

# High Performance Nanocomposites of Polyurethane Elastomer and Organically Modified Layered Silicate

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**ABSTRACT:** High performance nanocomposites comprising a polyurethane elastomer (PUE) and an organically modified layered silicate are prepared. These nanocomposites are based on poly(propylene glycol), 4,4'-methylene bis(cyclohexyl isocyanate), 1,4-butanediol, and organoclay. The tensile strength and strain at break for these novel PUE nanocomposites increases more than 150%, but the hardness remains unchanged. The fatigue properties are significantly improved. With 3 wt % organoclay, the fatigue properties

are improved the most, which is important for the PU industry. The effects of the isocyanate index on the mechanical properties of the PUE nanocomposites are investigated. It is found that an isocyanate index of 1.10 results in the best improvement in stress and elongation at break. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3239–3243, 2003

**Key words:** polyurethane; nanocomposite; organoclay; fatigue

## INTRODUCTION

Polyurethane elastomer (PUE) and inorganic filler (such as glass microspheres and glass fibers) composites, which are widely used in the automotive and construction industries, have been studied for many years in order to improve their mechanical and thermal properties.<sup>1</sup> The addition of these inorganic fillers also reduces production costs. However, the disadvantages are that inorganic fillers worsen the fatigue properties and reduce the elongation at break.<sup>2</sup> Recently, in order to overcome these disadvantages, PUE and organically modified layered silicate (organoclay) nanocomposites<sup>3,4</sup> have been developed.

The structure of the layered silicates leads to hybrids with nanoscale phase dimensions.<sup>5</sup> The layered silicates (alternatively referred to as 2:1 layered clay) possess the same structural characteristics as the well-known minerals talc and mica.<sup>6</sup> Their crystal structure consists of 2-dimensional layers (1-nm thickness) formed by fusing two silica tetrahedral sheets with an edge-shared octahedral sheet of either alumina or magnesia. Stacking of the layers leads to van der Waals gaps or galleries. The galleries (alternatively referred to as interlayers) are occupied by cations, which balance the charge deficiency that is generated by isomorphous substitution within the layers. In contrast to pristine mica-type silicates, which contain alkali metal and alkali earth charge-balancing cations, organoclay contains alkylammonium or alkylphos-

phonium cations.<sup>7</sup> The presence of these organic modifiers in the galleries renders the originally hydrophilic silicate surface organophilic. Depending on the functionality, packing density, and length of the organic modifiers, organoclay can be engineered to optimize their compatibility with a given polymer.<sup>8–10</sup>

There are three different approaches to preparing polymer-layered silicate nanocomposites: melt intercalation, solution intercalation, and *in situ* polymerization. The *in situ* polymerization method was first introduced in the preparation of polymer-layered silicate nanocomposites by Japanese researchers,<sup>9</sup> who synthesized nylon 6 layered silicate nanocomposites in which 1-nm thickness silicate layers of clay minerals are dispersed homogeneously in the nylon 6 matrix. The *in situ* polymerization method, which is suitable for thermoset polymer systems, is also suitable for the preparation of polymer nanocomposites.

Polymer-layered silicate nanocomposites exhibit various superior properties such as high strength, high modulus, and a high heat distortion temperature, compared to the pristine polymer.<sup>10</sup> The most characteristic feature of polymer nanocomposites is that the drastic changes in these properties can be derived with a few percents of the layered silicate. Numerous polymers have been successfully prepared as polymer-layered silicate nanocomposites including epoxies,<sup>11–13</sup> unsaturated polyesters,<sup>14</sup> poly( $\epsilon$ -caprolactone),<sup>15</sup> poly(ethylene oxide),<sup>16</sup> silicone rubber,<sup>17</sup> polystyrene,<sup>18</sup> polypropylene,<sup>19</sup> and PU.<sup>3,4,20,21</sup>

Studies of PUE–organoclay nanocomposites have mainly focused on the tensile properties<sup>3,4,20,21</sup> and permeability.<sup>22</sup> The effect of the nanofillers on the fatigue properties of PUE nanocomposites has not

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**TABLE I**  
**List of Samples**

Sample	Organoclay (wt %)	Isocyanate Index
Iso105	5	1.05
Iso110	5	1.10
Iso115	5	1.15
Iso120	5	1.20
Iso130	5	1.30
A0	0	1.10
A1	1	1.10
A3	3	1.10
A5	5	1.10
A7	7	1.10

been reported. This article reports on the effect of organoclay on the fatigue life of PUE nanocomposites.

## EXPERIMENTAL

### Materials

Poly(propylene glycol) (Lupranol 2090, molecular weight = 6000, function = 3), was kindly provided by Elastogran U.K. Ltd. 4,4'-Methylene bis(cyclohexyl isocyanate) and 1,4-butandiol were provided by the Aldrich Chemical Company. Dabco-33LV was obtained from Air Products and Chemicals. Stannous 2-ethyl hexanoate was provided by Sigma Chemical Company. The organoclay used in our experiments was C20, which was purchased from Southern Clay Products.

### Preparation of PUE-organoclay nanocomposites

A series of PUE-organoclay nanocomposites were prepared. The compositions of the nanocomposites are listed in Table I. The polyether polyol and the organoclay were blended at 60°C and stirred for different mixing times. The mixture (100 g, mixed for 24 h) was blended with 2.25 g of 1,4-butandiol, 0.75 g of Dabco-33LV, 0.75 g of stannous 2-ethyl hexanoate, and 15.5 g of 4,4'-methylene bis(cyclohexyl isocyanate) at room temperature for 5 min. Then the mixture was poured into an O-ring mold and cured at 80°C for 24 h.

### Characterization

X-ray diffraction experiments were performed on film samples on a Bruker X-ray diffractometer (AXS D8 Advance) using  $K\alpha$  ( $\lambda = 0.154$ ) radiation. Samples were scanned at a rate 0.24°/min from about 1 to 20° in 2 $\theta$ .

Mechanical tests were performed according to the relevant ASTM standards. The tensile strength was measured using a Lloyd material tester at room tem-

perature. All the reported results are an average of at least five measurements for tensile determinations.

Hardness tests were performed according to DIN 5305 at room temperature. The cyclic fatigue life of the PU nanocomposites was measured in uniaxial tension in a Hampden dynamic testing machine (Northampton, U.K.) using dumbbell test pieces. The tests were performed at a constant maximum deflection of 200% and a test frequency of 2 Hz. The test temperature was about 18°C, and the strain on each test piece was returned to zero at the end of each cycle.

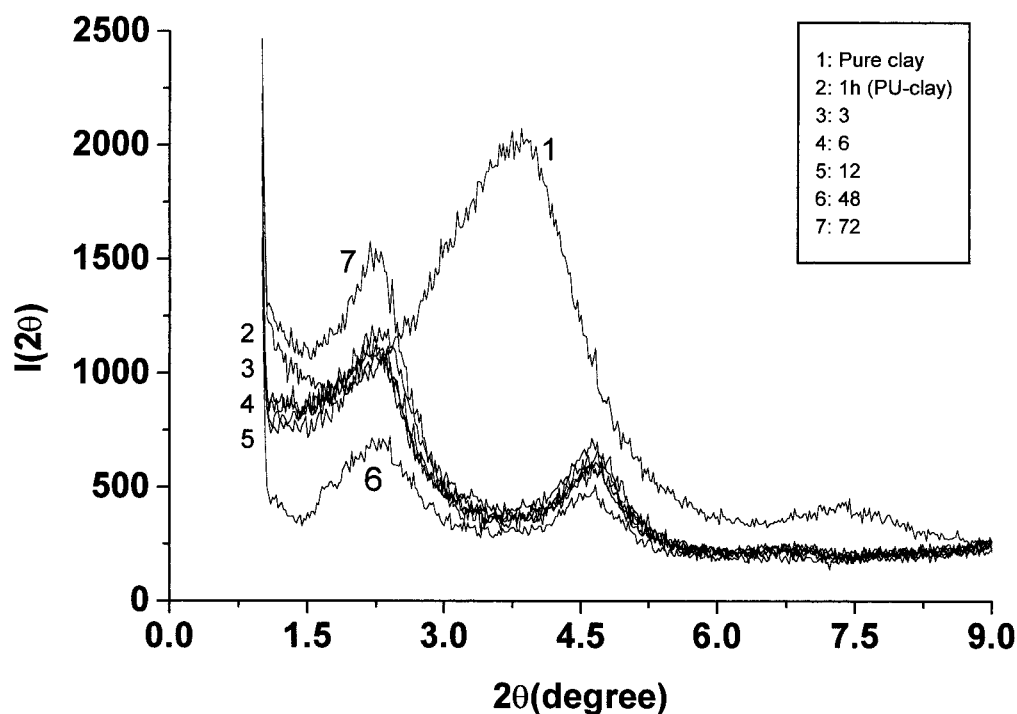
The measurement of the heat flow versus the temperature for the PU-organoclay blends was performed using a modulated differential scanning calorimeter (TA Instruments 2920 calorimeter). An oscillation amplitude of 1.0°C and an oscillation period of 60 s with a heating rate of 3°C/min were used for the study.

## RESULTS AND DISCUSSION

There are two kinds of polymer-layered silicate nanocomposites: intercalated nanocomposites and exfoliated nanocomposites. Wide-angle X-ray diffraction (WAXD) is an effective method for the evaluation of the intercalation capability of polymers. The expansion of layers of organoclay can be detected by means of WAXD. In intercalated nanocomposites, the diffraction peak shifts toward lower diffraction angles. In exfoliated nanocomposites, no diffraction peaks are shown.

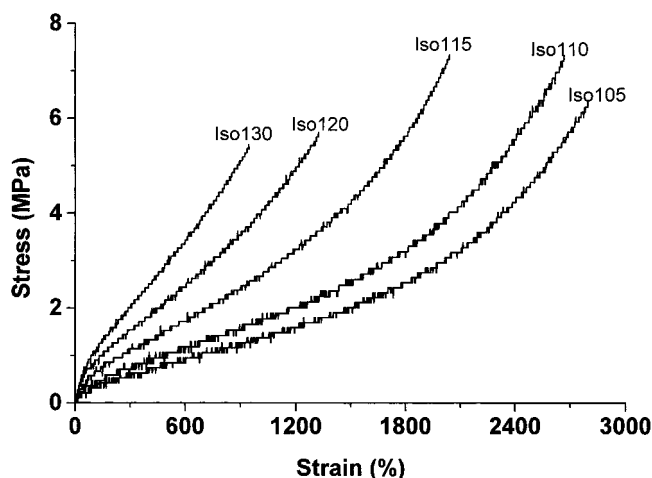
Figure 1 illustrates the WAXD patterns of the PUE-organoclay (10 wt %) nanocomposites for different mixing times. It is clear that the diffraction peaks shift to a lower diffraction angle. This indicates that some polyether polyol molecules have been intercalated into the layers of the organoclay, leading to the expansion of these layers. The WAXD results also show that the diffraction peaks remained unchanged with increasing mixing time. The minimum mixing time that we tried was 1 h. This means that 1 h is enough for the intercalation.

The WAXD results indicate that there are two diffraction peaks in the organoclay. The WAXD curve shows that the interlayer spacings of the organoclay are 1.1 and 2.3 nm. This result demonstrates that the organoclay is a mixture of inorganoclay (1.1-nm interlayer spacing) and organoclay (2.3-nm interlayer spacing). In the PUE-organoclay nanocomposites, the interlayer spacing of inorganic clay expanded from 1.1 to 1.7 nm. This shows that part of the polyether polyol molecules were intercalated into the interlayer of the inorganic clay. The interlayer spacing of the organoclay expanded from 2.3 to 3.8 nm, indicating that the fraction of polyether polyol molecules was intercalated into the interlayer of the organoclay.



**Figure 1** Wide-angle X-ray diffraction patterns of the PUE-organoclay nanocomposites with different intercalation times (10 wt % organoclay).

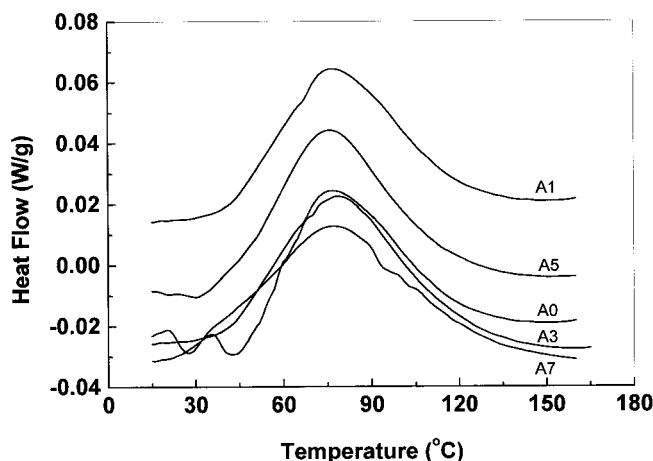
The isocyanate index, which is the molar ratio of NCO and OH groups, is an important parameter in the preparation of PUEs. This value has significant influence on the curing dynamics and physical properties of PUEs. Generally, an NCO:OH value of 1.05 has been chosen in the preparation of the PUs. Because of the existence of equilibrium water in layered silicates,<sup>23</sup> it is necessary to know what isocyanate index is suitable for the preparation of PUE nanocomposites. Figure 2 shows the effect of



**Figure 2** Stress-strain curves of the PUE-organoclay (5 wt %) nanocomposites with different isocyanate indexes.

the isocyanate index on the tensile behavior of the PUE-organoclay nanocomposites in which 5 wt % organoclay was used. Sample Iso105 was sticky. Note from Figure 2 that with an increasing isocyanate index, the stress strength and elongation at break decrease with the exception of the Iso105 sample. Comparing Iso105 and Iso110, it can be seen that the stress strength of Iso110 is higher than that of Iso105, but the elongation is almost the same. Generally, an increase in the isocyanate index results in an increase of the crosslink density in PUEs. The increase of the crosslink density reduces the molecular mobility and restricts microphase separation.<sup>1</sup> Because of the stickiness of the Iso105 sample, it can be deduced that the reactions between isocyanate and equilibrium water in the organoclay reduce the effectiveness of isocyanate. The results shown in Figure 2 indicate that it is clearly necessary to choose a suitable isocyanate index in the preparation of PUE-organoclay nanocomposites.

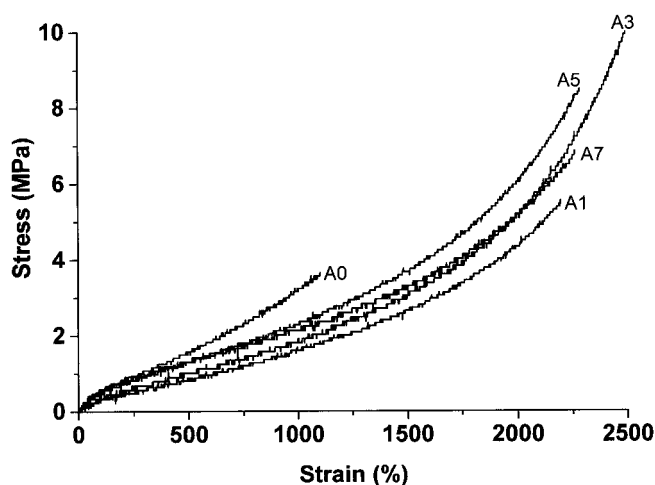
Figure 3 shows the effect of the organoclay content on the curing dynamics of the PUE nanocomposites in which the isocyanate index was 1.10. The results in Figure 3 indicate that there is no significant effect of the organoclay content on the curing dynamics when the isocyanate index is 1.10. The details of the effects of the organoclay and isocyanate index on the curing dynamics of the PUE nanocomposites will be published elsewhere.<sup>24</sup>



**Figure 3** The heat flow versus the temperature for the PUE-organoclay blends with an isocyanate index of 1.10.

In this study, as isocyanate index of 1.10 was chosen for the preparation of the PUE-organoclay nanocomposites. The stress and strain curves of these nanocomposites with different organoclay contents are shown in Figure 4. Compared with the pristine PU, we found that the properties of the nanoclay PUEs were significantly improved. Even when adding only 1 wt % organoclay, the tensile strength and elongation at the break were increased by more than 100%. When 3 wt % organoclay was added, the tensile strength and elongation at break reached maximum values. The tensile strength and elongation at the break were both increased by more than 150%.

In order to reduce the cost and improve the thermal properties, conventional inorganic fillers have been used in PUEs. Although the thermal properties and modulus were improved, the elongation at break de-



**Figure 4** Stress-strain curves of the PUE-organoclay nanocomposites (isocyanate index = 1.10) with different organoclay contents.

**TABLE II**  
Effect of Isocyanate Index on Hardness of PUE Nanocomposites

Sample	Iso105	Iso110	Iso115	Iso120	Iso130
Hardness (Shore A)	30	35	40	45	55

creased significantly. According to published data, not only can organoclay improve thermal properties, but it can also increase the tensile strength and elongation at break.<sup>4,25</sup>

Hardness, which is related to yield stress and modulus, is another important parameter of PUEs. Tables II and III show the effects of the isocyanate index and organoclay content on the hardness of the PUE nanocomposites.

It is reasonable that, with an increasing isocyanate index, the hardness of the PUE nanocomposites will increase. This is due to the increase in the crosslink density with an increasing isocyanate index. From Table III it is found that, contrary to the case of adding conventional fillers, with the addition of organoclay, the hardness of the PUE nanocomposites remained unchanged up to 5 wt %. This could result from the plastisizing effect of the organoclay on the PU matrix.<sup>26</sup>

Fatigue life is a key parameter in the application of PUEs. Fatigue is a property that is usually associated with aging.<sup>1</sup> It is defined as the ability to withstand repeated flexing without the development of severe cracking. Fatigue failure occurs in some cases as a result of the propagation of unstable cracks or defects under the application of cyclic force. Table IV shows the effect of the organoclay on fatigue life. These results clearly indicate that organoclay can significantly improve the fatigue properties of PUE. The addition of 3 wt % organoclay led to the best result for these PUEs.

We can speculate that there are two kinds of interactions between PU molecules and organoclay, which result from the absorption of PU molecules onto the surface of organoclay particles and from the intercalation of PU molecules into the clay galleries. The surface absorption may be considered as giving rise to mobile 2-dimensional physical crosslink points. The intercalated organoclay particles can be considered as entanglement points. Intercalated macromolecules may be able to slip from one location to another location in the occupied layer or on the surface of organo-

**TABLE III**  
Effect of Organoclay Content on Hardness of PUE Nanocomposites

Sample	A0	A1	A3	A5	A7
Hardness (Shore A)	35	35	35	35	38

**TABLE IV**  
**Effect of Organoclay Content on Fatigue Life**  
**(Isocyanate index = 1.10)**

Sample	A0	A1	A3	A5	A7
Number of cycles	55,160	310,267	821,352	122,153	64,874

clay particles when cyclic force is applied. The slipping of the silicate layers in organoclays can also occur when a force is applied. Such physical crosslink points, layer slipping, and entanglement points may release the concentrated stress and allow more frictional energy dissipation. This may avoid localized energy concentrations, which lead to crack growth.

### CONCLUSIONS

Organoclay can dramatically improve the mechanical properties of PUEs. The tensile strength and elongation at break of the PUE nanocomposites increased by more than 150%, but the hardness remained unchanged. The fatigue properties were significantly improved. We found that adding 3 wt % organically modified layered silicate improved the fatigue behavior the most. There was also an obvious effect of the isocyanate index on the mechanical properties of these PUE nanocomposites. An isocyanate index of 1.10 resulted in the best improvement of the mechanical properties.

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