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Preparation and characterization of poly(vinyl chloride)/layered double hydroxide nanocomposites with enhanced thermal stability

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ABSTRACT

Poly(vinyl chloride)/layered double hydroxide (PVC/LDH) nanocomposite has been prepared via solution intercalation process using dodecyl sulfate (DS^-) or stearate anion modified LDH. XRD and TEM results give evidence that the inorganic LDH particles were dramatically exfoliated into nanoscale and homogeneously dispersed in PVC matrix. The enhanced thermal stability was confirmed by conventional Congo Red test. The nanocomposite containing Mg_3Al–LDH-stearate had the maximum of increased dehydrochlorination time, 15 times of that of neat PVC, and more than twice of that of PVC/LDH-NO_3 composite and PVC/LDH-DS nanocomposite at 5 wt% loading. Furthermore, its thermal stability time increased with the LDH content. At 10 wt% loading of Mg_3Al–LDH-stearate, it reached 20 times of that of PVC, and obviously larger than that of the previously reported nanocomposite using alkyl phosphonate (AP) grafted LDH. The reason may lie on the absorption of the released HCl during degradation by both nanoscale dispersed LDH particles and stearate anions.

1. Introduction

It is well known that poly(vinyl chloride) (PVC) has a strong tendency to degrade when exposed to heat, shear or radiation (such as UV-light) during melt-processing and practical applications [1]. The degradation begins with a dehydrochlorination reaction and is subsequently accelerated by the released hydrogen chloride (HCl). Since the HCl is believed to sustain the auto-catalytic process [2], stabilizers that can irreversibly bond HCl are expected to prevent or delay the degradation process. At present, lead salts, metal soaps and organtin compounds are mainly used for this purpose. However, they have obvious disadvantages in terms of toxicity, environmental pollution, efficiency and cost. For example, lead salts are toxic and result in pollution; metal soaps are generally not used singly due to their low efficiency; organtin compounds are expensive. As a consequence, novel PVC resins with enhanced thermal stability or stabilizers are strongly desired considering the overall properties of non-toxicity, environmental friendliness, high efficiency and low price.

Layered double hydroxides (LDHs), important layered inorganic materials, have an HCl absorption capacity [3–6] and may be used as PVC thermal stabilizer. Unfortunately, they are conventionally used as micron-scale fillers, and their thermal stability is rather limited. LDHs are generally represented by the formula $[M^{II}_{1-x}M^{III}_{x}(OH)_2]\ (A^{m-})_{x/m}\cdot mH_2O$, wherein M^{II}, M^{III}, and A represent divalent (or monovalent) cation, trivalent cation and the interlayer anion, respectively. The interlayer anion (A^{m-}) may vary over a wide range and has an exchangeable capacity [7]. When certain organic anions are present in the interlayer space, the surface of LDHs can be rendered from hydrophilic to hydrophobic and the resultant organo-LDHs may be applied to prepare polymer/LDH nanocomposites [8–13].

Polymer/inorganic nanocomposites, wherein the inorganic components are dispersed in nanometer scale and thus can maximize their functions, have attracted much of current interests [14–18]. LDHs have a high surface charge and the interlayer anions cannot be exchanged easily, therefore, the preparation of polymer/LDH nanocomposites is difficult relative to that of the extensively studied polymer/clay nanocomposites (PCNs). Indeed, there are few publications about PVC/LDH nanocomposites [19–22]. Moreover, in most of the previous reports [19–21], the dehydrochlorination test has not been conducted, although the nanoscaly dispersed LDH particles are expected to greatly increase the thermal stability time. Bao et al. [22] achieved PVC/LDH nanocomposites using alkyl phosphonate (AP) grafted commercial nanoscale LDH, and found that the nanocomposites presented an enhanced thermal stability and an obvious increase of the dehydrochlorination time. We note that AP no exfoliation of LDH occurred in their study. If the organic surface modifying agent has an intrinsic ability of HCl absorption and the LDH particles have

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a higher extent of exfoliation, an unusual significant increase of the thermal stability and a dramatical increase of dehydrochlorination time can be expected for the resulting nanocomposite.

In this study, potassium stearate was adopted due to its intrinsic HCl absorption ability, and sodium dodecyl sulfate (SDS) was applied for comparison which does not contribute to the dehydrochlorination process itself. Two PVC/LDH nanocomposites have been obtained using LDHs with stearate and dodecyl sulfate ($C_{12}H_{25}OSO_3^-$, DS^-) as interlayer organic anion, respectively. The dispersion state of the nanocomposites was characterized by combination of X-ray diffraction (XRD) and transmission electron microscopic (TEM) techniques. And the thermal stability of the PVC/LDH composite or nanocomposites was investigated by conventional Congo Red tests.

2. Experimental part

2.1. Materials

The PVC resin (SG-5 type, suspension grade) was kindly provided by Beijing Huaer Company Limited. All of the chemical reagents employed in this study are of A.R. grade. The deionized water was distilled twice to get rid of carbon dioxide (CO_2).

2.2. Preparation of Mg_3Al–LDHs

Mg_3Al–LDHs with interlayer anions of nitrate (NO_3^-), DS^- and stearate ($C_{17}H_{37}COO^-$) were synthesized by a typical one-step co-precipitation method. Briefly, an aqueous solution containing 1 mol L^{-1} of magnesium nitrate ($Mg(NO_3)_2$) and aluminum nitrate ($Al(NO_3)_3$) with molar ratio of 3:1 was added drop-wise into an aqueous mixture of sodium hydroxide (NaOH) and sodium nitrate ($NaNO_3$) or SDS or potassium stearate in nitrogen atmosphere. To maintain the pH value of 10.0 of the system, an aqueous solution of 1 mol L^{-1} of NaOH was titrated simultaneously. Then, the mixture was heated and kept at 80 °C for 6 h. Finally, the product was washed for 4 times, dried and ground into powers to afford LDH-NO_3 or LDH-DS or LDH-stearate with Mg/Al of 3:1.

2.3. Preparation of PVC/LDH composite or nanocomposites

PVC was first dissolved in tetrahydrofuran (THF) at 50 °C, and LDH with anion of NO_3^- or $C_{12}H_{25}OSO_3^-$ or $C_{17}H_{37}COO^-$ was ultrasonically dispersed in cyclohexanone. Then, the LDH suspension was added into the PVC solution and fluxed for 30 min. Finally, the product was washed and dried to obtain PVC/LDH composite or nanocomposites.

2.4. Characterization

XRD patterns were collected on a Rigaku D/max 2400 diffractometer with Cu Kα radiation ($\lambda = 0.15418$ nm) measured at a scanning rate of 8°/min. TEM images were obtained with a Hitachi H-800 electron microscope operated at an accelerated voltage of 100 kV. The Fourier transform infrared (FTIR) spectra were recorded on a Perkin–Elmer System 2000 FTIR spectrophotometer that ranged 4000–400 cm^{-1} at a nominal resolution of 4 cm^{-1}.

2.5. Thermal stability measurements

Conventional Congo Red test was employed to study the thermal stability of PVC, PVC/LDH composite or nanocomposites according to the standard of ISO 182/1-1990. The time of the color change (discoloration) on Congo Red paper induced by reaction with released HCl was determined at 175 °C.

3. Results and discussion

The synthesized LDHs including Mg_3Al–LDH-NO_3, Mg_3Al–LDH-DS and Mg_3Al–LDH-stearate, prepared by one-step co-precipitation, are characterized by XRD (Fig. 1) and FTIR (Fig. 2) techniques. In Fig. 1(a), a series of sharp peaks are observed, characteristic of an ordered layered structure for Mg_3Al–LDH-NO_3. The basal spacing derived from the peak of the (003) plane ($2\theta = 10.9°$) can be calculated to be 0.81 nm. As for Mg_3Al–LDH-DS and Mg_3Al–LDH-stearate, their characteristic peaks of (003) plane shift to low 2θ angle at 3.20° and 2.62°, respectively. According to the well-known Bragg equation, their basal spacing is 2.76 nm and 3.37 nm, respectively, obviously larger than that of Mg_3Al–LDH-NO_3. This suggests that that the DS^- and stearate anions were present in the interlayer of LDHs. Additionally, the absence of the diffraction peak of (003) plane of Mg_3Al–LDH-NO_3 with $2\theta = 10.9°$ in Fig. 2(b) and (c) indicates that in the synthesized Mg_3Al–LDH-DS and Mg_3Al–LDH-stearate, the organic anions dominate while other anions such as NO_3^- does not exist in the interlayer space. This suggests that the present one-step co-precipitation procedure has an obvious advantage over two-step synthesis. In typical two-step synthesis procedure, LDH-NO_3 is synthesized first by co-precipitation, and then organic anions are intercalated into the LDH interlayer.

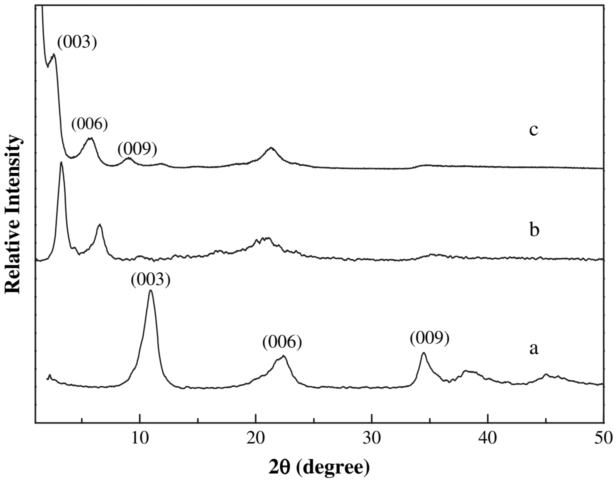

Fig. 1. XRD patterns of (a) Mg_3Al–LDH-NO_3, (b) Mg_3Al–LDH-DS and (c) Mg_3Al–LDH-stearate.

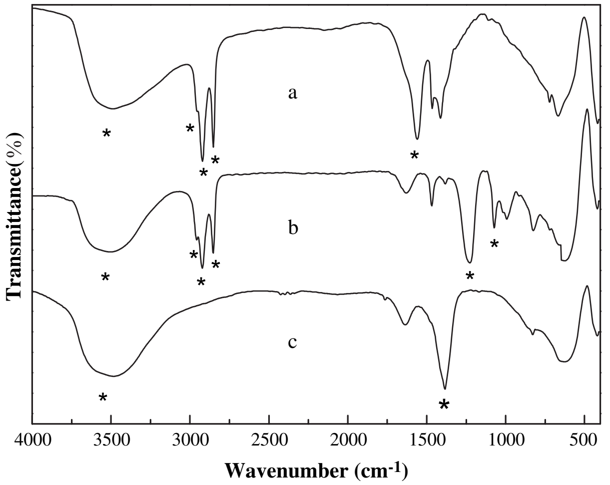

Fig. 2. FTIR spectra of (a) Mg_3Al–LDH-NO_3, (b) Mg_3Al–LDH-DS and (c) Mg_3Al–LDH-stearate.

Mixtures of organo-LDHs and LDH-NO_3 usually coexist in the product via two-step process, and retained XRD peaks of unorganically modified LDH-NO_3 can often be clearly observed [23].

Fig. 2 shows the FTIR spectra of Mg_3Al–LDH-NO_3 (a), Mg_3Al–LDH-DS (b) and Mg_3Al–LDH-stearate (c). A broad absorption band around 3500 cm^{-1} is assigned to O–H group stretching arising from both hydroxide layers and interlayer water molecules. A strong absorption band at 1384 cm^{-1} in Fig. 2(a) is associated with the asymmetric stretching vibration of the NO_3^- anions [24]. The FTIR spectrum of Mg_3Al–LDH-DS contains strong absorptions at 1226 and 1072 cm^{-1} and is assigned to the stretching of RSO_4 [25]. In Fig. 2(c), the band at 1542 cm^{-1} may result from the carboxylate asymmetric stretching [26]. In addition, characteristic absorption bands of $-CH_3$ and $-CH_2$ groups can be clearly observed at 2800–3000 cm^{-1} in Fig. 2(b) and (c). Please note that the samples for FTIR measurements were washed several times before use. The fact that Mg_3Al–LDH-DS and Mg_3Al–LDH-stearate still maintained the characteristic absorption bands of the corresponding organic anions demonstrates that the organic anions were strongly adsorbed on the surface of LDHs. As a consequence, the interaction and compatibility between PVC and LDHs matrix could be greatly increased, which is helpful for the followed preparation of PVC/LDH nanocomposites.

In this study, a solution intercalation process was applied to prepare PVC/LDH nanocomposites by mixing LDH dispersion with PVC solution. First, a stable dispersion of LDH is required before mixing with PVC solution. Fig. 3 shows the sedimentation experimental results of LDHs with different interlayer anions in cyclohexane. The dispersions were homogenized by a high-speed shear homogenizer, ultrasonicated and then stood for 1 h. Precipitation can be obviously seen at the bottom of the vial for Mg_3Al–LDH-NO_3 (a), and the upper supernatant is clear and transparent. In sharp contrast, stable homogenous dispersions of Mg_3Al–LDH-DS (b) and Mg_3Al–LDH-steatrate (c) are still maintained; no obvious precipitation can be discernible. This means that both Mg_3Al–LDH-DS and Mg_3Al–LDH-stearate can form a stable dispersion in cyclohexanone. Furthermore, cyclohexanone is miscible with tetrahydrofuran (THF), a good solvent of PVC resin. Therefore, PVC/LDH nanocomposites may be prepared by mixing of LDH/cyclohexanone stable dispersion with PVC/THF solution under desired conditions.

The dispersed and exfoliated state of LDHs in the PVC matrices was studied by combination of XRD and TEM techniques. Fig. 4 shows the XRD patterns of pure PVC (a), PVC/LDH-NO_3 composite (b), PVC/LDH-DS (c) and PVC/LDH-stearate (d) nanocomposites (containing of 5 wt% of LDHs). It can be seen that there are two broad diffraction peaks at $2\theta = 17.3°$ and $24.5°$ characteristic of the pure PVC resin. As for the PVC/LDH-NO_3 composite in Fig. 4(b), a sharp peak characteristic of Mg_3Al–LDH-NO_3 can still be observed at 2θ around 10.7°, indicating that the LDHs were not intercalated by PVC macromolecular chains and dramatically exfoliated. To our delight, no obviously sharp peak of LDHs but only broad bands characteristic of PVC are observed in the PVC/LDH-DS (c) and PVC/LDH-stearate (d) nanocomposites. Generally, the disappearance of any sharp XRD peak in low 2θ angle suggests that the ordered layered structure had been greatly destroyed. Therefore, the 2D inorganic layers of Mg_3Al–LDH-DS and Mg_3Al–LDH-stearate might be dramatically exfoliated and homogenously dispersed in the PVC matrix.

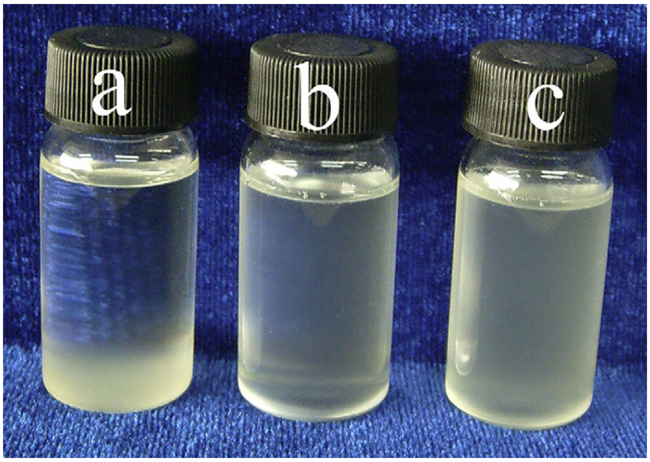

Fig. 3. Vials of dispersions of cyclohexanone containing (a) Mg_3Al–LDH-NO_3, (b) Mg_3Al–LDH-DS, and (c) Mg_3Al–LDH-stearate.

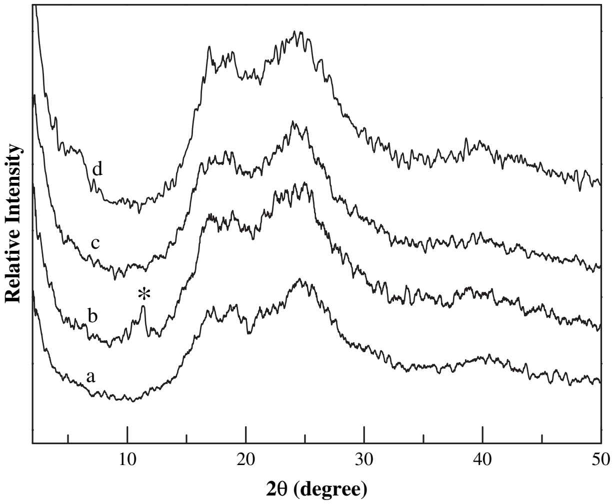

Fig. 4. XRD patterns of (a) pure PVC, (b) 5 wt% PVC/LDH-NO_3 composite, (c) 5 wt% PVC/LDH-DS nanocomposite and (d) 5 wt% PVC/LDH-stearate nanocomposite.

The microstructure of the PVC/LDH composite, PVC/LDH-DS and PVC/LDH-stearate nanocomposites was further studied by TEM technique, which reveals detailed information of local microstructure, different from XRD patterns showing global information. A miscellaneous structure can be seen in Fig. 5(a) and (b), including nanoscale particles together with larger particles with thickness even about 500 nm. This may be due to the strong attraction force of Mg_3Al–LDH-NO_3 layers and the difficulty for PVC macromolecular chains to intercalate and exfoliate. Fig. 5(c)–(f) shows the TEM micrographs of PVC/LDH-DS (c and d) and PVC/LDH-stearate (e and f) nanocomposites, respectively. No large aggregates with thickness of larger than 100 nm are observed, and the particles with thickness of 20–40 nm are prevalent. Combination of XRD and TEM results show that organo-LDHs containing DS^- and stearate anions can be significantly exfoliated into nanometer scale and homogeneously dispersed in PVC to afford PVC/LDH nanocomposites via the solution intercalation procedure.

Fig. 6 shows the influence of LDHs on the thermal stability and the dehydrochlorination process of PVC resins measured by the conventional Congo Red method. The thermal stability time of the pure PVC is only about 5 min. After addition of 5 wt% Mg_3Al–LDH-NO_3, the time extends to 27 min, which is more than five times of that of the neat PVC. This phenomenon indicates that LDHs themselves can contribute to the HCl adsorption during the PVC degradation, although they were not exfoliated and dispersed very well. As for the 5 wt% PVC/LDH-DS nanocomposite, the time is increased further to 32 min, longer than that of PVC/LDH-NO_3 composite. Please note that the inorganic LDH accounts for only 50.6 wt% (elemental analysis result) in the LDH-DS, which means there are only 2.53 wt% (5 wt% × 50.6%) of the inorganic LDH dispersed in the PVC/LDH-DS nanocomposite. This strongly

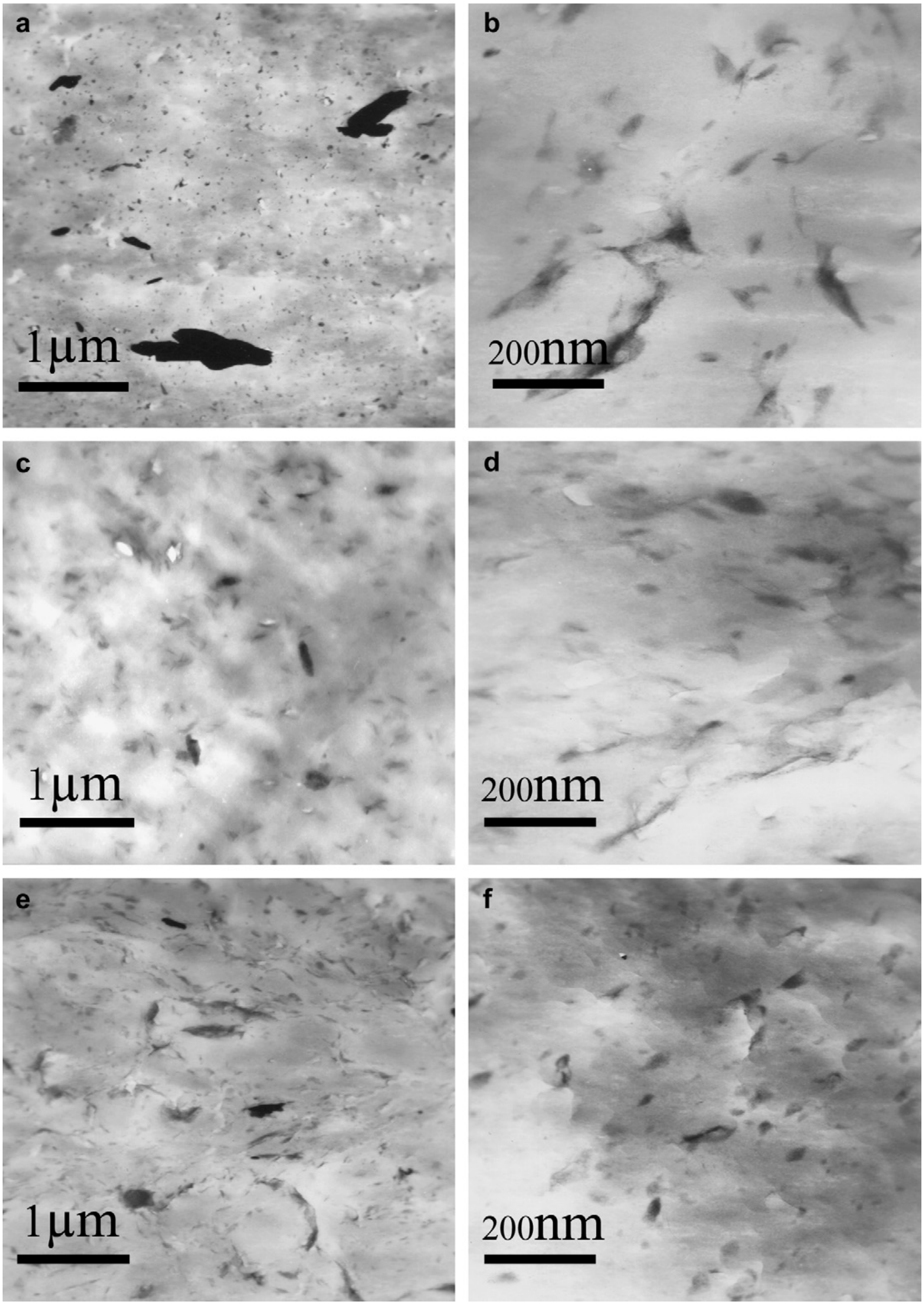

Fig. 5. TEM micrographs of (a,b) 5 wt% PVC/LDH-NO_3 composite, (c,d) 5 wt% PVC/LDH-DS nanocomposite and (e,f) 5 wt% PVC/LDH-stearate nanocomposite.

supports that the nanoscale dispersion has obvious effect on the absorption capacity of the released HCl. As for the PVC/LDH-stearate nanocomposites, it is interesting that the dehydrochlorination time even increases to 75 min, 15 times of that of the pure PVC, and more than twice of that of PVC/LDH-NO_3 composite and PVC/LDH-dodecyl sulfate nanocomposite. Here, the content of the inorganic LDH is about 2.44 wt% (5 wt% × 48.74%). This prominent increase of the dehydrochlorination time and the improvement of the thermal stability may be attributed to both the effects of the nanoscale dispersed LDH and the stearate anions. On one hand, the LDH particles were exfoliated into nanoscale and homogeneously dispersed in PVC matrix, resulting in enormous interface area and strong interfacial interaction between PVC and LDH. This will definitely increase the thermal stability of PVC. On the other hand, unlike DS^- anions, the stearate anions themselves are a kind of thermal stabilizer of PVC. In the present Congo Red test, they exhibited significant HCl absorption capacity when compared with DS^- and contributed to the PVC thermal stability.

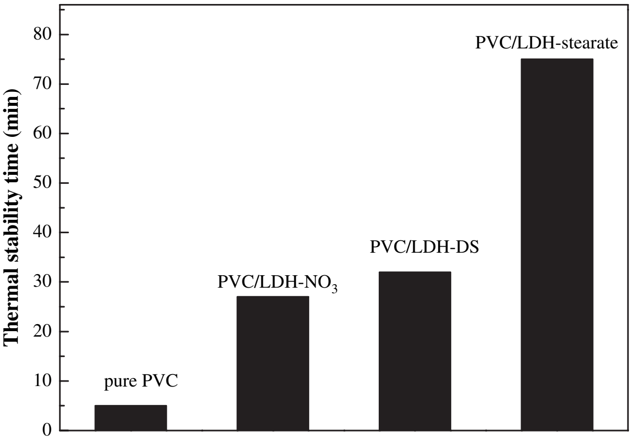

Fig. 6. Thermal stability time of PVC, PVC/LDH-NO$_3$ composite, PVC/LDH-DS nanocomposite and PVC/LDH-stearate nanocomposite measured by Congo Red test.

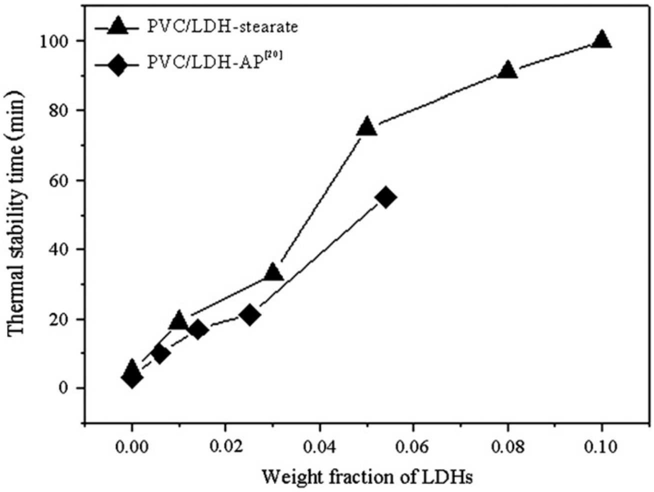

Fig. 7. Thermal stability time as a function of LDH weight fraction for PVC/LDH-stearate and PVC/LDH-AP nanocomposites.

The effect of Mg$_3$Al–LDH-stearate weight fraction on the thermal stability is shown in Fig. 7. It can be seen that the thermal stability time of the PVC/LDH-stearate nanocomposites is much longer than that of pure PVC resins (about 5 min) even at low content of 1 wt%, and increases with the weight fraction of Mg$_3$Al–LDH-stearate. When the content of Mg$_3$Al–LDH-stearate reaches 10 wt%, the thermal stability time is as long as 100 min, 20 times of that of the pure PVC resin. In addition, compared with the previous investigation of the PVC/AP-grafted-LDH nanocomposite [22], the present result shows an obviously further enhanced thermal stability and the discoloration time. The reason may lie on two aspects from microstructure and chemical contributions. The extent of exfoliation of LDH in the present study is much higher than AP-grafted-LDH, since no exfoliation occurred in their study. In addition, the interlayer stearate anion has an intrinsic and superior HCl absorption ability than AP during the dehydrochlorination process in degradation. We also note that the thermal stability of PVC/AP-grafted-LDH nanocomposite is superior to PVC/LDH-DS nanocomposite and PVC/LDH-NO$_3^-$ composite. Since AP has two hydroxyl groups in its molecular structure, we believe that there existed some un-reacted hydroxyl groups in the AP-grafted-LDH, which resulted in further increase of the thermal stability time by reacting with the released HCl vapor.

4. Conclusion

PVC/LDH nanocomposites can be successfully prepared via solution intercalation process using organo-LDHs with DS$^-$ and stearate anions in the interlayer space. The PVC/LDH-DS nanocomposite exhibits obviously enhanced thermal stability and increase of dehydrochlorination time in Congo Red tests relative to the neat PVC resin and the PVC/LDH-NO$_3$ composite. More importantly, the nanocomposite containing Mg$_3$Al–LDH-stearate shows a further significant increase of thermal stability and dehydrochlorination time compared to PVC/LDH-DS and PVC/LDH-AP nanocomposites, because the interlayer stearate anions have the intrinsic HCl absorption ability. Since many other properties of PVC are strongly dependent on the dehydrochlorination process, we believe that this study of the dramatically enhanced thermal stability of the PVC/LDH nanocomposites is helpful to exploit novel PVC resins with promoted thermal stability, photo-stability, flame retardancy and smoke suppression properties. Further detailed studies are currently under way and will be reported in the future.

Acknowledgements

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