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Tensile Yield-Stress Behavior of Glassy Polymers

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Synopsis

It is shown that, at the yield stress, glassy polymers exhibit viscous flow which is in agreement with the generalized theory of Eyring. The study of the yield stress over a wide range of temperatures and strain rates provides evidence on the secondary transitions found by other methods. From our measurements we conclude that every secondary transition corresponds to the liberation of one of the degrees of freedom of a segment of the main chain.

Introduction

In a previous paper¹ we showed for the first time that the yield stress of poly(methyl methacrylate) (PMMA) reveals a secondary transition due to the local relaxation mode. It was possible to calculate the activation energy associated with this transition by assuming that at the yield point a high polymer exhibits pure viscous flow, in agreement with Eyring's theory of non-Newtonian viscosity.^{2,3} Our results were unknown to Roetling, and independently he described the yield-stress behavior of three glassy polymers⁴⁻⁶ by the Eyring viscosity theory.

It is the purpose of this paper to give two other examples.

Experimental

We have measured the yield stress of two glassy polymers over a wide range of temperatures and rates of strain. The tensile stress-strain curves were obtained with an Instron testing machine. The temperature was regulated by an Instron environmental chamber and measured with a thermometer placed near the specimen in the chamber. The tests were made after the specimen had remained in the chamber for 1/2 hr at the required temperature.

Strain rates were calculated from the crosshead speed. The errors generally introduced when this procedure is used are due to parasitic deformations (for example: the Hookean deformation of the machine and the grips). These errors vanish if one calculates the strain rate corresponding to the yield point of the tensile curve, because at this point the rate of change of load is zero.

We have chosen bisphenol A polycarbonate (first investigated by Robertson⁷ over a very narrow range of strain rates) because this substance fits



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Eyring's first theory over a wide range of temperature. On the other hand, we have chosen poly(vinyl chloride) (PVC) (not previously investigated) because this substance exhibits a well known secondary transition in the plastic deformation range.

Test specimens of polycarbonate (Makrolon, Bayer) were cut from commercially available sheets 0.2 cm thick; their length was 4 cm and their width 0.8 cm. Test specimens of PVC (Solvic 227, Solvay et Cie) were 0.18 cm thick, 4 cm long, and 0.8 cm wide.

There was evidence of crazing on all the specimens of polycarbonate and PVC prior to yielding but the length and the number of the crazes varied with temperature and strain rate.

Yield-Stress Behavior of Polycarbonate: First Theory of Eyring

Eyring considers the viscous flow produced under the action of a high single shear stress. The deformation occurs along a set of parallel layers in the direction of the shear stress. The fundamental process consists of the jump of a molecular patch from one equilibrium position to another (in glassy polymers, these flow patches are segments of macromolecules). We assume that this type of deformation takes place at the yield point of the tensile curve. At this point the strain does not exceed 2% and appears to be uniform; for these reasons, we think that pure viscous flow just begins there. Of course, this assumption is a simplification, because the deformation at this point may entail delayed elasticity, adiabatic heating, and dilatation effects not considered in the theory of non-Newtonian viscosity.

It is not the purpose of this paper to discuss in details what the parameters of Eyring's theory do mean; for a first approach, we have neglected the processes whose contribution to the yield stress are not significant compared to the viscous contribution (adiabatic heating and high elasticity are only important during neck formation where local strain becomes large).

If pure viscous flow takes place at the yield point, we must write Eyring's equation for normal stresses and take into account the relations between normal and shear stresses and between normal and shear rates established by Bauwens.⁵

From these relations and from Eyring's first theory in the special case where

$$\sinh X \approx 1/2 \exp X$$

the following expression for the yield stress σ_e is derived:

$$\begin{aligned} \frac{\sigma_e}{T} &= \frac{4\sqrt{3}k}{v_0\gamma_0} \left(\ln \frac{\sqrt{3}}{2\gamma_0 J_0} \dot{\epsilon} + \frac{Q}{RT} \right) \\ &= A [\ln 2 C \dot{\epsilon} + (Q/RT)] \end{aligned} \quad (1)$$

where T is the absolute temperature, $\dot{\epsilon}$ is strain rate, v_0 is the shear volume, γ_0 is the elementary shear, J_0 is a rate constant (containing an entropy factor) for the jumping patches when no stress is acting, Q is the activation energy, k is Boltzmann's constant, and R is the universal gas constant.

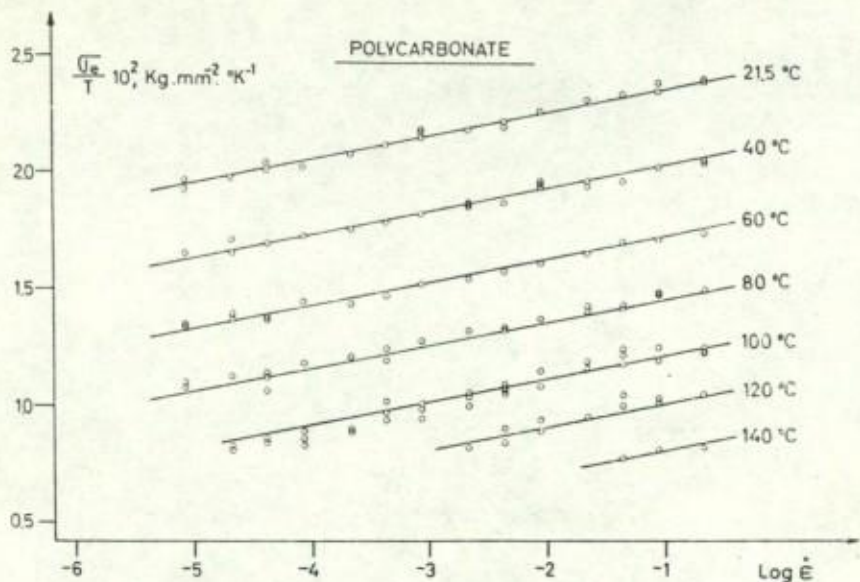


Fig. 1. Measured ratio of yield stress to temperature as a function of logarithm of strain rate ($\dot{\epsilon}$ in sec^{-1}). The set of parallel straight lines is calculated from eq. (1).

Equation (1) does not take into account the influence of the hydrostatic stress which has been evaluated in a previous paper.⁵ In a tensile test, the contribution of the hydrostatic stress does not affect the formalism of eq. (1) and concerns only the meaning of parameter A ; thus we have neglected it for a first approximation.

Eyring⁷ and others, such as Lazurkin⁹ and Robertson,⁷ have applied non-Newtonian viscosity theory to the cold drawing of plastics. They consider that the shear volume v_0 is proportional to temperature and that the yield stress may be written;

$$\sigma_e = \text{constant}(1/T) + \text{constant}(\log \dot{\epsilon}) \quad (2)$$

We have measured the yield stress of bisphenol-A polycarbonate over a wide range of strain rates, from 20°C to the glass temperature (145°C). From our data we find that the plot of σ_e versus $\ln \dot{\epsilon}$ at different temperatures gives a set of concurrent straight lines which do not fit eq. (2). But the plot of σ_e/T versus $\ln \dot{\epsilon}$ at different temperatures gives a set of parallel straight lines which fit eq. (1) fairly well. Our data are given in Figure 1. The graph consists of a set of parallel straight lines calculated from eq. (1) and is the experimental proof that v_0 and Q are constant over a range of temperatures covering at least 120°C. This is not surprising because in the glassy state when no stress is acting the equilibrium positions are frozen. The constants A , Q , and C of eq. (1) are evaluated as follows. We first draw the set of straight lines which best agrees with the data. The mean

slope is taken as A ; from the mean displacement of these lines we calculate Q , and from the mean extrapolated value of the abscissas for $\sigma_e = 0$ we calculate C . The graph of Figure 1 is recalculated from the following values of A , Q , and C :

$$A = 4.16 \times 10^{-4} \text{ kg/mm}^2\text{-}^\circ\text{K}$$

$$Q = 75.5 \text{ kcal/mole}$$

$$C = 10^{-31} \text{ sec}$$

We have performed tests near the glass temperature, but the data are not given here because we intend to come back to this subject in a future paper. We have mentioned the existence of a minimum yield stress σ_{ec} below which eq. (1) is no longer valid. We have found for polycarbonate that $\sigma_{ec} = 3.2 \text{ kg/mm}^2$.

The results of Roetling⁵ on poly(ethyl methacrylate) tend to show that eq. (1) is still valid just above the glass temperature; we believe that this is because his data correspond to very high strain rates for which σ_e is still higher than σ_{ec} .

Yield-Stress Behavior of Poly(vinyl Chloride): the Generalized Theory of Eyring

Our data for polycarbonate fit eq. (1) because the range of temperatures and rates explored does not include a secondary transition. However the set of curves, $\sigma_e/T = f(\ln \dot{\epsilon})$, at constant T is capable of revealing secondary transitions if the data cover the range where these begin to make a significant contribution to the stress. In this case the variation of the yield stress with strain rate and temperature can be described by the generalized theory of non-Newtonian viscosity proposed by Ree and Eyring² to represent the viscosity of rubbers, solutions of high polymers, and polymers in the rubbery state. In a previous paper¹ we applied this last theory to the yield-stress behavior of poly(methyl methacrylate) (PMMA) and attributed the observed transition of this polymer to the local relaxation mode of the main chain.¹⁰

Unfortunately, in the case of PMMA, mechanical losses reveal only two transitions, the first, called the β transition, is associated with the side-chain relaxation; the other one is the glass transition. The transition that we have observed is too close to the glass transition to be measured through mechanical losses at the usual frequencies, but it has been determined dilatometrically.¹¹

To compare the transition conditions determined from the yield stress with those from mechanical loss we have studied the yield stress of PVC, a high polymer having a secondary transition due to the local relaxation mode which is often revealed by measurements of electrical and mechanical losses.¹²⁻¹⁴ The activation energy associated with this transition has been measured by several authors and has been found to equal 14 kcal/mole.

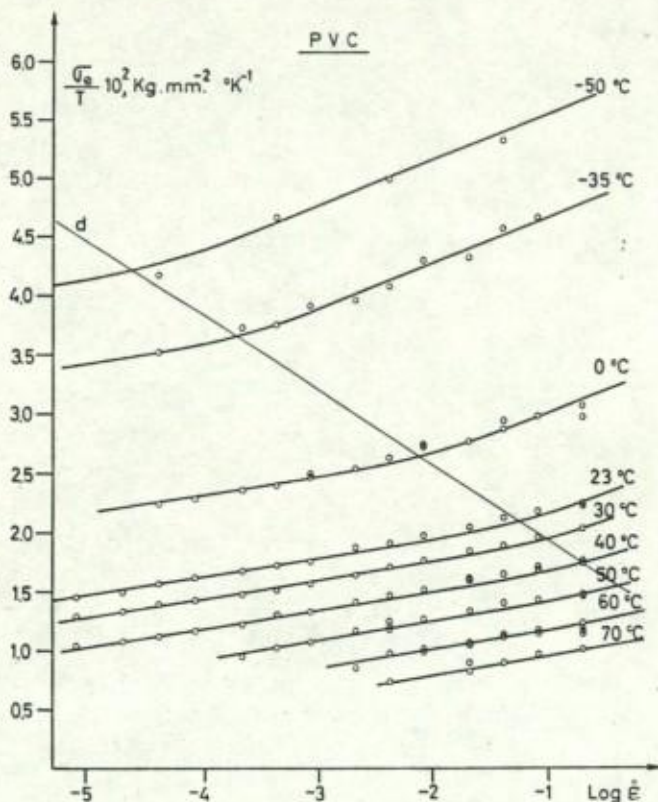


Fig. 2. Measured ratio of yield stress to temperature as a function of logarithm of strain rate ($\dot{\epsilon}$ in sec^{-1}). The set of parallel curves is calculated from eq. (3).

Our data are given in Figure 2 and fit fairly well the equation derived from the Ree-Eyring theory:

$$\begin{aligned} \frac{\sigma_a}{T} &= \frac{4\sqrt{3}k}{v_{\alpha\alpha}\gamma_{\alpha\alpha}} \left(\ln \frac{\sqrt{3}}{2\gamma_{\alpha\alpha}J_{\alpha\alpha}} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + \\ &\quad \frac{4\sqrt{3}k}{v_{\beta\beta}\gamma_{\beta\beta}} \sinh^{-1} \left(\frac{\sqrt{3}}{4\gamma_{\beta\beta}J_{\beta\beta}} \dot{\epsilon} \exp \left\{ \frac{Q_{\beta}}{RT} \right\} \right) \\ &= A_{\alpha} [\ln 2C_{\alpha} \dot{\epsilon} + (Q_{\alpha}/RT)] + A_{\beta} \sinh^{-1} (C_{\beta} \dot{\epsilon} \exp \{Q_{\beta}/RT\}) \quad (3) \end{aligned}$$

Equation (3) is merely a generalization of eq. (1). The curves represented in Figure 2 are calculated from eq. (3) with the following values for the constants:

$$\begin{aligned} A_{\alpha} &= 7 \times 10^{-4} \text{ kg/mm}^2 \cdot ^\circ\text{K} \\ Q_{\alpha} &= 70.5 \text{ kcal/mole} \\ C_{\alpha} &= 10^{-38} \text{ sec} \\ A_{\beta} &= 10.1 \times 10^{-4} \text{ kg/mm}^2 \cdot ^\circ\text{K} \\ Q_{\beta} &= 14 \text{ kcal/mole} \\ C_{\beta} &= 4.26 \times 10^{-10} \text{ sec.} \end{aligned}$$

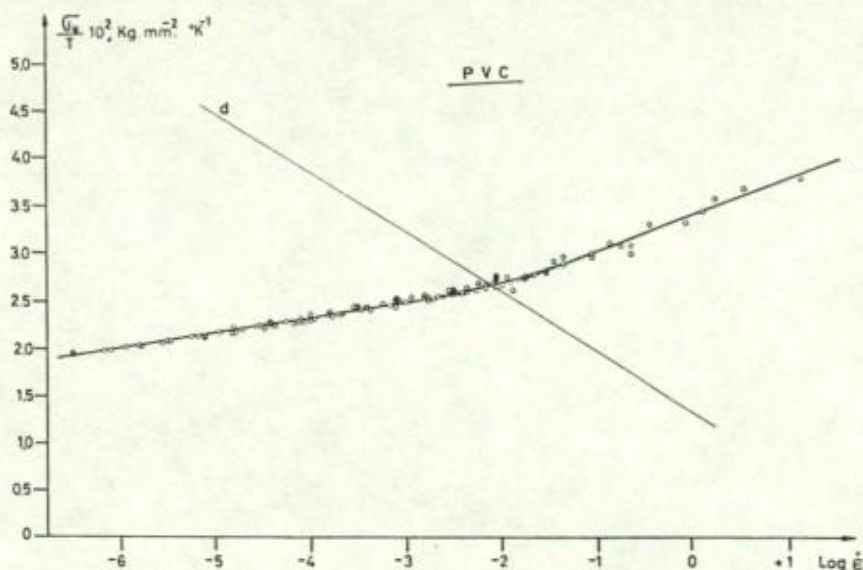


Fig. 3. Master yield stress curve reduced to 0°C for PVC ($\dot{\epsilon}$ in sec^{-1}).

The set of parallel curves shown in Figure 2 can be looked upon as generated by the shift of one curve along line d ; i.e., the locus of the intersections of the asymptotes of each curve.

We give in Figure 3 the master curve, reduced to 0°C, corresponding to the graph of Figure 2. From this graph it is possible to extrapolate the yield stress value to rates which cannot be reached experimentally.

Here, the shift of each curve is not along the horizontal axis as in the time-temperature-superposition principle of Tobolsky; this is due to the fact that the yield stress depends on two processes each characterized by its own activation energy.

The shift factor has two components, one along the horizontal axis:

$$s_x = (Q_\beta / 2.303 R) [(1/T) - (1/273)] \quad (4)$$

the other along the vertical axis:

$$s_y = - [A_\alpha (Q_\alpha - Q_\beta) / R] [(1/T) - (1/273)] \quad (5)$$

The tabulated values of s_x and s_y are given in Table I.

What is the physical meaning of the two processes involved? We can roughly separate the graphs of Figures 2 and 3 into two ranges; the α range, below d , where the term containing the β variables of eq. (3) can be neglected; and a range above d where the two terms of eq. (3) are important.

The intersection of every curve with d is thus the character of a secondary transition. From the value of the activation energy, 14 kcal/mole, and from the range of temperatures and strain rates where it occurs, we can identify this transition as the β transition of PVC.

TABLE I
Components of the Shift Factor Corresponding to the Master
Curve Reduced to 0°C for PVC

Temperature, °C	s_x	s_{y1} (10^{-1} kg/mm ² ·°K)
-50	2.52	-1.64
-35	1.64	-1.07
23	-0.87	0.56
30	-1.10	0.72
40	-1.42	0.93
50	-1.73	1.12
60	-2.01	1.31
70	-2.27	1.48

This secondary transition is due to the local relaxation mode of chains of macromolecules and is revealed by measurements at -30°C of mechanical losses at 10 cps.

The molecular motions which take place under the action of the yield stress in the α range may correspond to the translational mode of the main chains. The same kind of motion occurs at the yield point, in the range above d , but to produce such movements, it is necessary first to liberate the local relaxation modes of the chains.

As in the case of polycarbonate, we find that the theory is not in agreement with data when the yield stress is lower than $\sigma_{ec} = 3.4$ kg/mm².

Conclusions

The generalized theory of Eyring can describe fairly well the deformation of glassy polymers at the yield point, if one considers: (1) that the shear volume does not change with temperature; (2) that the different kinds of processes involved correspond to the degrees of freedom that must be activated if a segment of the main chain is to move. We confirm the existence of a critical value of the yield stress below which the theory is no longer valid. This critical stress seems to be a characteristic constant for each material.

The study of the yield stress of glassy polymers over a wide range of temperatures and rates is of use in revealing secondary transitions, especially when these transitions are too close to be distinguished by measurements of mechanical and electrical losses.

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