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“High-Frequency Viscoelastic Properties of Filled Polymer Blends”

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ABSTRACT

It has been reported that the wet traction of tires is associated with the high-frequency viscoelasticity of tire compounds.. An automated acoustic spectrometer was built to measure the high-frequency viscoelastic properties of filled blends of BR/NR and blends of SBR/BR. Effects of carbon black loading, polymer blend composition, blend system, and mixing technique on the high-frequency viscoelasticity of rubber vulcanizates were studied. The behavior of compositional dependence of α_L at room temperature depends on the miscibility of polymer blends system studied. The α_L of filled BR/NR blends as a function of temperature appears to follow linear additive rule with blend composition. For filled SBR/BR blends, α_L was found to have a negative deviation from linearity with blend composition. The mixing technique used was found to have only a small effects on the attenuation coefficient of filled SBR/BR blends.

INTRODUCTION

Tires under use are subjected to dynamic deformations at various frequency, strain, and temperature. The deformation of rolling of a tire is in the range of 60 Hz of frequency and 20 % strain. However, during braking, the deformation of tread is in the range of MHz but at relatively low strains, considering the speed of a vehicle being as fast as 100 Km/h and the aperture of road surface being as small as 1 mm. It is well recognized that to obtain information that can be related to the performance of tires, the test conditions used are to match the application conditions as close as possible. Because of the limitation of frequency attainable in dynamic mechanical testing, time temperature superposition principle is often used in order to broaden the frequency range.

However, for filled rubbers, filler network is dominant, as compared with polymer network, in determining the low-strain dynamic mechanical properties at temperatures far above the glass transition temperature of the polymer matrix. As a result, the time temperature superposition principle is generally considered not applicable to filled rubber. One approach to attaining high-frequency deformation is the use of acoustic wave, typically in the frequency range of 1 K to 10 M Hz. The deformation of specimen subjected to acoustic wave is as low as 10^{-9} m.

Both immersion bath and direct coupling methods can be used for the measurement of acoustic properties of rubbers. Immersion bath method has the advantage that the reflected acoustic energy at medium-specimen interface can be taken into account by using specimens with various thickness. The calculation of dynamic storage and loss moduli of the material from the acoustic measurement has been

developed. Both shear wave and longitudinal waves can be used. However, shear wave does not propagate at temperature far above the glass transition temperature of polymer.

The acoustic spectrometer has been used extensively for the study of thermal and dynamic characteristics of unfilled polymers. Very few studies on acoustic attenuation of filled polymers were made. In a recent study by Nikiel et. al. , effects of carbon black type, carbon black loading, degree of curing of polymer matrix and of filler dispersion, on acoustic properties of filled rubbers, particularly at room temperature, were investigated. It was found that the longitudinal attenuation coefficient of filled rubbers at room temperature was quite independent of grade of carbon black used, but increases with increasing carbon black loading, degree of curing of polymer matrix , and to a less extent, degree of filler dispersion. This has been attributed to the increased filler-polymer interface and immobilized polymer chains.

For polymers investigated in the previous study, the temperature at which the longitudinal attenuation coefficient, α_L , has a maximum , referred to as $T_{\alpha_L\max}$ or $T_{g\ 1\text{ MHz}}$ was found to be higher by about 40 C than the Tg obtained with differential scanning calorimetry (DSC), which is in the time scale of 50 Hz range. As compared with unfilled rubber, the $T_{\alpha_L\max}$ for filled rubbers was reported to shift to a higher temperature and the degree of which increases with increasing filler-polymer interaction.. In addition, the broadness of the peak of attenuation coefficient vs. temperature curve was found to increases with increasing polymer- filler interaction.

It was shown that for a given tire design, the wet traction of tires, in particular on a rough surface such as macadam, correlates fairly well with the high-frequency viscoelastic properties of tread compounds, i.e. attenuation coefficient α_L at 1 MHz and room temperature . The correlation is improved with increasing vehicle speed.

As polymer blends are often used in tires, it is of importance to develop an understanding of high-frequency viscoelastic properties of polymer blends. The objective of the present work is to study effects of carbon black loading, polymer blend system , and mixing technique on the high-frequency viscoelastic properties of filled rubbers at a wide temperature range. Focus is placed on the compositional dependence of high-frequency viscoelastic properties, i.e., attenuation coefficient for blend systems with different miscibility and on the effect of mixing technique on the attenuation coefficient.

EXPERIMENTAL

The attenuation coefficient of rubber compounds was measured by immersion method. In this method, the intensity of acoustic wave after passing the immersion liquid, the specimen, and then immersion liquid, was measured for specimens of various specimens. The attenuation coefficient was calculated from the slope of logarithm of intensity versus thickness by using the Bear's law.

For this study, an immersion bath chamber, 150 by 200 by 250 mm in dimension was built. Two acoustic transducers manufactured by Mattech were used, one as the

pulsar and the other as the receiver. These transducers have a relatively broad band with the maximum intensity at about 1 MHz and the full width at half height (FWHH) is about 0.82 MHz. The acoustic transducers are located near the bottom of the chamber. A rotating sample holder with six cavities was used to accommodate specimens with different thickness and was attached to a stepping motor. Two temperature probes were used, one for controlling and the other for measuring specimen temperature. Liquid nitrogen was used for cooling and electrical cartridge heaters were used for heating the medium and specimens. Ethylene alcohol was used as the coupling medium in order for the measurement to be conducted at a wide temperature range. The experimental setup is shown schematically in Figure 1.

Cylindrical specimens with diameter of 35.1 mm and thickness ranging from 2 to 12 mm were used.. Specimen to be measured was first rotated to a position in line with transducers. Measurements were made from -90 to 60 °C at a heating rate of 0.5 °C/min. The specimens were first cooled to -90 °C, and maintained at this temperature for 30 min to ensure that thermal equilibrium is reached. To stabilize the signal after the rotation of sample . a 10 sec delay was used before taking the measurement. Both the signal of acoustic wave as measured by the receiver and the temperature of specimen were acquired by using a Tektronix Digital Oscilloscope (TDS 524A) with a sampling rate of 100 MHz. Fast Fourier transform (FFT) was used to convert the signal from time domain to frequency domain and the area under the curve at frequency domain was used as the intensity. The acquired data from the oscilloscope was then sent to and stored in the computer via the GPIB IEEE488. The details of experimental technique used was well documented in the previous paper

Polymer blend systems studied are blends of butadiene rubber (BR, **** Budene 1201) and natural rubber (NR, ***) and blends of styrene-butadiene copolymer (SBR, DSM Copo 1500) and BR (Budene 1201) at various blend composition. Both unfilled and N234 carbon black filled polymer blends were used. Carbon black loading used ranges from 0 to 50 phr. Formulation of compounds used were ASTM D3191 except for the carbon black loading. Both natural distribution (ND) and forced distribution (FD) techniques were used for preparing the filled polymer blends. For the ND, the two constituent polymers together with carbon black were introduced into the mixer in the beginning of mixing. For the FD, the filled homopolymer polymer were mixed first and then two filled homopolymers were blended with a two-roll mill for 3 min to homogenize the mixture .

Two-stage mixing was used for compounding. In the first stage, all ingredients except curatives were mixed. The mixing was conducted with an internal mixer, Haake Rheocord System 90, at a starting temperature of 50 °C and a rotor speed of 50 rpm for 5 min. In the second stage, curatives were mixed with compounds at a starting temperature of 25 °C and a rotor speed of 30 rpm for 3 min. The t'90 of compounds was obtained with Monsanto Rheometer at 160 °C. Curing conditions used were 160 °C and t'90 +20%.

In addition, the dynamic mechanical properties of polymer blends were measured with Rheometric Scientific Advanced Rheometrics Expansion System (ARES) in torsion rectangular mode. Specimen geometry used was approximately 2 X 10X 25 mm.

Measurements were taken in temperature sweep mode from -120 to -40 C at a heating rate of 1 C/min. The frequency and strain used were 1 Hz and 0.5 %, respectively.

RESULTS AND DISCUSSION

The morphology of unfilled polymer blends depends on the blend composition, processing conditions, rheological properties of constituent component, and thermodynamic miscibility of blend system. Depending on the blend composition, either one phase forms the continuous phase and the other the discrete phase or co-continuous phases may exist. For filled polymer blends, the distribution of filler between polymer phase and the dispersion of filler in individual phase plays a role in determining the physical/mechanical properties. The results of BR/NR blends will be reported first, followed by those SBR/BR blends.

BR/NR Blends

The loss modulus G'' as a function of temperature for the unfilled BR/NR blends is given in Figure 2. The temperature at which G'' has a maximum, referred to the glass transition temperature T_g , is found to be about -100 °C for unfilled BR homopolymer and -60 °C for unfilled NR homopolymer. It can be seen in Figure 2 that there exist two discernible glass transitions for unfilled blends at all blend ratio investigated, indicating that unfilled BR/NR blends are immiscible.

The α_L as a function of temperature for unfilled BR/NR blends is given in Figure 3. There, it can be seen that the temperature at which α_L has a peak, referred to as, $T_{g_{1Mz}}$, is about -60°C for unfilled NR and -20°C for unfilled BR. The peak tends to be broader for unfilled blends than for unfilled homopolymers. For the NR rich unfilled blends studied, the α_L has a peak at about -20°C , corresponding to the $T_{g_{1Mz}}$ of unfilled NR, and the value of the peak decreases with increasing volume fraction of BR. The α_L vs. temperature curves of unfilled blends shows a shoulder at low temperatures and become broader, being attributable to existence of the glass transition of BR phase.

Figure 4 shows the calculated α_L for unfilled blends as a function of temperature from the data of unfilled homopolymers by using the linear additive rule of blend composition. Although the absolute values of calculated α_L do not agree well with experimental data, the features of the curves appear to be similar to those of experimental results. The calculated maximum value of α_L of NR rich unfilled blends agrees with experimental data. This may suggest that the contribution of interface between NR and BR phases to the acoustic attenuation due to differences in impedance between phases as compared to the weighted sum of BR and NR phases.

The plot of α_L vs. temperature for filled BR/NR blends prepared with forced distribution technique is shown in Figure 5. As found with unfilled polymer blends, NR rich filled BR/NR blends exhibit a peak at around -20°C and a shoulder at lower temperatures. Similar to the results found with the unfilled BR/NR blends, the calculated α_L based on linear additive rule as a function of temperature for filled BR/NR, as shown in Figure 5, appear to agree with experimental values. It is interesting to note that the

BR/NR=80/20 blend has a wide peak which in essence consists of peaks of NR and BR phases. The reason for the greater discrepancies found between experimental peak value and the calculated peak value for this blend composition than for BR/NR blends at other blend composition is not clear.

It has been reported that the attenuation coefficient at room temperatures increases with carbon black loading and then levels off, and to a less extent with degree of filler dispersion as varied by mixing time. This can be attributed to the increased interphase of filler and polymer matrix. In addition, for filled polymer blends, uneven filler distribution between polymer phases often exists, thereby affecting the attenuation coefficient of filled polymer blends. The use of forced distribution technique to prepared filled polymer blends is expected to minimized the extent of uneven filler distribution.

For filled polymer blends with a wide differences in attenuation coefficient of between the filled constituent homopolymers, it is expected that the attenuation coefficient of the blend depends in large part on blend composition per se rather than phase morphology, polymer interfaces, and possible uneven filler redistribution due to filler migration between phase. The nearly linear dependence of α_L on blend composition observed in Figure 6 for BR/NR blends filled with various loading of N234 further demonstrates this

SBR/BR Blends

Unlike the unfilled BR/NR blends, the unfilled SBR/BR Blends exhibit a single peak in the plot of loss modulus versus temperature, as given in Figure 7, except for BR rich blend, suggesting that the SBR/BR blend system studied is partially miscible.

The α_L versus temperature plot for unfilled SBR/NR blends is given in Figure 8. There, it can be seen that there exists a single peak and the peak is broader for the blends than for the homopolymers. In contrast to the unfilled BR/NR blends, the temperature at which α_L has a peak increases with increasing volume fraction SBR for SBR/BR blends as found in the glass transition temperature from loss modulus as a function of temperature shown in Figure 9.

Similar results can be found for filled SBR/BR blends as shown in Figure 10.

In addition, it can be seen in Figure 11 that the calculated attenuation coefficient obtained by using linear additive rule for blend composition do not agree well with the experimental data for filled SBR/BR blend, particularly at temperatures near the peak. As this blend system appears to be partially miscible and the glass transition temperature of the blend varies with blend composition, it is not surprising that the attenuation coefficient of the blend does not follow the linear additive rule with blend composition. This behavior can be more clearly observed in the plot of α_L versus blend composition for both unfilled and filled SBR/BR blends, as shown in Figure 12. This is mainly associated with the fact that as the SBR concentration of the blend is increased, there is a steeper change in attenuation coefficient of blend with temperature at room temperature, resulting from the increased $T_{g \ 1 \text{ MHz}}$ of the blends with increasing SBR concentration.

Moreover, the FD and ND mixing techniques give comparable values in α_L for SBR/BR blends.

SUMMARY AND CONCLUSION

High-frequency viscoelastic properties of unfilled and carbon black filled blends of BR and NR and blends of SBR and BR were measured by using an automated acoustic spectrometer. The compositional dependence of longitudinal attenuation coefficient at room temperature of both unfilled and filled BR/NR blends was found to follow the linear additive rule. However, a negative deviation from linearity was found for SBR/BR blends.

For filled BR/NR blends, the plot of attenuation coefficient versus temperature shows show a peak at $-20\text{ }^\circ\text{C}$, which corresponding the $T_{g\ 1\text{MHz}}$ for NR and a shoulder at lower temperatures, which is associated with the glass transition of BR phase. The calculated α_L based on linear additive rule agrees with the experimental data for BR/NR blends, indicating that BR/NR blends are immiscible. In contrast, a single glass transition was found for SBR/BR blends for SBR rich blends and the glass transition temperature increase with increasing SBR concentration. This result suggests that SBR/BR blends are partially miscible. A large discrepancies between calculated attenuation coefficient by using linear additive rule and the experimental results were found for SBR/BR blends. The FD and ND mixing techniques give comparable values in α_L for SBR/BR blends.

The acoustic spectrometer provide us with a technique for the study of miscibility of polymer blends, giving results which are consistent with those obtained with mechanical spectrometer. Applications of acoustic spectrometer include the study of phase transition of polymers and phase separation of polymer blends. Further study on effects of processing oil, degree of curing, and filler-polymer interactions on the high-frequency viscoelastic properties of rubber compounds are being pursued.

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