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# Effects of Silicone Surfactant on the Cell Size and Thermal Conductivity of Rigid Polyurethane Foams by Environmentally Friendly Blowing Agents

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**Abstract:** Rigid polyurethane foams (PUF)s were synthesized with environmentally friendly blowing agents such as a cyclopentane/distilled water (10.0/1.0, pphp) mixture and distilled water only for four different silicone surfactants having different silicone/polyether ratios. An attempt was made to reduce the thermal conductivities of the PUF samples by varying the concentration and the silicone/polyether ratio of the various silicone surfactants. The scanning electron microscopy (SEM) results indicated an optimum concentration of the silicone surfactant of about 1.5 to 2.5 phpp for various surfactants to reduce the cell size and lower the thermal conductivity. The silicone surfactant having a higher silicone/polymer ratio showed a smaller cell size and, therefore, demonstrated the lower thermal conductivity of the PUF samples. From the relation between the thermal conductivity and the cell size of the PUF samples, the smaller cell size improved the thermal insulation property of the rigid PUF for both the PUF samples blown by the cyclopentane/distilled water (10.0/1.0, pphp) mixture and distilled water only. If the blowing agent is fixed, then the cell size is an important factor to decrease the thermal conductivity of the PUF samples. These results indicated that rigid PUF samples having lower thermal conductivity can be obtained by choosing a silicone surfactant containing a higher silicone/polyether ratio, as well as an optimum content of the surfactant.

*Keywords*: rigid polyurethane foam, silicone surfactant, blowing agent, thermal conductivity.

## Introduction

Rigid polyurethane foam (PUF) has been used as a thermal insulation material due to its superior thermal insulation property which is basically influenced by thermal conductivity of the material.[1-19] Thermal insulation property is mainly determined by the types of blowing agent added in the system. Trichlorofluoromethane (CFC) and HCFC-141b have offered the rigid PUF a good thermal insulation as blowing agents.[20] However, halogenated compounds such as CFC and HCHF-141b were designated as environmentally regulatory materials since they were known to destroy ozone layer.[20-23] Therefore, it has become necessary to find blowing agents to replace CFC and many researches have been done to develop environmentally friendly blowing agents such as cyclopentane and water. Unfortunately, rigid PUFs produced with environmentally friendly blowing agent show poorer thermal insulation property than the PUF with CFC. Therefore, it is believed that researches have to be conducted to improve thermal insulation property of rigid PUF by environmentally friendly blowing agent.[22-27]

Recently, Cao *et al*.,[28] Widya and Macosko,[29] Seo *et al*.,[26] and Kim *et al*.[27] have shown that organoclay particles played an important role to create small and uniform cells in the rigid PUF. The results also suggested that good thermal insulation property was obtained due to the thermal barrier effect of clays in the rigid PUF. Even though the clay shows a good possibility to improve thermal insulation of PUF, the use of clay may be complicate because of the precipitation of the clay in the mixture of raw materials when the clay is stored in the storage tank for long time.

Another candidate for improvement of thermal insulation without complicating the process can be surfactants. Surfactants are essential ingredients to control the cell size of PUF.

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They stabilize the gas bubbles formed during nucleation and inhibit the coalescence. One of typical surfactants is silicone surfactant which is a grafted copolymer of polysiloxane backbone with polyether side chain. Silicone surfactants can prevent coalescence of the cells due to their ability to lower surface tension.

Zhang *et al.*[30] have studied that the increase of silicone/polyether ratio in the silicone surfactant may result in lowering the surface tension of the foaming system and this leads to a decrease in bubble size. Grimminger and Muha[31] have studied the effects of various silicone surfactants on the closed cell content, and they have shown that about 93.3 to 96.7% of closed cell was observed for the rigid PUF.

In this study, investigations were conducted to evaluate the effect of surfactants on the cell size and thermal conductivity of the rigid PUF. In the preparation of rigid PUFs using environmentally friendly blowing agents, an attempt to evaluate the relation among the cell size, thermal conductivity and the silicone/polyether ratio of the various silicone surfactants is the uniqueness in this study. Rigid polyurethane foams were prepared from polyether polyols, polymeric 4,4-diphenylmethane diisocyanate (PMDI) and environmentally friendly blowing agents such as distilled water and cyclopentane. By varying the amount and chemical structures of silicone surfactants, we obtained rigid polyurethane foam samples with various cellular structures and thermal properties. The cellular structure and thermal property were studied with a scanning electron microscopy (SEM), thermal conductivity analyzer, respectively. Structure of the surfactant was also investigated using FTIR and NMR spectroscopy.

## Experimental

**Materials.** The materials used in this study were obtained from commercial sources. Polymeric 4,4′-diphenylmethane diisocyanate (PMDI) was supplied from BASF Korea Ltd. (Seoul, Korea). The average functionality of PMDI was 2.7 and NCO content was 31.5 wt%. Pentaerithritol and glycerin base polyether polyols were supplied from KPC Co. (Ulsan, Korea). Distilled water used as a chemical blowing agent was generated in our laboratory. Gelling catalyst was triethylene diamines dissolved in dipropylene glycol from Air Product, and blowing catalyst was pentamethyldiethylene from Chemicals, Inc. (Allentown, USA). Four different kinds of polysiloxane ether surfactants were used from different suppliers such as GE Bayer Silicones (Erkrath, Germany), Air Products, Chemicals, Inc. (Allentown, USA), and Goldschmidt's (Essen, Germany). The polyols were dehydrated at 90 °C for 24 h in a vacuum oven before use and the other chemicals were used as received. The chemical compositions of the materials used in the preparation of rigid polyurethane foams are shown in Table I.

**Sample Preparations.** Rigid polyurethane foams (PUF) were synthesized by two-shot method. At first, polyol mixture, catalysts and surfactant were put into a reactor and mixed for 15 sec using brushless type stirrer at the rotating speed of 2,500 rpm. After premixing, blowing agent was put into the mixture of reactants and mixed for 10 sec using brushless type stirrer at 3,000. PMDI then was put into the reactants and all the reactants were mixed for 7 sec using brushless type stirrer at 5,000. Finally, the reactants were poured into the open mold (250 mm × 250 mm × 250 mm) to produce free-rise foams and cured for 1 week at room temperature. In order to avoid the change of thermal conductivity and mechanical strength, the curing was done at room temperature. The amount of surfactants varied from 0.5 to 3.0 parts per hundred polyol by weight (pphp). When the distilled water was used as a blowing agent alone, the amount of distilled water was 2.0 pphp. Also, when the mixed blowing agent was used, the amount of mixed blowing agent was cyclopentane/distilled water (10.0/1.0, pphp). The amount of blowing agent was controlled to set the density of 50 kg/cm$^3$ for all PUF samples.

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

| Chemicals | | Weight(g) |
|---|---|---|
| PMDI | | 142.8 |
| Polyol | | 100.0 |
| Surfactant | | 0.5,1.0,1.5,2.0,2.5,3.0 |
| Blowing Agents | Distilled water | 2.0 |
| | Cyclopentane/Distilled water | 10.0/1.0 |
| Catalyst | | 1.0 |

**Density Measurements.** Density of PUF sample was measured according to ASTM D1622. The dimension of the specimen was 30 × 30 × 30 mm (width × length × thickness). Measurements were conducted five times per sample and average value was used.

**Analysis of Surfactants.** Infrared spectra of surfactants used in this study were obtained using a Perkin-Elmer fourier transform infrared spectroscopy (FT-IR) over the frequency range from 750 to 4000 cm$^{-1}$. The FTIR measurements were carried out at 26 °C and the spectra were collected at a resolution of 8 cm$^{-1}$ and 16 scans were accumulated. The proton nuclear magnetic resonance ($^1$H NMR) spectra of surfactants dissolved in deuteroacetone ($CD_3COCD_3$) were also recorded on a Varian NMR-AS500 spectrometer at room temperature.

**Scanning Electron Microscopy.** The morphology of the PUF sample was observed using an S-4300SE field emission scanning electron microscope (Hitachi, Tokyo, Japan). The samples were cryogenically fractured and the surface was coated by gold before scanning. The accelerating voltage was 25 kV. We have counted 20 cells from the largest cells and then the cell size was measured from the selected

20 cells out of all the cells.

**Thermal Conductivity Measurements.** Thermal conductivity was measured using thermal conductivity analyzer (model TCA Point2, Anacon) according to ASTM C518. A sample was placed in the test section between two plates which are maintained at different temperatures during the test. Dimension of the specimen was 200 × 200 × 25 mm (width × length × thickness). The thermal conductivities of three specimens per sample were measured and averaged.

## Results and Discussion

Figure 1 shows the FTIR spectra of four different kinds of silicone surfactants named as surfactant A, B, C and D. It seems that the four different silicone surfactants have a similar structure. These surfactants are all grafted copolymers which consist of a polydimethylenesiloxane backbone and polyethylene oxide-*co*-propylene oxide side chain. In order to investigate the silicone/polyether ratio in the silicone surfactant, the surfactants (A to D) were investigated $^1$H NMR spectroscopy. The chemical structure of silicone surfactants used in this study is shown in Figure 2. It is believed that the surfactants A to D have different silicone contents according to the different ratios of backbone/side chain (silicone/polyether).

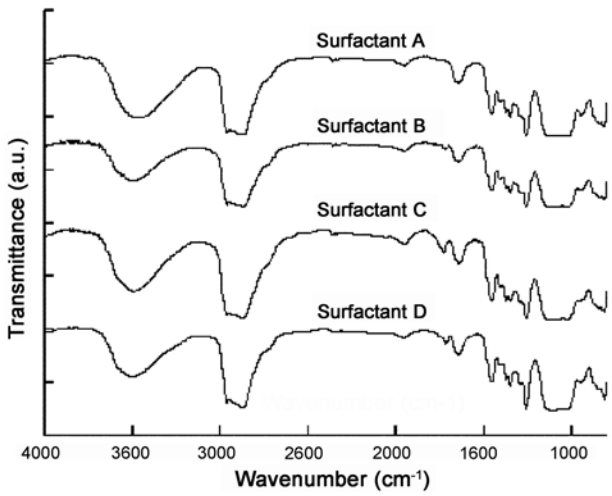


**Figure 1.** FTIR spectra of four different silicone surfactants (A, B, C and D).

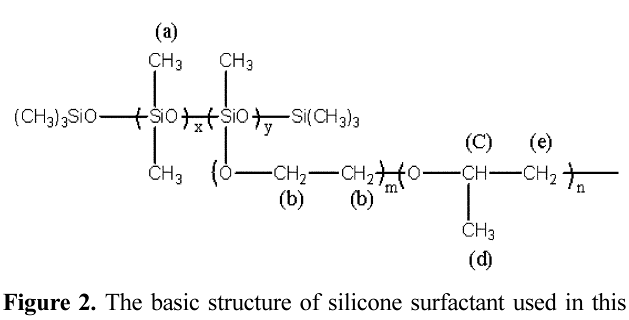


**Figure 2.** The basic structure of silicone surfactant used in this study.

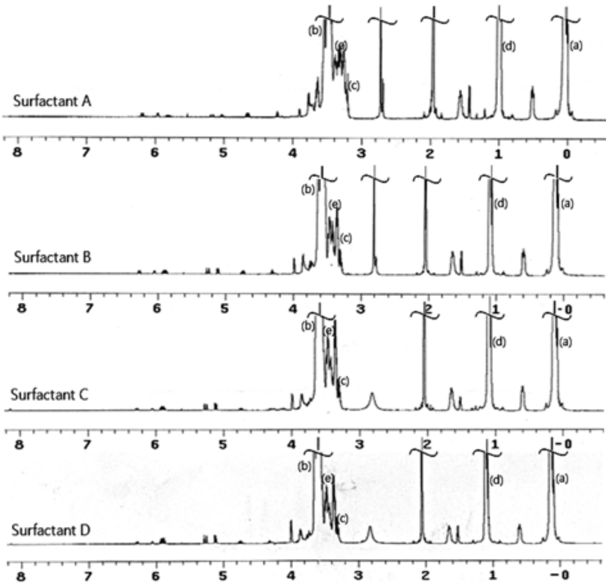


**Figure 3.** $^1$H NMR spectra of four different silicone surfactants (A, B, C and D).

Figure 3 shows the $^1$H NMR spectra of the silicone surfactants. The signal at $\delta$=0.1 (a) and $\delta$=3.6 (b) ppm is attributed to the protons of Si-$CH_3$ bond and O-$CH_2$-$CH_2$ bond, respectively. The signals at $\delta$=3.3 (c), $\delta$=1.1 (d) and $\delta$=3.5 (e) ppm are ascribed to the protons of O-CH($CH_3$)-$CH_2$ bond orderly.[32-34]

The silicone/polyether ratio of each silicone surfactant can be obtained by estimating area of each signal which indicates the number of protons exists. The silicone/polyether ratio of silicone surfactants A, B, C and D are shown in Table II. The results shown in Table II indicate that silicone/polyether ratio of the surfactant A is higher than other silicone surfactants. The relationship between the silicone/polyether ratio in surfactant and cell size will be discussed in the following section. The shape and size of cell of the polyurethane foams are important in the thermal conductivity of the rigid PUF since the thermal conductivity can be lowered by reducing the cell size of the rigid PUF.[26,27]

Figure 4 shows the effect of surfactant content on the cell morphology of rigid PUF blown by cyclopentane/distilled water (10.0/1.0, pphp). From the results of Figure 5, it is observed that the cell size of Figure 4 (a) to (f) is 500, 380, 358, 310, 460 and 490 $\mu$m, respectively. The cell size of polyurethane foam starts to decreases from 500 to 310 $\mu$m and, then, increases from 310 to 490 $\mu$m as the content of the surfactant A increases. In other words, there is an inflection point at the surfactant content of 2.0 pphp indicating the optimum content of surfactant and it is designated as critical micelle concentration (CMC). The surfactant-polymer chains seems to aggregate together when added more than the optimum content. When excessive amount of surfactant is added to the system, self aggregation can occur, then, the

**Table II. Each Signal's Area and Silicone/Polyether Ratio of Surfactants from NMR Spectroscopy**

| | (a) | (b) | (c) | (d) | (e) | Silicone/Polyether Ratio (%) |
|---|---|---|---|---|---|---|
| Surfactant A | 19.04 | 28.41 | 2.18 | 7.70 | 3.96 | 45.1 |
| Surfactant B | 15.77 | 28.00 | 1.88 | 5.53 | 2.66 | 41.4 |
| Surfactant C | 14.66 | 24.22 | 2.37 | 6.99 | 2.98 | 40.1 |
| Surfactant D | 18.05 | 39.48 | 1.06 | 3.38 | 2.48 | 38.8 |

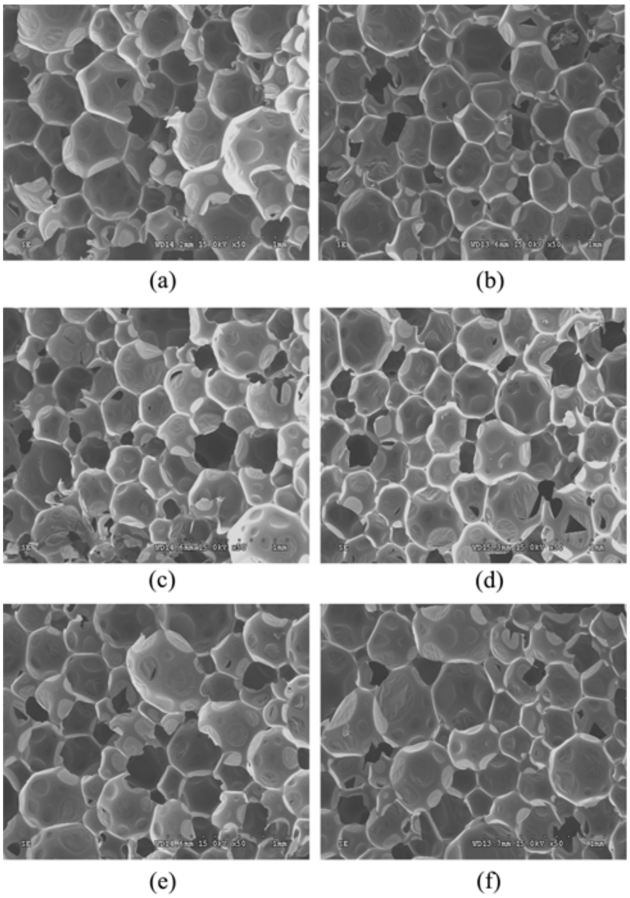

**Figure 4.** Scanning electron micrographs PUFs blown by cyclopentane/distilled water (10.0/1.0 pphp) mixture with the content of surfactant A (pphp): (a) 0.5, (b) 1.0, (c) 1.5, (d) 2.0, (e) 2.5, and (f) 3.0.

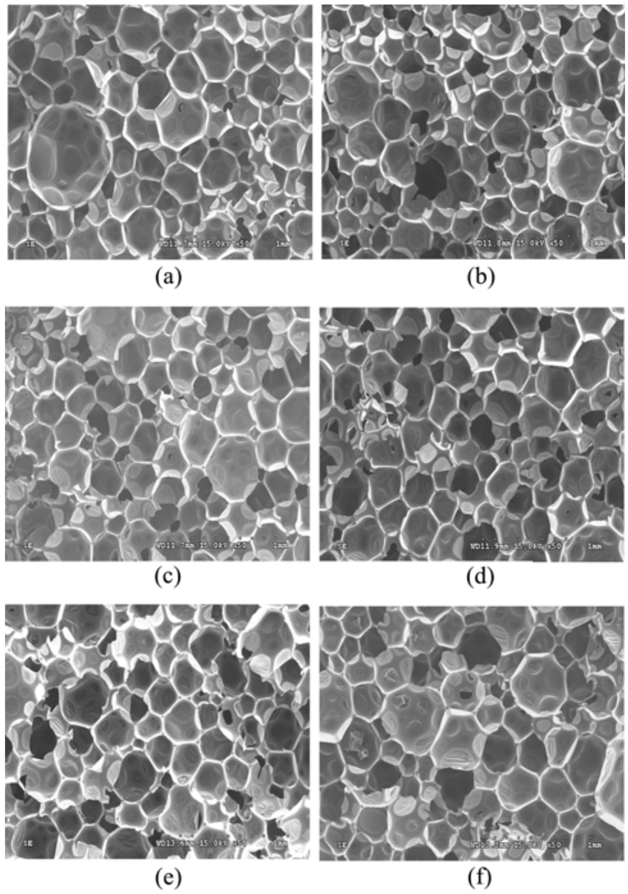

**Figure 5.** Scanning electron micrographs PUFs blown by distilled water with the content of surfactant A (pphp): (a) 0.5, (b) 1.0, (c) 1.5, (d) 2.0, (e) 2.5, and (f) 3.0.

pressure in the bubbles increase due to low surface tension. Consequently, the size of the cell increases due to the coalescence of the cells.

Figure 5 shows the effect of surfactant content on the cell morphology of rigid PUF blown by distilled water only. From the results of Figure 5, it is observed that the cell size of Figure 5 (a) to (f) is 330, 290, 263, 232, 277 and 310 $\mu$m, respectively. The cell size of polyurethane foam starts to decreases from 330 to 232 $\mu$m and, then, increases from 232 to 310 $\mu$m as the content of the surfactant A increases. The smallest and the uniform cells of the PUF could be obtained when the content of the surfactant A was 2.0 pphp in case of using distilled water as well as cyclopentane/distilled water (10.0/1.0, pphp) mixture as blowing agents. From the results of Figure 5(a) to (f), the standard deviation of the cell size was observed to be 52, 45, 32, 24, 43 and 53 $\mu$m, respectively. From the result of standard deviation, it is also suggested that the cell size becomes more uniform when the content of the surfactant is 2.0 pphp since the standard deviation of the cell size shows the smallest value at 2.0 pphp.

The cell size of the PUF produced by chemical foaming such as distilled water is known to be smaller than that produced by physical foaming such as cyclopentane.[26,27] The data obtained in this study showed similar results when compared the cell size obtained from Figures 4 and 5.

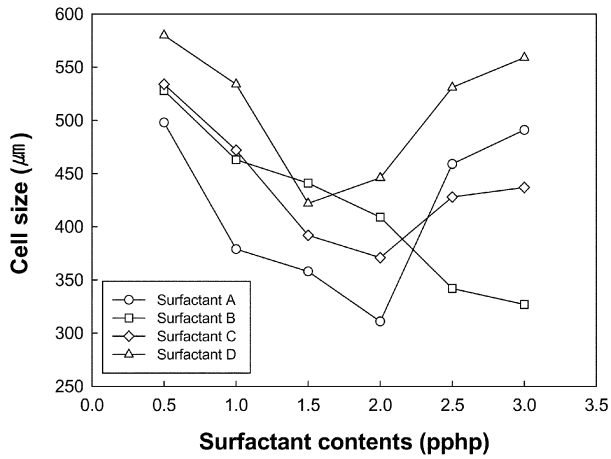


**Figure 6.** Cell size of PUFs with the surfactant content for the four different silicone surfactants (A, B, C and D). PUF samples were blown by cyclopentane/distilled water (10.0/1.0 pphp) mixture.

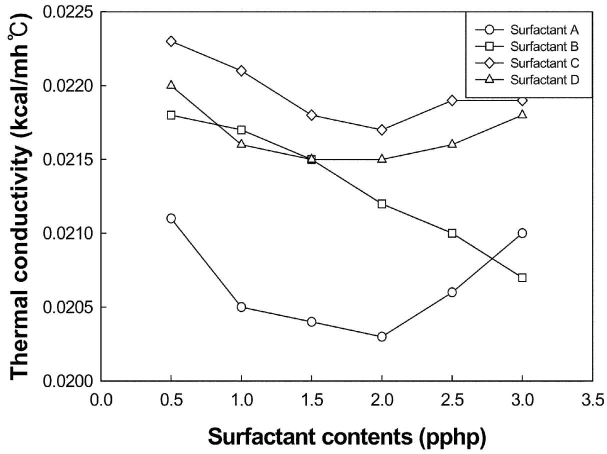


**Figure 8.** Thermal conductivity of PUFs with the surfactant content for the four different silicone surfactants (A, B, C and D). PUF samples were blown by cyclopentane/distilled water (10.0/1.0 pphp) mixture.

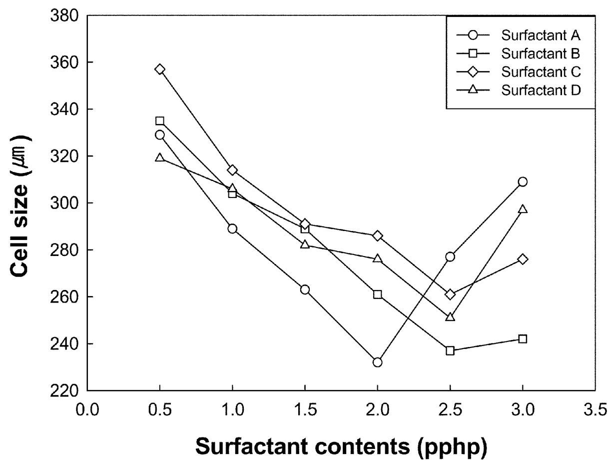


**Figure 7.** Cell size of PUFs with the surfactant content for the four different silicone surfactants (A, B, C and D). PUF samples were blown by distilled water.

Figures 6 and 7 show the effects of surfactant content on the cell size of rigid PUF for the surfactants A to D blown by cyclopentane/distilled water (10.0/1.0, pphp) mixture and distilled water only, respectively. From the results of Figures 6 and 7, it is shown that the silicone surfactant A leads to the lowest cell size of PUF probably due to the higher surface activity. Silicone surfactant A having higher silicone/polymer ratio seems to induce lower surface tension and it prevents the coalescence of the cells in the PUF. The smallest cells of the PUF are shown when the content of the surfactant A was about 2.0 pphp. This inflection point in cell size was also shown for other surfactants such as C and D, however, the optimum content for each surfactant was varied a little probably because of the difference in surface activity due to structural difference. For the surfactant B, the cell size is seen to decrease continuously up to 3.0 pphp and the inflection point in cell size may be observed when the content of surfactant is over 3.0 pphp.

Thermal conductivity is the most important factor for thermal insulating materials. Figure 8 shows the effect of surfactant content on the thermal conductivity of rigid PUF blown by cyclopentane/distilled water (10.0/1.0, pphp) mixture for the four different surfactants (A to D). As shown in Figure 8, the thermal conductivity of PUF using surfactant A shows the lowest value. The thermal conductivity of PUF decreased from 0.0211 to 0.0203 kcal/mh°C when the content of surfactant A is decreased from 0.5 to 2.0 pphp and, then, increased from 0.0203 to 0.0210 kcal/mh°C when the content of surfactant A is increased from 2.0 to 3.0 pphp. The repeatability of the measurements of thermal conductivity was very high, therefore, the standard deviation was observed to be about 0.00005 kcal/mh°C for each PUF samples.

Figure 9 shows the effect of surfactant content on the thermal conductivity of rigid PUF blown by distilled water for the four different surfactants (A to D). As shown in Figure 9, the thermal conductivity of PUF using surfactant A shows the lowest value. The thermal conductivity of PUF decreased from 0.0242 to 0.0221 kcal/mh°C when the content of surfactant A is decreased from 0.5 to 2.0 pphp and, then, increased from 0.0221 to 0.0233 kcal/mh°C when the content of surfactant A is increased from 2.0 to 3.0 pphp. From the results of Figures 8 and 9, it is suggested that the PUF using silicone surfactant A has better thermal insulation property than PUF using other surfactants such as surfactant B, C, and D. The results also indicate that the silicone surfactant A is more surface active and induces lower surface tension to the foaming system due to higher silicone/polymer ratio as shown in the results of cell size.

When the amount of surfactant A is 2.0 pphp in Figures 8

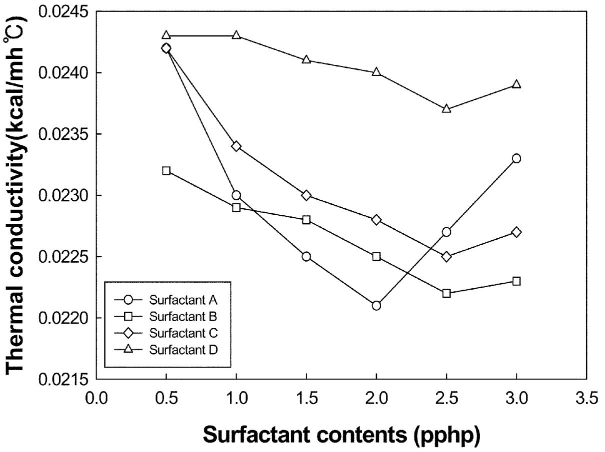


**Figure 9.** Thermal conductivity of PUFs with the surfactant content for the four different silicone surfactants (A, B, C and D). PUF samples were blown by distilled water.

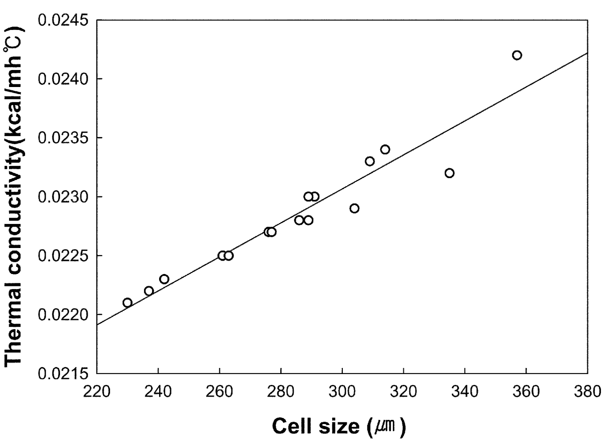


**Figure 10.** Relation between thermal conductivity and cell size of polyurethane foams blown by distilled water only.

and 9, the thermal conductivity of the PUF sample blown by cyclopentane/distilled water (10.0/1.0, pphp) mixture shows 0.0203 kcal/mhºC which is lower than the thermal conductivity of the PUF sample blown by distilled water (0.0221 kcal/mhºC) only, even though the cell size of the PUF blown by water is smaller than that blown by cyclopentane. This difference is maybe due to the difference of the thermal conductivities of the blowing gases used in this study such as cyclopentane and $CO_2$ which are 0.0110 and 0.0153, respectively.

Figure 10 shows the relation between the thermal conductivity and cell size of rigid PUF blown by distilled water. Thermal conductivities of the PUF decreased as the cell size of the PUF decreased. From the results of Figure 10, it is suggested that smaller cell size improves the thermal insulation property of the PUF samples. For relation between thermal conductivity and cell size of the PUF samples blown by cyclopentane/distilled water (10.0/1.0, pphp) mixture, similar behavior was observed with the results shown in Figure 10. If the blowing agent is fixed, then, the cell size is an important factor to decrease the thermal conductivity of the PUF samples. From the above results, it is suggested that the rigid PUF samples having lower thermal conductivity can be obtained by choosing the silicone surfactant containing higher silicone/polyether ratio. Also, the optimum content of silicone surfactant is an important factor to obtain the lower thermal conductivity of the PUF samples.

## Conclusions

Rigid polyurethane foams (PUFs) were synthesized with environmentally friendly blowing agents such as cyclopentane/distilled water (10.0/1.0, pphp) mixture and distilled water only with four different silicone surfactants having different silicone/polyether ratio, and an attempt was made to reduce the thermal conductivities of PUF samples.

From the results of scanning electron microscopy, optimum concentration of silicone surfactant was found to be about 1.5 to 2.5 phpp for the surfactants A to D to obtain the smaller cell size and lower thermal conductivity. Silicone surfactant having the higher silicone/polymer ratio showed smaller cell size and therefore, showed the lower thermal conductivity of the PUF samples.

From the relation between thermal conductivity and cell size of the PUF samples, smaller cell size improved the thermal insulation property of the rigid PUF for both the samples blown by cyclopentane/distilled water (10.0/1.0, pphp) mixture and distilled water only. If the blowing agent is fixed, then, the cell size is an important factor to decrease the thermal conductivity of the PUF samples. From the above results, it is suggested that the rigid PUF samples having lower thermal conductivity can be obtained by choosing the silicone surfactant containing higher silicone/polyether ratio. Also, the optimum content of silicone surfactant is an important factor to obtain the lower thermal conductivity of the PUF samples.

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