경질 폴리우레탄 폼 제조에 사용되는 원료물질들이 폼의 물성에 미치는 영향

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Effects of Raw Materials on the Properties of Rigid Polyurethane Foam

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Introduction

Polyurethane foams (PUF) are used in applications such as insulation materials, cushioning, automotive parts, and energy absorption materials.[1-3] In the preparation of PUF, physical and/or chemical blowing agent can be used. Distilled water is one of the widely used chemical blowing agent. Distilled water reacts with diisocyanate generating carbon dioxide while polyol reacts with diisocyanate. The most widely used physical blowing agents are chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs).[1-3] Limitations on the use of CFCs and HCFCs have arisen due to the environmental problems such as ozone destruction and global warming.[3,4] Substitutes for CFCs and HCFCs such as hydrofluorocarbon (HFC), cyclopentane, and water have been developed and their applications for cellular materials have been studied.[3-8] In our earlier studies, we reported the effects of water on thermal properties, mechanical properties, and morphology of PUF blown by a mixture of water and HCFC 141B.[9,10]

In this study, the effects of additives used in preparation of PUF on the thermal properties, mechanical properties, morphology, and reactivity of the rigid PUFs blown by water alone were investigated. Thermal properties such as glass transition temperature (T_g), cellular structure, and mechanical properties such as compressive, flexural, and tensile strength of the PUF samples were studied using differential scanning calorimeter (DSC), scanning electron microscopy (SEM) and a universal testing machine (UTM).

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 polyols were supplied from KPC Co. (Ulsan, Korea). Distilled water was generated in our laboratory. Amine based catalysts were supplied from Air Products and Chemicals, Inc. (Allentown, USA). Polysiloxane ether used as a surfactant was supplied Osi Specialties, Inc. (USA). The polyether polyols was dehydrated before use at 90 ℃ for 24 hours in a vacuum oven. The other chemicals were used as received.

Sample Preparations Rigid PUF samples with various densities were synthesized with a one-shot method. All chemicals were put into the reactor and mixed for 60 seconds with a brushless-type stirrer. The stirrer speed was set at 3000 rpm throughout the mixing. After mixing, the reactants were poured into an open mold (250 ㎜ × 250 ㎜ × 100 ㎜) to produce free-rise foams, which were cured for 1 week at room temperature. Distilled water was used as a blowing agent. Three replicates were made of all the foams.

The amount of polyether polyol was set at 100 parts by weight. The amount of PMDI required for the reaction with polyether polyol and water was calculated from their equivalent weights. To ensure complete reaction, excess PMDI (ca. 5wt %) was used in all formulations.

RESULTS AND DISCUSSION

1. Effects of Surfactant on the Properties of PUF

To investigate the effects of surfactant content on the properties of the PUFs, the amount of polysiloxane ether was varied from 0 to 2.00 parts by weight, while the amount of polyether polyol, PMDI, distilled water, and triethylene diamine were fixed at 100, 145.3, 1.5, and 0.7 parts by weight, respectively. In the sample code (SUR Z), Z denotes the amount of surfactant used.

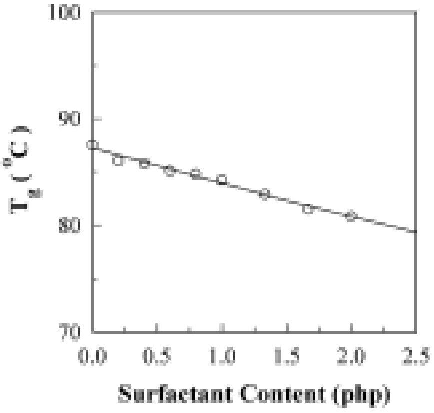


Figure 1 Effect of surfactant on the T_g of the PUF samples (SUR-Z).

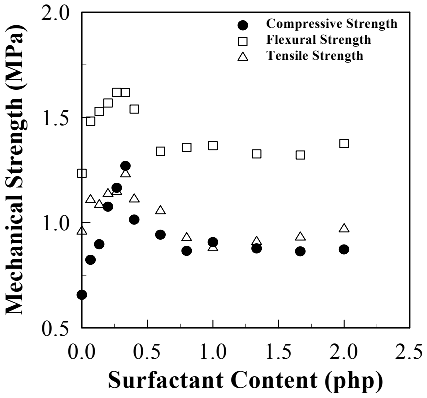
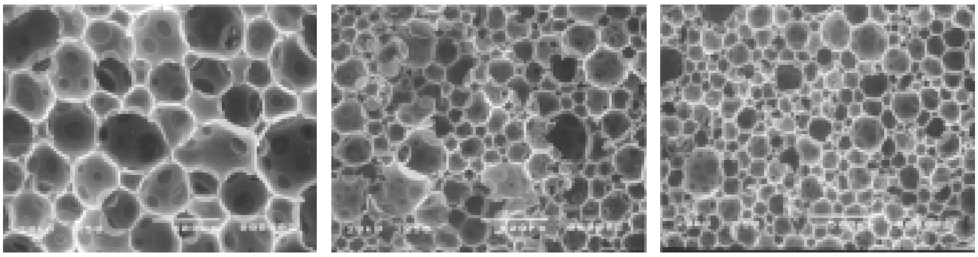


Figure 3 Mechanical strength of the PUF samples with surfactant at equal density and water content (SUR-Z).

The effect of the surfactant on the T_gs of the PUF samples is shown in Figure 1. From Figure 1, the T_gs of the PUF samples decrease from 87.5 to 80.9 ℃ as the amount of the surfactant increases from 0 to 2.0 php, respectively. For the mixing between the two miscible components, one component acts as a plasticizer to the other.[11] Therefore, adding the surfactant to the PUF reduces the T_g of PUF.



(a) (b) (c)

Figure 2 Scanning electron micrographs of the PUF samples with surfactant (SUR-Z): (a) SUR-0.00; (b) SUR-0.33; (c) SUR-2.00.

Figure 2 shows the micrographs of the PUF samples with different surfactant content. From Figure 2 (a-c), it is observed that the cell size of the PUF samples is shown to be 360, 146, and 142 ㎛ at the 0, 0.33, and 2.00 php surfactant content respectively. The cell size becomes smaller from 360 to 146 ㎛ with an increase in surfactant from 0 to 0.33 php, but the cell size does not change significantly when the surfactant content exceeds 0.33 php. It is known that the silicone surfactant lowers surface tension between cells and stabilizes the cell walls.[1-3] The silicone surfactant prevents the coalescence of the PUF cell so it makes the cell size smaller. Generally, it is known that the PUF with the small cell structure shows good mechanical properties and low thermal conductivity.[1-3]

The compressive strength, flexural strength, and tensile strength of the PUF samples having equal densities are shown in Figure 3. From Figure 3, maximum mechanical strength is observed at the 0.33 php surfactant content. This can be compared to the results obtained from the morphology and thermal analysis studies. The increase of the mechanical strength from the 0 to 0.33 php surfactant content is attributed to the decrease of the cell size of the PUF samples, and the decrease of the mechanical strength with a surfactant content greater than 0.33 php content may be due to the plasticizing effect of the PUF samples

2. Effects of Polyols on the Properties of PUF

To investigate the effects of polyols on the properties of the PUFs, various polyether polyols, which were supplied from KPC Co. (Ulsan, Korea), were used. The characteristics of the polyols used in this study are shown in Table 1. The amount of each polyol was fixed at 100 parts by weight and the amount of triethylene diamine and polysiloxane ether were fixed at 0.7 and 1.0 parts by weight respectively. The amount of distilled water was varied from 1.0 to 3.5 parts by weight with increment of 0.5 parts by weight. The amount of PMDI required for the reaction with polyether polyol, and the amount of distilled water required was calculated from their equivalent weights. For the completion of the reaction, excess PMDI (ca. 5wt %) was used. In the sample code (POL F-O) used in this study, F and O denote the functionality and the hydroxyl (OH) value of the added polyol respectively.

Table 3. Characteristics of the Polyether Polyols Used in This Study[a]

Polyether polyols	Functionality	Hydroxyl value	Equivalent weight (g/mol)
Polyol 3 - 290	3	290	193
Polyol 3 - 400	3	400	140
Polyol 3 - 670	3	670	84
Polyol 4 - 400	4	400	140
Polyol 4~5 - 360	4~5	360	156
Polyol 4~5 - 450	4~5	450	125
Polyol 4~5 - 490	4~5	490	114
Polyol 6 - 490	6	490	114

Figures 4, 5, and 6 show the results of this study, but only a part that can show the major results is expressed in these Figures. The densities of the PUF samples (POL F-O) blown by distilled water are shown in Figure 4. From Figure 4, when the OH value of trifunctional polyols increases from 290 to 670, the density of the PUF samples (POL 3-O) increases from 116.1 to 129.2 kg/㎥ at 1.0 php water content. As the OH value of the polyol increases, the equivalent weight of the polyol is lowered. In addition, PMDI is more likely to react with the polyol having lower equivalent weight. Therefore, as the OH value of added polyol is increased, the density of the PUF sample is higher because of an increase in PMDI content. In addition, from Figure 4, when the functionality of polyols with OH values of 400 increases from 3 to 4, the density of the PUF samples (POL F-400) increases from 118.4 to 128.1 kg/㎥ at 1.0 php water content.

Figure 5 shows the variation in compressive strength of the PUF samples (POL F-O) with distilled water content. From Figure 5, when the OH value of trifunctional polyols increases from 290 to 670, the compressive strength of the PUF samples (POL 3-O) increases from

0.92 to 1.48 ㎫ at 1.0 php water content. When the functionality of polyols with OH values of 400 increases from 3 to 4, the compressive strength of the PUF samples (POL F-400) increases from 1.17 to 1.26 ㎫ at 1.0 php water content. As the OH value and functionality of polyols are increased, the degree of crosslinking is higher.[1] Therefore, the compressive strength of the PUF sample synthesized with the polyol having high OH value and functionality increases because of an increase in degree of crosslinking.

For flexural strength of the PUF samples (POL F-O) with changing distilled water content, when the polyol functionality is low, the flexural strength of the PUF samples shows similar behavior to results obtained in compressive strength tests. However, where the polyol functionality is high, the flexural strength of the PUF samples does not always show similar behavior to the results of compressive strength tests of the PUF sample. When the functionality of polyols with OH values of 490 increases from 4~5 to 6, the flexural strength of the PUF samples (POL F-490) decreases from 2.19 to 1.82 ㎫ at 1.0 php water content. As the OH value and functionality of the polyol increases, brittleness as well as the degree of crosslinking increases.[1] Therefore, excessive crosslinks decrease rather then increase the flexural strength of the PUF sample.

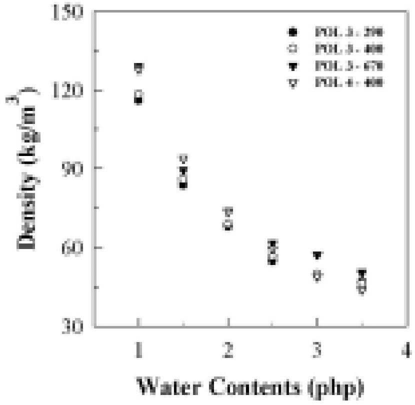


Figure 4 Effect of polyols on the PUF density (POL F-O).

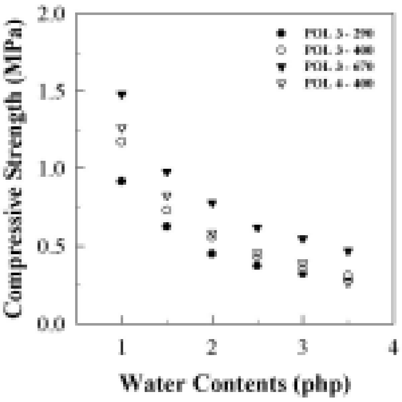


Figure 5 Effect of polyols on compressive strength of the PUF (POL F-O).

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