

Effect of Epoxy Resin on Morphology and Physical Properties of PVC/Organophilic Montmorillonite Nanocomposites

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ABSTRACT: Poly(vinyl chloride)/organophilic montmorillonite (PVC/OMMT) nanocomposites were prepared by means of melt blending. A liquid epoxy resin was used to aid PVC chains in intercalating into silicate layers. The effects of the preparation methods and epoxy resin contents on the melt intercalation of PVC were investigated. The morphology development, mechanical properties and optical properties of the PVC/OMMT composites were tested as functions of epoxy resin content and OMMT content. Wide-angle X-ray diffraction, transmission electron microscopy and scanning electron microscopy were used to characterize the morphology of the resulting composites. After being pretreated by the epoxy resin, the OMMT layers were largely intercalated into the PVC matrix, and even exfoliated at high epoxy resin content. The addition of epoxy resin led to a decrease in optical clarity of the composites but improved the processing stability, as indicated by yellowness

index and haze measurement. However, the optical clarity of the composites containing 4 phr of epoxy resin (PVC/E-OMMT) was improved by increasing the OMMT content, as shown by light transmission. Both the tensile strength and notched Izod impact strength of the PVC/E-OMMT composites reached their maximum values when the OMMT content was 0.5 phr and the epoxy resin content was 2 phr. With further increase of the OMMT content and the epoxy resin content, the tensile strength decreased but was still higher than that of original PVC. The method of addition of epoxy resin had little effect on the physical properties but mainly influenced the morphology of PVC/OMMT nanocomposites. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2184–2191, 2003

Key words: PVC; nanocomposites; resins

INTRODUCTION

Polymer-layered silicate nanocomposites (PLSNs) exhibit outstanding properties, such as superior mechanical properties, gas permeability barrier and flame retardancy, which are not shared by conventional composites.¹ To achieve such properties in PLSNs, it is very important to finely disperse the silicate layers at the nanoscale and strengthen the interfacial interactions between the polymer matrix and the silicate layers. Therefore, prior to application, the layered silicates are generally rendered organophilic by means of cation exchange of intergallery sodium cations with cationic surfactants to improve the silicate layers' affinity for the polymer matrix. Alkylammonium salts are often utilized to modify the silicate layers and expand the basal spacing.²

Previous studies of poly(vinyl chloride)/organophilic montmorillonite (PVC/OMMT) nanocomposites reported that OMMT modified with alkylammo-

nium salts could promote the dehydrochlorination reaction of PVC during melt processing, which in turn influences the formation and physical properties of the resulting nanocomposites.^{3–5} It is known that PVC exhibits low thermal stability and begins to dehydrochlorinate at about 100°C,⁶ which induces the formation of polyene sequences and the discoloration of PVC. Blends of PVC and OMMT were visibly discolored from yellow to purple, suggesting that OMMT could catalyze the degradation of PVC.³ It can be inferred from these results that avoiding contact between PVC chains and alkyl ammonium salts tethered in OMMT layers may depress PVC degradation.³

More recently, Ishida et al.^{4,7} proposed a new approach for the preparation of PLSNs. They used an epoxy resin as a compatibilizer, namely a swelling agent, in promoting intercalation and exfoliation in a wide variety of polymer nanocomposites. They found that both monomers and polymers that are known to intercalate or exfoliate layered clay could be used to aid in swelling silicate layers. This allows a polymer that typically will not interact with clay to form a nanocomposite, or to increase the degree of such formation. Ishida et al.⁴ showed that an epoxy resin could help PVC exfoliate clay layers as well as suppress PVC degradation. Since then, epoxy resin has been used as

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a compatibilizer in the preparation of some PLSNs, such as poly(butylene terephthalate)/clay⁸ and polyamide 66/clay nanocomposites.⁹

PVC is compatible with epoxy resin. Furthermore, epoxy groups can act as scavengers to absorb liberated hydrogen chloride (HCl) gas and prevent autoacceleration of the dehydrochlorination reactions.¹⁰ Therefore, a liquid epoxy resin was chosen as a co-intercalator for the melt intercalation of PVC and OMMT in this study. The effects of the epoxy resin on the melt intercalation, morphology development and physical properties of the PVC/OMMT nanocomposites were all investigated. In order to improve the compatibility between OMMT and epoxy resin, sodium montmorillonite modified by a dimethyl bis (hydrogenated tallow) ammonium salt was used. The epoxy resin content was varied from 0 to 8 phr in order to evaluate the proper amount of epoxy resin required to improve the dispersion of OMMT layers and the physical properties of the resulting nanocomposites.

EXPERIMENTAL

Materials

A suspension PVC (WS 800S) with a degree of polymerization of 800 was obtained from Shanghai Chlor-Alkali Chemical Co., Ltd., China. Dimethyl bis (hydrogenated tallow) ammonium exchanged montmorillonite clay (OMMT) is a commercial product provided by Zhejiang Huate Group Co., China. The liquid epoxy resin was a diglycidyl ether of bisphenol A with an epoxy equivalent weight of 180~200. It was produced by Shanghai Resin Factory, China. The PVC processing additives, such as organic tin stabilizer (TM181), plasticizer (DOP) and lubricant (stearic acid) were all industrial grade products.

Sample preparation

The liquid epoxy resin was mixed with OMMT at 80°C in a beaker with continuous stirring for 30 min to obtain a gray, viscous mixture. This pretreated OMMT mixture was denoted as E-OMMT. The contents of epoxy resin and montmorillonite were based on 100 parts of PVC by weight.

PVC/E-OMMT composites were prepared by melt mixing PVC, E-OMMT and various processing additives in a Haake Rheometer RC90 at 175°C and 50 rpm for 8 min. PVC/OMMT and PVC/OMMT/epoxy composites were also prepared under the same melt processing conditions used for the PVC/E-OMMT. In these composites, the OMMT was not first premixed with the epoxy resin. Instead, PVC, OMMT and the epoxy resin were mixed at the same time.

The above composites were compression molded into sheets of 1 and 3 mm in thickness at 175°C and 20

MPa for 10 min, followed by cooling to room temperature under a pressure of 5 MPa. The sheets were prepared for structure characterization and property measurements.

Measurements

Wide angle X-ray diffraction (WAXD) measurements were carried out using a Dmax-rC X-ray diffractometer with a CuK_α radiation ($\lambda = 0.154$ nm) and a scanning rate of 4°/min. The generator was operated at 40 kV and 100 mA. The basal spacing of the silicate layers, d , was calculated according to Bragg's equation, $\lambda = 2d\sin\theta$.

The composite samples for transmission electron microscopy (TEM) observation were microtomed into ultrathin sections using a diamond knife. The samples were then strained in osmium tetroxide vapor. The transmission electron micrographs were obtained with a JEM-1200EX apparatus running at an acceleration voltage of 80 kV.

The composites were cryo-fractured in liquid nitrogen and subsequently examined in a scanning electron microscope (SEM, HITACHI-S-2150). The fractured surfaces were coated with a thin layer of gold prior to SEM examination.

The light transmission and haze of the composites were measured by a Spherical Hazemeter M57 from Diffusion Systems, Ltd. (U.K.) at room temperature. The composite samples were 3 mm thick sheets prepared by compression molding at 175°C.

The yellowness index (YI) was measured according to ASTM D1925, using a Macbeth Color Eye 7000A spectrophotometer produced by Kollmorgen Instruments Corporation, Germany.

Tensile tests were performed according to ASTM D638M-93/89 at a crosshead speed of 10 mm/min using an Instron 4465 Universal Tensile Tester. Notched Izod impact tests were performed with a RAY-RAN Universal Pendulum Impact Tester according to ASTM D256-97, with a hammer speed of 3.5 m/s and pendulum weight of 0.818 kg.

RESULTS AND DISCUSSION

Effects of epoxy resin and addition method on microstructure of composites

Figure 1 shows the WAXD patterns of OMMT and PVC/OMMT, PVC/OMMT/epoxy resin and PVC/E-OMMT composites with the same clay content of 3 phr. The WAXD pattern of pristine OMMT exhibits two distinct peaks at $2\theta = 2.8^\circ$ and $2\theta = 5.6^\circ$, corresponding to the interlayer spacings of 3.2 nm and 1.6 nm, respectively. Because amorphous PVC does not have any diffraction peak in the 2θ region from 1° through 10° , diffraction peaks appearing in the WAXD

patterns of the three composites should be attributed to the diffraction peaks of OMMT.

As shown in Figure 1, the WAXD patterns of the PVC/OMMT, PVC/OMMT/epoxy resin and PVC/E-OMMT composites exhibit only one diffraction peak, corresponding to the interlayer spacings of 3.6, 3.9 and 4.2 nm, respectively. The enlarged interlayer spacing of OMMT in the PVC/OMMT composite implies that a small number of PVC chains have intercalated in the OMMT layers and expanded the basal spacing. It may be attributed to the interaction between polar chloride atoms in PVC chains and polar hydroxyl groups of alkyl ammonium molecules tethered in the OMMT layers.

The PVC/OMMT/epoxy resin and PVC/E-OMMT composites have the same composition but different methods of addition of epoxy resins. They have larger interlayer spacings of OMMT than does the PVC/OMMT composite, indicating that the epoxy resin could facilitate intercalation of PVC chains into OMMT layers. Because the PVC/E-OMMT composite has the largest interlayer spacing of OMMT, the method of addition of epoxy resin through pre-swelling OMMT is recommended for the sake of the intercalation of PVC into OMMT.

Effect of epoxy resin content on microstructure of composites

Epoxy resin content has a significant effect on the interlayer spacing of OMMT in PVC/E-OMMT nanocomposites, as shown in Figure 2. With increasing epoxy resin content from 2 to 6 phr, the interlayer spacing of OMMT increases from 4.1 to 4.7 nm. When the epoxy resin content is 8 phr, the diffraction peak of OMMT disappears, indicating the exfoliation of OMMT layers by epoxy resin and PVC chains. There-

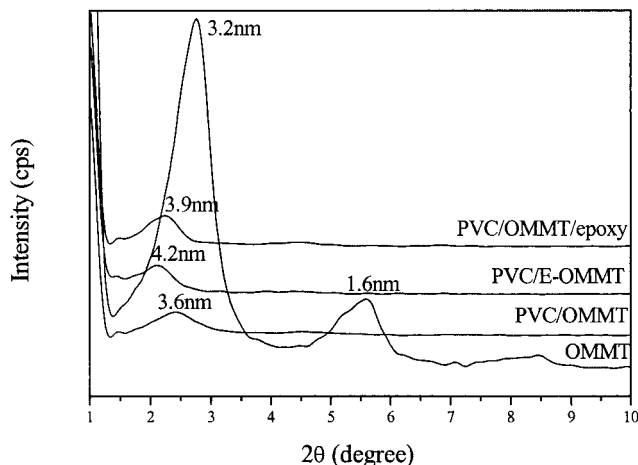


Figure 1 WAXD patterns of OMMT and PVC/OMMT composites. Formulation: PVC 100 phr; clay 3 phr; epoxy resin 2 phr.

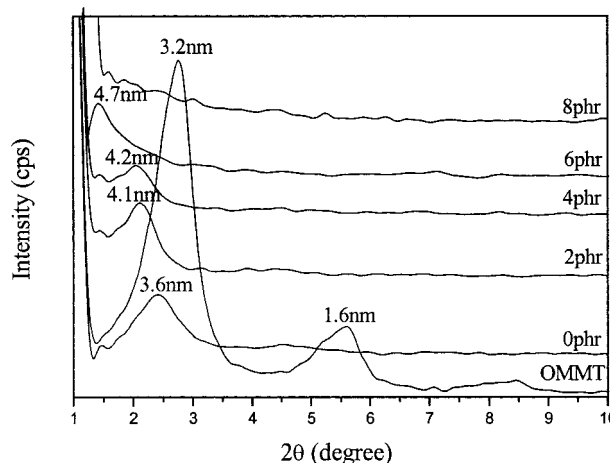


Figure 2 WAXD patterns of PVC/E-OMMT composites. Formulation: PVC 100 phr; E-OMMT 3 phr; epoxy resin variable.

fore, a high content of epoxy resin facilitates the intercalation and exfoliation of OMMT layers in the PVC matrix.

TEM characterization can directly demonstrate the microstructure of the PVC/E-OMMT composites. The effect of epoxy resin content on the microstructure of the PVC/E-OMMT composites is shown in Figure 3. The black lines are the cross sections of clay layers and the gray shadow is the stained epoxy resin phase. For the PVC/OMMT composite, a few intercalated clay layers and clay aggregates exist in the PVC matrix, as shown in Figure 3(a).

Two typical zones of TEM micrographs of the PVC/E-OMMT composite containing 2 phr epoxy resin are shown in Figure 3(b,c). The E-OMMT layers are intercalated and arranged in parallel directions, and the thickness of each aggregate of OMMT is about 25 nm, as shown in Figure 3(b). The interlayer spacing of OMMT is 4.1 nm for the PVC/E-OMMT composite containing 2 phr epoxy resin, as mentioned above, so each aggregate of OMMT should consist of five stacked layers. In Figure 3(c), the thickness of each aggregate of OMMT is about 10–15 nm, corresponding to 2–3 stacked layers. Therefore, 2 phr epoxy resin can effectively aid PVC to delaminate silicate layers and lead the layers to disperse in a disorderly fashion in the PVC matrix.

When the epoxy resin content is 4 phr, the E-OMMT layers are exfoliated and well dispersed in the PVC matrix, as shown in Figure 3(d).

There are several main reasons epoxy resin facilitates the melt intercalation and exfoliation of PVC/OMMT nanocomposites. During the pre-swelling process, the organophilic nature of OMMT makes it possible for epoxy resin to access the clay gallery surfaces. At 75°C, epoxy resin molecules can intercalate into the OMMT galleries and interact with hydroxyl groups

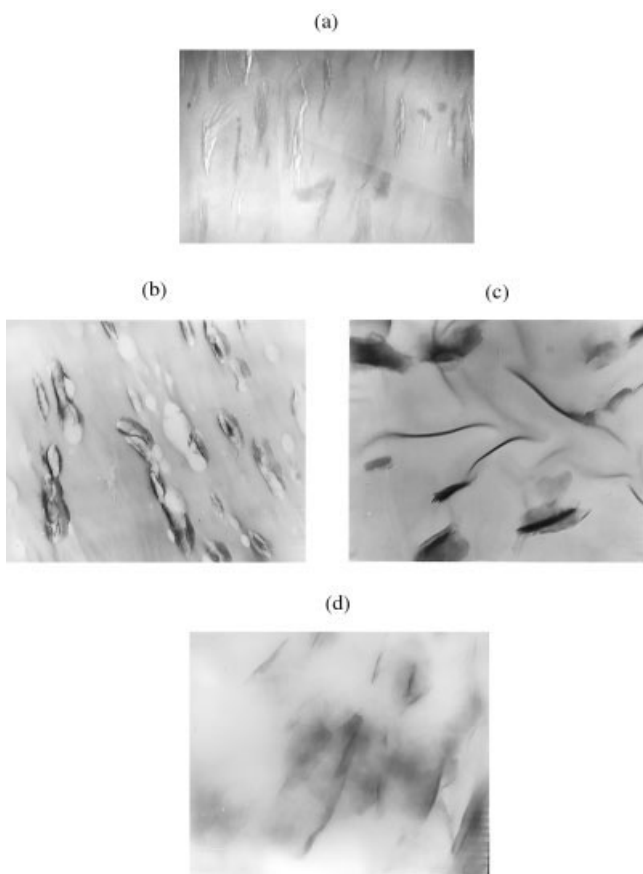


Figure 3 TEM micrographs of PVC/E-OMMT composites. Formulation: PVC 100 phr; E-OMMT 3 phr; epoxy resin variable: (a) 0 phr epoxy resin; (b), (c) 2 phr epoxy resin; (d) 4 phr epoxy resin.

and ammonium ions in the galleries through hydrogen bonds.¹¹ Upon epoxide intercalation into the clay layers, the alkylammonium ions can change their original orientations from the initial paraffin-like orientation to a more vertical orientation, which results in the enlargement of the basal spacing of the clay.¹¹ In addition, the interactions between the epoxide or hydroxide groups on epoxy resin molecular chains and the chlorines or α -hydrogens of PVC have been suggested as an enthalpic driving force to aid miscibility, and the resultant epoxy-solvated organophilic clay can strengthen the compatibility of the clay layers with PVC.¹² During melt-mixing process, more PVC chains may enter into E-OMMT layers through both solvation and dipolar interactions than those that enter into OMMT layers merely through dipolar interactions in the absence of epoxy resins. For PVC/OMMT/epoxy composites, the epoxy resin should act primarily as a thermal stabilizer during melt processing, which is supported by the less enlarged d spacing of the OMMT layers than that in the PVC/E-OMMT composites. Therefore, the OMMT pre-swelled by epoxy resin is more favorable for melt intercalation of

PVC; moreover, such solvation interactions will become stronger with an increased epoxy resin content.

Optical properties

PVC is sensitive to dehydrochlorination during processing and application.¹⁰ During the PVC melt-mixing processing, sequences of conjugated double bonds are formed in the molecular chains, resulting in the discoloration of the PVC matrix.¹³ Ishida et al.⁴ found that PVC visibly degrades during the preparation of PVC/clay composites without epoxy resin addition. When the clay was added at 170°C, PVC quickly turned purple, then black.⁴ A similar phenomenon

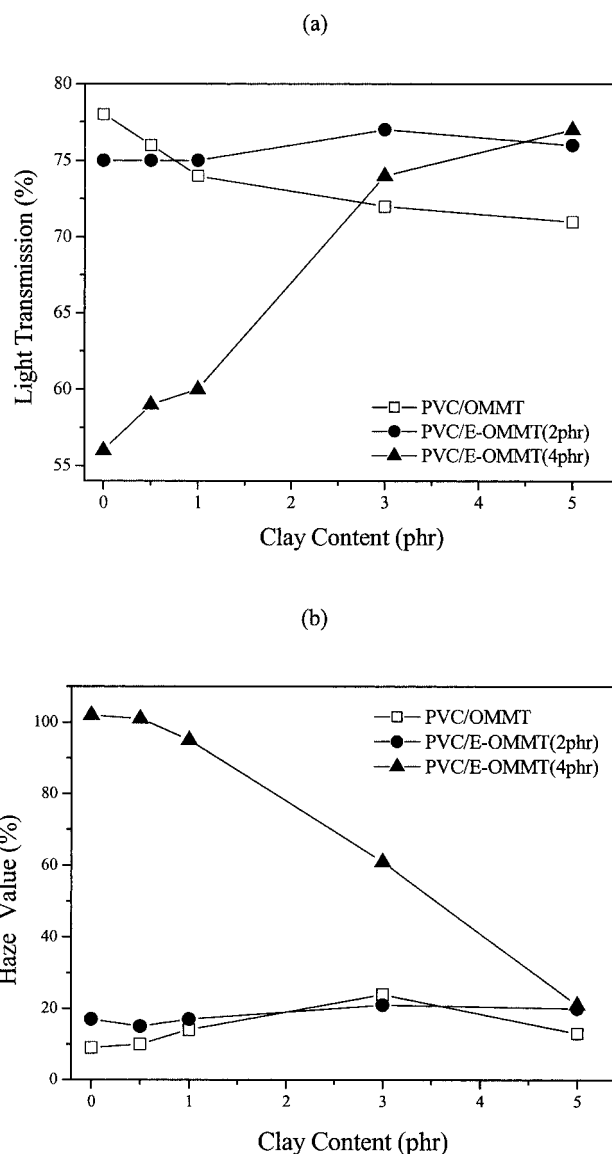


Figure 4 Effect of clay content on the optical clarity of PVC/clay composites: (a) light transmission; (b) haze measurements. Data in parentheses indicate epoxy resin content. Formulation: PVC 100 phr; epoxy resin 0, 2, 4 phr; clay variable.

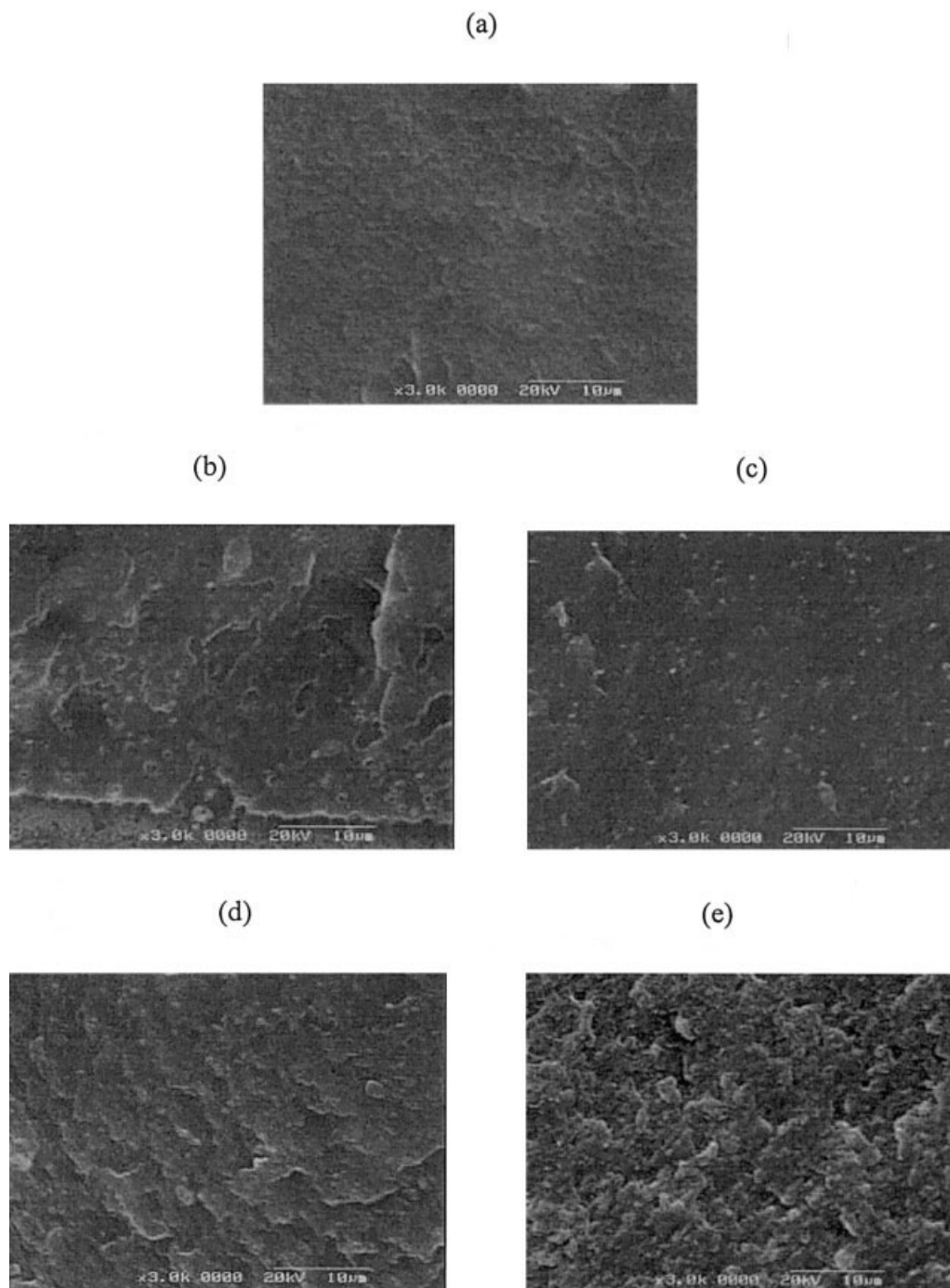


Figure 5 SEM micrographs of fracture surface of PVC/E-OMMT composites. Formulation: PVC 100 phr; epoxy resin 2 phr; E-OMMT variable: (a) original PVC; (b) 0 phr E-OMMT; (c) 1 phr E-OMMT; (d) 3 phr E-OMMT; (e) 5 phr E-OMMT.

was also reported by Trilica et al.³ Therefore, characterization of optical clarity of the composites can evaluate the thermal stability of the composites as well as the dispersion extent of clay in PVC matrix.

Figure 4 shows the light transmission and haze of the PVC/E-OMMT composites as functions of the E-OMMT content. The optical clarity of the original PVC was used as a control. All of the composites samples were transparent, independent of the epoxy resin con-

tent and E-OMMT content. All of the composites had lower light transmission and higher haze than the original PVC. The decreased optical clarity may be related to the presence of epoxy resin.

With an increasing clay content, the light transmission of PVC/OMMT composites decreases, but the light transmission of the PVC/E-OMMT (4 phr) increases, as shown in Figure 4(a). The clay content has a slight effect on the light transmission of the PVC/E-

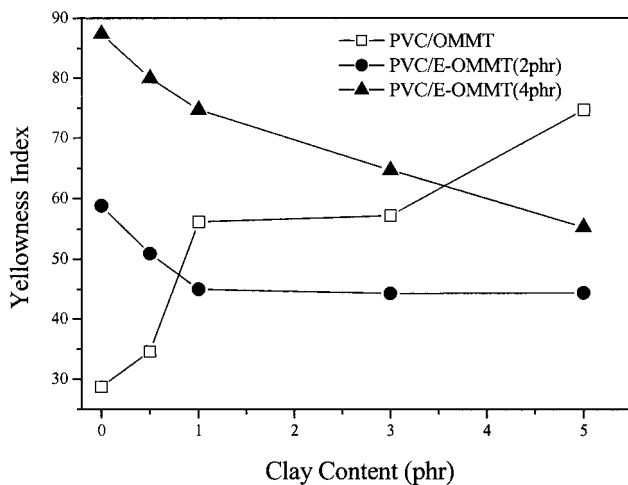


Figure 6 YI curves of PVC/clay composites as functions of clay content. Data in parentheses indicate epoxy resin content. Formulation: PVC 100 phr; epoxy resin 0, 2, 4 phr; clay variable.

OMMT (2 phr) composites. The PVC/epoxy (100 : 4) blend has the lowest light transmission.

It is interesting to note that with increased E-OMMT content, the light transmission of the PVC/E-OMMT (4 phr) composites increases significantly, and exceeds

that of the PVC/OMMT and PVC/E-OMMT (2 phr) composites at an OMMT content of 5 phr.

The PVC/E-OMMT (4 phr) composites have high haze values, as shown in Figure 4(b), but their transparency is significantly improved by increasing the E-OMMT content. Although the epoxy resin decreases the transparency of the composites, the addition of E-OMMT can offset the negative effect of the epoxy resin and increase the transparency of the composites.

Figure 5 shows SEM micrographs of fracture surfaces of PVC/E-OMMT composites containing 2 phr epoxy resin. The fracture surface of the PVC sample is glossy and smooth, as shown in Figure 5(a). Some microvoids of about 1 μm in diameter are randomly dispersed on the fracture surface of the PVC/E-OMMT composites containing 2 phr epoxy resin, as shown in Figure 5(b). Increasing the E-OMMT content from 1 to 5 phr causes the size of microvoids to become smaller and less numerous.

The liquid epoxy resin molecules with low molecular weight tend to coalesce in the continuous PVC matrix. In this case, the microvoids of about 1 μm in diameter make visible light scatter, resulting in the clouding of the PVC/epoxy resin blend. After the addition of clay, some epoxy resin molecules should enter into the clay galleries and interact with the clay

TABLE I
Mechanical Properties of PVC/E-OMMT Composites

Epoxly resin content (phr)	Clay content (phr)	Tensile strength (MPa)	Notched Izod impact strength (J/m)
0	0	51.3	29.0
0	0.5	63.6	34.0
0	1	56.6	33.0
0	3	56.4	27.0
0	5	54.9	20.8
2	0	58.0	28.0
2	0.5	64.4	30.0
2	1	59.5	29.7
2	3	58.6	29.3
2	5	57.4	25.8
4	0	62.9	19.5
4	0.5	61.7	26.0
4	1	62.0	22.8
4	3	58.3	21.5
4	5	56.8	26.5
6	0	57.2	22.0
6	0.5	61.1	20.0
6	1	59.7	17.0
6	3	58.3	21.0
6	5	58.0	16.0
8	0	58.7	18.4
8	0.5	60.8	18.5
8	1	57.0	18.0
8	3	60.1	19.8
8	5	57.6	15.5

^a Formulation: PVC 100; epoxy resin 0 \approx 8; clay 0 \approx 5 phr.

^b PVC/E-OMMT composites consist of PVC and OMMT pretreated by epoxy resins (E-OMMT).

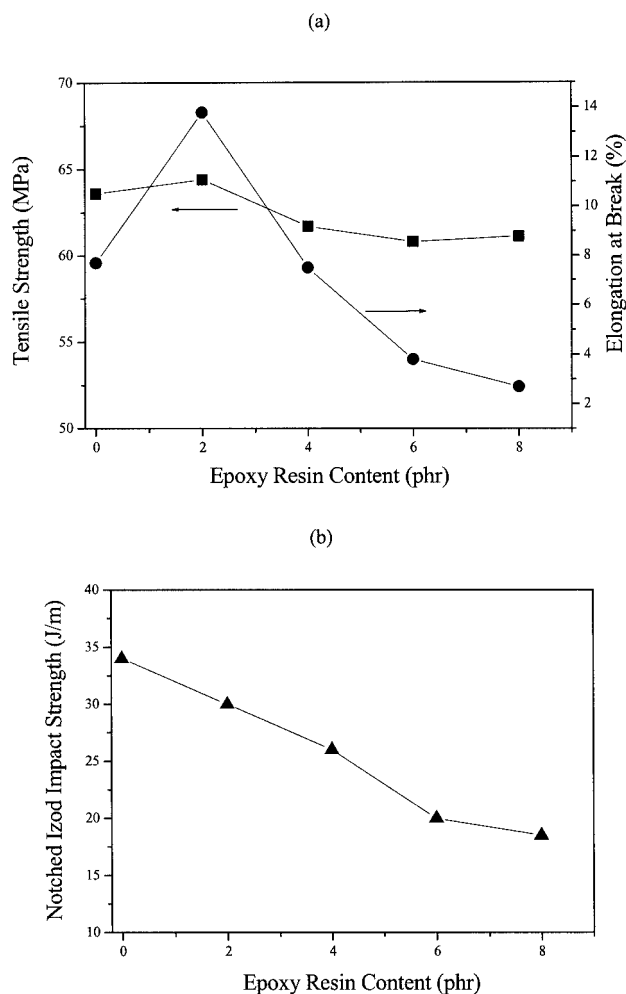


Figure 7 Effect of epoxy resin content on tensile and impact properties of PVC/E-OMMT composites: (a) tensile strength and elongation at break; (b) notched Izod impact strength. Formulation: PVC 100 phr; E-OMMT 0.5 phr; epoxy resin variable.

layers. This hinders the epoxy resin coalescence. That is why the transparency of PVC/E-OMMT composites is improved by increasing the E-OMMT content.

Figure 6 shows the YI values of the PVC/E-OMMT composites as functions of E-OMMT content. High YI indicates the discoloration of PVC.¹⁴ With increasing clay content, the YI values of the PVC/OMMT composites increase, implying an increase in discoloration. With increasing the clay content, the YI values of the PVC/OMMT composites containing epoxy resin decrease, implying the stabilization effect of epoxy resin on the PVC.

High clay content will usually lead to high YI values in the PVC/OMMT composites. An unusual phenomenon is that high clay content leads to decreased YI values in the PVC composites containing OMMT pre-swelled with epoxy resin. Because epoxide groups can react with the liberated HCl from PVC chains to form chlorohydrins, the autocatalytic effect of HCl is reduced during the course of PVC processing. Therefore, epoxy resin has two functions in the preparation of PVC/OMMT composites, to hinder discoloration and to aid in intercalation and exfoliation.

Mechanical properties

Table I shows the mechanical properties of PVC/E-OMMT composites. When the OMMT content is 0.5 phr, the tensile strength and the notched Izod impact strength of the composites reach their maximum values. When the OMMT content increases from 1 to 5 phr, the tensile strength of the composites decreases to a small extent, but all of the composites have higher tensile strength than the original PVC.

The notched Izod impact strength of the composites depends on the epoxy resin content and the clay content. When the clay content is equal to or lower than 3 phr, the composites have higher notched Izod impact strength than the PVC or corresponding PVC/epoxy resin blends. Although inorganic silicate layers of high aspect ratio could effectively reinforce the PVC matrix, OMMT particles tend to agglomerate when introduced at high content. Such OMMT aggregates may act as defects and induce stress concentration. The

TABLE II
Mechanical Properties of PVC/E-OMMT Composites Before and After Curing

Epoxy resin content (phr)	Clay content (phr)	Tensile strength (MPa)		Notched Izod impact strength (J/m)	
		Before curing	After curing	Before curing	After curing
2	0	58.0	59.6	28.0	31.5
2	0.5	64.4	57.5	30.0	30.0
2	1	59.5	55.4	29.7	25.8
2	3	58.6	52.8	29.3	23.6
2	5	57.4	49.1	25.8	21.5
4	0	62.9	50.9	19.5	21.5
4	0.5	61.7	47.3	26.0	19.6
4	1	62.0	46.7	22.8	17.0
4	3	58.3	45.3	21.5	16.2
4	5	56.8	42.8	26.5	14.0

impact modification of OMMT for the PVC is very limited.

The effect of epoxy resin content on mechanical properties is shown in Figure 7. When the epoxy resin content is 2 phr, the PVC/E-OMMT composite has a maximum tensile strength and elongation at break. A high content of epoxy resin leads to decreased tensile strength, impact strength and elongation at break. The mechanical properties of the cured PVC/E-OMMT composites are shown in Table II. Both the tensile strength and notched Izod impact strength of the composites are lower than those of the uncured composites, especially at the epoxy resin content of 4 phr. This indicates the curing of the epoxy resin results in high brittleness of the cured composites. In addition, the curing agent type, curing condition and epoxy content should be considered carefully in order to improve the mechanical properties of the cured composites.

CONCLUSIONS

The nanocomposites of PVC and OMMT have partially intercalated and exfoliated structures. Pretreatment of epoxy resin on OMMT is favorable; PVC expands the interlayer spacing of OMMT and even exfoliates the OMMT layers when the content of epoxy resin is greater than or equal to 2 phr. With an increasing clay content, the PVC/OMMT nanocomposites have decreased transparency and increased YI values, but the PVC/E-OMMT nanocomposites have increased transparency and decreased YI values. The

optical clarity of the PVC/E-OMMT nanocomposites containing 4 phr epoxy resin is second to that of the PVC/E-OMMT nanocomposites containing 0~2 phr epoxy resin, but it becomes better with increasing the E-OMMT content. When the E-OMMT content is 0.5 phr, the PVC/E-OMMT nanocomposites have the best mechanical properties, independent of the epoxy resin content, in the range of 0~5 phr E-OMMT content.

References

1. Michael, A.; Philippe, D. *Mater Sci and Eng* 2000, 28, 1.
2. Marco, Z.; Sergei, L.; Giovanna, C. *Macromol Mater Eng* 2000, 279, 1.
3. Trilica, J.; Aliachemj, C.; Patra, N. *SPE ANTEC* 2001, May 6~10, 2162.
4. Ishida, H. U.S. Pat. 6,271,297 (2001).
5. Wang, D. Y.; Parlow, D.; Yao, Q.; Wilkie, C. A. *J Vinyl & Addit Technol* 2001, 7, 203.
6. Dietrich, B. *J Vinyl & Addit Technol* 2001, 7, 168.
7. Ishida, H.; Campbell, S.; Blackwell, J. *Chem Mater* 2000, 12, 1260.
8. Li, X.C.; Kang, T. Y.; Cho, W.J.; Lee, J. K.; Ha, C. S. *Macromol Rapid Commun* 2001, 22, 1306.
9. Liu, X. H.; Wu, Q. J.; *Macromol Mater Eng* 2002, 287, 180.
10. Benaniba, M. T.; Belhaneche, B. N.; Gelbard, G. *Polym Degrad and Stab* 2001, 74, 501.
11. Tie, L.; Padmananda, D. K.; Thomas, J. P. *J Phys Chem Solids* 1996, 57, 1005.
12. Sang, J. K.; Byung, K. K.; Han, M. J. *J Appl Polym Sci* 1994, 51, 2187.
13. Minsker, K. S.; Koselov, S. V.; Zaikov, G. E. In *Degradation and Stabilization of Vinyl Chloride Based Polymers*; Pergamon Press: New York, 1988; p 76.
14. Chantara, T. R.; Khairul, Z. *Polym Degrad and Stab* 1999, 65, 99.