

Rectorite/Thermoplastic Polyurethane Nanocomposites. II. Improvement of Thermal and Oil-Resistant Properties

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ABSTRACT: Organ-rectorite/thermoplastic polyurethane (OREC/TPUR) nanocomposites were synthesized via melt intercalation. The dynamic mechanical properties by dynamic mechanical analysis (DMA), thermal and oil-resistant properties were investigated. The results show that the storage modulus (E'), loss modulus (E''), and glass-transition temperature (T_g) of the nanocomposites have an increase to some extent than those of pure TPUR. The thermal stability of nanocomposites was also studied in detail by thermal gravity analysis (TGA), which was higher than that of pris-

tine TPUR matrix when the content of organic REC is at 2 wt %, and the decomposition temperature at 10% weight loss of OREC/TPUR is greatly increased up to 330°C from 315°C. Oil uptake of the composites is also significantly reduced in comparison with TPUR matrix, which is ascribed to the good barrier effect of nanosheets of OREC. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1165–1169, 2005

Key words: rectorite; thermoplastic polyurethane; nanocomposites; thermal properties; oil resistance

INTRODUCTION

Nanocomposite materials consisting of inorganic nanolayers of clay, such as montmorillonite (MMT), and polymer matrix have recently attracted intense research interest. Presumably because of the nanoscale dispersion of the fillers and the local interaction between the filler and matrix, the nanocomposites can exhibit improved modulus, lower thermal expansion coefficient and gas permeability, higher swelling resistance, and enhanced ionic conductivity compared with the pure polymers.

In the past few years, much attention has been paid to preparation methods,^{1–3} dispersed structure and morphology,^{4–6} mechanical properties,^{7–9} etc. More recently, their fire retardance and thermal behavior, conductivity, gas barrier, and optical, magnetic, and electrochemical properties also attracted many researchers' interest.^{10–13} A lot of polymer/clay nanocomposite material systems were developed by dispersing organic clay in various polymeric matrices.

The current favorite clay for polymeric nanocomposite is MMT, that belongs to the general family of 2:1 layered silicates. It is an 1 nm thick and 30- to 2000-nm-long sheet consisting of oxide layers with exchangeable cations between layers. Rectorite (REC) is another kind of layered clay with specific texture

similar to that of MMT, which is a regularly interstratified clay mineral of dioctahedral mica-like layer (non-expandable) and dioctahedral smectite-like layer (expandable) in a 1:1 ratio. The mica layer displays high temperature-resistant property, and the smectite layer has the capability of cation exchange.

However, REC is also hydrophilic. To render it more hydrophobic, the hydrated cations between the silicate layers need to be exchanged with cationic surfactants such as organic quaternary ammonium salt (QAS), as shown in Figure 1. The modified clay with lower surface energy will become organophilic and will be more compatible with polymer matrix.

In this study, the organic rectorite (OREC) was dispersed well in thermoplastic polyurethane (TPUR) by melt-intercalation as shown in our previous work. Our objective was to examine the thermal, oil-resistant properties of fabricated OREC/TPUR nanocomposites.

EXPERIMENTAL

Materials

Sodium rectorite (Na^+ -REC) refined from the clay minerals was provided by Hubei Mingliu Inc. Co. (Wu Han, China) and the CEC is 45 meq/100 g, which was tested in our lab by using ammonium acetate alcohol as extractant according to the reported method.¹⁵ Na^+ -REC was suspended in hot deionized water by using a stirrer. Dodecyl benzyl dimethyl ammonium bromide (QASI) (supported by Shanghai, China) was

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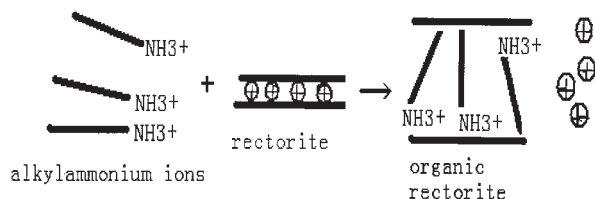


Figure 1 Cations exchange process of organic cations for alkyl ammonium ions. (a) Storage module E' curves for TPUR and its nanocomposites. (b) Loss module E'' curves for TPUR and its nanocomposites. (c) TAN curves for TPUR and its nanocomposites.

dissolved in water, then added into the clay suspension with vigorous stirring, and heated to 85°C for several hours. The product (OREC1) was washed several times, filtered, and then dried under vacuum at 100°C for several hours. Polyester-typed elastomer rubber (TPUR) was supplied by Da Qiu Zhuang (Tianjin, China).

OREC1 and TPUR were melt-mixed at 130–135°C in a twin-roller mixer; then additional fillers such as stearic acid were added in the designed sequence. The time of blending was about 15–30 min. In this article, 2, 5, and 8 wt % of OREC1 was filled in TPUR, and the resultants of the composites were termed OREC1/TPUR2, OREC1/TPUR5, and OREC1/TPUR8, respectively.

Characterization

Dynamic mechanical analysis (DMA) was performed by using DDV-III-EA (Toyo Baldwin Co. Ltd.), and the testing was carried out in three-point bending mode at a vibration frequency of 11 Hz in a temperature range from -100°C to 100°C at a heating rate of $2^{\circ}\text{C}/\text{min}$. Thermogravimetric analysis of OREC1/TPUR was carried out on a SDT 2960 simultaneous DTA–TGA by TA Instruments at a heating rate of $10^{\circ}\text{C}/\text{min}$ under nitrogen. Accelerated aging was conducted in an air-oven to provide a rough estimate of this property, according to GB3512-83. All of the samples were put into an air-oven and kept for different aging times such as 24, 48, and 72 h at 120°C and then their tensile strength was tested to evaluate the thermal air-resistant properties of the nanocomposites.

Oil-resistance experiments of the composites were carried out in 40 weight oil at room temperature according to GB1690-82. The samples were dried in an oven at 104°C for 2 h to achieve the dry weight; then they were immersed in oil and kept for different given times. After taking them out, they were quickly placed between sheets of dry cloth to remove the excess solvents and immediately weighed to get the oil-absorption weight. Tensile strength was tested to compare with original values and the weight-change ratio was

calculated from the increase in the weight of the samples. The percentage of oil absorption was calculated on the basis of

$$\text{Oil absorption (\%)} = [(W_1 - W_0)/W_0] \times 100\%$$

where W_1 and W_0 represent OREC/TPUR composites' oil-absorption weight and original dry weight in air, respectively.

Tensile strength were carried out on a ZGMi 250 tester at a crosshead speed of 500 mm/min according to the specifications of GB/T 528-1998. All samples, prepared on B230-H press machine (City of Industry, USA) were 2 mm thickness, and the data of properties were determined from the average value of at least five tests for each group of specimens.

RESULTS AND DISCUSSION

Thermodynamic properties

DMA for the OREC1/TPUR nanocomposites was carried out to monitor the effect of clay nanolayers on the thermodynamic properties of TPUR composites. The storage modulus (E'), loss modulus (E''), and loss factor ($\tan \delta$) are plotted in Figure 2. It can be seen that the nanocomposites have higher E' values than that of the pure TPUR over the whole temperature range [Fig.2(a)]. However, there is different magnitudes of enhancement in moduli at various temperature stages, indeed, it is much higher than that of pure TPUR, especially above glass-transition-temperature (T_g) for all kinds of nanocomposites. With the clay content increasing, the OREC1/TPUR nanocomposites show a substantial increase in E' , and the maximum storage modulus of these nanocomposites is in the case of OREC8/TPUR. The loss modulus of organic OREC1/TPUR also increases with the organoclay increasing, as shown in Figure 2(b).

Dynamic relaxation peaks of TPUR and OREC1/TPUR composites can be observed in Figure 2(c), and the dominant relaxation appearing at around -30°C is the T_g of TPUR matrix, which is caused by the movement of large-chain segments. The secondary relaxation peak, such as β - or γ -relaxation, which is attributed to a relaxing unit consisting of a few chain segments, seems not to be apparent within the range of testing temperatures. The glass transition peak of the OREC1/TPUR2 is almost at the same position as that of the pure TPUR. It is shown that a small amount of OREC1 added in TPUR will not affect the T_g of TPUR, and the nanocomposite can be used like pure TPUR in low temperature. However, with the OREC1 content increasing, there is a substantial enhancement in $T_{g'}$ which indicates that high temperature-resistant properties with them can be improved. The phenomena can probably be explained by the interaction, increas-

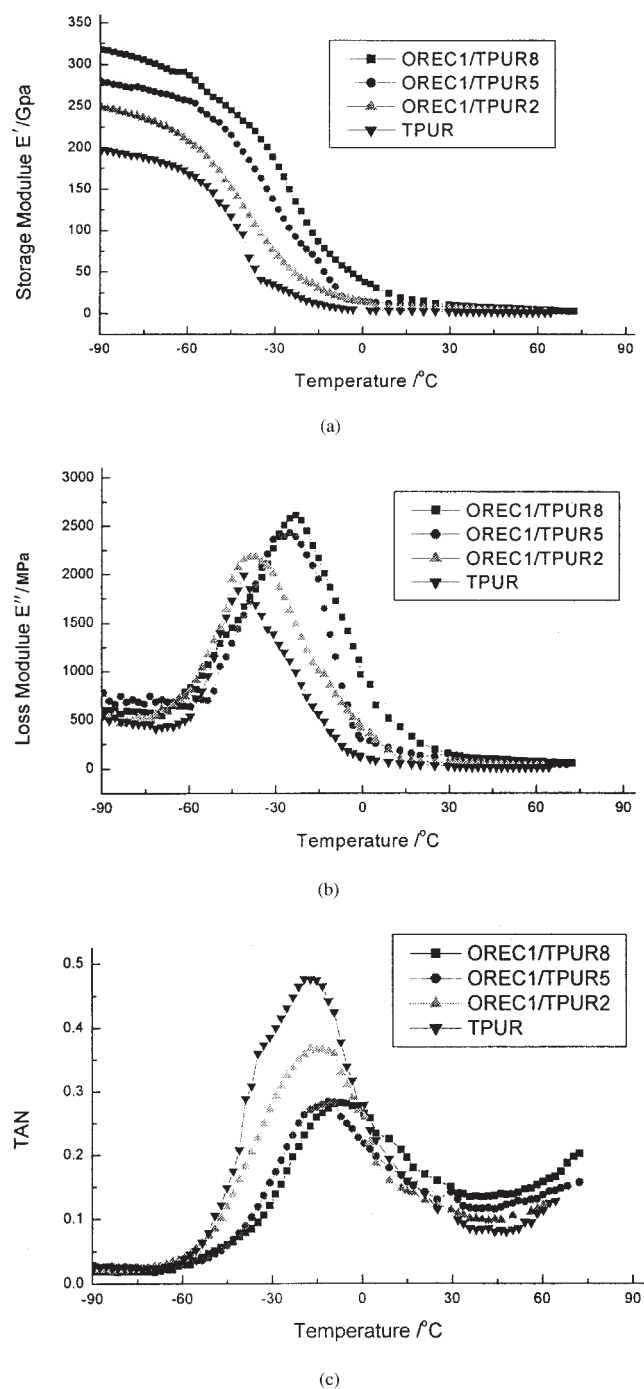


Figure 2 The curves of dynamic mechanical properties for TPUR and its nanocomposites.

ing with the clay content, between the clay as the hard segment and TPUR molecule chain, which results in the enhancement of T_g and the modulus.

The storage moduli (E') and loss moduli (E'') of the samples at different temperatures are shown in Table I. The peak storage moduli is 6.62 times higher (from 18.6 to 83.1 MPa) than that of pure TPUR at -20°C , and the peak loss moduli is 7.96 times higher (from 15.2 to 75.4 MPa) than that of pure TPUR at 40°C ,

which is much higher than that of conventional composites with platelike filler.

Thermal stability

Thermal stability of TPUR matrix and its composites with various OREC1 contents can be evaluated by thermogravimetric analysis (TGA), as shown in Figure 3. It was found that the thermal stability of nanocomposites adding a small content of OREC1 (2%) is higher than that of natural TPUR. This result may be attributed to a good nanometer-size dispersion of organic clay and the stable structure of REC possessing high temperature-resistant mica layers. The decomposition temperature at 10% weight loss is greatly increased to 330°C from 315°C . The similar conclusion also can be drawn from the percentage of weight loss at 500°C , which decreases from about 83% to about 72%. However, when the clay loading increases from 5 to 8 wt %, the TGA traces of the two kinds of composites are both similar to that of OREC1/TPUR2, which indicates that the decomposition temperature of composites having different clay contents is nearly invariable. The same phenomena in thermal stability were also reported for PP/clay,¹⁶ polyimide/clay,¹⁷ and PS/MMT.¹⁸ This is mainly due to the presence of well-dispersed OREC1 sheets, which will hinder the permeability of volatile decomposed products out of the composites in comparison with the natural TPUR. That is to say, the byproducts and heat of decomposition will be difficult to penetrate into the composites in this case. When the clay content is higher, above 5 wt %, there will be more agglomeration domains, and the effect of thermal resistance will be lost.

Two temperature stages of maximum weight-loss rate, about $320\text{--}360$ and $380\text{--}420^\circ\text{C}$, also can be observed on the TGA curves. As is well known, the high-temperature stage is attributed to the TPUR matrix's degradation and the low-temperature stage may be explained by the following two factors: first, a small

TABLE I
Dynamics Storage Moduli (E') and Loss Moduli (E'') of the Samples at Various Temperatures

Samples	-80°C	-20°C	40°C
	E' (GPa)		
TPUR	191 (1.00)	18.6 (1.00)	1.82 (1.00)
OREC2/TPUR	240 (1.26)	42.0 (2.26)	4.13 (2.27)
OREC5/TPUR	273 (1.43)	83.1 (4.47)	8.97 (4.93)
OREC8/TPUR	310 (1.62)	123.1 (6.62)	7.87 (4.27)
	E'' (MPa)		
TPUR	463 (1.00)	863 (1.00)	15.2 (1.00)
OREC2/TPUR	480 (1.01)	1350 (1.56)	40.7 (2.67)
OREC5/TPUR	707 (1.53)	2310 (2.68)	75.4 (7.96)
OREC8/TPUR	589 (1.27)	2563 (2.97)	105 (6.90)

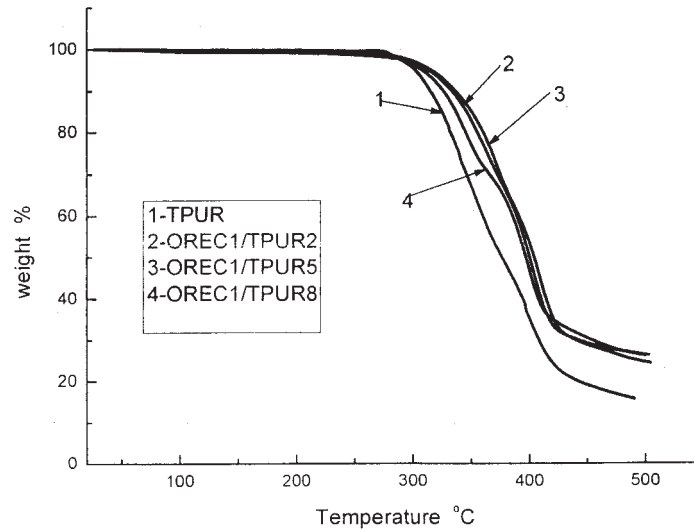


Figure 3 TGA curves of TPUR and OREC/TPUR composites.

amount of modifier molecules (dimethyl dodecane benzyl ammonium) intercalated into the REC gallery tends to degrade slightly faster than the TPUR matrix, which results in the additional weight loss in the composites at the low decomposition temperature. Second, the added lubricant such as stearic acid reducing the adhesive ability to the twin-roller mixer may volatilize above its boiling point.

Accelerated-aging in thermal air

Just like the conclusion drawn from the DMA and TG analyses, the presence of OREC1 sheets in composites also tends to enhance the aged strength of TPUR matrix. From Figure 4, we can see that the retained ratio of strength decreases with clay loading increasing. As

is well known, aging invariably occurs when the composites are used in fixed conditions on time passed. However, the OREC2/TPUR's strength only has a slightly decrease, which may result from the exfoliated OREC sheets' hindering to the heat and oxide molecule.

Oil-resistant properties

Tensile strength and oil absorption were measured to evaluate the reinforcing and barrier effect of the organic clay on nanocomposites in oil. The tested curves are represented in Figure 5. It can be seen that all curves show a similar change in the testing stage. As time passed, the tensile strength decreased slightly and the weight increased for all composites. However,

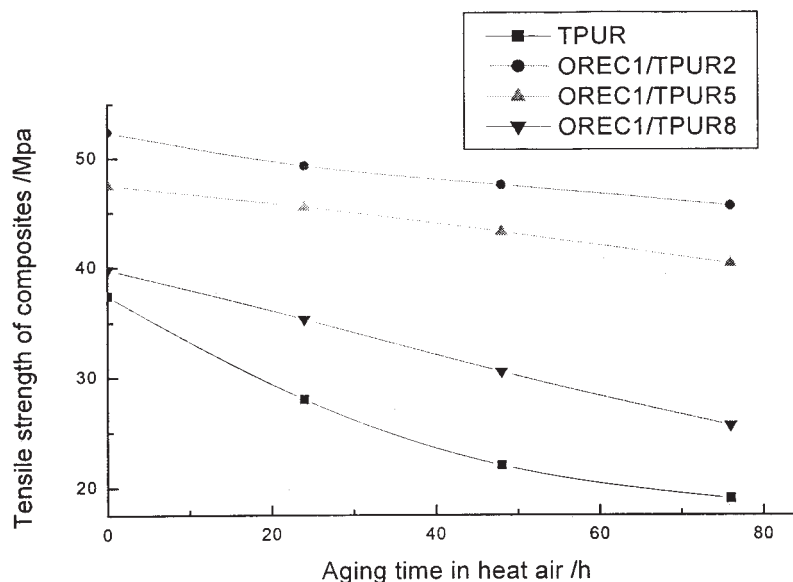


Figure 4 The composites' tensile strength after accelerated-aging in thermal air. (a) The tensile strength of composites in oil aging. (b) The weight change of composites in oil aging.

the tensile strength of OREC1/TPUR2 is improved greatly and the weight became lower in comparison with natural TPUR and the other composites. This may be attributed to the homogeneous dispersion of the OREC1 sheet in TPUR matrix and its barrier properties in nanocomposites. As we know, many factors, for instance, clay loading, sheet orientation, state of delamination or agglomerate, etc., influence the properties of composites, but only in low clay loading nanodispersion can we achieve the desired improvement in properties of TPUR nanocomposites. The presence of well-dispersed platelike clay makes the penetrant inevitably travel along a tortuous path in the composites, as shown in Figure 6(a), which decreases the relative permeability and improves the barrier properties of nanocomposites. However, the agglomerate of multiple OREC1 sheets will form at high clay loading and lead to the immiscibility between OREC1 and TPUR, which only forms conven-

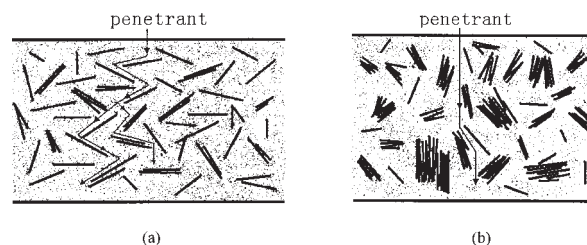


Figure 6 Schematic illustration of the penetrant's traveling path.

tional composites with poor barrier, as shown in Figure 6(b).

CONCLUSION

OREC/TPUR nanocomposites were developed. The OREC1/TPUR2 nanocomposites can exhibit excellent thermal and oil-resistant properties, which are attributed to the intercalation/exfoliation of OREC1 platelets in the TPUR matrix and makes the penetrant inevitably travel a long tortuous path in the composites. A significant improvement in the storage modulus and T_g for OREC1/TPUR2 nanocomposites are observed from DMA patterns. The initial decomposition temperature at 10% weight loss is greatly increased by about 15°C, and the tensile strength of OREC1/TPUR2 by accelerated-aging in thermal air or oil only has a slight decrease compared with TPUR matrix and other composites.

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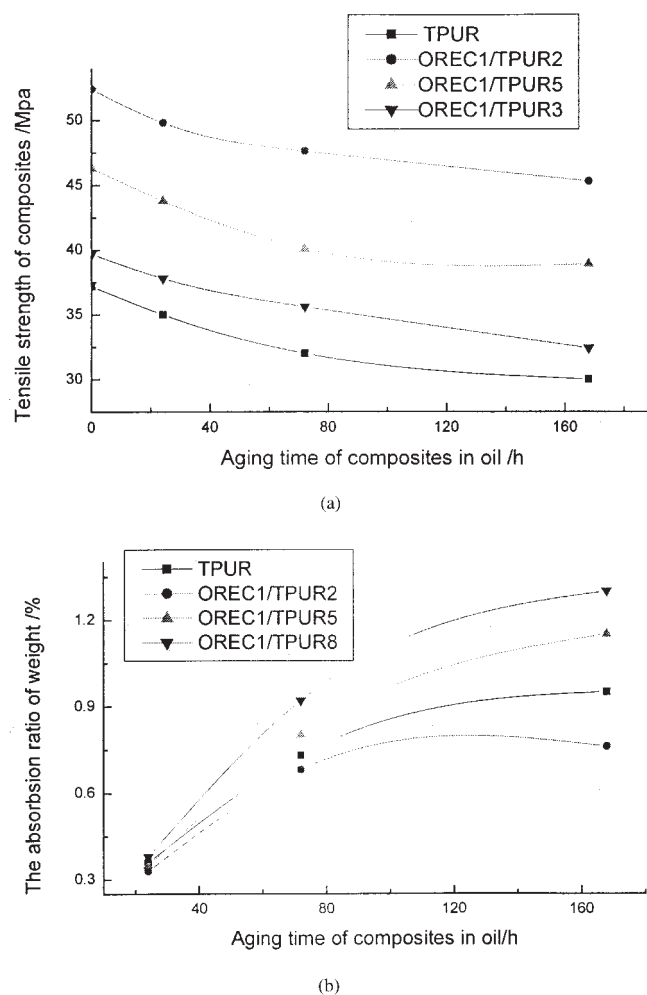


Figure 5 The influence of the properties of composites in oil aging.