A Novel Mechanism of Exfoliation and Physical Properties of PU/Organoclay Nanocomposites

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ABSTRACT: The novel mechanism of exfoliation of silicate was investigated. Exfoliation and intercalation was achieved even at 15 wt % in the polyurethane (PU) matrix via *in situ* polymerization. Through using IR consumption graph of curing agent, crosslinking equation could be derived. The diffusion rate of curing agent, Isophorone diisocyanate, brought the different morphologies as well as crosslinking densities of nanocomposites. Dodecylamine, the organifier having similar hydrogen-bonding component with Isophorone diisocyanate than octadecylamine, affected the faster diffusion of isophorone diisocyanate in hydroxyl terminated polybutadiene/organoclay composite. This phenomenon was confirmed by DSC graph, XRD, SAXS, and TEM images. The nanocomposites showed high physical properties until at 10 wt % clay. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2013

INTRODUCTION

Polymer-layered silicate nanocomposites have attracted great interest, because they have shown significant improvements in mechanical, thermal, and barrier properties.[1–5] Generally, the exfoliated polymer-layered silicate nanocomposites have shown more excellent properties than intercalated ones, because they have larger surfaces of silicates to interact with polymers. Accordingly, many researchers have tried to achieve exfoliation and published many successful reports on exfoliation of clay layers in polymers. However, there have been many tries to achieve exfoliation at low clay concentration rather than high clay concentration because of the dispersion problem even if nanocomposites with high clay concentration has limitless potential to enhance the properties of nanocomposites such as flammability and physical and mechanical properties. Achieving exfoliation at high concentrations is still remaining as an unresolved task as well as revealing the mechanism.

To achieve excellent exfoliation and intercalation, researchers seek to develop many methods. One of the popular methods is to use organic modifier before polymerization. The organic modifier is intended to make the gap between the clay layers as wide as possible, which make polymers penetrate into clay layer more easily. Organic modifier such as alkylammonium or alkyl-phosphonium cations, present inside the gallery, can act as a catalyst during the polymerization.[6,7] Researchers indicate that *in situ* polymerization is also one of the effective methods to obtain the exfoliation in composites rather then solution and melt processing.[8–10] Briefly, *in situ* polymerization consists of two steps: First, monomer molecules are allowed to diffuse into clay galleries, leading to the increase of *d*-spacing. Then, the polymerization with monomer makes the large polymer molecules form between the clay layers. Recently, there have been many attempts to achieve exfoliation through crosslinking of prepolymers. In this case, electrostatic attractive forces between the ammonium ions of organic modifiers and the negatively charged clay particles prevent crosslinked, prepolymer chains from recoiling, and the chains are able to widen the gap between the clay layers.[11] The speed of diffusion of curing agents and the curing temperature also revealed to affect the speed of gelation.[6] As the gelation occurs faster, the greater extent of exfoliation is achieved.[11]

Hydroxyl terminated polybutadiene (HTPB) is a very effective polymer for achieving exfoliation, because it has end functionalized hydroxyl groups with a hydrophobic main chain.[12,13] In this experiment, we achieved exfoliation even at 15 wt % of clay through crosslinking HTPB and adjusting organic modifiers. Surprisingly, the organoclay treated with dodecylamine crosslinked faster with IPDI than did octadecylamine and showed almost complete exfoliation. Through monitoring the

Table I. Designation of Organoclay

Designation of organoclay	Ion exchanged organic modifier
C12	Dodecylamine (12)
C18	Octadecylamine (18)

consumption of isocyanate by FTIR and DSC results, we were able to reveal the mechanism of exfoliation. We also found the fact that mechanical properties increased continuously until 10 wt % of clay.

EXPERIMENT

Twenty grams of pristine montmorillonite (southwestern clay) were dispersed in 1000 mL of H_2O and stirred for 24 h before using. Octadecyl amine and dodecyl amine were purchased from Aldrich Chemical, and these materials were notated as 18 and 12, respectively. Each of those organic modifiers (equal to 1.5 mequiv/g per mol of montmorillonite) was reacted with HCl of in 500 mL of H_2O for 2 h before the cation exchange reaction to change amine group of organic modifier to quaternized ammonium. Then, the solution was poured into the montmorillonite solution and stirred at 85°C for 4 h. The exchanged clay was washed several times with distilled water and checked with $AgNO_3$ for Cl^- residue. It was completely dried using a freeze dryer at −47°C for 5 days and in a vacuum oven at 60°C for 1 day.

The process of making organoclay was repeated three times, and then the clays were mixed to make the condition of clay same.

HTPB (hydroxyl terminated polybutadiene) was supplied by Agency for Defense Development, and its M_n was measured as 3700 by GPC and its polyfunctionality is 2.7.

Organoclay was mixed with HTPB by rotating and revolving materials with an R&R mixer, mixing for 10 min at 2000 rpm and defoaming for 10 min at 2200 rpm. The content of clay was calculated on the basis of pure clay. We used 5, 10, and 15 wt % of pure clay in the HTPB/organoclay composite. Then, the composite was preserved in an oven at 60°C for 2 days and then reacted with IPDI (isophorone diisocyanate), which was purchased from Aldrich Chemical, in the R&R mixer. The mass ratio of IPDI to HTPB was based on the ratio of NCO:

Table II. Swelling Results of PU(HTPB)/Organoclay Nanocomposites

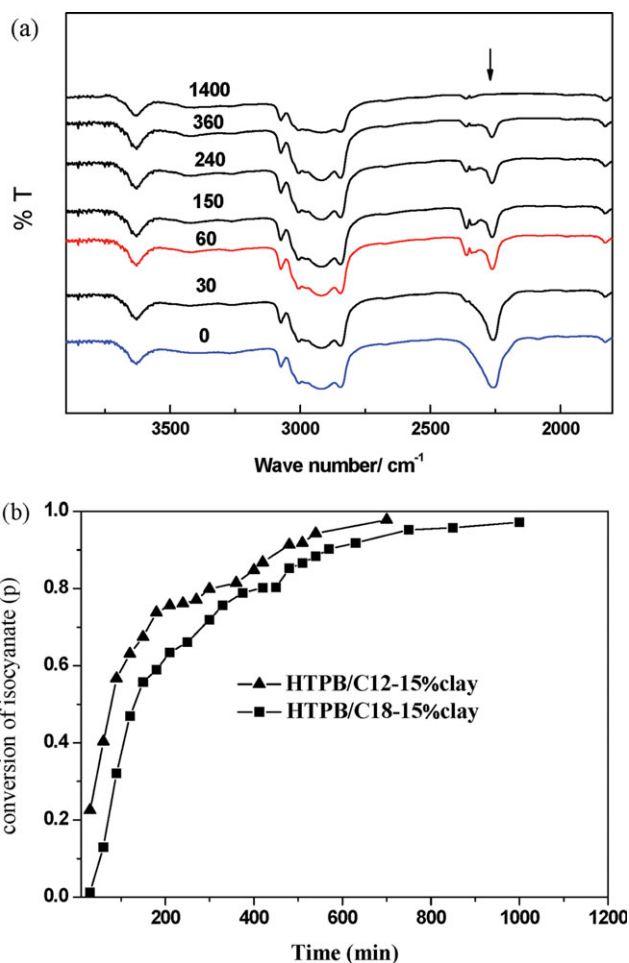| Clay type	wt % of clay	Swelling ratio
None	0	7.554
C12	5	8.37
	10	8.202
	15	5.685
C18	5	8.56
	10	11.039
	15	11.22

Figure 1. (a) IR curves of HTPB/C12-15% clay crosslinked with IPDI at different time. (b) The isocyanate conversion of HTPB/C12-15% clay and HTPB/C18-15% clay during crosslinking vs. time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

OH = 1.1:1. The product was casted in a Teflon Mold for 7 days, using triphenyl bismuth, which used as a catalyst.

Characteristics

The sample names in this research are given in Table I. C means clay, and 12 and 18 indicate the number of carbon atoms in the organic modifier. C12 and C18 mean organoclay which were formed through using dodecylamine and octadecylamine, respectively. The content of the organic modifier in the organoclay was measured by TGA. HTPB/C12-5% clay means the composite of HTPB and C12 with 5 wt % of content inorganic silicate. After this nanocomposite was reacted with IPDI, the product was designated as PU(HTPB)/C12-5% clay, which contains 5 wt % of pristine clay. The amount of IPDI was very small in the PU nanocomposite (9 wt% of HTPB). The PU(HTPB)/organoclay composite at 10 and 15 wt % are also designated following the same convention.

X-ray diffraction was performed using a Rigaku X-ray diffractometer (Cu Kα radiation with $\lambda = 0.15418$ nm) to measure the d-spacing and dispersion state. For accurate measurement, small-angle X-ray scattering (SAXS) was performed by
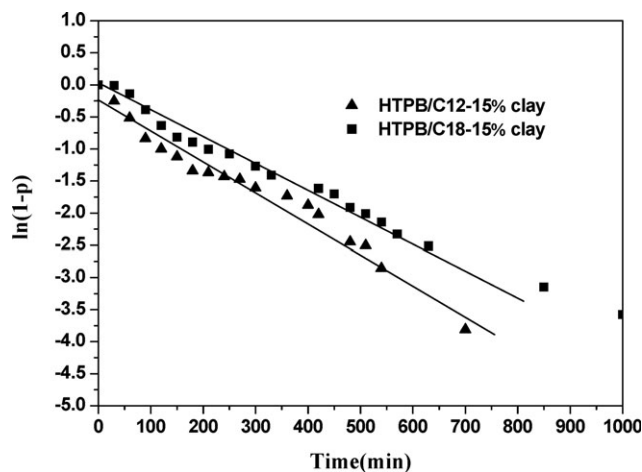
Figure 2. Relationship between isocyanate conversion(p) of HTPB/C12-15% clay and HTPB/C18-15% clay during crosslinking vs. time.

D/MAXIIC at 50 kV and 100 mA. The samples were radiated in D/MAXIIC for 2 h and the graphs were obtained.

To obtain TEM data, the PU nanocomposite was sectioned with a thickness of 100 nm by using CryoUltra microtoming and laid on a copper grid. TEM micrographs were obtained by using a Phillips CM 20 at 160 kV.

Swelling tests were performed to measure the degree of crosslinking. The volume of sample was measured before the swelling test, and it was measured again after 7 days in THF, tetrahydrofuran. The results are shown in Table II. The stress-elongation property was measured by using an Instron 5573 machine with a crosshead speed of 50 mm min^{-1}, and at least three specimens were used for the test. Rheological properties of nanocomposite were obtained using a parallel plate Rheometer, ARES 500, at 5% strain, 0.1 rad s^{-1}, at 60°C.

During the crosslinking reaction, DSC and IR experiments were performed. Using a differential scanning calorimeter (DSC, Q500, TA instrument), the amount of heat flow was measured. The heating rate of DSC was 20°C min^{-1}, from 35 to 300°C. After the HTPB/organoclay composite was mixed with IPDI, it was coated on the KBr platelet and put into the oven at 60°C. Every 30 min, IR graphs were obtained.

In Figure 1(a), the isocyanate absorption band is presented at 2300–2200 cm^{-1} in the mid-infrared spectrum. For scaling the decrease of the isocyanate absorbance, the C—H stretch absorption (2960 cm^{-1}) was chosen as an internal standard. Baseline corrections were fitted to all absorption peak areas. It was assumed that the side reaction would be negligible.

Table III. The Reaction Parameters During Crosslinking Process

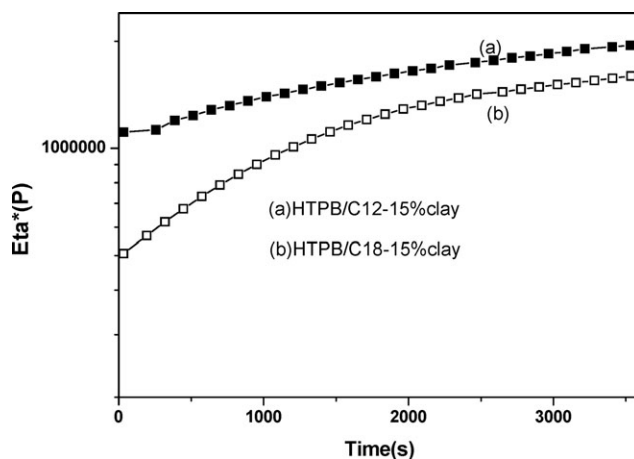| PU parameters	HTPB/C12–15% clay	HTPB/C18–15% clay
k_0	-4.86×10^{-3}	-4.175×10^{-3}
C	-0.242	0.0415

Figure 3. The viscosities at 0.1 rad s^{-1} of (a)HTPB/C12-15% clay and (b)HTPB/C18-15% clay after mixing with IPDI vs. time.

Hence, the isocyanate conversion was calculated by the following equation:

$$\text{Isocyanate conversion (p)} = 1 - \frac{A_t - A_\infty}{A_0 - A_\infty} \qquad (1)$$

where A_0 is the normalized area of the absorption at the initial time; A_t is the normalized area of the absorption at a certain time during the crosslinking; A_∞ is the final normalized area of the absorption at infinite time. The results are shown in Figure 1(b).

The Speed of Gelation. When an HTPB/organoclay nanocomposite was mixed with IPDI, HTPB was reacted with IPDI and crosslinking was achieved. After the reaction, PU(HTPB)/organoclay nanocomposite could be obtained. During the crosslinking reaction, the isocyanate conversion, p, of the reaction can be represented as:
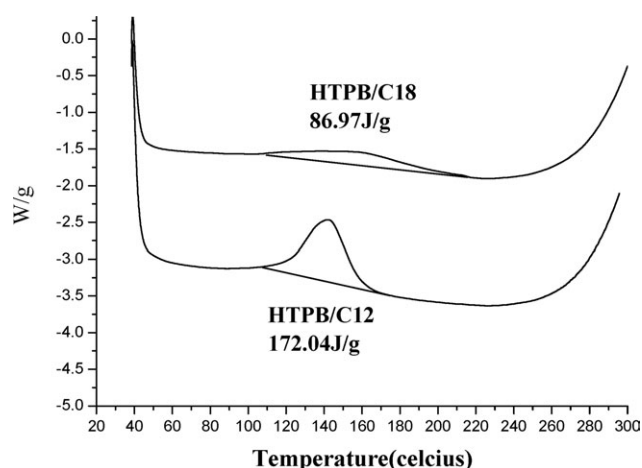
$$p(t) = \int_0^t dp \qquad (2)$$

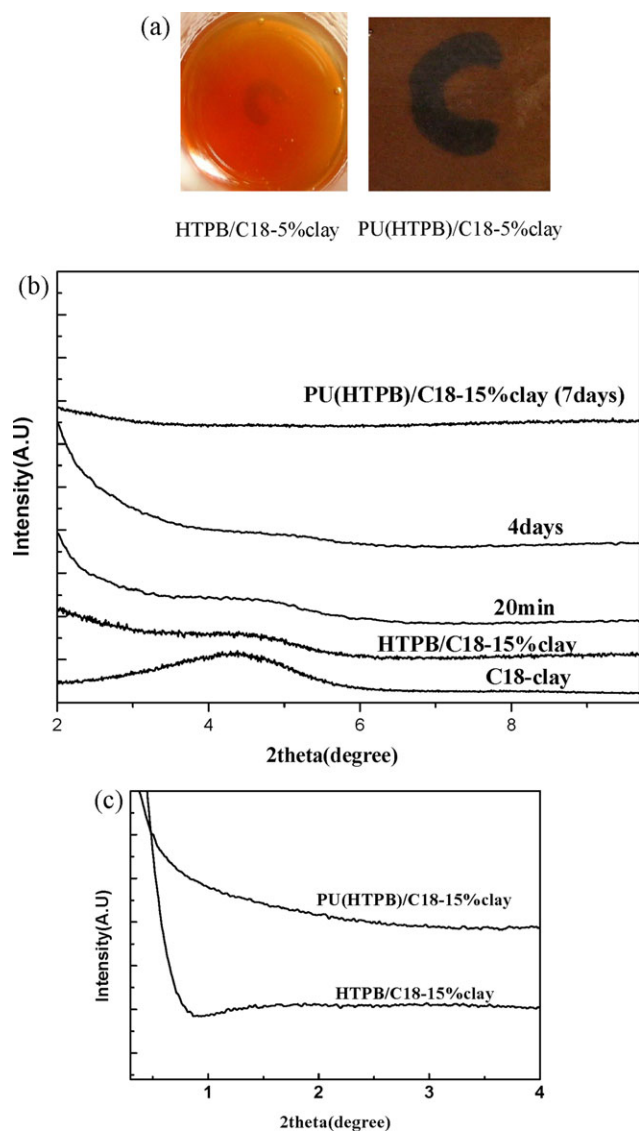**Figure 4.** DSC graph of HTPB/C12-15%clay and HTPB/C18-15% clay after mixing with IPDI vs. temperature.

Figure 5. (a) Transparent characteristics of HTPB/C18-5% clay, PU(HTPB)/C18-5% clay. (b) The XRD patterns of organoclay (C18), HTPB/C18-15% clay and HTPB/C18-15% clay crosslinked with IPDI at different time. (c) The SAXS pattern of HTPB/C18-15% clay and PU(HTPB)/C18-15% clay. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Through using the nth-order method, which is widely used for curing kinetics in the thermosetting materials, the reaction can be expressed by.[14]

$$\frac{dp}{dt} = k_0(1 - p^n) \quad (3)$$

The reaction constant k_0 is reaction rate, which depends on temperature. When $n = 1$, we can fit the theory to the experiment. Equation (3) can be transformed like below.

$$n = 1, \ \ln(1 - p) = k_0 t + C \quad (4)$$

Through calculating p according to time suggested in eq. (1), constant k_0 and C could be obtained. The experimental results

are shown in Figure 2 and the obtained value of k_0 and C is represented in Table III. HTPB/C12-15% clay and HTPB/C18-15% clay show almost the same value of k_0, but those have quite different values of C. Surprisingly, if the line for HTPB/C12-15% clay moves upward with the value of C, it is almost overlapped on the line for HTPB/C18-15% clay. It might be interpreted that they have similar reaction rate.

During the first 30 min, the consumption rate of IPDI for HTPB/C12-15% clay was much higher than that of HTPB/C18-15% clay. This explains why the integration constant C for HTPB/C12-15% clay has a larger value than that for HTPB/C18-15% clay. It seems a little bit strange due to following point. In our previous report, HTPB/C18 was more exfoliated than HTPB/C12.[13] Hence, the more exfoliated structure provide the possibility for IPDI molecules to penetrate into clay layers faster during the reaction with IPDI, but the reaction was slower in HTPB/C18. However, C12 has more compatibility with IPDI than C18 because the hydrogen-bonding component (δ_h) of the solubility parameter of C12 is 4.5, that of C18 is 4.0, and that of IPDI is 5.5. Accordingly, the diffusion rate of IPDI may be faster in HTPB/C12 than HTPB/C18.

Before the reaction, the viscosity of HTPB/C18, measured at 0.1 rad s^{-1}, was higher than that of HTPB/C12 due to more
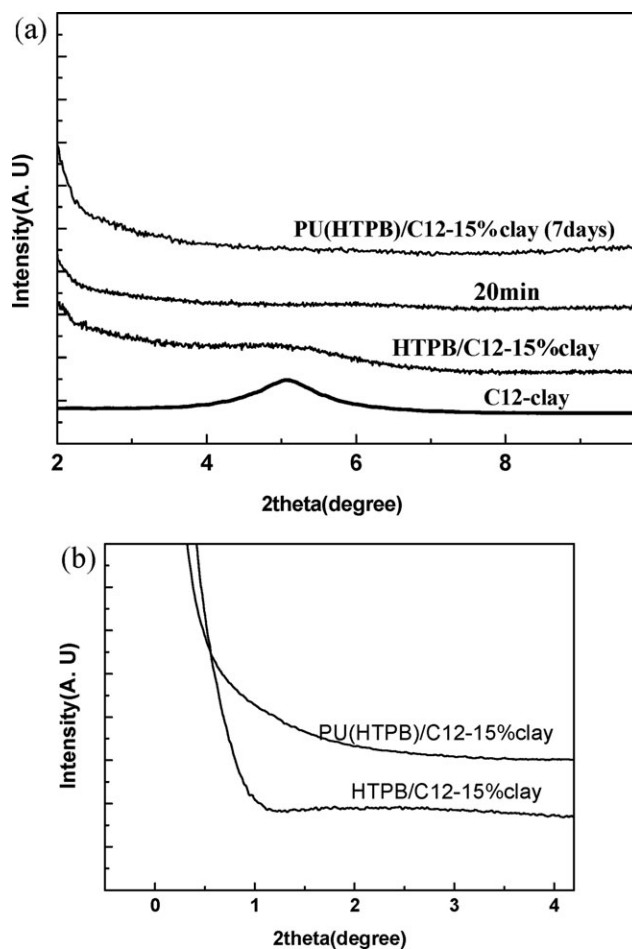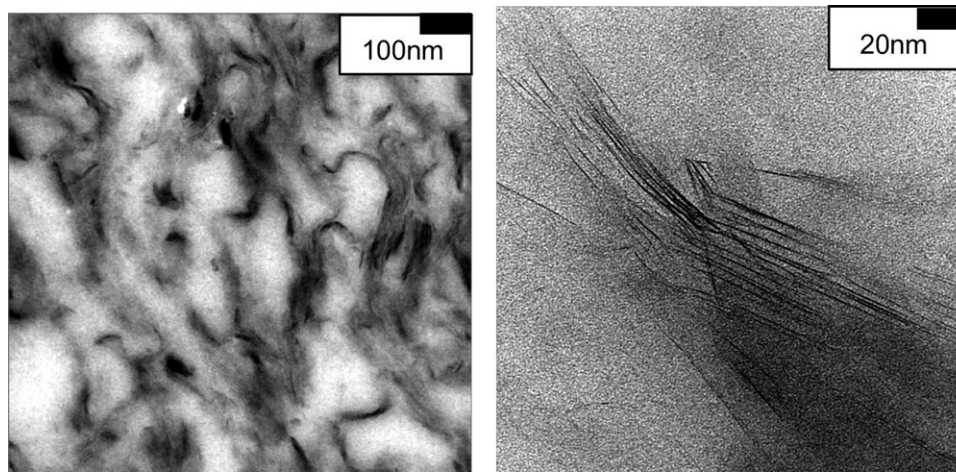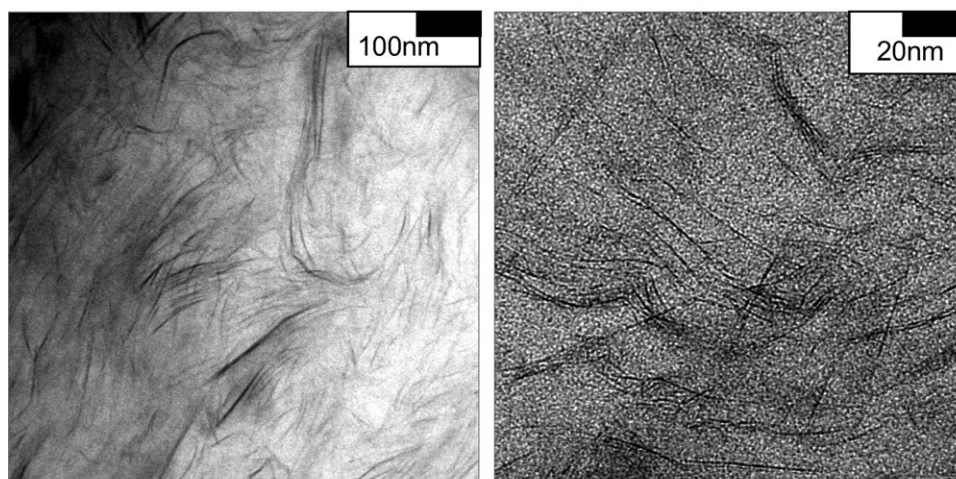

Figure 6. (a) The XRD patterns of organoclay (C12), HTPB/C12-15% clay and HTPB/C12-15% clay crosslinked with IPDI at different time. (b) The SAXS patterns of HTPB/C12-15% clay and PU(HTPB)/C12-15% clay.

(a) PU(HTPB)/C18-15%clay

(b) PU(HTPB)/C12-15%clay

Figure 7. (a) TEM image of PU(HTPB)/C18-15% clay. (b) TEM image of PU(HTPB)/C12-15% clay.

exfoliation.[13] During the mixing, due to the faster penetration of IPDI in HTPB/C12 composites, the viscosity of HTPB/C12-15% clay could be highly increased and it could exceed that of HTPB/C18-15% clay. After mixing, as shown in Figure 3, the viscosity of the HTPB/C12 reacted with IPDI shows higher viscosity than that of HTPB/C18.

Furthermore, from the DSC result in Figure 4, HTPB/C12 shows crosslinking reaction in a narrower temperature range than HTPB/C18. It represents the faster crosslinking of HTPB/C12. The relative crosslinking density can be examined by measuring the energy during the crosslinking reaction.[15] Comparing the energy during crosslinking in Figure 4, the PU(HTPB)/C12 has a higher degree of crosslinking than PU(HTPB)/C18. Furthermore, this phenomenon was also confirmed through the swelling measurements, shown in Table II. PU(HTPB)/C12 has a lower swelling ratio than PU(HTPB)/C18 at the same clay concentration, as shown in Table II.
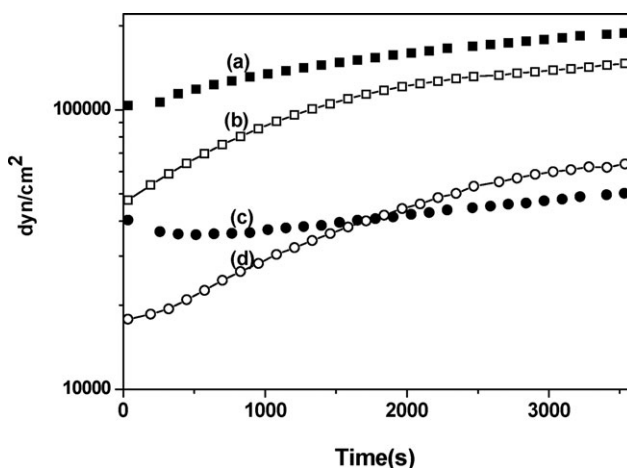

Figure 8. Growth of (a) G' of HTPB/C12-15% clay (b) G' of HTPB/C18-15%clay (c) G'' of HTPB/C12-15% clay (d) G'' of HTPB/C18-15% clay after mixing with IPDI at 0.1 rad/s vs. time.
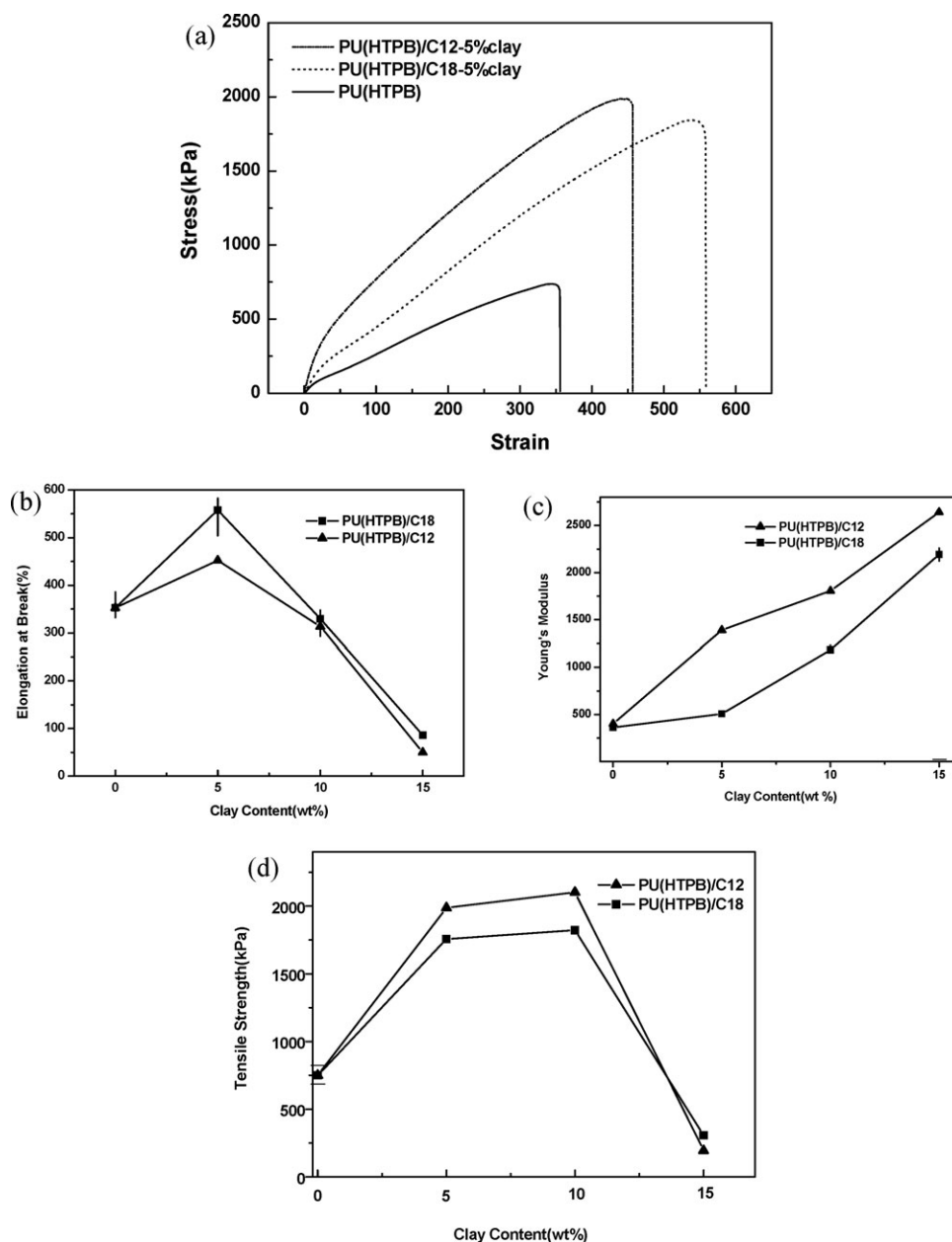
Figure 9. (a) Stress–elongation curve of PU(HTPB) without clay, PU(HTPB)/C12-5% clay and PU(HTPB)/C18-5% clay nanocomposites, (b) Young's modulus of PU(HTPB) nanocomposites, (c) Tensile strength of PU(HTPB) nanocomposites, and (d) elongation at break of PU(HTPB) nanocomposites at 0, 5, 10, 15% of clay.

Morphologies. In Figures 5 and 6 of SAXS and XRD results, HTPB/C12 and HTPB/C18 at 15 wt % of clay shows a broad hump. These graphs indicate that HTPB/C12 and HTPB/C18 at 15wt% of clay show exfoliated/intercalated state. HTPB/C18 composite shows more exfoliation than HTPB/C12 both in SAXS and WAXD graph. Especially in SAXS, HTPB/C18-15% clay has more swelling tactoids than HTPB/C12-15% clay because it shows broader hump than HTPB/C12-15% clay.

After crosslinking reaction, PU(HTPB)/C12 and PU(HTPB)/C18 shows no broad hump, which provides the evidence of the exfoliation in both composites. Comparing the XRD and SAXS graph of the composites in Figures 5 and 6, it might be

interpreted that the morphology change from HTPB/C12-15% clay to PU(HTPB)/C12-15% clay is more than that of HTPB/C18-15% clay.

Furthermore, PU(HTPB)/C18-15% clay became more transparent comparing HTPB/C18-15% clay, which is shown in Figure 5(a). The character is seen more clearly in PU(HTPB)/C18-5% clay than in the previous state. It may be interpreted that clays are well dispersed in PU at nanoscale. Some people may suggest that the transparency may due to by addition of IPDI, not by exfoliation of clay. However, it is not convincible because the loading of IPDI is relatively small (9 wt% of HTPB) to HTPB.

During the crosslinking reaction, HTPB/C12-15% clay is almost exfoliated in 20 min (Figure 6a), whereas HTPB/C18-15% clay takes 7 days to be exfoliated (Figure 5b). In Figures 5 and 6, PU(HTPB)/C18-15% clay and PU(HTPB)/C12-15% clay show the exfoliated structure. In the TEM result Figure 7, PU(HTPB)/C12-15% clay shows more complete exfoliation than PU(HTPB)/C18-15% clay.

It is evident that the speed of crosslinking is faster in HTPB/C12 than HTPB/C18, as shown in Figure 4. Under faster crosslinking conditions, the polymer chains have very little time to experience stress relaxation, then those store much more residual energy than under slow crosslinking conditions.[6] Considering that HTPB has end functional groups and a hydrophobic main chain, the crosslinked prepolymers become more hydrophobic as the reaction progresses. Accordingly, as the reaction becomes faster, more crosslinked macromolecules can be formed and those have more possibility to push out the hydrophilic clay layers effectively. Furthermore, besides the compatibility effect between organic modifier and polymers, the chain slippage may attribute to slower crosslinking in HTPB/C18 composites than HTPB/C12. In our previous report, HTPB/C18 showed the chain slippage phenomenon due to a greater extent of organic modifier than that of HTPB/C12.[13] Therefore, the loss modulus, G'', of PU(HTPB)/C18 may increases and exceeds the G'' of PU(HTPB)/C12, as shown in Figure 8 due to slippage effect. This phenomenon may hinder the exfoliation of clay in HTPB/C18 during crosslinking.

The Mechanical Properties of PU(HTPB)/Organoclay Nanocomposite. Stress–elongation curves of PU(HTPB)/organoclay nanocomposites containing 5 wt % clay are shown in Figure 9(a). Modulus, tensile strength, and the elongation at break of PU(HTPB)/organoclay increases than PU(HTPB) without organoclay. PU(HTPB)/C12 has a higher Young's modulus and tensile strength than PU(HTPB)/C18 because of the higher degree of crosslinking and exfoliation.

In Figure 9(b), the escalation of Young's modulus with clay concentration is attributed to the reinforcement provided by the dispersed silicate layers. In Figure 9(c), elongation at break decreases with increases in the values of Young's modulus. In Figure 9(d), tensile strength increases as the organoclay loading increases until 10 wt % of clay is reached. As clay loading increases, the interaction area between the organoclay and the polyurethane matrix is increased until 10 wt % of clay is reached. Many polymer–clay nanocomposites have shown the abrupt decrease in tensile strength over at least 5 wt % of clay content[16,17] due to the dispersion problem of clay. However, this composite shows highest value at 10wt%, so we can interpret high qualified dispersion state is achieved. The tensile strengths of PU(HTPB)/organoclay nanocomposites decreased when the wt % clay increased above 10 wt %. High loadings of inorganic clay usually make the polymers not to endure stress, and, finally, rupture occurs in the tensile test.[18]

CONCLUSIONS

The diffusion rate of IPDI in HTPB/organoclay composite was affected by the compatibility with organic modifier in the organoclay. Dodecylamine, the organic modifier having similar hydrogen bonding component with IPDI than octadecylamine, affected the faster diffusion of IPDI. That resulted different exfoliation state as well as crosslinking densities of the nanocomposite. Both nanocomposites showed high physical properties until a clay concentration of 10 wt % was reached. PU(HTPB)/C12 showed the higher tensile strength and Young's modulus than PU(HTPB)/C18.

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