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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

APR 7 1972

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

(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 – 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

or $\dot{\epsilon}$ change alone. Constant structure also implies that the sample must be deforming in a macroscopically homogeneous fashion. Hence we determine V^* here in the uniform cold-drawing regime beyond the Lüders strain (which is small in AC 1220). Also implicit in our experiments is the assumption that the ratio of applied stresses pertaining to a change of strain rate or pressure is equal to the ratio of the effective stresses acting on the mobile species. If the applied stress τ_a is unequal to the effective stress, either because τ_a is screened by a long-range internal stress τ_i or because τ_a is amplified by a stress concentration factor K , we assume that τ_i or K does not change during P or $\dot{\epsilon}$ cycling.

Therefore, with these qualifications the experiments proceed as indicated by the test record reproduced in Fig. 1. At pressure P_1 the sample is deformed plastically to tensile stress σ_1 at which point the deformation rate is cycled by a factor of ~ 5 , i. e., increased briefly and then decreased to the original value. On increasing $\dot{\epsilon}$ the flow stress is raised to σ_2 . On decreasing $\dot{\epsilon}$ the stress reaches σ_3 from where it is then reduced to zero. The pressure is then raised to P_2 , and on reloading there is an increase in flow stress from σ_3 to σ_4 . The deformation rate is cycled again, then load released, and the pressure is reduced once more to P_1 , and so on, until the sample fails. The parameter m is computed at each pressure from the ratio of stresses, i. e., $\ln(\dot{\epsilon}_2/\dot{\epsilon}_1)/\ln(\sigma_2/\sigma_1)$, etc. (It is not necessary to resolve to the shear component for the stress ratio.) The value of V^* computed for an increase or decrease of pressure is assigned to the mean

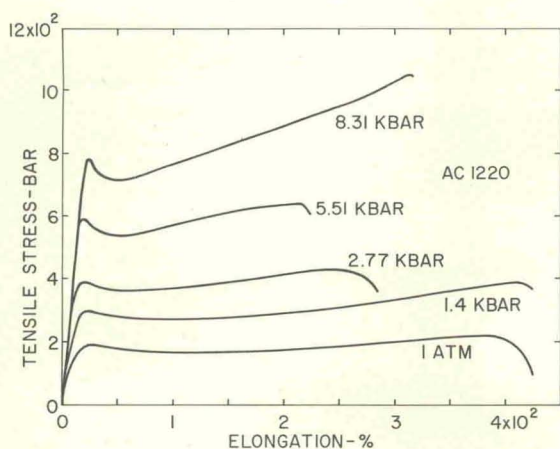


FIG. 1. Cyclic load (nominal stress)-elongation curves for AC 1220 PE indicating the change of stress with pressure and strain rate; $\dot{\epsilon}_2/\dot{\epsilon}_1 \approx 5.9$ at 6.22 kbar and 4.8 at 7.58 kbar.

pressure by using the geometric mean value of m (the variation of $\ln m$ with P is approximately linear) for the two pressures and the ratio of stresses, i. e., $\ln(\sigma_4/\sigma_3)$; ΔP is $\sim 20\,000$ psi (1.38 kbar) except for the lowest mean pressure (0.35 kbar) where it is $\approx 10\,000$ psi. It is found that during a time period (~ 25 min) equal to that required to unload the sample, change pressure, and attain thermal equilibrium, aging of the specimen occurs, i. e., after unloading, the stress required to reinitiate flow on reloading (at the same pressure) is $\sim 1-2\%$ higher (approximately independent of pressure). Hence the apparent relative change of stress due to pressure is greater on increasing as opposed to decreasing pressure (as much as 30% at higher pressures where the relative change of σ with P is smaller). To account for this effect the values of V^* reported are the mean of successful determinations with increasing and decreasing pressure (or vice versa). Figure 1 also indicates that we determine the flow stress after a pressure (or $\dot{\epsilon}$) change by the extrapolation technique.

Because we measure ratios of stresses (actually loads) it is not essential to know the true stress along the τ - ϵ curve to determine V^* . We should, however, correct for the small change of cross-sectional area which occurs when the pressure is changed. The correction amounts to $\frac{2}{3}mkT\beta$, where β is the volume compressibility. We have determined β from the results of Pastine¹¹ (see his Table VII) for an isotropic PE of 0.954-g/cm³ density. The calculated correction is thus slightly less than necessary for our lower-density material (0.90-0.935 g/cm³) in the isotropic state, but this is probably compensated by a reduced area compressibility of the specimen when in the cold-drawn state. It is found that an increase of m with pressure just compensates the decrease in β so that the correction term is almost constant at 8 \AA^3 .

The experiments are conducted at room temperature ($\sim 22^\circ \text{C}$).

RESULTS

Figure 2 shows several representative load-elongation curves for AC 1220 PE tested in water. It can be noted that the yield drop in this material is quite small. Also both the yield stress and the rate of work hardening increase with increasing pressure; the total elongation to failure decreases moderately with increasing pressure. The variation of the tensile yield stress with pressure is shown more clearly in Fig. 3; the circles correspond to specimens tested in water and the triangles correspond to those tested in pentane. The solid line shown is a quadratic least-squares fit to the water data. The yield-stress values

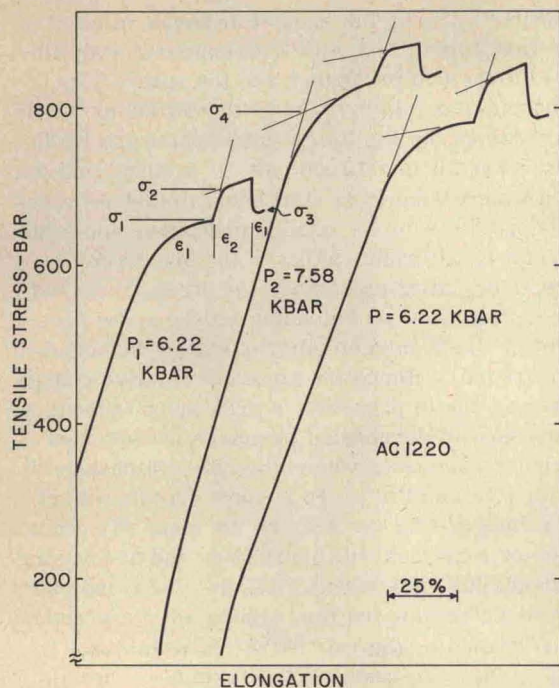


FIG. 2. Nominal stress-elongation ($\Delta L/L_0$) curves for AC 1220 PE tested at several pressures in water (stress uncorrected for the reduced area of the specimen resulting from hydrostatic compression).

in pentane fall below the solid line depending on the amount of pentane absorbed. The lowest points at a given pressure occur near saturation (> 24 h soaking in pentane).

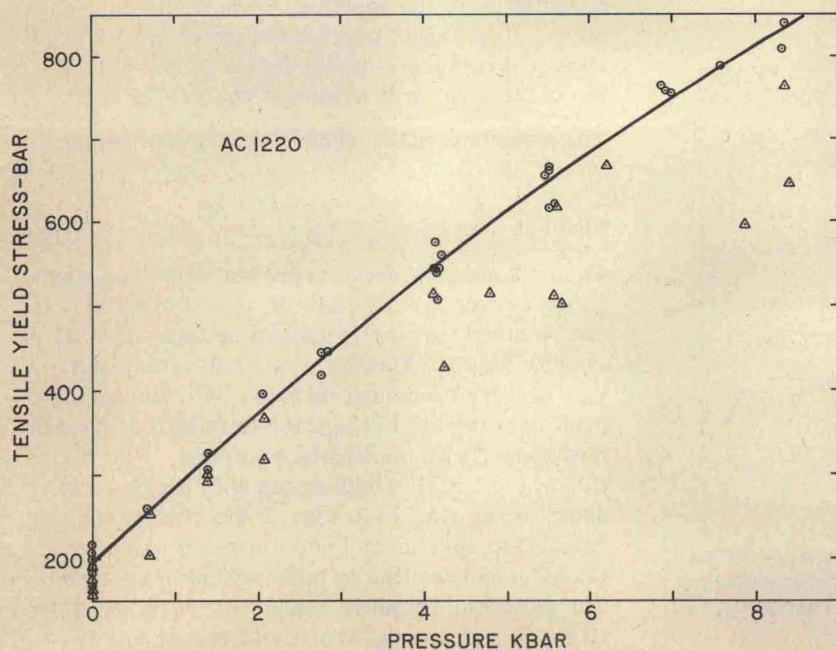


FIG. 3. Tensile yield stress (nominal) as a function of pressure for samples tested in water (circles) and pentane (triangles). The solid curve is a quadratic least-squares fit of the water data; $\sigma = 195 + 92.7P - 1.92P^2$, where σ is in bar for P in kbar. The stress is corrected for the compressibility of the samples according to the data of Pastine (Ref. 13) noted in the text.

The variation of the inverse strain-rate sensitivity of the flow stress $(\partial \ln \dot{\epsilon} / \partial \ln \sigma)_{T,P} \equiv m$, is given as a function of strain (at several pressures) and pressure (at several strains) in Figs. 4 and 5, respectively. It is evident in all cases that m decreases with increasing strain and increases strongly with increasing pressure. The slope of the curve $\ln m$ vs P in Fig. 5 is ~ 0.125 kbar $^{-1}$; the apparent strain dependence of this slope falls within the experimental uncertainty. According to Eq. (4) m is one of the two parameters needed to calculate V^* ; the other is the partial derivative $(\partial \ln \sigma / \partial P)_{T,\dot{\epsilon}}$. This is shown in Fig. 6 for samples tested in water (circles) and pentane (triangles); the data at each pressure are obtained from 1-3 specimens. If one evaluates the derivative at each pressure from the solid curve in Fig. 3, the dashed curve in Fig. 6 is obtained. It is apparent that the data points generally fall somewhat above the yield-point curve; they also seem to follow a curve of slightly different shape. Both of these features may be accounted for to a large degree by the fact that $\partial \ln \sigma / \partial P$ increases with increasing strain at a given pressure.

We calculate V^* then by multiplying the data in Fig. 6, point by point, by the appropriate values of m and kT . Because the relative strain dependences of m and $(\partial \ln \sigma / \partial P)_{T,P}$ are nearly equal and of opposite sign, V^* is only slightly dependent on ϵ at lower pressures and apparently independent of ϵ at higher pressures. This is indicated for a few cases in Fig. 7. In an attempt to account for this small strain dependence in a final plot of V^* vs P we choose a reference strain $\epsilon = 1.25$ which

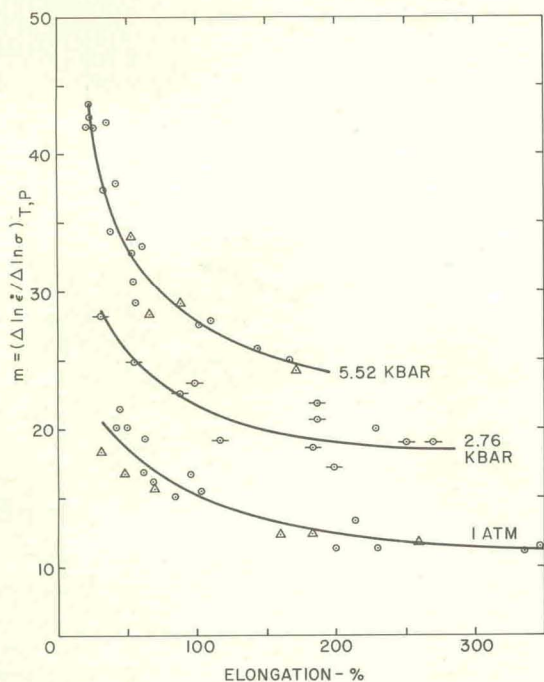


FIG. 4. Dependence of the inverse strain-rate sensitivity m on strain at several pressures. Elongation $= \Delta L/L_0$.

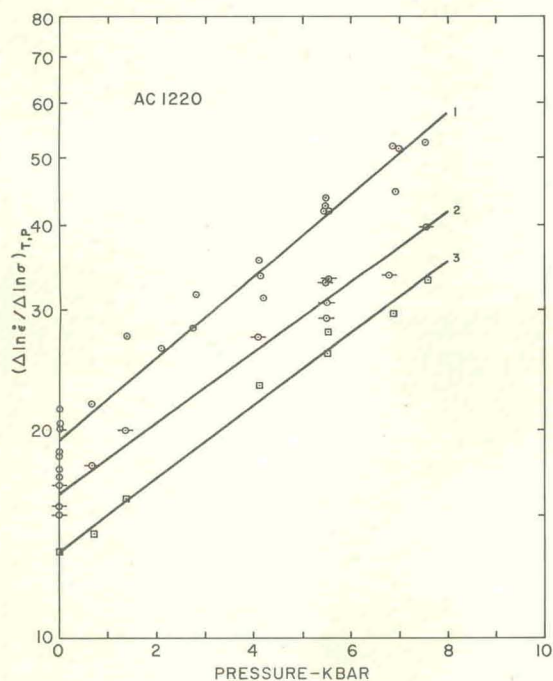


FIG. 5. Dependence of m on pressure at several strains, corresponding approximately to $\epsilon = \Delta L/L_0 = 0.3, 0.65,$ and 1.25 for curves 1, 2 and 3, respectively.

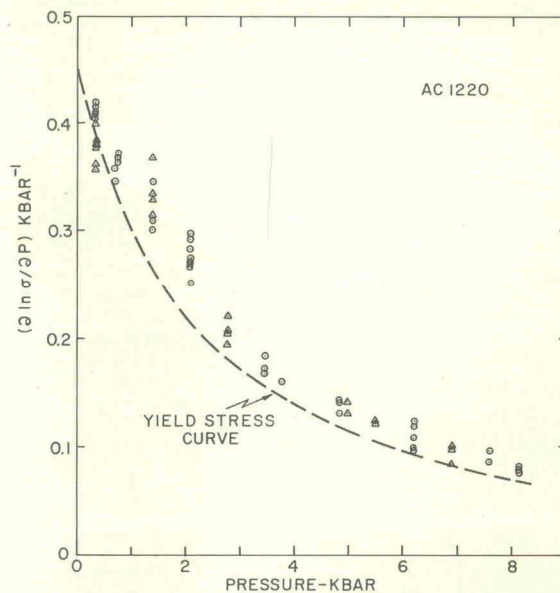


FIG. 6. Influence of pressure on the partial derivative $(\partial \ln \sigma / \partial P)_T$. The dashed curve shown for comparison is derived from the solid curve in Fig. 3.

is bracketed by most of the data. (As above, we recognize that fixed ϵ is not necessarily fixed structure.) The result is shown in Fig. 8, where the error bars ($\sim \pm 6\%$) represent our estimate of the total uncertainty arising in the experiments. Within the accuracy of the data one may approximate the decrease of V^* at low pressure as being linear; at high pressure, V^* appears to change very little with pressure. For specimens deformed in water V^* decreases from about 266 \AA^3 at 1 atm to about 135 \AA^3 at 8 kbar; the initial rate of decrease is $\sim -27 \text{ \AA}^3/\text{kbar}$. For samples tested in pentane the initial rate of decrease is smaller ($\sim -19 \text{ \AA}^3/\text{kbar}$) and the value of V^* is reduced at lower pressures ($\sim 230 \text{ \AA}^3$ at 1 atm as opposed to 266 \AA^3). At 0.35 kbar this difference arises because both m and $\partial \ln \sigma / \partial P$ are smaller (see Figs. 4 and 6); at 1.4 and 2.78 kbar it appears that the difference lies mainly in m . At any rate it is evident that pentane absorption causes a significant change of V^* at low pressure. If Fig. 8 were plotted for a different value of strain, the slope would decrease slightly with increasing strain, e.g., at $\epsilon = 2$, V^* would be $\sim 250 \text{ \AA}^3$ at 1 atm in water. As V^* in pentane seems to be somewhat less strain dependent, the results for pentane and water would be less divergent at high strains.

DISCUSSION

As is noted above, because deformation is a kinetic process, the appropriate measure of the pressure dependence of plastic flow is the activation

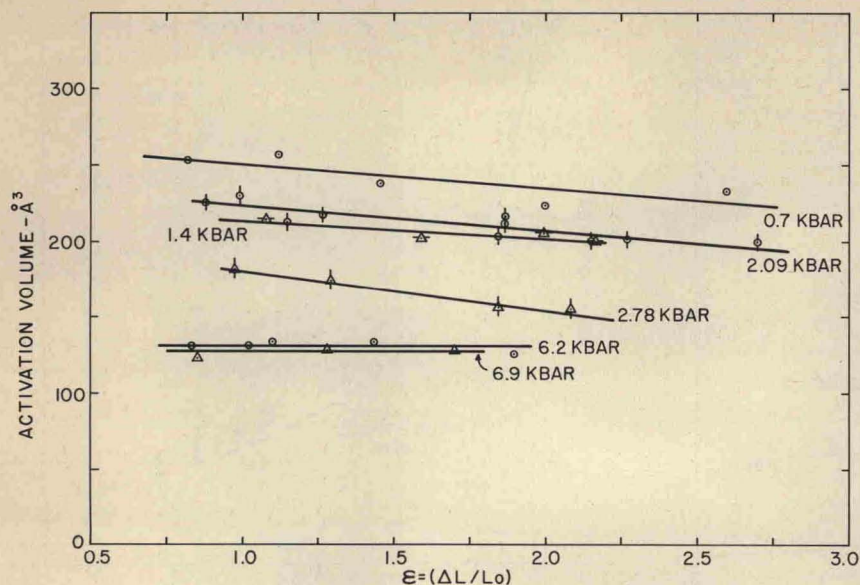


FIG. 7. Change of activation volume with strain for samples tested in water at 0.7, 2.09, and 6.2 kbar (circles) and for samples tested in pentane at 1.4, 2.78, and 6.9 kbar (triangles).

volume V^* . Here we find for high-molecular-weight PE (AC 1220) that V^* is $\sim 266 \text{ \AA}^3$ at 1 atm. As expected, this value is considerably greater than is found, for example, for creep in metals where V^* is of the order of $10\text{--}50 \text{ \AA}^3$, i.e., of the order of the atomic volume.¹² We also find (Fig. 8) that V^* decreases with pressure. Examining the parameters which determine V^* [Eq. (4)] we note that $(\partial \ln \sigma / \partial P)_{T,P}$ decreases by a factor of ~ 5 over the pressure range 1 atm to 8 kbar (Fig. 6); over the same range m increases to ~ 2.5 times its 1-atm value (Fig. 5). Hence V^* de-

creases by a factor of ~ 2 . For the case of a creep test [Eq. (2)] where the stress is held constant, one could assign this decrease in volume entirely to the increased pressure. In the present case, however, σ increases with P and hence one must examine the relationship between the change of V^* with P at constant stress and at constant strain rate. This is given by

$$\left(\frac{\partial V}{\partial P}\right)_\sigma = \left(\frac{\partial V}{\partial P}\right)_\epsilon - \left(\frac{\partial V}{\partial \sigma}\right)_P \left(\frac{\partial \sigma}{\partial P}\right)_\epsilon \quad (5)$$

For convenience the last term in Eq. (5) may be

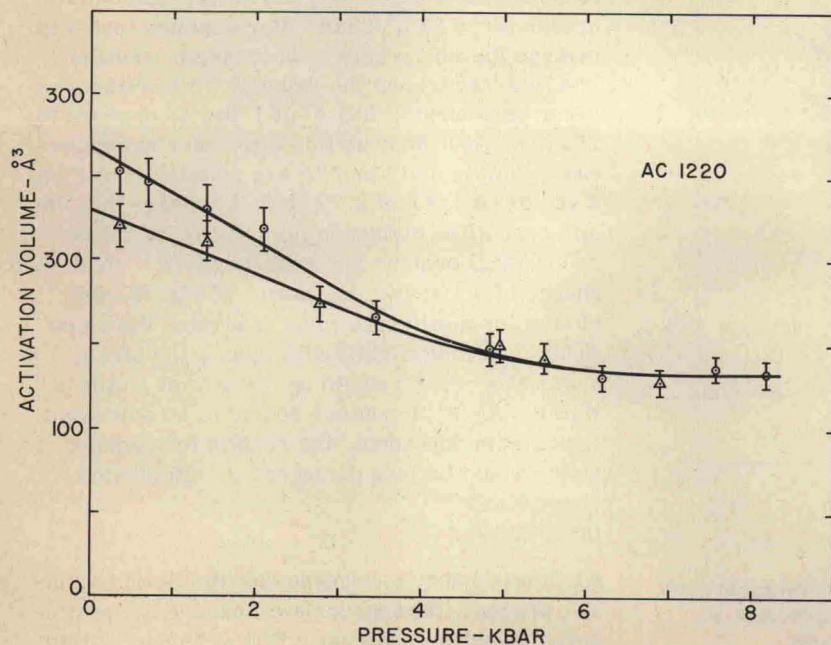


FIG. 8. The activation volume as a function of pressure for samples tested in water (circles) and pentane (triangles) at $\epsilon \approx 1.25$.

modified to $(\partial V/\partial \ln \sigma)_P (\partial \ln \sigma/\partial P)_\epsilon$; and the latter derivative may be found in Fig. 6. For the change of volume with stress we estimate the true stress by multiplying the nominal stress by $1 + \Delta l/l_0$. For the region beyond the Lüders strain, with which we are concerned, this is a reasonably reliable procedure. The values of $(\partial V/\partial \ln \sigma)_P$ thus obtained scatter between -14 and -64 \AA^3 over the range of 1 atm to 5 kbar for samples tested in water; we approximate the derivative in this region with a mean value of -37 \AA^3 . Above 5 kbar, $\partial V/\partial \ln \sigma$ is ~ 0 . For pentane, $\partial V/\partial \ln \sigma$ is $\sim -26 \text{ \AA}^3$ from 0–4 kbar and 0 at higher pressures. From these data, and from those in Figs. 6 and 8, one can then estimate $(\partial V/\partial P)_\sigma$ and this is shown in Fig. 9 for the (nominal) tensile stress appropriate to a value of $V^* \sim 266$ at 1 atm in water (~ 195 bar) and 230 \AA^3 in pentane (~ 180 bar).

It is evident that the decrease of V^* with P at constant stress is only about 60% of that at constant strain rate. We also note in Fig. 9 that V^* in pentane is always less than that in water; the coincidence of V^* at high pressure in Fig. 8 is caused by a combination of high pressure and high stress. At 8 kbar V^* is decreased by $\sim 30\%$ relative to its value at 1 atm. Some of this decrease must be ascribed to the hydrostatic compression of the material, which for the bulk polymer amounts to $\sim 10\%$ at 8 kbar. On the other hand, because pentane influences V^* and it is expected that the pentane is absorbed primarily in the amorphous region, this suggests that the decrease of V^* might reflect the compression of the amorphous

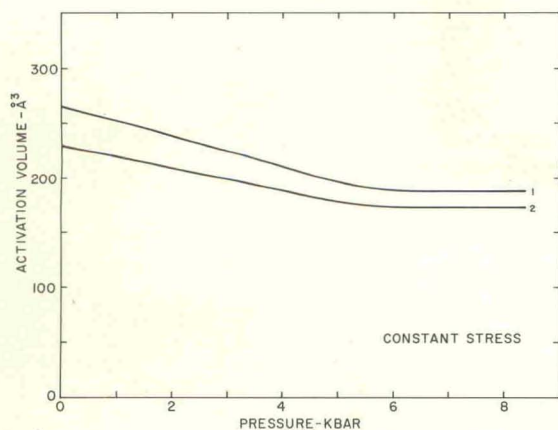


FIG. 9. Activation volume as a function of pressure at constant (nominal) stress equal to ~ 195 bar for curve 1 (water) and ~ 180 bar for curve 2 (pentane), which corresponds roughly to the 1-atm flow stress at $\epsilon = 1.25$ in each case; the true stresses are in approximately the same ratio. If the same true stress were used for both curves, the spread between the two curves would be slightly greater.

ous component. According to the work of Pastine¹³ this amounts to about 16% at room temperature and 8 kbar. At any rate, for the condition of constant stress and allowing for the compressibility of the material, V^* decreases by only 15–20% at 8 kbar. Such a decrease has also been found for metals.^{14,15}

The ultimate goal in determining the activation parameters which characterize plastic flow is to understand the nature of the micromechanical deformation mechanism. In this regard the influence of pentane on V^* is important, because it suggests that the rate-limiting step controlling deformation (beyond the Lüders strain) may operate in the amorphous region. One can imagine that in the already swollen polymer the difference in volume between the ground state and the activated state will be smaller except, apparently, under a combination of high pressure and high stress. According to the model of deformation developed by Peterlin¹⁶ the structure of cold-drawn PE is characterized by stacked crystalline lamellae interconnected by many tie molecules which bridge the quasiamorphous region between lamellae. The formation of free radicals on deformation, as detected by electron-spin resonance experiments,¹⁷ suggests that in order for plastic flow to proceed it is necessary to sever the tie molecules. We suggest then that the transient local volume change, which occurs in the unswollen polymer (AC 1220) at 1 atm during rupture of a tie molecule, probably amounts to $\sim 265 \text{ \AA}^3$. Because the activation energies of mechanical destruction and thermal degradation in many polymers are approximately equal,¹⁸ we speculate that the activation volume for the process of thermal degradation of PE is also approximately of this magnitude. The analogous situation for metals is the correspondence of the activation volumes of creep and diffusion.

The strain dependence of the parameter m observed here for PE offers an interesting contrast with that generally observed for metals. As noted above, m decreases with increasing strain while for metals m usually increases with strain. In the latter case it is believed that the applied stress σ_a is separable into the sum of two components, a long-range internal stress σ_i , and an effective stress σ_e acting on a mobile unit.⁴ By definition⁴ m is given by $\partial \ln \dot{\epsilon}/\partial \ln \sigma_e$. It is assumed that the change of applied stress $\delta \sigma_a$ which occurs in a cyclic test is equal to the change of effective stress $\delta \sigma_e$. However, $\delta \sigma_e/\sigma_e > \delta \sigma_a/\sigma_a = \delta \sigma_e/(\sigma_e + \sigma_i)$ if σ_i is not small. As σ_i increases, m will increase and hence work hardening in metals is ascribed to the generation of a long-range internal stress which screens the applied stress from the mobile unit. In the present case m decreases with strain

and hence work hardening is probably not associated with an increasing internal stress.

It has been noted that the ratio of yield stress to Young's modulus σ/E for polymers is approximately independent of T , $\dot{\epsilon}$, and P ¹⁹; this is roughly true in the present work. In the case of metals this is taken as evidence for an athermal process because E is not rate dependent, i. e., thermally activated, in the normal testing range and $\sigma_i \approx \sigma_a$. For polymers, however, both E and σ are rate dependent, and constant σ/E implies that they have similar activation parameters (though not necessarily similar mechanisms).

CONCLUSIONS

It is found that the inverse strain-rate sensitivity, m , of AC 1220 high-molecular-weight PE increases with pressure and decreases with strain (Figs. 4 and 5). The pressure derivative of the flow stress $(\partial \ln \sigma / \partial P)_T$ for this material decreases strongly with pressure (Fig. 6) and increases with strain. As the strain and pressure dependences of these parameters are of opposite sign, on calculation of the activation volume V^* from their product (and kT) it is found that V^* is only a moderately decreasing function of pressure, especially at constant stress (Fig. 9); it is only slightly dependent on ϵ at low pressure and independent of ϵ at high pressure. Samples tested in pentane are observed to have a lower activation volume than samples tested in water, except under a combination of high pressure and high stress. As pentane is absorbed primarily in the amorphous region, the influence of pentane on V^* suggests that the thermally activated mechanism which controls deformation probably operates in the amorphous region. We suggest that V^* may be the transient local volume change which occurs

on the breaking of a tie molecule during deformation.

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