

A Chemorheological Equation of State for the Stress Relaxation of Elastomers

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ABSTRACT: A chemorheological equation of state for the stress relaxation of elastomers has been derived. This equation of state provides a general relationship between stress ratio and aging time.

KEY WORDS Stress Ratio / Chemorheology / Aging Function / Primary Transient Network / Secondary Transient Network / Cross-Linking / Scission /

Elastomers under aging tests show the changes of the structures. These include the average molecular weight, the molecular weight distribution, the effective cross-linking density, and the transient networks, such as the entanglement density. Consequently, the properties of the elastomer system will also change. A useful method for determining the change in mechanical properties is the chemical-stress relaxation test.¹⁻³ Detail information for the chemical-stress relaxation test can be found in the work by Kusano, Tamura, and Murakami.⁴ In their work, the plots between the logarithmic stress ratio and the aging time exhibit a family curves corresponding to various stretch ratios for a given elastomer. By defining the slope obtained from large aging time periods, they concluded that the apparant rate constant for an aging reaction is a function of the stretch ratio, the vibrational frequency, and the temperature.

From the chemorheological point of view, a chemorheological equation of state, obtained from a good mechanical constitutive equation and a good aging kinetics for the elastomer system, is required.

THEORY

Under uniaxial tensile deformation, a new

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** During the preparation of this paper, we deeply regreted the loss of Professor Mitchel Shen.

mechanical constitutive equation for gum elastomers has been derived by Lee and Williams⁵ in the form,

$$\sigma_E = G(2C_3/G)^{\lambda^{-|b|}}(\lambda - \lambda^{-2}) \quad (1)$$

where

$$2C_3 = 2C_2 + G$$

Equation 1 is valid for elastomers which follow the Gaussian-chain dynamics during deformation. The term $2C_2$ is the shear modulus due to the transient network, and G is the shear modulus due to the chemical cross-links. The rate and temperature dependences of G are given as

$$G = G_0(d)^g \exp(h/T) \quad (2)$$

where G_0 is the zero shear modulus, T , the temperature, and d , the second invariant of deviatorial deformation rate tensor. The material constants g and h can be determined experimentally.

Chemorheological Equation of State

Based on eq 1, we now derive the chemorheological equation of state for gum elastomers. The shear modulus, $2C_2$ is attributed to the transient networks such as the effective entanglements. Physically, $2C_2$ contains two parts. They are

$$2C_2 = 2C_{21} + 2C_{2II} \quad (3)$$

The first part, $2C_{21}$ is the shear modulus due to the primary transient networks. The primary transient

networks exist even without cross-linking reactions. The second part, $2C_{2II}$ is the shear modulus due to the secondary transient networks. The secondary transient networks are produced by chemical cross-linking reactions, and can be positive, null or negative depending on the chain morphology in which the cross-linking reaction occurs.

For example, if we consider the transient networks are composed of entanglements only, then an effective entanglement can be produced if the cross-linking reaction occurs at a proper site as shown in Figure 1. However, if the cross-linking reaction happens at the site of the entanglement which has already existed before the cross-linking reaction, then we have a negative secondary entanglement. Figure 2 illustrates the point we have just discussed. The secondary transient network is caused only by the cross-linking reaction. Consequently, the shear

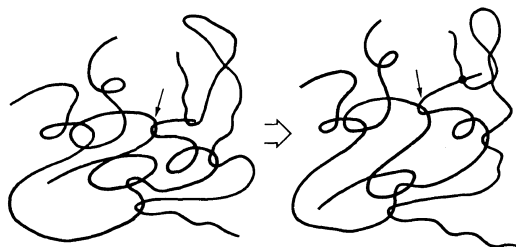


Figure 1. The evolution of a positive secondary entanglement in a cross-linking process. The dot indicates the cross-linking site, and the arrow indicates the entanglement site, which is an ineffective entanglement before the cross-linking reaction.

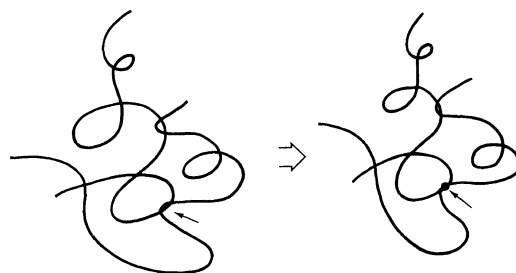


Figure 2. The evolution of a negative secondary entanglement in a cross-linking process. The arrow indicates an entanglement, and the dot indicates a cross-linking site. In this case the cross-linking reaction occurs at the entanglement site.

modulus $2C_{2II}$ is only a function of the shear modulus G , and G is a function of the chemical cross-linking density. We accordingly define the relationship between $2C_{2II}$ and G as

$$2C_{2II} = r(G)^v \quad (4)$$

where r and v are two material constants which can be determined experimentally. The value of v is always greater than zero. However, the parameter r has the following properties:

$$\begin{aligned} r > 0 &\text{ implies } 2C_{2II} > 0 \\ r = 0 &\text{ implies } 2C_{2II} = 0 \\ r < 0 &\text{ implies } 2C_{2II} < 0 \end{aligned}$$

Combining eq 3 and 4 leads to

$$2C_2 = 2C_{2I} + r(G)^v \quad (5)$$

The schematic plots of eq 5 are shown in Figure 3. The first systematical experiment for the transient network was investigated by Moore and Watson.⁶ Based on their experimental data for natural rubber, we obtain $2C_{2I} = 0.13 \text{ MNm}^{-2}$, $v = 1$ and $r = 0.205$. The results are shown in Figure 4.

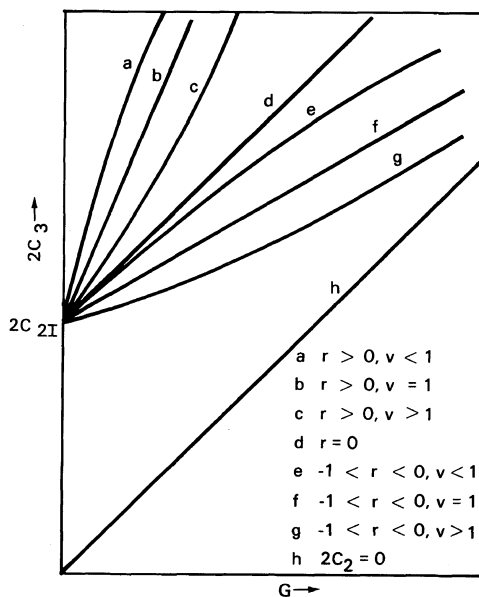


Figure 3. A schematic plot between the total shear modulus $2C_3$ and the shear modulus due to permanent cross-links G . In this figure, eight different cases are plotted.

Flory⁷ has established a relationship between the shear modulus and the cross-linking density in the form,

$$G(t) = N(t)RT \quad (6)$$

Consequently, we obtain

$$G(t)/G(0) = N(t)/N(0) \quad (7)$$

In eq 7, $G(t)$ and $N(t)$ are the shear modulus and the cross-linking density at aging time t respectively, and $G(0)$ and $N(0)$ are the initial shear modulus and the initial cross-linking density, respectively.

We now define the aging function for a chemorheological elastomer system as

$$A(t) = N(t)/N(0) \quad (8)$$

Under a constant stretch ratio λ , eq 1 leads to the stress ratio as

$$\frac{\sigma_E(t)}{\sigma_E(0)} = \left[\frac{G(t)}{G(0)} \right] \left[\frac{2C_3(t)G(0)}{2C_3(0)G(t)} \right]^{\lambda-b} \quad (9)$$

Finally, combining eq 8, 5, and 9, we obtain

$$\frac{\sigma_E(t)}{\sigma_E(0)} = A(t) \left[\frac{1 + r\{G(0)\}^{v-1}\{A(t)\}^{v-1} + A(t)^{-1}\{2C_{21}/G(0)\}}{1 + r\{G(0)\}^{v-1} + 2C_{21}/G(0)} \right]^{\lambda-b} \quad (10)$$

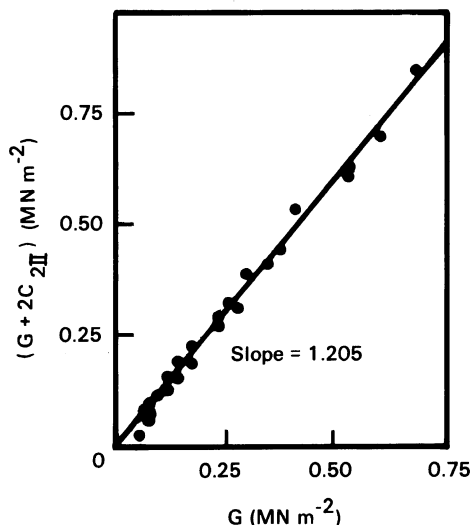


Figure 4. A plot between the secondary transient shear modulus $2C_{2II}$ and the shear modulus due to permanent cross-links G for peroxide cured natural rubber. Data are taken from Moore and Watson (1965).

Equation 10 is the chemorheological equation of state for the stress-relaxation test of gum elastomer.

It is noteworthy that $2C_{21}$ in eq 10 is assumed to be time-independent on the basis that the primary transient network represents a steady-state value of network density even without the cross-linking reactions.

Aging Function $A(t)$ and Chemical Reactions

For a system with i parallel reactions, the overall aging function can be expressed as

$$A(t) = \sum A_i(t) \quad (11)$$

where $A_i(t)$ is the aging function of the i th reaction. For a system with i sequential reactions, the total aging function can then be expressed as

$$[1/A(t)] = \sum [1/A_i(t)] \quad (12)$$

For example, if a system has a m th-order chemical reaction, then the aging function can be expressed as

$$A(t) = \{ [G(0)/RT]^{1-m} (1-m)Kt + 1 \}^{1/(m-1)} \quad (13)$$

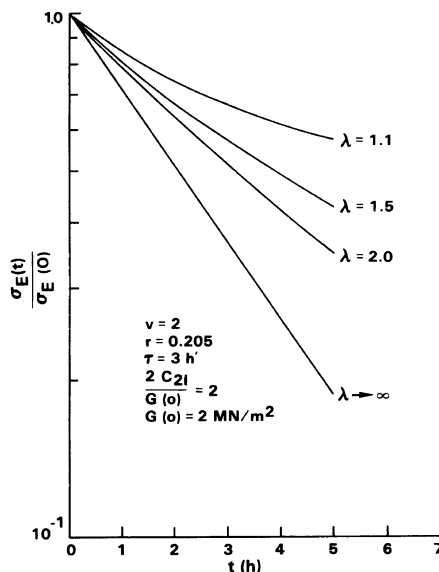


Figure 5. A theoretical prediction between the stress ratio and aging time under various stretch ratios of a chemical-stress relaxation test.

It is important to note that in this case the aging function depends on the cross-linking density as well as on the apparent rate constant, K .

Consider a system with n parallel first-order reactions, then the aging function can be expressed as

$$A(t) = \sum \exp(-K_i t) \quad (14)$$

where

$$W(t) = \left[\frac{1 + r\{G(0)\}^{v-1} \exp\{-(v-1)t/\tau\} + \{2C_{21}/G(0)\} \exp(t/\tau)}{1 + r\{G(0)\}^{v-1} + 2C_{21}/G(0)} \right]^{\lambda-b}$$

In eq 16, the stress ratio not only depends on the rate and temperature through $G(0)$, but also on the stretch ratio. A theoretical prediction of eq 16 is shown in Figure 5. It is important to note that the chemical-stress relaxation curve depends on the stretch ratio, even though the apparent rate constant is constant.

If $2C_2$ is zero, which implies null transient network in the system, eq 15 reduces to

$$\frac{\sigma_E(t)}{\sigma_E(0)} = \exp(-t/\tau) \quad (17)$$

Equation 17 has the same form that was suggested by Tobolsky.⁸

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First-Order Chain Scission Reactions

For a first-order chain scission reaction, the aging function $A(t)$ can be expressed as

$$A(t) = \exp(-Kt) = \exp(-t/\tau); \quad K > 0 \quad (15)$$

It is noteworthy that $A(t)$ depends only on the apparent rate constant in this case. Combining eq 15 and 10, we obtain

$$\frac{\sigma_E(t)}{\sigma_E(0)} = \exp(-t/\tau) [W(t)] \quad (16)$$

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