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Synthesis of exfoliated polystyrene/montmorillonite nanocomposite by emulsion polymerization using a zwitterion as the clay modifier

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Abstract

Montmorillonite (MMT) was modified with zwitterion aminoundecanoic acid (AUA). First AUA was protonized to facilitate molecules to get into the galleries of the montmorillonite to accomplish ion exchange, and the carboxyl groups were then ionized in the alkaline aqueous media to enable exfoliation of the clay. It was demonstrated by rheological measurements and atomic force microscopic studies that exfoliation of the clay driven by the electrostatic repulsion took place in an alkaline medium. Polystyrene/montmorillonite (PS/MMT) nanocomposite was synthesized via emulsion polymerization in the presence of the modified MMT. The exfoliated microstructure of the composites was studied by the X-ray diffraction and transmission electron microscopy. The exfoliated PS/MMT nanocomposite showed a greatly improved modulus, a higher glass transition temperature and a better thermal stability compared to the neat polystyrene and the intercalated PS/MMT composites.

Keywords: Nanocomposite; Emulsion polymerization; Polystyrene; Montmorillonite; Aminoundecanoic acid

1. Introduction

Polymer/layered silicate nanocomposites have been extensively studied in recent years [1–5]. By virtue of the layered silicate, these nanocomposites show many desirable properties, such as improved modulus and strength, higher heat distortion temperature, enhanced barrier characteristics and reduced gas permeability. Depending on the microstructure of the clay dispersed in the polymer matrix, two different types of composites can be obtained. In the intercalated composites, polymer chains are inserted into the interlayer space of the stacking silicate platelets, but the silicate layers are still well ordered although the basal space is greatly expanded. In the exfoliated composites, the discrete clay layers are randomly dispersed in the continuous polymer matrix. The exfoliated nanocomposites are desirable for property enhancement.

Polystyrene (PS) is a commercialized and mass-productive polymer. Hence, continuing research efforts have been devoted to the development of polystyrene/montmorillonite (PS/MMT) nanocomposites. Various methods based on simple mechanical mixing, bulk polymerization, solution polymerization and emulsion polymerization have been employed. Among the approaches

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mentioned above, emulsion polymerization is more attractive for the ease of manipulation, low cost and environmental friendliness.

Noh and Lee [6] and Kim et al. [7] have synthesized intercalated PS/MMT nanocomposites by emulsion polymerization in the presence of pristine MMT. In order to improve the compatibility with hydrophobic polymer, the clay was organically modified. Thus Laus et al. [8] and Qutubuddin et al. [9] prepared PS/reactive organoclay intercalated nanocomposites by emulsion polymerization. On the other hand, polar monomers have been introduced to copolymerize with styrene to increase the polarity of the polymer matrix, Choi and coworkers synthesized a series of MMT nanocomposites with PS [10], poly (methyl methacrylate-co-styrene) [11] and poly (styrene-co-acrylonitrile) [12] by soap-free emulsion polymerization using an ionic comonomer 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) to stabilize the latex.

So far the majority of PS/MMT nanocomposites prepared via emulsion polymerization showed an intercalated morphology. In this paper, we use a novel zwitterion amino acid to modify the clay, and PS/MMT composite is synthesized via emulsion polymerization in the presence of the modified clay. This approach is proved to be effective for the preparation of water-borne exfoliated polymer/clay nanocomposites. For comparison, emulsion polymerization in the presence of cetyltrimethyl ammonium bromide-modified MMT or pristine sodium montmorillonite are also studied.

2. Experimental

2.1. Materials

Sodium montmorillonite (Na-MMT) with a cation-exchange capacity (CEC) of 100 meq/100 g was supplied by Zhangjiakou Clay Mineral Corp. (Zhangjiakou, China). Styrene was of polymerization grade from Beijing Chemical Factory, and was distilled under reduced pressure before use. Ammonium persulfate (APS), sodium dodecyl sulphate (SDS), and cetyltrimethyl ammonium bromide (CTAB) were chemical reagents from Beijing Chemical Reagents Company. Aminoundecanoic acid (AUA) was purchased from Aldrich Chemical Co., Inc.

2.2. Preparation of modified MMT

2.2.1. The organoclay modified with AUA

Na-MMT (10 g) was dispersed in 1000 ml deionized water, and the dispersion was stirred vigorously overnight. AUA (3.0 g) was dissolved in 100 ml deionized water, and the pH value was adjusted to 3 using 0.1 mol/l HCl solution to protonize AUA. The AUA solution was slowly added to the clay suspension, and the mixture was stirred for 24 h at room temperature. The ion-exchanged clay was filtered, thoroughly washed with acidified water (pH 3) and dried at 50 °C in a vacuum oven. The organically modified MMT is denoted as A-MMT.

2.2.2. The organoclay modified with CTAB

Na-MMT (10 g) was dispersed in 1000 ml deionzed water, and the dispersion was stirred vigorously overnight. 5.5 g CTAB was dissolved in 100 ml deionized water. The CTAB solution was slowly added into the clay suspension, the mixture was stirred for 24 h at room temperature. The ion-exchanged clay was filtered, thoroughly washed with deionized water and dried at 50 °C in a vacuum oven. This organically modified MMT is denoted as C-MMT.

2.3. Synthesis of polystyrene/MMT composites via emulsion polymerization

2.3.1. The polystyrene/Na-MMT composite

Na-MMT (1 g) was dispersed in 110 ml deionzed water, and the dispersion was stirred vigorously overnight. Styrene (20 g), 0.2 g APS, and 0.2 g SDS were then introduced. After agitating for 30 min at room temperature under a nitrogen stream, the mixture was heated to 75 °C and kept for 6 h to effect polymerization.

2.3.2. The polystyrene/C-MMT composite

C-MMT (1 g) and 20 g styrene were mixed and treated in an ultrasonic bath for 30 min at 0 °C. 0.2 g APS and 0.2 g SDS were dissolved in 110 ml deionized water. Then the styrene/C-MMT mixture was introduced. After agitating for 30 min at room temperature under a nitrogen stream, the mixture was heated to 75 °C and kept for 6 h to effect polymerization.

2.3.3. The polystyrene/A-MMT nanocomposite

A-MMT (1 g) was dispersed in 110 ml deionzed water; the pH value was adjusted to 10 using 0.1 mol/l NaOH solution. The A-MMT suspension was stirred at room temperature overnight. Styrene (20 g), 0.2 g APS and 0.2 g SDS were then introduced. After agitating for 30 min at room temperature under a nitrogen stream, the mixture was heated to 75 °C and kept for 6 h to effect polymerization.

2.4. Characterization

Size exclusion chromatography (SEC; Waters, U.S.A.) was used to determine the molecular weights and polydispersity indices of PS. For the PS/MMT composites, the polymer was recovered by extraction with THF in a Soxhlet extractor.