

# Mechanical, Morphological, and Thermal Properties of Rigid Polyurethane Foams Blown by Distilled Water

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**ABSTRACT:** Rigid polyurethane foams (PUFs) were prepared from polymeric 4,4'-diphenylmethane diisocyanate (PMDI), polyether polyol, 1,4-butanediol, silicone surfactant, and distilled water. The properties of the synthesized PUF samples were investigated with differential scanning calorimetry, scanning electron microscopy, and a Universal testing machine. The density of the PUF was decreased from 173.7 to 41.7 kg/m<sup>3</sup> with an increase in distilled water from 0.5 to 3.0 parts per hundred polyol by weight (php), respectively, with 0 php butanediol. The cell size of the PUF sample increased from 115 to 258  $\mu\text{m}$  with an increase in distilled water from 0.5 to 3.0 php, respectively, with 10 php butanediol. From the results of the thermal analysis of the PUF sample, it was found that the glass-transition temperatures of the PUF samples were increased from 49.5 to 80.8°C with an increase in distilled water from 0.5 to 3.0 php, respectively, with 0 php butanediol. The results of the in-

vestigation of the mechanical properties of the PUF samples showed that the mechanical strength of the PUF samples was increased with the distilled water at equal density. The surfactant effect on the properties of the PUF was studied, and it was observed that the cell size of the PUF samples decreased from 360 to 146  $\mu\text{m}$  with an increase in surfactant from 0 to 0.33 php, respectively. However, the cell size did not change significantly when the surfactant exceeded 0.33 php. The increase of the mechanical strength from 0 to 0.33 php surfactant was attributed to the decrease of the cell size of the PUF samples, and the decrease of the mechanical strength with more than 0.33 php surfactant might be due to the plasticized effect of the PUF samples. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 12–21, 2003

**Key words:** rigid polyurethane foam; density; glass-transition temperature; morphology; mechanical property

## INTRODUCTION

Polyurethane foams (PUFs) are used in many applications such as insulation materials, cushioning, automotive parts, and energy absorption materials.<sup>1–3</sup> Physical and/or chemical blowing agents can be used in the preparation of PUFs. Distilled water is one of the widely used chemical blowing agents. It reacts with diisocyanate and generates carbon dioxide, and polyol reacts with diisocyanate. The widely used physical blowing agents are chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). PUF is based on the reaction of diisocyanate with polyol. The reaction is exothermic and the reaction heat can be used to form a cellular structure by evaporating the physical blowing agents. The foaming process can be explained by the nucleation and growth mechanism.<sup>1–3</sup>

The limiting of the use of CFCs and HCFCs has arisen because of environmental problems such as ozone destruction and global warming.<sup>3,4</sup> Substitutes for CFCs and HCFCs, such as hydrofluorocarbon, cyclopentane, and distilled water, have been developed and their applications for cellular materials have been studied.<sup>3–8</sup> To establish the PUF system, it is necessary to understand the effects of distilled water on the physical properties, thermal properties, microscopic morphology, and mechanical properties.<sup>5–9</sup> In our earlier studies we reported the effects of distilled water on the thermal properties, mechanical properties, and morphology of PUF blown by a mixture of distilled water and HCFC 141B.<sup>10,11</sup>

In this study the effects of distilled water and surfactant on the thermal properties, mechanical properties, and morphology of the rigid PUFs blown by only distilled water were investigated. The rigid PUFs were prepared from polymeric 4,4'-diphenylmethane diisocyanate (PMDI) with a functionality of 2.9 and polyether polyol with an average functionality of 3.0. Distilled water was used as a chemical blowing agent. By varying the compositions and amount of the blowing agent, rigid PUF samples with various densities were obtained. The thermal properties, such as the glass-transition temperature and cellular structure, and me-

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TABLE I  
Characteristics of Materials Used in Study<sup>a</sup>

Materials	Functionality	Equiv. weight (g mol <sup>-1</sup> )	Comments
4,4'-Diphenylmethane diisocyanate <sup>b</sup>	2.9	133.5	NCO content: 31.5%
Polyether polyol <sup>c</sup>	3.0	234.7	OH value: 239 mg KOH/g
1,4-Butanediol <sup>d</sup>	2.0	45.1	Chain extender
Distilled water <sup>e</sup>	2.0	9.0	Chemical blowing agent
Triethylene diamine <sup>f</sup>	—	—	Catalyst
Polysiloxane ether <sup>g</sup>	—	—	Surfactant

<sup>a</sup> Data from suppliers.

<sup>b</sup> Supplied by BASF Korea Co. (Seoul, Korea).

<sup>c</sup> Supplied by KPC Co. (Ulsan, Korea).

<sup>d</sup> Supplied by Junsei Chemical Co. (Tokyo).

<sup>e</sup> Synthesized in our laboratory.

<sup>f</sup> Supplied by Air Products and Chemicals, Inc. (Allentown, PA).

<sup>g</sup> Supplied by OSI Specialties, Inc.

chanical properties, such as the compressive, flexural, and tensile strengths, of the PUF samples were studied with differential scanning calorimetry (DSC), scanning electron microscopy (SEM), and a Universal testing machine (UTM), respectively.

## EXPERIMENTAL

### Materials

The materials used in this study were obtained from commercial sources. The PMDI was supplied by BASF Korea Co. (Seoul, Korea). The polyether polyol, synthesized from glycerine, was procured from KPC Co. (Ulsan, Korea). 1,4-Butanediol was purchased from Junsei Chemical Co. (Tokyo). Distilled water, which was used as a chemical blowing agent, was generated in our laboratory. Triethylene diamine dissolved in dipropylene glycol to 33 wt %, which was used as a catalyst, was supplied by Air Products and Chemicals, Inc. (Allentown, PA). Poly(siloxane ether), which was used as a surfactant, was supplied by Osi Specialties, Inc. The characteristics of the materials are shown in Table I. The polyether polyol and 1,4-butanediol were dehydrated before use at 90°C for 24 h in a vacuum oven. The other chemicals were used as received.

### Sample preparations

The rigid PUF samples with various densities were synthesized with a "one-shot method." All chemicals were put into the reactor and mixed for 60 s with a brushless-type stirrer, which had a ring guard propeller for protecting the wall or sensors in the reactor. The stirrer speed was set at 3000 rpm. After mixing, the reactants were poured into an open mold (250 × 250 × 100 mm) to produce free-rise foams and they were cured for 1 week at room temperature. Distilled water was used as a blowing agent. Three replications were executed for all of the foams.

Distilled water reacts with PMDI and then generates polyurea and carbon dioxide. Carbon dioxide inflates the reactants; as a result, a cellular structure is formed. Therefore, additional PMDI (133.5 g PMDI/9.0 g H<sub>2</sub>O) is needed because distilled water reacts with PMDI.<sup>12</sup> Carbon dioxide is a CFC-free blowing agent. Therefore, it is very important to establish the system of PUF blown by distilled water.

Tables II and III (PUF X–Y) show the chemical compositions of the PUF samples blown by distilled water. Note from the tables that the amount of polyether polyol was fixed at 100 by weight, and the amounts of the catalyst and surfactant were fixed at 0.7 and 1.0 php, respectively. In the sample code (PUF X–Y) used in this study, X denotes the amount of 1,4-butanediol and Y denotes the amount of distilled water. The amount of PMDI required for the reaction with polyether polyol, 1,4-butanediol, and distilled water was calculated from the equivalent weight. For the completion of the reaction, excess PMDI (ca. 5 wt %, NCO/OH = 1.05) was used.

To investigate the effect of the surfactant contents on the properties of the PUFs, the amount of poly(siloxane ether) was varied from 0 to 2.00 php while the amount of polyether polyol, PMDI, 1,4 butanediol, distilled water, and triethylene diamine were fixed at 100, 145.3, 20, 1.5, and 0.7 php, respectively. Table IV (SUR-Z) shows the chemical compositions of the PUF samples blown by distilled water with the surfactant content. In the sample code (SUR-Z), Z denotes the amount of surfactant used.

### Measurements

The density of the PUF samples was measured according to ASTM D 1622. The size of the specimen was 30 × 30 × 30 mm (width × length × thickness). The densities of five specimens per sample were measured and averaged.

**TABLE II**  
**Chemical Compositions<sup>a</sup> of Polyurethane Foam (PUF X-Y, X = 0–20)<sup>b</sup> Blown by Distilled Water**

PUF sample code	Polymeric 4,4'-diphenylmethane diisocyanate <sup>c</sup>	1,4-Butanediol	Distilled water
PUF 0–0.5	67.5	0	0.5
PUF 0–0.9	73.7	0	0.9
PUF 0–1.0	75.3	0	1.0
PUF 0–1.2	78.4	0	1.2
PUF 0–1.5	83.1	0	1.5
PUF 0–2.0	90.9	0	2.0
PUF 0–2.5	98.6	0	2.5
PUF 0–3.0	106.4	0	3.0
PUF10–0.5	98.6	10	0.5
PUF10–0.7	101.7	10	0.7
PUF10–1.0	106.4	10	1.0
PUF10–1.3	111.1	10	1.3
PUF10–1.5	114.2	10	1.5
PUF10–1.6	115.7	10	1.6
PUF10–2.0	122.0	10	2.0
PUF10–2.2	125.1	10	2.2
PUF10–2.5	129.8	10	2.5
PUF10–3.0	137.5	10	3.0
PUF20–0.5	129.7	20	0.5
PUF20–0.8	134.3	20	0.8
PUF20–1.0	137.5	20	1.0
PUF20–1.2	140.6	20	1.2
PUF20–1.5	145.3	20	1.5
PUF20–1.8	149.9	20	1.8
PUF20–2.0	153.1	20	2.0
PUF20–2.5	160.9	20	2.0
PUF20–3.0	168.7	20	3.0

<sup>a</sup> Parts by weight based on 100 parts of the polyether polyol.

<sup>b</sup> X denotes the amount of 1,4-butanediol and Y denotes the amount of distilled water.

<sup>c</sup> An excess PMDI of 5 wt % was used for the completion of the polyurethane reaction.

The thermal properties of the PUF samples were measured with a Perkin–Elmer (Norwalk, CT) DSC 7 differential scanning calorimeter. Temperature calibration was performed with indium ( $T_m = 156.6^\circ\text{C}$ ,  $\Delta H_f = 28.5 \text{ J/g}$ ). The PUF samples were investigated in a nitrogen atmosphere from 0 to  $220^\circ\text{C}$  at a heating rate of  $20^\circ\text{C}/\text{min}$ . After  $320^\circ\text{C}/\text{min}$  programmed cooling, the samples were reheated at a heating rate of  $20^\circ\text{C}/\text{min}$ . The DSC curves taken for the analysis were obtained from the second run.

The morphology of the PUF samples was studied with a Jeol JSM 5200 scanning electron microscope. The samples were cryogenically fractured and gold coated before scanning. The accelerating voltage was 25 kV. The JSM 5200 was used to observe the size of the cells on the PUF samples, which was measured with an Image-Pro Plus image analyzer and averaged, except for the largest and smallest cells.

The mechanical properties of the PUF samples were measured under ambient conditions with an Instron UTM (model 4467, Canton, OH). A compressive test was performed according to ASTM D 1621. The size of the specimen was  $30 \times 30 \times 30 \text{ mm}$  (width  $\times$  length  $\times$  thickness), and the speed of crosshead movement

was  $3.00 \text{ mm}/\text{min}$ . A flexural test was performed according to KS M3830. The size of the specimen was  $25 \times 120 \times 20 \text{ mm}$  (width  $\times$  length  $\times$  thickness). The span distance was 100 mm, and the crosshead speed was  $10.00 \text{ mm}/\text{min}$ . A tensile test was performed according to ISO 1926. The size of the specimen was  $20 \times 100 \times 6 \text{ mm}$  (width  $\times$  length  $\times$  thickness). The gauge length was 50 mm, and the crosshead speed was  $2.54 \text{ mm}/\text{min}$ . The strengths of five specimens per sample were measured and averaged for each mechanical test.

## RESULTS AND DISCUSSION

### Density measurements

The densities of the PUF samples (PUF X–Y) blown by distilled water are presented in Figure 1. When the distilled water increases from 0.5 to 3.0 php, the densities of the PUF samples (PUF 0–Y) decrease from 173.7 to  $41.7 \text{ kg}/\text{m}^3$ , respectively, at the 0 php butanediol content, as shown in Figure 1. When the butanediol increases from 0 to 40 php, the densities of the PUF samples (PUF X–1.0) increase from 109.1 to  $180.9$

**TABLE III**  
**Chemical Compositions<sup>a</sup> of Polyurethane Foam (PUF X-Y, X = 30-40)<sup>b</sup> Blown by Distilled Water**

PUF sample code	Polymeric 4,4'-diphenylmethane diisocyanate <sup>c</sup>	1,4-Butanediol	Distilled water
PUF30-0.5	160.9	30	0.5
PUF30-1.0	168.6	30	1.0
PUF30-1.4	174.8	30	1.4
PUF30-1.5	176.4	30	1.5
PUF30-1.7	179.4	30	1.7
PUF30-2.0	184.2	30	2.0
PUF30-2.1	185.7	30	2.1
PUF30-2.5	192.0	30	2.5
PUF30-2.9	198.1	30	2.9
PUF30-3.0	199.8	30	3.0
PUF40-0.5	191.9	40	0.5
PUF40-1.0	199.7	40	1.0
PUF40-1.1	201.2	40	1.1
PUF40-1.5	207.5	40	1.5
PUF40-1.9	213.6	40	1.9
PUF40-2.0	215.3	40	2.0
PUF40-2.3	219.9	40	2.3
PUF40-2.5	223.1	40	2.5
PUF40-3.0	230.9	40	3.0
PUF40-3.3	235.4	40	3.3

<sup>a</sup> Parts by weight based on 100 parts of the polyether polyol.

<sup>b</sup> X denotes the amount of 1,4-butanediol and Y denotes the amount of distilled water.

<sup>c</sup> An excess PMDI of 5 wt % was used for the completion of the polyurethane reaction.

kg/m<sup>3</sup>, respectively, at the 1.0 php water content. Figure 1 suggests that the densities of the PUF samples decrease with the water content and increase with the butanediol content.

**Morphology**

The cross-sectional surfaces of the PUF samples observed with SEM are shown in Figures 2. Figure 2(a,b)

shows the micrographs of PUF 10-0.5 (density = 208.5 kg/m<sup>3</sup>) and PUF 10-3.0 (density = 44.1 kg/m<sup>3</sup>), respectively, blown by distilled water. The cellular structures of the PUF samples were observed in the free-rising direction. Observe from Figure 2 that the cell size of the PUF sample increases from 115 to 258 μm with the increase of the distilled water from 0.5 to 3.0 php, respectively, at the 10 php butanediol content.

**TABLE IV**  
**Chemical Compositions<sup>a</sup> of Polyurethane Foam (SUR-Z)<sup>b</sup> with Surfactant [Poly(siloxane ether)] Content**

PUF sample code	Polyether polyol	Polymeric 4,4'-diphenylmethane diisocyanate <sup>c</sup>	1,4-Butanediol	Distilled water	Triethylene diamine <sup>d</sup>	Poly(siloxane ether) <sup>e</sup>
SUR-0	100	145.3	20	1.5	0.7	0
SUR-0.07	100	145.3	20	1.5	0.7	0.07
SUR-0.13	100	145.3	20	1.5	0.7	0.13
SUR-0.20	100	145.3	20	1.5	0.7	0.20
SUR-0.27	100	145.3	20	1.5	0.7	0.27
SUR-0.33	100	145.3	20	1.5	0.7	0.33
SUR-0.40	100	145.3	20	1.5	0.7	0.40
SUR-0.60	100	145.3	20	1.5	0.7	0.60
SUR-0.80	100	145.3	20	1.5	0.7	0.80
SUR-1.00	100	145.3	20	1.5	0.7	1.00
SUR-1.33	100	145.3	20	1.5	0.7	1.33
SUR-1.67	100	145.3	20	1.5	0.7	1.67
SUR-2.00	100	145.3	20	1.5	0.7	2.00

<sup>a</sup> Presented in parts by weights based on 100 parts of the polyether polyol.

<sup>b</sup> Z denotes the amount of the surfactant.

<sup>c</sup> Excess PMDI of 5 weight % was used for the completion of the polyurethane reaction.

<sup>d</sup> Dissolved in dipropylene glycol by 33 wt%.

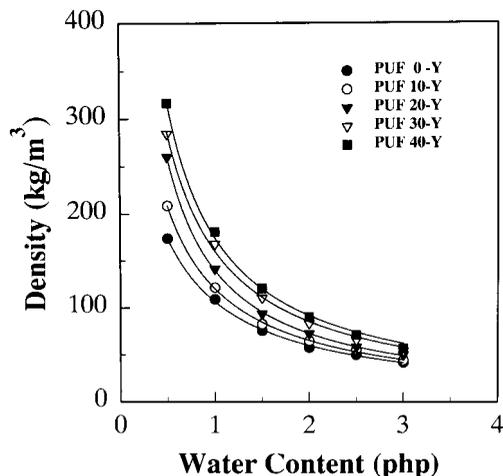
<sup>e</sup> Surfactant.

The size of the PUF cell is important in the mechanical properties and thermal conductivity of PUF.<sup>1,2,13,14</sup> A chemical blowing agent such as distilled water generates carbon dioxide through the chemical reaction with diisocyanate accompanying the exothermic reaction heat. Because of the increase of the temperature of the reactants' mixture, the concentration of blowing gas in the mixture exceeds its solubility limit and a nucleation of bubbles begins. During the rise time, the already formed bubbles grow and new bubbles nucleate.<sup>1,2,13,14</sup> The increase of distilled water generates more bubbles, and the increased bubbles coagulate much more with each other. Therefore, the cell size of the PUF increases with the increase of the distilled water content.<sup>14</sup>

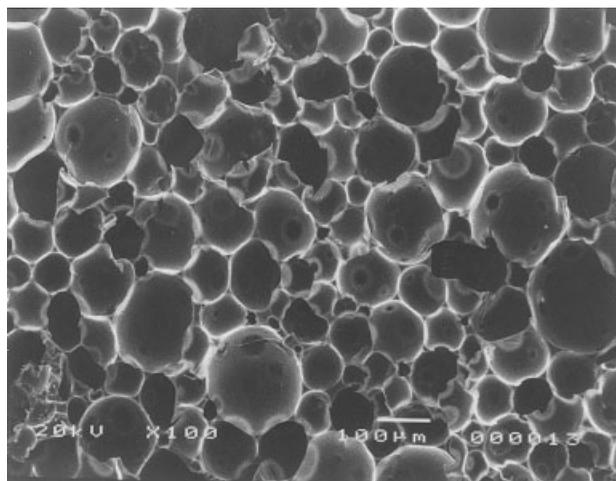
Figure 3(a,b) shows the micrographs of PUF 30–0.5 (density = 284.3 kg/m<sup>3</sup>) and PUF 30–3.0 (density = 54.1 kg/m<sup>3</sup>), respectively. The figure also shows that the cell size of the PUF sample increases from 113 to 255  $\mu\text{m}$  with the increase of distilled water from 0.5 to 3.0 php, respectively, at the 30 php butanediol content. From Figures 2 and 3 it is observed that the cell size appears to be equal between the Figure 2(a) and Figure 3(a), for which the butanediol contents are 10 and 30 php, respectively. Therefore, this suggests that the cell size of the PUF is not affected by the butanediol content.

### Thermal analysis

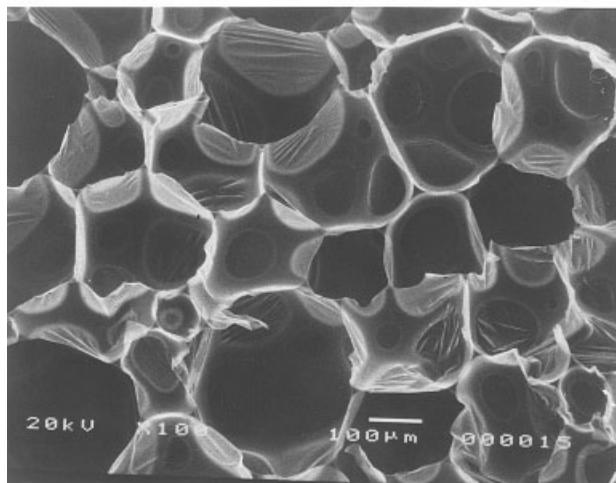
The glass-transition temperatures ( $T_g$ ) of the PUF samples measured by DSC are shown in Figure 4. Note from Figure 4 that when the distilled water increases from 0.5 to 3.0 php, the  $T_g$  values of the PUF samples (PUF 0–Y) increase from 49.5 to 80.8°C, respectively, at the 0 php butanediol content. When the butanediol increases from 0 to 40 php, the  $T_g$  values of the PUF



**Figure 1** The effect of distilled water on the PUF density (PUF X–Y).



(a)

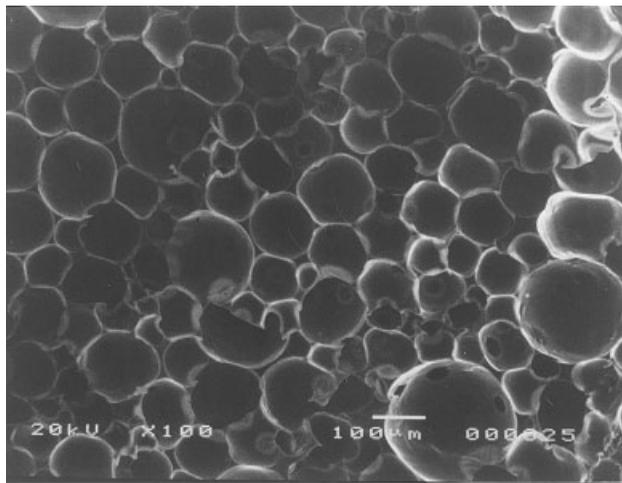


(b)

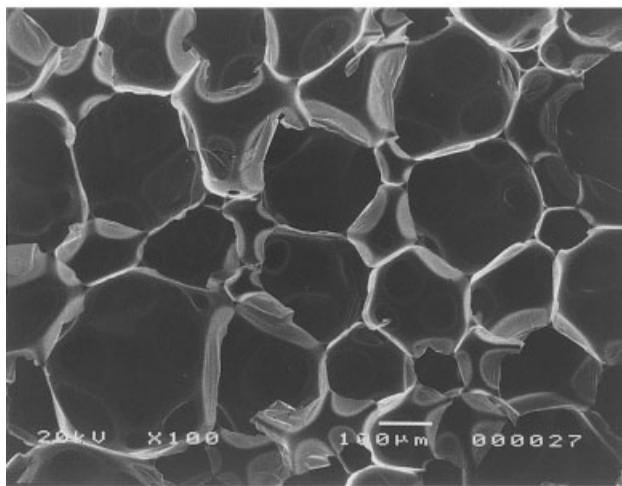
**Figure 2** Scanning electron micrographs of the PUF samples: (a) PUF 10–0.5 (density = 208.5 kg/m<sup>3</sup>) and (b) PUF 10–3.0 (density = 44.1 kg/m<sup>3</sup>).

samples (PUF X–1.0) increase from 62.1 to 95.4°C, respectively, at the 1.0 php water content.

Distilled water as a chemical blowing agent reacts with the isocyanate group to generate carbon dioxide and polyurea with the release of exothermic reaction heat. Polyurea is known to be more rigid than PU.<sup>1,2</sup> Therefore, when distilled water is used as a blowing agent, the chain mobility of the polymer chains can be decreased and the  $T_g$  of the polymer may increase.<sup>1,2,11</sup> In addition, a urea group can react with PMDI to generate biuret, which introduces additional networks to the PUF samples.<sup>1–3</sup> Therefore, when distilled water is used as a blowing agent, the increases of the  $T_g$  of the PUF may be due to the introduction of a polyurea and an additional network in the PUF.



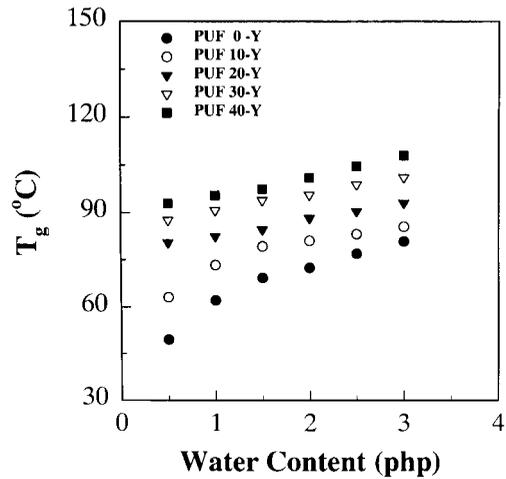
(a)



(b)

**Figure 3** Scanning electron micrographs of the PUF samples: (a) PUF 30-0.5 (density = 284.3 kg/m<sup>3</sup>) and (b) PUF 30-3.0 (density = 54.1 kg/m<sup>3</sup>).

Figure 4 shows that the  $T_g$  values of the PUF samples are increased with an increase in butanediol from 0 to 40 php at an equal content of distilled water. It is known that an increase of the butanediol increases the hard segment content of the PUF samples.<sup>1</sup> The hard segment is organized with urethane and a urea group, and the soft segment is organized with a polyol group. The urethane and urea group are more rigid than the polyol group. In addition, butanediol, which is used as a chain extender, acts like a crosslinking agent, so it introduces additional networks into the PUF sample.<sup>1</sup> Therefore, when the amount of butanediol is increased, the increase of the  $T_g$  of PUF may be due to the increase of the hard segment content and the additional networks in the PUF.

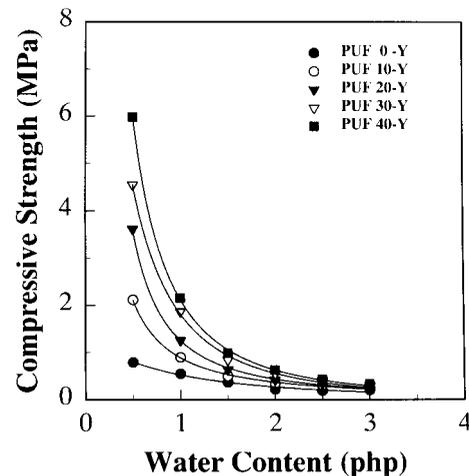


**Figure 4** The glass-transition temperatures ( $T_g$ ) of the PUF samples with distilled water (PUF X-Y).

**Mechanical properties**

Figure 5 shows the compressive strength of the PUF samples with the distilled water content. When the distilled water increases from 0.5 to 3.0 php, the compressive strength of the PUF samples (PUF 0-Y) decreases from 0.79 to 0.20 MPa, respectively, at the 0 php butanediol content. However, when the butanediol increases from 0 to 40 php, the compressive strength of the PUF samples (PUF X-1.0) increases from 0.55 to 2.16 MPa, respectively, at the 1.0 php water content. It is generally known that the mechanical properties of a cellular material mainly depend on its density. A simple power law can be used to depict the relationship between the mechanical properties, such as the compressive strength and the density.<sup>1,2,15-17</sup>

$$\text{strength} = A(\text{density})^B \tag{1}$$



**Figure 5** The compressive strength of the PUF samples with distilled water (PUF X-Y).

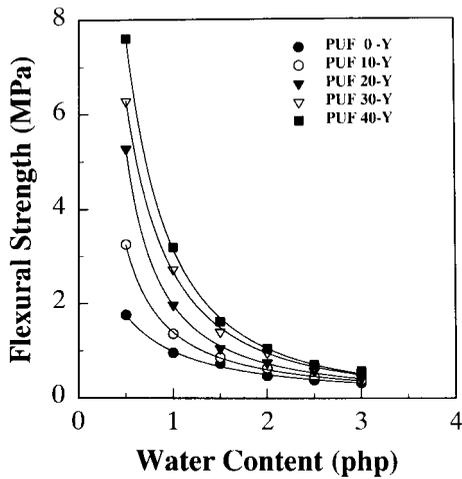


Figure 6 The flexural strength of the PUF samples with distilled water (PUF X-Y).

where  $A$  is a constant related to the temperature and physical properties of the resin and  $B$  is related to the deformation mechanics of cellular materials. The results of the density measurement demonstrate that the density of the PUF samples decreases with the water content and increases with the butanediol content. Therefore, the results of the density measurement and eq. (1) suggest that the compressive strength of the PUF samples decreases with the water content and increases with the butanediol content.

Figures 6 and 7 show the flexural and tensile strengths, respectively, of the PUF samples with the distilled water. In these figures the flexural and tensile strengths of the PUF samples decrease with the water and increase with the butanediol, which is similar to the results of the compressive strength of the PUF samples.

Figures 8, 9, and 10 show the compressive strength, flexural strength, and tensile strength, respectively, of

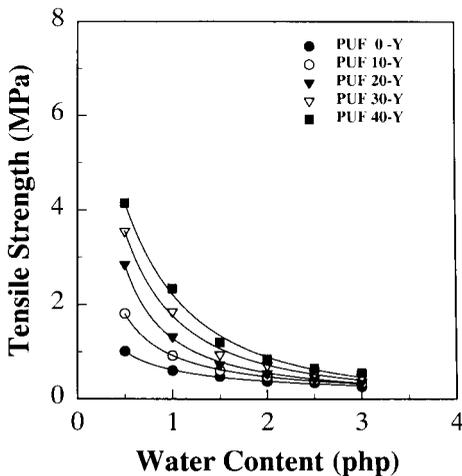


Figure 7 The tensile strength of the PUF samples with distilled water (PUF X-Y).

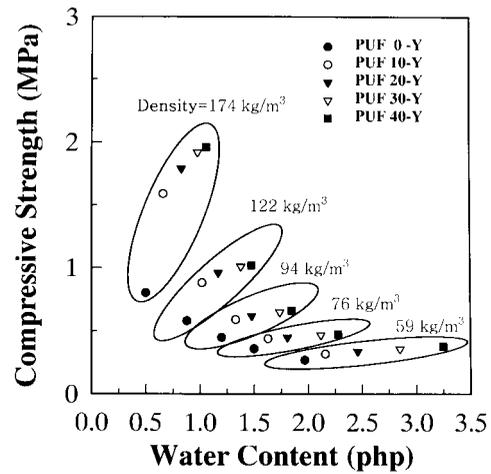


Figure 8 The compressive strength of the PUF samples with distilled water at equal density (PUF X-Y).

the PUF samples having equal density as the distilled water. Additional experiments were conducted in order to plot the compressive, flexural, and tensile strengths of the PUF samples versus the water content at the same density. The detailed compositions of the experimental results shown in Figures 8–10 are expressed in Tables II and III. As shown in Figure 8, when the density of the PUF samples is equal, the compressive strength of the PUF samples increases with the increase of the distilled water content. For example, for the PUF samples having a density of  $122 \text{ kg/m}^3$ , the compressive strength of the PUF samples increases from  $0.58$  to  $1.02 \text{ MPa}$  with the increase of the distilled water from  $0.88$  to  $1.48 \text{ php}$ , respectively. As mentioned previously, distilled water is known to produce additional crosslinks. In addition, the hard segment content of the PUF samples increases with the increase of the distilled water because additional PMDI is needed for the reaction with the distilled

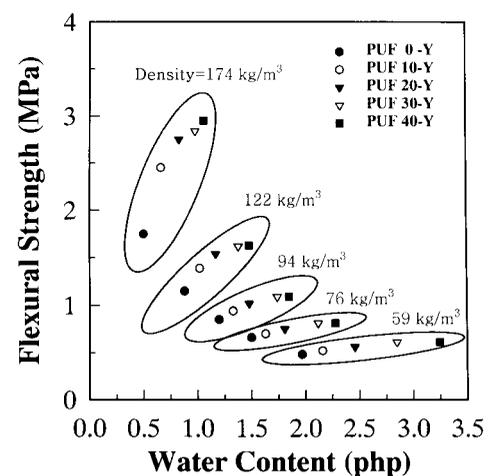
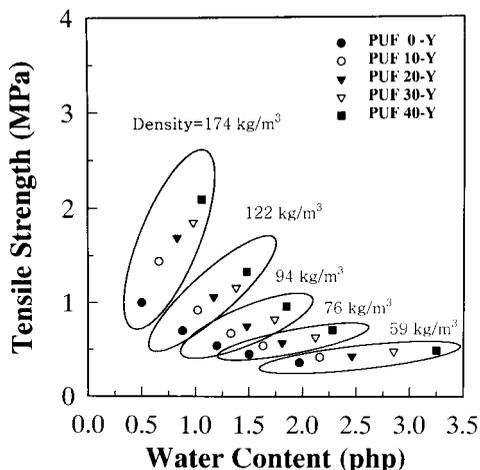


Figure 9 The flexural strength of the PUF samples with distilled water at equal density (PUF X-Y).

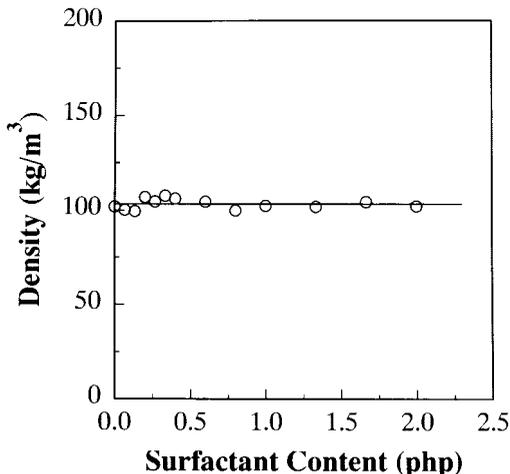


**Figure 10** The tensile strength of the PUF samples with distilled water at equal density (PUF X-Y).

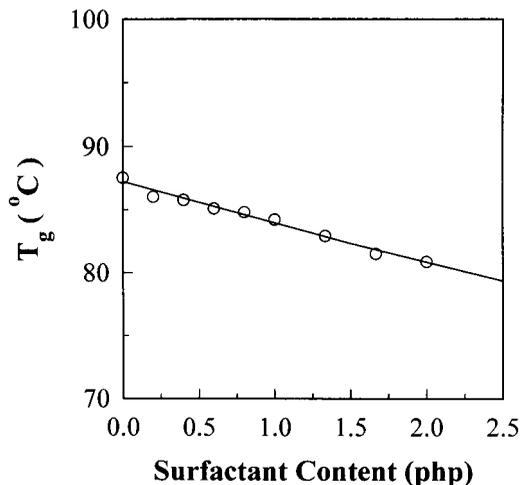
water. Therefore, it is possible that the increase of the compressive strength of the PUF samples having equal density may be due to the increase of rigid polyurea, the biuret produced by the reaction between distilled water and PMDI, and the hard segment. Figures 9 and 10 demonstrate that both the flexural and tensile strength of the PUF samples having equal density increase as the distilled water increases, which is similar to the results of the compressive strength of the PUF samples.

**Effects of surfactant on properties of PUF**

Table IV shows the chemical compositions of the PUF samples that are used for investigating the effects of surfactant on the properties of PUF. Figure 11 shows the effect of the surfactant on the density of the PUF sample. We can observe from the figure that the density of the PUF samples (SUR-Z) is about 103 kg/m<sup>3</sup>



**Figure 11** The effect of the surfactant on the PUF density (SUR-Z).



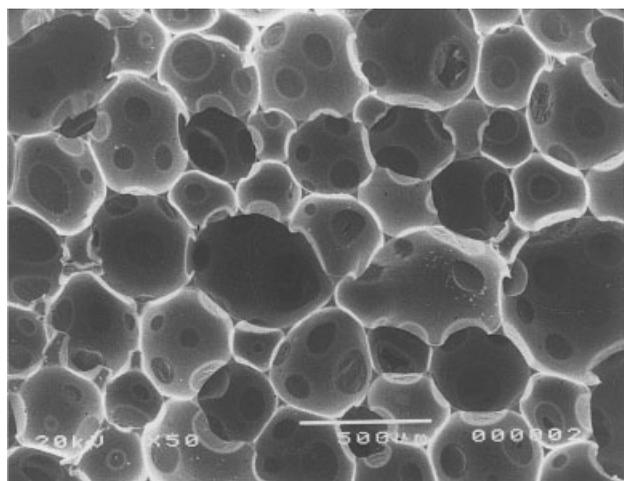
**Figure 12** The effect of the surfactant on the glass-transition temperatures ( $T_g$ ) of the PUF samples (SUR-Z).

and it does not change significantly with the surfactant content.

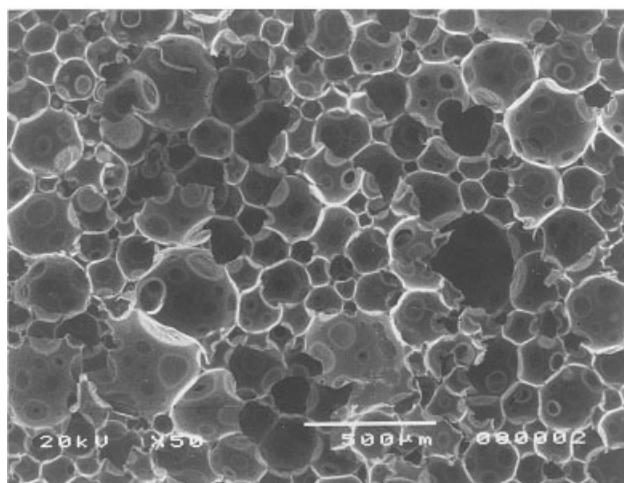
The effect of the surfactant on the  $T_g$  values of the PUF samples is shown in Figure 12. The  $T_g$  values of the PUF samples decrease from 87.5 to 80.9°C as the amount of the surfactant increases from 0 to 2.0 php, respectively. For the mixing between the two miscible components, one component acts as a plasticizer to the other.<sup>18</sup> Therefore, adding the surfactant to the PUF reduces the  $T_g$  of PUF.

Figure 13 shows the micrographs of the PUF samples with different surfactant contents. The cell size of the PUF samples is 360, 146, and 142  $\mu\text{m}$  at 0, 0.33, and 2.00 php surfactant contents, respectively [Fig. 13(a-c)]. The cell size decreases from 360 to 146  $\mu\text{m}$  with an increase in the surfactant from 0 to 0.33 php, respectively, but the cell size does not change significantly when the surfactant content exceeds 0.33 php. In this study poly(siloxane ether) was used as a surfactant in the preparation of the PUF samples. It is known that this silicone surfactant lowers the surface tension between cells, and it stabilizes the cell walls.<sup>1-3</sup> The silicone surfactant prevents the coalescence of the PUF cell, so it makes the cell size smaller. It is general knowledge that a PUF with a small cell structure shows good mechanical properties and low thermal conductivity.<sup>1-3</sup>

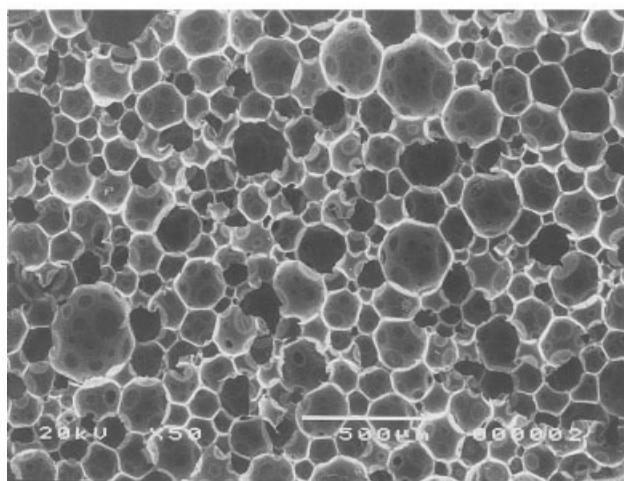
The compressive strength, flexural strength, and tensile strength of the PUF samples with equal densities are shown in Figure 14. The maximum mechanical strength is observed with the 0.33 php surfactant content, and the maximum strength may be related to the results obtained from the morphology and thermal analysis studies. The increase of the mechanical strength from the 0 to 0.33 php surfactant content is attributed to the decrease of the cell size of the PUF samples, and the decrease of the mechanical strength



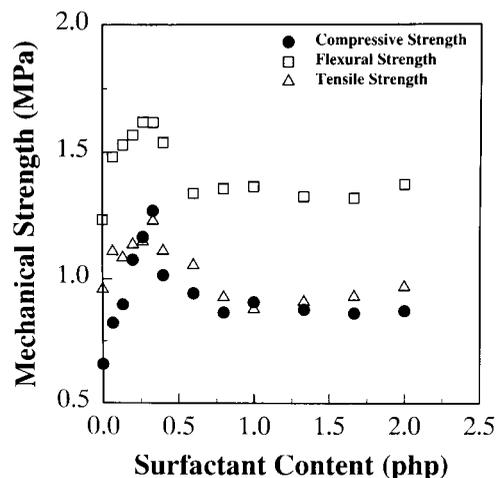
(a)



(b)



(c)



**Figure 14** The mechanical strength of the PUF samples with the surfactant at equal density with the water content (SUR-Z).

with a surfactant content of more than 0.33 php may be due to the plasticized effect of the PUF samples.

## CONCLUSIONS

Rigid PUFs were prepared with PMDI, polyether polyol, 1,4-butanediol, silicone surfactant, and distilled water as a blowing agent. The density of the PUF samples was decreased from 173.7 to 41.7 kg/m<sup>3</sup> with an increase in water from 0.5 to 3.0 php, respectively, at 0 php butanediol. We concluded from the results of the density measurements that the density of the PUF samples decreases with the water and increases with the butanediol.

The results of the morphology by SEM demonstrated that the cell size of the PUF samples increased from 115 to 258 μm with an increase in water from 0.5 to 3.0 php, respectively, at 10 php butanediol, and from 113 to 255 μm, respectively, at 30 php butanediol. Therefore, we concluded that the cell size of the PUF increases with the water and the cell size is not affected by the butanediol.

As seen in the DSC results, the  $T_g$  values of the PUF samples were increased from 49.5 to 80.8°C with an increase in water from 0.5 to 3.0 php, respectively, at 0 php butanediol. In addition, the  $T_g$  values of the PUF samples increased from 62.1 to 95.4°C with an increase in butanediol from 0 to 40 php, respectively, at 1.0 php water. Therefore, we concluded that the  $T_g$  of the PUF sample increases with the water and butanediol.

As seen in the results of the mechanical properties by the UTM, the compressive strength of the PUF

**Figure 13** Scanning electron micrographs of the PUF samples with surfactant (SUR-Z): (a) SUR-0, (b) SUR-0.33, and (c) SUR-2.00.

samples decreased from 0.79 to 0.20 MPa with an increase in water from 0.5 to 3.0 php, respectively, at 0 php butanediol. The compressive strength of the PUF samples increased from 0.55 to 2.16 MPa with an increase of butanediol from 0 to 40 php, respectively, at 1.0 php water. Therefore, we concluded that the compressive strength of the PUF samples decreases with the water and increases with the butanediol.

The compressive strength of the PUF samples having an equal density of 122 kg/m<sup>3</sup> increased from 0.58 to 1.02 MPa with an increase in water from 0.88 to 1.48 php, respectively. We suggest that the increase in the compressive strength of the PUF samples was related to the formation of rigid polyurea and additional crosslinks that arose from biuret formation by a reaction between distilled water and PMDI. The flexural strength and the tensile strength of the PUF samples showed similar behavior as the results of the compressive strength of the PUF samples.

The study of the surfactant effect on the morphology of the PUF clarified that the cell size of the PUF samples was decreased from 360 to 146  $\mu\text{m}$  with an increase in surfactant from 0 to 0.33 php, respectively, but the cell size did not change significantly when the surfactant exceeded 0.33 php.

The investigation of the surfactant effect on the compressive strength, flexural strength, and tensile strength of the PUF samples showed that the maximum mechanical strength was with 0.33 php surfactant. We suggest that the increase of the mechanical strength of the PUF samples from 0 to 0.33 php surfactant is attributable to the decrease of the cell size of the PUF samples and the decrease of the mechanical

strength with more than 0.33 php surfactant may be due to the plasticized effect of the PUF samples.

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