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SHORT COMMUNICATION

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Exfoliation of layered double hydroxide in polystyrene by in-situ atom transfer radical polymerization using initiator-modified precursor

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Abstract Exfoliated nanocomposite, based on Zn, Al layered double hydroxide (LDH) and polystyrene (PS), has been achieved by in-situ atom transfer radical polymerization reaction from initiator-modified LDH. The exfoliated structure is characterized by X-ray diffraction and transmission electronic microscope. The results suggest that the exfoliated ZnAl(DS) LDH sheets with a thickness of less than 1 nm disperse individually in the PS matrix, and the thermal stability of the nanocomposite shows a marked improvement. When the 50 wt% weight loss is selected as a comparison point, the decomposition temperature of PS/LDH nanocomposite is about 45 °C higher than that of pure PS.

Keywords Polystyrene · Intercalation nanocomposite · Layered double hydroxide · Thermal stability

Introduction

Layered double hydroxides (LDHs), known as hydrotalcite-like materials, are anion clays, which consist of positively charged brucite [$Mg(OH)_2$]-like layers with divalent cations partly substituted by trivalent cations in octahedral sites, separated by interlayer anions and water molecules [1]. Their idea structures are represented by the formula $[M^{2+}_{1\text{-}x}M^{3+}_{x}(OH)_2]^{x+}\ A^{n-}_{x/n}\cdot mH_2O$, where M^{2+} and M^{3+} are divalent and trivalent metal cations, such as Mg^{2+}, Al^{3+}, respectively, A is an anion, such as Cl^-, CO_3^{2-}, SO_4^{2-}, and NO_3^- . These compounds have received considerable attention, in recent years, because of theirs technological importance as catalyst, optical materials, and anion exchangers [2]. Because of their highly tunable properties, LDHs are considered as a new emerging class of the most favorable layered crystals for preparation of multifunctional polymer/layered crystal nanocomposites [3].

A large variety of polymers, such as poly(styrene sulfonate) [4, 5], polyacylate [6], and poly(vinyl achol) [7, 8], have been intercalated into the interlayers of LDHs by ion-exchange reaction or in-situ polymerization. However, the exfoliation of LDHs layers is very difficult because their layers are tightly bound together by the high layer charge density [9]. Most discussions of polymer/LDHs composites mainly focused on the intercalation reaction of the polymer molecule chains into the

LDHs galleries. However, the exfoliation reaction of polymer/LDHs systems was rarely discussed in recent literature.

Recently, exfoliated polymer/LDHs nanocomposites was developed in several polar polymers. O'Leary et al. [10] have reported that delamination of the MgAl-LDH in polar acrylate monomers with the help of high shear, subsequent polymerization of the monomers containing the LDH dispersion gave exfoliated polyacrylates/LDH nanocomposites. Hsueh et al. [11, 12] have obtained the polyimide/LDH and epoxy/LDH nanocomposites by grafting the polymer chains on the surfactant intercalated in LDH. Exfoliated polyethylene-*g*-maleic anhydride/MgAl-LDH nanocomposites were synthesized by the solution intercalation at the authors' laboratory [13].

The delamination of LDH in nonpolar polymers was prepared by refluxing of organo-modified LDH in polyethylene solution [14]. However, complete delamination of LDHs in nonpolar polymer by in-situ polymerization has not yet been reported. In this study, we develop a novel approach of exfoliating LDH by in-situ atom transfer radical polymerization (ATRP) reactions in styrene, i.e., anchoring an ATRP initiator inside the galleries of LDH hosts followed by intercalation and polymerization of styrene gives directly dispersed polystyrene (PS)/LDH nanocoposites.

Experimental

All reagents used in this work are analytical grade obtained from China National Medicines Group (Shanghai Chemical Reagents Company) and used without further purifications expect for styrene (St).

The $Zn_3Al(OH)_8Cl$ LDH precursor [$Zn_3Al(Cl)$] was prepared by the coprecipitation method previously described by Bonnet et al. [15]. A mixed solution of zinc chloride (0.75 M) and aluminum chloride (0.25 M) was slowly pumped into 150 mL decarbonated water under flowing N_2 gas, at a constant pH $= 8.0 \pm 0.2$ adjusted by simultaneously drop-wise addition of a 1.0 M NaOH solution. The resulting suspension was aged in the mother liquid at 60 °C for 1 day, and then it was recovered by six dispersion and centrifugation cycles in deionized water. The surfactant modified LDH [$Zn_3Al(DS)$] was obtained from the anion exchange reaction of 1.0 g of $Zn_3Al(Cl)$ with 100 ml 0.1 M sodium dodecyl sulfate at 60 °C. Exchange of dodecyl sulfate for α-bromobutyrate was carried out in ethanol/deionized water (5 %v/v) at 20 °C, yielding $Zn_3Al(DS\text{-}BrB)$.

In a typical polymerization, a 10-mL flask was charged with 0.1 g $Zn_3Al(DS\text{-}BrB)$ (0.076 mmol initiator). A solution containing 2.0 g styrene (19.2 mmol), 0.011 g CuBr (0.076 mmol), and 0.036 g 2,2′-bipyridinyl (0.228 mmol) was added to the flask. The content was then frozen with liquid nitrogen and purged with nitrogen by applying a vacuum, then an exhausting-refilling process was operated three times. Polymerization was carried out at 120 °C for 12 h. The viscous mixture was diluted with xylene and the polymer-grafted LDH was precipitated in ethanol. The solid material was collected and dried at 80 °C under vacuum to constant weight.

For comparison, a radical polymerization was performed on 2.0 g of styrene containing of 0.1 g of $Zn_3Al(DS)$ or $Zn_3Al(DS\text{-}BrB)$ initiated by BPO (0.2 wt%) at 80 °C for 12 h.

Elemental chemical analyses for Zn, Al were carried out by atomic emission spectroscopy (ICP/AES) in an Atomscan Advantage (Thermo Jarrell Ash Corporation (USA)) instrument after dissolving the samples in nitric acid. Carbon analysis was carried out in a VARIO EL III elemental analyzer. The X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max-rA rotating anode X-ray diffractometer equipped with a Cu Kα tube and Ni filter ($\lambda = 0.1542$ nm). The transmission electron microscopy (TEM) image was obtained on a Hitachi H-800 transmission electron microanalyzer with an accelerated voltage of 200 kV. The sample was ultramicrotomed with a diamond knife on an LKB Pyramitome to give 100-nm thick slices. The thermogravimetric analysis (TGA) was preformed on a Shimadzu TGA-50H thermoanalyzer under an airflow rate of 6×10^{-5} m^3/min at a scan rate of 10 °C/min.

Results and discussions

A Zn:Al ratio of $3.08 \pm 0.03{:}1$ was found for $Zn_3Al(Cl)$, $Zn_3Al(DS)$, and $Zn_3Al(DS\text{-}BrB)$. The ratio of dodecyl sulfate to α-bromobutyrate determined by the element analysis was 0.52:0.46 in $Zn_3Al(DS\text{-}BrB)$. The total amount of organics is slightly lower than one. This was attributed to the presence of a small amount of intercalated CO_3^{2-} in the starting LDH, which cannot be substituted. Actually, the very small amount of $Zn_3Al(CO_3^{2-})$ has no effect on the exfoliation of $Zn_3Al(DS)$. A similar observation has been reported in the literature [10, 13, 16].

Figure 1a shows the XRD patterns of $Zn_3Al(DS)$. The interlayer's distance is about 2.64 nm inducing from the reflection peak at 3.4°, which gives the straightforward evidence for intercalation of dodecyl sulfate anions. The basal spacing of the ZnAl(DS) decreases from 2.64 nm to 2.42 nm (Fig. 1b) with the intercalation of BrB anions, which indicates that dodecyl sulfate anions have been partially substituted by BrB anions and a rearrangement of the DS chains happened. The change of the DS orientation with the intercalation of BrB anions was driven by entropy gain. When the longer DS

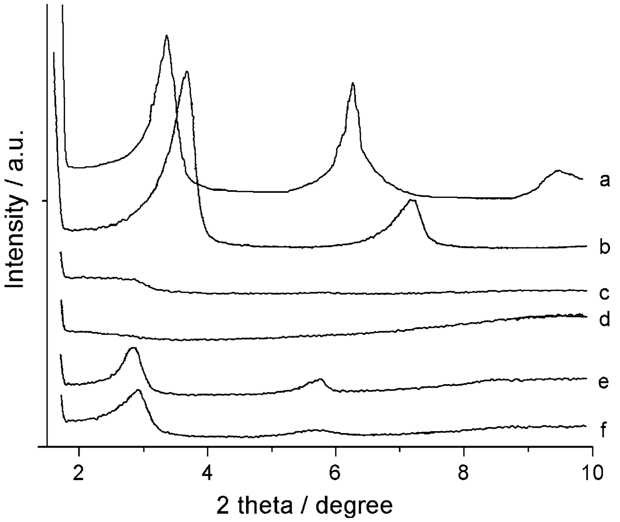


Fig. 1 The X-ray diffraction patterns of **a** $Zn_3Al(DS)$, **b** $Zn_3Al(DS\text{-}BrB)$, **c** composite after 8 h time of polymerization, **d** composite after 12 h time of polymerization, **e** composite of $Zn_3Al(DS)$ from thermal polymerization, and **f** composite of $Zn_3Al(DS\text{-}BrB)$ from thermal polymerization

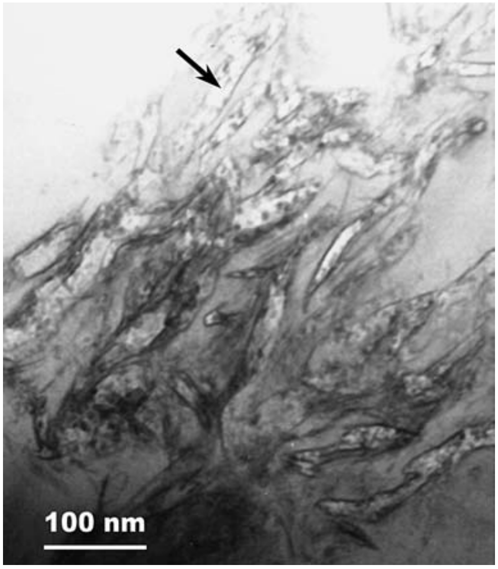


Fig. 2 Transmission electron microscopic image of exfoliated PS/LDH nanocomposite

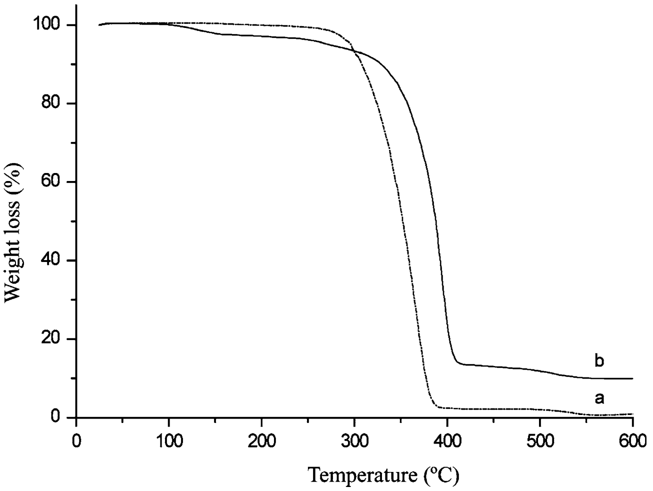


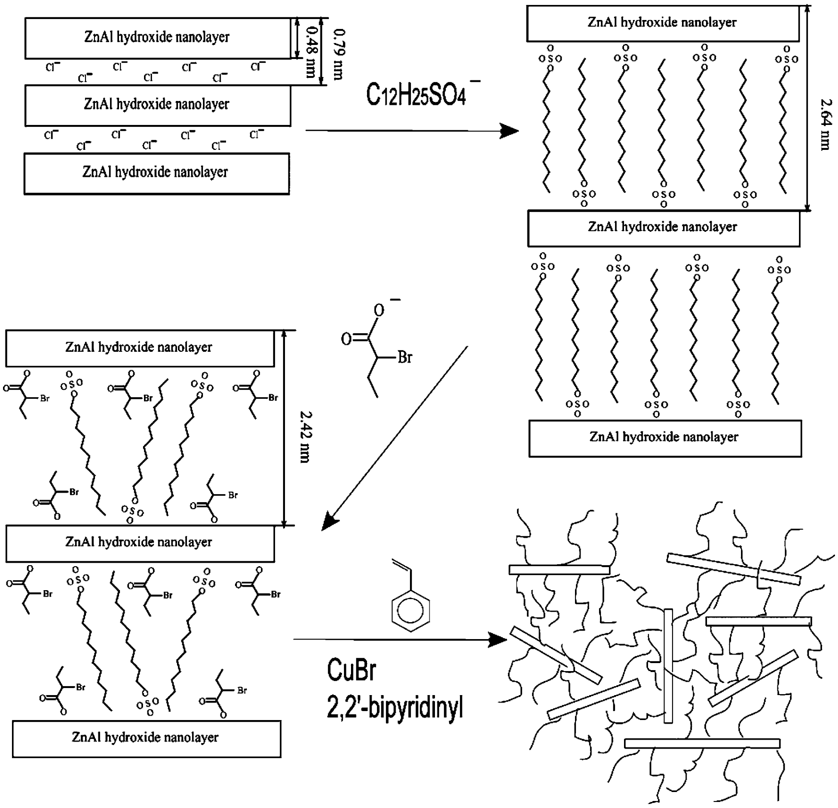
Fig. 3 Thermogravimetric analysis profiles for **a** pure PS and **b** exfoliated PS/LDH

chains were exchanged by the shorter BrB chains, the free space in the galleries of DS/LDH increased, which may allow the leftover DS chains to adopt a more disordered orientation structure to obtain entropy gain.

Polymerization of the composite was monitored by XRD. After a polymerization time of 8 h, the pattern (Fig. 1c) shows a weak diffraction peak, which suggests that the galleries of LDH are expanded and the layers of LDH are partially exfoliated. However, the (001) diffraction peak of LDH component (Fig. 1d) disappears completely in the composite polymerized for 12 h, which indicates the LDH layers are delaminated in PS matrix. The delamination of LDH is obtained by the swelling process arising from the transport of styrene molecular into the galleries of LDH. During polymerization, the styrene was polymerized from the BrB chains and was grafted on the surface of the ZnAl nanolayers. The gallery space is swelled and delaminated finally with increasing of the molecular weight of PS in the galleries. Scheme 1 illustrates the process of the exfoliating LDH layers in PS matrix. The modification of the LDH basal surfaces by dodecyl sulfate provides a hydrophobic environment and an enlarged interlayer distance to allow catalyst molecules and monomers to enter the LDH galleries.

The TEM image of exfoliated PS/LDH nanocomposite is shown in Fig. 2. It can be seen that some of the single exfoliated LDH layers are slant to the grid surface with certain angles, while most of them are vertical to the grid surface as point out by arrow. The thickness and the width/length of the single exfoliated LDH layers are measured to be 1.5–2 nm and 15–120 nm, respectively. This result gives positive evidence of good dispersion of exfoliated LDH layers in PS matrix.

To obtain conclusive evidence that the ATRP graft polymerization process results in delamination of LDH rather than bulk polymerization, a radical polymerization was performed on styrene containing of $Zn_3Al(DS)$ or $Zn_3Al(DS\text{-}BrB)$. The diffraction patterns of these composites show one strong reflection corresponding to a basal spacing of 3.04 nm for $Zn_3Al(DS)$ (Fig. 1e) and 3.16 nm for $Zn_3Al(DS\text{-}BrB)$ (Fig. 1f) and several weaker reflections, which indicate that the PS matrix has been intercalated into the galleries but exfoliated PS/LDH



Sch. 1 Process of exfoliating LDH by in situ ATRP reactions

nanocomposite could not be obtained by this method. Previous efforts involving in-situ soap-free polymerization of styrene also did not produce and exfoliated nanocomposite [17].

Figure 3 illustrates the TGA curves of pure PS and exfoliated PS/ZnAl-LDH nanocomposite. The thermal decomposition of pure PS sample (Fig. 3a) occurs in the weight loss at the range of 230–550 °C and no residues are left above 550 °C. Around 2.6 wt% weight loss for PS/LDH nanocomposite (Fig. 3b) at about 100 °C is due to the evaporation of physically absorbed water in the galleries. When the 50 wt% weight loss is selected as a comparison point, the decomposition temperature of PS/LDH nanocomposite is about 45 °C higher than that of pure PS. The tempera0ture corresponding to the maximum rate of weight loss is 365.5 and 393.8 °C, respectively for pure PS and the PS/LDH nanocomposite. These results suggest that the thermal stability of the exfoliated material improves markedly. The enhancement of thermal stability for the nanocompsite may be ascribed to a decrease in oxygen and volatile degradation products permeability/diffusivity deriving form the barrier effect of the exfoliated ZnAl hydroxide nanolayers in the PS matrix, as commonly founded in polymer/silicate nanocomposites [18].

In summary, this report clearly demonstrates that exfoliated PS/LDH nanocomposite can be achieved by in-situ ATRP reaction from initiator-modified LDH. The thermal stability of the nanocomposite shows a marked improvement. To the best of our knowledge, the exfoliation of LDH in non-polar polymer by in-situ polymerization has never been reported. Although our research is concentrated on the PS/ZnAl-LDH, this technique could be widely applied to many other polymers. It is also expected that block copolymer/LDHs nanocomposites can be synthesized by in-situ block copolymerization due to the living characteristics of ATRP, which has been achieved in silicate system [19].

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