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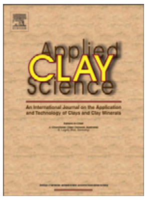

Research paper

Thermal stability and decomposition kinetics of styrene-butadiene rubber nanocomposites filled with different particle sized kaolinites

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ABSTRACT

A series of styrene-butadiene rubber (SBR) nanocomposites filled with different particle sized kaolinites are prepared via a latex blending method. The thermal stabilities of these clay polymer nanocomposites (CPN) are characterized by a range of techniques including thermogravimetry (TG), digital photos, scanning electron microscopy (SEM) and Raman spectroscopy. These CPN show some remarkable improvement in thermal stability compared to that of the pure SBR. With the increase of kaolinite particle size, the residual char content and the average activation energy of kaolinite SBR nanocomposites all decrease; the pyrolysis residues become porous; the crystal carbon in the pyrolysis residues decrease significantly from 58.23% to 44.41%. The above results prove that the increase of kaolinite particle size is not beneficial in improving the thermal stability of kaolinite SBR nanocomposites.

1. Introduction

Polymers filled by layered clay mineral particles have gained a significant research interest in the past two decades since the invention of nylon–clay based nanocomposites by the Toyota R&D group (Pavlidou and Papaspyrides, 2008). The clay minerals modified by organic coupling agents can be endowed with good compatibility and dispersibility (Bergaya et al., 2011). The incorporation of modified clay minerals can remarkably improve the properties of clay polymer nanocomposites (CPN), such as mechanical, thermal and barrier properties (Choudalakis and Gotsis, 2009; Coleman et al., 2011; Lagaly, 1999). The organo-clay minerals were used in various polymer systems (Bergaya et al., 2013). Rubber in particular is an important class of polymer material due to their specific applications. Much research about clay rubber nanocomposites has been carried out (Galimberti, 2011; Gu et al., 2009; Liu et al., 2008; Shi et al., 2007; Varghese and Karger-Kocsis, 2003; Vinay Kumar and Prakash Chandra, 2010; Yahaya et al., 2009; Zhang et al., 2010). Some improved results in mechanical and thermal properties of the rubber nanocomposites were observed.

Kaolinite has a wide variety of applications in industry, including ceramic materials, paper fillers, coating pigments, an extender in water-based paints and rubber fillers (Bergaya et al., 2013; Liu et al., 2008; Zhang et al., 2010) and other polymeric materials (Gardolinski et al., 2000; Xia et al., 2010). Kaolinite is a 1:1 type layer structure with the basic unit consisting of a tetrahedral sheet of SiO_4 siloxane units and an octahedral sheet of AlO_2 $(OH)_4$. Kaolinite particles after modification can be evenly dispersed in a polymer matrix. The layered structure can act as the barrier cell in polymers and improve the thermal stability (Mohan et al., 2011), gas barrier (Stephen et al., 2006), heat shielding and flame retardant property of kaolinite polymer nanocomposites (Chen et al., 2009; Gardolinski et al., 2000; Gilman, 1999).

In this paper a series of experiments are undertaken to investigate the relationships between the thermal stability of the filled SBR nanocomposites and the kaolinite particle size. The thermal stability and thermal decomposition behaviour of the SBR nanocomposites filled with different particle sized kaolinites are characterized by TG, DTG and thermal decomposition kinetics parameters. The microstructure changes of the pyrolysis residues are measured by digital photography, SEM micrographs and Raman spectroscopy which further explains the influence of the kaolinite particle size on the thermal stability and thermal decomposition behaviour of kaolinite SBR nanocomposites.

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2. Experimental

2.1. Preparation of the kaolinite samples

The raw kaolinite originates from Zhangjiakou in China, and belonged to a kind of clay with hydrothermal alteration origins. Four kaolinite samples are obtained by a free settling method. Firstly, the raw kaolinite is blended with water at a mass ratio of 1:4, and 0.5% sodium hexametaphosphate is added as dispersant. The pH of the dispersion was adjusted to 10.0 using a sodium hydroxide solution. The dispersion was stirred for 2 h. Then, the upper dispersion is extracted to another container with a siphon method after settling for 10 min. The sand and mud at the bottom are separated from the kaolinite dispersion. The new dispersion is resettled according to a specified set time. After settling for 480 min, the upper dispersion of 2 cm height is extracted to a selecting container and labelled as Kaol-1; the remaining dispersion is stirred for 1 h and resettled for 184 min. The upper dispersion of 1 cm height is obtained through siphoning, and labelled as Kaol-2. The remaining dispersion is stirred for 1 h again and resettled for 114 min; the upper dispersion of 1 cm height is extracted through siphoning, and labelled as Kaol-3. The residual dispersion is labelled as sample Kaol-4. The particle size characteristics are shown in Table 1.

2.2. Preparation of the kaolinite rubber nanocomposites

Firstly, a 2.0% silane coupling agent (KH-Si69) is added into the kaolinite dispersion and stirred for 1 h using a mechanic mixer at around 80 °C. The modified kaolinite samples are blended with SBR1500 latex (22.4% solid content) for around 20 min under a low stirring rate, and flocculated with the dilute hydrochloric acid solution (1.0%). The compounds are dried in a vacuum drier at around 80 °C. Then the dried compounds are processed into kaolinite SBR nanocomposites using a two roll mill (Gu et al., 2009; Lagazzo et al., 2010). The formulation of kaolinite SBR nanocomposites (phr) is as follows: SBR, 100.00; zinc oxide, 3.00; stearic acid, 1.00; accelerator NS, 1.00; sulphur, 1.75; kaolinite, 50; phr is the abbreviation of mass parts per 100 mass parts rubber. The preparation procedure of kaolinite rubber nanocomposite is briefly described as follows: the dried compound contained kaolinite and raw rubber are plasticized for 3–5 min in the XK-160 open mill around 40 °C, the spacing between the rolls is about 7 mm, and the roller rate is 6.98 m/min; then ZnO, stearic acid, accelerator NS and sulphur are added into the plasticized compounds; in turn, the roller spacing was adjusted to 3–4 mm and mixed evenly for 12–15 min at 60 °C. A small part of the obtained kaolinite rubber compounds (12.0 g) is used to test the optimum cure time in a ZWL-III non-rotor vulkameter. The rest of the kaolinite rubber compounds are put into a 150 × 150 × 2 mm mould and vulcanized on a 25QLB vulcanizing machine at 153 °C and 10.0 MPa pressure up to the optimum cure time. The cured rubbers are cooled rapidly in air at the end of the curing cycle. At last, four SBR nanocomposites filled by Kaol-1, Kaol-2, Kaol-3 and Kaol-4 are obtained, and individually labelled as Kaol-1 SBR, Kaol-2 SBR, Kaol-3 SBR and Kaol-4 SBR.

2.3. Characterization

The particle size distribution of the four kaolinite samples is measured by using a Mastersizer 2000 laser particle size analyser of Malvern company (wet, cycle injection mode, and test time: 1–2 min).

Table 1
Particle size characteristic ($D_{10}D_{50}D_{90}$) and specific surface area (S_{BET}).

Samples	D_{10} (μ m)	D_{50} (μ m)	D_{90} (μ m)	S_{BET} (m^2/g)
Kaol-1	0.466	1.004	2.115	7.01
Kaol-2	0.655	1.401	2.590	5.13
Kaol-3	0.804	1.935	3.871	3.99
Kaol-4	0.796	2.184	6.305	3.69

The thermal stability of kaolinite and kaolinite SBR nanocomposites are characterized with a Setaram Evolution 2400 analyser by heating from 21 to 600 °C under a nitrogen atmosphere at a heating rate of 3, 5, 10 and 20 K/min. In order to investigate the influence of kaolinite particle size on the thermal stability of kaolinite SBR nanocomposites and the structure properties of decomposition residues, kaolinite SBR nanocomposites are put in an alumina crucible and heated for 1 h under a nitrogen atmosphere in a tubular furnace (SK-G06123K) at the selected temperatures (550 and 600 °C). The structural changes of the pyrolysis residues are characterized using digital photography and electron microscopic examination. The digital photos are obtained using the FUJIFILM S2900 HD digital camera. The pyrolysis residues of SBR composites are adhered to Cu stubs using a conductive adhesive, and scanning electron microscopy (SEM) micrographs are obtained with a S4800 LV electron microscope under 3.0 kV accelerating voltage.

The Raman spectra are recorded at a resolution of 4 cm^{-1} using an inVia Laser confocal Raman spectroscopy system, at conditions of 514.5 nm laser wavelength, 65 um slit-width, 10 s time constant and 3 scanning times. The laser power of the incident beam on the sample is kept below 2 mW to prevent irreversible thermal damage to the sample. The samples are scanned between 4000 cm^{-1} and 400 cm^{-1}, with a data acquisition time of 20 s. The spectral regions of 1800–1000 cm^{-1} and 3400–2200 cm^{-1} are studied by curve fitting with PeakfitV4.0 software. Peak decomposition is accomplished using the Gaussian/Lorentzian functions. The parameters are fitted to the original data using the standard error ($SE < 10^{-2}$) and the correlation coefficient ($R^2 > 0.999$) as metrics for goodness of fit. The influence of the baseline is reduced by performing baseline correction before curve fitting. The spectral regions provide the most valuable data on the microstructure of carbons resulting from the pyrolysis of kaolinite SBR nanocomposites. The band positions, intensities, widths and area are determined. The defects of microcrystalline carbon for the samples are calculated from the integrated intensities of the D and G bands on the Raman spectra, equal to the area ratio of the D_1 and G bands. The relative concentration of amorphous carbon is calculated from the intensity of peaks at around 1530 cm^{-1} (D_3) and 1200 cm^{-1} (D_4) relative to that of D_1 and G bands (Potgieter-Vermaak et al., 2011; Reich and Thomsen, 2004).

2.4. Kinetics calculation

For kinetic analysis, it is assumed that a solid (polymer) will decompose into a new solid and some gases. The thermogravimetric rate is given by Eq. (1) according to the Arrhenius equation and the non-isothermal kinetics theory (Flynn and Wall, 1966).

$$\frac{\mathrm{dC}}{\mathrm{dT}} = \frac{A}{\beta}(1-C)^n e^{-E/RT} \tag{1}$$

where C is defined as the degree of conversion, equals the mass of material loss divided by the total mass loss as T or t; T, absolute temperature; β, constant heating rate; A, pre-exponential factor of the Arrhenius equation; E, activation energy; and R, the gas constant.

Eq. (1) is the basic expression for the investigation of thermal decomposition kinetics. According to the Flynn–Wall differential method (Flynn and Wall, 1966; Koga, 2013) and the Ozawa integral method (Ozawa, 1965, 1992; Park et al., 2000), the thermal kinetics parameters are obtained from the Eq. (2).

$$\lg\beta = \lg\frac{AE}{R} - lgF(C) - 2.315 - 0.4567\frac{E}{RT} \tag{2}$$

$F(C)$ is a function of degree of conversion. Therefore, from mass loss vs. temperature thermograms at several heating rates, one may determine the corresponding temperatures at a constant mass loss. Then, from the slope of a plot of $\lg\beta$ vs. $1/T$, the activation energy can be calculated using Eq. (2).