



Material properties

Interfacial mechano-chemical grafting in styrene-butadiene rubber/halloysite nanotubes composites

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ABSTRACT

SBR/unmodified HNT composites were prepared by open-mill mixing and vulcanization. The results showed that HNT could decrease the scorch and optimum cure time, and play a significant role in reinforcing SBR vulcanizates. Mechano-chemical grafting at the interface between HNT and SBR was investigated by using infrared spectroscopy, X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), solid-state ¹³C NMR spectra and bonded rubber content, etc. The results showed the shearing force during the mixing process can impel the grafting reaction of SBR onto the surfaces of HNT, which leads to interfacial chemical bonding between phenyl's α -H of SBR and the surface groups of HNT with Si-OH or Al-OH. Thus, the mechanical properties of the composites were significantly enhanced.

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1. Introduction

Since the late twentieth century, rubber-based nanocomposites prepared by rubber and inorganic nanomaterials have attracted much attention from researchers. The formation of the nanocomposites not only leads to a remarkable reinforcing effect, but can also provide the rubbers with new properties or functions. Therefore, these nanocomposites have been an important research direction in the current field of rubber science and technology [1,2].

Halloysite nanotubes (HNT) are a natural inorganic nanomaterial with nanotubular structure and the same composition as kaolinite. It may also be regarded as a silicate with SiO₂/Al₂O₃ molar ratio of 1:1. Also, it has multi-walled nanotube structure formed under natural conditions, in which SiO₂ forms the outer layer of the tube while Al₂O₃ forms the inner layer. The outside diameter and inside diameter of HNT are 10–50 nm and 5–20 nm, respectively, and the maximum length is about 2–4 μ m [3]. In 2006, our research team [4] reported polypropylene/HNT nanocomposites. Since then, our team and many researchers around the world have studied the nanocomposites formed by HNT and different polymers such as chitosan [5,6], polypropylene [7], epoxy resin [8,9], polystyrene [10], nylon [11], polyethylene [12], polyvinyl chloride [13], polyvinyl

alcohol [14], rubbers [15], and so on. The results showed that HNT has significant reinforcing and modification effects on polymers [16].

Among the nanocomposites of rubbers and HNT, the rubbers studied include styrene-butadiene rubber (SBR) [17–22], natural rubber (NR) [23,24], nitrile-butadiene rubber (NBR) [22], ethylene-propylene-diene monomer (EPDM) [25–27], carboxylated styrene butadiene rubber [28] and fluororubber [29], etc. There is a common characteristic among these rubber/HNT composites, namely, an interfacial modifier is generally added to disperse HNT in the rubber matrix and to strengthen the interfacial bonding between HNT and rubber. Taking the SBR/HNT composite as an example, the interfacial modifiers reported include a complex of resorcinol and formaldehyde (RH) [17], epoxidized natural rubber (ENR) [18], ionic liquids [19], methacrylic acid [20], sorbic acid [21], and so on. Our researches [17,18] showed the interfacial modifiers RH and ENR can promote nanodispersion and orientation of HNT in SBR matrix. They can also strengthen the interfacial interaction between HNT and SBR by forming hydrogen bonds and covalent bonds.

In general, in the rubber-based nanocomposites without interfacial modifiers, the rubber matrix and the filler are bonded to each other by physical interactions, and the interfacial covalent bonding is rarely involved. If the filler is dispersed in rubber matrix at nanometre level and the interface between the two phases forms chemical bonding, nanocomposites with significantly improved properties can be obtained. The polar groups on the surface of HNT particles are less than those on silica, and so agglomeration

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between particles is not as severe as in silica. Thus, it is easier for HNT to disperse in rubber than silica without additional interfacial modifier. Also, tubular nanoparticles can orientate in the rubber matrix, which can improve the mechanical properties of the nanocomposites favorably.

In this paper, to investigate the interfacial interaction between HNT and rubber, SBR and unmodified HNT were mixed on an open-mill to prepare SBR/HNT composites without adding any modifier. Further, the SBR/HNT model compounds without any other additive were prepared. The interfacial interaction between HNT and SBR was characterized by bonded rubber content, infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), solid-state ^{13}C NMR, transmission electron microscopy (TEM) and so on. The results showed that a mechano-chemical grafting reaction between SBR molecular chains and the active groups on the surface of the HNT particles was produced under the effect of mechanical forces during the mixing process. As a result, firm interfacial chemical bonding was produced between the filler and rubber. Therefore, the unmodified HNT can promote the vulcanization of the SBR/HNT compounds and reinforce the SBR vulcanizates significantly.

2. Experimental

2.1. Raw materials

Styrene-butadiene rubber (SBR) with a trade name 1502 was produced by Jilin Chemical Industrial Company, Ltd, China. Halloysite nanotubes (white powder) was produced in Hubei, China, and was dried and sieved before using. Other ingredients are commercially available industrial products and used as received.

2.2. Preparation of SBR/HNT composites

Basic formula (mass parts): SBR 100, HNT 0–60, zinc oxide 5, stearic acid 2, sulfur 1.5, N-cyclohexyl-2-benzothiazolesulfenamide (accelerator CZ) 1.5, N-isopropyl-N'-phenyl-p-phenylene diamine (antioxidant 4010NA) 1.5, benzothiazole disulfide (accelerator DM) 0.5. SBR and various ingredients were mixed on XK-160 open-mill. Roll speed ratio was 1:1.2. Optimum curing time (T_{90}) was determined at 150 °C by UR-2030 oscillating disk rheometer made by U-CAN Dynatex Inc., Taiwan. The compounds were held at room temperature for 2–4 h, and then vulcanized on a KSH R100 flat vulcanizing machine made in Dongguan City Kesheng Machinery Co., Ltd, China.

2.3. Preparation of SBR/HNT model compounds

SBR/HNT model compounds with different mass ratios were prepared on a LRMR-S-150/0 (Lab Tech Engineering Company LTD.) open mill at 40 °C for 10min. No other additives were added in the whole process. Then, all compounds were tested to obtain rheological parameters by UR-2030 oscillating disk rheometer and the bonded rubber content. The compound with SBR/HNT ratio of 100/50 was selected to obtain the ^{13}C solid-state NMR spectra. After that, it was extracted with xylene for 72 h in Soxhlet extractor to remove the physical adsorbed SBR from HNT. Then, the extracted residuum was collected to meet the tests of FTIR, XPS and TEM etc for investigating the interaction between SBR and HNT.

2.4. Testing and characterization

2.4.1. Determination of curing characteristics and temperature sweep

Vulcanization curves and vulcanization characteristic parameters of the compounds were determined at 150 °C by a U-CAN UR-

2030 oscillating disk rheometer. Temperature sweep of uncured rubber composites was conducted by a RPA2000 Rubber Processing Analyzer from 60 to 200 °C at a constant frequency of 1.67 Hz and strain 14%.

2.4.2. Mechanical properties

Tensile properties of the vulcanizates were determined following ISO 37-2005 at 25 °C using a U-CAN UT-2060 instrument. Tear strength was determined following GB/T529-1999. The determination of Shore A hardness was performed following ISO standard 7619-1986 using a XY-1 durometer (Shanghai).

2.4.3. Crosslink density

The apparent crosslink density of the vulcanizates was measured by the equilibrium swelling method. First, the sample (weighed as m_0) was soaked in toluene for 72 h at room temperature. Then it was removed and wiped quickly to remove solvent on the surface. The sample was immediately weighed as m_1 , dried in a vacuum oven at 80 °C for 36 h to remove the residual solvent, and then reweighed (m_2). The mass increase (in percent) was calculated by Eq. (1):

$$\text{swollen mass increase(\%)} = \frac{m_1 - m_0}{m_0} \times 100\% \quad (1)$$

The crosslink density was measured by applying the Flory-Rehner equation [30–32] as given in Equations (2)–(4) below:

$$M_c = \frac{-\rho_p V_s V_r^{1/3}}{\ln(1 - V_r) + V_r + \chi V_r^2} \quad (2)$$

$$V_r = \frac{(m_2 - m_f) / \rho_p}{(m_2 - m_f) / \rho_p + (m_1 - m_2) / \rho_s} \quad (3)$$

$$V_c = \frac{1}{2M_c} \quad (4)$$

where, M_c is the molecular weight between crosslinking points, m_f is the weight of the non-extractable filler in the sample. ρ_p is the density of cured rubber. V_s is the molar volume of the toluene (107 cm³/mol) [33]. V_r is the volume fraction of the swollen rubber. ρ_s is the density of toluene (0.866 g/cm³) [33] and V_c is the degree of crosslink density. χ is the SBR–toluene interaction parameter and is taken as 0.0653 calculated according to reference [33].

2.4.4. Determination of bonded rubber

Bonded rubber contents of SBR/HNT model compounds were obtained via soaking method. 0.2 g sample was immersed in 25 ml xylene for 7 days. The HNT-gel component was filtered and then dried for 1 day in air at room temperature. After that, the gel part was dried in an oven at 70 °C until constant weight. The bonded rubber content was determined [34] from Eq. (5):

$$R_b(\%) = \frac{W_{fg} - m_f}{m_p} \times 100\% \quad (5)$$

where R_b is bonded rubber content, W_{fg} is the weight of HNT-gel, and m_f and m_p are the weights of filler and polymer in the compound, respectively, which could be calculated from the compound formula.

2.4.5. Fourier transform infrared spectroscopy (FTIR)

FTIR analysis of SBR/HNT specimens was carried out by a Vector

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