# Liquid-type nucleating agent for improving thermal insulating properties of rigid polyurethane foams by HFC-365mfc as a blowing agent

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**ABSTRACT:** The effects of liquid-type additives on the morphology, thermal conductivity, and mechanical strength of polyurethane (PUR) foams were investigated. The PUR foams synthesized with perfluoroalkane showed a smaller average cell diameter and a lower thermal conductivity than PUR foams prepared with propylenecarbonate or acetone. The average cell diameter of the PUR foams decreased from 228 to 155 $\mu$m and the thermal conductivity decreased from 0.0227 to 0.0196 kcal/mh °C when the perfluoroalkane content was 0.0 to 2.0 php (parts per hundred polyol by weight). The perfluoroalkane likely acted as a nucleating agent during the formation of the PUR foams. The addition of perfluoroalkane induced the smaller cells size of the PUR foams probably due to lower surface tension of the polyol and perfluoroalkane mixture, resulting in high nucleation rate. The smaller cell size appears to be the main reason for the improvement in the thermal insulating and the mechanical properties of these PUR foams. The compressive strength of the PUR foams prepared with perfluoroalkane was higher than the PUR foams prepared with the propylenecarbonate and acetone. Based on the morphology, thermal conductivity, and compressive strength, it is suggested that the perfluoroalkane is an efficient liquid-type additive for the improving the thermal insulation of PUR foams. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43557.

## INTRODUCTION

Rigid polyurethane (PUR) foams provide outstanding thermal insulating properties.[1–3] Since the thermal conductivities of the PUR foams are much lower than those of other insulating materials, PUR foams have been widely used as thermal insulating materials in building construction,[4–7] liquefied natural gas (LNG) storage tanks,[8,9] refrigeration,[10] and acoustic damping and composite materials.[11–19] The thermal insulating properties as well as the mechanical strength of the cell structured PUR foams are mainly dependent on the size and uniformity of the cell structure. It has been shown that the cell size of the PUR foams can be controlled during nucleation and the growth step of the foaming process.[6,9,20]

There were some studies to control the cell size using catalysts, silicone-type surfactants, and nucleating agents, which induce the formation of bubbles during PUR foaming by cyclopentane and water as blowing agents.[5,6,10,21,22] The foaming process can be explained by the nucleation and growth mechanism. Many bubbles are generated if there are many nucleation sites during the polymerization reaction and foams having small cells can be produced if the coalescence of bubbles is prohibited by reducing the surface tension of the polyol and diisocyanate mixture during the growth process. Therefore, the addition of nucleating agents is important in order to create enough nucleation sites.

In our early studies, an attempt was made to find possible nucleating agents such as nanoparticles, for the preparation of PUR foams.[7,10] In the case of the solid nucleating agents, nanoparticles effectively reduced the cell size of PUR foams and produced high mechanical strength. However, when solid particles such as organoclay were used in the PUR foam, the production process was more complicated because of the precipitation of solid particles. Liquid-type nucleating agents can be nucleating

**Table I.** Chemical Compositions Used in the Preparation of PUR Foams

| Materials | Description | Weight (g) |
|---|---|---|
| Polyol | Polyether/polyester polyol | 100.0 (50/50) |
| MDI | Polymeric 4,4′-diphenylmethane diisocanate | 124.0 |
| Surfactant | Silicone type (L6900) | 3.0 |
| Catalyst | Pentamethyldiethyltriamine (PC5) | 0.03 |
| | Dimethylcyclohexylamine (PC8) | 0.07 |
| Blowing agent | HFC-365mfc | 9.2 |
| Liquid-type additives | Perfluoroalkane | 0.5 – 2.0 |
| | Propylenecarbonate | 0.5 – 2.0 |
| | Acetone | 0.5 – 2.0 |

agents for reducing cell size in PUR foam as well.[6,7] There were some attempts to reduce the cell size of the PUR foams using the silane compound as an efficient liquid-type nucleating agent such as hexamethyldisilazane (HMDS)[6] and tetramethylsilane (TEMS).[7] In case of HMDS and TEMS, uniform dispersion of the agent in the polyol solution was reported and the cell size was also decreased. There is, however, a disadvantage of the TEMS that it has a high-vapor pressure and highly flammable, and that TEMS and HMDS are very costly.

The purpose of this study is to find more efficient liquid-type nucleating agent. In this study, the effects of three different liquid-type additives (perfluoroalkane, propylenecarbonate and acetone) on cell morphology, thermal insulation and mechanical properties of rigid PUR foams blown by HFC-365mfc were studied using scanning electron microscopy (SEM), thermal conductivity, and a universal testing machine, respectively. The addition of perfluoroalkane may induce the smaller cells size of the PUR foams probably due to lower surface tension of the polyol and perfluoroalkane mixture, resulting in high nucleation rate. For the propylenecarbonate and acetone, they are low viscosity liquids. The lower viscosity of the polyol mixtures are expected to form well-mixed solution and smaller cells. The prepared rigid PUR foams can be used as a thermal insulating material in LNG carrier.

## EXPERIMENTAL

### Materials
The materials used in this study were obtained from commercial sources. Polymeric 4,4′-diphenylmethane diisocyanrate (MDI) was supplied by BASF Korea Ltd. (Daejeon, Korea). The average functionality of MDI was 2.9 and the NCO content was 31.2 wt %. The polyols used in this study were polyether type and polyester type polyols. Pentaerithritol (OH value = 560 mg KOH/g) and sucrose-based polyether polyol (OH value = 490 mg KOH/g) were supplied by BASF Korea Ltd. Glycol-based polyester polyol (OH value = 300 mg KOH/g, 3200 cps) was also supplied by BASF Korea Ltd. The weight ratio of pentaerithritol-based polyether polyol, sucrose-based polyether polyol, and glycol-based polyester polyol used in this study was 30:20:50 wt %, respectively. HFC-365mfc was used as a physical blowing agent. Pentamethyldiethyltriamine (PC 5) and dimethylcyclohexylamine (PC 8), which were supplied by

Air Products and Chemicals, Inc. (Allentown, PA), were used as catalysts. Silicone-type surfactant (NIAX silicone L6900) was supplied from Momentive Co. (USA). The hydrophile-lipophile balance (HLB) value of the surfactant is 8.47. Three different types of liquid-type additives were used (perfluoroalkane, propyenecarbonate and acetone). Perfluoroalkane (PF 5056) was supplied by 3M Co. (USA). The chemical compositions of the materials used in the preparation of the PUR foams are shown in Table I. The NCO index of the PUR foams prepared according to Table I was 126.3.

### Preparation of Polyurethane Foams
First, polyols, catalyst, and surfactant were put into a reactor and mixed for 90 seconds. Rotating speed started at 300 rpm and gradually increased up to 3000 rpm. Low speed at the initial stage of mixing is desirable for homogeneous mixing of highly viscous polyols and additives of low viscosity. Then, the blowing agent and the liquid-type additive (perfluoroalkane, propyenecarbonate or acetone) were added and the reactants were mixed again at 3000 rpm for 60 seconds. The liquid additive was added in the amounts of 0.5, 1.0, 1.5 and 2.0 parts per hundred polyol by weight (php). Next, MDI was added and all the reactants were mixed for 90 seconds using a brushless type stirrer at 7000 rpm. Finally, the reactants were poured into an open mold (250 mm × 250 mm × 250 mm) to produce free-rise foams. They were cured for 1 day at room temperature to prevent deterioration of thermal conductivity and mechanical properties.

### Cell Morphology
The morphology of the PUR foam was studied with a field emission scanning electron microscope (FE-SEM) (Hitachi Model S-4300SE, Tokyo, Japan). The samples were cryogenically fractured and the surface was coated with gold before scanning. The accelerating voltage was 15 kV. We counted 50 cells from the obtained SEM pictures and then the cell size was measured and averaged from the selected 50 cells.

### Surface Tension Measurements
Surface tensions of the liquid-type additive (perfluoroalkane, propyenecarbonate or acetone) and polyol and additive mixtures were measured using contact angle analyzer (model GonioStar 150, Surfacetech, Korea). Droplets of the solutions were dropped on the surface of glass palte. After that, contact

angle between droplet and glass plate was measured. The surface tension is calculated using eq. (1)[23]:

$$\cos\theta = 2\varnothing \left(\frac{\gamma_S}{\gamma_L}\right)^{\frac{1}{2}} - 1 \qquad (1)$$

where is the contact angle, $\varnothing$ the ratio of molar volume of liquid and solid which is approximated to 1.0, $\gamma_S$ the surface energy of solid which is glass plate (24.8 mN/m), and $\gamma_L$ the surface tension of liquid.

### Viscosity Measurements

Viscosity of the polyol and additive mixtures was measured using cone and plate rheometer (model AR 2000, TA Instruments). Cone angle and diameter of the fixture were 2 degree and 40 mm, respectively. Shear rate sweeps from 0.1 to $10^3$ s$^{-1}$ were performed at room temperature. The shear viscosity was obtained at the low shear rate range.

### Thermal Conductivity Measurements

The thermal conductivities of PUR foams were measured using a thermal conductivity analyzer (model TCA Point2, Anacon) according to the ASTM C518 standard test method.[5] The PUR foam sample was placed in the test section between two plates, which were maintained at different temperatures during the test. The temperatures of the upper and bottom plates were 37.7 and 10 °C, respectively. It took about 20 min. to obtain steady state between the plates. Upon achieving thermal equilibrium and establishing a uniform temperature gradient throughout the sample, the thermal conductivity of the PUR foams was determined. The size of the specimen was 200 mm × 200 mm × 25 mm (width × length × thickness). The thermal conductivities of three specimens per sample were measured and averaged.

### Mechanical Properties

The mechanical properties of PUR foam samples were measured under ambient conditions using a universal testing machine (Instron 4467). A compressive test was performed according to the ASTM D1621 test method. The size of each specimen was 50 mm × 50 mm × 50 mm (width × length × thickness), and the speed of crosshead movement was 5.00 mm/min. The strengths of 10 specimens per sample were measured and averaged for each mechanical test.

## RESULTS AND DISCUSSION

### Cell Morphology of PUR Foams

To evaluate the effects of liquid-type additives on the cell morphology, the cross-sectional surfaces of the PUR foams were observed using SEM. Figure 1(a–c) shows the cell morphology of the PUR foams with perfluoroalkane content of 0.0, 1.0, and 2.0 php, respectively. As shown in Figure 1(a–c), the cell size of the PUR foams decreased with the increase of perfluoroalkane content and was found to be 228, 205, and 155 $\mu$m, respectively. Figures 1(d–e,f–g) show the cell morphology of the PUR foams with propylenecarbonate and acetone with content of 1.0 and 2.0 php, respectively. As shown in Figure 1(d,e), the cell size of the PUR foams does not change significantly with the addition of propylenecarbonate content and was found to be 238 and 237 $\mu$m, respectively. For the PUR foams with acetone, the cell
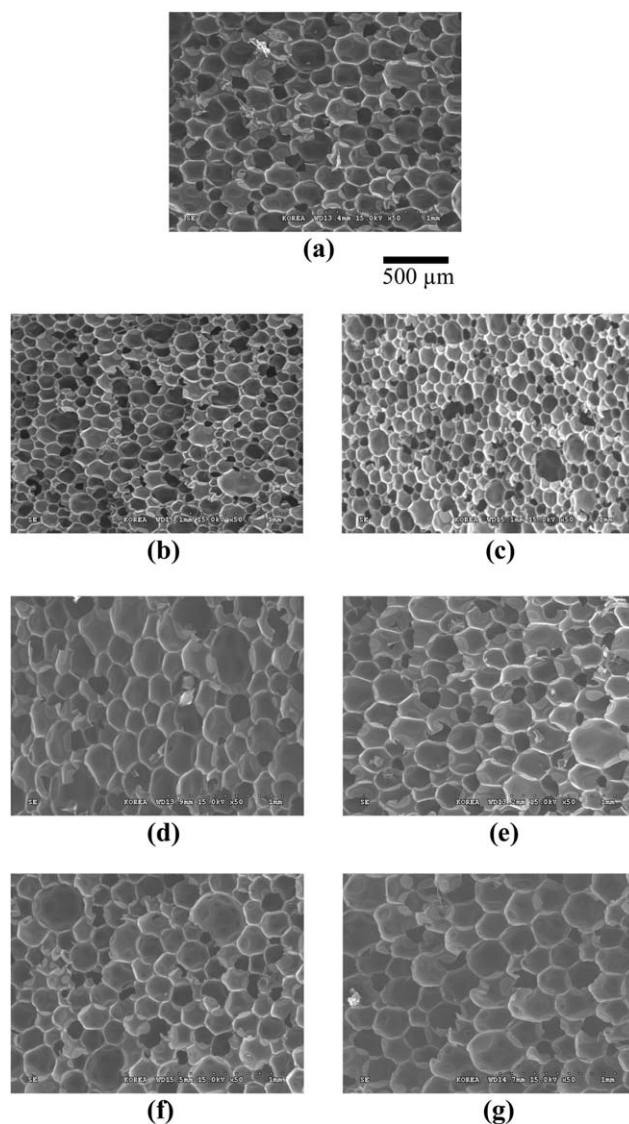


**Figure 1.** Scanning electron micrographs of PUR foams with varying additive species and concentrations (php): (a) without additive, (b) perfluoroalkane 1.0, (c) perfluoroalkane 2.0, (d) propylenecarbonate 1.0, (e) propylenecarbonate 2.0, (f) acetone 1.0, (g) acetone 2.0.

size increased with the addition of acetone content and was found to be 241 and 323 $\mu$m, respectively. In Table II shows the average cell size and standard deviation of the each foam. From Table II, standard deviations for the PUR foams without additive, with perfluoroalkane, propylenecarbonate and acetone are observed to be 51, 29, 62 and 56 $\mu$m, respectively. From these results, it is suggested that perfluoroalkane may contribute to reduce cell size of the foams as well as reducing cell size distribution.

Figure 2 shows average cell diameter of the PUR foams with additive species and concentrations. The average cell diameter of PUR foams with perfluoroalkane is the smaller than those of the foams with propylenecarbonate and acetone. Figure 1 also shows that the cell distribution is more uniform for the foams with perfluoroalkane compared with the propylenecarbonate

**Table II.** Cell Size and Density of PUR Foams with Additives

| Additive (php) | Without additive | Perfluoroalkane | | Propylene carbonate | | Acetone | |
|---|---|---|---|---|---|---|---|
| | | 1.0 | 2.0 | 1.0 | 2.0 | 1.0 | 2.0 |
| Cell Size (μm) | 228 | 205 | 155 | 238 | 237 | 241 | 323 |
| Standard Deviation (μm) | 51 | 40 | 29 | 60 | 62 | 70 | 56 |
| Density (kg/m$^3$) | 115.2 | 114.1 | 114.5 | 114.0 | 113.7 | 99.6 | 94.3 |

and acetone. These results are likely due to the lower surface tension of the perfluoroalkane, which allows it to be well-mixed in the polyol solutions and consequently a higher nucleation rate.[24] It seems that the low-surface tension of the polyol and perfluoroalkane mixture prohibits the coalescence of bubbles and it promotes the formation of dense and small cells. Table III shows the viscosity of the polyol solution without additive (6.78 Pa s) and the polyol and various additive mixtures such as perfluoroalkane, propylenecarbonate and acetone which are 2.50, 4.42 and 3.79 Pa s when the additive content are 2.0 phr, respectively. This result suggests that the lower value of viscosity of the polyol and the perfluoroalkane mixture has attributed to form well-mixed solution and smaller cell.

The data in Figure 2 suggest that propylenecarbonate does not affect the cell size of the PUR foams, however, it can be used as a chain extender in the preparation of PUR foams. Therefore, mechanical strength of the PUR foams may be increased with the addition of propylenecarbonate; the result will be shown in the compressive strength section of this study. The cell size of PUR foams that were prepared with acetone increased with increasing the acetone content. Since acetone is a low viscosity liquid, it is expected to increase the mixing efficiency when it is added to the polyol mixture. The lower viscosity of the polyol and acetone mixture was expected to form well-mixed solution and smaller cells.[25,26] However, acetone did not produce small cells size. Acetone acted more like a blowing agent and the cell wall of the foams became rather thinner. The density of the PUR foams with acetone is appeared to decrease from 115.2 to 94.3 kg/m$^3$ when the acetone content increases from 0.0 to 2.0 php, which are shown in Table II. Of course, lowering the foam
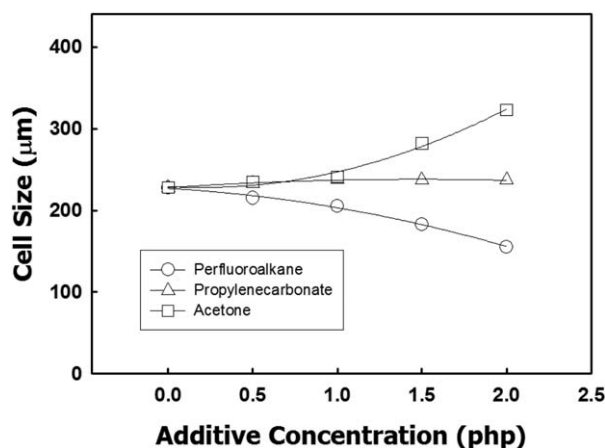
density results into the increasing of foam cell sizes. As a result, the cells coalesced, lowering the compressive strength which will be shown in the compressive strength section.

**Surface Tension of Polyol Solutions**
Figure 3(a–d) shows the contact angle measurements of the polyol solution without additive (65.9 degree) and the polyol and various additive mixtures such as perfluoroalkane, propylenecarbonate and acetone which are 52.2, 57.4 and 53.5 degrees when the additive content is 2.0 phr. The surface tensions of additives such as perfluoroalkane, propylenecarbonate and acetone were also obtained from the contact angle measurements and found to be 13.9, 40.3 and 25.1 mN/m, respectively. Table III shows the surface tensions of the polyol solution without additive (50.1 mN/m) and the polyol and various additive mixtures such as perfluoroalkane, propylenecarbonate and acetone which are 21.4, 41.9 and 39.0 mN/m when the additive content is 2.0 phr. From Table III, the surface tension of the polyol and the perfluoroalkane mixture showed the lowest value among the polyol and the propylenecarbonate or acetone mixtures. From the results of morphology and surface tensions shown in Figures 1 and 3, it is suggested that the lower value of the surface tension has affected the polyol and perfluoroalkane mixture to create enough nucleation sites and it promotes the formation of dense and small cells.

**Thermal Conductivity of PUR Foams**
Thermal conductivity is one of the important factors in thermal insulating PUR foams. Effects of three different liquid-type additives on the thermal conductivity of the PUR foams are shown in Figure 4. When the additive concentration of perfluoroalkane is increased from 0.0 to 2.0 php, the thermal conductivity of the PUR foams decreased from 0.0227 to 0.0196 kcal/mh °C. For the PUR foams with propylenecarbonate and acetone, the thermal conductivities were observed to be from 0.0227 to 0.0233 and from 0.0227 to 0.0234 kcal/mh °C with the increase of additive concentrations, respectively.

Figure 4 shows that PUR foams with perfluoroalkane as a nucleating agent have lower thermal conductivity than neat PUR foams because of their smaller average cell diameter. The PUR foams with perfluoroalkane showed the lowest thermal conductivity relative to PUR foams with propylenecarbonate and acetone. This is probably because PUR foams with perfluoroalkane provided the smallest cell size. It is thought that the perfluoroalkane creates considerable bubble nucleation during the foaming process by reducing the critical activation energy for nucleation.

Figure 5 shows the relationship between the thermal conductivity and average cell size of the PUR foams with the three



**Figure 2.** Average cell size of PUR foams with various additives at different concentrations.

**Table III.** Viscosity and Surface Tension of Polyol Mixtures with Additives

| Additive (php) | Without additive | Perfluoroalkane | | Propylene carbonate | | Acetone | |
|---|---|---|---|---|---|---|---|
| | | 1.0 | 2.0 | 1.0 | 2.0 | 1.0 | 2.0 |
| Viscosity (Pa s) | 6.78 | 4.01 | 2.50 | 4.46 | 4.42 | 4.33 | 3.79 |
| Surface tension (mN/m) | 50.1 | 23.1 | 21.4 | 44.0 | 41.9 | 42.4 | 39.0 |

different additives (perfluoroalkane, propyenecarbonate and acetone). Thermal conductivity of the PUR foams prepared with perfluoroalkane, propyenecarbonate or acetone is decreased with a decrease of the cell size, which explains that small cell size improves the thermal insulating property.
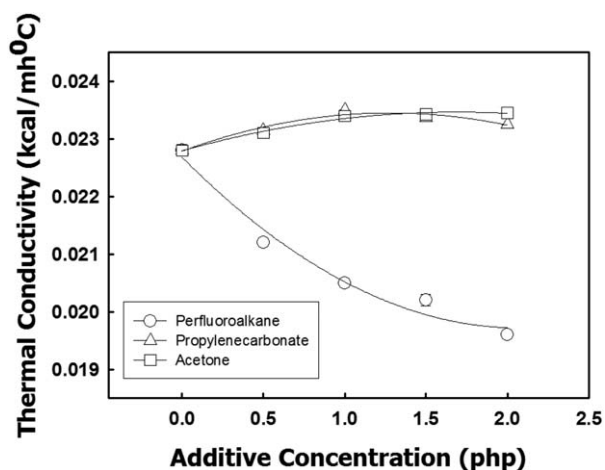
**Compressive Strength of PUR Foams**

Figure 6 shows the compressive strength of the PUR foams prepared with the three additives at different concentrations. The compressive strength of the PUR foams with perfluoroalkane and propylenecarbonate increase slightly with an increase of additive contents. Densities of the PUR foams prepared with perfluoroalkane and

propylenecarbonate were about 114 kg/m$^3$ (Table II). The compressive strengths of the PUR foams with the perfluoroalkane were found to be 1.230, 1.361, and 1.312 MPa for the additive content of 0.0, 1.0, and 2.0 php, respectively. Esmaeilnezhad et al.,[27] reported that there is a direct correlation between the microstructure and mechanical strength of the foams. From the results of cell size and compressive strength of the PUR foams shown in Figures 5 and 6, it is suggested that the increase of compressive strength of the PUR foams with the perfluoroalkane can be explained by the smaller cell size.

For the PUR foams prepared with propylenecarbonate, the compressive strength was found to be 1.230, 1.320, and 1.305
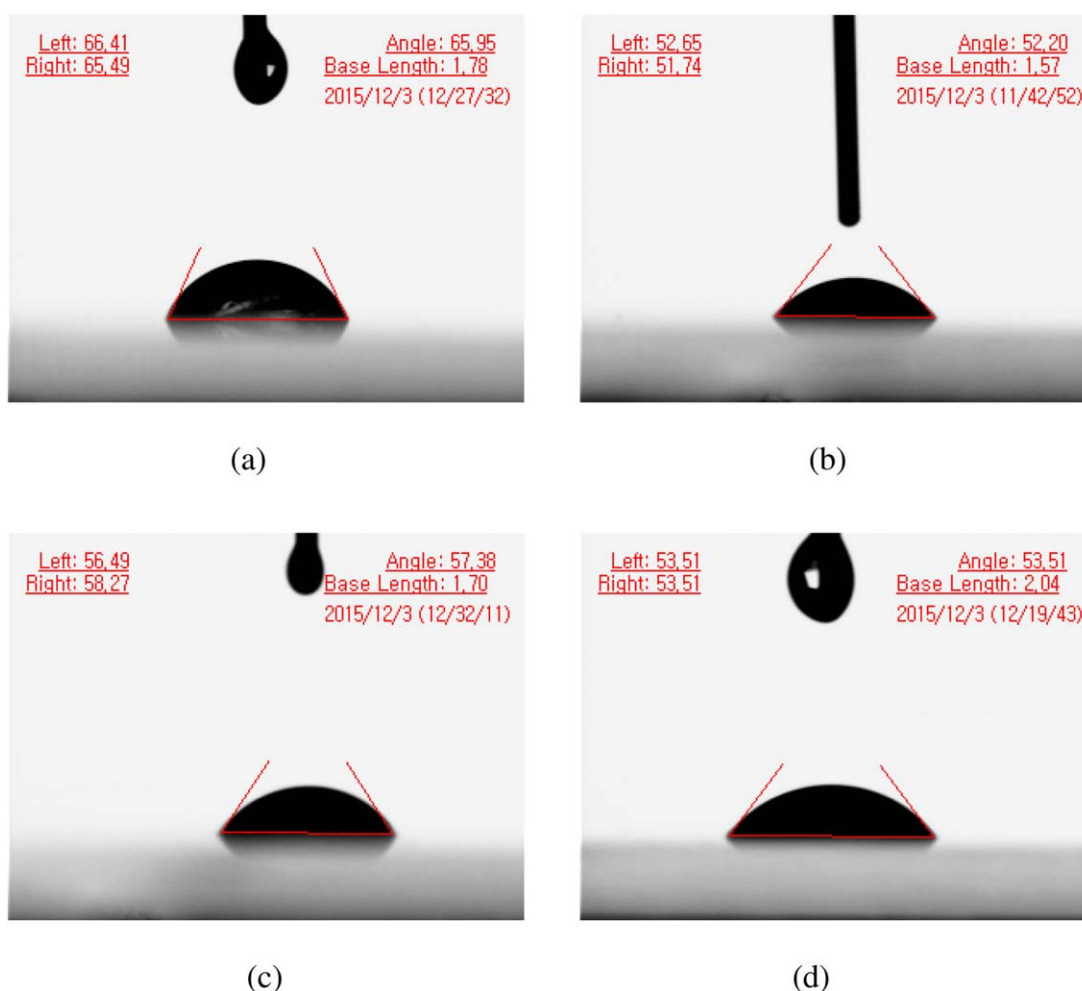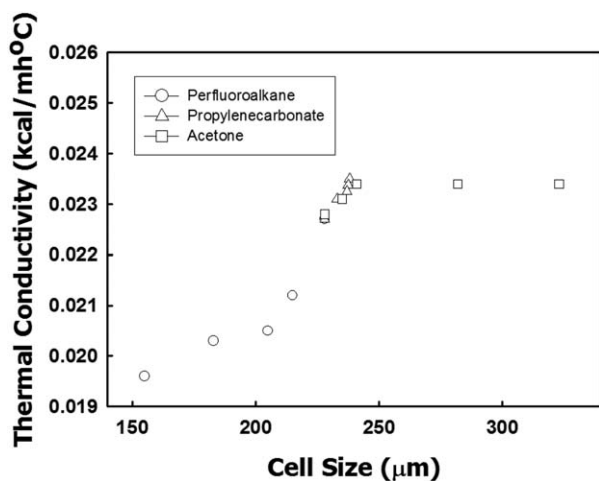


**Figure 3.** Measurements of contact angle of polyol and various additive mixtures: (a) polyol solution without additive, (b) polyol with perfluoroalkane 2.0 php, (c) polyol with propylenecarbonate 2.0 php, (d) polyol with acetone 2.0 php. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

**Figure 4.** Thermal conductivity of PUR foams with various additives at different concentrations.
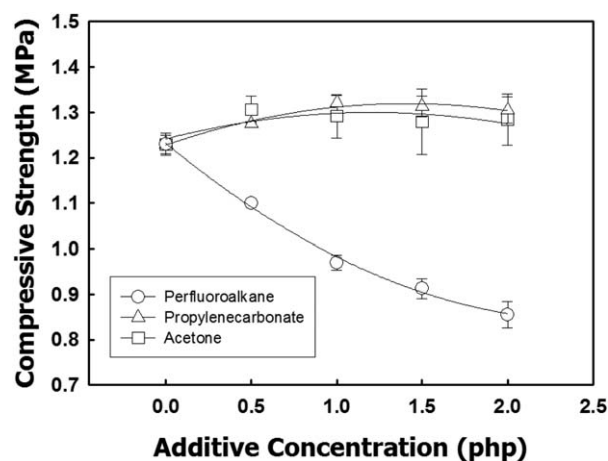


**Figure 6.** Compressive strength of PUR foams with various additives at different concentrations.

MPa for the additive content of 0.0, 1.0, and 2.0 php, respectively. Densities of the PUR foams did not change greatly with the increase of the propylenecarbonate, which were 115.2, 114.1, and 113.7 kg/m$^3$ when the propylenecarbonate content was 0.0, 1.0, and 2.0 php, respectively (Table II). The slight increase of compressive strength of the PUR foams with the propylenecarbonate is possibly because the propylenecarbonate acts as a chain extender in the preparation of the PUR foams. However, the compressive strength of the PUR foams with the acetone decreased from 1.230 to 0.855 MPa when the acetone content increased from 0.0 to 2.0 php. The decrease in compressive strength of the PUR foams with acetone is mainly due to the decrease of densities from 115.2 to 94.3 kg/m$^3$ when the acetone content increases from 0.0 to 2.0 php, which are shown in Table II.

Figure 7 shows the relationship between the compressive strength and density of the PUR foams with the three different additives (perfluoroalkane, propyenecarbonate and acetone). Compressive strength of the PUR foams with the three different additives is increased with the increase of density of the foams.

Mechanical properties of the rigid PUR foams depend mainly on the density of the foams. For the PUR foams with the acetone, the cells seemed coalesced because of the larger cell size compared those of the foams with the perfluoroalkane and propylenecarbonate. This caused decreased density and consequently decreased compressive strength of the PUR foams with the acetone.

## CONCLUSIONS

In this study, the morphology, thermal conductivity, and mechanical strength of PUR foams with the three different liquid-type additives (perfluoroalkane, propylenecarbonate, and acetone) were investigated. From the results of the morphology and the thermal properties of the PUR foams, it is suggested that foams prepared with perfluoroalkane were characterized by smaller average cell diameter and lower thermal conductivity compared with the PUR foams that were prepared with propylenecarbonate or acetone. The addition of perfluoroalkane seems to induce smaller cell size, probably due to lower surface tension of the polyol and perfluoroalkane mixture, resulting in high nucleation rate of the PUR foams.



**Figure 5.** Relationship between thermal conductivity and cell size of PUR foams with various additives at different concentrations.
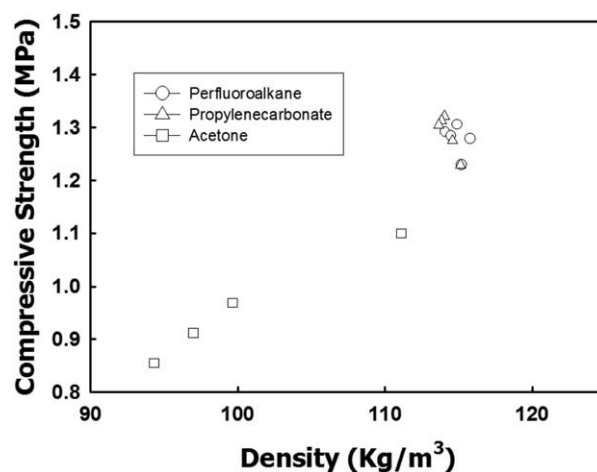


**Figure 7.** Relationship between compressive strength and density of PUR foams with various additives at different concentrations.

From the results of compressive strength of the PUR foams, it is suggested that the increase of compressive strength of the PUR foams with the perfluoroalkane can be explained by the smaller cell size of the foams. The smaller cell size appears to be an important reason for the improvement of thermal insulating and mechanical properties of PUR foams. The results of morphology, thermal conductivity, and compressive strength of the PUR foams suggest that perfluoroalkane may be the efficient liquid-type additive for the improvement of the thermal insulation property of the PUR foams.

## ACKNOWLEDGMENTS

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