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# Morphology and Properties of PVC/Clay Nanocomposites via *in Situ* Emulsion Polymerization

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**ABSTRACT:** PVC/Na<sup>+</sup>-montmorillonite (MMT) nanocomposites were prepared via a simple technique of emulsion polymerization at several different MMT clay concentrations. X-ray diffraction and transmission electron microscopy studies revealed the formation of a mixture of intercalated and exfoliated nanostructure. Tensile testing results showed that the tensile modulus of the nanocomposites increased with the addition of clay, while the tensile strength decreased little. The notched impact strength of the nanocomposites was also improved. For systems containing clay in the range of 2.1 to 3.5 wt %, the impact strength was almost two times as large as that of pure PVC. However, those mechanical properties began to decrease with the con-

tinuously increasing amount of clay. The fracture surface of pure PVC and the nanocomposites was observed by scanning electron microscope. Thermal properties of the nanocomposites were found to increase as a result of clay incorporation. The glass transition temperatures of the PVC/clay nanocomposites were nearly identical to that of pure PVC. The Vicat softening points exhibited a progressively increasing trend with the clay content added. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 277–286, 2004

**Key words:** poly(vinyl chloride) (PVC); clay; nanocomposites

## INTRODUCTION

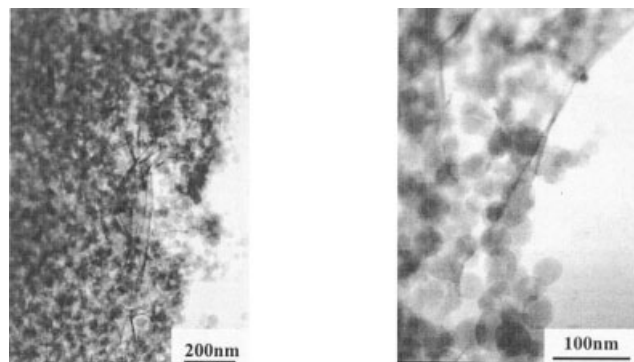
Poly(vinyl chloride) (PVC) is one of the most important commercial plastics owing to its wide applications and low cost. Despite its enormously technical and economic importance, PVC still possesses many problems, such as low thermal stability and brittleness. These inherent disadvantages limit the use of PVC and its composites in some applications. Therefore, it is necessary to develop new PVC products with high quality and good properties to broaden PVC applications.

Recently, polymer/clay nanocomposites have attracted much attention as examples of a newly developed polymer reinforcement technique. Owing to the nanometer-size dispersion of clay, polymer/clay nanocomposites usually exhibit improved mechanical properties, thermal stability, flame retardancy, gas barrier properties, ionic conductivity, etc. compared to the pristine polymers.<sup>1</sup> Polymer/clay nanocomposites have been more widely investigated, probably because the starting clay materials are easily available and because their intercalation chemistry has been studied for a long time.<sup>2</sup> While many polymer/clay

nanocomposites have been reported, PVC/clay nanocomposites have not attracted enough attention. Ishida et al.<sup>3</sup> applied a novel approach to nanocomposite preparation in which PVC was blended with a tin stabilizer in the presence of clay and epoxy; only X-ray diffraction (XRD) results have been reported. Wang et al.<sup>4</sup> prepared PVC/clay nanocomposites by melt blending of the polymer with an organically modified clay. The thermal and mechanical properties of these nanocomposites vary, depending upon the amount of clay and di(2-ethyl-hexyl)phthalate (DOP) that is present. However, they found that the organic clay had an effect on the course of the degradation of the PVC. Wan et al.<sup>5</sup> prepared three kinds of PVC/MMT nanocomposites by melt blending with Na<sup>+</sup>-MMT and two organically modified MMTs. They reported that the silicate modification and MMT content could affect the morphology, relaxation behavior, and mechanical properties of the composites. They also reported that, when comparing PVC/Na<sup>+</sup>-MMT with PVC/organic MMT nanocomposites, the former was more stable than the latter during melt processing. We have also studied the preparation of PVC/organic clay nanocomposites before.<sup>6</sup>

As inorganic materials, MMT has been adopted in the field of nanocomposites.<sup>2,7,8</sup> The basal space of the pristine silicate is smaller than the radius of gyration of general polymers. General polymers may experi-

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**Figure 1** TEM images of the emulsion of PVC/MMT6.0% nanocomposites.

ence difficulties to penetrate into silicate layers, because of size and hydrophobic character of polymers.<sup>9</sup> However, exfoliation adsorption in an emulsion with  $\text{Na}^+$ -MMT, known to readily delaminate clay in water, was studied to promote the intercalation of water-insoluble polymers.<sup>10</sup> In some articles, it was confirmed that a simple one-step emulsion polymerization could offer a new approach to the synthesis of a nanocomposite.<sup>11,12</sup> Since the interlayers of  $\text{Na}^+$ -MMT are filled with sodium cations, the hydrophilic properties are enhanced and lead to a high degree of swelling in water. We can use water to widen the basal space of silicate layers without any chemical treatment and performed the polymer intercalation into the silicate layers by emulsion polymerization rather than melt or solution intercalation. Furthermore, we can avoid the bad affection of the organic clay's modification in PVC/clay nanocomposites.

In this study, an emulsion polymerization, in which a vinyl chloride monomer (VCM) was dispersed in a water phase and polymerized with a water-soluble radical initiator, had been carried out in the presence of  $\text{Na}^+$ -MMT. The formation of a nanocomposite structure and the mechanical and thermal properties were investigated.

## EXPERIMENTAL

### Materials

Cloisite  $\text{Na}^+$  (Cation Exchange Capacity, CEC = 92.6 mEq/100 g) supplied by Southern Clay Products Inc.

is a  $\text{Na}^+$ -exchanged MMT. Vinyl chloride (VC), above 99.99 wt % purity, was supplied by the Tianjin Chemical Plant. Sodium dodecylsulfate (SDS), chemically pure, was used as an emulsifier; potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ), chemically pure and recrystallized, was used as an initiator; sodium hydroxide (NaOH), chemically pure, was used as a pH modifying agent; calcium stearate, stearyl alcohol, chemically pure, and organotin stabilizer, commercial grade, were supplied by the Tianjin Chemical Company. All of the water used was deionized.

### Preparation of hybrid

The preparation of nanocomposites with various amounts of  $\text{Na}^+$ -MMT was carried out in the following way: 4.00 g of SDS, 1.20 g of  $\text{K}_2\text{S}_2\text{O}_8$ , and a certain amount of  $\text{Na}^+$ -MMT were dispersed in 1,000 mL of water by agitation. The weight percentage of  $\text{Na}^+$ -MMT in PVC/ $\text{Na}^+$ -MMT nanocomposites is represented by X (2.1%) and is denoted by PVC/MMTX (PVC/MMT2.1%). NaOH solution (1 wt %) was added to adjust the pH of the mixture between 9 and 10. After standing overnight, the mixture solution was poured into a 2-L stainless-steel autoclave. VCM (400 g) was introduced, and the contents were stirred at the speed of 250 rpm for 2 h. The emulsion polymerization then was carried out at 50°C. After the pressure was reduced by 0.4 MPa, the reaction mixture was then cooled to room temperature. The resin was obtained from the emulsion by freeze at -20°C, filtration, and washing with water several times and then was dried in an oven at 50°C for 24 h under reduced pressure.

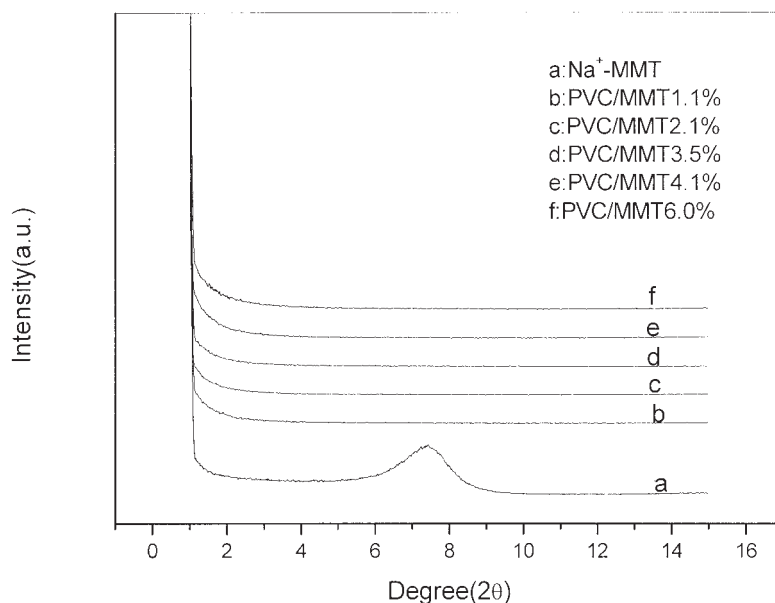
The resulting powder and other necessary reagents were mixed at a definite weight ratio, which presents in the formulation (resin: organotin stabilizer: calcium stearate: stearyl alcohol = 100 : 4 : 0.8 : 0.8). All components were first mixed in a high-speed mixer at room temperature and then milled on a laboratory two-roll mill between 170 and 175°C for 5 min. The pellets were molded into sheets of 4 mm at 180°C and 15 MPa, followed by cooling to room temperature at 5 MPa.

### Characterization and measurements

X-ray diffraction measurements were carried out by using a DMAX-RC X-ray generator (Cu  $\text{K}\alpha$  radiation)

**TABLE I**  
Mean Particle Diameters of PVC/MMT Nanocomposites

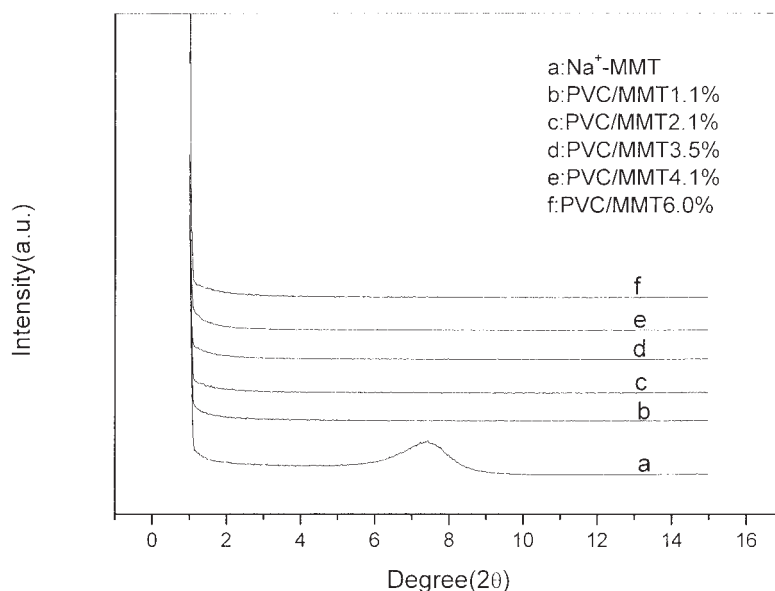
Clay content (wt %)	Intensity mean (nm)	Volume mean (nm)	Number mean (nm)
0	72.6	46.9	22.4
1.1	76.1	54.5	24.0
2.1	73.4	52.2	25.3
6.0	75.2	49.8	24.7



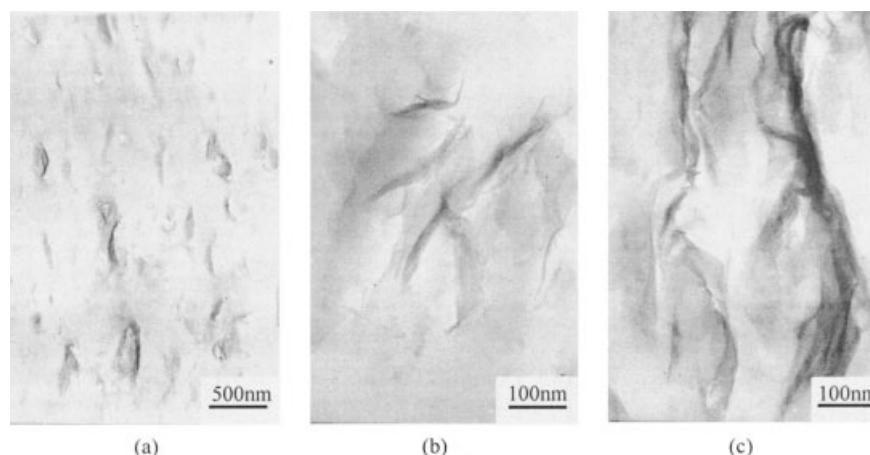
**Figure 2** XRD patterns of MMT and the PVC/MMT hybrids powder with different clay content.

at room temperature. Patterns were recorded by monitoring those diffractions that appeared in the  $2\theta$  range of  $1\text{--}15^\circ$  at a rate of  $1^\circ/\text{min}$ . Samples were  $\text{Na}^+$ -MMT and PVC/MMT nanocomposites. Transmission electron microscopy (TEM) images of samples were taken from a Hitachi H-800 TEM. The particle diameters were measured by Zetasizer 3000HSA (Malvern Instruments Ltd., United Kingdom). Weight average molecular weights were determined by using GPC. The samples were the polymer, which recovered from the powder that was extracted with hot tetrahydrofuran (THF) for 38 h by means of the Soxhlet extraction.

GPC analysis was performed at a flow rate of THF 1.0 mL/min at  $35^\circ\text{C}$  using a Waters GPC system equipped with styragel HR columns and the columns were calibrated with well-characterized monodisperse PS. Tensile strength testing was performed using a CMT-6104 electronic tensile tester with a computer controlling system. The dumbbell-shaped samples were cut from the above sheets. Tests were conducted at an extension rate of 5.0 mm/min at  $21^\circ\text{C}$ . Notched impact strength was carried out on a XCJ-40 Charpy impact tester. Size of the sample for the notched impact test was  $55 \times 6 \times 4 \text{ mm}^3$ , the notch depth was



**Figure 3** XRD patterns of MMT and the sheets of PVC/MMT hybrids.



**Figure 4** TEM images of PVC/MMT2.1% nanocomposites.

equal to 1/3 of the thickness of the sample. The fracture surface morphology of samples was characterized by Philips XL30 scanning electron microscope (SEM). The fractured surface of the notched impact bar was coated with a thin layer of gold under vacuum. Thermogravimetric analysis (TGA) was carried out using a TA Instruments SDT-2960. The samples were gradually heated to 700°C in N<sub>2</sub> at a rate of 20°C/min. Differential scanning calorimetry (DSC) was performed using a TA Instruments DSC-2910. The samples were heated to 120°C in N<sub>2</sub> at a rate of 10°C/min. The second scanning data were accepted. Vicat softening points (VSP) of samples were determined by a XWB-300F heat-distortion and Vicat softening point apparatus with computer controlling system. Tests were conducted from room temperature up to 150°C at a heating rate of 50°C/h.

## RESULTS AND DISCUSSION

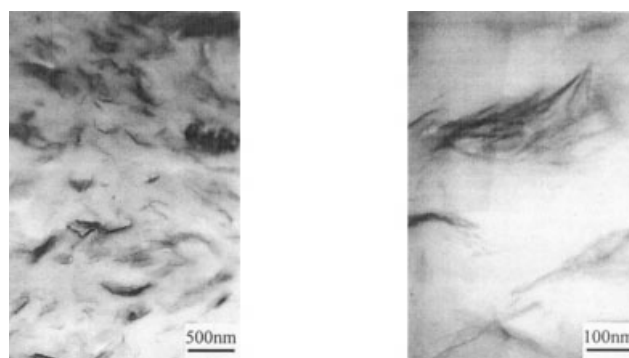
### Structure and morphology

Figure 1 shows the TEM photographs of the emulsion of PVC/MMT nanocomposites (with MMT content of 6.0 wt %). It can be seen that the diameters of the droplets were between ~ 20 and 40 nm; the clay was exfoliated into thin layers (thickness ≤ 7nm) and well mixed with the PVC emulsion droplets. From Table I, the table of mean particle diameters of PVC/MMT nanocomposites, we can see that the presence of the nanoclay and its concentration did not affect the size of the emulsion droplets.

X-ray diffraction is a useful technique for the characterization of polymer/clay nanocomposites. It allows the precise measurement of silicate layer spacing and monitors the intercalation behavior of polymer chains. Figure 2 shows the XRD patterns of MMT and the PVC/MMT hybrids powder with different clay

contents. It can be seen that the characteristic diffraction peak of MMT was at  $2\theta = 7.43^\circ$ , corresponding to a basal spacing of 1.19 nm. The original peak of pristine MMT disappeared in PVC/MMT hybrids, indicating that MMT may be delaminated into nanoscale layers. We obtained the dry powder of composites by washing, filtration, and drying after freeze coagulation of the emulsion. In the resulting emulsion powder, some of the silicate layers may be embedded in the resin particles, some may be segregated at the surface of the particles.

Figure 3 shows the XRD patterns of MMT and the sheets of PVC/MMT hybrids. From Figure 3, it can be seen that the original peak of pristine MMT disappeared in PVC/MMT hybrids, indicating that MMT may be delaminated into nanoscale layers in the PVC matrix. It should be noted that, in the exfoliated or delaminated state where the periodic arrangement of clay is lost, XRD does not provide definitive information regarding the structure of the nanocomposite. XRD can also suffer from problems of weak peak intensity with a bias toward surface region, and poor peak resolution, particularly in these composites



**Figure 5** TEM images of PVC/MMT6.0% nanocomposites.

TABLE II  
Molecular Weight Results of PVC/MMT Nanocomposites

Composites	Pure PVC	PVC/MMT2.1%	PVC/MMT3.2%	PVC/MMT6.0%
$M_w$	125,000	88,000	89,000	86,000

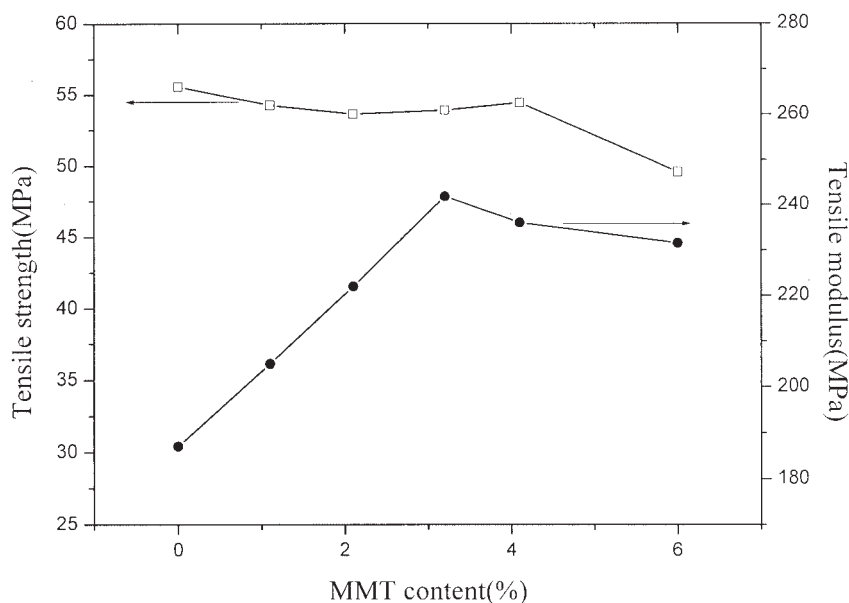


Figure 6 Tensile properties as a function of MMT content for PVC/MMT nanocomposites.

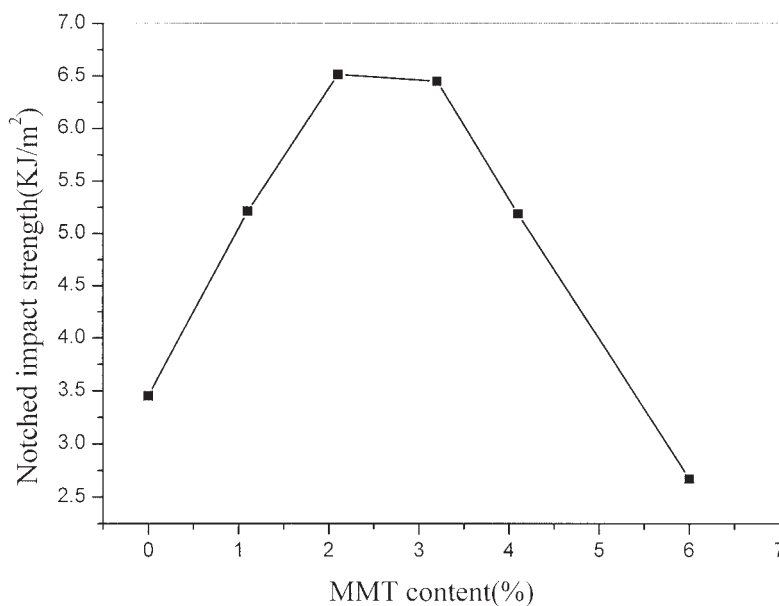


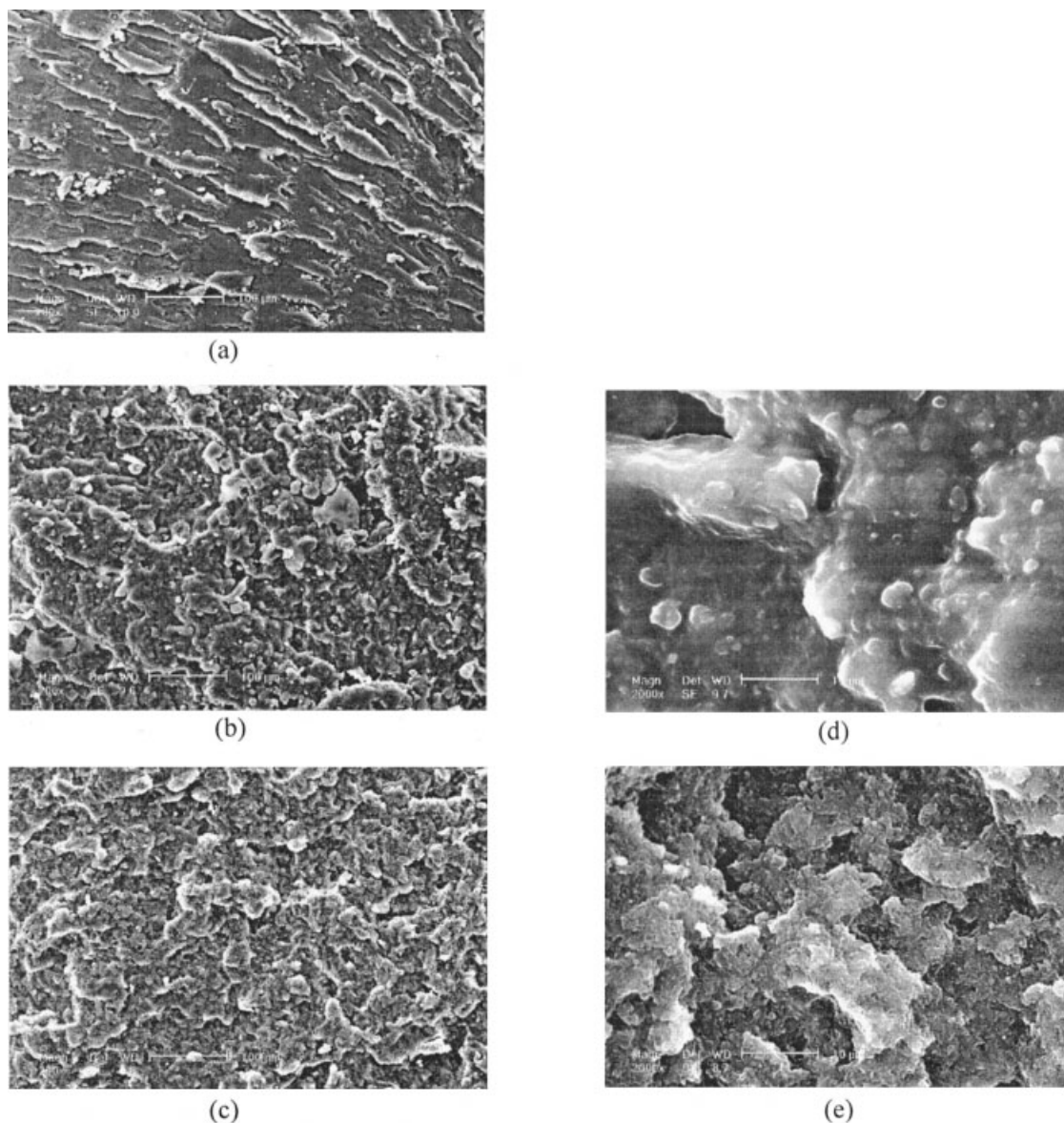
Figure 7 Notched impact strength as a function of MMT content for PVC/MMT nanocomposites.

where the clay content is small.<sup>6</sup> In fact, it was extensively reported that some polymer layered silicate nanocomposites show featureless XRD patterns when they exhibited exfoliated or delaminated structures, even for some partially exfoliated cases.<sup>13</sup> Therefore,

conclusions concerning mechanisms of hybrid formation and hybrid microstructure based solely on XRD results are not adequate.

In contrast to the global averaging of XRD, conventional TEM can provide information in real space on





**Figure 8** SEM images of the fracture surface of (a) pure PVC; (b) PVC/MMT2.1%; (c) PVC/MMT6.0%; (d) PVC/MMT2.1% at higher magnification, and (e) PVC/MMT6.0% at higher magnification.

morphology and spatial distribution of the various phases.<sup>14</sup> When XRD data exhibit featureless diffraction patterns it is necessary to use TEM to determine the nature of the hybrids and to provide additional information. Figure 4 shows TEM photographs of the PVC/MMT hybrid in which MMT content is 2.1 wt % at two magnifications. It can be observed from Figure 4(a) that MMT has been delaminated into nanoscale layers and is dispersed throughout PVC matrix. Figures 4(b) and (c) are higher magnification photographs of the hybrid. In Figure 4(b), it can be observed that some of the MMT particles have been partially exfoliated into single layers and thin multilayer stacks. There are still some intercalated layers, which are less

than 50 nm in thickness and 400 nm in length, as shown in Figure 4(c). It is evident that the PVC/MMT hybrid shows a mixture of intercalated and exfoliated nanostructure.

Figure 5 presents TEM images of the PVC/MMT hybrid in which MMT content is 6.0 wt % at two magnifications. As shown in Figure 5, some silicate still dispersed in nanoscale, however, some clay aggregates could be observed clearly in the matrix and were dispersed irregularly with the clay content increased.

Molecular weights of the nanocomposites are listed in Table II. Weight-average molecular weights ( $M_w$ ) decreased after the addition of MMT. However, the

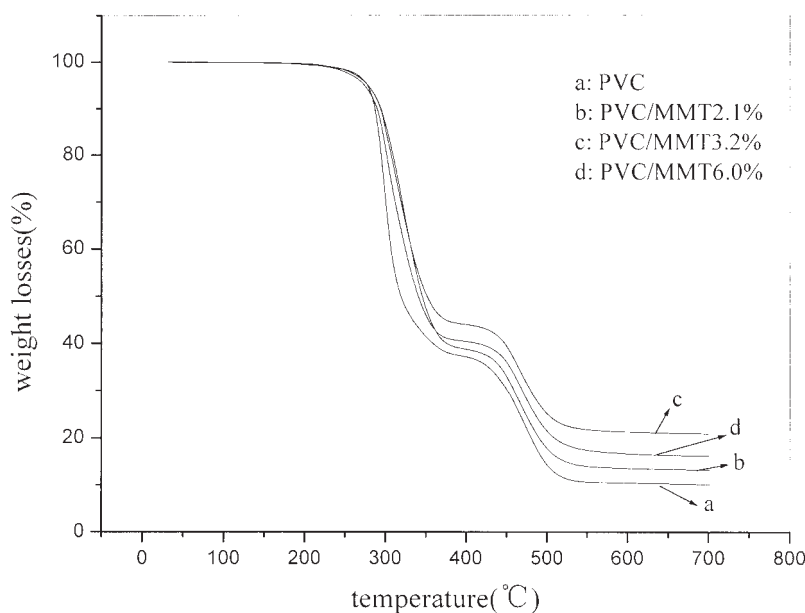


Figure 9 TGA curves of PVC/MMT nanocomposites with different MMT content.

$M_w$  of the composites did not change much with the concentration of MMT.

### Mechanical properties

The properties of composite materials are greatly influenced by the degree of mixing between the two phases. Generally, the strengthening of a polymer filled with inorganic materials is related to the thickness of the interlayers and the degree of interfacial interactions. In conventionally filled polymers, the micrometer-sized particles and the poor physical attraction between the organic and inorganic components lead to weaker materials. In nanocomposites, because of the very large surface area of the nanoscale filler, the interfacial interaction between the filler and the matrix is very strong even without a compatibilizer.<sup>10</sup> Due to the nanoscale reinforcement, the nanocomposite will exhibit markedly improved mechanical properties, such as an increased modulus and strength. In this study, because of the nanoscale silicate layers dispersed in the PVC and the stronger interactions between silicate layers and PVC, the mechanical properties of the nanocomposites are greatly improved.

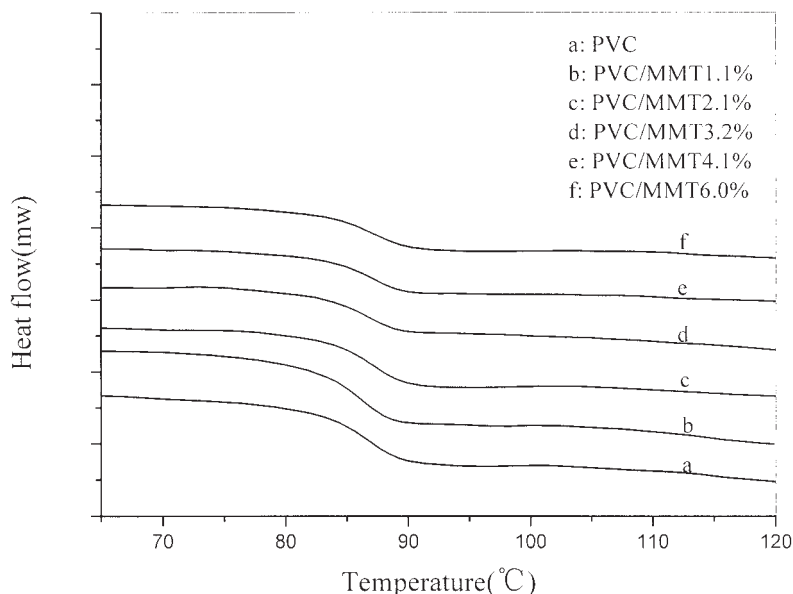
Figure 6 shows the tensile properties as a function of clay loading for PVC/MMT nanocomposites. It can be seen that the tensile strength of the nanocomposites decreases little and the tensile modulus increases with the MMT added. When the MMT content is 3.2 wt %, the modulus of the nanocomposites is 1.29 times that of pure PVC. As the amount of clay continuously increases, the modulus and the tensile strength begin to decrease. Mica-type silicate platelets are highly anisotropic, which complicates the analysis significantly. The experimental results would be further complicated by the fact that particle aggregation influences the modulus of the composites.<sup>15</sup>

The notched impact strength of the nanocomposites against MMT content is shown in Figure 7. It can be seen that the impact strength of the nanocomposites increases as a result of MMT incorporation. Here, pure PVC has the impact strength of 3.45 KJ/m<sup>2</sup>. For systems containing MMT in the range of 2.1 to 3.5 wt %, the impact strength of the nanocomposites is almost two times as large as that of pure PVC. The strength then decreases with a continuously increasing MMT content. From Figure 5 we can see that some clay aggregates formed with the increasing clay content.

TABLE III  
TGA Data of PVC/MMT Nanocomposites

Composites	Pure PVC	PVC/MMT2.1%	PVC/MMT3.2%	PVC/MMT6.0%
$T_{0.1}(^{\circ}\text{C})$	286	293	293	289
$T_{0.5}(^{\circ}\text{C})$	319	345	351	340



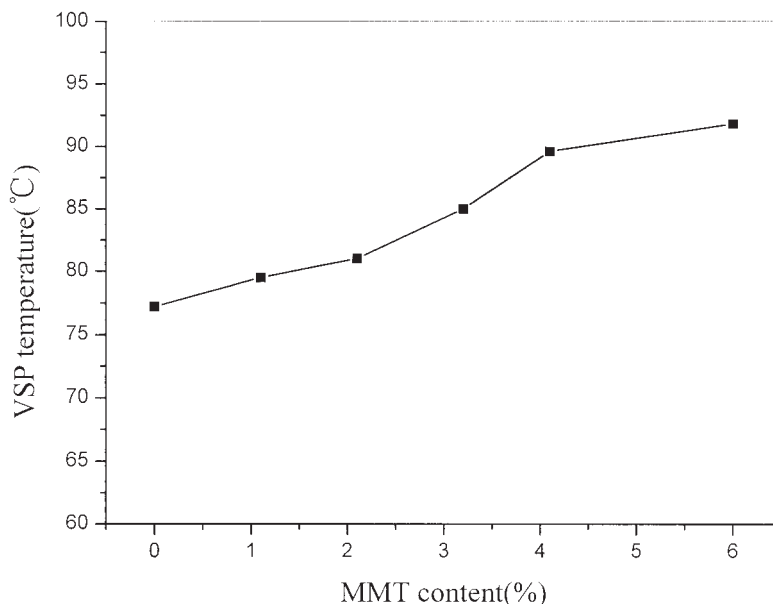


**Figure 10** DSC curves of PVC/MMT nanocomposites with different MMT content.

The formation of large silicate stacks, which effectively reduces the interfacial area available for polymer–clay interactions and acts as stress concentrators, results in poor mechanical properties.

Figure 8 shows the SEM observation of the fracture surface of pure PVC and PVC/MMT nanocomposites with different MMT contents. It is obviously seen that the morphological structure of the nanocomposites is greatly changed owing to the addition of the MMT. For pure PVC [Fig. 8(a)], the fracture surface is clear and sharp, typical of a brittle material.<sup>16</sup> For the PVC/

MMT nanocomposite with 2.1 wt % MMT [Fig. 8(b)], the fracture surface is rough and rugged, and the firm morphology is apparent. The presence of nanoscaled MMT forces the crack to progress along a more tortuous path, which increases the fracture surface area of materials and its toughness. Furthermore, the individual silicate layers are extremely strong and are unlikely to break during crack growth. Hence, the mechanical properties are improved with the addition of clay. A SEM photograph of the nanocomposite with 6.0 wt % MMT is shown in Figure 8(c). It can be seen



**Figure 11** Influence of MMT content on VSP of PVC/MMT nanocomposites.

from Figures 6 and 7 that mechanical properties of PVC/MMT6.0% are even worse than that of pure PVC. Comparing Figures 8(c) with (b), we can see that the morphology of the fracture surface in 8(c) is looser and collapsed. This maybe due to the bad dispersion of MMT at high MMT content. Further indications of the differences of the morphological characteristics between Figures 8(c) and (b) are clearly shown in Figures 8(d) and (e) at higher magnification.

### Thermal properties

It is known that PVC is one of least stable thermoplastics and will degrade during melt processing if no stabilizer or plasticizer is present.<sup>4</sup> One of the most important property enhancements exhibited by polymer/clay nanocomposites is their increased thermal stability at a quite low filling level. Because of the thermal insulation effect of MMT, the formation of a polymer nanocomposite can retard the thermal degradation. The much better thermal stability can also be affected by other factors, such as the type of polymer and the experimental conditions of the material degradation.<sup>2</sup> Wang et al.<sup>4</sup> reported that the addition of clay caused an initial drop in the onset of degradation in PVC/MMT nanocomposites. Apparently, the thermal stability of the nanocomposites could be slightly improved by the addition of MMT. Wan et al.<sup>5</sup> also reported that, when comparing PVC/Na<sup>+</sup>-MMT with PVC/organic MMT nanocomposites, the former was more stable than the latter. Figure 9 shows the TGA curves for PVC and PVC/MMT nanocomposites, whereas the data for the nanocomposites are listed in Table III. The data in Table III indicate the temperature at which 10 wt % degradation occurs,  $T_{0.1}$ , and the temperature at which 50% degradation occurs,  $T_{0.5}$ .  $T_{0.1}$  is representative of the onset of the degradation, whereas  $T_{0.5}$  also provides some information on the course of the degradation. It is obvious that the nanocomposites show higher thermal stability than pure PVC. The addition of inorganic MMT could play a more effective role in stabilizing PVC. The  $T_{0.5}$  value of the nanocomposites is at least 20°C higher than that of PVC. It is surprising to observe that the values of  $T_{0.1}$  and  $T_{0.5}$  of PVC/MMT6.0% are actually lower than that of PVC/MMT2.1% or PVC/MMT3.2%. This may be due to the aggregation of MMT and the poor combination between polymer and silicates when the MMT content increased.

DSC traces of both pure PVC and PVC/MMT nanocomposites are illustrated in Figure 10. In Figure 10, PVC exhibits a glass transition temperature ( $T_g$ ) at 87°C. The  $T_g$ s of the nanocomposites are nearly identical to that of the pure PVC. This indicates that the small amount of dispersed silicate layers in PVC is insignificant to influence the  $T_g$  of pure PVC.<sup>17</sup>

VSP tests were performed on PVC/MMT nanocomposites with MMT loading varying from 0 to 6.0 wt %. Figure 11 shows the VSP of PVC and nanocomposites. It can be found that the VSP of nanocomposites exhibits a progressively increasing trend with increasing clay content. When MMT content is 6.0 wt %, the VSP of the nanocomposite is 91.8°C, which is 14.6°C higher than that of the pure PVC. The enhanced VSP temperature with the increasing amount of MMT is undoubtedly the consequence of the increased thermal insulation effect of MMT.

### CONCLUSION

Emulsion polymerization is an easy, convenient, and cheap method to prepare nanocomposites. In this article, PVC/MMT nanocomposites were successfully prepared through a simple emulsion polymerization without employing any modification of clay or special coupling agents. The XRD patterns and the TEM photographs showed that MMT particles were delaminated into nanoscaled layers, which were dispersed throughout PVC matrix. The PVC/MMT hybrids showed a mixture of intercalated and exfoliated nanostructure. The tensile modulus of the nanocomposites was improved, while the tensile strength was almost unchanged. The notched impact strength was also improved with the addition of MMT. However, those mechanical properties of the nanocomposites began to decrease with the continuously increasing amount of MMT. The results of SEM study on the fracture surface of samples showed that the addition of MMT greatly changed the morphology structure of the nanocomposites. The thermal stability of composites was improved by the addition of MMT. The DSC curves showed that glass transition temperatures of PVC/MMT nanocomposites were nearly identical to that of pure PVC.

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