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Preparation of silica-supported 2-mercaptobenzimidazole and its antioxidative behavior in styrene-butadiene rubber

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ABSTRACT

A novel type of rubber antioxidant, silica-supported 2-mercaptobenzimidazole (SiO_2-s-MB), was prepared by reacting 2-mercaptobenzimidazole (MB) with chlorosilane-modified silica (m-SiO_2). Raman spectroscopy, FT-IR, XPS and TGA confirmed that MB was chemically bonded onto the surfaces of silica particles. SEM observation showed that SiO_2-s-MB was homogeneously dispersed in the styrene-butadiene rubber (SBR) matrix. Based on the measurement of oxidation induction time (OIT) of SBR/SiO_2-s-MB and SBR/m-SiO_2/MB composites containing equivalent antioxidant components, it was found that the antioxidative efficiency of SiO_2-s-MB was superior to that of the corresponding low molecular MB. By determining the changes of tensile strength, elongation at break and crosslinking density of SBR composites during long-term accelerated aging, it was shown that the thermal oxidative stability of SBR/SiO_2-s-MB composites was much higher than that of SBR/m-SiO_2/MB composites. Furthermore, the color contamination, migration and volatility of SiO_2-s-MB were lower than those of MB, indicating that SiO_2-s-MB is environmentally friendly.

1. Introduction

To extend the service life and improve the performances of polymer materials, antioxidants are added into polymeric products [1]. Since Goodyear set up the first rubber factory in the world in 1839, the antioxidants were used in vulcanizates in the form of organic compounds with low molecular weight. However, there are many disadvantages for the antioxidants with low molecular weight, such as low antioxidative efficiency, easy migration [2,3], easy volatility at high temperature [4], the pollution to the products and environment, etc. To overcome these disadvantages, polymer antioxidants have been prepared by the reaction of low molecular antioxidants with polymer chains [5–11]. The polymer antioxidant could dramatically reduce the migration and volatility of the antioxidant, and its aging resistant efficiency was superior to that of corresponding low molecular antioxidant. Recently, another novel method to overcome the disadvantages of low molecular antioxidant has been reported. The method was to chemically immobilize the low molecular antioxidant onto the surfaces of inorganic fillers. The nanosilica-immobilized antioxidant was firstly applied in plastics such as low density polyethylene [12] and polypropylene [13–15]. Begum et al. [16] reported a kind of antioxidant-modified precipitated silica, which could reduce the hydrophilicity of silica and hence achieved easy incorporation of silica into rubber, and the curing and mechanical properties of the composites with the modified silica were superior to those of unmodified silica composites. Lei et al. [17] prepared a new nanosilica-based antioxidant by the modification of nanosilica with a silane coupling agent and p-aminodiphenylamine (RT), which could be homogeneously dispersed in natural rubber matrix. The thermal oxidative stability of the vulcanizates with the nanosilica-based antioxidant was improved to a greater extent than that of the vulcanizates with other fillers. Pan et al. [4] synthesized antioxidant functionalized silica through the reaction of precipitated silica with a silane coupling agent functionalized antioxidant. This antioxidant functionalized silica was incorporated into SBR composites. The tensile strength of the SBR composites with antioxidant functionalized silica was much higher than that of the SBR composites with neat silica. Furthermore, the stability in thermal oxidative aging and damp heat aging for the SBR with antioxidant functionalized silica was greatly improved.

Many types of antioxidants, such as amines [18], will cause color contamination of rubber products and even pollute the materials attached to vulcanizates. These antioxidants have been extremely

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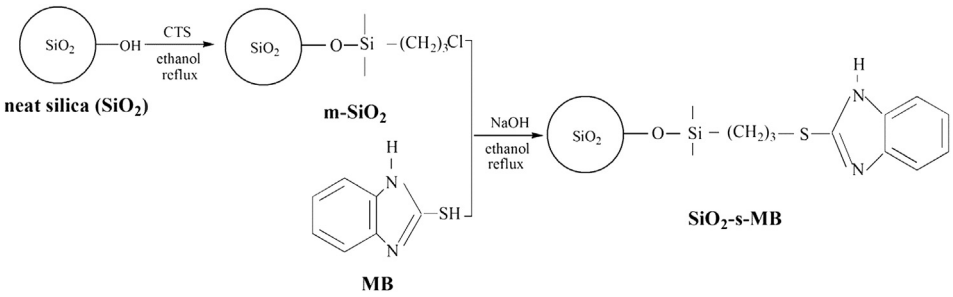

Fig. 1. Synthesis route of SiO_2-s-MB.

restricted in white and light-colored rubber products. 2-mercaptobenzimidazole (MB), one of the rare rubber antioxidants without color contamination, has been used in transparent and light-colored rubber products, such as transparent cables, electric wire and rubber products used in food service industry. However, MB is easy to volatilize at high temperature during polymer processing and to migrate and extract during long-term service due to the low molecular weight. Thus, the poor antioxidative performance of MB significantly limits the application. How to overcome these drawbacks of low molecular antioxidant MB is challenging. Xie et al. [19,20] prepared rare earth complexes of MB which greatly improved the thermal oxidative stability of NR vulcanizates. It could be attributed to the thioether bonds which can decompose the hydroperoxide and the rare earth ions which can capture and inactivate the oxy radicals. According to our recent works, the most effective novel method of improving the properties for antioxidant MB should be the preparation of "supported antioxidants" by chemically immobilizing the antioxidant with low molecular weight onto the surfaces of inorganic fillers or other supporter. The resistance to migration, volatilization and extraction can be improved through this method. Furthermore, the anti-aging efficiency can be enhanced by improving the dispersion of antioxidant in rubber matrix and enlarging the contact area between antioxidant and rubber matrix.

In this article, a novel supported antioxidant, silica-supported MB (SiO_2-s-MB), was prepared by the reaction of MB with chlorosilane-modified silica (m-SiO_2). In this novel antioxidant, MB molecule was chemically bonded onto the surfaces of silica particles which were used as the supporter. The preparation, structure and properties of the SiO_2-s-MB and its application in SBR were investigated by Raman spectroscopy, FT-IR, XPS, TGA, SEM, elemental analysis, etc. Oxidative induction time (OIT) at 180 °C was adopted to evaluate the antioxidative efficiency of SiO_2-s-MB during short-term oxidation in comparison with MB. The thermal oxidative stability of SBR composites during long-term thermal aging was evaluated by the changes of tensile strength, elongation at break and crosslinking density before and after aging.

2. Experimental

2.1. Materials

Precipitated silica (SiO_2) was produced from Huiming Chemical Co., Ltd., Jiangxi, China, and dried in a vacuum oven overnight at 100 °C before use. γ-chloropropyltriethoxysilane (CTS) was obtained from Wanda Chemical Co., Ltd., Shandong, China. SBR (1502) was offered by Guangzhou Institute of Rubber Products, China. MB, zinc oxide (ZnO), stearic acid (SA), accelerator N-cyclohexylbenzothiazole-2-sulphenamide (CBS) and insoluble sulfur (S) were industrial grade products and used as received. Sodium hydroxide (NaOH), absolute ethanol and toluene were analytical reagents and used as received.

2.2. Preparation of silica-supported antioxidant

The synthesis route of SiO_2-s-MB is shown in Fig. 1. 5.0 g of SiO_2 was dispersed in 350 mL of absolute ethanol, and then 15 g of CTS was added into the suspension. The mixture was stirred for 24 h at 50 °C. The product was filtered and then washed with 350 mL of anhydrous toluene (4 times) and 350 mL of absolute ethanol (4 times). The modified silica (m-SiO_2) was dried in a vacuum oven to constant weight at 50 °C.

1.8 g of MB and 0.45 g of NaOH were added into the suspension of obtained m-SiO_2 in 300 mL of absolute ethanol. The mixture was stirred for 24 h at 50 °C under nitrogen atmosphere in a three necked flask equipped with a reflux condenser. The product was filtered and washed with 300 mL of anhydrous toluene (4 times), 300 mL of absolute ethanol (4 times) and 300 mL of deionized water (2 times). The silica-supported antioxidant (SiO_2-s-MB) was dried at 50 °C under vacuum condition to constant weight.

2.3. Preparation of SBR composites

The compositions of SBR composites are shown in Table 1. The antioxidant contents of different composites were fixed at 1 phr (weight parts per 100 weight parts of rubber). The contents of SiO_2 and m-SiO_2 were determined by the residues of thermogravimetric analysis (TGA). The contents of SiO_2 and m-SiO_2 were 28 phr which was equivalent to the molar fraction of the modified silica in SBR/SiO_2-s-MB composites.

To obtain the sheets of SBR composites, the ingredients were first mixed for 8 min in an φ160 × 330 mm open mill at room temperature and the rotors were operated at a speed ratio of 1 (front): 1.22 (back), then the compounds were vulcanized in an electrically heated press at 170 °C for the optimum cure time (Tc90), which was previously determined by an Alpha RPA 2000 rubber processing analyzer.

2.4. Characterization of SiO_2, m-SiO_2 and SiO_2-s-MB

Raman spectra were determined using a HJY LabRAM Aramis microprobe Raman spectroscopy. Fourier transform infrared (FTIR) spectroscopy was recorded on a Bruker Vector 33 FT-IR spectrometer with KBr pellets in the range of 4000 cm^{-1} to 400 cm^{-1}. X-ray

Table 1
Composition of SBR composites.

Sample	Component (phr)						
	SBR	Filler	ZnO	SA	Antioxidant	CBS	S
SBR/SiO_2	100	28 (SiO_2)	5	2	–	2	1.6
SBR/m-SiO_2	100	28 (m-SiO_2)	5	2	–	2	1.6
SBR/m-SiO_2/MB	100	28 (m-SiO_2)	5	2	1 (MB)	2	1.6
SBR/SiO_2-s-MB	100	–	5	2	29 (SiO_2-s-MB)	2	1.6