Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Effect of Blowing Agent Type in Rigid Polyurethane Foam

Sung Hee Kim[a]; Ho Lim[b]; Jin Chul Song[a]; Byung Kyu Kim[a]
[a] Department of Polymer Science and Engineering, Pusan National University, Pusan, Korea [b] Korea Polyol Co., Ulsan, Korea

To cite this Article Kim, Sung Hee , Lim, Ho , Song, Jin Chul and Kim, Byung Kyu(2008) 'Effect of Blowing Agent Type in Rigid Polyurethane Foam', Journal of Macromolecular Science, Part A, 45: 4, 323 — 327
To link to this Article: DOI: 10.1080/10601320701864260
URL: http://dx.doi.org/10.1080/10601320701864260

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry (2008) **45**, 323–327
Copyright © Taylor & Francis Group, LLC
ISSN: 1060-1325 print / 1520-5738 online
DOI: 10.1080/10601320701864260

Effect of Blowing Agent Type in Rigid Polyurethane Foam

SUNG HEE KIM,[1] HO LIM,[2] JIN CHUL SONG,[1] and BYUNG KYU KIM[1]

[1]*Department of Polymer Science and Engineering, Pusan National University, Pusan, Korea*
[2]*Korea Polyol Co., Ulsan, Korea*

Received July, 2007, Accepted October, 2007

Rigid polyurethane foams have been fabricated from polymeric MDI and polypropylene glycols (PPG) synthesized with two different initiator compositions using two different types of blowing agents, viz., the conventional HCFC 141b and environmently friendly HFC 365 mfc. It was found that the two blowing agents gave identically the same cream time, gel time, and tack-free time. The HFC 365 mfc gave foams with smaller cell size, greater core density and compression strength, whereas HCFC 141b gave better dimensional stability and thermal insulation. For the same type of blowing agent, the initiator containing more toluene diamine gave greater core density, compression strength and thermal insulation

Keywords: rigid polyurethane foam; cell structure; core density; compression strength; dimensional stability; thermal conductivity

1 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 foams, coatings, adhesive, elastomers, and fibers (4). Among them, rigid polyurethanes foams (RPUFs) find such applications as insulations of refrigerators, freezers, piping, tanks, ship building, and LNG cargos (5). In these applications, high compression strength, especially at low temperature, as well as extremely low thermal conductivity, are properties of prime importance (6, 7).

The foaming process includes both the gelling reaction and the actual foaming process. First, reactions between isocyanate and polyol produce polyurethane linkages with the emission of heat of reaction. Second, the blowing agent vaporizes due to the heat of reaction and the gas is trapped in the closed cells of the foam to give extremely low thermal conductivity of RPUFs (physical blowing). In the presence of water, isocyanate also reacts with water to form urea linkage and carbon dioxide (chemical blowing) (8, 9).

The properties of RPUFs are considerably influenced by the type and content of the blowing agents. 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 (10, 11, 12). Consequently, the use of environmentally friendly blowing agents has become an important and urgent issue in the synthesis of polyurethane foam. Water has replaced such environmentally hazardous blowing agents (13). 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 (14).

We synthesized RPUFs from polymeric MDI and polypropylene glycols (PPG) prepared using two different compositions of initiators containing sorbitol and toluene diamine. Two types of blowing agent i.e., conventional HCFC 141b (CH_3CCl_2F) and environmentally friendly HFC 365mfc ($CF_3CH_2CF_2CH_3$) have been employed, and their performance has been analyzed in terms of reaction time, cell morphology, and mechanical and thermal properties of the foams.

2 Experimental

2.1 Raw Materials

Two types of PPG synthesized using different initiators, viz. sorbitol (OHV: 480, E.W.: 116.7)/toluene diamine (OHV: 400, E.W.: 140.0) = 6/4, and 8/2 were provided by Korea Polyol (Korea). Polymeric MDI was provided by Kumho Mitsui Chemicals (Korea). HCFC 141b and HFC 365mfc, as physical blowing agents, were provided by Solvay Chemicals (Belgium). D33LV (Air Products) was used as a gelling catalyst. Surfactant (B8462) was provided by Goldschmidt AG (Germany) Polyols were dehydrated before use at 90°C for 24 h in a vacuum oven. Other chemicals were used as received.

Address correspondence to: Byung Kyu Kim, Department of Polymer Science and Engineering, Pusan National University, Pusan 609-735, Korea. E-mail: bkkim@pnu.edu

2.2 Preparation of Samples

The RPUFs were synthesized by a one shot method. All materials were first put into a mixing cup and mixed thoroughly at 3000 rpm until they become homogeneous. Then the mixtures were poured into an open mold (200 × 200 × 100 mm) and cured for 1 week at room temperature. Blowing agents were used to prepare the foams. The amount of polyol, surfactant, and NCO index (Isocyanate equivalents/polyol equivalents) were respectively fixed at 100, 3, and 110 pphp (parts per 100 polyol by weight). The basic formulations are given in Table 1.

2.3 Characterization

Core density of the foam was measured according to ASTM D 1622 with a sample size of 30 × 30 × 30 mm (Width × Length × Thickness), and an average of at least five measurements was taken to report. 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). Mechanical properties were measured using a Universal Testing Machine (LLOYD Instruments, England) at room temperature. Compression strength was determined by ASTM D 1621 at a crosshead speed of 3.00 mm/min with the sample dimension of 30 × 30 × 30 mm (W × L × T) (15). Dimensional stability tests were done following ASTM D2126 at 80°C and -30°C.

3 Results and Discussion

3.1 Blowing Agent Type vs. Processing Characteristics

Reaction time is of importance in the foaming process. Table 2 shows that cream time, gel time and tack-free time for the two types of blowing agents were identically the same, which favors the use of the environmentally friendly blowing agent.

3.2 Blowing Agent Type vs. Cell Morphology

Figure 1 shows cell structures of the foams synthesized with the two different types of blowing agents. It is seen that the foams consist of well defined closed cells regardless of the blowing agent type. However, it is noted that HFC 365 mfc gives finer cells with uniform distribution than HCFC 141b, probably due to the larger amount of fluorine atoms of the former provide the growing gas bubbles with less surface energy than the latter one. Blowing agents having lower surface free energy create more surfaces to give smaller cells.

Table 2. Blowing agent type vs. reaction time

	HCFC 141b	HFC 365mfc
Cream time (s)	15∼17	16∼17
Gel time (s)	98∼100	98∼100
Tack free time (s)	137∼140	135∼140

3.2 Initiator Type and Blowing Agent Type vs. Core Density

Density is a most important parameter to control the mechanical and thermal properties of closed celled foams. The core densities of the foams are around 120 (kg/m^3) (Figure 2). The slightly higher density cells obtained with more toluene diamine (T4 series) suggest that the gelling reactions have possibly been catalyzed by the toluene diamine during the foaming process since urethane polymerization reactions are catalyzed by amine. Regarding the effect of different blowing agents, environmentally friendly HFC 365mfc gives a bit higher density than the HCFC 141b, however the difference is marginal.

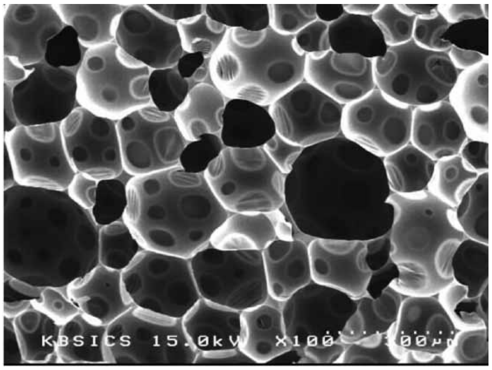
3.3 Blowing Agent Type vs. Compression Strength

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 celled foams. As the temperature goes up, gas pressure inside the cell increases, and the pressure difference relative to the atmospheric pressure becomes greater. 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 (8). The compression strengths of our foams are

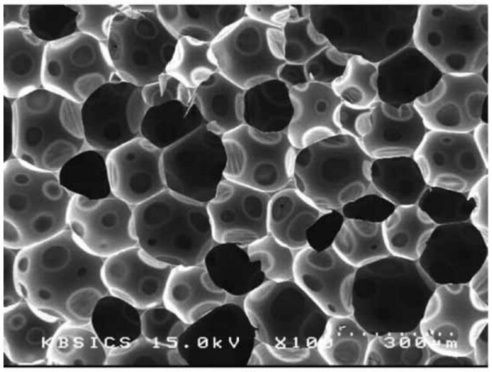
Table 1. Blowing agent type, initiator combination and catalyst content based formulations

	Polyol					
Samples	Sorbitol	TDA	HCFC 141b	HFC 365mfc	Surfactant	33LV
T2B9	80	20	9.5	0	3	0.8
T4B9	60	40				
T2M12	80	20	0	12		
T4M12	60	40				

The formulation is based on 100 parts of the polyol by weight.



(a)



(b)

Fig. 1. Cell size vs. type of blowing agent. (a) T4B9 (b) T4M12 The apparent cell wall "holes" correspond to junctions between neighboring cells.

about 1.1 MPa. Regarding the effect of blowing agent type, HFC 365mfc gives a slightly higher compression strength than HCFC 141b, due to the higher density of the foam as described above, since linear relationships between core density and compression strength are often obtained (8, 16). As expected, higher content of toluene diamine (T4 series) gives higher compression strength for both of the blowing agents due, again, to the higher densities of the foams. It is seen that the effect is more pronounced with HCFC 141b (Figure 3).

3.4 Blowing Agent Type vs. Dimensional Stability

Next to density, dimensional stability is the most often tested property to characterize closed celled foams. Closed celled foams shrink at low temperature and expand at high temperature. Typically, less than 1% of shrinkage is desired for sufficient strength.

Among the two types of blowing agent, HCFC 141b gives better dimensional stability both under compression and expansion (Figure 4). This implies that the dimensional stability is not necessarily related to the compression strength, especially when the foams are blown with different types of blowing agents. For the same type of blowing agents, a lower content of toluene diamine gives better dimension stability, both at low as well as high, temperatures. This is in contrast to the effect of initiator on compression strength, suggesting that the bulky structure of the toluene diamine initiator which becomes a fragment of the polymer is vulnerable to the permeation of gas molecules, especially at high temperature.

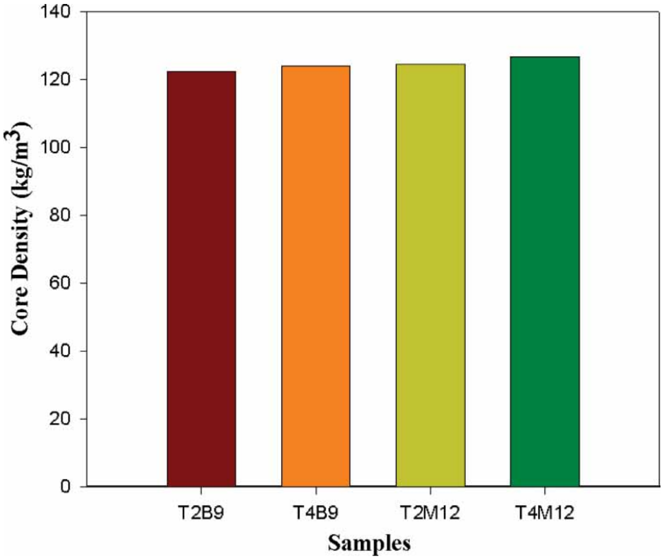


Fig. 2. Core density vs. type of blowing agent.

3.5 Heat Transfer Through the Foam

Heat conduction through the closed celled foams can be approximated by a series model which is composed of polymer walls and gas cells in series (17). Conductive heat flux (q) through the composite wall is given by:

$$q = \frac{\Delta T}{R} \tag{1}$$

where ΔT is the temperature drop across the foam and R is the

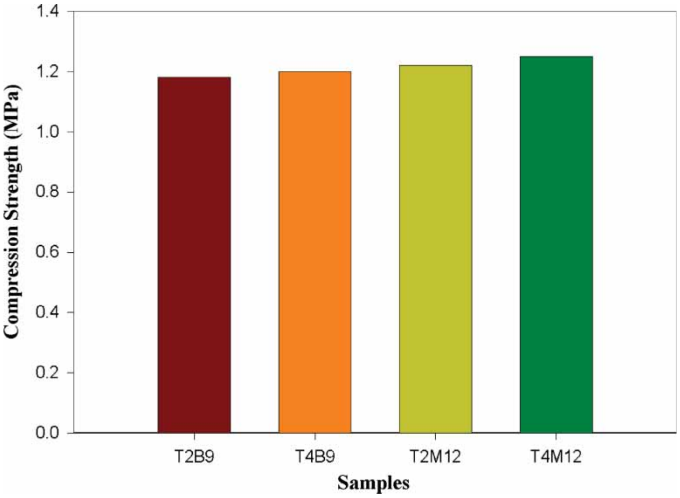


Fig. 3. Compression strength vs. type of blowing agent.

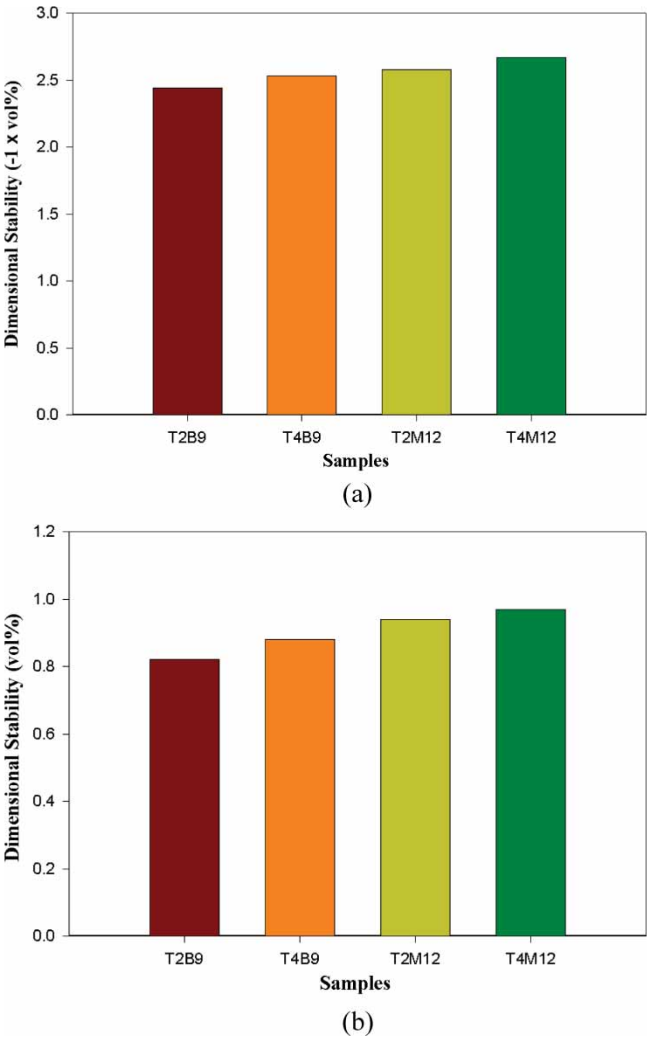


Fig. 4. Dimensional stability vs. type of blowing agent. (a) −30°C, (b) 80°C.

conduction resistance given by the following equation:

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

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:

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

In a typical closed celled foam, the polymer walls occupy 3–6 volume % 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:

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

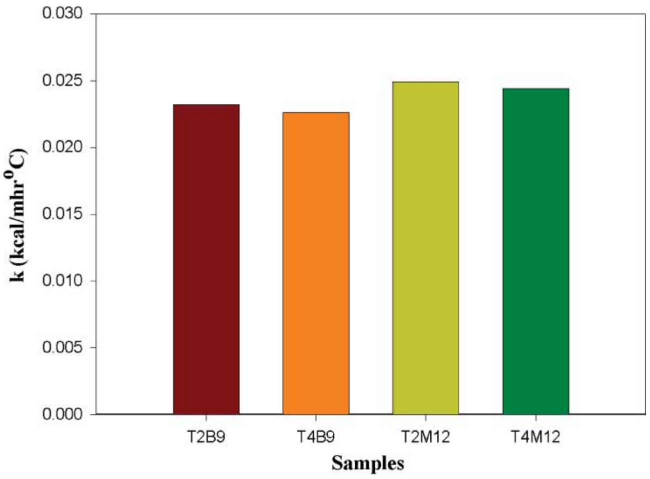


Fig. 5. Thermal conductivity vs. type of blowing agent.

The above simple analysis shows that the thermal insulation of closed celled foams increase linearly with the number of closed cells, that is the effective insulation increases as the cell size decreases.

The thermal conductivity of the closed celled foams is greater with HFC 365mfc than with HCFC 141b (Figure 5). For the same type of blowing agent, initiator containing less toluene diamine gives higher thermal conductivity. The greater thermal conductivity with HFC 365mfc is primarily caused by the higher thermal conductivity of this gas (0.00902 kcal/mhr°C) than the HCFC 141b (0.00679 kcal/mhr°C) since the conductivity of closed celled foams is mainly governed by the conductivity of the gas inside the cells, as shown by the above analysis (Equation (4)). On the other hand, higher thermal conductivity for the lower diamine content is related to the poor dimensional stability of the foams allowing more leaks of the gas.

4 Conclusions

Rigid polyurethane foams have been fabricated from polymeric MDI and polypropylene glycols (PPG) which were synthesized with different amounts of the two initiators viz. sorbitol and toluene diamine, using two different types of blowing agents, viz., the conventional HCFC 141b and environmently friendly HFC 365mfc.

Regarding the processability, the two blowing agents gave identically the same cream time, gel time, and tack free time, which favors the use of the environmentally friendly blowing agent.

The HFC 365mfc gave foams with smaller size, higher core density and higher compression strength whereas HCFC 141b gave better dimensional stability and better thermal insulation. The lower thermal stability of HCFC 141b blown foam is mainly due to the lower thermal conductivity of the gas.

For the same type of blowing agent, initiator containing more toluene diamine gave higher core density and compression strength due, presumably, to the catalytic activity of amine for gelling reactions, and poorer dimensional stability and thermal conductivity due to the bulky structure of the aromatic ring.

5 Acknowledgments

This research was financially supported by the Ministry of Commerce, Industry and Energy (MOCIE) and Korea Industrial Technology Foundation (KOTEF) through the Human Resource Training Project for Regional Innovation. BKK is also indebted to the NCRC organized at PNU.

6 References

1. Hapburn, C. *Polyurethane Elastomers*; Elsevier: Oxford, 1, 1991.
2. Kim, B.K. and Paik, S.H. (1999) *J. Polym. Sci. Part A: Polym. Chem.*, **37**, 2703.
3. Goods, S.H., Neuschwanger, C.L., Whinnery, L.L. and Nix, W.D. (1999) *J. Appl. Polym. Sci.*, **74**, 2724.
4. Seo, W.J., Park, J.H., Sung, Y.T., Hwang, D.H., Kim, W.N. and Lee, H.S. (2004) *J. Appl. Polym. Sci.*, **93**, 2334.
5. Cao, X., Lee, L.J., Widya, T. and Macosko, C. (2005) *Polymer*, **46**, 775.
6. Mondal, P. and Khakhar, D.V. (2004) *Macromol. Symp.*, **216**, 241.
7. Szycher, M. *Szycher's Handbook of Polyurethanes*; CRC Press: New York, p. 8.1, 1999.
8. Oertel, G. *Polyurethane Handbook*; Hanser Publishers: New York, p. 161, 1985.
9. Harikrishnan, G. and Khakhar, D.V. (2007) *J. Appl. Polym. Sci.*, **105**, 3439.
10. Widya, T. and Macosko, C.W. (2005) *Macromol. Sci. Part B-Phys.*, **44**, 897.
11. Wu, J.-W., Sung, W.-F. and Chu, H.-S. (1999) *Int. J. Heat. Mass. Transf.*, **42**, 2211.
12. Antolini, B., Bianchi, F., Bottazzi, M., Careri, M. and Musci, M. (2004) *Chromatographia*, **60**, 323.
13. Li, X.-B., Cao, H.-B., Zhang, Y. and Guan, T. (2006) *J. Appl. Polym. Sci.*, **102**, 4149.
14. Heintz, A.M., Duffy, D.J., Hsu, S.L., Suen, W., Chu, W. and Paul, C.W. (2003) *Macromolecules*, **36**, 2695.
15. Seo, W.J., Jung, H.C., Hyun, J.C., Kim, W.N., Lee, Y.B., Choe, K.H. and Kim, S.B. (2003) *J. Appl. Polym. Sci.*, **90**, 12.
16. Kim, S.H., Lim, H. and Kim, B.K. (2007) Polyurethane Rigid Foams from Environmentally Friendly Blowing Agent, paper presented at J. Polym. Environ, July 18.
17. Bird, R.B., Stewart, W.E. and Lightfoot, E.N. *Transport Phenomena*; Wiley, 303, 2006.