The Effect of Swelling Agents and Characterization of Polyurethane/Polymer Electrolytes/Clay Composites

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ABSTRACT: This study discusses the interaction model and characterization of a clay organic processed with different swelling agents blended with PU/polymer electrolytes. The change in *d*-spacing of the clay and modified clay in the PU/polymer electrolytes blends was analyzed using X-rays. A rigid-body pendulum rheometer was used to determine the curing behavior of PU/polymer electrolytes matrix in the clay and modified clay with different proportions. Dynamic mechanical analysis has been applied to discuss the intermolecular interaction between clay and organoclay with different proportions and PU/polymer electrolytes blends. We have also analyzed the mechanical properties, stress, and strain. As a result, the compatibility of polymer electrolytes, clay, and organoclay is better. The swelling agent that intercalated among the layers of clay will be crowded out and adsorbed onto the surface of clay. The curing time, intermolecular interaction, thermal properties, and mechanical properties of composites were clearly influenced by the clay and swelling agent. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 1206–1214, 2005

Key words: PU; polymer electrolyte; clay; swelling agent; composites

INTRODUCTION

Blending mixes two or more polymers of different proportions to achieve a certain expected performance.[1–3] Its advantages include simplicity, which was conducted by the existing equipment and technology,[4,5] and various predicted components as well as physical and chemical properties, which facilitate the evaluation of the properties of the mixture.

The molecular structure of polyurethane (PU) consists of urethane compounds (-NHCOO). In general, block copolymer PU is composed of rigid diisocyanate, short-chain diol, or diamine and polyol. Since it is chemical resistant, soft, waterproof, and weatherproof, it can be used for different purposes.[6] The application of polymer electrolytes is very broad. They are used in products including solid-state batteries, sensors, and display devices.[7–12]

PU/clay nanocomposites are a type of layered inorganic montmorillonite clay that disperses and reinforces PU polymer substrate. They help to increase heat resistance and mechanical and barrier properties of polymer composites significantly.[13–19] Besides, as hydrophilic clay is incompatible with hydrophobic polymer substrates in the PU/clay material system, a swelling agent is usually used to improve compatibility, and organoclay becomes a critical material of technological importance. For the types of intercalating agents used in the previous documents, Usuki and colleagues[20,21] used ω-amino acids of different carbon chains and clay for cation exchange. They found that amino acids with a carbon number lower than 8 were parallel to the paralleled silicate layers and those with a carbon number greater than 11 were slant among the clay layers. Modified clay dispersed more evenly and the cation exchange efficiency affected the compatibility between polymer and clay composites. Osman et al.[22] modified the clay with dialkylammonium SAMs and found that its thermal stability was better than that of monoalkyl derivatives. They also found that basal-plane spacing in the organic clay increased, which might be interesting for polymer business applications. Pinnavaia al.[23] utilized alkylammonium cation as an intercalating agent, which contributed excellent CO_2 barrier properties to polyimide/clay composites. The modified clay with the synthesized Qutubuddin intercalating agent[24,25] generated functionalized organoclay. In addition to self-polymerization, styrene monomers reacted with the intercalator after reacting with the clay layers. Heat resistance and mechanical strength of the compound material were also improved obviously. Ma et al.[26] modified the clay with *n*-dodecylamine, 12-aminolauric acid, and 1,12-diaminodecane and indicated that crystallization of polyamide 6 varied with different intercalators.

TABLE I
The Compositions of mPU/Clay Hybrids Containing Various Organoclay Concentrations (wt %)

Material										
mPU	98	98	96	96	94	94	92	92	90	90
Clay	2	—	4	—	6	—	8	—	10	—
Organoclay	—	2	—	4	—	6	—	8	—	10

Note. mPU, modifier of 10 wt % PEL content in PU; Organoclay; CTAB-OC, DDAC-OC, DDAB-OC.

Among the previous studies on polyelectrolyte/clay composites, Cheng et al.[27,28] proposed that the presence and compatibility of clay did benefit the conductivity of polymer electrolytes. Giannelis[29] added clay with the melt intercalation method and the conductivity of polyethylene oxide increased to 1.6 $\times$ 10^{-6} S/cm at room temperature. Viaia et al.[30] applied various approaches, including melt intercalation, *in situ* polymerization, and solution intercalation to combine polyethylene oxide and clay nanocomposites in which stiffness, strength, barrier properties, and thermal stability were improved significantly. The study on rheological properties of PEO/organoclay conducted by Hyun et al.[31] revealed that the shear viscosity increased with the clay content and the carbon length of amine.

However, the effects of the introduction of polymer electrolytes, clays, and organoclays to the PU matrix as well as their interaction and impact upon each other have not yet been studied. The main goal of this study was to evaluate the effect of the incorporation of clay and organoclay on the PU/polymer electrolytes (mPU) blends. Alkylammonium cation with a different carbon number was selected as an intercalator for clay modification. Basal-plane spacing changes of clay and organoclay in the PU/polymer electrolyte blends were observed by X-ray, and the curing behavior was detected by rigid-body pendulum rheometer. Dynamic mechanical analysis was used to explore the interaction among PU, polymer electrolytes, clay, and organoclay. The thermal stability was explored with thermogravimetric analysis. Last, the impact on PU physical properties by polymer electrolytes and organoclay was evaluated from the mechanical properties.

EXPERIMENTAL

Materials

The materials used (Table I) were PU (diphenylmethane diisocyanate, polypropylene glycol (soft segment), and polyethylene glycol (hard segment); product name, Corol, made by Kuan Je), liquid polymer elec-
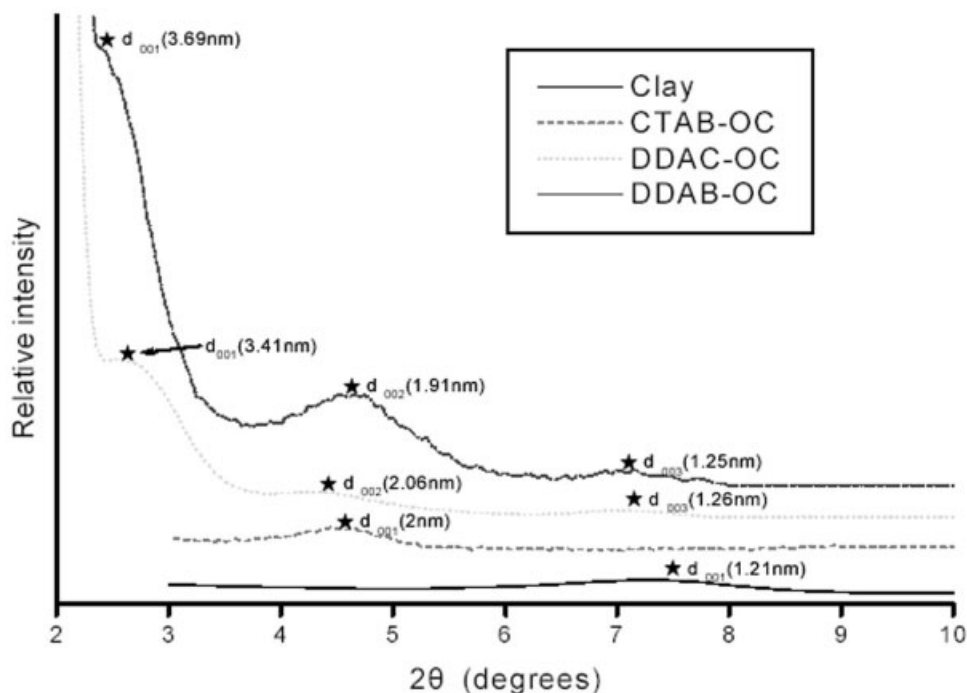

Figure 1 XRD patterns of organophilic clays: clay, CTAB-OC, DDAC-OC, DDAB-OC.
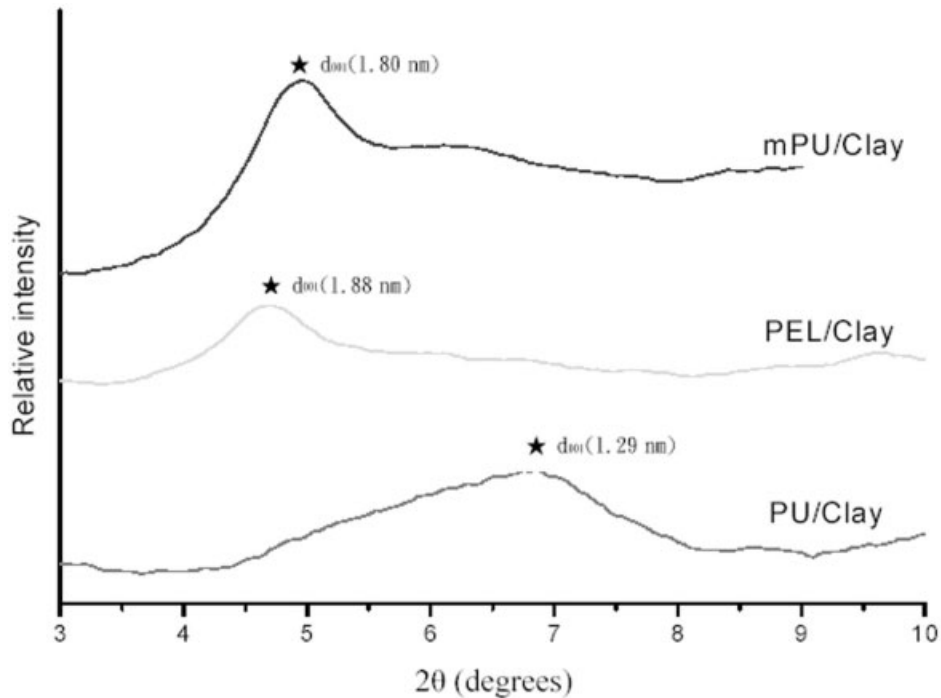
Figure 2 XRD patterns of clay in various polymers: mPU/clay, PEL/clay, PU/clay.

trolytes (polypropylene oxide–polyethylene oxide copolymer with $LiClO_4$ 20 wt % (PEL) manufactured by Japan Carlit), and Na+-montmorillonite (clay, Model No. PK805, from Pal Kong, Taiwan). Hexadecyldimethylethylammonium bromide (CTAB) was purchased from Acros. Dimethyldistearylammonium chloride (DDAC) and dimethyldipalmithylammonium bromide (DDAB) were purchased from TCI (Tokyo, Japan).

Preparation of organoclay

A total of 4.2 g CTAB (intercalative reagent) was dissolved in 250 mL distilled water under vigorous stirring to form a uniformly dispersed solution. Then, 5 g Na-montmorillonite was added to the solution and then stirred for 24 h, filtered, and washed three times with 400 mL of hot water to remove NaBr. After being washed with ethanol (250 mL) to remove residual ammonium salt, the modified clay was dried in a vacuum oven at 80 °C for 24 h. The above steps were repeated for 2.6 g of DDAC (intercalative reagent) and 2.5 g of DDAB (intercalative reagent) to obtain the DDAC-OC and DDAB-OC.

Preparation of specimen

The sample for testing was mixed with the proportions specified in Table I produced by mixing clay and organoclay (CTAB-OC, DDAC-OC and DDAB-OC) in PEL, before stirring with the PU, than placing in a mold. The mold was maintained at 30°C for a 48 h curing. After cooling, the test piece was removed from the mold and trimmed to a proper size for testing.

X-ray measurements

Wide-angle X-ray diffraction experiments were conducted on a Rigaku D/Max RC X-ray diffractometer using CuK_α radiation (λ = 1.5418 A) at 40 kv and 100 mA with a scanning rate of 2°/min.

Rigid-body pendulum rheometer measurements

Curing process measurements were taken with a rigid-body pendulum rheometer (Model No. α-100) manufactured by Tohoku Electronic Industrial Co., Ltd. (Japan). A frame-type pendulum (FRB-100) with knife edge (RBE-130) was chosen.

Dynamic mechanical properties analysis

The 2-mm-wide composites were trimmed to a specification of 2 × 10 × 5 mm. Dynamic mechanical analysis, Model No. TA2980, was used with a temperature rising rate of 5 °C/min within the range from −100 to 50 °C at a frequency of 1 Hz for temperature scanning.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was carried out using a thermogravimetric analyzer (TA instrument)
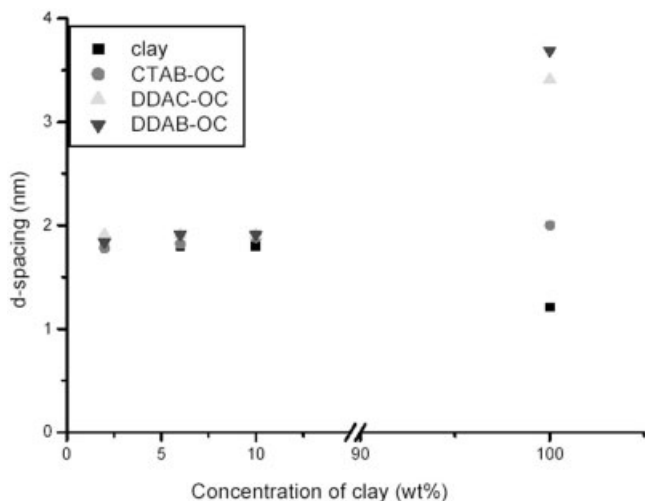
Figure 3 The *d*-spacing of mPU/clay hybrids containing various organophilic clay concentrations (wt %): mPU/clay, mPU/CTAB-OC, mPU/DDAC-OC, mPU/DDAB-OC.

in a nitrogen atmosphere from 30 to 600 °C at a heating rate of 20 °C/min.

Mechanical properties test

Tensile stress and strain were measured by a Universal tensile tester with a tension velocity of 500 mm/min in compliance with the specifications of ASTM D412C.

RESULTS AND DISCUSSION

The gallery distance of clay and organoclay in mPU blends

The surface of clay can attract positive ions, which makes clay hydrophilic. Organic polymer chains, mostly composed of hydrocarbons, are hydrophobic. Each polymer chain is so large that it can't easily enter the clay gallery to form intercalated composites. Therefore, this experiment mainly uses CTAB, DDAB,

and DDAC of the surfactant, which had an "ion exchange" with the Na^+ ions of the clay resulting in ionic bonds. The bulky alkylammonium molecules cause a larger interlayer spacing. The modified clay is hydrophobic with a lower surface energy, which is more compatible with organic polymers. The effect of organic modifiers on the intercalating behavior of the polymer can also be confirmed by an XRD pattern. As expected, the intercalation of the polymer chains further increases the interlayer spacing of the clay over that of pure clay, shifting the diffraction peak toward lower θ.

Figure 1 shows the diffraction features of the scattered and absorbed X-ray after the clay was organically processed with CTAB, DDAC, and DDAB ammonium salts. Before swelling, the *d*-spacing of clay was 1.21 nm ($2\theta = 7.3°$). After swelling by CTAB, the diffraction peak for the clay changed from the original $2\theta = 7.3°$ to a lower scattering angle of $2\theta = 2.6°$. At this time, the gallery distance was 2 nm. The diffraction peak of the clay (DDAC-OC) with swelling by DDAC was at $2\theta = 2.6°$. The interval distance increased to 3.4 nm. The diffraction peak of the clay (DDAB-OC) with swelling by DDAB was at $2\theta = 2.4°$. The gallery distance expanded to 3.6 nm. This makes an intercalation to the structure of clay layers and holds open the gallery distance between layers. The clay that was changed through the DDAB possesses large gallery distances between silicate layers.

Second, the unswelling clay is blended into PU, PEL, and mPU blends (Fig. 2. This shows that the *d*-spacing of the unswelling clay is not affected by the PU polymer. The PU polymer can clearly hold open the *d*-spacing of the unswelling clay to 1.88 nm. This illustrates that PEL is a polypropylene oxide–polyethylene oxide copolymer with 20 wt % $LiClO_4$. The content of 20 wt % $LiClO_4$ can interact with the clay with negative charge and with the ether oxygen chain of PEL. So the PEL polymer can get into the structure of the clay layers and hold open the clay *d*-spacing. The PEL polymer chain lies inside the structure along
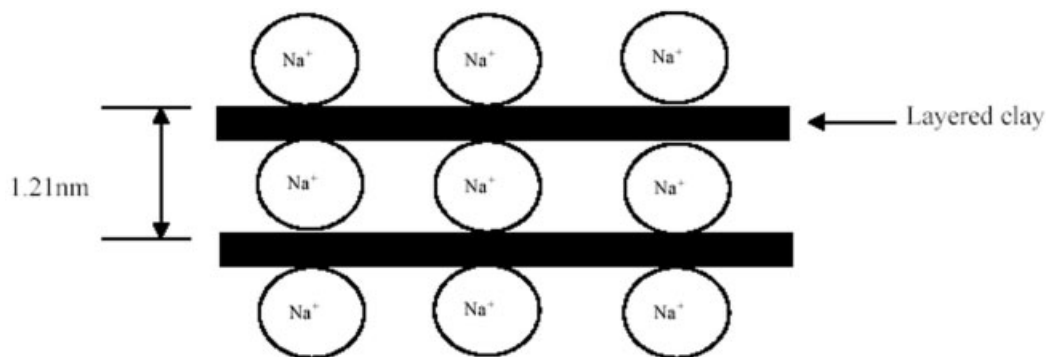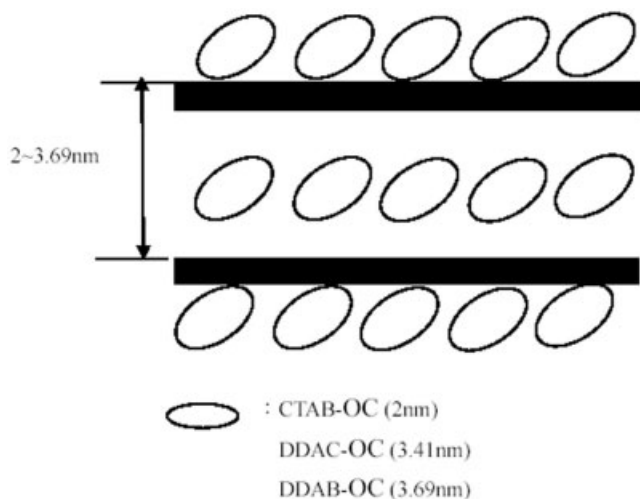

Figure 4 Structure of layered clay.

Figure 5 Structure of organoclay.

Figure 6 Structure of PU/clay composites.

with the long side of the clay layer. Then we tried to blend the unswelling clay into mPU blends; the d-spacing of clay is 1.80 nm. This explains that the d-spacing of the clay in the PU polymer matrix is not clearly influenced.

In the past, the PEO/clay nanocomposites reported by Cheng et al.[16] indicated that the d-spacing of the unswelling clay was about 1.24 nm. After swelling by DDAC and poly(oxypropylene) diamine (d2000), the d-spacing increased to 2.08 and 3.17 nm, respectively. Upon adding the swelling clay to the PEO polymer electrolyte (the consistency of lithium salts is fixed to PEO/Li = 8), we find that the d-spacing of the interval distance for unswelling clay layers is about 1.78 nm, with the existence of polyethylene oxide. When 2.9 wt % of DDAC-OC blends into the polyethylene oxide, it shows the status of coming off. When the proportion of the swelling clay in the polyethylene oxide is increased up to 16.7 wt %, the clay itself produces agglomeration and crowds the tetrabutylammonium portion existing inside the layers. Hence, the d-spacing of DDAC-OC is reduced to 3.92 nm. Meanwhile, the PEO polymer chain cannot easily access the clay layers and lower the compatibility between polyethylene oxide and swelling clay. The same thing happens with the d-spacing of d2000-OC under PEO polymer. The d-spacing change of the polymer is similar to that of the DDAC-OC/PEO system, whereas the d2000-OC inside the polyethylene oxide appears to intercalate. When the clay is processed by swelling, the compatibility between PEO and the clay is raised. We tried to blend the clay, CTAB-OC, DDAB-OC, and DDAC-OC into the mPU blends to be able to observe changes in the d-spacings of the clay. As shown in Figure 3, the unswelling clay was influenced by blends and its d-spacing was increased to 1.80 nm. Upon continuous addition of clays, no change in the d-spacing occurred.
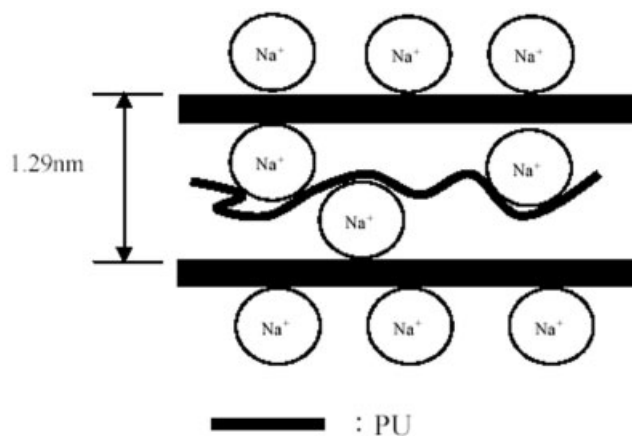
When the swelling clay is blended into the mPU in different proportions, its d-spacing was reduced, nearing the d-spacing (about 1.78–1.91 nm) of the PEL/clay nanocomposites. These results show that if mPU blends clay with different swelling agents, it is impossible to increase the compatibility of mPU blends. The clay in the mPU blends displays the status of intercalation. This illustrates that there is an interaction between lithium salts of the PEL polymer and clay, which would then result in the intercalation of PEL polymer into clay, and the crowding causes swelling of the clay layers. In the meantime, the d-spacing of the clay was reduced. Even the PEL/organoclay material system that went into the PU polymer had the d-spacing of the clay and was not influenced. According to the results shown above, Figures 4–8 show the interaction model among the clay, swelling agent, and mPU blends. Figure 4 shows that the d-spacing of the swelling clay is 1.21 nm. When the clay was organically processed by CTAB, DDAC, and DDAB swelling
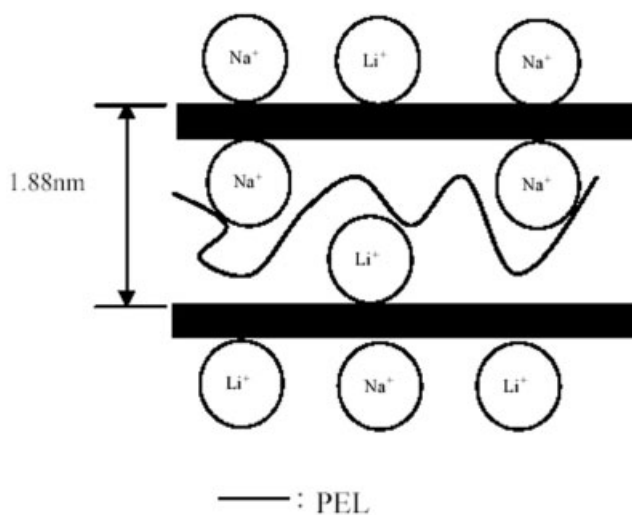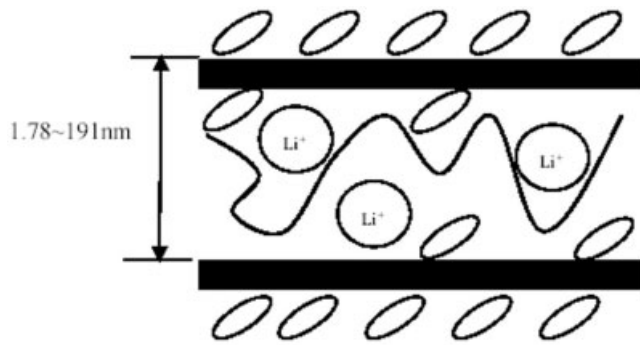

Figure 7 Structure of PEL/clay composites.

Figure 8 Structure of mPU/organoclay composites.

Figure 10 Change of vibration wave in the curing process.

agent, the d-spacing of the swelling clay wase 2, 3.41, and 3.69 nm, respectively, as shown in Figure 5. The effects of PU polymer and PEL polymer to the unswelling clay are shown in Figures 6 and 7. The d-spacing for these materials is 1.29 and 1.88 nm, respectively. The mode diagram in Figure 8 shows that the clay, after swelling, will be blended into the mPU blends, which has a d-spacing of about 1.78–1.91 nm. This proves that only the PEL polymer can intercalate into the clay layers and crowd the swelling agent out and, consequently, be absorbed onto the surface of the clay. From the XRD experimental results, we know that the compatibility is better between PEL and clay. In other words, PEL can be treated like a swelling agent for clay. Therefore, we select clay and CTAB-OC in the PU/polymer electrolyte blends to evaluate the curing behavior, intermolecular interaction, thermal stabilities, and mechanical properties. Besides, we also use it to understand the effect of swelling agent for the composite material system.

Curing behavior of clay and organoclay in mPU blends

In this study we used a rigid-body pendulum rheometer[32–36] to observe the changes in the properties of the composite curing process under the 30 °C reaction system. In the exper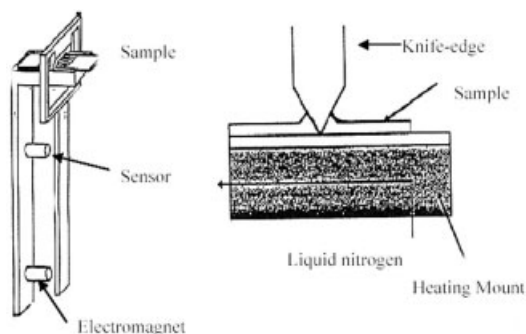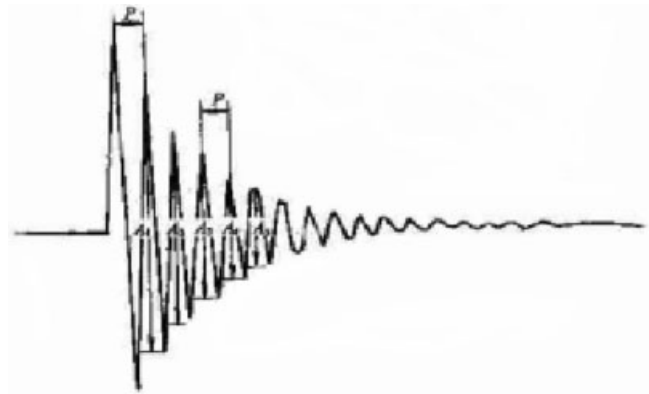iment, the sample was placed on a heating platform. Then, the knife of the pendulum was allowed to swing freely on the surface of the testing sample (Fig. 9). In the process of transition from liquid to solid phases of the blends, the amount of viscosity will be increased. Also, the vibration of the pendulum will change (Fig. 10). P is the cycle time for each swing and A is the amplitude of vibration, which is the maximum distance that the pendulum swings each time. Due to the consumption of the conglomerate, the amplitude will be reduced. From A, we can get the decrease in the logarithmic damping ratio Δ, which is defined as the natural logarithmic damping ratio of two near vibrations, that is:

$$\Delta = \ln A_1/A_2 = \ln A_2/A_3 = \ldots = \ln A_n/A_{n+1}.$$

A_1, A_2, A_3. . . A_n, $A_{n + 1}$ represent the width of the1, 2, 3. . . n, $n + 1$ amplitudes of the vibration. From the changes in the occurrences of vibration, we can get the rate of decrease of the logarithmic damping ratio. When the curing action of blends is completed, the logarithmic damping ratio rate of decrease will reach a balance, thus showing that the mapping time is the
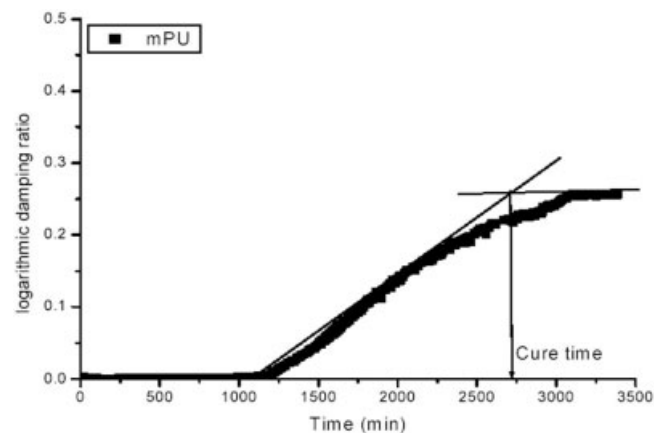

Figure 9 System of the instrument.

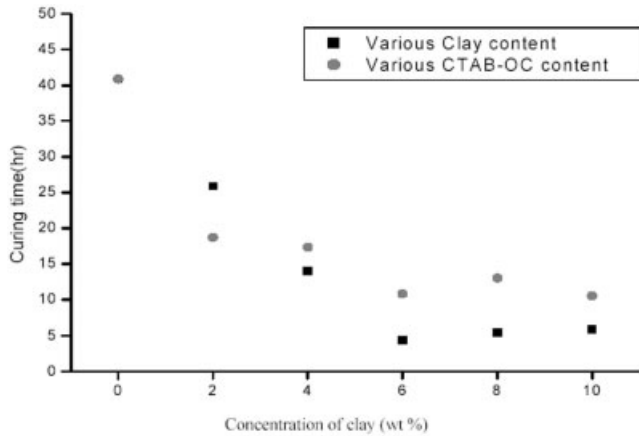**Figure 11** PU/PEL blend curing behavior.

Figure 12   Curing time of mPU/Clay blends with various clay and CTAB-OC content.
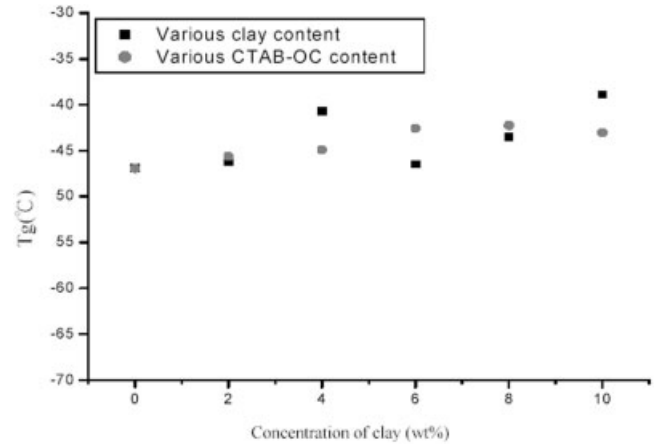

Figure 13 T_g of mPU/clay blends with various clay and CTAB-OC content.

curing time. From Figure 11, we know that the curing time for the mPU blends is 45.1 h. Moreover, we can observe the effects of different proportions of clay to the mPU blends curing procedure. The measured times of curing are shown in Figure 12, which shows that after adding clays, the curing time for blends shortens and the clay containing 6 wt % will balance in curing. In addition, the curing time of the mPU/CTAB-OC composites is shorter than that of the mPU/clay. This situation is similar to the one derived in the experimental results. Due to the good compatibility between the PEL and clay, the mPU blends can be added by following the clay addition procedure. Thus, one can intercalate more PEL polymer into the clay

layers. The entire contact area will be enlarged and the interaction would increase, thus speeding up the crosslinking reaction of mPU blends. In the mPU/CTAB-OC, the swelling of CTAB-OC will be crowded out and be absorbed on the surface of the clay. The other end of the swelling of hydrophobic adsorption of alkyl chains will interact with the blend interface. The curing time of the mPU/CTAB-OC composites will also be reduced by the addition of CTAB-OC.

Intermolecular interaction of clay and organoclay in mPU blends

The effects of clay and organoclay with different proportions of mPU blends are shown in Figure 13. From
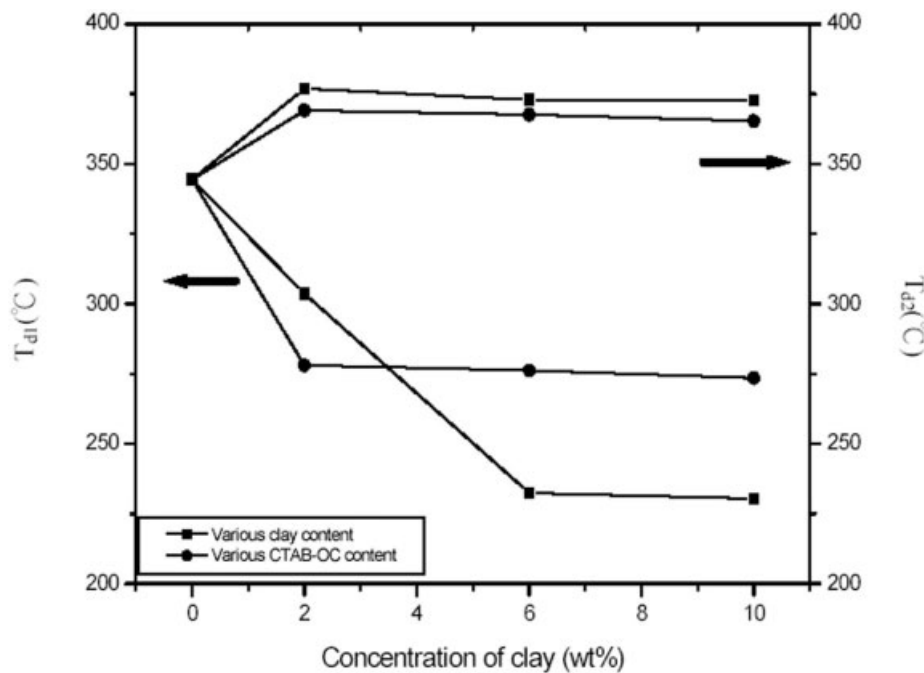

Figure 14   TGA curves of mPU blends with various clay and CTAB-OC content.

this figure, we can observe that the glass transition temperature (T_g) of mPU blends is −46.93 °C. After adding the clay, the T_g peak will shift to a higher range of temperature from −46.19 to −38.91 °C. This shows that the interaction occurs between the clays and mPU blends. In addition, the mPU/clay curve shows that when the amount of clay is lower than 6 wt %, the T_g will decrease by about 6 °C. This is due to the increase in the clay layers intercalated with the PEL polymer; yet the interaction between PU polymer and clay interface remains less. Slipping occurs under such circumstances. In the mPU/CTAB-OC curve, the swelling will be crowded out and be absorbed to the surface of the clay. This will enhance the interaction of the PU and clay layers. Consequently, it will reach a balance when the substance of CTAB-OC is 6 wt %. This shows that the interaction of mPU and clay and CTAB-OC is clearly influenced by the clay and the swelling agent.

TGA analysis of clay and organoclay in mPU blends

The thermal stabilities of clay and CTAB-OC in mPU blends are shown in Figure 14. The figure shows that the thermal degradation temperature (T_d) of mPU blends is 344.44 °C and that the clay and CTAB-OC can increase the thermal stabilities of the mPU blend. After adding the clay and CTAB-OC, two transition temperatures were obtained. Its first degradation temperature (T_{d1}) was the PU and the second degradation temperature (T_{d2}) was the PEL intercalation within the clay layers. Besides, after treating the clay with the swelling agent, the polymer chains can't easily enter into the clay layers and the effect of swelling agent leads to crowding out, so the T_{d2} of mPU/clay was better than that of the mPU/organoclay composites.
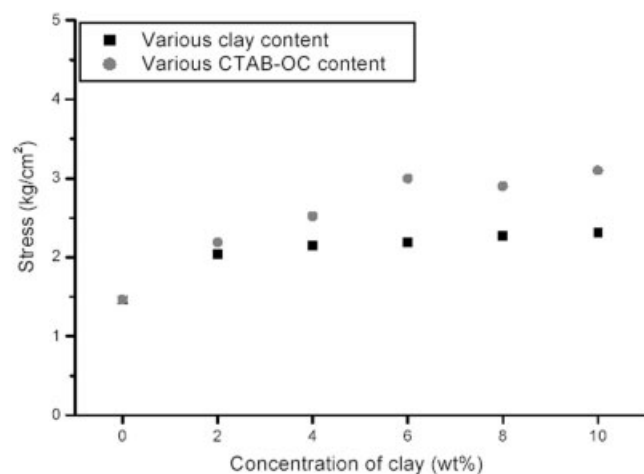

Figure 15   Stress of mPU/Clay blends with various clay and CTAB-OC content.
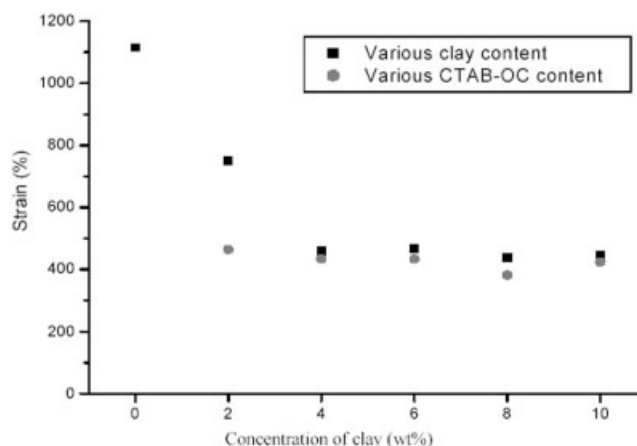

Figure 16   Strain of mPU/clay blends with various clay and CTAB-OC content.

Effect of mechanical properties of clay and organoclay in mPU blends

Figure 15 shows the stress curve diagram of mPU/clay nanocomposites with different proportions of clay. It shows that raising the clay content increases the stress of blends. The mPU/clay curve diagram shows that we can estimate the clay content in 2 wt % and further illustrates that a balance of stress is achieved. The tensile stress of mPU/CTAB-OC will reach a balance in 6 wt % and is better than that of the unswelling clay. From the test results, we conclude that the PEL polymer intercalated between the CTAB-OC layers will increase by adding clay. The ammonium salt was beneficial to the interaction between the PU and clay. It is also helpful for the improvement of the mechanical properties of the blends. Figure 16 shows the relation of strain and stress. In addition, the mPU/CTAB-OC composites can keep a good strain.

CONCLUSIONS

Based upon the experimental results of the X-ray, the clay organic processed with different swelling agents was added into the mPU blends. The *d*-spacing of PEL/clay was minimal. This means that in the PEL polymer, the swelling between clay layers of the composites system is crowded out and adsorbed onto the surface of the clay. Only the PEL polymer can be intercalated to the clay layers. Thus, the clay can maintain a complete gallery structure that disperses the mPU matrix and form intercalated composites accompanying increased contents of clay and organoclay in the mPU blends. This would result in a shorter curing time, increase in interaction, thermal stability increase, and enhancement of the mechanical properties. This explains the important role of clay and swelling agent in the physical properties of mPU blends.

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