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Material Properties

Performance improvement in nano-alumina filled silicone rubber composites by using vinyl tri-methoxysilane

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ABSTRACT

The performance of inorganic filler filled rubber composites is mainly affected by filler-rubber interface interactions. In this work, vinyl tri-methoxysilane (VTMS) was employed during the preparation of nano-alumina filled silicone rubber (SIR) composites, serving as the molecular bridge between SIR matrix and nano-alumina filler to strengthen the interfacial interaction. Through the reaction with the hydroxyl and carboxylic acid groups on the nano-alumina surface, VTMS connected the nano-alumina particles with the rubber chains during the curing process, improving the filler-rubber interaction while decreasing the filler-filler interaction. Compared to pristine nano-alumina filled SIR composites, the incorporation of VTMS resulted in better filler dispersion in the as-prepared composites, which exhibited enhancement of thermal conductivity, breakdown strength and mechanical properties, and reduction of dielectric constant and dielectric loss.

1. Introduction

Composite insulators are increasingly used in power transmission and distribution lines. Silicon rubber (SIR) is one of the major components in composite insulators, owing to its superior features such as good electrical insulation, excellent hydrophobicity, chemical inertness and high resistance to various types of irradiation [1]. However, when in service, heat build-up easily occurs for the insulators under high operating voltage, resulting in acceleration of rubber aging [2]. To alleviate the heat accumulation, the thermal conductivity of SIR needs to be enhanced, usually through the addition of thermally conductive fillers [3–5].

Among the various thermally conductive fillers, alumina has been one of the most widely used types for commercial applications because it has the advantages of low cost, electrical insulation and relatively high thermal conductivity [6]. However, due to the poor compatibility between hydrophilic alumina and hydrophobic SIR, the dispersion of alumina in rubber matrix is usually relatively poor and the interactions between alumina and rubber is quite weak, causing poor performance of the composites.

Silane coupling agents, serving as the molecular bridges between organic rubbers and inorganic fillers, are commonly used to promote interface adhesion so as to improve the performance of filler filled rubber composites [7–13]. Bis(triethoxysilylpropy1)tetrasulfide-modified, clay filled styrene butadiene rubber (SBR) nanocomposite [10] had tensile strength improved from 8.8 MPa to 14.5 MPa and the stress at 100% strain enhanced from 3.1 MPa to 8.3 MPa. Using the same silane coupling agent [8], thermal conductivity of 10.5 vol% boron nitride filled SBR composite enhanced from $0.43\,W\,m^{-1}\,K^{-1}$ to $0.57\,W\,m^{-1}\,K^{-1}$. As for SIR based composites, Yan et al. [11] modified fumed silica with hexamethyldisilazane and methacryloxy propyl trimethoxyl silane to improve the compatibility with SIR in order to achieve better reinforcement. Mei et al. [9] utilized pre-synthesized macromolecular silane coupling agent to bridge fumed silica with SIR so as to improve the composite mechanical properties.

In literature, there have also been studies investigating the influences of particle size, geometry and size distribution on the thermal conductivity of alumina filled SIR composites [6,14–17]. However, to the best of our knowledge, the breakdown strength and dielectric properties of these composites were rarely investigated, which are very important for SIR composites applied in high voltage fields. Therefore, in this work, commercially available nano-alumina was investigated as

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the filler to prepare SIR composites, and vinyl tri-methoxysilane (VTMS) was employed during the preparation of nano-alumina filled SIR composites to improve the composite performance. The effect of VTMS on thermal conductivity, dielectric properties, breakdown strength and mechanical properties of the SIR composites were investigated.

2. Experimental

2.1. Materials

Methyl vinyl silicone rubber (MVQ110, vinyl content of 0.23 wt%, molecular weight of 680,000) was purchased from Zhejiang Xin'an Chemical Group Co. Ltd., China. Nano-alumina (Aeroxide Alu C, density of 3.97 g cm^3, specific surface area of 100 $m^2 g^{-1}$) was provided by Evonik Industries AG, Germany. VTMS was provided by Nanjing Shuguang Chemical Co. Ltd., China. 2,5-bis(tert-butylperoxy)-2,5-dimethyl hexane was purchased from Akzo Nobel Cross-Linking Peroxide Co. Ltd., China.

2.2. Sample preparation

Nano-alumina and other ingredients were mixed into the gum SIR on a 6-in. two-roll mill to prepare SIR/alumina or SIR/alumina-VTMS compound, which was then cured in a standard mold using a hydraulic hot press (XLB-D 350, Huzhou Dongfang Machinery, Co., Ltd., China) at 160 °C and 15 MPa to obtain SIR/alumina or SIR/alumina-VTMS composites. The recipe (parts by weight) for the sample preparation was as follows: SIR, 100.0; 2,5-bis(tert-butylperoxy)-2,5-dimethyl hexane, 0.5; nano-alumina, variable; VTMS, variable (the weight ratio of nano-alumina and VTMS was always set as 100:1 in SIR/alumina-VTMS composites).

In order to investigate the reaction between nano-alumina and VTMS, model compound (labeled as alumina-VTMS) was prepared as follows: first, VTMS (0.5 g) was added to 100 mL ethanol suspension of nano-alumina (1 mg/mL) and stirred at 70 °C for 24 h; then the reaction product was centrifuged and washed three times with ethanol to remove unreacted VTMS, followed by drying under vacuum at 50 °C for 12 h. The obtained model compound was mainly used for the FTIR characterization.

2.3. Measurements

The morphologies of the tensile fracture surface of composites were observed on a scanning electron microscope (SEM) (S-4700, Hitachi, Japan) with an acceleration voltage of 20 kV.

Strain sweep of the composites was tested using a RPA 2000 rubber process analyzer (RPA) (Alpha Technologies, USA) at 60 °C and 1 Hz.

Infrared spectra were obtained from a TENSOR27 FTIR spectrometer (BRUKER OPTIK GMBH, Germany) with an accumulation of 100 scans at a resolution of 2 cm^{-1}. Samples were mixed with KBr powder and pressed into a disc.

Differential scanning calorimetry (DSC, NETZSCH, Germany) was used to evaluate the specific heat (C_p) of the composites under nitrogen atmosphere with a heating rate of 10 °C·min^{-1}. The samples used for DSC measurements were prepared with similar dimension and weight (~20 mg) to minimize experimental error. A density tester (MH-300A, MatsuHaku, Taiwan, China) was used to measure the density (ρ) of the samples. Thermal diffusivity (α) measurement was performed on a laser flash apparatus (LFA 427, NETZSCH, Germany) at room temperature. Thermal conductivity (κ) was calculated by the equation: $\kappa = \alpha \times C_p \times \rho$.

Breakdown strength was measured by a dielectric strength tester (HCDJC-50kV, Beijing Huace Testing Instrument Co. Ltd., China) at ambient temperature with an increasing alternating voltage of 1 kV/s. The specimens sandwiched between two copper rod electrodes with a diameter of 25 mm were immersed in pure silicone oil to prevent surface flashover.

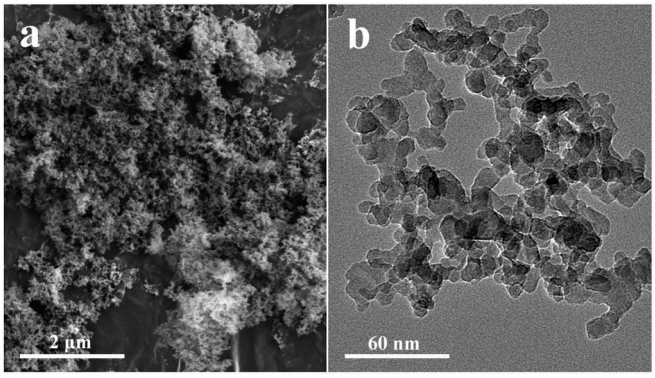

Fig. 1. (a) TEM and (b) SEM images of nano-alumina.

The dielectric properties of the composites were measured at ambient temperature using a Novocontrol GmbH concept 80 Broadband Dielectric Spectrometer over a frequency range of 0.1 Hz–1 MHz.

Mechanical property measurements were conducted using an tensile tester (GT-TC2000, Gotech Testing Machines, Co. Ltd., China) at the speed of 500 mm min^{-1} at room temperature according to ISO 37–2011. Shore A hardness was measured using LX-A rubber hardness apparatus (Liuling Instrument, Shanghai, China) according to ISO 7619-1-2004.

3. Results and discussion

3.1. Characteristics of nano-alumina

According to the TEM image in Fig. 1a, nano-alumina particles are mainly spherical, and the particle size ranges from 10 to 15 nm in diameter. The small size and high specific surface area of nano-alumina would be beneficial for strengthening the rubber composites. As shown in the SEM image in Fig. 1b, nano-alumina particles display a very loose structure. However, they tend to aggregate together due to the high surface energy.

Untreated and VTMS modified nano-alumina particles were characterized by FTIR and XPS to examine whether the chemical reactions occur during the in situ modification. The FTIR results are presented in Fig. 2. For the untreated nano-alumina, the broad band ranging from

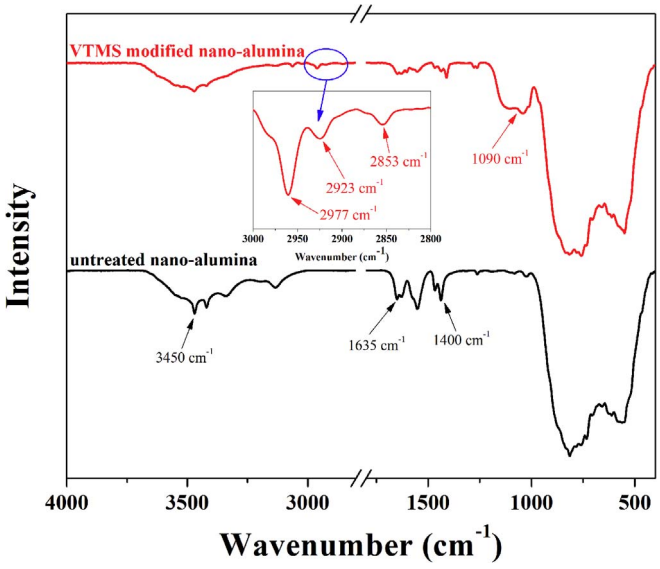

Fig. 2. FTIR spectra of nano-alumina and VTMS modified nano-alumina.