Material behaviour

Effect of isocyanate molecular structures in fabricating flexible polyurethane foams on sound absorption behavior

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Abstract

Flexible polyurethane foams have attracted significant attention as sound absorption materials for automotive components. Molecular structure of isocyanate components in the fabrication of the foams has a strong effect on the formation of interconnecting pores. Two competitive mechanisms of microphase separation and drainage flow in the polyurethane urea matrix determine the fractional ratio of closed, partially and fully open pores. This fractional ratio of pore types is crucial for the sound absorption efficiency of the final foam materials. The addition of modified isocyanate containing uretonimine linkages increases, not only the microphase separation of hard domains in the matrix, but also drainage flow in the cell wall. In addition, the decrease of toluene diisocyanate content increases the phase separation of hard domains in polyurethane urea matrix. The optimum amount of uretonimine linkages in the isocyanate for good sound absorption is 4.3 × 10−3 mol/g, showing the highest partially open pore fraction. Foam properties were analyzed by Fourier transform infrared spectroscopy, atomic force microscopy and scanning electron microscopy. Sound absorption efficiency was analyzed with an impedance tube.

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1. Introduction

Automotive noise pollution such as structural-borne noise and airborne noise is a serious problem in the automotive industry and, therefore, considering the sound absorption efficiency in designing sound absorbing materials is very important [1–4]. In general, a notable portion of the structural-borne noise can be guided in the low frequency regime (30–500 Hz), and airborne noise is mainly explored in the medium and high frequency regimes (500–8000 Hz) [5]. Major mechanisms of absorbing sound waves are friction with air molecules and damping with absorbing materials. In terms of material developments, sound absorption by damping plays an important role in achieving high absorption efficiency with improved sound dissipation by the conversion of sound energy to thermal energy through hysteresis [6]. In addition, sound absorption can be affected by various non-acoustic factors such as porosity, air resistivity, tortuosity and viscous thermal length. Many modeling studies [4,7–11] for the effect of non-acoustic parameters on sound absorption behavior showed a significant relationship with microcellular structure of the porous materials. Consequently, the sound absorption efficiency of the materials can be improved by modifying the cellular structure of flexible polyurethane foams.

Flexible polyurethane foams are considered as good sound absorption materials owing to their high damping for airborne sounds, and thus they have been widely used as a noise absorption material in the area of transportation because of low density, malleability and easy fabrication [12,13]. Other studies also reported that the morphological properties such as cavity and pore sizes, distribution of cavity and pores, and thickness of struts significantly affect the sound absorption of flexible polyurethane foams [14–16]. In the fabrication of flexible polyurethane foams, the cellular structure is directly affected from the use of the main ingredients such as polyols, isocyanates, chain extenders, water, silicon surfactants, blowing agents and catalysts [17,18]. In this study, flexible polyurethane foams were manufactured by one-shot polymerization with varying uretonimine contents in isocyanate mixtures by fixing other experimental parameters to examine the effect of uretonimine linkage on the sound absorption behavior. The properties of cellular morphology in the flexible polyurethane foams were investigated, and their relationship with
the sound absorption efficiency was also analyzed. The microphase separation of the hard segment domains in the flexible polyurethane matrix was explored by FTIR and AFM analyses, and the pore structure (closed, partially open and fully open) was carefully analyzed to understand the relationship with sound absorption efficiency. The physical properties (tensile and compression strengths) of the flexible polyurethane foams were also measured as guidance for long-term usage in applications of materials for automotive components.

2. Experimental

2.1. Base materials

Flexible polyurethane foams were manufactured using a polyether based alcohol (KE-810, OH value 28 ± 2, KPX Chemical) and two types of isocyanate. KE-810 triol has a weight average molecular weight of 6000 g/mol. For the isocyanates, KW 5029/1C-B (%NCO 35 ± 0.5, BASF) and COSMONATE LL (%NCO 29 ± 0.5, Kumho Mitsui Chemicals) were used for polymerization reactions. KW 5029/1C-B consists of ~60% monomeric methylene diphenyl disocyanate (MDI), ~15% polymeric MDI, and ~20% toluene disocyanate (TDI). COSMONATE LL is composed of ~75% modified MDI containing carbodiimide linkage mixed with monomeric MDI and ~25% modified MDI containing uretonimine linkage. Fig. 1 shows the detail molecular structures for the various isocyanates used in this study.

2.2. Materials synthesis

For the preparation of flexible polyurethane foams, various ingredients such as gelling and blowing catalysts, H2O as a blowing agent, a chain extender, and a surfactant were used. Dabaco 33LV (33% triethylenediamine (TEDA) and 67% dipropylene glycol) purchased from Air products and Chemicals were used as gelling and blowing catalysts. As a chain extender, diethanolamine (DEOA) was used for cross-linking reactions, and de-ionized (DI) water was used as the blowing agent. Silicon surfactant L-3002 (Momentive Corp) was used for the stabilization of cavities and interconnecting pores in the foams. The formulation details are listed in Table 1.

One-shot bulk polymerization was applied without a prepolymer synthesis step. First, the polyols systems (premixture containing alcohol, chain extender, gelling and blowing catalyst, DI water and silicon surfactant) were weighed in a 400 mL paper cup and mixed for 20 min at 1700 rpm using a mechanical stirrer. Subsequently, pre-weighed isocyanate mixtures following the formulations were added to the polyol systems and mixed further for 10 s at 6000 rpm. After the mixing process, the final mixtures were poured in an aluminum mold (400 × 400 × 30 mm3), and the mold was tightly closed with a mold cover and kept at 60 °C for 10 min. The isocyanate contents were calculated based on Equation (1) by keeping the NCO index as 1.0.

\[
\text{NCO Index} = \frac{\text{Isocyanate A}(g) \times (\% \text{NCO of Isocyanate A})/4200 + (\text{Isocyanate B}(g) \times (\% \text{NCO of Isocyanate B})/4200)}{(\text{Alcohol (g}) \times (\text{OH value of alcohol})/56100).}
\]
Fig. 1. Various isocyanate structures of monomeric MDI, polymeric MDI, TDI, and MDI containing carbodiimide and uretonimine linkages.

Table 1
Experimental formulations for synthesizing flexible polyurethane foams.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Content (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alcohol (KE-810)</td>
<td>300</td>
</tr>
<tr>
<td>Isocyanate A (COSMONATE LL)</td>
<td>111 88 66 44 33 22 11 0</td>
</tr>
<tr>
<td>Isocyanate B (KW 5029/1C-B)</td>
<td>92 110 129 147 157 166 175 184</td>
</tr>
<tr>
<td>L-3002</td>
<td>4.0</td>
</tr>
<tr>
<td>BL11</td>
<td>0.2</td>
</tr>
<tr>
<td>Dabco 33LV</td>
<td>2.1</td>
</tr>
<tr>
<td>DEOA</td>
<td>2.0</td>
</tr>
<tr>
<td>Water</td>
<td>12.0</td>
</tr>
<tr>
<td>Uretonimine&lt;sup&gt;b&lt;/sup&gt; (&lt;i&gt;×&lt;/i&gt;10&lt;sup&gt;-5&lt;/sup&gt;, mol/g)</td>
<td>21.1 17.0 12.8 8.6 6.4 4.3 2.2 0.0</td>
</tr>
</tbody>
</table>

<sup>a</sup> NCO index: 1.0.
<sup>b</sup> Moles per total mass of ingredients.

Fig. 2. Schematic illustration of an impedance tube with sample diameters of 30 mm and 60 mm (A) for high and low frequency measurements.
sample in the frequency range from 50 Hz to 2500 Hz with two 1/4 inch microphones. The absorption coefficient is defined as the difference in incident and reflected acoustic energies. The thickness of all the samples was 20 mm, and the diameters for high (500–2500 Hz) and low frequency (50–800 Hz) measurements were 30 and 60 mm, respectively. The results of each sample were merged using the software VA-LAB (BSWA Technology Co., Ltd.) for single range sound absorption coefficient [4]. The schematic illustration of an impedance tube system including a foam sample is shown in Fig. 2.

2.3.4. Physical properties

The tensile and compression strengths were measured at room temperature using a universal test machine (UTM, LS1, Lloyd Instruments Ltd.) according to AS 2282.6-1999 at a crosshead speed of 300 mm/min and KS M ISO 3386-1 at a crosshead speed of 100 mm/min, respectively. Dumbbell samples for the tensile measurements were used, and the sample dimensions for the compression tests was 60 mm in diameter with 20 mm thickness. The compression tests were performed for 40% and 70% strain conditions.

3. Results and discussion

3.1. FTIR spectra analysis

As mentioned in section 2.3.1, FTIR-ATR is a useful technique to detect, not only urethane and urea functional groups, but also the internal hydrogen bonds within flexible polyurethane materials. Band locations from free urethane and urea groups generally appear at 1730 cm\(^{-1}\) and 1710 cm\(^{-1}\), but they are shifted under hydrogen bonding conditions. For example, the band positions of the hydrogen-bonded urea appear at 1660 cm\(^{-1}\) and 1640 cm\(^{-1}\) for monodendate and bidendate cases, respectively, and thus these hydrogen bonds shift the peaks to the lower wavenumber position.

Fig. 3 shows the FTIR spectra of the foam samples recorded at different uretonimine contents through baseline correction. The absorbance differences of the flexible polyurethane foams can be clearly seen in two different regions: monodendate urea absorbance differences of the different uretonimine contents through baseline correction. The gated hard domain leads to the microphase separation.

Fig. 4 shows the schematic illustrations of the phase separation phenomenon under the inclusions of uretonimine functionalities. The uretonimine linkages in the modified MDI mixtures could be partially degraded into the monomeric MDI and MDI containing carbodiimide functionality (Fig. 1) at 60 °C mold temperature because the decomposition of the uretonimine linkages was observed at 40 °C mold temperature, as reported elsewhere [28].

From this partial decomposition of uretonimine linkages, the increased mobility of the mixtures can improve the possibility of forming bidendate urea linkages with strong hydrogen bonding compared to the formation of monodendate urea. In other words, the isocyanate mixtures with lower content of uretonimine linkages and higher amount of polymeric MDI can have low mobility because of the high chances of crosslinking reactions. Therefore, the higher content of uretonimine linkages in the isocyanate mixtures can lead to higher mobility and higher bidendate urea formation in the products [22,23,29]. Additionally, as uretonimine contents increase in isocyanate mixture, TDI contents decrease. This further leads to increase of hard segment size (i.e. the higher electron density of uretonimine than TDI) [30]. Furthermore, TDI and polymeric MDI reduce the degree of phase separation by interfering aligned hard domain [31]. As a result, the degree of phase separation increases with the decrease of TDI and polymeric MDI contents. Further evidence of phase separation phenomenon depending on the contents of uretonimine linkages is discussed based on the AFM morphology in the following section.

3.2. AFM analysis

Atomic force microscope-based phase imaging in air is capable of elucidating variations in material properties such as sound absorption behavior of materials. In general, in AFM phase images, microdomains with higher modulus appear lighter phase images than that with lower modulus [25,32–35]. Therefore, it is very useful to understand the distributions of the hard and soft phases in the flexible polyurethane foams using the phase images.

Fig. 5 shows the AFM phase images of flexible polyurethane foams with various amounts of uretonimine linkages. As the uretonimine content increases, the light area of urea rich phases (or urea aggregates) in color images becomes sharper, because of the increments of bidendate urea formations, as shown by the FTIR results in Fig. 3 and schematic illustrations in Fig. 4. Therefore, at low uretonimine contents, well-dispersed hard domains in the matrix can have high resistance to penetration by the gases formed from urea formation reactions, and thus they can lead to low chances of open pore formation. In contrast, at high uretonimine contents, highly aggregated hard phases can increase the possibility of open pore formations. This phenomenon is further discussed in the following section with the SEM results.

3.3. SEM analysis

In addition to the AFM results, SEM images can also be used for understanding the phase behavior of the hard domains in the flexible polyurethane foams. The hard phases separated in the flexible polyurethane matrix can exhibit extensional thinning and stress concentration points, which can promote cell opening by cell rupture [31]. During cell formation, cell rupturing results from the draining process of the flexible polyurethane matrix, and it can be directly affected by the molecular properties of matrix materials. The lower the molecular weight and viscosity of matrix material, the higher the drainage process in cell formation [36]. Therefore, examining the cellular characteristics of the flexible polyurethane foams depending on the molecular properties of materials used is meaningful.

Fig. 6 shows the SEM images for the flexible polyurethane foams

![Fig. 3. FTIR absorbance spectra for various uretonimine contents.](image-url)
including uretonimine functionality in the range up to $2.1 \times 10^{-4}$ mol/g content, and the arrows indicate the closed or partially open pores. At high uretonimine contents, most of the pores reveal fully open forms, but partially open or closed pores coexist at low uretonimine contents.

To obtain the cavity size and the fractional ratio of the pore types, several hundreds of pores from ~10 images were analyzed for each sample. The average diameter of the cavity size in our experimental ranges of uretonimine contents was ~520 μm, and there were no significant differences between flexible polyurethane foam samples. In contrast, a significant difference was observed in the fractional ratio of the pore types.

Fig. 4. Schematics of phase separated morphology depending on inclusions of uretonimine linkages.

Fig. 5. AFM phase images (5 μm × 5 μm) at various uretonimine contents ($\times 10^{-5}$, mol/g), A: 0.0, B: 12.8, and C: 21.1.

Fig. 7 shows the relative ratio of the closed, partially and fully open pores as a function of uretonimine content in isocyanate. At uretonimine contents lower than $4.3 \times 10^{-5}$ mol/g in isocyanate, the fractional ratio of the partially open pores increases, but it starts to decrease at $4.3 \times 10^{-5}$, probably because of the degree of the microphase separation of flexible polyurethane matrix depending on the uretonimine contents, as demonstrated by the FTIR and AFM results. With increasing degree of microphase separation, transient extensional thinning behavior and stress concentration are triggered in the cell window, as reported elsewhere [37,38]. Extensional thinning and stress concentration can be focused on the low viscosity region in the cell window, and thus the formations of the
partially or fully open pores occur preferentially with increasing uretonimine content. In addition to the microphase separation phenomenon, the draining process of the matrix polymer is also an important aspect to understand the formation mechanism of cavities and pores in the foam materials.

Fig. 8 shows schematic illustrations of forming closed, partially or fully open pores by the draining process of the flexible polyurethane matrix. The viscoelastic drainage flow is strongly dependent on the strength of the polymer matrix and the molecular properties such as molecular weight and chemical structure [36]. For example, high molecular weight polymer generally exhibits low drainage flow, because of high strength and high resistance to deform or flow. In other words, low molecular weight modified MDI leads to the low molecular weight flexible polyurethane with increased drainage flow rate during foaming. As explained in the above FTIR section, the partially decomposed uretonimine functionalities can help the drainage flow with decreased molecular weight of the resulting polymer products. Therefore, high drainage flow during foaming caused by low molecular weight and low viscosity increased the ratio of the fully open pores, as shown in Figs. 6 and 7, and it was also reported that the low molecular weight polyurethane increased the open-cell content by delaying the NCO-water reaction in the polymer system [39,40].

3.4. Acoustic properties

In sound absorption, various parameters such as vibration and dissipation of the cell walls, air inside cavities and stiffness of cell walls affect the resulting absorption efficiency of flexible polyurethane foams [14,41–44]. For example, a flexible polyurethane matrix containing a large portion of the soft region can lead to the dissipation of the sound energy through thermal hysteresis. The sound energy can be dissipated because of the viscous friction and heat exchange in porous materials [45]. Therefore, flexible polyurethane foams with a low degree of soft region slowly dissipate the sound energy and decrease the sound absorption coefficient. In analyzing the sound absorption efficiency, the noise reduction coefficient (NRC, arithmetic mean of absorption coefficients at 250, 500, 1000, and 2000 Hz) is generally used for interpretation of the acoustic properties [46–48]. Fig. 9a and b shows the NRC and absorption coefficient at 2.5 kHz as a function of uretonimine content.
respectively.

In Fig. 9a, the NRC shows two distinct regions depending on the uretonimine content. The NRC increases with increasing uretonimine to $4.3 \times 10^{-5}$ mol/g content, probably because of increasing degree of microphase separation, as explained by the FTIR, AFM and SEM results. A high degree of microphase separation can increase the fractional ratio of partially open pores and can increase the airflow resistivity and collisions of sound waves with struts. As a result, the increased partially open pores can improve the absorption efficiency of the flexible polyurethane foams. In addition, with increasing uretonimine content, the ratio of partially open and closed pores decreased, as shown in section 3.3, leading to easy penetration of sound waves and reduced airflow resistivity, and thus the NRC resulted in low values.

As mentioned in the introduction, the airborne noise is generated in the high frequency regime. Especially, the noise from the engine is mainly distributed at 1600–4000 Hz [49], but the NRC could not contain higher frequencies than 2 kHz. For this reason, the absorption coefficient at 2.5 kHz is also demonstrated in Fig. 9b, and it shows a similar sound absorption behavior (highest NRC at $4.3 \times 10^{-5}$ mol/g). Therefore, the sound absorption behavior can be understood with the synergistic actions between the microphase separation and drainage flow in the flexible polyurethane matrix. The flexible polyurethane foams with the optimum condition for microphase separation and drainage flow are recommended for effective sound absorption materials, for example, at $4.3 \times 10^{-5}$ mol/g uretonimine content in our experimental system.

3.5. Physical properties

For application of flexible polyurethane foams in sound absorption materials, it is important to maintain their mechanical properties such as tensile and compression strengths for long term usage. The tensile and compression strengths as a function of uretonimine contents are shown in Fig. 10.

By increasing the uretonimine content, both strengths increase similarly, probably because of the increased amount of microphase separated hard domains. Each hard domain in the flexible polyurethane foams acts as a physical crosslinking site and contributes to cohesive force and stiffness of flexible polyurethane matrix [50,51]. As a result, the increase in the cohesive force attributes a high level of tensile strength and can increase the endurance properties of flexible polyurethane foams. In addition, the compression strength of the flexible polyurethane foams was measured at 70% and 40% strain conditions. The compression strength also increased with increasing uretonimine content which can be because of the same reasons, such as physical crosslinking phenomenon.
4. Conclusions

Flexible polyurethane foams were synthesized with various uretonimine contents to examine the effects of uretonimine linkages on the microphase separation, cell morphology and sound absorption behavior. The results of the FTIR and AFM analyses showed that the degree of microphase separation in the flexible polyurethane matrix increased with increasing uretonimine content by forming a high amount of bidendate urea (low monodendate urea formation), and also with increasing hard segment size at reduced TDI content. This microphase separation promoted the formations of partially open pores by extensional shearing. However, the partial decomposition of the uretonimine linkages under the experimental conditions decreased the matrix viscosity, and thus improved the formation of fully open pores by the increased drainage flow of the flexible polyurethane matrix. With these two competitive mechanisms, an optimum amount of the uretonimine content in manufacturing the flexible polyurethane foams is essential to achieve good acoustic properties with a high percentage of partially open pores, as observed from the SEM analysis. A high level of uretonimine content accelerated the drainage flow rate, and thus the sound absorption revealed the reverse effect because of the increased amount of the fully open pores. Therefore, $4.3 \times 10^{-5}$ mol/g uretonimine linkages was the optimum in our flexible polyurethane system for delivering good acoustic performance.

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References


