

Synthesis and Characterization of PE-g-MA/MgAl-LDH Exfoliation Nanocomposite via Solution Intercalation

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An organo-modified MgAl-layered double hydroxide (OMgAl-LDH) was successfully exfoliated in the xylene solution of polyethylene-grafted-maleic anhydride (PE-g-MA) under refluxing condition. A PE-g-MA/MgAl-LDH exfoliation nanocomposite was formed after the precipitation of PE-g-MA from the dispersion system. The structure and thermal property of the PE-g-MA/MgAl-LDH exfoliation nanocomposite were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and thermogravimetry analysis (TGA). The disappearance of d_{001} XRD peak of OMgAl-LDH at $2\theta = 3.2^\circ$ suggests that the MgAl hydroxide sheets are exfoliated in the nanocomposite. The TEM image shows that the MgAl hydroxide sheets of less than 70 nm in length or width are exfoliated and dispersed disorderly in PE-g-MA matrix. TGA profiles indicate that the PE-g-MA/MgAl-LDH nanocomposite with 5 wt% OMgAl-LDH loading shows a faster charring process in temperature range from 210 to 390 °C and a greater thermal stability beyond 390 °C than PE-g-MA does. The decomposition temperature of the nanocomposite is 25 °C higher than that of PE-g-MA as measured at 50% weight loss. The PE-g-MA/MgAl-LDH nanocomposite is promising for application of flame-retardant polymeric materials.

Keywords polymer/layered double hydroxide nanocomposites, exfoliation, thermal stability

In recent years, polymers doped with inorganic compounds at the nanoscale level, named polymer/inorganic nanocomposites, have caused considerable interest in the field of materials chemistry owing to their unique properties, such as enhanced mechanical property, increased thermal stability, improved gas barrier property, and reduced flammability.¹⁻⁵ To date, however, the inorganic compounds investigated in polymer/inorganic nanocomposites have been mainly focused on the layered silicates systems, while the layered double hydroxide (LDH) systems are much less discussed in literature.⁶⁻⁹

The LDHs can be represented by the ideal formula $[M_1^{2+}_x M_2^{3+}_x (\text{OH})_2]^{x+} A_n^{n-} \cdot m\text{H}_2\text{O}$, where M_1^{2+} and M_2^{3+} are divalent and trivalent metal cations, such as Mg^{2+} , Al^{3+} , respectively, A is an anion, such as CO_3^{2-} , SO_4^{2-} , and NO_3^- . LDHs are of great importance in application

fields of catalyst, flame retardant, stabilizer, medicine, and so on.¹⁰ Therefore, LDHs are considered as new and promising layered crystals for preparation of multifunctional polymer/inorganic nanocomposites.⁶ However, LDHs have much higher charge density in the interlayer and stronger interaction between the hydroxide sheets than layered silicates, making the exfoliation of LDHs much more difficult.¹¹⁻¹³ In the present work we report the exfoliation of organo-modified MgAl layered double hydroxide (OMgAl-LDH) layers in xylene solution of polyethylene-graft-maleic anhydride (PE-g-MA) to form PE-g-MA/MgAl-LDH nanocomposite for the first time. Dodecyl sulfate (DS) ions were intercalated into the MgAl layered double hydroxide (MgAl-LDH) to weaken the electrostatic forces between the hydroxide sheets and render the LDH layers hydrophobic. The obtained polymer/LDH nanocomposite shows enhanced flame-retardant property and thermal stability.

MgAl-LDH was obtained by adding 100 mL of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.075 mol) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.025 mol) aqueous solution into 100 mL of Na_2CO_3 (0.025 mol) and NaOH (0.2 mol) aqueous solution. The obtained slurry was then aged for 12 h at 70–75 °C with pH = 8–9 adjusted by NaOH ($1 \text{ mol} \cdot \text{L}^{-1}$). The precipitate was washed with distilled water and dried in oven at 75–80 °C. The OMgAl-LDH sample was obtained from rehydration process of calcined MgAl-LDH. 1 g of MgAl-LDH sample was calcined at 500 °C for 6 h, and then suspended in 100 mL of aqueous solution containing 1 g of sodium dodecyl sulfate under refluxing condition for 6 h, yielding a white powder OMgAl-LDH. The PE-g-MA/MgAl-LDH exfoliation nanocomposite was obtained by refluxing OMgAl-LDH (0.20 g) in the solution of PE-g-MA (3.80 g) with 50 mL of xylene for 24 h. The dispersion system was then poured out into 100 mL of ethanol. The precipitate, PE-g-MA/MgAl-LDH nanocomposite, was filtered and dried under vacuum at 100 °C for 24 h.

The X-ray diffraction (XRD) data were collected on a D/Max-rA rotating anode X-ray diffractometer (Rigaku

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Co., Japan) equipped with a Cu K α tube and Ni filter ($\lambda = 0.1542$ nm). The transmission electron microscopy (TEM) image was obtained on an H-800 transmission electron microanalyzer (Hitachi Co., Japan) with an accelerated voltage of 200 kV. The thermogravimetry analysis (TGA) curves were recorded on a Shimadzu TGA-50H thermoanalyzer. In each case an 18 mg sample was examined under an air flow rate of 6×10^{-5} m³/min at a scan rate of 5 °C/min from room temperature to 800 °C.

Results and discussion

Fig. 1 shows the XRD patterns at the range of $2\theta = 1.5^\circ$ – 10° for OMgAl-LDH and PE-g-MA/MgAl-LDH nanocomposite samples. The basal spacing of OMgAl-LDH is determined to be 2.75 nm from the (001) diffraction peak at $2\theta = ca. 3.2^\circ$ in Fig. 1A, which indicates that the DS ions have been intercalated into the interlayers of LDH. However, the (001) diffraction peak from OMgAl-LDH component in PE-g-MA/MgAl-LDH nanocomposite sample was not observed in Fig. 1B. This indicates that the OMgAl-LDH layers, *i.e.* $[Mg_{1-x}^{2+}Al_x^{3+}(OH)_2]^{x+} \cdot (DS)_x$, are exfoliated in the PE-g-MA matrix and the previous PE-g-MA solution in xylene. In other words, the PE-g-MA/MgAl-LDH exfoliation nanocomposite has been prepared successfully.

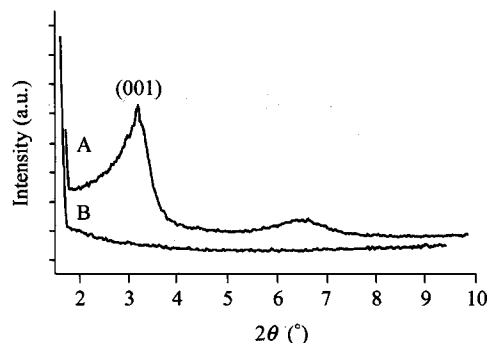


Fig. 1 XRD patterns of (A) OMgAl-LDH and (B) PE-g-MA/MgAl-LDH nanocomposite in the range of $2\theta = 1.5^\circ$ – 10° .

The typical morphology of PE-g-MA/MgAl-LDH exfoliation nanocomposite with 5 wt% OMgAl-LDH is shown in Fig. 2. It is found that the TEM micrograph from the PE-g-MA/MgAl-LDH nanocomposite is very different from those of polymers/layered silicates exfoliation nanocomposites in which the exfoliated clay layers are often face-face orientated due to the very high aspect ratio.¹⁴ In the case of PE-g-MA/MgAl-LDH exfoliation nanocomposite, the exfoliated MgAl hydroxide sheets combined with DS anions are dispersed disorderly in the PE-g-MA matrix. While some exfoliated MgAl hydroxide nanolayers are nearly vertical to the cutting section of the TEM specimen, most of them are slant to the cutting section at some large angle. These results give positive evidence of molecular dispersion of OMgAl-LDH layers in the PE-g-MA matrix. The data determined from the TEM image show that the length or

width of these nanolayers is about 70 nm.

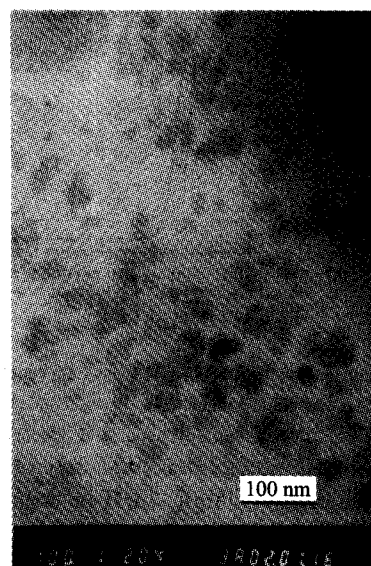


Fig. 2 TEM image of PE-g-MA/MgAl-LDH nanocomposite.

Fig. 3 shows the TGA curves of pure PE-g-MA and PE-g-MA/MgAl-LDH exfoliation nanocomposite. About 5% weight loss of PE-g-MA at the temperature range of 225 to 370 °C is due to the volatilization of a small amount of thermo-oxidative product of PE-g-MA. In the case of PE-g-MA/MgAl-LDH nanocomposite, about 31% weight loss at the range of 210 to 390 °C can be attributed to the decomposition of OMgAl-LDH and the thermo-oxidation of PE-g-MA. It is found that a successful charring process in flame retardant polymeric materials must occur at a temperature greater than the processing temperature of polymer but much lower than the decomposition temperature of polymer.¹⁵ Therefore, this kind of weight loss at the first step of decomposition is highly advantageous to promote the charring process and enhance the fire safety of the nanocomposite. The weight loss rates of both pure PE-g-MA and PE-g-MA/MgAl-LDH nanocomposite increase rapidly with the increasing decomposition temperature from 370 to 475 °C. However, the TG curve of PE-g-MA sample after 370 °C shows one step of 95% weight loss and almost no residue is left at 500 °C, while about 5% white powder residue is still left in the PE-g-MA/MgAl-LDH nanocomposite after 475 °C until 800 °C. In this decomposition step, the nanocomposite has a 25 °C higher decomposition temperature than PE-g-MA as measured at the point of 50% weight loss. So both the fast charring process at a low temperature and the enhanced thermal stability at a high temperature can improve fire safety performance of PE-g-MA/MgAl-LDH nanocomposite.

In conclusion, PE-g-MA/MgAl-LDH exfoliation nanocomposite was successfully synthesized via solution intercalation of PE-g-MA chains into the galleries of organo-modified MgAl-LDH, *i.e.* OMgAl-LDH, under refluxing condition in the xylene solution of PE-g-MA. The (001) diffraction peak of OMgAl-LDH is not observable in the

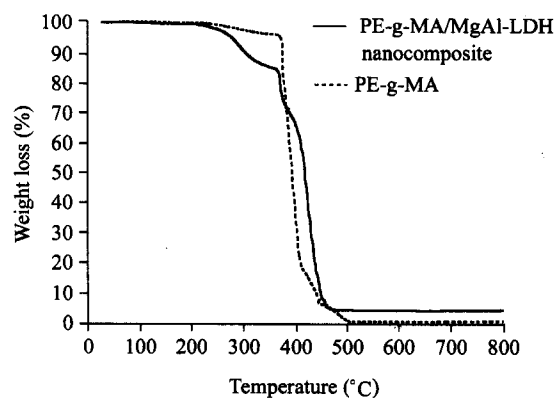


Fig. 3 TGA profiles for pure PE-g-MA and PE-g-MA/MgAl-LDH exfoliation nanocomposite.

PE-g-MA/MgAl-LDH exfoliation nanocomposite, which indicates the exfoliation of OMgAl-LDH layers. The exfoliated OMgAl-LDH layers of less than 70 nm in length or width are dispersed disorderly in the PE-g-MA matrix. With 5 wt% OMgAl-LDH loading, the PE-g-MA/MgAl-LDH exfoliation nanocomposite has a faster charring process in temperature range from 210 to 390 °C and a greater thermal stability beyond 390 °C than PE-g-MA does. The decomposition temperature of the nanocomposite is 25 °C higher than that of PE-g-MA as measured at 50% weight loss. The PE-g-MA/MgAl-LDH nanocomposite is promising for application of flame-retardant polymeric materials.

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