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Improved dynamic properties of natural rubber filled with irradiation-modified carbon black

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HIGHLIGHTS

- Irradiated CBs had more oxygen-containing groups than original CBs.
- Irradiated CBs had smaller particle sizes than original CBs.
- NR filled with irradiated CBs has lower abrasion than NR filled with untreated CBs.
- NR filled with irradiated CBs has lower rolling resistance than NR filled with untreated CBs.

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ABSTRACT

In this work, carbon black particles (CBs) were modified by high-energy electron beam (EB) irradiation at different doses. The influence of EB irradiation on the surface and particle size of CBs was investigated. Then, the CBs were compounded with natural rubber (NR), and the mechanical properties and dynamic properties of CBs/NR composite were further researched. The results showed that the irradiated CBs had more oxygen-containing groups and smaller particle sizes than original CBs. After irradiation, the content of bound rubber around the irradiated CBs increased, and the mechanical properties of CBs/NR composite were improved. Most importantly, NR filled with irradiated CBs has lower abrasion, higher wet skid resistance, and lower rolling resistance than NR filled with untreated CBs.

1. Introduction

Carbon black particles (CBs) have been used in the rubber industry for more than 100 years. As a reinforcing material, CBs play an important role in the tire industry. CB is made up of a turbostratic aggregation of very small graphene sheets which contain interesting defects called fullerene-like defects (Cataldo, 2002; Ban et al., 2011; Hulicova-Jurcakova et al., 2010). These fullerene-like sites in CBs act as free radical acceptor sites, which can attract the rubber-chain radicals formed by chain scission or hydrogen abstraction during the mixing process to form a thin layer called "bound rubber" (Ansarifar et al., 2004; Robisson, 2010; Sobral et al., 2003). The bound rubber has a strong interaction with CBs and cannot be separated from CBs even in some solvents for rubber. The rubber properties including mechanical and dynamical properties are correlated to the content of bound rubber around the CBs (Wang et al., 2009; Morozov et al., 2010).

Currently, surface grafting of fillers is a common chemical method to improve the properties of rubber for improving the interaction between the CBs and rubber molecules (Arroyo et al., 2003; Joly et al., 2002). For example, Sini and Arup prepared surface-modified CBs (N330) by treating it with pentaerythitol, a combination of pentaerythitol and pyrogallol, and a combination of pentaerythitol and resorcinol. It was found that CBs modified with pentaerythitol and resorcinol showed more pronounced effect than the other two (Sini et al., 2009). Ganguly et al. attempted to modify the surface of CBs (N330) by the interaction with aromatic derivatives. Two aromatic polyhydroxy compounds, namely 1,2 dihydroxy benzene (catechol) and 1,2,3 trihydroxy benzene

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(pyrogallol) were chosen as surface modifiers. The surface of CBs was modified when compounded with natural rubber. The results indicated that there was an obvious enhancement of filler–polymer interaction with a reduction of filler–filler networking (Ganguly et al., 2005). But those modifying chemicals could not completely react with oxygen-containing functional groups or rubber molecules. The residual of surfactants is harmful to not only the environment, but also the rubber properties.

In recent years, electron beam (EB) irradiation has been used in polymer processing and material modification (Coqueret et al., 2009; Kumar et al., 2012; Chmielewski et al., 2005). Shanmugharaj used EB irradiation to modify a dual-phase filler composed of CBs (N220) and silica. He managed to increase the C/O ratio of the dual-phase filler by electron spectroscopy for chemical analysis (ESCA) (Shanmugharaj, 2002). Evora and Klosterman used a high-energy electron beam to oxidize the surface of vapor-grown carbon nanofibers. The results showed that the O 1s/C 1s ratio increased by a factor of approximately 4 after the carbon nanofibers were irradiated at 3500 kGy (Evora et al., 2013). However, there are a few reports about the EB treatment on the CBs and the rubber filled with the irradiated CBs.

The objective of this study is to investigate the influence of EB irradiation on CBs and the properties of nature rubber (NR) filled with the irradiated CBs. First, CBs (N234) were exposed to EB irradiation. The irradiated CBs were then compounded with nature rubber (NR). The microstructure and properties of CBs and NR/CBs composites were fully investigated. The results showed that the irradiated CBs had high bound rubber and strong interaction with NR molecules. The rolling resistance, abrasion resistance, and wet-skid resistance of irradiated CBs/NR composites were all higher than those of composites without EB irradiation. The optimum irradiation dose was 400 kGy. These features enable irradiated CBs to be good candidate fillers for tires with low oil consumption and high safety on wet roads.

2. Experimental

2.1. Materials

NR (RSS3) was obtained from Yunnan Natural Rubber Industry Co., Ltd. CBs (N234) were purchased from Tianjin Haitun Carbon Black Industry. Other materials were commercial products.

2.2. Sample preparation

The CBs were exposed to EB irradiation in a glass box. The acceleration energy and beam current were 10 MeV and 10 mA, respectively. The scan current is 6.5 A. The irradiation was carried out on conveyor. A dose of 50 kGy irradiation was given in each pass, and the irradiated samples were subsequently cooled down with a blower before the next pass. In this study, the speed of conveyor is 0.24 m/min/mA. The total irradiation dose given to each sample was controlled by the total number of passes. The difference between the actual absorbed dose and the irradiation dose was within 10%. To study the effect of irradiation dose on the CBs, a wide range of irradiation doses (0, 100, 200, 300, 400, 500, 600, and 700 kGy) were given at room temperature (25 ± 2 °C). The formulation of the NR filled with the irradiated CBs is shown in Table 1. The optimum cure time (t_{90}) of the compounds was determined by a P3555B2 Disc Vulkameter (Beijing Huanfeng Chemical Machinery Trial Plant, Beijing, China). The compounds were vulcanized at 143 °C and a pressure of 15 MPa for t_{90} in a standard mold to form the composites.

Table 1
Formulation of the NR filled with the irradiated CBs.

Ingredient	Loading/phr[a]
NR	100
CB	48
Zinc oxide	3
Stearic acid	1
Antioxidant 4020[b]	1.5
Antioxidant RD[c]	1.5
Paraffin wax	1.5
Accelerator CZ[d]	1.1
Accelerator TBBS[e]	1
Sulfur	1.4

[a] Parts-per-hundred rubber.
[b] N-(1,3-Dimethylbutyl)-N′-phenyl-p-phenylenediamine.
[c] Poly(1,2-dihydro-2,2,4-trimethylquinoline).
[d] N-Cyclohexyl-2-benzothiazolesulfenamide.
[e] N-tert-Butyl-2-benzothiazolesulfenamide.

Table 2
Particle size distribution of CBs.

Dose /kGy	0	100	200	300	400	500	600	700
Z-average /d.nm	319	265.1	240.5	238.6	232.9	220.8	242.7	247.5
PDI	0.436	0.306	0.258	0.202	0.107	0.17	0.228	0.28

2.3. Characterizations

The *Z*-average particle size of the CBs was measured on a Laser Particle Size Analyzer (Mastersizer 2000) at 25 °C. The CB concentration in water was 0.01 g/L, and the solution was treated in an ultrasonic apparatus for 2 h before testing. The specific surface area (BET) of the samples was calculated by BET method based on the N_2 adsorption isotherm data. Sedimentation experiment of the CBs in water was carried out for one month at room temperature. Contact angle measurements of the vulcanized rubber filled with treated and untreated CBs were performed by using the sessile drop method. Each reported data represents an average value of three different contact angles tested in different locations on a given NR vulcanizate film.

X-ray photoelectron spectroscopy (XPS) measurements were obtained on a JEOL JPS-9000MX spectrometer. An MgKα radiation ($h\nu = 1253.6$ eV) was used for excitation. All the binding energies of elements were referenced to the C 1s peak at 284 eV of the surface adventitious carbon.

For the measurement of bound rubber content (BRC), an uncured rubber sample (m_1, g) was cut in small pieces and added to a steel wire basket (m_2, g). The basket was suspended in toluene in a vessel, which was enclosed with a piece of aluminum foil to minimize the evaporation of solvent. The solvent was agitated with a magnetic stirrer for 72 h at room temperature. Afterwards, the basket was removed from the solvent and dried in vacuum for 24 h at 40 °C. Complete drying was confirmed by a constant final weight (m_3, g) of the basket. The content of bound rubber is given by

$$\mathrm{BRC} = \left(\frac{m_3 - m_2 - m_1 \times M_1}{m_1 \times M_2}\right) \times 100 \quad (1)$$

where m_1, m_2, and m_3 are the mass values of the original sample, basket, and basket with rubber after immersion, respectively, and M_1 and M_2 are the mass fractions of CB and rubber in the uncured rubber sample, respectively (Leblanc, 2002).