New Facile Preparation of a Poly(vinyl chloride)/Layered Double Hydroxide Nanocomposite via Solution Intercalation

Jun Liu,[1,2] Guangming Chen,*[1] Jiping Yang,[2] and Yongmei Ma[1]
[1]*Beijing National Laboratory for Molecular Sciences (BNLMS), Laboratory of New Materials,*
Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, P. R. China
[2]*School of Material Science and Engineering, Beihang University, Beijing 100083, P. R. China*

(Received September 19, 2007; CL-071037; E-mail: chengm@iccas.ac.cn)

A poly(vinyl chloride)/layered double hydroxide (PVC/LDH) nanocomposite was successfully prepared via solution intercalation for the first time. Its microstructure was characterized by XRD, TEM, TGA, and IR, which clearly demonstrates that LDH particles were exfoliated into nanometer scale and homogeneously dispersed in the PVC matrix.

Recently, polymer/inorganic nanocomposites have been the focus of considerable research interest since these materials exhibit various greatly enhanced unique properties compared with their corresponding polymer and inorganic counterparts. Layered double hydroxide (LDH) is an important layered inorganic material, having a stacking of positively charged octahedral sheets with $[\mathrm{M^{II}}_{1-x}\mathrm{M^{III}}_{x}(\mathrm{OH})_2]$ $(\mathrm{A}^{m-})_{x/m}\cdot m\mathrm{H_2O}$ composition, wherein $\mathrm{M^{II}}$, $\mathrm{M^{III}}$, and A represent divalent (or monovalent) cation, trivalent cation, and the interlayer anion, respectively. Since LDHs have higher charge densities in the interlayer than other common layered materials such as clay, the intercalation of polymer into LDHs to prepare polymer/LDH nanocomposites is obviously more difficult than polymer/clay nanocomposites.[1–3] Fortunately, after appropriate organic surface modification, LDHs can also be employed to obtain polymer nanocomposites, such as polystyrene/LDH[4] and polyamide 6/LDH[5] nanocomposites. To the best of our knowledge, the study of poly(vinyl chloride) (PVC)/LDH nanocomposites is very scarce. In most of the previous publications, the exfoliation and dispersion state of LDHs in PVC by an electron microscope was not reported,[6–8] it least not in nanometer scale.[9] Bao et al.[10] obtained a PVC/LDH nanocomposite by in situ suspension polymerization. And we succeeded in exfoliation of LDH particles in nanometer scale in PVC by melt intercalation process using a twin-screw extruder.[11] Compared with the in situ polymerization and melt-blending processes, wherein special vessels are required and the toxic monomer is used, solution intercalation is a facile and effective method, especially for laboratory investigations. Here, we first report a new facile preparation of PVC/LDH nanocomposite via solution intercalation procedure. Its microstructure was studied by combination of X-ray diffraction (XRD), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), and Fourier-transform infrared (FT-IR) spectroscopy.

Figure 1 shows the schematic representation of the preparation procedure of PVC/LDH nanocomposite via solution intercalation. The procedure can be divided into two steps, i.e., coprecipitation and PVC intercalation. The organo-LDH was prepared by a typical coprecipitation method. In brief, an aqueous solution containing of 1 mol·L^{-1} of magnesium nitrate ($\mathrm{Mg(NO_3)_2}$) and aluminum nitrate ($\mathrm{Al(NO_3)_3}$) with a molar ratio of 3:1 was added dropwise into an aqueous mixture of sodium hydroxide (NaOH) and sodium dodecyl sulfate (SDS) in nitrogen atmosphere. To maintain the pH value of 10.0 of the system, a 1 mol·L^{-1} aqueous solution of NaOH was added simultaneously. Then, the mixture was heated and kept at 80 °C for 6 h in order to get high crystallinity. Finally, the product was washed with deionized water four times, dried and ground into powers to afford SDS–LDH with Mg/Al ratio of 3:1. The preparation of the PVC/LDH nanocomposite is briefly described as follows. PVC was first dissolved in tetrahydrofuran (THF) at 50 °C, and SDS–LDH was ultrasonically dispersed in cyclohexane. Then, SDS–LDH was added into the PVC solution and mixed for 30 min. Finally, it was washed and dried to obtain PVC/LDH nanocomposite.

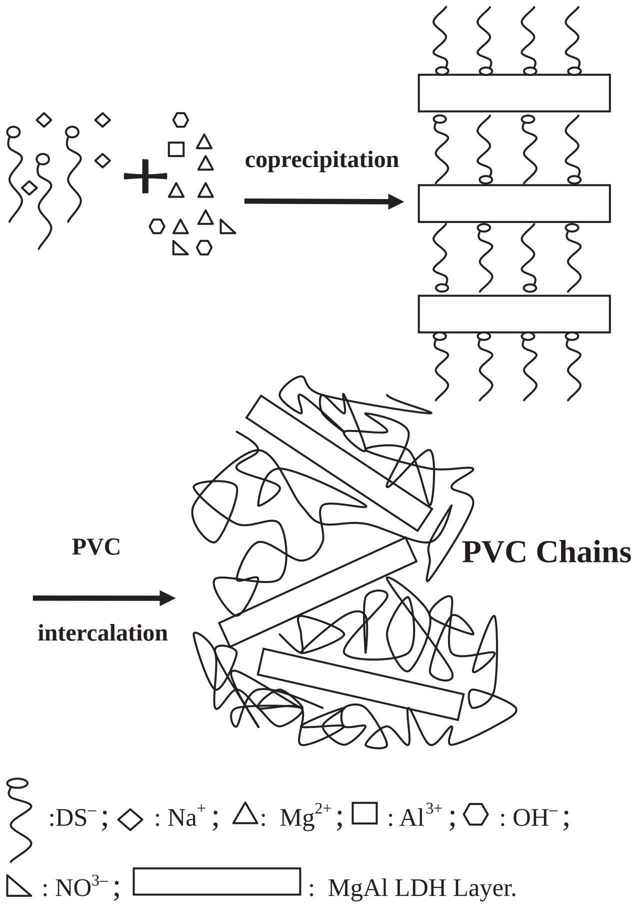

Figure 1. Schematic representation of the preparation procedure of PVC/LDH nanocomposite via solution intercalation.

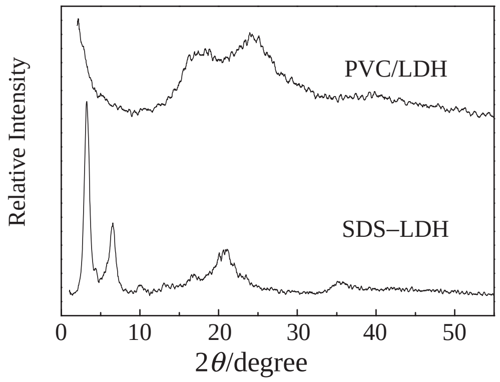

Figure 2. XRD patterns of SDS–LDH and PVC/LDH nanocomposite.

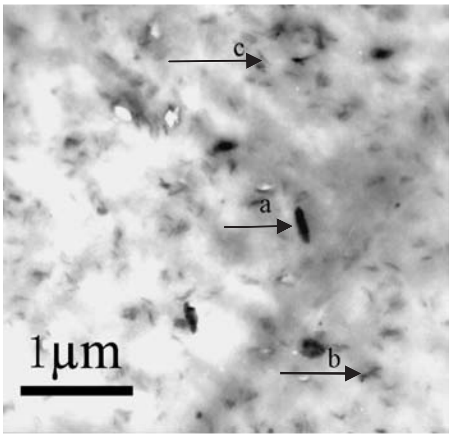

Figure 3. TEM micrograph of PVC/LDH nanocomposite.

The XRD patterns of SDS–LDH and PVC/LDH nanocomposite (containing of 5 wt % of SDS_LDH) are shown in Figure 2. The presence of a series of sharp diffraction peaks for SDS–LDH indicates an ordered lamellar structure. And the peak at $2\theta = 3.24^\circ$ corresponds to the basal spacing (d_{003}) of 2.72 nm. Considering the dimensions of individual LDH platelets and DS$^-$ anions, the anions of DS$^-$ may adopt a monolayer perpendicularly inclined structure in the interlayer space of the LDH. As for the XRD pattern of the PVC/LDH nanocomposite, no obvious sharp peak but only broad bands characteristic of PVC can be observed. Generally, the disappearance of any sharp XRD peak in low angle of $2\theta < 10^\circ$ suggests that the ordered layered structure have been greatly destroyed. Therefore, the 2D inorganic particles of SDS_LDH might be dramatically exfoliated and homogeneously dispersed in the PVC matrix.

The microstructure of the PVC/LDH nanocomposite was further studied by TEM technique, which reveals detailed information of local microstructure, different from XRD showing global information. Although XRD result shows that the SDS–LDH has been dramatically exfoliated, the typical TEM image of the PVC/LDH nanocomposite (Figure 3) demonstrates that there are still few primary particles with thickness of 70–90 nm (a). The particles with a thickness of about 30 nm are prevalent (b). Additionally, individual layers of LDHs can be also observed (c). Combination of XRD and TEM results show that LDH can be exfoliated into nanometer scale and homogeneously dispersed in PVC via solution intercalation procedure.

TGA results for pristine PVC and PVC/LDH nanocomposite show that the addition of the nanometer-scale-dispersed LDH particles can obviously increase the thermal stability of PVC. They exhibit two-stage decomposition processes. The onset decomposition temperatures were increased from 280 to 443 °C for neat PVC and from 284 to 454 °C for PVC/LDH nanocomposite containing of 5 wt % of SDS–LDH, respectively. This agrees very well with the above XRD and TEM results that the LDH particles have been greatly exfoliated and well dispersed in the PVC matrix, since the nanometer-scale-dispersed planar inorganic particles and layers can greatly increase the pathway for the diffusion of the decomposed gases and result in the obvious improvement of the thermal stability.[12]

FT-IR spectroscopy was also applied to investigate the microstructure of the PVC/LDH nanocomposite. The absorption bands at 1064 cm^{-1} characteristic of SDS–LDH can be observed obviously in the PVC/LDH nanocomposite. Note that the samples for IR measurements were collected randomly and that the content of the SDS–LDH is as low as 5 wt %. Therefore, the presence of the characteristic bands of SDS–LDH in the PVC/LDH nanocomposite suggests that the LDH was dramatically exfoliated and homogeneously dispersed in the PVC matrix as well.

In summary, we have developed a new facile preparation procedure to obtain PVC/LDH nanocomposite, whose microstructure was confirmed by XRD, TEM, TGA, and FT-IR techniques. More detailed studies are currently under way. The present work may open new avenues for development of polymer/inorganic nanocomposites with facile preparation procedures, deepen our understandings of polymer-based nanocomposites, and be expected to find their potential applications.

The authors thank financial support by the National Natural Science Foundation of China (No. 50603026).

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Published on the web (Advance View) November 10, 2007; doi:10.1246/cl.2007.1454