

Preparation of halloysite nanotubes supported 2-mercaptobenzimidazole and its application in natural rubber



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ABSTRACT

To improve the antioxidative efficiency of 2-mercaptobenzimidazole (MB) and strengthen the interaction between halloysite nanotubes (HNTs) and natural rubber (NR), HNTs supported 2-mercaptobenzimidazole (HNTs-s-MB) was prepared by reacting MB with chlorosilane modified HNTs (m-HNTs). FTIR, XPS and TGA confirmed that MB was chemically bonded onto the surface of HNTs. HNTs-s-MB could be homogeneously dispersed in the NR matrix and there was a strong interfacial interaction between HNTs-s-MB and NR, leading to the better mechanical performances of NR/HNTs-s-MB nanocomposites than those of NR/HNTs nanocomposites. Based on the measurements of the thermo-oxidation activation energy of NR/HNTs-s-MB and NR/m-HNTs/MB nanocomposites containing equivalent antioxidant component, it was found that the antioxidative efficiency of HNTs-s-MB was superior to that of the corresponding low molecular MB owing to the much lower migration and volatility of HNTs-s-MB than those of MB.

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1. Introduction

Natural rubber (NR) has been a base material of choice for soft materials. To modify the matrix by interaction during processing, make new functional materials with improved mechanical properties and cut down the material costs, commercial NR products are produced as nanocomposites with fillers of nanometer size [1]. It is well known that natural nanomaterials existing in nature world are rare. Halloysite nanotubes (HNTs) are one of a few natural nanomaterials, which are a type of natural silicates with nanotubular particles. Chemically similar to kaolin, HNTs have a molecular formula of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$. The nanotubular structure is evolved by rolling up the layers of kaolinite under natural conditions. Comparing with other nanotubes, such as carbon nanotubes (CNTs), the naturally occurred HNTs are easily available and much cheaper. Typically, the outer diameter and inner diameter of HNTs are about 10–50 nm and 5–20 nm, respectively, while the length of HNTs is about 0.5–2 μm . HNTs are an environmentally-friendly natural inorganic nanometer material [2], which has been widely used in polymers as inorganic filler to promote the properties of polymeric materials [3–13]. Accordingly, the dispersion of particulate nano-fillers in polymer matrix and the filler-rubber

interaction are two critical factors in determining the ultimate performance of polymer/HNTs nanocomposites.

Antioxidant is an essential component for NR products to protect them from degradations. However, many types of antioxidants, such as amines [14], will cause color contamination of rubber products and even pollute the materials attached to the vulcanizates. These antioxidants have been extremely 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. On the other side, MB is easy to volatilize at high temperature during polymer processing and to migrate during long-term service due to the low molecular weight, which deteriorates the antioxidative performance of MB and apparently limits its application. To overcome these drawbacks of low molecular MB is challenging and meaningful for practical application. Recently, a novel method to overcome the disadvantages of low molecular antioxidants has been reported. The method is to chemically immobilize the low molecular antioxidants onto the surface of silica. The nanosilica immobilized antioxidants were firstly applied in plastics such as low density polyethylene [15] and polypropylene [16–18], and then, several kinds of antioxidants modified silica were reported and used in rubber [19–21]. To the best of the authors' knowledge, there have been no reports about supporting MB onto the surface

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of HNTs to prepare HNTs supported antioxidants and no reports about the mechanistic understanding that how the filler–polymer interface is controlled by the surface modification of filler with antioxidants.

In this paper, to strengthen the interaction between HNTs and NR matrix and to avoid the volatility and migration of MB, a novel supported antioxidant, HNTs supported MB (HNTs-s-MB), was prepared by the reaction of MB with chlorosilane modified HNTs (m-HNTs). In HNTs-s-MB, MB molecules were chemically bonded onto the surfaces of HNTs. The preparation and structure of HNTs-s-MB, together with its effect on the performances of NR nanocomposites, especially reinforcement and antioxidation, were studied. Besides, in order to further understand how the filler-supported antioxidant affects the performances of nanocomposites, the filler–filler interaction, filler–rubber interaction and the characteristics (volatility and migration) of the antioxidants were also systematically investigated.

2. Experimental

2.1. Materials

Halloysite nanotubes (HNTs), mined in Hubei, China, were purified according to the reported method [22]. γ -chloropropyltriethoxysilane (CTS) was a commercial product supplied by Wanda Chemical Co., Ltd., Shandong, China. Natural rubber (NR) was offered by Guangzhou Institute of Rubber Products, China. Antioxidant MB, zinc oxide (ZnO), stearic acid (SA), accelerator N-cyclohexylbenzothiazole-2-sulphenamide (CBS) and insoluble sulfur (S) were industrial grade and used as received. Sodium hydroxide (NaOH), absolute ethanol and toluene were analytical reagent and used as received.

2.2. Preparation of HNTs supported antioxidant

The synthesis route of HNTs-s-MB is shown in Fig. 1. 5.0 g of HNTs were 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 HNTs (m-HNTs) were 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-HNTs in 300 mL of absolute ethanol. The mixture was stirred for 24 h under nitrogen atmosphere in a three necked flask equipped with a reflux condenser at 50 °C. 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 HNTs-supported antioxidant (HNTs-s-MB) was dried under vacuum condition to constant weight at 50 °C.

2.3. Preparation of NR nanocomposites

The compositions of NR nanocomposites are tabulated in Table 1. The antioxidant contents of different nanocomposites were fixed at 1 phr (weight parts per 100 weight parts of rubber). The contents of HNTs and m-HNTs were determined by the residues of thermogravimetric analysis (TGA). The contents of HNTs and m-HNTs were both 29 phr which was equivalent to the molar fraction of the modified HNTs in NR/HNTs-s-MB nanocomposites.

NR and unmodified or modified HNTs were compounded with rubber additives with a two-roll mill at room temperature. The compound was press-cured to a 1-mm-thickness sheet at $143\text{ °C} \times \text{Tc}90$ and then cut into specimens for measurements.

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

Fourier transform infrared (FTIR) spectroscopy was recorded on a Bruker Vector 33 FTIR spectrometer with KBr pellets in the range of 4000 cm^{-1} to 400 cm^{-1} . X-ray photoelectron spectroscopy (XPS) analysis was performed using a Kratos Axis Ultra (DLD) with an aluminum (mono) $K\alpha$ source (1486.6 eV). It should be noted that the samples for FTIR and XPS testing were extracted by a Soxhlet extractor for 72 h with toluene in advance to remove the unreacted CTS and MB. Thermogravimetric analysis (TGA) was conducted under nitrogen atmosphere with a NETZSCH TG209F1 at a heating rate of 10 °C/min from 30 °C to 700 °C .

2.5. Morphology analysis

The dispersion of HNTs and HNTs-s-MB in NR matrix was examined using a ZEISS scanning electron microscope (SEM) machine. Samples were fractured after cooling by immersing in liquid nitrogen, and then coated with a thin layer of gold before any observations.

2.6. The structural characterization and the determination of properties for NR unvulcanizate compounds and NR nanocomposites

The strain dependence of G' for the filled NR unvulcanizate compounds was determined by an Alpha RPA 2000 rubber processibility analyzer. The condition of measurement was at a frequency of 1 Hz, a temperature of 60 °C , and a strain range from 0.28% to 280%.

Heat capacity curves were obtained using a NETZSCH Instruments DSC 204 F1. The instrument was calibrated as

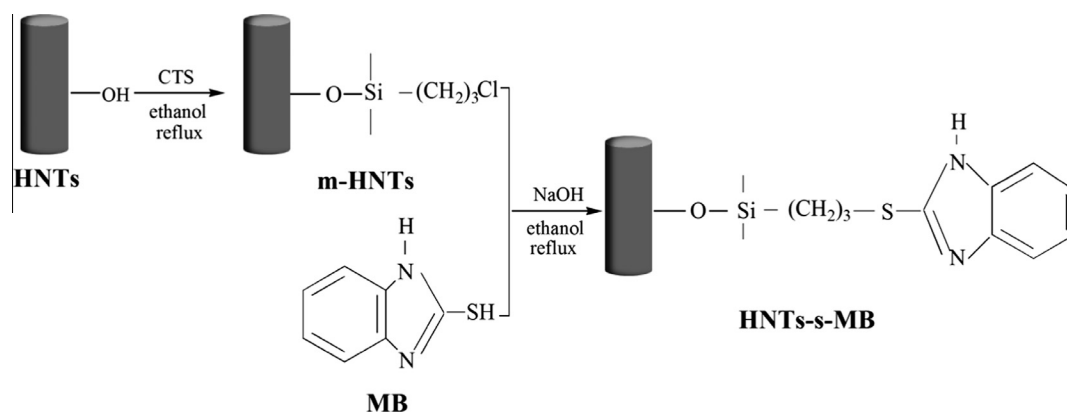


Fig. 1. Synthesis route of HNTs-s-MB.

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