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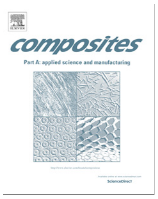

Effect of the temperature on surface modification of silica and properties of modified silica filled rubber composites

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ABSTRACT

The modified silica at different temperature (MSaDT) with bis(3-triethoxysilylpropyl)tetrasulfide (TESPT), and MSaDT filled solution styrene butadiene rubber (SSBR) composites were prepared to investigate the effect of temperature on surface modification of silica. The results showed that TESPT was successfully bonded on the surface of silica by chemical bonds. The grafting degree (K) of MSaDT of 50 °C was 62.2% and higher than that at the other temperatures. The thermal weight loss and the size distribution of MSaDT showed that the silanol of TESPT hydrolysates reacted with the surface hydroxyl groups of silica, decreasing the average size and agglomeration of modified silica. For 50 °C modified silica/SSBR composite, the static mechanical properties and rubber–filler interaction of the composite were better than those of the others. As far as dynamic mechanical properties are concerned, the 50 °C modified silica/SSBR composite owned a best combination of low rolling resistance and high wet skid resistance.

1. Introduction

In the rubber industry, nanosilica is one of the most important reinforcing fillers and has been researched and applied in depth [1,2], regarded as a replacement for carbon black [3], and applied in green tire preparation [4,5], since it can provide a combination of good mechanical properties [6], high wet skid resistance, and low rolling resistance [7].

However, the compatibility between the rubber matrix and nanosilica is rather poor because of the large quantities of hydroxyl groups on the surface of nanosilica and high surface energy, resulting in severe agglomeration and weak rubber–filler interaction [8,9]. Surface modification [10] of nanosilica can reduce the surface hydroxyl density and thus improve the compatibility of nanosilica with the rubber matrix, leading to the improvement of filler dispersion and performance of the rubber composite [11].

The silane coupling agents (SCAs) are widely used in the modification of several kinds of fillers, such as nanotubes [12], glass fiber [13], and nanosilica [14]. Bis(3-triethoxysilylpropyl)tetrasulfide (TESPT) has been successfully applied in the modification of nanosilica [15,16]. Some researchers blended TESPT with silica and rubber in an open or internal mixer at high temperatures [17] or combinations of room and high temperatures [18]. Other researchers applied pre-modification of silica with TESPT and then mixed the pre-modified silica with rubber according to compounding procedures. Such pre-modification of silica is always accomplished by simply dipping the silica into organic solutions, for example ethanol [19], leading to the uncertain physical or chemical adsorption of TESPT on the surface of silica. As is well known, the most effective modification of silica with a kind of SCAs such as TESPT involves the chemical bonding between the SCAs and silica particles, which is originated from the condensation of the silanols of hydrolyzed TESPT with the surface hydroxyl groups of silica. However, the above mentioned modification methods do not definitely involve the hydrolysis of TESPT, making the modification reaction uncontrollable and difficult to identify. In our previous study [20], we investigated surface modification of silica by Two-Step-Method and the influence of TESPT amount for the performance of rubber composites, indicating that 8 wt% TESPT amount was the best to decrease the agglomeration of silica and the processing energy consumption during the compounding of rubber and silica. Nevertheless, we just analyzed the effect of TESPT amount on the modification of silica at constant temperature. Furthermore, for surface modification of silica, many reports focused only on the kinds of SCAs [21,22], paying hardly any attention to the effect of temperature during the modification procedure. From the perspectives of chemical reaction kinetics,

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the high temperature may promote the grafting reaction between hydrolyzed TESPT and silica. In other word, we considered that differences in the chemical reactivity of the hydrolysate of TESPT and silica at different temperatures resulted in different degrees of grafting modification.

In this study, we prepared the hydrolysates as same as our previous study [20] at constant temperature firstly, mixed the hydrolysates of TESPT with silica to prepare modified silica at different temperature (MSaDT) and investigated the effect of temperature on the surface modification of silica. The rubber composites filled with MSaDT were fabricated to evaluate the improvement in the performances of the composites. The comparison of the silica before and after modification was carried out by using Fourier transform infrared (FTIR) spectroscopy, thermal gravimetric analysis (TGA), and dynamic light scattering (DLS). For MSaDT/SSBR composites, transmission electron microscope (TEM), rubber process analyzer (RPA), and dynamic mechanical thermal analysis (DMTA) were used to determine the dispersion of MSaDT, filler network structure, and dynamic mechanical properties of the composites, respectively.

2. Experimental

2.1. Materials

Commercial SSBR (Buna VSL 5025-2HM), composed of 75% butadiene with a 50% vinyl content, and 25% styrene content, extended with 37.5 phr treated distillate aromatic extracts (TDAE) oil, was purchased from Lanxess Chemical Industry Co., Ltd. (Germany). Precipitated silica of Tixosil 383 [median diameter (d50) is 13.7 μm, DOP (dioctyl phthalate) oil absorption is 2.66 mL/g, CTAB (cetyltrimethyl ammonium bromide) specific surface area is 163 m^2/g] was produced by Rhodia France (Qingdao, China). Bis(3-triethoxysilylpropyl)tetrasulfide (TESPT) was obtained from Nanjing Shuguang Chemical Group Co., Ltd. (China). All other materials were commercially available.

2.2. Surface modification of silica nanoparticles

TESPT hydrolysates were prepared according to our previous reported procedure [20]. Absolute ethanol 1000 mL and deionized water 30 mL were added to a beaker, and acetic acid was used to adjust the pH value to approximately 4.5. TESPT 8 g (mass ratio of TESPT to Silica = 8%) was added to the solution and hydrolysis of TESPT was allowed to proceed for 10 h, resulting in the transformation of ethyoxyl to hydroxyl. Silica nanoparticles 100 g were dispersed in TESPT hydrolysate in a three-necked flask under stirring for 48 h at different temperatures (30 °C, 40 °C, 50 °C, 60 °C, and 70 °C). Finally, the slurry was dried in a vacuum oven to obtain MSaDT powder. For the assessment of the surface modification of silica, a part of MSaDT was extracted in a Soxhlet extractor by toluene for 48 h to remove the un-grafted TESPT, and then dried in a vacuum oven at 70 °C for 24 h. The remainder of the MSaDT was compounded with rubber to prepare the MSaDT filled SSBR composites.

2.3. Preparation of MSaDT/SSBR composites

The formulation for the preparation of MSaDT/SSBR compounds is shown in Table 1. Firstly, the zinc oxide, stearic acid, N-Isopropyl-N′-phenyl-1,4-phenylenediamine, paraffin wax and MSaDT were directly compounded with SSBR base gum, and then all of the other ingredients were uniformly blended on a 6-inch two-roll mill (Shanghai Rubber Machinery Works No. 1, China) at room temperature. The optimum cure time (t_{90}) of the compounds were obtained by a P3555B2 Disc Vulkameter (Beijing Huanfeng Chemical Machinery Trial Plant, China). The composites were prepared by a XLB-D350 × 350-type Automatic Operation Vulcanizing Press (Huzhou Dongfang Machinery Co., Ltd., China). The compounds were vulcanized at 160 °C for t_{90} in a standard mold to produce the MSaDT/SSBR vulcanizates.

Table 1
Formulation of MSaDT/SSBR compounds.

Materials	Amount/phr[a]
SSBR	137.5
MSaDT	75
Zinc oxide	3.5
Stearic acid	2.0
N-Isopropyl-N′-phenyl-1,4-phenylenediamine	1.3
Paraffin wax	1.5
N-Cyclohexyl-2-beozothiazole sulfonamide	1.5
1,3-Diphenyl guanidine	2.0
Tetramethylthiuram disulfide	0.4
Sulfur	1.4

[a] Parts per hundred of rubber.

2.4. Characterizations

The difference in reactive groups between pure silica and MSaDT was identified on a Tensor 27 FTIR spectrometer (Bruker Optik Gmbh Co., Germany). The samples were pressed into pellets together with potassium bromide (KBr). The spectra were recorded in the wavenumbers range 500–4000 cm^{-1}. The organic degree [23,24] of MSaDT was obtained from the grafting degree, which is calculated according to Eq. (1):

$$K = (R - r)/R \times 100\%, \quad (1)$$

where K is the grafting degree of the hydroxyl, R is the ratio of the hydroxyl peak areas at 3447.35 cm^{-1} and 1108.32 cm^{-1} in the spectrum of pure silica, and r is the ratio of the hydroxyl peak areas at 3447.35 cm^{-1} and 1108.32 cm^{-1} in the MSaDT spectrum.

The weight loss measurements of pure silica and MSaDT were performed on a TGA STARe system (Mettler-toledo Co., Switzerland) under nitrogen atmosphere. The samples for TGA tests were heated at a heating rate of 10 °C/min.

The particle size distributions of pure silica and MSaDT were characterized by dynamic light scattering (DLS) on a Malvern ZEN3600 NanoZS Analyzer (Malvern Instruments Co., England). The samples were dispersed in ethanol for 2 h by ultrasonic technology before it was put in the instrument for particle size distribution measurements.

The filler dispersion was investigated on a Tecnai G2 20 TEM (FEI Co., USA) with an accelerating voltage of 200 kV. The thin sections for TEM observations were cut by a microtome at −100 °C and collected on copper grids.

The static mechanical properties of the composites were measured according to ASTM D638 by a CMT4104 Electrical Tensile Tester (Shenzhen SANS Test Machine Co., China) at a tensile rate of 500 mm/min.

The dynamic rheological properties of the composites were analyzed by RPA 2000 (Alpha Technologies Co., USA) at 60 °C. For the rubber compounds, the strain amplitude was varied from 0.1% to 400% at the test frequency of 1 Hz. For the rubber vulcanizates, the strain amplitude was varied from 0.1% to 40% at the test frequency of 10 Hz.

The viscoelastic properties of the composites were measured on a VA3000 DMTA (01 dB-Metravib, France) in the tension mode. The temperature was from −60 °C to 100 °C, the heating rate was 3 °C/min, the frequency was 10 Hz, and the strain amplitude was 0.1%.