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A New Rheological Constitutive Equation for the Network Model of Polymer Melts

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Synopsis

A new network model is suggested and a constitutive equation is developed on the basis of the assumed validity of Boltzmann's superposition principle for the shear stress. The predictions of the model concerning the relaxation behavior of polymer melts after steady shear or instantaneous deformation are compared to Lodge's theoretical results and to experimental data from the literature.

INTRODUCTION

Many attempts[1-9] have been made to extend the molecular network theory of rubber-like elasticity for permanently crosslinked rubbers so as to apply to concentrated high polymer solutions and melts.

Common to all such theories is the assumption that the stress is determined, apart from an additive isotropic pressure, by the deformation history of an impermanent molecular network whose junctions are created and lost during the deformation.

The theory of Lodge gives constitutive equations which account for large viscosity, positive primary normal stress difference, and large elastic recoil.
In the case of melts, solvent viscosity may be disregarded and stresses at any instant may be uniquely referred to the space distribution of network segments at that time.

The fundamental task of Lodge's and similar theories is thus the determination of an equation capable of relating the spatial distribution of network segments to macroscopic flow history. This task is accomplished in Lodge's theory starting from the following assumptions: (1) affinity between chain segment distortion and macroscopic deformation; (2) constant and stress-independent probability of junction loss; (3) isotropic generation of network segments; and (4) Gaussian network.

Experimentally, the relaxation modulus is nonexponential, and this observation forces Lodge to subdivide the network junctions into classes, each of which is characterized by a particular relaxation time τ.

The theory of Lodge is capable of predicting second-order effects, such as normal stresses, but it furnishes a viscosity which is independent of shear rate.

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Yamamoto[6-8] accounts for non-Newtonian behavior by modifying assumptions (3) and (4) of Lodge: (5) anisotropic generation of chain segments; and (6) non-Gaussian network.

Kaye[9] explains non-Newtonian behavior by assuming that the junction loss probability depends on the stress tensor.

Mills[10] has investigated experimentally the relaxation behavior of poly(dimethylsiloxane) after both steady shear flow and instantaneous deformation. He takes into consideration both tangential stress and normal stress difference. From Mills' data, it is possible to test the following predictions of Lodge's theory:

$$P_{12}^{s} = -\dot{P}^{s}/2\dot{\gamma} \tag{1}$$

$$\dot{P}_{12}^{s}/\dot{\gamma} = -P_{12}^{i}/\gamma \tag{2}$$

$$P^{i} = \gamma P_{12}^{i} \tag{3}$$

where P denotes the primary normal stress difference during relaxation, P_{12} the tangential stress during relaxation, and all quantities appearing in eqs. (1)–(3) refer to experiments of relaxation after steady shear (superscript s) or instantaneous deformation (superscript i); $\dot{\gamma}$ and γ are, respectively, the steady shear velocity gradient and the instantaneous deformation. Comparison with Mills' data shows that only eq. (2) fits experimental results.

In all cases, the normal stress seems to decay much more slowly than predicted by Lodge. Mills concludes that it is necessary to find two separate memory functions for tangential and normal stress. For incompressible materials this task cannot be accomplished within the framework of a linear viscoelastic theory.

In this paper we show that strong disagreements between the theory of Lodge and the experimental data on relaxation may be explained by introducing a new network model without requiring "ad hoc" nonlinearity considerations, at least for sufficiently low $\dot{\gamma}$.

BASIC ASSUMPTIONS OF A NEW PROPOSED MODEL

It may easily be shown that eq. (2) can be deduced not only from Lodge's theory, but from any linear visco-elastic theory, since it is a necessary consequence of Boltzmann's superposition principle. The observed agreement of eq. (2) with the experimental data therefore supports a linear analysis, but may not be considered as a proof of the validity of Lodge's theory.

In proposing a new network model, we shall give an equation relating the segment distribution function to the flow history:

$$n(\mathbf{r},t) = \mathfrak{L}[\dot{\gamma}(t')] \tag{4}$$

the main task of our paper being the determination of the actual form of the functional $\mathfrak{L}$. The stresses can then be calculated as moments of the distribution function $n(\mathbf{r},t)$ (see, e.g., ref. 11, eq. 3.37).

Adapting the results to a Gaussian network and assuming for simplicity that all segments contain the same number ν of free units, each of length l, we obtain for shear flow

$$P_{12} = 2kTb \int xyn(\mathbf{r},t)d^{3}\mathbf{r} \tag{5}$$

$$P = 2kTb \int (x^2 - y^2)n(\mathbf{r},t)d^3\mathbf{r} \tag{6}$$

where the x direction is flow parallel; b stands for $3/2\nu l^2$; k is the Boltzmann constant; and T is absolute temperature. In order to calculate $n(\mathbf{r},t)$, we shall formulate some conditions which restrict the possible forms of $\mathfrak{L}$.

We make no specific assumption as to the kinetics of segment generation and dissociation, but according to Mills' results, we require that the shear stress as calculated from eq. (5) must obey Boltzmann's superposition principle for an arbitrary flow history $\dot{\gamma}(t')$:

$$P_{12} = \int_{-\infty}^{t} G(t - t')\dot{\gamma}(t')dt' \tag{7}$$

where G is the memory function for shear stress, better known as the relaxation modulus. Furthermore, we require that no separate memory function need be introduced in order to explain normal stress relaxation. As a consequence of this assumption, we establish a principle of correspondence between memory functions, stating that $\mathfrak{L}$ must not contain material time constants not appearing also in the constitutive equation (7).

Other restrictions to the possible forms of $\mathfrak{L}$ can be derived from normalization conditions, asymptotic considerations, and invariance principles. A complete list of our assumptions is given below:

1. Unique derivability of stresses from the deformation state of a Gaussian network.
2. Uniform molecular weight of segments.
3. Validity of Boltzmann's superposition principle for the shear stress.
4. Existence of a principle of correspondence for memory functions referring to P_{12}, P, $\mathfrak{L}$.
5. Normalization condition for the distribution function

$$\int n(\mathbf{r},t)\, d^3\mathbf{r} = n_0. \qquad (n_0 = \text{constant})$$

6. Reduction of $n(\mathbf{r},t)$ to the Gaussian distribution function $n_{iso} = n_0(b/\pi)^{3/2}$ exp $(-br^2)$ for a vanishing flow history $[\dot{\gamma}(t') \to 0]$.
7. Invariance of $\mathfrak{L}$ with respect to a uniform shift in the time scale.

Assumptions 3 and 5 are seemingly not true for high enough flow rates, so that the applicability of our model is restricted to the region of Newtonian behavior. Within this limitation, the new model, though semiphenomenological in nature, can be applied to general network systems, such as the energetic model of Lodge-Yamamoto or a sliding contact network model.[12,13]

MODEL SOLUTION

There are at least two independent (and probably only two) functionals $\mathfrak{L}[\dot{\gamma}(t')]$ satisfying all requirements 1–7, as may be seen by inspection:

$$\mathfrak{L}_1[\dot{\gamma}(t')] = \int_{-\infty}^{t} \frac{[-\dot{G}(t - t')]}{n_0kT}\, n^*\, dt' \tag{8}$$

$$\mathfrak{L}_2[\dot{\gamma}(t')] = \int_{-\infty}^{t} \frac{G(t - t')}{n_0kT(t - t')}\, (\bar{n} - n_{iso})dt' + n_{iso} \tag{9}$$

where n^* and $\tilde{n}$ are defined by

$$n^* = n_0\left(\frac{b}{\pi}\right)^{3/2} e^{-b\{[x-y\gamma(t)+y\gamma(t')]^2+y^2+z^2\}} \tag{10}$$

$$\tilde{n} = n_0\left(\frac{b}{\pi}\right)^{3/2} e^{-b\{[x-y\dot{\gamma}(t')(t-t')]^2+y^2+z^2\}} \tag{11}$$

Formally, n^* may be associated with a network state characterized by a macroscopic deformation $\gamma(t) - \gamma(t')$, whereas $\tilde{n}$ may be associated with a state of flow $\dot{\gamma}(t')$ starting at time t'.

$\mathfrak{L}_1$ leads to the following equation:

$$P_{12} = \int_{-\infty}^{t} [-\dot{G}(t-t')][\gamma(t) - \gamma(t')]dt' \tag{12}$$

which, after integration by parts and with reasonable restrictions on $G(t)$, reduces to eq. (7): (I) $G(0)$ finite and equal to $n_0 kT$; (II) $G(\infty) = 0$. Actually, restriction (I) is also needed to satisfy the normalization requirement.

On the other hand, no such restriction is necessary for functional $\mathfrak{L}_2$. When substituting $\mathfrak{L}_2$ in eq. (5), we get Boltzmann's superposition principle in the standard form (7).

Putting $n(\mathbf{r}, t) = \mathfrak{L}_1[\dot{\gamma}(t')]$ and making use of eqs. (5) and (6), we obtain, in the case of stress relaxation, the set of results (1), (2), and (3) obtained by Lodge. In fact eq. (8) is nothing but the characteristic time evolution equation of the distribution function according to the theory of Lodge for the case of a uniform segment length. Thus, eq. (8) has quite an obvious structural meaning; it suggests the existence of a temporary network which deforms in an affine fashion.

Equation (9) has no well-known structural counterpart and leads to completely new connections between the tangential and normal stresses during relaxation. A discussion of the structural implications of this new model will be given after the experimental check on its predictions given in the following section.

COMPARISON OF LODGE'S THEORY AND NEW MODEL WITH EXPERIMENTAL DATA ON RELAXATION

Equation (9), when applied to relaxation processes, gives the following connection between the tangential and normal stresses:

$$\dot{P}^s/\dot{P}_{12}{}^s = \dot{\gamma}t \tag{13}$$

$$P^i/P_{12}{}^i = \gamma t/\epsilon \tag{14}$$

where time t is measured from the instant of flow interruption. Equation (13) refers to relaxation after steady shear $\dot{\gamma}$; eq. (14) applies to relaxation after a quasi-instantaneous deformation γ; ϵ is the time duration of the deformation impulse which is presumed to be applied at constant shear rate γ/ϵ. The validity of eq. (14) is obviously subject to the condition $t \gg \epsilon$. Equations (13) and (14) correspond to eqs. (1) and (3) of Lodge, to which they have been compared using Mills' experimental data as a reference.

Differentiating eq. (1) with respect to time we get

$$|\dot{P}_{12}{}^s| = \ddot{P}^s/2\dot{\gamma} \tag{15}$$

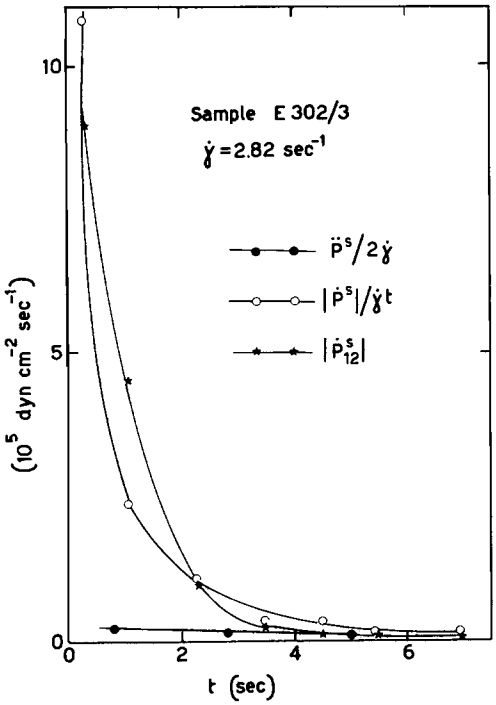

Fig. 1. Mills' data on relaxation after steady shear plotted for a comparative check of eqs. (15) and (26).

which is to be compared with the alternative equation

$$|\dot{P}_{12}{}^s| = |\dot{P}^s|/\dot{\gamma}t. \tag{16}$$

Mills' data for $|\dot{P}_{12}{}^s|$, $P^s/2\dot{\gamma}$, and $|\dot{P}^s|/\dot{\gamma}t$ referring to an experiment of relaxation after steady shear performed on the author's sample E 302/3[10] were plotted in Figure 1 against time for a comparative check of eqs. (15) and (16). Similarly, we get from eqs. (3) and (14)

$$P_{12}{}^i/\gamma = P^i/\gamma^2 \tag{17}$$

$$P_{12}{}^i/\gamma = \epsilon P^i/\gamma^2 t. \tag{18}$$

Equations (17) and (18) have been comparatively checked by plotting Mills' data referring to experiments of relaxation after instantaneous deformation performed on sample E 302/1C (see Fig. 2). The value for ϵ was known from experiment.

It may be seen from Figures 1 and 2 that the new model fits the experimental data much more closely.

By making a linear superposition of $\mathfrak{L}_1$ and $\mathfrak{L}_2$, we obtain a more general (seemingly the most general) form of functional $\mathfrak{L}$, satisfying all the prescribed requirements 1–7:

$$\mathfrak{L}_q = q\mathfrak{L}_1 + (1 - q)\,\mathfrak{L}_2 \tag{19}$$

where q is a dimensionless numerical constant expressing the relative weight of the Lodge component $\mathfrak{L}_1$.

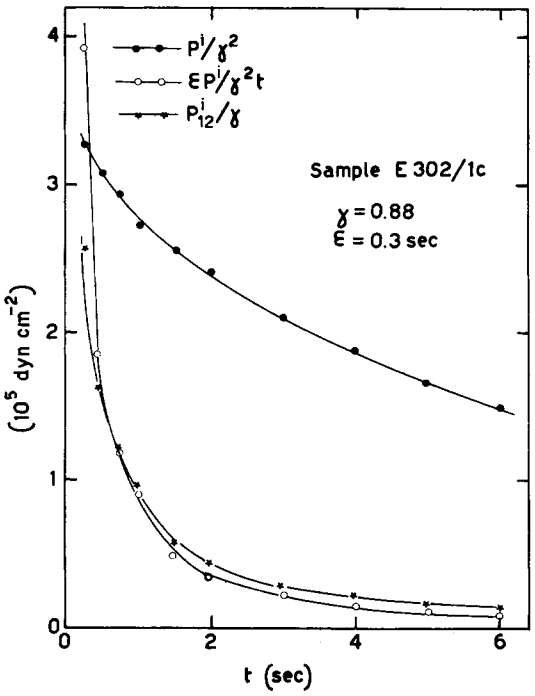

Fig. 2. Mills' data on relaxation after instantaneous deformation plotted for a comparative check of eqs. (17) and (18).

From eq. (19) we obtain

$$|\dot{P}^s(0)| = 2\,\dot{\gamma}\,q\,P_{12}{}^s(0). \tag{20}$$

Comparison with experimental data gives, as expected, quite a low value for the relative weight of the Lodge component:

$$q \simeq 0.1. \tag{21}$$

CONCLUDING REMARKS ON THE STRUCTURAL INTERPRETATION OF THE NEW MODEL

Considering a polymer network in conditions of steady flow or stress relaxation, we remark that its most general state, according to eq. (9), results from the superposition of two states: a rest state n_{iso} and a flow state $\tilde{n}$, into which activated segments are forced. We observe that, according to eq. (9), even in conditions of steady shear, a nonvanishing number of segments may be left in a rest state. On the other hand, eq. (9) suggests that, after flow interruption, some segments still remain in a state of distortional motion, their progressive decay into the isotropic rest state being responsible for the relaxation of stresses.

Such a strongly nonaffine behavior seems to be incomprehensible within the domain of the temporary network model, but it becomes acceptable if we think of a polymer melt as a collection of entangling molecules. In fact, it is quite reasonable to assume that network segments belonging to such a system are repeatedly swept across flow-activated states and isotropic rest states. Furthermore, it is not surprising that an instantaneous flow interruption does not freeze

the entangling molecules, but rather leaves activated segments in a state of distortional motion, as predicted by eq. (9).

Our feeling is that the observed agreement of the new model with experimental data on stress relaxation seems to support the entanglement hypothesis.

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