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Environmental crazing and intrinsic tensile deformation in polymethylmethacrylate

Part 2 *Morphology*

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The modes of deformation and fracture were observed by optical microscopy in specimens of PMMA which had been deformed in tension. The deformation took place in N_2, Ar, O_2, CO_2, water and He from 77 to 363 K and under varying partial pressures of the environmental gases. The differences between intrinsice and environmental crazing and the relationship between crazes and shear bands, and between crazing and fracture are presented.

1. Introduction

It was only after Parrish and Brown [1] showed N_2 was a crazing agent at low temperatures that the intrinsic tensile deformation of polymers was observed at low temperatures. This paper makes a clear distinction between the intrinsic behaviour of PMMA and environmental effects. Part 1 [2] is concerned with the tensile stress–strain behaviour of PMMA from 77 to 360 K as it is effected by the various environments, N_2, Ar, O_2, CO_2, water and He. He is completely inert in this entire temperature range. The partial pressure of the active environmental gases was varied from 0 to 1 atm. This paper is concerned with the modes of deformation and fracture.

Based on the mechanical behaviour and the morphology of the deformation, the modes of yielding and fracture can be classified as follows: (1) environmental crazing, (2) intrinsic crazing, (3) intrinsic brittle fracture, (4) environmental brittle fracture, and (5) shear. The shear has two forms, (a) gross localization of shear as shown by the necking of the specimen and (b) micro-shear bands. Under some conditions more than one type of deformation could be observed in the same specimen. The relationship of the various modes will be considered. For example, all brittle fractures showed evidence of crazing. Brady and Yeh [3] emphasized the connection between crazing and shear bands. This investigation re-enforces the idea that shear bands and crazes are intimately related and that this relationship plays a fundamental role in the growth of crazes.

Rabinowitz and Beardmore [4] have reviewed the morphology of crazes. They made a distinction between high and low temperature crazes whereas this paper shows that another distinction can be based on the difference between environmental and intrinsic crazes. At the time that Rabinowitz and Beardmore wrote their review, they did not know that the crazes that were observed in PMMA, after it was deformed in liquid nitrogen, were caused by the liquid nitrogen. Olf and Peterlin [5] have recently observed intrinsic crazing in polypropylene from 77 to 373 K; the morphology of the intrinsic crazes changed markedly with temperature so that it can be said that temperature *per se,* as well as the environment, determines the morphology. Olf and Peterlin [5] also observed the modes of deformation and failure in environments of N_2, Ar, O_2, and CO_2 for PP whose structure varied from "smetic" to highly crystalline. The effect of structure on the deformation was secondary compared to the effects of temperature and the environments. The results of this paper agree with the statement by Olf and Peterlin [5] that crazing is an "ubiquitous" mode of deformation since over the entire range of temperature and for all environments some evidence of crazing could always be detected in PMMA.

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2. Experimental

The PMMA was Plexi-Glass G from Rohm and Haas in the form of 0.6 mm sheet. The specimens from Part 1 were optically examined in transmitted and reflected light. Sometimes polarized light was used to enhance the contrast of the micro-deformation bands and to show the orientation within the massive crazes. The specimens were deformed at the same strain–rate of 1% min^{-1} over a temperature range of 77 to 373 K. The environments consisted of mixtures of each of the following gases with He at partial pressures of 0 to 1 atm: N_2, Ar, O_2 and CO_2. Distilled water was another environment.

3. Results

3.1. Macroscopic observations

An over-view of the deformation and fracture modes in the various ranges of temperature is presented in Fig. 1 where the tensile strength is shown

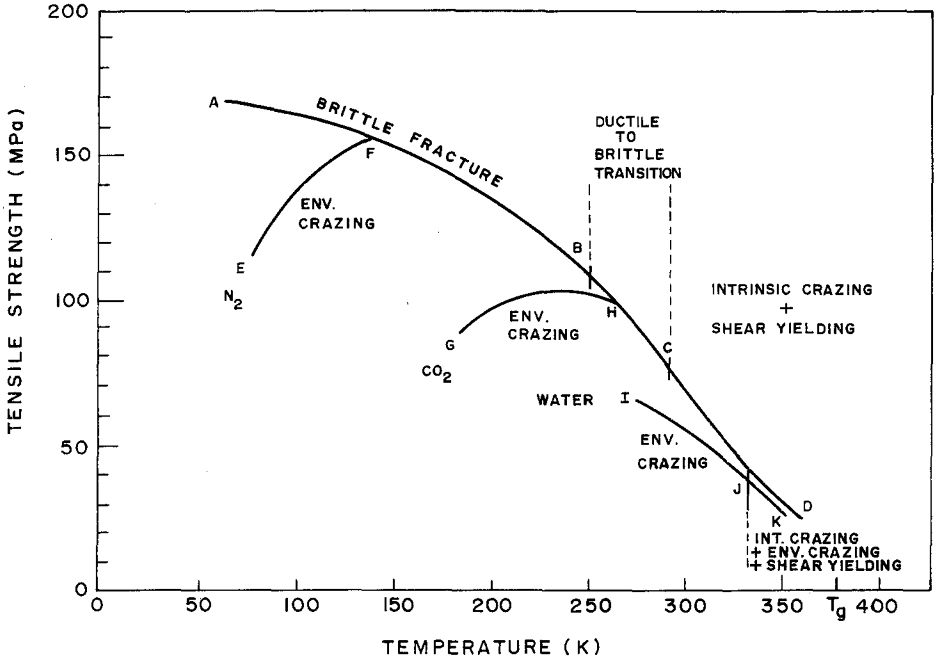


Figure 1 Tensile strength versus temperature and modes of deformation and fracture in different temperature ranges and environments. Curve ABCD is intrinsic behaviour. EF in N_2, GH in CO_2 at 1 atm, and IJK in water.

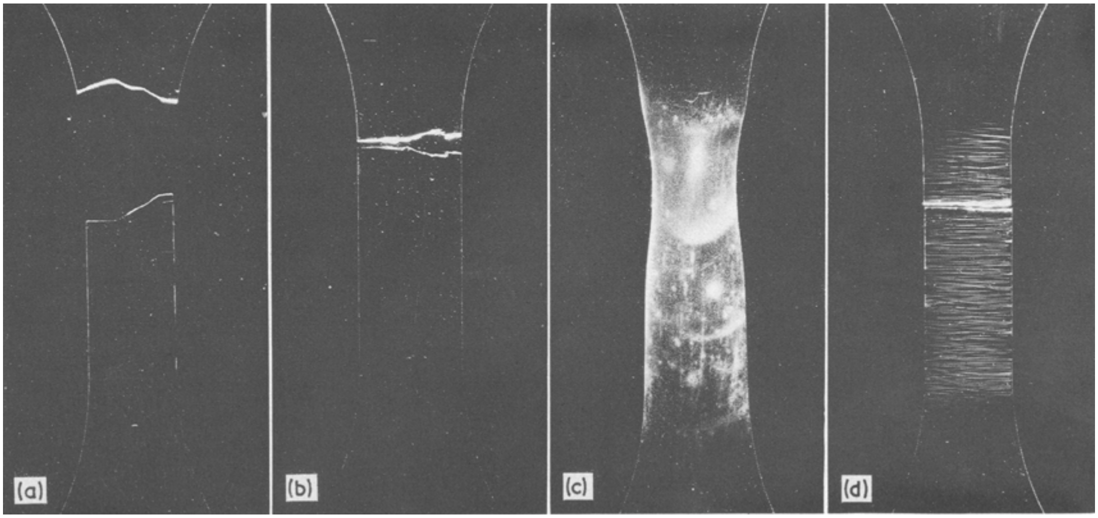


Figure 2 Typical examples of the various modes of deformation and fracture. (a) Fracture in He from 77 to 250 K, (b) fracture in He 250 to 283 K, (c) deformation in He above 283 K, (d) crazing in N_2 below 140 K. The tensile stress is verticle in Figs. 2 to 10 and 12.

as a function of temperature for inert and active environments. ABCD is the intrinsic behaviour; from 77 to 250 K, brittle fracture occurs; from 250 to 283 K is the brittle to ductile zone where there is a gradual increase in fracture strain; above 283 K, a shear yield point occurs along with intrinsic crazing. Fig. 2a to c shows examples of these modes of deformation and fracture. In the completely brittle region the specimen fractures in several pieces (Fig. 2a). In the brittle-to-ductile transition region, the specimen breaks into two pieces with some evidence of plastic deformation at the edge of the fracture (Fig. 2b). Above 283 K shear yielding and necking is seen, and the intrinsic crazes causes whitening or "blushing" or the specimen (Fig. 2c).

Environmental effects are represented in Fig. 1 by the branch EF for N_2, GH for CO_2, and IK for water. Each environment has its particular range of temperature and pressure where it acts as a crazing agent as shown in Part 1 [2]. The deformation and fracture mode in these active environments are typified by the crazed and fractured specimen shown in Fig. 2d. What is called intrinsic behaviour is not necessarily observed only in He or vacuum; intrinsic behaviour can be observed in any environment if the temperature is sufficiently high or the pressure is sufficiently low so that the environment becomes inactive. It is possible that He produces crazes in the temperature range in the neighbourhood of its boiling point.

3.2. Environmental crazing

Figs. 3a to c, 4 and 5 show typical environmental crazes that formed in all the active environments including water. The individual crazes have the same following characteristics: (1) they tend to grow very long, (2) their thickness tends to be thin and uniform except near the tip, and (3) shear bands were not observed at the tip. The only differences that were observed in environmental crazes involved their density (no./area) and length. Appreciable differences in their thickness were not apparent.

As shown in Figs. 4 and 5, an increase in the partial pressure of the environment decreased the craze density and increased the average length of the craze. The decrease in density with increasing pressure is understandable because the maximum stress to which the tensile was exposed prior to fracture also decreases with increasing pressure of the environmental gas [2, 6]. As shown by Brown and Fischer [7] the density of crazes increases strongly with the maximum stress to which the specimen was exposed. It might be expected that the increase in partial pressure of the environmental gas would make it easier to nucleate a craze for a given stress; this effect is obscured if one only observes the specimen after fracture by means of a stress–strain test where the stress change with time.

The increase of craze length with the increase in partial pressure (Figs. 4 and 5) depends on two factors, the craze velocity and the time that the specimen was under stress. The craze velocity depends on the stress and the concentration of the environmental gas. The time under stress

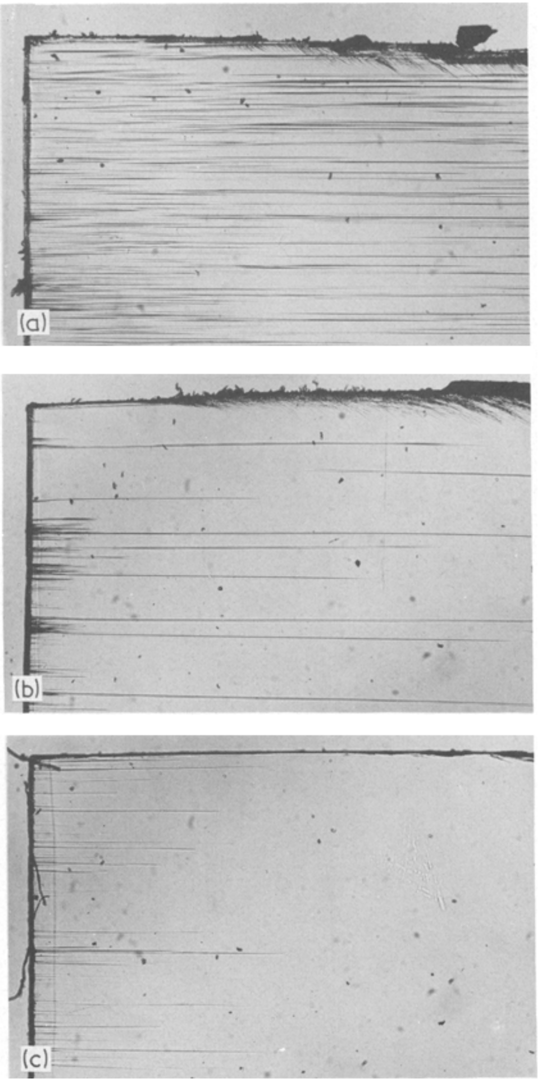


Figure 3 Typical environmental crazes in (a) N_2 77 K, (b) CO_2 196 K, (c) water 273 K, × 35.

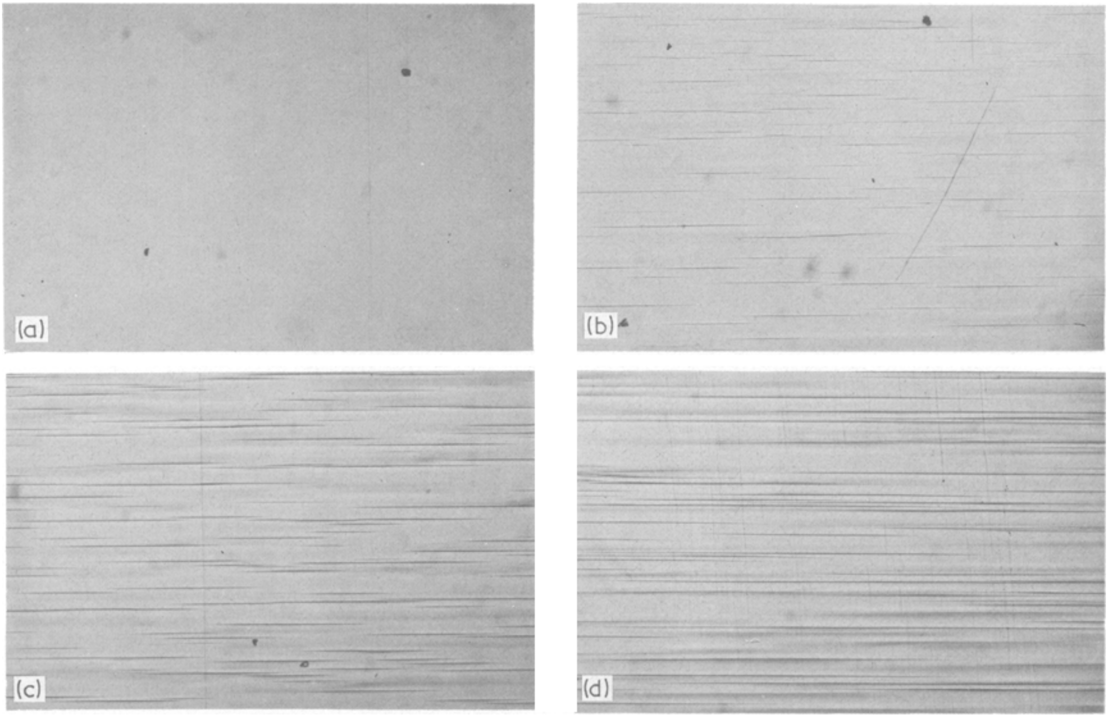


Figure 4 Effect of partial pressure of N_2 77 K on craze length and density × 35. (a) 0 atm, (b) 0.25 atm, (c) 0.50 atm, (d) 1.0 atm.

depended on the fracture strain and the strain–rate. The strain–rate was the same for all specimens and the fracture strain was not greatly different (see Part 1). The average stress to which the specimen was exposed decreased with increasing partial pressure. These results lead to the conclusion that the increase in craze length with increasing partial pressure was primarily caused by the increase in craze velocity. The connection between craze velocity and partial pressure of the environmental gas will be analysed further in the discussion.

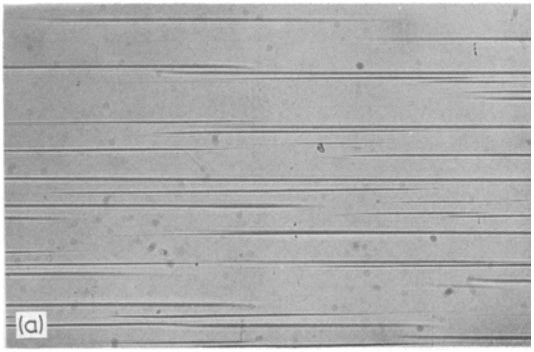
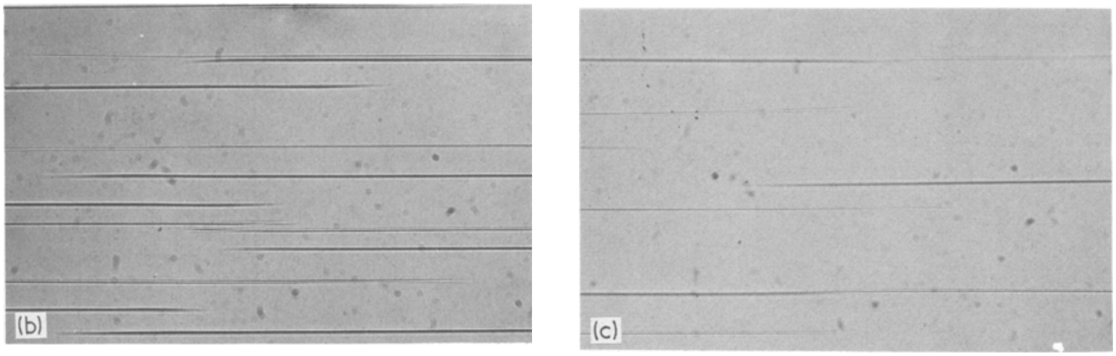


Figure 5 Effect of partial pressure of CO_2, 197 K, × 35. (a) 0.25 atm, (b) 0.50 atm, (c) 1.0 atm. At 0 atm, same as Fig. 4a.



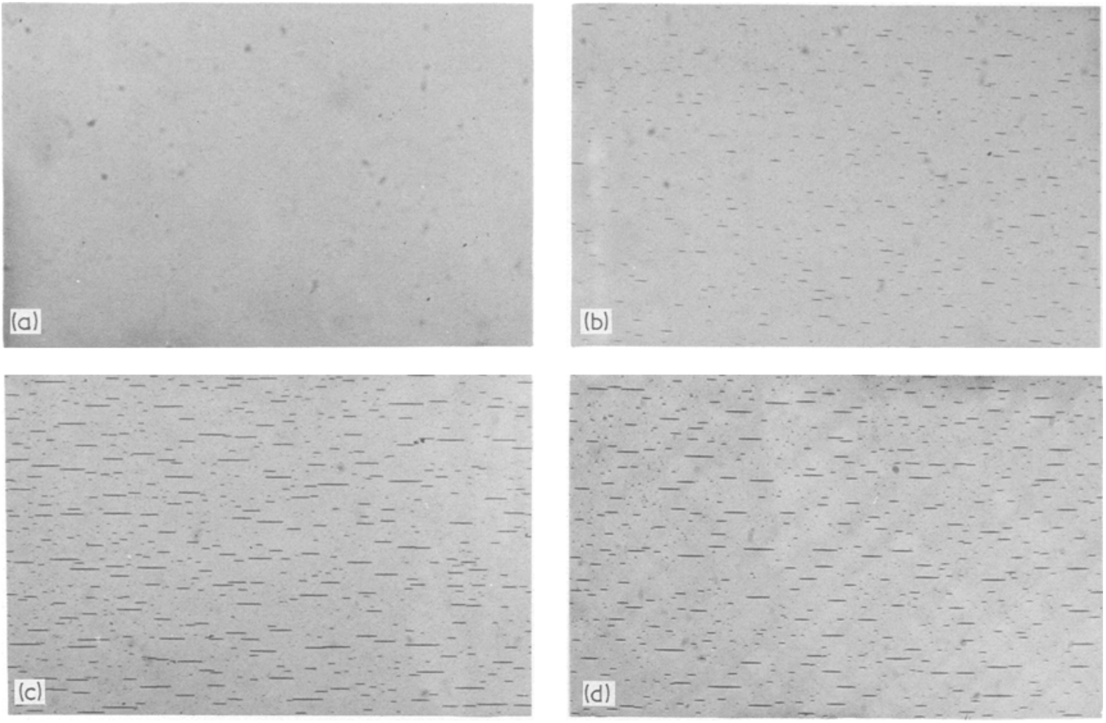


Figure 6 Intrinsic craze density as a function of temperature × 112. (a) 2.3 × 10^5 cm^{-2} at 283 K, (b) 3.4 × 10^5 cm^{-2} at 298 K, (c) 4.6 × 10^5 cm^{-2} at 319 K, (d) 4.9 × 10^5 cm^{-2} at 330 K.

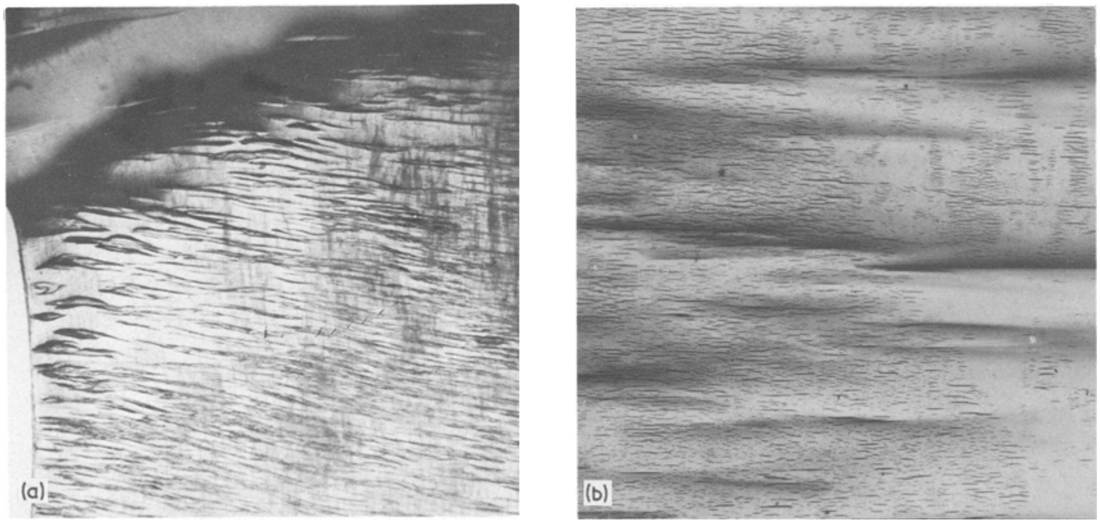
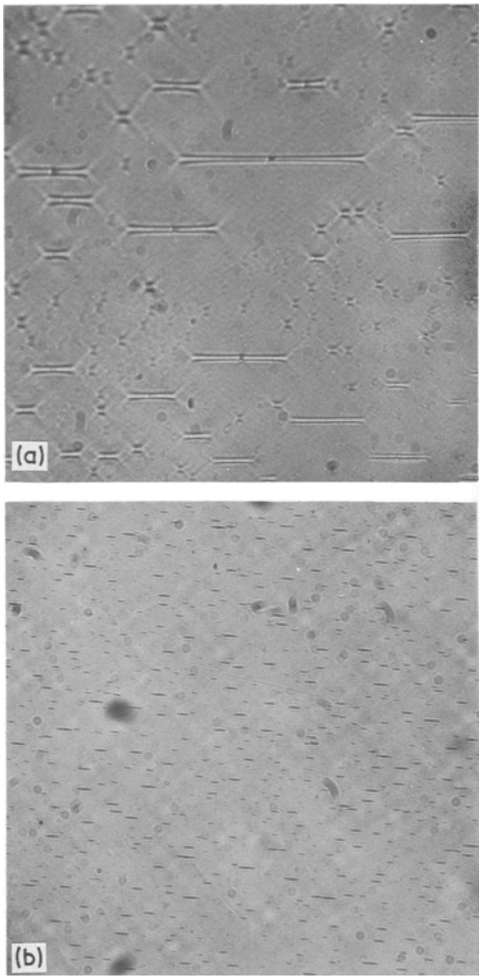


Figure 7 After 15% deformation in water at 333 K, (a) only extrinsic crazes are resolved at × 21, (b) shows short intrinsic and long environmental crazes at × 85.

3.3 Intrinsic crazing

Intrinsic crazing in He was first observed at temperatures above 283 K. Fig. 6 shows the intrinsic crazing at various temperatures. The most obvious difference between intrinsic and environmental crazes is in their length. The intrinsic crazes do not become very long. A good comparison of intrinsic and environmental crazing is provided by Fig. 7 where both types of crazes were produced at 333 K in water; the environmental crazes are 30 to 40 times longer.

The intrinsic crazes first appeared at 283 K, and their density increased with increasing temperature as follows: the density varied from 2.3 × 10^5 to



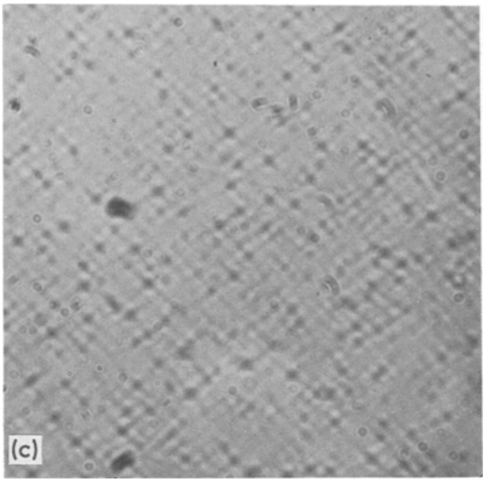


Figure 8 Intrinsic crazes and micro-shear bands. (a) 330 K, × 800 slightly out of focus, (b) 296 K, × 100 in focus, (c) same as (b) out of focus.

4.9×10^5 cm^{-2} as the temperature increased from 283 to 330 K. This is a true temperature effect since the maximum stress to which the specimens were exposed decreased with increasing temperature.

The intrinsic crazes were observed at 298 K as a function of strain. The crazes were first observed at 5% strain which is just prior to yield strain of 6%. As the strain changed from 5% to 20%, the length and density of the crazes remained nearly constant. The primary effect of the strain was to make the crazes more easily visible, presumably by making them thicker. The relationship between the intrinsic crazes and the strain became more apparent when the specimen surface was viewed slightly out of focus and shear bands were observed as shown in Fig. 8a to c. These shear bands were only observed at the ends of intrinsic crazes but not with environmental crazes. The shear bands made an angle of 45° with the craze. As mentioned above, the greater the strain the more readily visible the intrinsic crazes: the reason for this behaviour is shown in Fig. 9, where a craze at the edge of the specimen has widened considerably. This widening is attributed to the broad intense shear bands which emanate from the ends of the craze. In a following section the relationship between crazes and shear bands will be discussed more fully.

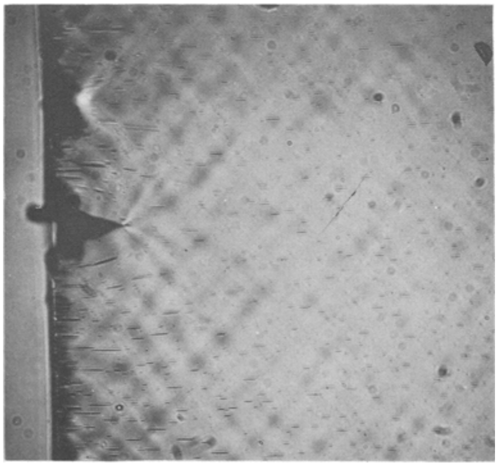


Figure 9 Widening of an intrinsic craze at edge of specimen. Shear bands emante from tip, 296 K, × 94.

3.4. Crazing in water

The stress–strain behaviour in distilled water was observed from 273 to about 333 K. The behaviour was brittle up to 319 K and only a few environmental crazes were observed in the fractured specimen. At about 333 K the specimen became very

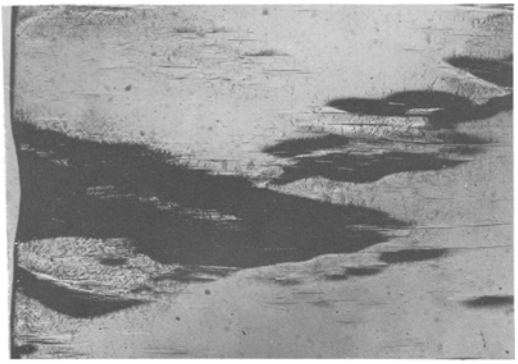


Figure 10 Same specimen as Fig. 7, but in drawn region after necking. Dark regions are massive crazes formed by the joining together of intrinsic crazes (Fig. 7a) × 14.

ductile and an upper yield point occurred. In the ductile range both environmental and intrinsic crazes occurred as shown in Fig. 7, because at about 333 K the intrinsic strength in He became nearly equal to the tensile strength in water (Fig. 1). Also at and above 333 K broad and irregular craze-like regions were observed as shown in Fig. 10. Analysis with polarized light showed that the dark regions were highly oriented parallel to the stress. It appeared that the craze density became very high in certain regions so that the smaller crazes joined together to form a massive craze.

3.5. The fracture surface

The fractured surfaces were observed after brittle fracture in He and in an active environment (Fig. 11). In all cases, part or all of the fractured surface showed crazing. Although in He no crazes were visible in the gauge section, except for a few short ones at the fracture edge, the fractured surface was partially crazed prior to fracture. Thus, it can be stated that a fracture tends to be preceded by a craze. When the fracture occurs at a very high velocity, the surface becomes very rough so that it is difficult to say whether crazing then precedes fracture. The distinction between intrinsic brittle fracture and environmental brittle fracture is arbitrary and does not involve different mechanisms. The environment only makes it possible to form a craze at a lower stress; therefore, the environmental craze can usually grow longer than the intrinsic craze before fracture occurs.

4. Discussion

4.1. Environmental crazing

As pointed out in Section 3.2, the increase in craze length with increasing partial pressure of the environmental gas is based on the increase in craze velocity. Brown [8] has suggested that for a given stress the velocity of an environmental craze depends on the diffusion coefficient of the gas into the polymer and on the surface concentration of the gas. The suggestion is based on the model of crazing where the gas very rapidly traverses the pores of the craze until it reaches the tip; then the rate determining factor is the diffusion of the gas into the tip. It is assumed that for the craze to grow, the tip must be plasticized by a critical amount depending on the stress. The critical amount of plasticization involves two factors: a critical concentration of sorbed gas and a critical depth of penetration. The above statement can be

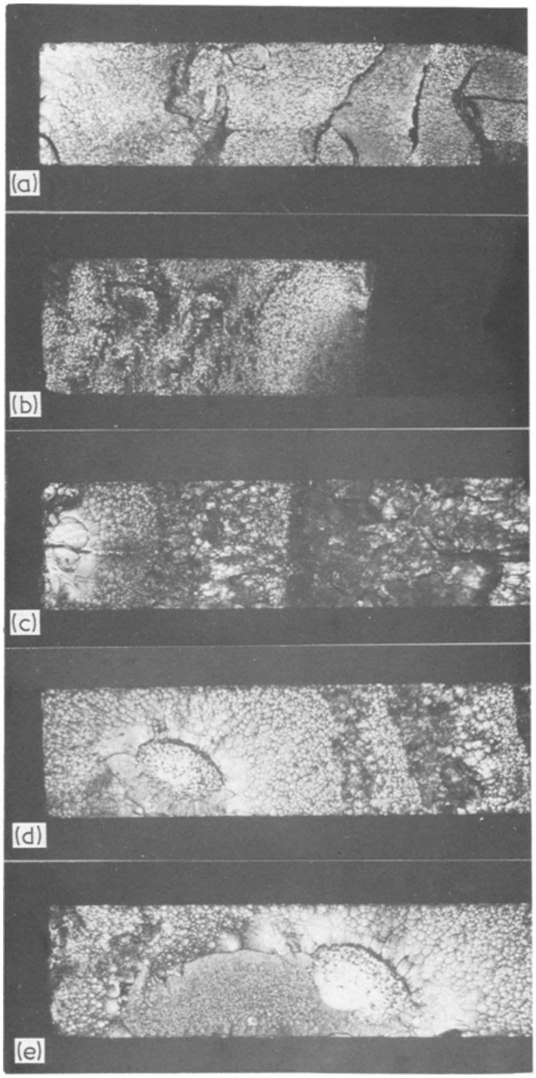


Figure 11 Fractures surface × 25. (a) 77 K in N_2, (b) 77 K in He, (c) 275 K in He, (d) 273 K in water, (e) 296 K in water.

formulated in the following equation.

$$C_c = C \exp(-X_c^2/Dt_c) \qquad (1)$$

where C_c is the critical concentration of the environmental gas; X_c is the critical depth of penetration as measured from an inner surface of the craze into the uncrazed polymer; C is the concentration of gas at the inner surface at a pressure, P; t_c is the time for the gas to penetrate the distance X_c, and D is the diffusion coefficient. The exponential in Equation 1 is a simplifying approximation to the error function which is generally more appropriate. After the polymer is plasticized to the depth X_c, the craze lengthens by an amount X_c so that the observed craze velocity v is given by

$$v = X_c/t_c. \qquad (2)$$

The surface concentration, C, depends on the partial pressure of the environmental gas.

$$C = AP \qquad (3)$$

where A is related to the adsorption coefficient. Combining Equations 1, 2 and 3

$$C_c = AP \exp |-X_c v/D|. \qquad (4)$$

As P increased, v increases in accordance with the experimental observation. The best method for quantitatively checking the relationship between v and P is the creep test where the stress is kept constant and the velocity of the individual crazes is observed directly.

4.2. Intrinsic crazing

Intrinsic crazes were observed throughout the specimen at temperatures above 283 K. Below 283 K the only evidence of crazing was on the fractured surface (Fig. 11). The intrinsic crazes were associated with micro-shear bands and they became more visible as the strain increased. The results suggested that the shear bands tend to widen the intrinsic crazes and at the same time tend to limit their growth by reducing the stress concentration at the tip (Fig. 9). In order for a craze to continue growing it must maintain the stress concentration at the tip. A similar situation occurs in metals where crack growth is impeded by blunting of the crack by plastic deformation. Olf and Peterlin [5] observed that intrinsic crazes became shorter and wider in polypropylene as the temperature increased; this observation is consistent with our suggestion that the greater ease of shear deformation involved at the higher temperature tends to blunt and widen crazes.

4.3. The relationship of crazes and shear bands

It is suggested two that shear bands occur at each tip of all crazes when the craze is first nucleated since the shear bands tend to be formed by the stress field of the craze. The double shear tends to cavitate the polymer at the tip and cause the craze to grow in length; at the same time the double shear tends to blunt the existing craze. Whether growth or blunting predominates depends on the extent of the shear bands as shown in Fig. 12. In Fig. 12a the shear bands are wide and long so that the blunting process predominates as is the case for intrinsic crazes. The large shear bands would be encouraged by a low shear yield strength throughout the polymer as is expected at high temperatures.

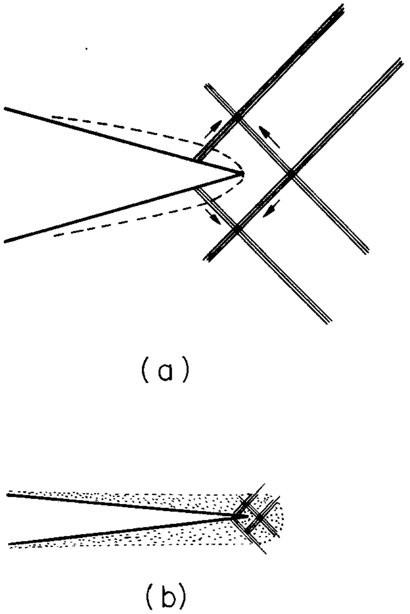


Figure 12 Model showing relationship of craze and shear bands. (a) Broad shear bands tending to widen craze. Arrows show directions of shear; tensile stress is vertical; (b) environmental craze with surrounding plasticized region (dotted). Smaller shear bands confined to plasticized region. Stress as in (a).

The case of environmental crazes is shown in Fig. 12b when there is only a small plasticized micro-volume of polymer at the tip of the craze. Under these conditions the shear bands are narrow and short. The double shear causes craze growth, but the bands are too narrow to blunt the existing craze. The bands are also so short that they are continually obliterated as the craze grows into the plasticized micro-volume of material that surrounds it. Long, narrow intrinsic crazes can also occur at low temperatures as observed by Olf and Peterlin [5] in PP because at low temperatures the shear yield stress is very high so that it can only be exceeded at the high stresses very near the tip. In the case of PMMA, similar behaviour is expected at low temperatures, but its shear yield point is so very high compared to its fracture strength that the very first craze that forms is immediately preceded by brittle fracture before other crazes can be nucleated. Matsushige *et al.* [9] investigated the effects of hydrostatic pressure on crazing and shear bands in PMMA; they also emphasized the point that "shear bands function as craze stoppers."

5. Summary and conclusions

Environmental crazes tend to grow long before they are terminated by fracture, and shear bands are not observed at their tips because environmental craze growth involves only a micro-volume of plasticized polymer.

The craze velocity increases with the partial pressure of the environmental gas because the rate determining factor is the diffusion of the gas into the polymer at the tip of the craze.

Intrinsic crazes are terminated by shear bands in PMMA. These shear bands, at elevated temperature, tend to limit the growth by blunting the tip of the craze.

All brittle fractures, both intrinsic and environmental, are preceded by a craze at least during the initial stage of fracture.

Almost any environment under the proper conditions of stress, temperature, and pressure, can enhance crazing in PMMA.

Acknowledgements

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