HIGH FREQUENCY VISCOELASTIC PROPERTIES OF NANO PARTICLES-FILLED RUBBER COMPOUNDS BY ULTARSONIC MEASUREMENT

Tetsuya Kunizawa*, Qing-Qing Ni**
*Graduate School of Shinshu University, ** Shinshu University

Keywords: *Composite materials, Viscoelasticity, Ultrasonic wave, Friction, Tribology*

Abstract

In this paper, a viscoelastic measuring method by using the ultrasonic device at a high frequency range was proposed for rubber compounds. The measurable frequency is usually lower than 10^2 Hz by the conventional dynamic viscoelasticity method because of the limit of machinery, while it is possible to measure the viscoelasticity at high frequency of 10^6 Hz level or more in case of using the ultrasonic device. The viscoelastic properties by the dynamic mechanical analysis (DMA) and ultrasonic method were compared using several rubber samples. As a result, some differences are observed between these two methods. In addition, the maximum friction coefficient (Max-μ) at wet condition was investigated for several rubber samples and the relationship between Max-μ and $tan\delta$ was made clear. It is shown that ultrasonic viscoelasticity is very beneficial one for estimating frictional characteristics and physical properties in a high frequency region for rubber compounds.

1 Introduction

One of the important subjects for tire development from a viewpoint of safety is to shorten braking distance. Braking distance of a tire is strongly influenced by the friction behavior between tread rubber (the part of contact with road) and road surface. In many previous researches [1]-[4], it is reported that the friction behavior is related strongly with viscoelastic properties of rubber compounds. On the other hand, in practical use, the evaluation of frictional behavior with a simple and precision way is required at laboratory level without taking off tires [5]-[6]. When a tire is rolling, the frequency of vibration that the tread surface receives from the unevenness of an asphalt road surface is relatively high to be in megahertz range. However, in the conventional method of dynamic mechanical analysis (DMA), the measurable frequency is less than 10^2 Hz because of the limit of mechanical capability of equipment and then the viscoelastic properties at high frequency are predicted by temperature-time conversion rule, which may be one of problems for rubber compounds. Thus, the big difference of vibration frequency between practical use and experimental level should be focused in tire development. It is necessary to develop a new method to directly measure viscoelastic properties at high frequency and avoid the use of temperature-time conversion rule for practical convenience and reliability. So far, sound velocity and attenuation coefficient have been investigated using ultrasonic devices at high frequency for rubber compounds [7]-[11]. But the samples were measured in the liquid and there existed difficulties in simple characteristic and applicability. Omata [12] et al. and authors [13] measured ultrasonic properties by attaching rubber sample to the transducer directly and calculated the viscoelastic parameters for rubber samples at high frequency. It is indicated that the ultrasonic parameters have a good correlation with the friction characteristics.

In this paper, the further investigation on viscoelastic properties by both DMA method and ultrasonic wave method is conducted. Their results for some rubber composites at high frequency are compared. The friction coefficient at wet condition was also investigated and the relationship between the friction coefficient and *tanδ* are discussed.

2 Approach of Ultrasonic Viscoelasticity

In ultrasonic viscoelasticity, the attenuation coefficient and sound velocity for rubber samples were measured by the ultrasonic echo waves. Then, storage modulus (L'), loss modulus (L'') are calculated with complex theory of elasticity. The

$tan\delta$ is defined by the ratio of L''/L' designate as a parameter for viscoelastic appraisal. The measuring schematic of the ultrasonic device used in the experiments is shown in Fig. 1. The reflected waves (see Fig. 2) between buffer and air, buffer and sample surface and sample base and air are marked as U_{A0}, U_A and U_B, respectively. One of the reflected waveforms is shown in Fig. 3. The amplitude spectrum A_0, A, and B corresponding to the waveforms U_{A0}, U_A and U_B, respectively were obtained by Fast Fourier Transform (FFT). For the case of air complete reflection, the formulae of A_0, A, and B can be represented with the amplitude reflectance (R) between buffer and sample surface and attenuation coefficient (α) of a sample as follows.

$$A_0=U \qquad (1)$$

$$A=U \cdot R \qquad (2)$$

$$B=U(1-R^2)exp(-2h\alpha) \qquad (3)$$

where, U is the amplitude of incident wave including attenuation at inside of buffer and characteristics of reflection and transmission between transducer and buffer, h is sample thickness. The attenuation coefficient (α) is represented in following formula.

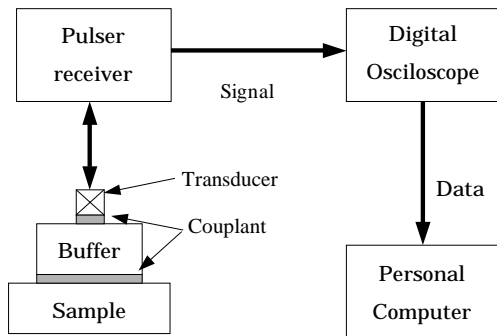$$\alpha=ln((A_0^2-A^2)/A_0B))/2h \qquad (4)$$

Fig. 1. Schematic of experimental device

Concerning sound velocity measurement, the group velocity calculated according to the propagation distance and time difference between the zero cross points or peaks of the surface reflected wave and base reflected wave is the simplest method. However, it is not suitable to use the group velocity because that the rubber materials have the characteristics of large attenuation and frequency dispersion. In this case, the phase velocity according to the phase difference in phase spectrum of the
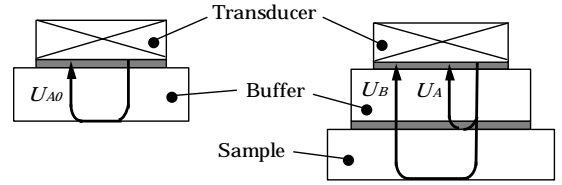

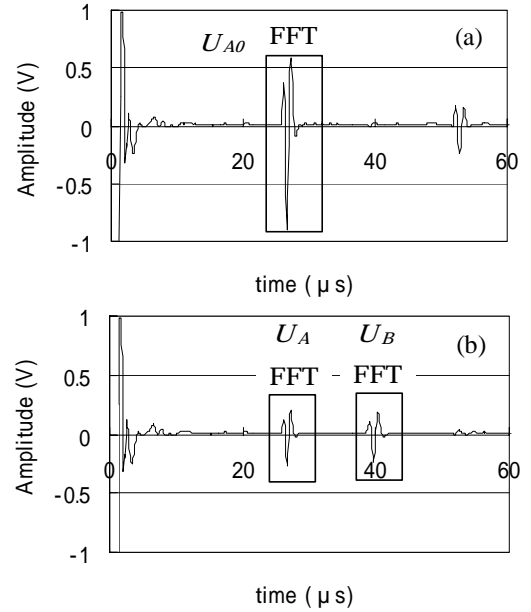Fig. 2. Reflected wave in the experimental model

Fig. 3. Reflected waves, (a) U_{A0}, (b) U_A, U_B and windows detection for FFT analysis

reference wave and the echo at a specified frequency is an effective parameter.

Phase velocity (V_P) is defined by the following formula (5), where, ω and κ are angular velocity and wave number, respectively. In the measurement, κ is expressed by formula (6) from the phase difference with a propagation distance.

$$V_P=\omega/\kappa \qquad (5)$$

$$\kappa=-\Delta\theta/2h \qquad (6)$$

Then, phase variation ($\Delta\theta$) due to the propagation distance can be calculated by the difference of phase spectrum θ_A and θ_B with the revision of the start time for FFT window cutting. If the difference of start time in FFT window of U_A and U_B is T, and then $\Delta\theta$ is represented by the formula (7) and V_P will be obtained as the formula (8).

$$\Delta\theta=(\theta_B-\omega T)-\theta_A \qquad (7)$$

$$V_P=2h\omega/(\theta_A-\theta_B+\omega T) \qquad (8)$$

Based on the above results and the complex theory of elasticity, the viscoelastic parameters of storage modulus (L'), loss modulus (L'') and $tan\delta$ (L'' / L') for the longitudinal ultrasonic wave in a wide medium can be obtained in formulae (9), (10) and (11), where supposing that $\alpha/V_P\omega \ll 1$ and ρ is density of sample.

$$L'=\rho V_P^2 \quad (9)$$

$$L''=2\alpha\rho V_P^3/\omega=2\alpha V_P L'/\omega \quad (10)$$

$$tan\delta=L''/L'=2\alpha V_P/\omega \quad (11)$$

3 Experimental

3.1 Rubber samples

The following three kinds of rubber samples were prepared using the materials that are generally adopted for tires. The content of carbon black (CB) or silica (Si) is changed while the kind of the polymer to styrene-butadiene rubber (SBR) is fixed, and the ratio of natural rubber (NR) to SBR is changed. The cure condition is 170 C° and 12 min.

3.2 Measurement of Dynamic viscoelastic property

DMA tests were conducted by using viscoelastic spectrometer (TYPE VES-F- made by IWAMOTO SEISAKUSHO). The thickness, width and length of a rubber sample were 2 mm, 4 mm and 40 mm, respectively. The gage length between the chucks was 30 mm. The temperature varied from -70 to 60 C° at the heating rate of 2 C° per min. The static strain, the dynamic strain and frequency were set as 10%, ± 0.5% and 10 Hz, respectively. In order to examine the viscoelastic characteristics at high frequency range, the master curve of $tan\delta$ using temperature-time conversion rule with base temperature (T_S) of Tg (glass transition point) + 50 C° was obtained. Tg was determined by the peak temperature in the $tan\delta$ curve. On the other hand, in order to investigate the influence of amplitude on the DMA results, in the measurement changing amplitude we measured by given the by the dynamic strain of ± 0.05, 0.1, 0.3, 0.5 and 1.0% were specified with accompanying the initial static extension of 10 % and the frequency of 10 Hz.

3.3 Measurement of ultrasonic viscoelasticity

The ultrasonic viscoelasticity instrument used for the measurement of ultrasonic echoes is the experimental model NC2 KA-EXTRA-URM0003 (OMRON Corporation). The sensor was contacted to rubber sample through a buffer and couplant. The amplitude spectrum of U_A and U_B from the boundary of sensor and rubber sample and the bottom of rubber sample, respectively, are shown in Fig. 2. Then the attenuation coefficient is obtained from the formula (4). The samples with different thicknesses (h) were also prepared for clarifying the measurable sample size. The measurement temperature was 25 C°.

3.4 Measurement of friction coefficient

The test pieces of cylinder type (outside-diameter 100 mm, inner 70 mm and width 20 mm) were fabricated for each sample. Measurement of friction coefficient was carried out using the flat belt friction tester (FR-5010) made by UESHIMA SEISAKUSHO. The pressure force 4 kgf, initial velocity 20 km/h and the slip ratio varying from 0 to 60 % are used in the test. The slip angle was 0°, and the safety walk (#240) was used to simulate the road surface. The water of 25 C° was supplied during testing. Each sample was measured eight times and the maximum friction coefficient (Max-μ) was calculated by the average of five times except the data for first time, the maximum and the minimum value. The general relation between friction coefficient (μ) and slip ratio is shown schematically in Fig. 4.
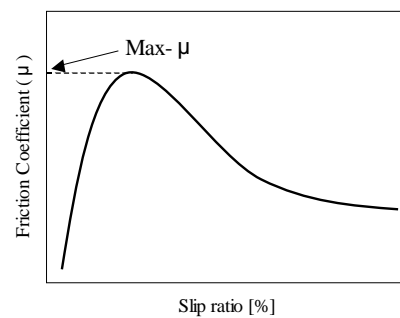

Fig. 4. Model of μ-S curve

4 Results and Discussion

4.1 Sample thickness

If the delay time of the reflected wave U_A and U_B is not enough these two waveforms may overlap and this will result in a difficulty for signal analysis. The delay time of two reflected waves depends on

the sample thickness directly. Here the thickness of rubber sample is changed with 1, 2, 5 and 10 mm to find out a suitable one (see Fig. 5). It is shown that the sample thickness over 5 mm is necessary for carving each reflected wave and a correct result of FFT analysis can be obtained. Thus, the sample thickness of 10 mm is adopted in the experiments afterward.

4.2 Amplitude dependence of *tanδ* in DMA

In order to compare DMA results in high frequency region with ultrasonic viscoelasticity, the temperature of DMA is usually converted into high frequency using the WLF formula (12). It is known that WLF formula is applicable regardless of polymer type in many macromolecule solids. The WLF formula has also been the rubber composites with fillers [2]-[4]. C_1 and C_2 in WLF formula (12) are constant with the values of 8.86 and 101.6, respectively. These values can be used when T_S is Tg + 50 ($\pm$ 5) C°. Since the amplitude of vibration in ultrasonic viscoelasticity is very small compared with DMA, it is necessary to investigate the influence of the amplitude on the elastic property. The *tanδ* curves with different strain amplitudes are shown in Fig. 6. Although it is only limited within the DMA test conditions there is no obvious shift of frequency peak in *tanδ* curves due to the variation of amplitude. Therefore, for the WLF conversion there may be no necessity to take into consideration of the amplitude.

$$log\alpha_T = -C_1(T-T_S)/(C_2+T-T_S) \qquad (12)$$

4.3 Comparison of DMA and ultrasonic viscoelasticity

The *tanδ* measured by DMA and ultrasonic viscoelasticity for different contents of CB, Si or ratios of NR to SBR are shown in Fig. 7, 8 and 9, respectively. The *tanδ* of DMA in the high frequency region is obtained by converting the temperature change to frequency shift according to the WLF formula (12). In these figures, the *tanδ* increased with an increment of frequency in both of DMA and ultrasonic viscoelasticity in the megahertz region. This tendency is considered to be appropriated since Tg is near - 30 C° and the peak *tanδ* will be in the higher frequency side due to -20 C° roughly corresponding to 1 MHz from formula (12).

In Fig. 7, *tanδ* of ultrasonic viscoelasticity tends to increase with the increment of CB fillers, but for *tanδ* of DMA, this tendency is not obvious.

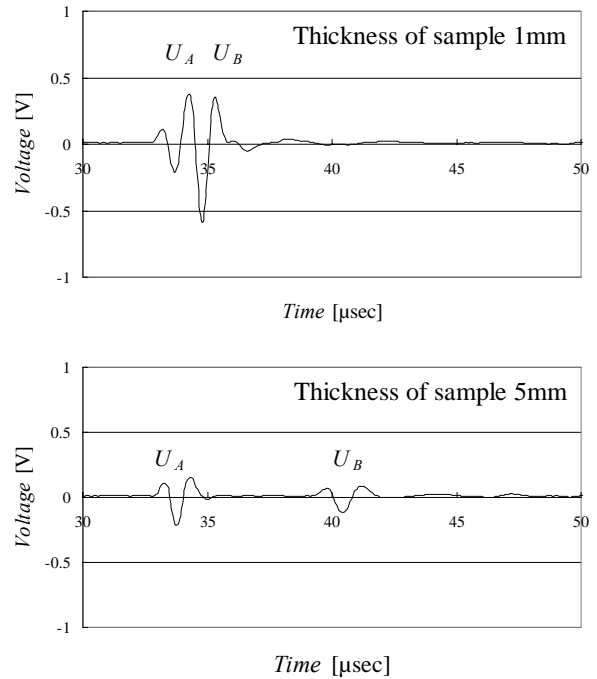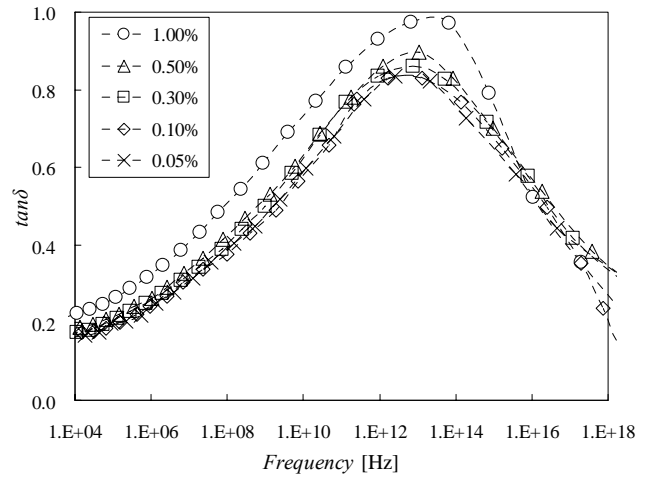Fig. 5. U_A and U_B in the different thickness of samples

Fig. 6. Master curve of *tanδ* changing amplitude

When changing the content of Si as shown in Fig. 8, the dependence of *tanδ* on Si contents is just similar to that of CB. On the other hand, *tanδ* tends to increase in both of ultrasonic viscoelasticity and DMA as the ratio of SBR increases, which is different from the influence of CB or Si fillers (see Fig. 9).

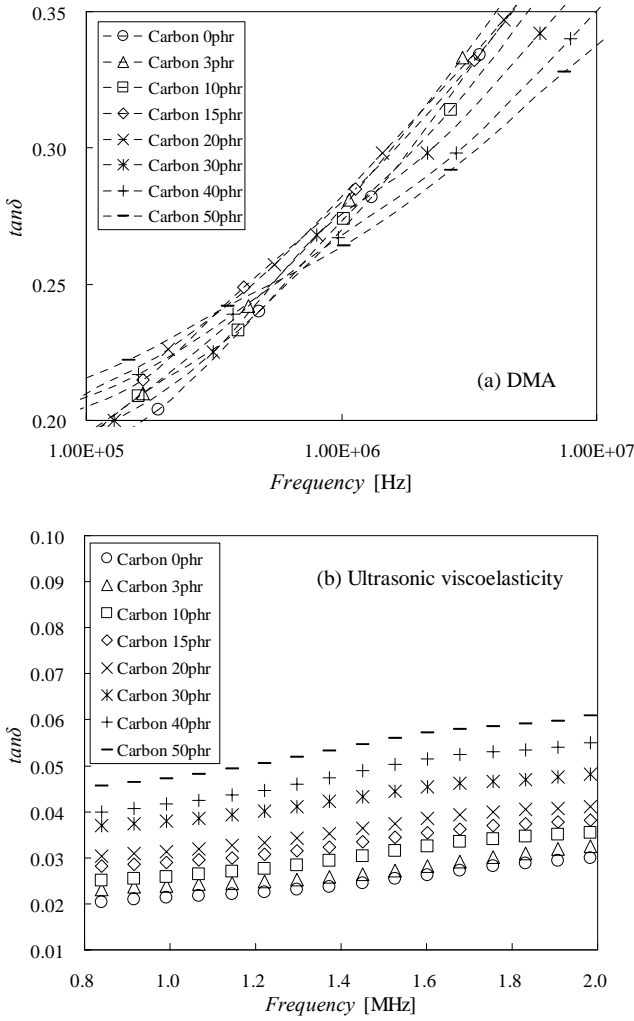It is thought that both of the characteristics of polymer itself and the interaction between polymer

Fig. 7. *tanδ* behavior for (a) DMA and (b) ultrasonic viscoelasticity in the sample with different CB contents at high frequency

Fig. 8. *tanδ* behavior for (a) DMA and (b) ultrasonic viscoelasticity in the sample with different Si contents at high frequency

and filler have affected the viscoelasticity. Since the diameter of primary particle of fillers is about 20 nm, the range of the interaction between polymer and fillers is expected as nano-order. Thus, it is considered that contribution of the interaction between polymer and fillers in the viscoelastic characteristics becomes large in micro deformation. In this experiment, the vibration strain of rubber sample in DMA is in milli-order, but it is considered that the strain in ultrasonic viscoelasticity is in micro- or nano-order [12], therefore it is thought that DMA shows the characteristics mainly resulted from the whole rubber, while ultrasonic viscoelasticity reflects the influence of the interaction between polymer and fillers more strongly rather than DMA. This may be the reason for the difference in these two methods. On the other hand, in Fig. 9, since not
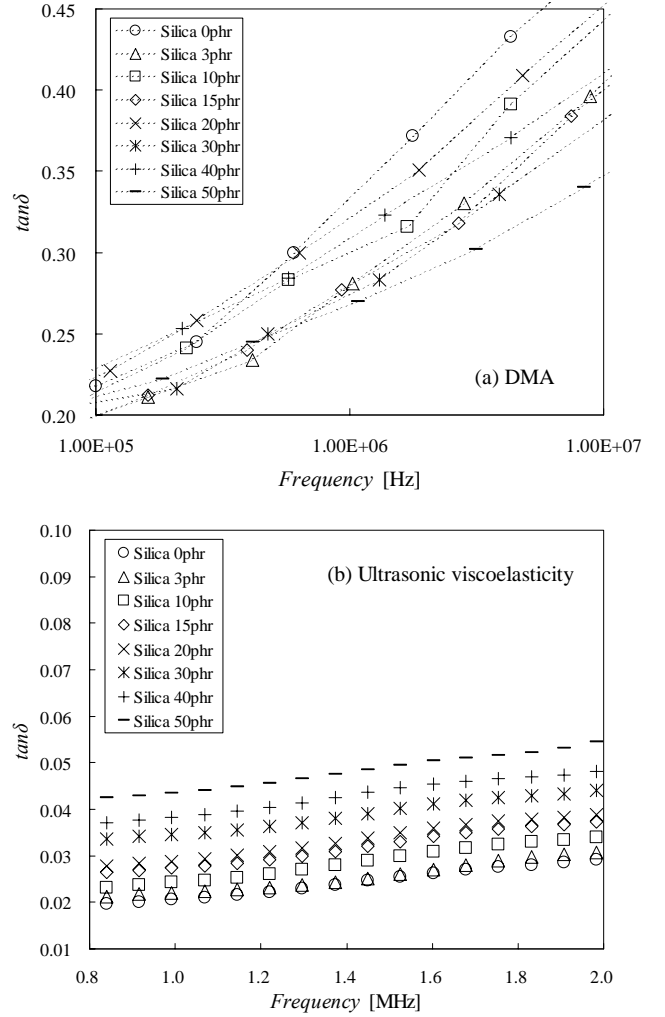
filler but polymer is changed, the same tendency is shown in both of DMA and ultrasonic viscoelasticity.

4.4 Relation between Max-*μ* and *tanδ*

Relationship between the *tanδ* measured by DMA and ultrasonic viscoelasticity and Max-*μ* at wet condition for three kinds of samples (CB, Si, polymer) is shown in Figs. 10 and 11. In Fig. 10, the *tanδ* of DMA is the value at 1MHz that calculated by interpolating Figs. 7 (a), 8 (a) and 9 (a). The *tanδ* in ultrasonic viscoelasticity is also the value at 1MHz (Fig. 11). It is evident that Max-*μ* can be estimated using the *tanδ* by ultrasonic viscoelasticity better than by DMA irrespective of the kind of polymer or fillers. Especially, in the samples with different contents of fillers, a good correlation
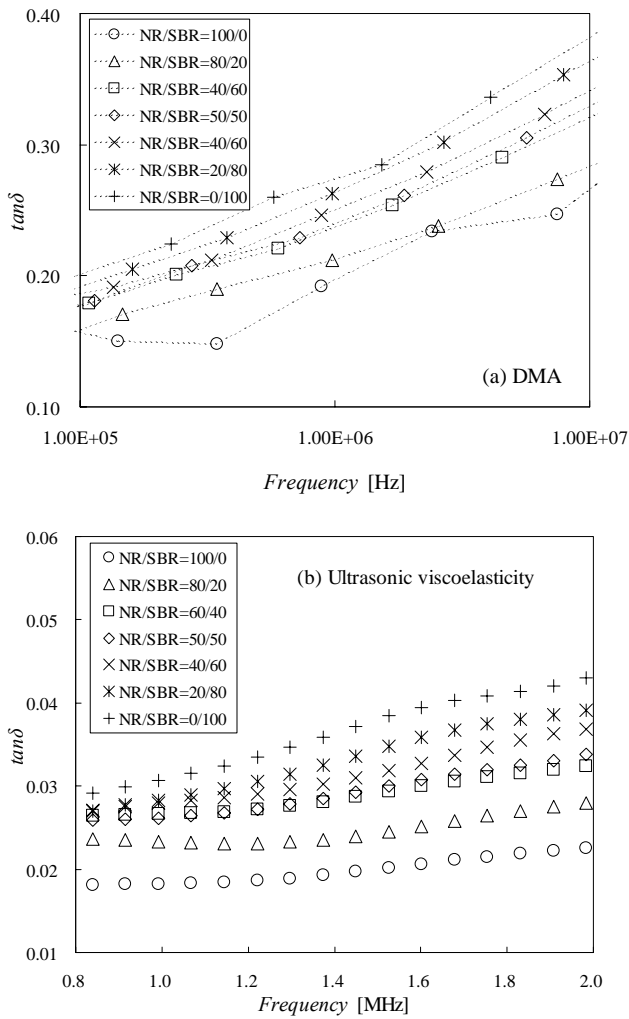
Fig. 9. *tanδ* behavior for (a) DMA and (b) ultrasonic viscoelasticity in the sample with different ratio of NR and SBR at high frequency

Fig. 10. Relationship between Max-*μ* and *tanδ* of DMA at the value correspond to 1 MHz

between Max-*μ* and *tanδ* is observed.

The vibration that rubber sample receives from the unevenness of the road surface is high frequency. And in this experiment, when the filler content or filler type changed, the interaction between polymer and fillers would also change. From these two points, it is considered that the ultrasonic viscoelasticity measurement is more suitable for estimating Max-*μ* since the characteristics can be expressed more exactly than DMA.

In general, the friction characteristic is explained from two terms, hysteresis friction and adhesion friction. Because *tanδ* is contributed by the hysteresis, the adhesion term of Max-*μ* is expected by the extrapolation of *tanδ* to be zero in Fig. 11. The value for the extrapolation was 0.81 and constant. The reason for the term of adhesion being constant is due to that the effect by changing the kind of rubber samples on adhesion is small since
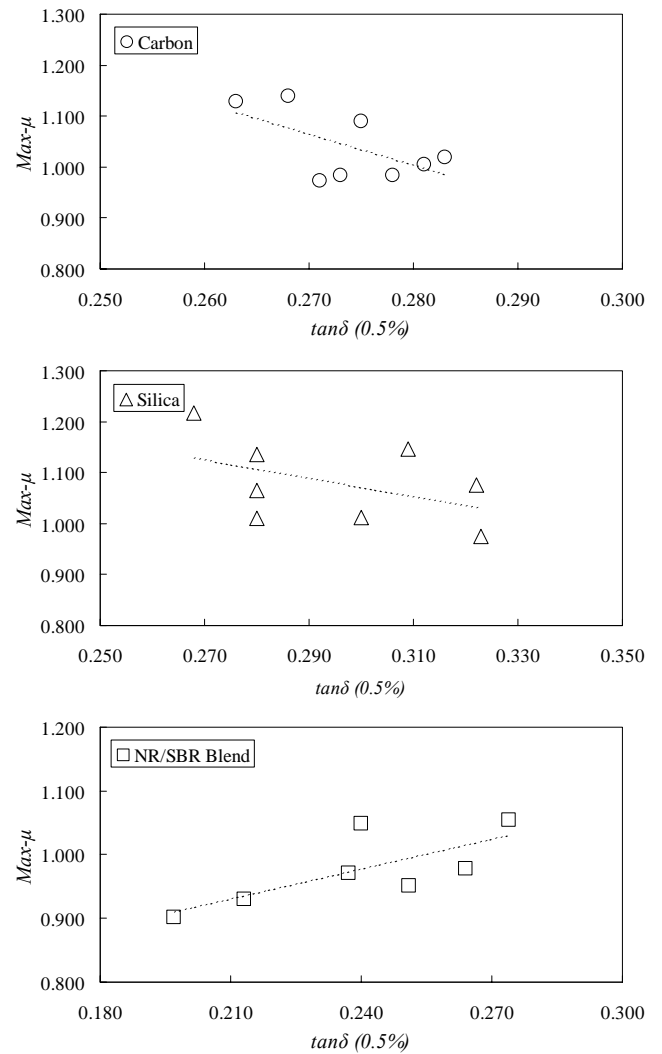
water always exists between rubber sample and road surface.

5 Conclusions

In this research, we tried to measure the viscoelastic characteristics at high frequency that was difficult in the conventional DMA. The rubber compounds with different filler types, filler contents and ratios of NR and SBR were fabricated. In the conventional DMA measurements, the temperature varied and high frequency property was calculated by using the WLF formula. At the same time, the samples were measured by the direct method of ultrasonic viscoelasticity. The *tanδ* in DMA and ultrasonic measurements was compared at the high frequency range of megahertz level. It was found that the viscoelastic behavior in DMA and ultrasonic
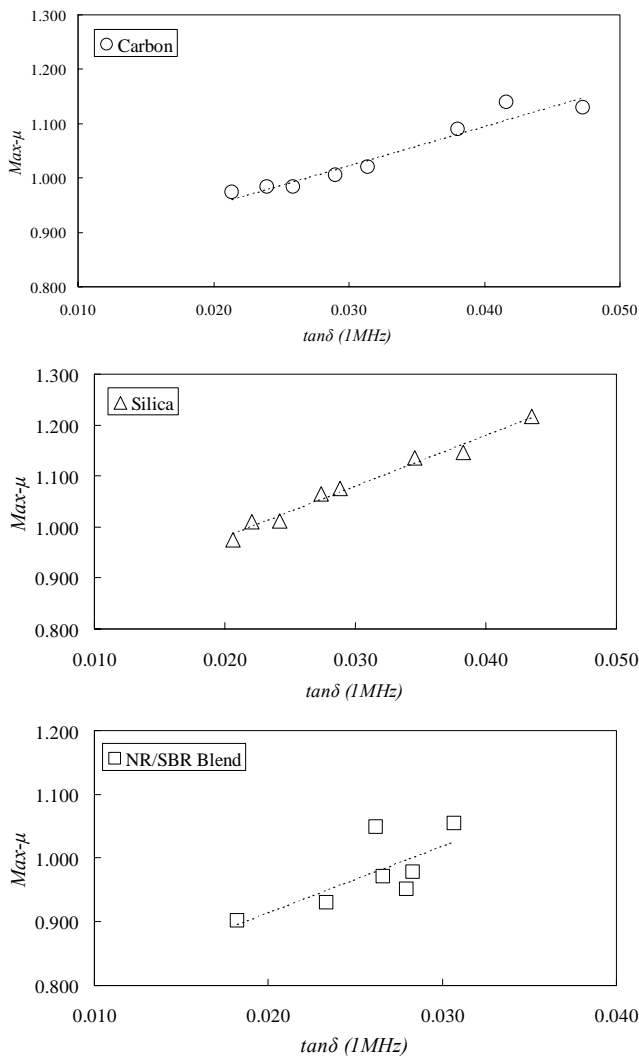
Fig. 11. Relationship between Max-μ and $tan\delta$ of ultrasonic viscoelasticity at 1 MHz

measurements differs for the rubber compounds with fillers of CB or Si. The reason for this difference was discussed from the vibration amplitude and the interaction between polymer and fillers. Based on the various observations, it is shown that the phenomenon, which may be unobservable with conventional DMA, can be caught by using ultrasonic viscoelasticity. In addition, the relationship between Max-μ at wet condition and $tan\delta$ in DMA and ultrasonic measurements was investigated as one of the applications for the ultrasonic viscoelasticity. It is found there exists a good correlation between Max-μ and ultrasonic $tan\delta$. It is suggested that the ultrasonic viscoelasticity as direct measurement will be a useful way for evaluating friction and viscoelastic characteristics of rubber compound at high frequency.

References

[1] Saito Y. "New Polymer Development for Low Rolling Resistance Tyres". *Kautschus Gummi Kunststoffe*, Vol. 39, No.30, pp 30-32, 1986.

[2] Amino N. et al. "Studies on the Friction Mechanism of Silica-Filled and Carbon Black-Filled SBRs - Friction on a Dry Surface -". *Journal of the Society of Rubber Industry, Japan*, Vol. 74, No.3, pp 110-115, 2001.

[3] Amino N. et al. "Studies on the Friction Mechanism of Silica-Filled and Carbon Black-Filled SBRs, Part 3. The Friction of Carbon Black-Filled and Silica-Filled SBR Blends". *Journal of the Society of Rubber Industry, Japan*, Vol. 75, No.1, pp 32-38, 2002.

[4] Amino N. et al. "Studies on the Friction Mechanism of Silica-Filled and Carbon Black-Filled SBRs". *Journal of the Society of Rubber Industry, Japan*, Vol. 77, No.5, pp 173-179, 2004.

[5] Muraoka K. "Viscoelastic properties for tyre rubber compounds (in Japanese)". *Journal of the Society of Rubber Industry, Japan*, Vol. 74, No.6, pp 242-247, 2001.

[6] Kawakami A. et al. "Prediction of braking distance temperature dependence through bench test". *Preprints of Meeting on Automotive Engineers*, No.71, pp 13-18, 2004.

[7] Gendron R. et al. "Ultrasonic behavior of polymer blends". *Polymer Engineering and Science*, Vol. 35, No.1, pp 79-91, 1995.

[8] Gerspacher M. et al. "High frequency viscoelasticity of carbon black filled compounds". *Rubber Chemistry and Technology*, Vol. 69, No.5, pp 786-800, 1996.

[9] Youssef M. H. "Influence of sulfur content and curing time on the glass transition parameters in SBR Vulcanizates: an ultrasonic study". *Polymer Testing*, Vol. 22, pp 235-243, 2003.

[10] Eckert-Kastner S. et al. "Investigation of the dynamic high frequency properties of elastomers using an ultrasonic spectrometer". *Kautschus Gummi Kunststoffe*, Vol. 57, No.9, pp 423-429, 2004.

[11] Manneville S. et al. "High-frequency ultrasonic imaging: A spatio-temporal approach of rheology". *Colloids and surface A: Physicochem. Eng. Aspects*, Vol. 270, pp195-204, 2005.

[12] Omata N. et al. "High frequency dynamic viscoelasticity measuring method for frictional characteristics evaluation of rubber roller for paper handling (Part 2)". *Journal of Japanese Society of Tribologists*, Vol. 50, No.3, pp 238-245, 2005.

[13] Kunizawa T. et al. "Viscoelastic properties at high frequency and wet friction behaviour of carbon black and silica filled rubber compounds". *Transactions of the Japan Society of Mechanical Engineers (A)*, in press.