

## PROPERTIES AND MORPHOLOGY OF UNSATURATED POLYESTER/ACRYLATE-TERMINATED POLYURETHANE/ORGANO- MONTMORILLONITE NANOCOMPOSITES\*

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**Abstract** Unsaturated polyester resin (UPR)/acrylate-terminated polyurethane (ATPU)/organo-modified montmorillonite (OMMT) nanocomposites were prepared by the *in situ* intercalative polymerization method. Samples were prepared by the sequential mixing, *i.e.* mixture of the ATPU and styrene (S) and OMMT were prepared in the first step; UPR was then added to the pre-intercalates of ATPU/S/OMMT. Results indicate that the mechanical properties and thermal properties of UPR/ATPU/OMMT nanocomposites greatly depend on the amount of ATPU and OMMT. Results show that the addition of ATPU could increase the impact strength of UPR/ATPU composites, but the tensile strength, flexural strength and heat resistance of the materials are obviously decreased. When the weight ratio between UPR, ATPU and OMMT were 82:15:3, the impact strength and heat distortion-temperature of nanocomposite were greatly improved, meanwhile there was little change for other properties of the nanocomposites. The synergistic enhancement effects of ATPU and OMMT on the composites were observed. The structures and morphology of the composites were investigated by X-ray diffraction, scanning electron microscopy and transmission electron microscopy.

**Keywords:** Unsaturated polyester; Acrylic terminal polyurethane; Organo-modified montmorillonite; Nanocomposite.

### INTRODUCTION

Unsaturated polyester resins (UPR) are widely used in the automobiles, constructions and electrical appliances, coatings *etc.* They offer reasonably good mechanical properties and are relatively inexpensive. The thermal cycles leading to the final products generally include curing and post-curing periods. After crosslinking reactions, the final products exhibit thermosetting characteristics such as insolubility and infusibility. Usually, cured unmodified UPRs have low strength and elongation at break, and are subjected to stress cracking and brittle fracture. The properties of the cured resins can be enhanced by adding various additives to the unsaturated polyester resins. Conventional composites are based on microscale reinforcement, and improvement in the impact resistance could be achieved by the addition of a second polymeric phase. With the development of the technique of inorganic particles micro-dispersion and the technique of surface treatment of particles, the toughening of plastics has changed the utilization of elastic bodies such as rubber of filling, which can damage the rigidity, the dimensional stability and the heat resistance of the modified materials.

For composite materials, rigid inorganic particles can also withstand tensile stress and further increase the toughness and strength of the resin matrix if they have an excellent binding effect in the matrix. Thus composite materials with excellent properties are obtained. Recently, a new approach has been investigated. The dispersion of inorganic fillers at the nanometer scale has led to significant improvements of properties in the polymer nanocomposites<sup>[1]</sup>. Nanostructured materials often show a combination of physical and mechanical properties not available with conventional composites<sup>[2]</sup>.

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Amongst all potential nanocomposite precursors, those based on clay and layered silicates have been most widely investigated because of their low cost, their availability, and their non-isometric structure derived from a high aspect ratio, which can maximize the reinforcing effect in terms of mechanical, thermal, and barrier properties. Montmorillonite (MMT) is the most commonly used layered silicate<sup>[3]</sup>.

In order to achieve the improvements in properties, good dispersion of nanoclay in the polymer matrix and a good interface between the two phases are essential.

In general, there are two methods of making nanocomposites melt intercalation and *in situ* intercalative polymerization of monomers. Melt intercalation of high polymers is a powerful new approach for synthesizing polymer-layered silicate nanocomposite. This method is quite general and is broadly applicable to many commodity polymers. The nanocomposites of thermoset can be prepared by the *in situ* intercalative polymerization method<sup>[4]</sup>; phenol resins, epoxy resins<sup>[5]</sup> and unsaturated polyester resins<sup>[6,7]</sup> are included in this category.

In our previous studies, the tensile strength and the heat distortion temperature of nanocomposites of UPR with organo-montmorillonite were improved, but a little improvement in impact strength and flexural strength was observed<sup>[8]</sup>. The UPR composites with acrylate-terminated polyurethane (ATPU) had great effect on toughening and shrinkage controlling of UPR. The results of DSC and SEM analyses showed that ATPU was partially compatible with UPR, where the compatibility depended on the type of both reactive end groups of ATPU and UPR; they can partially participate in UPR cure reactions, strengthening the surface combination between ATPU and UPR matrix<sup>[9]</sup>.

Homogeneous dispersions of the silicate layers can be obtained when the polymer contains polar functional groups which are compatible with the polar carboxyl groups of the silicate layers<sup>[10]</sup>. The objective of this study is to investigate the properties and formation mechanism of UPR/acrylate-terminated polyurethane (ATPU)/organo-modified montmorillonite (OMMT) composites prepared by sequential mixing method. The effects of the amount of ATPU and OMMT on the properties of the composites were discussed.

## EXPERIMENTAL

### Materials

Cetyltrimethyl ammonium bromide (C.P. grade) was provided by Shanghai Yuanshengwu Sci & Tech Ltd, China. Montmorillonite (800 mesh, its cation exchange capacity = 100 mmol/100 g) was supplied by Nanhai Non-metal Mineral Co., China. Polyethylene Glycol ( $M_n = 2000$ , C.P. grade) and 2,4(2,6)-toluene diisocyanate (C.P. grade), and hydroxy ethyl methacrylate (C.P. grade) and di-*n*-butylamine (A.R. grade) were bought from Shanghai Chemical Agents Factory. Methyl ethyl ketone peroxide and cobalt naphthenate were supplied by Guangzhou Nanfei Trading Co.. Other reagents were used without further purification.

### Preparation of OMMT

OMMT was prepared in our laboratory. First, MMT was dispersed in distilled water with vigorous stirring, and then trimethyl hexadecylammonium bromine was poured into the MMT-water solution and reacted for 8–10 h at 60–80°C. The precipitate formed were separated by filtration and dried to yield an organophilic MMT.

### Synthesis of ATPU

A weighted quantity of polyethylene glycol dried prior at 100–120°C for 1–2 h was charged into a flask equipped with stirrer, thermometer, dropping funnel, gas inlet and air condenser. During flushing with a slow stream of nitrogen, an excess of TDI was added to the flask. The mixture was heated and stirred for 2–3 h. After adding an equivalent ratio of HEMA, the reaction was carried out at a temperature below 70°C under nitrogen blanket and continued to obtain the theoretical value of NCO content. NCO content was determined by titration method using di-*n*-butylamine according to the procedure described in ASTM D-2572.

### **Preparation of UPR/ATPU/OMMT Composites**

The composites were prepared by sequential mixing, *i.e.* mixture of ATPU, styrene (S) and OMMT were prepared in the first step; UPR was then added to the pre-intercalates of ATPU/S/OMMT. After the accelerator and the curing agent were added, the sample was poured into a mould, and cured for 24 h at room temperature and postcured for 4 h at 80°C.

### **Extraction analysis**

The samples were extracted with acetone by a Soxhlet extractor for 48 h, and then dried until constant weight.

### **Instrumentation**

Dumbbell-shaped samples were cut from the molded sheets according to GB/T 10654-2001. Tensile testing was carried out with a Tensometer LJ-1000 (Shanghai, China) at a crosshead speed of 500 mm/min.

Notched Izod impact testing was performed according to GB/T 1843-1996 with an Impact Tester UJ-4 (Tianjin, China) at room temperature.

Flexural strength testing was performed according to GB/T 14208-1993.

Hardness was measured according to GB/T 6269-1997 with a HD-1875 Barcol Durometer, the diameter of the steel ball was 5.0 mm, and the loading was 62.5 kg.

The heat distortion temperature testing was performed according to GB1634-79 with a Weicar heat distortion tester. Testing conditions: heating medium was silicon oil, loading on the sample for maximum direct stress was 4.6 kg/cm<sup>2</sup>, and heating rate was 5 K/min.

The X-ray diffraction (XRD) pattern were recorded on a D/max-rB diffractometer (Japan) using CuK $\alpha$  radiation at room temperature in the range of  $1^\circ \leq 2\theta \leq 70^\circ$  with a scanning rate of 2°/min.

Dynamic mechanical properties of nanocomposites were measured with a DMA2980 Dynamical Mechanical Analyzer (TA Instrument, USA) in fixed frequency mode at 1 Hz, from 100°C to 250°C at a heating rate of 5 K/min. The sample size was 30 mm  $\times$  5 mm  $\times$  2 mm.

Microstructure of the impact-fractured surfaces was examined by using a scanning electron microscope Model JSM-5910 (Germany). Before taking photomicrographs, the samples were coated with a thin layer of gold.

Transmission electron microscopy (TEM) photomicrographs were obtained on a Model JEM-100CX II TEM (Japan) microscope, using an accelerating voltage of 120 kV. The TEM specimens were cut with the aid of LKB-2088 microtome.

## **RESULTS AND DISCUSSION**

### **Effect of ATPU Content on the Mechanical Properties of Composites**

Figures 1, 2, 3 and 4 show that the mechanical properties of the UPR/ATPU composites with and without OMMT. ATPU has strong influence on the properties of the composites, especially the impact strength. Without OMMT, an increase in the concentration of ATPU in the composites resulted in a noticeable increase in the impact strength of the obtained composites (Fig. 1). When the amount of ATPU was 15 wt%, the impact strength of the composite was increased by about one-fold, and upon filling with 30 wt% of ATPU a two-fold increase of the impact strength is obtained. But a drop in the tensile strength, flexural strength and Barcol hardness of UPR/ATPU/OMMT nanocomposites is triggered by dispersing increasing amount of ATPU, which is caused mainly by the addition of ATPU with a low modulus (Figs. 2, 3 and 4). The main shortcoming of the elastomers toughening is the significant reduction of the rigidity of polymer blend. Therefore, a higher content of ATPU in the composites can enhance their impact strength, but sacrifice other properties of the materials.

To obtain more information on the effects of ATPU, the samples of UPR/ATPU/OMMT nanocomposites were extracted with acetone. Table 1 lists the extraction data for UPR/ATPU/OMMT nanocomposites. It can be seen that the amount of extractable substance for UPR/ATPU/OMMT nanocomposites without ATPU is small. During the styrene-unsaturated polyester crosslinking copolymerization, the initiator decomposes and creates free radicals in the systems. The free radicals grow and form long-chain molecules by connecting styrene monomers with unsaturated polyester molecules by both inter- and intra-molecular reactions. After complete cure, it forms three dimensional crosslinking networks, resulting in a few extractions.

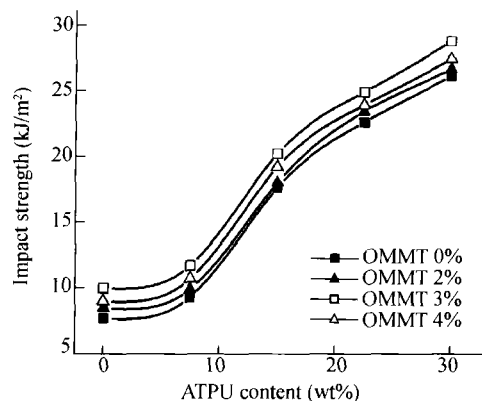


**Fig. 1** Effect of ATPU content on impact strength of UPR/ATPU/OMMT nanocomposites

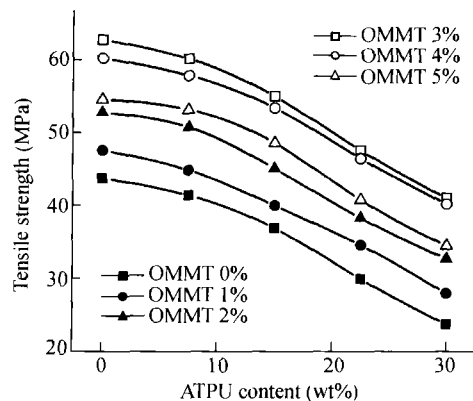


**Fig. 2** Effect of ATPU content on tensile strength of UPR/ATPU/OMMT nanocomposites

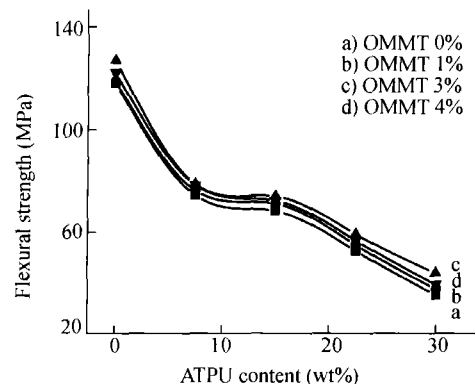


**Fig. 3** Effect of ATPU content on flexural strength of UPR/ATPU/OMMT nanocomposites

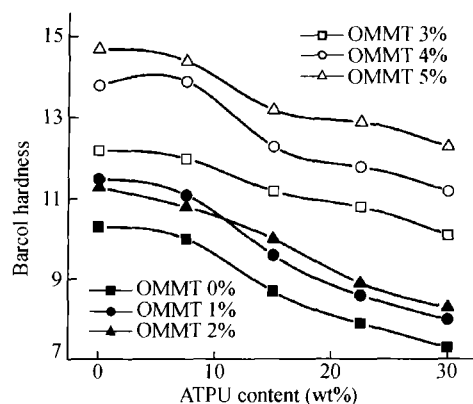


**Fig. 4** Effect of ATPU content on Barcol hardness of UPR/ATPU/OMMT nanocomposites

In our experiment, after ATPU was mixed with the curing agent and the accelerator for 24 h, no curing reaction occurred. But as shown in Table 1, the composites containing ATPU have a certain amount of extractable substance, which is about half of the ATPU amount incorporated into the composites. This result suggests that ATPU do participate in the curing of UPR and the double bonds at both ends of ATPU can crosslink with styrene and UPR, the extractable substance from the composites consists of mostly ATPU which does not take part in the crosslinking.

**Table 1.** Extraction data for UPR/ATPU/OMMT\* nanocomposites

| Amount of ATPU (wt%) | Amount of extractable substance (wt%) |
|----------------------|---------------------------------------|
| 0                    | 0.16                                  |
| 7.5                  | 4.11                                  |
| 15                   | 7.89                                  |
| 22.5                 | 10.88                                 |
| 30                   | 16.24                                 |

\* OMMT = 2 wt%

The cured pristine UPR resins, being crosslinked, are rigid and do not flow on heating, which do not absorb much energy upon vibration and impact. This is the main reason why cured unmodified UPR has low strength and elongation at break, and are subjected to stress cracking and brittle fracture. After co-curing of ATPU and UPR, the soft regions of ATPU become amorphous in which the disposition of molecules is random. The hard

segments such as benzene rings in UPR and ATPU tend to form a crystalline phase in regular order. This -UPR-ATPU-UPR block structure results in good bonds between the crystalline phase and the interphase of matrix. When composites are subjected to impact force, the amorphous phase becomes extended under tension. This extension of the amorphous phase absorbs energy and resists further crack growth. Good combination between the interphases also rendered the material absorbed a large quantity of impact energy. Consequently, the toughness of the material was increased greatly.

It is worth noting that with the increase in the amount of ATPU, the tensile strength, flexural strength and Barcol hardness of composites decrease while the impact strength increases. It is a baffling problem that the traditional polyurethane toughened unsaturated polyester faces. In the UPR/ATPU/OMMT nanocomposites, some of the problem could be solved by adding OMMT with the *in situ* intercalative polymerization method.

#### ***Effect of OMMT on the Mechanical Properties of the Composites***

For most polymers, montmorillonite is an excellent reinforcing material. Its advantage is believed to stem from the high aspect ratio and high modulus of the silicate platelets. The key to such performance rests in the ability to exfoliate and disperse individual, high-aspect ratio silicate platelets within the polymer matrix.

The impact strength, tensile strength, and flexural strength of UPR/ATPU composites with OMMT are also shown in Figs. 1, 2, and 3. It is remarkable to observe that the impact strength, tensile strength and flexural strength of all the nanocomposites increase with the increase in OMMT content up to OMMT content of 3 wt%. With 15 wt% of ATPU, the tensile strength is increased by about 50% while the impact strength and flexural strength are increased by about 8.6% and 10.3%, respectively when 3 wt % of OMMT is introduced. In general, the presence of MMT increases the impact strength, possibly due to modification of the matrix. In addition, MMT may absorb the impact energy and slow down the crack propagation. Furthermore, modification of the fracture mechanism in the presence of clay probably accounts for the improvement of impact strength<sup>[11]</sup>.

The influence of the OMMT content upon the Barcol hardness of UPR/ATPU composites is shown in Fig. 5. The Barcol hardness of the composite exhibits a linear increase with an increase in the OMMT content. It is due to the well-dispersion of OMMT in the matrix by the *in situ* intercalative polymerization method.

These strengthening and toughening effects may result from the strong interfacial interactions between UPR and ATPU molecules and OMMT particles, which lead to the formation of physical crosslinking. The strength and the toughness of the composites are dependent upon the crosslink density. In an appropriate range of the crosslink density, the crosslinking could exhibit both the strengthening and toughening effects. When the OMMT content exceeds 3 wt%, the impact strength, tensile strength and flexural strength are all decreased. This decrease may be caused by the aggregation of OMMT, which leads to the loss of the features of a nanometer composite.

#### ***Effect of ATPU Content on the HDT of Nanocomposites***

From Fig. 6, it can be seen that the heat distortion temperature (HDT) decreases with the content of ATPU. When 30 wt% of ATPU was added, the HDT of the composite decreased about 8–10°C, due to the introduction of soft segments in the network structure. Figure 6 also shows that the HDT increases with OMMT content. It seems obvious that the introduction of nanoscale of OMMT produces an obstacle on the molecular chains movement; that is, the lamellar space of OMMT confines the molecular chains movement and the nanoscale OMMT does exert shielding effect on molecular chains subjected to external heat, and gives a high heat distortion temperature. The increase in the heat distortion temperature can also be attributed to the high thermal stability of montmorillonite and the existence of strong interaction between the montmorillonite and polymers.

#### ***XRD Measurement***

XRD is often performed as an important technique to determine the structure of the organoclay in the nanocomposite. Figure 7 presents the XRD curves of OMMT, uncured pre-intercalative composite and composite after curing. In the curve of OMMT, a prominent peak corresponding to the basal spacing of OMMT can be seen at 2.31 nm (Fig. 7a). Since the stacking of the silicate nanolayers is held by a weak dipolar or van der Waals force<sup>[12]</sup>, the increase of interlayer distance lowers the interlayer attraction force. The larger interlayer

distance also facilitates the intercalation of UPR, ATPU and styrene molecules. The basal spacing increased from 2.31 to 2.90 nm after the OMMT was mixed with UPR, ATPU and styrene (Fig. 7b). This increased spacing suggests the molecules of UPR, ATPU and styrene intercalate into the gallery of MMT and expand it<sup>[13]</sup>. After curing, the prominent peaks are absent in the curve of UPR/ATPU/OMMT nanocomposites (15 wt% ATPU, 3 wt% OMMT), the remnant shoulder at about 4 nm in the curve indicates the presence of intercalated nanocomposite (Fig. 7c).

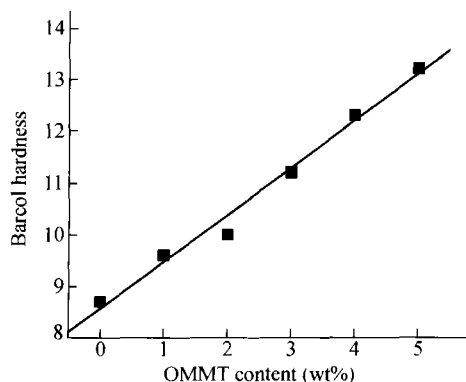


**Fig. 5** Effect of OMMT content on Barcol hardness of UPR/ATPU/OMMT nanocomposites (15 wt% ATPU)

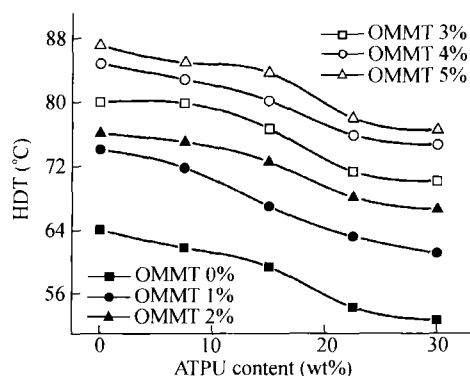


**Fig. 6** Effect of ATPU content on HDT of UPR/ATPU/OMMT nanocomposites

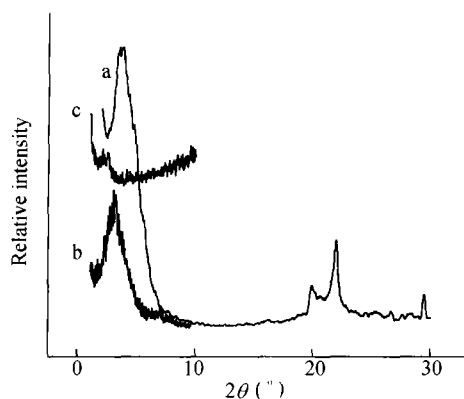


**Fig. 7** XRD curves of OMMT and UPR/ATPU/OMMT nanocomposites (15 wt% ATPU, 3 wt% OMMT)

a) OMMT; b) Uncured pre-intercalative composite; c) Composite after curing

Dynamic mechanical analysis is sensitive to a variety of transitions and relaxation processes of polymers over a wide range of temperatures and frequencies. Dynamic storage modulus ( $E'$ ) is an important way of assessing the load-bearing capability of a composite material. Figure 8 shows the temperature scans of  $E'$  for cured UPR, UPR/ATPU, UPR/OMMT and UPR/ATPU/OMMT nanocomposite samples. The dynamical modulus of nanocomposites with OMMT is higher than those of pristine UPR and UPR/ATPU composite samples for temperature below 100°C as shown in Fig. 8. The higher modulus of nanocomposites is attributed to a combination of the dynamic effects of the particles embedded in the matrix and the mechanical restraint introduced by the MMT nanolayers that reduce the mobility and deformability of the matrix.

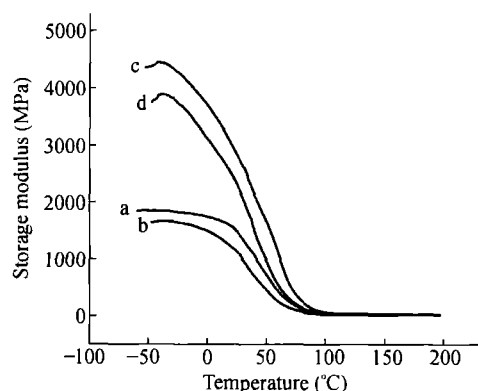


**Fig. 8** Storage modulus of UPR/ATPU/OMMT nanocomposites

a) Pristine UPR; b) ATPU 15%, OMMT 0%;  
c) ATPU 0%, OMMT 3%; d) ATPU 15%, OMMT 3%

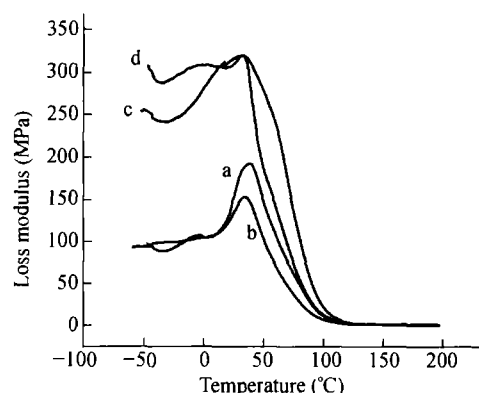


**Fig. 9** Loss modulus of UPR/ATPU/OMMT nanocomposites

a) Pristine UPR; b) ATPU 15%, OMMT 0%;  
c) ATPU 0%, OMMT 3%; d) ATPU 15%, OMMT 3%

Figure 9 presents the dynamic loss modulus ( $E''$ ) for cured UPR, UPR/ATPU, UPR/OMMT and UPR/ATPU/OMMT nanocomposite samples. Like rubber-modified UPR, the UPR/ATPU/OMMT nanocomposite also contains two peaks in loss modulus, corresponding to the UPR phase and ATPU phase, respectively.

### Morphology

The fracture surfaces of pristine UPR samples were observed using SEM (Fig. 10). They are relatively even and smooth, showing a brittle failure feature in a homogeneous material (Fig. 10a). Figure 10b shows the fracture surface of the modified UPR with 7.5 wt% ATPU content. The white lines are due to tearing of the materials between two crack planes, causing a surface step. On the other hand, the fracture surface of a nanocomposite with 3 wt% OMMT loading exhibits very different failure mode and it looks like that of filler-modified UPR (shown in Fig. 10c). Therefore, the toughening mechanisms of ATPU and OMMT are different. When the UPR was modified with both ATPU and OMMT at low OMMT loading, the fracture surfaces show both features of fracture surface described above. Especially, for UPR containing both 15% of ATPU and 3 wt% of OMMT, the void is serious, which becomes the main impact energy dissipation mechanism. It suggests that the nanocomposites may have some degree of toughness in comparison with pristine UPR.

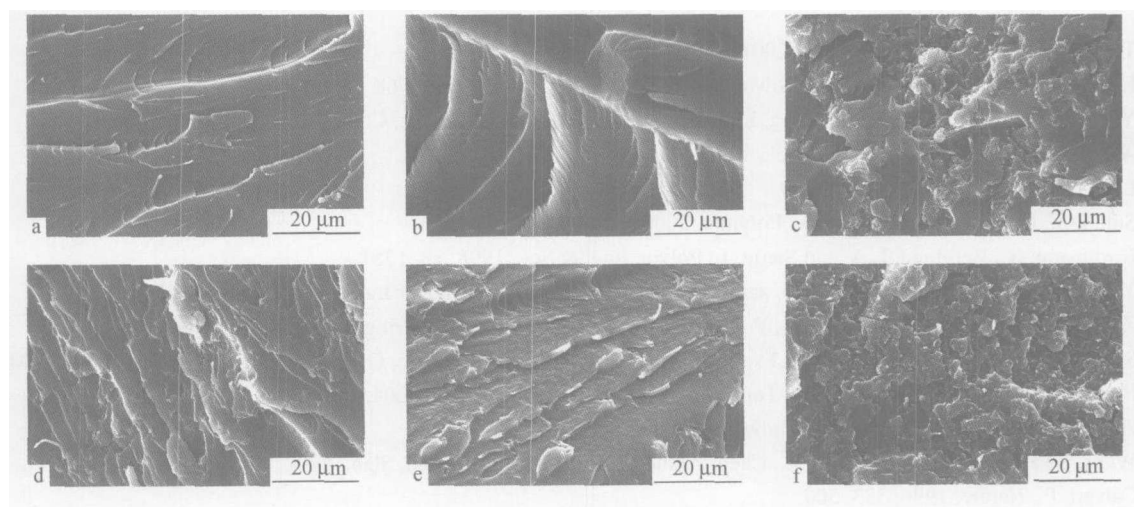


**Fig. 10** SEM microphotographs of UPR/ATPU/OMMT nanocomposites

a) Pristine UPR; b) 7.5% ATPU, 0% OMMT; c) 0% ATPU, 3% OMMT;  
d) 7.5% ATPU, 1% OMMT; e) 15% ATPU, 1% OMMT; f) 15% ATPU, 3% OMMT

In order to investigate the nanostructure feature of UPR/ATPU/OMMT nanocomposites directly, TEM was used to study the dispersibility of clay in the polymer matrix. Figure 11 shows the TEM image of the UPR with 15 wt% of ATPU and 3 wt% OMMT. Figure 11(a) represents a TEM image showing fairly well-dispersed clay. The composite exhibits a nanoscale dispersed morphology containing both individual silicate sheets and intercalated structure (Fig. 11b). Thus, UPR/ATPU/OMMT composite belongs to nanocomposite as defined by Calvert<sup>[14]</sup>. According to the intercalative polymerization mechanism, during the polymerization, small UPR molecules in the galleries grow to form the UPR macromolecules. The size of which is about several hundredths of a nanometer. Therefore, some of the layered structures of the clay are destroyed by the growing UPR macromolecular chains. The thickness of most dispersed phase is about 30–60 nm, which is equal to the thickness of several dozen of layers of montmorillonite and a small amount of original montmorillonite are left in the composites.

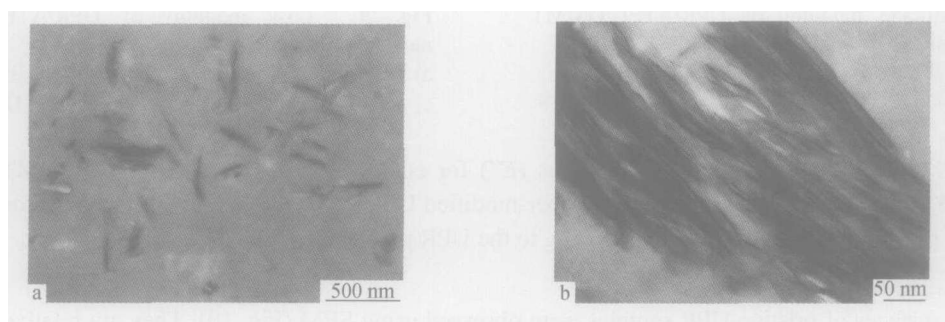


**Fig. 11** TEM microphotographs of UPR/ATPU/OMMT nanocomposites (15% ATPU, 3% OMMT)

It could be concluded from the above observation that in a certain OMMT content range the introduction of OMMT to UPR/ATPU composites would lead to both the reinforcing and toughening effects. Liu<sup>[15]</sup> found that there was a superposition effects on fracture toughness of the hybrid epoxy nanocomposites modified with both rubber and organoclay. This may be regarded as a feature of a nanometer-composite. It suggests that OMMT can improve compatibility and wetting of UPR and ATPU<sup>[16, 17]</sup>.

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