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The mechanical behaviour of high-impact polystyrene under pressure

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High-impact polystyrene [HIPS], a two-phase polymeric system, has been investigated studying the pressure dependence of stress–elongation behaviour in tension over the range from atmospheric pressure to 4 kbar at room temperature and constant strain-rate. A comparative study of polystyrene [PS] was also undertaken. HIPS sealed from the environment exhibited ductile behaviour at all pressures. Surprisingly, specimens exposed to silicone oil environment exhibited two transitions as the applied hydrostatic pressure was raised: a ductile-to-brittle followed by a brittle-to-ductile transition. Stress-whitening was suppressed at relatively low pressures. The dilational requirement for profuse crazing was restrained by the combined effect of fluid under pressure resulting in the suppression of the energy absorption mechanism.

Analysis of the stress–elongation curves for sealed specimens indicated that the pressure dependency of craze-initiation stress differs from that of shear band initiation stress. The brittle-to-ductile transition occurred when the initiation stresses of both processes became equal. The principal stress for craze initiation showed almost no pressure dependency, suggesting that crazes initiate when the principal stress level of the tensile specimen reaches a critical value irrespective of the applied hydrostatic pressure. A value for the proposed triaxial tension around the rubber particles was determined from the experimental results and found to be in good agreement with a calculated value. A general mechanics argument was used to explain the existence of the ductile-to-brittle and the brittle-to-ductile transition in HIPS, and also to predict the pressure dependencies of brittle-fracture stress and craze-initiation stress for sealed and non-sealed specimens.

Nomenclature

P,	hydrostatic pressure, here taken as always positive
BD,	brittle-to-ductile transition
CS,	craze-to-shear band transition
σ_T,	observed tensile stress
σ^1,	the first principal stress
σ_f^s,	fracture stress for sealed specimens
σ_f^{ns},	fracture stress for non-sealed specimens
σ_y,	yield stress
σ_f,	fracture stress
σ_{ci},	craze initiation stress

1. Introduction

One of the most important and versatile thermoplastic materials is high-impact polystyrene [HIPS], a two-phase polymeric system in which a rubbery phase is incorporated into polystyrene [PS] facilitating improved toughness and elongation. Our study of HIPS was conducted using material prepared by the polymerization described by Amos *et al.* [1] and Molau and Keskkula [2] of a solution of uncrosslinked rubber in vinyl monomer. Micrographs of the final product revealed a material with a solid dispersion of rubber particles in a matrix of polystyrene. Molau and Keskkula [2] showed that the rubber particles also contained occlusions of polystyrene. While most commercial HIPS contains about 3 to 10% by weight of polybutadiene, the presence of polystyrene occlusions gives rise to a volume fraction of 10 to 40% of the composite-reinforcing rubber phase [3].

Merz *et al.* [4] first suggested in 1956 that energy absorption occurs through the stretching of the rubber phase. Willersinn [5] similarly suggested in a 1966 review that the cross-linked but finely divided rubber phase acts as an energy absorber. Impact energy is converted to heat, thus rendering HIPS impact-resistant. He added that good "anchoring" is required, through grafting of the elastomer into the rigid matrix.

Ductility and stress-whitening of HIPS were ascribed by Bucknall and Smith [6] and Kambour [7] to the generation of multiple crazes which initiate at the rubber–polystyrene interface. Based on this crazing mechanism, Rosen [8], in a review in 1967, concluded that impact strength should improve as the number of sites for craze initiation is increased. However, Schmitt [9] has suggested that energy absorption is mainly accomplished by interfacial separation of the numerous rubber particles from the polystyrene matrix followed by the formation of a multitude of microcracks. He demonstrated that this driving force for interfacial separation is possibly due to a triaxial tension which exists at the interface. Adhesion needed for rubber particles to exist in a state of triaxial tension is provided by grafting reactions during the manufacturing process. Internal breaks of the rubber particles are prevented by cross-linking the rubber. It is not unlikely that all of these energy absorbing mechanisms do occur even simultaneously in a single material.

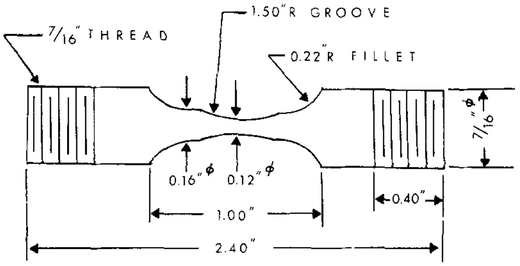
Crazing involves localized volume increases [10, 11] associated with macroscopic yielding; consequently, both craze yielding and fracture are strongly influenced by pressure. Mechanical properties of HIPS were investigated at high pressure under uniaxial tension by Biglione *et al.* [10]. They showed that stress-whitening was prevented at relatively low pressures and brittleness was exhibited at 2 kbar*. It was suggested that the presence of the rubber dispersion markedly lowers the yield stress but has essentially no effect on the fracture stress.

The purpose of the work described here was to study in much greater detail the mechanical properties of HIPS under high hydrostatic pressures. In particular, environmental effects on these properties due to sample immersion in the pressure-transmitting fluid were emphasized. The ductile-to-brittle transition and a second brittle-to-ductile transition are discussed, as well as the criteria for craze initiation, yielding and ductile fracture under pressure. A comparison is made with polystyrene (of similar molecular weight) tested under high pressure by Matsushige *et al.* [11].

2. Experimental details

High-impact polystyrene and polystyrene were received from the Dow Chemical Company in 1 in. thick compression-moulded blocks. Round test samples were machined to the shape illustrated in Fig. 1a. After machinining, the specimens were carefully polished using no. 600 sand paper followed by no. 2/0 emery polishing paper. Polishing was completed using water-soaked cotton wool and 0.3 μm alumina powder. This procedure was adopted to minimize possible surface roughness effects on mechanical behaviour. All HIPS specimens were annealed in vacuum for 24 h at 70° C and permitted to cool in air at room temperature. Sealing of the test samples from the pressure-transmitting environmental fluid was accomplished as shown in Fig. 1b. First, Teflon tape was wrapped tightly around the gauge length, and then this entire area was covered with translucent silicone rubber (RTV 108-GE) which was cured for 2 days at room temperature.

(a) SPECIMEN GEOMETRY



(b) SEALED SPECIMEN

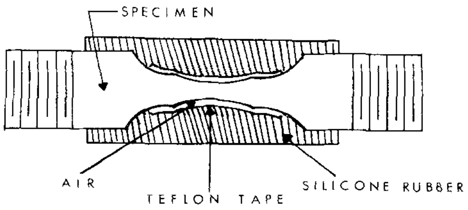


Figure 1 (a) Sample geometry; all dimensions are in inches. (b) Sealed specimen.

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*1 bar = 10^6 dyn cm^{-2} = 0.9869 atm = 1.020 kg cm^{-2}
= 750.06 mm Hg (Torr) = 14.50 psi
= 100 kPa.

The high-pressure apparatus used in this study, described previously elsewhere [12, 19], is a tensile testing machine contained in a pressure chamber filled with silicone oil (Dow Corning 200 fluid, 500 cS) which acts as the pressure-transmitting fluid. In the case of non-sealed samples the silicone oil is in direct contact with the specimen surface. The entire specimen (whether sealed or non-sealed) is subjected to a hydrostatic compressive force at all points including the end faces so that a state of hydrostatic compression exists within the specimen. The effect of environment was also studied using various silicone oils of 5, 1000, and 12 500 cS (Dow Corning 200 fluid). Applied stress versus elongation curves were obtained by pressurizing the chamber to the desired pressure followed by straining the sample at a constant cross-head speed of 1.30 ± 0.15 min^{-1} at room temperature.

Owing to the design limitations of the strain-gauge load cell, accurate modulus data could not be obtained. For this reason, the initial slope of all stress–elongation curves was drawn as a dashed line. The pressure range for study was from atmospheric pressure to 4 kbar.

3. Results

3.1. Environmental effect

Comparative studies using uni-axial tensile deformation at high pressure were conducted to observe the effect of the environment on the mechanical properties of HIPS. Silicone oil, considered to be inactive for polymers, has essentially no environmental effect at atmospheric pressure. In Fig. 2, non-sealed specimens (a) and (b) were pressure-soaked in silicone oil (500 cS) at 2 kbar for 30 min and at atmospheric pressure for 1 month, respectively. The control specimen (c) was not soaked. However, when the silicone oil transmits an applied hydrostatic pressure directly to the surface of the non-sealed specimen, an environmental effect is observed (Fig. 3). Surprisingly, specimens exposed to the silicone oil environment exhibited nearly brittle fracture, whereas sealed samples failed in a

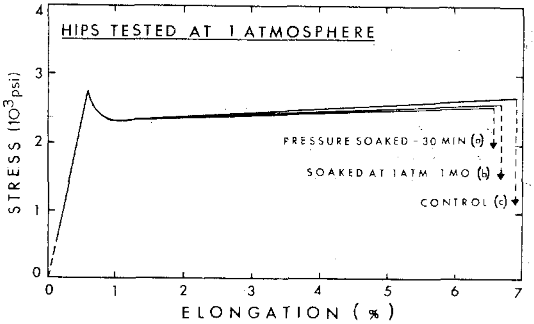

Figure 2 Stress–elongation curves of high-impact polystyrene tested at 1 atm under different surface conditions; (a) pressure soaked for 30 min at 2 kbar, (b) soaked at 1 atm for 1 month, (c) control (non-soaked).

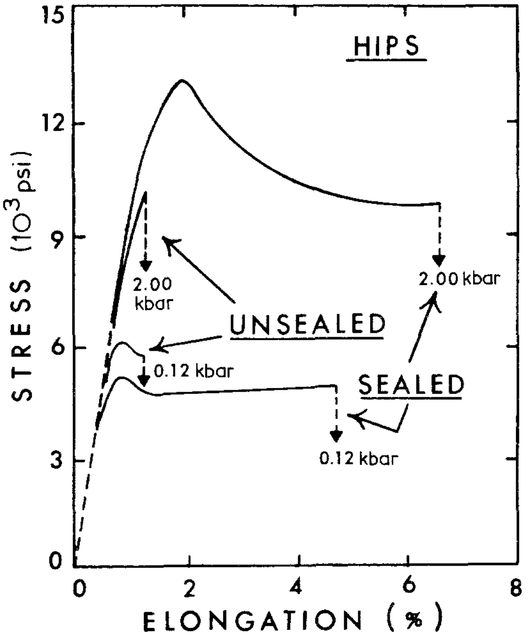

Figure 3 Stress–elongation curves of high-impact polystyrene sealed and non-sealed at 0.12 and 2.00 kbar.

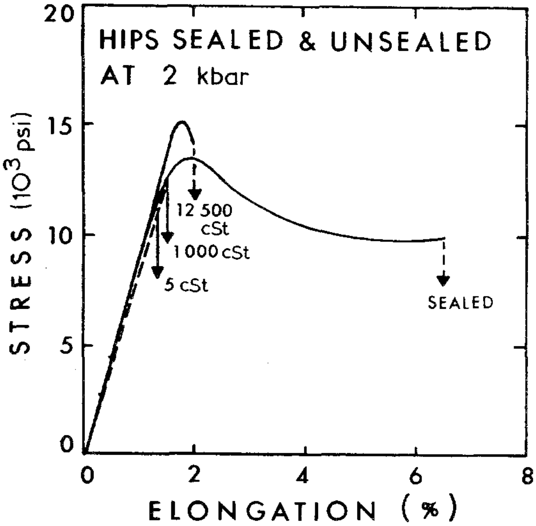

Figure 4 Effect of the viscosity of the silicone oil on stress–elongation curves of high-impact polystyrene at 2.00 kbar.

ductile manner as expected. The non-sealed specimens in the tests at 0.12 kbar did show some sign of yielding, but the elongation-to-failure was drastically reduced. Above 0.12 kbar stress-whitening was prevented and at 2.0 kbar fracture occurred in a brittle manner.

Some insight into the environmental effect was obtained by varying the viscosity of the silicone oil (Fig. 4). The fracture stress increased with increasing viscosity until yielding occurred at a viscosity of 12 500 cS. Examination of this tensile specimen revealed slight necking and ductile failure. A test on a sealed specimen can be thought of as being equivalent to a test on a non-sealed specimen with a silicone oil environment of infinite viscosity. The experiments clearly show that the mechanical properties of HIPS are drastically affected at high pressures when exposed to the pressure-transmitting fluid. Similar behaviour has been reported for polystyrene by Matsushige *et al.* [11, 13].

3.2. Stress–elongation behaviour for sealed HIPS

Stress–elongation curves for HIPS sealed from the environment are shown in Fig. 5 as a function of hydrostatic pressure. All tests indicated distinct yielding, failure occurring in a ductile manner over the entire pressure range studied. As expected, the yield and fracture stress increased with increasing applied hydrostatic pressure. An initial reduction in the elongation-to-break occurs until a minimum is reached at around 0.45 kbar and then the elongation increases again with pressure. This minimum corresponds to the disappearance of stress-whitening, which can be seen from the photographs in Fig. 6. A gradual decrease in stress-whitening occurs as the applied pressure is raised, until at 0.5 kbar when crazing is virtually suppressed. Specimens strained at pressure greater than 0.25 kbar displayed necking behaviour. In essence, the overall behaviour can be characterized in three pressure regions. Region one corresponds to the pressure range between 1 atm and 0.12 kbar where stress-whitening was the only major microdeformation mechanism. Region two corresponds to the pressure range between 0.12 and 0.40 kbar where both stress-whitening and necking (shear banding) occurred simultaneously. Finally, in region three, which corresponds to pressures greater than 0.4 kbar, shear banding alone is the major microdeformation mechanism.

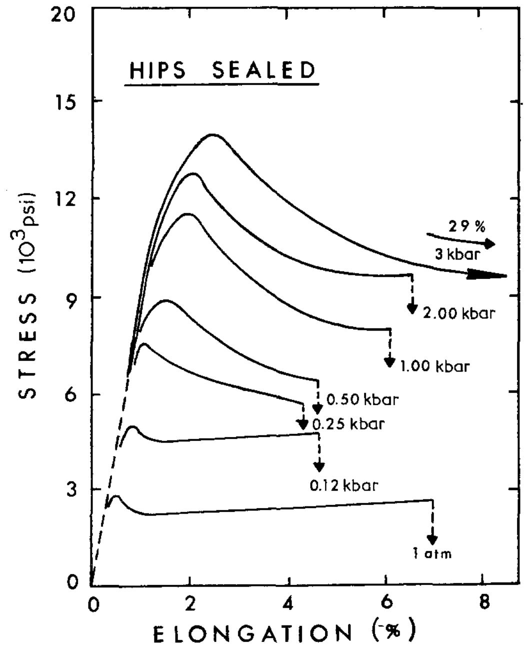

Figure 5 Stress–elongation curves of sealed high-impact polystyrene specimens as a function of applied hydrostatic pressure.

Fig. 7 shows the pressure dependencies of the fracture and the upper yield stresses in sealed PS and HIPS specimens. The arrows BD and CS indicate the brittle-to-ductile and craze-to-shear band transition for PS and HIPS, respectively. The change in slope of the curves indicates a change in fracture mechanism. The steeper slope of both

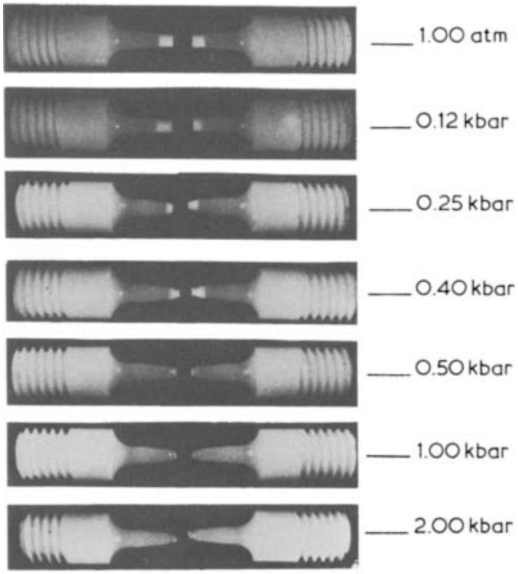

Figure 6 Sealed specimens of high-impact polystyrene after straining at various pressures.

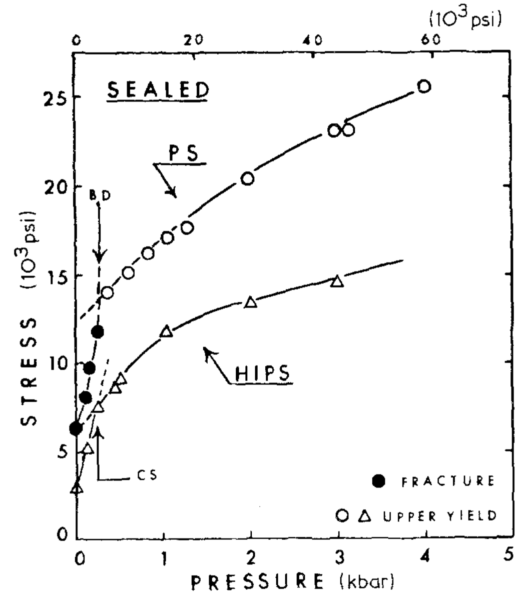

Figure 7 Pressure dependencies of fracture and upper yield stress in sealed specimens of polystyrene and high-impact polystyrene. Arrows BD and CS indicate the brittle-to-ductile and craze-to-shear band transition in polystyrene and high-impact polystyrene, respectively.

curves is characterized by void formation (crazes). The lesser slope of the curves corresponds to ductile failure (shear banding) with minimal volume change. A sharp CS transition was not apparent because the two mechanisms responsible for the change in fracture mode overlapped. As pointed out by Nielsen [14] and as can be seen in Fig. 7, rubber particles act as stress concentrators and tend to reduce the average tensile strength of the rigid matrix.

Pressure dependencies of the craze and the shear band initiation stresses for PS and HIPS are shown in Fig. 8. Below the BD transition for PS, Matsushige *et al.* [11] have defined the stress which corresponds to the limit of proportionality on the stress–strain curve (where marked non-linearity occurs) as the "craze initiation" stress, while the maximum stress is called the "craze yielding" stress. Above the BD transition they defined the limit of proportionality as the shear band" initation stress and the maximum, or upper yield, as the "shear-yielding" stress. These definitions have been adopted in this paper. The craze initiation stress for HIPS showed a slightly greater dependence on pressure than that of PS. The intersection of the extrapolated crazing and shear banding curves in Fig. 8 indicates, for both PS and HIPS, the pressure at which shear banding is first observed. For PS the craze-to-shear band transition is sharp. However, in the case of HIPS, crazing is not completely suppressed until about 0.5 kbar.

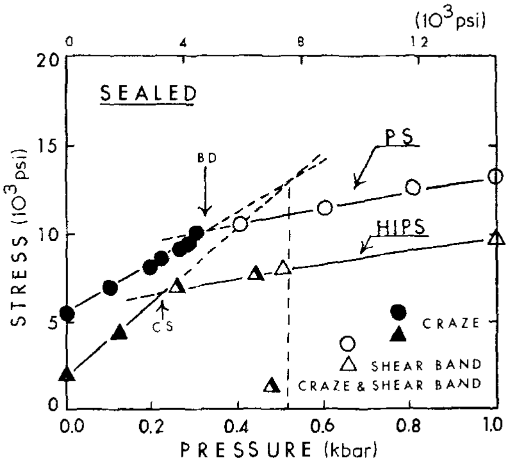

Figure 8 Pressure dependencies of craze and shear band initiation stress in sealed polystyrene and high-impact polystyrene specimens. Arrows BD, and CS indicate the brittle-to-ductile and craze-to-shear band transition in polystyrene and high-impact polystyrene, respectively.

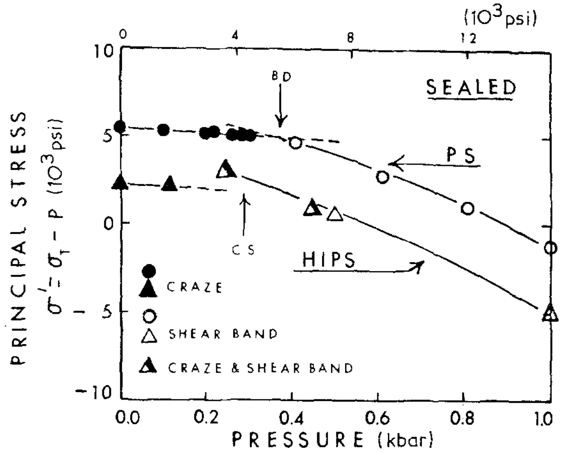

Figure 9 Pressure dependencies of "principal" craze and shear band initiation stress in sealed polystyrene and high-impact polystyrene specimens. Arrows BD and CS indicate the brittle-to-ductile and craze-to-shear band transition in polystyrene and high-impact polystyrene, respectively.

By subtraction of the applied hydrostatic stress component from the observed tensile stress (σ_T), the pressure dependency of the principal stress ($\sigma^1 = \sigma_T - P$) parallel to the tensile direction was calculated. In Fig. 9, the pressure dependencies of principal stress for craze and shear band initiation for sealed PS and HIPS are shown. As with PS, the principal craze initiation stress for HIPS shows almost no pressure dependency. This suggests that crazes initiate when the principal stress level of the tensile specimen reaches a critical value irrespective of the applied hydrostatic pressure. Although the principal shear-band-initiation stresses are also lower for HIPS, both materials behave similarly.

3.3. Stress–elongation behaviour of HIPS specimens exposed to silicone oil

The stress–elongation curves for HIPS exposed to silicone oil (500 cS) as a function of applied hydrostatic pressure are illustrated in Fig. 10. It is surprising to observe that as the pressure was raised HIPS exhibited two transitions: ductile-to-brittle then brittle-to-ductile. As is usual, the yield stress increased with increasing pressure. However, the fracture stress increased initially with pressure to 1.0 kbar then decreased reaching a minimum at the BD transition around 2.25 kbar. Necking and failure occurred in the samples which were strained above 2.25 kbar.

Fig. 11 shows the pressure dependencies of fracture and upper yield stress for PS and HIPS when exposed to the silicone fluid environment. The arrows (BD) indicate the brittle-to-ductile transitions. The changes in the fracture stress with pressure in HIPS and PS were similar, whereas the pressure dependency of upper yield stress was quite different for the two materials. Optical observations of the fracture surfaces of the HIPS specimens confirmed the transition from brittle failure to ductile failure with increasing pressure. As the applied pressure was raised from atmospheric to the BD transition pressure, the fractured surfaces became progressively smoother with crack lines radiating from the origin of failure on the outer surface.

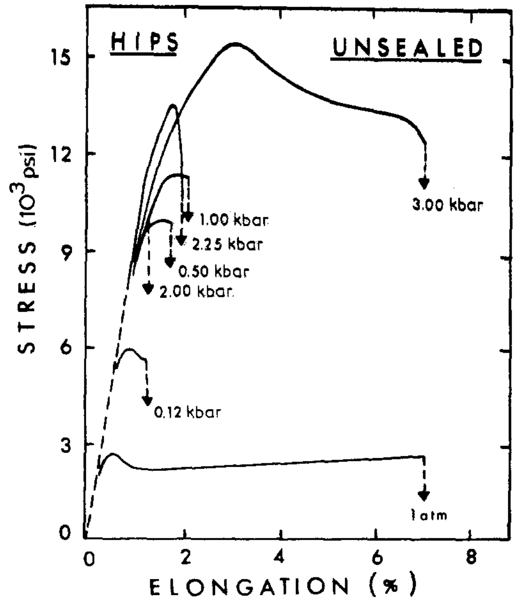

Figure 10 Stress–elongation curves of unsealed (exposed to silicone oil) high-impact polystyrene specimens as a function of applied hydrostatic pressure.

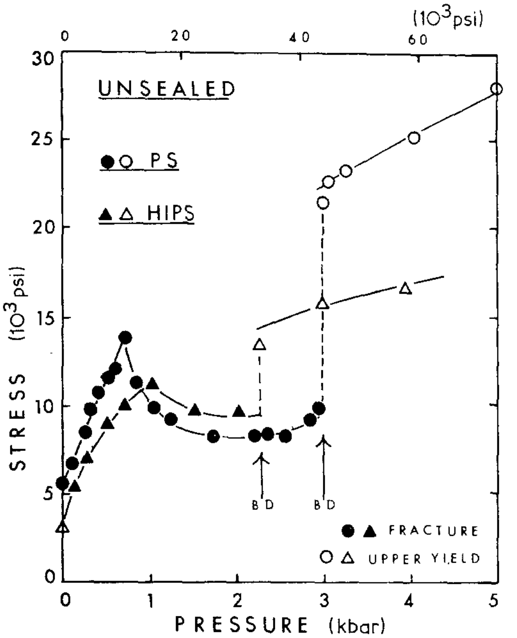

Figure 11 Pressure dependencies of fracture and upper yield stress in non-sealed specimens of polystyrene and high-impact polystyrene. Arrows BD indicate the brittle-to-ductile transitions.

4. Discussion

4.1. Microdeformation mechanisms

High-impact polystyrene, unlike PS, was found to be ductile over the entire pressure range when sealed from the pressurizing medium. However, elongation-to-fracture did change with increasing applied pressure. To illustrate this behaviour, a cross-plot of elongation-to-fracture versus pressure is shown in Fig. 12. The minimum in elongation coincides with the pressure at which stress-whitening was suppressed.

The change in slope in the plot of fracture and upper yield stresses versus pressure (Fig. 7), a minimum in the elongation-to-fracture versus pressure plot (Fig. 12), and a change from stress-whitening to shear banding (Fig. 8), all occurred at about 0.4 kbar. This indicates a change in the dominant microdeformation mechanism at this pressure. Plastic deformation of HIPS at atmos-

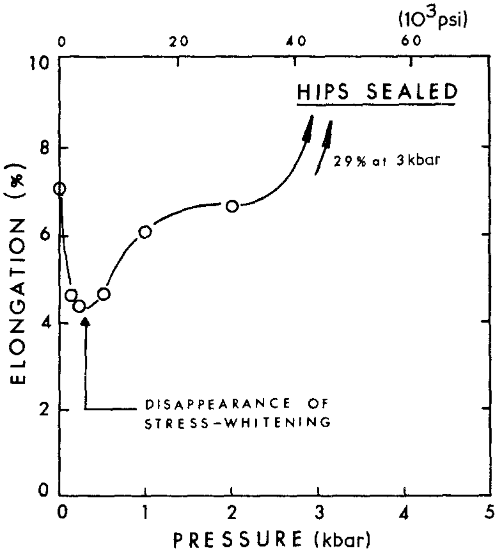

Figure 12 Pressure dependencies of % elongation in sealed high-impact polystyrene specimens.

pheric pressure is known to occur by the production of many crazes aligned perpendicularly to the applied stress; these crazes are responsible for stress-whitening. At 0.4 kbar, the energy needed to create crazes or initiate shear bands became equal, since above this pressure only shear bands were observed.

Crazing also occurs in unmodified polystyrene but to a lesser extent, resulting in a lower craze density. Since the results for PS were similar to those obtained by Matsushige *et al.* [11] comparisons of HIPS were made with these published data. The average distance between crazes in HIPS is such that the strain fields associated with the tips of the crazes can interact to inhibit lateral growth, effectively pinning the crazes. This reduces the probability that a craze can grow sufficiently to become a crack, which could lead to catastrophic failure. Nielson [14] gives a detailed description of how crazes can be responsible for large elongations in HIPS when strained.

4.2. Triaxial stress at rubber–PS interface

The intersection at approximately 0.5 kbar of the extrapolated craze-initiation stress versus pressure curves for HIPS and PS (Fig. 8) suggests that at this pressure the stress starts at the potential craze nuclei in the two materials would be the same. If it is assumed that crazes nucleate at small voids in PS and at the interfaces of rubber particles in HIPS, then, since the radial stress at the surface of a void is always zero, the radial stress at the surface of the rubber particles must also be zero at this pressure. Therefore, the triaxial-tensile stress is cancelled by this value of hydrostatic pressure, i.e. 0.5 kbar.

The triaxial tensile stress at the PS–rubber interface is associated with the volume strain which resulted from the difference in coefficients of thermal expansion of the polybutadiene and polystyrene on cooling from the glass-transition temperature to room temperature during processing. Taking the coefficients of thermal expansion for PS and polybutadiene as 1.7×10^{-4} and $6.6 \times 10^{-4}\,{}^\circ\mathrm{C}^{-1}$, respectively, and the compressibility of polybutadiene (25% PS) as 5.3×10^{-4} MPa^{-1}, the value of the triaxial stress is calculated as 0.46 kbar (46 MPa). This is in good agreement with the value of 0.5 kbar derived above from the experimental data.

The radial-tensile stress around the rubber particles may reduce the measured value of the yield stress (if the PS-butadiene interface is normal to the direction of applied stress) by locally increasing the total stress to the value of the yield stress of unmodified polystyrene. From the above, it would be predicted that the measured yield stress of HIPS would be 0.5 kbar (7×10^3 psi) lower than that of PS, and this is in agreement with the measurements up to 1 kbar (Figs. 7 to 9). The reason for the divergence of the curves above this value is, as yet, unknown. The reason for the increase in the applied stress needed to initiate a craze in HIPS as the pressure is raised (Fig. 8) can also be related to the radial tensile stress. Increasing the applied pressure probably reduces the contribution of the triaxial tension; that is, additional load must be applied to generate the critical stress needed to initiate a craze (Fig. 9).

When HIPS specimens were exposed to the environment and strained under pressure (Figs. 10 and 11), the material tended to behave similarly to PS. Above 0.5 kbar the rubber particles tend to function as "voids" and/or defects in the bulk material where their role to stop crazes has been eliminated by the combined influence of the silicone oil and pressure.

4.3. Crack propagation in sealed, and non-sealed specimens

The differences in the mechanical properties of the specimens exposed to the pressure-transmitting fluid and the sealed specimens can be understood by considering the energy balance in the propa-

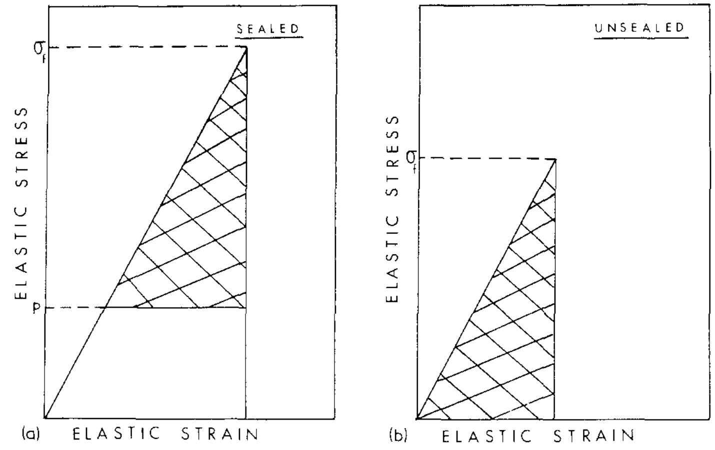

Figure 13 Stress–strain curves for a Hookeian material in which the cross-hatched area represents the energy recovered due to stress relief at newly-formed crack faces: (a) non-sealed pressurizing fluid can act on crack face, (b) sealed.

gation of a pre-existing crack. Griffith [15] has suggested that for catastrophic crack propagation the energy released by a crack when it spreads must be equal to (or greater than) the work done in spreading the crack. Thus, the brittle behaviour would be influenced by changes in either the energy released or the work required in crack propagation. The effect of the medium on the latter in decreasing the surface energy of the crack faces or plasticizing the material at the crack tip has been considered previously [16, 17]. However, a change in the energy released would also be important. The energy released is the elastic stored energy in the material which undergoes stress relaxation as the crack spreads. The shaded area under the stress–strain curve in Fig. 13a represents the energy released during crack propagation at $P = 0$. This energy is equal to the work done in propagating the crack. If it is initially assumed that the elastic modulus is not pressure dependent, then Fig. 13a also represents the energy release for propagation in a non-sealed specimen, because hydrostatic pressure within the polymer and the pressure in the fluid which penetrates the crack cancel at the crack face. If, however, the specimen is sealed from the pressurizing medium and the polymer specimen is again under a hydrostatic pressure, then fluid cannot perform work by assisting the contraction of the material at the crack faces as it can in the non-sealed specimen, hence, the energy released by crack propagation would be lower for the sealed specimen at the same value of tensile stress. Consequently, for the same energy release the stress must be greater. This is illustrated in Fig. 13b. Assuming that the elastic modulus is independent of pressure, then, the fracture stress for sealed specimens, σ_f^s, and non-sealed specimens σ_f^{ns} can be expressed as:

$$\sigma_f^{ns} = \sigma_f^s + P.$$

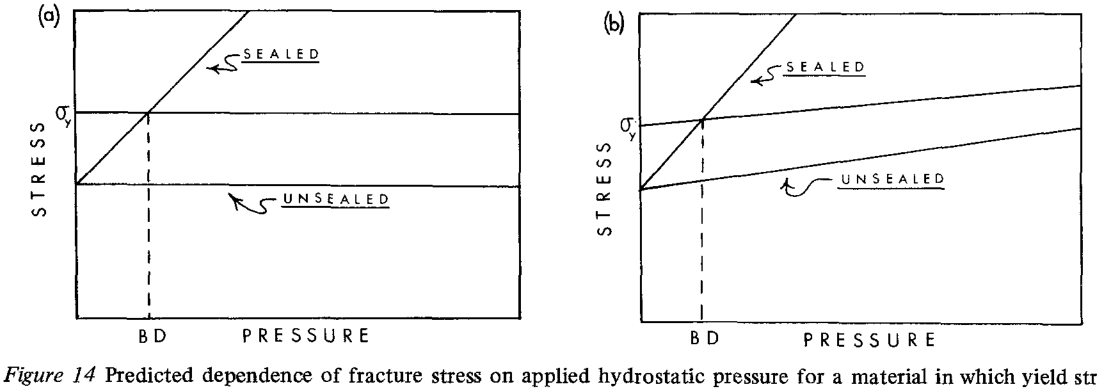

Figure 14 Predicted dependence of fracture stress on applied hydrostatic pressure for a material in which yield stress, σ_y, and elastic modulus; (a) are non-pressure dependent, (b) increase with pressure. BD indicates a brittle-to-ductile transition for the sealed samples.

Fig. 14a illustrates the predicted dependence of the brittle fracture stress on the applied hydrostatic pressure in an ideal case. The line $\sigma = \sigma_y$ represents the yield stress (assumed independent of hydrostatic pressure). There is a pressure above which the stress for cataclysmic brittle fracture in sealed specimens is greater than the yield stress, and, hence, the material is ductile above this pressure. This is the observed brittle–ductile transition.

Fig. 14b shows a more realistic situation for a glassy polymer for which both the elastic modulus and yield stress increase with increasing pressure, N.B. as the modulus increases a greater stress is required to produce the same elastic stored energy. The relative pressure dependencies of the yield stress and modulus would control the brittle–cutile transition pressure for the non-sealed specimens.

It should be pointed out that the above deals only with the catastrophic propagation of a crack. Obviously, a crack capable of growth must first exist or be created, and this crack nucleation may become the limiting process.

As a craze can be regarded as a crack [18] for the purpose of analysing growth behaviour, the above may also be valid for the understanding of craze growth. Again, it is not the nucleation that is being considered, but the subsequent growth to a size which is, for example, observable optically. This is the craze-initiation stress that is plotted in Fig. 8. It is now possible to compare the predictions of the above analysis with the experimental observations of the pressure dependency of the fracture stress and craze-initiation stress (Fig. 15) for sealed and non-sealed specimens are directly dependent on the applied hydrostatic pressure, such that $(\sigma_f - P)$ and $(\sigma_{ci} - P)$ are constants, and in the case of the non-sealed specimens the slight pressure dependency can be attributed to the increase of the elastic modulus with pressure.

4.4. Ductile–brittle transition in non-sealed HIPS specimens

The decrease in the ductility of non-sealed HIPS specimens at low pressure can be understood by considering the situation immediately after craze nucleation. As the same stress is required to nucleate a craze in both the sealed and non-sealed specimen the stored-elastic energy is the same prior to nucleation (Fig. 16). If the pressurizing

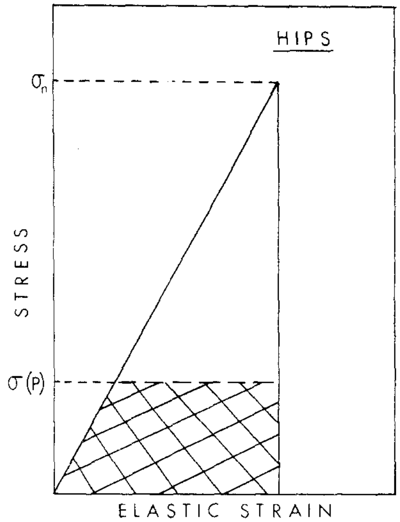

Figure 15 Elastic (Hookeian) stress–strain curve for HIPS specimens. σ_n the craze nucleation stress increases with applied hydrostatic pressure and is assumed the same for sealed and non-sealed specimens. The stored-elastic energy released on nucleation will be less for sealed specimens by an amount represented by the cross-hatched area.

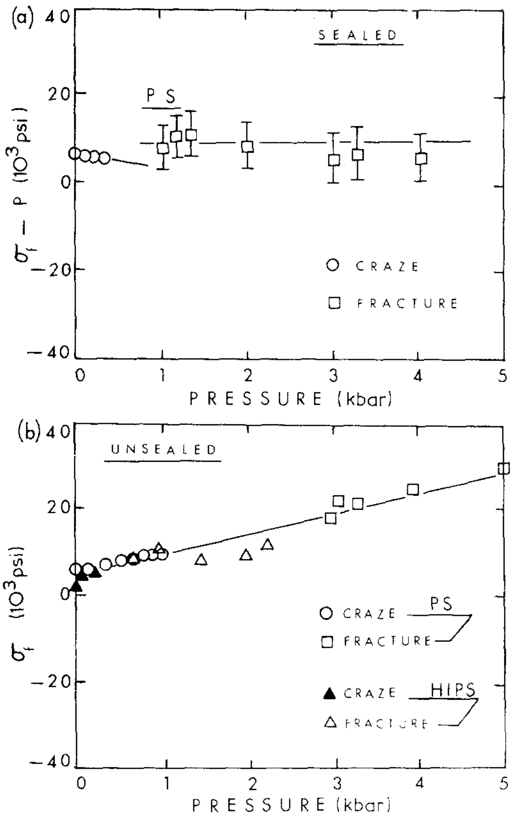

Figure 16 (a) Plot of fracture stress minus pressure against pressure for tensile specimens of polystyrene sealed from the pressurizing medium. HIPS is not included, because fracture was ductile. (b) Plot of fracture stress against pressure for non-sealed tensile specimens of polystyrene and high-impact polystyrene.

medium can flow or diffuse into the craze, then the energy released at the craze immediately after nucleation will be greater for the non-sealed case, N.B. this energy is greater than that for propagation of the craze. The energy released will increase with pressure and a value will exist which is sufficient to fracture the rubber particle from the PS matrix to form a crack which can lead to failure. Thus, it would be predicted that there would be a low pressure ductile–brittle transition, and that at pressures above this HIPS would behave in a manner similar to unmodified polystyrene. This agrees with the observations reported.

4.5. Effect of viscosity of fluid

The discussion so far has assumed that the pressurizing medium acts instantaneously on the newly created crack surfaces. However, if the rate of flow or diffusion along the crack is less than the rate of crack growth, then the pressure transmitted to the crack faces will be only a fraction of the applied pressure depending on the viscosity of the fluid. As the viscosity tends to infinity the behaviour tends to that of the sealed specimens. This is confirmed by the experimental observations shown in Fig. 4. It appears unlikely that the observations reported are due to any chemical or plasticization effect of the silicone oil on polystyrene as specimens soaked in silicone oil for times of up to 1 month exhibited no significant differences in behaviour (Fig. 2) compared to non-soaked specimens. Comparing the results of Fig. 2 with those of Fig. 4 suggests that the environmental effect is enhanced by a stress-activated diffusion of silicone oil into the polymer. "Inert" liquids such as silicone oil [11, 13] became strong stress-cracking agents under pressure (Fig. 10).

5. Conclusions

Tensile experiments on high-impact polystyrene under pressure showed that the mechanical properties of HIPS (as well as PS) are strongly affected by silicone oil. Studies on sealed specimens enabled us to observe the experimental criteria for the inherent craze initiation, yielding, and ductile failure processes.

The major conclusions of this study may be summarized as follows:

(1) Silicone oil used as a pressure-transmitting fluid is a strong stress crazing and cracking agent under pressure. High-impact polystyrene exhibits a ductile-to-brittle followed by a brittle-to-ductile transition as the pressure is increased.

(2) Stress-whitening was suppressed at relatively low pressures indicating that this mechanism involves a volume increase of the kind expected for craze formation.

(3) The craze and shear band initiation stresses have different pressure dependency curves. Above the transition pressure shear bands initiate at lower stress levels than crazes, thereby suppressing craze formation.

(4) The principal craze initiation stress shows almost no pressure dependency suggesting that crazes initiate in HIPS when the principal stress level reaches a critical value irrespective of the applied pressure.

(5) The role of the rubber particles to stop craze and crack propagation was inhibited when test samples under pressure were exposed to the silicone oil environment.

(6) A value of 0.5 kbar for the triaxial stress at the rubber–PS interface was deduced from the experimental data, and is in good agreement with a value of 0.46 kbar calculated using accepted material constants.

(7) Using a general mechanics argument, it was possible to explain the existence of a brittle-to-ductile transition pressure for sealed specimens. This analysis predicts that, depending on the pressure dependencies of the elastic modulus and yield stress, a BD-transition may exist for non-sealed specimens at a higher pressure.

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