$  gum used, the concentration of condensed aromatics also increases, causing the vulcanizates to be in a state of "lack of cure" when using usual amount of DBPMH as initiator. So, to obtain samples with good vulcanization characteristics, the amount of DBPMH used must increase with the increase of amount of  $\text{C}_1$  gum used.

#### Processing

Referring to the literature,<sup>9</sup> materials were compounded and then vulcanized at  $170^\circ\text{C}$  for 30 min under 10 MPa, and postcured at  $190^\circ\text{C}$  for 2 h under ambient pressure to obtain vulcanizates.

#### Irradiation

The silicone rubber samples were irradiated with  $\gamma$ -rays from a Co-60 source in vacuum (1.4 Pa). The total dose was chosen as 300, 500, and 1000 kGy, and the dose rate was 150 Gy/min.

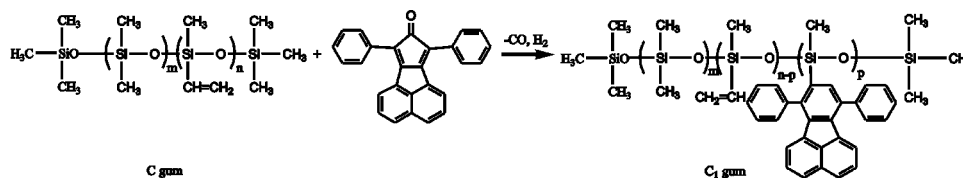
### Measurements and testing

The mechanical properties of vulcanizates were measured on a XLS-a rubber test instrument.

The samples were swollen in toluene at  $25^\circ\text{C}$  for 10–15 days. By the toluene-swelling method, average molecular weight between crosslinks can be calculated by the formula.<sup>13,14</sup>

$$M_c = -\rho V_0 \phi^{1/3} / [\ln(1 - \phi) + \phi + X\phi^2] \quad (1)$$

where  $M_c$  is the average molecular weight between crosslinks;  $\phi$ , the volume fraction of the swollen vul-



Scheme 2 Synthesis of  $\text{C}_1$  gum.

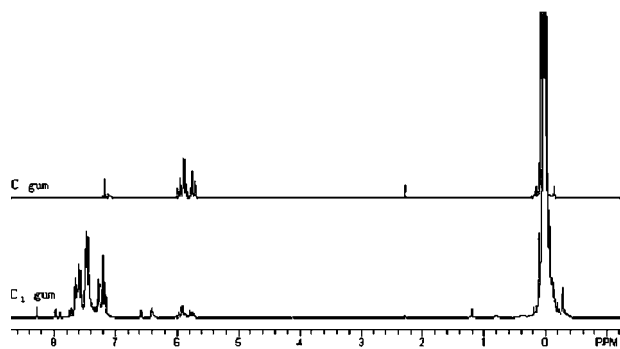


Figure 1  $^1\text{H}$  NMR spectra of C gum and  $\text{C}_1$  gum.

canizate;  $X$ , the macromolecule–solvent interaction efficiency, value is  $0.465^{11,12,15}$ ;  $\rho$ , the density of vulcanizate, and  $V_0$ , the mole volume of toluene.

$$\phi = (W_1/\rho)/((W_2 - W_1)/\rho_1 + W_1/\rho) \quad (2)$$

where  $W_1$  is the initial weight of vulcanizate;  $W_2$  is the weight of swollen vulcanizate; and  $\rho_1$  is the density of toluene (25°C).

## RESULTS AND DISCUSSION

### $M_c$ 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. The higher the crosslink density is, the smaller the  $M_c$  is. When silicone rubber is irradiated by  $\gamma$ -rays, both crosslinking and scission reactions of molecular chains occur simultaneously with different rates.<sup>16,17</sup> Many researchers have reported that crosslinking reactions predominate over scission reactions when polysiloxanes or silicone rubber is irradiated in vacuum.<sup>18–24</sup> From the data in Table II, it can be found that the  $M_c$  of all irradiated vulcanizates decreases after  $\gamma$ -radiation, indicating that the crosslinking

TABLE I  
Formula of Silicone Rubber<sup>a</sup>

Sample no.	Silicone gum	No. 4 fumed silica	$\text{D}_4^{\text{N}}$	$\text{C}_1$ gum	DA	DBPMH
1	100	50	8	0	0	0.83
2	100	50	8	2	0	0.92
3	100	50	8	4	0	1.08
4	100	50	8	6	0	1.33
5	100	50	8	8	0	1.50
6	100	50	8	10	0	1.81
7	100	50	8	12	0	2.1
8	100	50	8	14	0	2.65
9	100	50	8	0	4.17	0.83

<sup>a</sup> All values are expressed as (phr) by weight.

density increases and that the crosslinking reactions induced by radiation are predominant. It is consistent with the results that have been reported. After 300, 500, and 1000 kGy radiation, the  $M_c$  of sample 1 without  $\text{C}_1$  gum decreases from 4681 to 2369, 1306, and 827, respectively. It shows a remarkable decrease in  $M_c$  at different radiation dose. For samples with various amount of  $\text{C}_1$  gum, the  $M_c$  is quite different. For example, when the amount of  $\text{C}_1$  gum used is 2 phr (sample 2), the  $M_c$  is 2501 (300 kGy) and 1411 (500 kGy). Compared with sample 1, the protection effects of  $\text{C}_1$  gum begins to appear. With the increase of amount of  $\text{C}_1$  gum, the protection effects of  $\text{C}_1$  gum show more and more obviously. For example, when the amount of  $\text{C}_1$  gum used is 8 phr (sample 5), the  $M_c$  is 2898 (300 kGy) and 1913 (500 kGy); for sample 8 with 14 phr  $\text{C}_1$  gum, the  $M_c$  is 3123 (300 kGy) and 2237 (500 kGy), respectively. This illustrates that  $\text{C}_1$  gum has obvious protection effects on radiation of silicone rubber and its radiation protection effects increase with the increase of its concentration. When the radiation dose is 1000 kGy, the  $M_c$  of all samples varied from 827 to 990, no apparent difference exists in the  $M_c$  of these samples. It can be concluded that serious crosslinking reactions occurs in the rubber system at the dose of 1000 kGy even when  $\text{C}_1$  gum of 14 phr was used.

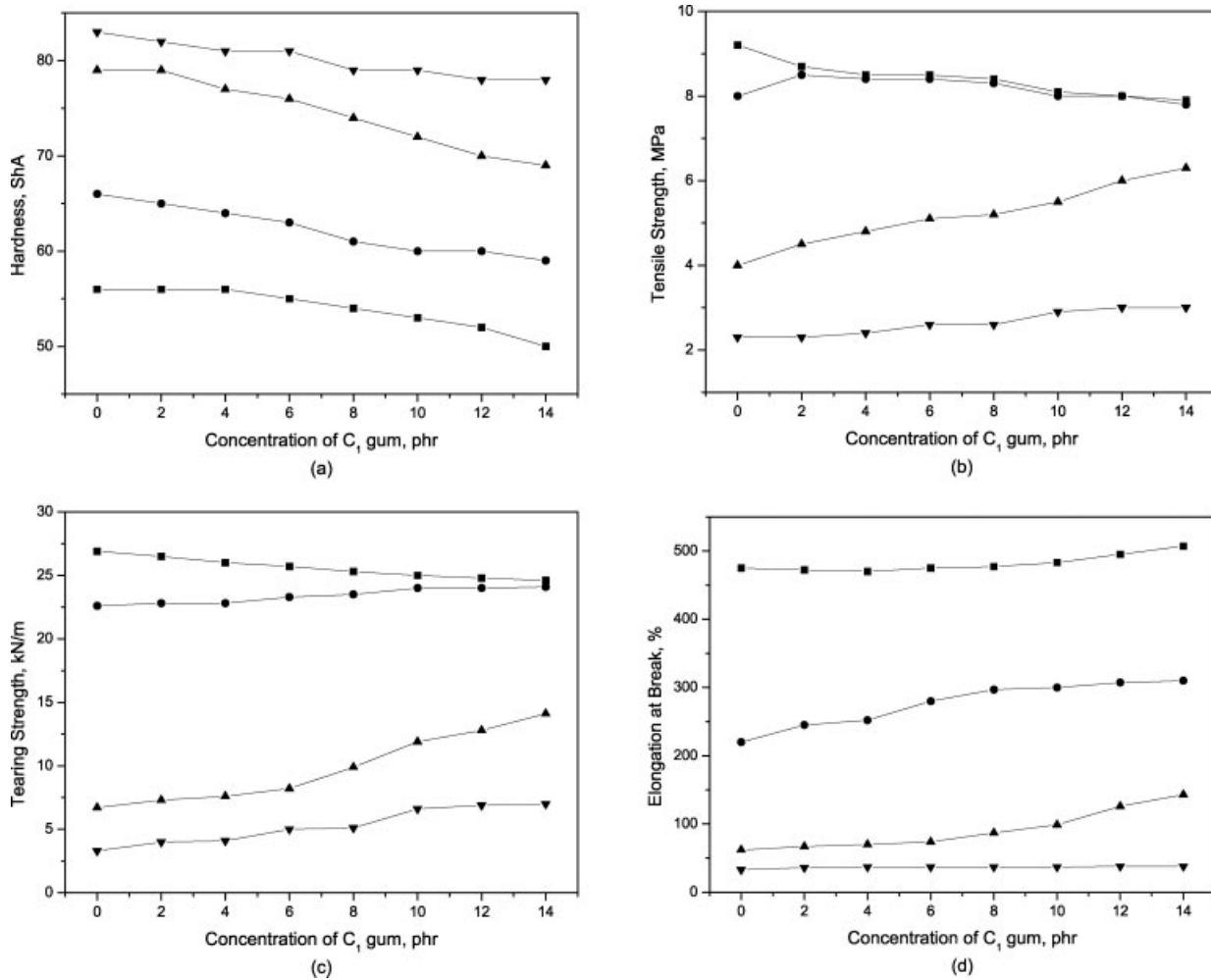
Theoretically, the radiation resistance of silicone rubber can be improved by using large amounts of  $\text{C}_1$  gum. But when the amount of  $\text{C}_1$  gum used exceeds 14 phr, the sample is hard to cure, leading to a state of “lack of cure.” Even when more DBPMH was used, it is difficult to obtain samples with good vulcanization characteristics.

### Effects of $\text{C}_1$ gum on the mechanical properties of silicone rubber

Figure 2 illustrates the effects of  $\text{C}_1$  gum on the mechanical properties of vulcanizates before and after radiation. As shown in Figure 2(a), the hardness increases with increasing radiation dose, which are mainly attributed to the higher crosslinking density

TABLE II  
 $M_c$  of Vulcanizates Before and After Radiation

Sample no.	Before radiation	300 kGy radiation	500 kGy radiation	1000 kGy radiation
1	4681	2369	1306	827
2	4696	2501	1411	834
3	4708	2612	1445	916
4	4793	2806	1677	944
5	4875	2898	1913	964
6	4899	3005	1958	978
7	4973	3089	2008	985
8	5102	3123	2237	990



**Figure 2** Effects of C<sub>1</sub> gum on the mechanical properties of vulcanizates before and after radiation: (■) before radiation; (●) 300 kGy; (▲) 500 kGy; (▼) 1000 kGy.

induced by radiation. For sample 1 without C<sub>1</sub> gum, the hardness is 66 Sh A (300 kGy), 79 Sh A (500 kGy), and 83 Sh A (1000 kGy); while for sample 8 with 14 phr C<sub>1</sub> gum, the hardness is 59 Sh A (300 kGy), 69 Sh A (500 kGy), and 78 Sh A (1000 kGy). It can be found that the hardness of samples containing C<sub>1</sub> gum is lower than that of sample 1 without C<sub>1</sub> gum after the same radiation dose.

Figure 2(b) shows a reduction of tensile strength after radiation. The tensile strength of sample 1 without C<sub>1</sub> gum decreases from 9.2 to 8.0 MPa (300 kGy) and 4.0 MPa (500 kGy). When the amount of C<sub>1</sub> gum used is 8 phr, the tensile strength decreases from 8.4 to 8.3 MPa (300 kGy) and 5.2 MPa (500 kGy); when the amount of C<sub>1</sub> gum used is 14 phr, the tensile strength decreases from 7.9 to 7.8 MPa (300 kGy) and 6.3 MPa (500 kGy). Similar results can be found on the changes of tearing strength [Fig. 2(c)] and elongation at break [Fig. 2(d)]. It can be seen that the mechanical properties of vulcanizates containing C<sub>1</sub> gum are better than those without C<sub>1</sub> gum after radiation. The higher the concen-

tration of C<sub>1</sub> gum is, the better the mechanical properties of vulcanizates are. When the dose is up to 1000 kGy, the mechanical properties of silicone rubber are seriously deteriorated whether the rubber contains C<sub>1</sub> gum or not. However, it can be concluded that C<sub>1</sub> gum is an effective antirads to improve the radiation resistance of silicone rubber.

#### The radiation protection mechanism of C<sub>1</sub> gum

There are vinyl groups on the side chains of C<sub>1</sub> gum (4.50 mol %), which can react with vinyl groups on the side chains of silicone gum during curing. As a result, a crosslinking network between silicone gum and C<sub>1</sub> gum could be formed.<sup>9-11,15,25</sup> Thus, the condensed aromatics could be incorporated onto the molecular network of silicone rubber, and become parts of molecular structure of silicone rubber. So, the radiation protection effects of C<sub>1</sub> gum could be characterized as internal protection.<sup>7</sup> When samples are irradiated, the absorbed energy from  $\gamma$ -rays can

TABLE III  
Effects of C<sub>1</sub> gum and DA at the Same Molar Concentration on the Mechanical Properties of Silicone Rubber Before and After Radiation

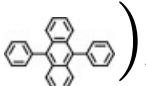
Samples	Hardness (Sh A)		Tensile strength (MPa)		Tearing strength (kN m <sup>-1</sup> )		Elongation-at-break (%)	
	B <sup>a</sup>	A <sup>b</sup>	B <sup>a</sup>	A <sup>b</sup>	B <sup>a</sup>	A <sup>b</sup>	B <sup>a</sup>	A <sup>b</sup>
Sample 1	56	79	9.2	4	26.9	6.7	475	62
Sample 8	50	69	7.7	6.3	23.4	14.1	507	143
Sample 9	56	79	8.3	4.1	18.9	6.8	372	60

<sup>a</sup> Before radiation.

<sup>b</sup> After 500 kGy radiation.

migrate onto the condensed aromatics and dissipate in the large conjugated structure before bond rupture occurs. Then, the reactions induced by radiation can be inhibited to a certain extent.

To improve the radiation resistance, it's an easy way for silicone rubber to be processed by using aromatic compound as additive. In this article, 9,10-

diphenylanthracene (DA, ) , which also

contains large conjugated structure, was chosen. Its effects on the radiation resistance of silicone rubber were studied. To compare the radiation protection effects of DA with C<sub>1</sub> gum, 4.17 phr DA was added to silicone rubber (sample 9) to make sure that the molar concentration of DA is the same as that of the condensed aromatics groups in C<sub>1</sub> gum in sample 8. The results show that DA does not exhibit good radiation protection effects as C<sub>1</sub> gum does on silicone rubber (Table III). This may be attributed to the different radiation protection mechanism of DA and C<sub>1</sub> gum. During the processing of silicone rubber, DA is compounded with silicone gum by mechanical force operated by a two-roll mill. Because DA is not incorporated onto the main chain of silicone gum, it is dispersed in the rubber matrix and the compatibility of DA is not as good as that of the condensed aromatics rings in C<sub>1</sub> gum. So, the radiation protection effects of DA can be characterized as external protection. The energy absorbed by the rubber network cannot effectively migrate onto the conjugated structure of DA, which influences its radiation protection efficiency. Theoretically, the larger the conjugated structure of aromatic additive is, the better the radiation protection is. But the experiment indicates that it is difficult to improve rubber's radiation resistance by using aromatic compound with large conjugated structure. Only when the large conjugated structure was incorporated onto the molecular structure of silicone rubber, the good radiation protection effects could appear, because internal protection occurs more readily than external protection.<sup>7</sup>

## CONCLUSIONS

As an additive of heat-curable silicone rubber, polyvinylsilicone oil with condensed aromatics (C<sub>1</sub> gum) can effectively inhibit the crosslinking reactions induced by  $\gamma$ -irradiation, and the radiation protection effects increase with the increase of C<sub>1</sub> gum used from 2 to 14 phr. When the radiation dose is 300 or 500 kGy, the mechanical properties of silicone rubber containing C<sub>1</sub> gum are better than those of rubber without C<sub>1</sub> gum. When the dose is up to 1000 kGy, the mechanical properties of silicone rubber are seriously deteriorated whether the rubber contains C<sub>1</sub> gum or not. However, it can be concluded that C<sub>1</sub> gum is an effective antirads to improve the radiation resistance of silicone rubber.

The better radiation protection effects of C<sub>1</sub> gum are due to the condensed aromatics on the side chains, which provide internal protection and dissipate the absorbed energy in the large conjugated structure before bond rupture occurs. When 9,10-DA is used as an additive in silicone rubber, it does not exhibit good radiation protection effects as C<sub>1</sub> gum does on silicone rubber, because the internal protection of condensed aromatics in C<sub>1</sub> gum could easily occur than the external protection of DA.

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