Effects of high hydrostatic pressure on the mechanical behaviour of homogeneous and rubber reinforced amorphous polymers

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Summary

The pressure dependence of the true stress-true strain behavior in tension of polystyrene, as an example of an amorphous glassy polymer, has been investigated over the range from atmospheric pressure to 6 kilobars at room temperature and constant strain rate with the principal objectives of elucidating the factors controlling plastic flow and fracture. Some preliminary measurements of the influence of pressure on the propagation velocity of artificially induced cracks were made. A comparative study of polystyrene containing a second-phase rubber dispersion (high-impact polystyrene) was undertaken, together with similar observations on an acrylonitrile-butadiene-styrene (ABS) material and a rubber-reinforced polymethylmethacrylate.

A pressure-induced transition from brittle to ductile behavior was observed between 2 to 3 kilobars. Crack velocity measurements showed that above the critical pressure any inherent flaws developed during straining grow only slowly and are stopped by crack blunting and stress relaxation at the tip. In all the rubber-reinforced polymers examined, stress whitening is prevented at relatively low pressures. Additional evidence was obtained that the rubber does not simply stop cracks and that stress whitening is a major mechanism for energy absorption involving a volume increase similar to microcrazing.

Introduction

In a previous paper from this laboratory, it was demonstrated that an improved understanding of the mechanical behavior of crystalline polymers could be obtained from investigation of the influence of high environmental pressure [1]. The present contribution extends this approach to the case of a representative glassy amorphous polymer.

Brittle glassy polymers such as polystyrene exhibit, when stressed in tension, a particular kind of inhomogeneous deformation known as crazing [2-4] that is associated with the onset of macroscopic fracture. The crazes, which are expanded structures containing approximately 60% polymer and 40% voids [5], start to develop at an applied tensile stress lower than the fracture stress and continue to the point of fracture, which can occur before any appreciable deformation takes place in the uncrazed material. It is well known that brittleness in glassy polymers can be overcome by introduction of an elastomeric phase. Most of the theories advanced to explain the toughening effect of such rubber additions [6-12] invoke mechanisms involving localized increases in volume and it is interesting to note that one of the approaches [9] implies that the 'stress-whitening' normally exhibited by these rubber poly-blends under tensile stress is associated with the formation of microscopic crazes in the glassy matrix adjacent to the rubber particles and, as such, is simply another aspect of the larger scale crazing exhibited by the homo-polymer. Since these various crazing phenomena appear to involve localized increases in volume and since macroscopic yielding in several glassy polymers has been shown to likewise involve volume increases [13], it is apparent that both flow and fracture should be influenced strongly by applied hydrostatic pressure.

The limited previous investigations of the effects of pressure on the tensile behavior of brittle amorphous polymers [14-16] have indicated increases in both the fracture stress and strain. For the particular case of glassy amorphous polymers, Holliday *et al.* [15] compared the tensile behavior of polystyrene at atmospheric pressure and 7·6 kilobars, and Ainbinder *et al.* [16] examined the behavior of polystyrene and polymethylmethacrylate up to 2 kilobars. These studies were directed primarily to the effects on engineering stress-strain properties and little attention was given to the detailed interpretation of yielding or to the crazing phenomenon.

In the light of the above considerations, the present study of the pressure dependence of the tensile behavior of polystyrene was undertaken with the principal objectives of elucidating the factors involved in the mechanisms of flow and fracture in this class of polymeric material. Such a study is also of potential technological importance in view of the recent increased interest in the application to polymers of cold-forming processes involving high compressive stresses. The selection of polystyrene has the additional interest that styrene-based rubber-reinforced polymers ('high-impact polystyrenes') have had wide engineering application, but the mechanism by which the presence of the second-phase dispersion of rubber particles influences the mechanical behavior is still uncertain. In the experimental approach adopted, tensile stress-strain measurements on polystyrene at room temperature were conducted for a series of pressures up to 6 kilobars. Some preliminary measurements of the pressure dependence of the crack propagation velocity were also carried out. Additional observations were made on several reinforced polymers—high impact polystyrene, the more complex multiphase polymer ABS (acrylonitrile-styrene) and a rubber-modified polymethylmethacrylate.

Experimental procedures and materials

The polymers used in this study were as follows: polystyrene of number-average molecular weight $\bar{M}_n = 93,430$ and weight-average molecular weight

$\bar{M}_w = 288,350$ ($\bar{M}_w : \bar{M}_n \simeq 3{\cdot}1 : 1$) obtained in the form of 0·5 in diameter extruded rod (a general purpose commercial grade from Dow Chemical Co.); high-impact polystyrene containing 4% butadiene in a matrix having $\bar{M}_n = 81,500$, $\bar{M}_w = 193,900$, ($\bar{M}_w : \bar{M}_n \simeq 2{\cdot}4 : 1$) obtained in a similar form from the same source; ABS containing 20% butadiene in a copolymer matrix having a styrene: acrylonitrile ratio of 2·2 : 1 and $\bar{M}_w$ of 75-90,000 (a commercial grade from Marbon Chemical Company) and a rubber-reinforced polymethymethacrylate (transparent acrylic polymer XT, American Cyanamid Company).

Tensile specimens were machined from these four materials (in the case of the ABS and XT materials, the machining was carried out by the manufacturers) to the shape and dimensions shown in Fig. 1 (a). The reduced diameter at the center section of the gage length was adopted after preliminary tests on the most brittle material (polystyrene) showed that fracture did not occur in this region in its absence. For the measurements of crack propagation velocity in the polystyrene, special flat section specimens with a sharp edge-notch were machined to the dimensions shown in Fig. 1 (b). For both types of specimens, the gage lengths were polished carefully after machining in order to minimise possible surface effects on the mechanical behavior.

The apparatus used for the tensile straining experiments, which has been described previously elsewhere [17], is essentially a constant strain-rate tensile machine contained within a pressure chamber filled with a fluid, the pressure of which can be maintained constant at a selected value during specimen straining. The tensile load applied to the specimen is measured by a strain-gage load cell within the pressure chamber and connected to the specimen at its fixed end. The specimen strain during the test is monitored in two ways—as elongation from the 'crosshead travel' at the movable end of the specimen by means of a linear transducer and as reduction in area from direct photographic observation through windows mounted on a cross-bored hole in the cylinder. In the present studies, the pressure fluid was castor oil and the specimens were strained at a constant crosshead speed on 10^{-2} in $\sec^{-1}$.

A curve of applied tensile load versus extension was obtained directly during each test by feeding the outputs from the load cell and transducer to an X-Y potentiometric recorder. The corresponding changes in specimen diameter were recorded from timed photographs taken with a 35 mm still camera. From these measurements, curves of both engineering stress versus elongation and true-stress versus true-strain were computed. A minimum of two tests were carried out for each condition to establish reproducibility. The true stress data obtained were also used to determine the point of plastic instability (corresponding to yielding or necking) by means of Considère's construction. The construction, which assumes that no volume change occurs during straining, was applied here by plotting [18] true stress versus ratio R, the ratio of the original area of specimen cross-section to the actual area. The point of tangency to the curve from $R=0$ corresponds to the point of plastic instability and gives a value for the true yield stress. Although the constancy of volume requirement is not met for polymers in the pre-yield stages of straining, the resulting error appears less than that involved in estimating the point of plastic instability from the true-stress/stress-strain curves.

In the case of the notched specimens, the load and extension were recorded as above and the fracture process was observed continuously by means of an 8 mm movie camera operating at a speed of 18 frames sec^{-1}. The crack propagation velocity was measured from subsequent examination of the enlarged film.

Results and discussion

Preliminary experiments were conducted to examine the possible influence of the pressure-transmitting fluid and of pressurisation [19] on the stress-strain behavior of the polymers under study. Comparative tensile tests were made in the high pressure apparatus at atmospheric pressure (a) in air, (b) in the pressure fluid and (c) in the fluid after first subjecting the specimen to a pressure of 5 kilobars for a time similar to that involved in the tensile tests at high pressure. In the case of the polystyrene, the specimens exhibited similar stress-strain behavior under all three conditions. For high-impact polystyrene and ABS, pressurisation did not change the behavior but the tests in the fluid medium gave slightly smaller elongations to fracture compared with those in air. However, despite these indications of some influence of the fluid environment on the behavior, all these materials exhibited marked increases in fracture strain when tested *at* high pressure, as is discussed later.

In the following, the effects of pressure on the behavior of polystyrene are considered first and then those on the characteristics of the several reinforced polymers:

A. Polystyrene

The changes in the tensile behavior of polystyrene with increasing environmental pressure up to 6 kilobars are shown in Fig. 2 in the form of relationships between engineering stress and strain (Fig. 2 (a)) and true stress and true strain (Fig. 2 (b)). Another set of measurements reported very recently [20] of the pressure dependence of the tensile load-elongation curve for polystyrene is in good agreement with the results shown in Fig. 2 (a). The principal features of the changes in behavior illustrated in these figures are seen to be a progressive increase in the modulus with increase in pressure and a similar initial rise in fracture stress followed by a discontinuous increase in the pressure range between 2 and 3 kilobars. The increase corresponds to a pressure-induced transition from brittle to ductile behavior and plastic yielding precedes fracture at all higher pressures. The transition and the pressure dependence of the true yield and fracture stresses are shown more clearly in Fig. 3.

The low level of tensile fracture stress at atmospheric pressure is in agreement with the well-established tensile behavior of unoriented polystyrene and, likewise, extensive crazing was observed to develop at relatively low stresses. The crazes lay perpendicular to the tensile axis and the transverse brittle fracture took place approximately parallel to them. At 2 kilobars, the fracture was again transverse but the fracture stress increased, no crazing was seen and the fracture surface was very smooth and planar. Crazing was absent at all higher pressures also. Above the brittle-ductile transition, the specimens exhibited necking and developed prominent shear deformation bands in the neck region – Fig. 4. Such bands have not been observed previously in unoriented polystyrene in tension as fracture normally precedes plastic yielding. However, bands similar to those here have been reported recently [21] for unoriented polystyrene in compression and for preoriented material in both compression and tension. Thus, this form of inhomogeneous deformation is seen to be generally characteristic of the yield process in polystyrene. An additional feature of the observations at pressure is that the bands became less evident as the tensile strain was increased at a given pressure and also as the test pressure was increased. The fracture process above the transition pressure occurred consistently by cracks initiating at the surface and spreading slowly (tearing) across the cross-section. As illustrated in Fig. 5, the crack develops in the neck region, although not always at the smallest cross-section, and additional cracks frequently developed at other parts of the surface before complete failure occurred.

In order to clarify the most prominent effect induced by pressure, namely, the brittle-ductile transition, it will be necessary to consider the results of the crack propagation velocity measurements. However, so as to establish a more complete background for that discussion, the observed changes in modulus and yield stress will be examined first. Although the method of tensile testing used here does not give precise measurement of the modulus, it is the relative change with pressure which is of interest. Using the secant modulus at a fixed strain (0·01 in cross-head displacement), the increase to 6 kilobars is found to be approximately 50%. This change is small compared with that of some 300% over the same range for the semi-crystalline polymer, polyoxymethylene (POM) [1]. In the case of the latter, stress-relaxation measurements at pressure indicated that the modulus change was associated with a pressure-induced increase in the temperature of the β relaxation process [1]. The fact that polystyrene does not exhibit any strong relaxation process below the glass transition temperature suggests that the small increase in its modulus reflects mostly changes in van der Waal's forces resulting from the hydrostatic compression of the polymer, which amounts to some 8% at 6 kilobars [22].

The yield behavior of polystyrene exhibited at pressures above the critical transition region has two particularly significant characteristics – there is an intrinsic yield drop (i.e., a fall in true stress on yielding) and the yield stress increases with pressure. The first characteristic – which indicates that the stress for yield initiation is greater than the stress for its propagation—is well known in many metals and crystalline inorganic materials but has not been recognised as having possible significance for polymers until the recent work of Brown and Ward [23] demonstrated the phenomenon in polyethylene terephthalate. In the case of polystyrene, the fact that a yield drop occurs under compressive loading at atmospheric pressure [13] (when crazing and brittle fracture are suppressed) already points to the possibility of an intrinsic yield drop and the present data under tensile loading at high pressure clearly establishes it as a characteristic of the yield process in that material also. However, it is interesting to note that the phenomenon is not a necessary feature of yielding in polymers – for the semi-crystalline polymer, POM, the earlier measurements in this laboratory [1] showed that yielding occurs without an intrinsic drop in stress. It is apparent that a better understanding of the nature of yielding in polymers, and possibly of the cold-drawing phenomena, depends in part on a clarification of the factors which determine whether yielding is discontinuous or not in any given polymer. The second characteristic – a pressure dependent yield stress – was also shown for polyoxymethylene [1] and the rate of increase with pressure is similar for both polymers. The linearity of the pressure dependence for polystyrene indicates that the Mohr (Coulomb-Navier) [24] continuum criterion for yielding, which involves a linear dependence of the yield stress on the mean normal stress, may provide a useful approximation for the polymer. However, in this connection it is of concern to note that the tensile yield stress for unoriented polystyrene at atmospheric pressure obtained by extrapolation from the high pressure data is similar to that reported [13] for the compressive yield stress. The applicability of the Mohr criterion implies that there would be a difference in these two stresses, as is found for polyoxymethylene [1]. Pre-oriented polystyrene does exhibit a lower tensile yield stress [13] than that reported for compression, but it is not certain that the pre-orientation itself has no effect on the yield process. Resolution of this question by means of comparative measurements of true yield stress in compression for the identical polymer used here has not been feasible in the present study. Despite the uncertainties as to the behavior at atmospheric pressure, the measured pressure dependence of the tensile yield stress does lend support to arguments that a relative volume dilation [13] observed to be associated with compressive yielding in several amorphous glassy polymers (including polystyrene) indicates that there should be a significant influence of hydrostatic pressure on yielding.

Returning now to the discussion of the pressure dependence of the fracture behavior, it is helpful to examine briefly current ideas on fracture in polystyrene. The brittle fracture exhibited by many glassy amorphous polymers at atmospheric pressure has been described [25, 26] with some success in terms of the Griffith theory [27] by which catastrophic growth of inherent cracks occurs in an ideal brittle-elastic solid when the work to produce the corresponding new fracture surface (i.e., the increase in total surface energy) equals or is less than the decrease in elastic strain energy. For glassy polymers, the surface energy computed on the basis of this theory from tensile measurements on specimens containing artificial cracks [25] is found to be considerably higher than expected from chemical measurements or calculations based on molecular structure. Following Orowan's proposal [28] to account for similar discrepancies in metals, the higher measured work of crack propagation has been attributed to additional energy consumed by plastic deformation in the highly stressed material at the crack tip. In the case of polystyrene, Berry [25] has shown that the measured value of this 'effective surface energy' indicates that the tensile fracture stress in the absence of artificial cracks corresponds to that predicted for material containing inherent flaws some 0·04 in long. While there is no evidence that flaws of such large size are present initially, crazes develop extensively at low tensile stresses in polystyrene, grow in size as the applied stress is increased and are associated with the initiation of catastrophic fracture. Accordingly, it has been deduced that the crazes grow until they can act in a manner equivalent to Griffith flaws with an 'effective crack-size' of 0·04 in. Further support for this interpretation is provided by the well-known fact that tensile pre-orientation of polystyrene results both in a higher fracture stress (macroscopic yielding occurs before fracture) and the inhibition of the formation of crazes.

Against this background, the observations made here of the changes in fracture behavior with increase in environmental pressure can be interpreted as follows. Initially, suppression of the formation of crazes occurs (as at 2 kb) with an associated increase in the brittle fracture stress corresponding to the operation of 'inherent flaws' of a size smaller than 0·04 in. The apparent flaw size computed from the Griffith relation and Berry's data, but based only on the observed increase in fracture stress, is approximately 0·010 in. However, the actual flaw size will depend also on any changes with pressure in the other parameters in the Griffith relation – the elastic modulus, Poisson's ratio and the effective surface energy. At 3 kb, the catastrophic growth of inherent flaws is suppressed and the specimens sustain a tensile stress which is large enough to cause macroscopic plastic yielding. At 3 kb and higher pressures, the final fracture initiates at the specimen surface and proceeds by slow crack growth, presumably by plastic tearing, across the specimen cross-section. With increasing pressure in this region, the fracture stress increases and the general path of fracture approaches the direction of maximum shear stress.

The above interpretations are further clarified by the preliminary measurements of the pressure dependence of the crack propagation behavior in the notched tensile specimens. The results obtained at atmospheric pressure, 2 and 3 kb are presented in Fig. 6 in the form of the increase in crack length with time during continuous extension of the specimens. At atmospheric pressure, crack growth initiated at an applied tensile stress (nominal) of 2400 psi and continued at a slow rate until the stress reached some 3300 psi, at which point very rapid growth occurred. Crazing developed generally in the specimen during the period of load increase. In contrast, none was observed in the specimens tested at high pressures. At 2 kb, rapid crack growth initiated at some 2800 psi without a detectable prior stage of slow growth. At 3 kb, crack growth initiated at some 2700 psi and proceeded slowly up to some 5000 psi, when the growth appeared to stop. On continuing to increase the applied stress, fracture was initiated near the threaded grip-portion of the specimen (outside the field of view). Three particularly significant features of these observations are that (a) rapid crack growth begins at atmospheric pressure when the crack developing from the highly stressed region at the notch attains a length similar to that discussed earlier as the 'effective critical crack-size' for catastrophic failure in polystyrene, i.e., approximately 0·04 in, (b) at 2 kb, when visible crazing is suppressed, no slow growth is detected and rapid growth occurs immediately on reaching a critical applied stress and at velocities apparently similar in magnitude to the high values at atmospheric pressure*, and (c) at 3 kb, where crazing is likewise not seen, the crack developed at the base of the notch grows only slowly and eventually stops. The cessation of crack growth at 3 kb appears analogous to the phenomenon which occurs in some metals of crack blunting and stress relaxation by plastic deformation in the region ahead of the tip. Possible support for similar behavior in the polymer is provided by the recent observations of Vincent [29] in glassy polymers at atmospheric pressure of elongated plastic zones which form at crack tips and grow in extent as the crack length increases.

Considering the crack velocity data in relation to the effects of pressure on the overall fracture process, it appears unlikely that, when the pressure has been raised sufficiently to suppress macroscopic crazing, any extension of the inherent flaws occurs by crazing on a microscopic scale as the applied tensile stress is increased up to fracture. Kambour [30] has demonstrated by optical interference techniques that a slowly propagating crack in polystyrene at atmospheric pressure is preceded by a finite length of craze ahead of the crack tip. However, at the high pressure, in addition to the absence of macroscopically visible crazes, no changes were observed in the optical characteristics of the unnotched specimens. Finally, the discontinuous increase in fracture stress in the region of the brittle-ductile transition pressure is seen to be due principally to the inability of an inherent flaw (or one developed during the increase in applied stress to the level required to induce macroscopic plastic yielding) to propagate catastrophically. Above the transition pressure, fracture initiates only after the specimen has been strained beyond the discontinuous yield point and, due to strain-hardening, the nominal true stress exceeds the yield stress. In this region, fracture initiation appears to be associated with micro-structural changes involved in the macroscopic plastic deformation and crack propagation is by a slow tearing process.

B. Rubber-reinforced polymers

As expected and in marked contrast to the polystyrene, the composite structure of a dispersion of soft rubber particles in a glassy polystyrene matrix (high impact polystyrene), behaved in a ductile manner when strained in a tension at atmospheric pressure – exhibiting a discontinuous yield drop and extensive cold drawing before fracture. The material yielded at approximately half the fracture stress of polystyrene alone, as shown in Fig. 7 (it should be noted that the true stress–true strain form of plot does not reflect the cold drawing since that occurs at constant true stress and strain), and exhibited pronounced stress-whitening over the gage length and on the fracture surfaces. At 2 kilobars, stress whitening was completely absent, the modulus increased and the material extended without yielding until it fractured in a brittle manner at a tensile stress close to the fracture stress for polystyrene at the same pressure. The fracture appearance for both materials at this pressure was almost identical – a smooth planar fracture surface, perpendicular to the tensile axis. On increasing the pressure further to 3 kilobars, the high impact polystyrene again behaved in a ductile manner but with both the yield and fracture stresses substantially higher than the fracture stress at the lower pressure. Although a true yield drop was not apparent, a yield plateau occurred which was followed by a short region of work-hardening before fracture. Despite the larger total true strain (Fig. 7), no cold drawing took place and the specimens necked directly to fracture. No stress whitening occurred at any stage. At higher pressures, the behavior was generally similar but with a progressive increase in the yield and fracture stresses. The pressure dependence of these stresses is shown in Fig. 8, together with similar data for polystyrene (from Fig. 3).

The principal features of the pressure-induced changes in the tensile behavior of the rubber-reinforced polystyrene are a complete suppression of

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* It is appreciated that the methods of velocity measurement used here are crude relative to the increasingly high velocities characteristic of an accelerating crack in a glassy polymer [26], but the present observations are nevertheless useful for the present purpose.

stress-whitening (supplementary tests indicated that stress-whitening was absent at pressures as low as 0·5 kilobars) accompanied at low pressures by a suppression of yielding and an increase in fracture stress, but with failure in a brittle manner. At higher pressures, the material behaves in a manner very similar to that observed for polystyrene alone – it undergoes a brittle-ductile transition in the region between 2 and 3 kilobars and subsequently yields followed by necking to fracture. The prominent yield drop for polystyrene is replaced by a yield plateau and the value of the yield stress at a given pressure is lower. However, the fracture stresses are almost identical for the two materials and the rates of increase in yield stress with pressure are very similar.

The two other rubber-reinforced polymers exhibited an identical pressure response to that of high impact polystyrene (HIPST) in that stress-whitening was absent in all tests at high pressure. The effect of pressure on the mechanical behavior of the ABS polymer was generally similar to that of HIPST in that the modulus and strength increased and a transition to more ductile behavior occurred with pressure. However, complete embrittlement at an intermediate pressure was not observed. As shown in Fig. 9, the yield drop exhibited at atmospheric pressure is accompanied by stress whitening, no cold drawing takes place, and fracture occurs in the neck at a total elongation very much less than that for HIPST. At 1 and 2 kilobars, the yield stress was progressively increased, but cracking developed on yielding. Propagation to fracture was rapid for the several cracks formed at the lower pressure, whereas at 2 kilobars only a single crack formed and extended slowly a considerable amount before growing rapidly. Thus, the apparent fall in stress after yielding at these pressures is largely attributable to the decrease in actual cross-section due to the cracking. Above 2 kilobars, a transition to more ductile behavior occurs with the development of substantial necking. Considerable work-hardening occurs in the necked region before fracture initiates. In the case of the XT polymer (reinforced polymethyl methacrylate), tensile tests were conducted only at atmospheric pressure and 2 kilobars, but the material exhibited similar changes in behavior to that of ABS under the same conditions. A particularly significant observation in the XT polymer, which unlike other reinforced polymers is optically transparent, is that it could be seen that no stress whitening occurred at pressure either on the surface or in the interior of the specimen.

The characteristics of the changes induced by pressure in the tensile behavior of these reinforced polymers permit a reassessment of the possible mechanisms by which the rubber dispersion improves resistance to catastrophic fracture in glassy amorphous polymers. In the case of HIPST, the facts that the rubber particles are ineffective in preventing brittle failure of the material in the relatively low pressure range up to the transition and that stress-whitening does not occur under pressure point clearly to a

relationship between these two phenomena. Although rubbers undergo a transition from rubbery to glassy behavior with increasing pressure, as shown by Patterson [31], the pressures required are such that the dispersion in the ABS can be expected to still be rubbery at 2 kilobars. Hence, an immediate consequence of the brittle behavior observed at 2 kilobars is that rubber particles, at least in the concentration present in this particular material, do not influence fracture by a crack stopping mechanism. Instead, the pressure results provide clear evidence that the mechanism must involve the stress-whitening and that the latter is associated with a volume dilation. Thus, the suggestion made in recent years by Bucknall and Smith [9] and Matsuo [10] that the rubber particles prevent fracture by promoting the transformation of the adjacent glassy matrix to a fine-scale craze structure (stress-whitening) appears validated. Kambour [12] has shown that such a mechanism would inhibit both crack formation and the propagation of any existing cracks since the spongy craze-structure absorbs energy in its formation and is capable of sustaining large strains before failure.

A restriction of possible importance in the above discussion is that the experiments referred to deal with tensile behavior at moderate strain rates. It is well known that such behavior does not necessarily reflect the characteristics of a material when stressed at high rates, i.e. the conditions of impact loading. Schmitt and co-workers [7, 11] have proposed an alternative reinforcement mechanism in which the rubber particles promote the growth of numerous energy-absorbing microcracks. Recently this hypothesis has been tested under impact loading conditions using a miniature dart drop test on the surface of polystyrene, rubber-modified polystyrene and intermediate blends of the two. As the rubber content was increased the cracks radiating from the impact point reduced in length, increased in number and an increasing density of stress-whitening developed. From the observation of partial separation of rubber particles from the polystyrene matrix and associated microcracks in the dilute blends, it was concluded that such separation and microcrack formation are the major cause of the high impact strength. It is suggested that the separation and cracking are facilitated (i.e., 'weakness' is built-in at the particle) by the triaxial tension within the rubber particle arising from its coherence with the matrix and differential contraction of rubber and matrix during cooling from the polymer melt. Although particle separation and microcracking were also observed in normal tensile tests on a dilute blend, only separation was found in the undiluted material. It must be noted that the interpretation of the point-impact tests on dilute blends is not unequivocal—the shortening of impact cracks with increasing rubber content is accompanied by increased stress-whitening and toughness. Thus, while the particle separation will involve energy absorption, it may also represent a deterioration of the effectiveness of the particle compared with maintenance of coherence accompanied by stress whitening due to microcraze formation in the adjacent matrix.

Unfortunately, the present pressure experiments do not permit a determination of the relative importance of these two mechanisms. However, it is significant that the lowering of the yield stress of polystyrene by the rubber additions is not necessarily due to a particle separation mechanism [11] since the present measurements at high pressure, where stress whitening is absent, show clearly (Fig. 8) that the yield stress of the rubber-modified polystyrene is consistently the lower. The complete understanding of the mechanism of rubber-reinforcement requires a more extensive study than has yet been reported in which the influence of important microstructural variables such as particle size, volume fraction, dispersion type of grafting and matrix are examined. Measurements at high pressures appear to provide a significant additional approach to the elucidation of this important phenomenon.

Conclusions

1. Crazing in polystyrene can be suppressed at relatively low pressures. However, at 2 kb fracture is still brittle suggesting the operation of inherent flaws at that pressure and that crazing is the mechanism of fracture initiation at atmospheric pressure.

2. There is a pressure-induced transition from brittle to ductile behavior which is associated with the fact that above this critical pressure any inherent flaws or cracks developed during straining grow only slowly and are stopped by crack blunting and stress relaxation at the tip.

3. The yield stress exhibits a linear dependence on the applied pressure, which supports the volume dilation model for yielding and indicates the usefulness of a Mohr type of continuum criterion for yielding.

4. Polystyrene exhibits a drop in true stress on yielding accompanied by shear bands indicative of inhomogeneous deformation.

5. In all the rubber-reinforced polymers examined, stress whitening is prevented at very low pressures indicating that this phenomenon does involve a volume increase of the type expected if it is a form of microcrazing.

6. In high impact polystyrene, brittleness was exhibited at intermediate pressures indicating that the rubber itself does not act simply as a crack stopping mechanism and that the microcracking (stress whitening) is a major mechanism of energy absorption.

7. In high impact polystyrene above the transition pressure, the presence of a rubber dispersion markedly lowers the yield stress, even in the absence of stress whitening, but has essentially no effect on the fracture stress.

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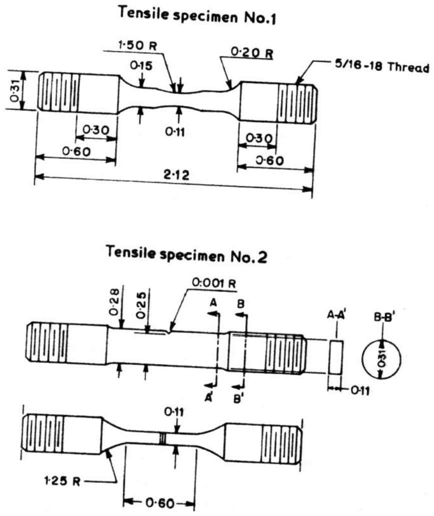

Fig. 1. Geometr y of unnotched and notched tensile specimens.

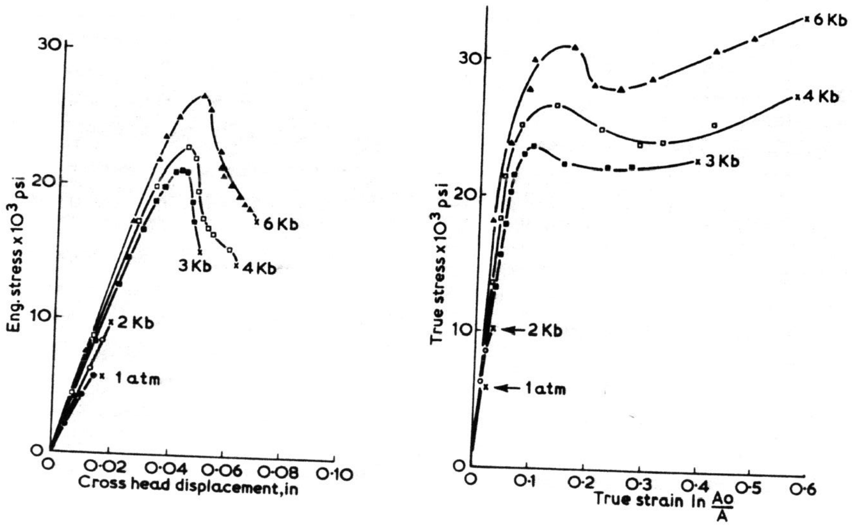

Fig. 2. (a) Engineering stress-strain curves of polystyrene at various pressures.
(b) True stress-strain curves of polystyrene at various pressures.

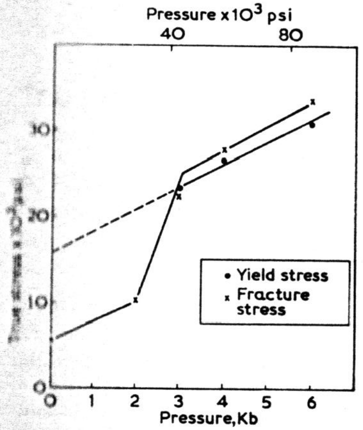

Fig. 3. Effect of pressure on yield and fracture stress of polystyrene.

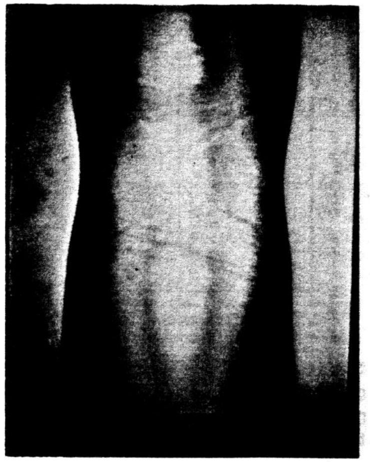

Fig. 4. Polystyrene plastically strained beyond the yield at 3 kb to illustrate necking and deformation bands.

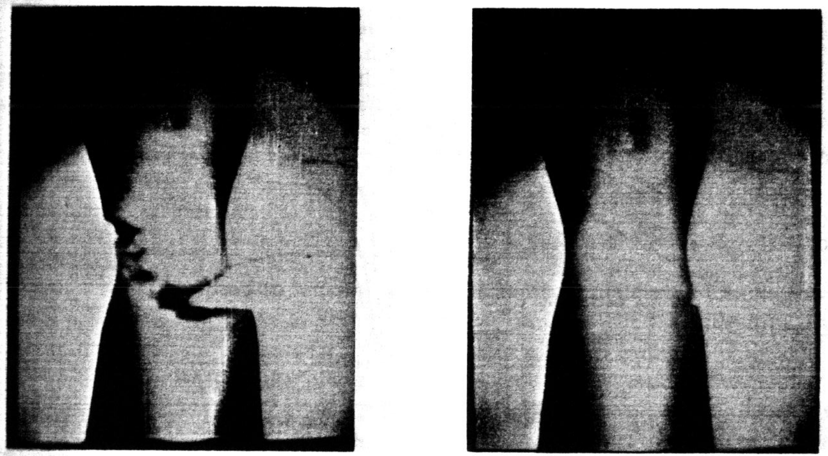

Fig. 5. Successive photographs showing the initiation and progress of a crack in polystyrene at 6 kb (fracture does *not* occur at the point of maximum stress).

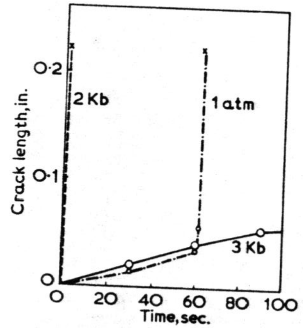

Fig. 6. A comparison of crack propagation velocities in polystyrene at one atmosphere, two and three kilobars.

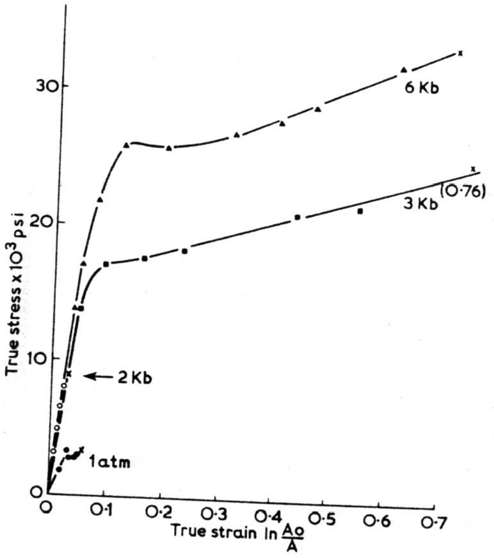

Fig. 7. True stress-strain curves of 'high impact' polystyrene at various pressures.

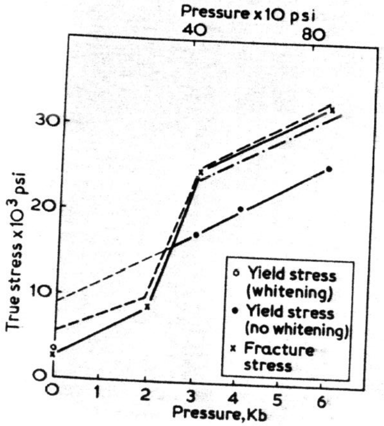

Fig. 8. Effect of pressure on yield and fracture stress of 'high impact' polystyrene (- - - - polystyrene fracture stress· . - . - . - polystyrene yield stress)

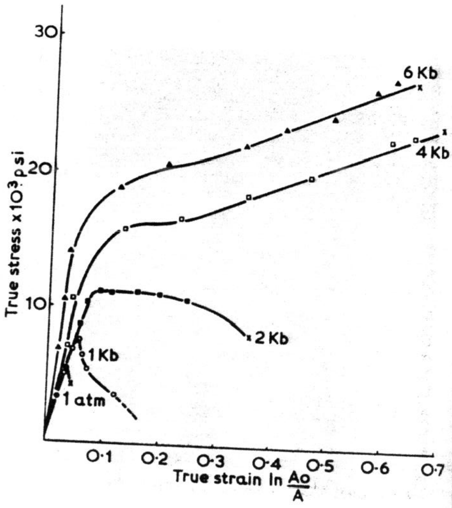

Fig. 9. True stress-strain curves of ABS polymer at various pressures.