



Novel functional silica nanoparticles for rubber vulcanization and reinforcement



Lijuan Chen, Zhixin Jia*, Yuhan Tang, Lianghui Wu, Yuanfang Luo, Demin Jia

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

ARTICLE INFO

Article history:

Received 12 August 2016

Received in revised form

5 November 2016

Accepted 8 November 2016

Available online 9 November 2016

Keywords:

Nano particles

Particle-reinforced composites

Curing

Interface

Surface treatments

ABSTRACT

A high reactive sulfocompound, sulfur monochloride, was chemically supported onto the surface of silica (silica-s-S₂Cl₂) by the reaction between chloric atom and silanol hydroxyl to obtain a novel vulcanizing agent, silica supported sulfur monochloride (silica-s-S₂Cl₂). Silica-s-S₂Cl₂ can be homogeneously dispersed in SBR matrix as a modifier and cure the styrene-butadiene rubber (SBR) without sulfur as a novel high-efficiency vulcanizing agent. The sulfur and Bis[3-(triethoxysilyl)propyl] Tetrasulfide (TESPT) silane coupling agent vulcanized SBR composites were mainly polysulfide crosslinks, on the contrary, the vulcanization by silica-s-S₂Cl₂ give priority to the mono- and disulfides crosslinks. The highlight of this work lies in the fact that apparent improvement has been achieved by novel and high efficient functional particles due to the silica surface supported with sulfur monochloride, which may open up new opportunities for the preparation of functional nano-fillers in rubber industry.

© 2016 Elsevier Ltd. All rights reserved.

Contents

1. Introduction	11
2. Experimental	12
2.1. Materials	12
2.2. Preparation of silica-s-S ₂ Cl ₂ vulcanizator	12
2.3. Preparation of SBR composites	12
2.4. Characterization	12
3. Results and discussion	13
3.1. Surface modification of silica particles with S ₂ Cl ₂	13
3.2. Cure properties of SBR compounds	13
3.3. Dispersion of fillers in SBR composites	13
3.4. Crosslink density and mechanical properties of SBR composites	15
3.5. The free sulfur of SBR composites and vulcanizing process for the SBR/silica-s-S ₂ Cl ₂ composite	16
4. Conclusions	17
Acknowledgements	17
References	17

1. Introduction

In 1839, the process of sulfur vulcanization of rubbers was

invented by Charles Goodyear and as a result of his discovery the rubber industry was explosively developed to this day [1–3]. Although the sulfur vulcanization of rubbers has been widely applied in industry, there are many disadvantages for the traditional vulcanization method. The low solubility of sulfur in rubber matrix will lead to its migration and blooming to the surface of products, and the nonuniform distribution of insoluble sulfur will

* Corresponding author.

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

lead to the uneven crosslinking structure and poor properties of the vulcanized rubber. Moreover, incomplete vulcanization reaction of sulfur particles might give rise to remain a considerable proportion of free sulfur, which is a disadvantageous for the properties of the vulcanized rubber and saving resources [4,5]. Sulfur vulcanization of rubbers form polysulfide crosslinking bonds frequently in normal conditions. The polysulfide crosslinks are thermally less stable than mono- and disulfides which sulfur atoms are not exchangeable. Polysulfides cause the reversion of vulcanization, which results in a reduction of mechanical properties when the vulcanization is carried out for a long time. Thus, it is crucial to decrease the polysulfide crosslinks in rubber vulcanization [6].

Most industrial applications rubbers need to be reinforced with certain content of reinforcing fillers such as carbon black, silica, graphene and carbon nanotubes, and so on. To prepare high performance rubber nanocomposites, the improvement of filler dispersion and filler–rubber interaction is generally acknowledged to be the key issue [7–9]. Tang et al. incorporated a graphene-like layered material, molybdenum disulfide to partly substitute carbon black in styrene butadiene rubber/CB composites and primarily focus on the filler dispersion and network with different content of MoS₂ [10]. Rooj et al. reported that the ‘expanded organoclay’ assisted dispersion of multiwall carbon nanotubes in natural rubber (NR) compounds and the electrical and mechanical behavior of NR composites were simultaneously improved [11]. Yang et al. prepared a novel covalent interface in graphene/SBR nanocomposites based on ortho-quinone-thiol chemistry to improve the dispersion and interfacial interaction, and drastically decreased energy loss in graphene/SBR nanocomposites [12].

Silica as one kind of important nanofiller is widely used in rubber reinforcement. However, silica surface is occupied by acidic hydroxyl, siloxane and silanol groups, which adsorb accelerators by the surface hydrogen bonds, deactivate them and slow down the rate and degree of vulcanization. Therefore, silica surface modification has been considered in order to reduce silanol groups of silica surface and their adverse effects on the vulcanization reactions [13–18].

Recently, our team has proposed a novel concept about supported rubber additives, and via the surface chemical modification of nanofillers with rubber additives to prepare different kinds of supported antioxidants and supported accelerators [19,20]. The filler-supported additives can not only remarkably increase the aging resistance or accelerating efficiency of the traditional additives, but also obviously improve the mechanical properties of the nanocomposites. Besides, they can overcome the weakness of easy volatility, migration and dissolution of the small molecular additives [21,22].

In this article, we prepared a novel supported vulcanizing agent, silica supported sulfur monochloride (silica-s-S₂Cl₂) by the reaction between chloric atom of S₂Cl₂ and silanol hydroxyl of silica surface, and vulcanized styrene-butadiene rubber (SBR) with the novel supported vulcanizing agent instead of sulfur. For this functional nanoparticle, it acts as not only novel vulcanizator to form the covalent crosslinking between rubber and filler, but also modified filler to improve the filler–rubber interaction. The crosslink densities and types for vulcanized SBR composites were determined by the method of chemical detection agent and the equilibrium swelling method. Finally, based on the analysis of the large strain behavior and the types of crosslink bonds for SBR composites, the difference in vulcanized effective between silica supported S₂Cl₂, sulfur and TESPT was analyzed and substantiated. The desirable vulcanizing agent silica-s-S₂Cl₂, which is excellent than sulfur and TESPT, together with its significant advantages of high performance, low free sulphur and environmental friendliness, make it

good candidate for the preparation of functional nano-fillers in rubber industry.

2. Experimental

2.1. Materials

Styrene-butadiene rubber SBR1502 (SBR) was received from Guangzhou Institute of Rubber Products, China. Precipitated silica with the primary particle of 10–20 nm diameter and the specific surface of 200–220 m²/g was produced from Huiming Chemical Co., Ltd., Jiangxi, China. Sulfur monochloride (S₂Cl₂) was obtained from Aladdin Chemical Co., Ltd., China. Bis[3-(triethoxysilyl)propyl] Tetrasulfide (TESPT) was purchased from Alfa Aesar. 2-Mercapto-benzothiazole, zinc oxide (ZnO), stearic acid (SA) and insoluble sulfur (S) were industrial grade products and used as received. Petroleum ether, acetone and n-heptanes were analytical reagents and used as received.

2.2. Preparation of silica-s-S₂Cl₂ vulcanizator

The synthesis route of silica-s-S₂Cl₂ is shown in Fig. 1. 10 g of silica was dispersed in 200 ml of petroleum ether, and then 5 g of S₂Cl₂ was added into the suspension. The mixture was stirred for 6 h at 60 °C under nitrogen atmosphere in a three necked flask equipped with a reflux condenser. The product was filtered and then washed with 300 ml of anhydrous toluene (3 times) and 300 mL of petroleum ether (5 times). The modified silica(silica-s-S₂Cl₂) was dried in a vacuum oven to constant weight at 80 °C.

2.3. Preparation of SBR composites

SBR composites filled with silica-s-S₂Cl₂ particles were prepared according to the formulas in Table 1. The constant filler content for each sample was 50 phr, and sufficient TESPT was added directly during mixing as vulcanizing agent. The mixing of components was carried out in a two-roll mill for 10 min. After homogenization the rubbers were vulcanized at 160 °C for the optimum cure time (t_{c90}).

2.4. Characterization

Fourier transform infrared (FTIR) measurement was carried out on a Bruker Vector 33 spectrometer. Thermogravimetric analysis (TGA) was conducted under nitrogen atmosphere with a TA Q5000 at a heating rate of 20 °C/min from 30 to 700 °C. Differential scanning calorimeter (DSC) (NETZSCH 204 F1) with a heating rate of 5 °C/min was used to study the melting point of sulfur and novel vulcanizator. The loading efficiency C_A [23] of S₂Cl₂ was determined by the weight loss from Thermogravimetric analysis and calculated with Eq. (1):

$$C_A = (1 - w_{\text{silica-s-S}_2\text{Cl}_2} / w_{\text{silica}}) \times 100\% \quad (1)$$

where, C_A is the loading efficiency of S₂Cl₂; w_{silica-s-S₂Cl₂} is the weight of S₂Cl₂-loaded silica at 700 °C; and w_{silica} is the weight of silica at 700 °C. Curing characteristics were determined at 160 °C by a U-CAN UR-2030 vulcameter. Scanning electron microscopy (SEM) was performed on a ZEISS Merlin. Transmission electron microscopy (TEM) was conducted on a JEOL2100. A tensile test was performed on a U-CAN UT-2060 instrument according to ISO standard 37–2005. The free sulfur content of each samples were detected by an ELEMENTAR elemental analyzer. Each sample was extracted in acetone solvent for 0 h, 12 h, 24 h, 48 h, and 72 h, respectively. The content of free sulfur can be proved by the analysis of the sulfur element from the extracted rubber.

Download English Version:

<https://daneshyari.com/en/article/5022182>

Download Persian Version:

<https://daneshyari.com/article/5022182>

[Daneshyari.com](https://daneshyari.com)