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Tunable Properties of Exfoliated Polyvinylalcohol Nanocomposites by In Situ Coprecipitation of Layered Double Hydroxides

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Abstract. Poly(vinyl alcohol) (PVA) nanocomposites were prepared by a “one step” method based on the coprecipitation of layered double hydroxide (LDH) nanosheets in the polymer aqueous solution. The morphology, fire resistance properties, mechanical and optical properties of the PVA/LDH nanocomposites were studied. The LDH nanosheets were homogeneously dispersed in the PVA matrix as indicated by X-ray diffraction (XRD) pattern and transmission electron microscopy (TEM) characterization. Meanwhile, the peak of heat release rate (pHRR) and total heat release (THR) were decreased by 58% and 28%, respectively. Storage modulus at 30 oC was increased, and the transmittance of more than 90% at the visible region was obtained upon addition of 5 wt% LDH.

1. Introduction
Poly(vinyl alcohol) PVA is a water soluble polymer with biocompatibility and biodegradability that allows penetration into various fields such as proton-exchange membranes and polymer electrolyte fuel cells [1], separation apparatus [2], permeability membranes [3], drug delivery [4], and membrane manufacturing [5]. However, PVA is highly flammable. Thus, the investigations on halogen-free flame retardant PVA have been one of the most substantial research topics for the PVA modification. Recently, nanocomposite technology has brought a revolutionary advancement in the area of fire retardation. In the past few decades, the addition of nanofillers such as montmorillonite, layered double hydroxides (LDH), carbon nanotube, graphene/graphite oxide, etc, exhibits favorable effect on improving the flame retardancy, thermal stability and mechanical properties of polymer materials simultaneously at low loading [6, 7]. As the important layered inorganic materials, LDHs are widely applied in catalysis, optical, medical and flame retardant fields [8, 9] Many kinds of nanocomposites based on LDHs and polymeric materials could be prepared with improved properties. As is well-known, the dispersion of nanoadditives in a polymer matrix is a key factor for property enhancements [10]. However, LDH usually stacks together to form layered structure with thickness of tens nanometers due to the strong interlayer electrostatic interactions. Pristine LDH is not suitable for the penetration of giant polymer chains or chain segments into their gallery space. Based on this idea, we prepared exfoliated polymer nanocomposites by a “one step” method based on the coprecipitation of
LDH nanosheets in the PVA aqueous solution. The PVA solution acts as a dispersant medium that prevents the stacking of the generated sheets, which leads to the exfoliated morphology.

In this work, we reported the synthesis of PVA/LDH nanocomposites using a “one step” method, which led to a well-dispersed nanosheets with an exfoliated structure. The incorporation of LDH nanosheets not only enhanced the modulus and flame-retardant properties, but also maintained the optical transparency of PVA.

2. Experimental

9.0 g PVA was dissolved in a 100 mL solution of distilled water under stirring 80 °C. When the solution turned transparent, the solution was left to cool down at room temperature. A solution of Zn(NO$_3$)$_2$·6H$_2$O (0.1672 g) and Al(NO$_3$)$_3$·9H$_2$O (0.1052 g) was added dropwise with vigorous stirring under nitrogen. The colloid solution was left for 3h with constant stirring until using the addition of NaOH (0.5 M) to maintain a constant pH of 9. At last the colloid solution was cast onto glass plates and dried at room temperature for 1 day and further heated at 60 °C for 3 h to remove residual water. The nanocomposite films were washed by Soxhlet extraction in methanol for 24 h to remove NaNO$_3$ and residual unreacted salts. The total amount of metallic salts was chosen to yield PVA/LDH nanocomposites with 1 wt% filler loading if complete coprecipitation occurred. PVA nanocomposites with different LDH concentrations (3.0 and 5.0 wt%) were also prepared. Table 1 lists the formulations of the PVA/ZnAl-LDH nanocomposites.

3. Results and discussion

The formation of a layered ZnAl-LDH structure in the PVA solution by coprecipitation was analyzed by TEM. Fig. 1e displays the TEM image of the PVA3 obtained after the in situ coprecipitation of ZnAl-LDH in an aqueous solution of PVA. The TEM image reveals that the presence of single layers of inorganic materials in the PVA matrix, which correspond to exfoliated and disorderly LDH nanocomposites. XRD analyses were required to complement the data from the TEM experiments and to further confirm that the platelets were formed by the “one-step” nanocomposite preparation method corresponding to the LDH exfoliated sheets. The diffraction peak of pure PVA (Fig. 1a) is located at 2θ = 19.5°. The XRD patterns of the PVA nanocomposites (Figs. 1b and c) after coprecipitation only show the diffraction peak from PVA and no noticeable reflections related to the stacked ZnAl-LDH, which indicate that the disordered or exfoliated layers structure in the PVA matrix. In XRD pattern of PVA3 with higher inorganic content, there are two new weak diffraction peaks corresponding to the (003) and (006) reflection of the ZnAl-LDH phase (JCPDS 22-0700). This peaks may be due to the formation of intercalated/exfoliated nanocomposite, which indicates that the ZnAl-LDH has been partially intercalated and exfoliated in the PVA matrix [11]. In the case of hydrothermal treatment, the (00l) reflections are characterized by high intensities combined with narrow peak widths, indicating that the LDH phase presents a relatively high crystallinity.

Table 1. Formulation and microcombustion calorimeter (MCC) data of PVA and PVA/LDH Nanocomposites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Component</th>
<th>PHRR (W/g)</th>
<th>THR (kJ/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA0</td>
<td>PVA</td>
<td>431</td>
<td>28.6</td>
</tr>
<tr>
<td>PVA1</td>
<td>PVA/1 wt% ZnAl-LDH</td>
<td>355</td>
<td>24.9</td>
</tr>
<tr>
<td>PVA2</td>
<td>PVA/3 wt% ZnAl-LDH</td>
<td>258</td>
<td>23.2</td>
</tr>
<tr>
<td>PVA3</td>
<td>PVA/5 wt% ZnAl-LDH</td>
<td>181</td>
<td>20.6</td>
</tr>
</tbody>
</table>
Figure 1. (a) - (d) XRD patterns of PVA and PVA nanocomposites; (e) TEM image of PVA2 ultrathin section.

Figure 2. (a) Dynamic mechanical analysis (DMA) curves of PVA nanocomposites; (b) transmittance properties of PVA nanocomposites in the wavelength range of 300-900 nm.

DMA was carried out to evaluate the mechanical properties. The storage modulus and loss tangent curves are shown in Fig. 2a. The storage modulus is a measure of the stiffness, and it increased in all of the PVA/LDH nanocomposites. PVA3 had the largest increase compared with PVA0 at 30 °C. The strong hydrogen bonds between LDH nanosheets and PVA matrix and the homogeneous dispersion of the LDH nanosheets explain the observed increase.

MCC is an effective bench scale methods for investigating the combustion properties of polymer materials. Several parameters can be obtained from MCC, such as heat release rate (HRR) and total heat release (THR), the corresponding combustion data are presented in Table 1. Compared to the neat PVA, the PVA nanocomposites acquire significant improvements in flame resistance. With the increase of LDH, PHRR decreased from 431 to 181 w/g. Meanwhile, THR decreased from 28.6 to 20.6 kJ/g, which indicated that LDH is an effective material to improve the flame retardancy.

As mentioned above, PVA is widely used in packing and coating materials, which require high transparency in practical applications. Thus, a transparence measurement based on UV-vis transmittance analysis was performed. Fig. 2b shows UV visible transmission spectra of all nanocomposites produced. It can be seen that the optical transparency of PVA/LDH nanocomposites films are very high, even for the case of 5 wt% LDH content. The average transmittance of the PVA/LDH composite films is about 90%, which is almost equal to the neat PVA film. This can be attributed to the UV absorbance of the nanoscale dimensions of the nanosheets in the PVA matrix, which has been reported in many previous literatures. The good compatibility and strong interfacial adhesion between the well dispersed LDH and PVA matrix also play a role in the enhancement of optical transparency.

4. Summary
In this work, LDH nanosheets were incorporated into PVA by a direct coprecipitation method of LDH nanoplatelets within the polymer solution. The LDH nanosheets were homogeneously dispersed in the PVA matrix. By incorporating the LDH nanosheets, mechanical properties and fire resistance
properties were significantly enhanced. Meanwhile, the nanocomposites are highly transparent in the visible region.

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