POLYMERS FOR ADVANCED TECHNOLOGIES
Polym. Adv. Technol. 2008; **19**: 1729–1734

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Effects of the hydroxyl value of polyol in rigid polyurethane foams

Ho Lim[2], **Sung Hee Kim**[1] **and Byung Kyu Kim**[1]*
[1] Department of Polymer Science and Engineering, Pusan National University, Busan 609-735, Korea
[2] Korea Polyol Co., Ulsan, 680-090, Korea

Received 12 December 2007; Revised 8 April 2008; Accepted 17 April 2008

Rigid polyurethane foams (RPUFs) have been fabricated from crude MDI (CMDI) and polypropylene glycols (PPGs) of various hydroxyl values (OHVs) of 300–600 with an environmentally friendly blowing agent (HFC 365*mfc*). The closed cell content, compression strength, and dimensional stability of the foam increased with increase in the OHV due to the increased crosslink density, which was evidenced from the increased glass transition temperature (T_g). The cream time, gel time, tack-free time, and density of the foam showed a minimum at 500OHV. The decrease and increase around the minimum were, respectively, interpreted in terms of increased mixture mobility and extensive allophanate crosslinks, which retard gelling as well as foaming reactions. The thermal conductivity also showed a small minimum at 500OHV. Copyright © 2008 John Wiley & Sons, Ltd.

KEYWORDS: rigid polyurethane foam; hydroxyl value; cell structure; dimensional stability; thermal conductivity

INTRODUCTION

Polyurethanes (PUs) are used as coatings, adhesives, sealants, elastomers (CASE), and fibers as well as flexible, semi-rigid, and rigid foams.[1–3] Rigid polyurethane 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, RPUFs find such applications as insulation of refrigerators, freezers, piping, tanks, ship building, and liquefied natural gas (LNG) cargoes.[5–7]

The foaming can be done using a 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. Typically, thermal conductivity of the blown gas is very low. This, together 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.[2,8]

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 their use has been regulated in many countries. So, the use of environment friendly blowing agents has become an important and urgent issue in the synthesis of polyurethane foam.[9–11] 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.[2,3,12]

The reaction kinetics of RPUF formation mainly depends on the rates of blowing and gelling reactions, which on the other hand are governed by an amine and a tin catalyst, respectively.[4,6] On the other hand, the properties of the foam mainly depend on the characteristics of polyol such as functionality and hydroxyl value (OHV), and type and amount of surfactant, and blowing agent. To reinforce the foam, composites formation with particle, clay, and fiber are being considered.[13–17]

We synthesized various types of RPUF from crude methylene diphenyl diisocyanate (CMDI) and polypropylene glycols (PPG) with an environmentally friendly physical blowing agent, *viz.* HFC 365*mfc* ($CF_3CH_2CF_2CH_3$). The effects of OHV on the performance of foams have been extensively analyzed in terms of forming kinetics, cell morphology (cell size, closed cell content), compression strength, dimensional stability, dynamic mechanical, and thermal properties of the foams.

EXPERIMENTAL

Raw materials

Four types of PPG having OHV (mg KOH g^{-1} of sample) of 300, 400, 500, and 600 (GSF4-300, GSF4-400, GSF4-500,

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**Correspondence to*: B. K. Kim, Department of Polymer Science and Engineering, Pusan National University, Busan 609-735, Korea.
E-mail: bkkim@pnu.edu

Table 1. Formulations to synthesize RPUFs

	Polyol (g)							
Samples	GSF4-300	GSF4-400	GSF4-500	GSF4-600	HFC 365*mfc* (g)	8404 (g)	PC 8 (g)	CMDI (g)
OH3	52.63	—	—	—	4.41	0.81	0.41	41.73
OH4	—	45.78	—	—				48.59
OH5		—	40.49	—				53.88
OH6		—	—	35.95				58.42

GSF4-*n* is PPG of hydroxyl number of *n*.

GSF4-600, functionality = 4) were provided by Korea Polyol Co. (Korea). CMDI was provided by Huntsman (Suprasec-5005), HFC 365*mfc* 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 hr 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 7000 rpm. Then the mixtures were discharged to an open mold (200 mm × 200 mm × 200 mm) and the foam cake was cured for 1 week at room temperature. The NCO index (100× isocyanate equivalents/polyol equivalents) was fixed at 110. The basic formulations are given in Table 1.

Characterizations

Density of the foam was measured according to ASTM D 1622 with a sample size of 30 mm × 30 mm × 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 mm × 50 mm × 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 compression 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^{-1} with the sample dimension of 30 mm × 30 mm × 30 mm.[11] 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 hr following ASTM D 2126.

Table 2. Reactivity and foam properties

	OH3	OH4	OH5	OH6
Cream time (s)	95	92	90	91
Gel time (s)	259	240	228	230
Tack-free time (s)	314	281	245	260
Density distribution (%)	3.48	2.06	1.83	0.43
Compression strength (MPa)	0.98	1.12	1.15	1.25
Compression strength anisotropy (%)	1.36	1.59	1.69	1.87

RESULTS AND DISCUSSION

Kinetics of foaming process

Kinetics of the foam formation are typically followed by the 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 formation 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 2 shows that cream time, gel time and tack-free time decrease with increasing OHV showing a minimum at 500OHV, beyond which they increase. For example, the tack-free time is 314 sec for OH3, 245 sec for OH5, and 260 sec for OH6. The increased kinetic rate is primarily due to the increased mobility by the decreased molecular weight (M_n) of the PPG. On the other hand, the decreased kinetic rate with 600OHV implies that excessive allophanate crosslinkings between the urethane linkages and free isocyanate groups provide the mixture

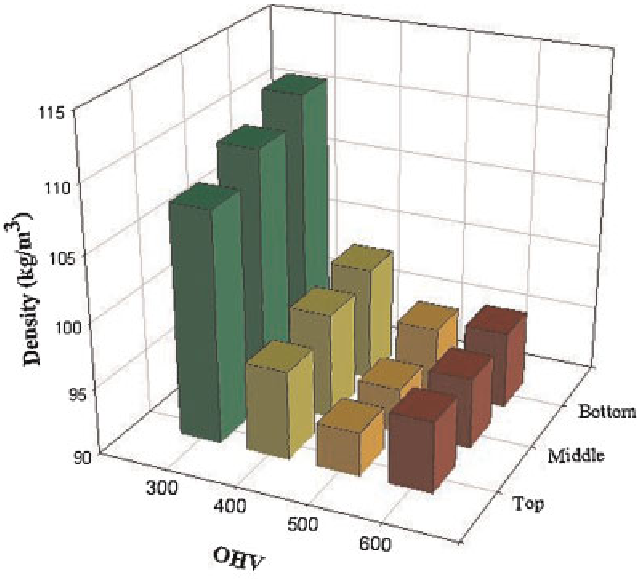
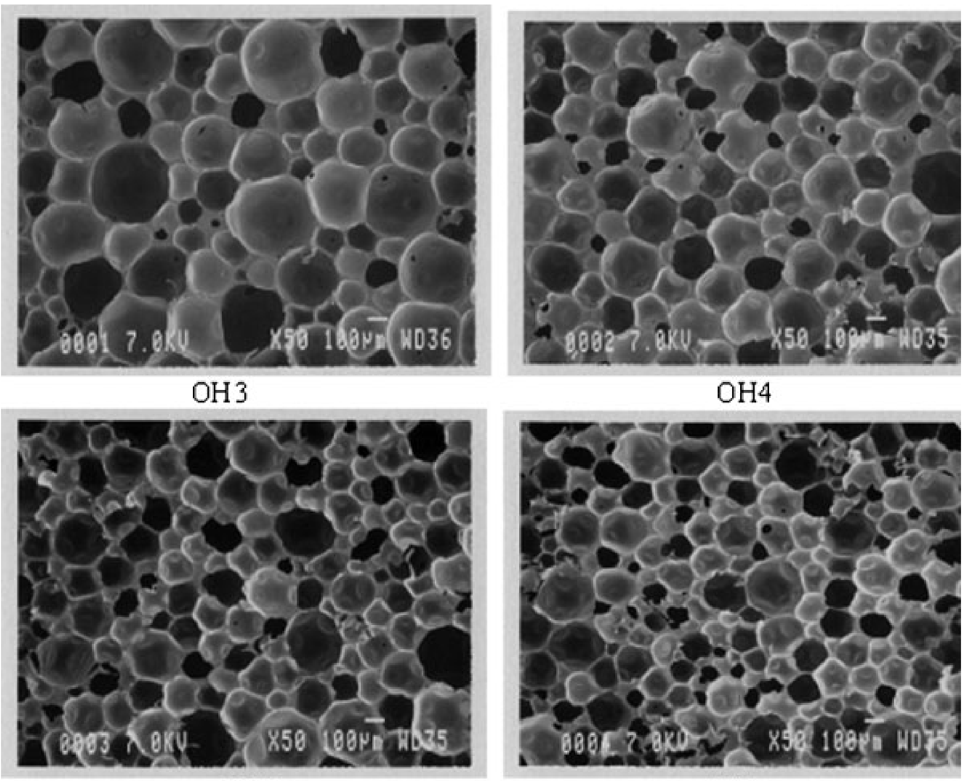


Figure 1. Densities of RPUFs versus OHV. This figure is available in colour online at www.interscience.wiley.com/journal/pat

DOI: 10.1002/pat



OH3 OH4

OH5 OH6

Figure 2. SEM morphologies of the RPUFs versus OHV.

with high viscosity which retards gelling and urethane foaming reactions.

Foam density and density distribution

Foam density (Fig. 1) decreases with increasing OHV showing a minimum at 500OHV, beyond which it increases. Density decrease is an indication of increased blowing efficiency which is due to the increased mixture mobility as the M_n decreases.[18,19] On the other hand, increase beyond the minimum is most likely due to the intensive formations of allophanate crosslinks which retard foaming reactions due to the increased mixture viscosity. The allophanate crosslinks are likely to increase with decreasing M_n of polyol due to the increased number of isocyanate group added to the formulation (Table 1) and urethane linkages to be formed.

Regarding the density distribution (Table 2), density decreases along the bubble rising direction, i.e. from bottom to top, and the effect is less pronounced with increasing OHV. The vertical distribution is mainly due to the gravity effect giving rise to great compression at bottom. On the other hand, high OHV provides cell walls with great elasticity by great crosslink density, and the walls are less vulnerable to deformation. Table 2 shows that the density distribution monotonically decreases with increasing the OHV, and it is 3.48 for OH3 and 0.43% for OH6, implying that more or less uniform distribution is obtained with high cell wall elasticity.

Cell morphology foam diameter

Fig. 2 shows the SEM morphology of the cell as a function of OHV, with the average size and closed cell content in Fig. 3. It is seen that the foams consist of spherical and polyhedral shapes and the size decreases as the OHV increases. The closed cell content asymptotically increases from about 88 to 94% while the cell size decreases from about 350 to 160 nm as the OHV increases from 300 to 600.

Regarding the formation of cells, exothermic heat of reaction causes the supersaturation of the reaction 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.[20] Then, the nuclei grow into bubbles and spherical cells by adopting more gases or by coalescing with neighboring ones. As the blow ratio increases, the spherical bubbles are eventually separated by the cell membrane and become polyhedral. Obviously, the bubble coalescence becomes difficult as the elasticity of the cell wall increases. That is, with the increase in OHV or

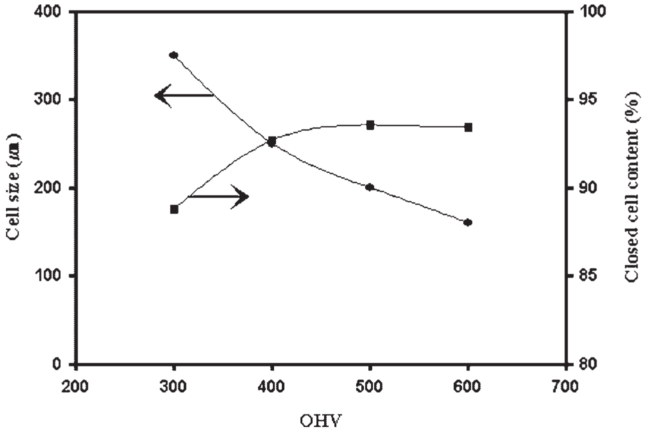


Figure 3. Cell sizes and closed cell contents of the RPUFs versus OHV.

decrease of M_n, crosslink density increases due to the increased allophanate reactions and the elasticity of the cell wall increases. This gives small cells.

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 recommended for closed cell foam.[3] The compression strength of our foam is greater than 0.97 MPa, and it monotonically increases with OHV from 0.98 (OHV3) to 1.25 MPa (OHV6), together with its anisotropy (strength ratio of parallel to perpendicular direction) (Table 2) due to the increased cell elasticity. The elasticity of crosslinked polymer is given by[21]

$$G_N^\circ = \frac{\rho RT}{M_c} \tag{1}$$

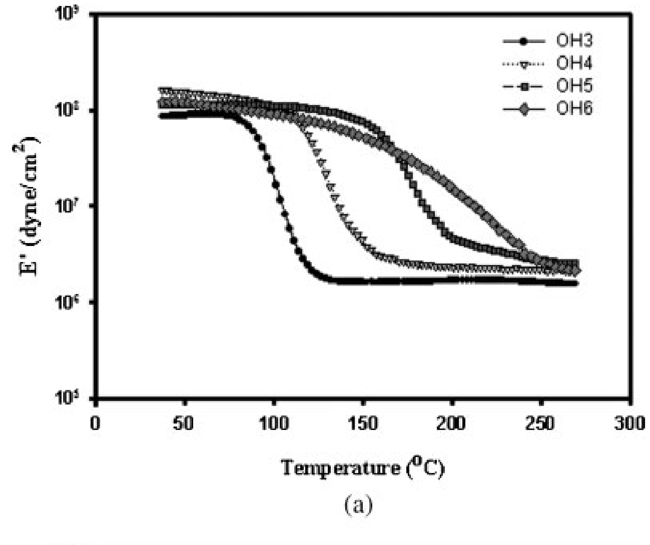
Here, G_N°, ρ, R, T, and M_c are is the rubbery plateau modulus, density, gas constant ($8.314\,\mathrm{m^3 Pa\,mol^{-1}\,K^{-1}}$), temperature, and molecular weight between crosslinks, respectively. Since OHV is inversely proportional to the M_n of polyol for given equivalent weight, large OHV corresponds to the small Mc since the urethane linkages are the sites for allophanate crosslinks. This will be seen by the increased glass transition temperature (T_g) with increasing OHV from the dynamic mechanical measurements to follow.

Dynamic mechanical analysis

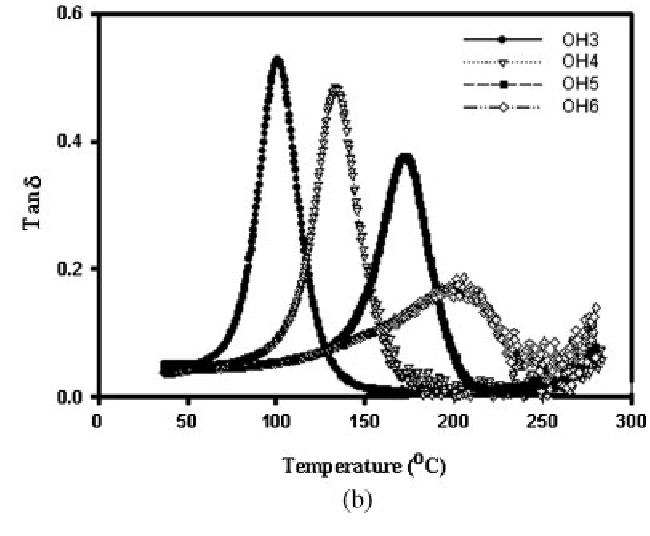
The dynamic mechanical properties of the foams are shown in Fig. 4 where the rubbery plateau modulus and tanδ peak temperature of the foam increase as the OHV increases.[22] The increase in plateau modulus is an indication of increased crosslink density (Eqn (1)). This states that more of the allophanate crosslinks are formed with the increase in OHV. The tanδ peak temperature corresponds to the T_g of the foam. Based on this, the T_g of the foams are about 100 (OH3), 133 (OH4), 179 (OH5), and 205°C (OH6), respectively. As the crosslink density increases, the glass-rubber transition becomes less pronounced.

Dimensional stability

Closed cell foams shrink at low temperature and expand at high temperature. Typically, less than 1% of volume change



(a)



(b)

Figure 4. Storage modulus (a) and tanδ peaks (b) of the RPUFs versus OHV.

DOI: 10.1002/pat

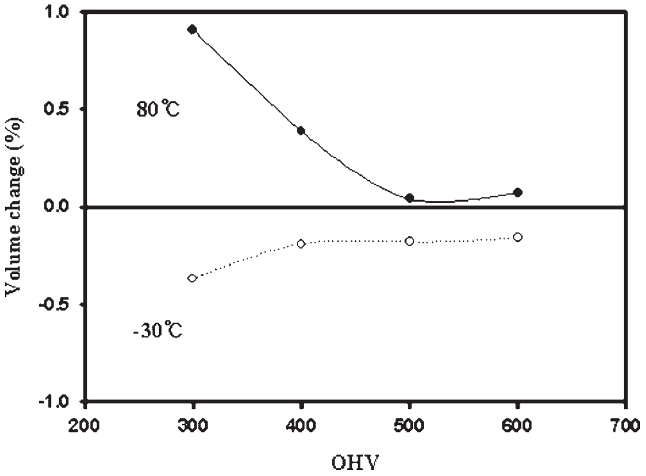


Figure 5. Volume changes of the RPUFs for the duration of 24 hr versus OHV.

is desired for sufficient strength. Fig. 5 shows that the volume change asymptotically decreases with increasing OHV, and the largest volume change is less than 1%. The shrinkage at −30°C is smaller than the expansion at 80°C. The smaller volume change *viz.* the greater dimensional stability with greater OHV is due to the increased elasticity of cell wall introduced by the allophanate crosslinks.

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.[23] Conductive heat flux (q) through the composite wall is given by

$$q = \frac{\Delta T}{R} \tag{2}$$

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

$$R = \sum_{i=1}^{n} \left(\frac{X_{W,i}}{k_W} + \frac{X_{G,i}}{k_G} \right) \tag{3}$$

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

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

In a typical closed cell foam, the polymer walls occupy 3–6 vol% of the foam.[3] 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

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

The above simple analysis shows that the thermal insulation of closed cell foam increases linearly with the number of closed cells, i.e. effect of insulation increases as the cell size decreases.[24]

The thermal conductivity of our foam decreases from 0.0242 (OH3) to 0.0222 (kcal mhr^{-1} °C) (OH5) and it stays more or less at the same value with 600OHV (Fig. 6). The decrease is mainly due to the decreased cell size giving a large number of n as analyzed above. With 600OHV, it seems that decreased cell size is more or less balanced with increased foam density giving rise to small change in thermal conductivity.

CONCLUSIONS

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

The compression strength and dimensional stability of the foam increased with increasing OHV due primarily to the increased crosslink density, which is accompanied by the decreased cell size and increased closed cell content. Direct evidence of the increased crosslink density was seen from the increased T_g as well as the increased rubbery plateau modulus.

The cream time, gel time, tack-free time, and density of the foam showed a minimum at 500OHV. The decrease up to the minimum is due to the increased mixture mobility, whereas

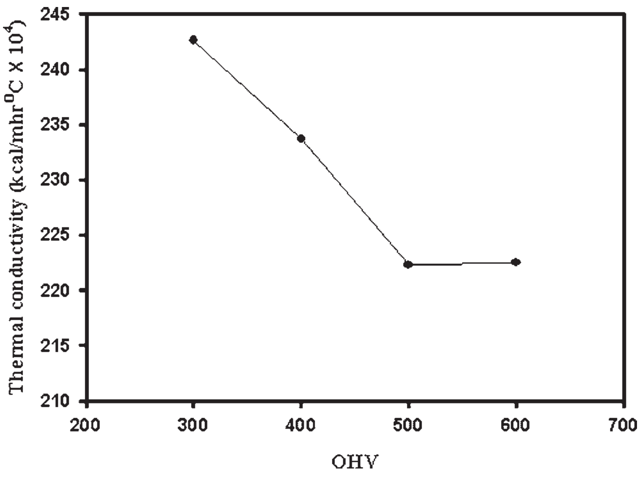


Figure 6. Thermal conductivities of the RPUFs versus OHV.

DOI: 10.1002/pat

the increase beyond the minimum by the extensive allophanate crosslinks which retard foaming reactions.

Thermal conductivity of the foam decreased with increasing OHV up to 500OHV, beyond which it stayed almost constant. The decrease is mainly due to the decreased cell size coupled with the decreased density. On the other hand, decreased cell size is more or less balanced, with increased foam density with 600OHV giving rise to no change in thermal conductivity.

Acknowledgments

This research was financially supported by the Ministry of Education, Science Technology (MEST), 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.

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DOI: 10.1002/pat