

# Effects of Ultrasound on the Synthesis and Properties of Polyurethane Foam/Clay Nanocomposites

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**ABSTRACT:** Polyurethane foam (PUF)/clay nanocomposites were synthesized with clay modified by polymeric 4,4'-diphenylmethane diisocyanate (PMDI) with the application of ultrasound. Transmission electron micrographs showed that the interlayer distance increased for the polyurethane (PU)/clay nanocomposites where ultrasound was applied. The results of the transmission electron microscopy and X-ray measurements suggest that the application of ultrasound to the clay modification with PMDI improved the efficiency of the clay modification by the effective breakup of the clay agglomerates and intercalation of the silicate layers. In the mechanical tests of the PUF/clay nanocomposites, the flexural and tensile strengths of the PUF/clay nanocomposites showed the maximum value at 3.0 wt % clay content based on PMDI. These results suggest that the increases in the flexural and tensile strengths were perhaps due to the uniform dispersion of

the clay by the application of ultrasound. At the same modified clay content, the fire resistance properties were increased for the PUF/clay nanocomposites with the application of ultrasound compared to the PUF/clay nanocomposites without the application of ultrasound. The cell size and thermal conductivity were decreased for the PUF/clay nanocomposites with the application of ultrasound compared to the PUF/clay nanocomposite without the application of ultrasound. Because of these results, we suggest that the smaller cell size and lower thermal conductivity of the PUF/clay nanocomposites were mainly due to the enhanced dispersion of the clay by the application of ultrasound to the mixture of PMDI and clay. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3764–3773, 2006

**Key words:** clay; foams; mechanical properties; nanocomposites; polyurethanes

## INTRODUCTION

The dispersion of layered silicate and properties of nanocomposites depend on various factors, including intercalation method (melt, solution, *in situ* polymerization), mixing temperature, mixing time, used solvent, size of monomer or polymer, and intercalation agent. When the clays are dispersed in a polymer matrix, they are either intercalated by macromolecules or exfoliated.<sup>1–5</sup> The best performances are commonly observed for exfoliated nanocomposites. However, this is very difficult to attain by simple mixing methods. Therefore, many researchers have been interested in the application of ultrasound to the synthesis of polymer/clay nanocomposites to overcome the limitations of existing methods.<sup>6,7</sup>

Polyurethane foams (PUFs) with a cellular structure are used for many engineering applications, such as insulation materials, cushioning, automotive parts, and structural materials.<sup>8–13</sup> PUF is based on the reaction of a diisocyanate with a polyol. The reaction is exothermic, and the reaction heat can be used to form a cellular structure by the evaporation of the physical blowing agents, such as chlorofluorocarbons, hydrochlorofluorocarbons, pentanes, and hydrofluorocarbons. The cellular structure of the PUF can be generated from chemical blowing reactions also. Some chemicals are reacted with the components generating the gas molecules, which yield the bubbles. One widely used chemical blowing agent for the synthesis of PUF is distilled water, which reacts with the diisocyanate to generate carbon dioxide.<sup>8–10</sup>

In a previous article,<sup>14</sup> we presented the technology of clay modification with polymeric 4,4'-diphenylmethane diisocyanate (PMDI) and the synthesis of PU nanocomposites with clay modified with PMDI. In this study, we used ultrasound in the clay modification with PMDI. A sonication process with ultrasonic waves was used to enhance the nanoscale dispersion of the clay and clay layers during the clay modification. For effective mixing, a special intensive mixer equipped

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with the ultrasonic generator was used. Thus, ultrasonic-assisted clay modification was expected to help us achieve the effective breakup of the clay agglomerates and the dispersion of the silicate layers and, thereby, an improvement in the efficiency in the clay modification. In addition, we examined the effects of ultrasound on the mechanical, thermal, and morphological properties of the PUF/clay nanocomposites produced by the blowing process of the PU/clay nanocomposites.

## EXPERIMENTAL

### Materials

The materials used in this study were obtained from commercial sources. PMDI was supplied from BASF Korea, Ltd. (Seoul, Korea). The average functionality of PMDI was 2.7, and the NCO content was 31.5 wt %. The equivalent weight and viscosity of PMDI were 135.0 g/mol and 550 cps, respectively. Pentaerythritol-base polyether polyol supplied from KPC Co. (Ulsan, Korea) was used for the preparation of the nanocomposites. Amine-treated organoclay, which was supplied from Southern Clay Co. (Gonzales, Texas, USA), was used in this study. Dimethylcyclohexylamine, which was supplied from Air Products and Chemicals, Inc. (Hamilton, Pennsylvania, USA), was used as a catalyst. Polysiloxane ether, used as a surfactant, was supplied from Osi Specialties, Inc. (Sisterville, West Virginia, USA). Distilled water, used as a chemical blowing agent, was generated in our laboratory. The polyol and clay were dehydrated before use at 90°C for 24 h in a vacuum oven. The other chemicals were used as received.

### Sample preparations

#### Clay modification with ultrasound

The organoclay and PMDI were premixed at 3000 rpm with a mechanical stirrer in an oil bath for 2 h. The temperature of the oil bath was maintained at 50°C on a hot plate, and the relative humidity was maintained below 30%. The organoclay content was fixed at 3 wt % on the basis of PMDI. When the mixing was started at a high speed, the clays did not disperse well and were aggregated each other. Therefore, the mixing was started at a low speed of about 400 rpm and was gradually increased to 3000 rpm.<sup>14</sup> After premixing, ultrasound (40 kHz, Bolt Clamped Langevin Type, Seoul, Korea) was applied to the mixture of the organoclay and PMDI for 15 min; then, the clay that was modified with PMDI was obtained. With our ultrasound equipment, a particular cooling system was not used because an appreciable temperature difference was not observed.

#### PU/clay nanocomposite

The PU/clay nanocomposite was synthesized by the reaction between the polyol and PMDI, which con-

tained the clay modified with ultrasound. The PMDI, clay with modified PMDI, polyether polyol, and amine catalyst were used for the preparation of the PU/clay nanocomposite. All chemicals were put into the reactor and mixed for 30 s with a brushless-type stirrer. The stirrer speed was set at 3000 rpm. The amounts of the polyether polyol and catalyst were fixed at 100.0 and 1.0 by weight, respectively. The amount of PMDI containing the modified clay required for the reaction with the polyether polyol was calculated from the equivalent weight. For the completion of the reaction, excess PMDI (ca. 5 wt %, NCO/OH = 1.05) was used. The composition of the PU/clay nanocomposite is summarized in Table I. In our previous article, a detailed scheme of the PU synthesis was provided.<sup>14</sup>

#### PUF/clay nanocomposites

The PU/clay nanocomposites were synthesized by the reaction between the polyol and PMDI that contained the clay modified with ultrasound. The PUF/clay nanocomposites were synthesized by a blowing reaction between the blowing agent (water) and PMDI. The amount of the clay was varied from 0 to 5 wt % (on the basis of PMDI). The PMDI, clay modified with PMDI, polyether polyol, amine catalyst, surfactant, and distilled water were used for the preparation of the PUF/clay nanocomposites. The amounts of the polyether polyol, catalyst, surfactant, and distilled water were fixed at 100.0, 1.0, 1.5, and 1.5 by weight, respectively. The amount of PMDI required for the reaction with the polyether polyol and distilled water was calculated from their equivalent weights. For the completion of the reaction, excess PMDI (ca. 5 wt %, NCO/OH = 1.05) was used. All chemicals were put into the reactor and mixed for 30 s with a brushless-type stirrer.<sup>11-14</sup> The stirrer speed was set at 3000 rpm throughout the mixing. After mixing, the reactants were poured into an open mold (250 × 250 × 100 mm) to produce free-rise foams and were cured for 1 week at room temperature. Three replications for all the foams were executed.

### Characterization

#### Wide-angle X-ray diffraction (WAXD)

The distribution of clay layers in the PU/clay nanocomposites was measured by an X-ray diffractometer

TABLE I  
Composition of the PU/Clay Nanocomposites

	PMDI	Polyether polyol	Catalyst	Clay <sup>a</sup>
Weight (g)	130.0	100.0	1.0	1.0, 3.0, 5.0

<sup>a</sup> The unit of the clay was parts per hundred resin, which was based on 100 g of the PMDI.

(model MXP-18, Mac Science, Tokyo, Japan). Cu K $\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) was used as an X-ray source at a generating voltage of 40 kV and a current of 100 mA. WAXD scans were obtained in reflection mode with an incident X-ray wavelength of 1.54  $\text{\AA}$  at a scanning rate of 2.0 deg/min. The  $d$ -spacing was calculated by Bragg's law ( $d = n\lambda/2 \sin \theta$ , where  $n$ : integer and  $\theta$ : glancing angle) from the position of the (001) or (002) plane peak in the WAXD pattern.

#### Transmission electron microscopy (TEM)

The TEM specimen was prepared by an epoxy embedding method at an ambient temperature. Transmission electron micrographs were obtained with a Fei Tecnai G<sup>2</sup> transmission electron microscope (Hillsboro, Oregon, USA) without the staining of the specimen.

#### Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis measurements were carried out with an advanced rheometric expansion system in oscillatory torsional mode at a strain of 0.1% and a frequency of 1 Hz. The temperature was scanned between 30 and 200°C at a rate of 5°C/min.

#### Mechanical properties

The mechanical properties of the PU/clay and PUF/clay nanocomposite samples were measured under ambient conditions with an Instron Universal Testing Machine (UTM) (model 4467, Canton, OH). Tensile tests for the PU/clay nanocomposites were performed according to ASTM D 638. The size of the specimen was 10  $\times$  63  $\times$  3 mm (Width  $\times$  Length  $\times$  Thickness). The gauge length was 13 mm, and the speed of crosshead movement was 1.5 mm/min. Flexural tests for the PUF/clay nanocomposites were performed according to KS M3830. The size of the specimen was 25  $\times$  120  $\times$  20 mm (Width  $\times$  Length  $\times$  Thickness). The span distance was 100 mm, and the speed of crosshead movement was 10.00 mm/min. Tensile tests for the PUF/clay nanocomposites were performed according to ISO 1926. The size of the specimen was 20  $\times$  100  $\times$  6 mm (Width  $\times$  Length  $\times$  Thickness). The gauge length was 50 mm, and the speed of crosshead movement was 2.54 mm/min. The strengths of 10 specimens per sample were measured and averaged for each mechanical test.

#### Thermogravimetric analysis (TGA)

The thermal stability of the PU/clay nanocomposites was observed with a thermogravimetric analyzer (TGA 2950, DuPont Instruments, New Castle, Delaware, USA) at a heating rate of 10°C/min from 50 to 800°C/min under a nitrogen atmosphere.

#### Fire resistance

The inflammability of the PUF/clay nanocomposites was measured according to ASTM D 4986. The size of the specimen was 50  $\times$  150  $\times$  13 mm (Width  $\times$  Length  $\times$  Thickness). The flame was adjusted to 6.5 mm for the inner flame and 38 mm for the outer flame. Test specimens were placed in the flame for 60 s and were then removed to a distance at least 150 mm from the flame. The time from beginning of exposure of the test piece to the flame to the extinguishing of the fire of the test piece (ignition time) and the length of the longest portion in the burnt part of the test piece (ignition length) were measured. The fire resistance properties of five specimens per sample were measured and averaged.

#### Scanning electron microscopy

The morphology of the PUF/clay nanocomposites was studied with an S-4300SE field emission scanning electron microscope (Hitachi, Tokyo, Japan). The samples were cryogenically fractured and white-gold-coated before scanning. The accelerating voltage was 25 kV. The S-4300SE was used to observe the sizes of the cells on the PUF/clay nanocomposite samples, which were measured with an Image-Pro Plus image analyzer (Media Cybernetics, Silver Spring, MD) and averaged, except for the largest and smallest cells.

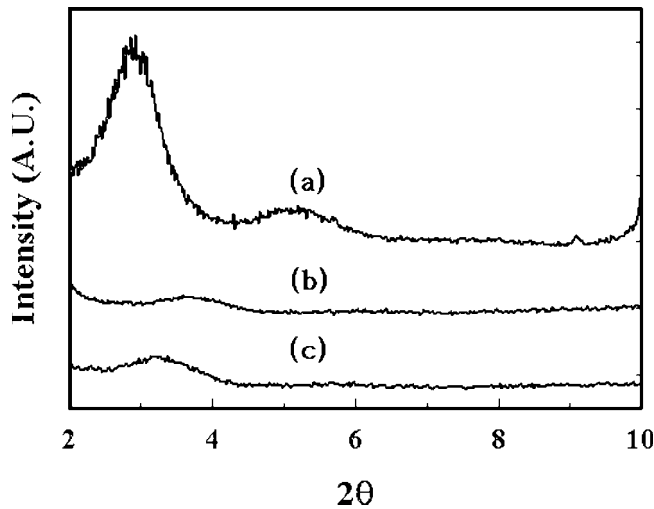
#### Thermal conductivity measurements

The thermal conductivity of the PUF/clay nanocomposites was measured with a Holometrix Micromet (model Lambda 2000, Boston, Massachusetts, USA) according to ASTM C518. A sample was placed in the test section between two plates that were maintained at different temperatures during the test. On the achievement of thermal equilibrium and the establishment of a uniform temperature gradient throughout the sample, the thermal conductivity of the PUF/clay nanocomposite samples was determined. The size of the specimen was 300  $\times$  300  $\times$  50 mm (Width  $\times$  Length  $\times$  Thickness). The thermal conductivities of three specimens per sample were measured and averaged.

## RESULTS AND DISCUSSION

### WAXD pattern of clay modified with PMDI

The silanol group ( $-\text{SiOH}$ ) located on the surface of the clay, which had a layered structure, could react with the isocyanate group ( $-\text{NCO}$ ) of PMDI, which had a high reactivity with hydroxyl groups ( $-\text{OH}$ ). In this study, we modified the clay with PMDI by a reaction that included the formation of urethane linkage ( $-\text{SiOCONH}-$ ). In our previous study,<sup>14</sup> it was shown from Fourier transform infrared analysis that an NCO characteristic peak was observed from the clay modified with PMDI. During the process of clay



**Figure 1** WAXD patterns of the clays: (a) pure organoclay, (b) clay modified without ultrasound, and (c) clay modified with ultrasound.

modification in this study, we applied ultrasound to the mixture of PMDI and clay. The sonication process with ultrasonic waves can enhance the nanoscale dispersion of the clay and clay layers during clay modification. Ultrasonic-assisted clay modification was expected to help us achieve effective breakup of the clay agglomerates and exfoliation of the silicate layers and, thereby, improve the efficiency in the clay modification.<sup>6,7</sup>

Figure 1(a–c) shows the WAXD patterns of the pure organoclay, the clay modified with PMDI without

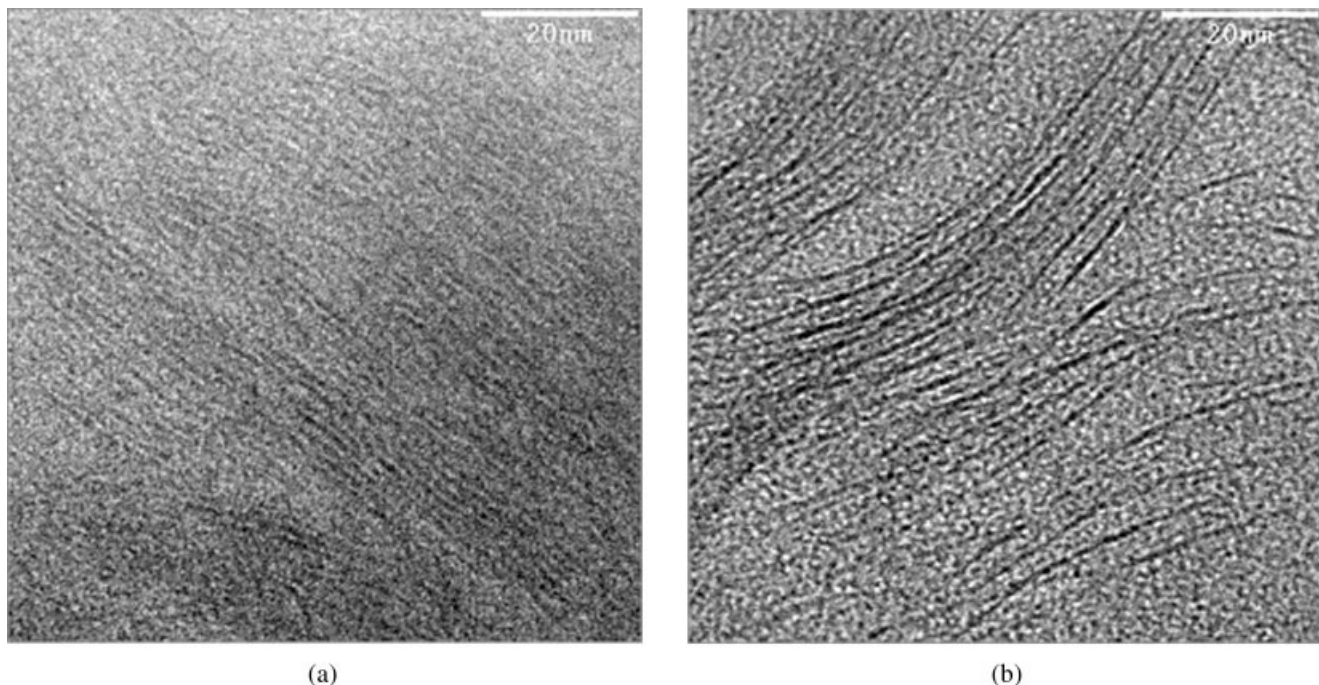
ultrasound, and the clay modified with PMDI with ultrasound, respectively. Generally, as the  $d$ -spacing of the clay layer was increased, the  $2\theta$  peak of the clay decreased. As shown in Figure 1(c), after clay modification with PMDI with ultrasound, the  $2\theta$  peak ( $d_{002}$ ) of the clay decreased from 5.2 [Fig. 1(a)] to 3.2 [Fig. 1(c)]. From these results, we calculated that the  $d$ -spacing of the clay layer increased from 3.3 [Fig. 1(a)] to 5.4 nm [Fig. 1(c)]. Therefore, after clay modification with PMDI with ultrasound, the  $d$ -spacing of the clay layer was increased by PMDI intercalated to the clay layers during the clay modification.<sup>6,14</sup>

As shown in Figure 1, the  $2\theta$  peaks ( $d_{002}$ ) of the clay modified without ultrasound and the clay modified with ultrasound were 3.7 [Fig. 1(b)] and 3.2 [Fig. 1(c)], respectively. Because of this result, we suggest that after clay modification with PMDI, the  $d$ -spacing of the modified clay increased from 4.7 [Fig. 1(b)] to 5.4 nm [Fig. 1(c)] with the application of ultrasound to the mixture of PMDI and clay. From this result, we expected that ultrasound assisted the clay modification to achieve the effective breakup of the clay agglomerates and intercalation of the silicate layers.

## PU/clay nanocomposite

### TEM

The PU/clay nanocomposite was synthesized by the reaction with polyol, PMDI, and clay modified with PMDI with and without sonication. Figure 2(a,b) shows the morphology by TEM of the PU/clay nano-



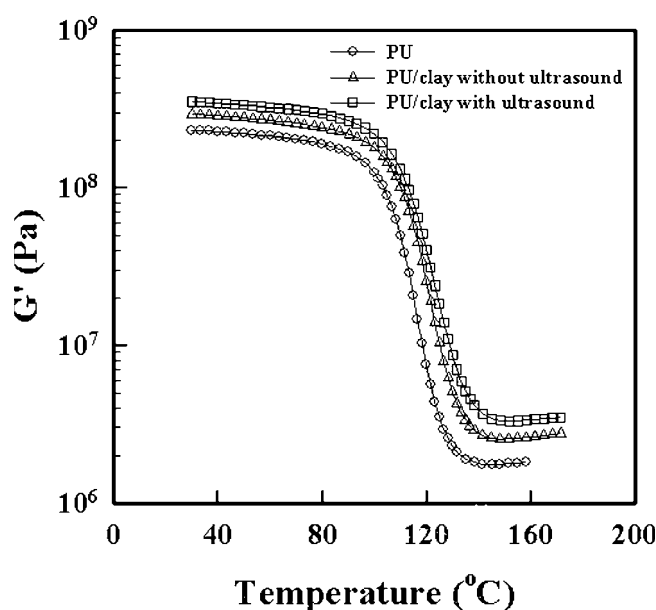
**Figure 2** Transmission electron micrographs of the PU/clay nanocomposites: (a) clay modified without ultrasound and (b) clay modified with ultrasound.

composites synthesized with the clay modified with ultrasound and without ultrasound, respectively. As shown in Figure 2 (b), the interlayer distance increased with the clay modified with ultrasound compared with the clay modified without ultrasound. The intercalation of the clay layers was achieved for the PU nanocomposite with the application of ultrasound to the clay modified with PMDI. This result was consistent with the results of WAXD pattern of the clay modified with PMDI, which is shown in Figure 1.

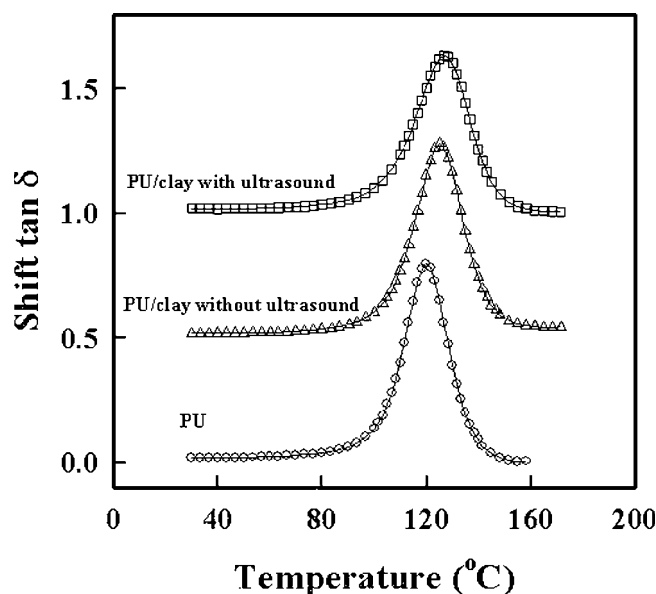
### Dynamic mechanical properties

Figure 3 shows the storage modulus ( $G'$ ) of the PU and PU/clay nanocomposites with and without sonication. As shown in Figure 3, the storage of the PU and PU/clay nanocomposites maintained a plateau below the glass-transition temperature ( $T_g$ ) and decreased through the glass-transition process. For the PU/clay nanocomposites, the values of  $G'$  were higher than those of the PU without clay. Also, the values of  $G'$  of the PU/clay nanocomposites with sonication were higher than those of the PU/clay nanocomposites without sonication.

Figure 4 shows shifted  $\tan \delta$  versus temperature for the PU and PU/clay nanocomposites with and without sonication (each sample was vertically shifted for clarity).  $T_g$ , corresponding to the temperature of the maximum  $\tan \delta$  peak, of the PU/clay nanocomposites increased compared to that of PU. Also,  $T_g$  increased with sonication in the PU/clay composites.  $T_g$ 's of the PU and PU/



**Figure 3**  $G'$  of the PU and PU/clay nanocomposites with and without ultrasound: (○) PU; (△) PU/clay nanocomposites without ultrasound; (□) PU/clay nanocomposites with ultrasound.



**Figure 4** Shifted  $\tan \delta$  versus temperature for the PU and PU/clay nanocomposites with and without ultrasound: (○) PU; (△) PU/clay nanocomposites without ultrasound; (□) PU/clay nanocomposites with ultrasound.

clay nanocomposites with and without sonication were observed at 119.8, 126.5, and 124.9°C, respectively.

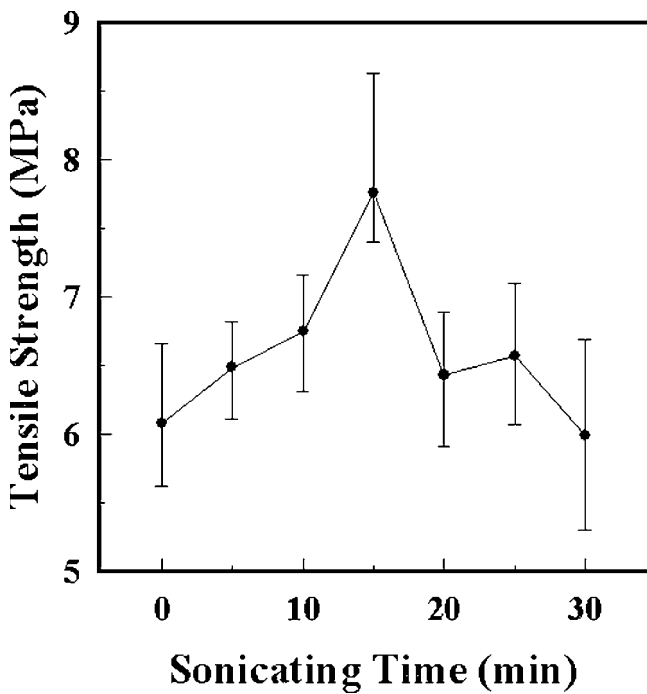
### Mechanical strength

Figure 5 shows the tensile strength of the PU/clay nanocomposites synthesized with the clay modified by the variation of the sonication time from 0 to 30 min. As shown in Figure 5, when the sonication time was increased from 0 to 15 min, the tensile strength of the PU/clay nanocomposites increased from 6.08 to 7.76 MPa; then, the tensile strength decreased with increasing sonication time.

Ultrasonic-assisted clay modification was expected to help us achieve the effective breakup of the clay agglomerates and exfoliation of the silicate layers and, thereby, improve the efficiency of the clay modification. The energy emitted by ultrasound, however, can activate the reactivity of PMDI, and so excess energy can make the isocyanate groups of PMDI covalently bonded to the clay layers be consumed. Therefore, we suggest that the decrease in the tensile strength with a sonication time over 15 min may have been due to the exhaustion of the isocyanate groups of PMDI covalently bonded to the clay layers. From this result, the optimum sonication time of the clay modification was 15 min in this study.

### Thermal stability

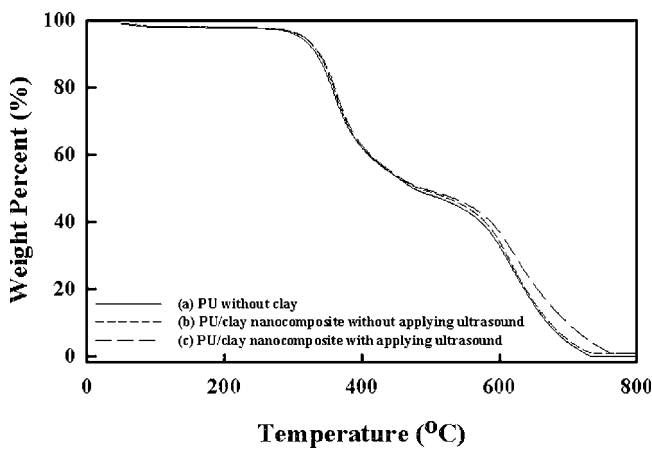
Thermal degradation was investigated by TGA under a nitrogen atmosphere at a heating rate of 10°C/min.



**Figure 5** Effect of the sonication time on the tensile strength of the PU/clay nanocomposite.

As shown in Figure 6, the PU/clay nanocomposite without ultrasound [Fig. 6(b)] degraded at a higher temperature than the PU without clay [Fig. 6(a)]. In addition, Figure 6 shows that the PU/clay nanocomposite with ultrasound [Fig. 6(c)] degraded at a higher temperature than the PU/clay nanocomposite without ultrasound [Fig. 6(b)].

This beneficial effect can be explained by a decrease in the diffusion of oxygen and volatile products throughout the nanocomposite material. In the presence of the clay layers, because the diffusing gas could not penetrate the clay layers, the pathway of the diffus-



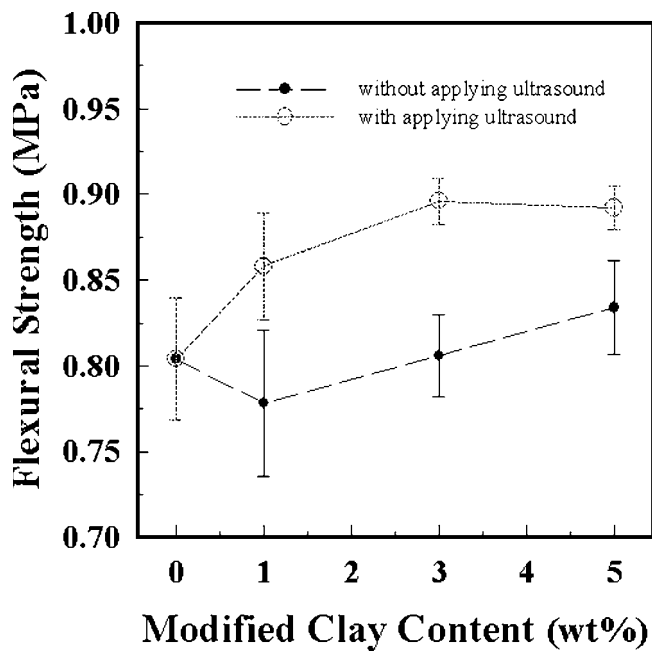
**Figure 6** TGA thermograms with temperature: (a) PU without clay, (b) PU/clay nanocomposite synthesized with the clay modified without ultrasound, and (c) PU/clay nanocomposite synthesized with the clay modified with ultrasound.

ing gas was remarkably extended. In addition, the effective breakup of the clay agglomerates and exfoliation of the silicate layers made the pathway of the diffusing gas be extended more. As mentioned previously, ultrasound-assisted clay modification achieved the effective breakup of the clay agglomerates and exfoliation of the silicate layers in comparison with the clay modification without ultrasound. Therefore, we suggest that the increase in the degradation temperature of the PU/clay nanocomposite may have been due to the extended pathway by effective breakup of the clay agglomerates and intercalation of the silicate layers by ultrasound.

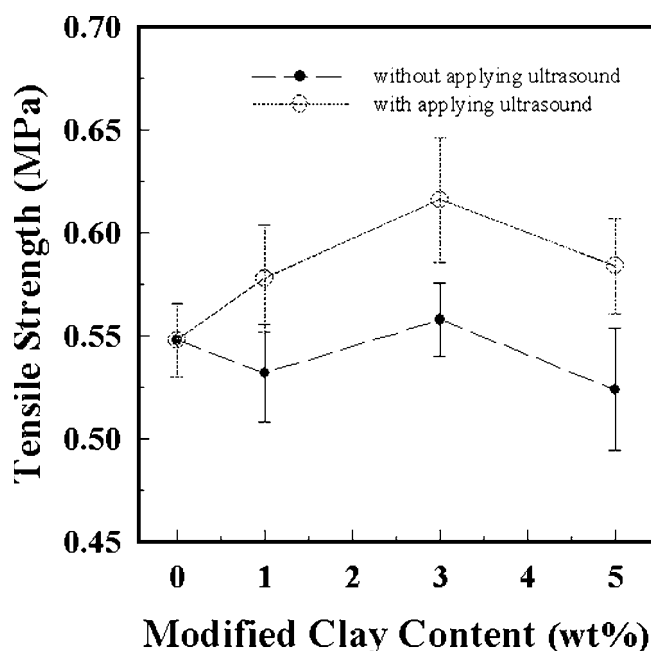
**PUF/clay nanocomposite**

**Mechanical strength**

Figure 7 shows the flexural strength of the PUF/clay nanocomposites with the modified clay content with and without applying ultrasound. It is known that the mechanical properties of cellular materials depend mainly on their density.<sup>8-10</sup> In this experiment, the densities of the PUF/clay nanocomposites were set at 90 kg/m<sup>3</sup> for each sample. As shown in Figure 7, the flexural strengths of the PUF/clay nanocomposites were 0.80, 0.78, 0.81, and 0.83 MPa for the 0.0, 1.0, 3.0, and 5.0 wt % modified clays, respectively, when ultrasound was not applied. As shown by the previous results, the improvement of the flexural strength of the PUF/clay nanocomposite without ultrasound was not



**Figure 7** Effect of the modified clay content on the flexural strength of the PUF/clay nanocomposite: (●) PUF/clay nanocomposite synthesized with the clay modified without ultrasound and (○) PUF/clay nanocomposite synthesized with the clay modified with ultrasound.



**Figure 8** Effect of the modified clay content on the tensile strength of the PUF/clay nanocomposite: (●) PUF/clay nanocomposite synthesized with the clay modified without ultrasound and (○) PUF/clay nanocomposite synthesized with the clay modified with ultrasound.

significant. To synthesize a nanocomposite with good mechanical properties, a uniform dispersion of the clay is important. Therefore, we suggest the use of the application of ultrasound to the mixture of PMDI and clay during clay modification.

As shown in Figure 7, the flexural strengths of the PUF/clay nanocomposites were 0.80, 0.86, 0.90, and 0.89 MPa for the 0.0, 1.0, 3.0, and 5.0 wt % modified clays, respectively, when ultrasound was applied. In comparison with the results of the PUF/clay nanocomposite without ultrasound, the flexural strength was improved. As shown by the results in Figure 7, the

application of ultrasound to the clay modification enhanced the dispersion of the clay. Therefore, we suggest that the increase in the flexural strength of the PUF/clay nanocomposites may have been due to the uniform dispersion of the clay by ultrasound.

Figure 8 shows the tensile strength of the PUF/clay nanocomposites with the clay content with and without ultrasound. As shown in Figure 8, the tensile strengths of the PUF/clay nanocomposites were 0.55, 0.58, 0.62, and 0.58 MPa for the 0.0, 1.0, 3.0, and 5.0 wt % modified clays, respectively, when ultrasound was applied. From the results of Figure 8, we suggest that the increase in the tensile strength of the PUF/clay nanocomposites may have been due to the uniform dispersion of the clay by ultrasound.

#### Fire resistance properties

PUFs are very easily ignited, so we used tris-2-chloropropyl phosphate as a flame-retarding agent; the tris-2-chloropropyl phosphate was added in the amount of 10 wt % based on the polyol throughout the synthesis of the PUF/clay nanocomposites. The results of the fire resistance test of the PUF/clay nanocomposites are shown in Table II. As shown in Table II, as the amount of the clay increased, the ignition time decreased, and the ignition length decreased for the PUF/clay nanocomposites with and without ultrasound. In addition, at the same clay content, the properties of fire resistance were increased more for the PUF/clay nanocomposite with ultrasound than for the PUF/clay nanocomposite without ultrasound. For example, at a clay content of 3.0 wt %, the ignition time and ignition length of the PUF/clay nanocomposite decreased from 71 to 67 s and from 62 to 54 mm, respectively, with ultrasound. The increase of the fire resistance could be explained by a decrease in the diffusion of oxygen and volatile products throughout the nanocomposite material. In the presence of the clay layers, because the diffusing gas

**TABLE II**  
Fire Resistance Properties of the PUF/Clay Nanocomposites with the Modified Clay Content and with the Application of Ultrasound

Modified clay content (wt %) <sup>a</sup>	PUF/clay nanocomposite without ultrasound <sup>b</sup>		PUF/clay nanocomposite with ultrasound <sup>c</sup>	
	Ignition time (s) <sup>d</sup>	Ignition length (mm) <sup>e</sup>	Ignition time (s) <sup>d</sup>	Ignition length (mm) <sup>e</sup>
0.0	75	70	75	70
1.0	73	66	69	60
3.0	71	62	67	54
5.0	68	54	66	50

<sup>a</sup> Based on PMDI weight.

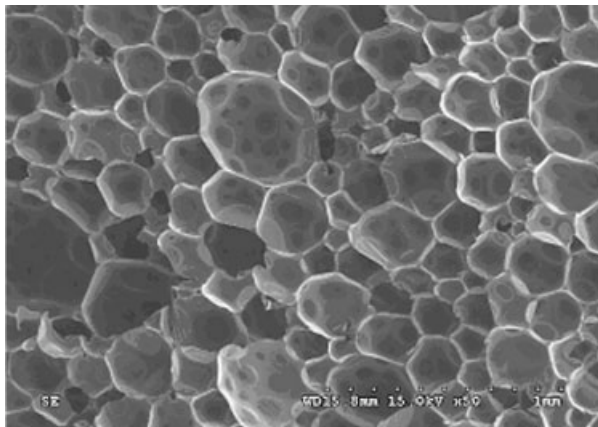
<sup>b</sup> PUF/clay nanocomposite synthesized with the clay modified without ultrasound.

<sup>c</sup> PUF/clay nanocomposite synthesized with the clay modified with ultrasound.

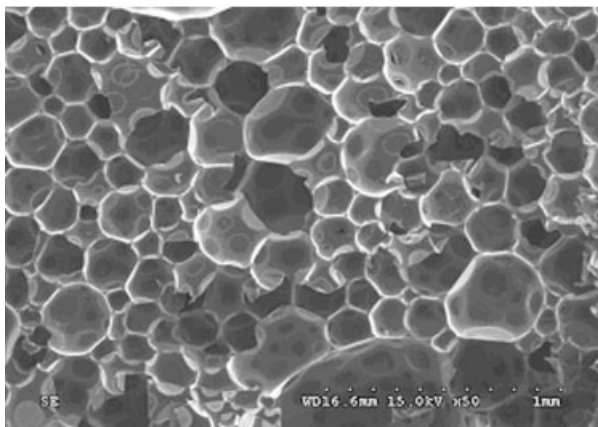
<sup>d</sup> The time from beginning of exposure of the test piece to the flame to the extinguishing of the fire of the test piece. The real ignition time was the ignition time minus 60 s.

<sup>e</sup> The length of the longest portion in the burnt part of the test piece.

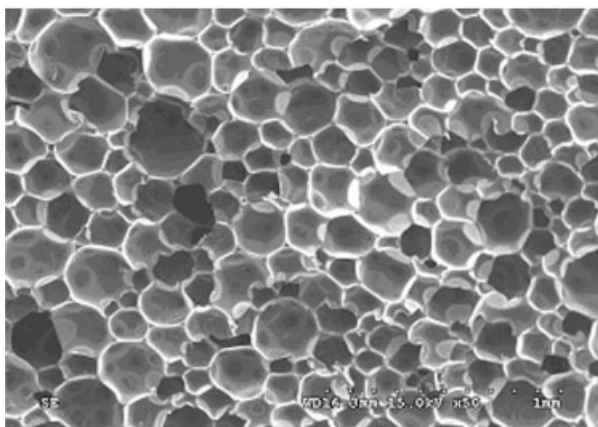




(a)



(b)



(c)

**Figure 9** Scanning electron micrographs of the PUF/clay nanocomposites: (a) PUF without clay, (b) PUF/clay nanocomposite without ultrasound, and (c) PUF/clay nanocomposite with ultrasound.

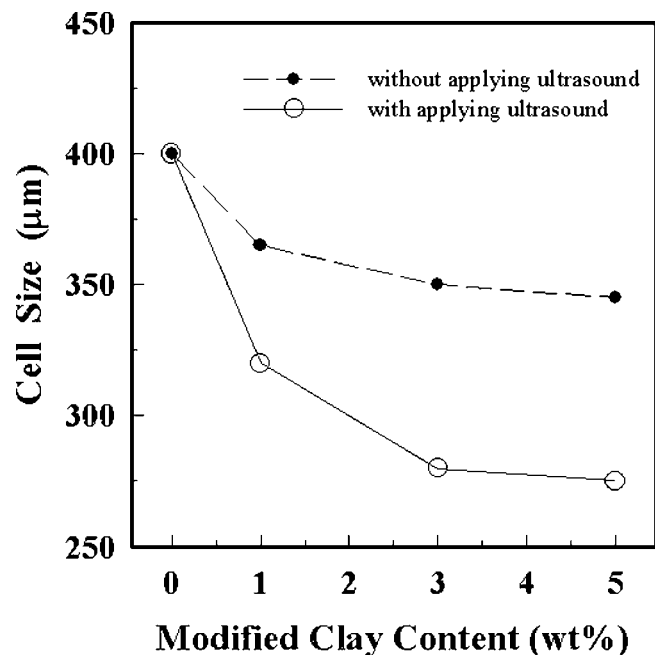
cannot penetrate the clay layers, the pathway of the diffusing gas is remarkably extended. In addition, the effective breakup of the clay agglomerates and exfoliation of the silicate layers make the pathway of the diffusing gas be extended more. As mentioned previously,

ultrasound-assisted clay modification achieved the effective breakup of the clay agglomerates and exfoliation of the silicate layers in comparison with the clay modification without ultrasound. Therefore, we suggest that the increase in the fire resistance property may have been due to the extended pathway of the PUF/clay nanocomposite caused by the effective breakup of the clay agglomerates and intercalation of the silicate layers by ultrasound.

**Cell morphology and thermal conductivity**

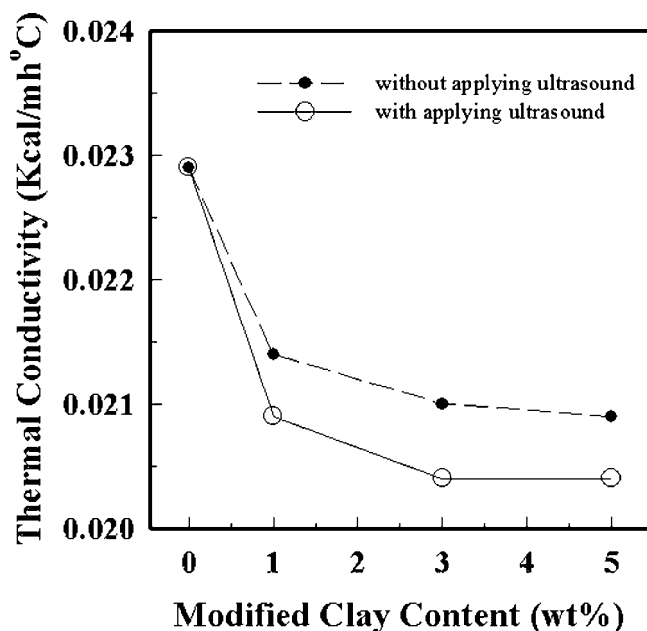
The effects of ultrasound on the cell morphology and thermal conductivity of the PUF/clay nanocomposites are shown in Figures 9–11. Figure 9(a–c) shows the micrographs of the PUF without clay, PUF/clay nanocomposite without ultrasound, and PUF/clay nanocomposite with ultrasound. The cell size of the PUF without clay was 400  $\mu\text{m}$  [Fig. 9(a)]. However, the cell sizes of the PUF/clay nanocomposites without and with ultrasound were 350  $\mu\text{m}$  [Fig. 9(b)] and 280  $\mu\text{m}$  [Fig. 9(c)], respectively.

Exfoliated clay layers can act as nucleation agents and serve as sites for bubble growth, with the formation of new bubbles not being necessary.<sup>8–10</sup> Therefore, we suggest that the reduction in the cell size of the PUF/clay nanocomposites may have been due to the nucleation effect of the clay. In addition, we suggest that the smaller cell size of the PUF/clay nanocomposite with ultrasound [Fig. 9(c)] may have been due to the enhanced dispersion of the clay.



**Figure 10** Effect of the modified clay content on the cell size of the PUF/clay nanocomposite (●) without ultrasound and (○) with ultrasound.





**Figure 11** Effect of the modified clay content on the thermal conductivity of the PUF/clay nanocomposite (●) without ultrasound and (○) with ultrasound.

Figure 10 shows the effects of the modified clay content and ultrasound on the cell size of the PUF/clay nanocomposites. As shown in Figure 10, as the amount of the clay increased, the cell size decreased for the PUF/clay nanocomposites with and without ultrasound. In addition, at the same clay content, the cell size decreased more for the PUF/clay nanocomposite with ultrasound than for the PUF/clay nanocomposite without ultrasound. As mentioned previously, exfoliated clay layers can act as nucleation agents and serve as sites for bubble growth with the formation of new bubbles. As the amount of nucleation agents increases, the bubble size decreases, and the number of the bubbles increases. Therefore, we suggest that the reduction in the cell size of the PUF/clay nanocomposites with the clay content may have been due to the increase in the amount of nucleation agents. In addition, the application of ultrasound to the clay modification with PMDI could have increased the dispersability of the clay within the PUF/clay nanocomposites in comparison with the clay modification with PMDI only.<sup>6,7</sup> Therefore, the PUF/clay nanocomposite with ultrasound had a smaller cell size than the PUF/clay nanocomposite without ultrasound at the same modified clay content.

As shown in Figure 10, the cell size did not decrease significantly when the modified clay content exceeded 3 wt % based on PMDI. In our previous work,<sup>14</sup> there was a saturation point in the exfoliated clay layers, and it was 3 wt % modified clay content based on PMDI. Therefore, we suggest that the small decrease in the cell size for more than 3 wt % clay content may have been due to the saturation of the clay layers.

The effects of the modified clay content and ultrasound on the thermal conductivity of the PUF/clay nanocomposites are shown in Figure 11. It is known that PUF with a small cell structure shows low thermal conductivity.<sup>8–11</sup> As shown in Figure 11, as the amount of the clay increased, the thermal conductivity had a lower value for the PUF/clay nanocomposites with and without ultrasound. In addition, at the same clay content, the thermal conductivity decreased for the PUF/clay nanocomposite with ultrasound compared to that without ultrasound. As shown in Figure 11, the thermal conductivity did not decrease significantly when the modified clay content exceeded 3 wt % based on PMDI. The results of the cell size show similar behavior with the results of the thermal conductivity with the clay content of the PUF/clay nanocomposites. Therefore, we suggest that the lower thermal conductivity was attributable to the smaller cell size of the PUF/clay nanocomposites.

## CONCLUSIONS

Clay was modified with PMDI via a reaction including the formation of urethane linkages ( $-\text{SiOCONH}-$ ) with the application of ultrasound. PU/clay and PUF/clay nanocomposites were synthesized by the reaction with polyol, PMDI, and clay modified with PMDI.

From the results of WAXD analysis, the *d*-spacing of the clay modified with ultrasound was wider than those of the virgin clay and the clay modified without ultrasound. From the results of the morphology by TEM, the interlayer distance was increased for the PU/clay nanocomposites with ultrasound. Also, in the study of the dynamic mechanical properties,  $G'$  increased for the PU/clay nanocomposites with ultrasound. From these results, we concluded that ultrasound can assist clay modification to achieve effective breakup of the clay agglomerates and intercalation of the silicate layers. From the results of thermal analysis by TGA, the PU/clay nanocomposite with ultrasound degraded at higher temperatures.

From the results of mechanical testing, the flexural and tensile strengths of the PUF/clay nanocomposites showed a maximum value at 3.0 wt % clay content based on PMDI. As seen in the results of the fire resistance tests, as the amount of the modified clay increased, the ignition time shortened and the ignition length decreased for the PUF/clay nanocomposites with and without ultrasound. In addition, at the same modified clay content, the fire resistance properties were increased for the PUF/clay nanocomposite with ultrasound compared to those for the PUF/clay nanocomposite without ultrasound.

In the study on the cell morphology and thermal conductivity, as the amount of the modified clay increased, the cell size and thermal conductivity

decreased for the PUF/clay nanocomposites with and without ultrasound. In addition, the cell size and thermal conductivity decreased for the PUF/clay nanocomposite with ultrasound compared to those for the PUF/clay nanocomposite without ultrasound. From these results, we suggest that the smaller cell size and lower thermal conductivity of the PUF/clay nanocomposite were mainly due to the enhanced dispersion of the clay by the application of ultrasound to the mixture of PMDI and clay.

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