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폴리우레탄 평판 음향 윈도우 제조와 수중에서 기계적 및 음향적 특성 연구

조미숙 · 최재석 · 이수정* · 윤석왕* · 구자춘 · 이영관†**

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Fabrication of Polyurethane-sheet Acoustic Windows and Their Mechanical and Acoustic Properties in Water

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초록: 가교제인 trimethylol propane(TMP)의 함량변화에 따라 다양한 폴리우레탄(PU) 평판을 제작하였다. DMA 측정을 통하여 TMP 함량에 따라서 PU의 T_g는 34.8 ℃에서 49.9 ℃로 증가를 확인하였다. TMP의 함량이 4%에서 12%까지 증가함에 따라 탄성률은 322 MPa에서 423 MPa로 증가하였고, 인장강도는 10.6 MPa에서 14.8 MPa로 다소 증가하였으며, 신율은 62.8%에서 49%로 감소하였다. 음향특성의 경우, TMP의 함량이 증가함에 따라 가교 정도가 높아지며, 음속은 증가하였으나 음향감쇠계수는 감소하였다. 제작한 PU 평판은 4주간 수중에서 안정적임을 보여 주었다.

Abstract: Polyurethane (PU) sheets were fabricated by the reaction of polypropylene glycol (PPG) and liquid diphenyl methane diisocyanate (L−MDI) with various trimethylol propane (TMP) contents. The T_g value was varied from 34.8 ℃ to 49.9 ℃ according to the TMP content. As the content of TMP was increased from 4 to 12 wt%, the modulus of the PU sheet was increased from 322 MPa to 423 MPa, its tensile strength was increased from 10.6 MPa to 14.8 MPa, and its elongation was decreased from 62.8% to 49%. In case of acoustic properties, the sound speed of PU sheet was increased while its attenuation coefficient was decreased as the content of TMP was increased. The fabricated PU sheet was stable in water bath for 4 weeks.

Keywords: PU sheet, crosslinking, acoustic window, attenuation coefficient.

Introduction

For successful anti−submarine operation of a surface ship, the mounted−type sonar on the ship must have sufficient detection ranges. To achieve this, the fluid−flow noise around the sonar dome and the self−structural noise of the sonar dome must be blocked during the sonar operation. A design that minimizes the transmission loss and the distortion of the acoustic wave that arises from the sonar dome itself is essential in improving the operation of the sonar. To address this requirement, the acoustic window that surrounds the sonar dome must be manufactured with a highly transmissive compound material, which can be selected based on the results of this study on the acoustic characteristics of various materials.

Polymer materials are widely used for the damping of acoustics and vibration.[1,2] Polyurethane (PU) is often used in studies on acoustic characteristics. It is highly wear−resistant and has the characteristics of both rubber and plastic. It consists of polyol in its soft part and diisocyanate in its solid part. Depending on its diverse chemical structures, it has a wide range of glass transition temperatures (T_g).[3] It is generally known that a polymer with a low T_g can convert acoustic or vibration energy into thermal energy.[4,5]

Weibo manufactured a compound with PU and epoxy, and reported its damped vibration characteristic.[6] Foam−type PU and multi−layered PU were manufactured using polypro−

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pylene glycol (PPG) with a molecular weight of 1000 g/mol or 2000 g/mol, and their excellent sound absorption characteristics at a frequency of 1000 Hz or higher were reported.[7,8]

In this study, a PU flat-sheet acoustic window that has diverse T_g values due to the varied contents of its cross-linking agent was manufactured, and its acoustic characteristics, including sound speed and sound attenuation were examined.

Experimental

Materials. Liquid diphenyl methane diisocyanate (L-MDI) and PPG (Mw: 1000 g/mol and 3000 g/mol, respectively) were used to manufacture the PU flat-sheet window, and trimethylol propane (TMP) was used as a cross-linking agent for the control of the PU's rigidity. Kumho Mitsui Chemical supplied the L-MDI, and KPX Chemical supplied the PPG. The TMP was purchased from BASF Korea.

Manufacture of the PU Sheet. In the preparation of the prepolymer, PPG with a molecular weight of 3000 g/mol and L-MDI were mixed at a normal temperature and stirred at 75 ℃ for 2 h and 30 min. The mole ratio of prepolymer, PPG: MDI was 0.7: 1. The reaction occurred in the vacuum oven while the foam was being removed. The prepolymer solution was stored in an oven at 70 ℃. Then PPG with a molecular weight of 1000 g/mol and TMP were mixed at specific content ratios and kept in the oven at 70 ℃ for 8 h: MDI/PPG/TMP= 2.4/1.06/0.8, 2.4/1.06/0.4, 2.4/1.06/1.3, respectively. The prepolymer was mixed in turn with the PPG/TMP mixture solution at room temperature and slowly stirred to minimize the creation of foam. The foam of the liquid-state PU was further removed in the vacuum oven. The liquid-state PU was poured into the die on the glass plate that had been preheated at 100 ℃, and after six hours in the oven, the solid-state PU sheet was obtained. Figure 1 shows the PU flat sheet that contained 4 wt% TMP. The size of the PU flat sheet was 30 ×30×10 mm, and it was transparent and uniformly sized, without foam.

Figure 1. Photo of PU sheet-window with 4% TMP (30×30×10 mm).

Measurement of the Mechanical and Thermal Characteristics of the PU Sheet. In order to check the T_g and elasticity of the PU, a dynamic mechanical analyzer (Seiko Exstar 6000, DMA/SS6100) was used to examine the dynamic viscoelastic characteristic. The temperature was raised at a rate of 10 ℃/min within the temperature range of 25-250 ℃ and at a 1 Hz frequency under an N_2 atmosphere. A force of 200 mN and the tension/sinusoidal mode were applied. This setup allowed us to obtain measurements of the storage and loss moduli (E' and E'') and the loss factor (tan δ), which is defined as the ratio of tan $\delta=E'/E''$.

In the tension test, the mechanical property was measured with tension specimens based on ASTM D 1708 at a cross-head speed of 10 mm/min using a universal tensile machine, UTM (Lloyd, Inc., LR 30 K).

Measurement of the Acoustic Characteristics of the PU Sheet. As the acoustic characteristics of PU depend on the contents of its cross-linking agent, the sound speed and sound attenuation coefficient were measured.

Time delay estimation based on the transmission method was used in the water. The time differences between the received signals with and without the specimen were used to determine the sound speed.[9] The sound speed of the specimen, c is determined with the equation (1):

$$c=\frac{d}{\frac{d}{c_w}-\Delta t} \tag{1}$$

The value d is the thickness of the specimen; c_w is the sound speed in the water; and Δt is the time difference between the received signals at the hydrophone with and without the specimen in the water. As an acoustic transmitter TKS IMA73 was used at 200 kHz while Reson TC4038 as a hydrophone. The temperature of specimen and water was kept constant at 28 ℃ during the experiments.

The sound attenuation coefficient of PU according to the contents of its cross-linking agent was also measured. TKS IMA73 and TKS IMA052 as acoustic transmitters and Reson TC4038 as a hydrophone were used for attenuation measurement around 200 kHz and 500 kHz, respectively. The attenuation coefficient α is determined as follows:

$$\alpha=-\frac{\ln\left(\frac{P_r}{P_{ref}(T_{ws}T_{sw})}\right)}{2d} \tag{2}$$

where,

Table 1. Mechanical and Thermal Properties of PU Sheets

Sample	TMP (wt%)	Tensile strength (MPa)	Strain (%)	Tensile modulus (MPa)	T_g (℃)	Density (kg/m^3)	Sound speed (m/s)	Impedance (MKS Mrayls)	Attenuation coefficient (Np/m),@ f (kHz)
1	4	10.6	62.8	322	34.8	1123	1942	2.18	1.7×10^{-1} x f
2	8	13.8	57.0	390	40.3	1141	2024	2.31	1.6×10^{-1} x f
3	12	14.8	49.0	423	49.9	1160	2076	2.37	1.5×10^{-1} x f

$$T_{ws} = \frac{2Z_w Z_s}{Z_w + Z_s} \tag{3a}$$

$$T_{sw} = \frac{2Z_s Z_w}{Z_s + Z_w} \tag{3b}$$

P_{ref} and P_r are the sound pressure amplitudes without specimen as reference and with specimen, respectively. T_{ws} is the pressure transmission coefficient from the water to the specimen, and T_{sw} is the pressure transmission coefficient from the specimen to the water. Z_w and Z_s are the characteristic impedances of water and specimen, respectively.

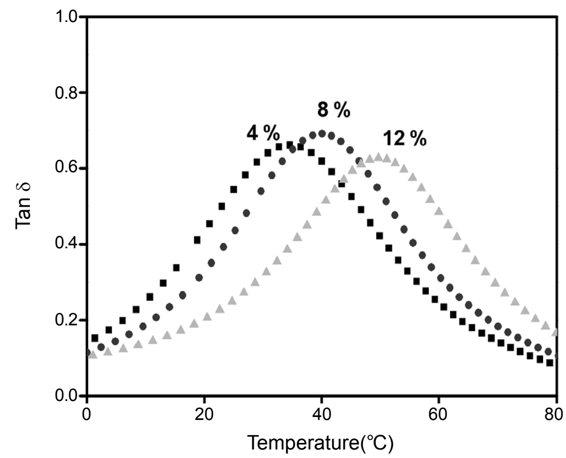

Figure 2. Tan δ curves of PU sheets with TMP contents as a function of temperature.

Results and Discussion

The TMP cross-linking agent was added to PU at contents of 4%, 8%, and 12%. The thermal, mechanical, and acoustic characteristics of the PU were compared according to their TMP contents.

Analysis of the Mechanical Properties. The mechanical properties of the diverse PU flat sheets according to their TMP content were measured using a UTM. Table 1 shows the mechanical strengths at a break point according to the TMP content. The PU flat sheet with a 4 wt% TMP content (Sample 1) showed a tensile strength of 10.6 MPa, an elasticity of 322 MPa, and an elongation percentage of 62.8%. The tensile strength and elasticity slightly increased with the increase in the TMP content from 8 to 12 wt%. The elongation decreased with the increase in the TMP content. The error-range of the value was 2.9%. This seems that higher cross-linking density allows enhanced mechanical strength with the increase in the TMP content in the flat sheet.

Analysis of the Dynamic Characteristics. Figure 2 shows the tan δ (ratio of loss-to storage moduli) curves under tension mode for the composites. It is a complex quantity defined with elastic (storage) and viscous (loss) components; denoted E' and E'', respectively. TMP was employed as a cross-linking agent in the PU matrix. The peak of the tan δ curve changed according to the TMP contents, and the fine transition phenomenon, an effect of the cross-linking agent, was observed. The T_g of the PU flat sheet was 34.8 ℃ for the 4% TMP content, 40.3 ℃ for the 8% TMP content, and 49.9 ℃ for the 12% TMP content, respectively. These data clearly show that T_g increased with the increase in the TMP content. This seems that cross-linking density increases with the increase in the content of the cross-linking agent, which was caused by the reduced free volume in the polymer as the result of the shortened chain distance between the cross-linking. The cross-linking agent content contribution to mechanical properties of PU sheet is shown in Table 1. Enhanced values of mechanical properties were observed according to the content of cross-linking agent.

Analysis of the Acoustic Characteristics. Figure 3 shows the sound speed of the PU specimen according to its TMP content. The sound speed increased with the increase in the TMP content, and the characteristic impedance, which is the product of the sound speed and the density, also increased. These indicated that the cross-linkage became strong with the increase in the TMP content, and the resulting reduction of the free volume of the polymer raised the sound speed, which increased with the increase in the tensile strength and the elasticity.

Figure 4 shows the sound attenuation coefficients of the PU specimens around the frequencies of 200 kHz and 500 kHz. The symbols represent the experimentally measured attenuation coefficients, and the lines represent the linear regression fittings with the measured values. The attenuation coefficient, which is depend on the cross-linking of material,

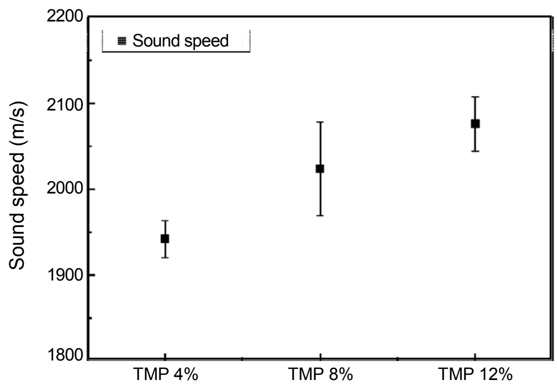

Figure 3. Sound speed of PU sheets with TMP contents.

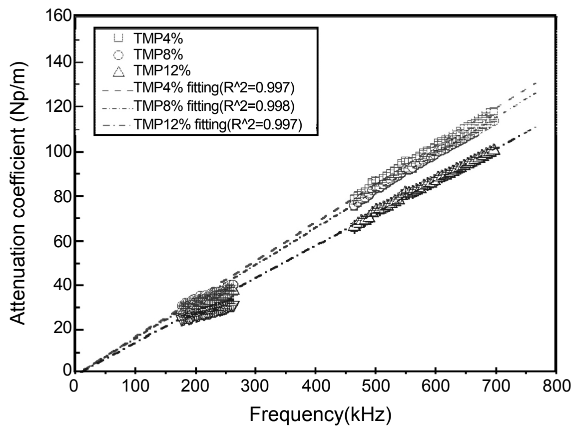

Figure 4. Attenuation coefficient (symbol: experiment, line: linear regression fitting) of PU sheets with TMP contents as a function of frequency.

meats the loss of sound energy by the absorption or diffraction of sound in material. They show that the attenuation coefficient linearly increased as a function of frequency.[10] It seems that the free volume of the polymer and the attenuation coefficient decreased with the increase in the TMP content. Table 1 shows the mechanical, thermal, and acoustic characteristics of PU according to the measured TMP content.

Underwater Stability Test. To examine the stability of the PU flat sheet in water, the PU flat sheet with a 4 wt% TMP content was kept in a water tank for one to four weeks, and its mechanical properties were measured according to the elapsed time. The size of the specimen was identical to the sizes of the specimens in the above-mentioned mechanical property analysis. As shown in Table 2, the tensile strength, elongation, and elasticity of the samples that underwent the acoustic tests had constant values, without special differences. That is, the PU was stable in the water after its four-week reaction in the water after acoustic tests. The length was also measured to examine the degree of expansion. It had constant values, which indicated the stability and reliability of PU in the water.

Table 2. Mechanical Properties of PU Sheets as a Function of Time

Period (week)	Strain (%)	Tensile strength (MPa)	Tensile modulus (MPa)	Depth (mm)
0	62.8	10.6	322.1	14.05
1	62.8	10.6	322.1	14.05
2	62.9	10.7	322.2	14.17
3	62.8	10.7	322.2	14.05
4	63.0	10.5	322.1	14.19

Conclusions

As the acoustic characteristics of PU depend on its cross-linking agent, its sound speed and sound attenuation coefficient were measured. Its sound speed increased with the increase in its cross-linking agent content from 4 to 12 wt%, but its sound attenuation coefficient decreased. These indicated that the cross-linking and elasticity became strong with the increase in the TMP content, and that the resulting reduction of the free volume of the polymer raised the sound speed, which increased with the increase in the tensile strength and the elasticity. The attenuation coefficient linearly increased with the increase in the frequency. The free volume of the polymer and its attenuation coefficient decreased with the increase in its TMP content. Thus, it is expected that the mechanical, thermal, and chemical properties of the polymer medium can be non-destructively predicted using acoustic characteristics, and that its properties can be closely monitored in a more non-interventional manner during its manufacture.

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