Damping Properties and Transmission Loss of Polyurethane. I. Effect of Soft and Hard Segment Compositions

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ABSTRACT: A series of polyurethane compositions with soft and hard segments were prepared, and the damping and mechanical properties of these materials were studied. The damping of polyurethane was decreased and shifted to the higher temperature with the content of butanediol (BD) used as a chain extender. The mechanical properties such as tensile strength and hardness (shore A) were increased with increasing BD contents. For application in noise reduction, the transmission loss of the mechanical vibration through solid structure was measured by two methods of extensional and constrained layer configuration. Polyurethane was used as a damping layer. The transmission loss of constrained layer configuration was larger than that of extensional configuration. Although the peak tanδ value of polyurethane having composition of BD 0.5 was lower than that of BD 0.4, its transmission loss was more effective at higher frequency. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 604–611, 2000

Key words: polyurethane; extensional configuration; constrained layer configuration; damping; transmission loss

INTRODUCTION

Polymers[1–4] are often used in sound and vibration damping areas. In general, one of the most important polymer properties of these applications is the glass transition. At the glass transition, a polymer is most efficient in converting sound and mechanical vibration energy into heat that results in absorption.

Polyurethanes[5–9] are particularly attractive for a study of the effect of chemical structure on damping because it is possible to change their glass transitions over a wide range of temperature. This corresponds to a damping peak location that spans more than 10 decades of frequency. In addition, changes in polyurethane structure can be used to produce a transition that can vary from narrow to broad. Polyurethanes are alternating block copolymers made of soft segments derived from polyester or polyether diols and hard segments that come from the diisocyanate and diol chain extender.[10] Because the soft and hard segments are chemically dissimilar, they tend to be incompatible and separate into different phases.

In this paper, a series of polyurethane compositions with soft and hard segments were prepared. We tried to find the optimum composition of soft and hard segments by measuring the damping and mechanical properties. For application in noise reduction, the transmission loss of

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the mechanical vibration through solid structure was measured.

EXPERIMENTAL

Materials

Poly(propylene glycol) (PPG), having molecular weight Mn = 1000, was obtained from Korea Polyol Co., Korea. 4,4′-Diphenylmethane diisocyanate (crude MDI, having functionality of 2.54) was obtained from Korea BASF Urethane, Korea. 1,4-Butanediol (BD), chain extender, was obtained from Junsei Chemical Co. Ltd., Japan.

Preparation of Prepolymers

In a four-necked flask, equipped with a mechanical stirrer, thermometer, nitrogen inlet, and outlet, a calculated quantity of MDI was added. The desired amount of PPG was added to the crude MDI. The reactants were stirred vigorously for 15 min at room temperature, and were reacted and degassed at 75°C for 15 min in a vacuum oven. After that, the reactants were stirred vigorously at room temperature, and then degassed for additional 15 min. After above methods were repeated two to three times, the liquid phase polyurethane prepolymer was obtained.

Preparation of Elastomers

The required amount of prepolymer and BD were stirred vigorously, degassed, and poured in a heated sheet mold and cured 100°C for 6 h in hot oven. The sheet of elastomers produced was 12 × 45 × 3.2 mm size. A solidified polyurethane was demolded and maintained for 18 h in hot oven. All the samples were postcured at room temperature for 7 days prior to testing. The ratio of MDI, PPG, and BD of the samples are listed in Table I.

Dynamic Mechanical Analysis

The dynamic storage and loss modulus were measured using a dynamic mechanical analysis (DMA) (DuPont DMA 983). The measurements were made at a frequency of $\omega = 1$ Hz in the temperature range of −50–150°C at a heating rate of 5°C/min.

Thermogravimetric Analysis

For thermogravimetric analysis, a DuPont thermal analyzer was used. The samples were tested at a heating rate of 20°C/min under nitrogen atmosphere.

Table I Molar Compositions of the Samples

Materials' Designation	Molar Ratio MDI : PPG : BD	Hard-Segment Content Mole% (MDI + BD)
BD0.1	1 (1.1)[a] : 0.9 : 0.1	55.0 (57.1)
BD0.2	1 (1.1) : 0.8 : 0.2	60.0 (61.9)
BD0.3	1 (1.1) : 0.7 : 0.3	65.0 (66.7)
BD0.4	1 (1.1) : 0.6 : 0.4	70.0 (71.4)
BD0.5	1 (1.1) : 0.5 : 0.5	75.0 (76.2)

[a] The value in parentheses indicates the equivalent molar ratio of NCO/OH, and OH consists of PPG and BD.

Mechanical Properties

The tensile properties, such as tensile strength at yield and elongation at break, were measured using an Instron model 4467 universal instrument. Measurements were made at room temperature at a constant crosshead speed of 50 mm/min on specimen. Data were taken as average of at least five measurements. The hardness of samples were measured using hardness tester (GS-710N shore A type, Tecklok).

Transmission Loss

In order to know the effect of polyurethane on transmission loss through solid structure, an apparatus shown in Figure 1 was used. Vibration source was speaker controlled from sound source controller, which gives the frequency range of 1 Hz–1 kHz. The signal detected by piezoelectricity (PZT) was analyzed. All the experimental runs were measured at 20°C, and data were taken as average of 100 measurements. All specimen used in acoustic experiment were 350 × 250 × 5mm size, and made as two types shown in Figure 2.

RESULTS AND DISCUSSION

Damping Properties

Because the soft and hard segments of polyurethane are chemically dissimilar, they tend to be incompatible and to separate into different phases. In order to improve the phase mixing and coordination of the segments motion, the equivalent ratio of isocyanate (NCO) and hydroxyl (OH)

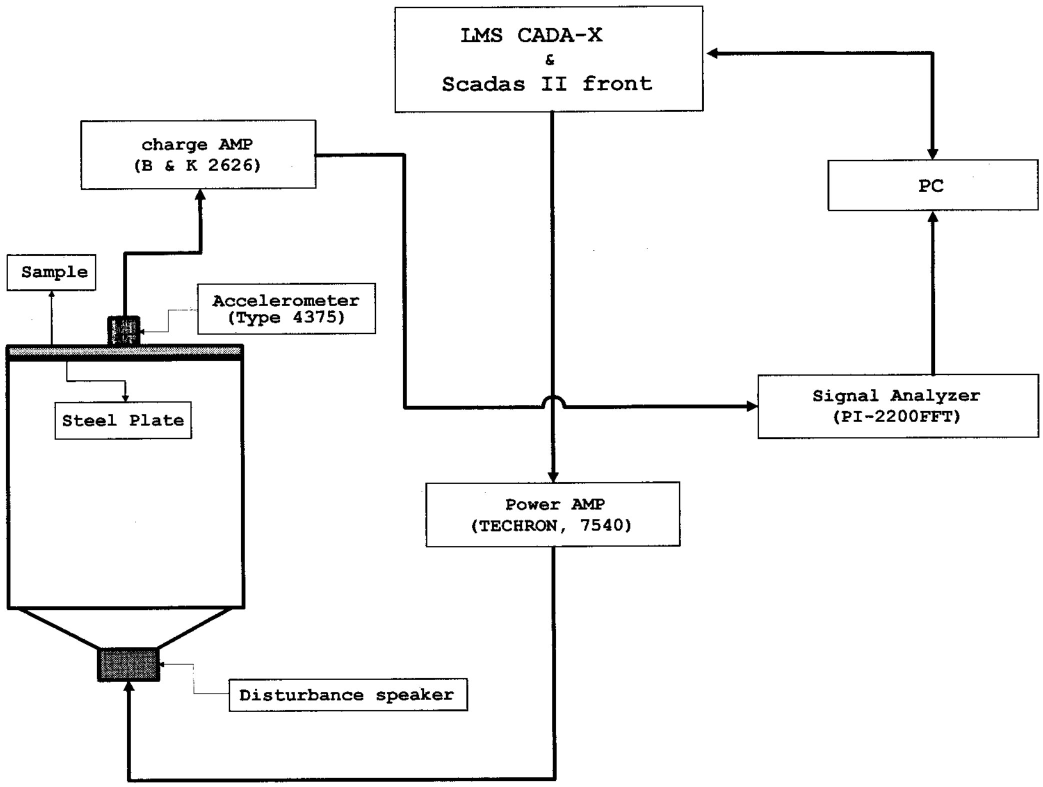

Figure 1 Acoustic apparatus for transmission loss.

was varied. This is one of the modifying methods to improve the compatibility.[11] Figure 3a,b shows that the loss factor (tanδ) of polyurethane prepared with the molar ratio of NCO/OH was 1 and 1.1, respectively. Detailed molar compositions are listed in Table I. The peak tanδ value of polyurethane decreases and is shifted to higher temperature with the increase of BD content because BD acts as a hard segment. The value of peak tanδ of polyurethane prepared with NCO/OH = 1 is higher than that of polyurethane having NCO/OH = 1.1. The decrease of the molar ratio of NCO/OH indicates that the crosslink density decreases. This is caused by the fact that the compatible degree of soft and hard segments increased as the crosslink density decreased. It results in the decrease of the motion resistance of hard segments, and the increase the value of tanδ.

In order to absorb the vibration through solid structure, the damping efficiency that indicates the area below the tanδ and temperature curve should be large. So polyurethane having the molar ratio of NCO/OH = 1 is effective in terms of damping.

Thermal Stability

Figure 4(a,b) shows the thermograms of polyurethane measured by thermogravimetric analysis with the content of BD for the molar ratio of NCO/OH = 1 and 1.1, respectively. It has been reported[12] that polyurethane elastomer based on MDI and aliphatic diamine as a chain extender starts decomposing at 280°C. Polyurethane prepared in this work starts decomposing at 330°C, which indicates that the crosslinking occurred. In addition to the starting temperature of decomposition, the increase of the thermal stability with increasing BD content was confirmed by the remaining char at 600°C. The effect is seen well in the higher molar ratio of NCO/OH in Figure 4(b).

Mechanical Properties

Table II shows the hardness (shore A), tensile strength at yield, and elongation at break with the content of BD for the molar ratio of NCO/OH. Tensile strength was found to increase continuously with increasing BD contents and molar ratio of NCO/OH. According to Smith,[13,14] the

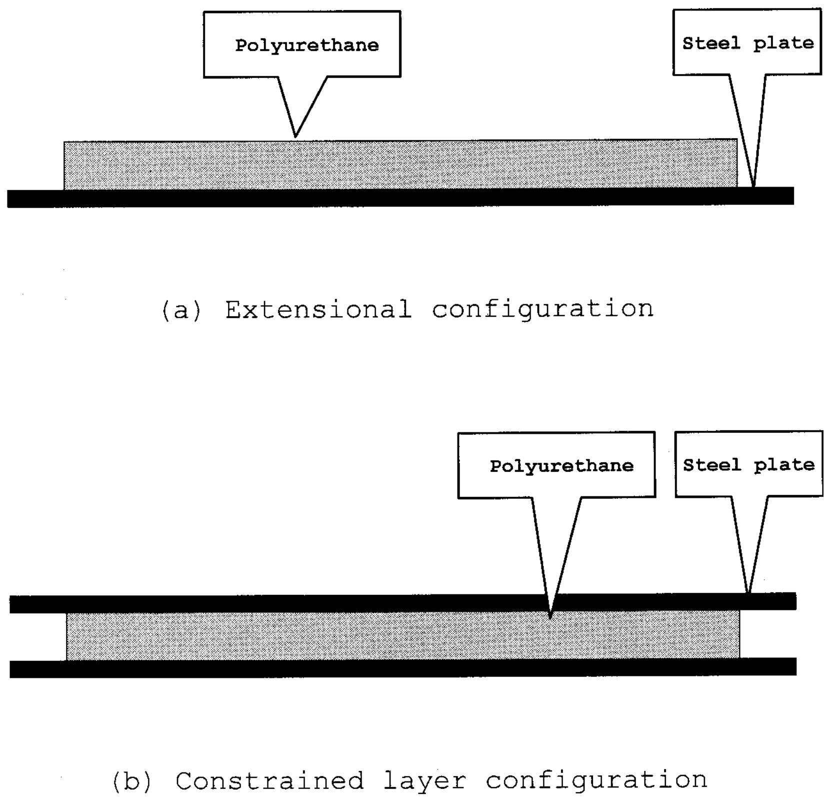

Figure 2 Test specimen for dynamic mechanical analysis and acoustic apparatus.

strength of elastomer is related to the relaxation time of mobil chains. Smith also found that hard segments in segmented polyurethane were highly effective sources of strength. It indicates that crosslinks slow down chain relaxation during extension. Hardness (shore A) with increasing BD contents and molar ratio of NCO/OH increased considerably. The mechanical properties depend on the hard segment in segmented polyurethane, and BD acts as a hard segment. In addition, excess MDI increased the crosslink density. These result in the increased mechanical properties.

Transmission Loss

The damping and mechanical properties of polyurethane were discussed with the content of BD and molar ratio of NCO/OH. In order to absorb the mechanical vibration through the solid structures, polymers coated on the solid surface should have the higher damping efficiency. As mentioned above, there is mutual relation between the damping and mechanical properties. In addition it is necessary to measure the damping at higher frequency because the $\tan\delta$ was measured at 1 Hz. So we measured the transmission loss (attenuation) of polyurethane having compositions of BD0.4 and BD0.5, which have considerable damping efficiency and mechanical properties among the compositions of polyurethane investigated. In acoustic terms, absorption can be expressed as $\alpha\lambda$, whereas in modulus terms, absorption can be expressed as $\tan\delta$. α and λ represent the attenuation coefficient and wavelength, respectively. So the acoustic and modulus approach are thus alternate and equivalent ways of describing the same physical phenomenon. For small $\tan\delta$, Ferry[15] pointed out that $\alpha\lambda = 8.686 \tan\delta$ in unit of dB.

Figure 5(a,b) shows the transmission loss of polyurethane having two compositions as a function of frequency for extensional and constrained layer configuration. Transmission loss of steel plate indicates the measured value without the damping layer (polyurethane). For extensional layer, polyurethane having composition of BD0.5 shows the larger transmission loss than that of BD0.4. However, the latter is more effective in a specified frequency range (200–370 Hz). For con-

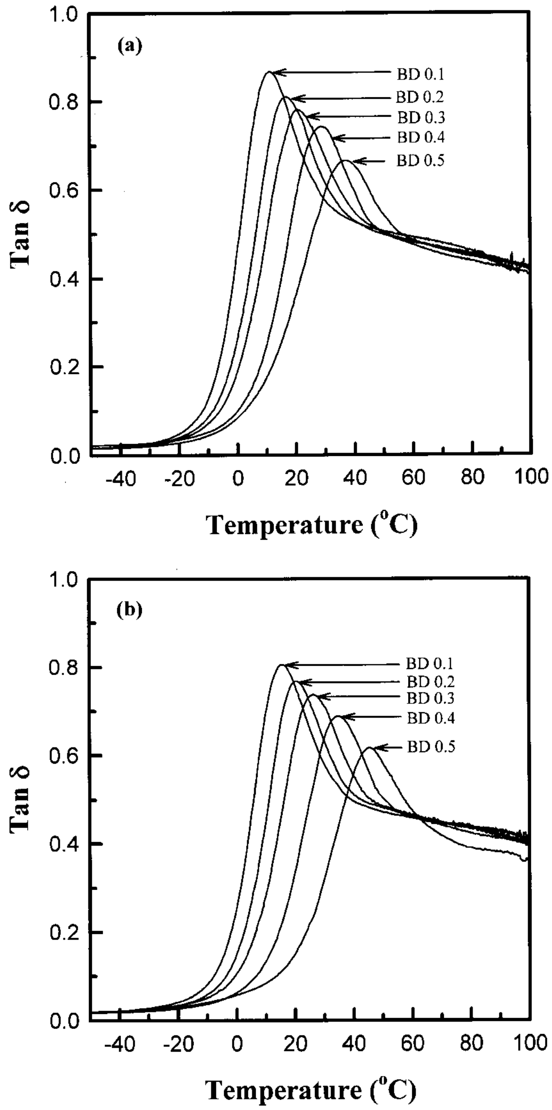

Figure 3 Tanδ curves of polyurethane with BD composition for the molar ratio of (a) NCO/OH = 1 and (b) NCO/OH = 1.1.

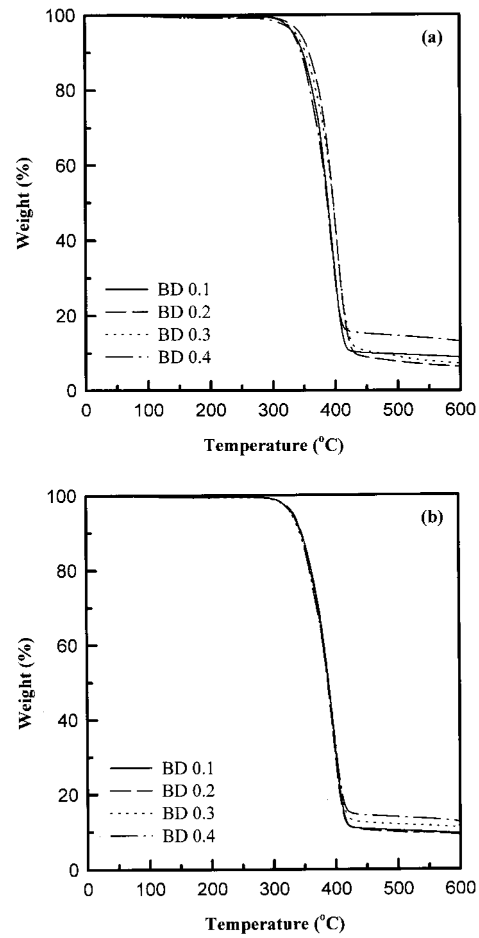

Figure 4 Thermogravimetric analysis of polyurethane with BD compositions for the molar ratio of (a) NCO/OH = 1 and (b) NCO/OH = 1.1 at 1Hz.

strained layer configuration, the similar behavior is observed. As shown in Figure 3(a), the polyurethane of two compositions has the different damping peak positions. The tanδ of polyurethane having BD0.4 is higher than that of BD0.5 up to 37°C, and then lower at higher temperature. From the present point of view, it must be noted that a decade of frequency increase is equivalent to an increase in temperature of approximately 6–7°C. The transmission loss was measured at 20°C. 37°C at 1 Hz corresponds to about 400 Hz at 20°C. So it can be explained that at low frequency (up to 400 Hz), the increase of transmission loss of polyurethane of composition of BD0.4 corresponds to the higher tanδ value at low temperature (below 37°C).

Table II Mechanical Properties of Polyurethane Elastomer

Materials	Hardness (Shore A)	Tensile Strength (MPa)	Elongation at Break (%)
BD0.1	30 (45)[a]	0.17 (0.15)	54.3 (26.9)
BD0.2	37 (50)	0.21 (0.35)	68.9 (50.1)
BD0.3	42 (54)	0.28 (0.68)	95.0 (93.0)
BD0.4	48 (58)	0.55 (1.20)	130 (140)
BD0.5	53 (63)	1.16 (2.12)	291 (193)

[a] The value in parentheses indicates the values of polyurethane prepared with the molar ratio of NCO/OH = 1.1.

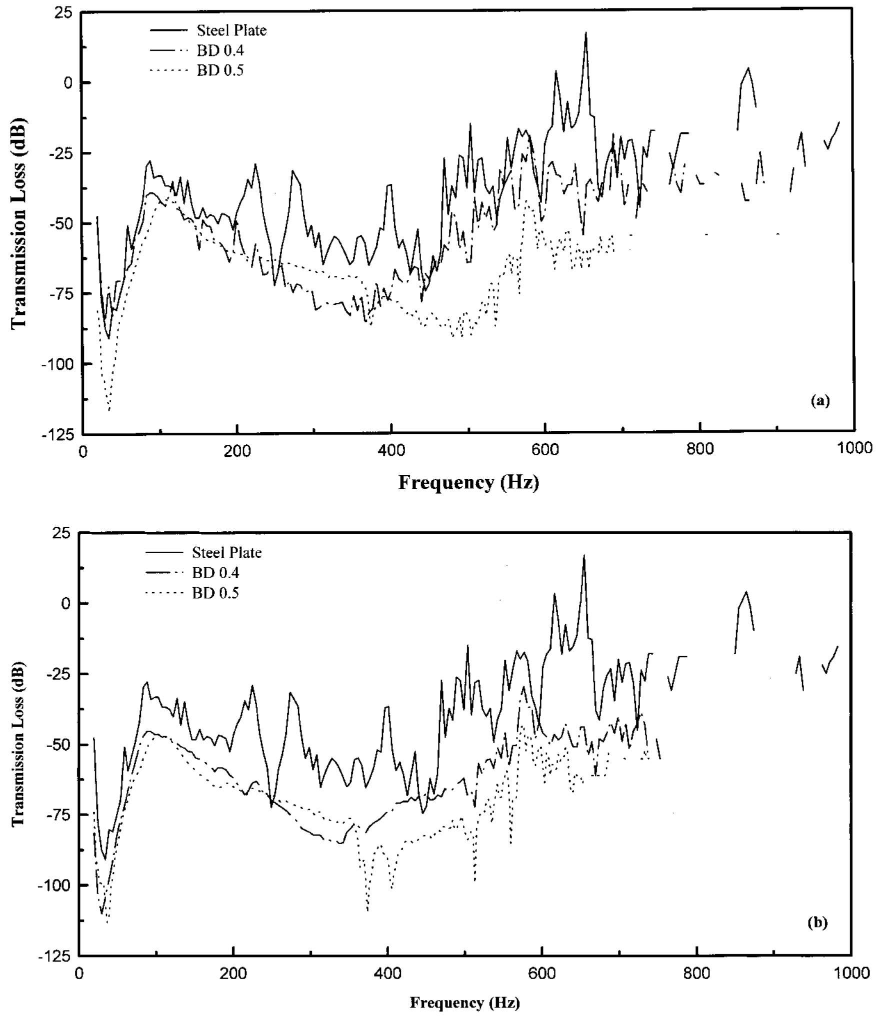

Figure 5 Transmission loss of polyurethane having compositions of BD0.4 and BD0.5 for (a) extensional and (b) constrained layer configuration. The thickness of damping layer (polyurethane) was 2.5 mm.

Figure 6(a,b) shows the thickness effect of polyurethane having composition of BD0.5 for extensional and constrained layer configurations, respectively. For extensional layer, transmission loss increases with the thickness of damping material at higher frequency than 400 Hz. For constrained layer configuration, however, the difference of transmission loss with the thickness of damping layer is not observed well. It was reported[8] that the damping efficiency was related to the sum of the thickness of constrained layer (upper steel) and damping material. We used steel as a constrained layer and did not change its thickness. The higher modulus constraining layer like steel will increase the shear motion of the damping layer and have a greater dissipation, but the thickness effect of damping layer without the increase of the thickness of constrained layer was less effective.

Figure 7 shows the difference of transmission loss between extensional and constrained layer configuration for polyurethane having composition of BD0.5. The latter is more effective than the former. Oberst[16] studied the extensional type damping and constrained layer damping, and reported that the latter yields better damping than the former. The constrained layer induces shear strain in the damping layer, and thus greater damping is produced.

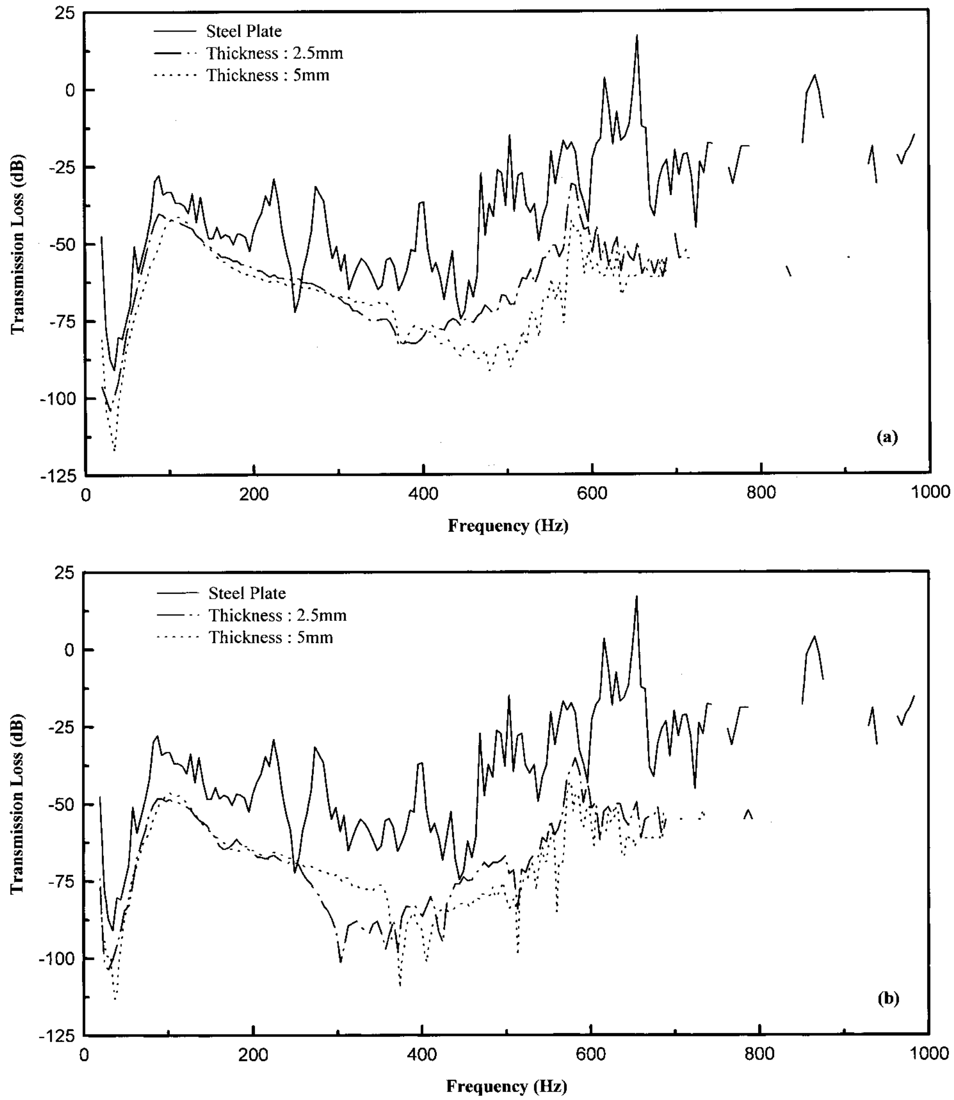

Figure 6 Transmission loss of polyurethane having composition of BD0.5 with the thickness of polyurethane for (a) extensional and (b) constrained layer configuration.

CONCLUSIONS

Polyurethanes are particularly attractive for a study of damping because it is possible to change their glass transition over a wide range of temperature through the changes in its structure. In this work, we measured the damping, mechanical properties, and transmission loss of polyurethane with soft and hard segment compositions. Because there is mutual relation between the damping efficiency and the mechanical properties, it was difficult to find the optimum composition of soft and hard segments. With polyurethane having the compositions of BD0.4 and BD0.5, which have considerable damping efficiency and mechanical property, the transmission loss of these materials was measured for application in noise reduction. As expected, the constrained layer configuration was more effective than extensional configuration. Although the peak tanδ value of polyurethane having BD0.5 was lower than that of BD0.4, its transmission loss was more effective at higher frequency.

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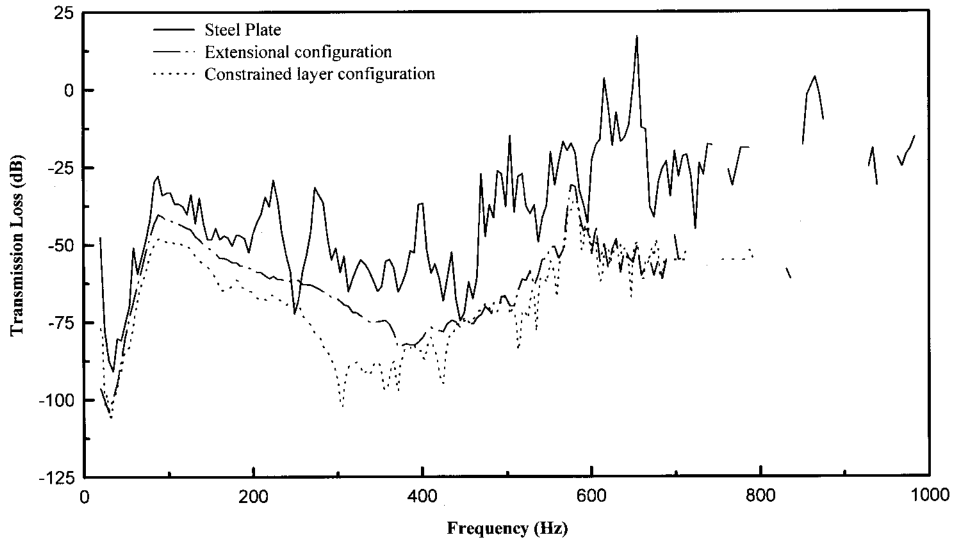

Figure 7 The difference of transmission loss between extensional and constrained layer configuration for polyurethane having composition of BD0.5. The thickness of polyurethane was 2.5 mm.

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