

# THE MECHANICS OF CRAZE GROWTH IN THE PRESENCE OF LIQUIDS

J. G. WILLIAMS, G. P. MARSHALL, I. GRAHAM\* and E. L. ZICHY†

*Department of Mechanical Engineering, Imperial College, London, UK*

## ABSTRACT

A model for the growth of crazes in the presence of liquids is described in which it is assumed that craze growth rate is controlled by the fluid flow through the porous structure of the craze. This model is used to describe observations on craze growth and the occurrence of crazes in unnotched specimens. The effects of soaking are also described and an explanation is suggested for the fact that degassing the liquid has a pronounced effect on craze growth.

## INTRODUCTION

The occurrence of fracture is one of the most important limiting factors on the increasing use of plastics. Brittle failures in supposedly tough materials are frequently encountered in the plastics industry and the advancement of some understanding of the subject is of commercial value as well as academic interest. Perhaps the most puzzling aspect of many failures in practice is the effect of fluids. Their bulk absorption by the polymer is generally rather slow but the presence of stress and small flaws leads to fracture in very short times. This paper looks at this problem from the somewhat unusual aspect of mechanics rather than that of physical chemistry in the hope of gaining a fresh perspective.

Fracture mechanics is concerned with describing stressed and flawed systems, and its utility when applied to polymers is now well established<sup>1</sup>. A model which explains fluid–solid interaction in terms of this theory has been proposed<sup>2,3</sup> and it will be used here. A series of observations on craze growth in polymers in the presence of fluids will be described and explanations for the effects observed will be proposed. It is hoped that these concepts will be of value in the more conventional chemical studies.

## AN OUTLINE OF BASIC CONCEPTS

The rapidity of action of some fluids is usually ascribed to the fact that the application of stress to a flawed structure results in a high strain concentration at the flaw tip. The material is extended in the direction of the load but constrained from lateral contraction by the surrounding material so that local voiding occurs. This results in porous material with a high area to

\* Now at Department of Polymer and Fibre Science, UMIST.

† ICI Plastics Division, Welwyn Garden City, Hertfordshire.

volume ratio at the flaw tip so that the fluid is absorbed very rapidly locally since the distance of penetration required is small. This causes plasticization of the deformed zone and a consequent reduction in load carrying capacity so that further material is highly deformed beyond the plasticized zone.

The plasticization leads to increased extension which sometimes gives immediate failure (a strain criterion in the tip zone is a reasonable concept) so that environmental stress cracking occurs. A stable porous structure, called a craze, can form at the flaw tip because of rapid work hardening of the ligaments within the structure. This process can occur in the presence of fluids since the extending ligaments can stabilize even when plasticized, leading to the growth of the craze from the flaw tip. The fluid must pass through the existing, softened craze to continue the plasticization process and there are two possible controlling rates. One is the bulk absorption within the craze, which is assumed to be fast, and the other is the flowrate through the pores.

It is assumed in the model used here that the latter is the slower and therefore controlling process. The formation of the new craze is assumed to open up voids with effectively zero internal pressure so that the driving force is the difference between the atmospheric pressure  $\bar{P}$  and the back pressure resulting from the pressure of the fluid in these voids. Darcy's law for porous flow is assumed to hold and the pore sizes are computed from the displacement at the flaw tip. This latter quantity, known as the crack opening displacement (COD), can be computed from the stress intensity factor  $K$  for any stress and crack system, together with the yield stress and the modulus of the material. For example, for an infinite plate under a stress  $\sigma$  and containing a crack of length  $2a$  we have

$$K = \sigma(\pi a)^{\frac{1}{2}}$$

and this may be combined with the general result for COD, i.e.

$$u = K^2/\sigma_y E$$

to find the appropriate value of  $u$ . The pore area is related to  $u$  by assuming a deformation model which results in

$$\text{void area} \propto u l_0$$

where  $l_0$  is the intrinsic distance between the pores, i.e. the void spacing. The combination of all these factors results in an expression for the velocity of flow of the form

$$\dot{x} \propto \frac{l_0 K^2}{\mu \sigma_y E} \times \frac{d\bar{P}}{dz}$$

where  $\mu$  is fluid viscosity and  $d\bar{P}/dz$  is the pressure gradient.

There are two types of behaviour which are observed with the usual single-edge notched specimens as shown in *Figure 1(a)*.

(a) End flow. In this case flow is directly along the craze so that  $d\bar{P}/dz = \bar{P}/x$ , and by integration we have an expression for growth in the form

$$x \propto K t^{\frac{1}{2}}$$

where  $t$  is the elapsed time.

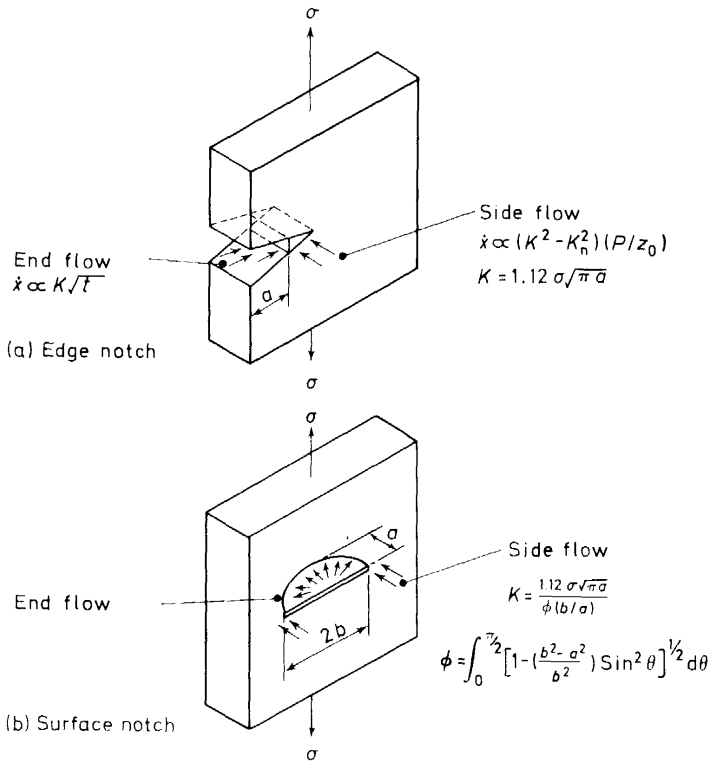


Figure 1. Fluid flow into crazes.

(b) Side flow. In this case the fluid enters the side of the specimen above some value of  $K$ , say  $K_n$ , so that the pressure drops over a constant distance, say  $z_0$ , and we have a constant speed

$$\dot{x} \propto (K^2 - K_n^2) \cdot \frac{\bar{P}}{z_0}$$

A surface notch is also shown in Figure 1(b) in which the penetration is of the end-flow type while the growth along the surface is at constant speed for  $K > K_n$ . The appropriate expressions for  $K$  for the two geometries are given in Figure 1.

These simple concepts will now be illustrated with data taken from some different test conditions.

### UNNOTCHED SPECIMENS

A series of tests were performed on unnotched PMMA specimens in which the central sections were completely immersed in a number of liquids. The specimens were then loaded at a fixed rate ( $0.5 \text{ cm min}^{-1}$ ) in an Instron testing machine and the load at which crazes were first observed was noted.

Table 1 gives the liquids used and the initiation stress  $\sigma_i$  together with values of the solubility parameter<sup>6</sup> and the fluid viscosity. It is apparent from the results that there are two distinct types of behaviour. The first three liquids in Table 1, namely acetic acid, methanol, and ethanol, give significantly lower values of  $\sigma_i$  than the rest listed. This difference is also shown in the crazing observed since all three gave a few well developed crazes as shown in Figure 2(a) for methanol while the rest gave a large number of small crazes as shown in Figure 2(b) for heptane. It would appear that if the liquid is a sufficiently good solvent then the smaller crazes are removed by surface plasticization while the larger ones grow rapidly at low stress levels. For the less effective solvents all the crazes continue to grow slowly and there is little surface plasticization.

Table 1

No.	Environment	Solubility parameter (cal cm <sup>-3</sup> ) <sup>‡</sup>	Viscosity (cP)	$\sigma_i$ (MN m <sup>-2</sup> )
1	Acetic acid	10.1	1.3	17.8
2	Methanol	14.5	0.59	21.2
3	Ethanol	12.7	1.22	21.5
4	Butanol	11.4	2.95	28.3
5	Hexane	7.3	3.33	31.0
6	Heptane	7.4	0.41	38.0
7	Formaldehyde	12.2	3.3	38.3
8	Carbon tetrachloride	8.6	0.97	40.0
9	Ethylene glycol	14.6	19.7	40.3
10	Paraffin	7.8	1.16	47.0
11	Water	23.5	1.0	52.4
12	White spirit	~ 6.9	0.87	59.6
13	Adinol (detergent)		350.0	64.3
14	Air		0.018	67.8

Bernier and Kambour<sup>4</sup> have pointed out that a propensity to stress cracking and crazing can be described in terms of the solubility parameter (SP) and Figure 3 shows  $\sigma_i$  as a function of SP. The curve is similar to that reported in reference 4 from quite different tests and shows a marked minimum in  $\sigma_i$  where there is a close match of solubility parameter between the fluid and the polymer [SP for PMMA  $\approx 11$  (cal cm<sup>-3</sup>)<sup>‡</sup>]. This simply means that good solubility of liquid and polymer results in preferential craze growth but while this is a necessary condition it is not sufficient<sup>5</sup>. This is illustrated by ethylene glycol which has a good solubility match but exhibits a high crazing stress. This may be attributed to the very high viscosity of ethylene glycol which inhibits craze growth even though there is high solubility.

The mechanics of how these crazes grow can be considered in terms of the model. Accordingly some tests were performed at various constant stresses with cells of one inch diameter filled with liquid and clamped to the surface to test its predictions. Only the low stress crazing liquids were

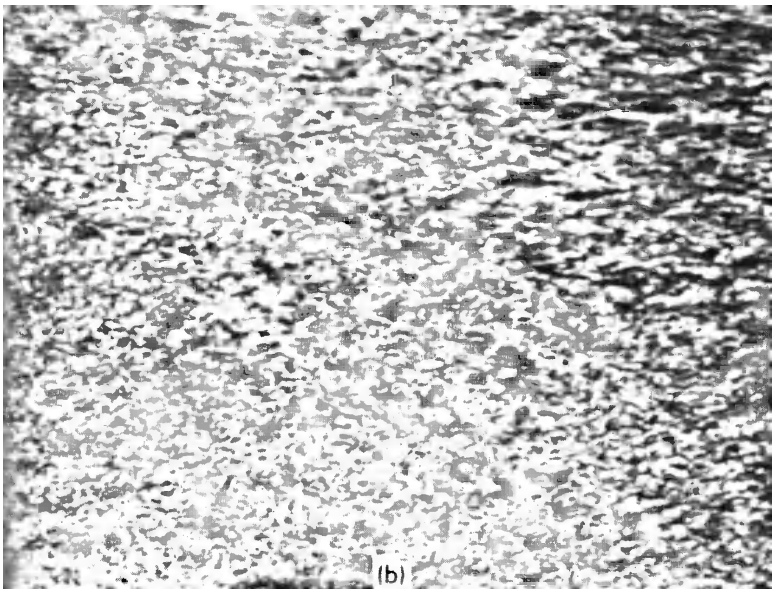


Figure 2. Types of crazing pattern : (a) methanol ; (b) n-heptane.

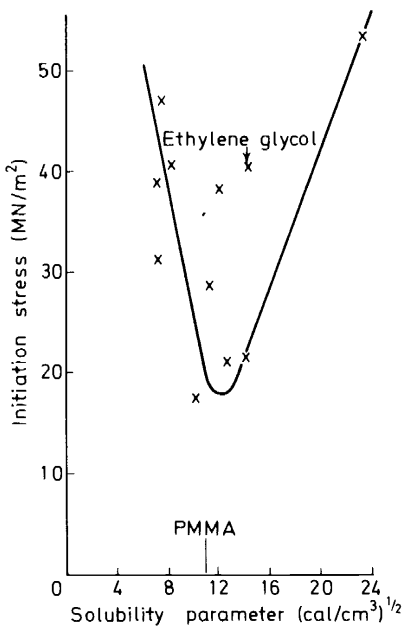


Figure 3. Craze stresses as a function of solubility parameter.

used so that there were few crazes and it was possible to determine by direct observation the number of crazes as a function of time and also the speed of growth of individual crazes. For example, *Figure 4* shows the growth curves for crazes in PMMA in methanol and the expected constant-speed behaviour is observed. Since data are known for induced cracks<sup>2</sup> and various stresses

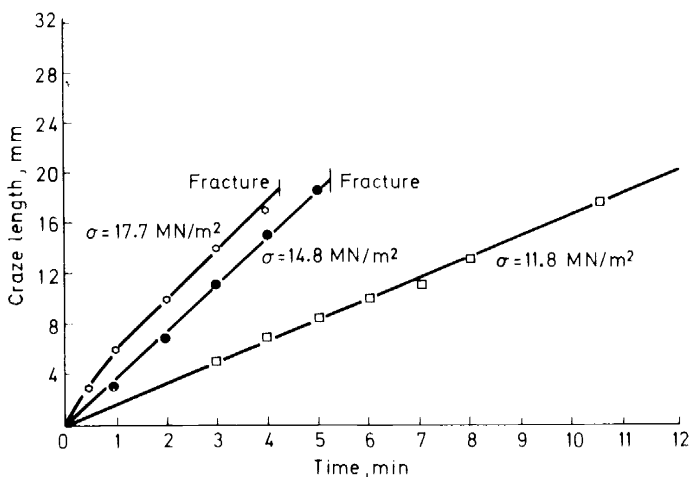


Figure 4. Craze growth in PMMA in methanol for unnotched specimens.

THE MECHANICS OF CRAZE GROWTH IN THE PRESENCE OF LIQUIDS

are used it is possible to deduce the average flaw size here in a similar manner to the usual Griffith analysis. This gives a value of around 1 mm which suggests that the flaws grow or perhaps amalgamate in the early stages of craze growth since this value is considerably greater than one would expect. Such flaws can be observed around the initiation area of the growing craze.

This constant-speed growth behaviour can be invoked to describe the occurrence of crazes as a function of time and it will be assumed that a craze may be identified when it achieves a length of  $x_0$ . Since

$$\dot{x} = c(K^2 - K_n^2)$$

where  $c$  is a constant and

$$K = \frac{1.12 \sigma(\pi a)^{\frac{1}{2}}}{\phi} \quad (\text{see Figure 1})$$

(since this is a surface craze), then the time for a flaw of depth  $a$  to achieve a length  $x_0$  (for  $b \ll x_0$ , where  $2b$  is the original flaw width) is given by

$$t = x_0/2c \left( \frac{1.24\sigma^2\pi a}{\phi^2} - K_n^2 \right)$$

and at this time all flaws with lengths of  $a$  or greater are therefore visible. If a cumulative distribution function of exponential form is used then

$$N = N_0 e^{-a/\bar{a}}$$

where  $N_0$  is the total number of flaws per unit area,  $N$  is the number whose size is  $a$  or greater and  $\bar{a}$  the mean size and we have

$$\ln \frac{N}{N_0} = - \frac{\phi^2}{1.24 \sigma^2 \pi \bar{a}} \left\{ K_n^2 + \frac{x_0}{2ct} \right\}$$

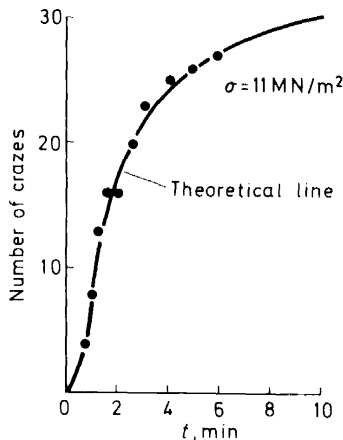


Figure 5. Crazes appearing in PMMA in the presence of ethanol.

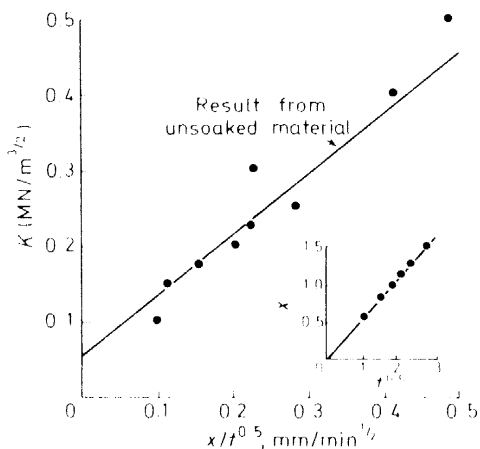
This function is shown in *Figure 5* plotted as  $N$  (here the number in a one-inch diameter circle) versus  $t$  with the constants fitted together with data obtained for PMMA in ethanol at a stress of  $11 \text{ MN m}^{-2}$ . The form is a reasonable fit to the points and preliminary results indicate that the various parameters are reasonable in magnitude (e.g.  $N_0 \approx 40 \text{ cm}^{-2}$ ).

### THE EFFECTS OF SOAKING

In unnotched specimens the effect of bulk absorption was apparent when good solvents were used since the plasticization of the surface removes the smaller flaws. If an edge notch is present, the model would predict that soaking should not effect end flow since there will simply be a thicker plasticized skin on the specimen surface. Tests were performed in methanol on edge-notched PMMA specimens which were soaked for twelve hours in methanol before testing. At low  $K$  levels, where there is end flow, it is convenient to plot  $K$  versus  $x t^{1/2}$  since

$$K \propto x t^{1/2}$$

and the line obtained for unsoaked material<sup>2</sup> is shown in *Figure 6* together with points obtained for the soaked specimens. As expected, there is no discernible effect of soaking.



*Figure 6.* The effect of prior soaking on end flow behaviour.

When side flow occurs, however, the model would suggest that  $z_0$ , the side-pressure drop distance, would increase giving slower speeds for a given  $K$ . *Figure 7* shows some results obtained with soaked specimens plotted as  $K^2$  versus  $\dot{x}$  and there is a significant decrease in speeds.  $K_n$  changes very little, if at all, but the implied change in  $z_0$  to, say,  $z_1$ , is given by the ratio

$$z_1/z_0 = 2.5$$

Since bulk absorption will be approximately proportional to  $t^{1/2}$  the ratio of



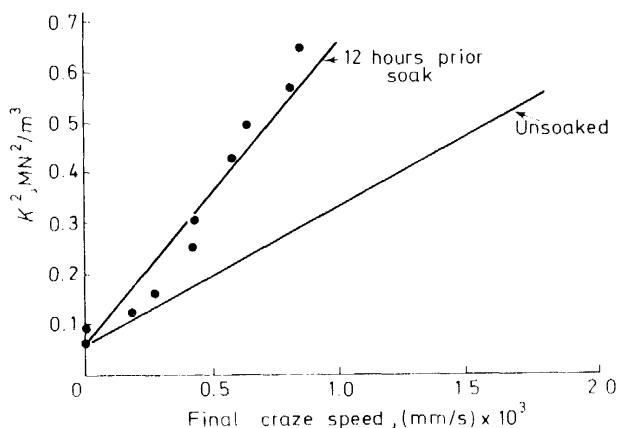


Figure 7. The effect of prior soaking on side flow behaviour.

penetration distances implies a soaking time ratio of about six, which is reasonable since tests normally lasted from two to three hours.

### THE EFFECTS OF DISSOLVED GASES

A related, and rather remarkable, phenomenon came to light during the course of these tests. It was sometimes observed that gas bubbles formed in the crazes and it was suggested that this may have been due to gas coming out of solution in the crazing agent in the low pressure of the craze cavities. To test this, some methanol was degassed by boiling under reflux and the tests repeated. There was a totally unexpected effect in that the crazes grew at much greater speeds in this liquid. The effect is well illustrated in *Figure 8* in which a craze is grown at a fixed  $K$  of  $0.65 \text{ MN m}^{-3/2}$  and the surrounding methanol changed. The degassed methanol gave a speed of  $3.90 \times 10^{-3} \text{ mm s}^{-1}$  compared with the expected value of around  $1.5 \times 10^{-3} \text{ mm s}^{-1}$ . If nitrogen was bubbled through the methanol as the test proceeded the speed dropped quite rapidly to a constant value of  $0.89 \times 10^{-3} \text{ mm s}^{-1}$ . Replacing the degassed methanol with 'natural' methanol resulted in a speed of  $1.54 \times 10^{-3} \text{ mm s}^{-1}$  as expected but nitrogen bubbled through this gave a similar speed to the previous case, i.e.  $0.85 \times 10^{-3} \text{ mm s}^{-1}$ . Returning to degassed methanol gave a similar speed to the original phase.

This observation can be accounted for by considering that the affinity of methanol to inert gas is much less than that of PMMA to methanol. Consequently methanol will lose part of its dissolved gas as it associates with and swells PMMA. The model predicts that the speed of craze propagation is proportional to the driving pressure difference, and one can estimate therefore the effective back pressure produced by 'natural' and gas-saturated methanol, if it is assumed that in the presence of excess (not yet adsorbed) of pure methanol in the voids, the back pressure equals its vapour pressure, i.e. at room temperature  $\sim 0.23 \text{ bar}$ . These estimates are  $0.45 \text{ bar}$  for 'natural'

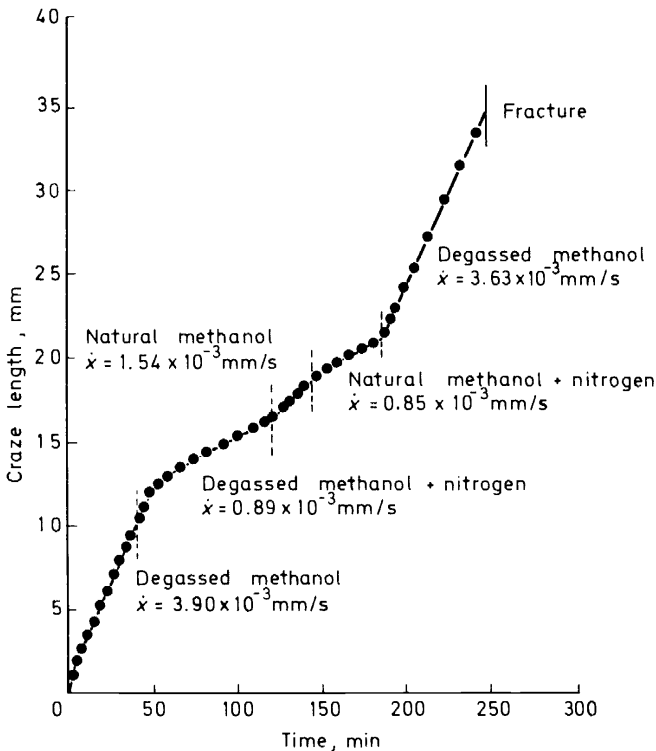


Figure 8. The effect of gas dissolved in methanol on craze growth in PMMA.

and 0.59 bar for gasified methanol. It is not possible to estimate the amount of gas lost from the methanol to produce these back pressures because the exact geometry of the voids is not known. However, one can calculate that a given volume of liquid methanol would have to release 0.0275 and 0.045 weight per cent of gas to produce these pressures in the same volume filled now with methanol vapour and gas. The figures seem reasonable given that the saturation concentration of nitrogen in methanol is quoted as  $\sim 0.024$  weight per cent<sup>7</sup>. This effect can be shown by the development of gas bubbles when finely divided PMMA and methanol are brought into contact.

## CONCLUSIONS

The various phenomena described here have all been capable of rational explanation by use of the porous-flaw model for craze growth. Some of the work is at an early stage but there are clear indications that the parameters involved give sensible numerical values. This quantitative predictive capability is a feature of the mechanics model of the process. It is felt that the results given here are further evidence that the model is essentially correct and likely to be of value.

ACKNOWLEDGEMENTS

The authors thank Mr. McDonagh who performed some of the unnotched tests. They also acknowledge the financial support of this work by S.R.C.

REFERENCES

- <sup>1</sup> G. P. Marshall, L. E. Culver and J. G. Williams, 'Crack and craze propagation in polymers: a fracture mechanics approach. Crack growth in polymethylmethacrylate in air', *Plastics and Polymers*, pp. 75-80 (1969).
- <sup>2</sup> G. P. Marshall, L. E. Culver and J. G. Williams, 'Craze growth in polymethylmethacrylate— A fracture mechanics approach', *Proc. Roy. Soc. A*, **319**, pp. 165-187 (1970).
- <sup>3</sup> G. P. Marshall and J. G. Williams, 'Thermal and environmental effects in craze growth and fracture', *Proc. Battelle Conference*, Kronberg (1972).
- <sup>4</sup> G. A. Bernier and R. P. Kambour, 'The role of organic agents in the stress crazing and cracking of poly-(2,6-dimethyl-1,4-phenylene oxide)', *Macromolecules*, **1**, 5, 393-400 (1968).
- <sup>5</sup> P. I. Vincent and S. Raha, 'Influence of hydrogen bonding on crazing and cracking of amorphous thermoplastics', *Polymer*, **13**, 283 (1972).
- <sup>6</sup> *Polymer Handbook*, pp. vi 347. (edited by J. Brandrup and E. H. Immergut). Interscience: New York (1966).
- <sup>7</sup> *Solubility of Inorganic and Organic Compounds*, Vol. 1, p. 1141, ed. H. Stephen and T. Stephen, Pergamon: Oxford (1963).