

The Steady Flow Shear Modulus of Polymer Melts

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Synopsis

Relaxation times of polyethylene melts have been measured by Aloisio, Matsuoka, and Maxwell. One implication regarding their observations is that the elastic properties of polymer melts must be time-dependent. In particular, the steady-flow shear modulus depends on the strain rate. Some interpretations of data in the literature have been based on concepts in rubber elasticity where the steady-flow modulus is an equilibrium value, independent of strain rate. We have used Pao's theory for viscoelastic flow together with measurements of relaxation times to discuss the strain rate dependence of the steady-flow shear modulus of melts. The existence of a strain rate-dependent shear modulus leads naturally to a nonlinear relation between shear stress and recoverable shear strain. The conclusions regarding the molecular weight dependence of the modulus also differ from interpretations based on rubber elasticity.

The elastic properties of polymer melts and solutions undergoing steady laminar shearing flow have received considerable attention in the recent literature. Generally, the elastic properties are specified in terms of a steady-flow shear modulus defined by

$$\tau = Gs \quad (1)$$

where τ is the shear stress, G is the modulus, and s is the recoverable shear strain. Since τ is a function of the rate of shear strain, $\dot{\gamma}$, in general both G and s may have shear rate dependence.

In 1947 Weissenberg¹ proposed a constitutive law for elastic fluids in which the recoverable shear strain is defined as

$$s = (P_{11} - P_{22})/\tau \quad (2)$$

where $(P_{11} - P_{22})$ is the difference between the normal stress components along coordinates in the direction of flow and in the direction of varying velocity respectively. This relation has been widely used by researchers with little experimental justification. Except for some recoil measurements by Philippoff and co-workers² on polyisobutylene, and by Pollett³ on low-density polyethylene, in which only very rough agreement with eq. (2) was obtained, there is little evidence to support the validity of this assumption for polymer melts. Since almost all measured values for steady-flow shear modulus are based on a recoverable strain calculated from eq. (2), serious errors may exist in the reported moduli.

Recently values of shear modulus independent of shear rate for polyethylene melt undergoing steady laminar flow have appeared in the literature. Dexter and co-workers⁴ obtained a value for G of 7.3×10^4 dynes/cm.² for low-density polyethylene from a plot of s versus τ measured in a concentric cylinder apparatus. Their experiments were performed at temperatures ranging from 130 to 170°C., yet all the data appear to scatter about a single straight line. Only one decade of shear rate was covered. For the data taken at 130°C., poor agreement was noted between the experimental values of s and those calculated from birefringence data through the use of eq. (2), though at higher temperatures reasonable agreement was observed.

Bagley^{5,6} obtained linear plots of s versus τ for both branched and linear polyethylenes at 190°C. from capillary end-correction measurements. This method assumes that s is given by eq. (2) (see, for example, Philippoff and Gaskins.⁷ From these plots he calculated shear moduli of 8.3×10^4 and 3.6×10^5 dynes/cm.² for the branched and linear material, respectively. In addition he proposed that the molecular weight of a linear polymer might be calculated from the constant-valued steady-flow shear modulus by the relation

$$G = RT\rho/M \quad (3)$$

where R is the gas constant, T is the absolute temperature, ρ is the polymer melt density, and M is the molecular weight. This equation was derived by Wall⁸ from a statistical treatment of rubber elasticity in which it is assumed that rubber obeys Hooke's law in shear. In Wall's treatment, M is molecular weight between crosslinks of the rubber network.

Recently Aloisio, Matsuoka, and Maxwell⁹ have demonstrated that a discrete relaxation spectrum for a polymer melt exists. In light of this development we do not believe that one is justified in assuming G is independent of the rate of shear in steady laminar flow. At low shear rates only the long relaxation times would contribute to the modulus, but at higher rates the shorter relaxation times have an increasing effect. Thus G would be expected to vary with rate of shear.

In view of this fact it is somewhat surprising that constant-valued shear moduli have been reported for polymer melts undergoing steady laminar flow. This might be attributed in part to the fact that the moduli were based on recoverable strains calculated from unsubstantiated relationships such as eq. (2) and to the relatively small intervals of shear rate thus far investigated. In addition because the recovery process is itself dissipative, observed values of recovered strain are less than the actual recoverable strain.

In rubber elasticity, where Hooke's law in shear is assumed, G is an equilibrium modulus and is independent of the rate of shear. In polymer melts, however, G should not be an equilibrium modulus if a relaxation spectrum exists but should be based on that spectrum. In addition, it

follows that the use of Wall's equation for determining the molecular weight of linear polymers is without theoretical foundation.

Pao's continuum theory for viscoelastic fluids^{10,11} assumes the existence of a relaxation spectrum for the polymer melt. In his theory, the material properties such as viscosity and steady-flow modulus are couched in terms of parameters which describe the relaxation spectrum. For steady laminar shearing flow, G is given by

$$G = K \left\{ \frac{\left[\sum_i \frac{G_{0i}/\tau_i}{(1/\tau_i)^2 + K^2} \right]}{\sum_i \frac{G_{0i}K}{(1/\tau_i)^2 + K^2}} + \sum_i \frac{G_{0i}K}{(1/\tau_i)^2 + K^2} \right\} \quad (4)$$

where the τ_i and G_i are the discrete relaxation times and moduli, respectively, and K denotes the velocity gradient ($= 2 \dot{\gamma}$). Figure 1 (curve *a*) shows the shear modulus calculated from Pao's theory as a function of shear rate for a high molecular weight linear polyethylene (MI = 0.9) at 190°C. The terminal region of the relaxation spectrum used was measured by Aloisio and co-workers.⁹ The rest of the spectrum was approximated according to their method. It is seen that G increases with rate of shear.

Because of this result it might be expected that shear stress versus recoverable strain should be nonlinear if the data cover a sufficiently large range of shear rate. Figure 2 shows a plot of s versus τ in which both values have been computed from Pao's theory. A nonlinear relationship is obtained, though over a limited range the curve can be represented quite adequately by a straight line.

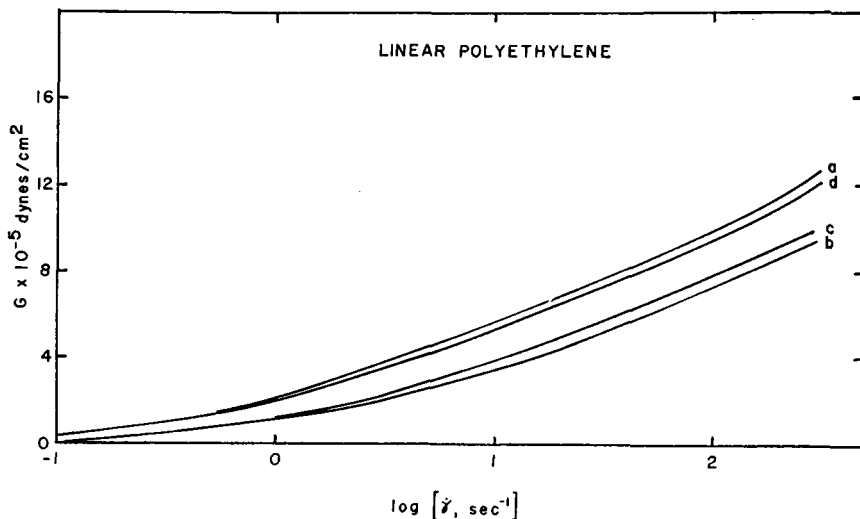


Fig. 1. Steady-flow shear modulus vs. strain rate for high molecular weight linear polyethylene (MI = 0.9) at 190°C. and low molecular weight linear polyethylene (MI = 5.0) at 200°C. and 190°C.

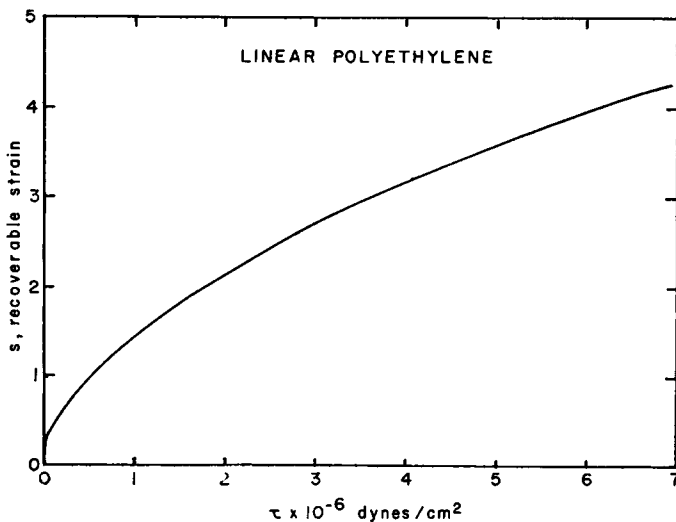


Fig. 2. Shear stress vs. recoverable shear strain for high molecular weight linear polyethylene at 190°C.

In finite elasticity, an equation similar to eq. (2) is a result of mechanics rather than a definition of strain. Likewise, in a rational viscoelastic theory, eq. (2) should not be taken to define the recoverable strain but, if applicable, it should be a result of the mechanics. The recoverable strain is not a kinematically determined quantity. However, Pao defined it by using an equivalent form of the constitutive equation involving the retardation spectrum. Since exact relations exist between the two spectra,¹² the two forms of the constitutive equation are internally consistent with one another. We have derived expressions for $P_{11} - P_{22}$ and τ for flow through a capillary tube by using Pao's viscoelastic theory. By comparing the ratio of these quantities to Pao's expression for recoverable strain, we obtain the result

$$s = (P_{11} - P_{22})/2\tau \quad (5)$$

Since this recoverable strain is one-half the value used by most other authors, our modulus values are roughly twice as large.

In the limit of very small shear stresses the steady flow shear modulus decreases to zero. This implies that the curve in Figure 2 approaches the recoverable strain axis asymptotically as we have indicated.

We do not wish to intimate that Pao's theory should give quantitative agreement with experimental observations merely because it is based on the relaxation spectrum of the polymer. This is a separate but important question still largely unsettled. We wish only to point out that the existence of a relaxation spectrum for polymer melts leads naturally to a strain rate-dependent shear modulus and a nonlinear relation between shear stress and recoverable shear strain in steady laminar flow.

A second implication regarding the shear modulus of polymer melts concerns molecular weight. It is generally accepted that the width of the plateau region of the viscoelastic spectrum is related to the molecular weight of the polymer.¹³ Two materials at the same conditions of temperature and shear rate but differing in molecular weight have different moduli. This is expected on the basis that the relaxation spectrum is extended to longer times as molecular weight increases, corresponding to an increase in the width of the plateau zone.

We have computed the shear modulus according to Pao's expression for another linear polyethylene (MI = 5.0) of lower molecular weight. The same method as before was used to obtain the relaxation spectrum. Figure 1 (curve *b*) shows the result for 201°C. In order to compare the two moduli at the same temperature we have shifted the data for curve *b* to 190°C. using an activation energy of 6 kcal./mol.⁹ Curve *c* in Figure 1 shows this result and illustrates that the shear modulus in this region of shear rates is less than the corresponding value for the higher molecular weight polymer.

The effect of molecular weight on G can be accounted for quantitatively according to the following considerations. From molecular theory the width of the plateau zone is predicted¹³ to be

$$D = 2.4 \log(\bar{M}_w/2M_e) \quad (6)$$

where D is the width on the $\log \tau$ axis, \bar{M}_w is weight-average molecular weight, and M_e is the molecular weight between entanglements. The increase in width due to a higher molecular weight can therefore be estimated from the ratio of molecular weights

$$\Delta D = 2.4 \log(\bar{M}_{w_1}/\bar{M}_{w_2}) \quad (7)$$

where \bar{M}_{w_1} and \bar{M}_{w_2} are molecular weights of the two materials. \bar{M}_{w_1} is reported to be about 130,000 and \bar{M}_{w_2} about 90,000. Using these values to estimate the relaxation spectrum at 190°C. of the higher molecular weight polymer from that of the lower at 190°C., we compute the shear modulus shown in Figure 1 (curve *d*).

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Résumé

Les temps de relaxation de polyéthylènes fondus ont été mesurés par Aloisio, Matsuoka, et Maxwell. Ces observations supposent que les propriétés élastiques des polymères fondus sont fonction du temps. En particulier le module de cisaillement stationnaire dépend de la vitesse de cisaillement. Certaines interprétations des données de la littérature ont été basées sur le concept d'élasticité caoutchouteuse lorsque le module d'écoulement stationnaire est une valeur à l'équilibre indépendamment de la vitesse de cisaillement. Nous avons utilisé la méthode de Rao pour l'écoulement viscoélastique simultanément à des mesures de temps de relaxation en vue de discuter la dépendance de la vitesse de cisaillement en fonction du module de cisaillement à l'écoulement stationnaire des polymères fondu. L'existence de modules de cisaillement dépendant de la vitesse de la tension amène naturellement à une relation non-linéaire entre la tension de cisaillement et la tension de cisaillement récupérable. Les conclusions concernant la dépendance du poids moléculaire du module diffèrent également de l'interprétation basée sur l'élasticité caoutchouteuse.

Zusammenfassung

Relaxationszeiten für Polyäthylenschmelzen wurden von Aloisio, Matsuoka, und Maxwell gemessen. Eine Folgerung aus ihren Beobachtungen ist, dass die elastischen Eigenschaften von Polymerschmelzen zeitabhängig sein müssen. Im besonderen hängt der Schubmodul für stationäres Fließen von der Verformungsgeschwindigkeit ab. In einigen Fällen erfolgte die Interpretation von Literaturdaten auf Grundlage von Konzepten bezüglich der Kautschukelastizität, in welchen der Modul für stationäres Fließen als Gleichgewichtswert, unabhängig von der Verformungsgeschwindigkeit, angenommen wird. Wir haben die Theorie des viskoelastischen Fließens von Pao zusammen mit Relaxationszeitmessungen zur Diskussion der Abhängigkeit des Schubmoduls für stationäres Fließen von Schmelzen von der Verformungsgeschwindigkeit benützt. Das Vorhandensein eines von der Verformungsgeschwindigkeit abhängigen Schubmoduls führt natürlich zu einer nicht linearen Beziehung zwischen Schubspannung und rückbildungsfähiger Schubverformung. Auch die Schlüsse bezüglich der Molekulargewichtsabhängigkeit des Moduls unterscheiden sich von den auf der Kautschukelastizität beruhenden.

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