Tensile deformation of polychlorotrifluoroethylene in He, N_2, Ar, O_2, and CO_2 environments

Yasufumi Imai* and Norman Brown
Department of Metallurgy and Materials Science and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pa. 19174, USA
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The tensile stress–strain behaviour of quenched polychlorotrifluoroethylene (PCTFE) was measured from 77K to T_g in gaseous environments of He, N_2, Ar, O_2, and CO_2 and in water. The partial pressure of the gas was varied from 0 to 1 atm. N_2, Ar, O_2 and CO_2 produced crazing and a lowering of the tensile strength relative to the intrinsic tensile strength at that temperature. The effect of pressure and temperature on the tensile strength was quantitatively similar to the effect of these gases on PC and PMMA, and could be described by an equation of the form: $\sigma_c/\sigma_i = [P\exp(Q/RT)/P^*]^{-0.10}$. The constants Q and P^* depended on the gas, and σ_i is the intrinsic strength. The Q values were approximately the same as the heat of vaporization for each gas. CO_2 produces crazing below as well as above its sublimation temperature. The intrinsic yield point varied from 0.033 to 0.054 of E, Young's modulus, as the temperature varied from 300 to 77K. The experimental value of the yield point extrapolated to $0.055E$ at 0K and compares favourably with existing theories for the yield point of glassy polymers.

INTRODUCTION

Gaseous environments such as N_2, O_2, Ar, and CO_2 are known to effect the tensile behaviour of glassy and crystalline polymers, usually by causing them to craze at low temperatures[1–8]. Quantitative studies of the range of temperature and pressure in which each gaseous environment causes crazing have been made with PC[9] and PMMA[10] whose behaviours were quite similar. The effect of temperature and pressure on the tensile strength in the gaseous environment, σ_c, relative to its tensile strength in an inert environment, σ_i, at the same temperature, could be described by the following equation for both PC and PMMA:

$$\sigma_c/\sigma_i = [P\exp(Q/RT)/P^*]^{-n} \qquad (1)$$

when P^*, Q, and n were constants, and n varied with the polymer but was independent of the environmental gas. For a given polymer, Q increased with the boiling point of the gas and approximated its heat of vaporization. One purpose of this paper is to determine the generality of the equation (1) by observing another polymer and to completely display the intrinsic tensile behaviour of PCTFE for the first time since all previous tensile data at low temperatures were influenced by the environmental effect. The tensile stress–strain behaviour of PCTFE was observed from 77K to T_g in He, N_2, Ar, O_2, CO_2, and H_2O at partial pressures which varied from 0–1 atm. In general the behaviour of PCTFE was similar to PC and PMMA with the exception that H_2O had no effect on PCTFE but did cause PMMA to craze.

EXPERIMENTAL

The PCTFE was commercial Kel-F 81 Plastic, Grade 3 by 3M Company. It was hot pressed by the Fluorocarbon Company in the form of 0.9 mm thick sheet, and called Lox–Grade which means it was uniformly water quenched from 300°C. Tensile specimens were cut by a milling machine; they had a 5 mm width and 12.7 mm uniform gauge length.

The desired partial pressure of each crazing gas was obtained by mixing it with He, which is inert. The flow rate of each gas was precisely maintained by manometer controlled flow meters so that the partial pressure of the crazing gas was constant within ±1% during the course of the experiments. The purity of the He, N_2 and Ar was within 99.99%; O_2 was 99.6%, and CO_2 was 99.5% pure. The water was distilled.

The temperature of the specimen and the surrounding gas was controlled by a cold bath and an electric heater. Three thermocouples along the gauge length were used to measure the temperature of the specimen and also the temperature gradient. It is estimated that the temperature gradient was within 2°C/cm, and the temperature was known within ±1°C. The temperature fluctuations were within ±1°C during the course of each test.

A preload was always used during the cooling or heating period, and was kept at 3–5% of the fracture load. The stress–strain data were obtained with an Instron machine. The crosshead speed for all experiments was 0.25 mm/min. The error in stress is primarily associated with the non-uniformity of the thickness of specimens and is about ±3MPa. The strain was calculated from the crosshead displacement and an effective gauge length of 25 mm. The stress–strain curves were calculated with an effective gauge

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* Permanent address: Nagasaki University, Nagasaki, Japan.

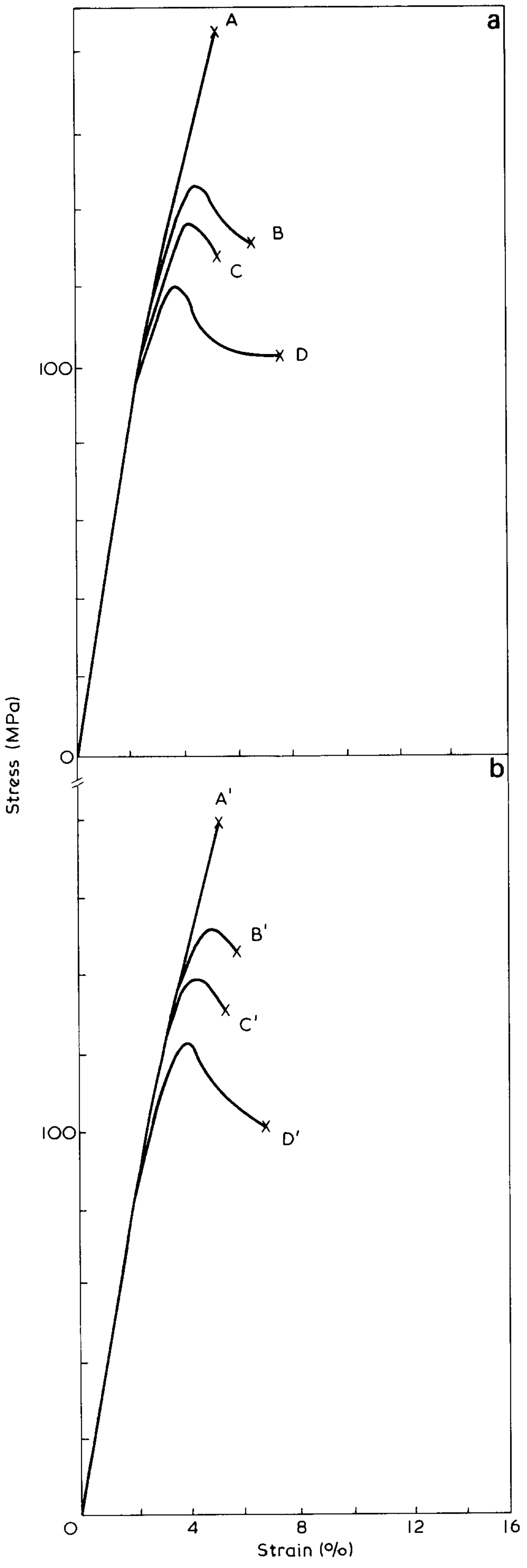

Figure 1 Stress–strain curves at various partial pressures. (a) In N_2 at 77K; (b) in Ar at 87K. A, A', 0.0; B, B', 0.25; C, C', 0.50; D, D', 1.0

length that was twice the uniform gauge length in order to obtain the best absolute value for the Young's modulus. The reported strain in the plastic region is smaller than its absolute value.

RESULTS

Figures 1a and *1b* show the stress–strain curves in N_2 and Ar for P varying from 0 to 1 atm and with T equal to the boiling point. Craze yielding occurred for all these tests except at $P = 0$ (pure He). Generally at each temperature, the tensile strength increases as P decreases. Young's modulus is independent of P. Micrographs of crazes (*Figure 2*) show that the craze density (number of crazes per unit area of the surface) increases with decreasing pressure; the results might appear contrary to expectations since the gas helps nucleate crazes. However, if it is realized that the maximum stress to which the specimen was exposed increases with decreasing pressure and that the density of crazes depends very strongly on the maximum stress[11], this result is understandable. The crazes fade-out with decreasing pressure because their average length decreases. The average length depends on the craze velocity which is very sensitive to the pressure at low partial pressures.

The effect of temperature on the intrinsic stress–strain behaviour which occurs in the inert environment of pure He is shown in *Figure 3a*; no crazes occur. Brittle fracture is observed up to 180K, and above 180K a shear yield point occurs. The tensile strength and Young's modulus decreases monotonically with temperature and approaches zero at T_g.

The effects of temperature in N_2 at $P = 1$ atm are shown in *Figure 3b*. The tensile strength *increases* with increasing temperature from 77 to 130K and then starts to decrease. This unusual behaviour occurs in the other gases and for all polymers[3,6,8–10]; it is a major characteristic of crazing in gaseous environments. The effect is caused by desorption of the gas from the surface as the temperature is increased[12]. Micrographs of crazes in N_2 are shown in *Figure 4* as a function of temperature. As the temperature increased beyond 130K, the craze density rapidly decreased until no crazes could be observed above about 185K. The last places where crazes could be observed were the sites of large inclusions as shown in *Figure 4d*. The deformation mode changed from craze yielding to shear yielding above about 185K; then intrinsic behaviour was observed even in N_2. The temperature above which intrinsic behaviour is observed decreases as the pressure decreases. O_2 and Ar give the same type of behaviour as N_2 except the transition temperatures and pressures from crazing to intrinsic behaviour are different. Young's modulus was not affected by the environmental gases and shows the same monotonic decrease with increasing temperature as in the inert He environment. The curves of tensile strength *versus* T in the various environments are shown in *Figure 5*.

In CO_2 crazing was observed below 220K. Above 220K the intrinsic shear yielding behaviour was observed in CO_2 at $P = 1$ atm, as shown in *Figure 5*. Between the sublimation temperature of 195 and 220K the behaviour was qualitatively similar to that in the other gases. Below 195K where the vapour was in equilibrium with the solid CO_2, the craze yield point increased with temperature until 160K where its tensile strength (brittle fracture stress) became equal to the intrinsic value. At 170K, for example, CO_2 has a vapour pressure of about 0.1 atm and the tensile strength was reduced ~10%. Between 150–160 K where

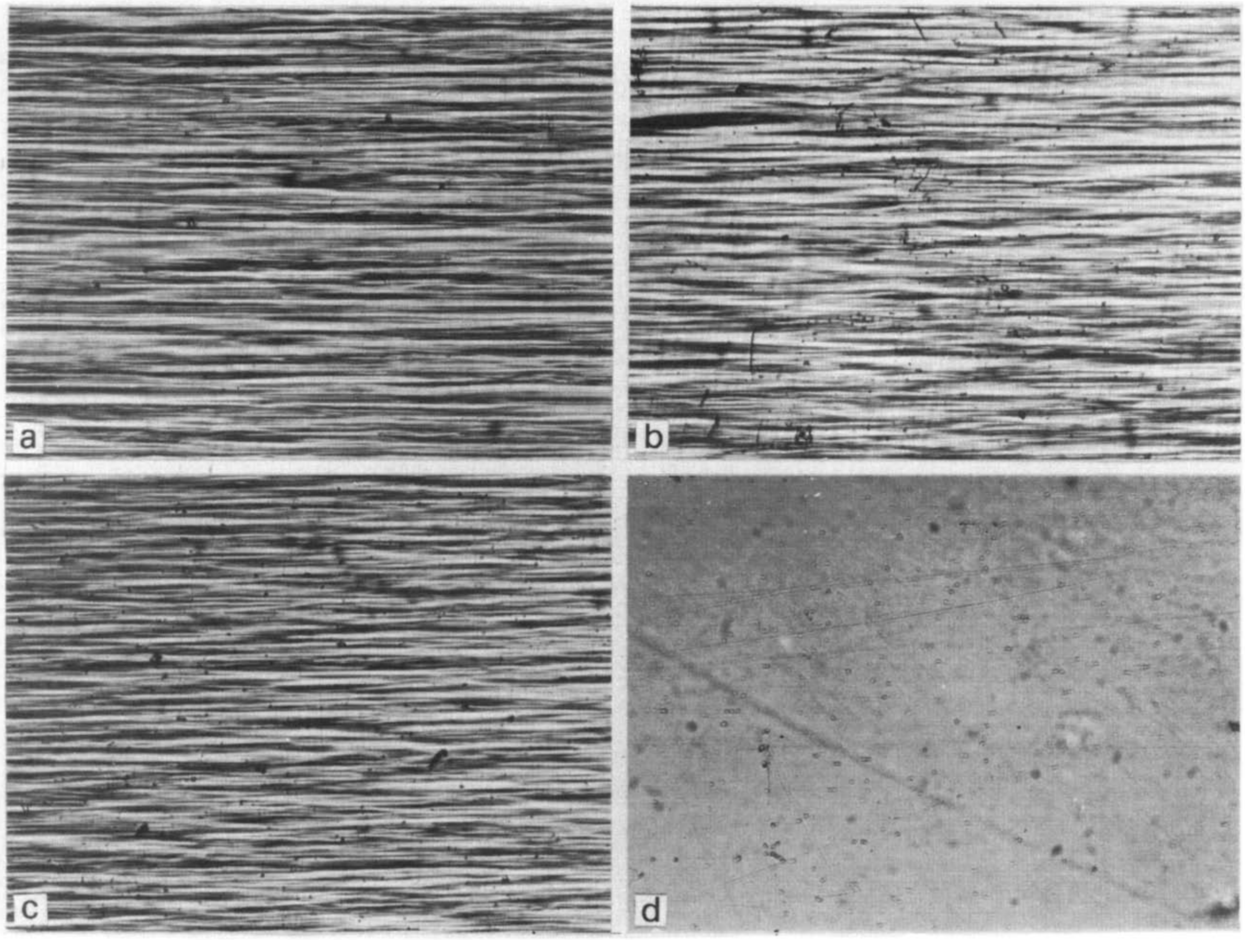

Figure 2 Crazes in tensile specimens fractured in N_2 at 77K at (a) 1 atm; (b) 0.50 atm; (c) 0.25 atm; (d) 0 atm. Length of each micrograph corresponds to 1.6 mm. Magnification 50X

the effect of CO_2 on the tensile strength becomes zero, the vapour pressure of the CO_2 is about 0.01–0.03 atm. Similar behaviour was observed with PMMA in CO_2[10].

In water, no crazing or other departure from the intrinsic behaviour could be observed (*Figure 5*).

SYNTHESIS

The effects on the craze yield point of all the environmental gases at various temperatures and pressures were synthesized by means of equation (1). In making the synthesis, it was desirable to compare the craze yield point with respect to the intrinsic shear yield point, but there was a problem since the PCTFE fractured before shear yielding (*Figure 3a*) for temperatures below 180K. Therefore extrapolated values of the shear yield point were used in the synthesis for temperatures below 180K. The extrapolated values are shown by the broken curve in *Figure 5*. There were two methods of extrapolation: (a) the curve of shear yield point *versus* elastic modulus was extrapolated and (b) the stress–strain curves of *Figure 3a* were used. Both methods gave about the same values. Thus, the effects of the environment on the craze yield point could be described by the following equation:

$$\sigma_c/\sigma_i = [P\exp(Q/RT)/P^*]^{-0.10} \qquad (2)$$

where the values of Q and P^* for each gas are given in *Table 1*. *Figure 6* shows all the data plotted in accordance with equation (2). Equation (2) is an empirical representation of the data and is useful for predictive purposes.

Equation (2) can be used to calculate the critical temperature and pressures which separate the domains of intrinsic behaviour from the domain of craze yielding as shown in *Figure 7*. For each gas there is a domain boundary[9,10]; to the left of the boundary intrinsic behaviour is observed and to the right craze yielding. Crazing is expected to occur at temperatures higher than those observed in this investigation for pressures higher than 1 atm. However at very high pressures, the hydrostatic stress effect would take over and eventually supress crazing.

DISCUSSION

Environmental effect

The magnitude of the environmental effect is given by the ratio of the craze yield point to the intrinsic shear yield point, σ_c/σ_i. Since this ratio is a function of the parameter, $P\exp(Q/RT)$, then sorption may be important. The value of Q should be equal to the heat of sorption[8,9,12] and therefore should be related to the latent heat of vaporization, as supported by *Table 1*. The question arises as to whether the phenomenon is one of adsorption[12] or absorption[8]. In general, it is expected that the heat of adsorption, ΔH_{ad}, and of absorption, ΔH_{ab}, are related to heat of vaporization, ΔH_v, as follows:

$$\Delta H_{ad} \geq \Delta H_v$$

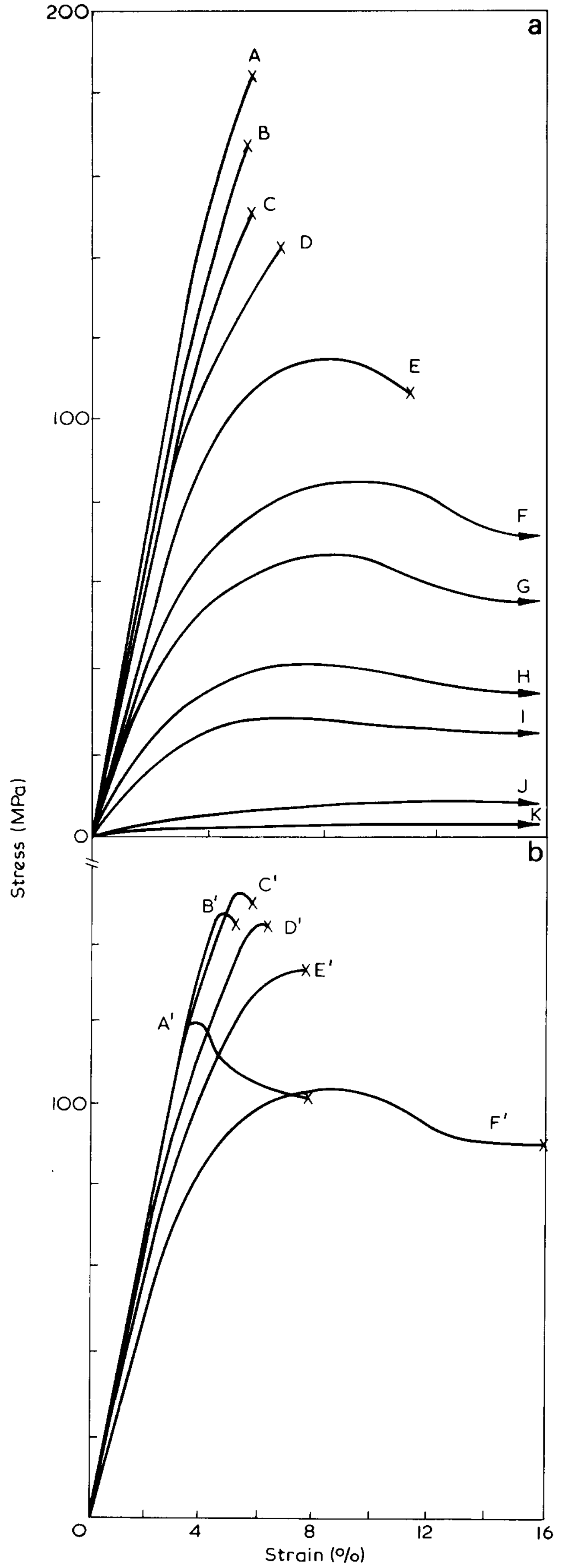

Figure 3 Stress–strain curves at various temperatures. (a) In He at 1 atm. A, 77; B, 118; C, 150; D, 169; E, 192; F, 220; G, 240; H, 275; I, 298; J, 340; K, 373K. (b) In N_2 at 1 atm. A', 77; B', 99; C', 138; D', 160; E', 179; F', 200

$$\Delta H_{ab} = \Delta H_v - \Delta$$

ΔH_{ad} should be greater than ΔH_v because the bonding energy between the small gas and the large polymer molecule is greater than between the two small gas molecules. ΔH_{ab} is less than ΔH_v because Δ, which is related to the Flory–Huggins interaction parameter, is always positive for saturated molecules. The Q values in *Table 1* are less than ΔH_v, which indicates that absorption is more important. However, the value of Δ is less than about 100 cal/mol and since the uncertainty in the Q values is greater than ±10%, a definitive statement cannot be made as to whether Q is determined by adsorption or absorption. Kinetic experiments[5] show that the gas acts at or close to the surface of the bulk polymer. Since the surface of the craze is very rough, a distinction between adsorption and subsurface absorption is difficult to define and measure. For PC[9] and PMMA[10] in the same gases, the Q values for PC were greater than ΔH_v and for PMMA less than ΔH_v. In all cases, however, Q was approximately equal to ΔH_v and always increased as the boiling point of the gas increased. Most likely, the gas causes crazing by plasticizing a microvolume of the polymer at the tip of the craze and by reducing its surface energy, and the effective concentration of the gas is directly related to the parameter $P\exp(Q/RT)$.

At this time the physical significance of the exponent n in equation (1) is not understood, but it is interesting to note that its value of 0.10 in PCTFE is close to the value of 0.08 and 0.13 for PC and PMMA, respectively.

Intrinsic stress–strain behaviour

The intrinsic tensile stress–strain behaviour as a function of temperature is shown in *Figure 3a*. The data below 180K are new because previous results were obscured by the environmental effect. *Figure 3a* has four important features: (a) the modulus and the strength increase together as the temperature decreases; (b) fracture precedes the shear yield point for temperatures below about 180K; (c) localized necking as indicated by the shear yield point gives way to homogeneous deformation above about 300K and (d) the yield strain is relatively insensitive to temperature. The transition from brittle fracture to shear yielding at 180K is attributed to the start of the γ-relaxation processes[13] as shown in *Figure 8*. The transition from localized necking at the yield point to homogeneous deformation at about 300K we attribute to the start of the β-relaxation processes.

That the intrinsic strength of a polymer strongly depends on the modulus is a general observation. Every factor that changes the modulus such as hydrostatic pressure, temperature and orientation changes the yield point in a like fashion[14,15]. Also the yield point of a polymer is very close to its theoretical strength[14], whereas the yield point of highly crystalline solids is usually much less. *Figure 8* shows that the ratio of the tensile yield point to Young's modulus increases from 0.033 to 0.055 as the temperature decreases to 0K. It is interesting to compare this experimental value of 0.055 at 0K with theoretical calculations of this ratio (*Table 2*). The Brown[16], Bowden–Paha[17], and Argon[18] theories were general for any linear polymer. The Yannas[19] theory is general, but it was applied to polycarbonate. The experimental value for polycarbonate was found to be 0.054 at 0K. The Bowden–Paha and Argon theories were for shear yield point relative to the shear modulus, and their results were converted to tensile

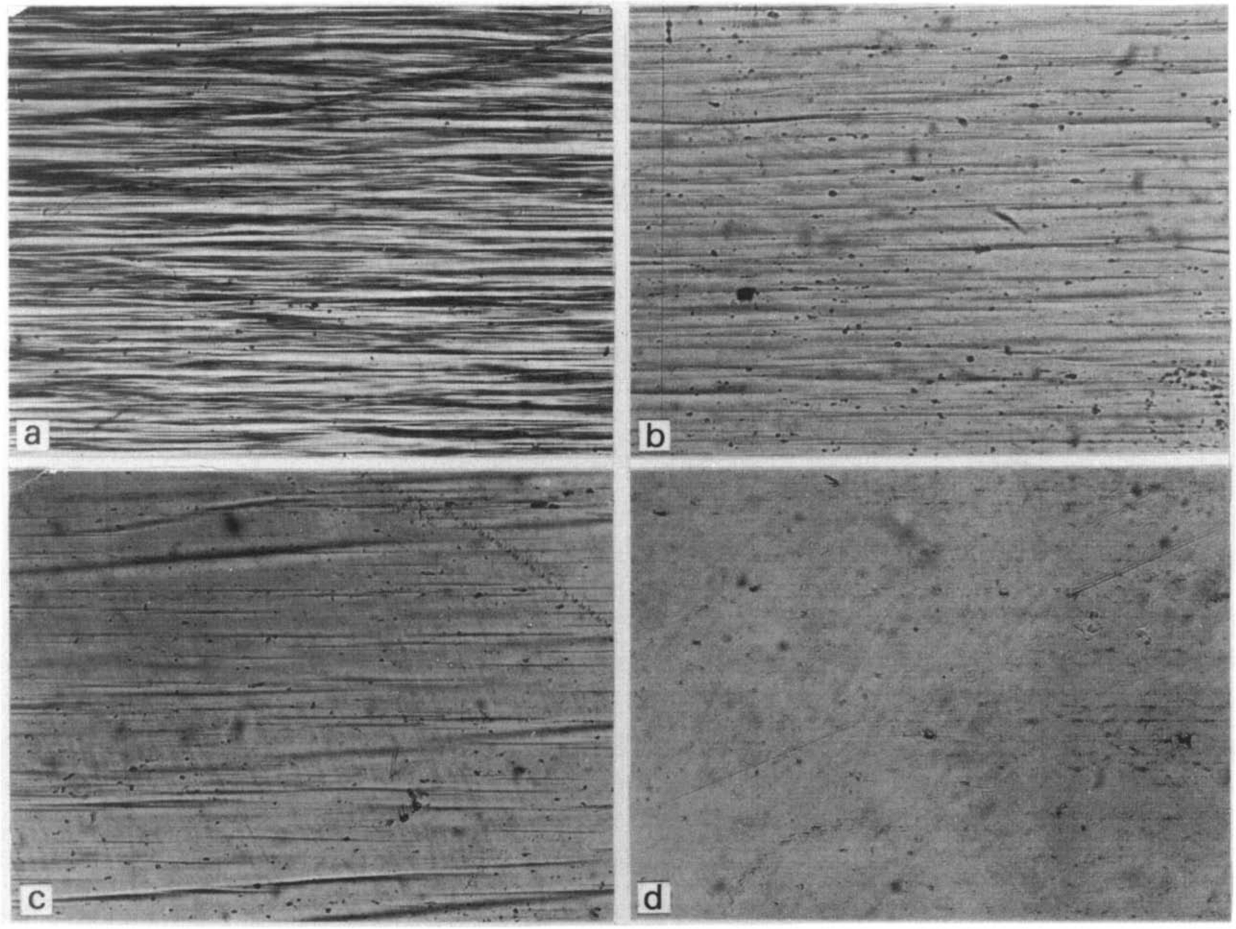

Figure 4 Crazes in tensile specimens fractured in N_2 at 1 atm. (a) 77K; (b) 138K; (c) 160K; (d) 179K

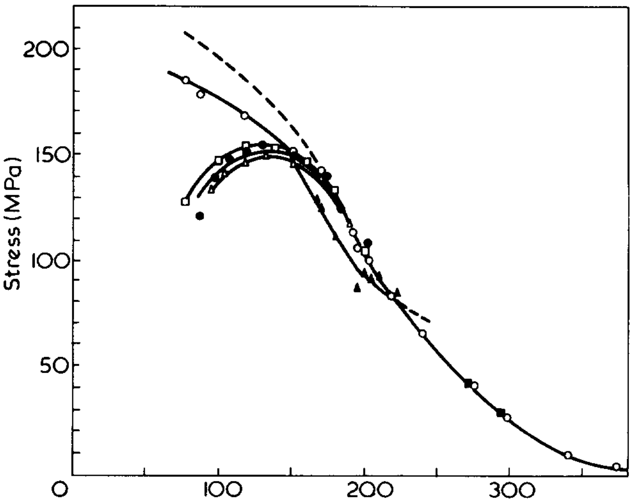

Figure 5 Tensile strength vs. temperature at 1 atm: ○, He; □, N_2; ●, Ar; △, O_2; ▲, CO_2; ■, H_2O; — — — —, extrapolated shear yield point

Table 1 Parameters in equation (2)

Environment	Q (cal/mol)	Heat of vaporization, ΔH_v(cal/mol)	P^* (bar)
N_2	1270	1335^a	31.6
Ar	1470	1501^a	61.6
O_2	1520	1630^b	57.5
CO_2	5450	6030^a	2.48×10^5

[a] Thermodynamic Function of Gases, (Ed. F. Din), Butterworth, London 1962

[b] O. Kubaschewski and E. Evans, 'Metallurgical Thermochemistry', 3rd Edn, Pergamon, London, 1958

yield point relative to Young's modulus by using a value of 0.37 for Poisson's ratio so that all theories and the experimental results could be compared on the same basis. The average value of all theories is 0.077 as compared to the experimental value of 0.055, which indicates that all the theories approximate the truth in spite of differences in the models. The agreement between theories and experiment is about as good as a similar comparison between theory and the observed strength of defect-free whiskers of highly crystalline solids[20]. Usually, in the case of highly crystalline solids the interaction of dislocations with defects in the lattice is the primary basis for determining the strength. In the case of environmental crazing, the craze yield point is a dynamic phenomenon which strongly depends on strain rate and the stress to nucleate a craze[21]. In the case of metals, the observed ratio of yield point to modulus can be as low as 10^{-6} [22], whereas in glassy polymers the shear yield point is always close to the theoretical value.

The systematic decrease in the ratio of yield point to modulus with increasing temperature (*Figure 8*) is attributed to the contribution of the process of thermal activation. However, even at 300K the ratio is still about 0.033

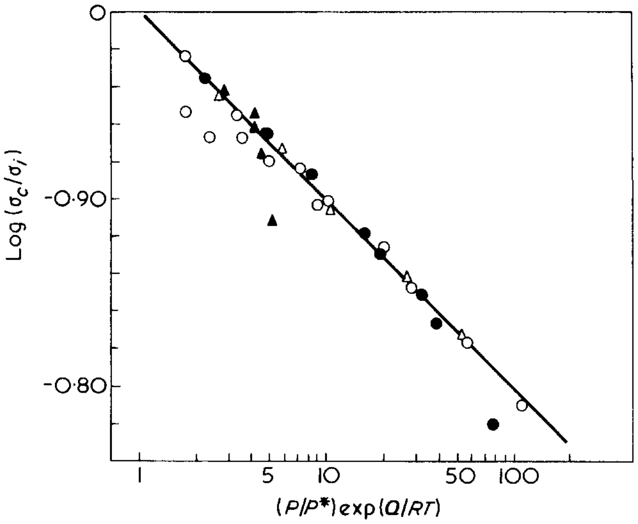

Figure 6 All the data showing the agreement with equation (2) and using the parameters in *Table 1*: ○, N$_2$; ●, Ar, △, O$_2$; ▲, CO$_2$

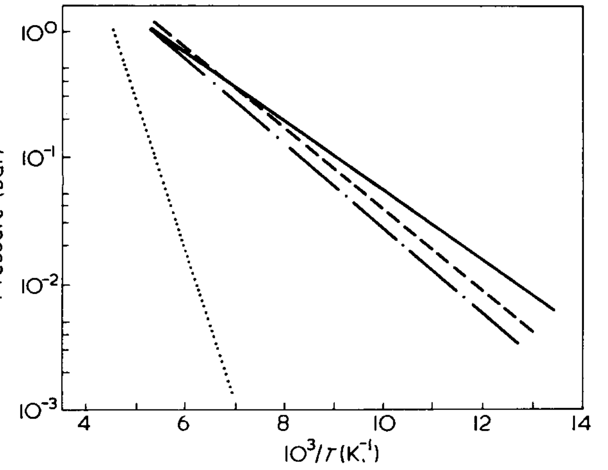

Figure 7 Boundary between the intrinsic domain and the domain of craze deformation. The intrinsic domain is to the left of each boundary. Each environment has its own boundary: ———, N$_2$; – – –, Ar; — · — · —, O$_2$; · · · · · ·, CO$_2$

which indicates that the theoretical strength is the primary basis for determining the yield point at a particular temperature. Thus, at the very highest strain rates, the yield point is expected to approach the theoretical strength which depends on the modulus for that temperature. How much the yield point can be reduced by thermal activation can only be determined by experiments. At very low stresses, the strain rate is so slow that the total strain remains small during the lifetime of the experiment. If the strain is less than a critical value, it is completely recovered after the stress is removed. The critical value of the yield strain is for most polymers within the range of 0.05 to 0.10 as typified by *Figure 3a*. The variations in the yield strain for a given polymer is usually less than the variation in stress that can be caused by thermal activation. The theory by Brown[16] indicates that the yield strain should be about 11%. It is suggested that a critical yield strain is a more constant criterion for yielding than the theoretical stress because it is less sensitive to hydrostatic pressure and thermal activation.

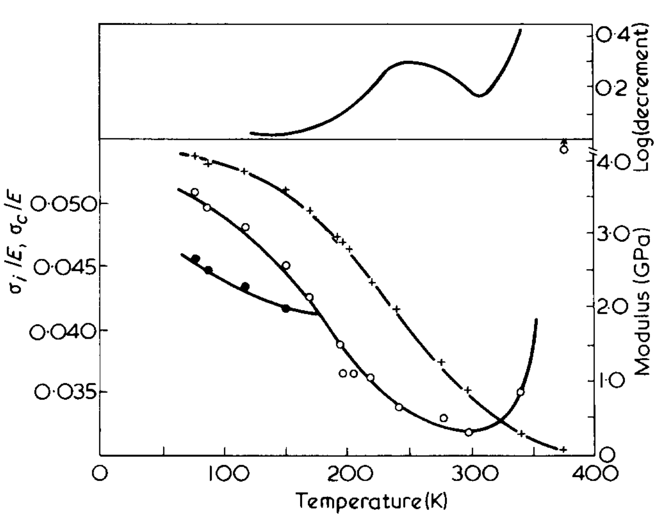

Figure 8 Log decrement (McCrum[23]) (———); Young's modulus (X); ratio of yield point over Young's modulus (○) and ratio of fracture stress over Young's modulus (●) *versus* temperature

Table 2 Theoretical strength of polymers at 0K relative to Young's modulus

$\sigma y/E$	Basis of theory	Source
0.037	Overcoming an average Lennard–Jones potential	Brown[16]
0.13	Nucleation of a slip patch	Bowden and Paha[17]
0.12	Nucleation of a pair of kinks in a polymer chain	Argon[18]
0.019	Strophons in a Lennard–Jones potential	Yannas[19]

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