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Registry No. Polyethylene, 9002-88-4; polystyrene, 9003-53-6; isotactic polypropylene, 25085-53-4.

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A Theoretical Basis for Viscoelastic Relaxation of Elastomers in the Long-Time Limit[†]

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ABSTRACT: A molecular interpretation of the viscoelastic behavior of elastomers at long times is developed. This interpretation is based on a model consisting of dangling chain ends (branches) in a cross-linked network with topological constraints (entanglements). We make use of results by de Gennes for the reptation of a single branched chain with topological constraints. We then sum over contributions to the relaxation modulus from a distribution of branch lengths. The distribution function for chain branches was obtained by assuming that the network was formed from primary molecules due to a random cross-linking process. This leads to a relaxation modulus having power law dependence on time as in the empirical Chasset and Thirion equation. The theory also predicts that the parameters in the Chasset and Thirion equation have a cross-link density dependence which is consistent with available experimental data on natural rubber. Furthermore, the present treatment predicts that relaxation curves of different cross-link density are approximately superposable along the log time axis. The shift factor is predicted to have power law dependence on cross-link density, as observed experimentally by Plazek. Finally, the present theory predicts that the Plazek exponent (x) for the shift factor is approximately related to the Chasset and Thirion exponent (m) for the relaxation modulus ($x \sim 2/m$) in a manner consistent with available experimental data.

Introduction

It is well-known[1,2] that elastomers undergo extremely long-term relaxation processes as seen in stress relaxation and creep experiments. Furthermore, the time required to achieve equilibrium decreases dramatically as the cross-link density increases. Ferry has suggested[2] that the molecular mechanism responsible for this long-term process is the diffusion of chain branches (dangling ends) in the presence of entanglements. Recently, de Gennes[3] analyzed the reptation of branched polymers in the presence of topological constraints. We feel that this approach may provide a molecular basis for certain empirical relationships which describe the viscoelastic behavior of elastomers in the terminal relaxation region. The purpose of this paper, therefore, is to compare these existing empirical observations with the predictions of the theories for reptation of branched chains.

Phenomenological Observations

Typical stress relaxation behavior[1] of elastomers at long times is shown in Figure 1 for natural rubber. Chasset and Thirion[1] recognized that an excellent representation of this data is given by

$$E(T) = E_\infty[1 + (t/\tau_0)^{-m}] \qquad (1)$$

for large times t, where $E(t)$ is the isothermal relaxation modulus. E_∞ is the equilibrium modulus, and m and τ_0 are material parameters. This relationship holds for temperatures below which no chemical reaction or degradation occurs during the experiment. In most systems the exponent m is approximately 0.1. A similar expression also holds for the time dependence of the creep compliance.[2] Equation 1 is an excellent representation of data for many systems and is sometimes used for estimating the equilibrium modulus E_∞ from stress relaxation experiments.

The relaxation behavior is strongly dependent on temperature and cross-link density. Plazek[4] and Dickie and Ferry[5] observed that viscoelastic curves at fixed cross-link

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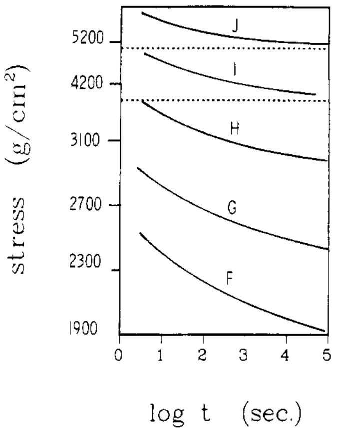

Figure 1. Stress relaxation data[1] of Chasset and Thirion on natural rubber at 30 °C and 50% elongation at various cross-link densities. The vulcanizates shown have the following cross-link densities: F, 0.46 × 10^{-4}; G, 0.62 × 10^{-4}; H, 0.80 × 10^{-4}; I, 1.20 × 10^{-4}; J, 1.69 × 10^{-4}.

density displayed conventional time–temperature superposition behavior.[2] This implies that only E_∞ and τ_0 in eq 1 depend on temperature. Plazek's results suggest that τ_0 in eq 1 can be written as

$$\tau_0(T,\nu) = \tau_0(T_0,\nu_0)a_T a_x \tag{2}$$

where T_0 and ν_0 refer to the reference temperature and cross-link density, and a_T and a_x represent shift factors for temperature and cross-link density. Plazek[4] observed a power law dependence of a_x on cross-link density ν

$$a_x = (\nu/\nu_0)^{-x} \tag{3}$$

where $x \sim 15$.

Dickie and Ferry[5] analyzed their results on natural rubber by fitting eq 1 to time–temperature master curves at each cross-link density. They found that not only E_∞ and τ_0 but also m depend on cross-link density.

Theory

Ferry[2] has speculated that the molecular process associated with this long-time behavior is related to the existence of branched structures in the presence of entanglements. These branched structures or dangling ends can eventually relax to their unperturbed conformations, even though the network to which they are attached remains in a state of strain. This process would be expected to be slow because of the presence of entanglements, which act as topological constraints.

de Gennes[3] has studied the reptation of a branched chain in the presence of fixed obstacles. In his study, de Gennes considered a branch or dangling chain end of n units that is *permanently* attached to a fixed point in space. Since one end of the chain is fixed, it cannot undergo conventional reptation.[3] de Gennes argued that the only way such a chain in a perturbed state can reach its equilibrium conformation is by retracting its path to the origin (or branch point). Using this reasoning, de Gennes showed that the reptation time t_n for a chain branch to reach equilibrium depends exponentially on the chain length n

$$t_n = \tau_1 \exp(\alpha n) \tag{4}$$

where τ_1 is only weakly dependent on n and α is a material constant. Furthermore, de Gennes argued[3] that the component of stress σ_n due to the dangling chain end is proportional to that part (l) of the chain (of n units) which has relaxed to equilibrium.

$$\sigma_n(t) \sim l(t) \tag{5}$$

Following de Gennes, a crude estimate of the time dependence of l can be found from eq 4 to be

$$l(t) = \alpha^{-1} \ln (t/\tau_1) \tag{6}$$

It can be observed from experiment (see Figure 1 and eq 1), however, that the relaxation behavior of elastomers is decidedly not logarithmic. The mechanism by which the dangling chain end approaches equilibrium can be visualized as a modified reptation process within a constraining tube. As the chain retraces its path from the free end, $l(t)$ of the n segments emerge from the original tube. Since excluded volume of the chain within the tube is not considered, the quantity $l(t)$ is independent of chain length n.

In this investigation, we make a different assumption than de Gennes' in eq 5 for the stress component[8]

$$\sigma_n(t) \sim n - l(t) \tag{7}$$

for $l \leq n$. This relation implies that the stress due to a dangling end of length n is proportional to that part of the chain which has *not* relaxed to equilibrium.

In general, we would expect a distribution of chain lengths n in a real elastomer because of the random nature of the cross-linking process. The total stress on the network would then be obtained by summing over contributions from all chain lengths n. At long times, when all other relaxation processes have relaxed to zero, we can then write the following expression for the relaxation modulus:

$$E(t) = E_\infty + k\sum_{n=l}^{\infty}[n - l(t)]P(n) \tag{8}$$

where k is a material constant and $P(n)$ is the probability of having a dangling end of n units.

The probability $P(n)$ can be easily determined for random cross-linking of a system of cross-link density ν having ρ chain segments per unit volume (see Appendix). For the case of interest, $\nu \ll \rho$ and $P(n)$ is given by

$$P(n) = q(1 - q)^{n-1} \tag{9a}$$

$$q = \nu/\rho \tag{9b}$$

If eq 9a is substituted into eq 8, the summation can be performed to give

$$E(t) = E_\infty + (k/q)(1 - q)^l \tag{10}$$

If we now substitute eq 6 into eq 10 and make use of the rubber elasticity[6] result for the equilibrium modulus, we obtain after rearrangement (for $q \ll 1$)

$$E(t) = E_\infty[1 + (t/\tau_{\text{av}})^{-q/\alpha}] \tag{11}$$

where the relaxation time τ_{av} is given by

$$\tau_{\text{av}} = \tau_1(k_{\text{B}}T\nu^2/k\rho)^{-\alpha/q} \tag{12}$$

Equation 11 is seen to have the same form as the empirical Chasset and Thirion relation in eq 1. Thus we can identify the exponent m and τ_0 in eq 1 as

$$m = a/\alpha = \nu/\alpha\rho \tag{13}$$

$$\tau_0 = \tau_{\text{av}} \tag{14}$$

Discussion

From the preceding arguments, it can be seen that a dangling chain model leads to an expression for the relaxation modulus which has the same form as the empirical Chasset and Thirion equation. Furthermore, we now have a theoretical interpretation of the empirical parameters m and τ_0 in this equation. We will now compare the

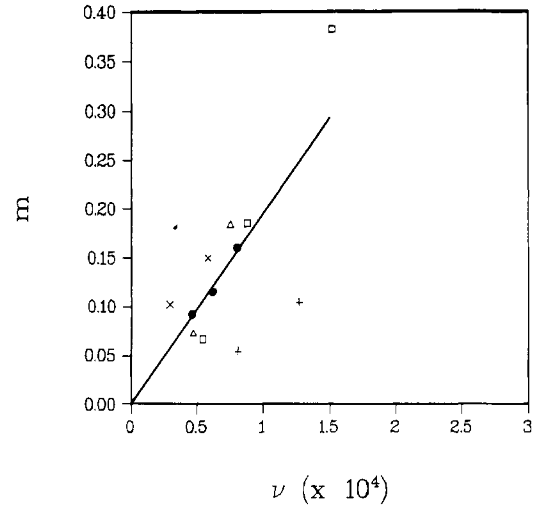

Figure 2. Parameter m in eq 1 obtained from the creep data[5] on various natural rubber samples. The samples shown by circles are the same as in Figure 1. The other samples have various initial molecular weights (before vulcanization) as follows: (△) 550 K; (+) 770 K; (×) 260 K; (□) 230 K. The straight line is drawn through the circles and the origin.

predictions of the theory with available experimental data.[4,5]

Cross-Link Density Dependence of m and τ_0. The present theory predicts that the parameters m should be linearly related to the cross-link density ν. Furthermore, eq 12–14 imply that

$$-m \log (t/\tau_1) = \log (k_B T/k\rho) + 2 \log \nu \qquad (15)$$

The above equation could be used to test the cross-link density dependence of τ_0 provided τ_1 is known.

Dickie and Ferry[5] performed long-term creep measurements on well-characterized samples of natural rubber. They then fitted their results to the analogous expression to eq 1 for the creep compliance $J(t)$.

$$J(t) = \frac{1}{G_\infty[1 + (t/\tau_0)^{-m}]} \qquad (16)$$

Equation 16 can be easily derived[2] from eq 1 for a linear viscoelastic material in the long-term limit. These workers indeed found that both τ_0 and m depend on cross-link density. Their results for m are shown in Figure 2. Unfortunately, the results show considerable scatter as can be seen in the figure. It should be noted, however, that most of the natural rubber samples were masticated to various degrees prior to curing with dicumyl peroxide.[5] Each set of symbols in Figure 2 represents samples having the same initial average molecular weight and distribution. The data shown by circles in Figure 2 represent the same samples as studied in ref 1 and were not masticated prior to curing. Perhaps the different initial molecular weight distributions are contributing to the scatter in these data. If one looks only at the samples that were not premasticated (circles), a reasonably good linear fit through the origin is seen, in accordance with our theoretical prediction.

Figure 3 shows a plot of $-m \log \tau_0$ vs. $\log \nu$ from the tabulated values of Dickie and Ferry.[5] As in the previous figure, we observe substantial scatter in the data. If, as before, we consider only samples that were not premasticated, we find a straight line of slope 2, in accordance with the theoretical prediction. This plot implies that the theoretical parameter τ_1 has a value of approximately 1 s to be consistent with eq 15.

Cross-Link Density Superposition. Plazek[4] performed creep experiments on the same natural rubber that was studied by Chasset and Thirion[1] and Dickie and Ferry.[5] As mentioned earlier, Plazek observed that his data at different cross-link densities could be superposed to a single master curve. The shift factors exhibited power law dependence on ν according to eq 3. On the surface, it appears that the theoretically and experimentally observed dependence of the exponent m on cross-link density precludes a superposition of curves observed by Plazek since superposition implies that

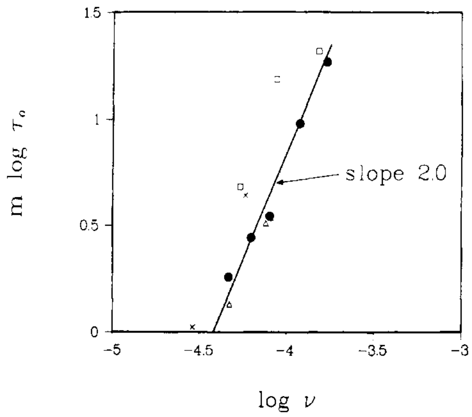

Figure 3. $-m \log \tau_0$ vs. $\log \nu$ for the same samples as in Figure 2. A straight line of slope 2, in accordance with eq 15, is drawn through the circles. Equation 15 implies that $\tau_1 \sim 1$ s.

$$E(t,\nu) = E(t/a_x) \qquad (17)$$

If, however, the parameter m is small compared to 1 ($m \ll 1$), the theoretical relaxation modulus can be shown to obey eq 17 to a good approximation. This can be seen by expanding eq 1 in a Taylor expansion about $t/\tau_0 = 1$. For times $t \gg \tau_0$ ($\sim$1 s), this expansion can be written as

$$\frac{E(t)}{E_\infty} = 2 + \sum_{i=1}^{\infty} \frac{(-1)^i}{i}\left(\frac{t}{\tau_i'} - 1\right)^i \qquad (18)$$

where

$$\tau_i' = \tau_1\left(\frac{k_B T \nu^2}{k\rho}\right)^{-1/m}\left[\frac{\Gamma(i)\Gamma(m)}{\Gamma(m+i)}\right]^{1/i} \qquad (19)$$

We now make use of the fact that $m \ll 1$, in which case eq 19 reduces to

$$\begin{aligned}\tau_i' &\cong \tau_1\left(\frac{k_B T \alpha^2 \rho}{k}\right)^{-1/m} m^{-(2/m+1/i)} \\ &\cong \tau_1\left(\frac{k_B T}{k\rho}\right)^{-1/m} \nu^{-2/m} \qquad (20)\end{aligned}$$

where we have made use of eq 13 for m. Thus, it can be seen that τ_i' is independent of i provided m is small, and eq 17 holds.

We can now obtain a theoretical expression for the shift factor a_x in eq 17

$$\begin{aligned}a_x &= \tau_i'(\nu)/\tau_i'(\nu_0) \\ &= \left(\frac{k_B T \nu^2}{k\rho}\right)^{-1/m_0(1-\nu_0/\nu)}\left(\frac{\nu}{\nu_0}\right)^{-2/m_0} \qquad (21)\end{aligned}$$

where ν_0 is some reference cross-link density and

$$\begin{aligned}m_0 &= m(\nu_0) \\ &= \nu_0/\alpha\rho \qquad (22)\end{aligned}$$

For ν close to ν_0, we recover the power law behavior observed empirically by Plazek[4]

$$a_x \sim (\nu/\nu_0)^{-2/m_0} \tag{23}$$

Furthermore, we note from eq 23 and 3 that the present theory predicts an approximate relationship between the phenomenological exponents m and x.[9]

$$x \sim 2/m \tag{24}$$

Since Plazek[4] found that $x \sim 15$, eq 24 implies that $m \sim 0.13$. This is approximately correct, as can be seen from the range of m values occurring in Figure 2.

Secondary Dangling Ends. It has been pointed out by Pearson and Graessley[7] that dangling chain structures, which themselves contain dangling ends, can occur in randomly cross-linked networks. In the present analysis we neglect these secondary branched structures. As pointed out by Pearson and Graessley,[7] the number of branch points per dangling end approaches zero rapidly as the cross-link density is increased above the gel point. Although we have not considered these secondary structures explicitly in the present analysis, it seems likely that they would approach their equilibrium conformation in a similar manner to the primary dangling ends (i.e., by path retracement).

Conclusions

Building on the work of de Gennes,[3] we have shown that a polymer network containing a random distribution of dangling chain ends leads to a relaxation modulus having the same form as the phenomenological Chasset and Thirion equation.[1] This supports the conjecture of Ferry[2] that dangling chain ends lead to extremely long viscoelastic processes. The present theory predicts a cross-link density dependence of the Chasset and Thirion parameters m and τ_0 which appears to be in accordance with experimental data on natural rubber. Further experiments on other well-characterized elastomers are clearly needed to demonstrate the generality of the theoretical predictions. The theory also predicts that for small m (as observed experimentally) viscoelastic curves of different cross-link density would be superposable along the log time axis. Furthermore, the shift factors approximately obey an empirical power law relationship seen by Plazek. Finally, the theory predicts that the phenomenological exponents m and x are related to each other in a way that is consistent with experiment.

Appendix

The probability $P(n)$ of having a dangling chain end can be determined for a randomly cross-linked system. Suppose we have a system of N chains per unit volume and a monomer density ρ. The average degree of polymerization r is then given by $r = \rho/N$ and the average number of cross-links per chain s is given by $s = \nu/N$, where ν is the cross-link density. If we consider a given chain, the first cross-link can occur on r sites. The probability q of any unit k $(1 \leq k \leq r)$ on the chain being cross-linked for a random process is thus

$$q = \frac{1}{r} + \frac{1}{r-1} + \ldots + \frac{1}{r-s+1} = \sum_{i=1}^{S}(r+1-i)^{-1} \cong -\ln(1-s/r) \cong s/r = \nu/\rho \tag{1A}$$

In eq 1A, we have assumed that the cross-link density ν is much less than the monomer density ρ (i.e., $s \ll r$).

The probability of having a sequence of exactly n units is then

$$P(n) = q(1-q)^{n-1} \tag{2A}$$

which is the probability of having $n - 1$ consecutive un-cross-linked sites followed by a cross-linked site. Equation 2A is identical with eq 9a in the text.

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(8) A somewhat different assumption, $\sigma_n \sim 1 - l/n$, can also be used in place of eq 7. This leads to results that are fundamentally the same as presented here, with only minor differences.

(9) The assumption $\sigma_n \sim 1 - l/n$ rather than eq 7 leads to $x \sim 1/m$ rather than eq 24.