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Note

Gas barrier properties and mechanism of kaolin/styrene–butadiene rubber nanocomposites

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ABSTRACT

A series of kaolin/styrene–butadiene rubber (SBR) nanocomposites were prepared by melt blending. The scanning electron microscopy images of the kaolin/SBR nanocomposites showed that the kaolin particles were disorderly and finely dispersed in the SBR matrix. The layer-like particles also had the diameters of 300 nm to 700 nm and the thicknesses of 50 nm to 150 nm. Compared with pure SBR, the kaolin/SBR nanocomposites exhibited excellent gas barrier properties, and the oxygen permeability of the kaolin/SBR nanocomposites decreased by 64% with increased kaolin content to 80 phr. The gas barrier properties of the kaolin/SBR nanocomposites were much better than those of SBR materials filled with precipitated silica or carbon black. The physical dispersion of kaolin layer-like particles had a significant effect on gas barrier property of kaolin/rubber composites. The gas barrier model of the kaolin/SBR nanocomposite was proposed based on the Nielsen model. The results showed that the overall orientation angle of the kaolin layer-like particles in the SBR matrix was approximately 30° to 45°, and which would decrease with increased kaolin content.

1. Introduction

Clay mineral polymer nanocomposites have received great interest from industry and academia researchers. Clay mineral polymer nanocomposites exhibit remarkable improvement in material properties compared with virgin polymer and conventional micro- and macrocomposites because of their ultra-fine phase dimensions and special phase structure (Y. Wang et al., 2005; Z.F. Wang et al., 2005; Ruiz-hitzky and Van Meerbeek, 2006; Pavlidou and Papaspyrides, 2008; Shapiro and Wesselingh, 2008; Zhang et al., 2010a). Improvements in materials caused by clay mineral polymer nanocomposites include increased moduli and strength, enhanced barrier property and thermal stability, and decreased flammability (Agag et al., 2001; Zanetti and Costa, 2004; Ruiz-hitzky and Van Meerbeek, 2006; Liu et al., 2008; Yahaya et al., 2009; Urresti et al., 2011; Zare Shahabadi et al., 2011). Many researchers have applied different approaches to modify clay minerals (Zare Shahabadi et al., 2011) and incorporate the modified clay minerals into polymer matrix by in situ polymerization, solution intercalation and simple melt mixing (Y. Wang et al., 2005; Z.F. Wang et al., 2005). The clay mineral polymer nanocomposites presented outstanding overall performance, and thus have received considerable attention as a new class of engineering material with excellent performance, low-cost, and extensive applications in various fields (Ruiz-hitzky and Van Meerbeek, 2006; Pavlidou and Papaspyrides, 2008; Zhang et al., 2010b).

Many researchers have recently focused on the gas barrier properties of clay mineral rubbery polymer composites because of the wide and mass applications of rubber material. The clay minerals with impermeable layered structure could lengthen the tortuous pathway for gas molecules to traverse the nanocomposites, which can be considered as natural barrier materials (Zhang et al., 2001; Liang et al., 2008; Choudalakis and Gotsis, 2009). Many studies have reported the excellent gas barrier property of rubber polymer material based on modified clay minerals, such as natural rubber, nitrile butadiene rubber, styrene–butadiene rubber and ethylene propylene–diene–terpolymer rubber (Alexandre and Dubois, 2000; Zhang et al., 2001; Gorrasi et al., 2003; Lu and Mai, 2007; Lu et al., 2007; Zhang et al., 2010b; Rattanasom and Prasertsri, 2012).

Previous works about the gas barrier property of clay mineral rubber polymer nanocomposites had focused on montmorillonite, but only a little on kaolin. Kaolin, is one of the important clay minerals, and could be used as functional filler for rubber because of its light color, special stratified structure and availability (Liu et al., 2008). Kaolin could significantly improve the gas barrier and other properties of rubber materials after being modified and finely dispersed into the rubber matrix. In this study, kaolin/styrene–butadiene rubber nanocomposites with excellent gas barrier property were prepared through melt-blending, and the dispersed state and barrier mechanism of kaolin in the rubber matrix were investigated.

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Table 1
The composition formulation of rubbers (%).

Ingredient	Rubber matrix	Zinc oxide	Stearic acid	Accelerant	Sulfur	Fillers
Content/phr	100	3	1	1	1.75	Variable

2. Experimental

2.1. Material

The raw kaolin sample was obtained from SanXing Advance-New Material Company of Zaozhuang Shandong, China, which is a sedimentary kaolin with disordered structure. The chemical component of this kaolin is SiO_2 45.74%, Al_2O_3 35.61%, Fe_2O_3 0.88%, TiO_2 1.23%, Na_2O 0.41%, K_2O 0.32%, MgO 0.11%, CaO 0.12% and MnO less than 0.01%. The silane coupling agent bis-(γ-triethoxysilyl-propyl)-tetrasulfide (Si-69) was supplied by ShuGuang Chemical Group Limited Company of Nanjing Jiangsu, China. Styrene butadiene rubber (SBR) 1500 was supplied by ShenHua Chemical Company of Nantong Jiangsu, China. Carbon black (CB) was obtained from Haitun Company in Tianjin, and precipitated silica (PS) was supplied by Shuanglong Limited Company Tonghua Jinlin. The other materials were available commercially.

2.2. The preparation of modified kaolin

The kaolin samples were dispersed in water with 30% and 0.5% of the dispersing agent, and were allowed to mix for 0.5 h at room temperature. Then, the surface modifier was added into the mixture and reacted with kaolin in the dispersion for 1 h–1.5 h at 60 °C. The modified kaolin was filtered and dried at 110 °C, and then was ground.

2.3. The preparation of rubber/kaolin composites

A series of kaolin rubber nanocomposites were prepared through melt blending. First, the gum rubber was laminated for ten times in an open two-roll mill around room temperature, and then the accelerant, activating agent, reinforcing agent, softening agent and sulfur were added into the laminated rubber successively. Their formulations are shown in Table 1. The mixtures were mixed for about 12 min to 15 min and thin-passed several times. The specimens of composites were cured at the condition of 153 °C/10 MPa × t_{90} and modeled using a 400 mm × 400 mm 25TQLB vulcanizer. The time to optimal cure (t_{90}) was measured by a C2000E non-rotor vulkameter.

2.4. Characterization and measurement

The morphology of kaolin/SBR nanocomposites was characterized using a scanning electron microscopy (SEM) observed by a S4800 low temperature field emission electron microscope produced by Rigaku Corporation, which can also characteristic the dispersion state of kaolin particles in the rubber matrix.

Gas barrier property of kaolin/SBR nanocomposites can be characterized by permeability measurements. The permeability is expressed as the volume rate of the oxygen penetrating the unit thickness rubber membrane at a constant temperature and pressure. The relative permeability is the ratio of the permeability of kaolin/SBR nanocomposites to that of the pure rubber. The permeability of kaolin/SBR nanocomposites was measured with a VAC-V1 gas leakage detector produced by Languang Company in Jinnan, Shandong province. The specimens with thickness of 1 mm and diameter of 70 mm were prepared for permeability measurement. The measurement atmosphere was implemented at 40 ± 0.5 °C and 0.1 MPa pressure of oxygen. Prior to test, the whole measurement system was sealed and evacuated until air vacuum reached a required condition, oxygen was then supplied to the test cell and was ended when the permeant concentration in the specimen reached a constant level, and at which the oxygen flux reached the steady-state value.

3. Results and discussion

3.1. Microstructure of kaolin/SBR nanocomposites

The microstructure of kaolin/SBR nanocomposite is shown in Fig. 1. The kaolin particles with layered structure were finely and disorderly dispersed in the composite matrix, and not obviously large kaolin aggregations were observed in the dispersed region. The layered-like particles of kaolin exhibited significant characteristics with the diameter of 300 nm to 700 nm and the thickness of 50 nm to 150 nm, and the average distances between layer-like particles ranged from dozens of nanometers to hundreds of nanometers. Moreover, the spatial orientation of the plate-like particles in the observed region presented a relatively disorderly state. These results indicate that the prepared kaolin/SBR nanocomposite is classified as flocculated nanocomposite (Gopakumar et al., 2002; Bergaya et al., 2006; Choudalakis and Gotsis, 2009). The kaolin layered-like particles with micro-nano scale presented finely physical dispersion and this could improve the mechanical properties and decreased the gas permeability of the composite.

3.2. Gas barrier property of kaolin/SBR nanocomposites

3.2.1. Influence of kaolin powder size

The obviously differentiated particle sizes of four kaolin samples are shown in Table 2. The oxygen permeability of the nanocomposites was decreased significantly and continuously with the reduction of the kaolin particles size (Fig. 2). The relative permeability was reduced to 0.46 when the powder size of kaolin reached the minimum of four samples. Compared with the pure SBR, the permeability of kaolin/SBR nanocomposites was decreased by 23% to 54%.

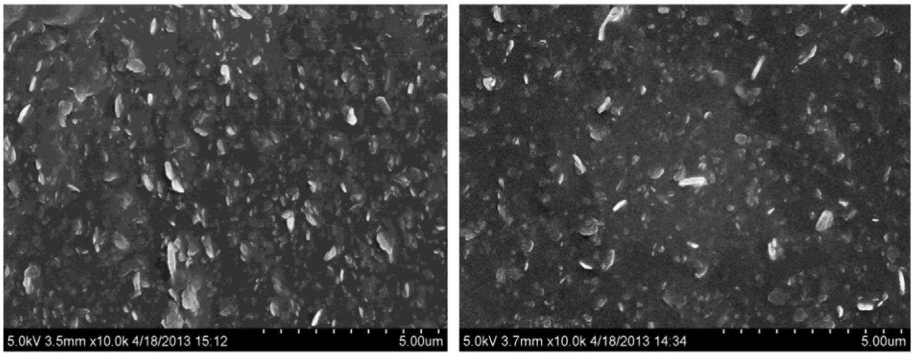

Fig. 1. The overall dispersed state of kaolin layers in the kaolin/SBR nanocomposite.