A Study on Viscoelasticity of Polyurethane–Organoclay Nanocomposites

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ABSTRACT: Polyurethane (PU)/organically modified layered silicate (organoclay) nanocomposites were prepared by *in situ* polymerization. The viscoelasticity of PU–organoclay nanocomposites was investigated. The results suggest that the addition of organoclay resulted in the increase in the elasticity of PU and the decrease in damping property, and improvement of the thermal stability of PU significantly. However, it was also found that the addition of organoclay did not enhance the modulus of PU significantly. It was found that at high contents of soft segments, the modulus of PU decreased with the addition of organoclay. Hysteresis results indicated that energy dissipation increased with increasing organoclay. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 99: 3677–3683, 2006

Key words: nanocomposite; clay; energy dissipation; polyurethane

INTRODUCTION

The study of polymer/layered silicate nanocomposites has still attracted academic and industrial interests in material science although a large variety of polymer/layered silicate nanocomposites has been developed during last decade by a number of methods, such as prepolymer from solution, *in situ* intercalative polymerization, and melt intercalation.[1–4] Because of the incorporation of nanosized layered silicates into polymer hosts by only a small amount (≤5 wt %), it has led to reports of pronounced improved mechanical, thermal, and other properties when compared with those of the host polymers. These improvements include a higher modulus,[1,5,6] increased strength,[7] increased fatigue durability[8] and heat resistance,[1,7] deceased gas permeability,[9,10] etc. These nanocomposites containing layered silicates also offer effective flame retardancy[11,12] without creating environmental problems in terms of combustion, recycling, and disposal of the end products. This is the most successful approach developed so far to reduce environmentally friendly flame retardant polymer.[11,12]

To understand why and how the small amount of layered silicates can improve physical properties of the material, many efforts have been made in last few years.[1] It has been concluded that the main reason for such improved properties in nanocomposites is the stronger interfacial interactions between the matrix and layered silicate and the size of the filler compared with conventional filler-reinforced system.[1] It has been also evidenced that the altered properties of the materials relies heavily on the molecular dynamics of polymers in addition to traditional filler reinforcement.[13] However, the mechanisms behind these improvements are still not well clearly understood at present. Now the continuous research on this topic is forward and many researchers have built some physical models or used computing simulation to investigate these questions.[1,14]

Polyurethane (PU), which is a segmented elastomer, is one of the most versatile materials due to its biocompatibility,[15] elasticity,[16] and abrasion resistance.[15] The physical properties of PU are derived from their molecular structure caused by interactions between the polymer chains. The segmental flexibility, the chain entanglement, and the crosslinkage are all factors that influence on the properties and determine the use of the end-products. As matter of fact, it was widely used in many industrial applications such as coatings, thermoplastic elastomers, and composite. One of the important applications of PU is as a damping material, for example as the spring aids in the automotive industry, which need to have excellent fatigue and tensile properties. To improve its mechanical properties, more recently, PU/layered silicate nanocomposite has received increasing interest.[17–19] From the investigation of the morphology and surface properties, it is known that the organoclay can reduce surface energy of the polymer,[20] which could provide the useful information to develop new antifouling coating material for marine applications. By X-ray dif-

TABLE I
Young's Modulus of PU Nanocomposites

Clay content (%)	Young's modulus (MPa)			
	Hard segment 18 wt %	Hard segment 26 wt %	Hard segment 32 wt %	Hard segment 36 wt %
0	0.926	1.931	2.735	4.133
1	0.848	1.839	2.844	4.184
3	0.745	1.609	2.931	4.251
5	0.839	1.977	3.067	4.485

fraction detection of compliance in PU nanocomposites it has been proposed a new concept of nanospring for better understanding why the fatigue durability of the nanocomposite is significantly enhanced when organoclay was incorporated.[8] This present work is to study the viscoelasticity of PU nanocomposites and to understand how the organoclay affects on the viscoelastic properties. The viscoelastic nature is associated with the energy dissipation when the material is subjected to oscillating stress.

EXPERIMENTAL

Materials

Poly(propylene glycol) (Luprane 2090, molecular weight = 6000, function = 3) was kindly provided by Elastogran UK Ltd. (Alfreton, UK) 4,40-Methylene bis(cyclohexyl isocyanate) and 1,4-butanediol were provided by Aldrich (Milwaukee, WI). Dabco-33LV was obtained from Air Products and Chemicals (Allentown, PA). Stannous 2-ethyl hexanoate was provided by Sigma (St. Louis, MO). The organoclay used in our experiments was Cloisite® 20A, which was purchased from Southern Clay Products, Inc (Gonzalez, TX). The organic modifier is dihydrogenated tallow, quaternary ammonium, and the modifier concentration is 95 meq/100 g clay.

Preparation of PU–organoclay nanocomposites

A series of PU–organoclay nanocomposites were prepared. The preparation process was as follows: the polyether polyol and the organoclay were blended and stirred for 4 h at 60°C. The mixture (100 g) was blended for a particular PU/clay nanocomposite with 2.25 g of 1,4-butanediol, 0.75 g of Dabco-33LV, 0.75 g of stannous 2-ethyl hexanoate, and 15.5 g of 4,40-methylene bis(cyclohexyl isocyanate) at room temperature for 1 min and was vacuum degassed for 5 min. Then the viscous prepolymer was poured into an O-ring metal mold and cured at 50°C for 24 h and 80°C for 1 week. According to above formula, PU/clay nanocomposites with different contents of hard segments were prepared.

Characterization

Dynamic mechanical thermal analysis

A bending mode was used in the test, in this research. Specimens were held by single cantilever clamp. The specimens were mainly tested from −80 to 200°C, at a frequency of 10 Hz and a strain of 4 times, with a heating rate of 3°C/min. The assembly was placed in the furnace, which was first cooled with liquid nitrogen to −90°C, and electrically heated at 3–200°C or more. The temperature near the clamps was measured using a platinum thermocouple. Small rectangular bar specimens of approximately 35 mm × 10 mm × 2 mm were tested in bending mode.

Mechanical tests

Mechanical tests (tensile and hysteresis) were performed according to the relevant ASTM standards. Tensile strength was measured using a Lloyd Material Tester at room temperature. The NLC 2.5 kN load cell was used. The normal rate of traverse of the moving grip was 500 mm/min. All the reported tensile determinations were an average of, at least, five measurements. The hysteresis was measured on the loading–unloading cycle. Permanent set was taken as the strain at which a zero load is measured on the unloading cycle.

RESULTS AND DISCUSSIONS

Tensile properties of PU nanocomposites

Segmented polyurethane elastomers are block copolymers with alternating soft and hard blocks that, due to structural differences, separate into two phases or domains. As matter of fact, hard domains serve as physical crosslinks and act as high modulus filler, whereas the soft phase provides extensibility.[15,16] For these reasons, in this research, the tensile properties of pure polyurethanes with different contents (by weight) of hard segments and their nanocomposites at various organoclay contents (by weight) were investigated, and all results are presented in Tables I–III.

TABLE II
Stress at Break of PU Nanocomposites

Clay content (%)	Stress at break (MPa)			
	Hard segment 18 wt %	Hard segment 26 wt %	Hard segment 32 wt %	Hard segment 36 wt %
0	2.05	4.19	8.51	10.34
1	3.53	6.14	10.79	15.03
3	3.88	9.03	12.76	16.90
5	3.80	9.77	13.77	15.58

It can be seen from Table I that when the PU has a lower content of soft segment, the addition of the organoclay into the PU leads to decrease in modulus of the PU nanocomposites. And then with increasing the organoclay to 5 wt % the modulus recover to about the value of the pure PU. These results express that the organoclay has different effect from conventional filler and has a function as plasticizer.[21] As PU has higher content of hard segment, the modulus of the PU nanocomposites significantly increased with increasing the organoclay, indicating that the organoclay also behave partly as conventional filler resulting in a reinforcing effect.

As shown from Tables II and III the stress and elongation at break dramatically increased when the organoclay was incorporated into the PU. When adding 3 wt % of the organoclay, the elongation at break increase about 1.5–2 times compared with that of the pure PU. Figure 1 shows the effect of hard segment content on the increment ratio (elongation of nanocomposite/elongation of the pure PU) of elongation at break for the PU nanocomposites. As indicated, when the organoclay content increases the increment ratio increased. At higher hard segment content in the PU, the increment ratio decreased for the PU nanocomposites containing 1 wt % organoclay. For the 3 wt % organoclay containing PU the ratio increased, then decreased with increase in the hard segment content. These results indicate that the organoclay and hard segment in the PU nanocomposites determine the mechanical properties, and both show opposite effects. The interactions between the organoclay and PU chains, which makes the movement ability of the PU segments decrease, and the plasticizer effect of the

alkylammonium ions could result in increase of the mobility of PU chains. Therefore, both hard segments and the organoclay could corporate to alter the mechanical properties of the material. For the PU–organoclay nanocomposites prepared by us, the optimizing condition is 26% hard segment with 3 wt % organoclay.

Dynamical mechanical behavior of PU nanocomposites

DMTA measures the response of a given material to an oscillatory deformation as a function of temperature. Figure 2 presents the temperature dependence of the storage modulus of the PU and its nanocomposites with different contents of the organoclay. It can be seen that at below glass transition temperature the storage modulus for the pure PU and its nanocomposites have no obvious difference. At above glass transition temperature the storage modulus was strongly increased, showing that addition of organoclay has strongly improved elastic property and thermal stability.

The storage modulus curves of the pure PU materials with different hard segment contents are presented in Figure 3. In comparison between Figures 2 and 3, there were no differences in the storage modulus in the glassy state and with increasing hard segment contents in the PU the enhancement in the modulus at above glass transition temperature was also observed. This means that the effect of clay on the storage modulus of the materials is hard segment-like, and the organoclay has the same reinforcing effect as conventional filler. Both hard segment and the organo-

TABLE III
Elongation at Break of PU Nanocomposites

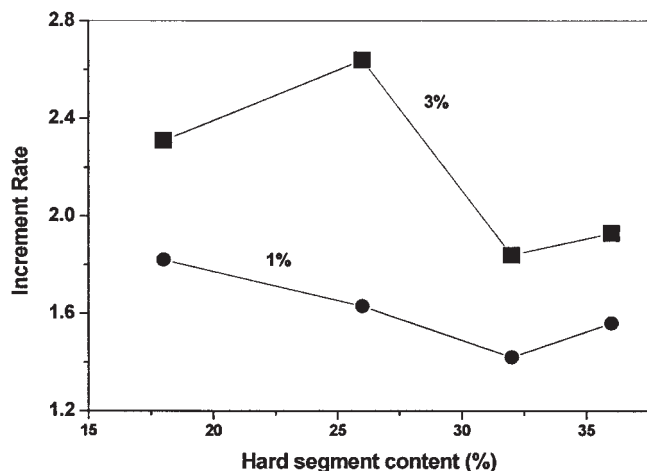| Clay content (%)	Elongation at break (%)			
	Hard segment 18 wt %	Hard segment 26 wt %	Hard segment 32 wt %	Hard segment 36 wt %
0	360	305	414	369
1	656	498	588	576
3	833	807	762	714
5	749	807	712	583

Figure 1 Increment ratio (elongation of nanocomposite/elongation of the pure PU) of elongation at break versus hard segment content for the PU nanocomposites.

Figure 3 Log E' as a function of temperature for pure PU with different contents of hard segments.

clay have strongly influenced on the damping and elastic properties of the material.

At above glass transition temperature, when materials become soft the movement of the polymer chains could be restricted by the organoclay. On other hand, all PU nanocomposites show a greater increase in storage modulus at higher temperature compared with that of the pure PU. This indicates that the reinforcement effect of the organoclay particles becomes prominent, resulted by both the organoclay particles and extended intercalation, at high temperature.[22]

The loss factors (tan δ) of the PU and its nanocomposites with different organoclay contents are presented as a function of temperature, shown in Figure 4. Obviously, the intensity of the tan δ peaks of the nanocomposites significantly decreased or narrower compared with that of the pure PU, indicating that
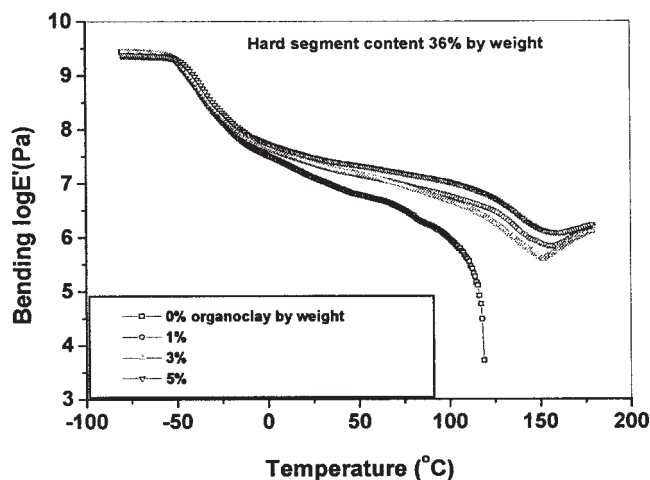
addition of organoclay resulted in reduction of damping ability of the PU nanocomposites. This indicates that polymer–filler interactions present in these systems contributed to hindering molecular motion.[13]

Figures 5 and 6 show the temperature dependence of loss factors of the pure PUs with different hard segment contents. With increasing hard segment content tan δ peak also decreases.

Figures 7 and 8 show the relationship between loss and storage modulus for the pure PU with different hard segment contents, and the PU nanocomposites with various organoclay contents, respectively. The results express that there are some different effects of organoclay and hard segment on the dynamic properties, obviously, at above glass transition temperature. With increasing hard segment content, the loss modulus (log E'') increase, resulting from more internal friction between hard and soft segments when the
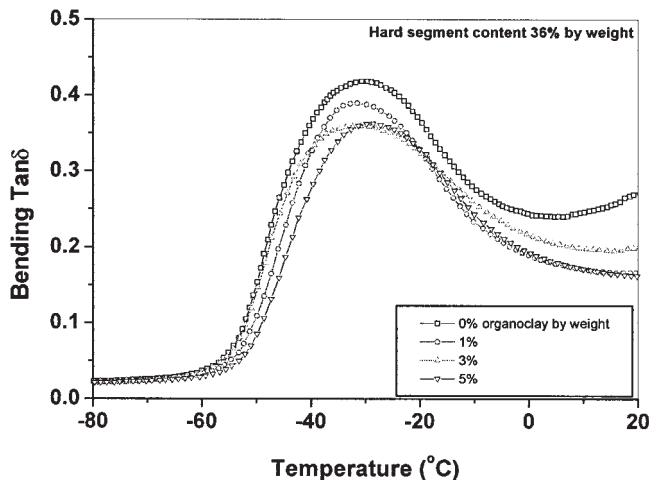

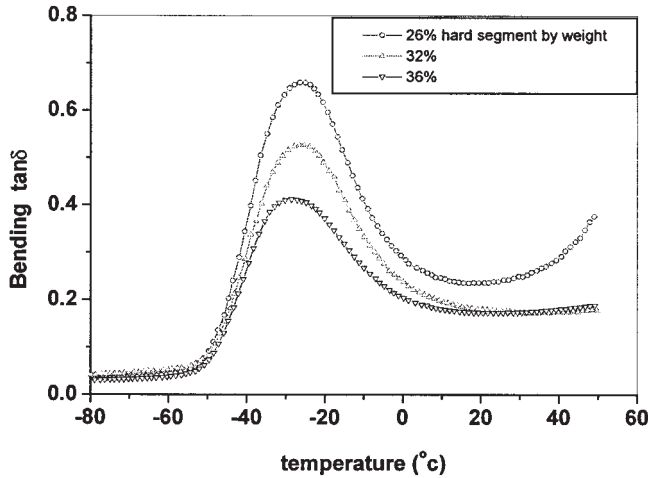**Figure 2** Log E' versus temperature for PU nanocomposites with different organoclay contents.

Figure 4 Tan δ versus temperature for PU nanocomposites with different organoclay contents.

Figure 5 Tan δ versus temperature for the pure PU with different hard segment contents.

Figure 7 Variation of the log E'' as function of log E' for the pure PU with different hard segment contents.

soft segment moves on the surface of the hard domain. This means that the increase in hard segment content increased damping capacity and reduced elastic properties of the PU. However, as seen in Figure 8, with increase in the organoclay, the loss modulus decreases, indicating that the addition of the organoclay leads to reduced viscosity and increase in elasticity of the materials. So both hard segment and organoclay contents have an opposite influence on the viscoelasticity of the materials and the incorporation of both can produce desirable viscoelasticity.

Hysteresis

Hysteresis experiment is a simple method for the analysis of the nature of energy dissipation of a polymer, which is contributed to internal friction between
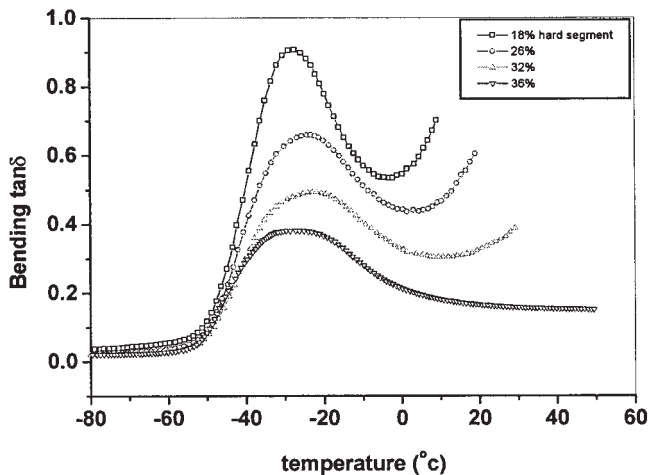
chains.[23] Stress–strain behavior observed upon deformation typically induces a significant strain energy contribution. As a viscoelastic material, when it is stressed, the molecular disentanglements cause the great resistance to deformation. This leads to substantial unrecoverable work of deformation and heat building, represented by dissipation energy of the material.[23] The area enclosed by the hysteresis loop corresponds to the dissipated energy for each cycle. For any given cycle (n), the dissipated energy is given by

$$\Delta E(n) = \oint \sigma \, d\varepsilon$$

where ΔE is the dissipated energy, σ is the stress, and ε is the strain.

Figure 9 shows the stress–strain curves in deformation of 200% for loading and unloading cycles 1, 2, 3, and 4, respectively. Obviously, the energy dissipated at the first cycle is greater than that at following cycles,

Figure 6 Tan δ versus temperature for PU nanocomposites (3% organoclay content) with different hard segment contents.

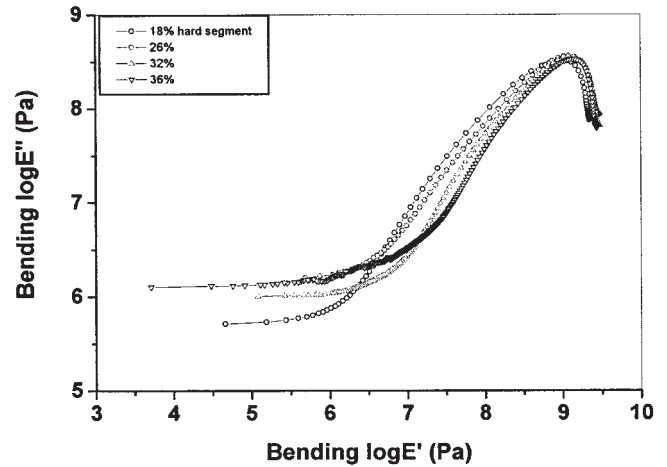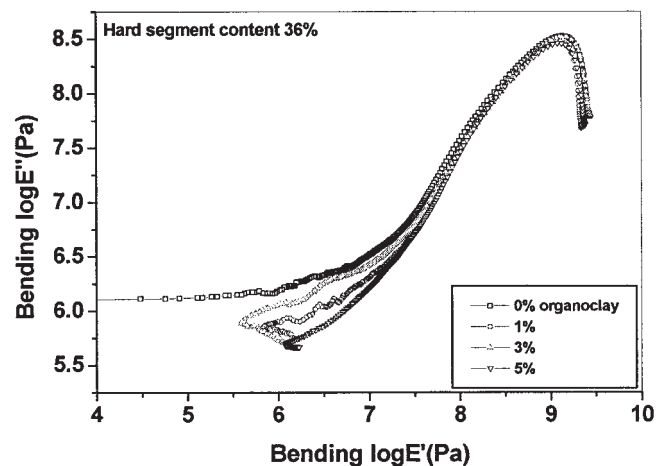**Figure 8** Variation log E'' as function of log E' for PU nanocomposites.
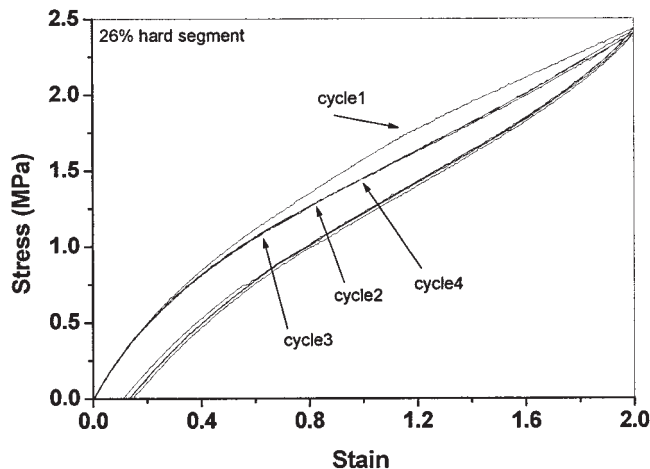
Figure 9 Stress–strain curves of the PU in 200% deformation for loading and unloading cycles

and the dissipation energies almost were almost the same at second, third, and forth cycle representing by the equal areas as shown in Figure 9.

Figure 10 shows plots of the dissipated energy of the PU nanocomposites versus the organoclay content at deformation of 50, 100, or 200% for first cycle, in which the dissipated energy of the pure PU was chosen as the reference. The results show that the addition of the organoclay caused the more energy dissipated and the dissipated energy greatly increased with increasing organoclay content.

The total of the dissipated energy of the PU nanocomposite could be roughly divided into three parts as follows:

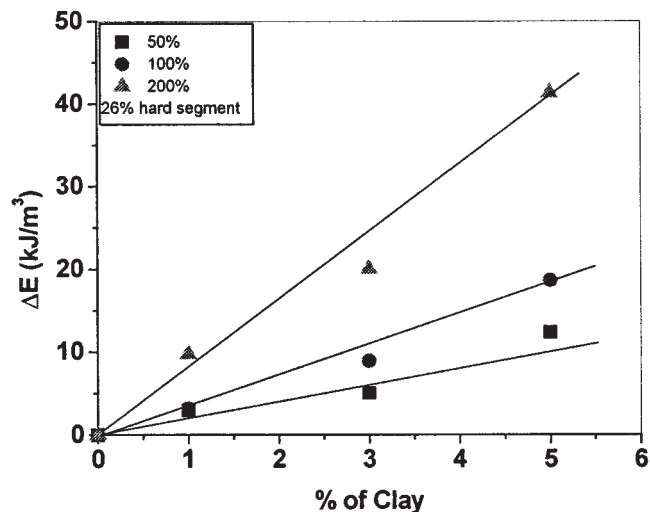$$\Delta E = \Delta E_1 + \Delta E_2 + \Delta E_3$$

Figure 10 Dissipated energy of the PU nanocomposites versus organoclay content at different deformations (first cycle).
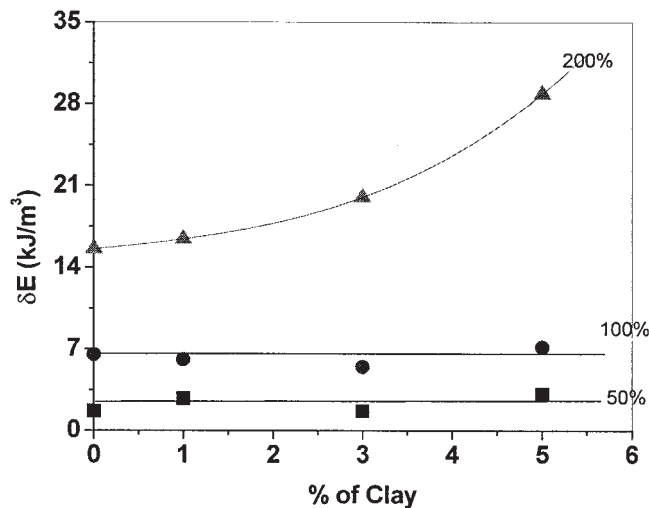

Figure 11 Difference of dissipated energy between in first and second cycles of the PU nanocomposites versus organoclay content.

ΔE_1 is the energy of hard domain deformation, ΔE_2 is the energy of the viscoelasticity of PU chains, and ΔE_3 is the energy of the organoclay orientation (including friction), respectively. For a given sample at a certain deformation, the total of dissipated energy is determined by the viscoelasticity of the PU chains and the orientation of the organoclay platelets. As discussed above the viscosity of the PU nanocomposites reduced compared with that of the pure PU. Therefore, the increased dissipated energy, as shown in Figure 10, was required for orientating the organoclay platelets and overcoming the interactions between the surface of the organoclay and PU molecules during the deformation. With increase in the organoclay content these could cause the more mechanic energy transfer to heat energy by internal friction. This in turn hinders the ability of the elastomers to relax. So the PU nanocomposite shows higher hysteresis than that of the pure PU.

Figure 11 shows plots of the difference of dissipated energy between in first and second cycles for the PU nanocomposites versus organoclay content. It can be seen that the difference of dissipated energy between two cycles at the deformation of 50 or 100% was almost the same with various organoclay contents. However, at high deformation of 200%, the difference of the dissipated energy clearly depends on organoclay content.

As indicated above at small deformation of 50 or 100%, the difference of dissipated energy between the two cycles was not affected by the organoclay. This means that the part of the domain deformation energy was the same for the PU nanocomposites at different organoclay contents. It demonstrates that the hard domain deformation was not disturbed by the orientation of the organoclay platelets at small deformation. At the larger deformation of 200% a mutual influence

between the domain deformation and the orientation of the organoclay platelets coexists. Therefore, during the larger deformation the extra energy was required to overcome the effect. The more organoclay incorporated in the PU, the more the dissipated energy was. However, it is necessary to note that the intercalation characteristic of organoclay by PU chains and the dispersion of organoclay in PU matrix could be key factors affecting the viscoelasticity of the composites. We will report the results systematically in next paper.

CONCLUSIONS

PU/organically modified layered silicate (organoclay) nanocomposites were prepared by *in situ* polymerization. The viscoelasticity of PU–organoclay nanocomposites was investigated. The results suggest that the addition of organoclay resulted in the increase in the elasticity of PU and the decrease in damping property, and improvement the thermal stability of PU significantly. However, it was also found that the addition of organoclay did not enhance the modulus of PU significantly. It was found that in high contents of soft segments, the modulus of PU decreased with the addition of organoclay. Hysteresis results indicated that energy dissipation increased with increasing organoclay.

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