Effects of additives on the radiation resistance of heat-curable silicone rubber

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ABSTRACT Effects of five kinds of aromatic additives (biphenyl, naphthalene, phenanthrene, benzophenone and-diphenylacetylene) on radiation resistance of heat-curable silicone rubber were studied. The changes in average molecular weight between crosslinks (M_c) and mechanical properties before and after γ-ray irradiation of 400 and 600kGy in vacuum were analyzed. Protection mechanisms of the aromatic additives are discussed. The results show that the aromatic additives, especially diphenylacetylene, can improve radiation resistance of silicone rubbers.

KEYWORDS Heat-curable silicone rubber, Additive, Radiation resistance, Radiation protection mechanism

CLC O631.3$^+$4, O621.25, TQ316

With fine electric insulation, good thermo-stability, excellent resistance to oxygen, ozone and sunlight, low toxicity and chemical reactivity, silicone rubbers have been used in aviation, nuclear power plants and military weapons, etc. Therefore, their radiation resistance is especially important. The effects of high-energy rays on silicone rubbers have been studied extensively over the past 50years[1-7]. It has been reported that, when silicone rubber is irradiated, phenyl substitution on silicon atoms offers partial protection to dimethyl siloxane units[8], and the radiation resistance of silicone rubber containing phenyl groups is better than that of polymethyl vinyl silicone rubber[5,6,9]. Delides[8] explained the protection effects of phenyl groups by the mechanism of electron migration: An electron removed by excitation might be replaced by electron migration through the main chain-Si-O-and its energy dissipated by the resonance structure of phenyl redical.

Some aromatic compounds, such as nanphthalene, phenanthrene and p-terphenyl, etc., can be used as anti-rads to prolong material's lifetime in high-energy radiation environment[10-13]. However, few publications can be found concerning the effects of aromatic additives on the radiation resistance of silicone rubber[14]. On the other hand, the distribution of additives in a rubber matrix is very important to the rubber system. It may affect mechanical properties of the rubber and radiation protection efficiency of the additives. The dispersion problem may be alleviated by aromatic additives with low melting points, selected according to curing temperature of a silicone rubber. When the rubber is vulcanized at 170℃ and 10MPa, the additives change into liquid phase and migrate in the rubber system, hence a better dispersion in the rubber matrix.

In this paper, biphenyl, naphthalene, phenanthrene, benzophenone and diphenylacetylene were examined to study their effects on radiation resistance of heat-curable silicone rubber, and the protection efficiency of the aromatic additives is discussed, in an attempt to find effective additives for improving radiation resistance of silicone rubbers.

1 Experimental

1.1 Materials

Polymethyl vinyl silicone gum (M_n, 5.0×10^5; vinyl group content, 0.15mol%), 4#fume silica (specific surface area, 176m^2/g), otamethylcyclotetrasilazane (D_4^N) and 2,5-bis(tert-butyl peroxy)-2,5-dimethyl hexane（DBPMH）were all industrial products. The aromatic additives, biphenyl (BP, , m.p.71℃), naphthalene (N,  , m.p.80.5℃),

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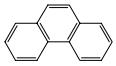
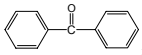
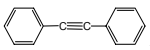
phenanthrene (P,  , m.p.101℃), benzophenone (BPN,  , m.p.48℃), diphenylacetylene (DPA,  , m.p.62℃) were obtained from Shanghai Chemical Reagent Co. and were used without further purification.

1.2 Preparation of silicone rubber

1.2.1 Formulation The formulation of silicone rubber is listed in Table 1.

Table 1 Formulation of silicone rubber (weight parts)

Silicone gum	4# fume silica	D_4^N	Additive	DBPMH
100	50	8	4.6	0.8

1.2.2 Processing Referring to Ref. [15], the materials were compounded and vulcanized at 170℃ for 30min under 10MPa.

1.3 Irradiation test

The silicone rubber samples were irradiated in vacuum to 400kGy or 600kGy by ^{60}Co γ-rays at a dose rate of 100Gy/min.

1.4 Measurements and testing

Mechanical properties of the vulcanizates were measured on an XLS-A rubber test instrument. The samples were swollen in toluene at 25℃ for 10—15 days. The average molecular weight between the crosslinks was calculated by the following equation [16-17].

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

where M_c is the average molecular weight between the crosslinks; X=0.465[18-20], macromolecule-solvent interaction efficiency; ρ, density of the vulcanizate; V_0, mole volume of toluene; and φ, volume fraction of vulcanizate in the swelling body;

$$\varphi=(W_1/\rho)/((W_2-W_1)/\rho_1+W_1/\rho)$$

where W_1 is initial weight of the vulcanizate; W_2, swollen weight of the vulcanizate; ρ_1, density of toluene at 25℃; ρ, the density of vulcanizate before swelling (25℃).

2 Results and discussion

2.1 M_c of pre- and post-irradiation vulcanizates

For silicone rubbers, average molecular weight between crosslinks (M_c) is an important structural parameter, which indicates the degree of crosslinking of vulcanizates. The higher the crosslink density is, the smaller the M_c becomes. Phenyl groups are stable against radicals from decomposition of catalyst[18, 20]. The aromatic additives used in this study have cure retardation to heat-cure silicone rubber: the Mc of 3970 of vulcanizate without additive is lower than that of vulcanizates containing additives DPA, P, BP and N (Table 2).

Table 2 M_c of vulcanizates and the Change in M_c

Additives	M_c		
	I	II	III
None	3970	3097	1408
Biphenyl	4278	3450	2305
Naphthalene	4655	3807	2297
Phenanthrene	4349	3684	2404
Benzophenone	3964	3446	2376
Diphenylacetylene	4166	4117	2431

I. Before irradiation II. 400kGy III. 600kGy

When silicone rubbers are irradiated by γ-rays, scission and crosslinking reactions occur simultaneously at different rates[21-22]. The changes in M_c before and after irradiation reflect changes in crosslink density of the vulcanizates. From Table 2 it can be found that the M_c of all irradiated vulcanizates decreases after irradiation, indicating that crosslinking reactions are predominant during the irradiation. After the 400 or 600kGy irradiation, M_c of the vulcanizate containing aromatic additives is higher than the vulcanizate without additives. This shows that the aromatic additives can inhibit the crosslinking reactions. It can be seen that DPA has the best inhibition effects among the aromatic additives, as M_c of the vulcanizate with DPA is the highest after irradiation.

2.2 Effects of additives on the mechanical properties of silicone rubber

After irradiation, hardness and modulus at 100% of the vulcanizates increased, while tensile strength, tearing strength and elongation at break decreased, as shown in Table 3. Just as discussed above, this is attributed to higher crosslinking density induced by the γ-rays. Mechanical properties of the vulcanizates containing aromatic additives are better than the vulcanizate without any additive. For example, after 600kGy irradiation, tensile strength of the vulcanizate without additive is 4.5MPa, while it is 6.2MPa for the vulcanizate containing DPA. Similar results can be found on tearing strength and elongation at break.It further indicates that the aromatic additives can improve radiation resistance of the silicone rubbers and DPA has the best radiation protection effects.

Table 3　Effects of additives on the mechanical properties of vulcanizates before and after irradiation

Additives	Hardness (Shore A)			Modulus at 100% /MPa			Tensile Strength /MPa			Tearing Strength (kN m^{-1})			Elongation at break/%		
	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III
None	56	62	69	1.6	2.1	—	9.2	8.1	4.5	29.2	27.1	9.6	470	336	80
Biphenyl	56	60	66	1.4	1.9	3.0	9.6	8.8	5.3	28.9	28.7	14.6	515	403	140
Naphthalene	54	60	66	1.2	1.8	2.9	9.8	8.2	5.2	29.3	27.2	15.0	613	403	145
Phenanthrene	54	59	66	1.1	1.8	2.8	9.3	8.5	5.5	28.5	28.1	16.7	575	408	173
Benzophenone	56	60	66	1.4	2.0	2.9	9.2	8.4	6.0	29.5	28.6	15.6	526	384	163
Diphenylacetylene	54	59	64	1.1	1.5	2.7	9.6	8.8	6.2	29.1	28.9	17.3	649	453	182

I. Before irradiation　II. 400kGy　III. 600kGy

2.3 Radiation protection mechanisms of aromatic additives

Among the aromatic additives, P, BP and N have the same radiation protection mechanism [10,13]. It is suggested that excess energy release may be one of the most important factors in appearance of the radiation protection effects. The absorbed radiation energy can be dissipated in the conjugated structure before bond rupture occurs, converted to heat or light and released to the environment [11, 12, 23]. As a result, the aromatic additives protect the macromolecules from the damage it would otherwise suffer. The protection efficiency of the additives is in relation with the lowest singlet energy (E_s). And it seems to decrease with increasing E_s. In addition, the additives can react with radicals or electrons, which are formed by bond rupture during the irradiation, preventing either further bond scissions or recombination of radicals. Tabuse[13] reported that the higher is the degree of aromaticity of additives, the higher is the reactivity of additives towards excited molecules, radical cations, and electrons. According to the results above, we can conclude that P has the better radiation protection effect than BP and N. This is consistent with the energy values of P (Table 4). Its resonance energy (RE) and electron affinity (EA) are the highest (1.924 eV, 0.269±0.035 eV), and its E_s is the lowest (346 kJ/mol).

Table 4　Several typical energy values of the aromatic additives used in this study[13]

Additives	Es[a] (kJ/mol)	EA[a] /eV)	RE[a]/eV)
Phenanthrene	346	<0.269±0.035	1.924
Biphenyl	418	<0.130±0.035	1.718
Naphthalene	385	0.140±0.050	1.325

BPN is usually used as ultraviolet absorbent in macromolecular materials. It is a good radical acceptor during radiation, thus it can inhibit the crosslinking or scission reactions induced by high-energy rays [14]. This is also indicated by the results in Table 2 and 3.

As mentioned above, DPA has the best radiation protection effect. This may be attributed to its special chemical structure. The unsaturated bond can be opened by γ-rays and more easily reacts with radicals formed during radiation. As a result, the crosslinking and scission reactions induced by radiation are effec-

tively inhibited. In such a course, by the recombination of radicals, DPA may polymerize or be grafted onto the rubber matrix[24-25], so its protection effect changes from “external protection” to “internal protection”, which is expected to occur more readily than external protection[8, 26]. In particular, external protection occurs when P, BP and N are mixed in the rubber system.

3 Conclusions

The aromatic additives (biphenyl, naphthalene, phenanthrene, benzophenone and diphenylacetylene) can improve radiation resistance of silicone rubbers obviously, and diphenylacetylene has the best radiation protection effect.

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添加剂对高温硫化硅橡胶耐辐射性能的影响

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摘要 研究了五种不同的芳香族添加剂（联苯、萘、菲、二苯甲酮、二苯乙炔）对高温硫化硅橡胶的耐辐射性能的影响。分析了在真空下经受 400kGy 和 600kGy 的 γ 射线辐照下，两交联点间有效链平均分子量 M_c 和力学性能的变化。讨论了芳香族添加剂的辐射保护机理。结果表明芳香族添加剂，尤其是二苯乙炔，能提高硅橡胶的耐辐射性能。

关键词 高温硫化硅橡胶，添加剂，耐辐射性，辐射保护机理

中图分类号 O631.3^{+}4，O621.25，TQ316