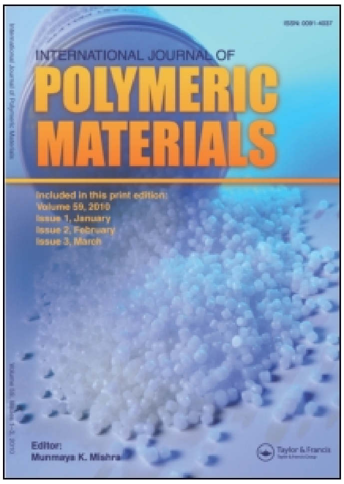

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Effects of Hydrostatic Pressure on the Mechanical Behavior of Polymers: Polyurethane, Polyoxymethylene, and Branched Polyethylene

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Effects of Hydrostatic Pressure on the Mechanical Behavior of Polymers: Polyurethane, Polyoxymethylene, and Branched Polyethylene

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The mechanical behavior of polyurethane, polyoxymethylene and branched low density polyethylene is evaluated at various levels of hydrostatic pressure from atmospheric up to 6.9 Kb. Polyurethane undergoes a "ductile–brittle–ductile" transition accompanied by decreased strain hardening and also exhibits intrinsic yield behavior in compressive tests at higher pressures. A study was made of polyoxymethylene with emphasis below 1.4 Kb and in the vicinity of 5.5 Kb. The effect on the mechanical behavior in the 5.5 Kb region is attributed to a possible pressure-induced shift of a β-transition. Additional data not reported by Sardar *et al.* are discussed. Tests on branched low density polyethylene show that it behaves under pressure in a way similar to that of medium density polyethylene. With increased pressure, failure of the specimens tested, occurs by necking to a fine point. The elastic modulus versus pressure data indicates a possible pressure-induced shift of a β-transition up to room temperature. Above this pressure (2.4 Kb) the rate of increase is slowed because the material is largely in the glass state. A modified form of the Hu–Pae yield criterion which predicts the linear dependence of the yield stress on the hydrostatic pressure is introduced.

INTRODUCTION

In this paper, the stress–strain behavior of polyurethane (PU), polyoxymethylene (POM), and branched low density polyethylene (LDPE), under different values of hydrostatic pressure up to 6.9 Kb, is examined. The PU specimens reveal a "ductile–brittle–ductile" transition accompanied by decreasing strain hardening. Since Sardar *et al.*[1] have reported on the general effects of pressure on POM, emphasis here is on the behavior at lower pressures (< 1.4 Kb) and on the variation of elastic modulus and tensile yield stress near 5.5 Kb. When possible, both continuum theory and molecular interpretations are used.

MATERIALS AND EXPERIMENTS

Density, crystallinity and the melting temperature for the materials tested are shown in Table I.

TABLE I

Material	Density (g/cm^3)	Crystallinity (%)	Tm (°C)	Remarks
PU	1.266	~20	~150	Polyester based resin
POM	1.425	~74	~182	Delrin 500
LDPE	0.9231	~51.6	~115	$\bar{M}w = 142{,}945$

These materials were obtained from commercial outlets in the form of 1.27 cm diameter rods. The specimens were machined into cylinders, having 1.27 cm diameter and 2.54 cm or 5.08 cm long, for compressive tests. For tensile testing, specimens having a 0.64 cm diameter by 2.54 cm long gage section with raised threaded ends were used.

Uniaxial tensile and compressive tests, under selected levels of hydrostatic pressure, were performed in a thick-walled cylindrical chamber. Details of this apparatus have been described elsewhere.[2] The pressure transmitting fluid is mainly kerosene mixed with a small amount of lubricating oil. No absorption of fluid or swelling was observed in all three materials when subjected to high pressure for several hours. Tests were conducted at room temperature (23°C) at a constant deformation rate of 0.254 cm per minute. Under these conditions, the deformation process is considered a quasi-static and isothermal one.

RESULTS AND DISCUSSION

a) Polyurethane

Nominal tensile stress–strain curves at various levels of hydrostatic pressure are shown in Figure 1. Several unusual features are present in addition to the usual increase of elastic modulus and yield stress with increasing pressure.

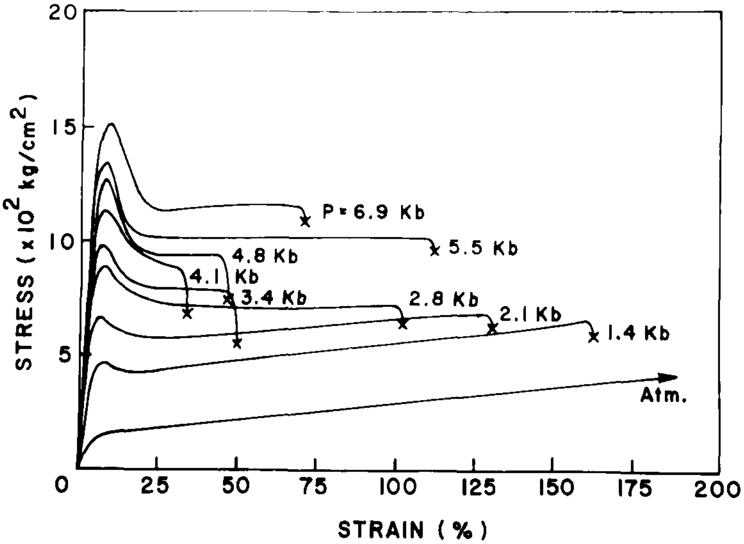

FIGURE 1 Nominal tensile stress–strain curves for PU at various pressures.

First, PU undergoes an apparent "ductile–brittle–ductile" transition. At one atmosphere, the specimen deforms in a ductile manner up to several hundred percent. Strain to fracture then gradually decreases with increasing pressure until a minimum value (33%) is reached at 4.1 Kb where this trend reverses and the elongation increases again. A similar pattern was observed when polyvinyl chloride specimens were tested in a high pressure environment.[3] Secondly, PU shows a gradual decrease in the strain hardening rate with increasing pressure (Figure 1) from one atmosphere up to 2.8 Kb and at higher pressures it completely vanishes. This is in contrast with tests on polytetrafluoroethylene (PTFE), where the strain hardening rate increased markedly with pressure.[4] Finally, at atmospheric pressure, PU specimens deform without necking by cold drawing uniformly in the same manner as PTFE.[4] However, at high pressure (> 1.4 Kb) the specimens develop a neck which propagates along the gage length (similar to polyethethylene and polypropylene under ambient conditions) and as a result the elongation depends on the amount of this propagation.[5]

Nominal compressive stress–strain curves obtained at various levels of hydrostatic pressure are shown in Figure 2. Clearly, the compressive elastic modulus and the yield strength increase with increasing pressure. At atmospheric pressure the compressive stress–strain curve shows a monotonically increasing stress with strain. An unusual feature of the compressive yield behavior in PU is the development of a distinct yield peak at high pressures,

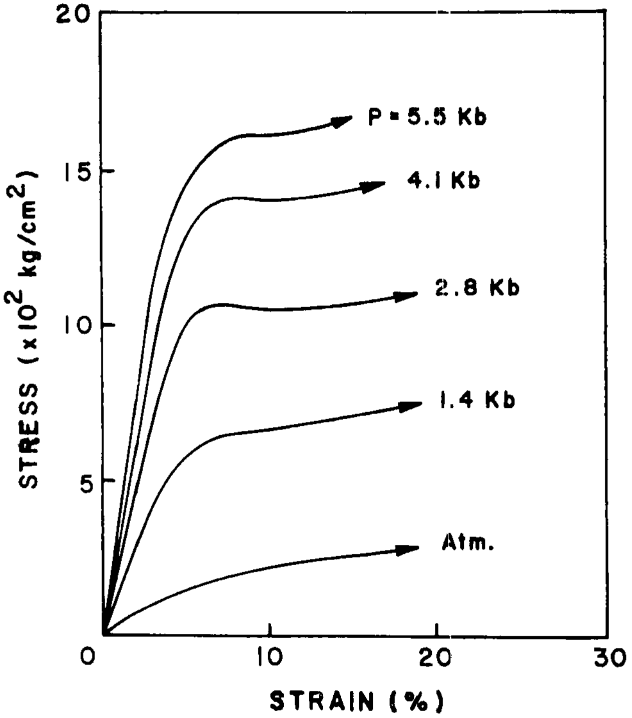

FIGURE 2 Nominal compressive stress–strain curves for PU at various pressures.

that is, at pressures greater than 2.8 Kb, yielding associated with an instability point, is observed. Since compressive yielding is not due to a geometrical change of the specimens, such as necking in tension, it must instead represent a true softening effect. Intrinsic yielding at ambient conditions is not a rare phenomenon but in PU an intrinsic yield drop developed only after the application of pressure and this is indeed an unusual property.[6] The opposite effect is, in fact, found in polyvinyl chloride and cellulose acetate,[3] that is, under applied pressure the yield drop present at ambient conditions gradually vanished.

The change in the compressive elastic modulus, determined from the initial slope of the stress–strain curves, with hydrostatic pressure is shown in Figure 3. This relationship between modulus and pressure is composed of two straight lines joined by a smooth curve at about 4.1 Kb. Since the slope of the straight line above 4.1 Kb is much lower than that of the straight line below 4.1 Kb, it can be assumed that the material passed through some kind of molecular transition. Pressure-induced shifts of the glass transition temperature in the range of 15–30°C per kilobar have been reported.[7,8] If a pressure-induced

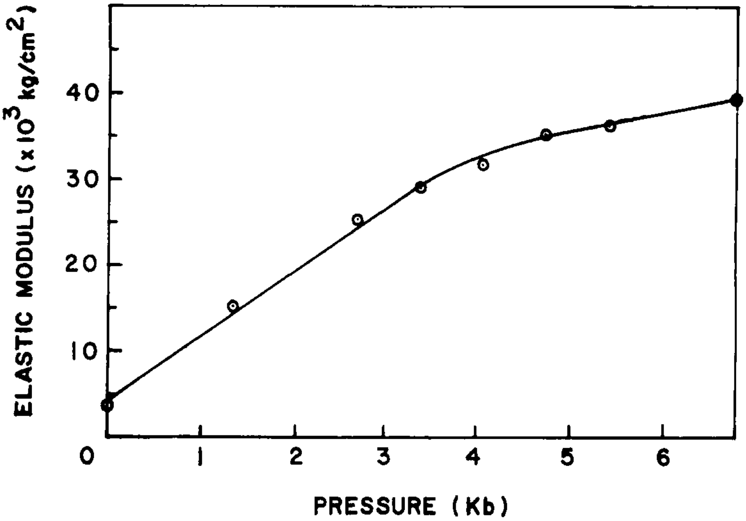

FIGURE 3 Pressure dependence of compressive elastic modulus for PU.

shifting of 20°C per kilobar of a molecular relaxation transition is assumed by this kind of reasoning, a transition may be assumed to exist near −60°C which is now raised to room temperature under 4.1 Kb.

The dependence of tensile yield stress on the applied pressure is shown in Figure 4. Yield stresses represent peak values except for atmospheric pressure which was determined by the 2% offset method. The dependence is piecewise linear with a sharp break appearing at 4.1 Kb. This break at 4.1 Kb coincides with the similar transition in the modulus versus pressure curve and thus supports the idea of the presence of a transition at this pressure. Obviously, a yield condition which incorporates the pressure dependence is needed and such a yield condition will be discussed later.

b) Polyoxymethylene

For this material, emphasis is placed on the stress–strain behavior below 1.4 Kb and in the vicinity of 5.5 Kb. During these tests more than 30 specimens were used in determining various properties. The results are comparable to those obtained by Sardar *et al.* for POM,[1] but some additional features not previously reported will be discussed.

Nominal tensile stress–strain curves at various pressures are plotted in Figure 5. At all pressures, the specimens exhibit linear elastic behavior followed by plastic deformation. Rather unusual behavior is observed for this polymeric material during the deformation process in the plastic range.

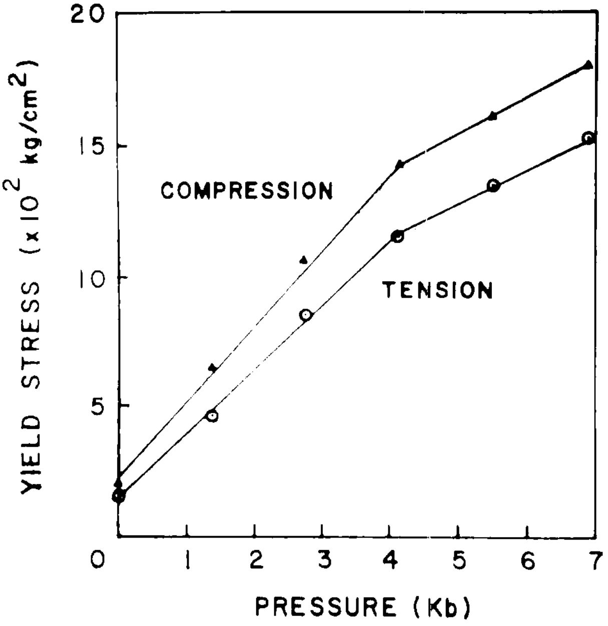

FIGURE 4 Pressure dependence of tensile and compressive peak yield stresses for PU.

At atmospheric pressure, linear elastic behavior is followed by perfectly plastic deformation without any distinct yield point or necking. The specimen is uniformly drawn until fracture occurs at approximately 9.5% strain. The fracture surface is sharp and perpendicular to the applied tensile stress direction. At pressures of 0.21 Kb and 0.34 Kb, the shape of the curves is basically unchanged from that at atmospheric pressure, although the elastic modulus, the yield strength, and the strain to fracture (13.5% and 22% respectively), all have higher values. The rapid increase in elongation with pressure without a change in the basic shape of the curves seems to indicate that the specimens tested at atmospheric pressure might have fractured prematurely because of the presence of inherent flaws. The application of pressures, as low as 0.21 Kb, suppresses flaw crack growth enough to delay crack propagation and ultimate fracture. There appears to be a formation of an instability point in the stress–strain curve at 0.34 Kb and 0.69 Kb, but the deformation process is still dominated by uniform cold drawing with only very little necking. At 0.69 Kb, the basic character of the curve remains essentially unchanged while the instability point has increased in prominence. A corresponding increase in the elongation (~25%) was observed as the maximum elongation attained at all pressure levels (Figure 5).

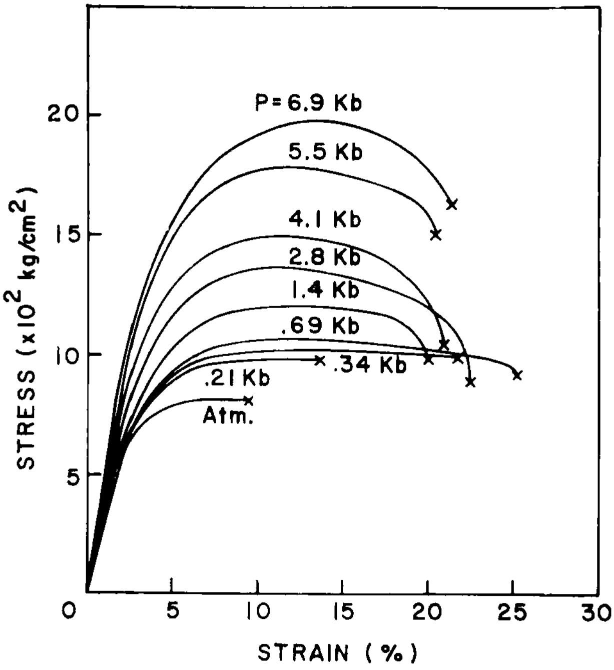

FIGURE 5 Nominal tensile stress–strain curves for POM at various pressures.

Between 0.69 Kb and 1.4 Kb fundamental changes occur in the form of the stress–strain curves. This new shape of the curve persists at all pressures up to 6.9 Kb and the data of Sardar *et al.* substantiates these results up to approximately 8 Kb. At these pressures, plastic deformation is due to the combination of uniform drawing and a necking process rather than by uniform drawing alone which occurs at and below 0.69 Kb. The amount of necking is increased with pressure. There is considerable strain hardening during the plastic deformation process preceding neck formation which is followed by continued necking of the material until fracture occurs. At pressures above 1.4 Kb, a neck was observed on the gage length of the specimen, but contrary to expectations, a rough crack propagation proceeded at an angle of about 50° with the specimen axis into the less oriented region above the necked section.

The dependence of the compressive elastic modulus, the tensile yield strength (1% offset), and the ultimate strength upon hydrostatic pressure is shown in Figure 6. All three curves have similar characteristics, namely, they are piece-wise linear with pressure with a break near 5.5 Kb except at low pressures. At low pressures, from one atmosphere to 0.69 Kb, the properties increase rapidly in a nonlinear fashion. The compressive elastic modulus

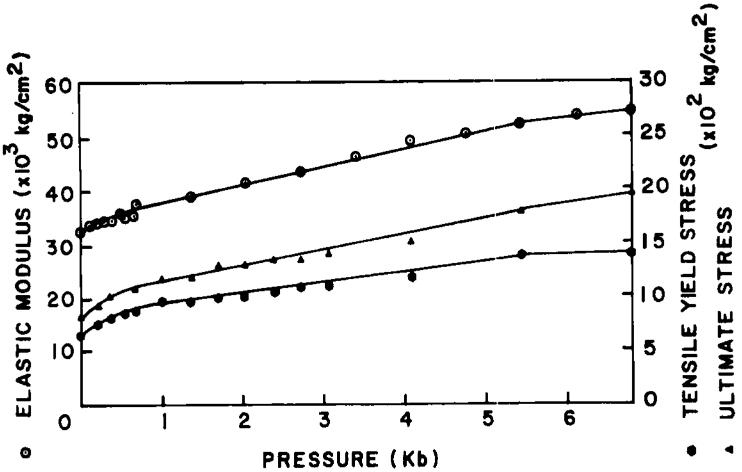

FIGURE 6 Compressive elastic modulus, tensile yield stress and tensile ultimate strength for POM at various pressures.

is determined from the initial slope of the stress–strain curves using a 2-inch long compressive sample. Increase in the modulus of elasticity with pressure may be associated with the pressure-induced shifting of the β-transition up to room temperature as was also pointed out by Sardar *et al.* The β-transition has been observed in the vicinity of $-75°C$ at atmospheric pressure[9,10] and is interpreted to be the result of segmental motion of the backbone chain in the amorphous region of POM. Therefore, the shift corresponds to approximately 18°C per kilobar of applied pressure. The rate of increase in the elastic modulus above 5.5 Kb is expected to be lower than that below this pressure level since amorphous regions of the material above the transition pressure respond like the glass state. Sardar *et al.* reported a linear increase of elastic modulus with pressure without a break near 5.5 Kb, although variations in the yield strength and fracture strength showed such a break. A possible reason for the absence of the break on the modulus versus pressures curves in their data might be due to the use of the secant modulus instead of Young's modulus.

c) Branched polyethylene

Nominal tensile stress–strain diagrams of branched low density polyethylene (LDPE) specimens tested at various levels of hydrostatic pressure are shown in Figure 7. The material is Hookean at all pressures within small strain. The elastic modulus increases significantly with increasing hydrostatic pressure. Clearly, the peak yield stress also increases appreciably with increasing pressure; thereby, extending the elastic range. The specimens tested

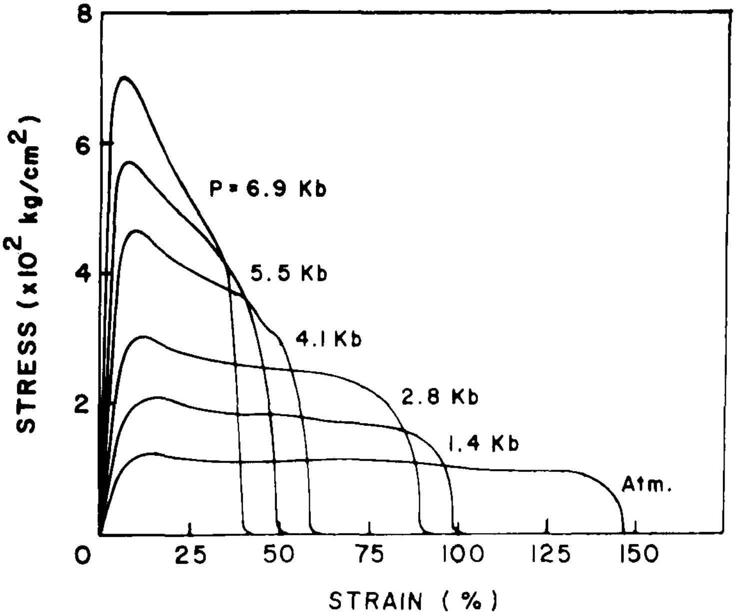

FIGURE 7 Nominal tensile stress–strain curves for LDPE at various pressures.

at atmospheric pressure undergo yielding followed by perfectly plastic deformation with failure occurring at about 150% nominal strain. At medium pressure levels the amount of plastic deformation is reduced and failure occurs by a reduction in the specimen cross section. At high pressures above 5.5 Kb the plastic deformation is suppressed and local necking predominates rather than neck extension.

Nominal compressive stress–strain curves for LDPE specimens tested at various pressures from atmospheric to 6.9 Kb are shown in Figure 8. These curves have a general form at all pressures with a linear elastic region followed by a strain hardening region. The magnitude of the yield stress increases markedly with pressure while the degree of strain hardening increases only slightly with increasing pressure.

The variation of the elastic modulus with pressure, which is determined from the compressive stress–strain curves at small strains, is shown in Figure 9, together with that of slightly branched medium density polyethylene (MDPE — $\rho = .9473$, $\bar{M}w = 170{,}729$, and $\chi = 67.7\%$) for comparison.[11] The moduli of both types of polyethylene are largely linear with pressure. The linear increase is expected as a first approximation result from elasticity theory when consideration is given to finite strains induced by the imposition of high pressure.[5]

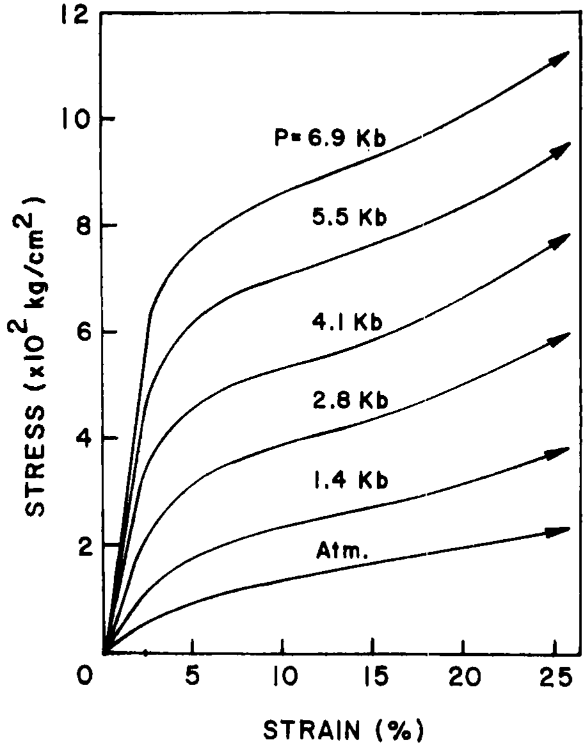

FIGURE 8 Nominal compressive stress–strain curves for LDPE at various pressures.

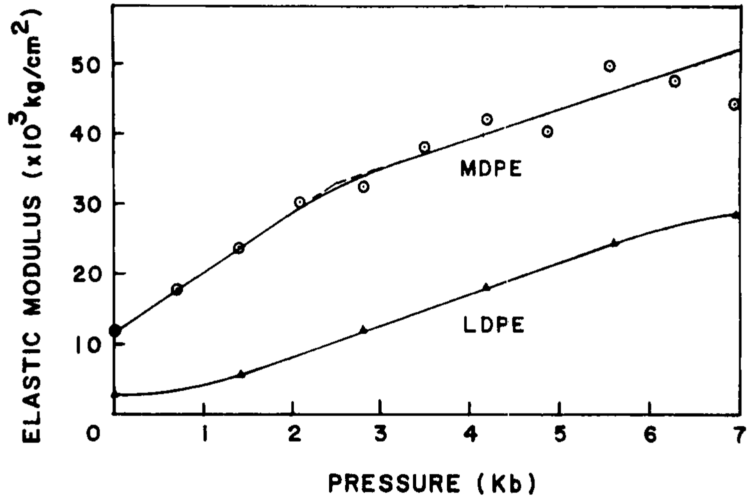

FIGURE 9 Variation of compressive elastic modulus with pressure for LDPE and MDPE.

A better indicator of the rapid increase in the elastic modulus with pressure is the diagram in Figure 10 of the logarithm of the elastic modulus versus the applied pressure. Clearly as expected the modulus of LDPE increases at higher rate than that of MDPE. This is due to higher compressibility of LDPE.

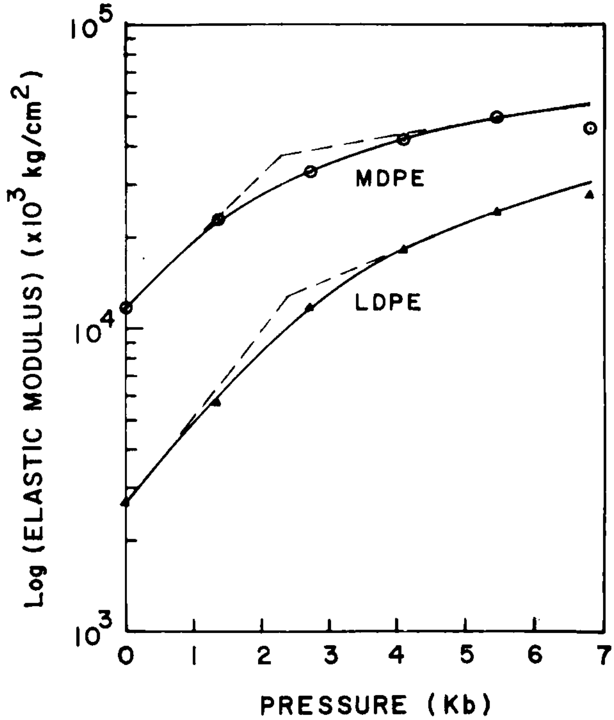

FIGURE 10 Variation of the logarithm of the compressive elastic modulus with pressure for LDPE and MDPE.

Intersecting tangent lines drawn on each curve are both located at the same pressure level (~2.4 Kb). It was noted in an earlier paper,[11] that this is due to the pressure-induced shift of the β-transition which occurs at atmospheric pressure near −10°C.[12]

The diagram in Figure 11 shows the pressure variation of the compressive yield stress (5% offset method) and the tensile yield stress as determined from peak values. Their variation is similar in nature to that observed for the elastic modulus, with the variation approximately linear at pressures above 1.4 Kb.

The changing nature of deformation and fracture under tensile loading with increasing pressure is quite marked. First, a neck is formed at some

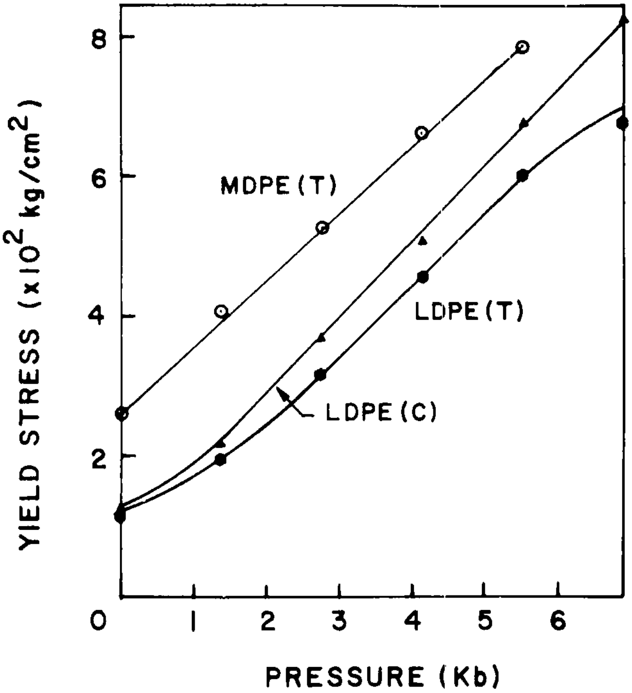

FIGURE 11 Pressure dependence of compressive yield strength and tensile peak yield stress for LDPE with tensile peak yield stress for MDPE.

point in the gage section at the peak stress value. At atmospheric pressure, the neck quickly propagates along the gage length, indicating that sufficient strain hardening due to orientation has occurred in the necked region to stabilize the neck despite its reduced cross section. Finally, fracture occurs after prolonged cold drawing by a combination of slip and tearing processes. At higher pressures up to 4.1 Kb, pressure seems to enhance the amount of localized necking as the difference between the upper and the lower yield stresses increases. This response is probably due to a reduction in strain hardening or in orientation. Fracture occurs by tearing and shearing in the necked region until the cross section is reduced to a fine point. At 5.5 Kb and higher, cold drawing is almost completely eliminated. Necking occurs at one specific cross section, probably where some flaw or stress concentration is present and then dominates the deformation process gradually reducing the necked cross section to a fine point. The specimens fail in the necked region by a shearing process. Thus, the fracture behavior of LDPE is "neck formation dominated" at high pressures and "neck propagation dominated" at low pressures.

It is instructive to compare the deformation behavior of LDPE with that of the MDPE specimens tested under similar conditions by Mears, Pae and Sauer.[5] The nominal stress–strain curves for the two materials are similar in form. The MDPE specimens, however, exhibited larger overall deformation at each pressure level. This may indicate a higher molecular weight for the MDPE specimens. At atmospheric pressure, the LDPE specimens fail at about 150% nominal strain, whereas, the MDPE samples did not fail even after several hundred percent nominal strain. Furthermore, as shown by Figure 9 and Figure 11, both the elastic modulus and the yield stress of MDPE is much higher than that of LDPE at all pressure levels. These differences in strength and stiffness are a result of the lower density, lower crystallinity, and the increased branching in LDPE as compared to MDPE.

The nature of yielding and plastic deformation processes in LDPE appears to be slightly different from that observed in MDPE.[5] In the MDPE specimens subjected to low applied pressures, local necking was quickly suppressed as a result of strain hardening at the critical cross section; hence, the necked region could then propagate along the entire length with fracture intervening. In fact, the specimens tested at atmospheric pressure and at 0.69 Kb did not fracture even when strained several hundred percent. At higher pressures (2.8 Kb and 4.1 Kb), however, the amount of cold-drawing decreased. Fracture apparently stems from slip processes in the cold drawn region for the 2.8 Kb specimens and from slip and tear processes for the 4.1 Kb specimens. At the highest pressure levels; that is, 5.5 Kb and 6.9 Kb, the neck remained localized and its diameter gradually reduced to a fine point before final separation followed.

d) Yield criteria

For all polymers studied, the yield strength in tension and in compression depends on the magnitude of hydrostatic pressure. Furthermore, the yield strength in compression is noticeably higher than that in tension. Since hydrostatic pressure plays such an important role in the initial yield of polymers, appropriate yield criteria, which includes the observed mechanical behavior, will be considered.

The Hu-Pae yield criterion[13] accounts for the influence of pressure on the yield strength by including J_1 in the expression for the initial yield surface, thus

$$f_0(J_1, J_2', J_3') = 0 \tag{1}$$

where

$$J_1 = \sigma_{kk}$$

$$J_2' = 1/2\sigma_{ij}'\sigma_{ij}'$$

$$J_3' = 1/3\sigma_{ij}'\sigma_{jk}'\sigma_{ki}'$$

As a special case Eq. (1) may be written as

$$(J_2')^{1/2} = \sum_{n=0}^{\infty} a_n J_1{}^n \tag{2}$$

where a_n are material constants. This will reduce to the von Mises criterion when $n = 0$. When $n = 1$ is taken, Eq. (2) becomes

$$(J_2')^{1/2} = a_0 + a_1 J_1 \tag{3}$$

Eq. (3) may be used to describe the yield behavior of most polymers studied. For a stress state produced by an uniaxial stress $\pm\, \sigma$, with superimposed hydrostatic pressure, $-P$, a_1 is evaluated to be a negative quantity and thus Eq. (3) becomes

$$\sigma = \left[\frac{(3)^{1/2}}{1 \pm (3)^{1/2}|a_1|}\right] \cdot (a_0 + 3|a_1|P) \tag{4}$$

where the plus sign refers to the tensile case and the minus sign to the compression. Eq. (4) predicts that the yield strength in tension and in compression are a linearly increasing function of hydrostatic pressure and that the yield strength in compression is higher than that in tension. The material constants a_0 and a_1 are listed in Table II for PU, POM, and LDPE.

TABLE II

Material		a_0		a_1	
PU	Tension	98.8 kg/cm^2	<4.1 Kb	−0.0542	<4.1 Kb
	Compression	10.49 kg/cm^2		−0.0531	
POM	Tension	514 kg/cm^2		−0.0182	
LDPE	Tension	17.0 kg/cm^2		−0.0210	
	Compression	15.8 kg/cm^2		−0.0201	

Another yield criterion developed by Sternstein *et al.*[14] to describe shear yielding in polymethylmethacrylate (PMMA) is expressed by

$$\tau_{oct} = \tau_s - \mu_m \sigma_m \tag{5}$$

where τ_{oct} = octahedral shear stress

τ_s = pure shear yield stress

μ_m = material constant

σ_m = mean stress.

This yield criterion follows directly from the more general Hu–Pae approach.

Since $$\tau_{oct} = (2/3J_2')^{1/2} \tag{6}$$

and $$\sigma_m = 1/3J_1, \tag{7}$$

the Hu–Pae yield criterion represented by Eq. (3) gives

$$\tau_{oct} = (\alpha_0 - 3|\alpha_1|\sigma_m) \quad (2/3)^{1/2} \tag{8}$$

which is identical to Eq. (5) above.

Acknowledgements

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