

# Properties of Water-Blown Rigid Polyurethane Foams with Reactivity of Raw Materials

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**ABSTRACT:** Rigid polyurethane foams (PUFs) were prepared from polymeric 4,4-diphenylmethane diisocyanate (PMDI; having functionality of 2.9), polyether polyols, silicone surfactant, amine catalysts, and distilled water. The effects of reactivity on the properties such as density, compressive and flexural strength, and glass-transition temperature ( $T_g$ ) of the PUF samples were studied. The kinetic rate of forming the PUF samples was increased with the catalyst and water content. With increasing OH value and functionality of the polyols, the density and compressive strength of the PUF samples also increased. For the PUF samples synthesized with polyols having high functionality (>5), the flexural strength of the PUF samples decreased with the functionality of the polyols. With increasing OH value and

functionality of the polyols, the  $T_g$  of the PUF increased because of an increase in the degree of crosslinking of the PUF samples. The  $T_g$  value and compressive strength of the PUF samples were observed to increase with the NCO index. From this result, it was suggested that the increase in the  $T_g$  value and compressive strength of the PUF samples may be attributable to the additional crosslinks that arose from allophanate and biuret formation by the supplementary reactions of excess PMDI. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2334–2342, 2004

**Key words:** reactive processing; glass transition; OH value; foams; NCO index

## INTRODUCTION

A polymer containing a functional group of urethane (–NHCOO–) or urea (–NHCONH–) is called a polyurethane. With the chemical component and composition, polyurethanes can be manufactured in an extremely wide range of grades, in densities from 6 to 1220 kg/m<sup>3</sup>, such as adhesives, binders, coatings, paints, elastomers, flexible foams, and rigid foams.<sup>1</sup> Polyurethane foams (PUFs) are generally created from a two-phase system that consists of a solid polymer matrix and a gaseous phase, gained through blowing agents. The cell geometry may be either open or closed cell. Closed-cell foams are most suitable for thermal insulation and are generally rigid. The foaming of polymeric materials can be carried out by mechanical, chemical, or physical means. Distilled water is one of the widely used chemical blowing agents. Distilled water reacts with diisocyanate, generating carbon dioxide, whereas polyol reacts with diisocyanate. PUF is based on the reaction of diisocyanate with polyol. The

reaction is exothermic and the reaction heat can accelerate the foaming reaction.<sup>1–3</sup>

The difference in reactivity of forming PUF is induced by differences in kinetic rate, which is increased by catalyst and temperature, and in the type and content of major reactants that are polyols and isocyanates.<sup>1</sup> The difference in the type and content of major reactants, in addition, causes a difference in the crosslinking density of various PUFs.<sup>1</sup>

Substitutes for chlorofluorocarbons and hydrochlorofluorocarbons such as hydrofluorocarbon, cyclopentane, and distilled water have been developed and their applications for cellular materials have been studied.<sup>3–8</sup> For establishing the PUF system, however, it is necessary to understand the effects of raw materials used for synthesizing water-blown PUF 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 and surfactant on thermal properties, mechanical properties, and morphology of the rigid PUFs blown by distilled water.<sup>10,11</sup>

In this study, the effects of reactivity on the physical, thermal, morphological, and mechanical properties of the rigid PUFs blown by distilled water were investigated. The rigid PUFs were prepared from the polymeric 4,4-diphenylmethane diisocyanate (PMDI), with a functionality of 2.9, and the polyether polyols having

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TABLE I  
Characteristics of the Polyether Polyols Used in This Study<sup>a</sup>

Polyether polyols <sup>b</sup>	Functionality	Hydroxyl value	Equivalent weight (g/mol <sup>-1</sup> )
Polyol 3-290	3	290	193
Polyol 3-400	3	400	140
Polyol 3-670	3	670	84
Polyol 4-400	4	400	140
Polyol 5-360	5	360	156
Polyol 5-450	5	450	125
Polyol 5-490	5	490	114
Polyol 6-490	6	490	114

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

<sup>b</sup> Supplied from KPC Co. (Ulsan, Korea).

various hydroxyl values (OH values) and functionalities.<sup>1</sup> Distilled water was used as a chemical blowing agent. Thermal properties, such as the glass-transition temperature ( $T_g$ ), cellular structure, and the mechanical properties such as compressive and flexural strength of the PUF samples, were studied with differential scanning calorimetry (DSC), field emission scanning electron microscopy (FE-SEM), and a universal testing machine (UTM), respectively.

## EXPERIMENTAL

### Materials

The materials used in this study were obtained from commercial sources. The polymeric MDI (PMDI) was supplied from BASF Korea Co. (Seoul, Korea). The polyether polyols, having various OH values and functionalities, were supplied from KPC Co. (Ulsan, Korea). The characteristics of the polyols used in this study are shown in Table I. Distilled water, used as a chemical blowing agent, was generated in our laboratory. Triethylene diamine dissolved in dipropylene glycol to 33 wt % and pentamethyldiethylene triamine, used as catalysts, were supplied from Air Products and Chemicals, Inc. (Allentown, PA). Polysiloxane ether, used as a surfactant, was supplied from Osi Specialties (now GE Bayer Silicones, Erkrath, Germany). The polyether polyols 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."<sup>10,11</sup> All chemicals were charged to a reactor and mixed for 60 s with a brushless-type stirrer, consisting of a ring-guard propeller for protecting the wall or sensors in the reactor, at ambient condition. 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. Distilled water was used as a blowing agent. Three replications for all the foams were executed.

To investigate the kinetic rate of forming PUF, triethylene diamine dissolved in dipropylene glycol to 33 wt % (gelling catalyst) and pentamethyldiethylene triamine (blowing catalyst) were used as catalysts. The amount of each catalyst was varied from 0.2 to 1.8 parts per 100 polyether polyol by weight (php) with the increment of 0.4 php, whereas the amounts of polyether polyol and polysiloxane ether were fixed at 100 and 1.0 php, respectively. The amount of distilled water was varied from 1.0 to 3.5 php. The amount of PMDI required for the reaction with polyether polyol and distilled water was calculated from their equivalent weights. For the completion of the reaction, excess PMDI (~ 5 wt %; NCO/OH = 1.05) was used.

To investigate the effects of the polyols on the properties of PUFs, various polyether polyols, shown in Table I, were used. The amount of each polyol was fixed at 100 php and the amounts of triethylene diamine and polysiloxane ether were fixed at 0.7 and 1.0 php, respectively. The amount of distilled water was varied from 1.0 to 3.5 php, at 0.5 php increments. The amount of PMDI required for the reaction with polyether polyol and distilled water was calculated from their equivalent weights. For the completion of the reaction, excess PMDI (~ 5 wt %; NCO/OH = 1.05) was used. In the sample code (POL F-OH) used in this study, F and OH denote the functionality and the OH value of the added polyol, respectively.

To investigate the effects of the PMDI on the properties of the PUF, the NCO index (% NCO/OH) was varied from 90 to 135. For varying NCO index from 90 to 135, the amount of PMDI, which was calculated from equivalent weights of polyether polyol and distilled water, was varied from 112.7 to 169.1 php, respectively. The amounts of polyether polyol, triethylene diamine, polysiloxane ether, and distilled water were fixed at 100, 0.7, 1.0, and 2.0 php, respectively.

TABLE II  
Effect of Catalysts on Kinetic Rate of Forming PUF

Catalyst content (php)	Water content (php)	Blowing catalyst <sup>a</sup>			Gelling catalyst <sup>b</sup>		
		Cream time (s)	Gel time (s)	Tack-free time (s)	Cream time (s)	Gel time (s)	Tack-free time (s)
0.2	1.0	45	480	780	51	225	378
0.6	1.0	28	293	400	48	158	335
1.0	1.0	24	210	250	37	108	200
1.4	1.0	17	142	195	26	72	173
1.8	1.0	14	106	153	21	55	141
0.2	3.5	32	359	713	49	232	302
0.6	3.5	22	191	372	35	120	239
1.0	3.5	17	159	253	26	85	210
1.4	3.5	15	91	170	18	72	152
1.8	3.5	13	62	141	16	59	130

<sup>a</sup> Pentamethyldiethylene triamine, supplied from Air Products and Chemicals, Inc.

<sup>b</sup> Triethylene diamine dissolved in dipropylene glycol to 33 wt %, supplied from Air Products and Chemicals, Inc.

## Measurements

The density of the PUF samples was measured according to ASTM D1622. The size of the specimen was 30 × 30 × 30 mm (width × length × thickness). The densities of five specimens per sample were measured and averaged.

The thermal property of the PUF samples was measured with a DSC7 differential scanning calorimeter (Perkin Elmer Cetus Instruments, Norwalk, CT). 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 30 to 220°C, at a heating rate of 20°C/min. After 20°C/min programmed cooling, the samples were reheated at a heating rate of 20°C/min. The DSC curves taken for the analysis were obtained from the second run.

The morphology of the PUF sample was studied with an S-4300SE field emission scanning electron microscope (Hitachi, Tokyo, Japan). The samples were cryogenically fractured and gold coated before scanning. The accelerating voltage was 25 kV. The S-4300SE was used to observe the size of the cells on the PUF samples, which was measured with an Image-Pro Plus image analyzer (Media Cybernetics, Silver Spring, MD) 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 D1621. The size of the specimen was 30 × 30 × 30 mm (width × length × thickness), and the speed of crosshead movement was 3.00 mm/min. A flexural test was performed according to KS M3830. The size of the specimen was 25 × 120 × 20 mm (width × length × thickness). The span distance was 100 mm, and the speed of crosshead movement was 10.00 mm/min. The strengths of five

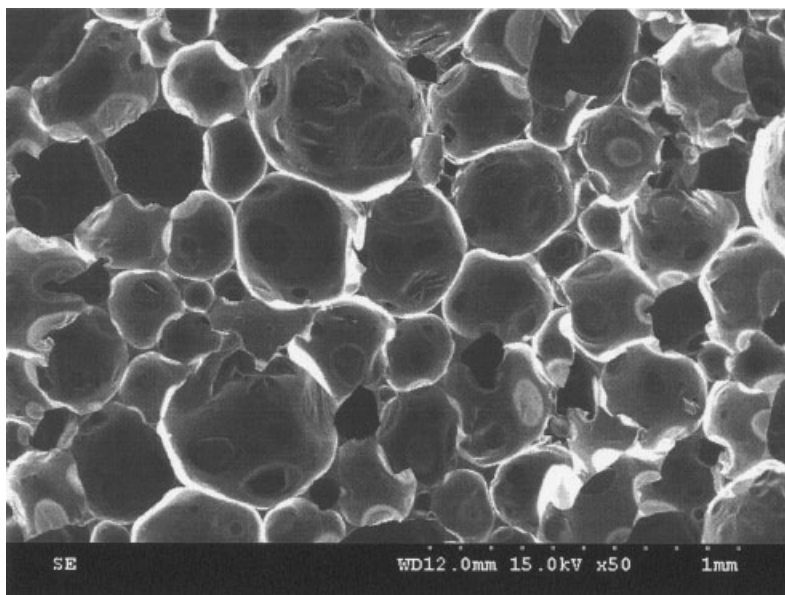
specimens per sample were measured and averaged for each mechanical test.

## RESULTS AND DISCUSSION

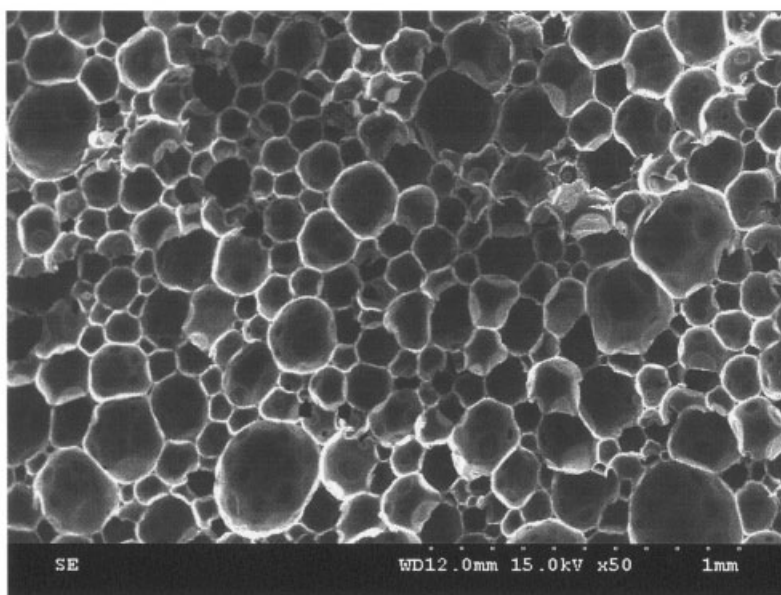
### Kinetic rate of PUF formation

The effect of a catalyst on the kinetic rate of forming the PUF samples is shown in Table II. The kinetic rate of forming the PUF was obtained from measuring cream time, gel time, and tack-free time. The cream time was the starting point of blowing and so was the time when the color of mixed reactants was brightened. The gel time was the starting point when the stable spatial shape was formed by the reaction of forming urethane and urea linkage and the crosslinking reaction. The tack-free time was the time when the perfectly crosslinked PUF could be detached from the mold. From Table II, the kinetic rate of forming the PUF is shown to increase with an increase in catalysts content regardless of the type, either blowing or gelling catalyst. Moreover, the kinetic rate of forming the PUF increases with an increase in water content because the temperature of the reactants is increased by the heat of reaction exerted by the reaction between water and PMDI. In addition, the blowing catalyst promotes the blowing reaction, relatively, which was confirmed by faster cream time, and the gelling catalyst promotes the gelling reaction, relatively, which was confirmed by faster gel time and tack-free time.

Figure 1 shows, in addition, the effect of a catalyst on the cell morphology of the PUF sample. The figure shows that the cell size of the PUF sample decreases from 307 to 132  $\mu\text{m}$  with the increase of the gelling catalyst from 0.6 to 1.8 php, respectively. Although not shown in Figure 1, the blowing catalyst shows a similar behavior, which may be attributable to an increase



(a)



(b)

**Figure 1** Scanning electron micrographs of the PUF samples with gelling catalyst content: (a) 0.6 php, (b) 1.8 php.

in the kinetic rate of forming blowing gas bubble with the catalyst content regardless of the type of catalyst.

Figures 2 and 3 show the effects of catalyst on the density and compressive strength of the PUF sample. From these figures, it is observed that the type and content of the catalysts used in this study have no significant influence on either the density or the compressive strength of the PUF sample. Therefore, for the

water-blown PUF, a catalyst affects the kinetic rate of forming the PUF but not the density and compressive strength of the PUF.

#### **Effect of polyols on the properties of PUF**

Figures 4–8 show the effects of OH value and functionality of the polyols on the density, compressive

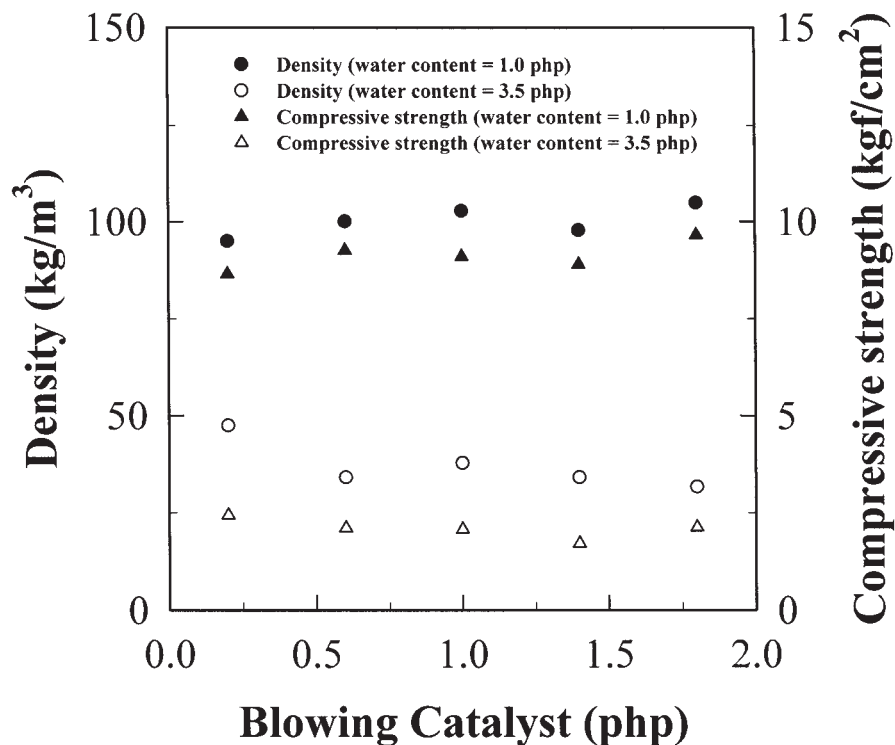


Figure 2 Density and compressive strength of the PUF samples with blowing catalyst content.

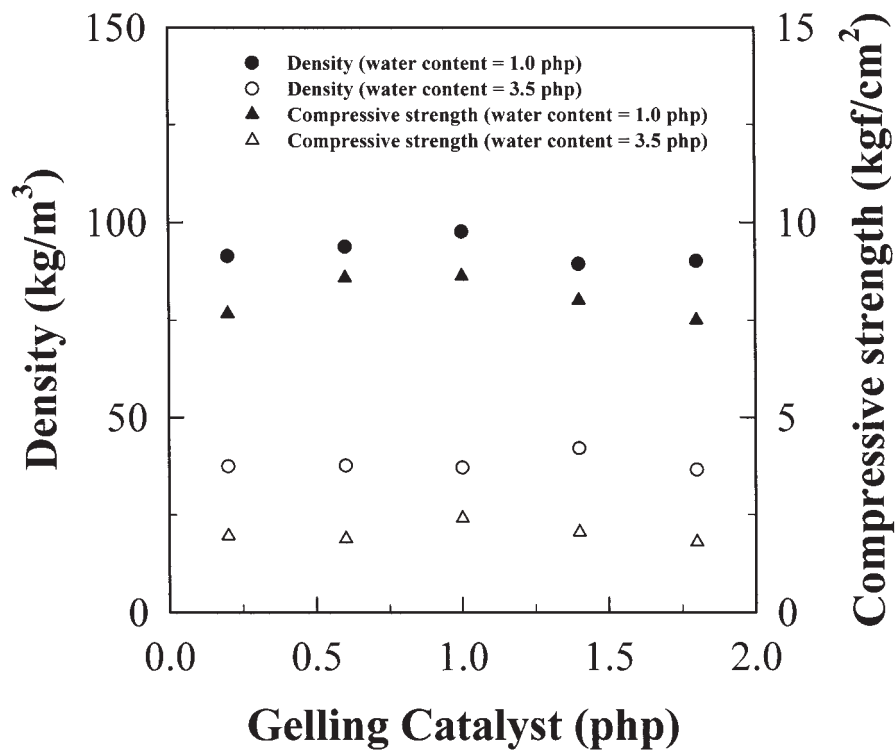


Figure 3 Density and compressive strength of the PUF samples with gelling catalyst content.

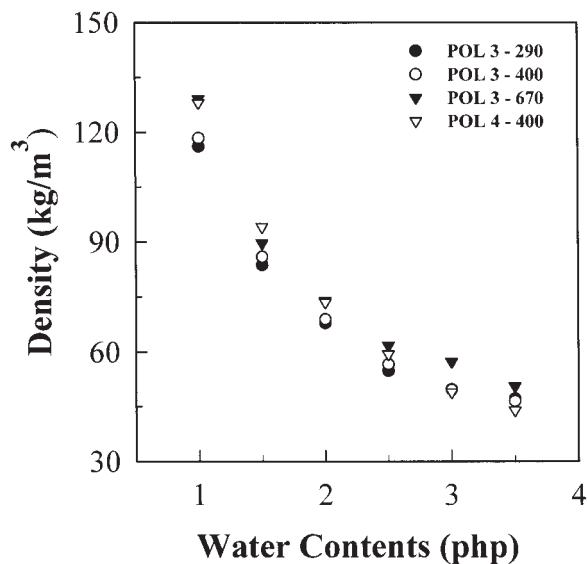


Figure 4 Effect of the polyols on the density of the PUF samples (POL F-OH).

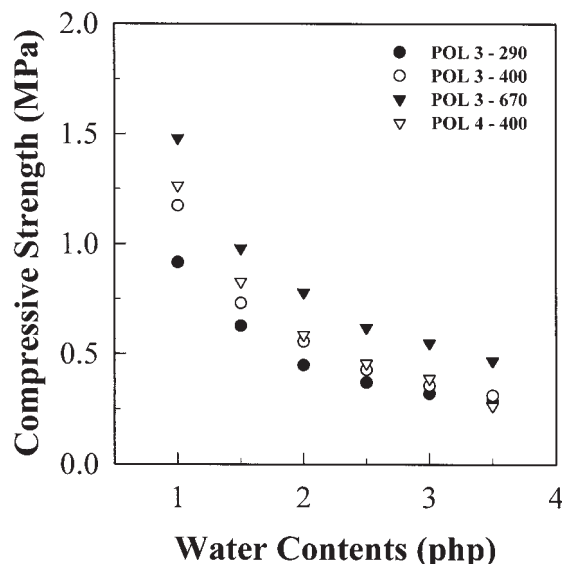


Figure 5 Effect of the polyols on the compressive strength of the PUF samples (POL F-OH).

and flexural strength, and glass-transition temperature of the PUF samples. The densities of the PUF samples (POL F-OH), blown by distilled water, are shown in Figure 4. From Figure 4, when the OH value of the polyols with trifunctionality increases from 290 to 670, the density of the PUF samples (POL 3-OH) increases from 116.1 to 129.2 kg/m<sup>3</sup>, respectively, at a 1.0 php water content. With increasing OH value of the polyol, the equivalent weight of the polyol is lower. The PMDI is needed more for the reaction with the polyol having the lower equivalent weight. Therefore, as the OH value of the polyol increases, the density of the PUF sample increases. In addition, from Figure 4, when the functionality of the polyols increases from 3 to 4, having an OH value of 400, the density of the PUF sample (POL F-400) increases from 118.4 to 128.1 kg/m<sup>3</sup>, respectively, at a 1.0 php water content. For the polyols having the functionality of 5 or 6, the density of the PUF samples showed similar behavior, with the result that is shown in Figure 4.

Figure 5 shows the compressive strength of the PUF samples (POL F-OH) with the distilled water content. From Figure 5, when the OH value of the polyols with trifunctionality increases from 290 to 670, the compressive strength of the PUF samples (POL 3-OH) increases from 0.92 to 1.48 MPa, respectively, at a 1.0 php water content. When the functionality of the polyols increases from 3 to 4, having an OH value of 400, the compressive strength of the PUF samples (POL F-400) increases from 1.17 to 1.26 MPa, respectively, at a 1.0 php water content. As the OH value and the functionality of the polyol increase, the degree of crosslinking of the PUF sample increases.<sup>1</sup> Therefore, the compressive strength of the PUF sample synthesized with the polyols having high OH value and

functionality increases because of an increase in the degree of crosslinking of the PUF sample. For the polyols having a functionality of 5 or 6, the compressive strength of the PUF samples showed similar behavior, with the result that is shown in Figure 5.

Figures 6 and 7 show the flexural strength of the PUF samples (POL F-OH) with the distilled water content. As shown in Figure 6, in the case where the functionality of the polyol is somewhat low, tri- or tetra-functionality shown in Figure 6, the flexural strength of the PUF samples showed similar behavior,

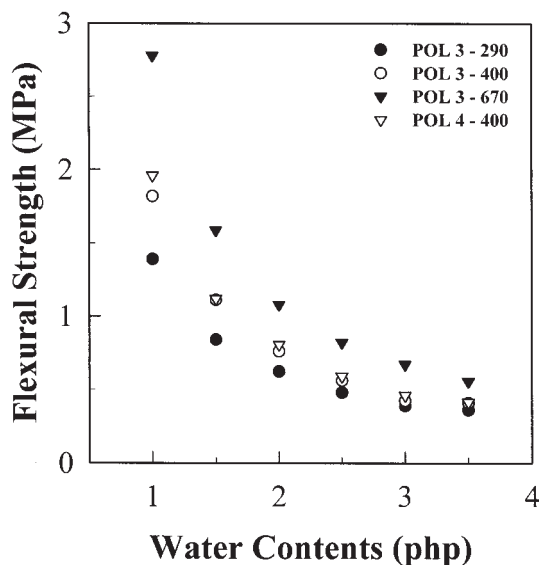
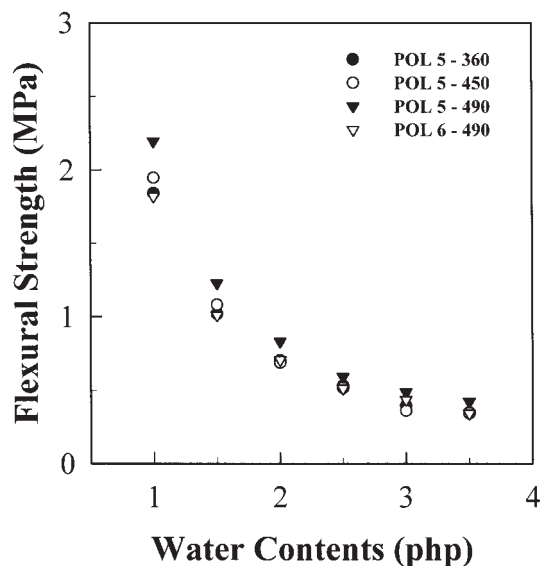


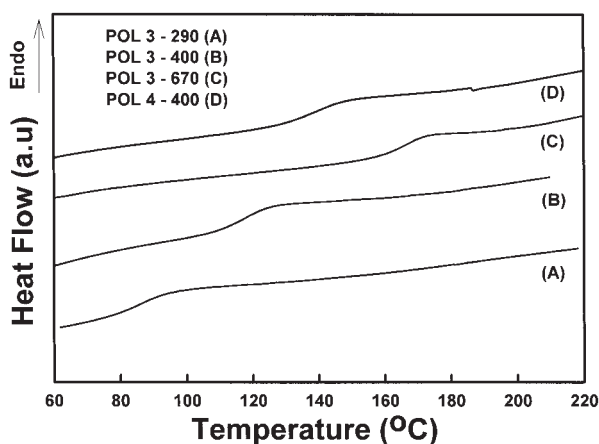
Figure 6 Effect of the polyols, having somewhat low functionality, on the flexural strength of the PUF samples (POL F-OH, where F is 3 or 4).



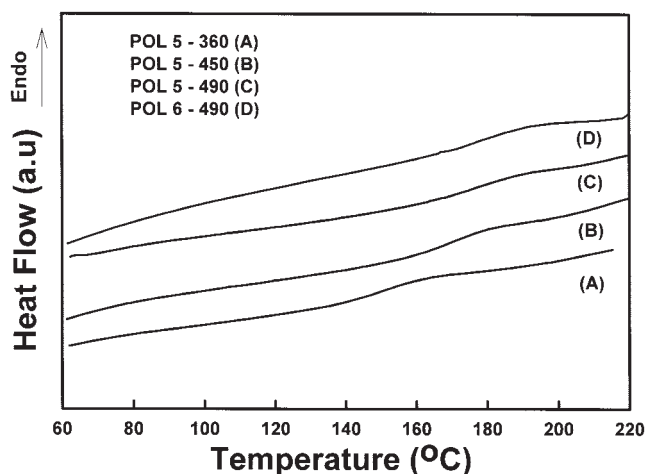
**Figure 7** Effect of the polyols, having somewhat high functionality, on the flexural strength of the PUF samples (POL F-OH, where F is 5 or 6).

with the result of the compressive strength shown in Figure 5. For the polyols having a functionality of 5 or 6, shown in Figure 7, the flexural strength of the PUF sample (POL 5-490) is shown to increase, compared to that of the PUF sample (POL 6-490), from 1.82 to 2.19 MPa, respectively, at a 1.0 php water content. As the functionality of the polyol increases, brittleness as well as degree of crosslinking of the PUF sample increase.<sup>1</sup> Therefore, excessive crosslinks somewhat decrease the flexural strength, rather than increase, the flexural strength of the PUF sample.

Glass-transition temperature ( $T_g$ ) of the PUF samples (POL F-OH) measured by DSC is shown in Figures 8 and 9. From Figure 8, for the PUF samples



**Figure 8** Effect of the polyols, having somewhat low functionality, on the glass-transition temperature ( $T_g$ ) of the PUF samples (POL F-OH, where F is 3 or 4).



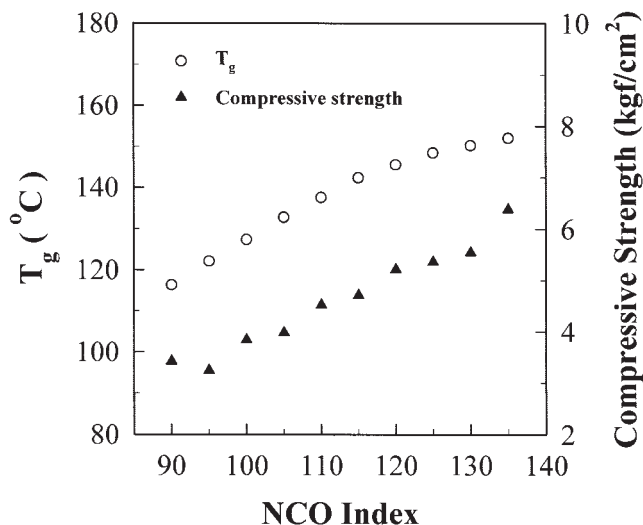
**Figure 9** Effect of the polyols, having somewhat high functionality, on the glass-transition temperature ( $T_g$ ) of the PUF samples (POL F-OH, where F is 5 or 6).

synthesized with the polyols having low functionality, such as POL 3-290 (A), POL 3-400 (B), POL 3-670 (C), and POL 4-400 (D), the  $T_g$  values of the PUF samples are shown to be 91, 125, 171, and 142°C, respectively. When the OH value of the polyols (tri-functionality) increases from 290 to 670, the  $T_g$  values of the PUF samples (POL 3-OH) increases from 91 to 171°C, respectively. When the functionality of the polyols increases from 3 (POL 3-400) to 4 (POL 4-400), having an OH value of 400, the  $T_g$  values of the PUF samples increase from 125 to 142°C, respectively.

From Figure 9, for the PUF samples synthesized with polyols having a high functionality, such as POL 5-360 (A), POL 5-450 (B), POL 5-490 (C), and POL 6-490 (D), the  $T_g$  values of the PUF samples are shown to be 163, 182, 187, and 190°C, respectively. Generally, as the degree of crosslinking of a polymer increases, the  $T_g$  of the polymer increases because of a decrease in chain mobility of the polymer chains.<sup>1,2,10,11</sup> Therefore, as the OH value and the functionality of the polyol increase, the  $T_g$  values of the PUF samples increase because of an increase in the degree of crosslinking of the PUF sample. In Figure 9, however, the change in the  $T_g$  value is small between samples C and D, which may be attributable to the saturation in the crosslinking densities between samples C and D. This result may be related to the result of the flexural strength of the PUF samples of POL 5-490 and POL 6-490, shown in Figure 7, that excessive crosslinking density affected the flexural strength of the PUF samples because of the increase in brittleness of the PUF (POL 6-490) sample.

#### Effect of PMDI on the properties of PUF

Figures 10 and 11 show the effects of the amount of PMDI [i.e., NCO index (% NCO/OH)] on the  $T_g$ , the



**Figure 10** Glass-transition temperature ( $T_g$ ) and compressive strength of the PUF samples with NCO index.

density, and the compressive strength of the PUF samples. The effect of NCO index on the  $T_g$  of the PUF sample measured by DSC is shown in Figure 10. From Figure 10, the  $T_g$  values of the PUF samples increase from 116.2 to 152.1 $^{\circ}\text{C}$  as the NCO index increases from 90 to 135, respectively. Excess PMDI can react with formed urethane groups, generating allophanate, which introduces additional networks to the PUF sample.<sup>1,2</sup> In addition, it can react with urea groups, which were formed from the reaction between water and PMDI, generating biuret, which also introduces additional networks to the PUF sample.<sup>1,2</sup> Therefore, as the NCO index increases, it is suggested that the increase of the  $T_g$  may be attributable to the additional networks in the PUF. Generally, as the degree of crosslinking increases, the mechanical strength increases.<sup>1,2</sup> From Figure 10, it is observed that the compressive strength of the PUF samples increases with the NCO index.

Generally, the density in the cellular materials is the main factor for determining the properties.<sup>1,2,10,11</sup> As the density of the cellular materials increases, the mechanical strength increases.<sup>1,2,10,11</sup> Figure 11 shows the effect of NCO index on the density and compressive strength of the PUF samples. From Figure 11, it is observed that the density of the PUF samples does not change until the NCO index reaches 110, after which the density increases slightly with the NCO index. The compressive strength of the PUF sample, however, increases significantly with the NCO index, compared to the density. Like the previous result of the  $T_g$  value (Fig. 10), excess PMDI can generate allophanate and biuret, which introduce additional networks to the PUF sample. Therefore, as the NCO index increases, it is suggested that the increase of the compressive strength, shown in Figure 10, is mainly attributable to the additional networks in the PUF.

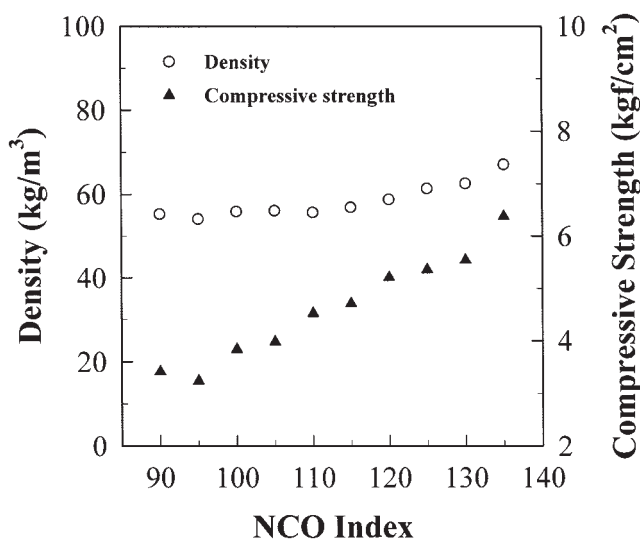
## CONCLUSIONS

Rigid PUFs were prepared with PMDI, polyether polyols, amine catalysts, silicone surfactant, and distilled water as a blowing agent. The kinetic rate of forming the PUF increased with the catalyst content regardless of type, either blowing or gelling catalyst. The kinetic rate of forming the PUF increased with an increase in water content because of the reaction heat exerted by the reaction between water and PMDI. Therefore, we concluded that the kinetic rate of forming the PUF increases with the catalyst and water content.

From the result of the effect of polyols on the properties of PUF, we concluded that the density and the compressive strength of the PUF increase, as the OH value and the functionality of the polyols are higher. For the PUF synthesized with polyols having high functionality ( $>5$ ), the flexural strength of the PUF samples decreased with the functionality of the polyols. From this result, we suggest that the decrease in the flexural strength of the PUF samples may be attributable to the increase in brittleness of the PUF sample.

As seen in the DSC results, as the OH value and the functionality of the polyols increased, the  $T_g$  of the PUF was increased. From this result, we suggest that the increase in the  $T_g$  of the PUF is related to an increase in degree of crosslinking. For the PUF samples, however, synthesized with polyols having high functionality ( $>5$ ), the change in the  $T_g$  value was negligible. From this result, we suggest that the slight change in the  $T_g$  value of the PUF samples may be attributable to the saturation in the crosslinking densities of the PUF samples.

From the result of the effect of NCO index on the  $T_g$  of the PUF, it was shown that the  $T_g$  values of the PUF



**Figure 11** Density and compressive strength of the PUF samples with NCO index.



samples increased from 116.2 to 115.2°C with an increase in NCO index from 90 to 135, respectively. We suggest that the increase in the  $T_g$  values of the PUF samples is related to the additional crosslinks that arose from allophonate and biuret formation by the supplementary reactions of excess PMDI.

The investigation of NCO index effects on the density and the compressive strength of the PUF samples demonstrated that the compressive strength of the PUF samples increased with the NCO index, even with only a slight increase in the density. From this result, we suggest that the increase in the compressive strength of the PUF samples may be attributable to the additional networks that arose from allophonate and biuret formation by the supplementary reactions of excess PMDI.

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