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Effects of Organoclay on the Thermal Insulating Properties of Rigid Polyurethane Foams Blown by Environmentally Friendly Blowing Agents

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Abstract: A process designed to synthesize rigid polyurethane foam (PUF) with insulative properties via the modulation of PUF cell size via the addition of clay and the application of ultrasound was assessed. The blowing agents utilized in this study include water, cyclopentane, and HFC-365mfc, all of which are known to be environmentally-friendly blowing agents. The rigid PUFs were prepared from polymeric 4,4'-diphenylmethane diisocyanate (PMDI) and polyether polyol with a density of 50 kg/m^3. In addition, rigid PUFs/clay nanocomposites were synthesized with clay modified by PMDI with and without the application of ultrasound. The PUF generated using water as a blowing agent evidenced the highest tensile strength. The tensile strength of the PUF/nanocomposites was higher than that of the neat PUF and the strength was even higher with the application of ultrasound. The cell size of the PUF/clay nanocomposites was less than that of the neat PUF, regardless of the type of blowing agent utilized. It appears that the higher tensile strength and lower cell size of the PUF/clay nanocomposites may be attributable to the uniform dispersion of the clay via ultrasonic agitation. The thermal conductivity of the PUF/clay nanocomposites generated with HCFC-141b evidenced the lowest value when PUF/clay nanocomposites were compared with other blowing agents, including HFC-365mfc, cyclopentane, and water. Ultrasound has also proven effective with regard to the reduction of the thermal conductivity of the PUF/clay nanocomposites with any of the blowing agents employed in this study. It has also been suggested that the uniformly dispersed clay particles in the PUF matrix function as diffusion barriers, which prevent the amelioration of the thermal insulation property.

Keywords: rigid polyurethane foam, PUF/clay nanocomposies, blowing agent, thermal conductivity.

Introduction

Rigid polyurethane foams (PUF) have been used for insulation of appliances such as freezers and refrigerators, and for the production of building insulation panels as well as many other applications.[1-8] Since the major interest in rigid PUF has been for thermal insulation, therefore, the primary importance of the rigid PUF is to decrease the thermal conductivity of the foams. Rigid PUFs have closed cell structures which are usually produced with a density of higher than 32 kg/m^3. The thermal conductivity of the closed-cell foams depends mainly on the total content and the thermal conductivity of entrapped blowing gas inside the cells.[1]

Trichlorofluoromethane (CFC) has been the most widely used blowing agent in the industry due to its lowest diffusion coefficient and thermal conductivity. Unfortunately, it is now prohibited to use CFC by the environmental regulations since it was turned out to be one of the materials destroying ozone layer on the earth. There are several alternatives such as cyclopentane, HFC-365mfc or water. However, they are not as effective as CFC in terms of thermal insulation because they have higher thermal conductivity and diffusion of gas is easier when they are used as blowing agents.[9,10] Moreover, Usage of HCFC-141b is also supposed to be prohibited after the year of 2030 for the same reasons as CFC.[9]

Many researches have been focused on water which has been regarded as an environmentally friendly blowing agent. Rigid PUF can be made by CO_2 gas produced by the reaction between water and isocyanate.[11-13] It is difficult to maintain good insulating property for the foams blown with water, however, because air is filled in cells of the PUF shortly due to high thermal conduction and diffusion rate of CO_2.

Thermal conductivity is very important property for insulating characteristics of PUF. Thermal conduction of PUF

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depends on conductivity of polyurethane itself, conductivity of blowing agent, radiation and convection through gas phase. Therefore, thermal conductivity of PUF (λ_{foam}) can be determined by the sum of four factors which are thermal conductivity of polyurethane (λ_s), thermal conductivity of blowing gas (λ_g), thermal conductivity of gas by radiation (λ_r) and thermal conductivity of gas by convection (λ_c) as shown in eq. (1).

$$\lambda_{foam} = \lambda_g + \lambda_s + \lambda_c + \lambda_r \quad (1)$$

Thermal conductivity of gas by convection is negligible.[10] Also, the thermal conductivities of PU (λ_s) have to be considered as constants because their values are inherent once the material is decided. In order to improve thermal insulating characteristic of PUF, therefore, thermal conductivity of gas by radiation (λ_r) is considered to be the major factor which is controllable by outside of the system.[1,14]

Biedermann *et al.* have shown the possibility to reduce the thermal conductivity of PUF by reducing radiative thermal conductivity of gas (λ_r) through the reduction of cell size of the PUF.[10] In order to reduce the radiative thermal conductivity, it is important to reduce the cell size of PUF. Addition of surfactants or catalysts may affect the size of the cells and also clay nanocomposite is known to be effective to reduce the cell size.[15-17] Moreover, clay is expected to reduce the thermal conductivity of gas diffusion since it can lengthen the pathways of gas diffusion. When synthesizing PUF/clay nanocomposites, uniform dispersion of clay is very important to make sure the cells in PUF are small enough.

In this study, investigation was conducted to evaluate the effect of clay nanocomposites on the thermal conductivity of PUF blown by environmentally friendly blowing such as water, cyclopentane and HFC-365mfc. Furthermore, the effect of ultrasound on the radiative thermal conductivity of the PUF was also studied. It is believed that the results obtained by applying ultrasound and nanoclay can contribute to the development of PUF having high insulating characteristics with green blowing agents.

Experimental

Materials. The materials used in this study were obtained from commercial sources. PMDI was supplied from BASF Korea Ltd. (Seoul, Korea). The average functionality of PMDI was 2.7 and NCO content was 31.5 wt%. The equivalent weight and viscosity of PMDI were 135.0 g·mol^{-1} and 550 cps, respectively. Pentaerithritol base polyether polyol supplied from KPC Co. (Ulsan, Korea) were used for the preparation of the nanocomposites. The organoclay (30B clay, organic modifier: $N^+(CH_2CH_2OH)_2CH_3T$, where T is tallow: C18/C16/C14 = 65/30/5) was supplied from Southern Clay Co. (USA). Dimethylcyclohexylamine, which was supplied from Air Products and Chemicals, Inc. (USA), was used as a catalyst. Polysiloxane ether, used as a surfactant, was supplied from Osi Specialties, Inc. (USA). Distilled water, used as a chemical blowing agent, was generated in our laboratory. The physical blowing agents, such as HCFC-141b, cyclopentane, and HFC-365mfc were used as received. The polyol and clay were dehydrated before use at 90 °C for 24 h in a vacuum oven.

Sample Preparations. The organoclay and PMDI were premixed by 3,000 rpm with mechanical stirrer in oil bath for 2 hours. The temperature of oil bath was maintained at 50 °C on the hot plate and the relative humidity was maintained below 30%. The organoclay content was fixed at 3 wt% based on PMDI. After premixing, ultrasound (40 kHz, BLT vibrator type) was applied to the mixture of the organoclay and PMDI for 15 min, then the clay which was modified with the PMDI was obtained. In our previous work,[16] we have demonstrated FT-IR analysis of the modified clay obtained by the reaction of clay modified with PMDI.

The PUF/clay nanocomposites were synthesized by the reaction between the polyol and PMDI that contained the modified clay with ultrasound. The amount of the clay was 3 wt% (based on PMDI). The PMDI, modified clay with the PMDI, polyether polyol, amine catalyst, surfactant, and distilled water were used for the preparation of the PUF/clay nanocomposites. For the completion of the reaction, excess PMDI (ca. 5 wt%, NCO/OH = 1.05) was used. Also, Various Blowing agents such as cyclopentane, HFC-365mfc, water, and HCFC-141b were used. For water, CO_2 is generated by the reaction between water and isocyanate to give amine compounds, this amine groups react again with isocyanate to form urea and biuret bond between polymer chains.

The amount of blowing agents was controlled to set the density of 50 kg/m^3 for all PUF samples. The composition of the materials used in the preparation of PUF/clay nanocomposites are shown in Table I. All chemicals were put into the reactor and mixed for 30 s with a brushless-type stirrer. The stirrer speed was set at 3,000 rpm throughout the

Table I. Composition of the Materials Used in the PUF/Clay Nanocomposites

Chemicals	Weight (g)	
PMDI	142.85	
Clay	4.45	
Polyol	100.00	
Surfactant	1.50	
Blowing Agents	Water	2.30
	HCFC-141b/water	14.00/1.00
	Cyclopentane/water	10.00/1.00
	HFC-365mfc/water	18.00/1.00
Catalyst	1.00	

mixing. After mixing, the reactants were poured into an open mold (250 × 250 × 100 mm) to produce free-rise foams and were cured for 1 week at room temperature.[18,19]

In order to investigate the effect of clay on the physical properties and thermal conductivity of PUF, neat PUF was also prepared and compared to PUF/clay composites. The PUF/clay nanocompisites were synthesized with and without ultrasound to study the effect of ultrasonic cavitation on PUF's properties.

Mechanical Properties. The mechanical properties of neat PUF and PUF/clay nanocomposite samples were measured under ambient conditions with an Instron UTM (model 4467, Canton, OH). A tensile test for neat PUF and PUF/clay nanocomposite was performed according to ISO 1926. The size of the specimen was 20 × 100 × 6 mm (width × length × thickness). The gauge length was 50 mm, and the speed of crosshead movement was 2.54 mm/min. The strengths of ten specimens per sample were measured and averaged for each mechanical test.

Scanning Electron Microscopy (SEM). The morphology of neat PUF and PUF/clay nanocomposites was studied with an S-4300SE field emission scanning electron microscope (Hitachi, Tokyo, Japan). The samples were cryogenically fractured and white 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/clay nanocomposite samples. 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 Measurement. The thermal conductivity of PUF and PUF/clay nanocomposites was measured with a Holometrix Micromet (model Lambda 2000) according to ASTM C518. 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/clay nanocomposite 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

Figure 1 shows the tensile strength of neat PUF and PUF/clay nanocomposites blown by four different blowing agents. The PUF/clay nanocomposites were prepared with and without ultrasonication. It is known that the mechanical properties of cellular material depend mainly on its density.[20-23] In this experiment, the densities of neat PUF and PUF/clay nanocomposites were set at 50 kg/m^3 for each sample.

From Figure 1, the PUF produced with water as a blowing agent showed the highest tensile strength. Tensile strength

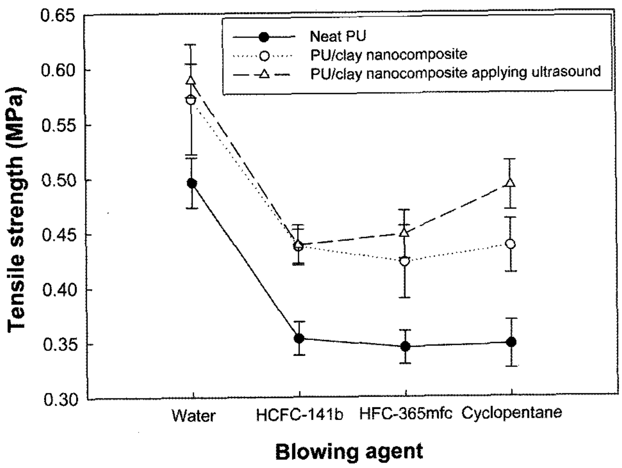


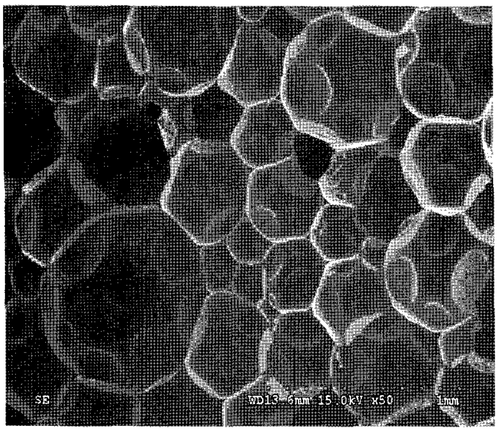
Figure 1. Tensile strength of neat PUF and PUF/clay nanocomposites with and without applying ultrasound. The foam was blown by four different blowing agents.

of the PUF/nanocomposite was higher than the neat PUF and the strength was even higher when ultrasound was delivered regardless of the types of blowing agents. It seems that the application of ultrasound to the clay modification could enhance the dispersion of the clay in polyurethane matrix. The increase of the tensile strength of the PUF/clay nanocomposites may be due to the uniform dispersion of the clay by ultrasonication. When water was used as a blowing agent, the tensile strength was the highest, and the increase of tensile strength may be due to the smaller cell size or more uniform dispersion of clay.

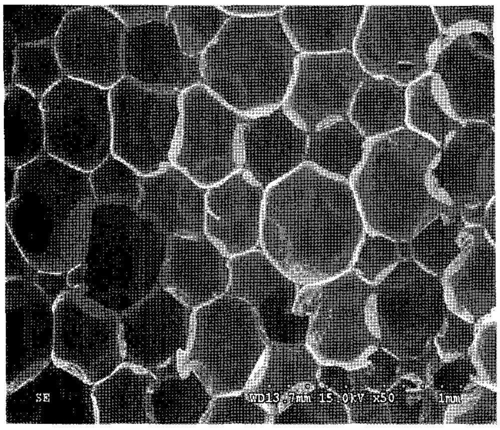
The effects of clay and ultrasonication on the cell morphology of PUF and the PUF/clay nanocomposites are shown Table II and Figure 2. Figure 2 shows scanning electron micrographs of PUFs blown by HFC-365mfc: (a) neat PUF, (b) PUF/clay nanocomposite, (c) PUF/clay nanocomposite with ultrasound. It seems cell size is getting more uniform and finer when clay was added. The cell size is even more uniform and finer after the ultrasound was applied. The cell size of the neat PUF was 514 μm and it was reduced down to 360 μm when modified by clay with ultrasound. From the results of Figure 2, it was observed that the cell size was decreased if clay was added and ultra-

Table II. Cell Size of Neat PUF and PUF/Clay Nanocomposites Blown by Four Different Blowing Agents with and without Applying Ultrasound

Blowing Agent	Cell Size (μm)		
	Neat PUF	PUF/Clay	PUF/Clay with Ultrasound
Water	423	310	296
HCFC-141b	529	481	421
Cyclopentane	558	479	384
HFC-365mfc	514	437	360



(a)



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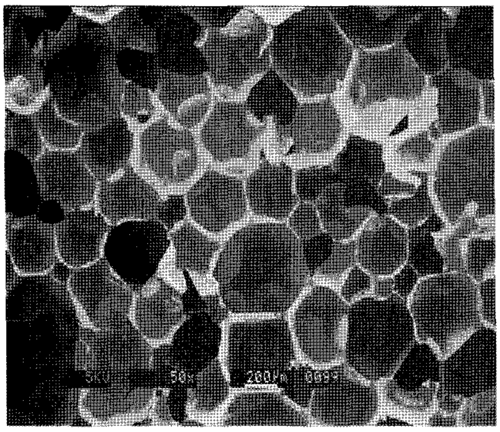

(c)

Figure 2. Scanning electron micrographs of PUFs blown by HFC-365mfc: (a) neat PUF, (b) PUF/clay nanocomposites, and (c) PUF/clay nanocomposites with ultrasound.

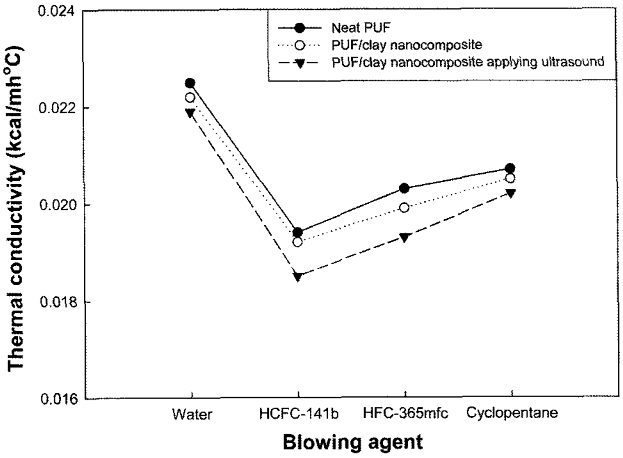

Figure 3. Thermal conductivity of neat PUF and PUF/clay nanocomposites with and without applying ultrasound. The foam was blown by four different blowing agents.

sound was applied regardless of the types of blowing agent. These results were summarized in Table II. Surfactant is very important to decrease the average cell size of PUF. When the amount of surfactant is increased, however, the cell size of PUF can be increased. Therefore we have used the optimum amount (1.5 wt% based on polyol) of surfactant to decrease the cell size of the PUF.

The exfoliated clay layers can act as nucleation agents and serve as sites for bubble growth.[11-13] 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 cell size of the PUF/clay nanocomposites may be due to the nucleation effect of the clay. In addition, the application of ultrasound to the clay modification with the PMDI can increase the dispersibility of the clay within the PUF/clay nanocomposite. Therefore, the PUF/clay nanocomposite with ultrasound has smaller cell size than the PUF/clay nanocomposite without ultrasound at the same modified clay content.

Thermal conductivities of PUFs and PUF/ clay nanocomposites blown by various blowing agents are shown in Figure 3. Thermal conductivities of neat PUF, PUF/clay nanocomposite and PUF/clay nanocomposites with ultrasound, in sequencies, was decreasing for all the blowing agents used in this study. This is maybe because that the uniformly dispersed clays of high aspect ratio seem to be barriers for gas diffusion when the clay exists at the cell wall of the PUF samples, as can be seen in Figure 4. Figure 4 shows the cell wall morphology of PUF/clay nanocomposite, blown by HFC-365mfc. From Figure 4, it is observed that the clay exists at the cell wall. We have seen that the thermal conductivity of the PUF/clay with ultrasound showed the lowest values among the samples from Figure 3.

Also, the clay itself can serve as a nucleating agent and much more bubbling is expected on the surface of finely dispersed clay. Therefore total numbers of cells are increased and size is decreased. From Figure 3, the thermal conductivity of the PUF sample (without clay) blown by HCFC-141b shows 0.0194 kcal/mh°C which is lower than

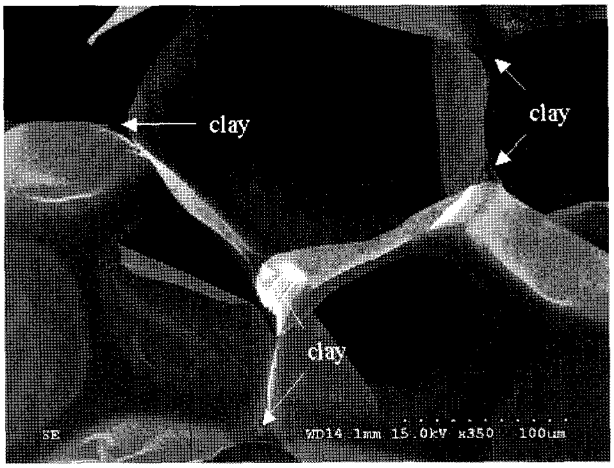

Figure 4. Scanning electron micrograph of cell wall structure of PUF/clay nanocomposite.

the thermal conductivity of the PUF sample blown by distilled water (0.0225 kcal/mh°C), cyclopentane (0.0207 kcal/mh°C) and HFC-365mfc (0.0203 kcal/mh°C). This difference is maybe due to the difference of the thermal conductivities of blowing gases used in this study such as HCFC-141b, CO_2, cyclopentane and HFC-365mfc which are 0.0079, 0.0153, 0.0110, and 0.0105 kcal/mh°C, respectively.

Figure 5 shows the relationship between the thermal conductivity and cell size of PUF samples with and without clay. Thermal conductivity of the PUF samples blowing by different kinds of blowing agent is decreased as the cell size is decreased, which explains that low cell size improves the insulation property of the PUF samples.[10,24,25] From the results of thermal conductivity, it is suggested that the thermal conductivity of the PUF samples strongly depends on the thermal conductivity of blowing agent as well as the additive such as organoclay and the processing condition

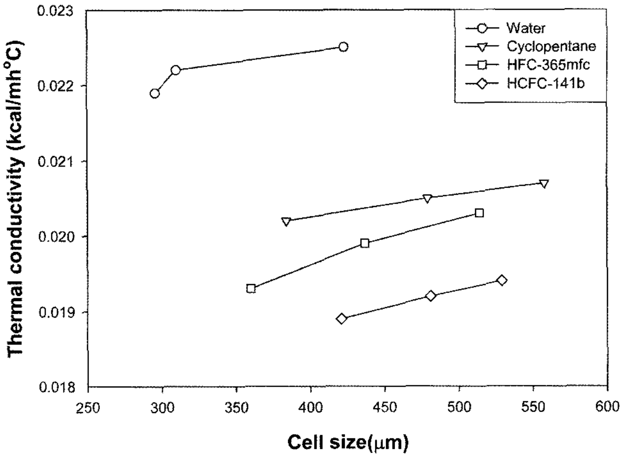

Figure 5. Relation between thermal conductivity and cell size of rigid polyurethane foams blown by four different blowing agents.

such as ultrasonication. If the blowing agent of the PUF sample is fixed, then, the cell size is an important factor to control the thermal conductivity of the PUF samples.

Conclusions

PUF /clay nanocomposites were synthesized with alternative blowing agents such as water, cyclopentane and HFC-365mfc, and an attempt was made to reduce the thermal conductivities of PUFs. Tensile strength of the PUF/clay nanocomposite showed higher value than that of the neat PUF. Application of ultrasound when synthesizing PUF/clay nanocomposite made the foam stronger.

Thermal conductivities of PUF/clay nanocomposites with ultrasound showed the lowest values when comparing with PUFs without clay for all the blowing agents used in this study. The application of ultrasound during the synthesis of PUF/clay nanocomposites showed quite effective way to reduce the cell size and thermal conductivity eventually.

From the results of this work, it is concluded that the thermal conductivity of the PUF samples strongly depends on the thermal conductivity of blowing agent itself as well as the additive such as organoclay and the processing condition such as ultrasonication. If the blowing agent of the PUF sample is fixed, then, the cell size is an important factor to control the thermal conductivity of the PUF samples. Also, it is suggested that the PUF having low enough thermal conductivity can be produced using alternative blowing agents such as cyclopentane or HFC-365mfc by adding organoclay as an additive as well as applying ultrasound during the synthesis of PUF.

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