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Synthesis and characterization of PVC/montmorillonite nanocomposite

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Nanocomposites, composed of clay and polymers, have been studied extensively in recent years and show some unique properties relative to the virgin polymer and to conventional inorganic-polymer composites [1, 2]. In general, there are four methods to prepare polymer-clay nanocomposites: exfoliation-adsorption [3], *in situ* intercalative polymerization [4], melt intercalation [5] and template synthesis [6]. Melt intercalation and *in situ* intercalative polymerization are conventional methods to prepare polymer-clay nanocomposites and have been shown to be efficient alternatives to other methods.

Polyvinyl chloride (PVC) is a thermoplastic material widely used because of its valuable properties, such as good mechanical properties, and high chemical and abrasion resistance [7]. Recently, the preparation and characterization of PVC/montmorillonite nanocomposites formed by both melt and solution blending were reported [8, 9]. However, the resultant nanocomposites required large amounts of additives or stabilizers, and a fine nanostructure was not apparent. In our work, a PVC/montmorillonite nanocomposite (nanoPVC) was successfully synthesized via *in situ* intercalative polymerization process and an exfoliated nanocomposite was obtained.

Na-montmorillonite (Heibei, China, abbreviated as MMT) was modified by dimethyl dialkyl ammonium chloride (in which alkyl: C_{18}, 75%; C_{16} 25%) to produce organo-montmorillonite (abbreviated as OMT) according to a method we reported previously [10]. Vinyl chloride monomer (supplied by Beijing No. 2 chemical company), OMT (monomer: OMT = 100:3 wt) and initiator were mechanically mixed in a vacuum reactor and then distilled water and dispersants were added to start the polymerization. The molecular weights and polydispersity indices (PDI) of the obtained nanoPVC were examined by gel permeation chromatography (GPC). The change of the interlayer spacing was investigated by X-ray diffraction (XRD), using a Rigaku *D*/max 2400 diffractometer with Cu K_α radiation ($\lambda = 0.154$ nm, 40 kV, 120 mA) at room temperature, scanning over the 2θ range from 1.5° to 15° in 0.02° steps, at a scanning rate of 8°/min. The nanostructure features were characterized by an H-800 transmission electron micorscopy (TEM) at 100 kV. The samples were ultramicrotomed with a diamond knife at room temperature to give 60–80 nm thick sections, which were transferred on to 200 mesh copper grids.

Table I is the number- and weight-average molecular weights (M_n, M_w) and polydispersity indices (PDI) of the PVC and the nanoPVC polymerized at two different temperatures measured by GPC. The data show the presence of OMT seems to have little effect on the average molecular weights of the PVC, and M_n (or M_w, PDI) of nanoPVC is observed to slightly increase with increase in polymeric temperature. The results suggest that the nanoPVC could be synthesized by a traditional suspending polymerization procedure without major amendment.

The nanostructure of polymer/clay nanocomposites is described as either intercalated or exfoliated, which are popularly characterized by XRD and TEM. Fig. 1 shows the XRD patterns of the MMT, OMT and the nanoPVC 2. The characteristics peaks correspond to

TABLE I M_n, M_w and PDI of the PVC and the nanoPVC of two different polymeric temperatures

Sample	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	PDI (M_w/M_n)
PVC	7.4	12.8	1.73
NanoPVC 1	7.3	13.1	1.79
NanoPVC 2	7.4	13.4	1.81

NanoPVC 1 was polymerized at 53 °C, nanoPVC 2 and PVC were polymerized at 57 °C.

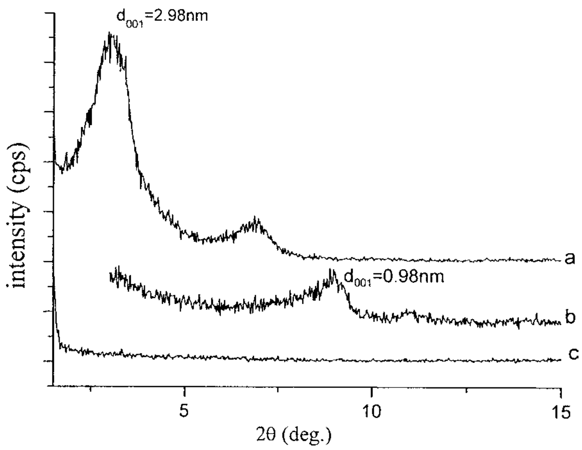

Figure 1 X-ray diffraction patterns of (a) OMT, (b) MMT, and (c) nanoPVC 2.

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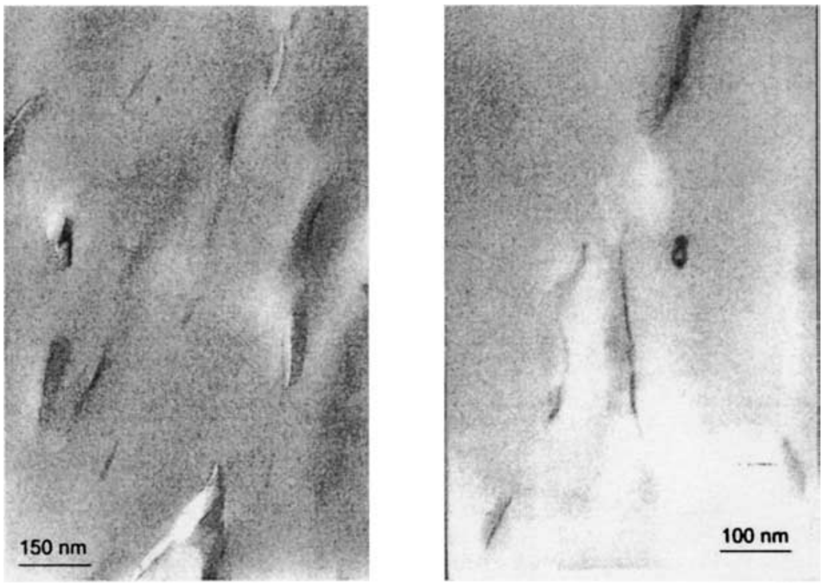

Figure 2 TEM images of the nanoPVC 2.

the (001) plane of the clays. The characteristic peak for the (001) plane of untreated Na^+-MMT appears at 9.0 °, showing the basal spacing (d_{001}) is 0.98 nm. After organic modification, the diffraction peak shifts to 2.96 °, showing the basal spacing (d_{001}) increases from 0.98 to 2.98 nm, and thus enable the small vinyl chloride monomers to easily penetrate the OMT galleries. While for the nanoPVC, the characteristic peak disappears, suggesting that the basal spacing may be expanded over 6 nm ($2\theta < 1.5\,°$) and exceeded our XRD instrument testing range (starting from 1.5 °). The absence of an XRD peak implies that during the polymerization, the layered structure of OMT was destroyed by the growing of the PVC macromolecular chains and voluminously exfoliated in the PVC matrix.

The exfoliated structure of the nanoPVC is further confirmed by TEM. Fig. 2 shows the TEM images of the nanoPVC 2. The black lines represent the clay layers. It can be seen that the clay layers are exfoliated into nano-scale layered blocks and dispersed homogeneously in the matrix. Such a nanostructure can be considered as exfoliated type. The mechanical and thermal properties of the obtained nanoPVC will be studied and reported later.

In conclusion, polyvinyl chloride/montmorillonite nanocomposites have been synthesized by *in situ* intercalative polymerization. The presence of OMT has no obvious effect on the suspending polymerization technique. Both XRD patterns and TEM images confirm that OMT is exfoliated and separated into nano-scale layered blocks.

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