

Effects of Nucleating Agents on the Morphological, Mechanical and Thermal Insulating Properties of Rigid Polyurethane Foams

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Abstract: This study examined the effects of liquid and solid additives on the morphological, mechanical and thermal insulating properties of rigid polyurethane foams (PUFs). The PUFs synthesized with tetramethylsilane (TEMS) as a liquid-type additive showed a smaller average cell size and lower thermal conductivity than those with the aerosil 200 and clay 30B as solid-type additives. When TEMS was added, the average cell size of the PUF became more uniform and finer due to the reduced surface tension of the polymer solution, which increased the nucleation rate and number of bubbles produced and reduced cell size. The PUFs with TEMS showed the highest closed cell contents among the PUFs prepared using TEMS, aerosil 200 and clay 30B. This suggests that the insulation properties of PUF can be determined by both the size of the cell structure and the amount of closed cell contents in the system. The compression and flexural strengths of the PUF increased slightly when the aerosil 200, clay 30B and TEMS were added compared those of the neat PUF. The reaction profiles of the PUFs showed a similar gel and tack free time with the reaction time among the PUFs synthesized with three different additives and neat PUF. This suggests that the nucleating additives used in this study do not affect the bubble growth of the chemical reaction, and the additives may act as nucleating agents during the formation of PUF. From the above results of the cell size, thermal conductivity, closed cell contents and reaction profile of the PUFs, liquid-type nucleating agent, such as TEMS, is more effective in decreasing the thermal conductivity of the PUF than solid-type nucleating agent, such as aerosil 200 and clay 30B.

Keywords: rigid polyurethane foam, thermal conductivity, morphology, mechanical property.

Introduction

Rigid polyurethane foams (PUFs) are widely used as a thermal insulating materials in building, transportation and refrigeration industries. Thermal conductivity of PUF is influenced by thermal conductivities of blowing agent and solid polymer of PUF itself, and cell size of the foam.¹⁻⁶ When blowing agent and solid polymer are fixed, an improvement of thermal insulation of PUF can be achieved by reducing the cell size of the foam. Many researchers have extensively studied to improve thermal insulation property of PUF by reducing cell size and improving uniformity of cell morphology in the foams.⁷⁻²⁰

The PUF is based on the reaction of a diisocyanate with a polyol. The reaction is exothermic and the reaction heat can be used to form a cellular structure by evaporating the physical blowing agents such as trichlorofluoromethane (CFC)

and HCFC.^{5,6} The cellular structure of the PUF can be also generated from chemical blowing reaction. One of the widely used chemical blowing agents for PUF is distilled water. Water reacts with diisocyanate and, then carbon dioxide is generated during the reaction.

The foaming process can be explained by the nucleation and growth mechanism.^{21,22} First of all, many bubbles are generated if there are many nucleation sites during the process and foams having small cell structure can be produced if coalescence of bubbles is prohibited by controlling reaction parameters or reducing surface tension of solution during growth process. There are possible nucleation sites such as blowing agent in the polyol and diisocyanate compound, other dissolved gas or air bubbles hiding on the rough surface of solid matters. Therefore, the addition of nucleation agent is essential to create enough nucleation sites.

Small amount of well-dispersed nanoparticles in the polyurethane matrix may yield copious bubble nucleation by reducing the critical activation energy for nucleation. Accord-

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ing to the results from recent investigations, nanoparticles effectively reduced the cell size of the foam and increased the cell density during foaming process.^{3,8,23,24} Especially, the presence of nanoparticles resulted in a pronounced improvement of thermal and mechanical properties. In our previous work, it has shown that the clay particles played an important role to create tiny bubbles, and uniform cells could be obtained.³ Even though the clay showed a good possibility to improve thermal insulation of PUF, the use of clay may make the production process more complicated because of the precipitation of solid particles. Another nucleating candidate for reducing cell size in PUF can be liquid type nucleating agents. Nucleating agents play a role as nucleation sites and surfactants as well. They stabilize the gas bubbles formed during nucleation and inhibit the coalescence.

An attempt was made to find optimum nucleating agent for the preparation of rigid polyurethane foams. In this study three different additives were used as nucleating agents. One liquid-type additive was silane compound such as tetramethylsilane (TEMS). Two solid-type additives were hydrophilic fumed silica particles such as aerosil 200 and organically-modified montmorillonite such as clay 30B. Effects of nucleating agents on the morphological, thermal insulating and mechanical properties of PUF were investigated by scanning electron microscopy (SEM), thermal conductivity analyzer and universal testing machine (UTM), respectively. Furthermore, an investigation was carried out to elucidate that the mechanism for the change of cell morphology would be due to whether nucleation process or polymerization reaction rate by comparison of reaction profiles of the PUFs.

Experimental

Materials. The materials used in this study were obtained from commercial sources. Polymeric 4, 4'-diphenylmethane diisocyanate (MDI) and polyether polyol were supplied from BASF Korea Ltd. (Daejeon, Korea). Distilled water used as a chemical blowing agent was generated in our laboratory. Amine type catalyst was supplied from Air Products and Chemicals, Inc. (Allentown, USA). Polysiloxane ether used as a surfactant was supplied from Degussa (Seoul, Korea). Tetramethylsilane (TEMS) as a liquid-type nucleating agent was purchased from Sigma-Aldrich Co. Closite 30B and aerosil 200 as solid-type nucleating agents were supplied from Southern Clay Products, Inc. (USA) and Degussa, respectively. Aerosil 200 having hydrophilic characteristic was not surface treated. The clay 30B was dried at 90 °C for 24 h in a vacuum oven before use and the other chemicals were used as received. Table I shows the chemical compositions for the preparation of rigid polyurethane foam samples.

Preparation of PUF. Rigid polyurethane foam (PUF) samples were prepared by mixing both polyol and the MDI at

Table I. Compositions of the Materials Used in the Polyurethane Foams

Chemicals	Description	Weight(g)
MDI	4,4'-diphenylmethane diisocyanate	145.7
Polyol	Polyether type	100.0
Surfactant	Silicone type	2.5
Blowing Agents	Cyclopentane/Water	16.5/1.95
Catalyst	Amine type	2.5
Additives	Tetramethylsilane	1.0, 2.0, 3.0
	Aerosil 200	1.0, 2.0, 3.0
	Clay 30B	1.0, 2.0, 3.0

20 °C using a mechanical stirrer. The chemical compositions used in the preparation of rigid PUF are listed in Table I. When the mixing was started directly at high speed, the fillers did not disperse well and they were aggregated each other. Therefore, the mixing was started from a speed of about 400 rpm and it was gradually increased to 3,000 rpm and mixed at 60 °C for 2 h. Then, water, catalysts and surfactant were added to 100 g of polyol in a polyethylene cup and they were mixed for 15 sec at 3,000 rpm using brushless type stirrer until the mixture was a homogeneous phase. After mixing, cyclopentane was put into the polyol mixture and mixed again for 10 sec using brushless type at 3,000 rpm. Since cyclopentane is very volatile, it was stored in a refrigerator before mixing. After that, MDI was added into the polyol mixture prepared by the process mentioned above at the rotation speed of 5,000 rpm for 5 sec at ambient temperature. Finally, the mixture was immediately poured into an open mold (250 mm×250 mm×250 mm) to produce free-rise foams, which was kept at room temperature for 8 min. The foam was then removed from the open mold and it was cured at room temperature for at least 1 day before characterization.

Thermal Conductivity Measurements. Thermal conductivities of PUF with three different additives were measured with a thermal conductivity analyzer (model TCA Point2, Anacon) according to ASTM C518. PUF sample was placed in the test section between two plates which are maintained at different temperatures during the test. Upon achieving thermal equilibrium and establishing a uniform temperature gradient throughout the sample, dimension of the specimen was 200×200×25 mm (width×length×thickness). The thermal conductivities of three specimens per sample were measured and averaged.

Scanning Electron Microscopy (SEM). Morphology of PUF 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 25 kV. We have counted 30 cells from the largest

cells and then the cell size was measured from the selected 30 cells out of all the cells.

Mechanical Properties. Mechanical properties of PUF were measured under ambient condition using an Instron universal testing machine (Model 4467, Canton, Ohio). Compressive strength tests were performed according to the ASTM D1621. The size of the specimen was 30 mm (W) × 30 mm (L) × 30 mm (T) and the speed of crosshead movement was 3.00 mm/min. The flexural strength tests were carried out according to the KS M3830. Specimens were cut to dimensions of 25 mm (W) × 120 mm (L) × 20 mm (T). The span distance was 100 mm, and the cross head speed was 10.00 mm/min. The strengths of 10 specimens per sample were measured and averaged for each mechanical test.

Closed Cell Content of PUF. Closed cell content of was determined by an Automatic Pycnometer (Model UPY-20F, Quantachrome instruments). The specimens had dimensions of 25 mm (W) × 25 mm (L) × 25 mm (T). For each data point, five samples were tested, and the average value was taken.

Reaction Profile of PUF. The reaction profile of the PUF was recorded under ambient condition with a foam qualification system (Model FOAMAT, Format Messtechnik GmbH). The rise profiles of the PUF were recorded for height with reaction time by mixing both polyol component and MDI at 20 °C.

Results and Discussion

Cell Morphology. The cell size and shape of the PUF is very important in thermal conductivity of the rigid PUF.²⁵⁻²⁷ The effects of nucleating additives on the cell morphology of the PUF are shown in Figures 1 and 2. From Figures 1 and 2, it seems that average cell size is getting more uniform and finer when the amount of additive is increased. Figure 1

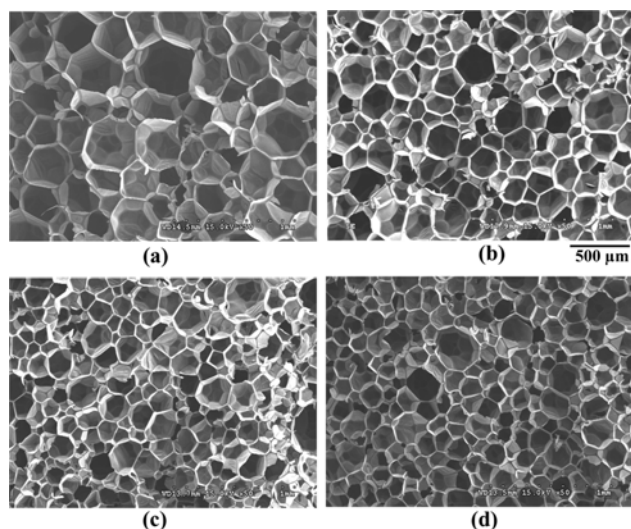


Figure 1. Scanning electron micrographs of polyurethane foams filled with tetramethylsilane (phr): (a) 0.0, (b) 1.0, (c) 2.0, (d) 3.0.

(a) to (d) shows the scanning electron micrographs of the cryogenically fractured cross-sectional surfaces of the PUF containing 0.0, 1.0, 2.0 and 3.0 phr (parts per hundred grams of polyol by weight) of TEMS, respectively. For Figure 1(a) to (d), the average cell size of the PUF is shown to decrease from 328, 245, 223 to 198 μm with the increase of TEMS content, respectively. From the results of Figure 1(a) to (d), the standard deviation of the cell size was observed to be 62, 36, 35 and 34 μm, respectively. It is known that the methyl groups on organic compound have intrinsically low surface energy, as a result of weak van der Waals attractive forces.²⁸ TEMS which has four methyl groups provides low surface tension to the foaming system. Uniform mixing can be obtained with the addition of TEMS since it lowers the surface tension and the viscosity of the solution. TEMS having low boiling point can also be an effective nucleating agent. Therefore, when TEMS is added, average cell size of the PUF is getting more uniform and finer because of the lowering the surface tension of the solution as the amount of this particular nucleation agent increases.

From the study by Colton and Suh,²⁷ homogeneous nucleation has been described as shown in eq. (1):

$$\Delta G^* = \frac{16\pi\sigma^3}{3\Delta P^2} \quad (1)$$

where ΔG^* is change in Gibbs free energy, σ is the surface tension and ΔP is the gas saturation pressure. The formula indicates that the decrease in the surface energy of polymer decreases the activation energy for nucleation. A dissolved nucleating additive, TEMS will reduce the activation energy for nucleation by reducing surface tension of the polymer, thereby increasing the nucleation rate and a number of bubbles produced and then cell sizes are smaller.

Figure 2(a) to (d) shows the scanning electron micrographs

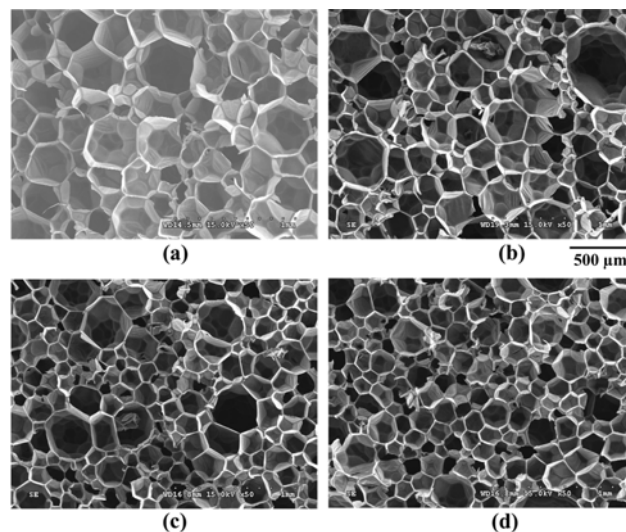


Figure 2. Scanning electron micrographs of polyurethane foams filled with aerosil 200 (phr): (a) 0.0, (b) 1.0, (c) 2.0, (d) 3.0.

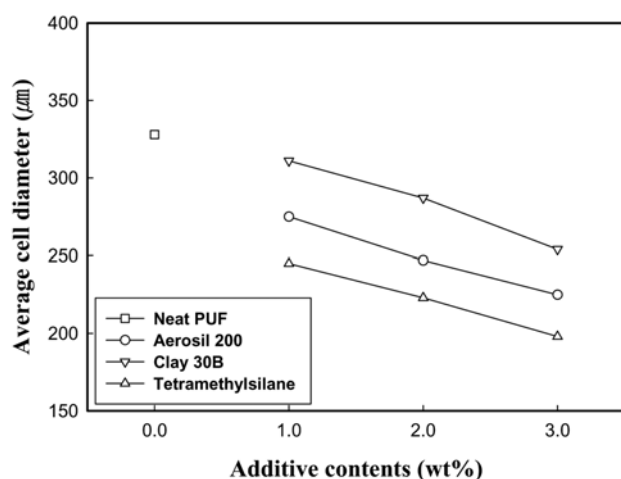


Figure 3. Average cell size of polyurethane foams with the additive contents for the three different additives of tetramethylsilane, aerosil 200 and clay 30B.

of the cryogenically fractured cross-sectional surfaces of PUF with aerosil 200 (hydrophilic SiO_2 powder), and the average cell size of PUF is decreased from 328, 245, 223 to 225 μm , respectively. Uniformly dispersed fillers could act as nucleation agents and serve as sites for bubble growth.²⁴ From this result, it is suggested that the aerosil 200 in the PUF may act as a nucleating agent for creating copious bubble nucleation during foaming process.

Figure 3 shows the effect of additive content on the average cell size of the PUFs. As the content of the additive is increased, the average cell size is decreased for PUFs with TEMS, aerosil 200 and clay 30B. PUF loaded with 3 wt% of TEMS showed the smallest average cell size and the average cell size of neat PUF was reduced from 328 to 198 μm . When the content of the clay 30B is increased up to 3 phr, average cell size of PUF is decreased from 328 to 254 μm . Exfoliated clay layers can act as nucleation agent and serve as sites for bubble growth with the formation of new bubbles.^{28,29} As the amount of nucleation agents increases, the bubble size decreases, and the number of the bubbles increases. Therefore we suggest that the reduction in the average cell diameter of PUF filled with clay 30B may have been due to the nucleation effect of the clay 30B. Hydrophilic clay 30B has a good affinity to polyol and it can also be an effective nucleating agent for small and uniform cell structure.

The reason that liquid-type additive is more effective than solids in reduction of cell size is that the addition of solid particles increases the viscosity of the solution and more energy is required for nucleation due to high surface tension. The number of heterogeneous nucleation sites is typically less than that of the homogeneous nucleation sites. However, one of each small particle can act as a nucleation agent and serves as sites for the bubble growth with the formation of new bubbles in heterogeneous system where ultra

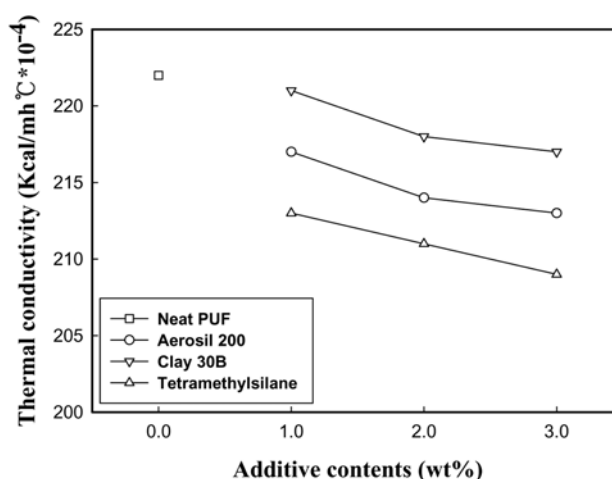


Figure 4. Thermal conductivity of polyurethane foams with the additive content for three different additives of tetramethylsilane, aerosil 200 and clay 30B.

fine solid particles are dispersed uniformly. As a result, whenever additives act as nucleating agents regardless of the phase, as the content of nucleation agent is increased, the bubble size is decreased and consequently the number of bubbles is also increased.

Thermal Conductivity. Thermal conductivity is one of the important factors in thermal insulating materials and it is influenced by several parameters. Thermal conductivities of rigid PUFs synthesized with three different nucleating additives are studied. Figure 4 shows the effect of additive content on the thermal conductivity of PUF. The contents of the additives were varied from 1 to 3 phr. From Figure 4, it shows that PUFs with TEMS, aerosil 200 and clay 30B as nucleating agents appear lower thermal conductivity than neat PUF because of their smaller average cell size. The PUF with TEMS showed the lowest thermal conductivity than other PUFs. This is probably because that the PUF with TEMS provides the smallest cell size and highest closed cell content values among the PUFs prepared using TEMS, aerosil 200 and clay 30B as nucleating agents. The TEMS creates copious bubble nucleation during foaming process by reducing the critical activation energy for nucleation.

Figure 5 shows the relationship between the thermal conductivity and average cell size of PUF with additives. Thermal conductivity of the PUFs with three different additives is decreased with the decrease of average cell size of the PUF, which explains that small cell size improves the thermal insulation property of the PUF. From the results of thermal conductivity shown in Figures 4 and 5, it is suggested that the thermal conductivity of PUF strongly depends on average cell size of the PUF.

Closed Cell Content of PUF. The closed cells of PUF are produced such that the cells are initially filled with gas that has a relatively lower thermal conductivity than that of air.

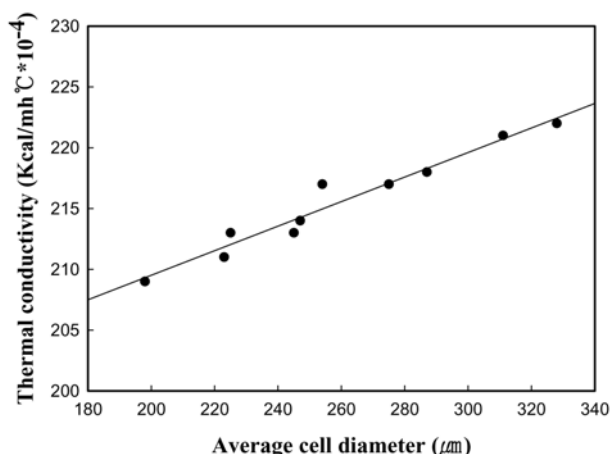


Figure 5. Relationship between thermal conductivity and cell size of polyurethane foams with the additives of tetramethylsilane, aerosil 200 and clay 30B.

Thus, thermal conductivity of PUF is mainly affected by the composition of the gas mixture in the cells of PUF. The thermal conductivity of PUF changes over time because produced gases diffuse out of the cell matrix and atmospheric gases diffuse into the cells. Therefore, a decrease of the closed cell content leads to higher thermal conductivity of the PUF because that the amount of blowing agent diffused out of the cells is increased with time. The insulation property of PUF can be determined by not only by the size of cell structure but by the amount of closed cells in the system.

Figure 6 shows the effect of additive content on the closed cell content of the PUF with three different additives. The additive content was increased from 1.0 to 3.0 wt%. When the TEMS was added, closed cell content of the PUF did not change as compared with that of the neat PUF. However, when the solid particles such as aerosil 200 and clay 30B

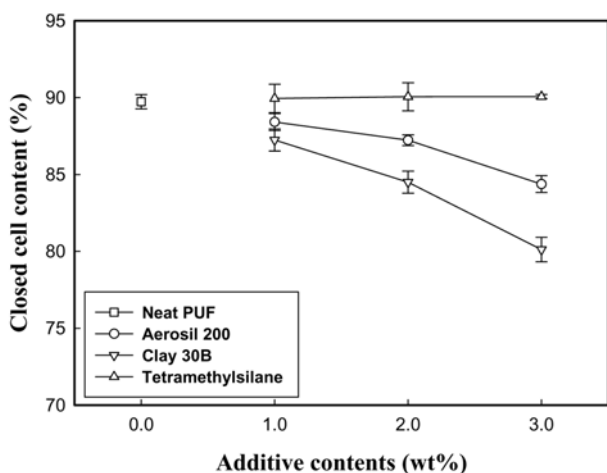


Figure 6. Closed cell content of polyurethane foams with the additive content for three different additives of tetramethylsilane, aerosil 200 and clay 30B.

were added, the closed cell content of the PUF was decreased with additive contents. This indicates that the windows of the PUF synthesized with solid particles are ruptured more easily during foam formation. Uneven dispersion of the fillers in the polymer matrix brings to no intercalation, exfoliation or disaggregation of the fillers and then, the fillers have micrometric dimensions. In presence of micrometric fillers, it is known that the fillers have negative effect on foam morphology because they interfere during foam expansion process, when the cell structure is growing, thus leading to a worse structure.²³ One of the reasons for the higher insulation property when adding TEMS is that the content of closed cell is higher because the cell walls are not broken.

Mechanical Properties. Mechanical properties of rigid PUF depend mainly on its density. In this study, the density of the PUF is about 30 kg/m³ and shows similar values for all the foams prepared in this study. Therefore, the effects of

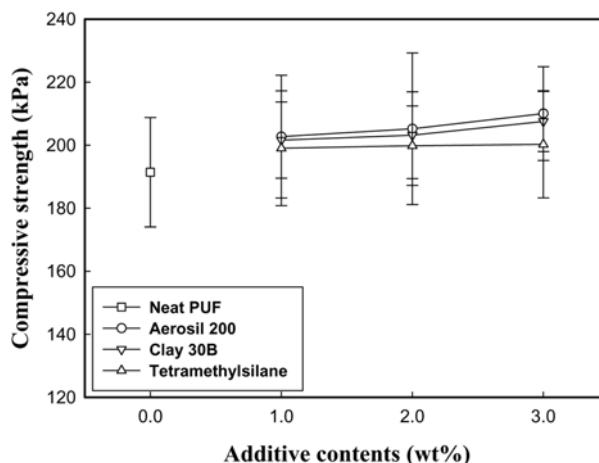


Figure 7. Compressive strength of polyurethane foams with the additive content for three different additives of tetramethylsilane, aerosil 200 and clay 30B.

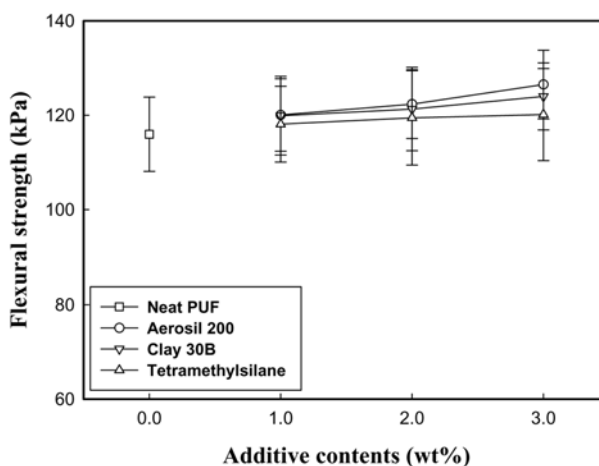


Figure 8. Flexural strength of polyurethane foams with the additive content for three different additives of tetramethylsilane, aerosil 200 and clay 30B.

additive type and content on the mechanical properties of PUF can be studied. Figures 7 and 8 show the compression and flexural strengths of the PUF. From Figures 7 and 8, it is observed that the compression and flexural strengths of the PUF increase slightly with the increase of additive contents for the aerosil 200 and clay 30B as a solid-type additive. However, when TEMS was added as a liquid-type additive, the compression and flexural strengths of the PUF did not change appreciably with the additive contents. From this result, it is suggested that the liquid-type additive such as TEMS do not affect the mechanical properties of PUF appreciably.

Reaction Profile of PUF. Polymerization reaction rate of PUF is a very important factor for final cell size. Usually, the growth of bubbles can be varied by controlling reaction using the addition of reaction catalyst. To produce microcellular structure, high nucleation rate should be obtained and bubble growth should be controlled and stopped before coarsening of bubbles. Thus, the final size of cells created during foaming process can be affected by growth of bubbles as well as nucleation of bubbles in PUF. In this study, foam rise profile was investigated to figure out whether or not the nucleating agent affects on the reaction rate which is related to bubbles growth.

The rate of synthesis of PUF is measured as cream time, gel time and tack free time. Viscosity influences bubble growth significantly because the growth of bubbles stop as the viscosity gets very high and solidification takes place. Viscosity of the polyurethane changes largely during gel time. The reaction profiles of PUF with and without additives are shown in Figure 9. From Figure 9, it is observed that the reaction profiles for PUFs with three different additives and neat PUF show similar gel and tack free time with the reaction time. From this result, it is suggested that the nucleating additives used in this study did not affect the bubble growth of chemical reaction because of their similar viscosity

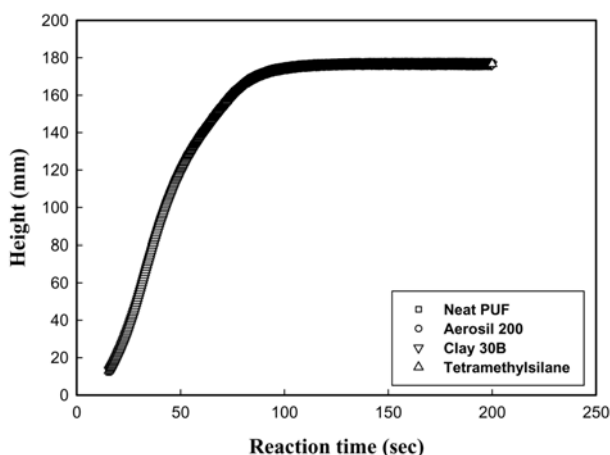


Figure 9. Reaction profile of polyurethane foams with reaction time for the three different additives of tetramethylsilane, aerosil 200 and clay 30B. The additive content was 3 phr.

change during foaming process. Therefore, in the conditions of this study, the average cell size of PUF was changed by bubble nucleation in the presence of liquid and solid types of additives and the additives may have acted as nucleating agents during the formation of PUF.

Conclusions

Rigid polyurethane foams were synthesized with tetramethylsilane, aerosil 200 and clay 30B as additives. Scanning electron microscopy and thermal conductivity measurements have shown that PUFs synthesized with TEMS as a liquid-type additive appeared the smaller average cell size and lower thermal conductivity than with the aerosil 200 and clay 30B as solid-type additives. From the above results, when the TEMS was added, it is suggested that average cell size of the PUF is getting more uniform and finer because of lowering the surface tension of the polymer solution, thereby increasing the nucleation rate and a number of bubbles produced and then cell size becomes smaller.

From the results of closed cell content of PUF, the PUF with TEMS provided the highest closed cell contents among the PUFs prepared using TEMS, aerosil 200 and clay 30B. From this result, it is suggested that the insulation property of PUF can be determined by not only the size of cell structure but the amount of closed cell contents in the system. Compression and flexural strengths of the PUF showed slightly increased values when the aerosil 200, clay 30B and TEMS were added compared those of the neat PUF.

The reaction profiles of PUFs with three different additives and neat PUF showed similar gel and tack free time with the reaction time. This result suggested that the nucleating additives used in this study did not affect the bubble growth of chemical reaction, and the additives may have acted as nucleating agents during the formation of PUF.

From the results of cell size, thermal conductivity, closed cell contents and reaction profile of the PUFs, it is concluded that nucleating agents are necessary gradient to produce uniform and fine cell structure of rigid polyurethane foams. As a result, liquid-type nucleating agent such as TEMS is more effective on lowering the thermal conductivity of the PUF than solid-type nucleating agent such as aerosil 200 and clay 30B.

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