

Rectorite/Thermoplastic Polyurethane Nanocomposites: Preparation, Characterization, and Properties

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ABSTRACT: A newly developed kind of layered clay, rectorite (REC), has been used to yield intercalated or exfoliated thermoplastic polyurethane rubber (TPUR) nanocomposites by melt-processing intercalation. Because of the swollen layered structure of REC, similar to that of montmorillonite, organic rectorites (OREC) can also be obtained through ion-exchange reaction with two different quaternary ammonium salts (QAS1, QAS2) and benzidine (QAS3). The microstructure and dispersibility of OREC layers in TPUR matrix were examined by X-ray diffraction and transmission electron microscopy, which revealed not only that

the composites with lower amounts of clay are intercalation or part exfoliation nanocomposites, but also that the mechanical properties of the composites were substantially enhanced. The maximum ultimate tensile strength for TPUR/OREC nanocomposites appeared at 2 wt % OREC loading. With increasing OREC contents, the tear strength of the composites increased significantly. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 608–614, 2004

Key words: nanocomposites; rectorite; clay; thermoplastic polyurethane rubber (TPUR); mechanical properties

INTRODUCTION

Nanocomposites based on a polymer matrix can provide mechanical, heat-resistance, barrier, and other functional properties compared with those of conventional microscale composites because of greatly enhanced filler–polymer interaction. Polymer/layered silicate clay nanocomposites display excellent mechanical properties compared to those of conventionally filled polymers.^{1,2} The dispersion of clay layers in the polymer matrix can result in the formation of three types of composite materials. The first type is conventional composites, containing clay tactoids, in which the layers aggregate in an unintercalated face-to-face form, in which the clay tactoids are dispersed simply as a segregated phase, resulting in poor mechanical properties of the composite materials. The second type is intercalated polymer–clay nanocomposites, which are formed by the insertion of one or more molecular layers of polymer into the clay host galleries. The last type is exfoliated polymer–clay nanocomposites, which are characterized by low clay content, a monolithic structure, and a separation between clay nanolayers. Exfoliated polymer–clay nanocomposites are especially desirable for improved properties because of the homogeneous dispersion of clay and large interfacial area between polymer and clay.

The current favored clay for polymeric nanocomposites is montmorillonite (MMT) that belongs to the general family of 2 : 1 layered silicates,³ which consists of two fused silicate tetrahedral sheets sandwiching an edge-shared octahedral sheet of either aluminum or magnesium hydroxide. The silicate layers are coupled through relatively weak dipolar and van der Waals forces, and the interlayer space is about 1 nm. The Na⁺ or Ca²⁺ residing in the interlayers can be replaced by organic cations such as alkylammonium ions by an ion-exchange reaction to render the hydrophilic layered silicate organophilic, so the polymer chains or molecule can be intercalated, thus causing the clay layer to be either swollen or exfoliated.

Rectorite (REC) is another kind of clay mineral,⁴ with structure and characteristics much like those of MMT. It is a sort of regularly interstratified clay mineral with alternate pairs of dioctahedral mica-like layer (nonexpansible) and dioctahedral smectite-like layer (expansible) in a 1 : 1 ratio. The cations of Na⁺, K⁺, and Ca²⁺ lie in the interlayer region of 2 : 1 mica-like layers and 2 : 1 smectite-like layers, whereas the exchangeable hydrated cations reside in the latter. The REC structure can also easily cleave between smectite-like interlayers, forming monolithic REC layers (2 nm thick). Thus the similar structure of REC to that of MMT imparts some excellent properties to their corresponding composites, such as good colloidal property in water, high heat resistance, good plastic index, and processing properties, which may provide the basis for many potential applications in industry, especially in modification of polymers. However, nearly no attention has been paid to the research of REC, on

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TABLE I
The Systems of Composites

Content of clay in TPUR (wt %)	System				
	REC/TPUR	OREC1/TPUR	OREC2/TPUR	OREC3/TPUR	OMMT/TPUR
2	REC/TPUR2	OREC1/TPUR2	OREC2/TPUR2	OREC3/TPUR2	OMMT/TPUR2
5	REC/TPUR5	OREC1/TPUR5	OREC2/TPUR5	OREC3/TPUR5	OMMT/TPUR5
8	REC/TPUR8	OREC1/TPUR8	OREC2/TPUR8	OREC3/TPUR8	OMMT/TPUR8

modifying polymer composites, until the high quality of REC deposits was discovered in Wuhan, China. As mentioned above, natural REC is hydrophilic and not interfacial-compatible with organic materials, which results in a poor-quality interface between REC and the polymer matrix, although it can be chemically modified by means of an ion-exchange reaction with cation surfactants, to render the surface of REC more hydrophobic. Just like organic MMT, the organically modified REC could also be used to improve the mechanical properties of polymer composites prepared by *in situ* intercalation polymerization, solution-mixing, and melt intercalation.

To investigate the microstructure and mechanical properties of polymer composites modified by OREC, we synthesized three different ORECs and one organic montmorillonite (OMMT). The corresponding OREC/thermoplastic polyurethane rubber (TPUR) and OMMT/TPUR composites were then prepared by means of melt-blending, which is the most versatile and environmentally benign processing method of all available methods, to prepare the polymer/OMMT clay nanocomposites,⁵ and it is also a practical method that has been broadly applied to many commodity polymers, from nonpolar polypropylene to strong polar nylon.^{6,7}

EXPERIMENT

Materials

Sodium montmorillonite [MMT; $M_{0.33}Al_{1.67}(Mg,Fe^{2+})_{0.33}[Si_4O_{10}](OH)_2$], supplied by the Fourth Reagent Factory (Shanghai, China), had a cationic exchanging capacity (CEC) of 60 meq/100 g, and the *d*-space was about 1.5 nm.

Sodium rectorite [REC; $Mica (Na,Ca,K)_2(Al_4)[Si_6Al_2]_8O_{20}(OH)_4$] and smectite [$E_{0.66}(Al,Mg)_4[Si,Al]_8O_{20}(OH)_4 \cdot nH_2O$] were refined from clay minerals available in Wuhan, China. The CEC is 45 meq/100 g, and the *d*-space of REC is 2.2 nm.

Polyurethane elastomer rubber (TPUR), polyester type 5290, was provided by the Foam Plastics Factory (Tianjin, China). Dodecyl benzyl dimethyl ammonium bromide (QAS1), hexadecyl trimethyl ammonium bromide (QAS2), and benzidine (QAS3) were obtained from Xi'an Chemical Agent Factory (China).

Synthesis of organic clay

Sodium REC or MMT was screened with a 300-mesh sieve to remove impurities. A certain amount of screened clay was suspended in deionized water in a glass vessel using a glass rod. The QAS1, QAS2, and QAS3 were dissolved in prescribed amounts of water, respectively, then added to the suspended clay-water solution, with vigorous stirring for several minutes at room temperature. The mixture was transferred to a three-neck flask, heated to 85°C, and stirred for 5 h. The treated products were washed and filtered repeatedly to ensure the complete removal of bromide ions; the filtrate was titrated with $AgNO_3$ until no $AgBr$ precipitate was found. The products were then dried under vacuum at 100°C for several hours, and designated OREC1, OREC2, OREC3, and OMMT, respectively[b].

Preparation of clay/TPUR nanocomposites

OREC and TPUR were melt-mixed for about 15–30 min at 130–135°C in a twin-roller mixer. In this work, we prepared composites containing different amounts of REC, OREC1, OREC2, OREC3, and OMMT, respectively, which are listed in Table I.

Characterization

FTIR was performed on an infrared spectroscopy of WQF-310. X-ray diffraction (XRD) scattering measurements were conducted using a D/max-3C Rigaku (Tokyo, Japan) X-ray automatic generator. The X-ray beam was derived from nickel-filtered $Cu-K_{\alpha}$ ($\lambda = 0.154$ nm) radiation in a sealed tube operated at 40 kV and 40 mA, and the scan range of 2θ was from 2 to 8 at room temperature. The dispersion state and layered structure of clay composites were inspected using a Hitachi H-800 transmission electron microscope (TEM; Hitachi, Osaka, Japan).

Tensile strength and tear strength tests were carried out on ZMGi 250 machine at a crosshead speed of 500 mm/min according to the specification of GB/T 528-1998 and GB/T 530-81. All samples, prepared by PHI, were 2 mm thick, and at least five tests were conducted for each group of specimens, and the reported standard deviation values were less than 10%.

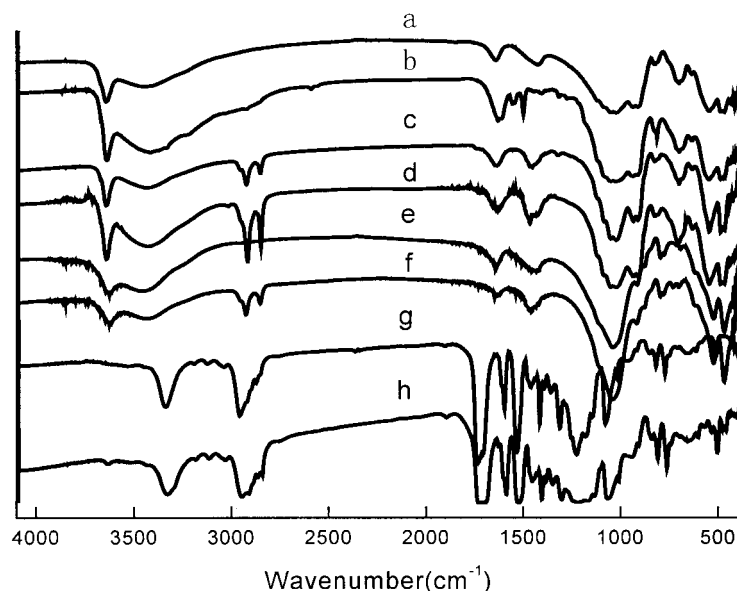


Figure 1 FTIR spectra of (a) REC, (b) OREC3, (c) OREC1, (d) OREC2, (e) MMT, (f) OMMT, (g) TPUR, and (h) TPUR/OREC1. Bands at 2927–2853 cm^{-1} : $-\text{CH}_2-$ and $-\text{CH}_3-$ stretching vibration; about 3300 cm^{-1} : $-\text{NH}-$ stretching vibration; around 1500 and 1550 cm^{-1} : $-\text{C}=\text{C}-$ stretching vibration in aromatic ring; 1628 cm^{-1} : $-\text{C}-$ in-plane vibrations; small peak at 3600 cm^{-1} : stretching vibration of $\text{Al}-\text{OH}$ in REC.

RESULTS AND DISCUSSION

In the present work, different organic modifying agents (QAS1, QAS2, and QAS3) were used for ion exchanging of Na^+ to modify the REC and MMT interlayer surface. The structure of natural clays, organic clays, and the composites can be characterized by FTIR spectra, as shown in Figure 1. The characteristic peaks confirm that the organic cations of quaternary ammonium salt and amine were exchanged with the interlayer Na^+ of REC or MMT.

Further analyses of X-ray diffraction (XRD) patterns for natural clay and organic clay are shown in Figure 2. We can obtain the interlayer distance (d -space) of the clays from their characteristic peaks, based on Bragg's equation. The d -spaces of OREC1, OREC2, and OREC3 are 2.57, 2.54, and 2.74 nm, respectively. All of these data values are greater than that of untreated REC (2.22 nm), which indicates that a cationic-exchange reaction occurred between the clay and swelling agent, and the galleries in the REC were filled with molecules containing organic cations. The larger the d -space, the greater the effect of intercalation. The d -space of OREC2 is smaller than that of OREC1, which may be attributed to the different chain structure of modifier; that is, QAS1 contains alkyl chain and benzyl chain, and QAS2 contains only alkyl group. The d -spaces of the OMMT are much larger than that of MMT, however, they are all smaller than that of OREC and REC, respectively, which may be determined by the structure of the natural REC and MMT.

The XRD patterns of composites with different amounts of clay are presented in Figure 3. The char-

acteristic diffraction peaks of the (001) plane at $2\theta = 2.10, 2.18,$ and 2.02° , corresponding to d -spaces of 4.20, 4.05, and 3.40 nm, respectively, are attributed to different contents of OREC1/TPUR [OREC1/TPUR2, OREC1/TPUR5, and OREC1/TPUR8 (Fig. 3(a))]. Figure 3(b) and (c) show the XRD patterns of OREC2/TPUR and OREC3/TPUR composites with different contents of clay. The d -space of OREC2/TPUR2 is 4.37 nm; OREC2/TPUR5, 4.05 nm; OREC2/TPUR8, 3.50 nm; OREC3/TPUR2, 3.84 nm; OREC3/TPUR5, 3.77 nm; and OREC3/TPUR8, 2.74 nm. The strong diffraction peaks can be observed as well-defined peaks for

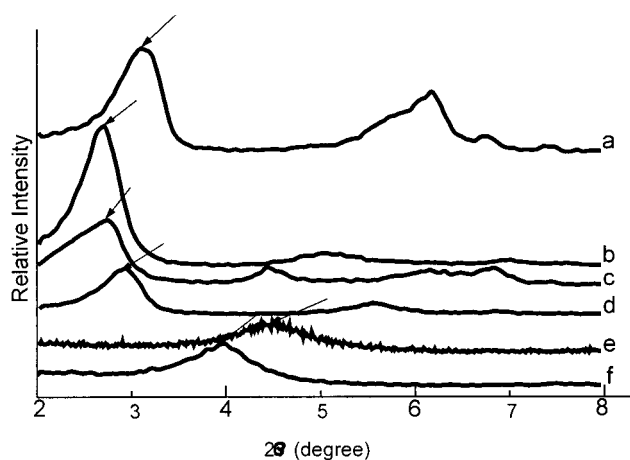


Figure 2 XRD patterns of REC and OREC: (a) REC, $d_{001} = 2.22$ nm; (b) OREC3, $d_{001} = 2.74$ nm; (c) OREC1, $d_{001} = 2.57$ nm; (d) OREC2, $d_{001} = 2.54$ nm; (e) MMT, $d_{001} = 1.50$ nm; (f) OMMT, $d_{001} = 1.70$ nm.

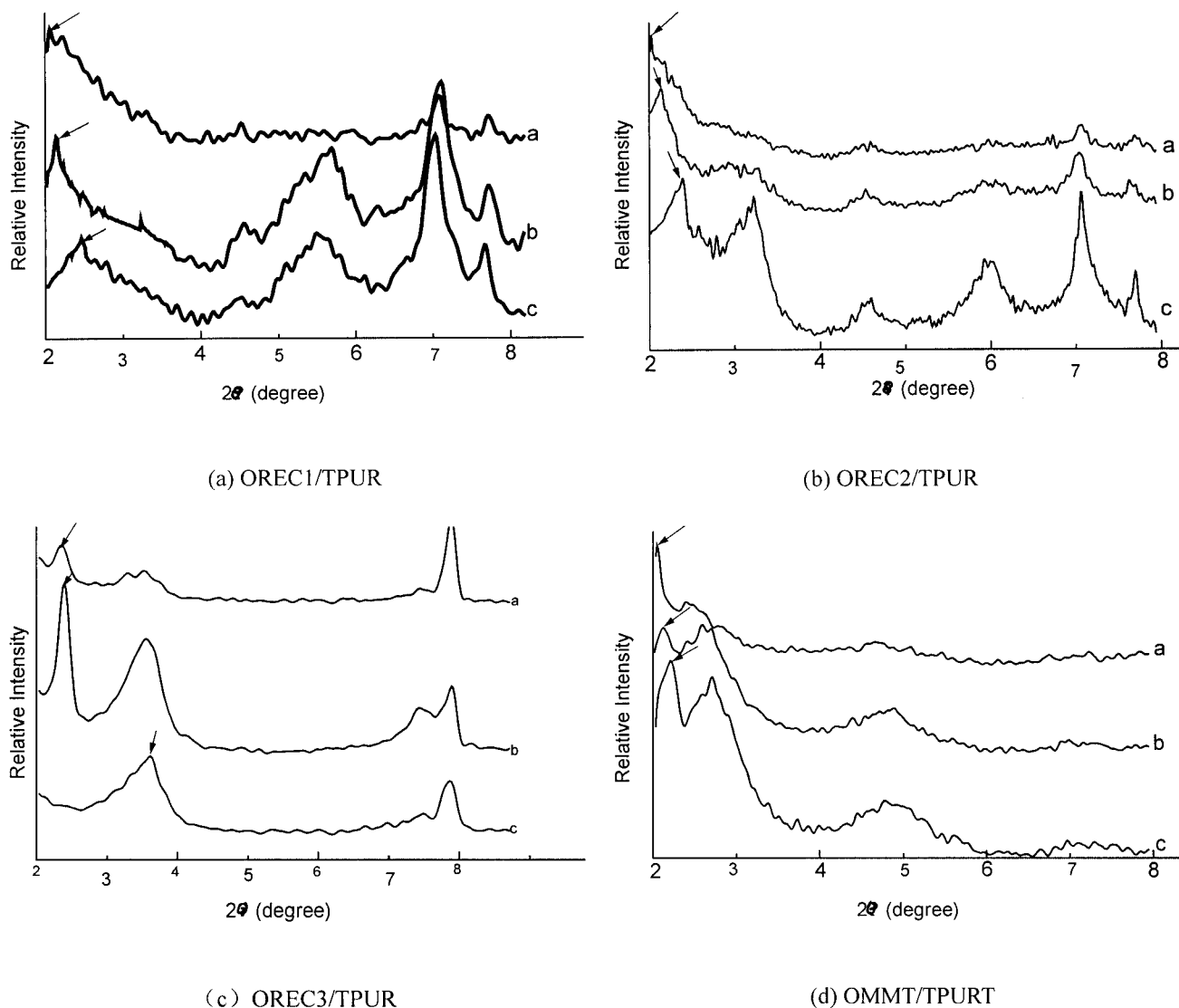


Figure 3 XRD patterns of nanocomposites with different amounts of clay: (a) OREC1/TPUR (a: OREC1/TPUR2, $d_{001} = 4.20$ nm; b: OREC1/TPUR5, $d_{001} = 4.05$ nm; c: OREC1/TPUR8, $d_{001} = 3.40$ nm); (b) OREC2/TPUR (a: OREC1/TPUR2, $d_{001} = 4.20$ nm; b: OREC1/TPUR5, $d_{001} = 4.05$ nm; c: OREC1/TPUR8, $d_{001} = 3.40$ nm); (c) OREC3/TPUR (a: OREC3/TPUR2, $d_{001} = 3.84$ nm; b: OREC3/TPUR5, $d_{001} = 3.77$ nm; c: OREC3/TPUR8, $d_{001} = 2.74$ nm); (d) OMMT/TPUR (a: OMMT/TPUR2, $d_{001} = 4.33$ nm; b: OMMT/TPUR5, $d_{001} = 3.91$ nm; c: OMMT/TPUR8, $d_{001} = 3.15$ nm).

OREC1/TPUR8, OREC2/TPUR8, and OREC3/TPUR8. These results demonstrate that the OREC1, OREC2, and OREC3 in TPUR may be intercalated and formed intercalated nanocomposites when the clay content is less than 5%, whereas in high clay loading, the layer may exist in the original state or agglomerate.

There are similarly diffracted curves for clay-modified epoxy,⁸ as may be observed from Figure 3(c): the X-ray curves of OREC3/TPUR2 and OREC3/TPUR5 (curves a and b) have two peaks in the range $2\theta < 4^\circ$, whereas curve c has only one peak. This may be associated with another competent factor caused by the two terminal $-\text{NH}_2$ in one QAS3 molecule. When the cationic ions between clay interlayers are ex-

changed with QAS3, the crosslinking bridge may be formed between the clay sheets and prevent the exfoliation of clay layers, and lead to the clay either being partly intercalated or holding the original structure. The first peak reflects the d -spaces of intercalation, and the second peak, the d -spaces of pristine clay. Curve c has one peak, and the d -space is identical to that of OREC3. This means that the OREC3 does not intercalate at all in the composites of OREC3/TPUR8.

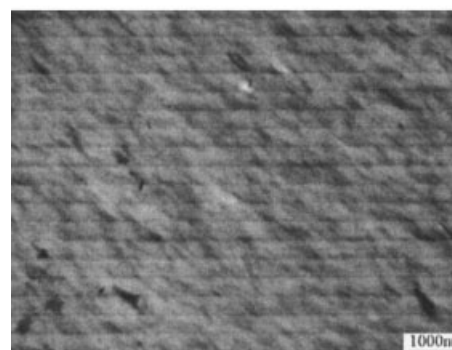
Figure 3(d) shows XRD curves of OMMT/TPUR composites, where one observes that the d_{001} peak of OMMT/TPUR composites is apparently present, although the calculated d -space of swollen OMMT in composites is larger than that of OMMT. This result means that the OMMT can also be swelled by TPUR.

We also investigated the morphology of OREC/TPUR by TEM images shown in Figure 4, which provides more direct evidence for the formation of a true nanocomposite. The dark lines represent clay, whereas the bright area represents the TPUR matrix. It can be seen from Figure 4(a) that the dispersion of the clay particles in TPUR polymer matrix is fine and uniform. Most of the organic clay particles exhibit parallel alignment to the sample surface in the case of low clay loading of 2 wt %. Moreover, some particles still exist in the original order, with swollen size of about 100 nm. However, most clay layers are partially or even completely exfoliated into well-dispersed OREC sheets, with size of about 10 nm, displayed apparently as dark lines for the OREC1/TPUR2 and OREC2/TPUR2 systems shown in Figure 4(a) and (c), respectively. This means that the thickness of stacked silicate layers is much thinner in systems with low content of clay than in those with high content. With clay content increasing to 8 wt %, the agglomerated structure forms and becomes denser in the polymer matrix. Thus the thicker lines occur in the TEM image of the composites of OREC1/TPUR8 and OREC2/TPUR8, as can be seen from Figure 4(b) and (d), respectively. In a word, we can conclude that the OREC/TPUR composites loading small content of OREC are intercalated nanocomposites.

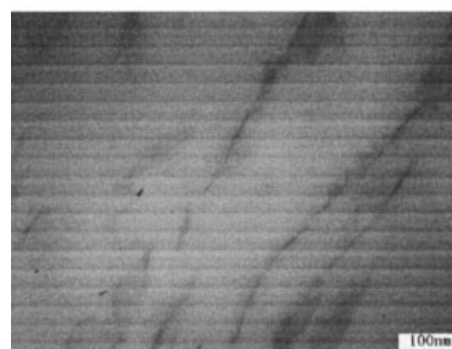
Figures 5 and 6 show the dependency of the tensile and tear strength of OREC/TPUR composites on the OREC content. The addition of a small amount of OREC to TPUR matrix can significantly enhance the mechanical properties of the composites. It can also be seen that tensile strength of composites of OREC1/TPUR, OREC2/TPUR, and OREC3/TPUR at 2 wt % clay loading is increased to 57.9, 49.3, and 41.0 MPa, respectively, which is about 52.0, 26.8, and 5.4% higher than that of pure TPUR accordingly. The tear strength of OREC1/TPUR and OREC2/TPUR composites nearly linearly increases with OREC loading, and it is enhanced by 34.0 and 40.0% at 2 wt % clay loading, compared with that of the pure TPUR. As is known, the existing agglomerate of clay particles and morphology separation of composites could substantially affect the mechanical properties; thus the achieved improvement of mechanical properties could be explained by the fine structure of nanocomposites, that is, the formation of large aspect ratio of clay particles in TPUR composites, as previously discussed in the literature.⁹ From analysis of XRD and TEM images of composites, we can see that because of the better dispersed nanometer-sized OREC platelets and the more uniform structure of OREC in the composites, the mechanical properties are more greatly enhanced. That is to say, the favorable properties are associated with the good compatibility and strong interaction between the clay and TPUR. On the contrary, the agglomerated structure, which can influence the me-



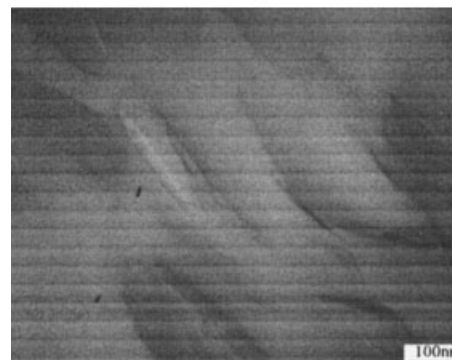
a: OREC1/TPUR2 10000 times



b: OREC1/TPUR8, 10000 times



c: OREC1/TPUR2, 100000 times



d: OREC1/TPUR8, 100000 times

Figure 4 TEM micrographs of OREC/TPUR nanocomposites: (a) OREC1/TPUR2 ($\times 10,000$); (b) OREC1/TPUR8 ($\times 10,000$); (c) OREC1/TPUR2 ($\times 100,000$); (d) OREC1/TPUR8 ($\times 100,000$).

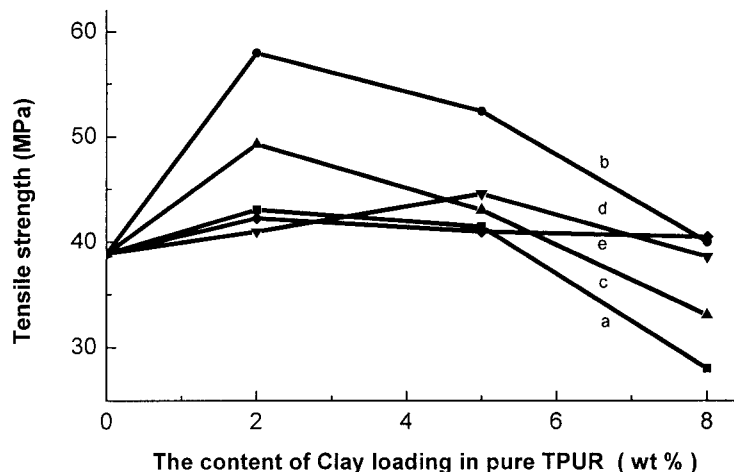


Figure 5 Tensile strength of composites of different contents: (a) REC/TPUR; (b) OREC1/TPUR; (c) OREC2/TPUR; (d) OREC3/TPUR; (e) OMMT/TPUR.

chanical strength, will be formed with the clay loading.

QAS3 has two terminal $-NH_2$ groups that may react with one $-NCO$ group, as mentioned in the literature,¹⁰ and form the crosslinking structure in TPUR. Therefore, the mechanical properties can be dramatically improved for nanocomposites. However, the tensile strength increases from 38.9 to only 44.6 MPa (by 14.6%) when the content of OREC3 is 5 wt %. When the content of OREC3 is 2 and 8 wt %, the tensile strength decreases. Simultaneously, the tear strength of OREC3/TPUR, containing only 5 wt % of OREC3, increases from 92.8 to 103.8 kN/m, whereas the tear strength decreases at 2 and 8 wt % clay loading. This collapse of the mechanical properties can be attributed to the aggregation of OREC3 as discussed above.

The mechanical properties of the OMMT/TPUR composite are also shown in Figures 5 and 6. The

tensile strength of OMMT/TPUR decreases with increasing OMMT content, which may be caused by low CEC (60 meq/100 g), smaller than that reported in the literature,¹¹ attributed to the abundance of impurities. On the other hand, the structure of MMT differs from that of REC, which may cause the difference of mechanical properties of composites.

Figure 7 illustrates the relationship between elongation at break of composites and clay loading, which provides evidence that the elongation at break does not show a simple dependency on clay loading.¹² The peak values are observed for OREC1/TPUR and OREC2/TPUR at 5 wt % clay. The elongation at break of other systems decreases compared with that of pure TPUR, indicating that the mechanisms of reinforcement and fracture are different between conventional composites and nanocomposites; thus further research is necessary.

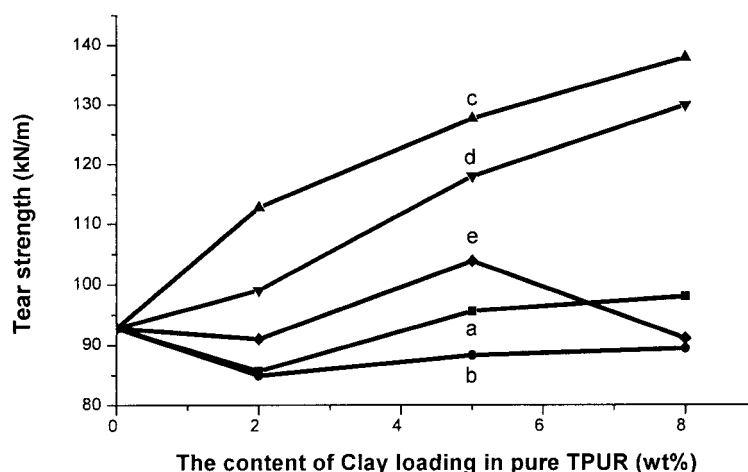


Figure 6 Tear strength of composites of different contents: (a) OMMT/TPUR; (b) REC/TPUR; (c) OREC1/TPUR; (d) OREC2/TPUR; (e) OREC3/TPUR.

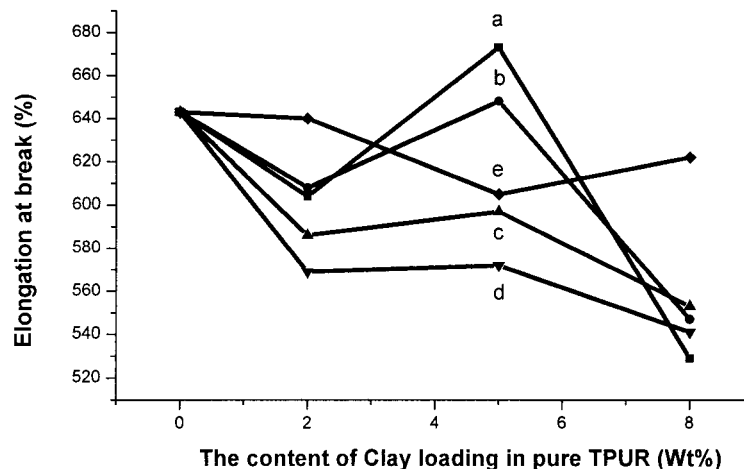


Figure 7 Elongation at break of composites of different contents: (a) OREC1/TPUR; (b) OREC2/TPUR; (c) OREC3/TPUR; (d) REC/TPUR; (e) OMMT/TPUR.

Table II shows the values of tensile modulus of nanocomposites such as OREC1/TPUR2, OREC2/TPUR2, and OREC3/TPUR2 in the case of 100 and 300% strain. The tensile modulus of the OREC1/TPUR2 and OREC2/TPUR2 systems significantly increased, although the tensile modulus of OREC3/TPUR2 is not noticeably enhanced. These results reflect the reinforcement effect attained by the dispersion of the clay nanolayer in TPUR.

CONCLUSIONS

This study illuminates that rectorite, a kind of natural silicate clay similar to MMT, is a good nanometer modifier for modifying polymers such as TPUR. First, natural REC must be modified by long-chain quaternary ammonium salts and organic amine salt through cationic-exchange reaction, and the modified REC (OREC) can be used to prepare OREC/TPUR nanocomposites by melt blending at lower clay loading.

TABLE II
Effect of Clay on Tensile Modulus of Nanocomposites at Room Temperature

Stress (MPa)	System			
	TPUR	OREC1/TPUR2	OREC2/TPUR2	OREC3/TPUR2
100%	7.1	15.9	12.1	8.1
300%	12.5	20.1	15.9	13.9

Mechanical properties of the OREC/TPUR nanocomposites can be substantially enhanced when the REC is modified by quaternary ammonium salts, and the maximum ultimate tensile strength can be obtained at 2 wt % OREC loading, whereas the tear strength also significantly increases with increasing amounts of OREC. When the REC is modified by binary organic amine, the mechanical properties are not so obviously improved.

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