Effect of Isocyanate Index on the Properties of Rigid Polyurethane Foams Blown by HFC 365mfc

Sung Hee Kim and Byung Kyu Kim*

Department of Polymer Science and Engineering, Pusan National University, Busan 609-735, Korea

Ho Lim

Korea Polyol Co., Ulsan 680-090, Korea

Abstract: Rigid polyurethane foams (RPUFs) were fabricated from crude MDI (CMDI) and polypropylene glycols (PPGs) of various isocyanate indices with a physical blowing agent (HFC 365mfc). There was a tendency for the gel time to decrease and the tack-free time to increase with increasing index value. With increasing index value the foam density and compression strength decreased and the glass transition temperature, dimension stability and thermal insulation increased, while the cell size and closed cell content were virtually unchanged. Allophanate crosslinks and condensation reactions between the isocyanate groups, which are favored with a high index value, exerted significant effects on the properties of RPUFs.

Keywords: rigid polyurethane foam (RPUF), isocyanate index, cell structure, density, compression strength, dimensional stability, thermal conductivity.

Introduction

Polyurethanes (PUs) are versatile engineering materials which find a wide range of applications because their properties can be readily tailored by the type and composition of their components.[1-3] PUs are used as coatings, adhesive, sealants, elastomers (CASE), and fibers as well as flexible, semi-rigid and rigid foams. Among them, rigid PU foams (RPUFs) have closed cell structure with low thermal conductivity, high compression strength, low density, high strength-to-weight ratio, and low moisture permeability.[2-4] Consequently, RPUF finds such applications as insulations of refrigerators, freezers, piping, tanks, ship building, and LNG cargos.[5-7]

The foaming can be done in one shot or two shot method. In one shot method, all materials are put into a mixing cup and mixed homogeneously before they are poured into a mold. In two shot method, all materials except the isocyanate are mixed before the isocynate is added. The foaming can be carried out with a physical blowing agent, chemical blowing agent, or mixture of the two.[5] In physical blowing, reactions between isocyanate and polyol produce polyurethane linkages with the emission of heat of reaction. Then, the blowing agent vaporizes and the gas is trapped in the

closed cells of the foam.[8] Typically, thermal conductivity of the blown gas is very low. This, with small closed cell structure gives extremely low thermal conductivity of the RPUF. In chemical blowing, water (most widely used blowing agent) reacts with isocyanate to form unstable carbamic acid which immediately decomposes into an amine and carbon dioxide.[2,9-11]

Recently, many of the conventional blowing agents such as monofluorotrichloromethane (R11) and difluorodichloromethane (R12) have been suggested to contribute to the depletion of the stratospheric ozone layer and the use has been regulated in many countries. Consequently, the use of environmentally friendly blowing agents has become an important and urgent issue in the synthesis of polyurethane foam.[12-14] Water can in part replace such environmentally hazardous blowing agents. However, the excessive use of water causes a negative pressure gradient due to the rapid diffusion of CO_2 through the cell wall causing cell deformation.[2,3,15]

The kinetics of RPUF formation mainly depends on the rates of blowing and gelling reactions, which on the other hand are respectively governed by an amine and a tin catalyst.[4,6] On the other hand, the properties of the foam mainly depend on the morphology of polyol such as functionality and hydroxyl value, and type and amount of surfactant, and blowing agent. To reinforce the foam, composites with par-

*Corresponding Author. E-mail: bkkim@pnu.edu

ticle, clays and fiber are being considered.[16-20]

We synthesized various types of RPUF from crude MDI (CMDI) and poly(propylene glycols) (PPGs) with an environmentally friendly physical blowing agent, viz. HFC 365mfc ($CF_3CH_2CF_2CH_3$). The effects of isocyanate index on the performances of the foams have been extensively analyzed in terms of reactivity, cell morphology, mechanical and dynamic mechanical properties, and thermal properties of the foams.

Experimental

Raw Materials. Two types of PPG having hydroxyl value (OHV, mg KOH/g of sample) of 450 (HR-450P) and 400 (KR-403) were provided by Korea Polyol Co. (Korea). Crude MDI (CMDI) was provided by Huntsman (Suprasec-5005). HFC 365mfc was provided by Solvay Chemicals (Belgium), whereas Polycat-8 (PC 8) as foaming catalyst by Air Products. Silicon surfactant (B 8404) was provided by Goldschmidt. Polyols were dehydrated before use at 90 °C for 24 h in a vacuum oven. Other chemicals were used as received.

Preparation of Samples. The rigid foams were synthesized by one shot method. All raw materials were first put into a mixing vessel (Utra-Turrox T-50, Ika-Werke) and mixed for 30 sec at 7,000 rpm. Then the mixtures were discharged to an open mold (200 × 200 × 200 mm) and the foam cake was cured for 1 week at room temperature. The NCO index (isocyanate equivalents/polyol equivalents × 100) controlled from 90 to 130. The basic formulations are given in Table I.

Characterizations. Density of the foam was measured according to ASTM D 1622 with sample size of 30×30×30 mm (width×length×thickness), and an average of at least five measurements was taken to report. The closed cell content was determined by an air pycnometer following ASTM D 2850 with specimen dimension 50×50×25 mm. Thermal conductivity was measured using HC-074 (Laser Comp) according to ASTM C 518. The cell morphology was observed under a scanning electron microscope (SEM, HITACHI S3500N). Samples were cryogenically fractured in liquid nitrogen and gold sputtered before they were scanned in the free rising direction. Dynamic mechanical tests were performed with a dynamic mechanical thermal analyzer (DMTA, Rheometrics MK-IV) from 30 to 250 °C at 10 hz and 2%

strain using tensile mode. Mechanical properties at room temperature were measured using a Universal Testing (Ametek, Lloyd). Compression strength was determined by ASTM D 1621 at a crosshead speed of 3.0 mm/min with the sample dimension of 30×30×30 mm.[7] The force required for at 10% deformation based on the original thickness has been taken as the compression strength of the foam. Dimensional stability was measured at 80 and -30 °C for the duration of 24 h following ASTM D 2126.

Results and Discussion

Reactivity of Foam Formation. Reactivity of the foam formation is followed by the physical change of the properties such as cream time, gel time and tack-free time.[4,6] The cream time corresponds to the start of bubble rise and hence color of the mixture becomes cream-like from dark brown due to the introduction of bubbles. Gel time is the starting point of stable network formation by intensive allophanate crosslinkings as well as urethane and urea linkages. At the tack-free time, the outer surface of the foam loses its stickiness and the foam can be removed from the mold.

Table II shows that cream time is insensitive to the index value. On the other hand, gel time decreases and tack-free time increases with increasing index value although the differences are small. The decreasing tendency of gel time is probably due to the increased mixture mobility and allophanate reactions which are favored with more of the free isocyanate. On the contrary, it is also more probable to produce more of low molecular weight polymers including the unreacted monomers as the stoichiometric imbalance between the reacting groups is increased. The low molecular weight species are preferably exposed to the free surfaces due to

Table II. Reactivity and Foam Properties

	90	110	130
Cream time (s)	60	61	61
Gel time (s)	208	206	204
Tack-free time (s)	245	250	254
Density distribution	4.7	3.16	2.59
Closed cell content (%)	92.50	92.71	91.36
Cell size (μm)	143	144	146

Table I. Formulations to Synthesize the RPUFs

Samples	Polyol(g)		HFC 365mfc (g)	B 8462 (g)	PC 8 (g)	CMDI (g)	NCO Index
	HR-450P	KR-403					
90	38.60	9.65				46.15	90
110	34.82	8.70	4.40	0.80	0.40	50.88	110
130	31.71	7.93				54.76	130

Figure 1. Densities of the RPUFs vs. isocyanate index.

(a) 90   (b) 110

(c) 130

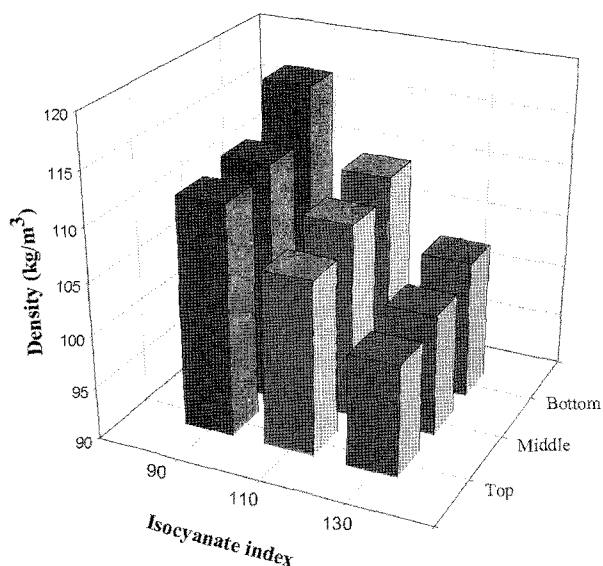**Figure 2.** SEM micrographs of the RPUFs vs. isocyanate index.

their low free energy and cause stickiness, which would give long tack-free time.

Foam Density and Density Distribution. Density is a most important parameter to control the mechanical and thermal properties of closed cell foams.[2,3] Figure 1 shows that the density decreases, i.e., blowing efficiency increases as the index increases. This is due to the combined effects of increased mixture mobility and additional blowing (other than the physical blowing) by the CO_2 produced from the condensation reactions between the isocyanate groups.[2,3]

$$-NCO + -NCO \rightarrow -NCN- + CO_2$$
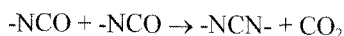
Regarding the density distribution, density decreases along the bubble rising direction i.e., from bottom to top, and the effect is less pronounced with increasing the index value. The vertical distribution of foam density is mainly due to the gravity effect giving rise to great compression at bottom. In addition, high index value provides cell walls with great elasticity by allophanate crosslinks, and the walls are less vulnerable to deformation.

Cell Morphology Foam Diameter. Figure 2 shows the SEM morphology of the cell as a function of index value. It is seen that the foams consist of spherical and polyhedral shape. Size and closed cell content (Table II) are virtually insensitive to the index value.

Regarding the formation of cells, exothermic heat of reaction causes the supersaturation of the reactive mixture, leading to phase separation into gas followed by diffusion into the nuclei which are small air bubbles entrapped during the mixing of raw materials.[21] Then the nuclei grow into bubbles and spherical cells by adopting more gases or by coalescence with neighboring ones. As the blow ratio increases the spherical bubbles are eventually separated by the cell
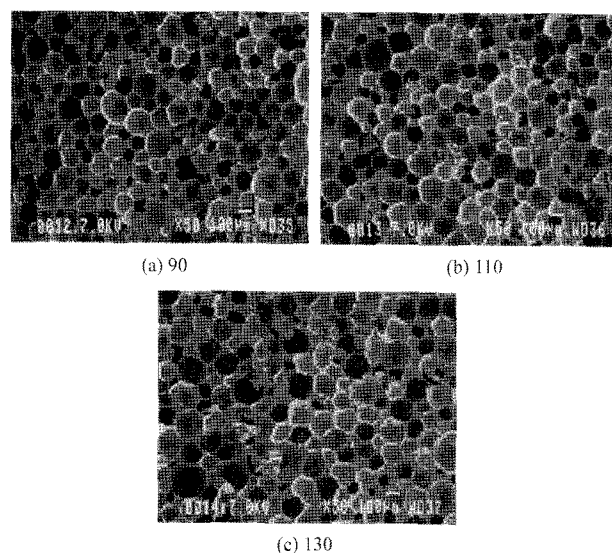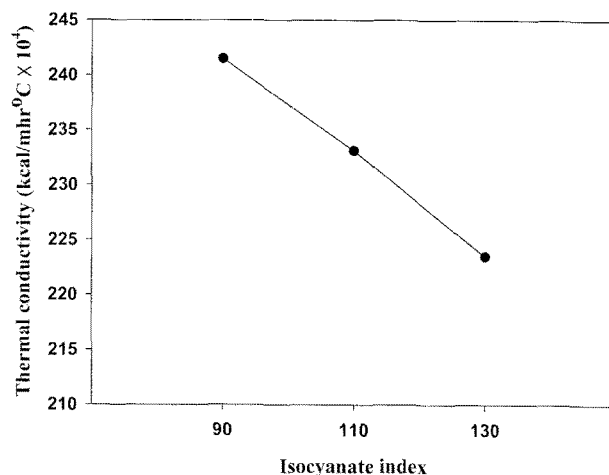

Figure 3. Thermal conductivities of the RPUFs vs. isocyanate index.

membrane and become polyhedral.

As the index value increases, elasticity of the cell wall increases by the allophanate crosslinks. Then the growth and coalescence of the bubbles become difficult. This would keep the bubble small. On the hand, CO_2 blows and expands new bubbles. It seems that the two conflicting forces are more or less balanced to give similar size of bubbles regardless of the index value.

Compression Strength. The compression strength is closely related to the dimensional stability of closed cell foams. As the temperature goes up, gas pressure inside the cell increases, and the pressure difference relative to the atmospheric pressure becomes great. If the foam is to be dimensionally stable under these conditions, the compression strength must be greater than the pressure rise.[2] A minimum compression strength of 0.1 MPa is generally
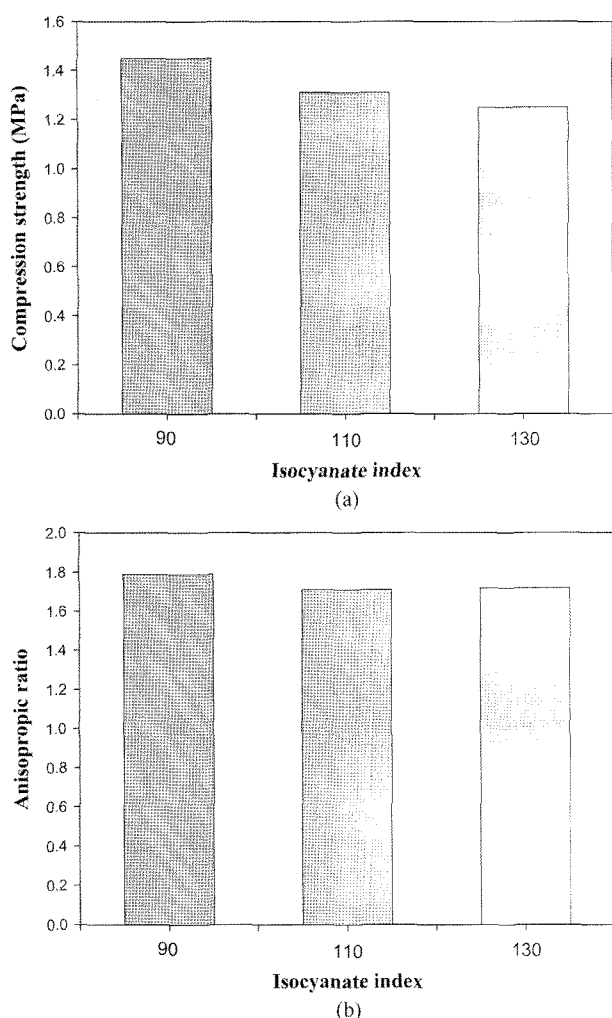
Figure 4. Compression strengths (a) and their anisotropies (b) of the RPUFs vs. isocyanate index.

Figure 5. Storage modulus (a) and tanδ peaks (b) of the RPUFs v.s isocyanate index.

recommended for closed cell foam.[3] The compression strength of our foam is greater than 1.2 MPa and its anisotropy (strength ratio of parallel to perpendicular direction) decreases with increasing the index value (Figure 4), due mainly to the decreased foam density although the cell elasticity is enhanced. The elasticity of crosslinked polymer is given by[22]

$$G_N^o = \frac{\rho R T}{M_c}$$

Here, G_N^o, ρ, R, T, and M_c are is the rubbery plateau modulus, density, gas constant (8.314 m³ Pamol⁻¹K⁻¹), temperature, and molecular weight between cross-links, respectively. As the index value increases more of allophanate crosslinks are introduced, which gives a decrease in M_c and an increase in elasticity. This will be seen as the increased T_g with increasing index value from the dynamic mechanical measurements.

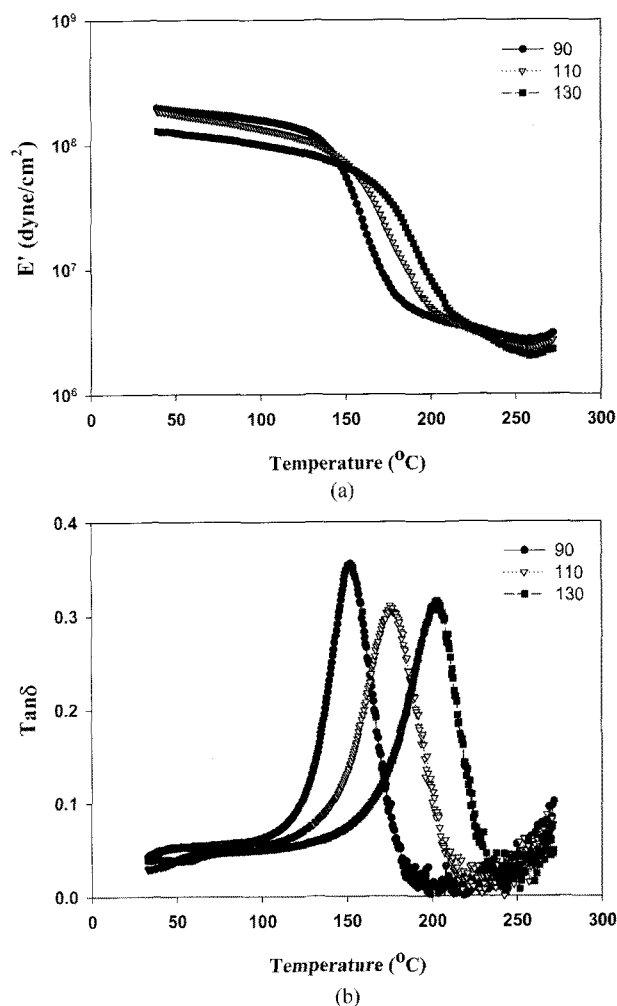**Dynamic Mechanical Analysis.** The damping character-

istics of the foams are shown in Figure 5 where the glass transition temperature (T_g) are seen in terms of tanδ peak. As expected, the T_g of PU increases with increasing the index value. Since T_g of polymer increases with increasing crosslink density,[23] this confirms that more of the allophanate crosslinks are formed as the index value increases.

Dimensional Stability. Closed cell foams shrink at low temperature and expand at high temperature. Typically, less than 1% of volume change is desired for sufficient strength. Figure 6 shows that the volume change asymptotically decreases with increasing the index value, and the largest volume change is less than 1%. The decrease is mainly due to the increased allophanate crosslinks of the foam with increasing the index value. The shrinkage at -30 °C is smaller than the expansion at 80 °C for index values of 110 and 130 due probably to the great elasticity of crosslinked cell wall at low temperature. However, the opposite is seen for index value of 90 where the allophanate crosslinks are presumably insignificant and properties at low temperature
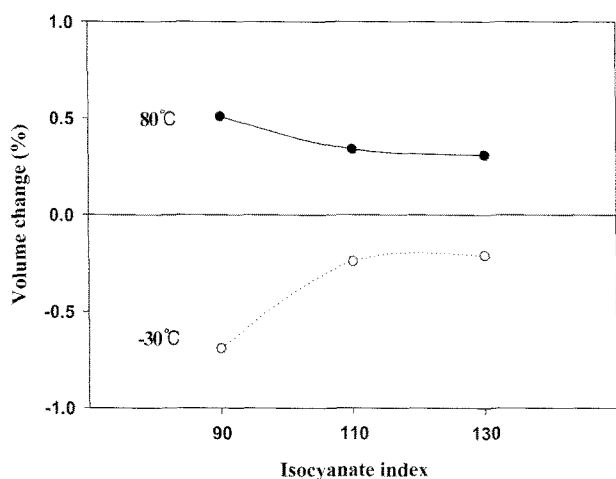
Figure 6. Volume changes of the RPUFs for a duration of 24 h vs. isocyanate index.

are mainly governed by the polyol.

Thermal Conductivity of the Foam. Heat conduction through the closed cell foams can be approximated by a series model which is composed of polymer walls and gas cells in series.[24] Conductive heat flux (q) through the composite wall is given by

$$q = \frac{\Delta T}{R} \qquad (1)$$

where ΔT is the temperature drop across the foam and R is the conduction resistance given by the following equation.

$$R = \sum_{i=1}^{n} \left(\frac{X_{W,i}}{k_W} + \frac{X_{G,i}}{k_G} \right) \qquad (2)$$

Here $X_{W,i}$ and $X_{G,i}$ are the cell wall thickness and cell dimension, and n is the number of polymer walls, respectively. For uniform cells, wall thickness ($X_{W,i}$) and cell dimension ($X_{G,i}$) are constant to give

$$R = n\left(\frac{X_W}{k_W} + \frac{X_G}{k_G} \right) \qquad (3)$$

In a typical closed cell foam, the polymer walls occupy 3-6 vol% of the foam. In addition, the conductivity of the polymer is much greater than that of the blowing gas. So, the first term, viz. polymer wall resistance can be neglected to give

$$R = n\left(\frac{X_G}{k_G} \right) \qquad (4)$$

The above simple analysis shows that the thermal insulation of closed cell foams increase linearly with the number of closed cells, i.e., effect of insulation increases as the cell size decreases.[25]

The thermal conductivity of our foam decreases with

increasing the index value (Figure 3). Since the cell size of our foams was virtually insensitive to the index value, thermal conductivity doesn't greatly depend on X_G in eq. (4) The decrease is in part due to the decreased density of the foam giving a larger value of 'n' which is caused by the additional blowing reactions between the isocyanates groups to produce CO_2 having much smaller thermal conductivity as compared with polymer walls.

Conclusions

RPUFs have been fabricated from CMDI and PPGs of various isocyanate indices with an environmentally friendly blowing agent (HFC 365mfc) and the following conclusions have been derived.

Though marginal, gel time decreased and tack-free time increased with increasing index value due respectively to the increased mixture mobility and allophanate crosslinks, and the presence of low molecular weight polymers which are preferentially exposed to the surface and cause stickiness.

Foam density decreased as the index value increased due to the additional blowing by the CO_2 which was produced from the condensation reactions between the isocyanates, followed by the decreased compression strength and decreased thermal conductivity. The low thermal conductivity of CO_2 has been considered as the prime reason for the low thermal conductivity of the foam.

The decrease of volume changes or the increase of dimensional stability of the foam with the increase of index value was caused by the increased glass transition temperature which on the otherhand was introduced by the increased allophanate crosslinks. A direct evidence of the increased crosslink density was seen from the increased glass transition temperature.

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