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Poly(ethylene terephthalate) nanocomposites with strong UV-shielding function using UV-absorber intercalated layered double hydroxides

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Reagents and Materials

All of the reagents, including hydrated magnesium nitrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), hydrated aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), sodium hydroxide (NaOH), urea and hexamethylenetetramine (HMT) are of analytical reagent pure (A.R.) grade. The UV absorber of 4,4'-diaminostilbene-2,2'-disulfonic acid (DDA) was bought from TCI company with purity higher than 95%. The neat PET was kindly provided by Professor Peng Chen at the Ningbo Institute of Material Technology & Engineering, Chinese Academy of Sciences. Before use, the deionized water was distilled to get rid of carbon dioxide.

Synthesis of small-sized LDH_ NO_3 particles.

The small-sized LDH_ NO_3 was synthesized by a typical coprecipitation method. In brief, an aqueous solution of $\text{Mg}(\text{NO}_3)_2$ (0.50 mol L^{-1}) and $\text{Al}(\text{NO}_3)_3$ (0.25 mol L^{-1}) and a solution of NaOH (1.0 mol L^{-1}) were added drop-wisely into the NaNO_3 solution (0.1 mol L^{-1}). During the adding process, the pH value was kept at $\text{pH} = 10.0$ under stirring in nitrogen atmosphere. Then, the mixture was aged at $80 \text{ }^\circ\text{C}$ for 8 h. Finally, the resultant was filtrated, washed with deionized water, and dried in a vacuum oven at $50 \text{ }^\circ\text{C}$ for 24 h.

Synthesis of large-sized LDH_ NO_3 particles.

The large-sized LDH_ NO_3 was obtained by synthesis of LDH_ CO_3 and subsequent decarbonation. First, large-sized LDH_ CO_3 was synthesized as follows. HMT solution with concentration of 0.075 or 0.0375 M was added into the mixed aqueous solution of $\text{Mg}(\text{NO}_3)_2$ (0.075 mol L^{-1}) and $\text{Al}(\text{NO}_3)_3$ (0.025 mol L^{-1}), wherein the total concentration of metal ions ($[\text{Mg}] + [\text{Al}]$) was 0.15 mol L^{-1} . The molar ratio of $\text{Mg}/\text{Al}/\text{urea}/\text{HMT}$ was 3:1:40:3. Then, the

mixture was heated to reflux for *ca.* 20 min under continuous stirring, a translucent dispersion appeared due to formation of precipitate was added. Then, 50 mL of NaOH solution (0.10 mol L⁻¹) was drop-wisely added in 30 min. The duration for the synthesis was about 28 h. Finally, the resultant precipitate was collected by filtration, washed, and dried in a vacuum oven at 50 °C for 24 h.

Then, the large-sized LDH_CO₃ was decarbonated to LDH_NO₃. About 0.10 g of the LDH_CO₃ was added into a mixed solution of 100 mL HNO₃-NaNO₃, in which the concentrations for the HNO₃ and NaNO₃ solutions were 0.005 and 5.0 mol L⁻¹, respectively. A subsequent ultrasonication treatment was carried out under nitrogen gas protection. Then, the vessel was stored with constant shaking at 25 °C for 48 h. Finally, the product was filtrated, washed and dried under vacuum at 50 °C for 24 h.

Synthesis of LDH_DDA.

The LDH_DDA with two different sizes were obtained by anion exchange reaction, which was completed in aqueous solution for 24 h. The main difference was the reacted temperature. The small-sized LDH_DDA was achieved at 80 °C, whereas the large-sized LDH_DDA was obtained at 60 °C.

Synthesis of PET/LDH Nanocomposites or Composite.

The PET nanocomposites or composite were prepared by a solution intercalation method. Typically, PET was first dissolved in m-cresol at 140 °C and LDH with anion of NO₃⁻ or DDA⁻ was ultrasonically dispersed in cyclohexanone by ultrasonic treatment. Then, the LDH

suspension was added into the PET solution and stirred for 30 min. After that, the mixture was immediately added into ethanol at the ratio of 1:1. Finally, the product was filtrated, washed and dried.

Characterizations.

X-ray diffraction (XRD) patterns were collected using a Rigaku D/max 2500 diffractometer with Cu K α radiation ($\lambda = 0.154$ nm) at a scanning rate of 4° min^{-1} in 2θ range of $3\text{--}70^\circ$. Fourier transform infrared (FTIR) spectra were recorded on a BRUKER TENSOR-27 FTIR spectrophotometer ranging from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} . The size and morphology of the LDHs were observed by a HITACHI S-4300 scanning electron microscopy (SEM). Its accelerating voltage was 15 kV. The transmission electron microscopic (TEM) images were obtained with a JEOL JEM-2011 electron microscope operated at an acceleration voltage of 100 kV, using ultra-thin films with thickness around 80 nm (from a melt injection-molded pellet by a CS-183 MMX Mini Max Molder) cut by a diamond knife. Ultraviolet-visible (UV-vis) absorption spectra were collected in the range from 290 to 800 nm on a Shimadzu UV-1601 spectrophotometer, with a slit width of 5.0 nm. The elemental analysis was carried out using a Carbon Sulfur Analyzer, CS-2008 apparatus (Beijing NCS Analytical Instruments).