

Synthesis and UV absorption properties of 2,3-dihydroxynaphthalene-6-sulfonate anion-intercalated Zn–Al layered double hydroxides

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ABSTRACT

An organic UV absorbent has been intercalated into a layered double hydroxide (LDH) host by ion exchange of a Zn–Al–LDH–nitrate precursor with a solution of 2,3-dihydroxynaphthalene-6-sulfonic acid (DNSA) sodium salt in water. After intercalation of the UV absorbent, the powder X-ray diffraction (XRD) pattern shows that the interlayer distance in the LDHs increases from 0.90 to 1.59 nm. The possible structure is that the interlayer DNSA anions arrange in a monolayer and in a perpendicular orientation toward the hydroxide layers. Infrared spectra and TG–DTA curves reveal the presence of a complex system of supramolecular host–guest interactions between layers. The thermal stability of the intercalated UV absorbent was investigated by TG–DTA and it was found that this material is more stable than the original organic UV absorbent at high temperature, showing that the thermostability is markedly enhanced after intercalation into the LDH host. The UV absorbent-intercalated LDHs exhibit excellent UV photostability in polypropylene composites.

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1. Introduction

2,3-Dihydroxynaphthalene-6-sulfonic acid (DNSA) is often used as a coupling agent to synthesize diazo sensitizer, as a color developing agent, photosensitive material, and food additive. Indeed, DNSA is an excellent UV absorbent and can absorb a majority of UV irradiation from the sunlight. Because DNSA is a small organic molecule and has poor thermal stability, it can be easily oxidized in polymer composite processing at higher temperature, which restricts its use as a photostabilizer in polymer composites. The chemical structural formula of DNSA is shown in Fig. 1.

Polypropylene (PP) is a widely used general-purpose plastic, but its photostability is poor. UV ray in sunlight can induce photo-oxidative degradation of PP, which has an adverse effect on its mechanical property [1]. To improve the anti-ultraviolet ability of PP, some kinds of photostabilizers must be added to the PP composite during the manufacturing process.

Layered double hydroxides (LDHs) are well known as a large class of anionic clays. LDHs possess a positively charged hydroxide basal layer, which are electrically balanced by the intercalation of anions in the interlayer space, and the interlayer anions can be replaced by other anions to form plenty of new functional materials. The general formula of LDHs can be represented by

$(M_{1-x}^{2+}M_x^{3+}(\text{OH})_2)(A_n^{n-}/m \cdot m\text{H}_2\text{O})$, where M^{2+} and M^{3+} are metallic cations such as Mg^{2+} , Ni^{2+} , Mn^{2+} , or Zn^{2+} and Al^{3+} , Cr^{3+} , or Fe^{3+} , and so forth. A^{n-} is an exchangeable inorganic anion [2] such as CO_3^{2-} , SO_4^{2-} , Cl^- , NO_3^- , or various organic anions, and x value is equal to the molar ratio $M^{3+}/(M^{2+} + M^{3+})$, and m is the number of water molecules located in the interlayer region together with the anions. Recently, LDHs have received considerable attention due to their potential applications as catalysts, catalyst supports, electrodes, sensitizers, anionic exchangers, adsorbents, and polymer additives [3–5].

Several examples of the intercalation of organic and inorganic compounds in LDHs have been reported in the literature [6–8]. After intercalation, the thermal stability of the guest anions stayed in the interlayer space of LDHs has been markedly improved. In our previous work, 5-benzotriazolyl-4-hydroxy-3-sec-butylbenzenesulfonic acid, 5-sulfosalicylic acid and 2-naphthylamine-1,5-disulfonic acid with better UV absorption ability and poor thermal stability were intercalated into the Zn–Al–LDH precursor, and their thermal stability and photostability have been markedly enhanced. The polypropylene composites containing the intercalated materials exhibit excellent UV photostability [9–11].

In this paper, we synthesize DNSA anion-pillared LDHs through the anion-exchange method and use it as a photostabilizer for PP. Because of the special substituted dihydroxynaphthalene structure of DNSA and the existence of various chemical interactions in intercalated material, DNSA anion-pillared LDHs show an excellent thermal stability and improve the anti-ultraviolet ability of PP composites greatly.

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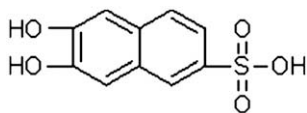


Fig. 1. Chemical structural formula of DNSA.

2. Experimental section

2.1. Chemicals

NaOH, HNO₃, Zn(NO₃)₂·6H₂O, and Al(NO₃)₃·9H₂O were all of A.R. grade. 2,3-Dihydroxynaphthalene-6-sulfonic acid (DNSA) was purchased from J&K Chemical. CO₂-free deionized water with conductivity less than 10⁻⁶ S cm⁻¹ was used in synthesis and washing steps. Commercial isotactic polypropylene (PP, S1003) was purchased from Yanshan Petrochemical Company (China).

2.2. Preparation of ZnAl-NO₃-LDHs

ZnAl-NO₃-LDH precursor was prepared by a method involving separate nucleation and aging steps (SNAS) developed in our laboratory [12]. For the sake of increasing the charge density of layer sheets, the Zn/Al molar ratio was fixed at 2. Zn(NO₃)₂·6H₂O (71.4 g, 0.24 mol) and Al(NO₃)₃·9H₂O (45.0 g, 0.12 mol) were dissolved in CO₂-free deionized water to make a mixed salt solution (300 mL). NaOH (28.8 g, 0.72 mol) was dissolved in CO₂-free deionized water to make an alkali solution (300 mL). These two solutions were simultaneously added to a Rotating Liquid Film Reactor at about 4000 rpm. The resulting slurry was removed into a four-necked flask as soon as possible and aged at 100 °C for 6 h under N₂ stream. After centrifugation and washing with CO₂-free deionized water and finally anhydrous ethanol, a filter cake containing 38.6 wt% solid was obtained.

2.3. Preparation of ZnAl-DNSA-LDHs

DNSA anion-pillared LDHs (ZnAl-DNSA-LDHs) were prepared by the anion-exchange method using ZnAl-NO₃-LDH as a precursor. ZnAl-NO₃-LDH filter cake (4.90 g) was sufficiently dispersed in CO₂-free deionized water (75 mL) to form a slurry. DNSA (2.40 g) was dissolved in CO₂-free deionized water to form an aqueous solution (75 mL). The pH value of the solution was adjusted to around 4 by adding an adequate amount of NaOH. DNSA solution was dropped to precursor slurry slowly by controlling the pH ≥ 4, followed by being aged at 100 °C for 6 h under a N₂ stream. The resulting precipitate was centrifuged, thoroughly washed (using CO₂-free deionized water and finally anhydrous ethanol), and dried at 70 °C overnight and kept in a sample bottle.

2.4. Preparation of ZnAl-DNSA-LDHs/PP, DNSA/PP, and pristine PP films

ZnAl-DNSA-LDHs and DNSA (1.0 wt%) were respectively mixed with PP in an SSR-Z4 double roller mixer at 165 °C for about 15 min. The resulting ZnAl-DNSA-LDHs/PP and DNSA/PP composites were molded into flakes of 80 × 100 × 1 mm³, and films with 0.05 mm thickness were then formed at 160 °C under pressure. The reference films of pristine PP were prepared under the same conditions.

2.5. Photostability of ZnAl-DNSA-LDHs/PP, DNSA/PP and pristine PP films

Samples of ZnAl-DNSA-LDHs/PP, DNSA/PP, and pristine PP films were photoaged in a UV photoaging instrument (UV high-pressure mercury lamp as the UV light source, 1000 W of power and

a wavelength range from 250 to 380 nm) with a temperature-controlling system. Diffuse reflectance UV-vis spectra were recorded after UV irradiation for 5 min. The above process was repeated 7 times, giving a total of 35 min of accumulated exposure for each sample.

2.6. Analysis and characterization

Powder X-ray diffraction (XRD) measurements were performed on a Shimadzu XRD-6000 X-ray powder diffractometer (Cu K α radiation, $\lambda = 0.15406$ nm) between 3 and 70°. The scan speed was 5° min⁻¹. IR spectra were recorded on a Bruker Vector 22 Fourier transfer infrared spectrophotometer using the KBr disk method with a ratio of sample/KBr of 1:100 by mass. Thermogravimetry and differential thermal analysis (TG-DTA) curves were obtained on a Beifen PCT-1A instrument in the temperature range of 25–700 °C with a heating rate at 10 °C min⁻¹ in air. Elemental analysis was carried out using a Shimadzu ICPS-7500 inductive coupled plasma (ICP) emission spectrometer. Diffuse reflectance UV-vis absorbance spectra were recorded using a Shimadzu UV-2501PC instrument with an integrating sphere attachment in the wave range 200–600 nm using BaSO₄ as reference. UV-irradiated samples were analyzed immediately after exposure.

3. Results and discussion

3.1. Structure analysis

The XRD patterns of ZnAl-NO₃-LDHs, DNSA, and ZnAl-DNSA-LDHs are shown in Fig. 2. The XRD pattern of the ZnAl-NO₃-LDH precursor (Fig. 2a) exhibits typical characteristics of the LDH phase. The (003), (006), and (009) diffraction peaks, which correspond to the basal and higher order reflections, appear at 9.76°, 19.77°, and 29.96°, respectively. The interlayer distance $d_{(003)}$ is 0.90 nm, which is close to the literature value of 0.89 nm [13]. The diffraction peaks in Fig. 2b indicate the typical structure of DNSA. After DNSA anions, which have a diameter of 0.94 nm, were intercalated into the interlayer galleries of ZnAl-NO₃-LDHs, the new (003), (006), and (009) diffraction peaks move to 5.56°, 11.26°, and 17.01°, as shown in Fig. 2c. The corresponding interlayer distance of $d_{(003)}$ is 1.59 nm, which indicates that DNSA anions have replaced NO₃⁻ in the interlayer galleries to form ZnAl-DNSA-LDHs. The strong sharp reflections indicate that the ZnAl-DNSA-LDHs have a well-formed crystalline-layered structure.

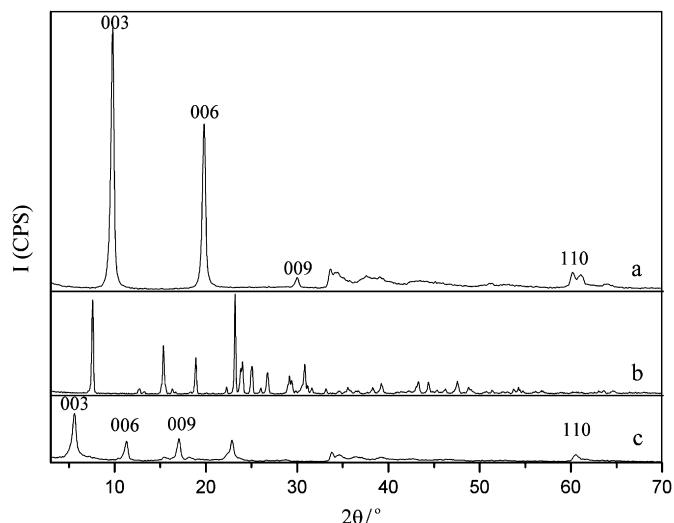


Fig. 2. XRD patterns of ZnAl-NO₃-LDHs (a), DNSA (b), and ZnAl-DNSA-LDHs (c).

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