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Research paper

Characterization of kaolinite/styrene butadiene rubber composite: Mechanical properties and thermal stability

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ABSTRACT

The processing, mechanical properties and thermal stability of kaolinite/styrene butadiene rubber (SBR) composite were investigated, and the influences of kaolinite particles size and filled contents on these properties were analyzed. The X-ray diffraction (XRD) patterns, Fourier-transform infrared (FT-IR) spectroscopy, Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) showed that the rubber chains may be confined within the interparticles space and the kaolinite particles presented a physical dispersion in SBR matrix. The scorch time (t_{s2}) and cure time (t_{c90}) of the kaolinite/SBR composites decreased simultaneously relative to those of the pure SBR. The minimum torque of the kaolinite/SBR composite increased relative to that of pure SBR, and it decreased with decreasing filler particle size and increased with increasing filler content. The modified kaolinite gave a progressive reinforcement on mechanical properties of the kaolinite/SBR composite, even at high filler content (80 phr).The tensile strength and tear strength of the kaolinite/SBR composite at 80 phr filler loading were 19.62 MPa and 40.63 kN/m respectively. The prepared composite exhibited significantly improvement in thermal stability compared with that of pure SBR. The characteristic decomposition temperatures of kaolinite/SBR composite gradually increased with decreasing particle size and increasing content. The improvement of mechanical properties and thermal stability of kaolinite/SBR composite is attributed to the fine dispersion of kaolinite particles in the rubber matrix and the strong interactions between kaolinite particles and rubber chains.

1. Introduction

Polymer composites are considered as one of the most interesting areas because of their advantages of lower weight, easy processing, and low cost when incorporating cheap fillers, and thus are interesting research subjects (Sudeepan et al., 2014). Polymer/layer silicate composite have recently gained significant research attention because they exhibit remarkably improved material properties when compared with virgin polymer or conventional micro-and macro-composites (Choudalakis and Gotsis, 2009; Sinha Ray and Okamoto, 2003; Villaluenga et al., 2007). Rubber, as a particular class of polymer materials, is widely used in the industry because of its outstanding and unique characteristics. Clay minerals modified with appropriate organic coupling agents can be endowed with good compatibility and dispersibility within a particular rubber matrix (Zhang et al., 2014a). The first step in obtaining clay-based nanocomposite products with homogeneous structure is the preparation of stable dispersions. The stability and dispersion properties of clay particles in a polymer matrix are very important for the final properties and formulation of a product, economic aspects of the process and storage stability of a product (Tunc et al., 2008, 2011, 2012). A significant amount of research on the preparation and properties of clay/rubber composite has been performed. Incorporation of organoclays into the rubber matrix can significantly improve the properties of clay/rubber composite, such as mechanical, thermal, barrier and dynamic properties of the resultant clay/rubber composite (Gu et al., 2009; Liang et al., 2008; Liu et al., 2008; Raka et al., 2009).

Kaolinite, a highly useful clay mineral, is the most common 1:1 (two-sheet) - type clay mineral with the basic unit consisting of a tetrahedral sheet of SiO_2 siloxane units and an octahedral sheet of AlO_2 $(OH)_4$ (Cheng et al., 2010a; Diar-Bakerly et al., 2014; Frost et al., 2001). Kaolinite is suitable for use as a functional filler to modify the properties of rubber and other polymer materials properties because of its whiteness, fine particle size, layered structure and low heat and electric conductivity (Cheng et al., 2014; Liu et al., 2008; Santos et al., 2012). This clay is an inexpensive additive and can improve the properties of some nanocomposite materials. It is widely used in various industrial applications such as paints, inks, ceramics, coatings, plastics, papers and wastewaters treatment (Duman et al., 2012). The fine dispersibility and compatibility of modified kaolinite can significantly improve the thermal stability, mechanical, gas barrier and flame retardant properties of kaolinite/rubber composite. However, there is little research about the influence of kaolinite particle size and content on the vulcanization,

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mechanical properties and thermal stability of kaolinite/rubber composites, and these properties are important for the actual industrial application of kaolinite/rubber composites.

The work presented in this paper focuses on investigating the effects of kaolinite particle size and kaolinite content on the vulcanization, mechanical properties, and thermal stability of kaolinite/styrene butadiene rubber (SBR) composite.

2. Experimental

2.1. Materials

The raw kaolin sample was obtained from Zhangjiakou, Hebei province in China, which belonged to a kind of kaolin deposit with hydrothermal alteration origins. The kaolinite content in kaolin sample is about 98%. The structure of kaolinite is well-ordered and its Hinckley index is 1.31. Kaolinite samples with different particle sizes were obtained using a disperser and relative material properties are presented in Table 1. The silane coupling agent bis-(γ-triethoxysilyl-propyl)-tetrasulfide (KH-Si69) was purchased from Nanjing Shuguang Chemical Group Co., Ltd, China. Styrene butadiene rubber (SBR) 1500 was supplied by ShenHua Chemical Company of Nantong Jiangsu, China. The viscosity value of pure SBR used in this study is $50ML_{1+4}^{100°C}$, and the mass fraction of bound styrene is 22.5–24.5%. Zinc oxide (ZnO), stearic acid, the accelerator *N-tert*-buylbenzothiazole-2-sulphenamide (NS), and sulphur were obtained from Sinopharm Chemical Reagent Co., Ltd.

2.1.1. Preparation of the modified kaolinite and the kaolinite/rubber nanocomposite

Kaolinite samples were dispersed in water at a final content of 25%, and the sodium polyacrylate with the average molecular weight of 3000–3500 was added to the mixture as a dispersant with 0.5% of the kaolinite mass. The pH of the suspension was maintained at 10.0 using a sodium hydroxide (NaOH) solution, subsequently, 0.5% modifier (KH-Si69) was added to the dispersion. The resulting dispersion was stirred for 1.5 h using a mechanical mixer at approximately 80 °C. Modified kaolinite powder was obtained by spray drying at 120 °C.

Kaolinite/SBR composites were prepared through melt blending. The preparation procedure is briefly described as follows. Raw rubber was plasticized for 3–5 min in an SK-160B open mill at room temperature. The spacing between the two rolls was about 0.15 cm, and the roll rate was 6.98 m/min. ZnO, stearic acid, NS, sulphur and various kaolinite samples were successively add into the plasticized compound successively. The two roll spacing was adjusted to 0.05 cm and uniform mixing was performed for 15 min (Gu et al., 2009; Lagazzo et al., 2010; Zhang et al., 2014a). The formulations of the kaolinite/SBR composites (phr) are shown in Table 2. The optimal cure time was determined using a ZWL-III non-rotor vulkameter. Kaolinite/SBR composite specimens were placed in a 150 mm × 150 mm × 2 mm mold and vulcanized in a 400 mm × 400 mm 25TQLB vulcanizing machine at 153 °C and 10.0 MPa until the optimal cure time was obtained. The cured rubbers were rapidly cooled in air.

Table 1
Particle sizes characteristic of kaolinite samples.

Samples	D_{10}/μm	D_{50}/μm	D_{90}/μm	% ⩽1 μm
Kaolinite-1 (K-1)	1.06	6.49	22.19	9.05%
Kaolinite-2 (K-2)	0.89	3.74	17.94	12.20%
Kaolinite-3 (K-3)	0.63	1.93	4.98	22.75%
Kaolinite-4 (K-4)	0.28	0.53	1.69	79.27%

Table 2
Composition formulation of kaolinite/SBR composites.

Ingredient	SBR	Zinc oxide	Stearic acid	Accelerant (TBBS)	Sulphur	fillers
Content/phr	100.00	3.00	1.00	1.00	1.75	Variable

phr is the abbreviation of mass parts per 100 mass parts rubber.

2.2. Characterization

The particle sizes of the kaolinite samples were measured using a Mastersizer 2000 laser particle-size analyzer (Malvern Company) in wet, cycle injection mode.

The XRD patterns of prepared samples were performed by using a Rigaku D/max 2500PC powder X-ray diffract meter operating at 40 kV and 150 mA. The Cu Kα radiation with 15.40596 nm was used. The scanning step size is 0.02°, and the slit width: DS = SS = 1°, RS = 0.3 mm. Measurements were performed in the range 2.6–60° in 2θ with the scanning rate of 2°/min.

Fourier-transform infrared spectroscopy (FT-IR) was undertaken using a Fourier transform infrared spectrometer (Magna-IR 750 Nicolet) at a resolution of 4 cm^{-1} in the region of 4000–400 cm^{-1}. The number of scans accumulated was thirty-two. The samples were prepared at potassium bromide (KBr) pellets (ca. 2% by mass in KBr).

The morphology of kaolinite/SBR composite was characterized using a scanning electron microscopy (SEM) observed using a S4800 low temperature field emission electron microscope produced by Rigaku Corporation, which was also used to study the dispersion state of kaolinite particles in the rubber matrix. The surface of the vulcanizate sample was treated with alcohol, then was coated with a thin layer of gold and observed by SEM using secondary electron detection and a voltage of 15 KV.

The TEM images of the kaolinite/SBR composites were characterized using an JEM-2100 transmission electron microscope (JEOL., Japan) with an acceleration voltage of 200 kV. Samples were prepared by ultramicrotomy of the bulk cured nanocomposites, to give a section of about 50 nm thickness.

The cure characteristics of the kaolinite/SBR composites were measured by a ZWL-III non-rotor vulkameter at 153 °C, and approximately 5 g of the rubber compounds was tested. Minimum torque (M_L), scorch time (t_{s2}), and optimal cure time (t_{c90}) were determined through a cure curve according to the definitions described in ISO 6502.

Dumbbell and crescent shaped samples were cut out of the molded sheet for measurement of tensile stress at 100% and 300%, tensile strength, and tear strength. Vulcanizate samples were measured using a universal testing machine (YHS-229WJ) in accordance with ASTM D624-86.

The thermal decomposition behavior of the kaolinite/SBR composite were characterized by a Mettler-Toledo TG-DSC I/1600 HT simultaneous thermal analyzer at a heating rate of 10 °C/min in a flowing nitrogen atmosphere (100 mL/min). Samples are heated from 25 °C to 600 °C.

3. Results and discussion

3.1. X-ray diffraction

The XRD patterns of pure SBR, kaolinite, kaolinite/SBR vulcanizate filled with 20 phr kaolinite and 50 phr kaolinite are shown in Fig. 1. The kaolinite showed two main reflections at 2θ = 12.3° and 24.9°, which correspond to a $d_{(001)}$-value = 0.714 nm and $d_{(002)}$-value = 0.357 nm of kaolinite. The other characteristic reflections of kaolinite at 2θ = 35.0°, 36.0°, 37.8°, 38.6°, and 39.3° were also present (Cheng et al., 2010a; Frost et al., 2001; Qiu et al., 2014; Štengl et al., 2014; Zhang et al., 2011, 2014b). The diffraction pattern of pure SBR vulcanizate exhibited a broad and amorphous reflection at approximately 2θ = 20°. The