THE EFFECT OF PRESSURE AND ENVIRONMENT
ON THE FRACTURE AND YIELD OF POLYMERS

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INTRODUCTION

Recent studies on the effect of hydrostatic pressure on the mechanical behaviour of polymers [1,2] have shown that the application of pressure increases both the modulus of the polymer and its yield stress; in fact for certain polymers the application of pressure has been observed to cause a transition in the mode of failure from brittle to ductile.

The presence of low molecular weight materials in polymers are generally known to plasticize them decreasing their modulus and yield stress. In some cases these low molecular weight materials, acting in a sense opposite to that of pressure, actually cause a transition from ductile to brittle behaviour. In the above context it is important to give cognizance to the effect of these fluids on the observed mechanical behaviour, a factor which has hitherto been ignored.

This paper presents an overview of earlier work in this laboratory [1,3,4] on the effects of high pressure and environment on the mechanical behaviour of polystyrene, (polymethylmethacrylate was also studied; the results for it are generally similar to polystyrene and are discussed in detail in [2,3,4]), and also recent results on the effects of high pressure and environment on the mechanical behaviour of the semi-crystalline polymers polyethylene, polypropylene and polyoxymethylene.

EXPERIMENTAL

Polystyrene samples were obtained as extruded rods 7/8 inches in diameter ($M_w = 104,100; M_n = 265,400$), a general purpose commercial grade manufactured by the Dow Chemical Co. Polyethylene, polypropylene and polyoxymethylene samples were obtained as extruded rods from Cadillac Plastics and Chemicals. The densities of these semi-crystalline polymers, as measured in a density gradient column at 23°C, were 0.956, 0.895 and 1.425 g/cm³, respectively. The samples used were machined directly from the rods and were of the standard round bar type (with threaded ends) having an overall length of 5 cm. After machining the samples were carefully polished using fine grade sandpaper, followed by soft paper and cotton wool to minimize surface roughness effects. Sealed samples were prepared by wrapping Teflon (carbon coating was used instead of Teflon in the polyethylene, polypropylene and polyoxymethylene samples) around the gauge length and then coating around the Teflon with a silicone rubber (RTV 180 from GE) which was cured for one day at room temperature.

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Polyoxymethylene: Stress-strain curves for polyoxymethylene samples in the silicon oil environment, Figure 5a, are in good agreement with those published earlier by Buida and Silano et al. [3] and Silano et al. [6]. The unsheared POM samples deform homogeneously at atmospheric pressure with fracture occurring before the yield peak is reached; with increasing pressure, however, deformation passes through a yield which is followed by a reduction in the cross-section area leading to failure; little or no plastic deformation is observed as illustrated in Figure 6. In the case of the sealed sample, Figure 5b, as pressure increases, yielding is observed which is followed by necking and cold drawing into the neck, failure occurring after the entire gauge length has drawn into the neck (Figure 6).

ANALYSIS AND DISCUSSION

Polyoxymethylene:

a) Brittle-ductile transition: The principal stress for craze initiation for sealed polyoxymethylene samples was observed to be independent of pressure, whereas the principal stress at which shear banding occurs decreases linearly with pressure for both sealed and unsealed samples, Figure 7. Studies on the temperature and pressure dependencies of these stresses [3] show that with increasing pressure and at all temperatures the craze initiation stress increases more rapidly than the shear banding stress. The pressure at which these stresses coincide with the observed transition from brittle to ductile behaviour at that temperature. Thus from the fracture mechanics point of view the brittle-ductile transition can be viewed as arising out of the difference in the pressure and temperature dependencies of these stresses; that these stresses have different pressure and temperature dependences is not unreasonable considering the different molecular mechanisms (brittle fracture formation with crazing and molecular slip with shear banding) with which these phenomena are associated.

b) Criteria for craze initiation: The observation that the principal craze initiation stress for sealed samples is independent of pressure and decreases linearly with pressure for unsealed samples suggests craze initiation criteria of the form

\[ \sigma = \text{constant} \quad \text{(for sealed samples)} \]

and

\[ \sigma = \sigma_0 - \Delta \sigma \quad \text{(for unsealed samples)} \]

The comparison of these results with various craze initiation criteria has been discussed elsewhere [1]. It is noted however that in the unsealed sample crazing is observed to occur only when the principal stress is negative i.e. in a net compressive field.

c) Environmental effects: As can be readily seen the silicon oil acts as a strong stress crazing agent. FTIR studies of cross-sections of unsealed samples which had failed in a brittle fashion, at pressures above the brittle ductile transition of sealed sample, showed that the silicon oil had penetrated up to the same depth as the crazes. It is reasonable to postulate therefore that crazing growth occurs by the oil diffusing into the craze and plasticizing the region just ahead of it. This lowers the craze propagation stress in the region just ahead of the craze such that the craze grows into it; propagation of the craze leading to failure occurs by a repetition of this process. The question that arises is why does not the silicon oil simply plasticize the polymer allowing yield to occur rather than...
Induce a transition from ductile to brittle behaviour? The answer, by analogy with the role of temperature and pressure on the brittle-ductile transition, is probably the stronger effect of silicon oil on the craze initiation stress as compared to the shear banding stress.

Polyethylene and Polypropylene: The stress-strain behaviour for unsealed polyethylene and polypropylene samples is similar to that observed by Mears, Pae and Sauer [7] (i.e., increasing pressure results in an increase in modulus, yield stress and decreases plastic deformation). Superposition of the true-stress strain curves of sealed and unsealed samples indicates that the silicon oil does not effect either modulus or yield stress. In the context of the previous discussion of FTIR results for polystyrene, this behaviour is consistent with the observation of Silano et al [6] that polyethylene does not absorb kerosene-oil when exposed to it under high pressure for long periods of time.

The role of silicon oil for these polymers, therefore seems to be restricted to decreasing the amount of possible plastic deformation at higher pressures by causing 'crack initiation'. Further studies to elucidate the mechanism of such 'crack initiation' are in progress.

Polyoxymethylene (POM): Results for unsealed POM are identical to earlier results obtained in this laboratory by Sardar, Radcliffe and Baer [5] and the more recent results of Silano, Bhatia and Pae [6]. In contrast to the plastic deformation inhibiting effect of pressure in unsealed samples that is observed in polyethylene and polypropylene, POM becomes more ductile with increasing pressure. This can be clearly seen in photographs of the unsealed samples which have failed at various pressures. As in the case of polyethylene and polypropylene, the only role of silicon oil, as evidenced by superposition of the true stress-strain curves up to the point of 'crack initiation' is to inhibit plastic deformation.

CONCLUSIONS

The effect of pressure on the mechanical behaviour of polymers is to increase their modulus and yield stress. In polystyrene, the application of pressure induces ductile behaviour. Silicon oil, which was used as a pressure transmitting fluid was observed to act as a strong stress-crazing solvent and shifts the brittle ductile transition to higher pressures relative to the sealed polymer. The brittle-ductile transition is conceived as arising out of the difference in pressure, temperature and environmental dependence of craze initiation and shear banding stresses. Crazing is observed in a net-compressive field. In the case of polyethylene and polypropylene, pressure increases modulus and yield stress but decreases the amount of plastic deformation that occurs before failure. In the case of polyoxymethylene, the modulus and yield stress increase with pressure as also the plastic deformation prior to failure. Silicon oil does not affect the modulus or yield stress of these polymers, but decreases the amount of plastic deformation for all three semicrystalline polymers by 'crack initiation'. Work is in progress to elucidate the mechanism by which the silicon oil acts to 'initiate cracks'.

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REFERENCES

Figure 2a Stress-Strain Curve for Unsealed PE Samples as a Function of Pressure

Figure 2b Stress-Strain Curves for Sealed PE Samples as a Function of Pressure

Figure 3 True Stress-Strain Curves for Sealed and Unsealed PP Samples as a Function of Pressure

Figure 4 Sealed and Unsealed PP Samples Tested at Various Pressures After Test Completion

Figure 5a Stress-Strain Curves of Unsealed POM Samples as a Function of Pressure

Figure 5b Stress-Strain Curves of Sealed POM Samples as a Function of Pressure
Figure 6  Sealed and Unsealed POM Samples Tested at Various Pressures after Test Completion

Figure 7  Pressure Dependency of Principal Craze Initiation and Shear Banding Stresses for Sealed and Unsealed PS