Carbon Black Effect on the Acoustic Properties of Nitrile Butadiene Rubber

Kyung-Il Jung,[1] Suk Wang Yoon,[1] Shi-Joon Sung,[2] Jung-Ki Park[2]

[1]*Department of Physics, SungKyunKwan University, Chunchun-dong, Changan-gu, Suwon, 440-746, Republic of Korea*
[2]*Department of Biomolecular and Chemical Engineering, Korea Advanced Institute of Science and Technology, 373-1 Guseong-dong, Yuseong-gu, Daejeon, 305-701, Republic of Korea*

Received 21 April 2003; accepted 14 April 2004
DOI 10.1002/app.20931
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Acoustic and mechanical properties of nitrile butadiene rubbers (NBR) with the variation of the carbon black contents were investigated. All the composition contents except carbon black were kept constant in the specimens. Acoustic measurements were performed in the frequency range of 300–800 kHz. Increase of the carbon black contents in the rubber resulted in an increase of the mechanical properties such as density, hardness, tensile strength, and glass transition temperature. The sound speed and attenuation in the specimen were mainly affected by the carbon black. The sound speed increased with the carbon black content and depended on the square root of the ratio of hardness to density. However, the sound attenuation was not affected by the carbon black content variation but by the existence of the carbon black. The results with carbon black content variation were also compared with those of the sulfur content variation having a fixed carbon black content (K. I. Jung et al., J Appl Polym Sci 85, 2764–2771, 2002). These results show that the variation of acoustic properties can be used to nondestructively evaluate mechanical properties and to estimate the carbon black content variation in NBR. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 678–683, 2004

Key words: nitrile butadiene rubber; acoustic properties; carbon black; nondestructive evaluation

INTRODUCTION

Studies on the acoustic properties of the polymeric materials have been attracted in the field of polymer physics by their abundant information related to polymer characterization in a nondestructive manner.[1,2] Acoustic analysis method can evaluate mechanical properties of complex composites with high accuracy. For example, acoustic measurements of rubber particles dispersed in the polymer matrix were reported to provide a toughened mechanism of rubber-toughened materials.[3,4] Acoustic analysis can be a powerful method, but there are few works in the acoustic property measurements of rubber except some reports on the relationship between composition and acoustic properties of the rubber itself.[5,6] Because rubbers in practical applications are complex composites that include raw rubber, filler, plasticizers, vulcanizing agents, and miscellaneous additives,[7] it is useful to understand the effects of various ingredients on the acoustic properties of the rubber.

Acoustic properties of nitrile butadiene rubber (NBR) with the content variation of vulcanizing agent sulfur were recently reported by Jung et al.[8] In their study, an increase of the sulfur contents resulted in the increase of the crosslinking density, and the increase of the sound speed and resulted in the increase of acoustic wave transmission.

In this study, the mechanical and acoustic properties of the NBR with constant sulfur content were measured with the carbon content variation. They are also compared with those of NBR with the sulfur content variation.[8]

EXPERIMENTAL

Materials

Stearic acid, ZnO, and sulfur were purchased from Aldrich (Milwaukee, WI). Dibenzothiazolydisulfide (DM) and tetramethylthiuramdisulfide (TT) as crosslinking coagents were obtained from TCI (Tokyo, Japan). Carbon black (HAF) and polymer of 2,2,4-trimethyl-1,2-dihydroquinoline (RD) as antioxidant were used. Carbon black (HAF) was provided from Hankock Tire Co. Ltd. (Darjun, Korea) and RD was provided from Kawaguchi Chemical Industry Co. Ltd. (Tokyo, Japan). Formulation of the NBR specimens[9] is shown in Table I.

NBR preparation

Rubber mixing was carried out by using an F-series Banbury mixer. The mixing procedure is divided into

Correspondence to: S. W. Yoon (swyoon@skku.ac.kr).

two steps. In the first step, carbon black is mixed with pristine NBR and, in the second step, crosslinking agent and coagents are mixed with the first-stage product mixture. The rubber mixes were vulcanized in a hydraulic press at 150°C. Vulcanization condition was determined previously by the viscosity change measurements.

Measurement of mechanical properties

The density of the NBR specimen was determined with the Archimedes principle at 25°C. Hardness of the specimen 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 tensile strength measuring instrument (Instron 4204) at the crosshead speed 500 mm/min following ASTM D412. Each value was averaged from five specimens.

Relative crosslinking density of the specimen 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

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

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.[9]

Measurement of glass transition temperature (T_g)

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 temperatures (T_g) of the NBR specimens were measured at the inflection point.

Measurement of acoustic properties

Four NBR specimens of 168 × 118 × 19.6 mm were prepared for acoustic properties measurements. One of the specimens was the control, without carbon black filler. Acoustic properties were measured by trough-transmission method.[10] The schematic diagram of the acoustic property measurement system is shown in Figure 1. 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 surface of specimen. Incident acoustic waves were generated by a transducer (Panametrics A301S or A302S) with a function generator (HP 3314A) and a power amplifier (ENI 2100L). The transmitted acoustic waves through the specimen were received by a transducer (Panametrics A301S or A302S) and analyzed by a digital storage oscilloscope (LeCroy LT322) with a wave-processing package.

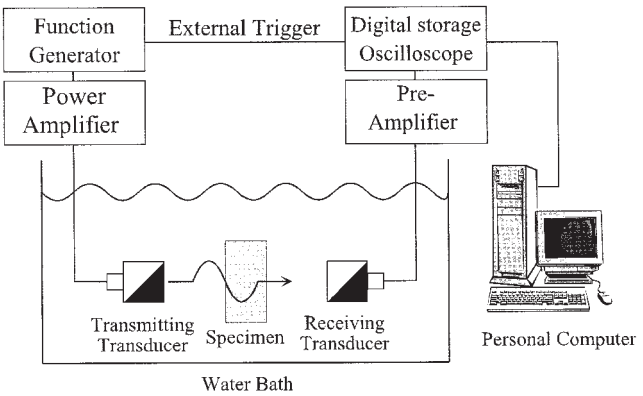

Figure 1 A schematic diagram of the acoustic property measurement system.

To investigate the frequency dependence of acoustic properties of NBR, acoustic measurements were carried out in the frequency range of 300–800 kHz. Because one transducer cannot cover all the operating frequency range, two pairs of transducers with the center frequencies of 500 and 800 kHz were used for measurements, respectively. The usable frequency range of the first pair of transducers was 300–600 kHz and that of the second pair of transducers was 500–800 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 carbon black contents

Properties of vulcanized rubber are affected by the various ingredients such as elastomer, vulcanizing agent, accelerator, reinforcer, plasticizer, and so forth. To investigate the effect of carbon black content variation in the NBR on the mechanical and acoustic properties, we modified the standard mixing recipe of the NBR (ASTM D3187-73). Table I shows the formulation of the prepared NBR. 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 lower than 0.2% of the total weight (2.1 kg). It means that all

TABLE I
Formulation of the NBR Specimens (phr)

	NC-0	NC-1	NC-2	NC-3
NBR	100	100	100	100
HAF	0	10	20	30
ZnO	5	5	5	5
St-acid	1.5	1.5	1.5	1.5
RD	1.5	1.5	1.5	1.5
Sulfur	2.0	2.0	2.0	2.0
DM	2.0	2.0	2.0	2.0
TT	2.0	2.0	2.0	2.0

RD: 2,2,4-trimethyl-1,2-dihydroquinoline; TT: tetramethylthiuram disulfide; DM: dibenzothiazoly disulfide.

the introduced carbon blacks are well distributed in the elastomer matrix.

As shown in Table II, density, tensile strength, and hardness increased with the increase of the carbon black contents. This is due to the reinforcing effect of carbon black in the NBR. Great improvement of tensile strength was observed. However, as shown in Table III, there was little change in the T_g between the presence and absence of the carbon black regardless of the carbon black contents. The variation of swelling ratio did not bring the change of glass temperature. Carbon black contents decrease the free-volume movement as shown in the change of swelling ratio. However, it is considered that the chain flexibility of rubber without carbon black is similar to the rubbers with carbon black by unchanged T_g. The decrease of swelling ratio with the increase of carbon black contents seems to be due to the presence of carbon black between the polymer chains and not due to the decrease of polymer chain–chain distance, itself.

Sound speeds in the NBR specimens with different carbon black contents

Sound speed was determined by the transmission 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 formula

$$c_s = \frac{d}{(d/c_w) - \Delta t} \tag{2}$$

TABLE III
Glass Transition Temperature of the NBR Specimens

Specimen	NC-0	NC-1	NC-2	NC-3
T_g (°C)	−13.5	−12.8	−12.9	−12.6

where c_s is the sound speed in the specimen, d is the thickness of the specimen, c_w is the sound speed in water at 20°C, and Δt is the flight time difference between time with and time without the specimen.

Figure 2 shows the sound speed variation as a function of acoustic frequency. The open symbol shows the sound speed in the controlled specimen without carbon black contents and the filled symbols show the sound speeds in the specimens with carbon black contents, respectively. The sound speed was increased with increasing the carbon black contents in the NBR. In Table II, the variations of density and hardness were around 3–5% and 8–9%, respectively. The variation of sound speed was 1–2%.

Figure 3 shows the relations of sound speed to density and hardness at 500 kHz. Sound speed depends on the square root of the ratio of modulus to density.[11,12] The sound speed can be dependent on the bulk and shear modulus of the specimen, and the hardness is correlated with the bulk and shear modulus. The variation of hardness is almost twice the degree of variation of density and the increases of hardness and density result in the increase of sound speed.[3]

The frequency dependence of sound speed was shown in Figure 4. Sound speed is different with frequency in the same hardness. These results show the NBR with carbon black is dispersive with frequency. However, the slopes of the sound speed variation to the hardness are almost the same in each frequency, even though the sound speed depends on the frequency. These results give the possibility of nondestructively estimating the variation of some mechanical properties by using sound speed measurement and predicting the carbon black content effect on the acoustic properties.

TABLE II
Mechanical Properties and Sound Speed of the NBR Specimens

Entry	Density (g/cm^3)	Hardness (Shore A)	Tensile strength (kg/cm^2)	Q (swelling ratio)	Sound speed at 500 kHz (m/s)
NC-0	1.030 ± 0.001	57 ± 0.7	36.3	95.5	1856.2
NC-1	1.080 ± 0.001	62 ± 0.8	60.6	84.0	1877.9
NC-2	1.112 ± 0.001	68 ± 0.6	102.7	78.7	1911.2
NC-3	1.142 ± 0.001	73 ± 0.7	143.4	74.1	1946.7

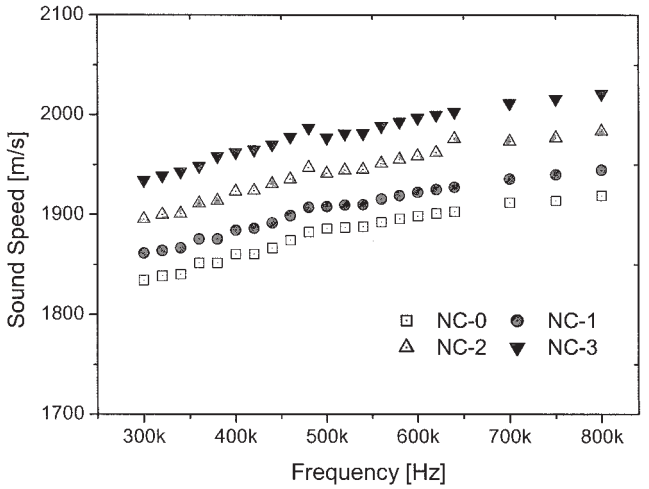

Figure 2 Sound speed as a function of acoustic wave frequency; sound speed of NC-0 (□), NC-1 (●), NC-2 (▲), and NC-3 (▼).

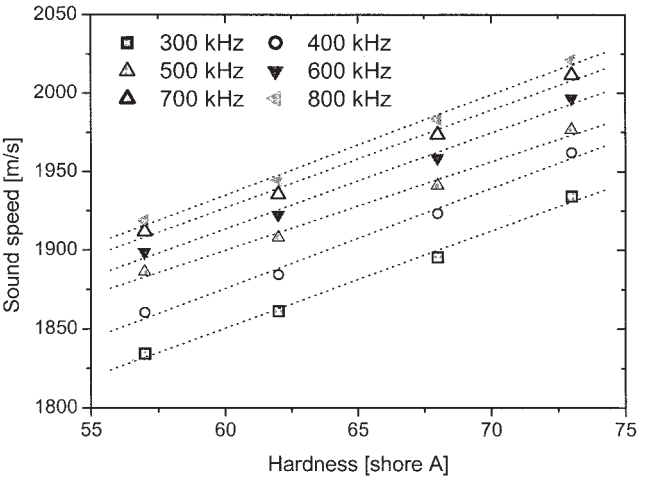

Figure 4 Sound speed as function of hardness at different frequencies. Sound speed at 300 kHz (■), 400 kHz (○), 500 kHz (▲), 600 kHz (▼), 700 kHz (△), 800 kHz (◀).

Acoustic wave transmission with different carbon black contents

Transmission coefficient, reflection coefficient, and attenuation were measured in the experimental setup shown in Figure 1. Acoustic pressure transmission coefficient T and reflection coefficient R are defined as

$$T = \frac{p_t}{p_i} \tag{3}$$

$$R = \frac{p_r}{p_i} \tag{4}$$

where p_i is the incident pressure wave and p_r and p_t are the reflected pressure wave and the transmitted pressure wave, respectively.

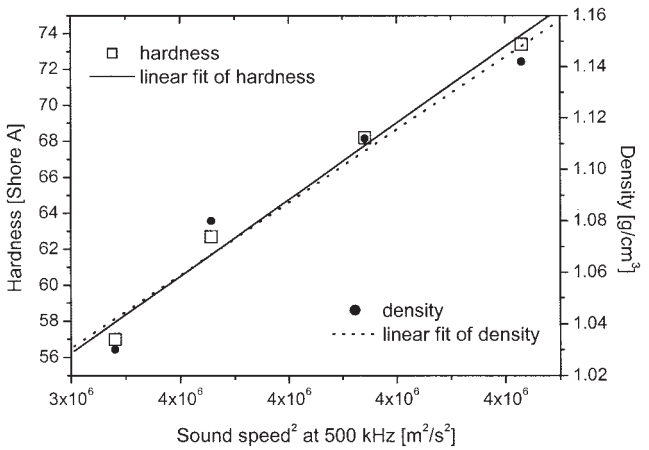

Figure 3 Density and hardness as a function of squared sound speed at 500 kHz; density (□) and hardness (●).

Attenuation α in the specimen can be determined from the transmission measurements with the formula

$$\alpha = 20\log\left(\frac{p_1}{p_2}\right)\frac{1}{\Delta d} \quad [\text{dB/cm}] \tag{5}$$

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

Figures 5 and 6 show the transmission coefficient and attenuation of the NBR specimens as a function of frequency. The acoustic wave transmission was increased with the increase of carbon black contents. However, the variation of transmission was not af-

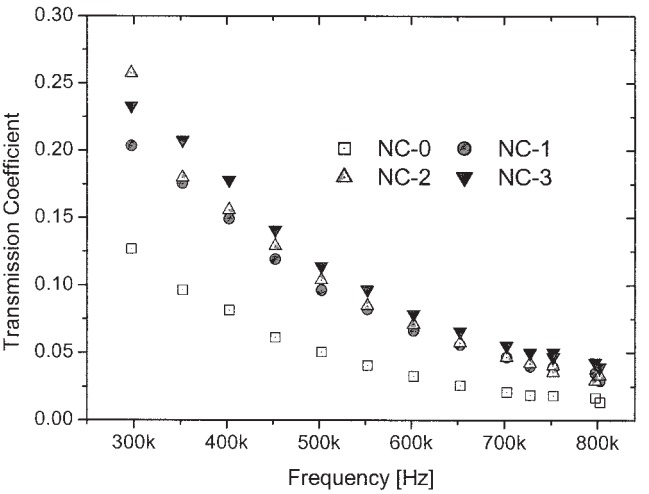

Figure 5 Acoustic transmission coefficient of the NBR specimens as a function of frequency; NC-0 (□), NS-1 (●), NS-2 (▲), and NS-3 (▼).

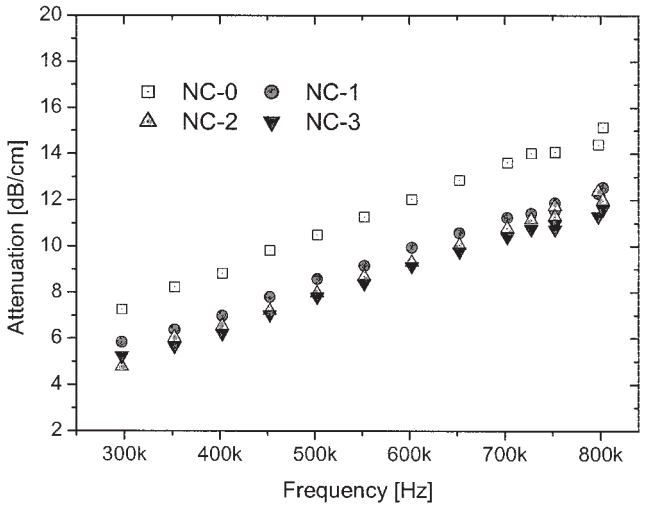

Figure 6 Attenuation of the NBR specimens as a function of frequency; NC-0 (□), NS-1 (●), NS-2 (▲), and NS-3 (▼).

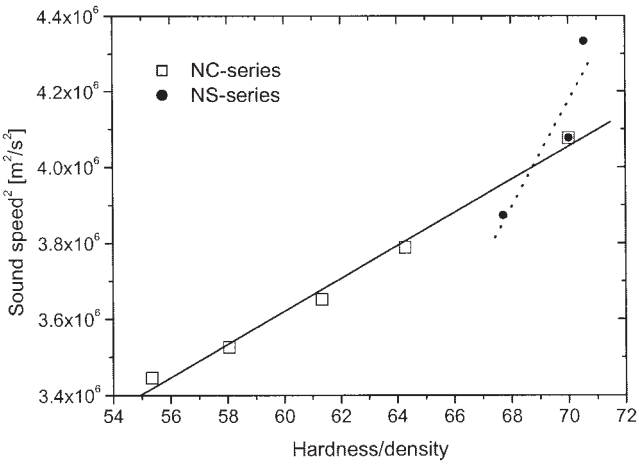

Figure 7 Squared sound speed variation of specimens as a function of hardness/density at 500 kHz; NC series (□) and NS series (●).

fected by the carbon black content variation but by the existence.

DISCUSSION

Table III shows the measured T_g of the NBR specimens. T_g is increased with the increase of carbon black content. However, the variation was small and not affected by the carbon black content variation but by the existence.

As shown in Table II, the increase of carbon black content decreases the free-volume movement in the polymer. The free-volume movement is related to the chain–chain distance. The chain–chain distance is related to the flexibility of polymer chain in the rubber media. To investigate the flexibility of rubber media, thermal properties of rubber were observed. The carbon filler also might be related to the free-volume movement. The movement of the carbon fillers in rubber media seems to reduce the energy of acoustic wave propagation because the applied acoustic energy is transformed 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. From the result of the T_g measurement, the flexibility was not changed with carbon black content. It was considered that the free-volume movement was not affected by the flexibility. These results show that the decrease of the free-volume movement is not due to the decrease of the chain–chain distance but due to the increase of carbon black content as the carbon blacks are placed between the polymer chains.

To qualitatively analyze the relations between mechanical and acoustic properties, we compared the results of the carbon black content variation with those of the sulfur content variation. Figure 7 shows the squared sound speed as a function of hardness/density, (s/ρ_s), where s and ρ_s are the hardness and the density of specimen, respectively. The open square symbols show the specimens of carbon black content variation (NC series) and the solid circle symbols show the specimens of sulfur content variation (NS series).[8] Both (s/ρ_s) dependences of the squared sound speeds of NC series and NS series show linearly increased trends, but the variations are clearly different. The variation of the NC series is smaller than that of the NC series. These results can be explained as the increase of the sulfur content directly decreases chain–chain distance, but carbon blacks are placed between chain and chain, so they indirectly decrease chain–chain distance. This could be also explained with the T_g. As shown in Table IV, T_g is increased with the sulfur content increase of the NS series. An increase of sulfur as a crosslinking agent directly decreases the chain–chain distance and the variation of sound speed is high. However, the T_g variation of the NC series was less affected by the carbon black content variation. Because the carbon blacks between polymer chains

TABLE IV
Glass Transition Temperature of NC-Series and NS-Series Specimens

Specimen	NC-0	NC-1	NC-2	NC-3	NS-1	NS-2	NS-3
T_g (°C)	−13.5	−12.8	−12.9	−12.6	−9.0	−5.2	−3.9

decrease the space between the chains, the carbon blacks decrease the chain–chain distance indirectly. Thus, the effect of carbon black on sound speed is smaller than that of sulfur. The sound speed variation can be correlated with the variation of a specific ingredient such as carbon black and makes feasible for estimating the mechanical properties of the NBR with specific content.

CONCLUSION

The acoustic property variations of NBR with an increase of carbon black contents and the relations between mechanical and acoustic properties were reported. The mechanical properties such as density, hardness, and tensile strength linearly depend on the carbon black contents in the specimens. Sound speed depends on the square root of the ratio of hardness to density. The acoustic transmission between presence and absence of the carbon black is clearly changed. However, there was little difference with the carbon black content variation. The variation of swelling ratio shows variations of the free volume in the rubber, but the T_g shows no change in the flexibility of polymer chain in the rubber media. The decrease of the free volume movement is not due to the decrease of the chain–chain distance, but to the increase of carbon blacks between the polymer chains. This result means that the small change of the acoustic wave transmission can be originated from the change of swelling ratio without T_g variation.

The mechanical and acoustic properties with carbon black content variation were also compared with those of the sulfur content variation. The variation of sound speed is smaller than the sulfur-cured series. From this result, the carbon black effect on the mechanical properties of NBR can be nondestructively estimated by the acoustic property such as sound speed. The acoustic properties with carbon black content also can be predicted by measuring the mechanical properties such as density and hardness. These results can make it easier to utilize NBR with desired mechanical and acoustic properties for the various underwater applications such as underwater acoustic window, backing, and anechoic coating materials.

This work was supported by the *Underwater Acoustics Research Center* (UA-33) in Korea (2002). The authors thank R&D Center of Hankook Tire Co. for supporting the preparation and characterization of NBR.

References

1. Desai, J. A.; Parsania, P. H. J Polym Mater 1996, 13, 79.
2. Van Krevelen, D. W. in Properties of Polymers; Elsevier Science: Amsterdam, 1990; Chapter 14.
3. Biwa, S.; Ito, N.; Ohno, N. Mech Mater 2001, 33, 717.
4. Koda, S.; Tsutsuno, N.; Yamada, G.; Nomura, H. J Appl Polym Sci 2001, 81, 2089.
5. Nolle, A. W. J Appl Phys 1952, 23, 888.
6. Horoshenkov, K. V.; Swift, M. J Appl Acoust 2001, 62, 665.
7. Barlow, F. W. Rubber Compounding; Principles, Materials, and Techniques; Marcel Dekker; New York, 1988.
8. Jung, K. I.; Yoon, S. W.; Cho, K. Y.; Park, J. K. J Appl Polym Sci 2002, 85, 2764.
9. Glazanov, V. E.; Mikhailov, A. V. Acoust Phys 2001, 47, 671.
10. Lee, K. I.; Roh, H. S.; Yoon, S. W. J Acoust Soc Am 2003, 115 (5), 2933.
11. Kinsler, L. E.; Frey, A. R.; Coppens, A. B.; Sanders, J. V. Fundamentals of Acoustics; Wiley: New York, 1982; Chapter 5.
12. Graff, K. F. Wave Motion in Elastic Solids; Dover Publishers: New York, 1991, Chapter 5.