

Properties of Rigid Polyurethane Foams Blown by HCFC 141B and Distilled Water

H. C. JUNG,¹ S. C. RYU,^{1,*} W. N. KIM,¹ Y.-B. LEE,² K. H. CHOE², S.-B. KIM³

¹ Department of Chemical Engineering, Center for Advanced Functional Polymers, Korea University, Anam-dong, Seoul 136-701, Korea

² R&D Center, Korea Gas Corporation, Ansan-City 425-150, Korea

³ Department of Chemical Engineering, Kyonggi University, Suwon 442-760, Korea

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ABSTRACT: Rigid polyurethane foams (PUFs) were prepared from polymeric 4,4'-diphenylmethane diisocyanate, polyester polyol, 1,4-butane diol, silicone surfactant, hydrochlorofluorocarbon (HCFC) 141B, and distilled water. The properties and structure of the PUFs were investigated with differential scanning calorimetry (DSC), scanning electron microscopy (SEM), and a universal testing machine. The density of the PUF blown by distilled water and/or HCFC 141B decreased from 175.7 to 28.2 kg/m³ with an increase of blowing agents. From the SEM results, the average cell size of the PUF blown by distilled water increased from 150 to 290 μm with the distilled water content. From the DSC results, the glass-transition temperature (T_g) of the PUF blown by distilled water increased from 85.7 to 101.7°C with increasing distilled water content, whereas the T_g of the PUF blown by HCFC 141B remained unchanged with HCFC 141B content. The compressive strength and modulus of the PUF blown by a mixture of distilled water and HCFC 141B was increased from 0.13 to 0.25 MPa and from 3.00 to 7.23 MPa, respectively, with the distilled water content at the sample density of about 44.0 kg/m³. The increase of the compressive strength and modulus of the PUF at the same density was related to the increase of the T_g from 86.0 to 100.9°C. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 486–493, 2001

Key words: rigid polyurethane foam; cellular materials; density; glass-transition temperature; compressive strength

INTRODUCTION

Polyurethane foams (PUFs) with a cellular structure are used for many engineering applications, such as insulation materials, cushioning, automotive parts, and structural materials.^{1–4} PUFs are

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 evaporation of the physical blowing agents, such as chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). The cellular structure of the PUFs can be generated from a chemical blowing reaction as well. Some chemicals are reacted with the components generating the gas molecules, which yield the bubbles. One of the widely used chemical blowing agents for creating PUFs is distilled water, which reacts with the

Correspondence to: W. N. Kim (kimwn@mail.korea.ac.kr).
*Present address: Samyang Central R&D Center, 63-2 Hwaam-dong, Yusung-gu, Taejeon 305-348, Korea.

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diisocyanate, generating carbon dioxide. The foaming process can be explained by the nucleation and growth mechanism.¹⁻⁴

These days, the use of CFCs is considered undesirable because of environmental problems such as ozone depletion and global warming. Substitutes for CFCs, such as HCFCs, hydrofluorocarbons, cyclopentane, and distilled water, have been developed, and their applications for cellular materials have been studied.¹⁻⁴

The final structure and properties of PUFs depend on the molecular architecture of the constituent polymer and processing conditions.⁵⁻⁷ However, many works have focused on the mechanical behavior related to the mechanics of cell deformation.⁸⁻¹⁷ Recently, Gibson and Ashby did an extensive review of the cell structure and properties over a wide range of cellular solids.^{4,14,15}

Rigid PUF polymers are known to have a network structure, whereas polyurethane elastomers and flexible PUFs have a microphase-separated segmented structure.^{1-4,18-23} In an earlier study, we investigated the thermal properties and degree of crosslinking of rigid polyurethanes synthesized from high-functional polymeric 4,4'-diphenylmethane diisocyanate (PMDI) and polyester polyol.²³

In this study, rigid PUFs were prepared from PMDI with a functionality of 2.9 and a polyester polyol with an average functionality of 2.0. HCFC 141B, distilled water, and a mixture of HCFC 141B and distilled water were used as blowing agents. By varying the amount of blowing agents, we obtained rigid PUF samples with various densities. The cellular structure, thermal properties such as glass-transition temperature (T_g), and mechanical properties such as compressive strength and compressive modulus were studied with a scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and a universal testing machine (UTM), respectively.

EXPERIMENTAL

Materials

The materials used in this study were obtained from commercial sources. The PMDI was supplied from BASF Co. (Seoul, Korea). The polyester polyol, synthesized from phthalic anhydride and diethylene glycol, was supplied from Stepan Co. (Northfield, U.S.A.). Distilled water was generated in our laboratory and used as a chemical

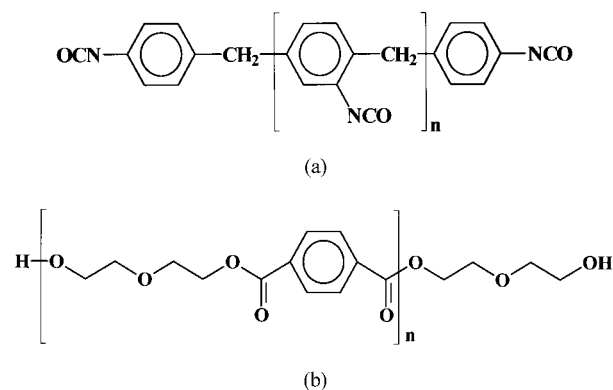


Figure 1 Chemical structure of the components: (a) PMDI, $n \cong 1.0$, and (b) phthalic anhydride-based polyester polyol, $n \cong 1.1$.

blowing agent. Triethylene diamine dissolved in dipropylene glycol to 33 wt % was supplied from Air Products and Chemicals, Inc. (Allentown, PA) and was used as a catalyst. The chemical structure and characteristics of the materials are shown in Figure 1 and Table I, respectively. The polyol and 1,4-butane diol 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. 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. Through annealing at elevated temperatures, the crosslink density, T_g , and, therefore, the mechanical strength of a PUF can be increased.²³ Also, the thermal conductivity of a PUF increases with the penetration of air replacing a blowing gas.¹⁻³ To avoid these problems and observe the properties of PUFs under processing condition, we performed the curing at room temperature. The amount of polyester polyol was set at 100 parts by weight, and the amount of 1,4-butane diol was set at 20 parts by weight. The amount of PMDI needed for reacting with polyester polyol and 1,4-butane diol was 135.5 parts by weight. Distilled water, HCFC 141B, and a mixture of distilled water and HCFC 141B were used as blowing agents.

When distilled water is used as a blowing agent, it reacts with PMDI to generate polyurea

Table I Characteristics of the Materials Used in This Study

Materials	Functionality	Equivalent Weight (g/mol)	Comments
4,4'-Diphenylmethane diisocyanate ^a	2.9	133.5	NCO content = 31.5%
Polyester polyol ^b	2.0	175.0	OH value = 300–330 mg KOH/g
1,4-Butane diol ^c	2.0	45.1	Chain extender
Distilled water ^d	2.0	9.0	Chemical blowing agent
HCFC 141B ^e	—	—	Physical blowing agent
Triethylene diamine ^f	—	—	Catalyst
Polysiloxane ether ^g	—	—	Surfactant

Data from suppliers.

^a Supplied from BASF Co. (Seoul, Korea)

^b Supplied from Stepan Co. (Northfield, U.S.A.)

^c Supplied from Junsei Chemical Co. (Tokyo, Japan)

^d Synthesized in our laboratory.

^e Supplied from Ulsan Chemical Co. (Ulsan, Korea)

^f Supplied from Air Products (Allentown, PA).

^g Supplied from OSI Specialties (U.S.A.).

and carbon dioxide. The carbon dioxide inflates the reactant, and as a result, a cellular structure is formed. Therefore, additional PMDI (133.5 g of PMDI/9.0 g of H₂O) is needed because distilled water is reacted with PMDI. When HCFC 141B is used as a blowing agent, it boils during the exothermic reaction and inflates the reactants.

Table II shows the chemical compositions of the PUF samples (PUF-X-Y) blown by distilled water and HCFC 141B. In the sample code (PUF-X-Y), X denotes the amount of distilled water used, and Y denotes the amount of HCFC 141B used. Excess PMDI (ca. 5 wt %; NCO/OH = 1.05) was used to assure the complete reaction of the polyol.

Measurements

Thermal properties of the PUF samples were measured on a PerkinElmer (Norwalk, U.S.A.) DSC7 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 -70 to 220°C at a heating rate of $20^\circ\text{C}/\text{min}$. The samples were then reheated at a heating rate of $20^\circ\text{C}/\text{min}$, followed by a $320^\circ\text{C}/\text{min}$ programmed cooling immediately between heats.

Mechanical properties of the PUF samples were measured under ambient conditions with an Instron (Canton, U.S.A.) 4467 UTM. Compressive

Table II Chemical Compositions^a of the Polyurethane Foam (PUF-X-Y)^b Blown by HCFC 141B and Distilled Water

Blowing Agent	PUF-0.5-0	PUF-1.0-0	PUF-1.5-0	PUF-2.0-0	PUF-2.5-0	PUF-3.0-0	PUF-0.0-Y
Polyester polyol	100.0	100.0	100.0	100.0	100.0	100.0	100.0
4,4'-Diphenylmethane diisocyanate	150.1	157.9	165.7	173.5	181.3	189.1	142.3
1,4-Butane diol	20.0	20.0	20.0	20.0	20.0	20.0	20.0
Distilled water	0.5	1.0	1.5	2.0	2.5	3.0	0.0
HCFC 141B	0	0	0	0	0	0	5–30 ^c
Triethylene diamine ^d	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Polysiloxane ether	2.0	2.0	2.0	2.0	2.0	2.0	2.0

^a Presented in parts by weight based on 100 parts of polyester polyol.

^b X denotes the amount of distilled water, and Y denotes the amount of HCFC 141B.

^c Five to 30 parts of HCFC 141B with an increment of 5 parts.

^d Dissolved in dipropylene glycol by 33 wt %.

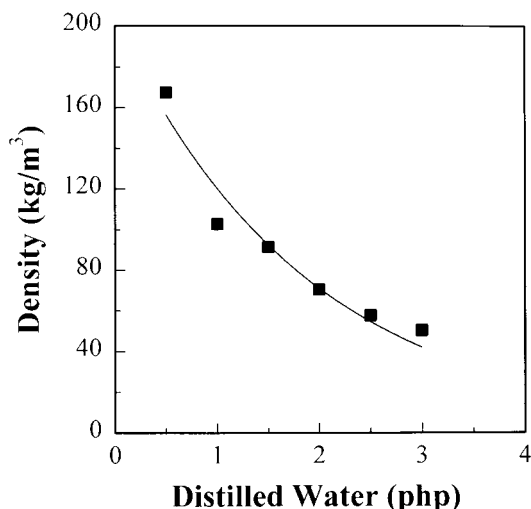


Figure 2 Density of the PUF samples blown by distilled water (PUF-X-0).

tests were performed according to ASTM D 1621. The size of the specimen was 30 mm (width) \times 30 mm (length) \times 30 mm (thickness), the speed of crosshead movement was 3 mm/min, and the strain rate was 0.1 min^{-1} . Compressive strengths of 5–7 specimens per sample were measured and averaged.

Morphology of the PUF samples was studied on a JEOL (Peabody, U.S.A) JSM 5200 scanning electron microscope. The samples were cryogenically fractured and gold-coated before scanning. The accelerating voltage used was 25 kV.

RESULTS AND DISCUSSION

Density Measurements

The densities of the PUF samples (PUF-X-0) blown by distilled water are shown in Figure 2. As shown in Figure 2, the density decreased from 167.5 to 50.3 kg/m^3 as the amount of the distilled water increased from 0.5 to 3.0 parts per 100 polyester polyol by weight (php), respectively. The densities of the PUF samples blown by HCFC 141B (PUF-0.0-Y) and by a mixture of HCFC 141B and distilled water (PUF-X-Y) are shown in Figure 3. As shown in Figure 3, the density of the PUF samples blown by HCFC 141B decreased from 175.7 to 40.8 kg/m^3 as the amount of HCFC 141B increased from 5 to 30 php, respectively. When the mixture of distilled water and HCFC 141B was used as a blowing agent, the density of the PUF samples ranged from 95.6 to 28.2 kg/m^3 .

Morphology

The cross-sectional surfaces of the PUF samples observed by SEM are shown in Figures 4 and 5. Figure 4(a,b) shows micrographs of PUF-0.5-0 (density = 167.5 kg/m^3) and PUF-3.0-0 (density = 50.3 kg/m^3), respectively, blown by distilled water. The cellular structures of the PUF samples were observed in the free-rising direction. Figure 5(a,b) shows micrographs of PUF-0.0-5 (density = 175.7 kg/m^3) and PUF-0.0-30 (density = 40.8 kg/m^3), respectively, blown by HCFC 141B. As shown in Figures 4 and 5, the PUF cells formed a spherical shape, and the cell size increased with the decrease in the density of the PUF samples.

The shape and size of the PUF cell are important to the mechanical properties and thermal conductivity of the PUF.^{1–4,24,25} The foaming process can be explained by nucleation and growth mechanism. When a polyol and an isocyanate react, the temperature of the mixture rises because of exothermic reaction heat. A physical blowing agent such as CFC 11 or HCFC 141B vaporizes, utilizing the reaction heat. A chemical blowing agent such as water generates carbon dioxide through the reaction with diisocyanate accompanying exothermic reaction heat. Because of the increase of temperature of the reactant mixture, the concentration of blowing gas in the mixture exceeds its solubility limit, and bubble nucleation begins. During the rise time, the already formed bubbles grow, and new bubbles nucleate.^{1–4,24,25} Niyogi et al. reported the cell-size distribution of the PUF from their simulation results.^{24,25} When

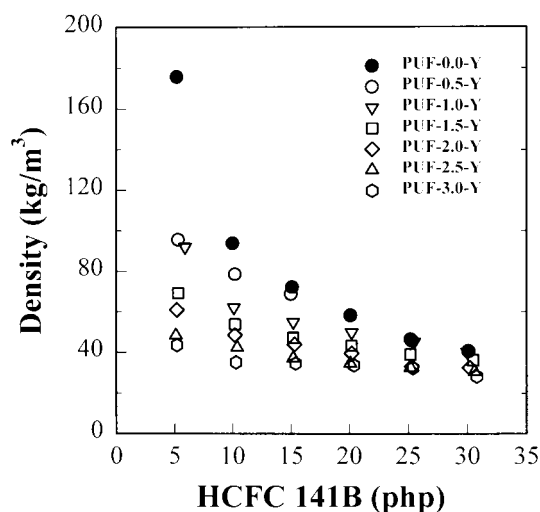
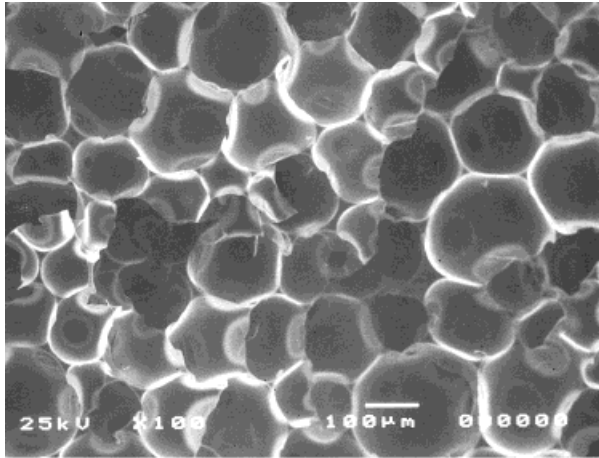
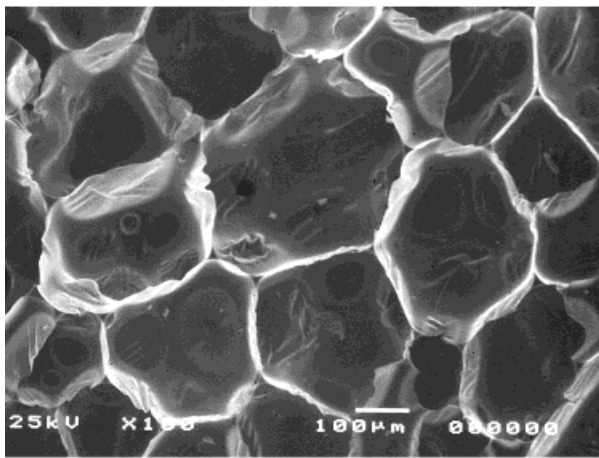


Figure 3 Density of the PUF samples blown by distilled water and HCFC 141B (PUF-X-Y).



(a)

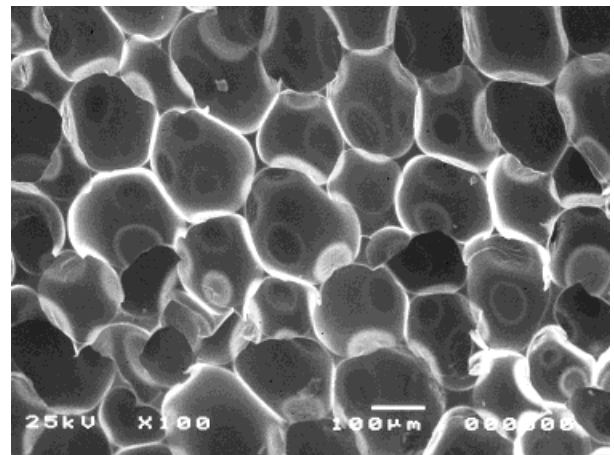


(b)

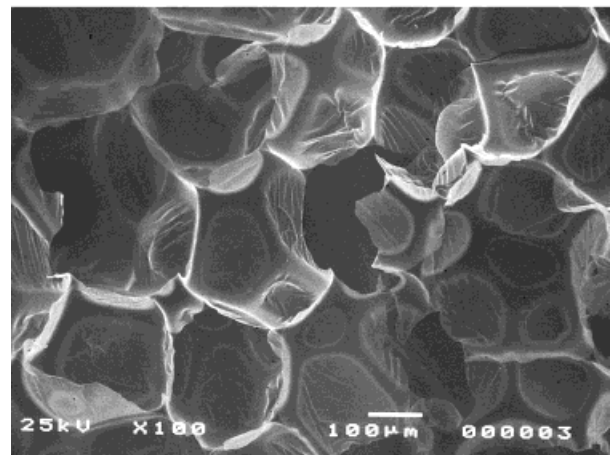
Figure 4 Scanning electron micrographs of PUF samples blown by distilled water: (a) PUF-0.5-0 (density = 167.5 kg/m^3) and (b) PUF-3.0-0 (density = 50.3 kg/m^3).

CFC 11 was used as a physical blowing agent, they reported that the rate of nucleation was smaller and the rise time was longer with a higher initial blowing-agent concentration. Hence, the average bubble size increased with the initial CFC 11 concentration.²⁴ When distilled water was used as a chemical blowing agent, they reported that the rate of nucleation was larger with a higher initial water concentration. The increase in the number of nuclei was more than the increment of carbon dioxide generation as the water concentration increased. As a result, the average bubble diameter decreased with a higher

initial water concentration.²⁵ However, as shown in Figures 4 and 5, the size and shape did not significantly change with the type of blowing agent. Also, the cell size of the PUF blown by either HCFC 141B or distilled water increased with the increase in the blowing-agent concentration. This may be a coalescence of PUF cells. Niyogi et al. assumed that no coalescence of bubbles occurred because of the presence of surfactants.^{24,25} However, the coalescence of bubbles cannot be completely prevented in the real system, although a surfactant is used. In this study, the amount of silicone surfactant was set at 2.0



(a)



(b)

Figure 5 Scanning electron micrographs of PUF samples blown by HCFC 141B: (a) PUF-0.0-5 (density = 175.7 kg/m^3) and (b) PUF-0.0-30 (density = 40.8 kg/m^3).

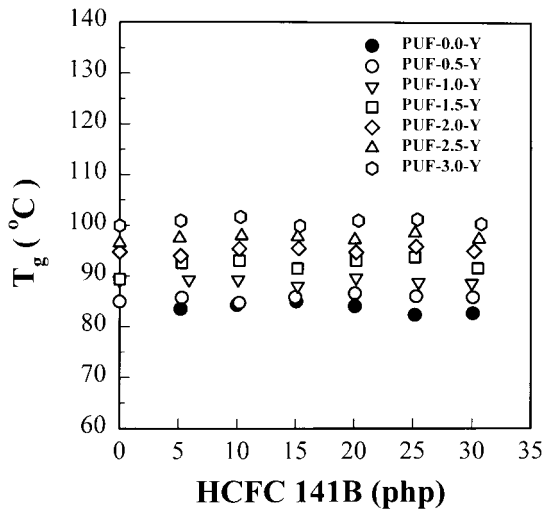


Figure 6 T_g of PUF samples blown by distilled water and HCFC 141B (PUF-X-Y).

php at all compositions. The cell size of the PUF samples blown by distilled water increased from 150 to 290 μm with an increase in distilled water from 0.5 to 3.0 php.

Thermal Analysis

The T_g 's of the PUF samples measured by DSC are shown in Figure 6. When HCFC 141B was used as a blowing agent (PUF-0.0-Y), the T_g 's of the PUFs were between 82.4 and 85.0°C and did not change significantly with the HCFC 141B content. When distilled water was used as a blowing agent with and without HCFC 141B, the T_g 's of the PUFs increased from 85.7 to 101.7°C.

When distilled water was added as a blowing agent, the T_g of the PUF samples increased from 85.7 to 101.7°C. 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. The polyurea itself is known to be more rigid than polyurethane. Therefore, when distilled water is used as a blowing agent, the chain mobility of the polymer chains can be restricted, and the T_g of the polymer may increase.¹⁻³

The polyurea content in the polymer can be measured with infrared spectroscopy. The peak at 1620–1750 cm^{-1} is characteristic of the carbonyl group in infrared spectroscopy. The peaks at 1731–1734 and 1715–1725 cm^{-1} are assigned to free (not hydrogen-bonded) urethane carbonyl and hydrogen-bonded urethane carbonyl, respectively. The peaks at 1695 and 1665–1675 cm^{-1}

are characteristic of free urea carbonyl and hydrogen-bonded urea carbonyl, respectively.^{26,27} The concentration of the urea can be analyzed by measuring the intensity of the urea carbonyl peak at 1665–1695 cm^{-1} with infrared spectroscopy. However, the peaks of carbonyl groups are broad and overlapped at 1620–1750 cm^{-1} . Therefore, it is difficult to measure the urea content quantitatively in this case.

The urea group can react with PMDI to form diamine. The diamine can also react with PMDI to generate biuret, which introduces additional crosslinks to the polymer.¹⁻⁴ Therefore, when distilled water was used as a blowing agent, the increases in the T_g of the PUF might have happened because of the introduction of polyurea and additional crosslinks in the PUF.

Mechanical Properties

In Figure 7, the compressive strength of the PUF samples with density is shown. As shown in Figure 7, the compressive strength of the PUF samples ranged from 0.05 to 1.78 MPa with density, and the compressive strength increased as the density of the PUF samples increased. It is known that the mechanical properties of a cellular material depend mainly on its density. A simple power law can be used to depict the relationship between mechanical properties, such as strength and modulus, and density.^{1-4,14-17}

$$\text{Strength or modulus} = A(\text{density})^B \quad (1)$$

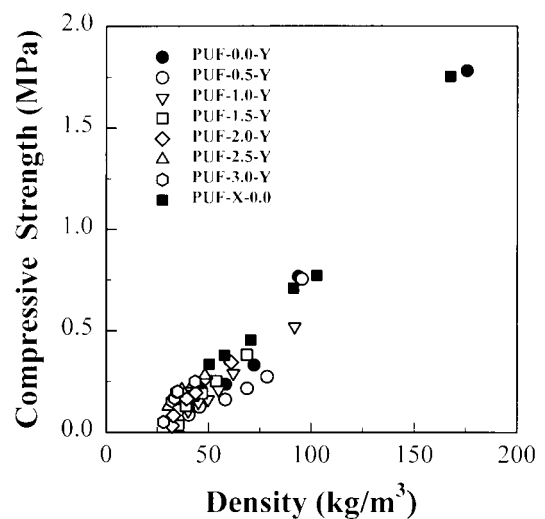


Figure 7 Compressive strength of PUF samples blown by distilled water and HCFC 141B (PUF-X-Y).

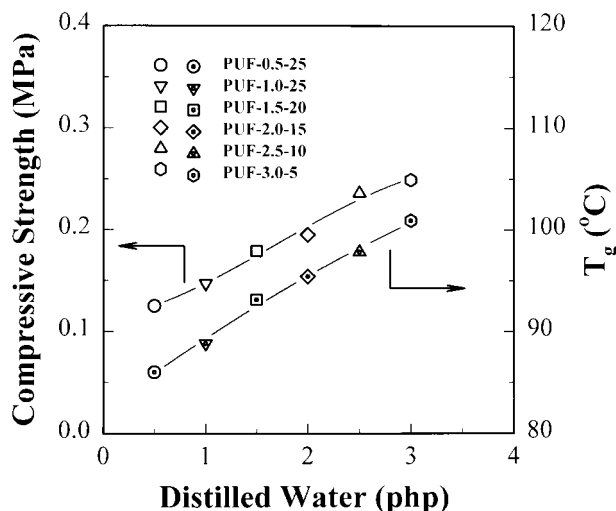


Figure 8 Compressive strength and T_g of PUF samples with a density of about 44.0 kg/m^3 blown by distilled water and HCFC 141B.

where A is a constant related to the temperature and physical properties of a resin and B is related to the deformation mechanics of cellular materials. The value of B is known to range from 1 to 2.^{14–17} In this study, the constant B ranged from 1.50 to 1.64.

To investigate the effect of blowing agents on the mechanical properties of the PUF samples, the T_g , compressive strength, and compressive modulus of the PUF samples, which had a density of about 44.0 kg/m^3 with distilled water and HCFC 141B, are shown in Figure 8 and Table III. The cell size and density of the PUF samples shown in Figure 8 and Table III were about equal in this study. However, the compressive strength and compressive modulus of the PUF samples increased from 0.13 to 0.25 MPa and from 3.00 to 7.23 MPa, respectively, with the increase on distilled water. As mentioned in the thermal analysis section, distilled water is known to produce polyurea, which may act as a filler and biuret, which may introduce additional crosslinks. As shown in Figure 8 and Table III, the compressive modulus and T_g of the PUF samples increased with an increase in distilled water. Therefore, it is suggested that the increase in the compressive strength of the PUF samples may be due to the polyurea and biuret produced by the reaction between the distilled water and PMDI.

CONCLUSIONS

Rigid PUFs were prepared with PMDI, polyester polyol, 1,4-butane diol, silicone surfactant, and

HCFC 141B and distilled water as blowing agents. The density of the PUF blown by distilled water and/or HCFC 141B decreased from 175.7 to 28.2 kg/m^3 with an increase in the blowing agents. As seen in the results of morphology by SEM, the cell size of the PUF samples increased from 150 to $290 \mu\text{m}$ with an increase in distilled water from 0.5 to 3.0 php, respectively. The cell size of the PUF samples blown by HCFC 141B and a mixture of HCFC 141B and distilled water exhibited behavior similar to the behavior of the PUF samples blown by distilled water.

As seen in the DSC results, the T_g 's of the PUF samples blown by distilled water increased from 85.7 to 101.7°C with an increase in distilled water from 0.5 to 3.0 php, respectively. The T_g 's of the PUF samples blown by HCFC 141B did not change significantly, varying from 82.4 to 85.0°C . When distilled water was used as a blowing agent, the increase of the T_g of the PUF might have been due to the rigid polyurea and additional crosslinks arising from biuret formation.

As seen in the results of the mechanical properties by UTM, the compressive strength of the PUF samples blown by distilled water increased from 0.34 to 1.75 MPa with an increase in density from 50.3 to 167.5 kg/m^3 , respectively. The compressive strength of the PUF samples blown by HCFC 141B and a mixture of HCFC 141B and distilled water exhibited similar behavior compared with the compressive strength of the PUF samples blown by distilled water alone.

The compressive strength and compressive modulus of the PUF samples at the same density of about 44.0 kg/m^3 increased from 0.13 to 0.25 MPa and from 3.00 to 7.23 MPa with an increase in distilled water. We suggest that the increase in the compressive strength of the PUF samples was related to the formation of rigid polyurea and

Table III Density, T_g , Compressive Strength, and Compressive Modulus of the PUF Samples Blown by Distilled Water and HCFC 141B

Specimen	Density (kg/m^3)	T_g ($^\circ\text{C}$)	Compressive Strength (MPa)	Compressive Modulus (MPa)
PUF-0.5-25	45.8	86.0	0.13	3.0
PUF-1.0-25	45.1	88.8	0.15	3.62
PUF-1.5-20	43.2	93.1	0.18	4.65
PUF-2.0-15	43.9	95.4	0.20	5.67
PUF-2.5-10	42.4	98.0	0.24	6.33
PUF-3.0-5	43.5	100.9	0.25	7.23

additional crosslinks that arose from biuret formation by a reaction between distilled water and PMDI.

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