

Effects of Isocyanate Index and Environmentally-Friendly Blowing Agents on the Morphological, Mechanical, and Thermal Insulating Properties of Polyisocyanurate-Polyurethane Foams

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Abstract: The effects of the isocyanate (NCO) index and blowing agent on the morphology, mechanical strength, thermal conductivity and thermal stability of the polyisocyanurate-polyurethane (PIR-PUR) foams were investigated. When the NCO index was increased, the isocyanurate ring content in the PIR-PUR foams was found to be increased regardless the type of blowing agents. As a results, the thermal stability of the PIR-PUR foams was improved. When the isocyanurate ring content in the PIR-PUR foams was increased, the cell size was slightly decreased. The decreased cell size of the foams affected the decrease in the thermal conductivity of the PIR-PUR foams regardless the type of the blowing agents. From the results of thermogravimetric analysis (TGA), the thermal stability of the PIR-PUR foams was found to increase with an increase in the NCO index. When the NCO index was 200, the compressive strength was maximal for the PIR-PUR foams regardless the type of the blowing agents. The compressive strength of the foams blown by cyclopentane was higher than that of the water blown foams. From the above results, it is suggested that the thermal insulation property and thermal stability of the PIR-PUR foams increased with an increase in the NCO index. However, the compressive strength of the PIR-PUR foams showed maximum value at a specific NCO index.

Keywords: polyurethane, foam, polyisocyanurate, thermal conductivity, morphology, blowing agent.

Introduction

Rigid, closed cell, polyurethane (PUR) foams provide outstanding insulation properties. Since the thermal conductivities of the PUR foams are much lower than those of other insulating materials such as polystyrene foams, glass wools, and rock wools, PUR foams have been widely used for building insulation panels, refrigerators, pipe insulation and liquefied natural gas (LNG) storage tanks.¹⁻⁷

One of the key materials for low thermal conductivity of rigid PUR foam is the blowing agent. In early times, chlorofluorocarbon (CFC) and hydrochlorofluorocarbons (HCFCs) have been used as blowing agents for rigid PUR foams owing to their low gas thermal conductivities. However, they are now known to be major causes of ozone layer depletion and global warming, and developed nations should strive towards the total phase out of production and consumption of CFC and HCFCs under the Montreal Protocol. The interest in finding alternative solutions grew as water and cyclopentane were chosen for alternative environmentally friendly blowing agents.^{8,9} Ozone depletion potentials (ODP) of these

environmentally friendly agents are equal to zero and the global warming potentials (GWP) are very low, however, one of disadvantages of these blowing agents is their high gas thermal conductivity. Therefore, research has been focused on decreasing thermal conductivity of the foams.^{10,11}

In previous studies, effects of surfactants and various types of additives on cell size and thermal conductivity of the foams have been investigated since small and uniform sized cells are effective to reduce the thermal conductivity of the PIR-PUR foams.^{10,11} Since the flame retardancy of the rigid PUR foams are low, rigid PUR foams require modification as a polyisocyanurate-polyurethane (PIR-PUR) foam in order to improve the flame retardant properties.¹²⁻¹⁶

PIR-PUR foam is produced by the reaction between polyol and excessive 4,4'-diphenylmethane diisocyanate (MDI) or toluene diisocyanate (TDI) (isocyanate (NCO) index > 180) when a certain catalyst exists in the system. The key structure of the PIR-PUR foams is isocyanurate rings produced by cyclotrimerization of excess isocyanate groups in polyurethane matrix. The isocyanurate ring improves the mechanical strength of the polymers and the ring structure also has effects to increase the thermal decomposition temperature of the PIR-PUR foams to 250-300 °C which is

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Table I. Chemical Compositions Used in the Preparation of Polyisocyanurate-Polyurethane Foams with Blowing Agents

Materials	W150 ^a	W200	W250	W300	M150 ^b	M200	M250	M300	C150 ^c	C200	C250	C300
Polyol	100	100	100	100	100	100	100	100	100	100	100	100
MDI	180	254	342	449	170	239	319	413	125	167	209	251
Surfactant	1.87	2.36	2.95	3.66	1.80	2.26	2.80	3.42	1.50	1.78	2.06	2.34
Catalyst	1.40	2.07	2.95	4.12	1.35	1.97	2.80	4.27	1.09	1.38	1.70	2.05
Water	2.43	2.89	3.54	4.39	1.98	2.37	2.94	3.59	-	-	-	-
Cyclopentane	-	-	-	-	1.98	2.37	2.94	3.59	9.39	11.58	13.90	15.78
NCO Index	150	200	250	300	150	200	250	300	150	200	250	300

^aW150 denotes polyisocyanurate foam blown by water when NCO index is 150. ^bM150 denotes polyisocyanurate foam blown by water/cyclopentane (50:50, wt%) when NCO index is 150. ^cC150 denotes polyisocyanurate foam blown by cyclopentane when NCO index is 150.

100 °C higher than PUR foams.¹⁷⁻²²

Many researchers¹⁻⁶ have studied the properties of rigid polyurethane (PUR) foams with the blowing agents and isocyanate index. However, it is believed that studies concerning PIR-PUR foam, which is obtained by the cyclotrimerization, are very few, especially for the foams blown using environmentally-friendly blowing agent. Cyclotrimerization can be obtained using the potassium 2-ethylhexanoate and the PIR-PUR foam used in the field of thermal insulating sandwich panels for the building construction because of the higher thermal stability compared to the polyurethane (PUR) foams.^{11,23} Since the global warming potential (GWP) of cyclopentane and water is very low compared to that of CFC, HCFC-141b or HFC 365mfc, in this study, we have used the environmentally-friendly blowing agents cyclopentane, water and the water/cyclopentane (50:50, wt%) mixture to see the effects of isocyanate index on the morphological, mechanical and thermal insulating properties of the PIR-PUR foams.

Experimental

Materials. The materials used in this study were obtained from commercial sources. Polymeric 4,4'-diphenylmethane diisocyanate (PMDI) was supplied from BASF Korea Ltd. (Seoul, Korea). The average functionality of PMDI was 2.7 and NCO content was 30.5 wt%. Polyether polyol and polyester polyol were used in this study. Pentaerithritol and glycerin based polyether polyol (OH value=370 mg KOH/g, 2050 cps) was supplied from KPX Chemicals Co. (Ulsan, Korea). Anhydride and glycol based polyester polyol (OH value=330 mg KOH/g, 2100 cps) was supplied from Aekyung Petrochemical Co. (Seoul, Korea). The weight ratio of polyether and polyester polyol used in this study was 40:60 in wt%. Cyclopentane and water were used as physical and chemical blowing agents, respectively. Cyclotrimerization catalyst was potassium 2-ethylhexanoate from OMG Americas, Inc. (Ohio, USA). Polysiloxane ether, used as a surfactant, was used from Goldschmidt's (Essen, Germany). The polyols

were dehydrated at 90 °C for 24 h in a vacuum oven before use, and the other chemicals were used as received. The chemical compositions of the materials used in the preparation of polyisocyanurate-polyurethane (PIR-PUR) foams are shown in Table I.

Preparation of Polyisocyanurate-Polyurethane (PIR-PUR) Foams. The polyisocyanurate-polyurethane (PIR-PUR) foams were prepared in laboratory scale. Polyols, catalyst, surfactant were mixed and stirred for 40 s at 2,500 rpm. Then blowing agent was mixed with premixed components for 20 s at the rotation speed of 500 rpm. PMDI was, then, added into the premixed components and mixed for 15 s at 5,000 rpm. Finally, the reactants were poured into the open rectangular mold (dimensions 250 mm×250 mm×250 mm) to produce free-rise foams. After foaming, the prepared foams were removed from the mold. They were cured for 24 h at room temperature. The amount of blowing agent was controlled to obtain the same density of 50 kg/m³ for all the samples.

FTIR Spectroscopy. The FTIR analysis of the PIR-PUR foams was performed on a Infinity gold FTIR Series (ThermoMattson, USA) in the mid-IR range from 4000 to 400 cm⁻¹. The FTIR measurements were carried out at 26 °C and the spectra were collected at a resolution of 8 cm⁻¹ and 16 scans were accumulated. The data, collected as transmittance values, were converted into absorbance which is directly related to the concentration of the functional group by Lambert-Beer's law of eq. (1):

$$A = (\epsilon b) C \quad (1)$$

where A is absorbance, ϵ is extinction coefficient, b is optical path and C is concentration.²⁴

Thermogravimetric Analysis (TGA). DSC2010 analyzer (TA instrument, USA) was used to study the thermal performance of the PIR-PUR foams. 4.5 mg in average of PIR-PUR foam sample (powder) was used to obtain TGA data profiles. The heating rate was set to 10 °C/min under nitrogen atmosphere (100 mL/min). The temperature range under analysis was from 25 to 800 °C. The results were obtained as weight loss (%) versus temperature.

Density Measurements. The density of the PIR-PUR foams were determined by averaging the mass/volume measurement results of five specimens per sample following the procedure described in ASTM D1622-98 standard. The shape of the sample was a cube (size: 30 mm×30 mm×30 mm).

Thermal Conductivity. Thermal conductivities of PIR-PUR foams were measured using a thermal conductivity analyzer (model TCA point2, Anacon) according to ASTM C518. PIR-PUR sample was placed in the test section between two plates which are maintained at different temperatures (37.8 and 10 °C, respectively) during the test. Dimension of the specimen was 200 mm×200 mm×25 mm (width×length×thickness).

Cell Morphology. Cell morphology of PIR-PUR foams was monitored by field emission scanning electron microscope (FE-SEM) (Hitachi Model S-4300SE, Tokyo, Japan). The samples were cryogenically fractured and the surface was coated with platinum (Pt) for 120 s before scanning. To measure cell size of PIR-PUR foams, we have used an image processing software (ImageJ). About 70 closed cells per sample were measured and averaged.

Compressive Strength. Compressive strength of PIR-PUR foams was measured under ambient conditions using an Instron universal testing machine (Model 4467, Instron). Compressive strength tests were performed according to the ASTM D1621. The size of the specimen was 30 mm×30 mm×30 mm and the speed of crosshead movement was 3 mm/min. Seven specimens per sample were measured and averaged.

Results and Discussion

FTIR Analysis. FTIR spectra of PIR-PUR foams blown by water, cyclopentane and water/cyclopentane (50:50, wt%) mixture, and cyclopentane alone are shown in Figure 1(a)-(c), respectively. The NCO index of all the foams is fixed by 300. The peak at wavenumber 1410 cm^{-1} is due to functional group of isocyanurate ring structure and the peak at wavenumber 1510 cm^{-1} is due to amine (-NH) groups (bend) that exist in urethane and urea linkage. The peak at 1710 cm^{-1} is due to carbonyl (-C=O) of urethane and urea, the peak at 1220 cm^{-1} is due to -CO single bond. The peak at 2280 cm^{-1} denotes functional group of isocyanate bond (-N=C=O).^{17,25,26} The wavenumber of about 3350 cm^{-1} is due to amine (-NH) group (stretch).²⁷ The peak intensity at 3350 cm^{-1} showed very weak in the analysis of the PIR-PUR foams.

From Figure 1, it is observed that the peak height is somewhat different depending on the type of blowing agents. The absorbance at 1510 cm^{-1} of the PIR-PUR foams blown by cyclopentane is lower than that of the foams blown by water. The reason is that urea bond is additionally formed when water is used as a blowing agent. Therefore, at the

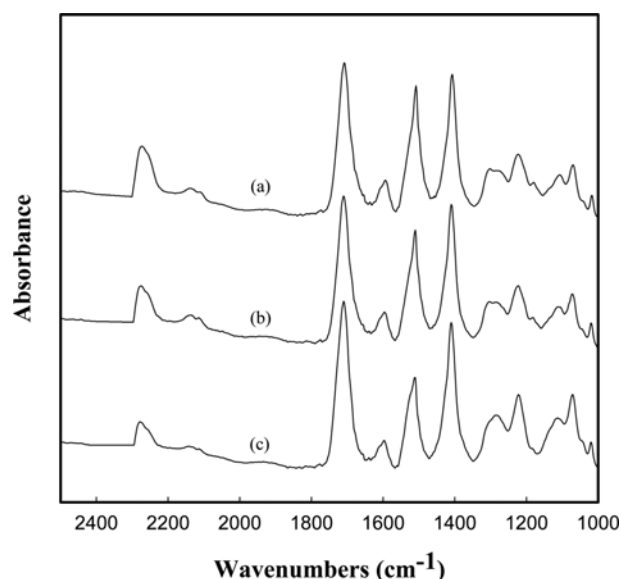


Figure 1. FTIR spectra of polyisocyanurate-polyurethane foams blown by: (a) water, (b) water/cyclopentane (50:50, wt%) mixture, and (c) cyclopentane.

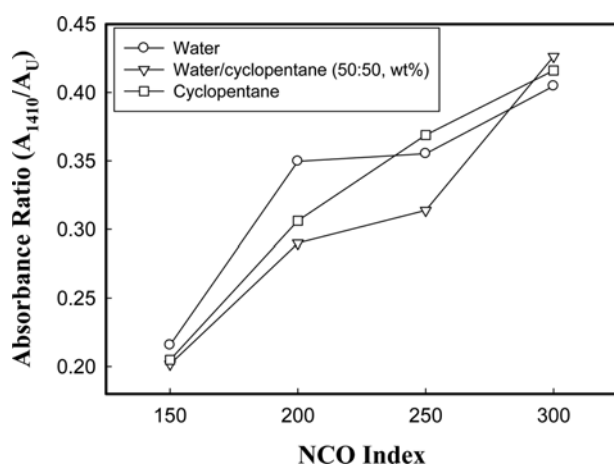
same NCO index, the amine group (-NH) is generated more in the foams blown by water than the foams blown by cyclopentane. The peak height at 1510 cm^{-1} of the foams blown by water/cyclopentane (50:50 wt%) mixture shows an average height compared to the peak height of the foams blown by each of the water and cyclopentane.

The peak intensity of the absorbance is directly related to the concentration of the functional group by Lambert-Beer's law which is shown in eq. (1). But, the absorbance data of FTIR cannot be directly used for a quantitative evaluation of isocyanurate content, because the extinction coefficient (ϵ) and optical path (b) product in the Lambert-Beer's law could not be obtained in this FTIR experiment. Although an absolute estimation of isocyanurate content is not possible, Modesti *et al.* suggested to obtain the comparative results using the ratio of the peak height between the isocyanurate and urethane groups.^{23,24} To express expediently, we abbreviated absorbance at 1410 cm^{-1} peak which denote isocyanurate ring content to A_{1410} . Also, it is abbreviated that the absorbance of urethane group to A_U which is characterized by the summation of the absorption bands at 1220, 1510, 1710, and 3350 cm^{-1} , that is $A_U = A_{1220} + A_{1510} + A_{1710} + A_{3350}$.

Table II shows the calculated data from the FTIR absorbance of the PIR-PUR foams. From Table II, it shows that the A_{1410}/A_U of the foams blown by water increases from 0.2157 to 0.4047 with the increase of the NCO index from 150 to 300. For the foams blown by water/cyclopentane mixture and cyclopentane alone, the same behavior is observed. Figure 2 shows the value of A_{1410}/A_U when the NCO index is increased from 150 to 300. The A_{1410}/A_U value is gradually increased when NCO index is increased, regardless of

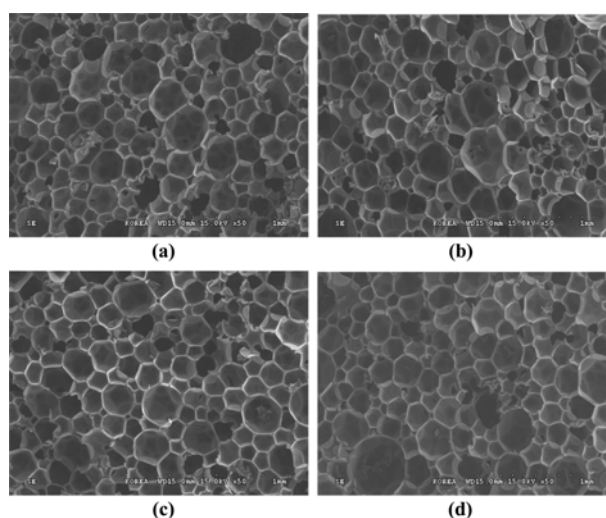
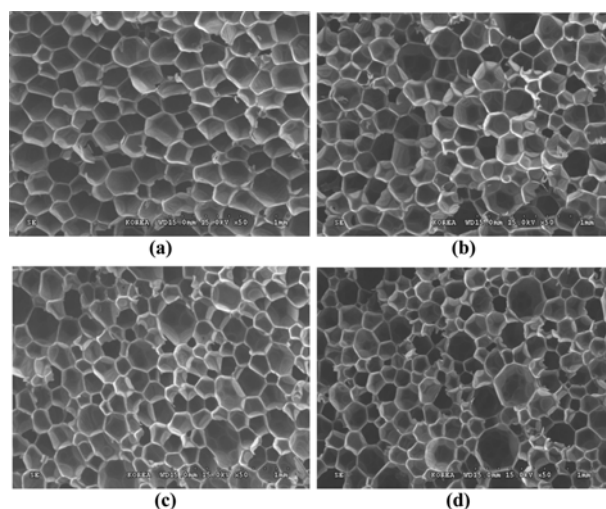
Table II. Absorbances at 1410 cm⁻¹ Peak (A_{1410}) and Urethane Group (A_U) from FTIR Analysis of Polyisocyanurate-Polyurethane Foams with Blowing Agents

Sample	A_{1410}	A_U	A_{1410}/A_U
W150	0.0217	0.1006	0.2157
W200	0.0292	0.0835	0.3497
W250	0.0282	0.0794	0.3552
W300	0.0382	0.0944	0.4047
M150	0.0166	0.0823	0.2017
M200	0.0194	0.0669	0.2900
M250	0.0262	0.0835	0.3138
M300	0.0382	0.0896	0.4263
C150	0.0142	0.0693	0.2049
C200	0.0237	0.0774	0.3062
C250	0.0422	0.1144	0.3689
C300	0.0419	0.1007	0.4161

**Figure 2.** The effect of NCO index on the isocyanate/urethane group ratio with blowing agents.

the type of blowing agents. From the FTIR results, it is suggested that when the NCO index is increased the isocyanurate content in the foam is also increased.

Morphology of the PIR-PUR Foams. To evaluate the effects of NCO index on the morphology, the cross-sectional surfaces of the PIR-PUR foams were observed using SEM. Figures 3 and 4 show the cell morphology of the PIR-PUR foams blown by water and cyclopentane, respectively. From Figures 3 and 4, both foams with increasing NCO index (from 150 to 300) tend to show smaller cell size. Figure 5 shows cell size distribution of the PIR-PUR foams blown by cyclopentanes and water when the NCO index is 250. From Figure 5, cell size distribution seems quite uniform. However, average cell diameter of the PIR-PUR foams blown by cyclopentane shows smaller than that of the foams blown by

**Figure 3.** Scanning electron micrographs of polyisocyanurate-polyurethane foams blown by water with NCO index: (a) 150, (b) 200, (c) 250, and (d) 300.**Figure 4.** Scanning electron micrographs of polyisocyanurate-polyurethane foams blown by cyclopentane with NCO index: (a) 150, (b) 200, (c) 250, and (d) 300.

water. For the foams with the other NCO index, similar behavior was observed.

Figure 6 shows the average cell diameter of the PIR-PUR foams with the NCO index and blowing agent. When the NCO index is increased from 150 to 300, the cell size of the water and cyclopentane blown foams is decreased from 226 to 206 μm and from 220 to 193 μm , respectively. For the PIR-PUR foams blown by water/cyclopentane (50:50 wt%) mixture, the cell size of the foams is decreased from 223 to 204 μm .

The decrease in the cell size with the increase of NCO index is probably due to the viscosity effect of the polyol and MDI as main ingredients for the synthesis of the foams. The viscosity of MDI is relatively lower than that of the

polyol. Therefore, when the NCO index is increased, the viscosity is decreased because the higher NCO index needs the larger amount of MDI. The lower viscosity of the polyol and MDI mixture may induce to form homogeneous and smaller cells because it makes it more uniform, well-mixed and allows the synthetic reaction to occur rapidly.^{28,29}

From Figures 5 and 6, it shows that the average cell size of the PIR-PUR foams blown by cyclopentane is smaller than that of the water blown foams. The decrease in cell size of the foams blown by cyclopentane can be explained such that expansion of a foam is achieved by evaporation of a physical blowing agent (cyclopentane) or gas generation reaction of a chemical blowing agent.³⁰⁻³² The exothermic reaction heat causes the increase of temperature of the reactants and at the vaporization of the physical blowing agent, the physical blowing evaporates extremely fast, since this gives little time for coalescence of the cells. A chemical blowing agent generates blowing gas by the chemical reaction with the reactants. The kinetic rate of the chemical

reaction increases with temperature of the reactants, and the blowing gas is generated gradually. The water as chemical blowing agent evaporates *via* the urea reaction step which emits carbon dioxide and the reaction speed is relatively slow. The foaming rate is a very important factor in the formation of the cell. Therefore, the cell size of the foams blown by cyclopentane becomes small compared to the foams blown by water.

Thermal Conductivity. Effects of NCO index and blowing agents on the thermal conductivity of the PIR-PUR foams are shown in Table III. When NCO index is increased from 150 to 300, the thermal conductivity of the foams tends to decrease slightly. When the PIR-PUR foams blown by water, the thermal conductivity of W150 and W300 is observed to be 0.0224 and 0.0221 kcal/mh°C, respectively. When the foams blown by cyclopentane, the thermal conductivity of C150 and C300 is 0.0201 and 0.0195 kcal/mh°C, respectively. When the foams blown by water/cyclopentane (50:50, wt%) mixture, the thermal conductivity of M150 and M300 is 0.0213 and 0.0221 kcal/mh°C, respectively. Figure 7 shows the relationship between thermal conductivity and cell size of the PIR-PUR foams with blowing agents. From Figure 7, it shows that when the cell size becomes smaller, the thermal conductivity is lowered proportionally.

TGA Analysis. Thermal gravimetric analysis (TGA) was

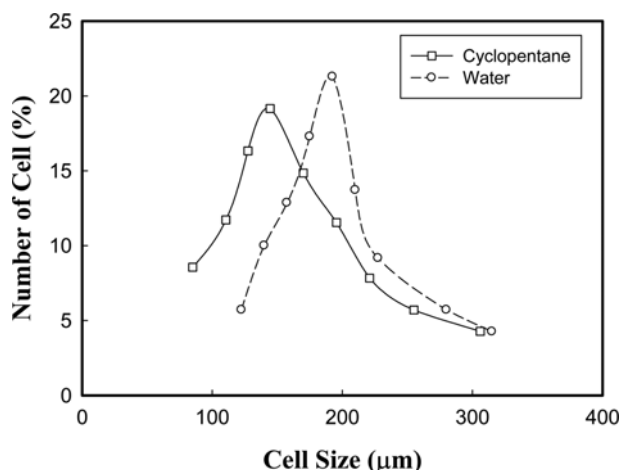


Figure 5. Cell size distribution of PIR-PUR foams blown by cyclopentane and water when NCO index is 250.

Table III. Thermal Conductivity of the PIR-PUR Foams with NCO Index and Blowing Agents (unit : kcal/mh°C)

Blowing Agent NCO Index	Blowing Agent		
	Water	Water/Cyclopentane Mixture	Cyclopentane
150	0.0224	0.0213	0.0201
200	0.0225	0.0213	0.0196
250	0.0222	0.0211	0.0196
300	0.0221	0.0211	0.0195

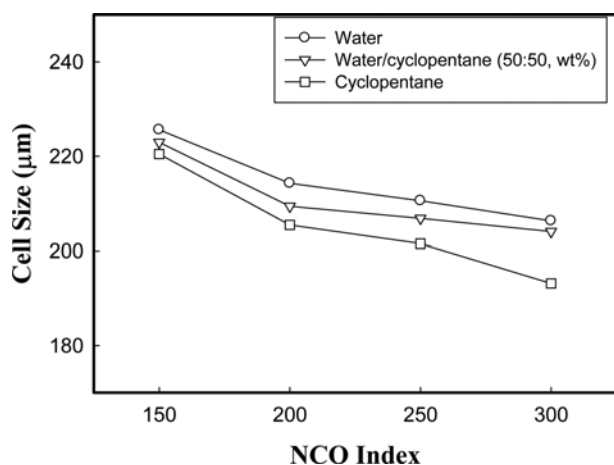


Figure 6. Cell size of polyisocyanurate-polyurethane foams with NCO index and blowing agents.

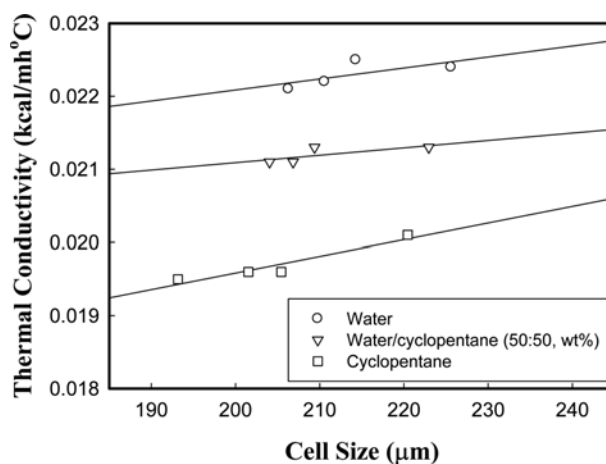


Figure 7. Relationship between thermal conductivity and cell size of polyisocyanurate-polyurethane foams with blowing agents.

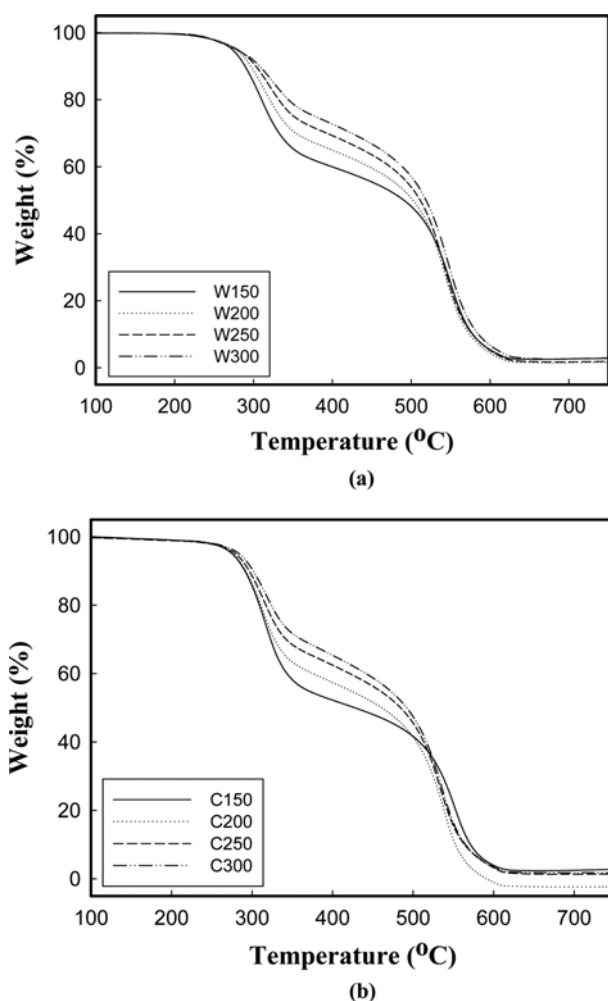


Figure 8. TGA of polyisocyanurate-polyurethane foams with NCO index: (a) blown by water and (b) blown by cyclopentane.

carried out to investigate the effect of NCO index on the thermal stability of the foams. Figure 8 shows TGA results of the PIR-PUR foams blown by water and cyclopentane, respectively. From Figure 8, it is observed that copolyurethane decomposition starts at about 200 °C. This is a simple depolymerization of the urethane bonds and it is intensified at about 260 °C (Table IV) to produce the starting materials (MDI and polyols) or some side products such as amines, olefins and carbon dioxide.^{23,33} Then, the polyol chain (soft segments) scission occurs at about 370-380 °C and produces

more volatile chain fragments.³⁴ The final stage at about 400-600 °C may be attributed to thermal decomposition of isocyanurate rings and carbodiimide linkages, which leads to the production of CO₂ and the formation of char in the solid state, which remained as residue.³³⁻³⁵ Isocyanurate ring is included in hard segment. Therefore, as the content of isocyanurate ring is increased in the foams blown by water and cyclopentane, the temperature of first degradation step is also getting increased.^{36,37}

The degradation process of the PIR-PUR foams is characterized by the onset and maximum degradation temperatures of the first and second steps, as summarized in Table IV. The onset degradation temperature of first step ($T_{1,on}$) of the water and cyclopentane blown foams is increased from 265.0 to 285.8 °C and 269.7 to 279.2 °C with increasing NCO index from 150 to 300, respectively. The maximum degradation temperature of the first step ($T_{1,max}$) is also increased with increasing NCO index from 150 to 300. This is because the isocyanurate content of the foams is increased.

The residual weight after degradation of the first step at 400 °C (W_{res}) of water blown foams is higher than that of the foams blown by cyclopentane. From Table IV, it shows that the W_{res} of W300 is 72.7% whereas the W_{res} of C300 is 65.3%. This is because that the urea group is additionally contained in the foams when water is used as a blowing agent. It is known that the decomposition temperature of urea (250 °C) is higher than that of the urethane (200 °C). From the results of TGA analysis, it is suggested that the foams blown by water show better thermal stability than that of the foams blown by cyclopentane.

Compressive Strength. Figure 9 shows the effects of NCO index on the compressive strength of the PIR-PUR foams with blowing agents. When the NCO index is 200, maximum value of the compressive strengths are observed which are 0.510, 0.480, and 0.469 MPa for the foams blown by cyclopentane, water/cyclopentane mixture and water, respectively. This is because the isocyanurate ring structure is rigid aromatic structure, and it affects the strength of the PIR-PUR foams. The foam consists of two parts: hard segment and soft segment. The hard segment is a functional group which is formed by reaction of the diisocyanate such as urethane, urea and isocyanate ring bond. They have a high density of PIR-PUR foams, and for this reason, they give rigid and strong PIR-PUR foams. The soft segment is the long chain part of polyol, so they give a flexibility and

Table IV. Characteristics of Decomposition Temperature and Residue Weight of PIR-PUR Foams from TGA Data

	W150	W200	W250	W300	M150	M200	M250	M300	C150	C200	C250	C300
$T_{1,on}^a$ (°C)	265.0	274.3	282.6	285.8	261.4	273.2	276.9	289.5	269.7	271.6	275.6	279.2
$T_{1,max}^b$ (°C)	308.1	314.5	320.3	324.7	307.6	311.6	312.3	324.0	313.6	314.5	315.5	317.4
W_{res}^c (%)	59.9	64.9	69.3	72.7	54.8	64.6	69.0	72.2	52.2	57.4	62.5	65.3

^a $T_{1,on}$ =Onset degradation temperature of the first step. ^b $T_{1,max}$ =Maximum degradation temperature of the first step. ^c W_{res} =Residual weight percent of PIR-PUR foams after degradation of the first step at 400 °C.

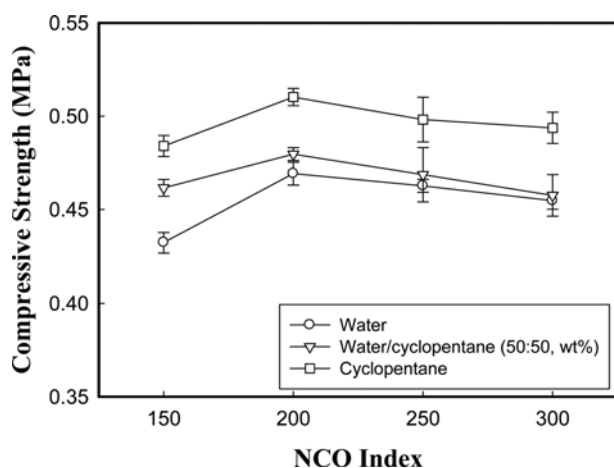


Figure 9. Compressive strength of polyisocyanurate-polyurethane foams with NCO index and blowing agents.

elasticity.^{36,38,39} However, the foams containing higher content of isocyanurate rings (NCO index is 300) are brittle and friable, therefore decrease the mechanical strength. Therefore, the appropriate content of isocyanurate rings increases the strength of the foams.

In general, higher isocyanate index gives more isocyanate group reactions to form carbodiimide and CO_2 .²³ This gives additional foaming and low density of the foams. Low density would give small compression strength, which is in agreement based on the 200 NCO index. The existence of the maximum compression strength shown in Figure 9 could be due to the balance between the decreased cell size and presumably decreased foam density with increasing NCO index. The compressive strength of the foams blown by cyclopentane is higher than that of the water blown foams. This may be due to the decreased cell size of the foams blown by cyclopentane compared to the foams blown by water.

Conclusions

In this study, the morphology, thermal conductivity and mechanical properties of the PIR-PUR foams were investigated with respect to the NCO index and blowing agents. The FTIR results showed that the isocyanurate ring was increased with the increase of the NCO index. When the isocyanurate ring content in the PIR-PUR foams was increased; however, the cell size was slightly decreased. The decreased cell size of the foams affected the decrease of the thermal conductivity of the PIR-PUR foams regardless of the type of the blowing agent. From the results of TGA, thermal stability of the PIR-PUR foams was increased with the increase of NCO index. Thermal stability of the foams blown by water were higher than that of the foams blown by cyclopentane because of the urea formation in the foams blown by water. When the NCO index is 200, a maximum value of

the compressive strength was observed for the PIR-PUR foams regardless of the type of blowing agent. The compressive strength of the foams blown by cyclopentane was higher than that of the water blown foams. This may be due to the decreased cell size of the foams blown by cyclopentane compared to the foams blown by water. From the above results, it is suggested that the thermal insulation property and thermal stability of the PIR-PUR foams are increased with the increase of NCO index. However, compressive strength of the PIR-PUR foams showed maximum value at a specific NCO index.

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