Journal of Alloys and Compounds 509 (2011) 3497–3501

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Preparation and investigation of the combustion behavior of polypropylene/organomodified MgAl-LDH micro-nanocomposite

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ARTICLE INFO

Article history:
Received 6 June 2010
Received in revised form
13 November 2010
Accepted 17 December 2010
Available online 25 December 2010

Keywords:
Polypropylene (PP)
Layered double hydroxide (LDH)
Combustion behavior
Micro-nanocomposite
Microscale combustion calorimeter (MCC)

ABSTRACT

Layered double hydroxides (LDHs) are considered as a new emerging class of clays and they have a promising future in the field of nanocomposites due to their highly tunable properties. In this research, polypropylene/organomodified magnesium–aluminum LDH (PP/O-MgAl-LDH) composites were prepared by direct melt compounding. X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used to characterize the samples. Both XRD and TEM images of the composites illustrate the formation of a mixed morphology of micro and nano scale dispersion of MgAl-LDH in the matrix. Its combustion behaviors were examined via microscale combustion calorimeter (MCC), and char residues investigated by SEM. The MCC results show that the addition of Mg-Al-LDH into PP can efficiently decrease the specific heat release rate (HRR), the heat release capacity (HRC), and total heat release (THR), indicating the flame retardancy of the composite are improved. Flame retardant properties of PP/O-MgAl-LDH micro-nanocomposite were further enhanced with the increasing amounts of MgAl-LDH concentration.

1. Introduction

Polypropylene (PP) is widely applied in engineering materials, electronic cases, interior decoration, etc. regarding its excellent insulation properties, low cost, ease of fabrication and processing. Many of these applications carry severe risk of flame related occasions and loss of valuable properties due to high flammability of polypropylene. Introducing flame retardant additives into matrix polymer, therefore, is an essential step and phosphorous or metal oxide containing flame retardants are mostly employed in this manner to maintain flame retardancy. Besides microscale conventional flame retardant technologies, nanocomposites seem to be a promising alternative and, most of the ongoing investigations focus on a sub-class of nanocomposites, polymer/layered silicate nanocomposites [1–3]. However, in the recent years, polymer/layered double hydroxide (LDH) nanocomposites have drawn an enormous attention among polymer-clay nanocomposites [4–6].

LDH is a host–guest material consisting of positively charged metal hydroxide sheets with intercalated anions and water molecules [7]. The surface characteristic of pristine LDH is hydrophilic and it is difficult to realize the intercalation of polymer into the interlayers because of the integrated hydrogen-bonding network between the hydroxide layers, intercalated anions and water molecules. Furthermore, the organo modification for LDH is often considered as an essential and vital step before further utilizing it as a nanofiller. In comparison to conventional modification methods, like regeneration or anionic exchange method, in latest study we have successfully prepared organomodified LDH via one step method without requirement of carbonate free environment [8,9].

In the present work, we reported the preparation of PP/O-MgAl-LDH micro-nanocomposites by melt compounding directly. O-MgAl-LDH was synthesized by one step method as previously reported and a third component, maleic anhydride grafted polypropylene (MAH-g-PP) was used to assist dispersion of the layered inorganic materials. The MgAl-LDH to MAH-g-PP weight ratio was kept constant (1:1) in all compositions. The structural characterizations of PP/O-MgAl-LDH mixed micro-nanocomposite and the residues after combustion test were investigated by wide angle X-ray scattering (WAXS) and transmission electron microscopy (TEM). Their combustion behaviors have been studied by microscale combustion calorimetry (MCC).

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doi:10.1016/j.jallcom.2010.12.138

2. Experimental

2.1. Materials

The metal nitrate salts ($Mg(NO_3)_2$, $Al(NO_3)_3$), and sodium dodecylbenzenesulfonate (Na-DBS, Purity: 91%) were obtained from Aldrich Chemical Company for the purpose of organomodified synthesis of Mg/Al-LDH and used without further purification. Deionized water was used to dilute the solutions and to wash the filtered precipitates. Polypropylene (PP, homopolymer, HD 120 MO) was purchased from Borealis, Porvoo, Finland. Maleic anhydride grafted polypropylene (MAH-g-PP, Exxelor PO1020) was supplied by the Exxon Mobil Chemical.

2.2. Preparation of organomodified MgAl-LDH samples via one step route [8]

The synthesis of organomodified MgAl-LDH was carried out by the slow addition of a mixed magnesium and aluminium metal salt solution (with Mg^{2+}:Al^{3+} ratio equal to 2:1 and a total metal ion concentration of 0.3 M) to a Na-DBS solution with a continuous stirring at 50 °C. During the synthesis the pH value was kept to be 10 ± 0.2 by adding required amount of 1 M NaOH solution. After the addition of the mixed metal salt solution, the resulting slurry was continuously stirred at the same temperature for 0.5 h and then thermal treatment was applied for the following 18 h at 75 °C. The final products were filtered and washed several times with distilled water to get rid of non-reacted surfactant molecules until the pH of the supernatant solution was about 7. Organomodified MgAl-LDH (O-MgAl-LDH) was then dried in oven at 80 °C till the constant weight. For the comparison, pristine MgAl-LDH was also synthesized using the same principle mentioned above.

2.3. Preparation of PP/O-MgAl-LDH samples

PP, MAH-g-PP and O-MgAl-LDH were melt-compounded by a corotating twin-screw microextruder (15 cm^3 microcompounder, DSM Xplore, Geleen, The Netherlands) based upon certain weight ratios. Melt-compounding conditions were defined as 190 °C, 200 rpm screw speed and 10 min mixing time. The concentrations of MgAl-LDH in the composites were determined based on an approximate metal hydroxide content of the filler in whole matrix-filler system. In this research, 1.2 wt%, 2.4 wt%, and 4.8 wt% concentrations of MgAl-LDH in the composites, were investigated.

2.4. Characterization

Wide angle X-ray scattering (WAXS) was performed using 2-circle diffractometer XRD 3003 θ/θ (GE Inspection Technologies/Seifert-FPM, Freiberg) with Cu-Kα radiation ($\lambda = 1.542$ Å) generated at 30 mA and 40 kV in the range of $2\theta = 0.5$–$25°$ using a scintillation detector (0.05° as the step length, 15 s as measuring time per step). The Fourier transform infrared spectra (FTIR) of the LDH materials were obtained using the BRUKER VERTEX 80V spectrometer over the wave number range of 4000–400 cm^{-1}. The powdered samples were mixed with KBr and pressed in the form of pellets for the measurement of FTIR analysis. The morphological analysis was carried out using transmission electron microscopy (TEM) with microscope LEO 912. The conditions used during analysis were room temperature, 120 kV acceleration voltage and bright field illumination. The ultra-thin sections of the samples were prepared by ultramicrotome at −120 °C with a thickness of 80 nm. Microscale Combustion calorimeter (MCC-1, FTT) was used to investigate the combustion behavior of PP and PP/O-MgAl-LDH micro-nanocomposites. In this system, about 5 mg samples were heated to 700 °C at a heating rate of 1 °C/s in a stream of nitrogen flowing 80 cm^3/min. Prior to entering a 900 °C combustion furnace the volatile, anaerobic thermal degradation products in the nitrogen gas stream were mixed with a 20 cm^3/min stream consisting of 20% oxygen and 80% nitrogen. The scanning electron microscopy (SEM) (microscope model: Ultra Plus, Carl Zeiss SMT) was used to study morphological features of the residues of samples. The voltage = extra high tension (EHT) and aperture size was standing in the picture in the annotation bar. The samples are sputtered with 2 nm platinum.

3. Results and discussion

3.1. Structural characteristics of O-MgAl-LDH and PP/O-MgAl-LDH micro-nanocomposite

The FTIR spectra of the unmodified MgAl-LDH and organomodified MgAl-LDH were shown in Fig. 1. In comparison to unmodified MgAl-LDH, the FTIR spectrum of the organomodified MgAl-LDH reveals the presence of DBS anion in the filler. The characteristic vibration bands were detected for SO_3^- stretchings (symmetric stretching at 1038 cm^{-1} and asymmetric at 1183 cm^{-1}), the benzene group (C–C stretching at 1460 cm^{-1}, C–H in plane bending at 1004 and 1140 cm^{-1}) and alkyl group (asymmetric stretching of CH_3 and CH_2 at 2963 and 2925 cm^{-1}, respectively; symmetric stretching of CH_3 and CH_2 at 2872 and 2851 cm^{-1}, respectively). The bands recorded below 800 cm^{-1}, especially the sharp and strong characteristic band around 452 cm^{-1} appear due to the vibration of metal-oxygen bond in the brucite-like lattice. Besides, more direct evidences can be obtained from WAXS in Fig. 2, which is one of the powerful technologies to characterize the layered structure of nano-materials. The WAXS patterns of unmodified MgAl-LDH and organomodified MgAl-LDH reveal that modifier anion was efficiently intercalated within the MgAl-LDH layers with respect to its first basal reflection (0 0 3) at $2\theta = 2.90°$ corresponding to an interlayer distance of 3.05 nm, while the interlayer distance of unmodified MgAl-LDH is 0.89 nm. All these evidences show that the DBS anion was successfully intercalated into the interlayers of Mg/Al-LDH, which is consistent with the previous report [8].

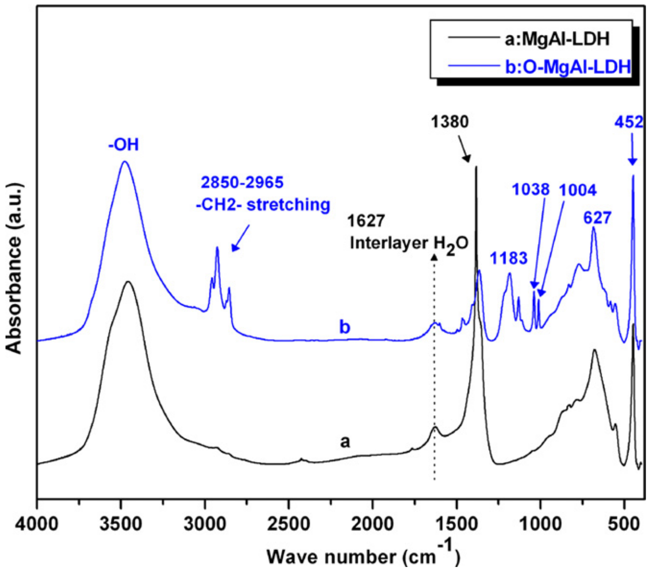

Fig. 1. FTIR spectra of (a) MgAl-LDH and (b) O-MgAl-LDH.

In comparison to (0 0 3) basal reflection of O-MgAl-LDH, PP/O-MgAl-LDH composites show almost no shift of the first basal reflection, while the second and the third basal reflections become weak and broad, or even non-existent for the composites with low LDH concentrations. This might be originated from a mixed morphology of micro- and nano-scale dispersion of MgAl-LDH in the matrix instead of complete nano-scale dispersion. The reason of inhomogeneous dispersion might be due to the difference in polar-

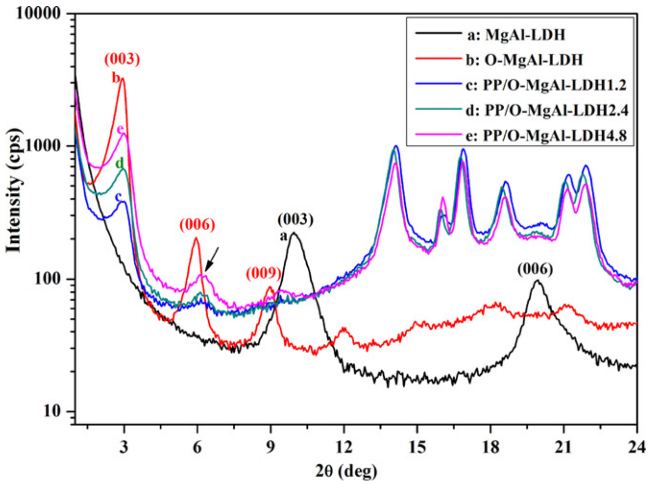

Fig. 2. WAXS patterns of MgAl-LDH, O-MgAl-LDH and PP/O-MgAl-LDH composites.