

# Protection of SEBS/PS Blends against Gamma Radiation by Aromatic Compounds

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**ABSTRACT:** We reported the effects of four kinds of aromatic compounds (diphenylacetylene, biphenyl, anthracene, pyrene) on the gamma-irradiation resistance of the styrene-ethylene-butylene-styrene/polystyrene (SEBS/PS) blends. It was found that, after gamma irradiation, the blends with aromatic additives had improved mechanical, dielectric, and thermal characteristics when compared with those samples without additives, and that among the four compounds, pyrene was shown to be the most effective additive. The rheological results were consistent with

the changes of mechanical, dielectric, and thermal properties, and the blends with pyrene had the lowest values of melt-flow rate after gamma irradiation. The possible mechanism of the effects of the aromatic compounds on the irradiation resistance SEBS/PS blends was also suggested. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1076–1081, 2009

**Key words:** SEBS/PS blends; irradiation; aromatic compounds; mechanical properties; dielectric properties

## INTRODUCTION

Polymer materials are widely used as dielectrics and electrical insulation because of their excellent mechanical, electrical, and processing properties. The mechanical and electrical performance of these materials can, however, be compromised by their working environment, and one of the most deleterious is that where nuclear radiation is present.<sup>1–3</sup> For electrical and electrical equipments used in nuclear power plants, e.g., control cable systems, it is extremely important to have some irradiation-resistance characteristics to keep their qualities in an accident. Of great importance is to choose the polymers with excellent irradiation-resistance as insulating materials of the equipments used in nuclear power plants. As an aromatic polymer, styrene-ethylene-butylene-styrene (SEBS) was considered to have a good radiation resistance. The near saturated ethylene/butylene mid-block of SEBS makes it more stable than styrene-butylene-styrene (SBS), offering higher processing temperatures, while it still retains the typical behavior of thermoplastic elastomers.<sup>5</sup> Steller<sup>4</sup> found that SEBS and its blends with polypropylene (PP) were more resistant toward the action with electron

beam in comparison with PP, SBS, and the SBS-based blends. Photooxidative degradation mechanisms in SEBS have been studied and it has been shown that the main-chain scission and oxidation occurred in the olefinic phase (EB phase) while less degradation occurred in polystyrene (PS) phase.<sup>6</sup> This may be attributed to that the degradative and oxidative reactions in PS phases were slowly controlled by the rate of diffusion of oxygen into the polymer because of the special volume of the PS benzene rings that restricted oxygen entering the matrix.<sup>7</sup>

For SEBS/PS blends, their irradiation stability could be improved by reducing the percentage of EB phase, whereas high PS concentration might deteriorate the mechanical properties, e.g., elongation at break of the blends. It has been shown in our previous work that SEBS/PS (60/40) had a better irradiation resistance and mechanical properties than pure SEBS and other SEBS/PS blends (80/20, 70/30, 50/50) under the dose of radiation of 0–2.0 MGy.<sup>8</sup> It was known that some aromatic compounds, such as naphthalene, phenanthrene, and *p*-terphenyl, etc., could be used as antirads to prolong the lifetime of polymeric materials under high-energy radiation environment.<sup>9,10</sup> There was, however, little information about the effects of aromatic additives on the irradiation resistance of SEBS/PS blends. This work aims to investigate the effects of diphenylacetylene (DPA), biphenyl (BP), anthracene (An), and pyrene (Py) on the  $\gamma$ -irradiation resistance of SEBS/PS

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(60/40) blends and to illustrate the corresponding mechanisms related with the improvement of the irradiation resistance.

## EXPERIMENTAL

### Materials

The SEBS (Kraton, G-1651H) with specific gravity of  $0.91 \text{ g/cm}^3$  and styrene/rubber ratio of 33/67 was supplied by Shell Chemical (Houston, TX). Polystyrene (STYRON, 666H) with specific gravity of  $1.04 \text{ g/cm}^3$  was supplied by Dow Chemical (Midland, MI). Both polymers were used without further purification.

BP was obtained from Sinopharm Chemical Reagent (Shanghai, China). DPA, An, and Py were obtained from Alfa Aesar China (Tianjin Corp.). All the aromatic compounds were used as received.

### Sample preparation

SEBS with 40 wt % PS was blended using a Haake Rheometer RC90 (Karlsruhe, Germany) at the temperature  $180^\circ\text{C}$  and the rotor speed of 80 rpm for 10 min. The concentration of each additive is 4 phr by weight. Sheets with a thickness of around 1 mm were obtained using compression molding at  $180^\circ\text{C}$  under a pressure of about 15 MPa. Then, the sheets in the mold were transferred to another compression molding machine, and the temperature of the sheets in the mold was slowly decreased to room temperature under the condition of the pressure of 15 MPa and the water cooling. Next, the sheets were removed from the mold. Polyethylene terephthalate films were used as backing.

### Gamma irradiation

The sheets were irradiated with a  $^{60}\text{Co}$  ( $7.4 \times 10^{15}$  Bq) gamma-irradiation source in Shanghai Heming Radiation Technology (Shanghai, China) at dose rate of 5.3 kGy/h. The sheets were irradiated to 0.5, 1.0, 1.5, and 2.0 MGy in air atmosphere at room temperature.

### Mechanical properties

Tensile strength and elongation at break were measured with a CMT 5305 Testing Machine (SANS, Shenzhen, China) according to ASTM D-638-2003 at a crosshead speed of 250 mm/min. For each sample, five determinations were performed, and the results are reported as the mean of five determinations. Measurements were carried out at room temperature.

### Dielectric properties

The DC volume resistivity was measured with the three-terminal technique after applying a dc voltage of 1000 V to the specimens for 1 min, using ZC-36 megohmmeter (Shanghai Precision and Scientific Instrument Corp., Shanghai, China). The dielectric dissipation factor was measured on a QS30 high-voltage bridge (Shanghai Huguang Corp., Shanghai, China) at the frequency of 50 Hz. All the measurements were performed at room temperature.

### Melt-flow rate measurements

Melt-flow measurements (MFR) were carried out on a MZ-2028 MFR tester (Jiangdu Mingzhu Experimental Instrument Corp., China) according to ASTM D-1238 at  $200^\circ\text{C}$  and with a load of 5 kg. For each sample, five measurements were performed, and the results are reported as the mean of five measurements.

### Thermogravimetric analysis

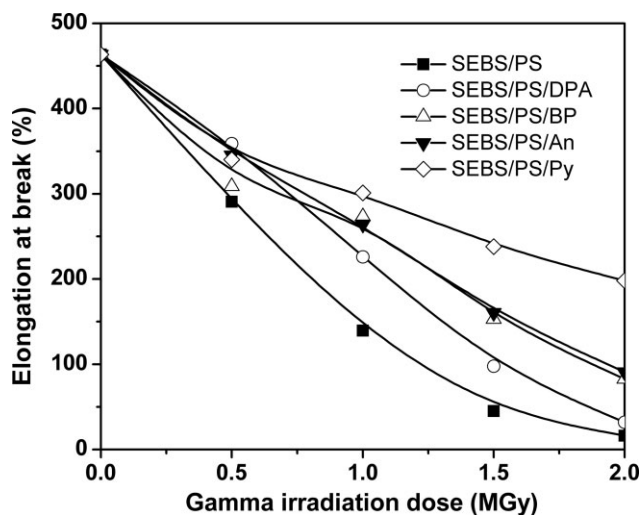
Thermogravimetric analyses (TGA) were carried out using the TGA 7 Thermogravimetric Analyzer (Perkin Elmer, USA) under nitrogen atmosphere. The samples were heated from room temperature to  $700^\circ\text{C}$  at a rate of  $20^\circ\text{C}/\text{min}$ .

## RESULTS AND DISCUSSION

### Mechanical properties

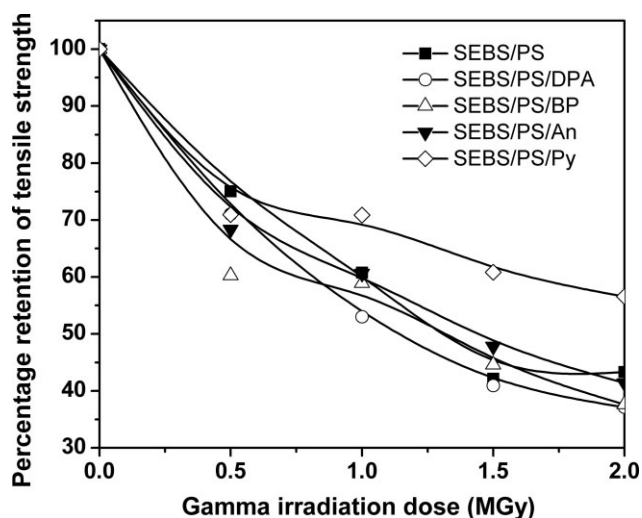
It was known that changes of mechanical properties before and after gamma irradiation, especially elongation at break,  $E_b$ , could offer a means for directly estimating polymer degradation phenomena.<sup>11</sup> Figure 1 shows the elongation at break of SEBS/PS blends with and without aromatic compounds as a function of gamma-irradiation doses. It could be observed that after gamma irradiation, the blend without aromatic compounds almost lost the ductibility and its  $E_b$  value was close to zero (16%), whereas those with aromatic compounds still kept relatively high values of  $E_b$ , and their  $E_b$  values decreased in the order of Py (198%) > An (91%) > BP(83%) > DPA (32%). These results indicated that the aromatic additives could improve the irradiation resistance of SEBS/PS blends, and Py had the best irradiation-resistance effect.

Figure 2 provides the changes of the tensile strength retention for all the samples before and after gamma irradiation. The values of tensile strength retention were calculated by dividing each value at a given dose by the corresponding initial value. The curves clearly reveal that gamma irradiation changed the tensile strength depending on what

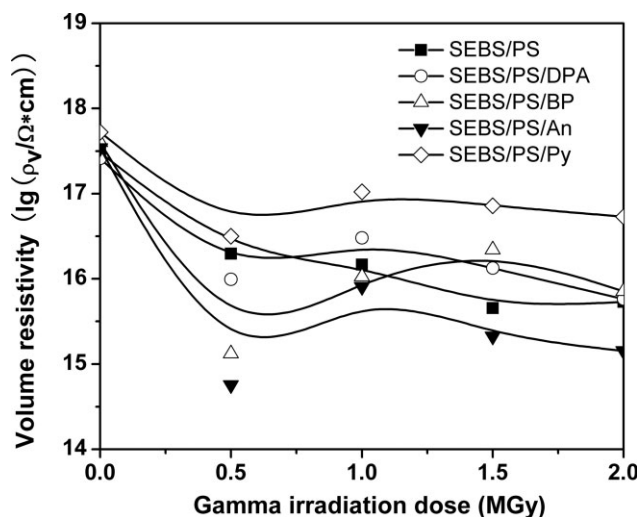


**Figure 1** Elongation at break of the SEBS/PS blends with and without aromatic compounds as a function of the irradiation dose.

kind of additive was added. With the changes of  $E_b$  values mentioned earlier, all the samples exhibited an initial sharp decrease in tensile strength, whereas at higher doses, the values of the samples showed a gradual decrease, especially for the blends with Py. As we could see from Figure 2, the samples had a decrease in tensile strength by more than 50%, except SEBS/PS/Py with 56.6% retention. These results also reveal that Py was effective in altering the radiation resistance of the SEBS/PS blends, giving us a hint that it could be quite possible to further improve the performance stability of the SEBS/PS blends under the condition of high-dose gamma radiation.



**Figure 2** Tensile strength of the SEBS/PS blends with and without aromatic compounds as a function of the irradiation dose.

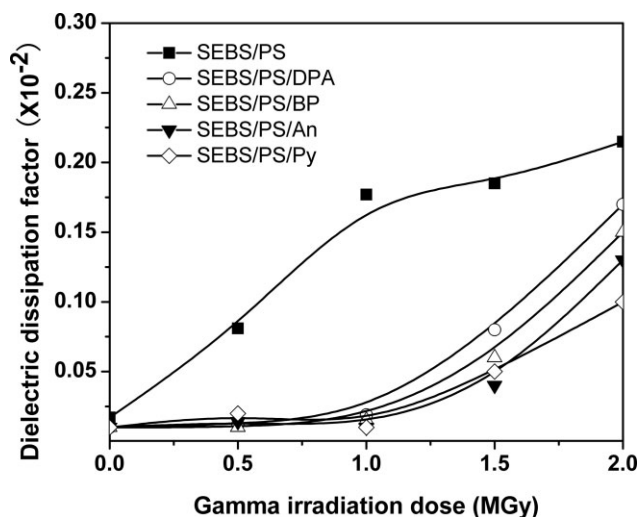


**Figure 3** Volume resistivity of the SEBS/PS blends with and without aromatic compounds as a function of the irradiation dose.

### Dielectric properties

The volume resistivity measurement results for SEBS/PS blends with and without aromatic additives are shown in Figure 3. A drastic decrease in the volume resistivity was observed at 0.5 MGy for the samples without additives as well as those with aromatic additives, indicating that radiation-induced degradation played an important role in the initial stage of gamma irradiation (0–0.5 MGy). As the result of chain scission and oxidation resulting from the degradation, the number of electric carriers and their mobility further increased, which could lead to the increase of the electrical conduction inside the samples, in other words, to the decrease of the volume resistivity.<sup>12</sup> It is well understood that volume resistivity of nonpolar polymers or their blends depends on the impurities because the base substance of those polymers could not be ionized, and that even very slight impurities can appreciably affect their conductivity.<sup>13</sup> As the radiation dose further increased up to 1.0 MGy, all the blends with additives showed higher volume resistivity when compared with those at 0.5 MGy. In the dose range over 1.0 MGy, the resistivity values of the blends with additives started to decrease gradually. These results meant that the radiation-induced crosslinking in the blends was much more apparent at the second stage of radiation dose (0.5–1.0 MGy). Beyond 1.0 MGy, the degradation of molecular chains became predominant again, and thus caused the decrease of the resistivity values. For the blends without additives, however, the changes of resistivity values had a different trend from those samples with additives, namely the resistivity of the blends without additives always decreased with the increasing radiation





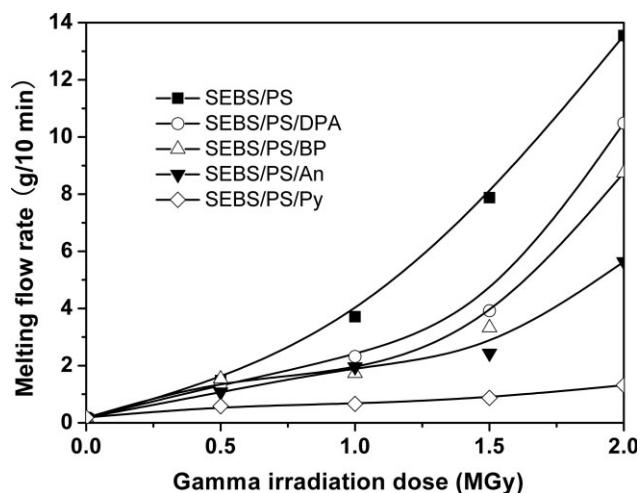
**Figure 4** Dielectric dissipation factor of the SEBS/PS blends with and without aromatic compounds as a function of the irradiation dose.

dose, indicating that the degradation of the molecular chains was always predominant in the samples without additives. These results were found to agree well with the dielectric loss results for those samples. As shown in Figure 4, the values of dielectric loss for the samples without additives always increased with the radiation doses increasing, whereas the blends with additives almost had the same changing tendency of dielectric loss with the conductivity behavior (reciprocal of the values of resistivity), which further validated the degradation and crosslinking mechanisms mentioned earlier. Figure 3 also clearly showed that, among the blends with aromatic compounds, the samples with Py had the highest volume resistivity all over the irradiation dose range, which indicated that Py could effectively protect the SEBS/PS blends against gamma radiation, and the results were consistent with the mechanical data.

Dielectric loss was attributed both to the electrical conductance (leakage loss) and to the relaxational polarization.<sup>14,15</sup> The aromatic compounds could retard the degradation of the molecular chains and, as a result, decreased the production of ionic and molecular mobility in the blends, which caused the decline of the dielectric loss of the samples.

### Thermogravimetric analysis

The thermal stability of the blends with and without additives has been investigated by TGA. Figure 5 shows the TGA curves of all samples with and without gamma irradiation (2.0 MGy). The decomposition temperatures at different weight losses and the temperature at maximum rate of decomposition



**Figure 5** TGA curves of the SEBS/PS blends applying and without applying 2.0 MGy dose of gamma irradiation.

( $T_{max}$ ) are given in Table I. It was found that, after gamma irradiation, the incorporation of aromatic additives led to the improvement of thermal stability of the blends: (i) the addition of aromatic additives led the TGA curves to shift toward higher temperatures, and the incorporation of Py could bring out the further improvement of the thermal stability; (ii) according to Figure 5, the samples with aromatic compounds showed increased  $T_{max}$  values, and the sample containing Py had the highest one; (iii) as shown in Table I, the listed decomposition temperatures for the SEBS/PS blends after gamma irradiation were lower than those of the samples before gamma irradiation, indicating the presence of degradation of polymer chains in the blends. The enhanced thermal properties might be attributed to the improved resistance of the blends against gamma irradiation. It was interesting to observe that the addition of aromatic additives made the irradiated blends have higher  $T_{max}$  values, indicating the presence of crosslinking reaction during the irradiation process. It should be noted from Figure 5 and

**TABLE I**  
Decomposition Temperatures at Different Weight Losses and Temperatures at Maximum Rate of Decomposition ( $T_{max}$ ) for the SEBS/PS Blends Applying and Without Applying 2.0 MGy Dose of Gamma Irradiation

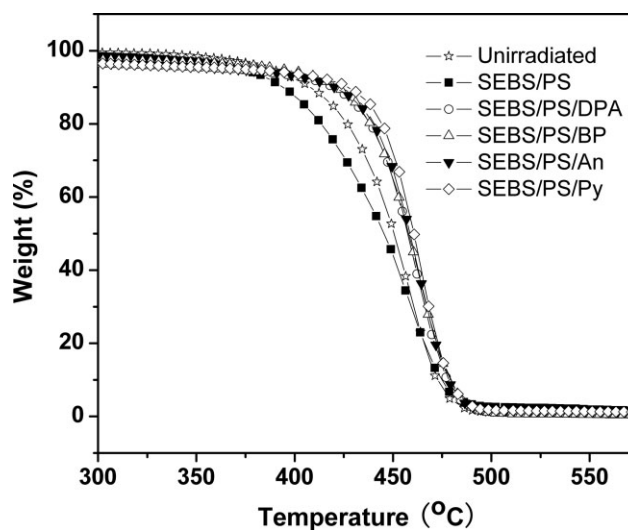
Sample	Decomposition temperature (°C)				
	$T_{5\%}$	$T_{10\%}$	$T_{30\%}$	$T_{50\%}$	$T_{max}$
Unirradiated SEBS/PS	387	408	437	450	457
SEBS/PS	373	394	426	445	456
SEBS/PS/DPA	370	419	447	457	461
SEBS/PS/DP	372	421	447	458	465
SEBS/PS/An	369	420	448	458	464
SEBS/PS/Py	372	427	451	460	466

Table I that, for the blends with aromatic additives, the decomposition temperatures at 5% weight loss ( $T_{5\%}$ ) were lower than that of the blend sample without irradiation, whereas the decomposition temperatures at 10, 30, and 50% and  $T_{\max}$  were all higher than those of the blends without irradiation. These results might be attributed to the poor thermal stability of additives and the presence of some small molecule species originating from the aforementioned degradation reaction of molecular chains.

### Melt-flow rate

Rheological information has been used for an approximate quantitative analysis of oxidative degradation.<sup>16</sup> MFR was a widely used empirical index to assess the rheological properties of polymeric materials.<sup>17</sup> Figure 6 shows the changes of the MFR for the SEBS/PS blends with and without aromatic additives as a function of gamma irradiation doses. It could be observed that, after gamma irradiation, the blends without additives had higher values of MFR in comparison with those without additives and the values of MFR increased with increasing radiation dose. For the samples with additives, however, the rate of MFR increment was lower than those samples without additives, and the blends with Py had the minimum values of both MFR and the rate of MFR increment. And also the values of MFR increased in the order of the stabilizer type, i.e., DPA > BP > An > Py. The MFR curves also showed that a fast increase in MFR occurred after 0.5 MGy for the SEBS/PS blends without additives, indicating the predominance of the aforementioned chain-scission reactions. The samples with additives showed an increase in MFR starting from almost 1.5 MGy. As concluded earlier, these results indicated that the aromatic additives could improve the stability of SEBS/PS blends and postponed the chain-scission reactions under the gamma-irradiation environment. Another feature of the results was that Py provided more excellent capacity of retarding the chain scission than the other stabilizers, which might be ascribed to its higher values of electron affinity and degree of aromaticity.

As discussed earlier, it could be concluded that, after gamma irradiation, the incorporation of aromatic compounds made the SEBS/PS blends have improved mechanical, dielectric, and thermal properties when compared with those blends without additives, and the aromatic compound Py had the best irradiation resistance effect of the blends against irradiation. As to the mechanism of irradiation resistance, it had been proposed that excess energy release via excitation energy and charge transfer played an important role in the process of radiation protection.<sup>9</sup> In this instance, the radiation energy



**Figure 6** Melting flow rate as a function of gamma irradiation dose for the SEBS/PS blends.

could be dissipated in the conjugated structure before the scission of macromolecular chains occurred or be released to the environment in the form of heat or light. It was also found that the efficiency of the aromatic compounds for the irradiation resistance was related to their electron affinity ( $E_A$ ). Tabuse et al.<sup>9</sup> reported that the degradation of *n*-alkanes showed a tendency toward the decrease along with the decrease of the values of  $E_A$ , which was in accordance with our results since the degree of degradation of the blends showed a tendency in order of Bp ( $E_A = 0.130 \pm 0.035$  eV) < An ( $E_A = 0.530 \pm 0.05$  eV) < Py ( $E_A = 0.591 \pm 0.008$  eV). In addition, aromatic compounds could react with the transient intermediates caused by gamma irradiation and protected polymers from a worsening in molecular scission. When polymers are subjected to gamma irradiation, their molecular degradation might produce a host of hydrocarbon radicals and other reactive intermediate species that could lead to the further degradation and oxidation of molecules or to the formation of the crosslinking between molecules. Tabuse et al.<sup>9</sup> also reported that higher the degree of aromaticity of aromatic additives, the higher became the reactivity of additives. Therefore, we conclude that, from the viewpoint of degree of aromaticity, the best irradiation protection effect of Py could also be attributed to its highest value of degree of aromaticity among the aromatic additives used in this work.

As reported in the literature,<sup>10</sup> the unsaturated bond of DPA could be opened by gamma rays and more easily reacted with the transient intermediates caused by gamma irradiation. Therefore, by the recombination of the transient intermediates, DPA might be grafted onto the polymer matrix and should have better protection effect when compared

with other additives. However, as observed earlier, the blends with DPA did not show any improvement of properties when compared with those samples containing other additives. These results indicated that, for aromatic compounds used in this work, the excess energy release via excitation energy and charge transfer might be more important than the reaction with the transient intermediates in protecting the blends against gamma irradiation.

### CONCLUSIONS

We have studied the effects of four kinds of aromatic compounds on irradiation resistance of SEBS/PS blends.

The results obtained in this study can be summarized as follows:

After gamma irradiation, all the blend samples showed deteriorated mechanical, dielectric, and thermal properties when compared with those samples without gamma irradiation, whereas the blends with aromatic additives had improved mechanical, dielectric, and thermal characteristics when compared with those samples without additives.

Py was the most effective additive in improving the gamma irradiation-resistance performance of the SEBS/PS blends among the aromatic compounds used in this work. MFR measurements indicated that polymer chain scission mainly occurred rather than crosslinking at high radiation doses and that aromatic additives could effectively prevent scission of polymer chains.

For the aromatic compounds, the excess energy release via excitation energy and charge transfer might play an important role than the reaction with

the transient intermediates in protecting the blends against gamma radiation.

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