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The tensile stress-strain behaviour of polystyrene in inert and gaseous environments

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For the first time the intrinsic tensile stress–strain behaviour of polystyrene was measured in an inert atmosphere (He) from 77 to 350 K. The intrinsic tensile strength decreases monotonically with increasing temperature with completely brittle behaviour below 231 K and crazing without shear flow at higher temperatures. The behaviour in N_2, Ar, CH_4, CO_2, H_2S, and N_2O was observed with the relative pressure being the important parameter. The softening depended on the square root of the relative pressure. A calculation was made of the concentration of absorbed gas to produce a given amount of softening. The question of why polystyrene is a brittle solid and thus crazes instead of shear flows is discussed.

1. Introduction

Polystyrene (PS) is an extensively used material and is often used as the prototype for a linear amorphous polymer. A gap exists in our knowledge of its intrinsic mechanical behaviour in tension at low temperatures because previous experiments [1, 2] were conducted in nitrogen which is an environmental crazing agent. This paper fills that gap and also presents the basic parameters that determine its tensile behaviour in gaseous environments.

The tensile behaviour of polyethylene terephthalate (PET) [3], polypropylene (PP) [4], polycarbonate (PC) [5], polychlorotrifluoroethylene (PCTFE) [6], polymethyl methacrylate (PMMA) [7], polytetrafluoroethylene (PTFE) [8], Nylon [9] and polyvinyldiene chloride (PVDC) [9] have been determined in gaseous and inert environments. It is interesting to compare PS with these polymers. PS crazes in gases such as N_2, O_2, and Ar at low temperatures as do these other polymers. In an inert environment PS exhibits only brittle fracture at low temperatures and crazing at higher temperatures, but all of the other polymers, even PMMA, exhibit some shear flow in tension especially at higher temperatures. PS does not show macroscopic shear flow in tension at any temperature below 350 K although it does show shear flow in compression.

As was shown in all previous investigations, the effectiveness of a gas in modifying the mechanical behaviour via crazing depends on its relative pressure, P_r, the ratio of its pressure divided by the vapour pressure in equilibrium with the liquid at a given temperature:

$$P_r = P\exp\left[-\frac{Q_v}{R}\left(\frac{1}{T_B}-\frac{1}{T}\right)\right], \qquad (1)$$

where P is in atmospheres, Q_v is the heat of vapourization and T_b is the boiling point. The relative pressure is important because the solubility and adsorption of a gas in a polymer increase with P_r. Van Amerongen [10] showed that the log of the solubility coefficient of gases in a polymer is a linear function of T_b. The solubility coefficient, S_o, is related to the concentration of dissolved gas, C, and the pressure by

$$C = S_oP. \qquad (2)$$

Van Amerongen [10] showed that at 25° C

$$S_o = A\exp(BT_b), \qquad (3)$$

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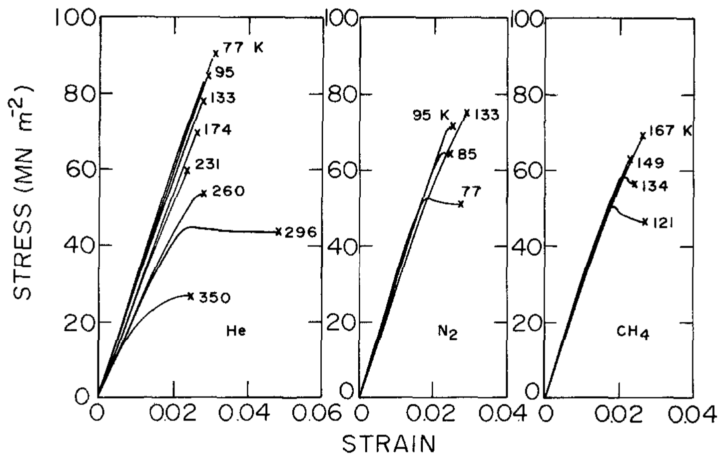


Figure 1 Stress–Strain curve at various temperatures (a) in He, (b) in N_2, (c) in CH_4.

where B is independent of the polymer, as pointed out by Stannet [11], and A depends somewhat on the polymer. Equation 3 can be related to Equation 1 by a thermodynamic argument where

$$B = S_v/RT , \qquad (4)$$

and S_v, the entropy of vapourization, equals Q_v/T_b. Since the entropy of vapourization of most gases is about 67 to 71 J mol^{-1} K^{-1}, it is understandable that B is a constant and that Equation 4 agrees with the experimental data of Van Amerongen [10] where $B = 0.028$ when $T = 298$ K and $S_v = 69$ J mol^{-1} K^{-1}. Combining Equations 2, 3 and 4 and using values of $A \approx 10^{-2}$ presented by Stannett [11]

$$C = 10^{-2} P \exp(8.25 T_b/T) = 38 P_r, \qquad (5)$$

where C has units of cm^3 (STP) per cm^3 of polymer and P is in atmospheres. The factor 10^{-2} varies with the polymer. Olf and Peterlin [4] have presented a more detailed theoretical expression for the solubility which includes an interaction energy between the polymer and the gas and is based on the theories of Hildebrand and Scott [12] and Flory [13]. Equation 5 is more useful because it relates the theory directly to experimental data.

2. Experimental procedure

The PS used was a commercial atactic material compression moulded by Westlake Plastics. It was used in previous investigations and found to have very reproducible mechanical behaviour. The values of the tensile strengths from this material are the same as those obtained by Hoare and Hull [1] so that the PS may be considered to be a standard commercial type. The PS was a compression moulded sheet 0.8 mm thick. The tensile specimens were milled to 5 mm width and 12.7 mm uniform gauge length.

The tensile tests were done in an environmental chamber where the environmental gas was mixed with He at a total pressure of 1 atm. The partial pressure of the environmental gas was precisely maintained manometer-controlled flow meters to an accuracy of within 1 % and the temperature was known within ± 1° C. The strain rate was 0.01 min^{-1} unless otherwise specified.

3. Results

3.1. Behaviour in an inert environment

The intrinsic stress–strain behaviour of PS in He is shown in Fig. 1 from 77 to 350 K. Below 231 K the stress–strain curve is linear up to the fracture stress and no crazing is observed. Crazing begins between 231 and 260 K and the crazing causes non-linear behaviour prior to fracture. A yield point is observed above 260 K. The fractured specimens are shown in Fig. 2 where it should be noted that there is no change in cross-sectional area. This means that all of the non-elastic deformation is caused by crazing and that shear flow was absent. PMMA on the other hand exhibited both crazing and shear in an inert environment around the temperature range where PS only crazed.

The variation of tensile strength with temperature is shown in Fig. 3. As with other polymers the tensile strength approaches zero at T_g and increases monotonically as the temperature decreases to 77 K. The fracture strain, Young's modulus, and tan δ for the β relaxation process are shown in Fig. 4 as a function of temperature. Young's modulus decreases slowly with increasing

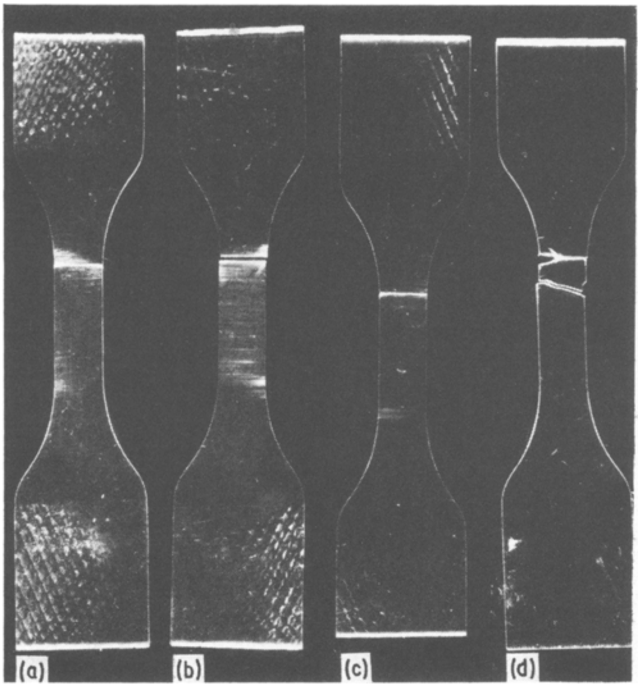


Figure 2 Fractured specimens in He at temperatures of (a) 350 K, (b) 296 K, (c) 260 K and (d) 231 K.

temperature prior to the beginning of the β relaxation , but since the fracture stress decreases more rapidly in this temperature range, the fracture strain decreases with increasing temperature up to 230 K. Above 230 K the fracture strain rises rapidly to a maximum at about 300 K and then rapidly decreases. The behaviour of the fracture strain above 230 K depends primarily on the amount of crazing that occurs prior to fracture and only secondarily on the fact that Young's modulus decreases rapidly in the course of the β relaxation. Fig. 5 shows that the maximum amount of crazing occurs at about 300 K where the fracture strain is also a maximum.

3.2. Behaviour in N_2

The stress–strain behaviour in N_2 at various temperatures for a partial pressure of 1 atm is shown in Fig. 1. The deformation from 77 to 150 K involves crazing. Crazing was not observed above about 150 K. The behaviour above about 150 K in N_2 is the same as in He; the decrease in craze density with increasing temperature is shown in Fig. 6. The dependence of tensile strength with temperature is shown in Fig. 3 where the N_2 curve joins the He curve at about 150 K. The N_2 curve in Fig. 3 is the same as the one obtained by Hoare and Hull [1]. That the effect of N_2 essentially disappears above about 150 K at 1 atm pressure is

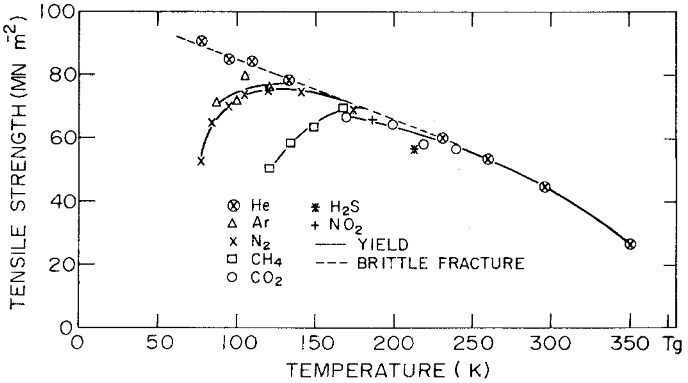


Figure 3 Tensile strength against temperature in various gases at $P = 1$ atm. The upper curve is the intrinsic strength in an inert environment.

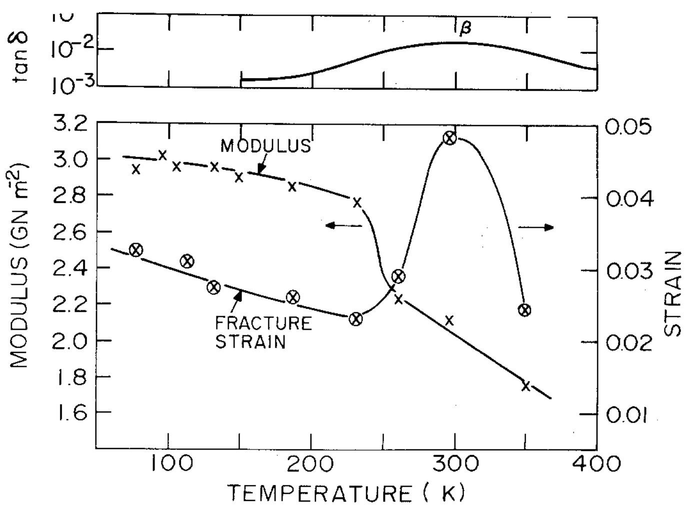
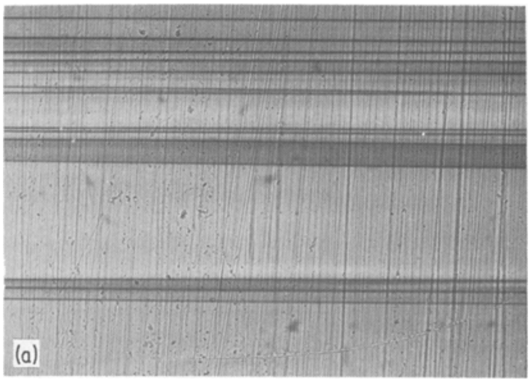


Figure 4 Young's modulus, fracture strain, and tan δ against temperature.

nearly independent of the polymer as shown in other investigations and depends primarily on the gas as will be shown in Section 4.

The stress–strain behaviour at various partial pressures at 77 K is shown in Fig. 7. Crazes may be observed in N_2 for partial pressures as low as about 0.02 atm at 77 K. The tensile strength varied linearly with the square root of the partial pressure as shown in Fig. 8.



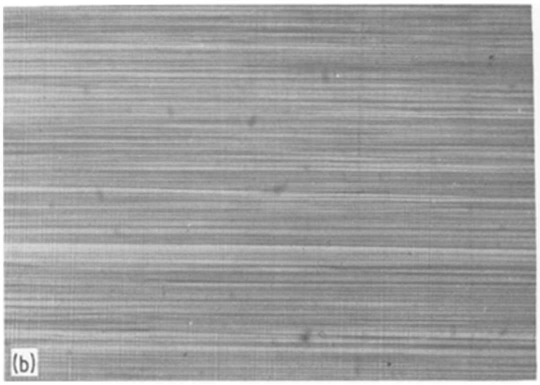
3.3. Strain rate effect

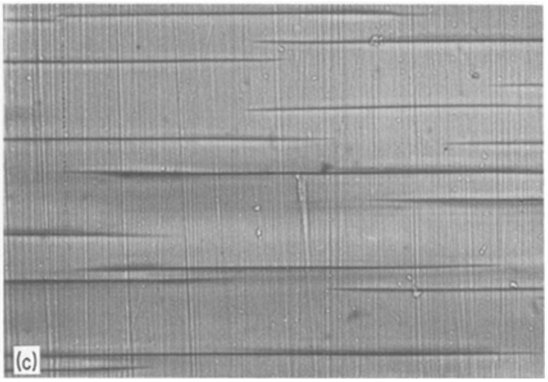
The effect of strain rate was investigated at low temperatures. As with other polymers at low temperature in an inert environment, there was almost no effect of strain rate on the tensile stress–strain behaviour. However in N_2 at low temperatures, strain rate has a very large effect on the tensile strength, as shown in Fig. 9. This large strain rate effect generally occurs in environmental gases for all polymers in the temperature range where the gas is effective. Note that the tensile strength is a non-linear function of the log of the strain rate.

3.4. Behaviour in H_2, CH_4, CO_2, H_2S and N_2O

The effects of the above gases are shown in Table I. All the gases except H_2 decreased the tensile strength relative to the value in an inert environment at the same temperature.

Figure 5 Crazing in an inert environment (He) at temperatures of (a) 260 K (b) 290 K and (c) 350 K.





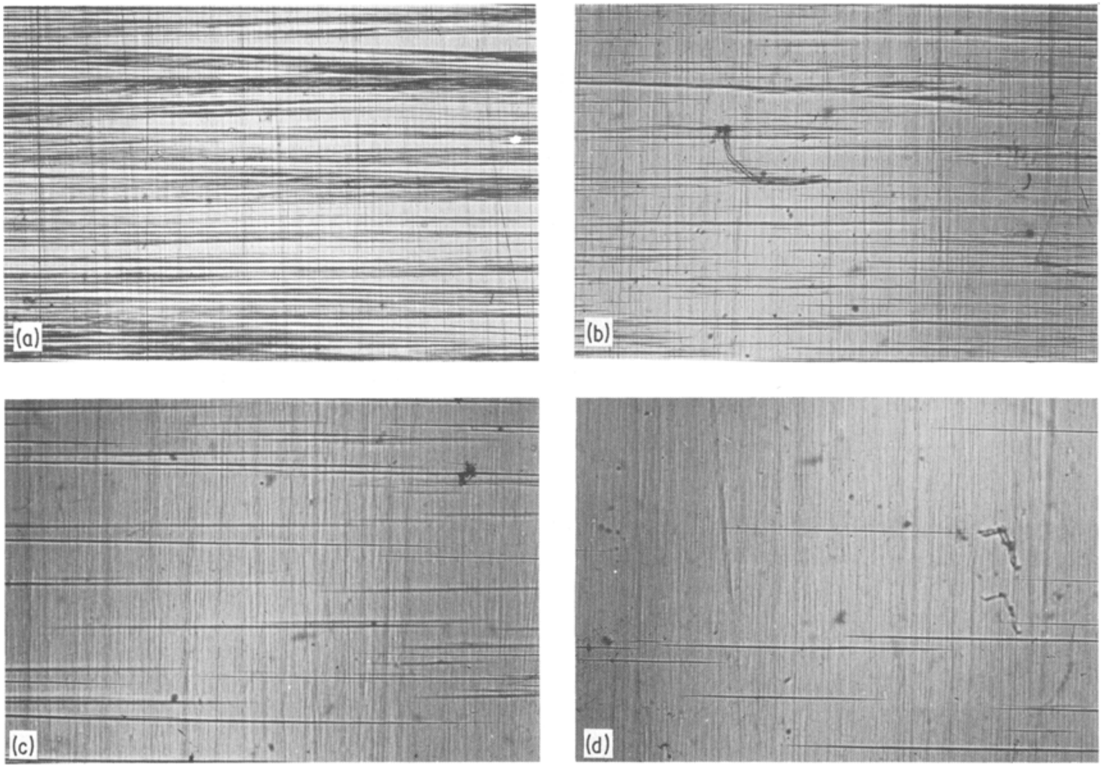


Figure 6 Crazing in N_2 at temperatures of (a) 77 K, (b) 85 K, (c) 95 K and (d) 105 K for $P = 1$ atm (X 19).

Fig. 3 shows the effectiveness of the various gases in reducing the tensile strength at various temperatures and at 1 atm pressure. It should be noted that CO_2 is effective below its sublimation temperature. Hiltner *et al.* [3] found that N_2 produced crazes down to 45 K whereas the freezing point is 63 K. In general the solid, liquid and gaseous states may act as an environmental agent.

Since the relative pressure of H_2 at 77 K and 1 atm is only 0.013 atm ($Q_v = 1.0\,\text{kJ mol}^{-1}$, $T_b = 21$ K), it is not expected that H_2 would be an environmental agent at 77 K. However, a few

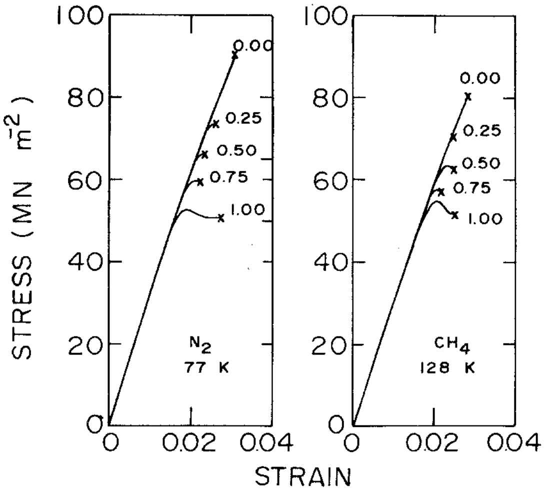


Figure 7 Stress–strain curves at various partial pressures (atm) for N_2 at 77 K and CH_4 at 128 K.

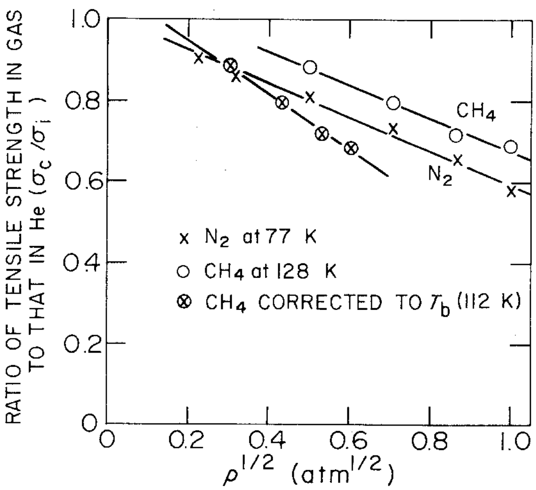


Figure 8 Ratio of tensile strength in N_2 and CH_4 relative to that in He against square root of the pressure.

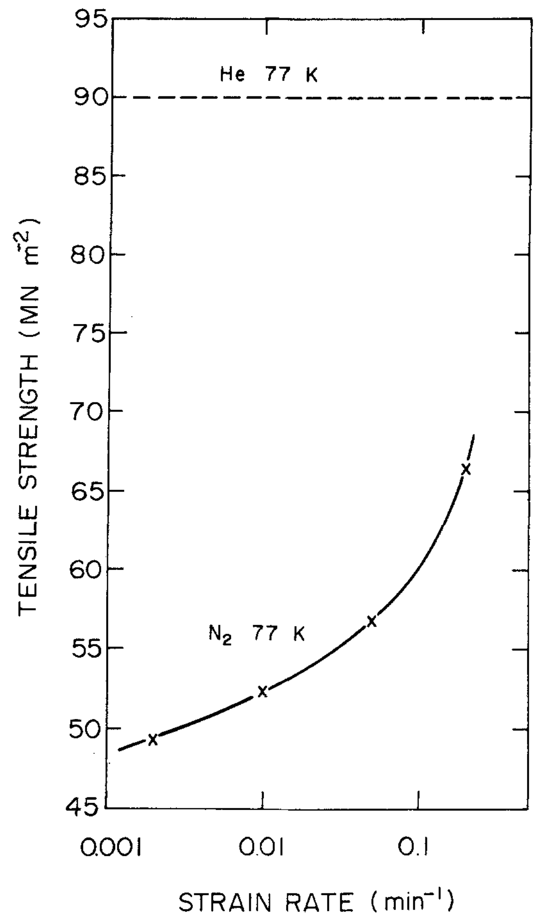


Figure 9 Tensile strength in N_2 against strain rate at 77 K. Dotted curve is for He at 77 K.

crazes were observed on the shoulder of the specimen in H_2, but no effect on the tensile strength was observed.

The effects of CH_4 were similar to N_2. The stress–strain curves at various temperatures and pressures are shown in Figs 1 and 7. Fig. 8 shows that the tensile strength in CH_4 varies as the square root of the pressure, as it does in N_2.

4. Discussion

4.1. Intrinsic behaviour

In an inert environment, the deformation behaviour of PS in tension from 350 K to the lowest temperature is very simple. From 350 K to about 231 K there is only elastic deformation and crazing and below 231 K there is only elastic deformation which leads to brittle fracture. By way of comparison PMMA exhibits both shear and crazing from T_g to about 240 K and then becomes completely brittle at lower temperatures.

The variation of ductility and fracture strain with temperature (Fig. 4) is readily understood. From 78 to 220 K the strain to fracture (fracture stress/modulus) decreases linearly with increasing temperature because the fracture stress and modulus are each a linear function of temperature and the fracture stress decreases more rapidly with increasing temperature than does the modulus. The increase in ductility from 220 to about 240 K is caused by the rapid decrease in modulus from the β transition and partly from the advent of crazing. Above 240 K the amount of crazing prior to fracture governs the ductility. The maximum in ductility at 300 K coincides with the maximum in the amount of crazing, as shown by Fig. 5.

It is of interest to answer the question of why PS begins to craze in an inert environment above 231 K. An absence of crazes does not necessarily mean that no crazes form. If the first craze that forms fractures before another craze appears, then it is not completely correct to say no crazing occurred. Observation of the fractured surface often indicates crazing prior to rapid fracture without other crazes being present. Thus, the real question to be answered in the case of PS is why the specimen fractures prior to the formation of other crazes for temperatures below about 231 K. The answer to the above question is complex since it depends on the time to fracture the first

TABLE I Softening effect of various gases at 1 atmosphere pressure, strain rate = 0.01 min^{-1}.

Gas	Boiling point (K)	Testing temperature (K)	$(\sigma_i - \sigma_c)/\sigma_i$ softening	Comments
H_2	21	77	0	Few crazes
N_2	77	77	0.42	Crazing yielding
A_r	81	81	0.20	Craze yielding
CH_4	112	121	0.38	Craze yielding
N_2O	185	187	0.04	Single craze fracture
CO_2	195 (Sublimes)	200	0.02	Single craze fracture
H_2S	212	213	0.12	Single craze fracture

craze as compared to the time to form additional crazes. Little is known about the stress and temperature dependence of the time to fracture craze fibrils, but the time to produce a given number of crazes at a given stress varies inversely with the temperature as indicated by the theory and experiments of Argon *et al.* [14]. If the time for fibril fracture increases with decreasing temperature less rapidly than does the time for craze initiation, then it is expected that there would be a temperature below which crazes would not be observed after the specimen is fractured.

Another important question is why PS crazes in an inert environment, instead of undergoing shear flow as do most other polymers above a certain temperature. Even PMMA goes from brittle to shear plus crazing behaviour in the higher temperature range. This basic question in modified form is often asked about all solid materials: Will it flow or fracture? Crazing fundamentally starts like a brittle fracture process. It starts at a point of stress concentration and follows a localized path perpendicular to the maximum tensile stress. The only reason that a polymer crazes instead of fracturing is the fact that the long-chain molecules hold together surfaces which would otherwise be fractured surfaces. They became fracture surfaces when the fibrils break or if the molecular length is too short to form bridging fibrils. The critical length for the formation of craze fibrils is about equal to the length of chain between random entanglements as shown by Kramer [15]. Thus, one may look at the initiation of crazing as being associated with the same fundamental factors as those that initiate fracture, and the basic question with a polymer, as with any other solid, is whether it will shear flow or fracture (craze).

An answer to the above question has been given for crystalline solids by Smith [16] who presented the general principles which determine whether a crystalline material is brittle or ductile (like Si or Au). The bonding between atoms in ductile materials is non-directional as for the metallic bond and that between brittle materials is highly directional as in the case of the covalent bond. The same principles can be applied to polymers. We suggest that directionality in the Van der Waal's bond depends on the flexibility and mobility of the polymer chain as well as the atomic structure of the mer. The more flexible and mobile a portion of the polymer chain is, the more isotropic is its bonding relative to its surroundings. Conversely, less flexible and less mobile molecular chains have a more directed bond to its neighbouring atoms. No doubt the large relatively immobile benzene ring reduces the chain flexibility, and also the directionality of the bonding around the benzene is highly anisotropic; thus PS is a brittle material which crazes instead of shear flows. Wellinghoff and Baer [17] have also addressed themselves to this fundamental question while investigating the ductile–brittle behaviour of PS–poly(phenelyne oxide) blends. They state that bulky side groups promote crazing and flexible backbone linkages promote shear flow. Our view is that the most fundamental basis for determining ductility or brittleness is the degree of directionality of the bonding.

4.2. The effect of strain rate

At 77 K, the tensile strength in He is practically independent of strain rate, but in N_2 there is a large strain-rate sensitivity, as shown in Fig. 9. The slope, $d\sigma/d\ln\dot{\epsilon}$, at low strain rates corresponds to an activation volume of $0.610\,\text{nm}^3$. At higher strain rates $d\sigma/d\ln\epsilon$ increases. The calculation of an activation volume, V, from the equation $V = kT\,d\sigma/d\ln\dot{\epsilon}$, is not thought to be meaningful at high strain rates because, as pointed out previously [18], the simple Eyring type of equation does not hold. At high strain rates two processes are involved: (a) the usual stress assisted thermal activated process and (b) a diffusion limiting process which is a function of strain rate.

An insight into the diffusion limiting process at high strain rates is obtained by determining the strain rate above which crazing is not observed in N_2. According to previous investigations [18, 19], if the strain rate is beyond a critical value, there is not sufficient time for the N_2 to penetrate the polymer and plasticize it. Thus, an upper limit for the diffusion coefficient can be estimated as follows. In order to plasticize the polymer, the N_2 must penetrate beyond the polymer–gas interface a distance δ. Thus, the time to penetrate is given by $t = \delta^2/D$ where D is the diffusion coefficient. If the critical strain rate above which no crazing is observed is $\dot{\epsilon}_c$, then $t = \epsilon_F - \epsilon_0/\dot{\epsilon}_c$, where ϵ_F is the strain at fracture for the critical strain rate and ϵ_0 is the strain at which a craze is nucleated. At low temperatures in N_2, ϵ_0 is insensitive to strain rate and thus can be obtained from the proportional limit in the stress–strain curves of Fig. 1. Thus $D = \delta^2 \dot{\epsilon}_c / (\epsilon_F - \epsilon_0)$. This equation is only an approximation since D is expected to be a function of ϵ_F as discussed below. $\dot{\epsilon}_c$ is the strain rate corresponding to a tensile stress of 90 MPa which is obtained in He at 77 K and is estimated to be 10 min^{-1} from Fig. 9. ϵ_F is the fracture strain in He at 77 K as given in Fig. 1 and is 0.03. ϵ_0 is the strain at the proportional limit of the curve at 77 K in Fig. 1b and is about 0.01. δ is not known, but the smallest value should be approximately a molecular diameter or about 0.5 nm. Thus, a lower limit for D is about 10^{-15} cm^2 sec^{-1}. The value of D for N_2 in PS at 77 K may be estimated by extrapolating measurements of D for simple gases in PS as measured at higher temperatures [11]. These measurements give a value for D at 77 K of 10^{-24} to 10^{-28} cm^2 sec^{-1}. This large discrepancy between the diffusion coefficients from the strain rate experiment and from the diffusion measurements has been explained by Olf and Peterlin [4] by assuming that the diffusion coefficient is enhanced by the applied stress at the points of stress concentration where the crazes are nucleated. The process is autocalytic in that the stress permits the penetration of some gas molecules which then plasticize the polymer making it easier for the stress to separate the polymer molecules further so that the diffusion coefficient is reduced even more. Thus, the craze nucleates and then grows under the combined effects of the plasticizing gas and the applied stress.

4.3. The effect of pressure and temperature of the environmental gas

Both the nucleation and growth of crazes are each functions of the relative pressure. Experiments at various temperatures and pressures in N_2 gave a value for Q_v (see Equation 1) of 6.10 kJ mol^{-1}. The handbook [20] value is 5.58 kJ mol^{-1}. For the experiments in CH_4, Q_v = 7.40 kJ mol^{-1}, compared to a handbook [20] value of 8.15 kJ mol^{-1}. The agreement is within the error of the experiment.

One may also estimate the temperature above which a particular gas is ineffective. Experiments show that for partial pressures less than about 0.02 the effect of the gas on the tensile strength is too small to measure. Thus, the temperature above which the effect of the gas is unobservable at a pressure of one atmosphere is given by

$$1/T < 1/T_b + \ln 0.02/(Q_v/R)$$
$$= \frac{1}{T_b}\left[1 + \frac{\ln 0.02}{(S_v/R)}\right] = 0.54/T_b. \qquad (6)$$

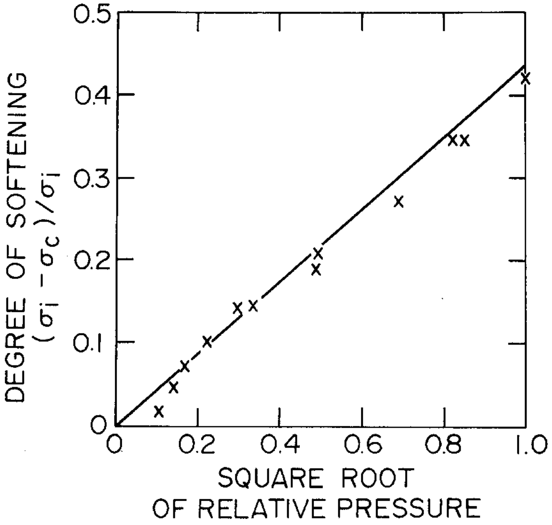


Figure 10 Softening, $(\sigma_i - \sigma_c)/\sigma_i$, against root of relative pressure of N_2 over temperatures of 77 to 260 K.

For N_2 and CH_4, the predicted temperatures above which the effect of the gas is not measurable are 143 K and 207 K whereas the experimental points are about 160 K and 185 K (Fig. 3). The factor 0.54 in the above equation was derived for an average value of S_v of 69 J mol^{-1} K^{-1} and also depends on the sensitivity of the tensile strength to the partial pressure and the precision of the experimental measurements.

It was found that the fractional change in the tensile strength varied linearly with the square root of the pressure as shown in Fig. 8. When all the data for N_2 at different temperatures and pressures was plotted as a function of the relative pressure (Fig. 10), the following relationship was obtained:

$$(\sigma_i - \sigma_c)/\sigma_i = 0.43 P_r^{1/2}, \qquad (7)$$

where σ_i and σ_c are the tensile strengths in the inert environment and N_2 respectively and P_r is the relative pressure. $(\sigma_i - \sigma_c)/\sigma_i$ is the degree of softening.

If the concentration of adsorbed gas is proportional to the relative pressure as given by Equation 5 then

$$(\sigma_i - \sigma_c)/\sigma_i = 0.07 C^{1/2}. \qquad (8)$$

Thus, an increment of concentration at low concentrations is more effective as a plasticizer than an increment at a higher concentration. It is most interesting to estimate the concentration of gas to produce a given amount of softening. From Equation 8, a degree of softening of 0.1 requires that $C = 2\,\text{cm}^3$ (STP) per cm^3 of polymer. Taking the density of PS as $1.05\ \text{gm cm}^{-3}$ [21], it is estimated that 0.01 N_2 molecules per monomer unit of PS reduces the intrinsic tensile strength by 10%. Knowing that the softening varies as the square root of the concentration of the absorbed gas and knowing the amount of gas that produces a given amount of softening should lead to an understanding of how the gas and polymer interact with the stress at the molecular level. It is our expectation that these results will eventually place the phenomenon of plasticization on a more fundamental and quantitative basis.

5. Conclusions

(a) The intrinsic tensile stress–strain behaviour of PS was measured from 77 K to 350 K in an inert atmosphere. Brittle behaviour occurs below 231 to 260 K and at higher temperatures crazing occurs.

(b) The tensile behaviour in various gases involves crazing and a reduction in the tensile strength which depends on the relative pressure.

(c) A quantitative estimate of the concentration of gas required for a given amount of softening was made.

(d) The softening effect of the gas was found to vary as the square root of the concentration of absorbed gas.

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