

The micromechanics and microstructure of CO₂ crazes in polystyrene

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Although CO₂ at 1 atmosphere pressure is not a crazing and/or cracking agent for polystyrene (PS), we have established that it becomes one at higher pressure. Crazes grown from cracks in PS thin films in high pressure CO₂ are investigated using transmission electron microscopy (TEM). The fact that broken craze fibrils retract strongly upon exposure to high pressure CO₂ gas suggests that the primary effect of the CO₂ is plasticization, not surface energy reduction. Quantitative analyses of TEM micrographs of crazes grown at CO₂ pressures in the range 5 to 100 MPa at 34°C and 45°C have been carried out to find the craze fibril volume fractions $v_f(x)$ and the surface displacements $w(x)$ along each craze. From the fibril volume fraction profile along the craze, the dominant craze thickening mechanism of CO₂ crazes is shown to be the same as that for air crazes, i.e. the surface drawing mechanism, and not the fibril creep mechanism. The craze surface stress profile is computed from the craze surface displacements using a distributed dislocation analysis. These profiles all show a stress concentration at the craze tip which falls to a roughly constant value σ_b over the rest of the craze. The fracture toughness G_{Ic} (and critical stress intensity factor K_{Ic}) for propagation of a crack in PS at these CO₂ pressures can also be computed. All these quantities (v_f , σ_b , G_{Ic} and K_{Ic}) show pronounced minima as a function of CO₂ pressure at 20 MPa, the same CO₂ pressure at which T_g of the polymer also reaches a minimum. These minima are more pronounced at 45°C than at 34°C. The G_{Ic} 's and K_{Ic} 's are depressed by orders of magnitude at the minimum, which corresponds to the qualitative observation that CO₂ becomes a severe cracking agent at these pressures. These observations provide additional confirmation that the major mechanism for the environmental crazing and cracking of PS by CO₂ is plasticization of the craze fibrils and surfaces.

Keywords Crazing; craze microstructure; environmental stress cracking; craze micromechanics; carbon dioxide crazes; polystyrene

INTRODUCTION

A characteristic feature of the fracture of glassy polymers is the appearance of crazes in the specimen prior to actual fracture. The mechanical behaviour of these crazes is important to all aspects of the fracture process in these materials. It is now widely accepted¹⁻³ that the relatively high fracture toughness of these materials is due to the plastic work done in generating a craze (or crazes) in front of the advancing crack tip. However, the fact that the fibrils within an isolated craze (not at a crack tip) eventually break down to form large voids which grow slowly to form cracks of critical size within the craze means that crazes are also a source of weakness in the polymer. The former process (craze generation) depends on the critical strain (or stress) for crazing; whereas the latter process (breakdown of crazes) depends on the stability of the craze fibril structure which in turn depends on the volume fraction v_f of craze fibrils and their mechanical properties⁴⁻⁶.

In the presence of certain environments, the fracture toughness and craze stability in glassy polymers decrease drastically^{7,8}. While it is well known that environmental crazes nucleate and grow at much lower applied stresses than in air, an important question remains: Is the plastic rupture of the craze fibrils accelerated by these environments? and if the answer is yes, what is the mechanism of environmental attack?

For knowledge of the processes leading to crack initiation, information is necessary on the micro-

mechanics of environmental crazes, i.e., local displacement stress and strain information at various points along the craze⁹. For example, from the measured volume fraction and primordial craze thickness profile along crazes, the dominant craze thickening mechanism can be determined; from the surface stress and the displacement profile along the craze, the fracture toughness (G_{Ic}) and the critical stress intensity factor (K_{Ic}) can be found.

Techniques are now available^{6,9} for generating isolated crazes at the tips of a crack embedded in a thin film of polymer. The volume fraction of craze fibrils as well as the displacements of the craze surface can be determined from a quantitative analysis of TEM micrographs. Several stress analysis methods^{6,9,10} can be used to solve the craze surface stress profile from the craze surface displacements along the craze.

The enhancement of crazing by the environment has been attributed to either a reduction in surface energy caused by the environment^{11,12} or a depression of the glass transition temperature T_g of the polymer swollen by the environment (plasticization)^{2,8,13}; in the former case the environmental molecules can decrease the surface energy required for forming the finely divided fibril structure of the craze whereas in the latter they can swell the polymer thereby reducing the flow stress of the glassy state and allowing plastic formation of the fibril structure to occur more readily. To decide between these two alternate mechanisms, one should perform model experiments in which the crazing is carried out in an environ-

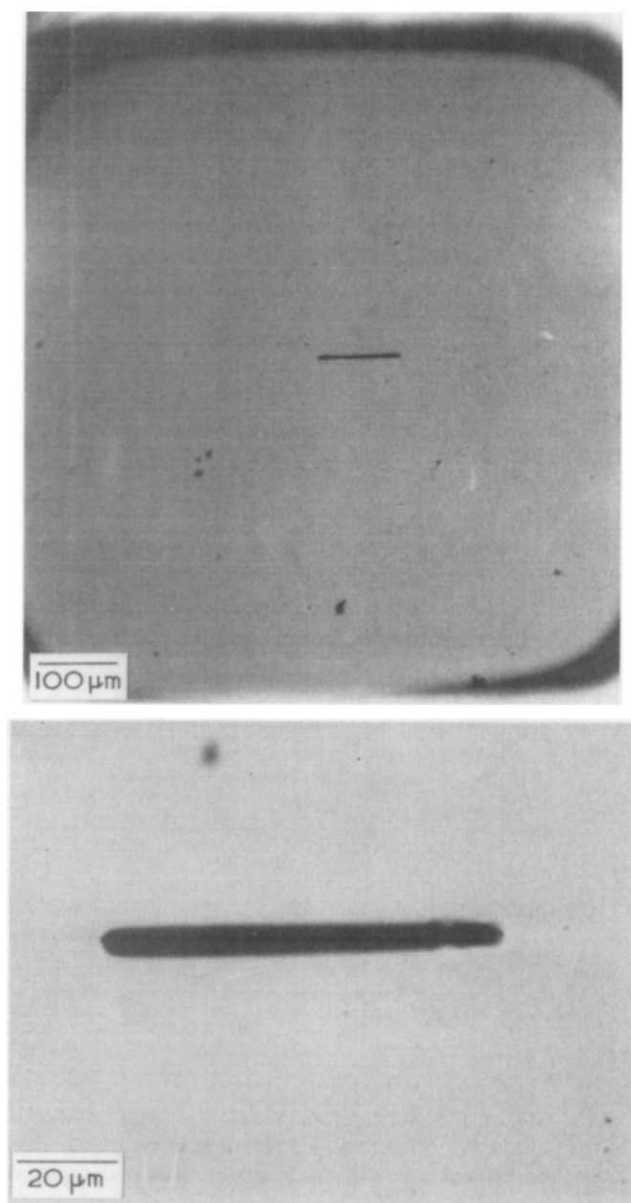


Figure 1 Precracked grid square

ment where the absorption and plasticization effect can be varied over a significant range.

Carbon dioxide gas is a suitable choice for this environment: it has a convenient critical temperature 31°C. Above this temperature the activity of the gas and thus plasticization of the gas in the polymer can be changed continuously by simply changing the pressure of the gas. Such changes in activity cannot be carried out for liquids⁸ in contact with polymers, unless various liquids with different activities in the polymer are used. But then it is hard to rule out specific chemical effects of particular liquids. Moreover, it will be demonstrated here that high pressure CO₂ is a crazing and cracking agent for polystyrene.

By combining experimental TEM measurements of CO₂ crazes with a new method of stress analysis, we present below results on the micromechanics of CO₂ crazes grown over a significant range of CO₂ pressures and ambient temperatures. The results leave little doubt that the major effect of the environment on craze formation and breakdown in this model system is T_g depression.

EXPERIMENTAL PROCEDURE

Polystyrene with a number average molecular weight $\bar{M}_n = 110\,300$, and a weight average molecular weight $\bar{M}_w = 264\,600$ is dissolved in toluene. Thin films of PS (with thicknesses in the range 0.45 ~ 0.75 μm) are produced by slowly pulling glass microscope slides from the solution. These films, after drying, are floated off the glass slides onto the surface of a water bath and are picked up on the copper grids which are precoated with PS⁹. The films are then bonded to the grid by exposing them briefly to the toluene vapour. After drying, a crack of controlled geometry is introduced into the film by 'burning' a slit with the intense electron beam of an electron microprobe. The geometry of the crack is chosen so that its long axis is normal to the direction in which the strain shall be applied. A typical precracked grid square is shown in Figure 1.

To determine whether CO₂ gas at high pressure is a crazing and/or cracking agent, the following procedures are used. A tensile stress is applied to the film by straining the copper grid in tension to a value which is below the critical strain for crazing in air. The copper grid deforms plastically and holds the polymer film under tension even when the applied force on the grid is removed. After straining, the film is examined in the optical microscope to ensure that no air crazes have formed. It is then placed in the high pressure CO₂ gas at a constant temperature. After 10 minutes, this film is taken out and examined again with the optical microscope.

The quantitative study of the CO₂ craze micromechanics requires two steps: (a) the displacement profile $w(x)$ along the crazes must be determined directly from experimental measurements and (b) a mathematical method must be applied to obtain the surface stresses on the craze from these displacements. The mathematical method used here has been developed in another paper¹⁴. This method of stress analysis can be applied to crazes which extend symmetrically from the tips of a double ended slit embedded in a linear elastic sheet under a tensile stress σ_∞ . By representing these crazes by distributed dislocation arrays (each dislocation having unit Burgers vector) with a density $\alpha(x) = -2 \frac{dw(x)}{dx}$, the surface stress

profile $S(x)$ along each craze as well as the applied tensile stress σ_∞ can be obtained from the displacements along the craze as follows¹⁴:

$$\sigma_\infty = (E^*/2\pi) \int_c^a dx \cdot \alpha(x) \cdot \frac{1}{(x^2 - c^2)^{1/2}}$$

and

$$S(x) = (E^*/2\pi) \cdot x \cdot (x^2 - c^2)^{1/2}$$

$$\int_c^a \frac{dx_1 \cdot \alpha(x_1)}{(x_1^2 - c^2)^{1/2}} \cdot \frac{1}{x^2 - x_1^2}$$

Here c is the half crack length, a is the half crack length plus craze length, $E^* =$ Young's modulus E for plane stress and $E^* = E/(1 - \nu^2)$ for plane strain where ν is Poisson's ratio.

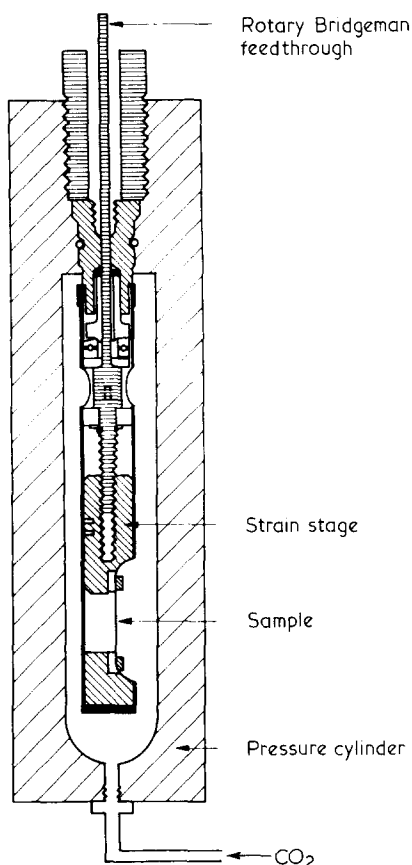


Figure 2 Straining stage in high pressure CO₂ environment

The value of Young's modulus E of polystyrene is needed in this stress analysis. Since it has been established that at high pressure, CO₂ is a severe plasticizer for polystyrene, the value of the modulus E varies with the surrounding CO₂ pressure and ambient temperature. A method has been developed to measure the modulus of bulk PS specimen at different CO₂ pressures and temperatures; the results are reported in another paper¹⁵. These results for E will be used here for the purposes of stress analysis.

To grow a craze at a fixed CO₂ pressure, it is desirable to apply the strain to the copper grid after this CO₂ pressure is reached instead of applying the strain first and then increasing CO₂ pressure to the desired value. For this purpose a strain frame was designed to strain the sample under high pressure. The copper grid with attached PS film is mounted in this strain frame, the whole unit (Figure 2) is immersed in an oil bath, and CO₂ gas is introduced. After the whole system reached equilibrium, sufficient tensile strain is applied to cause CO₂ crazes to nucleate at crack tips and grow to the desired length. A suitable craze is located and the corresponding copper grid square is cut out for TEM observations.

The displacement profiles along the crazes are obtained directly from the quantitative analysis of the TEM plates by a method developed by Lauterwasser and Kramer⁹. By using the relation

$$w(x) = \frac{1}{2} T(x) (1 - v_f(x))$$

they obtain the craze surface displacement at point x , $w(x)$ from the craze thickness $T(x)$ and volume fraction

of polymer fibrils $(v_f(x))$ at point x . The craze thickness profile is measured directly from the electron micrograph sequences along the craze. The local volume fraction of polymer material in the craze is determined from the microdensitometer measurements of the optical densities (on the electron image plate) of the craze $(\phi_c(x))$, the film (ϕ_f) and a hole in the film (ϕ_h) by using the equation

$$v_f(x) = 1 - \frac{\ln(\phi_c(x)/\phi_f)}{\ln(\phi_h/\phi_f)}$$

The displacement profiles of crazes grown at CO₂ pressures in the range 5 to 100 MPa at 2 different temperatures (34°C, 45°C) have been determined in this way. The surface stress profiles $S(x)$, as well as the applied stresses σ_∞ , corresponding to these displacement data are obtained using the distributed dislocation stress analysis.

RESULTS AND DISCUSSION

Effects of high pressure CO₂ on crazing and cracking of PS

An optical micrograph of a precracked PS film strained to $\epsilon = 0.1\%$ and then exposed to 10 MPa CO₂ pressure at 34°C is shown in Figure 3. A similar micrograph of a precracked PS film strained to $\epsilon = 0.15\%$ and exposed to 20 MPa CO₂ pressure at 45°C is shown in Figure 4. Two crazes have nucleated at the crack tips at $\epsilon = 0.1\%$ and 10 MPa CO₂ pressure at 34°C (Figure 3) but the crack has not yet propagated, while at $\epsilon = 0.15\%$ and 20 MPa pressure at 45°C (Figure 4) the crack has propagated through crazes grown from its tips. Precracked films of PS subjected to ϵ 's of 0.15% at either temperature do not show crazing or cracking in air or 1 atmosphere (0.1 MPa) CO₂ pressure. This result demonstrates that although at 1 atmosphere CO₂ is not a crazing and cracking agent for polystyrene, it is at higher pressures. The presence of high pressure CO₂ gas apparently decreases the critical strain for the craze nucleation as well as weakens the craze fibril structure leading to easy craze fracture.

Mechanisms for CO₂ gas crazing and cracking of PS

While there seems little doubt that various environments can decrease the critical craze nucleation strain and the load-bearing capacity of craze fibrils^{3,7}, it is still debatable what kind of a role the environment plays in

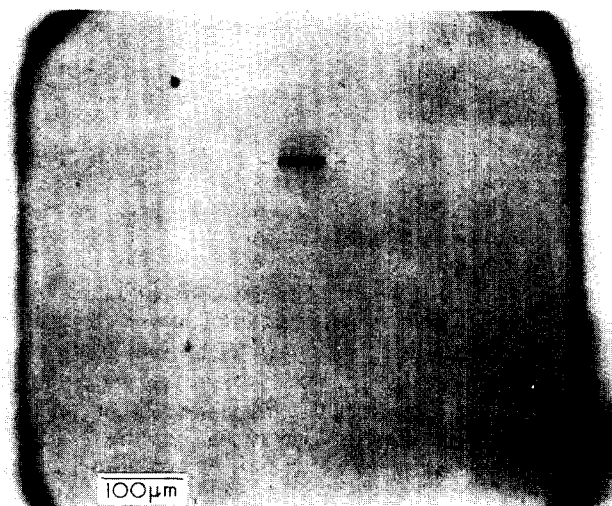


Figure 3 CO₂ crazes grown at 10 MPa CO₂ pressure, 34°C and 0.1% strain

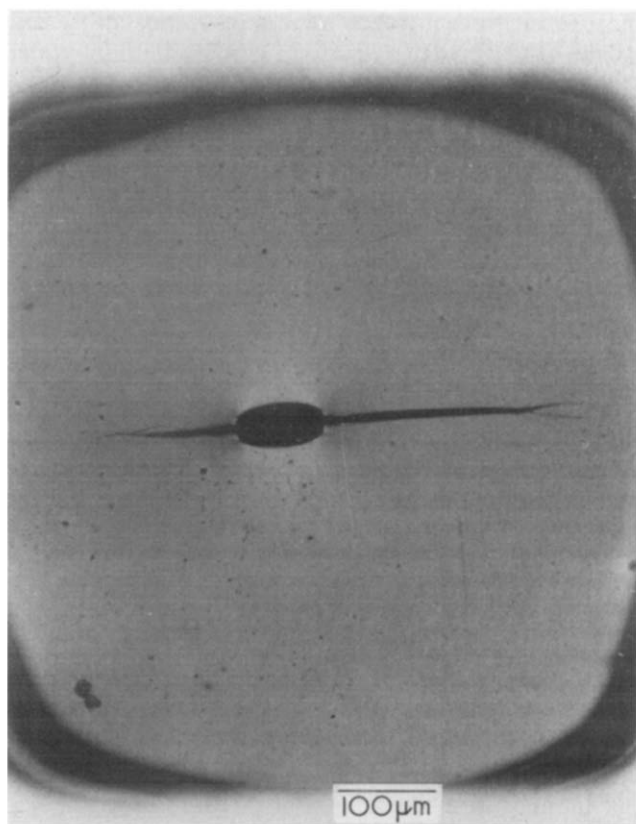


Figure 4 Propagation of a crack through crazes at 20 MPa CO₂ pressure, 45°C and 0.15% strain

strain, crazes nucleated at the crack tip and the crack propagated a few microns into one of the crazes. The broken craze fibrils behind the crack tip retracted partially but not completely as can be seen in Figures 5a and 5c. The film was then exposed to high pressure CO₂ for 10 minutes at 34°C. If the surface energy reduction of the craze fibrils were the major effect of the CO₂ gas, the fibrils should not shrink on exposure to CO₂ since the interfacial tension forces tending to contract the fibrils will be decreased.

If plasticization is the major effect however, fibril shrinkage is expected since relaxation times for the highly aligned polymer chains in the fibrils, to return to their random coil configurations under the entropic forces of rubber elasticity, become much shorter as T_g is depressed toward 34°C. The results of exposing the broken craze fibrils to CO₂ at 27.6 MPa and 55 MPa pressures (Figures 5b, 5d) show that substantial fibril retraction occurs at both pressures. The primary effect of the CO₂ is thus plasticization and not surface energy reduction. That T_g of PS is substantially depressed by CO₂ is confirmed by direct measurements of the creep compliance of bulk PS in CO₂. It is worth noting that since 34°C is above the critical temperature for CO₂, the fibril retraction cannot be the result of the action of a meniscus between liquid and gaseous CO₂; at this temperature the density of CO₂ gas increases continuously with pressure and there is thus no gas-liquid meniscus.

Micromechanics of CO₂ crazes

A craze grown by loading rapidly at 14.5 MPa CO₂ pressure and 45°C (Figure 6) is used as an example to compare with an air craze. Unlike an air craze in PS, there are non-fibrillated plastic zones observed at the craze tips of the CO₂ craze. The occurrence of these plastic zones is a common feature of all the crazes grown rapidly in PS films severely plasticized by high pressure CO₂ gas. The reason for formation of these plastic zones is not known yet. The volume fraction v_f , primordial craze thickness T_0 , and displacement w of this CO₂ craze versus position along the craze are shown in Figures 7, 8 and 9.

The v_f and T_0 profiles along the craze can be used to reveal the craze thickening mechanism^{3,7,9}. The growing craze can thicken by drawing new polymer from the craze surface into the craze fibrils maintaining the extension ratio of the fibrils constant for a given surface stress. This is called the surface drawing mechanism which provides stress relief without producing damage to the fibril structure. If crazes thicken by this mechanism, the extension ratio of the fibrils should maintain a constant value along the craze while the primordial craze thickness

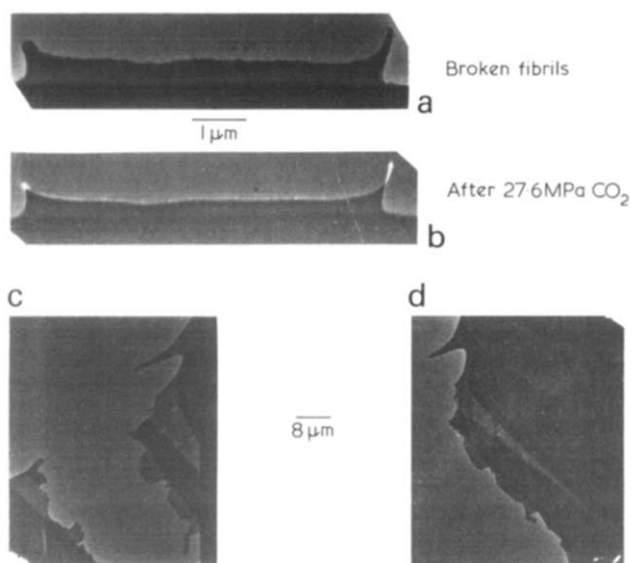


Figure 5 (a), (c): Broken fibrils before exposure to CO₂ gas. (b), (d): Broken fibrils after exposure to CO₂ gas

regard to these damaging effects. Two primary mechanisms have been proposed^{2,3} for the environmental effects: one is a decrease in the surface energy required for forming the finely divided fibril structure of the craze; the other is the plasticization (decrease in T_g of the polymer) which leads to a decrease in the flow (or drawing) stress of the polymer at the craze tip where fibrils are being formed (or at the craze surface where they are being drawn out). To decide which of these two alternative mechanisms is more important under high pressure CO₂, a craze fibril retraction experiment was performed.

A precracked PS film was strained 1.5% in air. At this

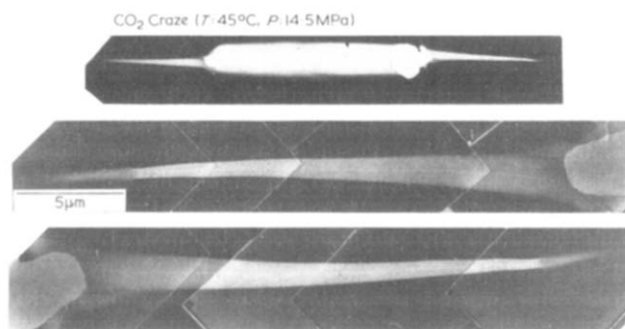


Figure 6 A craze grown by loading rapidly at 14.5 MPa CO₂ pressure and 45°C

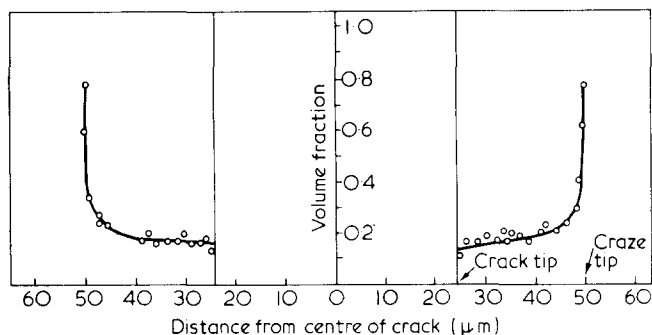


Figure 7 Fibril volume fraction profile

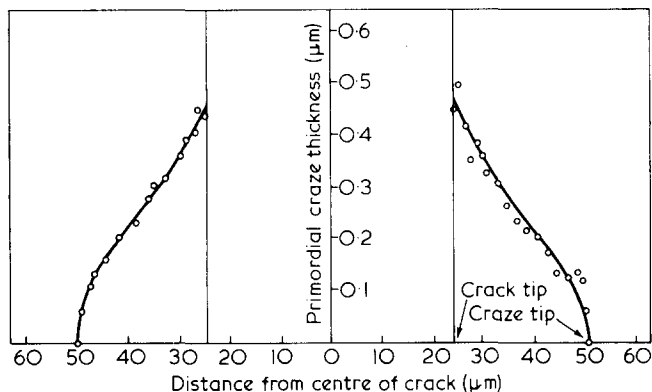


Figure 8 Primordial craze thickness profile

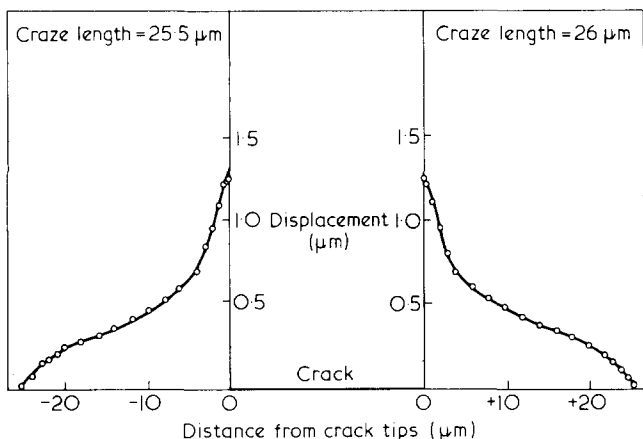


Figure 9 Craze opening displacement profile

should decrease toward the craze tip. However, the craze can thicken by increasing the extension ratio (decreasing the fibril volume fraction) of the already existing craze fibrils without drawing in any new polymer. This is the fibril creep mechanism which is inherently damage producing and ultimately leads to fibril failure. In this case, one would expect that the primordial craze thickness would be fixed not far behind the craze tip and that the extension ratio of the fibrils would increase drastically from the tip to the base (crack tip) to produce the observed thickness profile.

As shown in Figure 7, the fibril volume fraction increases slightly, away from the crack tip but then holds approximately constant until the plastic zone at the craze tip is reached. In the plastic zone, the fibril volume fraction increases to 1. The volume fraction profile, together with the primordial craze thickness profile (Figure 8) which decreases monotonically toward the craze tip, suggests

that the dominant craze thickening mechanism in CO₂ crazes is the surface drawing mechanism, the same mechanism which operates in air crazes. The result is different from that of the PMMA-methanol or PS-n-heptane systems studied by Krenz and Kramer⁵. Both systems exhibit the characteristics of the fibril creep mechanism (i.e. v_f decreases toward the crack tip and T_0 is roughly constant along the craze). The fact that CO₂ molecules diffuse much faster in PS ($D \sim 10^{-8} \text{ cm}^2 \text{ s}^{-1}$) than methanol or n-heptane molecules in PMMA or PS ($D \sim 10^{-11} \text{ to } 10^{-13} \text{ cm}^2 \text{ s}^{-1}$) eliminates any rate limitation of the surface drawing mechanism due to diffusion of the molecules at the craze-bulk polymer interfaces. The observation that the predominant mechanism of craze thickening is surface drawing rather than fibril creep in the CO₂ crazes thus seems reasonable.

The surface stress profile for the CO₂ craze in Figure 6 is shown in Figure 10. The stress profile as well as the stress profiles of other CO₂ crazes shows qualitatively the same characteristics as those of air crazes, i.e. the surface stress stays approximately constant along the craze and rises to a small stress concentration at the craze tip. Examining the TEM pictures of the CO₂ crazes, it is clear that the midrib, a region of lower fibril density running along the central plane of crazes, is present under all the CO₂ pressures and temperatures studied. This fact together with the similarity of the surface stress profile along the crazes also suggests that the mechanisms of craze tip advance and craze thickening are the same in the high pressure CO₂ environments as in air⁹. That is, the craze thickens as it grows in length by drawing new fibril material from the craze surfaces. The decrease in v_f in the midrib is due to the higher craze surface stress just behind the craze tip. This result agrees well with the volume fraction and primordial craze thickness profiles which suggest the surface drawing mechanism for craze thickening.

The stress levels of CO₂ crazes are much lower than those of air crazes because of the severe plasticization effect of CO₂ molecules in PS. The values of σ_b (the approximately constant stress along the craze) and σ_t (craze tip stress) of crazes grown at different CO₂ pressures at temperatures of 34°C and 45°C are listed in Table 1. The average fibril volume fraction along these crazes, as well as the measured Young's modulus of PS in the high pressure CO₂ environment are included in this Table. The craze stress σ_b and the average fibril volume fraction v_f along the craze are plotted vs. CO₂ pressure (at both 34°C and 45°C) in Figures 11 and 12 respectively. The values of σ_b and σ_t , which reflect the load-bearing ability of craze fibrils, decrease with the increasing degree of plastici-

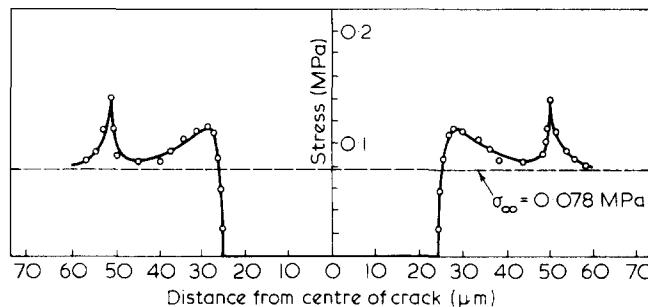


Figure 10 Craze surface stress profile calculated by distributed dislocation method

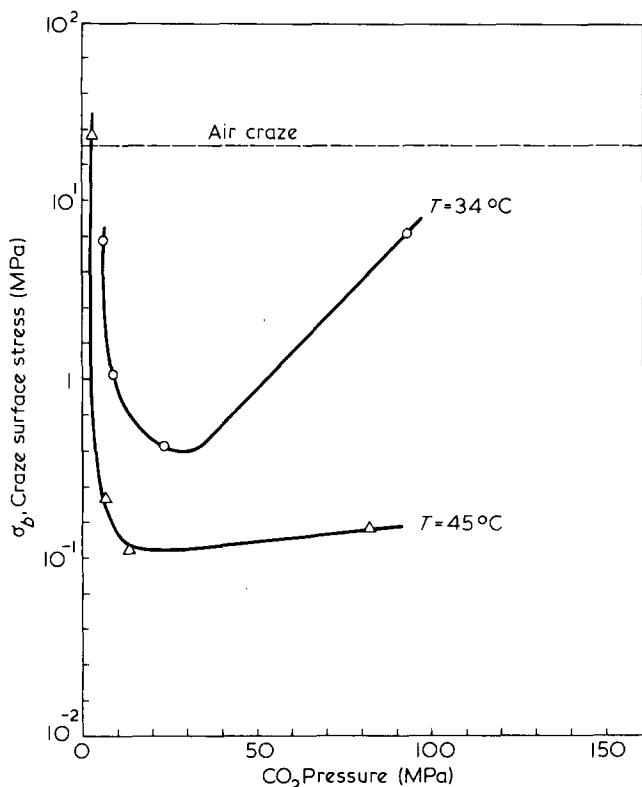


Figure 11 Craze stresses as a function of CO₂ pressure and temperature

zation of PS by the CO₂ molecules. Therefore the CO₂ crazes, although they thicken by the same mechanisms as air crazes, are plasticized and weakened by the CO₂ gas.

It is clear from Figure 12 that the volume fraction of craze fibrils grown at different CO₂ pressures and temperatures decreases with respect to the increasing degree of plasticization. It varies from 0.25 for air and slightly plasticized crazes to 0.12 for severely plasticized PS at 44.5°C, 14 MPa CO₂ pressure. It is known that diluting the polymer with a low molecular weight diluent increases the entanglement molecular weight^{8,16}

$$(M_c)_s = M_c / \phi_2$$

where M_c is the entanglement molecular weight for undiluted polymer, ϕ_2 is the polymer volume fraction in the polymer-diluent solution, and $(M_c)_s$ is the entanglement molecular weight of polymer in the solution. Assuming there is no slipping of entanglements, the entanglement molecular weight is related to the maximum extension ratio λ_m that can be achieved for a polymer as below⁸:

$$\lambda_m \propto ((M_c)_s)^{1/2}$$

Hence the maximum fibril extension ratio (minimum fibril volume fraction) in the swollen polystyrene plasticized by CO₂ molecules is given by

$$(v_f)^{-1} = (\lambda_m)_s \propto (M_c / \phi_2)^{1/2}$$

The absorption of CO₂ molecules which decreases the polymer volume fraction ϕ_2 in the solution therefore increases the maximum fibril extension ratio (decreases the volume fraction) of craze fibrils. However, this decrease in v_f is only 10% (the increased volume of polystyrene swollen by high pressure CO₂ gas is measured to be around 20%, which corresponds to $\phi_2 = 0.83$), much less than the 52% decrease in v_f actually measured (v_f is 0.25 in an air craze whereas it is 0.12 in a craze grown at 45°C, 13.8 MPa CO₂ pressure, Table 1). Therefore the decrease in v_f with increasing degree of plasticization is probably because the CO₂ molecules, as a plasticizer, cause an easier slippage¹⁷ (reptation) of molecular entanglements in the drawing fibrils.

At a constant applied stress the true stresses in the fibrils are higher in low fibril volume fraction crazes than in higher fibril volume fraction crazes (the true stress in the fibrils σ_{true} is the fibril surface stress divided by the fibril volume fraction)^{8,9}. This effect together with the weaken-

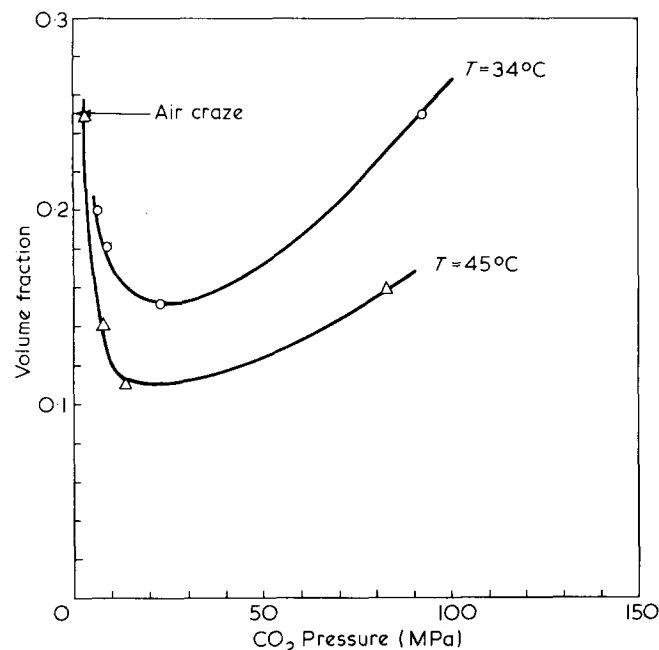


Figure 12 Craze fibril volume fraction as a function of CO₂ pressure and temperature

Table 1 Important parameters of CO₂ crazes: T , ambient temperature; P , CO₂ pressure; T_g , glass transition temperature; E , Young's modulus; σ_b , craze average stress; σ_t , craze tip stress; v_f , fibril volume fraction; G_{fC} , fracture toughness; K_{fC} , critical stress intensity factor

	(Air craze)			(CO ₂ Crazes)					
T (°C)	20	34	34	34	34	45	45	45	45
P (MPa)	0.1	6.79	9.31	22.8	93.1	4.83	7.53	13.8	82.6
T_g (°C)	100	43.8	38.7	36.8	41.5	53	46.6	41.7	43.4
E (MPa)	3000	173	20.3	6.78	212	2028	4.69	3.41	3.73
σ_b (MPa)	18	6.04	1.05	0.4	8.0	25	0.24	0.11	0.15
σ_t (MPa)	27	8.92	1.96	0.95	17.0	27.7	0.34	0.14	0.22
v_f	0.25	0.2	0.18	0.15	0.25	0.25	0.14	0.12	0.16
G_{fC} (J m ⁻²)	2430	18.1	3.93	3.01	39.1	67	1.46	0.26	0.54
K_{fC} (10 ⁻³ MPa(m) ^{1/2})	2700	56.0	8.93	4.52	91.0	369	2.62	0.95	1.41

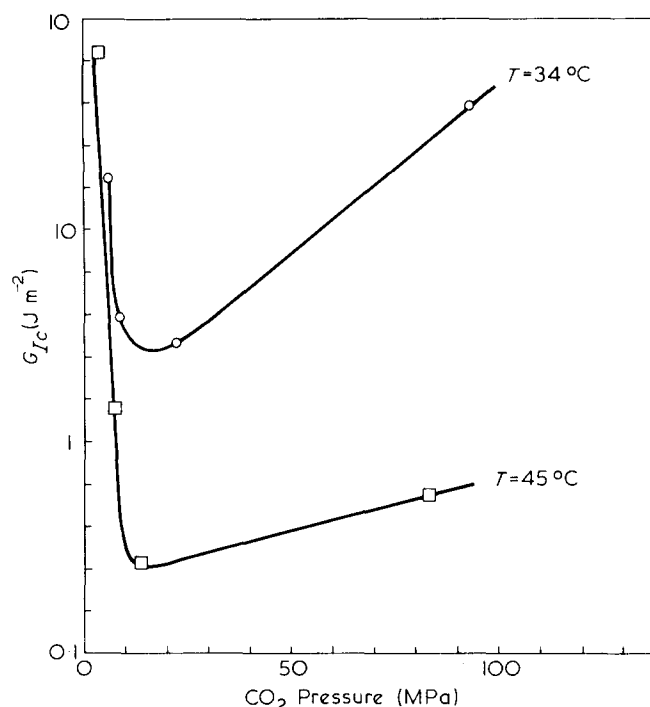


Figure 13 Fracture toughness of PS as a function of CO₂ pressure and temperature

ing of craze fibrils by CO₂ molecules leads to a more rapid nucleation and growth of cracks within the craze, and reduces the fracture toughness of PS accordingly.

In Table 1, at both 34°C and 45°C the modulus of PS goes through a minimum with increasing CO₂ pressure. This phenomenon is explained in another paper¹⁵ as follows: the initial decrease of modulus is caused by the plasticization effect by CO₂ molecules absorbed in PS. As the CO₂ pressure gets higher, this effect will be opposed by a stiffening (and an increase in T_g) of the polymer caused by the hydrostatic pressure alone. Due to the combined effect of these two counteracting mechanisms, the depression of T_g and E increases with CO₂ pressure, reaches a maximum around 20 MPa then decreases again. However, the surface energy reduction of the craze fibril surfaces exposed to CO₂ gas should increase monotonically as the CO₂ gas pressure increases. The difference can be used as another indicator to decide which mechanism is primarily responsible for the environmental damaging effect in this system. Both the values of v_f and σ_b of crazes grown at different CO₂ pressures decrease at first with increasing CO₂ pressure, reach a minimum and then increase again. The minimum in v_f and σ_b corresponds well with the pressure at which the depression of T_g of PS by CO₂ is a maximum. There is, therefore, little doubt that it is the plasticization effect of CO₂ molecules absorbed in PS which is responsible for the environmental damage of the fibril structure of crazes in PS.

If one makes the assumption that the craze at the crack tip propagates together with the crack and maintains a steady state displacement profile, the fracture toughness G_{Ic} (the work needed to advance the craze and crack per infinitesimal unit area) can be calculated* from the

* It might be argued that the cracks and crazes analysed are not in the ready-to-advance condition, hence the fracture toughness calculated is less than the value it should be. The cracks and crazes observed here however come from copper grids strained to such a degree that over 90% of the grid squares contain cracks that have already propagated through the crazes grown from their tips (Figure 4). Therefore, the cracks and crazes are very near if not exactly the ready-to-advance state.

displacement and surface stress profile along the craze as:

$$G_{Ic} = -2 \int_c^a S(x) \cdot (dw/dx) \cdot dx$$

$$= 2 \int_0^{w_c} S \cdot dw$$

where w_c is the craze surface displacement at the crack tip. In the Dugdale model, which assumes a constant surface stress σ_y along the plastic zone (craze), G_{Ic} can be easily calculated as^{3,4}:

$$G_{Ic} = 2w_c \cdot \sigma_y \quad (1)$$

Since the surface displacement and stress profile along the CO₂ crazes (Figures 9 and 10) are similar to those of Dugdale model, equation (1) is used to estimate the fracture toughness G_{Ic} of these CO₂ crazes (σ_y is replaced by σ_b). The values of the fracture toughness together with the critical stress intensity factor K_{Ic} ($K_{Ic}^2 = E^* \cdot G_{Ic}$) are listed in Table 1. The fracture toughness and critical stress intensity factor decrease drastically with the increasing degree of plasticization of polystyrene by CO₂ molecules as shown in Figures 13 and 14 respectively.

Therefore, although the surface drawing mechanism is still the dominant craze thickening mechanism of CO₂ crazes and little damage in the craze fibril structure will occur during the craze growth process, CO₂ molecules swell and plasticize polystyrene to facilitate the nucleation of crazes. Moreover, these CO₂ molecules enhance the slippage of molecular entanglements, decrease craze sur-

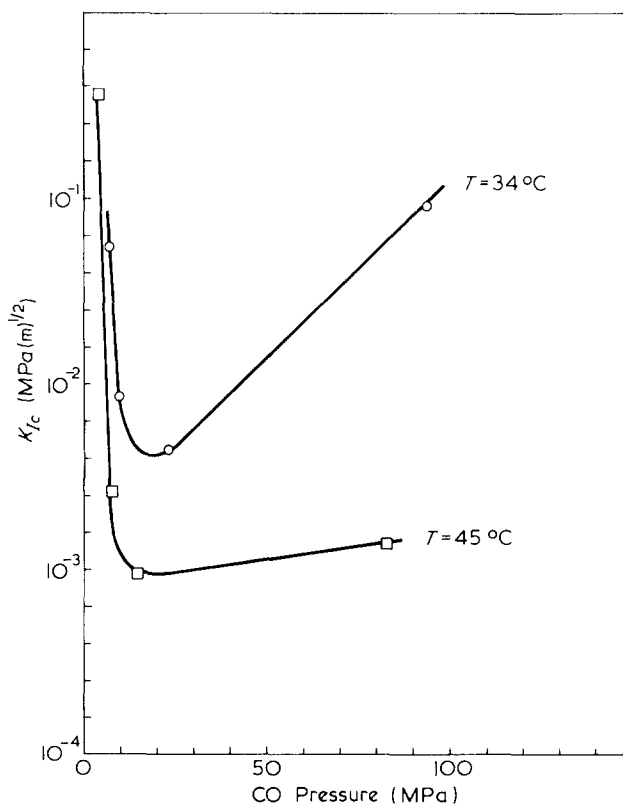


Figure 14 Critical stress intensity factor of PS as a function of CO₂ pressure and temperature

face stresses and lower the work necessary for the craze and crack to advance, leading to a large reduction in the fracture strength of polystyrene.

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