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A method to improve the mechanical performance of styrene-butadiene rubber via vulcanization accelerator modified silica

Bangchao Zhong, Zhixin Jia*, Yuanfang Luo, Demin Jia

School of Materials Science and Engineering, South China University of Technology, 381 Wushan Road, Guangzhou 510640, China

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ABSTRACT

Accelerator ethylenethiourea (ETU) was chemically grafted onto the surface of silane modified silica (m-silica) to obtain ETU-modified silica (silica-s-ETU). Silica-s-ETU could be homogeneously dispersed into the matrix of styrene-butadiene rubber (SBR) with fairly strong filler-rubber interaction and the grafted ETU molecules were still able to accelerate the sulfur vulcanization. Owing to the improved modification effect, the prepared SBR/silica-s-ETU nanocomposites showed more excellent mechanical properties than SBR/m-silica and SBR/silica nanocomposites containing equivalent accelerator component. Based on the results of immobilized polymer layer, the strengthening mechanism of silica-s-ETU was analyzed and substantiated. The highlight of this work lies in the fact that apparent improvement has been achieved by the surface modification of silica with vulcanization accelerator, which may open up new opportunities for the preparation of high performance rubber composites.

1. Introduction

In recent years, rubber/inorganic filler nanocomposites have become increasing important for science and technology [1–3]. It is generally accepted that the filler dispersion and filler-rubber interaction are two critical factors determining the performance of filled nanocomposites [4,5]. Styrene butadiene rubber (SBR)/silica composites have been established as one of the most important material systems in green tire. However, due to a high density of silanol groups on the surface, silica particles are hard to disperse uniformly with poor filler-rubber interaction in SBR [6], which extremely deteriorates the performance of SBR/silica composites. Fortunately, many efforts are underway to overcome this problem and the surface modification of silica seems to be a practical and effective approach. Bertora et al. [7] and Qu et al. [8] explored the effect of silane modified silica on the performance of SBR. The results showed that the as-prepared SBR composites presented much better filler dispersion and mechanical performances than those of SBR composites with unmodified silica. Ramier et al. [9] and Stockelhuber et al. [10] discussed many important topics in the specific impact of surface modified silica on the "Payne effect" of SBR composites. Mathew et al. [11] found that the surface treatment of silica with plasma could improve the filler dispersion and filler-rubber interaction, leading to high comprehensive properties of SBR composites. Hosseini et al. [12] demonstrated that silane modified silica played an important role in the cure properties of SBR/silica compounds. In summary, it is possible to promote better performances of SBR composites through finer filler dispersion and stronger filler-rubber interaction.

Moreover, vulcanization accelerator is an essential component for rubber products, which is available for improving the processing of rubber compounds. Mixed accelerators have been widely applied and known to give superior properties in rubber vulcanization reaction [13]. Thiourea and its derivatives were reported to be effective secondary accelerators with N-Cyclohexyl-2-benzothiazole sulfenamide (CBS) [14]. Due to the critical impact of filler and accelerator on the performances of rubber products, developing a unique technology which can realize the improvement of filler dispersion, filler-rubber interfacial interaction and efficiency of accelerator simultaneously is meaningful both in academy and in industry.

In this work, silica modified by (3-glycidoxypropyl)trimethoxysilane (m-silica) was reacted with accelerator ethylenethiourea (ETU) to prepare ETU-modified silica (silica-s-ETU), which was characterized by FTIR, XPS and TGA. The effects of silica-s-ETU on the cure property, filler-rubber interaction and mechanical performance of SBR nanocomposites were investigated. Besides, the strengthening mechanism of silica-s-ETU was studied.

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* Corresponding author.
E-mail address: zxjia@scut.edu.cn (Z. Jia).

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2. Experimental section

2.1. Materials

Precipitated silica with the primary particle of 10–20 nm diameter and 200–220 m^2/g surface area was produced by Huiming Chemical Co., Ltd., China, and dried in a vacuum oven overnight at 100 °C before use. (3-glycidoxypropyl)trimethoxysilane (A-187) was a commercial product from Wanda Chemical Co., Ltd., China. SBR (1502) was offered by Guangzhou Institute of Rubber Products, China. Stearic acid, ZnO, CBS, ETU, antioxidant N-1, 3-dimethylbutyl-N′-phenyl-p-phenylenediamine (DMPPD) and sulfur were industrial grade products. Absolute ethanol was analytical reagents.

2.2. Preparation of silica-s-ETU

Ring-opening reaction of epoxy group with amino group is classical [15]. Therefore, the silica-s-ETU designed in this work was prepared by the reaction of ETU with A-187. Excess ETU and proper temperature were used to make sure that one of the two amino groups in the structure of ETU [16] reacted with one epoxy group only. The synthesis route of silica-s-ETU is shown in Fig. 1.

5.0 g of silica was dispersed in 350 mL of absolute ethanol, and then 2.5 g of A-187 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 ethanol (4 times). The silane modified silica (m-silica) was dried in a vacuum oven to constant weight at 50 °C.

1.0 g of ETU was added into the suspension of obtained m-silica in 300 mL of absolute ethanol. The mixture was stirred for 6 h at 80 °C under nitrogen atmosphere in a three necked flask equipped with a reflux condenser. The product was filtered and washed with 300 mL of hot ethanol (4 times). The silica-s-ETU was dried at 50 °C under vacuum condition to constant weight.

2.3. Preparation of unfilled SBR and SBR nanocomposites

All compounds were based on the same composition, except for the type (silica, m-silica and silica-s-ETU) and content of filler, which were varied to prepare three kinds of SBR nanocomposites (SBR/silica, SBR/m-silica and SBR/silica-s-ETU) with increasing filler content from 0 (unfilled SBR) to 50 phr. The other ingredients in the rubber compounds were (in phr): rubber, 100; stearic acid, 2.0; ZnO, 5.0; DMPPD, 2.0; sulfur, 1.6. The accelerators consisted of CBS and ETU with the ratio of 3/2 were fixed at 2 phr. It should be pointed out that the content of grafted ETU determined by the residue weight after being heated to 700 °C in thermogravimetric analysis (TGA) for silica-s-ETU was calculated as part of the accelerator amount to make sure that all of the compounds contained equivalent accelerator component.

To obtain the sheets of unfilled SBR and SBR nanocomposites, the ingredients were first mixed for 8 min at room temperature in an open mill, and then the compounds were vulcanized in an electrically heated press at 160 °C for the optimum cure time.

2.4. Characterization

Fourier transform infrared spectrum (FTIR) was recorded on a Bruker Vector 33 with KBr pellets in 4000 cm^{-1} to 400 cm^{-1} range. X-ray photoelectron spectroscopy (XPS) analysis was performed using a Kratos Axis Ultra (DLD) with an aluminum (mono) Kα source (1486.6 eV). The samples for FTIR and XPS testing were extracted by a Soxhlet extractor for 72 h with hot ethanol in advance to remove A-187 and ETU. TGA was conducted on a NETZSCH TG209F1 under nitrogen from 30 °C to 700 °C at the rate of 10 °C/min. Scanning electron microscopy (SEM) was performed on a ZEISS Merlin. Transmission electron microscopy (TEM) was conducted on a JEOL2100.

The glass transition behaviors of unfilled SBR and SBR nanocomposites were detected by a NETZSCH DSC 204 F. The samples were isothermal for 5 min t −100 °C, followed by heating to 30 °C at a rate of 10 °C/min under nitrogen. The experimental parameters were assigned to the heat capacity step ΔC_{pn} and weight fraction of immobilized polymer layer χ_{im} [17,18]. ΔC_{pn} and χ_{im} were calculated as follows:

$$\Delta C_{pn} = \Delta C_p/(1-w) \tag{1}$$

$$\chi_{im} = \left(\Delta C_{p0} - \Delta C_{pn}\right)/\Delta C_{p0} \tag{2}$$

ΔC_p is the heat capacity jump at T_g. ΔC_{pn} is normalized to the polymer weight fraction. w is the weight fraction of filler. ΔC_{p0} referrers to the heat capacity jump at T_g of the unfilled polymer matrix. χ_{im} is the weight fraction of immobilized polymer layer. T_g was determined according to ASTM E1356-08, and ΔC_p was calculated by the software NETZSCH Thermal Analysis.

The cure characteristics of the SBR compounds were determined using an UCAN UR-2030 moving-die rheometer (MDR) at 160 °C. Tensile and tear tests were performed using an UCAN UT-2060 following ASTM D 412 and ASTM D 624, respectively. The dependence of the elastic modulus on the strains of the cured compounds was measured on a rubber processibility analyzer (Alpha, RPA 2000).

3. Results and discussion

3.1. Surface modification of silica particles with ETU

Fig. 2a shows the FTIR spectra of ETU, silica, m-silica and silica-s-

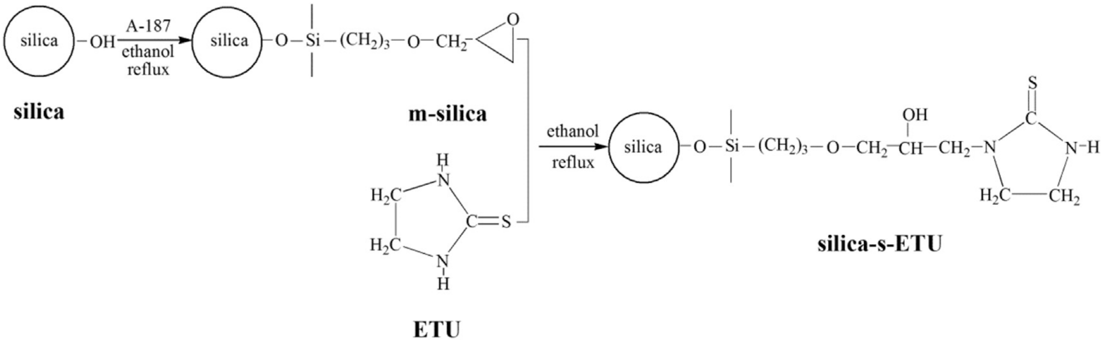

Fig. 1. Synthesis route of silica-s-ETU.