Effects of the Functionality of Polyol in Rigid Polyurethane Foams

Ho Lim,[1] Sung Hee Kim,[2] Byung Kyu Kim[2]

[1]Korea Polyol Co., Ulsan 680-090, Korea
[2]Department of Polymer Science and Engineering, Pusan National University, Busan 609-735, Korea

ABSTRACT: Rigid polyurethane foams (RPUFs) have been fabricated from crude MDI (CMDI) and polypropylene glycols (PPGs) of various functionalities (f) with HFC 365mfc as a blowing agent. Foam density increased, cell size and density distribution decreased with increasing f while the closed cell content was kept constant over 92%. The gel time, tack-free time, volume change, and the thermal conductivity of the foam showed a minimum with $f = 5$, and the existence of minimum has been explained in terms of a large mixture viscosity and cell wall resistance. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 49–54, 2008

Key words: density; mechanical properties; morphology; polyurethanes; thermodynamics

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, semirigid and rigid foams. Among them, rigid PU foams (RPUF) have closed cell structure with low thermal conductivity, high compression strength, low density, high strength-to-weight ratio, and low moisture permeability.[4,5] Consequently, RPUF finds such applications as insulations of refrigerators, freezers, piping, tanks, ship building, and LNG cargos.[6]

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 thoroughly 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. In physical blowing, reactions between isocyanate and polyol produce polyurethane linkages with the emission of heat of reaction.[7] Then, the blowing agent vaporizes and the gas is trapped in the closed cells of the foam. 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 that immediately decomposes into an amine and carbon dioxide.[8]

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.[9–11] Consequently, the use of environmentally friendly blowing agents has become an important and urgent issue in the synthesis of polyurethane.[12,13] 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.

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. 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.[14,15]

We synthesized various types of RPUF from crude MDI and polypropylene glycols (PPG) with an environmentally friendly physical blowing agent, viz. HFC 365mfc ($CF_3CH_2CF_2CH_3$). The effects of PPG functionality on the performances of the foams have been extensively analyzed in terms of kinetic rates,

TABLE I
Formulations to Synthesize RPUFs

Samples	Polyol (g)				HFC 365mfc (g)	B 8404 (g)	PC 8 (g)	CMDI (g)
	GS400-3	GS400-4	GS400-5	GS400-6				
F3	45.78				4.41	0.81	0.41	48.59
F4		45.78						
F5			45.78					
F6				45.78				

GSF400-n is PPG of functionality of n.

cell morphology (cell size, anisotropy, closed cell content), and mechanical, dynamic mechanical and thermal properties of the foams.

EXPERIMENTAL

Raw materials

Four types of PPG were synthesized with two types of initiators, viz. sorbitol, and sucrose/glycerine. The PPGs having functionalities of 3, 4, 5, and 6 (GS400-3, GS400-4, GS400-5, GS400-6, OHV: 400, E.W.: 140.25) were provided by Korea Polyol Co. (Korea). Crude MDI was provided by Huntsman (Suprasec-5005). HFC 365mfc, as physical blowing agents, 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 s at 7000 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) was fixed at 1.10. The basic formulations are given in Table I.

Characterizations

Kinetics of the foam formation are followed by the physical change of the properties such as cream time, gel time, and tack-free time.[8] The cream time corresponds to the start of bubble rise and hence color of the mixture becomes creamlike from dark brown due to the introduction of foam bubbles. Gel time is the starting point of stable network formation by intensive formations of urethane and urea linkages and crosslinkings by allophanate and biuret

reactions. At tack-free time, the outer surface of the foam loses its stickiness and the foam can be removed from the mold. These times were measured by a digital stop watch.

Density of the foam was measured according to ASTM D 1622 with sample size of 30 × 30 × 30 mm^3 (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^3. 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 compression mode. Mechanical properties at room temperature were measured using a Universal Testing Machine (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^3 (W × L × T).[11] Dimensional stability was measured at 80 and −30°C following ASTM D 2126. ATR-FTIR (Magna-IR 750, Nicollet) was used to confirm the conversion of NCO groups.

RESULTS AND DISCUSSION

Kinetics of foam formation

Reactivity is also of importance in the foaming process. Table II shows that cream time is virtually insensitive to the functionality (f) of PPG. Cream time is mainly controlled by the amine catalyst, whereas gel time and tack-free time by tin catalyst. It is seen that gel time and tack-free time decrease with the increase of f with a minimum at $f = 5$, beyond which they increase. The decrease of gel time and tack-free time is primarily due to the increased rate of network formation (increased f and

TABLE II
Various Properties of the RPUFs vs. PPG Functionality

	F3	F4	F5	F6
Viscosity (cps) at 25°C, polyol	420	4100	13,300	42,000
Cream time (s)	90	92	91	92
Gel time (s)	259	245	238	242
Tack free time (s)	315	281	267	285
Cell size (µm)	300	250	220	180
Closed cell content (%)	92.22	92.35	92.55	91.87
Compression strength (MPa)	1.05	1.12	1.13	1.23
Compression strength anisotropy (%)	1.39	1.58	1.57	1.72
Glass transition temperature (°C)	115.10	150.87	170.25	224.13
Conversion (%)	96.45	96.05	96.17	93.56
Thermal conductivity (kcal/m h °C) $\times 10^4$	235.1	233.7	232.4	235.9

increased content of sucrose based polyol having aromatic ring). However, the effect of mixture viscosity (Table II) seems more pronounced than the functionality effect with $f = 6$. This, together with the intensive network formation leads to slow gelling reactions.

Cell morphology foam diameter

Figure 1 shows cell structures of the foams as a function of PPG functionality, together with their cell size in Table II. It is seen that the foams consist of well defined closed cells of spherical and polyhedral shape, and the size decreases as the PPG functionality increases. The close cell content is over 92% and almost independent of cell size. Regarding the formation of cells, exothermic heat of reaction causes the supersaturation of the reactive mixture, leading to phase separation into vapor followed by diffusion into the nuclei which are small air bubbles entrapped during the mixing of raw materials.[4,16] Then the nuclei grows into bubbles and spherical cells by coalescence with neighboring ones. When the spherical bubbles are separated by the cell membrane, they become polyhedral. Obviously, the bubble coalescence becomes difficult as the elasticity of the cell wall becomes great. That is, with the increase in PPG functionality, the elasticity of the cell wall increases due to the increased crosslink density.

Foam density and density distribution

Density is a most important parameter to control the mechanical and thermal properties of closed cell foams. Figure 2 shows that the foam density increases with increasing f. It is also noted that the density increase is most pronounced as f increases from 3 to 6. Regarding the vertical distribution, cell size increases along the rising direction i.e., from bottom to top, and the effect is less pronounced with
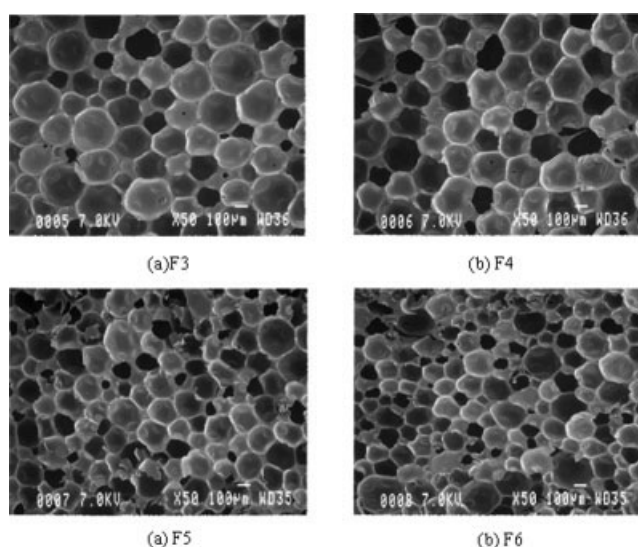

Figure 1 SEM morphologies of the RPUFs versus PPG functionality.
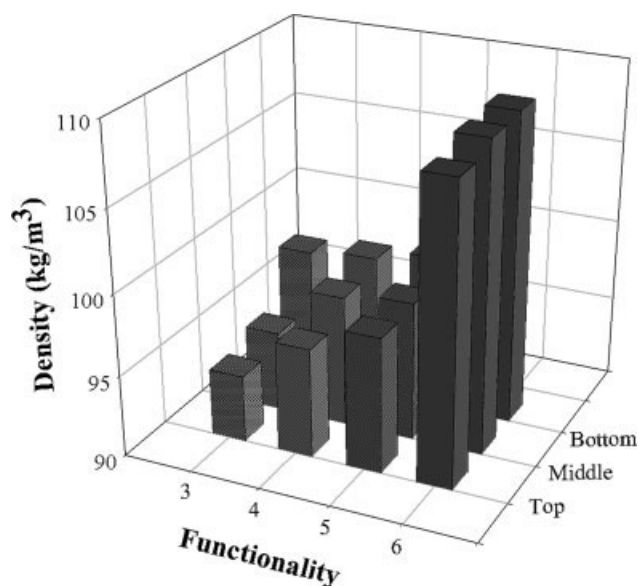

Figure 2 Densities of RPUFs versus PPG functionality.

increasing *f*. The vertical distribution is mainly due to the gravity effect giving rise to great compression at bottom. On the other hand, high functionality PPG provides cell walls with great elasticity by great crosslink density, and the walls are less vulnerable to deformation by compression as well as internal pressure.

Compression strength

The force required for 10% deformation based on the original thickness has been taken as the compression strength of the foam. 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. A minimum compression strength of 0.1 MPa is generally recommended for closed cell foam.[5] The compression strength as well as the anisotropy (strength ratio of parallel to perpendicular direction) of our foam generally increases with increasing *f* ranging from 1.05 (*f* = 3) to 1.23 (*f* = 6) MPa although there is little difference between *f* = 4 and *f* = 5 (Figs. 5 and 6). The compression strength increase is mainly due to the increased density, which on the other hand, is due to the decreased blowing efficiency.

Dynamic properties

The dynamic mechanical properties of foams are shown in Figure 3 where the rubbery modulus and tan δ peak temperature increase with increasing *f*. (Table II) The increase of plateau modulus is directly related to the crosslink density as[17]

$$G_N^o = \frac{\rho RT}{M_c} \qquad (1)$$

Here, G_N^o, ρ, R, T, and M_c are is the rubbery plateau modulus, density, gas constant (8.314 m^3 Pa mol^{-1} K^{-1}), temperature, and molecular weight between crosslinks, respectively.

On the other hand, the glass transition temperature (T_g) is inversely proportional to the M_c as[18]

$$T_g = A + \frac{B}{M_c} \qquad (2)$$

where *A* and *B* are constants. It is concluded that high functionality polyol gives high crosslink density which in turn gives high glass transition temperature. It is noted that for *f* = 6, the glass-rubber tran-
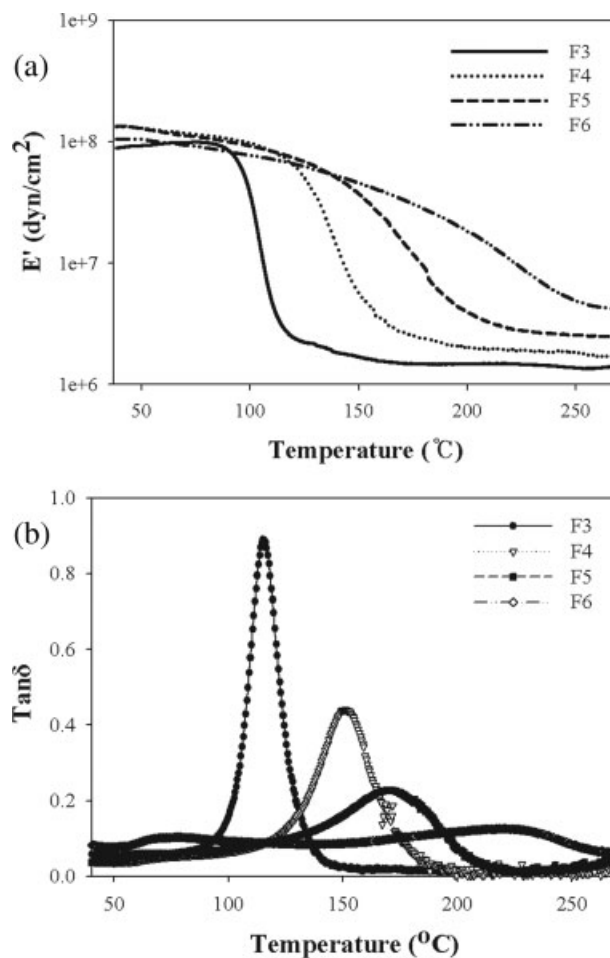
Figure 3 Storage moduli (a) and tan δ (b) of the RPUFs versus PPG functionality.

sition is less pronounced and the tan δ peak is mere a broad shoulder implying that the system is composed of various levels of crosslink density.

Dimensional stability

Closed cell foams shrink at low temperature and expand at high temperature. The dimensional stability of foam depends on a number of factors such as density or cell size, closed cell content, glass transition temperature, and compressibility of the gas. Typically, less than 1% of shrinkage is desired for sufficient strength. The largest volume change is less than 1% (Fig. 4), and foam is a bit more dimensionally stable at −30°C than at 80°C because of the increased elasticity of cell wall at low temperature. The volume change decreases with increasing functionality up to *f* = 5, beyond which it increases a bit and the tendency is similar to that of gel time and tack-free time. The smallest volume change viz the greatest dimensional stability obtained may imply that more crosslinks are introduced with *f* = 5 than
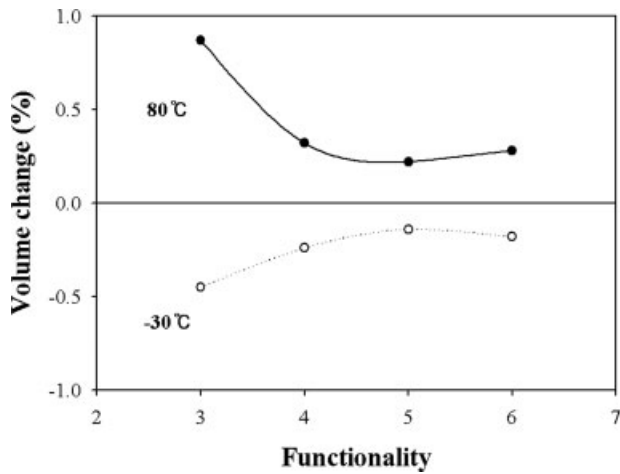
Figure 4 Volume changes of the RPUFs for a duration of 24 h versus PPG functionality.

Figure 6 Strength anistropy of RPUF vs. functionality of polyol.

with $f = 6$ since the compression resilience generally increases with crosslink density

To confirm this, the conversion of NCO groups has been determined using FTIR-ATR (Table II). For this, a calibration curve of NCO/R-H area ratio versus conversion has been prepared using known data. It is seen that the conversion is over 96% for $f = 3$–5, and it is less than 94% for $f = 6$. Probably, high viscosity of the reaction mixture with $f = 6$ would lower the final conversion as well as reaction rate as noted from the long gel time and tack free time, together with broad crosslink density distribution.

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. Con-
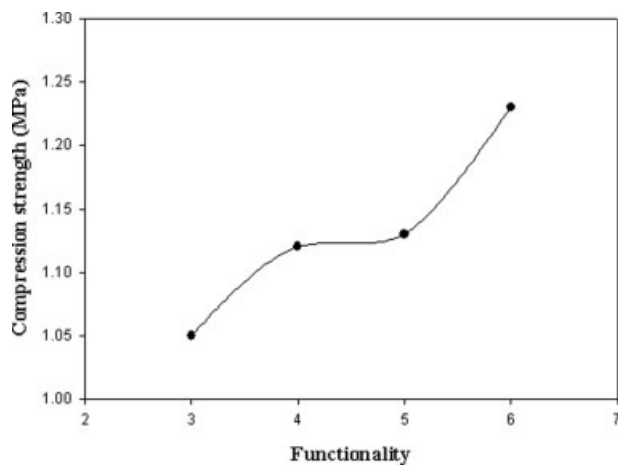
ductive heat flux (q) through the composite wall is given by[19]

$$q = \frac{\Delta T}{R} \tag{3}$$

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

$$R = \sum_{i=1}^{n} \left(\frac{X_{W,i}}{k_W} + \frac{X_{G,i}}{k_G} \right) \tag{4}$$

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

$$R = n \left(\frac{X_W}{k_W} + \frac{X_G}{k_G} \right) \tag{5}$$

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

$$R = n \left(\frac{X_G}{k_G} \right) \tag{6}$$

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. However, the thermal conductivity of our foams shows a minimum at $f = 5$ (Table II), although our cell size decreased monotonically with f. The increase with $f = 6$ is mainly due to the large increase in density giving rise to poor formation of foam. Then the second term of eq. (5) may be considered to give increased resistance and decreased thermal conductivity.

Figure 5 Compression strength of RPUF vs. functionality of polyol.

CONCLUSIONS

The RPUFs have been fabricated from CMDI and PPGs of various functionalities (f) with an environment friendly blowing agent, viz. HFC 365mfc and the following conclusions have been obtained.

As foam density increased, cell size and density distribution decreased with increasing f while the closed cell content was kept constant over 92%.

The compression strength and its anistropy generally increased with inncreasing f though no difference was found between $f = 4$ and $f = 5$.

The gel time, tack-free time, and volume change of the foam showed a minimum with $f = 5$, implying that high mixture viscosity of $f = 6$ retards the reaction and decrease the final conversion as verified from the conversion measurement.

On a difference basis, thermal conductivity decreased with increasing f showing a minimum at $f = 5$, followed by an increase with $f = 6$. The decrease is due to the decrease in cell size, whereas the increase is due to the large increase in foam density, which necessitates the incorporation of cell wall resistance.

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