Fabrication of host–guest UV-blocking materials by intercalation of fluorescent anions into layered double hydroxides

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Materials for blocking UV light play important roles in a variety of areas such as protecting the human skin and increasing the lifetime of polymers. In this work, a new type of host–guest UV-blocking material has been synthesized by the introduction of a fluorescent anion, 2-(2-[[2-(4-(2-(4-carboxyphenyl)vinyl)phenyl)-vinyl]benzoate (CPBA), into the interlayer galleries of a ZnAl–NO₃ layered double hydroxide (LDH) precursor by an anion-exchange method. The structure and the thermal and photostability of the intercalated ZnAl–CPBA-LDH were investigated by powder X-ray diffraction (XRD), infrared spectroscopy (FTIR), thermogravimetry and differential thermal analysis (TG-DTA), fluorescence spectroscopy and UV-vis spectroscopy. The supramolecular layered host–guest structure of ZnAl–CPBA-LDH enables both physical shielding and absorption of UV light. Furthermore, in contrast to conventional UV blocking materials—which convert UV light into thermal energy—the CPBA anions in the LDH interlayer galleries convert UV light (in the range 250–380 nm) into lower energy fluorescence emission ($\lambda_{em} = 430$ nm), thus reducing the thermal aging of the polymer composite materials. Intercalation of the CPBA anions into the LDH host also markedly enhances the thermal stability of CPBA. In polypropylene (PP) aging performance tests, after adding 1–5 wt% ZnAl–CPBA-LDH to PP, the resistance to UV degradation of the resulting ZnAl–CPBA-LDH/PP composites is higher than that of pristine PP or a CPBA/PP composite. Therefore, this work provides a way to construct a new type of host–guest layered material for UV-blocking applications.

1. Introduction

UV light radiation can produce highly reactive free radicals that can induce chemical reactions, resulting in subsequent photo-degradation, and color fading of polymers, pigments, and dyes, a process which is usually called aging. In addition to UV light aging, polymers also suffer from thermal aging, with both types of aging causing loss of mechanical strength of the polymers.

The development of additives able to protect materials against UV light aging has therefore attracted significant interest. UV blocking materials can be classified into two types—inorganic UV shielding materials and organic UV absorbing materials—on the basis of the blocking mechanism involved. A small number of inorganic shielding materials, such as titanium dioxide and zinc oxide, protect the skin or polymer materials by reflecting and scattering UV radiation. A wider variety of organic UV absorbing materials have been employed, including camphors, benzophenones, cinnamates, and triazines. However, organic UV absorbing materials have poor thermal and photostability which reduces their long-term efficacy as additives in polymers, and the radical species produced by decomposition of the organic UV absorbing material can even contribute to an enhanced rate of degradation of the polymer. Furthermore the UV energy absorbed by the organic material is generally dissipated as heat, which promotes the thermal aging of polymer materials to a certain extent. Incorporating organic UV absorbing materials in an inorganic host matrix offers several potential advantages. The resulting hybrid absorber can block UV light by both physical screening by virtue of the inorganic host and absorption by the organic guest. Furthermore incorporating an organic absorber in an inorganic host should increase its thermal and photostability when used as an additive in polymers. Host–guest materials also have potential advantages as sunscreen agents, since organic UV absorbing molecules pose problems in terms of both environmental pollution and health and safety, and incorporating them in an inorganic host will decrease their direct contact with the skin.
2. Experimental section

2.1. Reagents

Analytical grade Zn(NO$_3$)$_2$·6H$_2$O, Al(NO$_3$)$_3$·9H$_2$O, NaOH, H$_2$SO$_4$, and CPB were purchased from Beijing Chemical Co., Ltd. and used without further purification. CO$_2$-free deionized water was used in synthesis and washing steps. Commercial isotactic polypropylene (PP, S1003) was purchased from Yanshan Petrochemical Company, China.

2.2. Preparation of ZnAl–NO$_3$–LDH

The ZnAl–NO$_3$–LDH precursor was prepared by the method involving separate nucleation and aging steps (SNAS) developed in our laboratory.$^{14}$ A solution of Zn(NO$_3$)$_2$·6H$_2$O and Al(NO$_3$)$_3$·9H$_2$O with a Zn/Al ratio of 2.0 in CO$_2$-free deionized water ($[\text{Zn}^{2+}] + [\text{Al}^{3+}] = 0.9$ M) and a solution of NaOH (1.8 M) in CO$_2$-free deionized water were simultaneously added to a modified colloid mill with a rotor speed of 3000 rpm and mixed for 1 min. The resulting suspension was removed from the colloid mill as soon as possible and aged at 100 °C for 6 h under N$_2$ protection. The final suspension was washed several times with CO$_2$-free deionized water until the pH of the washings was around 7, separated by centrifugation, and finally dried at 60 °C for 24 h.

2.3. Preparation of CPB and ZnAl–CPBA-LDH

CPB was hydrolyzed to give CPB by heating at 130 °C with 50 wt% H$_2$SO$_4$ as a catalyst. CPB anion intercalated LDH (ZnAl–CPBA-LDH) was prepared by anion-exchange using ZnAl–NO$_3$–LDH as a precursor. ZnAl–NO$_3$–LDH (0.018 mol) was sufficiently dispersed in CO$_2$-free deionized water to form a slurry. CPB (0.03 mol) was dissolved in CO$_2$-free deionized water to form an aqueous solution. The pH value of the CPB aqueous solution was adjusted to around 8 by adding NaOH aqueous solution and it was then directly mixed with the precursor slurry, followed by aging at refluxing temperature for 6 h under N$_2$ protection. The resulting precipitate was centrifuged, thoroughly washed (using CO$_2$-free deionized water and finally anhydrous ethanol), and dried at 70 °C overnight.


0.5 g of ZnAl–CPBA-LDH, 0.5 g of CPB, 0.5 g of ZnAl–NO$_3$–LDH (1 wt%), 1.5 g of ZnAl–NO$_3$–LDH (3 wt%), and 2.5 g of ZnAl–NO$_3$–LDH (5 wt%) were mixed with separate portions of 50.0 g of PP in a Haake internal mixer (HAKE Rheomix 600 OS, Thermo Fisher Scientific, America) equipped with two counter-rotating rotors at 185 °C for about 10 min to produce the corresponding composites. The resulting composites were molded into flakes of 100 mm × 100 mm × 1 mm, and films with 0.05 mm thickness at 180 °C under pressure. Pristine PP films were also prepared under the same conditions as a reference.

Samples of ZnAl–CPBA-LDH/PP, CPBA/PP, ZnAl–NO₃-LDH/PP and pristine PP films were rapidly photo-aged in a UV photolaging instrument (with a UV high-pressure mercury lamp as the UV light source, a power of 1000 W and λ_max = 365 nm) with a temperature-control system holding the temperature at 60 °C. FTIR spectra were recorded after irradiation for 10 min. The process was repeated five times, giving a total of 50 min of accumulated exposure for each sample.

2.6. Characterization of samples

Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku XRD-6000 diffractometer, using Cu Kα radiation (λ = 0.15418 nm) at 40 kV, 30 mA, with a scanning rate of 5° min⁻¹, in the 2θ range from 2° to 70°. FTIR 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. Thermogravimetric (TG) analysis was performed on a PerkinElmer Lambda 950 instrument in the temperature range 25–700 °C with a heating rate of 10 °C min⁻¹ in air. Scanning electron microscopy (SEM) images were obtained using a Hitachi S-4700 scanning electron microscope operating at 20 kV. Transmission microscopy (SEM) images were obtained using a Hitachi S-4700 scanning electron microscope operating at 20 kV. Transmission microscopy (TEM) and high resolution TEM (HRTEM) observations were carried out on a JEOL JEM-2100 transmission electron microscopy (TEM) and high resolution TEM (HRTEM) scanning electron microscope. Di ff erentions were carried out on a JEOL JEM-2100 transmission electron microscopy (TEM) and high resolution TEM (HRTEM) scanning electron microscope operating at 20 kV. Transmission microscopy (SEM) images were obtained using a Hitachi S-4700 scanning electron microscope operating at 20 kV. Transmission microscopy (SEM) images were obtained using a Hitachi S-4700 scanning electron microscope operating at 20 kV. Transmission microscopy (SEM) images were obtained using a Hitachi S-4700 scanning electron microscope operating at 20 kV. Transmission microscopy (SEM) images were obtained using a Hitachi S-4700 scanning electron microscope operating at 20 kV.

3. Results and discussion

3.1. X-ray diffraction

The XRD patterns of ZnAl–NO₃-LDH and ZnAl–CPBA-LDH are shown in Fig. 1. The XRD pattern of the ZnAl–NO₃-LDH precursor (Fig. 1a) exhibits the typical characteristics of an LDH phase. The (003), (006), and (009) diffraction peaks, which correspond to the basal and higher order reflections, appear at 9.66°, 19.56°, and 29.36°, respectively. The interlayer distance d_003 is 0.90 nm, which is close to the value reported in the literature. After CPBA anions were intercalated into the interlayer galleries of ZnAl–NO₃-LDH, the main characteristic reflections of the product appear at 2.99° (003), 6.05° (006), 9.83° (009), and 60.68° (110) and the d_003 (2.903 nm), d_006 (1.445 nm) and d_009 (0.925 nm) spacings present a good multiple relationship for the basal, second and third-order reflections (Fig. 1b). The lattice parameter c can be calculated from averaging the positions of the three harmonics: c = 1/3 (d_003 + 2d_006 + 3d_009). The basal spacing for ZnAl–CPBA-LDH is 2.903 nm, indicating that CPBA anions have replaced NO₃⁻ in the interlayer galleries. Considering the thickness of the LDH layer (0.48 nm), the spacing of the gallery between the LDH layers is about 2.42 nm, which corresponds to a single layer of CPBA anions being intercalated perpendicular to the LDH layers.

3.2. FT-IR spectroscopy

The FT-IR spectra of ZnAl–NO₃-LDH, CPB, CPBA and ZnAl–CPBA-LDH are shown in Fig. 2. The broad absorption band around 3448 cm⁻¹ shown in the spectrum of the ZnAl–NO₃-LDH precursor (Fig. 2a) can be ascribed to the stretching vibration of the O–H groups of LDH layers and the interlayer water molecules. The sharp band around 1384 cm⁻¹ corresponds to the νs stretching vibration of NO₃⁻ groups and the band at 425 cm⁻¹ can be ascribed to O–M–O vibrations in the layers of LDH. The broad absorption peak at 2220 cm⁻¹ which can be assigned the stretching vibration of the C≡N groups in the CPB. In Fig. 2c, the absorption peak at 2220 cm⁻¹ has disappeared and a peak at 1684 cm⁻¹ which can be assigned to the C≡O stretching vibration of the carboxylic acid group is present, indicating the successful hydrolysis of CPB into CPBA.
In the spectrum of the ZnAl–CPBA-LDH obtained after intercalation (Fig. 2d), the O–H absorption band around 3421 cm\(^{-1}\) and the O–M–O vibration band at 425 cm\(^{-1}\) are similar to the corresponding bands in the spectrum of the ZnAl–NO\(_3\)-LDH precursor, while the characteristic peak of the nitrate group was absent, confirming that the nitrate ions have been displaced by the CPBA anions. The stretching vibration of the carboxylic acid group moved from 1684 cm\(^{-1}\) to 1540 cm\(^{-1}\) and 1400 cm\(^{-1}\) (the antisymmetric and symmetric stretching bands) of the carboxylic group (Fig. 2d), suggesting that the carboxylic acid group has been deprotonated to form an anion and has hydrogen bonding interactions with the LDH layers. These results are in agreement with those observed by XRD, further confirming the successful intercalation of the CPBA anions into the interlayer galleries of ZnAl–NO\(_3\)-LDH to form ZnAl–CPBA-LDH.

### 3.3. TG–DTA analysis

Fig. 3 shows the TG-DTA curves of CPB, CPBA, and ZnAl–CPBA-LDH. For CPB, the endothermic peak at 199 °C in the DTA curve correspond to the removal of adsorbed water and the partial decomposition, and the two strong exothermic peaks around 421 °C and 580 °C separately correspond to the further decomposition and complete combustion of CPB. After CPB was hydrolyzed into CPBA, the first exothermic peak occurred around 307 °C, and further decomposition and complete combustion followed around 464 °C and 559 °C, respectively, indicating CPBA has better thermal stability than CPB. The DTA curve for ZnAl–CPBA-LDH is quite different from those of CPB and CPBA. The first and second endothermic peaks marked at 125 °C and 307 °C in the DTA curve correspond to the removal of interlayer water and dehydroxylation, respectively. The DTA curve of ZnAl–CPBA-LDH has a strong exothermic band at 480 °C with a corresponding mass loss between 400 °C and 600 °C in the TG curve which is due to the combustion of the organic guest. The decomposition temperature of the CPBA occurs at 480 °C, suggesting that the intercalation of the CPBA anions into the interlayer galleries of the ZnAl–NO\(_3\)-LDH markedly enhances the thermal stability of the organic guest. This improvement in thermal stability can be ascribed to the interactions between the host brucite-like sheets and the intercalated guest anions, involving electrostatic attraction between opposite charges, hydrogen bonding, and van der Waals forces.

### 3.4. SEM and TEM

The surface morphology and particle size of ZnAl–NO\(_3\)-LDH and ZnAl–CPBA-LDH were investigated by SEM and TEM, as illustrated in Fig. 4. The expected hexagonal plate-like nature of the crystallites is clearly apparent in the micrographs of both ZnAl–NO\(_3\)-LDH and ZnAl–CPBA-LDH, indicating that the intercalation of CPBA does not change the morphology of the LDH crystallites, as shown by comparison of Fig. 4A and B. The diameter of the ZnAl–NO\(_3\)-LDH platelets is in the range 60–100 nm, while that of ZnAl–CPBA-LDH is in the range 100–150 nm; the increase in particle size after intercalation can be attributed to the ion-exchange reaction being carried out at high temperature. The TEM (Fig. 4C) and HRTEM micrographs of ZnAl–CPBA-LDH (Fig. 4D) show that the interlayer spacing increased to 2.9 nm after intercalation, which is in accordance with the XRD results.

### 3.5. UV absorption properties of ZnAl–CPBA-LDH

The UV-vis diffuse reflectance spectra of ZnAl–NO\(_3\)-LDH, CPBA and ZnAl–CPBA-LDH are shown in Fig. 5. The spectrum of ZnAl–NO\(_3\)-LDH (Fig. 5a) shows strong UV absorption between 200 and 320 nm due to the presence of nitrate anions in the interlayer galleries, as well as the shielding effect of the LDH layers. The UV absorbance curve of CPBA, as shown in Fig. 5b, indicates that CPBA has a broad UV absorption between 200 and 500 nm. After intercalation, ZnAl–CPBA-LDH exhibits excellent UV absorption ability below 400 nm, even better than pure CPBA,
which is due to the interactions between the guest and host layers (Fig. 6).

### 3.6. Fluorescence properties

The fluorescence spectra of CPB, CPBA and ZnAl–CPBA-LDH are shown in Fig. 7. The excitation spectrum and emission spectrum of CPBA both show a red shift when compared with CPB, due to the C=N groups in the CPB molecule being hydrolyzed into COOH groups. After intercalation, the emission spectrum of ZnAl–CPBA-LDH remains unchanged with the maximum emission wavelength ($\lambda_{\text{em}}$) located at 430 nm, while the excitation spectrum shows a slight blue shift from 364 nm to 352 nm, which can be attributed to intermolecular interactions between the excited guest and the LDH layers.\(^{18}\) The fluorescence lifetime of ZnAl–CPBA-LDH is 4.83 ns, significantly longer than the value of 1.26 ns for pristine CPBA; the photo-luminescence quantum yield (PLQY) of ZnAl–CPBA-LDH increases to 35.4%, compared with a value of 15.6% for pristine CPBA. The improvement of the fluorescence lifetime and PLQY can be assigned to the high degree of organization of the CPBA moieties in the interlayer galleries of the LDH layers, which suppresses the thermal vibration and rotation of the CPBA anions.\(^{19}\)

### 3.7. Photostability of ZnAl–CPBA-LDH/PP films

To evaluate the efficacy of ZnAl–CPBA-LDH as a UV blocking agent for polymers, we added ZnAl–NO$_3$-LDH, CPBA and ZnAl–CPBA-LDH to separate samples of PP and carried out UV aging tests. The FT-IR spectra of pristine PP, ZnAl–NO$_3$-LDH/PP, CPBA/PP, and ZnAl–CPBA-LDH/PP films after different UV exposure times are shown in Fig. 8. The photooxidative and thermal degradation mechanism of PP has been widely studied.\(^{20}\) The decomposition product shows two characteristic absorption peaks associated with carbonyl and hydroperoxide groups at 1710 and 3345 cm$^{-1}$, respectively. With increasing exposure time to UV light, the absorption intensities of PP at 1710 and 3345 cm$^{-1}$ show a gradual increase. The aging degree of the PP can be quantified by calculating the area of the carbonyl absorption band in the region from 1810 to 1660 cm$^{-1}$, as shown in Fig. 8.\(^{21}\) The integrated area of the carbonyl absorption band of ZnAl–CPBA-LDH/PP increases more slowly with time than those for pristine PP, ZnAl–NO$_3$-LDH/PP and CPBA/PP, suggesting that
ZnAl–CPBA-LDH can significantly inhibit the aging of PP. In particular, the area of the carbonyl absorption band for CPBA/PP increases significantly after irradiation for more than 30 min, indicating the poor photo- and thermal stability of the pristine PP. Therefore, the superior antiaging performance of ZnAl–CPBA-LDH compared with CPBA can be attributed to both the improvement in photo- and thermal stability of the organic guest by virtue of its interactions with the host layers, as well as the UV shielding properties of the inorganic layers. Additionally, the quantity optimization experiments showed that the adding amount of 3 wt% of ZnAl–CPBA-LDH can achieve the highest photostability of PP, and the adding amount more than 5 wt% of ZnAl–CPBA-LDH would influence the blending uniformity of PP/LDH composites.

4. Conclusion

A readily available fluorescent material CPB has been hydrolyzed into CPBA, and CPBA-intercalated LDH has been prepared by an ion-exchange method. Compared with the pristine CPBA, ZnAl–CPBA-LDH exhibits better UV blocking properties with longer fluorescence lifetime and higher photoluminescence quantum yield. Accelerated UV aging tests of PP samples containing CPBA and ZnAl–CPBA-LDH confirm the excellent UV blocking properties of the intercalated product, as shown by the significantly lower increase in the carbonyl band intensity during the aging of ZnAl–CPBA-LDH/PP when compared with pristine PP and CPBA/PP. Addition of only 3 wt% ZnAl–CPBA-LDH affords excellent UV aging resistance, highlighting the potential practical applications of this material as an additive for PP, as well as other polymer materials which are also prone to UV aging. The UV blocking properties of the supramolecular ZnAl–CPBA-LDH host-guest material involve both shielding by the LDH layers and UV light absorption by the interlayer organic species. Furthermore, in contrast to conventional UV absorbing materials, the absorbed UV light is converted into visible fluorescence emission instead of thermal radiation, thus reducing thermal aging of the polymer materials.

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Notes and references