Materials Letters 150 (2015) 31–34

Contents lists available at ScienceDirect

Materials Letters

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

The preparation and characterization of sulfamic acid-intercalated layered double hydroxide

Yu Jiang, Xiaoyu Gu, Sheng Zhang*, Wufei Tang, Jingran Zhao

Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, China

ARTICLE INFO

Article history:
Received 29 October 2014
Accepted 19 December 2014
Available online 29 December 2014

Keywords:
Layered double hydroxide
Intercalation
Composite materials
XPS
Flammability

ABSTRACT

$NH_2SO_3^{-1}$ was intercalated into layered double hydroxide to prepare a novel sulfamic acid-intercalated MgAl-LDH (SA-LDH). Fourier transform infrared (FT-IR) analysis confirmed the presence of sulfamic acid in LDH. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) were also used to characterize the structural morphology of SA-LDH, and the results revealed that the interlayer space of LDH had been enlarged from 0.76 to 0.91 nm and proved the formation of hydrogen bonds between SA-LDH. The SA-LDH was introduced into ethylene vinyl acetate (EVA) copolymer via melt blending, and the cone calorimetry test results demonstrated that the presence of SA-LDH could significantly improve the flame retardancy of EVA composite.

1. Introduction

LDH is a class of synthetic anionic clays with host-guest nanolayer material containing positively charged metal hydroxide sheets, intercalated anions as guest and water molecules [1–3]. LDHs have been widely investigated that was partly driven by the use of these materials as ion exchange hosts, fire retardant additives, catalytic agent, drug delivery and so on [4–7]. Its general formula is $M^{II}_{1-x}M^{III}_x(OH)_2(A^{n-})_{x/n}\cdot mH_2O$, where M^{II} and M^{III} are, respectively, divalent (Mg^{2+}, Zn^{2+}, Co^{2+}) and trivalent cations (Al^{3+}, Fe^{3+}, Mn^{3+}), and A^{n-} is the charge balancing interlayer anion [8–10]. Recently, most of the ongoing investigations focus on lamellar compounds for their unique anion exchange and intercalation properties [11–13].

The sulfamic acid (SA) with a molecular formula of NH_2SO_3H is an effective flame retardant for many polymers and textile materials, therefore, it is expected that the intercalation of $NH_2SO_3^{-1}$ can improve the flame retardancy of LDH, which has not been reported so far.

In this work, a novel sulfamic acid-intercalated MgAl-LDH (SA-LDH) was prepared and characterized. The interlayer anion of LDH was displaced through acid-base reaction between SA and CO_3^{2-}, and carbon dioxide generated in the reaction. The structure and morphology of intercalated LDH were characterized, and the effect of SA-LDH on the flammability behavior of EVA was investigated by using cone calorimeter.

2. Experimental

Preparation of SA-LDH: MgAl-CO_3^{2-}-LDH (LDH) was purchased from Nan Tong Advanced Chemicals Ltd., China.10 g MgAl-CO_3^{2-} LDH sample was firstly dispersed in 200 mL deionized water in a 500 mL three-necked flask before vigorously stirred by a magnetic stirrer for around 20 min, then 50 mL SA water solution which contained 10 g SA was added into the above slurry, and the mixture was stirred vigorously at 50 °C for 2 h. The precipitate was finally washed, filtered and dried at 50 °C for 10 h, and SA-LDH was obtained.

The EVA/SA-LDH composite were obtained by melt blending using a micro two-screw extruder. The temperature of the micro extruder from the hopper to the die was 90/110/120 °C, and the screw speed was 40 rpm.

Characterization: Wide angle X-ray diffraction (WXRD) were examined on a RigakuDmax2500VB2+/PC diffractometer with Cu-$K\alpha$ radiation source (λ=0.154 nm). X-ray photoelectron spectroscopy (XPS) was examined on ThermoVG ESCALAB 250. Fourier transform infrared (FTIR) spectra were recorded on a Thermo Nicolet Nexus 670 (USA). The surface morphology and particle size were examined with JAPAN JEM-3010 transmission electron microscopy (TEM). The analysis was performed at 200 kV acceleration voltage and bright field illumination under ambient temperature and the samples were obtained by dispersing the particles into alcoholic solution with ultrasonic impact treatment. Fire Testing Technology cone calorimeter

---

* Corresponding author. Tel.: +86 10 18610021239; fax: +86 10 64436820.
E-mail address: szhang1966@163.com (S. Zhang).

http://dx.doi.org/10.1016/j.matlet.2014.12.096
0167-577X/

was also used to evaluate the fire performance of the composite according to the standard ISO 5660 under a heat flux of 50 kW/m^2 with a sample size of 100 × 100 × 3 mm^3 in conditions comparable to a mild fire scenario.

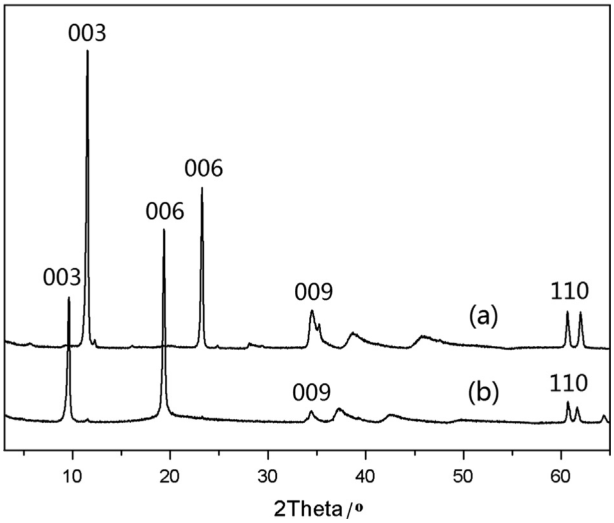


Fig. 1. XRD patterns of (a) LDH and (b) SA-LDH.

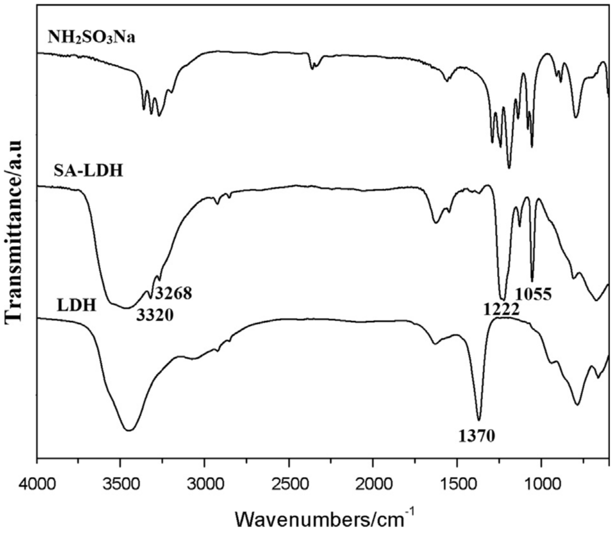


Fig. 2. FT-IR spectra of (a) LDH, (b) SA-LDH, and (c) NH_2SO_3Na.

3. Results and discussion

XRD analysis: Fig. 1 displays the XRD spectra of the LDH and SA-LDH. The patterns of LDH exhibits strong and sharp peaks of 0 0 *l* (*l*=3, 6, 9) at =11.2°, 23.30° and 34.50°, reflecting well-crystallized and ordered layered phases and the basal spacing of 0.77, 0.38 and 0.26 nm can be calculated, respectively, according to the Bragg equation. All diffraction peaks of 0 0 *l* (*l*=3, 6, 9) in SA-LDH left shift to 9.66°, 19.39° and 34.42°, indicating the corresponding basal spacing has been enlarged to 0.91, 0.76 and 0.26 nm, respectively. The increase in basal spacing indicates that $NH_2SO_3^-$ has been successfully intercalated into the interlayers of LDH.

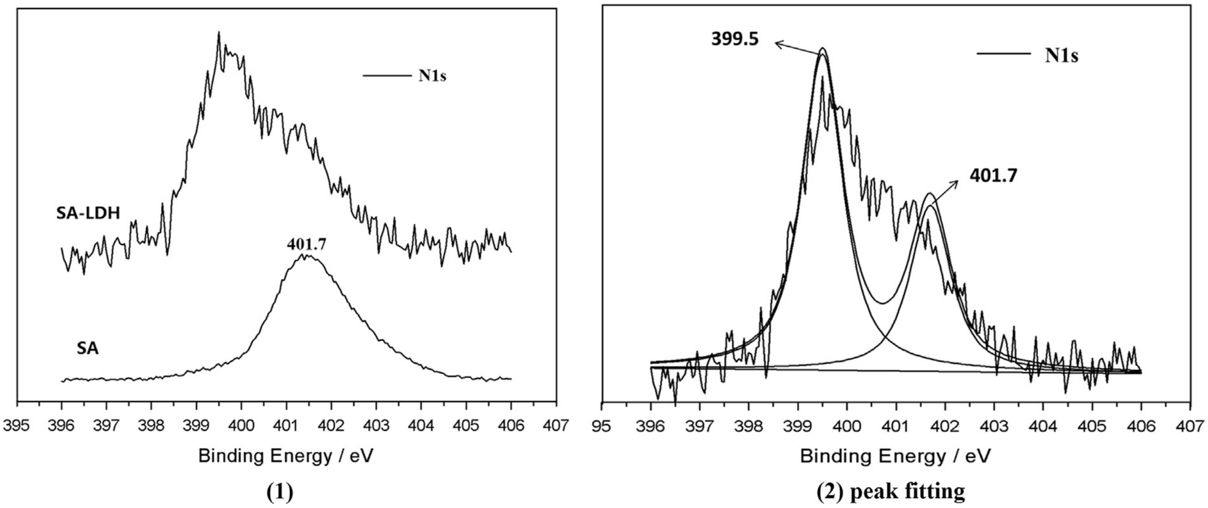
FT-IR spectra analysis: Fig. 2 displays the FTIRspectra of NH_2SO_3Na, LDH and SA-LDH.Both LDH and SA-LDH show the absorption bands of O–H stretching at about 3450 cm^{-1}, δ(H–OH) vibrations at about 1625 cm^{-1}, and the lattice vibration of the M–O and O–M–O (M= Mg and Al) groups in the low frequency region below 800 cm^{-1} [14].

The peak at 1370 cm^{-1} in the spectrum of LDH is assigned to the carbonate stretching, which has disappeared in the spectrum of SA-LDH with several emerged new peaks. Peaks at 1222, 1129, and 1055 cm^{-1} are corresponding to the vibrations of S=O and the peak at 810 cm^{-1} is assigned to S–O. Peaks at 3320 and 3268 cm^{-1} are corresponding to the stretching vibration of $-NH_2$ [15,16]. It could be concluded that $NH_2SO_3^{-1}$ has been successfully intercalated into the interlayers of LDH.

XPS and TEM analysis: The binding energy values for the N element of SA and SA-LDH have been measured by XPS. Fig. 3 shows the XPS spectra of SA and SA-LDH, and it can be seen the peak binding energy of N in SA appears at 401.7 eV, however, a new peak appears at 399.5 eV in SA-LDH. Based on the peak fitting result shown in Fig. 3 (2), the area ratio of peak at 399.5 eV and 401.7 eV is about 65.6% and 34.4%, respectively. In other words the binding status of about two thirds of N has been altered after intercalation. This may be attributed to the formation of hydrogen bonds between N and H atoms in $NH_2SO_3^-$ (the sketch map is shown in supporting information).

TEM images of LDH and SA-LDH are shown in Fig. 4. Plate like particles with edges can be observed. Compared with the homogeneous distribution of the LDH particles, intensive aggregation of SA-LDH particles is represented. This may be mainly due to the formation of hydrogen bonds between N, O and H in $NH_2SO_3^{-1}$, which is consistent with the XPS analysis.

Cone calorimeter analysis: Fig. 5 shows the cone test curves of EVA and its composites. One can see a second peak of heat release rate (PHRR$_2$) after the initial peak (PHRR$_1$) curve, which is presumably due to char-surface rupture or burn-out of the sample. PHRR$_1$ and



(1) (2) peak fitting

Fig. 3. XPS spectra of SA and SA-LDH.