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Deformation of Polyethylene at High Pressure

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The influence of pressure, deformation rate, and pressure fluid on the mechanical properties of high-molecular-weight polyethylene is examined. A miniature motor-driven testing machine which operates completely enclosed in a high-pressure vessel is employed. This device allows for the first time in any material measurement of the sensitivity of the flow stress σ to an instantaneous change of strain rate under superposed high hydrostatic pressure. From these data and the pressure dependence of σ it is possible to calculate the activation volume V^* for plastic flow as a function of pressure; it is suggested that V^* is the appropriate parameter to describe the pressure dependence of a kinetic process such as plastic deformation. It is found that samples deformed in *n*-pentane generally exhibit a reduced flow stress relative to those tested in water. In addition, it is observed that V^* for specimens tested in pentane is significantly less than for those tested in water ($\sim 230 \text{ \AA}$ at 1 atm as opposed to $\sim 266 \text{ \AA}^3$). In both cases V^* is observed to decrease moderately with increasing pressure.

INTRODUCTION

The plastic deformation of polymeric solids, such as polyethylene, is distinguished from that of metals and ceramics by its considerable dependence on the hydrostatic component P of the stress tensor. A number of recent reports have considered this phenomenon with a particular interest in establishing suitable yield criteria.¹⁻³ Such an approach is of practical interest in predicting the behavior of polymers in load-bearing applications, but it does not lead to an understanding of why plastic flow is pressure sensitive; this must be related to the micromechanical flow mechanism in the polymer. If we recognize that flow is a kinetic process which proceeds when some mobile species surmounts a potential energy barrier, we may write an expression relating the rate of plastic flow $\dot{\epsilon}$ to temperature T , pressure P , and shear stress τ , as follows⁴:

$$\dot{\epsilon} = \dot{\epsilon}_0 \exp(-\Delta G^*/kT)$$

$$= \dot{\epsilon}_0 \exp[-(U_0 - \int_0^\tau v d\tau + \int_0^P V^* dP)/kT], \quad (1)$$

where $\dot{\epsilon}_0$ is a constant related to the frequency at which the mobile species attempts to cross the barrier, U_0 is the activation energy at zero stress (deviatoric and hydrostatic), v is the stress activation volume, and V^* is the pressure activation volume. We note that Eq. (1) holds only when the probability of a reverse jump across the energy barrier is negligible; it does not require that v and

V^* be constants. The term τv is the work done by the applied stress in surmounting the energy barrier while the PV^* term is the work which must be done against hydrostatic pressure. If we derive the expression for $\ln \dot{\epsilon}$ from Eq. (1) and differentiate with respect to P , we have

$$V^* = -kT \left(\frac{\partial \ln \dot{\epsilon}}{\partial P} \right)_{T, \tau, \epsilon} \quad (2)$$

For v we find

$$v = kT \left(\frac{\partial \ln \dot{\epsilon}}{\partial \tau} \right)_{T, P, \epsilon} \quad (3)$$

In effect, then, V^* is the activation parameter related to the microscopic flow mechanism which determines the pressure dependence of a rate process. Assuming that deformation is controlled by a single thermally activated process, it is the transient increase in volume of the material when one activation event occurs. We suggest then that V^* is the critical parameter which should be derived from high-pressure deformation studies of polymers. It follows directly from the pressure dependence of creep according to Eq. (2). If, as in the present case, constant-strain-rate tests are performed, Eq. (2) is rewritten as

$$V^* = kT \left(\frac{\partial \ln \dot{\epsilon}}{\partial \ln \tau} \right)_{T, P, \epsilon} \left(\frac{\partial \ln \tau}{\partial P} \right)_{T, \dot{\epsilon}, \epsilon} \quad (4)$$

In this case then one must determine the pressure dependence of both τ and the inverse strain-rate sensitivity

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$$\left(\frac{\partial \ln \epsilon}{\partial \ln \tau}\right)_{T, P, \epsilon}$$

(defined in the following as m) in order to determine V^* as a function of P . This has been done here for high-molecular-weight polyethylene (PE). The results presented for the rate dependence of the flow stress under high hydrostatic pressure are the first measurements of their kind for any material.

EXPERIMENTAL PROCEDURE

Specimen Preparation

In this work we have studied a high-molecular-weight PE ($M_w \approx 2.8 \times 10^6$; $M_n \approx 6 \times 10^4$) designated AC 1220.⁵ Sheets of the polymer with dimensions $15 \times 15 \times 0.65$ cm are compression molded from powder according to the following procedure: (a) Powder in the mold is allowed to creep slowly at 170°C and low pressure for ~ 7 min; (b) a molding pressure of ~ 70 bar at 170°C is applied for about 3 min; and (c) the molded plate is then quenched in ice water. The solid product shows a poorly defined microspherulitic structure with a density in the range $0.93\text{--}0.935$ g/cm³. From this density the crystallinity is estimated to be $\sim 55\%$. From the molded sheets, small circular-cross-section specimens are machined with an over-all length of ~ 2.54 cm and a gauge section of 0.254 -cm diameter and 0.254 -cm length; the specimen ends (0.635 -cm diameter) are threaded for gripping. One sample was annealed after machining at 127°C for 42 h prior to testing (at 2.09 kbar in water); little difference in behavior is apparent.

Mechanical Testing Apparatus

The mechanical testing apparatus used (minitester) has been described in some detail by Gordon and Mike⁶ and Davis and Gordon.⁷ The barrel and grips in the present version are modified to allow tensile testing, but the other components are basically the same. The drive train of the system consists of a synchronous motor, a planetary gear system, and a 0.3175 -cm-pitch drive screw. By adjusting the gear ratio one can alter the deformation rate. In the present system, however, we have employed for the first time a unique variable-frequency power supply⁸ with push-button frequency selection, to effect instantaneous changes of deformation rate. The power frequency is switched between 82 Hz (motor speed = 2460 rpm at 1 atm) and 533 Hz (motor speed = 15 990 rpm at 1 atm) for a strain-rate ratio of 6.5. For the 12000:1 gear reduction employed and the 0.3175 -cm-pitch screw, the respective deformation rates are then 0.0651 and 0.423 cm/min, which, for

our samples, yield nominal strain rates of 4.27×10^{-3} and 2.78×10^{-2} sec⁻¹. At low frequency the motor speed is insensitive to pressure but above about 5 kbar viscous drag on the motor becomes significant in the high-speed mode. Hence the strain-rate ratio for the two frequencies noted above decreases from 6.5 at 5 kbar to about 4 at 8 kbar. (The motor speed is always insensitive to the load developed in the tester.)

Load is monitored by a thin-wall steel load cell affixed with two Al₂O₃-bonded strain gauges. A second dummy load cell placed in the pressure chamber compensates for pressure change. The active load cell is calibrated at 1 atm against a standard MTS⁹ load cell, and the change in its calibration with pressure is determined by using a stiff steel spring as a standard.⁷ For the particular load cell employed here, the calibration changes by about 0.7% per kbar (towards reduced sensitivity).

The minitester operates completely enclosed in a liquid-medium 200 000-psi-capacity Harwood¹⁰ pressure system. Pressure is monitored by a manganin cell with a precision of $\sim \pm 100$ psi below 50 000 psi, $\sim \pm 200$ psi from 50 000 to 100 000 psi, and ± 400 psi above 100 000 psi and with an accuracy given by these limits or $\sim 1\%$, whichever is greater. The influence of the pressure transmission fluid on the measured mechanical properties is of potential importance and this has been examined in the present case by using both water and *n*-pentane. In use the minitester stands in a vertical configuration with the bottom specimen grip in the form of a cylindrical-cross-section cup. The specimen may be immersed in the cup filled with water when the rest of the tester is immersed in a less dense, immiscible, nonpolar fluid such as pentane. Alternately, the water may be omitted so that pentane fills the cup and is in contact with the specimen. When saturated with pentane, the density of AC 1220 PE is ~ 0.90 g/cm³.

Test Procedure

The partial derivatives of Eq. (4) imply measurement of changes of τ with pressure or strain rate at constant structure, i. e., constant chemical, morphological, and defect structure. As one does not expect that two samples deformed continuously to the same strain at different pressures or strain rates will have exactly the same structure, V^* cannot be reliably determined by comparison of different continuous τ - ϵ curves (except, perhaps, right at yield).

Rather, differential tests are required, which is to say that we do not expect a sample deformed to a given strain to change structure just due to a P