Nonlinear Viscoelasticity of Rubber Materials:
Payne Effect and Differential Dynamic Modulus

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Abstract Rubber materials are used normally in large deformations, that is, in nonlinear conditions. So, nonlinear viscoelasticity is important for the characterization of rubber materials. So-called Payne effect, strain amplitude dependence of dynamic modulus, is one of the examples for nonlinear behaviors in rubber materials.

In linear viscoelasticity, we can determine experimentally peak stress, peak strain, and phase angle difference in stress and strain waves. Hence we can define storage and loss modulus, G’ and G”, respectively. In nonlinear viscoelasticity, however, stress wave deviates from a simple sinusoidal wave. Therefore, we may discuss Payne effect on rubber materials by absolute values of dynamic modulus, |G*|. We need additional information on viscoelasticity to discuss Payne effect.

In this work, strain amplitude, γL, and phase angle, ωt, dependence of differential dynamic modulus, G*(ω, γL; t) for carbon black filled, cured and unfilled, cured SBRs were tested in large amplitude oscillatory shear (LAOS) at γL=0.005 – 2.0 and νL=0.001 Hz (period T=1000 s) using self-made biaxial rheometer. Small oscillations (γS=0.005, νS=0.2 Hz) were superposed orthogonally on LAOS. Strain softening in G* was found depending on both γL and ωt. Unfilled, cured rubber showed affine-like change with LAOS in both G’ and G”, while filled, cured rubber did partial recovery in G’ at peak position of LAOS and additional enhancement in G”. As a result, filled, cured rubber showed much higher values of differential loss tangent (DLT) in LAOS than unfilled, cured one, indicating that DLT may be useful for novel index of heat generation in periodical deformations of rubber materials.

Keywords Rubber, Filler, Dynamic modulus, LAOS, Payne effect, Heat generation, Loss tangent.

1. Introduction

Linear viscoelasticity for filled rubbers is limited in a range of very low strain, 0.5% or lower in typical. Rubber materials are used in large deformations, that is, in nonlinear conditions. Rubber processing is made in nonlinear conditions, too. Hence nonlinear viscoelasticity is important for characterization of rubber materials.

Rubber materials are made of two networks, chemical and physical networks. In a physical network, filler plays an important role. Hence we call the latter “filler network”. Generally speaking, filler network may be much weaker than chemical one. Hence change in filler network may be a major reason for nonlinear viscoelasticity of rubber materials.

So-called Payne effect, strain amplitude dependence of dynamic modulus, is one of examples for nonlinear viscoelastic behaviors in rubber materials. Here it should be noted that the ordinate reported originally by Payne was absolute value of dynamic modulus, |G*|, defined as

\[ |G*| = \frac{\sigma_p}{\gamma_p} \]  

(1)

where \( \sigma_p \) and \( \gamma_p \) are peak values of dynamic stress and dynamic strain, respectively. After the Payne’s report, wide discussion has been made. In the discussions, however, storage modulus G’ and loss modulus G” have been used. As well known, G’ and G” are defined as

\[ G’ = |G*| \cos \delta \]  

(2)

\[ G” = |G*| \sin \delta \]  

(3)

where \( \delta \) is phase angle difference between stress and strain sinusoidal waves. \( \sigma_p \) and \( \gamma_p \) can be determined clearly in experiment. The phase angle difference \( \delta \) can be determined in linear viscoelasticity where \( \delta \) is independent of time, that is, phase angle. However, \( \delta \) cannot be defined uniquely in nonlinear viscoelasticity where oscillatory
stress deviates from sinusoidal wave and \( g \) changes with time. In the case of nonlinear viscoelasticity, therefore, we should analyze the phenomena using some methods different from that in linear viscoelasticity.

Several methods have been proposed. The first one is harmonic approximation.\(^{14}\) However, the approximation cannot be applied to very large strain amplitude such as \( ca. 50\% \) or higher. The second is the Fourier transform analysis where the nonlinearity is described by the amplitude of the higher harmonics.\(^{15–22}\) Otherwise, a graphical representation of the nonlinearity can be gotten with use of Lissajous curves.\(^{11}\) In the latter two cases, however, it is hard to get physical interpretation from the information obtained. Hence we need another method for analysis.

We have shown that the change and the recovery in entanglement network and nonlinear viscoelasticity of rubber-like polymers can be studied using dynamic modulus measured with small shearing oscillatory strain superposed on large shearing deformations.\(^{23–33}\) We have called it as differential dynamic modulus (DDM), \( G^*(\omega \gamma; t) \), where \( \gamma \) is large strain on which small oscillations are superposed. Change in network structure in a large deformation can be monitored using DDM. Nonlinear viscoelasticity discussed now may come from change in filler and chemical networks. DDM may give additional information on the change in filler and chemical networks.

The purpose of this work is to discuss nonlinear phenomena in large amplitude oscillatory shear (LAOS) from the viewpoint of change in filler and chemical networks using differential dynamic modulus.

### 2. Experimental

**2.1 Materials**

The rubber used was styrene-butadiene random copolymer (Nipol SBR-1502, Zeon Corporation). Carbon-black (CB) used was N330 (Mitsubishi Chemical Corporation). Other additives were Zinc Oxide (Shodo Chemical), Antioxidant (SANTOFKEX 6PPD, Flexsys), and Stearic Acid (Stearic Acid N for industrial use, Asahi-Denka). Details on compound formulation are shown in Table 1. CB master batches were prepared in 1L Kneader type mixer (DS1-5MHB-S, Moriyama) for 4.5 minutes at 353 K in the beginning (at \( ca. \) 383 K in the final stage). The curatives were mixed to the master batches using 6 inch open-roll mixer (Type 2533, Kansai Roll). The compound is cured for 15 minutes at 433 K.

**2.2 Measurements**

The apparatus used was biaxial rheometer made by ourselves.\(^{1,20–32}\) A servo-controlled hydraulic actuator (JT Toshi) drove relative motion along axis. A load cell (LRM-50K, Nihon Tokushu Sokki) and a cantilever spring type displacement transducer (CE-10, Tokyo Sokki) detected force and displacement, respectively. Special air bearings are equipped to prevent undesired rotation around the road cell axis. A stepping motor equipped with harmonic gear having no backrush (UDP556HG2-A2, minimum 1.8 x 10^{-5} deg/step, Oriental Motor) drove relative rotation around axis. A non-rotational type torque meter (TCF-01K, Nihon Tokushu Sokki) and a non-contact type Laser Feed Monitor (FC-2000, Keyence) detected rotational oscillatory torque and angle.

In this work, a Pochetitino-type and Couette-type of shear deformations were adopted for large shearing and small shearing oscillations, respectively. The special device for combination of the two types of deformations was the same as that used in previous works.\(^{27,30}\) The device consists of inner bob and outer cup, which can move independently. The Pochetitino-type and Couette-type shears can be obtained by their relative displacement along axis and relative rotation around axis, respectively. The samples were fixed to steel cup and bob using cyanoacrylate glue.

Figure 1 shows a sketch of the experimental procedures to obtain large oscillatory shear stress response against to large oscillatory shear strain, and orthogonal differential dynamic modulus, \( G^*(\omega \gamma_1; t) \), for small oscillatory shear given in the direction orthogonal to large oscillatory shears. Before giving large oscillatory shearing, dynamic modulus in linear viscoelasticity, \( G'(\omega, 0) \) and \( G''(\omega, 0) \), were measured. A large oscillatory shear started at time 0. Two cycles of oscillatory shear were given. Orthogonal DDM was measured intermittently at every phase angle of \( \pi/4 \) radian from zero-cross point. The period of the large oscillatory shear was 1000 s. The strain amplitude of oscillatory shear ranged from 0.005 to 2. The strain amplitude and the frequency of small oscillations were

### Table 1. Compound formulations (unit in phr)

| Sample Code | 1   | 2   | 3   | 4   |
|------------|-----|-----|-----|-----|
| SBR(1502)  | 100 | 100 | 100 | 100 |
| CB(N330)   | 50  | 50  | 50  | 50  |
| Anti-oxidant\(^a\) | 1   | 1   | 1   | 1   |
| Stearic Acid| 2   | 2   | 2   | 2   |
| ZnO        | 3   | 3   | 3   | 3   |
| Sulfur     | 1.5 | 1.5 | 1.5 | 1.5 |
| Accelerator (DPG)\(^b\)| 1   | 0.667 | 1 | 0.667 |

\(^a\) N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD)

\(^b\) 1,3-Diphenylguanidine
fixed to be 0.005 and 0.2 Hz (1.257 rad/s). All measurements were made at 293 K.

3. Results and Discussion

3.1 Strain Amplitude Dependent Dynamic Modulus in Large Amplitude Oscillatory Shear

Figure 2 shows strain amplitude dependence of absolute values of dynamic modulus, $|G^*(\omega, \gamma_L)|$. The unfilled, cured samples 1 and 2 shows linear or nearly linear viscoelasticity up to ca 0.1 in strain amplitude. However, the range of linear viscoelasticity for the filled, cured samples 3 and 4 is limited to strain amplitude less than 0.01. Such narrow range of linear viscoelasticity is the characteristic nature of filled vulcanizates. At larger strain amplitude, filled samples show strong nonlinear character. Especially, enhanced nonlinear behavior, upturn in curve, is observed for filled, cured sample at high shear strain. This is attributed to the cusps of the corresponding Lissajous’s figure.¹)

Figure 1. Schematic illustration of Experimental Procedure.

Figure 2. Shear strain amplitude, $\gamma_L$, dependence of absolute values of dynamic modulus $|G^*(\omega, \gamma_L)|$ for various samples.

Figure 3. Phase angle dependent differential dynamic modulus and loss tangent at various shear strain amplitudes of LAOS for sample 1. The curves were shifted along the ordinate by a factor of A denoted in the panels to avoid overlap. Various symbols denote the values measured at various phase angles of LAOS as schematically shown at the top.
3.2 Differential Dynamic Modulus during Large Oscillatory Shear Deformation

Figure 3 shows the values of orthogonal differential dynamic modulus, \( G^*(\omega, \gamma_L, t) \), for unfilled, cured sample 1 measured at various strain amplitude ranged from 0.01 to 2. Broken lines denote the values in linear viscoelasticity. Various symbols denote the values measured at various phase angles of large oscillatory shears as schematically explained at the top of Fig. 3. At very low strain amplitudes, \( \gamma_L = 0.1 \) or lower, all values of differential dynamic modulus and loss tangent show no change from the broken lines, indicating complete linear viscoelasticity. However, the change in \( G' \) and \( G'' \) become large with increase in strain amplitude. At large strain, \( \gamma_L = 1 \) or 2, phase angle dependence appears clearly in differential dynamic modulus. But there may be no chain scission at these levels of strain, and chemical network structure should take recovery at zero-cross strain. Chain anisotropy

**Figure 4.** Phase angle dependent differential dynamic modulus and loss tangent at various shear strain amplitudes of LAOS for sample 2. The curves were shifted along the ordinate by a factor of A denoted in the panels. The meanings of the symbols are the same as in Fig. 3.

**Figure 5.** Phase angle dependent differential dynamic modulus and loss tangent at various shear strain amplitudes of LAOS for the sample 3. The curves were shifted along the ordinate by a factor of A denoted in the panels. The meanings of the symbols are the same as in Fig. 3.
Figure 6. Phase angle dependent differential dynamic modulus and loss tangent at various shear strain amplitudes of LAOS for sample 4. The curves were shifted along the ordinate by a factor of A denoted in the panels. The meanings of the symbols are the same as in Fig. 3.

Figure 7. Strain amplitude dependence of differential dynamic modulus and loss tangent at various phase angle of LAOS for sample 1. The meanings of the symbols are the same as in Fig. 3.

Figure 8. Strain amplitude dependence of differential dynamic modulus and loss tangent at various phase angle of LAOS for Sample 2. The meanings of the symbols are the same as in Fig. 3.
in chemical network should depend on absolute value of strain. So DDM shows full-wave rectification-like change. \( G' \) and \( G'' \) have minimum and maximum at peak and zero-cross points of large oscillation, respectively. These are the reasons why \( G' \) and \( G'' \) for unfilled, cured rubber show affine-like relationship with large oscillations, and \( \tan \delta \) shows fluctuation-like change around the original value, \( \tan \delta(a,0) \). Figure 4 for the unfilled, lightly cross-linked sample 2 shows much the same features as the sample 1 in Fig. 3, indicating generality of nonlinearity observed in the phase angle dependent DDM.

Figures 5 and 6 show the results of \( G'/(\omega \gamma_L, t) \) at various strain amplitudes ranged from 0.01 to 2 for filled, cured samples 3 and 4, respectively. At low \( \gamma_L \), linear or nearly linear viscoelasticity is observed as expected. It may be, however, noted that \( G'' \) is more sensitive than \( G' \). At high \( \gamma_L \), nonlinear behaviors are observed in DDM. \( G' \) falls from the broken line, indicating network rupture due to large amplitude oscillatory shears. We can find phase angle effect on both \( G' \) and \( G'' \). Recovery of \( G' \) was observed at zero-cross points as well as change in \( G'' \). Such feature in recovery is similar to that for unfilled, cured samples. However, the behavior in \( G'' \) is different from that in \( G'' \) at the peak points of large oscillations. \( G'' \) shows minimum at the peak points of large oscillation. But \( G' \) shows recovery in part at the peak points. Lissajou’s figure for filled, cured sample shows cusp shape at the peak points of large oscillatory strain.\(^1\) At the peak oscillatory strain, rubber chain between cross-linking points should be extended too much. Partial rise in \( G' \) may correspond to the chain extension.

Strain amplitude dependent differential dynamic modulus and loss tangent at various phase angle for all samples 1–4 are summarized in Figs. 7–10. \( G' \) for unfilled, cured samples 1 and 2 is monotonically decreasing function of strain amplitude in LAOS, but \( G' \) at zero-cross points shows plateau like behavior due to partial recovery in shape at \( \gamma_L = 1 \) or higher. \( G'' \) also shows behavior similar to \( G' \), but strain amplitude dependence of \( G'' \) is larger than \( G' \). It recovers to the broken line (equilibrium value in \( G'' \)) at zero-cross points, irrespective of \( \gamma_L \). As a result, \( \tan \delta \) shows cyclic change around the equilibrium value. DDM

**Figure 9.** Strain amplitude dependence of differential dynamic modulus and loss tangent at various phase angle of LAOS for Sample 3. The meanings of the symbols are the same as in Fig. 3.

**Figure 10.** Strain amplitude dependence of differential dynamic modulus and loss tangent at various phase angle of LAOS for Sample 4. The meanings of the symbols are the same as in Fig. 3.
for filled, cured samples 3 and 4 shows $\gamma_L$ dependence similar to that for unfilled, cured samples. But $G^*$ shows additional energy dissipation probably due to filler network rupture,\(^3,4\) resulting in high values in $\tan\delta$ at larger strain amplitude.

It may be noted that there is clear difference between nonlinear behaviors for $\tan\delta(\omega, \gamma_L; t)$ in unfilled and in filled samples. Unfilled, cured samples show cyclic change around the equilibrium value (indicated by broken line), while filled, cured samples do cyclic change above the equilibrium value. Hence differential loss tangent in LAOS may give novel index for heat generation in periodical defoemations of filled rubber materials. This point will be discussed in a subsequent paper.

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