Sound Absorption Properties of Polyurethane/Nano-Silica Nanocomposite Foams

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ABSTRACT: In this study, polyurethane (PU)/nano-silica nancomposite foams were prepared. The effects of isocyanate index, cell size, density, and molecular weight of polyols on the sound absorption ratio of PU/nano-silica foams were investigated. With increasing nano-silica content, the sound absorption ratio of PU/nano-silica foams increases over the entire frequency range investigated in this study. Decrease of isocyanate index, cell size, and increase of density leads to the increase of sound absorption ratio of PU/nano-silica foams. PU/nano-silica foams have a broad T_g centered around room temperature by decreasing molecular weight of polyol resulting in good sound absorbing ability. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 2384–2390, 2012

Key words: polyurethane; nano-silica; nanocomposite; sound absorption; polyol

INTRODUCTION

Various kinds of undesired noise are often experienced in our living and working environment. Because of increased public concern regarding noise pollution, noise reduction becomes very important. Using sound insulating materials or sound absorption materials is the most popular means for noise reduction. Since sound insulation materials can only change the sound propagation path, and sound absorption materials can absorb sound waves directly, the improvement of sound absorption characteristics of polymer foams is investigated in this study.

Polymer foams have been widely used for sound absorption materials, because sound energy of incident sound wave is partially dissipated as heat due to air friction inside cells and viscous friction between adjacent polymer chains.[1] Polyurethane (PU) foams are widely used in applications such as seating, cushioning, insulation, and packing because of good sound damping, low thermal conductivity, and low density.[2–7] PU foams can be obtained from the reaction of an isocyanate with a polyol and water. Urethane bonds are formed by the reaction of the polyol with isocyanate while the reaction of isocyanate with water produces a transient carbamic acid which generates carbon dioxide. Carbon dioxide is an effective blowing agent for PU foams. It was reported that the sound absorption of PU foams can be improved by the incorporation of micro-sized fillers.[2,3]

In recent years, polymer/nano-silica nanocomposites have attracted considerable attention from both a fundamental research and an application point of view due to their remarkable improvement in materials properties.[8–16] Even though a lot of studies have been conducted on polymer/nano-silica nanocomposites, there have been few studies on the effect of nano-silica on sound absorption of polymer/nano-silica nanocomposites.

In this study, PU/nano-silica nancomposite foams were prepared and the effect of nano-silica on their sound absorption ratio was investigated. The effects of isocyanate index, cell size, density, and molecular weight of polyols on the sound absorption ratio of PU/nano-silica foams were investigated.

EXPERIMENTAL

Materials and nanocomposite foam preparation

Names and important characteristics of the materials used in this study are summarized in Table I. 4,4-Diphenylmethane diisocyanate (MDI) was provided from KMCI (Korea) under the trade name of CG-29N. Commercial polypropylene glycol (PPG) was supplied from SKC (Korea). The catalysts were amine, and the surfactants were silicon based surfactants. The catalysts, crosslinking agent and the

TABLE I
Important Characteristics of the Materials Used in this Study

Materials		Supplier	Characteristics
Isocyanate	4,4-Diphenylmethane diisocyanate (MDI, CG-29N)	KMCI, Korea	NCO %: 28.2, Molecular weight: 250
Polypropylene glycol (PPG)	PPGA (Y-3553)	SKC, Korea	M_n = 4800 g/mol, f = 3.0
	PPGB (DF-2000)	SKC, Korea	M_n = 2000 g/mol, f = 2.0
	PPGC (DF-1000)	SKC, Korea	M_n = 1000 g/mol, f = 2.0
	[a]PPGD (Y-7325N)	SKC, Korea	Hydroxyl value: 25 mg KOH/g
[b]Catalyst	Catalyst A (DABCO 33-LV)	Air-product, U.S.A	Amine value: 333 mg KOH/g
	Catalyst B (DABCO BL-11)		Amine value: 367 mg KOH/g
Cross-linking agent	Diethanol amine (DEOA)	DOW, U.S.A	Hydroxyl value: 1601 mg KOH/g
[c]Surfactant	B4113	Evonik, Germany	
	B8629	Evonik, Germany	
	L3184	Momentive, U.S.A	
Nano-silica	Aerosil-200	Evonik, Germany	Particle size : 12 nm, Specific Surface Area : 200 $\pm$ 25 m^2/g

[a] Polyether polyol with 30 wt% of SAN (Styrene-acrylonitrile copolymer).
[b] Amine catalyst.
[c] Silicon based surfactant.

surfactants widely used in the PU foam industry were chosen for this study.

Prior to the synthesis of PU nanocomposite foams, nano-silica was first mixed with PPG for 2 h using a high speed mixer (with sonication). Subsequently, the surfactant, catalyst, crosslinking agent and distilled water were added to the PPG/nano-silica mixture and mixed at 5200 rpm for 5 min. Finally, MDI was added and stirred for 6 s. The mixture was poured into a mold. The size of mold was 500 mm × 500 mm × 20 mm and the temperature of the mold was fixed at 65°C. Table II shows the recipes (in pbw) of PU/nano-silica nancomposite foams.

Measurements

The sound absorption ratio was measured on cylindrical foams, 100 mm in diameter and 20 mm thick. The frequency range of measures was from 100 to 1800 Hz. The sound absorption ratio (α) is defined as

$$\alpha = 1 - \nu/I \qquad (1)$$

ν, reflected sound intensity; I, incident sound intensity.

Reflected and incident sound intensity was measured using acoustic duct (Scien system-9301). The acoustic duct was manufactured according to ISO 10534 and JIS A1405.

Glass transition temperature (T_g) and tan δ of PU/nano-silica foams were measured using a dynamic mechanical analyzer (DMA Q-800, TA Instrument) in three-point bending modes. A frequency and a heating rate were fixed at 1 Hz and 5°C/min, respectively.

To investigate the cell structure of foams, samples of the PU/nano-silica nanocomposite foams were cry-

ogenically fractured in liquid nitrogen and were examined with Scanning Electron Microscope (SEM, JEOL JSM-4200). A Universal Testing Machine (UTM, Instron-5567) was used to obtain the tensile properties of the nanocomposite foams at room temperature. The crosshead speed was 500 mm/min. All measurements were performed for five replicates of specimens (JIS K-6301) and averaged to get the final result.

RESULTS AND DISCUSSION

Figure 1 shows the sound absorption ratio of PU/nano-silica foams with different nano-silica content. With increasing nano-silica content, the sound absorption ratio of PU/nano-silica foams increases over the entire frequency range investigated in this study. The addition of 0.2 pbw of nano-silica has relatively little effect, but the addition of 0.5 phw of nano-silica leads to a significant increase of absorption ratio. At the very lower frequency level (100 to 150 Hz), the sound absorption ratio is the best for unfilled sample. Such outcome can be due to resonance effect at lower frequency ranges. In fact, similar observations were reported by an earlier work for PU/clay flexible foam.[7] The improvement of sound absorption of the PU/nano-silica foams could be due to the increased energy dissipation as heat through hysteresis.[17,18]

Also, the increased energy dissipation is possible by increased scattering or reflection at the PU foam wall, as added silica can increase the stiffness of the foam wall. In addition, silica can act as wall for blocking the movement of sound wave. Tensile strength and Young's modulus of PU/nano-silica foams slightly increase with increasing nano-silica content, as shown in Table III and Figure 2. It is seen that the effect of nanosilica on the sound absorption ratio is noticeable in spite of the marginal

TABLE II
Recipes (in pbw*) of PU/Nano-Silica Nancomposite Foams

Variable	Polyol mixture					Isocyanate index	Remark	T_g^c (°C)
	Polyol	Surfactant	Cross-linker	Catalyst	Nano-silica			
Aerosil content	Polyol A/D (90/10)	B4113 (1.0)	DEOA (0.2)	Catalyst A/B (0.2/0.4)	Aerosil (0, 0.2, 0.5, 0.7, 1.0)	60		(−44.8, −43.7, −42.5, −41.1, −38.6)
Isocyanate Index[a]	PPG A/D (90/10)	B4113 (1.0)	DEOA (0.2)	Catalyst A/B (0.2/0.4)	Aerosil (0.5)	50, 60, 70, 80, 90		−46.0, −42.5, −41.4, −39.8, −37.5
Cell size	PPG A/D (90/10)	B4113 (1.0) B8629 (1.0) L3184 (1.0)	DEOA (0.2)	Catalyst A/B (0.2/0.4)	Aerosil (0.5)	60		
Density[b]	PPG A/D (90/10)	B4113 (1.0)	DEOA (0.2)	Catalyst A/B (0.2/0.4)	Aerosil (0.5)	60	70 kg/m³, 80 kg/m³, 90 kg/m³, 100 kg/m³, 110 kg/m³	
Molecular weight of Polyol	Polyol A/D (90/10)	B4113 (1.0)	DEOA (0.2)	Catalyst A/B (0.2/0.4)	Aerosil (0.5)	60	HR	−45.0
	Polyol A/C/D (40/50/10)						LR-1	20.0
	Polyol A/B/D (40/50/10)						LR-2	−5.8

[a] Isocyanate Index is adjusted with the ratio of polyol and isocyanate resin : index 50 (100:29), index 60 (100:34), index 70 (100:40), index 80 (100:46), index 90 (100:51).

[b] Density is adjusted with excess packing %:—70 kg/m³(110%), 80 kg/m³(125%), 90 kg/m³(141%), 100 kg/m³(156%), 110 kg/m³(173%).

[c] T_g data were taken from DMA measurements just for comparison. For exact values of T_g, refer to Figures 3 and 7, too. The order of T_g follows that of the recipes in the 6th, 7th, and 8th columns.

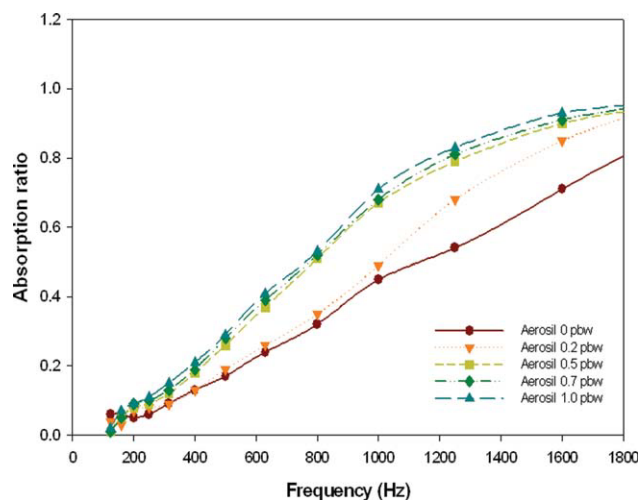*The unit of pbw stands for parts by weight per 100 parts of polyol.

Figure 1 Sound absorption ratio of PU/nano-silica foams with different nano-silica content; Isocyanate index was fixed as 60. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

differences in the tensile strength and the tensile modulus. The elongations at break of PU/nano-silica composite foams were higher than that of PU, regardless of the nanosilica contents, though the tendency was not consistent. The average cell size of the PU/nanosilica foams ranged from 160 to 400 μm. Our preliminary SEM results showed that the cell size of the nanocomposite foams was smaller with increasing the nanosilica contents, though the size differences were not so clearly observed.

Figure 3 shows the DMA thermograms of PU/nano-silica foams prepared with different isocyanate index. Glass transition temperature (T_g) decreases and the area of tan δ peak increases with decreasing the isocyanate index value. Crosslinking reactions are favored with more free isocyanates.[19] It should be noted, however, that the decrease of isocyanate index decreases the crosslink density, implying that the composite is not fully crosslinked. More detailed studies on this subject using DSC or FTIR spectroscopy are now underway. Since decreasing the index value means less free isocyanates, decreasing the
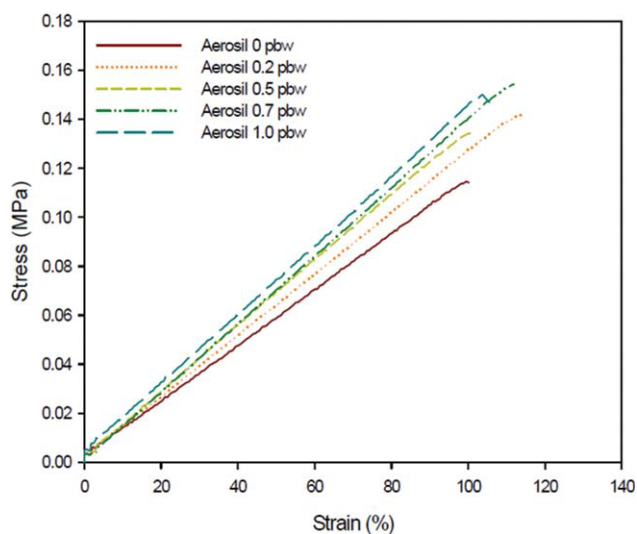
TABLE III
Tensile Strength and Young's Modulus of PU/Nano-Silica Foams

Content of aerosil (pbw)[a]	Tensile strength (MPa)	Young's modulus (MPa)
0.0	0.11 ± 0.01	0.11 ± 0.01
0.2	0.14 ± 0.02	0.12 ± 0.01
0.5	0.13 ± 0.01	0.13 ± 0.02
0.7	0.15 ± 0.01	0.14 ± 0.01
1.0	0.15 ± 0.02	0.14 ± 0.02

[a] The unit of pbw stands for parts by weight per 100 parts of polyol.

Figure 2 Typical stress–strain curves of PU/nano-silica foams with different nano-silica content; Isocyanate index was fixed as 60. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

index value leads to less crosslink density. Therefore, decreasing index value results in the decrease of glass transition temperature and increase of the area of tan δ peak. Increase of the area of tan δ peak indicates the increased energy dissipation as heat through hysteresis. The T_g values taken from DMA
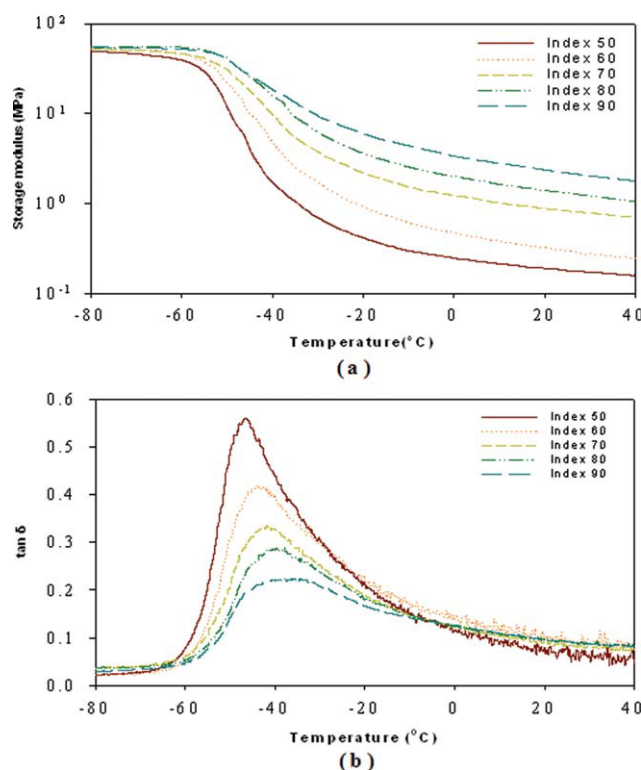

Figure 3 DMA thermograms of PU/nano-silica foams prepared with different isocyanate index (50–90) : (a) storage modulus, (b) tan δ.[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
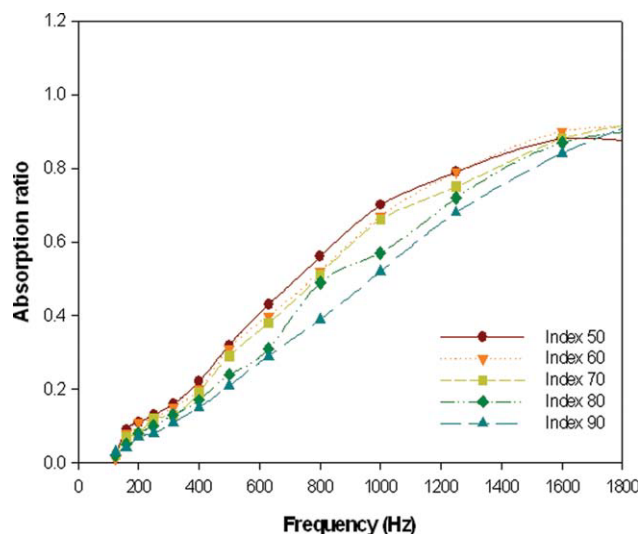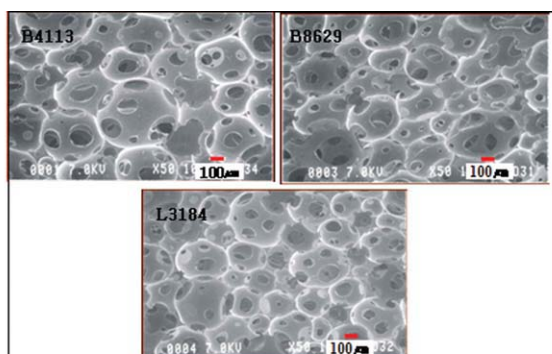
Figure 4 Sound absorption ratio of PU/nano-silica prepared with different isocyanate index (50–90). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

measurements were summarized in Table II for comparison.

The sound absorption ratio of PU/nano-silica prepared with different isocyanate index is illustrated in
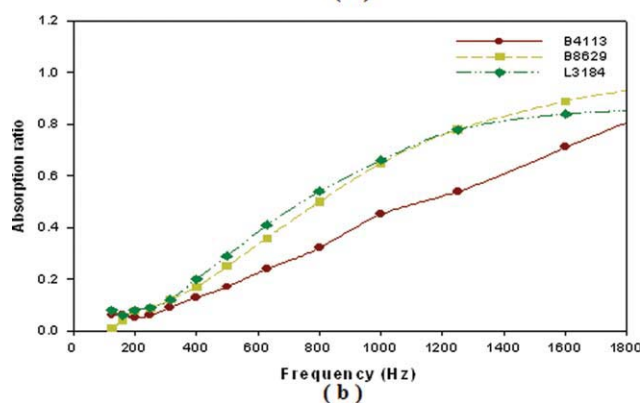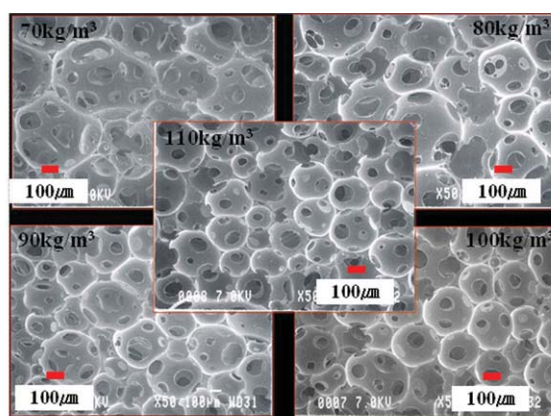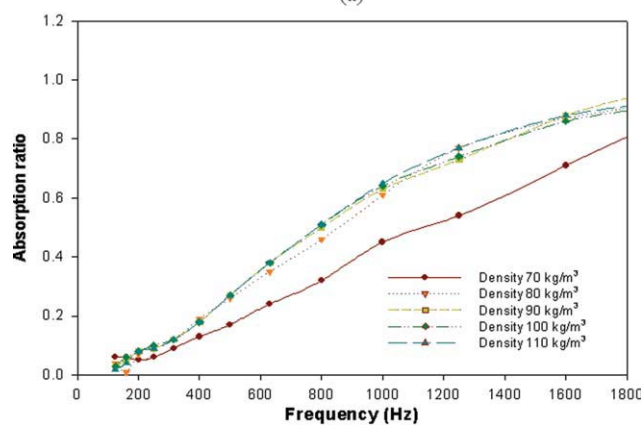

Figure 5 (a) SEM micrographs of the cross section and (b) the sound absorption ratio of PU/nano-silica foams prepared with three different surfactants; Isocyanate index was fixed as 60. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6 (a)SEM micrographs of the cross section and (b) the sound absorption ratio of PU/nano-silica foams with different density; isocyanate index was fixed as 60. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 4. With decreasing isocyanate index, the sound absorption ratio of PU/nano-silica foams increases over the entire frequency range investigated in this study. PU/nano-silica foams with larger area of tan δ peak have higher sound absorption ratio.

Figure 5 shows SEM micrographs of the cross section and the sound absorption ratio of PU/nano-silica foams prepared with three different surfactants. Generally silicone based surfactants are used to stabilize gas bubbles for PU foams. Different surfactants produce PU foams with different cell sizes. In Figure 5, PU foams prepared with B8629 and L3184 have smaller cell size and higher absorption ratio. The foams with small cell size absorb sound better than the foams with large cell size. Surfactants can change the interfacial energy of the silica-PU interface. It may also act as coupling agent that binds the two phases effectively. In this case, it may also attenuate sound energy and thus increase the sound absorption profile. Since the surfactants used in this study have similar chemical structures, it may be assumed that the interfacial energy has similar values for the three different surfactants.
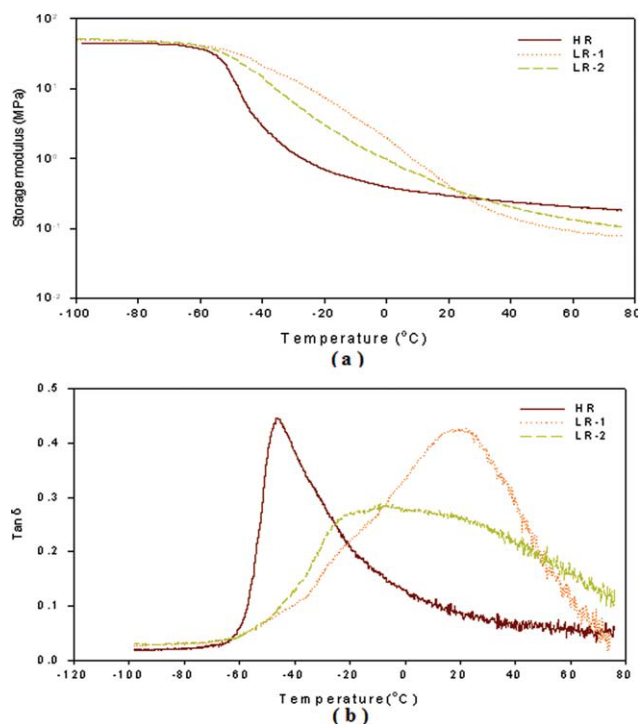
Figure 7 DMA thermograms of HR, LR-1, and LR-2: (a) storage modulus, (b) tan δ. Isocyanate index was fixed as 60. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

SEM micrographs of the cross section and the sound absorption ratio of PU/nano-silica foams with different density are given in Figure 6. With increasing density of the foams, their cell size decreases, and the sound absorption ratio of foams increases. Again, this confirms that foams with small cell size absorb sound better than the foams with large cell size. The sound waves lead to the vibration of the thin cell walls and air inside cells. The sound energy is dissipated through vibration damping of the cell walls and air. Better sound absorption ability of foams with small cell size could be due to the high cell density resulting in more dissipation through vibration damping of the cell walls and air. Up to a certain loading of silica, the absorption of sound is noted to increase substantially. Beyond a certain level, the absorption profile is not improved that much. In fact, after attaining the optimum level, further silica addition results in no change in the absorption characteristics. This has been explained on the basis of distribution profile of the silica in the PU foam walls. Very high loading can result in aggregate formation leading to no improvement in the stiffness of the cell wall. Of course, at very high loading, the uneven distribution of silica can affect the stiffness of the cell wall in such a way as to reduce the modulus and tensile strength of the foam. Besides, the accumulation of excess silica aggregate in void space of a cell can act as a barrier

to influence the movement of the sound wave inside a cell. It should be stressed that the presence and distribution of silica has a huge role to play in the nanocomposite especially at the higher silica loading. More details will be reported elsewhere on the distribution profile of silica in the foam either by TEM and energy-dispersive X-ray spectroscopy (EDX) or by SEM and EDX dot mapping.

Figures 7 and 8 show the DMA thermograms and the sound absorption ratio of high resilience (HR) foam, low resilience (LR-1) foam and LR-2 foam, respectively. In this study, three different PU foams were prepared using PPGs with different molecular weight. HR is the PU foam prepared with PPGA ($M_n = 4800$ g/mol). LR-2 is the PU foam prepared with PPGA and PPGB ($M_n = 2000$ g/mol). LR-1 is the PU foam prepared with PPGA and PPGC ($M_n = 1000$ g/mol). T_g of HR is around $-45°C$ and T_g of LR-1 and LR-2 is shifted to room temperature (see also Table II). Therefore, below 20°C, HR displays the lowest storage modulus, and LR-1 shows the highest storage modulus. However, above 20°C, LR-1 displays the lowest storage modulus, and HR exhibits the highest storage modulus because T_g of LR-1 is around 20°C. The order of area of tan δ peak is LR-1 > LR-2 > HR (Fig. 7). The order of absorption ratio at lower frequency range is LR-1 > LR-2 > HR (Fig. 8). It is well understood that glass transition temperature region is the region with potential for maximum sound energy dissipation. If PU foams have a broad T_g centered around room temperature, it is expected that the PU foams have a larger area of tan δ peak around room temperature and thus have good sound absorbing ability. PU foams are composed of hard segments and soft segments. One
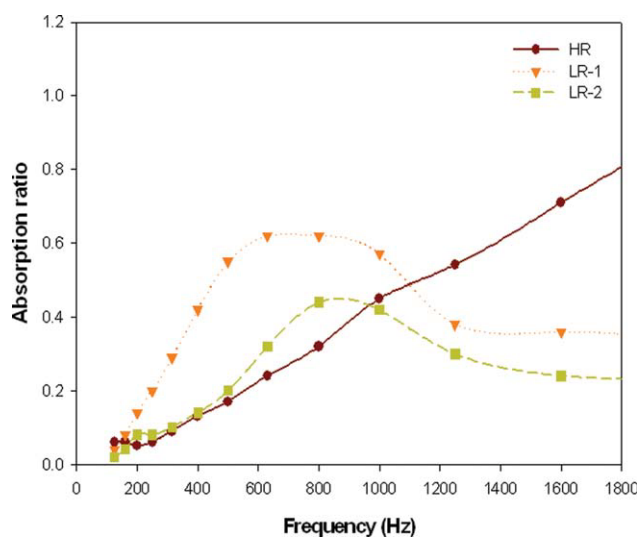

Figure 8 Sound absorption ratio of HR, LR-1, and LR-2; Isocyanate index was fixed as 60. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of the factors to affect T_g is molecular weight of soft segment (polyol). Generally, T_g of PU foams increases with decreasing molecular weight of polyol, as shown in Figure 7(b). Interestingly, the order of absorption ratio at high frequency range is completely changed (Fig. 8). Scattering or reflection may also be involved at high frequency regions at the PU foam wall as added silica can increase the stiffness of the foam wall. In Figure 8, the sound absorption ratio shows a maximum at a certain frequency for LR-1 and LR-2, while it shows a monotonous increase with frequency for HR. This is because the measurement was done at room temperature. The result in Figure 8 can be expected from the fact that HR is rubbery (Tg; ca. $-45°C$) but both LR 1 and LR2 (LR1 and LR2; T_g- ca. 20°C and $-6°C$, respectively) are in the transition state between rubber to glass, at room temperature. It is obvious that the sound absorption property is different inherently for rubbery materials and glassy materials.

CONCLUSIONS

Improvement of the sound absorption ability of PU foams was observed with addition of nano-silica. The addition of 0.2 in parts by weight (pbw) of nano-silica has relatively little effect but the addition of 0.5 phw of nano-silica leads to the significant increase of sound absorption ratio. The improvement of sound absorption of the PU/nano-silica foams could be contributed by polymer chain slipping at the PU/nano-silica interface, resulting in increased energy dissipation as heat through hysteresis.

Decrease of isocyanate index, cell size, and increase of density leads to the increase of sound absorption ratio of PU/nano-silica foams over the entire frequency range investigated in this study. PU/nano-silica foams have a broad T_g centered around room temperature by decreasing molecular weight of polyol resulting in good sound absorbing ability.

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