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Dynamic Mechanical Properties of Crosslinked Polyisoprene Under Deformation

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Summary

Molecular motions of elastomers under deformations were observed through dynamic mechanical measurements. Composite master curves of dynamic moduli E' and E" and loss tangent tanδ over a wide range of frequency and in a state of elongation were obtained by the time-temperature superposition procedure. It is found that both moduli increase with strain, γ. The slope of the dispersion curve of E' become more gradual with the increase in γ, while that of E" is almost unchanged. The increment of E' is generally larger than that of E", which does not agree with the N. W. Tschoegl prediction, $E^*_\gamma(\nu) = f(\gamma)\, E^*_0(\nu)$, where $E^*_\gamma(\nu)$ and $E^*_0(\nu)$ are complex moduli at the strain of γ and 0, respectively, and $f(\gamma)$ is the function of only γ. The difference in the strain dependence of E' from E" was found to correspond to the strain dependence of the equilibrium modulus.

Introduction

The elongation of elastomers can produce partially ordered orientation of molecules. The orientation is expected to affect the molecular motion in the elastomers, which results the viscoelastic behavior characteristic of the deformed elastomers. The dynamic measurement is useful to study the relation between the characteristic viscoelastic behavior and the molecular motion in the deformed elastomer. Practically most of elastomers have been used as mechanical components under their statically and dynamically deformed state. While the effect of temperature on molecular motion in elastomer is fairly well understood, relatively little information is available on the effect of elongation. In this study the sample is extended to several strains ranging from 0.1 to 4 and a small amplitude sinusoidal deformation is added on it. The temperature is changed from -60°C to 20°C.

Experimental

This work was carried out on a cis-1,4-polyisoprene distributed by the General Science Corp. Films of cis-1,4-polyisoprene were made by casting the concentrated benzene solution on a glass plate at room temperature. All films were dried for a week. Films were crosslinked by γ-ray irradiation at 10°C in vacuo. The amount of dose was 40 Mrad. The degree of crosslinking was determined to be 5.4×10^{-5} mol / cm^3 by measuring static Young's modulus. Wide angle x-ray diffraction patterns were obtained at 15°C for films under several strains between 1 to 3 (the strain was defined as $\gamma = (L - L_o)/L_o$ where L is the extended length and L_o is the initial length). At this temperature no crystallites were observed in the system up to the strain of 3.

At first the sample is extended to some strain, γ, and kept under this condition until the stress is nearly relaxed. Then a small sinusoidal deformation is added. The amplitude of this deformation, ε (= 0.04 cm), is 3.0 % of the initial length L_o. By observing the respondent stress to ε, the dynamic moduli at γ were obtained.

Two series of measurements were performed; (1) γ-dependence of the dynamic moduli $E'(\nu)$ and $E''(\nu)$ and loss tangent $\tan\delta(\nu)$ (= E''/E') at a constant temperature over γs ranging from 0.1 to 4.0; (2) temperature dependence of the moduli at several γs ranging from 1 to 3 over a temperature range from 20°C to -60°C.

According to Ferry reliable viscoelastic master curves can be obtained if the experimental window is sufficiently broad. In the present work, however, both series of measurements were performed over a frequency range from 0.1 to 1 Hz.

This deficiency was compensated by performing measurements of isothermal-isostrain segments for superposition at small intervals of temperature.

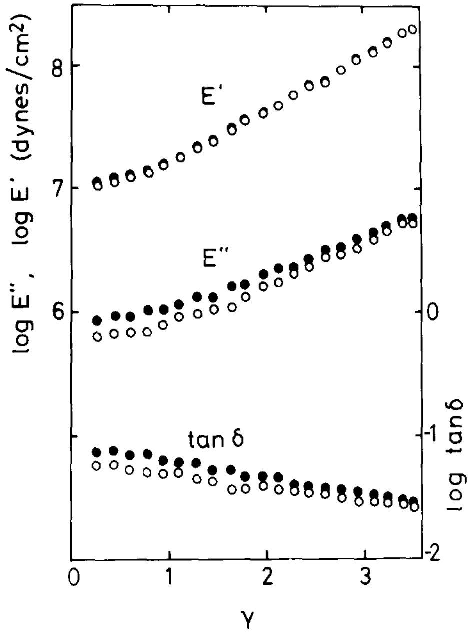

Figure 1. γ-dependence of E', E'', and tanδ measured at frequencies of 0.1 Hz (○) and 0.6 Hz (●), and at the temperature of 23°C.

Results and Discussion

In Figure 1, E', E'', and tanδ are plotted against the strain. Both moduli E' and E'' increase monotonously with γ. The slight difference in increasing rates with γ between E' and E'' is reflected in tanδ as a decreasing function. N. W. Tschoegl et al. presented the simplified superposition equation.[1-3] It is the type of variable separation and has been proved to be suitable to explain many experimental results. As for the complex modulus, the equation is described as follows,[2]

$$E^*_\gamma(\nu) = f(\gamma)\, E^*_0(\nu) \tag{1}$$

where $E^*_\gamma(\nu)$ and $E^*_0(\nu)$ are complex moduli under the strain γ and $\gamma = 0$, respectively, and $f(\gamma)$ is the function of γ expressed as

$$f(\gamma) = (3/2)(\alpha^{n-1} + 0.5\,\alpha^{-(n+2)/2}) \tag{2}$$

where $\alpha = \gamma + 1$ and n is a material parameter introduced by Tschoegl.[2] From this equation, it is easily deduced that tanδ(ν) should be independent of γ. The result shown in Figure 1 does not follow the equation on the point that tanδ decreases with γ. The Tschoegl equation has been derived on the basis that the relaxation spectrum would not be changed by the moderately large deformation. The reason of the dis-

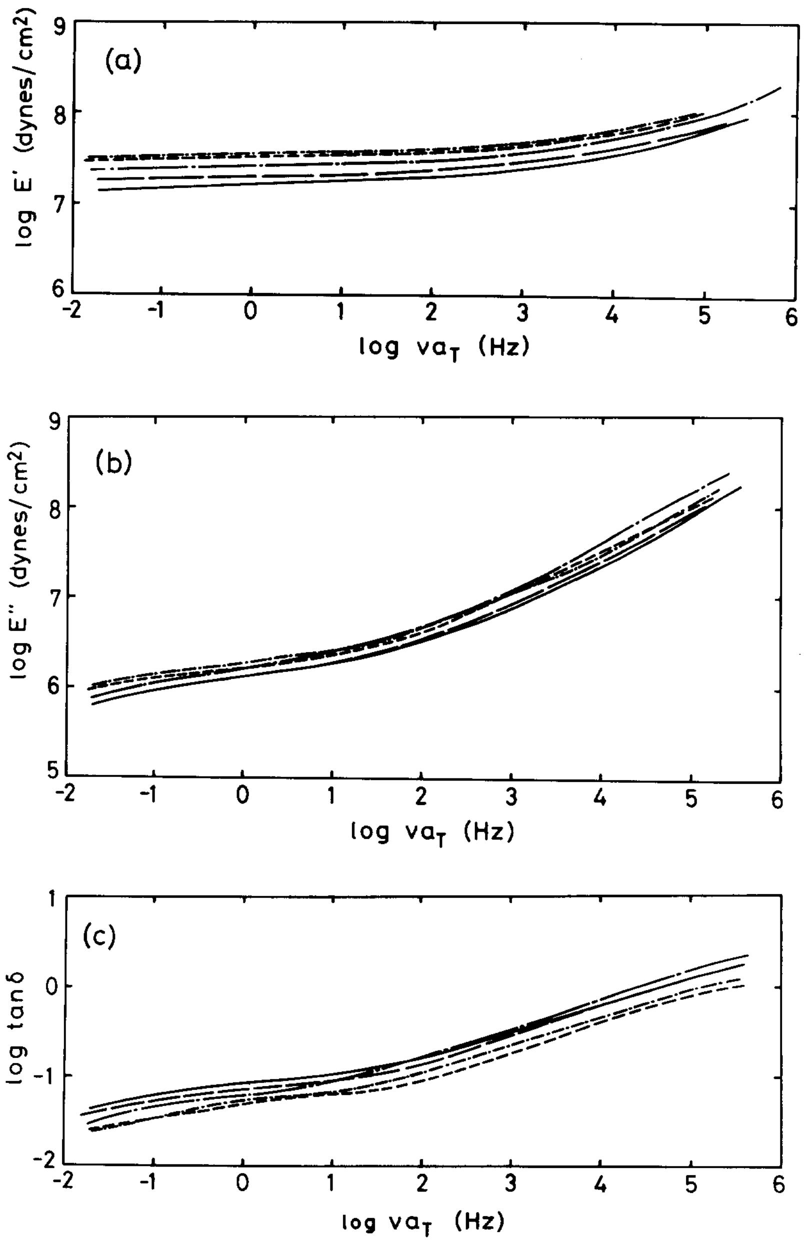

Figure 2. Composite master curves of (a) E', (b) E", and (c) tan δ reduced to 0°C for γ = 1.2,———, 1.8,—— ——, 2.0,———·——, 2.3,-------, and 2.4,——·——·—.

crepancy of our result from the Tschoegl equation was discussed as follows; in order to investigate the effect of elongation on the molecular motion, we consider the three cases (possible and sufficient) concerning the relaxation spectrum (the relaxation time spectrum) and each relaxation time τ_i : (1) The relaxation spectrum is conserved and the relaxation time does not change. (2) The relaxation spectrum is conserved and the relaxation time changes. (3) Both the relaxation spectrum and the relaxation time change. The Tschoegl equation is based on the case (1).

To examine whether the relaxation spectrum is conserved or not in the experimental results for several elongated states, the results obtained from several constant strains were composed to a master curve which covers a wide range of frequency. In Figures 2 (a), (b), and (c), master curves of E', E", and tanδ , respectively, for several strains are shown. Experimental points, which are widely dispersed, are omitted for the sake of clarity. Each composite matser curve is reduced to 0°C. In order to obtain smooth master curves of E' and E" at low temperatures (below -5°C) and for γs larger than 2, vertical shifts of each isothermal segment are needed. The necessity of the vertical shift to superpose the frequency dispersion curves reminds us of the vertical shift reported for crystalline polymers, for which the vertical shift should be related to a change in the degree of crystallinity with temperature or to that in the orientation of crystallites in the amorphous matrix.[4] It has also been known that if crosslinked natural rubber is maintained at a low temperature (e. g. 0°C or lower) or in a elongated state, it gradually crystallizes. A possible explanation of our case can be made in terms of crystallization caused by maintaining rubbers at low temperatures under strain.

It is found that both moduli increase with γ. The increment in E' is generally larger than that in E". In order to give more detailed informations, master curves of E' and E" were replotted in Figure 3 for $\gamma = 1.2$ and 2.4 where the dispersion of data points was smaller than others and the difference in γ was relevant to observe the effect of γ. The slope of the master curve of E' becomes more gradual with the increase in γ, while that of E" is almost unchanged. Remembering that the dispersion curve of E" is the zeroth approximation of the relaxation spectrum,[5] we are able to consider that in our result the relaxation spectrum would not be changed by the strain. In order to discuss the difference between behaviors of both moduli under the strain, which also causes the discrepancy of our result from the Tschoegl equation, the expression of the dynamic moduli by the relaxation spectrum H(τ) were appreciated,

$$E'(\nu) = E_e + \int_{-\infty}^{\infty} H(\tau)\,\frac{(2\pi\nu)^2\tau^2}{1+(2\pi\nu)^2\tau^2}\,d\ln\tau \qquad (3)$$

$$E''(\nu) = \int_{-\infty}^{\infty} H(\tau)\,\frac{2\pi\nu\tau}{1+(2\pi\nu)^2\tau^2}\,d\ln\tau \qquad (4)$$

where E_e is a modulus at an equilibrium state. The term which is responsible for the difference described above is guessed to be the additive term E_e in eq (3). When E_e increases with γ, the slpoe of the log E' vs log νa_T curve should become gradual, which was the case of Figure 3.

To estimate the increment in E_e with γ, E' is compared with E" as follows;

$$E'/E'' = \left[E_e + \int_{-\infty}^{\infty} H(\tau)\,\frac{(2\pi\nu)^2\tau^2}{1+(2\pi\nu)^2\tau^2}\,d\ln\tau\right] \Big/ \int_{-\infty}^{\infty} H(\tau)\,\frac{2\pi\nu\tau}{1+(2\pi\nu)^2\tau^2}\,d\ln\tau \qquad (5)$$

as the integral is independent of γ, E'/ E" would depend on E_e linearly. In Figure 4, E'/ E" is plotted against $\Delta\gamma = \gamma - \gamma_0$ where $\gamma_0 = 1.2$. From this curve, the relation between both values is described as,

$$\log(E'/E'') \propto \Delta\gamma \quad . \qquad (6)$$

Then empirically E_e can be expressed as

$$E_e(\Delta\gamma) = X\exp(A\Delta\gamma) + Y \qquad (7)$$

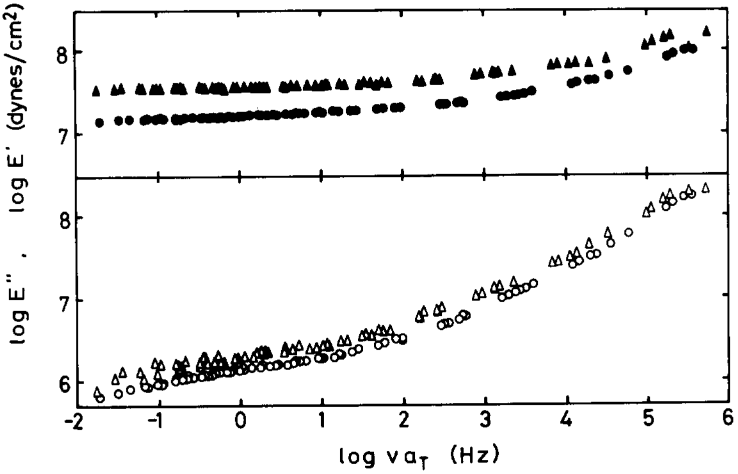

Figure 3. Composite master curves of E' for $\gamma = 1.2$ (●) and 2.4 (▲), and of E'' for $\gamma = 1.2$ (○) and 2.4 (Δ).

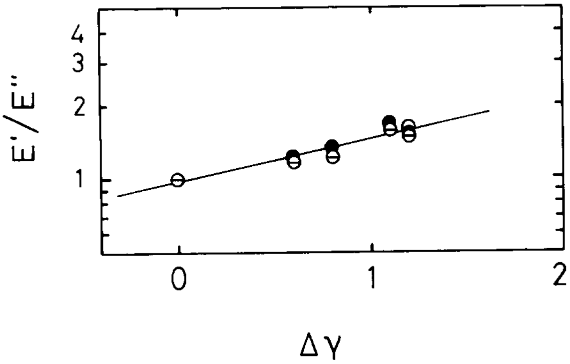

Figure 4. Δγ dependence of E'/ E'' for νa_T = 0.1 Hz (●), 1 Hz (○), and 10 Hz (⊖). $\Delta\gamma = \gamma - \gamma_o$ where $\gamma_o = 1.2$.

where A, X, and Y are constants independent of Δγ.

As mentioned in the experimental part, at 15°C even under strains up to 3, we did not observe crystallites in the system. As the dependence of E_e on γ is remarkable at room temperature, the crystallization by deformation is not responsible for the γ dependence of E_e. The exponential formed function in eq (7) is reminiscent of the correcting factor of the empirical or semiempirical expressions of the tensile stress-strain relation at an equilibrium state,[6-8]

$$S = E_e(\gamma)\left(\frac{1}{\alpha} - \frac{1}{\alpha^2}\right) \tag{8}$$

where S is the tensile stress based on the initial cross sectional area. As for $E_e(\gamma)$, exponential formed functions have been proposed; that presented by Blanchard and Parkinson (BP)[6]

$$E_e(\gamma) = E_e^o \exp C_1 \gamma \tag{9}$$

and a purely empirical expression discovered by Martin, Roth, and Stiehler (MRS),[7]

$$E_e(\gamma) = E_e^o \exp C_2 \left(\alpha - \frac{1}{\alpha} \right). \tag{10}$$

In both equations, E_e^o represents an equilibrium modulus at $\gamma = 0$ ($\alpha = 1$). For crosslinked natural rubber $C_1 = 0.5$ and $C_2 = 0.38$.[6,7] Our value of A in eq (7) was found to be 0.4, which accords well with these values. Qualitatively C_1 and C_2 are related to the finite degree of extension of polymer chains.[8] As BP and MRS equations deal with the equilibrium value of stress and modulus and our resultant equation (7) agrees with these equations, the exponential term in eq (7) is considered to be related to the exponential factors in both eqs (9) and (10). Thus, the dependence of E_e on γ would be concluded to be related also to the finite degree of extension of polymer chanis.

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