



Enhancing interfacial interaction and mechanical properties of styrene-butadiene rubber composites via silica-supported vulcanization accelerator



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ABSTRACT

To modify the filler surface and simultaneously elude issues related to the physical loss by migration of rubber additives, the concept of “supported rubber additives” was proposed and vulcanization accelerator 2-benzothiazolethiol (M) was chemically grafted onto the surface of silane modified silica (m-silica) to prepare silica-supported vulcanization accelerator (silica-s-M). Silica-s-M could be homogeneously dispersed into styrene-butadiene rubber (SBR). Besides, the interfacial interaction between silica-s-M and SBR was significantly enhanced, which was confirmed by the constrained rubber chains approaching the filler surface. Consequently, silica-s-M effectively reduced the activation energy of vulcanization and SBR/silica-s-M composites showed much better mechanical properties than SBR/m-silica and SBR/silica composites containing equivalent accelerator component. From this work, it is envisioned that this methodology for the surface treatment of silica to prepare supported accelerator may be extended for other nanofillers and functional rubber additives, which may be promising for the preparation of high-performance and functional rubber/nanofiller composites.

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1. Introduction

As one of the most important polymer materials, rubber exhibits remarkable properties, especially high elasticity, which enables rubber to become a non-replaceable material and find use in a multitude of applications. However, most of the synthetic rubbers, such as styrene-butadiene rubber (SBR), are mechanical weak and nanofillers are filled to get improved strength and controlled cost of rubber composites [1–5]. Among fillers for rubber, silica is attracting a great deal of attention and gaining increasing importance as non-black reinforcing filler. In particular, SBR/silica composites is one of the most important material systems in green tire, for the use of silica in tire results in lower rolling resistance and consequently fuel savings compared to carbon black [6]. It has been proved that homogenous dispersion and strong interfacial interaction are essential conditions to make the best of the extraordinary properties of nanofillers for reinforcement of rubber [7,8]. Nevertheless, due to a high density of silanol groups on silica surface, there will be a great chance to form hydrogen-bond interactions between silica particles. Therefore,

silica particles tend to exist as agglomerates and obtaining homogeneous dispersions in rubber is still a big challenge. To make matter worse, the interfacial interaction between hydrophilic silica and hydrophobic rubber is generally poor, leading to the greatly deteriorated performances of rubber/silica composites. Because of these issues, large experimental efforts are devoted to preparing high performance rubber/silica composites with uniform filler dispersion and strong filler-rubber interfacial interaction. In particular, surface treatment of silica is a promising and effective approach. For example, Mathew et al. [9] 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, while Liu et al. [10] used a novel method to investigate the modification of silica with bis(3-triethoxysilyl propyl)tetrasulfide and the results revealed that the nanoparticle size decreased and the agglomeration trend of silica weakened after modification. So far, silane coupling agents have been the most commonly used surface modifier of silica [11–13]. To the best of the authors' knowledge, vulcanization accelerators have not been used for silica surface modification except by our group.

It is known that traditional rubber additives (i.e. accelerator, antioxidant) are always organic molecules with low molecular weight. In addition to the poor compatibility with rubber, rubber

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additives often migrate and diffuse toward the surface of rubber vulcanizates in an event called “blooming” [14,15]. “Blooming” causes defect of microstructure, loss of efficiency of rubber additives and contamination of environment, which highly impedes the applications of rubber composites.

In this work, to achieve the homogeneous dispersion of silica, enhance the silica-SBR interfacial interaction and elude issues related to “blooming” of rubber additives, the concept of “supported rubber additives” was proposed and conventional vulcanization accelerator 2-benzothiazolethiol (M) was reacted with silanized silica (m-silica) to prepared silica-supported accelerator (silica-s-M). The effects of silica-s-M on the filler dispersion, filler-rubber interfacial interaction, curing kinetics and mechanical properties of SBR composites were fully investigated.

2. Experimental section

2.1. Materials

Silica was kindly provided by Huiming Chemical Co., Ltd., China. The primary silica particle was of 10–20 nm diameter and 200 m²/g to 220 m²/g surface area. γ -chloropropyltriethoxysilane (CTS) was from Wanda Chemical Co., Ltd., China. SBR (1502) was produced by Sinopec Group, China. Sulfur, stearic acid, zinc oxide, N-cyclohexyl-2-benzothiazole sulfenamide (CZ), accelerator M and N-1, 3-dimethylbutyl-N'-phenyl-p-phenylenediamine (antioxidant) were industrial grade products. Absolute ethanol and sodium hydroxide (NaOH) were analytical grade.

2.2. Synthesis of silica-s-M

The preparation processing of silica-s-M is illustrated in Fig. 1. The detailed procedures were as follows: firstly, 5.0 g of silica was dispersed in 350 mL of absolute ethanol, and then 2.5 g of CTS was dropped into the suspension. The mixture was stirred for 24 h at 50 °C. The product was then washed with absolute ethanol to remove the ungrafted CTS and dried in a vacuum oven to constant weight to prepare silane coupling agent modified silica (m-silica). Secondly, 1.6 g of M and 0.4 g of NaOH were dissolved in 300 mL of absolute ethanol under ultrasound, and then m-silica was further added. After stirring for 8 h at 70 °C under nitrogen atmosphere, the suspension was filtered and washed with absolute ethanol and deionized water. To obtain silica-s-M, the product was dried under vacuum condition at 50 °C to constant weight.

2.3. Preparation of unfilled SBR and SBR composites

For a better comparison, all compounds were based on the same composition, except for the content of filler (silica, m-silica and

silica-s-M), which was varied to prepare three kinds of SBR composites (SBR/silica, SBR/m-silica and SBR/silica-s-M) with the increment of 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; zinc oxide, 5.0; antioxidant, 2.0; sulfur, 1.6. The total content of vulcanization accelerator consisted of CZ and M with the weight ratio of 3/2 was fixed at 2 phr. The quantity of supported M determined by the residue weight after being heated to 700 °C in thermogravimetric analysis (TGA) for silica-s-M must be calculated as part of the accelerator content to ensure that all of the compounds contained equivalent accelerator component.

To obtain unfilled SBR vulcanizate and SBR composites, the compounds which were mixed for 8 min at room temperature in an open mill in advance were vulcanized in an electrically heated press at 160 °C for the optimum cure time (t_{90}).

2.4. Characterization

Fourier transform infrared spectrum (FTIR) was recorded by a Bruker Vector 33 with KBr pellets in the range of 4000–400 cm⁻¹. X-ray photoelectron spectroscopy (XPS) analysis was carried out on a Kratos Axis Ultra (DLD) with an aluminum (mono) K α source (1486.6 eV). To ensure the accuracy of FTIR and XPS results, m-silica and silica-s-M samples were extracted in advance by a Soxhlet extractor for 72 h with hot ethanol to get rid of the unreacted CTS and M. 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 by a ZEISS Merlin. Dynamic mechanical analysis (DMA) was performed using a TA DMA Q800 instrument using a tensile mode with a dynamic strain of 0.5%. The samples were heated from –80 °C to 70 °C at the rate of 3 °C/min. The frequency was fixed at 5 Hz.

The thermal behaviors of unfilled SBR and SBR composites in glass transition were recorded by a NETZSCH DSC 204 F. Samples were scanned from –80 °C to 20 °C at a rate of 10 °C/min under nitrogen. The heat capacity step ΔC_{pn} and weight fraction of constrained polymer layer χ_{im} [16] of SBR composites were calculated according to the following equations:

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

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

ΔC_p is the heat capacity jump at glass transition temperature (T_g), while ΔC_{pn} is normalized to the rubber weight fraction. w is the weight fraction of filler. ΔC_{p0} is the heat capacity jump at T_g of the unfilled rubber matrix. χ_{im} is the weight fraction of constrained rubber layer.

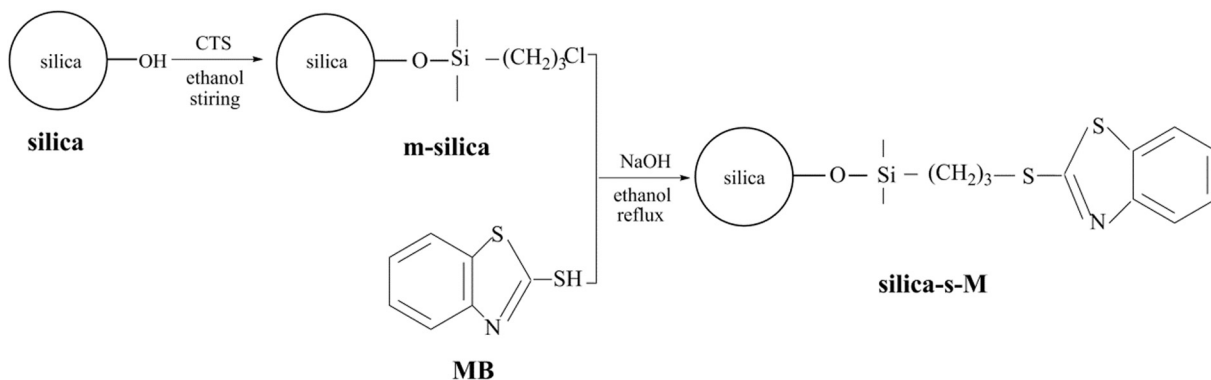


Fig. 1. Synthesis route of silica-s-M.

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