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Frequency- and strain-amplitude-dependent dynamical mechanical properties and hysteresis loss of CB-filled vulcanized natural rubber

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ABSTRACT

The dynamic mechanical behavior of carbon-black-filled vulcanized natural rubber is experimentally investigated by stretching the rubber strips with various strain amplitudes at different frequencies in a sinusoidal tension mode. The Payne effect is demonstrated and the frequency- and strain-amplitude-dependent hysteresis losses are determined by DMA measurements. The Kraus model is used for describing the Payne effect. The results show that hysteresis loss increases with increase in frequency and strain amplitude. A viscoelastic model, which correlates the hysteresis loss with strain amplitude and loss modulus, is used to calculate the energy dissipated in a full deformation cycle. The model prediction is shown to be in good agreement with the experimental result.

1. Introduction

Elastomers and filler reinforced elastomers are widely used in many engineering fields such as civil engineering, mechanical engineering, automobile engineering and aerospace engineering due to their high elasticity, high damping and larger elongation at failure. Natural rubber (NR) is one of the most important elastomers, and its properties can be tailored by incorporation with carbon black or silica of varying surface chemistry and aggregate size/aspect ratio to suit the concerned application. Many constitutive models have been proposed to reproduce the complex mechanical behavior of filled rubbers, such as hyperelasticity [1,2], viscoelasticity [3–5], Mullins effect [6] and Payne effect [7,8]. Tomita et al. developed a nonaffine chain network model, which accounts for the chain disentanglement due to deformation, to represent the orientation hardening behavior of amorphous polymers [9,10] and to model the hysteresis loss phenomenon of CB-filled rubbers under cyclic deformation [11]. In order to reproduce the rate-dependent response of CB-filled rubbers to monotonic and cyclic straining, Tomita et al. further proposed a visco-hyperelastic 8-chain network model that incorporates a nonlinear dashpot with Langevin springs [12]. The dashpot was modeled based on the reptation theory. The visco-hyperelasticity of filled rubbers was also investigated by Bergström and Boyce [5], Amin et al. [13] and Höfer and Lion [14], among others.

Viscoelastic properties of materials are often determined either with static measurements such as step-load creep or relaxation as well as slow ramp loading procedure or with steady-state oscillation tests [15]. The latter approach is usually referred to as dynamic mechanical analysis (DMA) or dynamic mechanical thermal analysis (DMTA). In this study, CB-filled rubber strip specimens are loaded with harmonic deformations under different frequencies and amplitudes and the steady-state stress responses are evaluated in terms of storage and loss modulus. The frequency- and amplitude-dependent dynamic modulus and hysteresis loss are then discussed and modeled.

2. Steady-state hysteresis loss and energy dissipation

When a viscoelastic material is subjected to a sinusoidal excitation

$$\varepsilon(t) = \varepsilon_0 + \Delta \sin(\omega t) \tag{1}$$

with a dynamic strain amplitude Δ, an angular frequency ω and a prestrain ε_0, the corresponding stress response is also sinusoidal if the dynamic strain amplitude is small, but is out of phase with

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strain excitation,

$$\sigma(t) = \sigma_0 + \Delta E^* \sin(\omega t + \delta) = \sigma_0 + \Delta[E' \sin(\omega t) + E'' \cos(\omega t)] \tag{2}$$

in which $E' = E^* \cos\delta$ and $E'' = E^* \sin\delta$ are storage and loss moduli; E^* is the absolute value of the complex modulus and δ the phase angle. The static stress σ_0 is a function of ε_0; in a linear approximation it is given by $\sigma_0 = E_\infty \varepsilon_0$, E_∞ is the equilibrium modulus.

The total work of deformation or, in other words, the mechanical energy absorbed per unit volume of the material in the deformation up to time t is given by

$$W(t) = \int_0^t \sigma(\tau)\dot{\varepsilon}(\tau)d\tau \tag{3}$$

This energy consists of the stored energy and dissipated energy; if the inertial effect during deformation is negligible, the stored energy is strain potential energy only. This potential energy is stored in the stretching of the molecular configuration changes and subsequently recovered completely on unloading. Therefore, the amount of energy dissipated in a full cycle of oscillatory straining as given in Eq. (1) can be calculated by integrating Eq. (3) over the cycle:

$$D = W_{\text{loop}} = \int_0^{\frac{2\pi}{\omega}} \sigma(\tau)\dot{\varepsilon}(\tau)d\tau = \pi \varDelta^2 E'' \tag{4}$$

This dissipated energy is also called hysteresis loss; it represents the area of the hysteresis loop and causes the temperature rise of the material [16–18]. It can be seen from Eq. (4) that the hysteresis loss is proportional to the loss modulus and the square of the strain amplitude.

3. Kraus model

The Payne effect is a particular feature of the stress–strain behavior of rubber, especially filled rubber. It manifests the fact that increase in amplitudes leads to a decrease in storage modulus and a maximum in loss modulus. Physically, the Payne effect can be attributed to deformation-induced changes in material's microstructure, i.e. to breakage and reforming of weak physical bonds between the filler aggregates. The first phenomenological model to represent and understand the Payne effect is the so-called Kraus model [19]. It reads as follows [20,21]:

$$E'(\varDelta) = E'_\infty + \frac{E'_0 - E'_\infty}{1 + (\varDelta/\varDelta_c)^{2m}} = E'_0 - \Delta E' + \frac{\Delta E'}{1 + (\varDelta/\varDelta_c)^{2m}} \tag{5}$$

$$E''(\varDelta) = E''_\infty + \frac{2(E''_m - E''_\infty)(\varDelta/\varDelta_c)^m}{1 + (\varDelta/\varDelta_c)^{2m}} \tag{6}$$

where $\varDelta_c$ is the characteristic value of the strain amplitude, at which the loss modulus reaches its maximum E''_m; E'_0 is the storage modulus for small strain amplitudes (usually < 0.01%); E'_∞ and E''_∞ are the asymptotic plateau values of the storage and loss moduli at large strain amplitudes, respectively; $\Delta E' (= E'_0 - E'_\infty)$ is the excess storage modulus; m is a non-negative phenomenological exponent to fit the experimental data. It was reported in the literature that the exponent m is nearly independent of temperature, frequency and carbon black content, and has the value of about 0.5 [21,22] or 0.6 [23]; however, as will be seen from the present experiments, m decreases slightly with increase in frequency, varying from 0.6 to 0.4.

4. Experimental

4.1. Material

Thin rectangular strips of length 35 mm and width 7 mm were cut from a 2-mm-thick vulcanized rubber sheet, which was generously provided by the Zhuzhou Times New Material Technology Co., Ltd. in China. The formulation of the rubber compounds was as follows: 100 phr NR (Thailand RRS3), 20 phr carbon black (N550), 10 phr zinc oxide, 5 phr antioxidant, 2.5 phr sulfur (200 meshes per square inch), 2 phr stearic acid, 2 phr micro-crystal wax, 2 phr solid Coumarone resin and 1.4 phr vulcanization activator.

4.2. Tests by DMA

In order to investigate the dynamic viscoelasticity and the Payne effect of the CB-filled rubber, dynamic mechanical tests were carried out with a *Gabo Eplexor 500N* working in the tensile mode. Isothermal dynamic sweep measurements were performed at 23 °C. In order to exclude the Mullins effect, i.e. the softening phenomenon during the first several deformation cycles, all specimens were mechanically preconditioned. Afterward the specimens were sinusoidally stretched under a prestrain of 10% and various frequencies, i.e. 3, 10, 20, 30, 40, 50, 60 and 70 Hz, and the superimposed strain magnitude was varied between 0.1% and 4% by steps of 0.05%. The stress responses to the strain excitations were recorded automatically, and from these measurements the tensile storage modulus E' and the loss modulus E'' were calculated, and the mechanical hysteresis loop in a full strain cycle was also constructed.

5. Results and discussions

Figs. 1 and 2 show the test results, where the storage and loss moduli are shown as a function of the applied frequency and strain amplitude. These results reveal a typical nonlinear viscoelastic behavior, i.e. the well-known Payne effect [7,8]. It was reported that both storage and loss modulus are independent of the strain amplitude in the cases where amplitudes are smaller than 0.01–0.1% [24,25], depending on the formulation of the

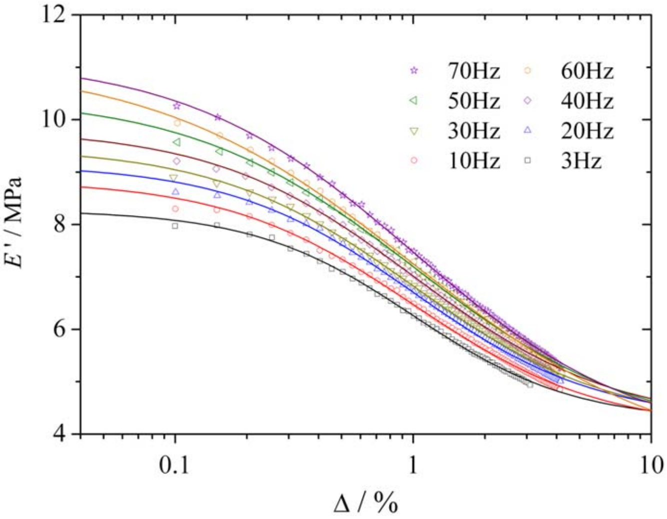

Fig. 1. Strain-amplitude-dependent storage modulus at various frequencies (open symbols denote the test data; lines represent the Kraus model fit using a constant characteristic strain amplitude, Δc=1%).