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Research paper

Preparation of functionalized kaolinite/epoxy resin nanocomposites with enhanced thermal properties

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ABSTRACT

In this study, kaolinite/epoxy resin nanocomposites were fabricated using functionalized kaolinite (KGS) as filler. The KGS was prepared by silylation of 3-aminopropyltriethoxysilane onto the surface of mechanically ground kaolinite. The addition of KGS into epoxy resin matrix improved the storage modulus and glass-transition temperature, compared to those of epoxy resin nanocomposites filled with raw kaolinite. Furthermore, with the increase of KGS loading, the coefficient of thermal expansion decreased gradually, and the dielectric constant slightly increased when compared to that of pure epoxy resin. The presence of kaolinite led to an improvement in the water resistance property of kaolinite/epoxy resin nanocomposites. This research provided guidance to construct high-performance kaolinite/epoxy resin nanocomposites.

1. Introduction

Inorganic particles-polymer nanocomposites including clay mineral-polymer nanocomposites (CPN) (Bergaya et al., 2013; Suter et al., 2015), carbon-polymer nanocomposites (Bai et al., 2011; Sun et al., 2013), ceramic-polymer nanocomposites (Dang et al., 2013), bioinspired nanocomposites (Bouville et al., 2014; Wegst et al., 2015), *etc.*, have attracted great attention during the past three decades, because they often exhibit remarkable thermal, mechanical, and barrier properties. Compared with each individual constituent, these inorganic particles-polymer nanocomposites combine the best properties of both phases, yielding potential performance well beyond those of each individual constituent material (Nair et al., 2010). Based upon these features, inorganic particles-polymer nanocomposites enjoy their applications in wide fields, such as medical devices, automotive and aerospace components, packaging, and building materials *etc.*

Among the various inorganic particles, clay minerals are one of the favorite choices, owing to their intrinsic properties such as chemical and thermal stability, easy processing, abundant resources and low cost. Since the first report on CPN in the early 1990s, there have been thousands of research investigations with the concept of clays as fillers for polymer matrices (Galimberti et al., 2013). Among them, montmorillonite is the most widely chosen filler, mainly due to its swelling property leading to exfoliation and high interlayer ion exchange capacity (Liu et al., 2011; Hasani-Sadrabadi et al., 2013; Huskic et al., 2013; Tong et al., 2014). Kaolinite is also an abundant clay mineral, which has been widely applied in ceramics, paper fillers, and also as adsorbents in pollution control processes. However, much less research has been done on kaolinite based polymer nanocomposites, compared with that on 2:1 layer type montmorillonite (Xia et al., 2010). Kaolinite is a dioctahedral 1:1 layer clay mineral with an ideal chemical formula of $Al_2Si_2O_5(OH)_4$. Its layer was constituted by superposition and bonding of a Si tetrahedral sheet with an Al octahedral sheet. Although both montmorillonite and kaolinite possess plate like structures, their cohesive energies between layers differ significantly. Kaolinite has no intercalated charge-balancing cations because of little or no isomorphous substitution in the tetrahedral and octahedral sheets unlike montmorillonite. Adjacent layers are linked by hydrogen bonds, which makes delamination or the direct intercalation of kaolinite with inorganic and/or organic molecules much harder than those of swelling clays (Tunney and Detellier, 1996; Letaief and Detellier, 2005; Detellier and Letaief, 2013). For the same reason, it is also hard to functionalize the surfaces of kaolinite leading to poor dispersion in polymer matrices. To solve these problems, a silylation reaction was performed on ground

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kaolinite and was successfully incorporated in polymer without resorting to the intercalation of highly polar, small molecules in kaolinite under severe reaction conditions (Tao et al., 2014b). The effect of such a functionalized kaolinite on epoxy curing was also evaluated by Tao et al. (2014a) who found that the addition of functionalized kaolinite could decrease activation energy and accelerate the curing reaction of epoxy resin.

In this work, kaolinite/epoxy resin (Kao/EP) nanocomposites were fabricated using KGS as filler and the effect of KGS on thermal properties of Kao/EP nanocomposites was investigated. The addition of KGS improved the thermal stability and glass-transition temperature (T_g) of the Kao/EP nanocomposites, compared to those CPN prepared by the addition of raw kaolinite. The coefficient of thermal expansion (CTE) values decreased with the increase in the KGS loading. Furthermore, the water absorption by the product decreased after the loading of KGS. This research is expected to provide guidance to construct kaolinite/polymer nanocomposite with high-performance and thus, may lead to new applications of kaolinite in polymer nanocomposites.

2. Experimental

2.1. Materials

An epoxy resin monomer, 3,4-epoxycyclohexylmethyl-3,4-epoxycyclo-hexane carboxylate (ERL 4221, Tetrachem, China) with an epoxy equivalent mass of 127.0 g mol^{-1} was used and purchased from The Dow Chemical Company. The curing agent used was methylhexahydrophthalic anhydride (MHHPA, ≥98%, Bangcheng CO. LTD, China) and activator was 2-ethyl-4-methylimidazole (EMI, 99%, Bangcheng CO. LTD, China). The raw kaolinite was obtained from Maoming Kaolin Science and Technology Co., LTD, China. The raw kaolinite had been already treated to remove impure minerals except quarts by supplier, and used in this study as received without further treatment. 3-Aminopropyltriethoxysilane (APTES) was purchased from Aldrich (≥98%) and was used as received.

2.2. Functionalization of kaolinite

A selected amount of kaolinite was ground for 6 h using a Fritsch pulverisette 5/2-type laboratory planetary mill at a rate of 370 rpm, according to a previous work (Tao et al., 2014b). 4.0 g of ground kaolinite was dispersed in 40 mL of cyclohexane and 4.0 g of APTES was slowly added into the clay dispersion under stirring. The mixture was then stirred for 24 h at 80 °C. The reaction product was collected by centrifugation and washed with cyclohexane in order to remove the excess silane. After drying at 80 °C for 24 h, the grafted product (designated as KGS) was collected for further reaction.

2.3. Preparation of the kaolinite/epoxy resin nanocomposites

KGS/epoxy resin nanocomposites with different amounts of KGS were prepared by a solvent-free method. In a typical process, a stoichiometric amount of epoxy resin, curing agent, activator, and KGS were mixed by a high speed mixer under vacuum. The uniform CPN dispersion was then gently poured into a mold, cured at 140 °C for 2 h, and then heated at 220 °C for further 2 h. The KGS loadings in the KGS/epoxy resin nanocomposites were 3 $_{wt}$%, 5 $_{wt}$% and 10 $_{wt}$%, respectively. The corresponding KGS/epoxy resin nanocomposites were designated as KGS-3/EP, KGS-5/EP, and KGS-10/EP, respectively. For comparison, pure epoxy and raw kaolinite/epoxy resin nanocomposite with 5 $_{wt}$% kaolinite loading (Kao-5/EP) were also prepared following the same procedure.

2.4. Characterization

The cross polarization magic angle spinning solid-state nuclear magnetic resonance spectra (^{29}Si CP/MAS NMR) were acquired using a Bruker Advanced 300 NMR spectrometer operating at 59.63 MHz. The contact time was 5 ms, the recycle delay was 3 s, and the spinning rate was 5.5 kHz. Tetramethylsilane was used as the external reference. The fractured surface morphologies of the CPN were examined by scanning electron microscopy (SEM, FEI Nova NanoSEM 450), working in the secondary electrons mode at a high voltage of 10 kV. The thermogravimetric analysis (TG) of the clays and CPN were conducted using a TA Instrument thermobalance (TA Q600), under 100 mL/min nitrogen flow. The samples were heated from 30 to 800 °C with a heating rate of 10 °C/min. Dynamic mechanical thermal analysis (DMA) was performed on a dynamic mechanical thermal analyzer (Q800, TA Instruments) in three-point bending mode at a frequency of 1 Hz with a constant heating rate of 3 °C/min ranging from 30 to 300 °C. Specimen dimensions were 30 mm × 6 mm × 2 mm. The T_g value was taken to be the temperature at the maximum of the tan δ peak.

The dielectric properties at room temperature were measured using an impedance analyzer (Agilent 4294A) in the frequency range of 100 Hz to 10 MHz. The samples were coated with silver paste for test. The CTE of CPN were obtained using Thermo-Mechanical Analyzer (TMA 402F3, Netzsch Instruments) by applying a force of 0.02 N with a heating rate of 10 °C/min from room temperature to 300 °C in a nitrogen atmosphere. CTE values were calculated by the following equation:

$$CTE = \frac{dL}{dT} \times \frac{1}{L_0} \tag{1}$$

where dL/dT was the slope of length-temperature curve for the sample, and L_0 is the initial length at room temperature.

Water absorption of the CPN was measured using weighing method. Firstly, the specimens with a dimension of 20 mm × 20 mm × 2 mm were put into oven at 80 °C for 24 h and then weighed. Secondly, the specimens were immersed in distilled water at a temperature of 25 °C. After 24 h, the specimens were taken out and wiped with absorbent paper to remove the water on the surfaces and then reweighed. The water absorptions (WA) of the samples were calculated by using following equation:

$$WA = \frac{W_1 - W_0}{W_0} \times 100\% \tag{2}$$

where W_0 and W_1 were the weight of dry material (the initial weight of materials prior to exposure to the water absorption) and weight of materials after exposure to water absorption, respectively.

3. Results and discussion

In a previous study, the effect of grinding on the resulting chemical structure of ground kaolinite had been investigated systematically (Tao et al., 2014b). It was demonstrated that physical grinding treatment would lead to layer disorder and fracture of kaolinite. Some interlayer surface hydroxyl groups of kaolinite would be exposed, and newly broken bonds with undercoordinated metal ions would generate after grinding, which provide new active sites for silanes to react under mild conditions. Here, solid-state ^{29}Si MAS NMR spectrum was used to identify the Si environments of the ground kaolinite and KGS (Fig. 1). Both ground kaolinite and KGS exhibit a resonance at −92.3 ppm (Q^3[$Si(OSi)_3OM$], where M represents Al, Fe, *etc.*), corresponding to the Si in the tetrahedral clay sheets. For KGS, a new resonance was observed at −66.7 ppm, which was attributed to the hydrolyzed tridentate bonding (T^3, [$Si(OSi)_3R$], where $R = CH_2CH_2CH_2NH_2$). This demonstrated the formation of different kinds of siloxane bonds between silane and kaolinite and among silane molecules (Tao et al., 2011). The degree of functionalization of the KGS was further estimated by TG. The thermal decomposition of KGS displayed two new mass losses at around 400 and 550 °C in the TG curves (Fig. 2). These mass losses could be attributed to the decomposition of the covalently