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A new method to prepare flame retardant polymer composites

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ABSTRACT

In water solution, ammonium polyphosphate (APP) and pentaerythritol (PER) were designed to intercalate into the galleries of layered double hydroxide (LDH). The X-ray diffraction (XRD) results, transmission electron microscopy (TEM) images and Fourier transform infrared (FTIR) spectra show that APP and PER were successfully intercalated into the interlayer of LDH. Compared with conventional method to prepare polypropylene (PP)/APP/PER/LDH composite, the new routine can provide the composite with excellent optical and mechanical properties. The thermogravimetric analysis (TGA) data indicate the thermal stability of the composite added by this new kind of LDH is close to that of the conventional PP/APP/PER/LDH composite by the melt mixture. Finally, the LOI values of new PP/APP/PER/LDH composite with the 30 wt% new kind of LDH are 31, and UL-94 test of it is measured up to V-1.

1. Introduction

Presently, a lot of interest is focused on the layered double hydroxide (LDH) as a kind of flame retardant reagent (Du et al., 2007; Xu et al., 2006; Ding et al., 2006; Zammarano et al., 2005) due to their novel mechanical, thermal, optical, and physico-chemical properties, which are rarely presented in the pure polymer or micro-scale composites (Ray and Okamoto, 2003; Alexandre and Dubois, 2000; Fournaris et al., 1999). LDH are host–guest materials consisting of positively charged metal hydroxide sheets with intercalated anions and water molecules (Chen and Qu, 2003). Several methods have been reported for the synthesis of polymer/LDH with good properties, including solution blending, melt blending, and situ preparation (Ding and Qu, 2005; Chen and Qu, 2005; Du and Qu, 2006). Among these methods, melt blending has been proved as a new and efficient method for the preparation of polymer/LDH composite (Ding and Qu, 2005). However, the polypropylene (PP)/ammonium polyphosphate (APP)/pentaerythritol (PER)/LDH composite directly by melt mixture showed that APP and PER make surface of the composites unclear because of segregation. On the other hand, with the addition of the filler, the optical and mechanical properties of the PP/APP/PER/LDH composite become worser than that of pure PP. In present work, LDH was designed as a kind of precursor, and sodium dodecyl sulfate (SDS) was used to enlarge the basal spacing of the LDH before melt blending. It is due to sufficient basal spacing of the interlayer of LDH that APP and PER can easily enter the galleries of LDH in the water solution. After the process above, APP and PER were saved between layers of LDH before melt mixture. Previous work proved that the melt mixture preparing polymer/LDH could make LDH disperse uniformly in the polymer matrix (Ding and Qu, 2006). So it is possible that modified LDH can disperse uniformly. Then, the problem of segregation could be solved when the LDH sheets are seen as baffle-wall, which can

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prevent the composites against segregation near the surface. At the same time, the mechanical and optical properties can be improved when the filler disperse uniformly in the polymer matrix.

2. Experimental

2.1. Materials

PP resin was supplied by Jinling Petrochemical Co., Ltd. (China). Pentaerythritol was provided by Sinopharm Chemical Reagent Co., Ltd. (China). Ammonium polyphosphate was supplied by Zhengjiang Xingxing Flame retardant Reagent Co., Ltd. (China). All the other chemicals, such as $Zn(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, NaOH, and sodium dodecyl sulfate were obtained from China Medicine (Group) Shanghai Chemical Reagent Corporation and used as received without further purification. Distilled water was used throughout.

2.2. Preparation of samples

ZnAl-LDH in the present study was prepared by co-precipitation method (Hsueh and Chen, 2003). The pH value of 30 mL aqueous solution containing a divalent metal, M(II), salt solution, a trivalent metal, M(III), salt solution and SDS at a desired M(II)/M(III) molar ratio was adjusted to desired pH value with 1 mol/L NaOH aqueous solution. The obtained slurry was aged for 3 days at 80 °C, then filtered, and washed with distilled water. A LDH (DS) powder was obtained by drying at 60 °C in an oven. The modified ZnAl-LDH was prepared by mixture with LDH (10 g), APP (10 g) and PER (5 g) in distilled water solution for 4 h at 60 °C, then, the resulting white slurry was desiccated at 60 °C in an oven. All the composite samples (Table 1) were prepared by melt mixture using an SXX-300 mixer with a rotor speed of 64 rpm at 150 °C for 15 min, and the samples were cooled at room temperature for upper testing. The sample code and compositions in this work are listed in Table 1.

2.3. Characterization

The X-ray diffraction (XRD) was performed using 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 and a camera length of 0.8 m. The Fourier transform infrared (FTIR) spectrum was recorded on a Nicolet MAGNAIR750 spectrometer. The thermogravimetric analysis (TGA) was preformed on a Shimadzu TGA-50H thermoanalyzer. In each case an 18-mg sample was examined under air flow rate of 6×10^{-5} m^3/min at a scan rate of 10 °C/min from room temperature to 700 °C. The mechanical properties were measured with an Instron Universal tester (model 1185) at 25 °C with a crosshead speed of 25 mm/min. The dumb-bell-shaped specimens were prepared according to ASTM D412-87. Three samples were analyzed to determine the average values in order to obtain reproducible results. The limiting oxygen index (LOI) was measured using a ZRY-type instrument (China) on sheets 120 mm × 60 mm × 3 mm according to the standard oxygen index test ASTM D2863. The vertical test was measured on sheets 127 mm × 12.7 mm × 3 mm according to the standard UL94 test ASTM D635

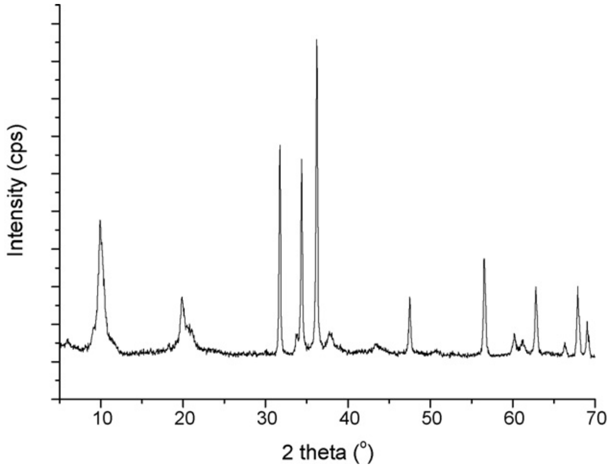

Fig. 1 – Wide-angle XRD patterns of ZnAl-LDH in the range of $2\theta = 5$–$70°$.

3. Results and discussion

3.1. Crystal morphologies and structures of LDH

Fig. 1 gives the wide-angle XRD patterns of ZnAl-LDH sample. Apparently the nanocomposite samples show some characteristic peaks in Fig. 1 corresponding to the diffractions of LDH layers (Leroux and Besse, 2001). This indicates that the LDH-layered framework form in the preparation of ZnAl-LDH. Fig. 2 shows the low-angle XRD patterns of ZnAl-LDH, modified ZnAl-LDH and new PP/modified ZnAl-LDH composite. The basal spacing of ZnAl-LDH is determined as being

Table 1 – Sample code and compositions

Sample	PP (g)	Modified LDH (g)	APP (g)	PER (g)	ZnAl-LDH (g)
PP/modified LDH-5	50	2.5			
PP/modified LDH-15	50	7.5			
PP/modified LDH	50	15			
PP/APP/PER/ZnAl-LDH	50		6	3	6
PP/APP/PER	50		10	5	
PP/ZnAl-LDH	50				1