Improving the Thermal Aging Resistance of γ-Vulcanized Polybutadiene Rubber (BR)/Nature Rubber (NR) Blends with Sulfur Added

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In this paper, sulfur was added into polybutadiene rubber/nature rubber (BR/NR) blends for improving the resistance of thermal aging. BR/NR blends with sulfur were vulcanized by 60Co γ radiation with different irradiation doses. Afterwards, the specimens underwent thermal aging by using air oven, the non-aged specimens without such process. It was found that the crosslink degree of BR/NR blends increased with the increase in the irradiation dose, according to the results of gel and molecular weight between crosslinks (Mg). Furthermore, the crosslink degree of BR/NR blends increased after thermal aging. This made the mechanical properties and initial degradation temperature (IDT) of aged BR/NR blends improve. Sulfur could improve thermal resistance of γ-irradiated BR/NR blends. Finally, the possible mechanism of improved crosslink degree in aged BR/NR blends was illuminated in the paper.

1. Introduction

Polybutadiene rubber (BR) is one of the largest synthetic rubber in the world, which is widely used in tire, glove, boot, seal, and other industrial products [1–7]. In general, BR is not used alone, because the mixture of the two types of rubber has superior properties not found in the component rubber [8, 9]. It makes BR/NR blends superior like wear resistance, bending resistance, tensile strength, and compression stiffness [10–13]. However, the performances of the BR/NR blends would gradually downturn during the service process, because the rubber materials are vulnerable to the aging when they are exposed to oxygen, ozone, light, heat, and so on [14–18].

It would result in the main manifestations of cracks, getting sticky, hardening, chalking, discoloration, and finally losing its value in application [19, 20]. Thermal aging is regarded as one of the main reasons for the deterioration of the rubber blends, and various chain-cleavage reactions may occur [21–25]. Antioxidants are often added into the rubber for slowing down the aging process [26, 27]. For instance, derivatives of aromatic or phenol are excellent antioxidants, which are mostly used for preventing the rubber from thermal aging [21, 28]. However, antioxidants would like to result in “blooming” phenomenon because antioxidants are inclined to diffuse toward the surface of the rubber [29]. It will bring side effects like defects of rubber, inferior antioxidant protection, and environment contamination. Antiblooming of antioxidants has been studied in recent years, but it is restricted by the complex operation and high costs [30]. In this study, antioxidants will not be used to slow down the thermal aging process.

Compared with sulfur vulcanization, radiation vulcanization is considered as an alternative method for improving the resistance of thermal aging [31, 32]. Carbon-carbon (C-C) crosslinks instead of carbon-sulfur (C-S)
crosslinks form during radiation vulcanization process [33]. The bond energy of C-C and C-S bond is 85 kcal/mol and 64 kcal/mol, respectively [32]. Therefore, the radiation-vulcanized rubber provides high stability and good mechanical and thermal properties [34–36]. Furthermore, radiation vulcanization has many advantages including operating at the room temperature, consuming less energy, being faster, and inherently clean technology [28, 29, 37]. It is a simple and an eco-friendly process, which has already been commercialized [38].

In this work, we studied the effects of sulfur on the thermal aging of irradiation-vulcanized BR/NR blends with different doses. Two groups of irradiation-vulcanized BR/NR blends were prepared: the aged one is with thermal aging, while the non-aged one is without such process. From the mechanical strength data, the aged BR/NR blends had higher tensile strength than that of non-aged ones, which contributed to the higher crosslink degree. The thermal aging could promote the new crosslink points form. Furthermore, the dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), and volume swelling measurements were conducted to study the resistance of the thermal aging, and the characteristics were analyzed as well.

2. Experimental

2.1. Materials. The BR used in this study was BR grade 9000 from Sinopec Beijing Yanshan Co., China. Its Mooney viscosity of raw rubber, ML1+4 at 100°C, is 45 ± 4. The mass fraction of volatile matter is no more than 0.50%. The NR was purchased from Yunnan Agricultural Reclamation Group Co. Ltd, China. Its Mooney viscosity of raw rubber, ML1+4 at 100°C, is 100–130. The sulfur is purchased from Hubin Chem. Co., China.

2.2. Preparation of Samples. The base formulation of the two rubber composites was described as follows (phr): BR, 70; NR 30; sulfur, 2.0. The samples were prepared by a two-roll laboratory mill with a roll diameter of 250 mm and a working distance of 750 mm. The roll temperature, mixing time, and mixing speed were 70°C, 10 min, and 40 rpm, respectively. After compounding, the rubber compounds were placed in the laboratory for 24 hours. Then, they were compressed at a condition of 100°C, 10 MPa for 2 min. All the samples were irradiated by 60Co radiation source (3.7 × 1016Bq, Beijing HYSFCo., China) with the irradiation dose from 50 to 250 kGy. Potassium (silver) Dichromate (JJF1018-90 Standard Method) was used to measure the absorbed radiation doses. The formulation of BR/NR blends is shown in Table 1.

Afterwards, the aged specimens underwent thermal aging, which was placed in the air oven at 100°C for 48 hours according to ISO 188:2011.

2.3. Instrumentation

2.3.1. Volume Swelling Measurements. The rubber specimens were firstly weighted ($w_1$) by analytical balance (ME-T, Mettler Toledo Co.). Then, they were left to swell in toluene for 24 hours at room temperature, which made them reach an equilibrium state. The swollen specimens were weighted ($w_2$) after the solvent was wiped out. Finally, the swollen specimens were dried in a vacuum oven and weighted accurately ($w_3$).

The gel fraction and the volume swelling ratio ($Q_v$) could be directly calculated according the following equations:

$$\text{Gel Fraction} = \frac{w_3}{w_1} \times 100\%,$$

$$\text{Swelling Ration} = \frac{(w_2 - w_1)\rho_r}{w_1\rho_s},$$

where the $\rho_r$ and $\rho_s$ are the density of rubber (1.10 g/cm³) and toluene (0.87 g/cm³), respectively [23]. The characteristics of swelling properties and gel fraction could be expressed by the Charlesby-Pinner equations [39]:

$$\varphi_r = \frac{1}{1 + Q_v},$$

$$M_c = \frac{\rho_r V_1 \left(\varphi_r^{1/3} - \varphi_r / 2\right)}{\ln (1 - \varphi_r) + \varphi_r + \chi_{12}\varphi_r^2},$$

where $V_1$ is the molar volume of the toluene (105.9 g/cm³); $\varphi_r$ is the volume fraction of rubber in the swollen gel; $\chi_{12}$ is the Flory-Huggins interaction parameter value used for $\chi_{12}$ is 0.27 [40]; $N$ is the Avogadro constant; $M_c$ is the molecular weight between crosslinks. Finally, the $Q_v$, and $M_c$ could be calculated according the above equations.

2.3.2. Mechanical Measurements. Tensile properties of the dumbbell samples were measured by using MTS Universal Testing machine, USA. Tensile strength and elongation at break were measured at 500 mm/min speed at room temperature, according to ASTM D412.

Hardness tests were carried out according to ASTM D 2240. The units of hardness were expressed in Shore A.

2.3.3. Dynamic Mechanical Analysis. The rubber specimens were measured by using Gabo (German) Epelxor 500 N dynamic mechanical analyzer under tension mode. The experiments were carried out at a frequency of 10 Hz and a heating rate of 2°C/min from −100°C to 100°C.

2.3.4. Thermogravimetric Analysis. TGA was performed with the Shimadzu TGA-50 system, Japan, and heated from room temperature to 550°C at a rate of 10°C/min under controlled dry nitrogen of flow of 20 ml/min.

3. Results and Discussion

3.1. Swelling Properties. Figure 1 shows the gel fraction as a function of radiation dose. The gel fraction of the nonaged BR/NR blends increased with the increase in the radiation dose from 68% to 85%. The gel fraction could be used to predict the extent of radiation-induced crosslinking of
polymer since the crosslinked parts would not be dissolved in the solvent [41]. In this study, the higher radiation dose could result in the larger crosslink density of BR/NR blends within 250 kGy. Furthermore, the gel fraction of BR/NR blends increased after the thermal aging process. From Figure 1, almost 16% to 5% increase of gel fraction took place when BR/NR blends underwent thermal aging process. However, previous studies suggested that the thermal aging process would lead to segmentation of the polymeric chain, which resulted in the decrease of gel fraction [42]. The increase of gel fraction confirmed new crosslinks formation during the thermal aging. We speculated that the crosslinking reaction was attributed to sulfur in BR/NR blends, which the C-S bonds form under the 100°C aging process.

Table 2 shows the volume swelling ($Q_v$) and the average molecule length between two crosslink points ($M_c$) with different radiation doses. $Q_v$ and $M_c$ reflect the crosslinking degree of the rubber. The smaller $M_c$ would result in a stronger constraint among the macromolecules, in which less small toluene molecules could dissolve into the crosslinked networks, and a smaller $Q_v$ value is obtained. From Table 2, the $M_c$ and $Q_v$ decreased with the increase in the irradiation dose. The higher the radiation dose, the greater the crosslinking degree of the rubber. During the radiation process, no carbon-sulfur (C-S) bonds formed since the C-S bonds formation was under an elevated temperature [43]. Furthermore, the thermal aging could improve the crosslink degree of irradiated BR/NR blends according to Table 2. Generally, the bond scissions would happen when the rubber undergoes thermal aging. It had a reverse result in this work. We speculated that the increased crosslinking degree could be attributed to the addition of sulfur. Thermal aging broke molecular chains and produced radicals at the same time. Sulfur could react with radicals at 100°C, in which it resisted the degradation of the vulcanized BR/NR blends. From Table 2 we can see that the crosslink degree increased when the specimens underwent the thermal aging.

Moreover, the radiation-chemical yield ($G(X)$) of vulcanization without main-chain scission could be calculated by the swelling methods [44], in which the equation is as follows:

$$G(X) = 4.82 \times 10^6 \frac{M_c}{4s_c}.$$  \hspace{1cm} (3)

The $G(X)$ could be calculated from the $M_c$ values in Table 2, and the results of $G(X)$ are shown in Table 3:
3.2. Mechanical Properties

3.2.1. Tensile Strength. The tensile strength of the non-aged and aged BR/NR blends is shown in Figure 2. With the increase in the radiation dose, the tensile strength of the non-aged BR/NR blends gradually increased from 5.0 MPa to 13.8 MPa, while that of the aged ones increased from 10.04 MPa to 18.32 MPa and then decreased to 17.18 MPa. The crosslink degree increased with the irradiation dose, according to Table 2. The increased crosslink degree could improve the tensile strength since higher energy dissipation was used to break the C-C or/and C-S bonds during stretching process. It provided the three-dimensional network with more integrity when the rubber specimens were pulled off. The tensile strength of the non-aged and aged BR/NR blends had the similar trend as the crosslinking degree. It was noticed that the non-aged BR/NR blend with 180 kGy had a higher tensile strength than the aged BR/NR blend with 90 kGy, while the crosslink degree of these two samples was converse. The Mc of the non-aged BR/NR blend with 180 kGy and aged BR/NR blend with 90 kGy is 7006 g/mol and 6922 g/mol, respectively. We speculated that the C-C bond content in the non-aged BR/NR blend with 180 kGy was higher than that of the aged BR/NR blend with 90 kGy. The C-C bond energy was larger than the C-S bond ones, which requires more energy dissipation during the stretching process. Thus, the tensile strength of the non-aged BR/NR blend with 180 kGy was higher than that of the aged BR/NR blend with 90 kGy.

Furthermore, hardness (shore A) of the non-aged and aged BR/NR blends is also shown in Figure 2. Despite the aged or non-aged BR/NR blends, the hardness increased with the increase in the irradiation dose. The aged BR/NR blends had a greater hardness than the non-aged ones at the same irradiation dose. This could contribute to the crosslink degree of the BR/NR blends. Higher crosslink degree could result in more stability and smaller deformation for the molecule network when external force pressed on the specimens, and a higher hardness is exhibited. From Figure 2 it is seen that the hardness of the non-aged and aged BR/NR blends increases from 30 to 43 and from 43 to 53, respectively.

Table 4 shows the elongation at break of BR/NR blends with and without thermal aging. The elongation at break of the non-aged and aged BR/NR blends gradually decreased with the increase in the irradiation dose. Compared with the non-aged BR/NR blends, the aged ones had smaller elongation at break at the same irradiation dose. This was attributed to the crosslink degree of the specimens, because molecule chains were restricted by the crosslink points when the specimens were put off. It exhibited inferior flexibility of BR/NR blends with high crosslink degree. Therefore, the elongation of the non-aged and aged BR/NR blends decreased from 755% to 668% and from 616% to 592%, respectively.

3.3. Dynamic Mechanical Analysis. Figure 3 shows the storage modulus (E′) of the non-aged and aged BR/NR blends with different radiation doses. For the non-aged and aged BR/NR blends, the dynamic storage modulus increased with the increase in the irradiation dose. The storage modulus had a close relationship with the crosslink degree, in which the higher crosslink in BR/NR blends would restrict the chain mobility and make the vulcanizates more rigid.
From Figure 3 it is seen that the $E'$ value of the non-aged and aged BR/NR blends increased with the increase in irradiation. It is also proved that the higher irradiation dose would result in an increase in the crosslink degree of BR/NR blends. Furthermore, the aged BR/NR blends had higher $E'$ value than the non-aged BR/NR blends at the same irradiation dose. It contributed to the increased crosslink degree after thermal aging.

The loss tangent ($\tan\delta$) of the non-aged and aged BR/NR blends is shown in Figure 4. $\tan\delta$ could predict the glass transition temperature ($T_g$), in which the temperature of chain segments starts moving [45]. It was sensitive to the molecule structure that differences in crosslink structure were presented [46]. From Figure 4 it is seen that the $T_g$ of the non-aged BR/NR blends and aged BR/NR blends increased with the increase in the irradiation dose. Moreover, the aged BR/NR blends had higher $T_g$ than that of the non-aged ones at the same irradiation dose. In the crosslinked polymer, the chemical crosslink points could restrict the molecule mobility, in which the transition point must shift to a higher temperature. Compared with the non-aged ones, the transition temperature in the aged BR/NR blends slightly increased to a higher temperature.

### 3.4. Thermogravimetric Analysis

Thermal stability of the BR/NR blends without and with thermal aging for increasing temperatures was delineated at a heating rate of 10°C/min, shown in Figure 5. Both the non-aged and aged BR/NR blends had the same terminal degradation temperature, which was nearly 500°C. However, the range of the initial degradation temperature (IDT, 1% weight loss) was different. The IDT of the aged BR/NR blends was higher than that of the non-aged ones. For industrial application, the IDT was much important since it was regarded as the upper limitation temperature (ULT) of the rubber application. The improved IDT was attributed to the higher crosslink degree of the aged BR/NR blends. Other literatures also reported similar conclusions [47]. Figure 6 shows the derivative thermograph (DTG) graphs of the non-aged and aged BR/NR blends with different irradiation doses. It clearly displayed two peak regions, which were related to different polymeric components in the BR/NR blends. The decomposition temperature of the first peak was defined as $T_{\text{max}}$.

The activation energy for decomposition, $E_a$, of the rubber blends can be calculated from the TGA curves by the integral method of Horowitz and Metzger [48] as given below:

$$\ln\left[\ln\left(1 - \alpha\right)^{-1}\right] = \frac{E_a\theta}{RT_{\text{max}}},$$  \hspace{1cm} (4)

where $\alpha$ is the decomposed fraction, $E_a$ the activation energy for decomposition, $T_{\text{max}}$ the temperature at maximum rate of weight loss, $\theta$ the decomposition temperature minus $T_{\text{max}}$, and $R$ the gas constant.

Figure 7 shows the plots of $\ln[\ln(1 - \alpha)^{-1}]$ versus $\theta$, with 1%, 5%, 25%, and 50% decomposition temperature used. The activation energy for decomposition could be calculated from the slope of the straight line in equation (4). As a result, $E_a$ of the non-aged and aged BR/NR blends was calculated and is presented in Table 5. The $E_a$ of the non-aged and aged BR/NR blends increased with the increase in the irradiation dose from 71.1 to 82.3 kJ/mol and from 84.0 to 87.1 kJ/mol, respectively. The $E_a$ value was related to the crosslink degree of the BR/NR blends, in which the higher crosslink degree would improve the $E_a$ value. Furthermore, the IDT of BR/NR blends and the $T_{\text{max}}$ were also exhibited in Table 4. It showed that the IDT of the aged BR/NR blends were higher than those of the non-aged ones at the same irradiation dose.
However, the change of $T_{\text{max}}$ was small. It seemed that the thermal aging had little effect on $T_{\text{max}}$. The higher crosslink degree could improve the thermal resistance of initial decomposition, in which it is associated with the higher $E_t$ value.

### 4. Discussion

In this study, BR/NR blends with sulfur were vulcanized by gamma radiation. The gamma ray could induce the free radicals, which reacted with each other to form a crosslinked network. The formed crosslink points contributed to the C–C bonds formation. It is shown in Figures 8(b) and 8(c). The crosslink degree increased with the increase in the irradiation dose within 250 kGy. Subsequently, the aged BR/NR blends underwent thermal aging, while the non-aged ones did not undergo such process. A previous study showed that thermal aging would cause molecule chain breakage and lower the crosslink degree [42]. However, the above data proved that the crosslink degree increased after thermal aging.

![Figure 4: The tanδ of non-aged and aged BR/NR blends at different radiation doses.](image)

![Figure 5: Thermal gravity analysis of BR/NR blends at different doses, non-aging and aging.](image)
Figure 6: TDG curves of BR/NR blends at different doses, non-aging and aging.

Table 5: Thermal stability parameters of the BR/NR blends.

| IDT  | IDT  | Tmax (°C) | E (kJ/mol) |
|------|------|-----------|------------|
| 50 kGy | 231.6 | 396.7     | 71.1       |
| 100 kGy | 244.9 | 400.3     | 73.7       |
| 150 kGy | 249.6 | 408.6     | 74.3       |
| 200 kGy | 251.8 | 407.1     | 77.7       |
| 250 kGy | 262.5 | 411.6     | 82.3       |
| 50 kGy  | 272.8 | 393.3     | 84.0       |
| 100 kGy | 273.5 | 400.5     | 85.3       |
| 150 kGy | 275.3 | 408.3     | 85.8       |
| 200 kGy | 282.3 | 409.2     | 87.1       |
| 250 kGy | 281.9 | 408.2     | 84.8       |

Figure 7: Plots of ln[ln(1 – α)^(-1)] versus θ for the decomposition activation energy, non-aging and aging.
aging. The increased crosslink degree after thermal aging was deduced from the contribution of sulfur that existed in BR/NR blends, because thermal aging resulted in molecule scissions, which produced radicals at the same time. The generated radicals reacted with sulfur under an elevated temperature environment, shown in Figures 8(d) and 8(e). The thermal aging mainly led to a crosslinking reaction, but side reactions might also happen and result in chain cleavage at a certain degree. In this paper, the BR/NR blends with sulfur added were vulcanized by gamma radiation. It increased the thermal resistance of BR/NR blends and maintained the performance of the BR/NR blends.

5. Conclusions

In this paper, BR/NR blends with sulfur were vulcanized by $^{60}$Co $\gamma$ radiation with different irradiation doses. Afterwards, the specimens underwent thermal aging process by using air oven. The remaining specimens were placed under the laboratory environment for comparison. It is found that the crosslink degree of BR/NR blends improved after thermal aging, according to the results of gel and $M_c$. This made the aged BR/NR blends have better tensile strength and higher hardness than the non-aged ones at the same irradiation dose. The $T_g$ value was improved after thermal aging due to the restriction of molecule mobility by increased crosslink points. From TGA data, the IDT of BR/NR blends was enhanced by thermal aging process, with a higher $E_t$ value. In conclusion, the sulfur could improve the thermal resistance of $\gamma$-irradiated BR/NR blends and maintain the performance of the BR/NR blends.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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