Acoustic Properties of Nitrile Butadiene Rubber for Underwater Applications

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Received 16 August 2001; accepted 18 November 2001

ABSTRACT: Acoustic properties of nitrile butadiene rubber (NBR) specimens with carbon black as filler were investigated with different sulfur contents in the frequency range of 300-1000 kHz. Their mechanical properties, such as density, hardness, tensile strength, were conventionally measured and correlated with their acoustic properties. Sound speeds in the specimens were increased with an increase in the sulfur content. The variation of sound speed was about 2–5% in the specimens, whereas the variation of density was less than 0.4%. Enhanced acoustic transmission was also observed with increasing sulfur content. It may be due to the hardness change from the increase of crosslinking density in the specimens. These results show that the mechanical properties of NBR can be nondestructively and accurately determined with the acoustic property measurements. By use of the desired mechanical and acoustic properties, the utilization of the NBR for underwater applications becomes less difficult. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 2764–2771, 2002

Key words: acoustic property; NBR; rubber; crosslinking

INTRODUCTION

Studies of acoustic property measurements in polymeric materials were attracted in the field of polymer science and physics because of their abundant information concerning polymer–solvent and polymer–polymer interaction.[1–3] The acoustic properties of polymeric materials can be determined by acoustic measurement technique with high accuracy. Such acoustic properties contain important information on the mechanical properties of polymers commonly used for underwater application materials. In early research, acoustic properties were investigated for commercially available polymers such as poly(methyl methacrylate),[4] rubber,[5] and polyurethane.[6] Recently, structural variations of polymer were also investigated to prepare appropriate polymer compositions for underwater applications.[7–10] Thompson et al.[7] reported intensive investigation of the effect of polyurethane structure on acoustic properties. Soft-segment polyurethane was shown as a major factor to determine sound speed.

Rubber is an excellent material usable for underwater applications because of its easy fabrication. However, not much research has been done on the relationship between mechanical proper-

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Contract grant sponsor: Underwater Acoustics Research Center; contract grant number: UA-33.

Journal of Applied Polymer Science, Vol. 85, 2764–2771 (2002)

Table I Formulation of the NBR Specimens (phr)

Ingredient	NS-1	NS-2	NS-3
NBR	100	100	100
HAF black	60	60	60
DOA	0.0	0.0	0.0
ZnO	5.0	5.0	5.0
Coumarone inden resin	0.0	0.0	0.0
Stearic acid	1.5	1.5	1.5
Sulfur	1.0	2.0	3.0
[b]RD	1.5	1.5	1.5
[c]CM	0.0	0.0	0.0
[d]TT	2.0	2.0	2.0
[e]DM	2.0	2.0	2.0

Note. The acrylonitrile (Percentage is 33% for all NBR specimens.
[a] RD, 2,2,4-trimethyl-1,2-dihydroquinoline.
[b] CM: *N*-cyclohexyl-2-benzothiazolysulfenamide.
[c] TT, tetramethylthiuram disulfide.
[d] DM, dibenzothiazolydisulfide.

ties and acoustic properties of rubber. In this article, we report on the acoustic properties of nitrile butadiene rubber (NBR) with different sulfur contents when carbon black filler was added.

EXPERIMENTAL

Materials

Acrylonitrile rubber (Hyundai Petrochemical Co.), stearic acid, ZnO and sulfur were purchased from Aldrich (Milwaukee, WI). Dibenzothiazolydisulfide (DM), tetramethylthiuramdisulfide (TT) and *N*-cyclohexyl-2-benzothiazolysulfenamide (CM) as crosslinking coagent were obtained from TCI (Tokyo, Japan). Carbon black (HAF) and polymer of 2,2,4-trimethyl-1,2-dihydroquinoline (RD) as antioxidant were donated by Hankook Tire Co. (Daejeon, Korea). Formulation of the NBR specimen[11] is shown in Table I.

Mixing Procedure

Rubber mixing was carried out by using an F-series Banbury mixer. The mixing procedure was divided into the two stages. In the first mixing stage, carbon black was mixed with pristine NBR, and in the second mixing stage, crosslinking agent and coagent were mixed with the first-stage product mixture. The rubber mixes were vulcanized in a hydraulic press at 150°C. Figure 1 shows the profiles of temperature, power loaded to mixer, and input power variation with the mixing time for the first and second mixing stages.

Measurement of Mechanical Properties

Density of the NBR specimens was determined with the Archimedes principle at 25°C, and hardness of the specimens was determined by a Shore A hardness tester following ASTM D 2240-68. Tensile strength and elongation at break of the specimens were measured by using an Instron (model 4204) tester at the crosshead speed of 500 mm/min, following ASTM D412. Each value was averaged from five specimens.

Relative crosslinking density of the specimens was estimated with the swelling method. The weights of the unswollen and swollen specimens were measured. For the swollen weight measurement, the specimens were soaked in toluene for 12 h and the swelling ratio was determined as follows:

$$Q = 100 \times (W_s - W_u)W_u \quad (1)$$

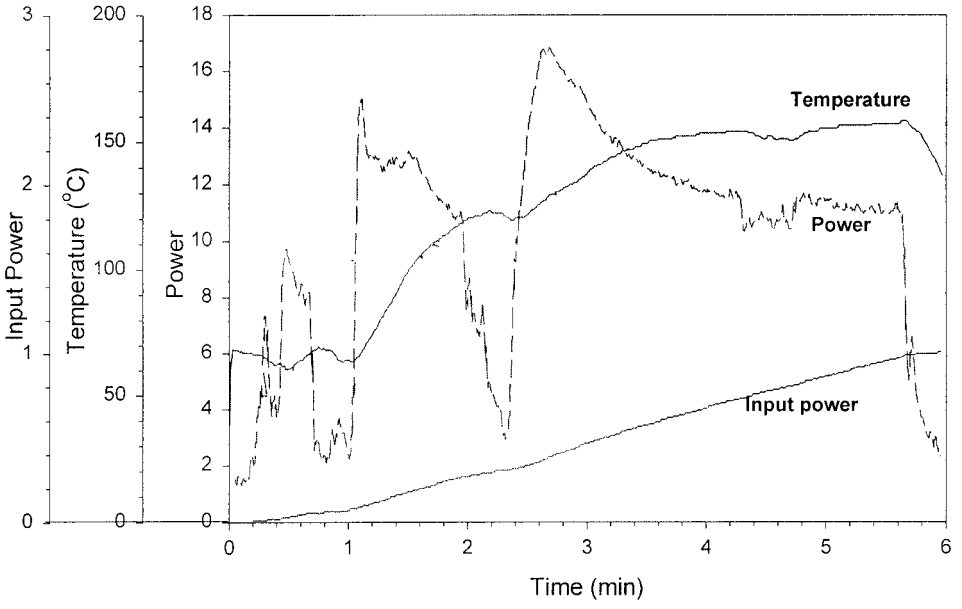
where W_s and W_u are the weights of the swollen and unswollen specimens, respectively. The reciprocal Q value gives the relative crosslinking density.[12]

Measurement of Glass Transition Temperature

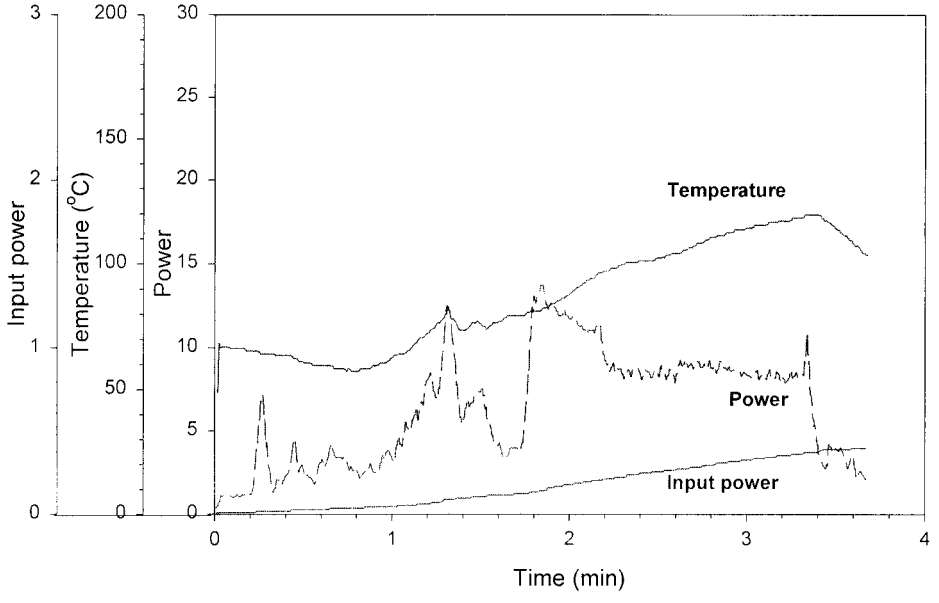
Differential scanning calorimetry (DSC) was carried out in the temperature range of 150–200°C by using the NBR mass of 7–9 mg. The heating rate was kept at 10°C/min in a nitrogen atmosphere. Glass transition temperature (T_g) of the NBR was measured at the inflection point.

Measurement of Acoustic Properties

Three NBR specimens of 168 × 118 × 19.6 mm with carbon black filler were prepared for acoustic property measurements. A schematic diagram of the acoustic property measurement system is shown in Figure 2. The system consisted of a pair of ultrasonic transducers mounted coaxially with 5 cm separation. Transducer alignment was adjusted to maximize the amplitude of a received reference signal transmitted through water. A specimen was immersed in a 20°C water bath and placed halfway between the two transducers. The acoustic beam axis was aligned normal to the



(a)



(b)

Figure 1 Profiles of the temperature, power loaded on mixer, and input power with the mixing time. (a) First mixing stage: raw rubber input ⇒ 20-s mixing ⇒ half amount of carbon black input ⇒ 60-s mixing ⇒ remaining carbon black input ⇒ 210-s mixing. (b) Second mixing stage: input of first stage mixes and sulfur with coagents ⇒ 110-s mixing.

surface of the specimen. Incident acoustic waves were generated by a transducer (Panametrics A301S or A302S) with a function generator (HP 3314A) and a power amplifier (ENI 2100 L). The transmitted acoustic waves through the specimen were analyzed by a digital storage oscilloscope (LeCroy LT322) with a wave-processing package.

To investigate the frequency dependence of acoustic properties of NBR, acoustic measurements were carried out in the frequency range of

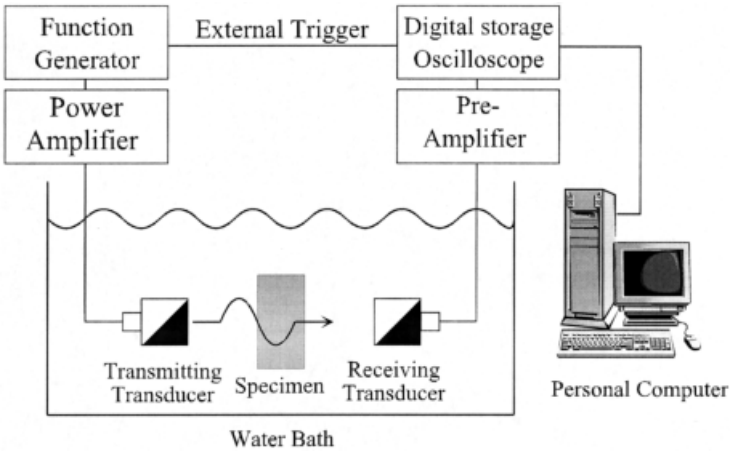


Figure 2 A schematic diagram of the acoustic property measurement system.

300-1000 kHz. Because one transducer cannot cover all the operating frequency ranges for our measurements, we measured the acoustic properties of the NBR by using two pairs of transducers with the center frequencies of 500 and 1000 kHz, respectively. The usable frequency range of the first pair of transducers was 300–600 kHz and that of the second pair of transducers was 500-1000 kHz. To verify accurate and reasonable measurements in the whole frequency range, the upper and lower usable frequency limits were overlapped in the frequency range of 500–600 kHz.

RESULTS

Mechanical Properties of the NBR Specimens with Different Sulfur Contents

Rubber products are generally composed of various ingredients such as elastomer, vulcanizing agent, accelerator, reinforcer, and plasticizer. To evaluate the effect of sulfur content in the elastomer on the mechanical and acoustic properties, we modified the standard mixing recipe of the NBR (ASTM D 3187-73). The formulation of the prepared NBR is shown in Table I. The NBR specimens with carbon black filler, NS-1, NS-2, and NS-3, were prepared with different sulfur contents to change crosslinking degree. In the mixing procedure, the NBR showed excellent compatibility with the applied carbon black. This was confirmed by the weight change before and after the first mixing stage. The mass loss during the mixing procedure was $<0.2\%$ of the total weight (2.1 kg), which means that all the introduced carbon blacks are well distributed in the elastomer matrix.

Mechanical properties of the NBR specimens are listed in Table II. There were little changes in the density with an increase in the sulfur content. Because of the increase of the crosslinking density, hardness was increased with an increase in the sulfur content. It was clearly shown that the sulfur content mainly affected the hardness rather than the density of the NBR specimen. The

Table II Mechanical Properties and Sound Speed of the NBR Specimens

Entry	Density (g/cm^3)	Hardness (Shore A)	Elongation at Break (%)	Tensile Strength (kg/cm^2)	Q (swelling ratio)	Sound Speed (m/s) (mean value)
NS-1	1.211 ± 0.001	82 ± 0.7	201 ± 27.0	243 ± 28.5	78.8	2005.5
NS-2	1.214 ± 0.001	85 ± 0.8	177 ± 9.3	276 ± 8.8	69.3	2070.9
NS-3	1.219 ± 0.001	86 ± 0.6	155 ± 15.1	264 ± 20.6	66.1	2147.3

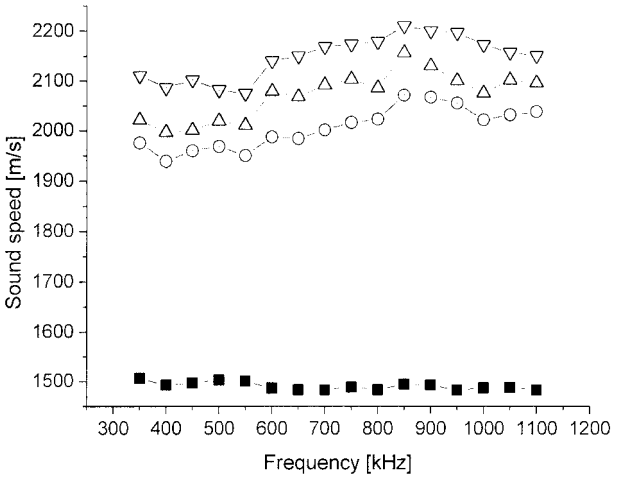


Figure 3 Sound speed variation as a function of acoustic wave frequency: sound speed of water (■); NS-1 (○); NS-2 (△); NS-3 (▽).

NS-2 specimen showed the optimum tensile strength.

Sound Speeds in the NBR Specimens with Different Sulfur Contents

Sound speed was determined by the time-delay method in water. The flight time difference with and without the specimen was measured with a digital oscilloscope (LeCroy LT322). The sound speed in the specimen can be determined from the following formula:

$$c_s = \frac{d}{\left(\frac{d}{c_0}\right) - \Delta t} \tag{2}$$

where c_s is the sound speed in specimen, d is the thickness of specimen, c_0 is the sound speed in water, and Δt is the flight time difference.

Figure 3 shows the sound speed variation as a function of acoustic frequency. The solid symbol shows the sound speed in water and the open symbols show the sound speeds in the specimens, respectively. The sound speed was increased with an increase in the sulfur content in the NBR. It shows the same trend as the hardness. In Table II, the variation of density was very small, around 0.3–0.4%, but the variation of sound speed was 2–5%. Because the sound speed can be correlated with the bulk and shear modulus of the specimen, and hardness is correlated with the bulk and shear modulus, the increase in hardness results in the increase of sound speed.[3]

Acoustic Wave Transmission with Different Sulfur Contents

Transmission coefficient and attenuation were measured in the experimental setup, shown in Figure 2. Acoustic pressure transmission coefficient T is defined by:

$$T = \frac{P_t}{P_i} \tag{3}$$

where p_i is the incident pressure wave and p_t is the transmitted pressure wave. Attenuation α in the specimen can be determined with the transmission measurement by the following formula:

$$\alpha = 20 \log\left(\frac{p_1}{p_2}\right)\frac{1}{\Delta d} \quad [\text{dB/cm}] \tag{4}$$

where p_1 and p_2 are the transmitted pressure amplitudes through thickness d_1 and d_2, respectively. Δd is the thickness difference between d_1 and d_2.

Figures 4 and 5 show the transmission coefficient and attenuation of the NBR specimens as a function of frequency. The transmission coefficient is increased with the increase of sulfur content in the NBR. The increase of hardness with

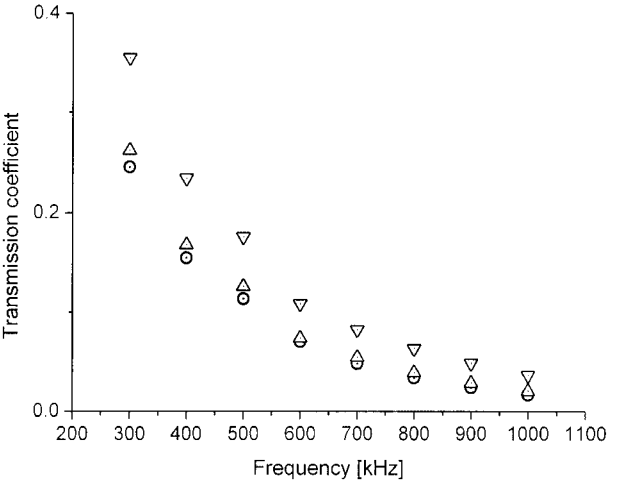


Figure 4 Acoustic transmission coefficient of the NBR specimens as a function of frequency: NS-1 (○); NS-2 (△); NS-3 (▽).

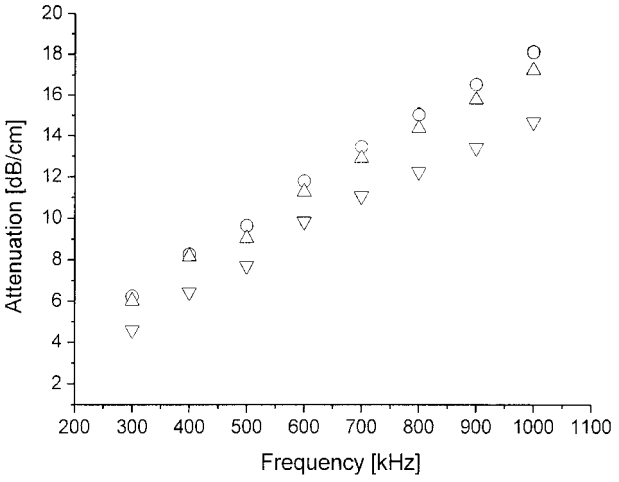


Figure 5 Attenuation of the NBR specimens as a function of frequency: NS-1 (○); NS-2 (△); NS-3 (▽).

sulfur content increases the transmission coefficient, and this results in the decrease of attenuation in the specimen. All specimens showed higher attenuation when the frequency increased.

DISCUSSION

In the three-medium propagation model shown in Figure 6 without considering attenuation in the specimen, the reflection and the transmission coefficient can be expressed by

$$R = \frac{i\left[\left(\frac{Z_s}{Z_0}\right) - \left(\frac{Z_0}{Z_s}\right)\right]\sin k_s d}{2\cos k_s d + i\left[\left(\frac{Z_s}{Z_0}\right) + \left(\frac{Z_0}{Z_s}\right)\right]\sin k_s d} \quad (5)$$

$$T = \frac{1}{1 + \frac{1}{4\left[\left(\frac{Z_s}{Z_0}\right) + \left(\frac{Z_0}{Z_s}\right)\right]^2 \sin^2 k_s d}} \quad (6)$$

where k_s is the wave number in the specimen, $Z_0 = \rho_0 c_0$ and $Z_s = \rho_s c_s$ are the characteristic acoustic impedance of water and specimen, respectively. ρ_0 and ρ_s are the densities of water and specimen, respectively.

From eqs. 5 and 6, the reflection coefficient and the transmission coefficient are determined by the characteristic impedance Z_0 and Z_s. The increase of density and sound speed in a specimen makes the difference of impedance large between Z_0 and Z_s. This makes reflection of acoustic wave from the specimen large, so the transmission coefficient without considering attenuation would be decreased with the increase in sulfur content. However, the transmission coefficient increases with increasing crosslinking density even though the difference of impedance between Z_0 and Z_s is large. This result can be explained with attenuation in the specimen.

Figure 7 shows a representative DSC thermogram of the NBR, and Table III shows the measured T_g of the NBR specimens' data. T_g is increased with the increase of sulfur content. The lowest sulfur content showed the highest chain flexibility (lowest T_g) for the specimens.

Crosslinking pulls the polymer chain closer. This reduces the free movement volume, and the flexibility of polymer chain in the rubber media is decreased. The flexibility of polymer chain is related to movement of carbon black filler in the rubber media. To investigate the flexibility of rubber media, rubber thermal properties were observed. The polymer chain flexibility of rubber media would make fillers move easier in the matrix for the filler containing system. The movement of the carbon fillers in rubber media seems to reduce the energy of acoustic wave propagation because the applied acoustic energy is trans-

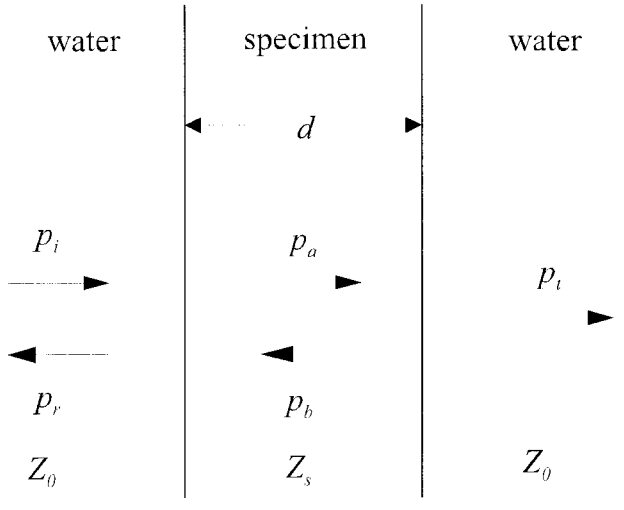


Figure 6 A schematic diagram of three-medium propagation model. p_i and p_r are the incident and reflected pressure waves, and p_a and p_b are the transmitted and reflected pressure waves in the specimen, respectively. Z_0 and Z_s are the characteristic acoustic impedances of water and specimen, respectively.

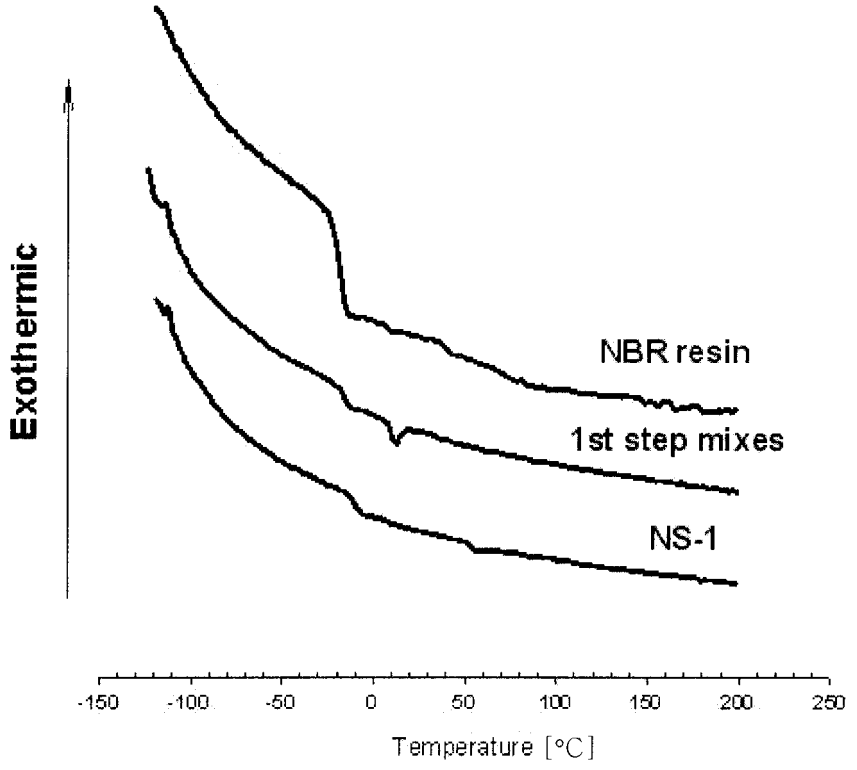


Figure 7 Representative DSC thermograms of the NBR.

formed to the movement of the carbon fillers itself. It is expected that the sound propagation becomes easier when the movement of the carbon black fillers is decreased in the rubber. Thus, an increase of crosslinking density with the sulfur content increase makes the movement of the carbon filler less. This makes the energy dissipation by flexibility low and the acoustic wave transmission[13] high.

CONCLUSION

In this article, we reported the acoustic property changes of NBR with increasing of sulfur content when carbon black filler was added. The variation of the sulfur content in the NBR specimen changed the mechanical properties such as crosslinking density and hardness. Even though the density variation with sulfur content was small, the hardness variation became high because of the crosslinking density change in the specimen. Because the increase in crosslinking density makes the free movement volume and the flexibility of polymer chain in the rubber media less, the sound speed and acoustic wave transmission may become higher. The variation of the sound speed was about 10 times as high as that of density. These results show that the mechanical properties of NBR can be nondestructively and accurately determined with the acoustic property measurement. It may be easier to utilize the NBR for underwater applications with the desired mechanical and acoustic properties such as acoustic transparent window, backing, and anechoic-coating material.

Table III Glass Transition Temperature of the NBR Specimen

Specimen	Raw NBR	First Stage Mixes	NS-1	NS-2	NS-3
T_g (°C)	−17.6	−16.4	−9.0	−5.2	−3.9

This work was supported by the Underwater Acoustics Research Center (UA-33) in Korea. Acrylonitrile rubber was kindly donated by Hyundai Petrochemical Co. Stearic acid, ZnO, sulfur, carbon black, crosslinking coagents (DM, TT, CM), and antioxidant (RD) were kindly supplied by Hankook Tire Co.

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