Properties of Rigid Polyurethane Foams Blown by HFC-365mfc and Distilled Water

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Abstract: Rigid polyurethane foams (PUFs) were prepared from polymeric 4,4-diphenylmethane diisocyanate (PMDI), polyether polyol, silicone surfactant, amine catalysts, and hydrofluorocarbon (HFC-365mfc) and distilled water as blowing agents. The density and compressive strength of the PUF samples were decreased with the increase of the blowing agent. This is mainly due to that the cell size of the PUF samples is increased with the increase of blowing agent. From the result of the effect of blowing agents on the thermal conductivity of the PUF samples, it was observed that, when the amount of the distilled water was fixed, the thermal conductivity of the PUF samples decreased with the increase of the amount of HFC-365mfc. Also, when the amount of HFC-365mfc was fixed, the thermal conductivity of the PUF samples decreased with the increase of the amount of distilled water. From the results of thermal conductivity of PUF samples, it is suggest that the thermal conductivity of the PUF samples depends on the thermal conductivity of blowing agent as well as the total amount of the entrapped blowing gas inside the closed cell of the PU foams. Also, PU foams blown by mixed blowing agent such as HFC-365mfc and distilled water may increase in the structural stability of the PU foams by matching of the rates of gelling and foaming reactions for the formation of desired foams compared the PU foams blown by HFC-365mfc or distilled water alone.

Keywords: polyurethane, foam, morphology, blowing agent, mechanical property

Introduction

Polyurethane foams (PUFs) have been commercially accepted in wide variety of applications since the 1940s. These foams surround us in today’s society, playing an important role in many industries from shipbuilding to footwear, construction to cars, insulation to furniture, and car seating to packaging and contribute greatly to our daily lives. Especially rigid polyurethane foam is one of the most important insulating materials used today in the construction industry and is the sole insulation used in global appliances industry like refrigerators and freezers [1-12].

Polyurethane foams are generally created from a two-phase system that consists of a solid polymer matrix and a gaseous phase gained through blowing agents. The most widely used system of producing foamed polymers involves dispersing a gas throughout a fluid polymer phase and stabilizing the resultant foam. In most of these systems, the foam is expanded by increasing bubble size before stabilizing the system [2,3].

These days, the use of chlorofluorocarbons (CFCs) is considered undesirable because of environmental problems such as ozone depletion. The ozone depletion potential of the CFC, HCFC-141b and hydrofluorocarbon (HFC-365mfc) is known to be 1.0, 0.1, and 0.0, respectively. Substitutes for CFC and HCFC-141b have been developed, and their applications for cellular materials have been studied. Therefore, HFC-365mfc and distilled water were used as blowing agents in this study because of the environmental problems [13].

Thermal conductivity is the most important property for the thermal insulating materials. The thermal conductivity of the closed-cell foams depends mainly on the total content and the thermal conductivity of entrapped...
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Table 1. Characteristics of Materials Used in This Study

<table>
<thead>
<tr>
<th>Materials</th>
<th>Comments</th>
<th>Functionality</th>
<th>Equivalent weight (g/mol)</th>
<th>Composition (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4,4'-diphenylmethane diisocyanate</td>
<td>NCO content: 31.5 %</td>
<td>2.9</td>
<td>133.5</td>
<td>142.7</td>
</tr>
<tr>
<td>(MDI)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyol</td>
<td>Polyether polyol</td>
<td>3.0</td>
<td>234.7</td>
<td>100.0</td>
</tr>
<tr>
<td>Triethylene diamine</td>
<td>Catalyst</td>
<td>-</td>
<td>-</td>
<td>0.9</td>
</tr>
<tr>
<td>Polysiloxane ether</td>
<td>Surfactant</td>
<td>-</td>
<td>-</td>
<td>1.5</td>
</tr>
<tr>
<td>Distilled water</td>
<td>Chemical blowing agent</td>
<td>2.0</td>
<td>9.0</td>
<td>0.5 ~ 3.0</td>
</tr>
<tr>
<td>HFC-365mfc</td>
<td>Physical blowing agent</td>
<td>-</td>
<td>-</td>
<td>5.0 ~ 30.0</td>
</tr>
</tbody>
</table>

*a data from the suppliers.

blowing gas inside the closed cells. The cell geometry may be either open or closed cell. Closed-cell foams are most suitable for thermal insulation and are generally rigid. In addition, the structure and structural stability of the foams also affect the thermal conductivity of the foams. For the PUF system, physical blowing agent such as HFC-365mfc expands the polyurethane (PU) material by vaporizing, and this reaction is endothermic. On the contrary, chemical blowing agent such as water expands the PU material by the blowing gas generated by the reaction between chemical blowing agent and raw materials, and this reaction is exothermic [14,15].

In this study, the effects of blowing agents on the density, the compressive strength, the cell morphology, and thermal conductivity of the rigid PUF samples were investigated. The rigid PUF samples were prepared from the polymeric 4,4-diphenylmethane diisocyanate (PMDI) with a functionality of 2.9 and the polyether polyl based on glycerine. HFC-365mfc was used as a physical blowing agent and distilled water was used as a chemical blowing agent. The cellular structure, the mechanical properties such as compressive strength, and the thermal conductivity of the PUF samples were studied with a universal testing machine (UTM), a field emission scanning electron microscopy (FE-SEM), and a heat flow meter, respectively.

**Experimental**

**Materials**

The materials used in this study were obtained from commercial sources. The polymeric MDI (PMDI) was supplied from BASF Korea Co. (Seoul, Korea). The polyether polyl based on glycerine was supplied from KPC Co. (Ulsan, Korea). Hydrofluorocarbon (HFC-365mfc, CF₃CH₂CF₂CH₃), which was used as a physical blowing agent was supplied from Solvay. Distilled water, which was used as a chemical blowing agent, was supplied from Air Products and Chemicals, Inc. (Allentown, USA). Polysiloxane ether used as a surfactant was supplied Osi Specialties, Inc. (USA). The characteristics of the materials are shown in Table I. The polyether polyl was dehydrated before use at 90 °C for 24 h in a vacuum oven. The other chemicals were used as received [10,16-19].

**Sample Preparations**

The Rigid PUF samples with various densities were synthesized with a “one-shot method” [16,17]. All chemicals were put into the reactor and mixed for 30 s with a brushless-type stirrer, which was ring guard propeller for protecting the wall or sensors in the reactor, at ambient condition. The stirrer speed was set at 3000 rpm throughout the mixing. After mixing, the reactants were poured into an open mold (250 mm × 250 mm × 100 mm) to produce free-rise foams and were cured for 1 week at room temperature. Three replications for all the foams were executed.

**Measurements**

**Density Measurement**

The density of the PUF samples was measured according to ASTM D1622. The size of the specimen was 30 × 30 × 30 mm (width × length × thickness). The densities of five specimens per sample were measured and averaged.

**Scanning Electron Microscopy**

The morphology of the PUF sample was studied with a HITACHI S-4300SE field emission scanning electron microscope. The samples were cryogenically fractured and gold coated before scanning. The accelerating voltage was 25 kV. The S-4300SE was used to observe the size of the cells on the PUF samples, which was measured with an Image-Pro Plus image analyzer and averaged, except for the largest and smallest cells.

**Universal Testing Machine**

The compressive strength of the PUF samples was
measured under ambient conditions with an Instron UTM (model 4467). A compressive test was performed according to ASTM D 1621. The speed of crosshead movement was 3.00 mm/min. The strengths of five specimens per sample were measured and averaged.

**Thermal Conductivity Measurement**

The thermal conductivity of the PUF samples was measured with a Holometrix Micromet (model Lambda 2000) according to ASTM C 518. A sample was placed in the test section between the two plates which were maintained at different temperatures during the test. Upon achieving thermal equilibrium and establishing a uniform temperature gradient throughout the sample, the thermal conductivity of the PUF samples was determined. The size of the specimen was 300 × 300 × 50 mm (width × length × thickness). The thermal conductivities of three specimens per sample were measured and averaged.

**Results and Discussion**

**Density of PU Foams**

The densities of the PUF samples (PUF-X-Y) blown by a mixture of distilled water and HFC-365mfc are shown in Figure 1. In the sample code (PUF-X-Y), X denotes the amount of distilled water used, and Y denotes the amount HFC-365mfc used. As shown in Figure 1, the density of the PUF samples blown by HFC-365mfc decreased from 180.3 to 55.3 kg/m$^3$ as the amount of HFC-365mfc increased from 5 to 30 php (parts per hundred polyol), respectively. When the mixture of distilled water and HFC-365mfc was used as a blowing agent, the density of the PUF samples ranged from 120.3 to 30.2 kg/m$^3$. From the results of Figure 1, densities of the PUF samples decrease with the increase of the blowing agents.

The cell size of the PUF samples is important in the density, mechanical properties and thermal conductivity of PUF samples. A chemical blowing agent such as distilled water generates carbon dioxide through the chemical reaction with diisocyanate in the PMDI accompanying the exothermic reaction heat. Because of the increase of the temperature of the reactants, the concentration of blowing gas in the mixture exceeds its solubility limit and a nucleation of bubbles begins. During the rise time, the already formed bubbles grow and new bubbles nucleate. The increase of distilled water generates more bubbles, and the increased bubbles coagulate much more with each other. Therefore, the cell size of the PUF samples increases with the increase of the amount of distilled water [1-3].

From Figure 1, it is observed that the density of the PUF samples is decreased with the increase of the distilled water content from 0.0 to 3.0 php when the HFC-365mfc is fixed. This is mainly because that the cell size of the PUF samples is increased with the increase of the distilled water content, therefore, density of the PUF samples is decreased. Figure 2 shows the effect of surfactant on the density of the PUF samples. As shown in Figure 2, the surfactant does not affect the density of the PUF samples when the surfactant is added in the amount of 0.0 to 3.0 php.

**Compressive Strength of PU Foams**

In Figure 3, the compressive strength of the PUF samples with the blowing agent is shown. As shown in Figure 3, the compressive strength of the PUF samples decreased from 2.21 to 0.37 MPa as the amount of HFC-365mfc increased from 5 to 30 php, respectively, when the distilled water was fixed at 0.0 php. From Figure 3, the compressive strength of the PUF samples is shown to decrease from 2.21 to 0.40 MPa as the amount of water is increased from 0.0 to 3.0 php when the
Table 2. Cell Size, Density and Thermal Conductivity of the Polyurethane Foam Samples with the Amount of Blowing Agents

<table>
<thead>
<tr>
<th>Sample</th>
<th>Distilled water (php)</th>
<th>HFC-365mfc (php)</th>
<th>Cell size (µm)</th>
<th>Density (kg/m³)</th>
<th>Thermal conductivity (kcal/mh°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.5</td>
<td>5.0</td>
<td>350</td>
<td>120.3</td>
<td>0.0284</td>
</tr>
<tr>
<td>B</td>
<td>0.5</td>
<td>10.0</td>
<td>360</td>
<td>90.3</td>
<td>0.0260</td>
</tr>
<tr>
<td>C</td>
<td>0.5</td>
<td>15.0</td>
<td>370</td>
<td>83.2</td>
<td>0.0257</td>
</tr>
<tr>
<td>D</td>
<td>0.5</td>
<td>20.0</td>
<td>400</td>
<td>70.4</td>
<td>0.0251</td>
</tr>
<tr>
<td>E</td>
<td>0.5</td>
<td>25.0</td>
<td>420</td>
<td>60.3</td>
<td>0.0234</td>
</tr>
<tr>
<td>F</td>
<td>0.5</td>
<td>30.0</td>
<td>450</td>
<td>52.3</td>
<td>0.0215</td>
</tr>
</tbody>
</table>

Figure 3. Compressive strength of the PUF samples with the amount of blowing agents.

amount of HFC-365mfc is fixed at 5.0 php. From the results of compressive strength, it is suggested that the compressive strength of the PUF samples is decreased with the increase of the blowing agent. This is because that the cell size of the PUF samples is increased with the increase of the blowing agent, therefore, the density of the PUF samples is decreased.

It is generally known that the mechanical properties of a cellular material mainly depend on its density. A simple power law can be used to depict the relationship between the mechanical properties, such as the compressive strength and the density [1,2,20].

\[ \text{Strength} = A(\text{density})^B \]  

where A is a constant related to the temperature and physical properties of the polymer and B is related to the deformation mechanics of cellular materials. The results of the density measurement demonstrate that the density of the PUF samples decreases with the increase of water and HFC-365mfc contents which are shown in Figure 1. Therefore, the results of the density measurement and equation (1) suggest that the compressive strength of the PUF samples decreases with the increase of water and HFC-365mfc contents which are shown in Figure 3.

Morphology of PU Foams

Figure 4 shows the effect of the blowing agent on the cell morphology of the PUF samples. From Figure 4(a) ~ (f), it is shown that the cell size of the PUF sample is increased from 350 to 450 µm as the amount of HFC-365mfc increased from 5 to 30 php, respectively. The amount of distilled water which was used as a chemical blowing agent was 0.5 php for all the PUF samples as shown in Figure 4. Detailed compositions of the blowing agents used in Figure 4(a) ~ (f) are shown in Table 2. Table 2 shows also the density and cell size of the PUF samples which are appeared in Figure 4(a) ~ (f).

From Table 2, it is shown that the cell size of the PUF samples increases with the increase of the amount of physical blowing agent (HFC-365mfc). And, therefore, the density of the PUF samples is decreased with the increases of the amount of blowing agent and cell size.

Generally expansion of the foam is achieved by evaporation of low boiling agents or gas generation reaction with chemical blowing agent. The polymerization and crosslinking reaction are highly exothermic. Exothermic reaction heat increases the temperature of the reactants. When the temperature of the reactants reaches the vaporization point of the physical blowing agent, the physical blowing agent evaporates extremely fast. In this case, the cell size of the PUF sample becomes small [1,14].

The blowing process of the water blown PUF is the reaction of isocyanate with water. Water as a chemical blowing agent reacts with the isocyanate group to generate carbon dioxide and polyurea with the release of exothermic reaction heat. The kinetic rate of the chemical reaction increases with temperature of the reactants and the blowing gas is generated gradually. Therefore, the cell size of the PUF sample blown by water becomes larger than the sample blown by physical blowing agent [10,14].

In this study, the physical blowing agent, HFC-365mfc, was used as a main blowing agent, and the chemical blowing agent, distilled water, was used as a support blowing agent. Generally polyurethane foams are produced by forming a PU with concurrent a gas evolution process. Provided these two processes are balanced, bubbles are trapped in the polymer matrix and a cellular
product is formed. If evolution of gas is too fast, the foam initially expands well but then collapses because the gelling process has not proceeded enough to retain the gas. The matching of the rates of gelling and foaming reactions is essential for formation of desired foams. In Table 2, this is the reason that the mixture of the physical and chemical blowing agents was used to match the rates of reactions to form the desired PU foams. The PU foams are widely used as thermal insulating materials with low thermal conductivity, and this is maybe because that the closed cell content shown in Figure 4 is about 95%. This high closed cell content contributes to the low thermal conductivity of the PU foams compared other thermal insulating materials.

Thermal Conductivity of PU Foams

The thermal conductivity of the PUF samples with the amount of blowing agents is shown in Figure 5. The thermal conductivities of HFC-365mfc and carbon dioxide that is generated by the reaction between water and polymeric MDI are 0.0105 and 0.0153 kcal/mh°C, respectively. Therefore, as shown in Figure 5, at the equal amount of the distilled water, the thermal conductivity of the PUF samples decreases with the increases of the HFC-365mfc. For example, as shown in Table 2, at the 0.5 php distilled water content, the thermal conductivity of the PUF samples is decreased from 0.0284 to 0.0215 kcal/mh°C as the amount of HFC-365mfc increased from 5 to 30 php, respectively.

From Figure 5, when the amount of the HFC-365mfc is fixed, the thermal conductivity of the PUF samples de-
creases with the increases of the distilled water. The increase of distilled water generates more bubbles, and the increased bubbles coagulate much more with each other. Then, the cell size of the PUF samples is increased with the increase of the amount of distilled water, therefore, the total content of the blowing gas in the PUF samples is increased. Also, when the amount of distilled water is fixed, the thermal conductivity of the PUF samples decreased with the increase of the amount of HFC-365mfc.

The thermal conductivity of the PUF sample (density = 55.2 kg/m$^3$) blown by HCFC-141b as a blowing agent, for example, shows 0.0194 kcal/mh$^o$C which is lower value than the thermal conductivity (0.0215 kcal/mh$^o$C) of the PUF sample blown by HFC-365mfc and distilled water at the same density (Table 2). This difference is maybe due to the difference of the thermal conductivities of HCFC-141b and HFC-365mfc which are 0.0090 and 0.0153 kcal/mh$^o$C, respectively. From the results of thermal conductivity of PUF samples, it is suggest that the thermal conductivity of the PUF samples strongly depends on the thermal conductivity of blowing agent as well as the total amount of the entrapped blowing gas inside the closed cell of the PU foams. If the blowing agent and density are fixed, then, the cell size could be an important factor to control the thermal conductivity of the PUF samples.

**Conclusion**

Rigid PUF samples were prepared with PMDI, polyether polyl, catalyst, surfactant, and HFC-365mfc and distilled water as blowing agents. The density and compressive strength of the PUF samples were decreased with the increase of the distilled water content from 0.0 to 3.0 php when the HFC-365mfc was fixed. This was mainly due to that the cell size of the PUF samples was increased with the increase of blowing agent. The surfactant did not affect the density of the PUF samples when the surfactant was added in the amount of 0.0 to 3.0 php.

From the results of compressive strength, it showed that the compressive strength of the PUF samples decreased with the increase of the amount of HFC-365mfc when distilled water was fixed. This was mainly due to that the cell size was decreased with the increase of the HFC-365mfc content, therefore, the density of the PUF samples was decreased.

From the result of the effect of blowing agents on the thermal conductivity of the PUF samples, at the equal amount of the distilled water, the thermal conductivity of the PUF samples decreased with the increase of the amount of HFC-365mfc. At the equal amount of HFC-365mfc, the thermal conductivity of the PUF samples decreased with the increases of the distilled water. The increase of distilled water generates more bubbles, and the increased bubbles coagulate much more with each other. Then, the cell size of the PUF samples is increased with the increase of the amount of the distilled water, therefore, the total content of the blowing gas in the PUF samples is increased.

At the equal amount of HFC-365mfc, the thermal conductivity of the PUF samples decreased with the increase of the distilled water. The increase of distilled water generates more bubbles, and the increased bubbles coagulate much more with each other. Then, the cell size of the PUF samples is increased with the increase of the amount of the distilled water, therefore, the total content of the blowing gas in the PUF samples is increased.

Also, at the equal amount of distilled water, the thermal conductivity of the PUF samples decreased with the increases of HFC-365mfc. From these results, it is suggested that the thermal conductivity of the PUF samples strongly depends on the thermal conductivity of the blowing agent as well as the total amount of the entrapped blowing gas inside the closed cell of the PU foams.

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