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Large Elastic Deformations of Polymers in Shear and Extensional Flows

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Using polystyrene as an example, we have demonstrated that the use of an elastic potential of the power type provides a satisfactory description of the dependence of stress on strain for various type of the stress state of a viscoelastic liquid in flow.

INTRODUCTION

The problem of a quantitative description of the rubber-like properties of polymers is extensively discussed in the scientific and technical literature on cured elastomers. The importance of this problem is shown by the fact that the dependence of the stress on strain in various deformations is the basic characteristic of the mechanical properties of these materials.

It is well known¹ that the stress-strain relationships for various loading conditions cannot be arbitrary since they must satisfy the requirement of invariance. The general method for the fulfillment of this requirement is the use of an elastic potential W , which is represented as a function of the invariants of the strain tensor. Various forms of the elastic potential have been proposed in the literature. Of these the Mooney-Rivlin two-constant equation is most widely used. With an appropriate choice of the constants it satisfactorily describes the dependence of stress on the extension ratio in uniaxial elongation, which is why this equation is extensively employed and the elucidation of the physical significance of its constants has been the subject of considerable effort. Much less attention has been paid to the fact that

in the case of simple shear this formula predicts a strictly linear relation between the shear stress, τ , and the amount of shear, ε . This relation is

$$\tau = 2(C_1 + C_2)\varepsilon \quad (1)$$

where C_1 and C_2 are the empirical constants of the Mooney–Rivlin equation, and the value $2(C_1 + C_2)$ must have the meaning of a constant shear modulus, but, in fact, depends on ε . The generally adopted way for improving the agreement between theoretical prediction and experiment consists in using many-term equations for the elastic potential incorporating an ever increasing number of constants which are arbitrarily varied. Thus, generally speaking, it is possible to describe experimental data with any degree of accuracy. But the success is achieved at a high cost because of the complicated calculations, the ambiguity of the choice of the constants and the lack of physical meaning of the analytical expressions used.

Of special interest in this respect is the so-called n -measure of strain, proposed by some authors (for the history of the problem, see Ref. 2) and widely used by Blatz, Sharda and Tschoegl,^{3,4} and Bloch, Chang and Tschoegl.⁵ This two-constant potential is written in the form

$$W = (2G/n^2)(\lambda_1^n + \lambda_2^n + \lambda_3^n - 3) \quad (2)$$

where G is the zero-shear modulus, n is an empirical constant and the λ_i are the principal extension ratios.

This formulation of W satisfies the invariance requirement since the principal values of the finite-strain tensor may be regarded as the invariants of that tensor. In this formula W refers, as usual, to the initial (undeformed) state since $W = 0$ if all the λ_i are equal to unity.

Equation (2) for W resembles the well known power law expression for the dependence of the apparent viscosity on the shear rate or the corresponding invariant form of the dependence of the energy dissipation on the invariants of the rate-of-strain tensor. This leads one to attempt to use Eq. (1) for describing the rubber-like properties of polymer melts and solutions, especially as it is known that these properties are also nonlinear in shear⁶ and, hence, are not described by equations such as the Mooney–Rivlin equation, for example, with its linear relationship (1).

Before we consider concrete analytical dependences and compare them with experiment, it is necessary to make one remark. For cured (non-fluid and non-relaxing) elastomers the elastic potential W expresses their equilibrium properties. The deformation of polymer solutions and melts is invariably associated with dissipative losses in flow. Therefore, the possibility of describing their behavior with the aid of an elastic potential remains controversial from the physical viewpoint. The controversy is underlined by the fact that in measurements of the elastic after-effect in fluid media there also

takes place a partial dissipation of the stored elastic energy. Nevertheless, such measurements give unambiguous results. In this respect, the concept of the elastic potential may be considered to be a useful (though, possibly, formal) method of generalizing experimental data obtained for polymer melts and solutions under various deformations. The use of this concept is based on the assumption that each steady flow state with its rate of deformation is associated with the structure of the material, which is retained for an indefinitely long time, and in this sense may be regarded as being in quasi-equilibrium. In this case, the behavior of the liquid under steady-state flow conditions may be described by two 'equilibrium' functions—the flow curve, which characterizes the flow properties, and the elastic potential which characterizes its rubber-like properties.

THEORY

The elastic potential must, in general, be represented as a function of the invariants of the strain tensor. If the material is incompressible (this assumption is quite valid for polymer solutions and melts), then there are two such invariants. The role of the invariants can be played, for example, by two of the principal extension ratios. The third invariant (i.e., the third principal extension ratio) is automatically eliminated through the condition that

$$\lambda_1 \lambda_2 \lambda_3 = 1. \quad (3)$$

If the function $W(\lambda_i)$ is known, we can calculate the stress-strain relations for any loading geometry. Thus, the stress σ_i which corresponds to the elongation λ_i , is expressed by

$$\sigma_i = \lambda_i (\partial W / \partial \lambda_i) \quad (4)$$

Of interest to the present discussion are two principal loading schemes: uniaxial tension and simple shear. The first is characterized by the magnitude of the equilibrium reversible elongation κ ; the second is characterized by the magnitude of the equilibrium elastic shear deformation ε . These quantities are used to express the invariants of the strain tensor—the principal elongations. For uniaxial tension the principal values are

$$\lambda_1 = \kappa; \quad \lambda_2 = \lambda_3 = \kappa^{-1/2}. \quad (5)$$

For simple shear the principal values are expressed in terms of ε by

$$\lambda_1 = \tan \chi; \quad \lambda_2 = \cot \chi; \quad \lambda_3 = 1 \quad (6)$$

where the angle χ is related to the amount of shear ε by the equation⁶

$$\chi = (1/2)\arctan(2/\varepsilon). \quad (7)$$

Note that the shear stress τ , which is the basic force characteristic of the state of stress in simple shear, is expressed in terms of W as

$$\tau = dW/d\varepsilon. \quad (8)$$

The equations given above yield the basic relationships expressing the dependence of stress on strain under various modes of deformation if the form of the elastic potential $W(\lambda_i)$ is known. For the elastic potential (2) the difference between the principal stresses σ_α and σ_β , which correspond to the extension ratios λ_α and λ_β , is given by

$$\frac{\sigma_\alpha - \sigma_\beta}{2G} = (\lambda_\alpha^n - \lambda_\beta^n)/n \quad (9)$$

It is not difficult to derive the following equations for the dependence $\sigma(\kappa)$ for uniaxial tension

$$\sigma = (2G/n)(\kappa^n - \kappa^{-n/2}) \quad (10)$$

and the dependence $\tau(\varepsilon)$ for simple shear

$$\tau = \frac{2G}{2^n n \sqrt{4+\varepsilon^2}} (\sqrt{4+\varepsilon^2} + \varepsilon)^n - (\sqrt{4+\varepsilon^2} - \varepsilon)^n \quad (11)$$

Now let us find the "initial" values of the elastic modulus in uniaxial tension, E_0 , and in simple shear, G_0 . These quantities are determined in the following manner:

$$E_0 = \lim_{\kappa \rightarrow 1} \sigma/(\kappa - 1) \quad (12)$$

$$G_0 = \lim_{\varepsilon \rightarrow 0} (\tau/\varepsilon) \quad (13)$$

It is evident that $G_0 \equiv G$, i.e. G has the meaning of the initial shear modulus, and in the limiting case of infinitesimal strains there is fulfilled the standard relationship, which is common to all incompressible bodies: $E_0 = 3G_0$.

Using Eq. (13) we can write Eqs. (10) and (11) in the following manner:

$$\frac{3\sigma n}{2E_0} = \kappa^n - \kappa^{-n/2} \quad (14)$$

and

$$\frac{\tau \varepsilon n}{2G_0} = \frac{\varepsilon}{2^n \sqrt{4+\varepsilon^2}} (\sqrt{4+\varepsilon^2} + \varepsilon)^n - (\sqrt{4+\varepsilon^2} - \varepsilon)^n \quad (15)$$

The left hand sides of these expressions exactly correspond to the left hand side of Eq. (9), and the right hand sides correspond to the right hand side of the same equation. If we now denote the left hand sides of Eqs. (14) and (15) by Y and the right hand sides by X , then the dependence $Y(X)$ must be

invariant to the form of the state of stress, provided, of course, that the potential (2) correctly represents the elastic deformation. Therefore a plot of the experimental data obtained through the use of different experimental schemes on a single graph in the coordinates Y and X and their coincidence would be the criterion for the validity of the form of the elastic potential for any material. Experimental testing of this conclusion is the central task of the present work.

EXPERIMENTAL

For experiments we used a commercial sample of atactic polystyrene with a wide molecular mass distribution because this material clearly displays pronounced non-linear properties both in shear and in extension. The viscosity-average molecular mass of the sample is 3×10^5 . The experiments were carried out at 130 and 150°C. The main difficulty was associated with the choice of a sample that could be tested over a sufficiently wide range of deformation rates both in shear and in uniaxial tension.

The experiments under the condition of uniaxial tension were conducted at various constant velocity gradients leading to steady-state flow conditions. These flow conditions can be attained for polystyrene; the relevant details of the experiment can be found in Ref. 7 where the results of various measurements made under the conditions of uniaxial tension are given.

The measurements in simple shear were carried out in a shear plastometer described in Ref. 8. The measurement error in all cases did not exceed ± 10 percent. The results of measurements of the dependences $\sigma(\kappa)$ and $\tau(\varepsilon)$ are given in Figures 1 and 2, respectively.

For the experimental data to be represented in invariant form it is necessary to know in advance the value of the exponent n . This difficulty can, however, be circumvented if use is made of the results of measurements over the range of values of ε greater than 1.15 and κ greater than 2.25, which does not limit the range of measurements too severely. In this case, Eqs. (14) and (15) may be given in the following approximate form:

$$\log \frac{3\sigma}{2E_0} = n \log \kappa - \log n \quad (16)$$

$$\log \frac{\tau \sqrt{4+\varepsilon^2}}{G_0} = n \log(\sqrt{4+\varepsilon^2} + \varepsilon) - [(n-1) \log 2 + \log n] \quad (17)$$

The form of the above expressions suggests a graphical method for the determination of the constant n by constructing a plot of $\log \sigma$ against $\log \kappa$ and/or a plot of $\log(\tau \sqrt{4+\varepsilon^2})$ against $\log(\sqrt{4+\varepsilon^2} + \varepsilon)$. This treatment of

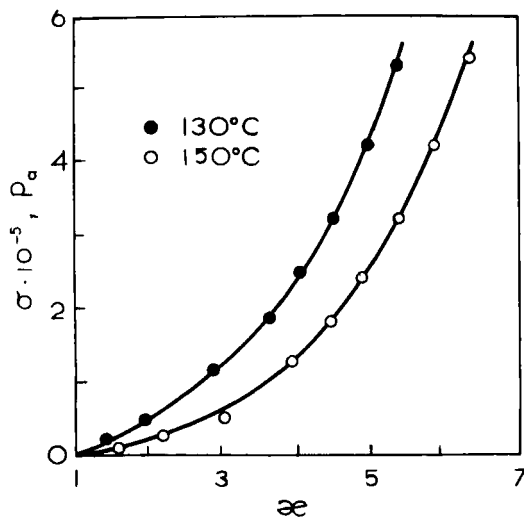


FIGURE 1 Dependence of stress on the extension ratio in uniaxial extension. Rates of deformation (from the lower points to the upper ones) at 130 and 150°C, 10^{-3} , s^{-1} : 0.137; 0.275; 0.74; 1.11; 2.0; 2.98; 4.56; 5.7; 12 (for 150°, only).

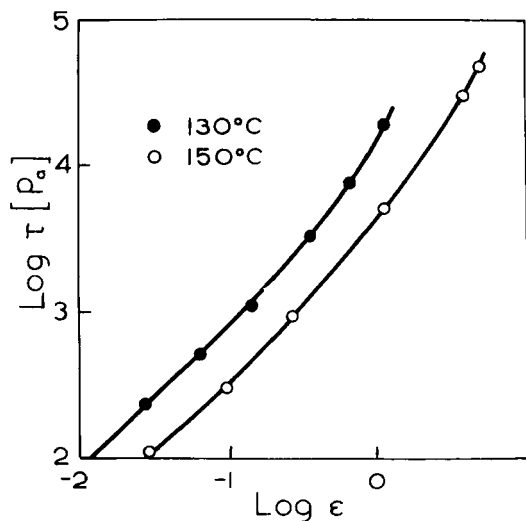


FIGURE 2 Dependence of shear stress on elastic deformation in simple shear. Rates of shear (from the lower points to the upper ones), $\times 10^{-3}$, s^{-1} ; at 130°C: 0.0083; 0.032; 0.1; 0.147; 0.152; 0.24; at 150°C: 0.046; 0.155; 0.525; 3.16; 12; 15, 8; 126.

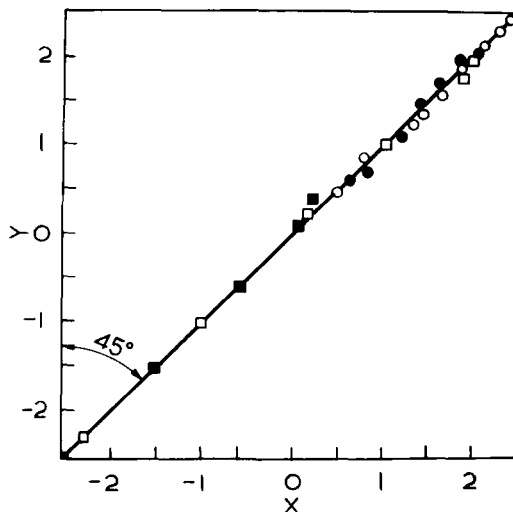


FIGURE 3 Invariant representation of experimental data on the dependence of stress on strain in uniaxial extension and in simple shear. The letter Y represents the left hand sides of formulas (14) and (15) and X, the right hand sides of the same formulas. The numerical data are the same as in Figures 1 and 2.

the experimental data for $\sigma(\kappa)$ and $\tau(\varepsilon)$ gave the same value of n , namely $n = 2.9 \pm 0.05$. This value does not depend on the rate of deformation, as the points in Figures 1 and 2 correspond to different rates of extension and shear. Now, knowing the value of n , we can make use of Eqs. (14) and (15); the experimental data can then be given in invariant form in the coordinates Y and X. This is done in Figure 3.

As seen, the use of the potential (2) enables one to attain an excellent agreement between the invariant representation of experimental data on shear and extension over a wide range of deformation rates and elastic deformations. This proves the applicability of the elastic potential given by Eq. (2) for a quantitative description of elastic deformations stored during the flow of polymers.

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