Preparation of a Poly(vinyl chloride)/Layered Double Hydroxide Nanocomposite with a Reduced Heavy-Metal Thermal Stabilizer

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ABSTRACT: A novel poly(vinyl chloride) nanocomposite with layered double hydroxide was successfully prepared via a melt-compounding process in which the positively charged platelets were dramatically exfoliated and homogeneously dispersed. Because of the absorption of the released hydrochloric vapor by both layered double hydroxide platelets and an organomodifier (stearate anions), the added amount of the conventional toxic heavy-metal heat stabilizer could be reduced. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 817–820, 2007

Key words: morphology; nanocomposites; nanolayers; nanotechnology; poly(vinyl chloride) (PVC)

INTRODUCTION

Polymer/inorganic nanocomposites exhibit dramatically increased or unique mechanical and physical properties superior to those of their conventional microcomposite counterparts because of the nanoscale dispersion, high interfacial area, and strong interfacial interaction,[1,2] and they have attracted much current interest in both industry and academia.[3–14] Poly(vinyl chloride) (PVC) is an important thermoplastic resin with versatile applications in pipes and tubing, window profiles, packaging films, belting, cable coverings, and so forth.[15,16] Unfortunately, in comparison with other polymers, studies of PVC-based nanocomposites[10–14,17] are scarce. In addition, among the few studies of PVC nanocomposites, most concern PVC/clay nanocomposites.[11–14]

Layered double hydroxide (LDH) is a layered inorganic material having a stacking of positively charged octahedral sheets with an $M^{II}_{1-x}M^{III}_{x}(OH)_2^{x+}(A^{m-})_{x/m}$ mH_2O composition, where M^{II}, M^{III}, and A represent a divalent (or monovalent) cation, a trivalent cation, and an interlayer anion, respectively.[18–22] Compared with clay minerals, LDH has a higher surface charge density. Its anion-exchange capacity is 200–470 mequiv/100 g,[23] whereas the cation-exchange capacity of montmorillonite is commonly 80–120 mequiv/100 g. Thus, the exfoliation of LDH platelets with a high surface charge density is very difficult to afford polymer/LDH nanocomposites. Fortunately, previous publications[24–26] have indicated that after appropriate surface organomodification, LDH can also be employed to prepare polymer-based nanocomposites. In light of its structural characteristics, because LDH itself can react and neutralize hydrochloride released during the thermal degradation of PVC,[27–31] it has obvious advantages in comparison with common layered inorganic materials used in PVC-based nanocomposites. In addition, some organic anions of PVC's heat stabilizer may be intercalated into the interlayer space via an ion-exchange reaction. In this way, the positive inorganic platelets may be exfoliated and homogeneously dispersed in the PVC matrix, and LDH and the organic modifier agent may contribute to the heat stabilization as well. Unfortunately, in most of the previous studies, LDHs were added either directly without any surface modification[28–31] or simply through a modification with a coupling agent,[32] and the exfoliation and dispersion states of LDH were not reported, or it was not fully exfoliated and homogeneously dispersed.[27–33] Here we report a novel PVC/LDH nanocomposite with a reduced heavy-metal thermal stabilizer, using sodium stearate (SS) as the organic intercalative agent.

In this study, we sought to make a novel PVC nanocomposite with SS as the organic modification agent in which two-dimensional positive inorganic platelets were fully exfoliated and homogeneously dispersed in PVC. Its microstructure was characterized by a combination of wide-angle X-ray diffraction (WAXD) and transmission electron mi-
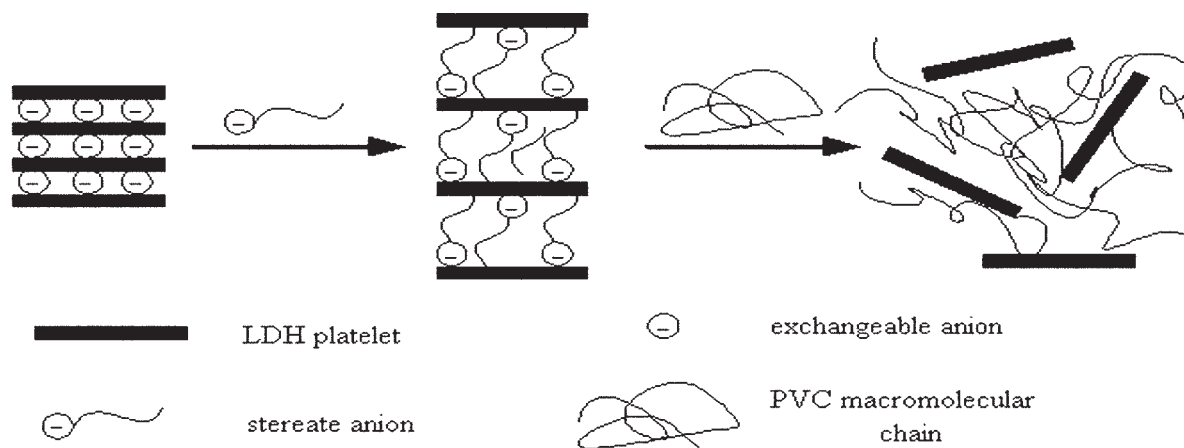
Figure 1 Schematic representation of the preparation of the PVC/LDH nanocomposite.

croscopy (TEM) techniques. The heat stabilization effect was studied through color changes.

EXPERIMENTAL

Materials

The PVC resin was a commercial suspension-polymerized product (SG5 type) supplied by Beijing No. 2 Chemical Co. (Beijing, China).

LDH was kindly provided by the Beijing University of Chemical Technology (Beijing, China). Its Mg/Al ratio was 2.

A commercialized Pb thermal stabilizer (BPR20) was purchased from Mitsui Chemical Co. (Tokyo, Japan).

SS was analytical-reagent-grade and was used without further purification.

Preparation of the PVC/LDH nanocomposite

Figure 1 shows a schematic representation of the preparation procedure for the PVC/LDH nanocomposite. First, the ion-exchange reaction was performed in a 1:1 (v/v) water/alcohol mixture with 3.0 g of SS and 1.0 g of LDH at 80°C with stirring for 4 h. Then, the PVC/LDH nanocomposite was obtained by a melt-blending procedure. The sheet samples of the PVC and PVC/LDH nanocomposite (1 mm thick) were prepared with a conical twin-screw extruder of a Hakke Rheocord 90 (Berlin, Germany). The temperatures of the extruder were 120, 150, 160, and 165°C from the hopper to the die, respectively, and the rotor speed was 50 rpm. In the melt-blending process, desired amounts of the Pb thermal stabilizer and LDHSS were added.

Characterization

WAXD tests were conducted on a Rigaku D/max 2400 diffractometer (Tokyo, Japan) with Cu Kα radiation

(0.15418 nm) scanned at room temperature. The voltage and current of the X-ray tubes were 40 kV and 120 mA, respectively. The measurements were performed within a 2θ range of 1.5–15° at a scanning rate of 8°/min. TEM photographs were obtained with a Hitachi H-800 electron microscope (Hitachi, Japan) operated at an accelerated voltage of 100 kV.

RESULTS AND DISCUSSION

In general, because of their hydrophilic surfaces and high surface energy, original inorganic particles are difficult to disperse homogeneously on a nanoscale, and fine inorganic particles, even nanoparticles, agglomerate automatically during a melt-mixing process with a polymer. Thus, the surface modification of inorganic particles with organic molecules or macromolecules is always necessary to change the surface from hydrophilic to hydrophobic and reduce the surface energy. In this work, the surface modification of the original LDH was accomplished by an ion-exchange reaction. The basal spacing of LDH was measured to be 7.5 Å (as shown in Fig. 2). After it was ion-exchanged with SS, the basal spacing of SS-intercalated LDH (LDHSS) increased dramatically to 38.8 Å (Fig. 2), and this indicated that the stearate anions were exchanged and intercalated into the interlayer space of the LDH platelets. Thus, the interlayer distance of LDHSS was enlarged to accommodate the PVC molecules. The surface of LDH was changed from hydrophilic to hydrophobic, as suggested by the good dispersion state of LDHSS in organic solvents such as cyclohexanone versus the quick precipitation of LDH in organic solvents.

After melt mixing, a PVC/LDH nanocomposite was successfully obtained, and its microstructure was characterized with a combination of WAXD (Fig. 2) and TEM (Fig. 3) techniques. In Figure 2, no obvious sharp peak can be observed at 2θ angles
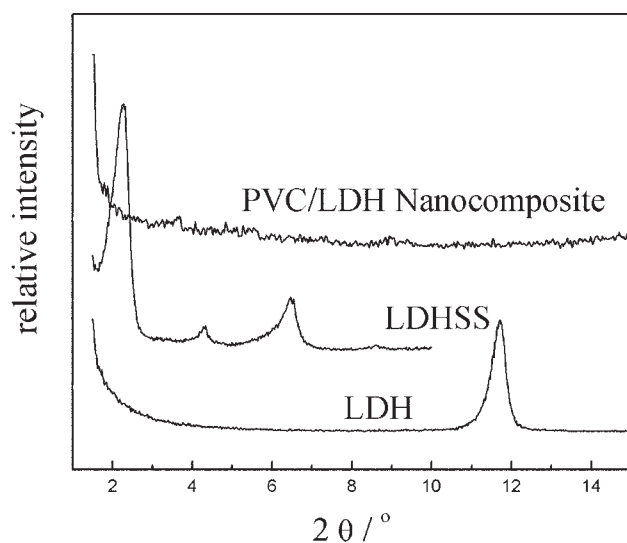
Figure 2 WAXD patterns of the LDH, LDHSS, and PVC/LDH nanocomposite (4 wt % Pb stabilizer + 2 wt % LDHSS).

lower than 10°, and this suggests that the ordered layered structure of the LDH platelets was destroyed, and the two-dimensional inorganic layers were dramatically exfoliated and homogeneously dispersed in the PVC matrix. Unlike WAXD patterns showing a global microstructure, TEM can reveal detailed information about a local microstructure. In Figure 3, a typical TEM image further demonstrates that the LDH platelets (dark lines) were exfoliated and dispersed homogeneously. Individual layers of LDH were prevalent, and some primary particles,
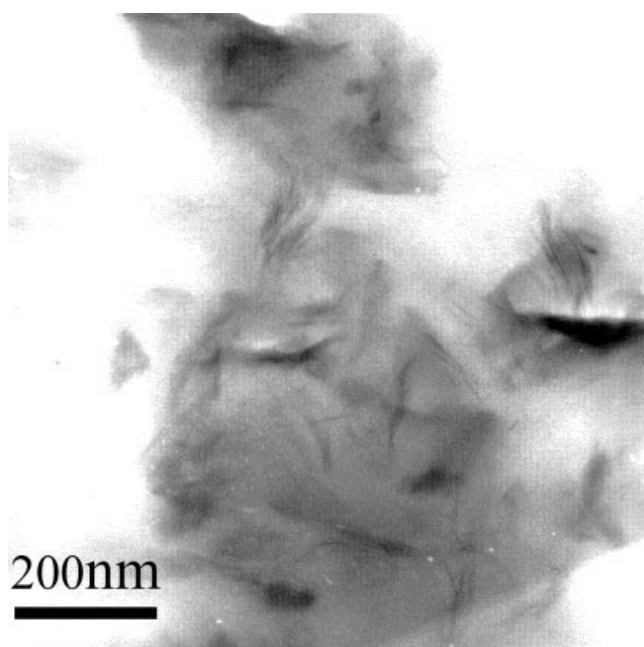
with their thickness less than 80 nm, were also observed. Therefore, after appropriate surface modification, LDH was exfoliated and dispersed in PVC on a nanometer scale to afford a new polymeric nanocomposite.

When there is not enough heat stabilizer in PVC melt processing, PVC degrades seriously. With an increase in the extent of degradation, an extruded sample becomes yellow, brown, red, purple, or even black and cannot be extruded at all.[1,2] In addition, when the degradation is serious, the material becomes brittle and loses its mechanical properties. In this study, when 5 wt % of the commercial product, the Pb heat stabilizer, was added, the PVC sheet sample was extruded very fluently, and its color was white [Fig. 4(a)]. When 2 wt % LDHSS was added to replace 1 wt % Pb stabilizer, that is, 4 wt % Pb stabilizer and 2 wt % LDHSS were added, the resulting PVC sheet sample could be extruded fluently, and its color became only slightly yellow, as shown in Figure 4(b), indicating that only slight degradation had occurred. If no Pb stabilizer was added, when the concentration of LDHSS was 8 wt %, the PVC sheet sample still could be extruded, but its color
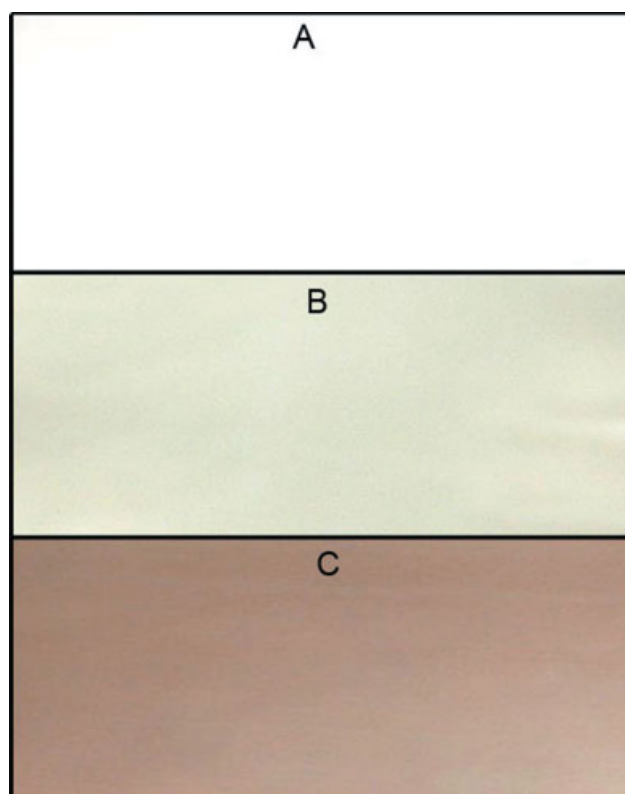

Figure 3 Typical TEM image of the PVC/LDH nanocomposite (4 wt % Pb stabilizer + 2 wt % LDHSS).

Figure 4 Extruded PVC and PVC/LDH nanocomposite sheet samples from a Hakker twin-screw extruder: (a) 5 wt % Pb stabilizer, (b) 4 wt % Pb stabilizer and 2 wt % LDHSS, and (c) 8 wt % LDHSS. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

was brown, indicating that a certain degree of heat degradation had occurred [Fig. 4(c)]. In this case, the sheet sample still kept its strength, rigidity, and modulus. If no LDHSS and no Pb stabilizer were added, PVC would become black soon and could not be extruded at all. Both results suggest that LDHSS can contribute greatly to the thermal stabilization of PVC and obviously replace and reduce the amount of the commercial Pb heat stabilizer. This may be because both interlayer anions, such as stearate anions, and the structural hydroxyl groups of LDH react with and neutralize the hydrochloride vapor that is released during the melt-processing procedure and thus stop the dehydrochlorination of the PVC chains in the autocatalytic degradation process.[19–24] As a result, LDHSS acts as a heat stabilizer and reduces the amount of the heavy-metal heat stabilizer.

CONCLUSIONS

A novel PVC/LDH nanocomposite with an obviously reduced amount of a heavy-metal thermal stabilizer was successfully prepared after the surface of the original LDH was appropriately modified via an anion-exchange reaction. The organomodified LDH may be used to reduce the toxic heavy-metal heat stabilizer as well. These results are of great importance for the development of novel polymeric nanocomposites and for the pursuit of novel low-toxicity and environmentally friendly heat stabilizers in the PVC industry. Further studies are in progress and will be reported in the future.

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