JOURNAL OF MATERIALS SCIENCE 17 (1982) 2047–2055

Fracture of a plasticized epoxide under superposed hydrostatic pressure

A. S. WRONSKI, T. V. PARRY
School of Materials Science, University of Bradford, West Yorks, UK

The deformation and fracture behaviour of rubber-coated and uncoated epoxy specimens has been studied under superposed hydrostatic pressures extending to 300 MN m^{-2}. Maximum shear stress at yield for this epoxy were about 25 MN m^{-2} at atmospheric pressure and rose to about 48 MN m^{-2} at 300 MN m^{-2} superposed pressure. Yielding and failure of all specimens tested beyond pressures of 75 MN m^{-2} took place when all the (macroscopic) principal stresses, though unequal, were compressive. Fractographic examination revealed three distinct zones of the failure surfaces at atmospheric pressure. The behaviour of all uncoated specimens and those coated and tested below 100 MN m^{-2} was similar. A fracture-mechanics interpretation of failure could be applied to these tests assuming the deformation-produced first zone was the fracture initiating site. Coated samples tested beyond 100 MN m^{-2} superposed pressure failed with no evidence of Zones II or III of failure; Zone I appeared to spread over the entire failure surface. An interpretation involving fluid penetration of Zone I failure nuclei, along the lines suggested by Duckett, can account for the failure stresses of the uncoated specimens but is not tenable for the coated samples. It appears that crack nucleation and (slow) growth, as opposed, perhaps, to (catastrophic) crack propagation, can take place in this polymer when all the principal stresses are compressive.

1. Introduction

Duckett has recently proposed for polymers an elegant interpretation of the transition from crazing or fracture to shear yielding and vice versa with increasing superposed pressure [1]. He considered the role of stress concentration sites in generating high local tensile stresses and showed that for both a large stress concentrator, K, and fluid penetration of the surface flaw, superposed pressure will have a negligible effect on crack propagation. This could thus take place when the nominal stress field was purely compressive. He distinguished between the behaviour of uncoated and coated specimens and concluded that, without fluid penetration, it is extremely unlikely that brittle failure will result from a flaw at high pressure.

Duckett's model satisfactorily interprets numerous results [1], but appears incompatible with failure taking place from an internal flaw when all the principal stresses, though unequal, are compressive. Such behaviour, however, has been reported by Wronski and Pick for an epoxide (see Fig. 5 of [2]). An additional general problem of interpretation of fracture of polymers which fail by crack propagation concerns those whose stress—strain curves (e.g., Fig. 1b) exhibit a maximum before the fracture stress is reached. A question arises as to why a flaw, if present at the surface or elsewhere, did not nucleate failure at the maximum stress. It seems that an interpretation requires a postulate of cracks which are nucleated and grow to the critical size by a crazing or shear yielding process [3]. It has been suggested that crazing itself is nucleated by micro-shear bands [4] and there is little evidence of it in epoxides [5]. Accordingly, it is considered that crack nucleation in epoxides can be a, possibly pressure dependent, process associated with post-yield straining. It should be added that, in another epoxide, orthogonal shear band were observed at about 45° to the straining direction in close proximity to the failure surfaces [2].

0022–2461/82/072047–09$03.58/0

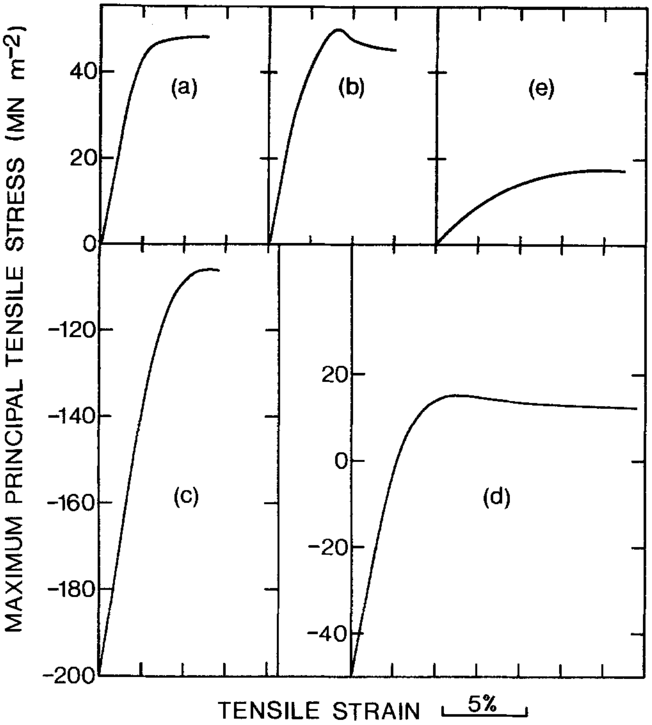

Figure 1 Nominal stress–nominal strain curves for epoxide specimens tested: (a) and (b) at atmospheric pressure and temperature, (c) and (d) under superposed pressures of 200 MN m^{-2} (uncoated) and 50 MN m^{-2} (coated), respectively, and (e) at 50° C at atmospheric pressure.

2. Experimental procedure

The epoxide for the investigation, in the form of 6 mm thick plate (normally used to manufacture photoelastic test specimens) was made by Norwood Instruments Co., of Huddersfield. The system was Ciba-Geigy MY 753/HT 901, bisphenol-A-diglycidyl ether monomer plasticized with dibutyl pthalate and cured with pthalic anhydride.

Double-shouldered round tensile specimens with a gauge length of about 12 mm and gauge diameter of about 2 mm were machined and polished prior to testing. This was performed in uniaxial tension at a cross-head speed of 10^{-4} mm sec^{-1} on a Hedeby Universal Testing Machine fitted with a Coleraine pressure cell, details of the technique have been given previously [2]. The pressurizing fluid was Plexol, a synthetic diester. Prior to testing, half of the specimens were coated with several layers of rubber, deposited from a solution, to prevent ingress of the fluid into surface flaws or deformation-induced cracks.

Specimen failure surfaces were examined using optical and scanning electron microscopes. Some samples were mounted in polyester resin, sectioned and polished parallel to the tensile axis for observation by reflection optical microscopy.

3. Results

In uniaxial tension at atmospheric pressure some specimens exhibited a load maximum (e.g., Fig. 1b) and some did not (e.g., Fig. 1a). For the former, the maximum force before the load drop and the original cross-sectional area were used to calculate the yield stress, of 49 ± 3 MN m^{-2}. This strength corresponds well with the stress at the apparent limit of proportionality, taken to be the yield stress for the latter specimens. Following yielding, deformation continued to about 6% strain and failure occurred by crack propagation (e.g., Fig. 2a).

When tensile tests were carried out under superposed pressure, the shear stress for yielding was found to increase with superposed pressure (see Fig. 3). The data are consistent with a pyramidal yield criterion [2] with the uniaxial tensile, uniaxial compressive and bi-axial compressive strengths being 49 ± 3, 67 ± 3 and 61 ± 3 MN m^{-2}, respectively. Again, some samples showed stress maxima (e.g., Fig. 1c) and some did not (e.g., Fig. 1d) before deformation to higher strains. There was no systematic variation of failure strain with superposed pressure; the strains in the uncoated specimens, however, were consistently smaller, never exceeding 10% (e.g., Fig. 1c). Drawing was observed in some coated specimens, such that nominal failure strains reached about 20% (e.g., Fig. 1d). The eventual separation was then observed to take place, sometimes through the

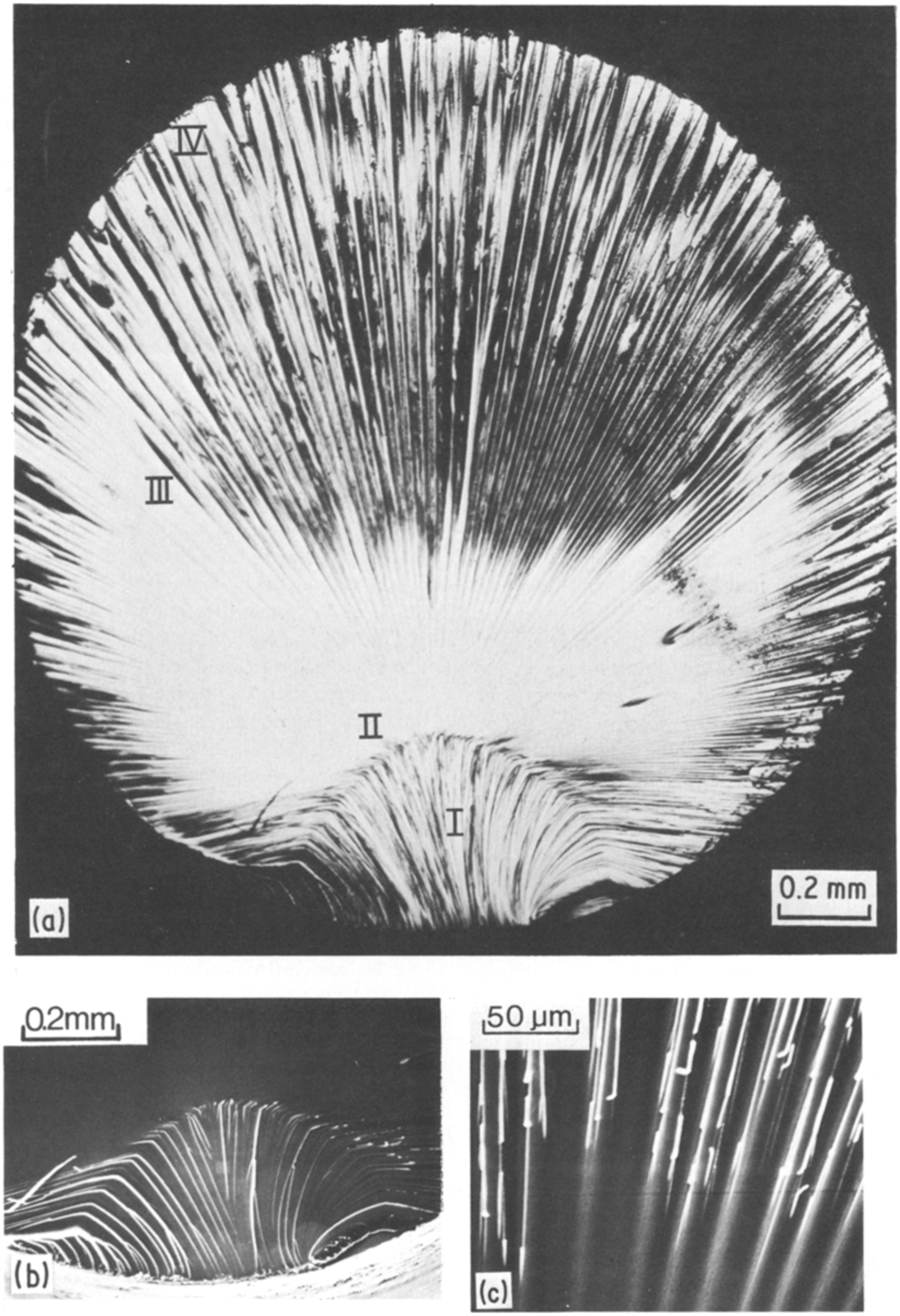

Figure 2 Fractographic observations of atmospheric failure: (a) general features with Zones I, II, III and IV indicated; (b) Zone I; (c) "ribs" in Zone III; (c) chips near the Zone I–Zone II boundary [from a different specimen from that in (a)]; and (e) "parabolic marking", Zone IV, at the extremity of Zone III.

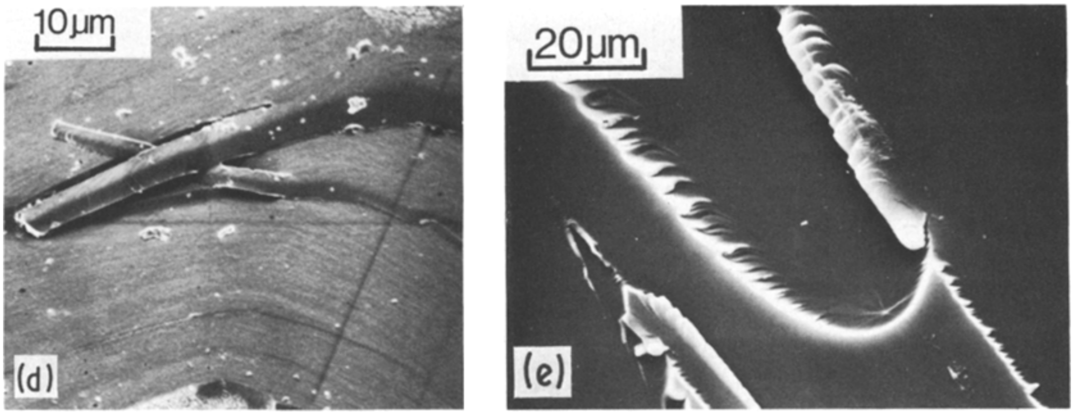

Figure 2 Continued.

drawn region (e.g., Fig. 4a), and at other times outside the drawn region (e.g., Fig. 4b). All the principal stresses were compressive for yielding and for failure of the uncoated specimens above 62 MN m^{-2} superposed pressure. For the coated specimens, the critical pressure for failure was 66 MN m^{-2}.

Stresses at failure were calculated from the fracture load and final cross-sectional area. For those samples that did not neck these values were consistent with calculations which assume deformation at constant volume. The data indicate that fractures took place at superposed tensile stresses not markedly different to those for yielding (see Table I).

When failed specimens were examined by optical and scanning electron microscopy, a large variation in the fractographic details of nominally identical specimens which failed in the same stress system was noted. Only general features therefore will be described. At atmospheric pressure there was always a failure-initiation region, approximately crescent-shaped and about 0.5 mm deep (e.g., Fig. 2b), which we term Zone I. From Zone I, cracking spread with a change in propagation direction into a fairly featureless Zone II and Zone III of the same direction of crack propagation. Zone III had easily discernible "ribs" parallel to the crack propagation direction (e.g., Fig. 2c). Other features, particularly near the Zone I–Zone II boundary, have been described as [6] "chips" (e.g., Fig. 2d, taken from another specimen). Zone I features resembled those of a region of "slow crack growth" reported for polysulfone [7]. Sometimes more than one Zone I-type region was found on the failure surface, but only the largest was associated with Zone II of crack propagation. Outside of Zone III there was sometimes an area of parabolic markings (e.g. Fig. 2e), Zone IV, whose features resemble those of the fast crack-

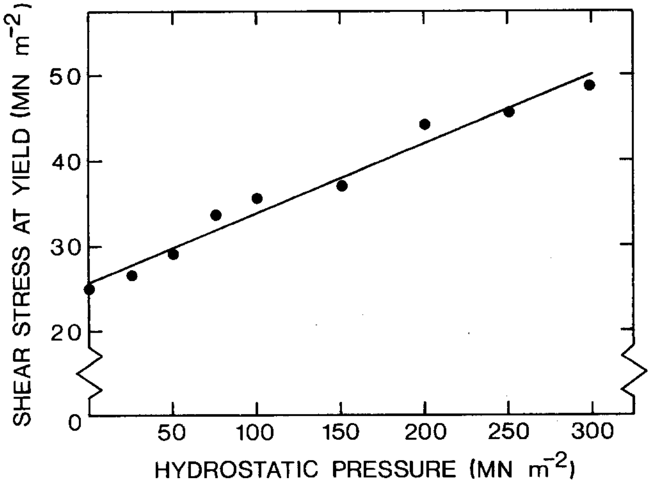

Figure 3 The dependence of maximum shear stress at yield on superposed hydrostatic pressure.

TABLE I Yield and fracture-strength data for coated and uncoated epoxide specimens tested in tension under superposed hydrostatic pressure.

Stress ($MN\ m^{-2}$)	Pressure ($MN\ m^{-2}$)								
	Atmospheric pressure	−25	−50	−75	−100	−150	−200	−250	−300
Maximum principal stress at yield	50 ± 3	28 ± 4	8 ± 6	−7 ± 7	−28 ± 5	−76 ± 3	−111 ± 4	−158 ± 3	−203 ± 4
Superposed tensile stress at yield	50 ± 3	53 ± 4	58 ± 6	68 ± 7	72 ± 5	74 ± 3	89 ± 4	92 ± 3	97 ± 4
Maximum principal stress at fracture (coated)	57 ± 6	29	13	−11 ± 4	−20	−55	−112	−144	−197 ± 3
Superposed tensile stress at fracture (coated)	57 ± 6	54	63	64 ± 4	80	95	88	106	103 ± 3
Maximum principal stress at fracture (uncoated)	57 ± 6	32	6	−11 ± 3	−30	−70	−110	−156	−195 ± 4
Superposed tensile stress at fracture (uncoated)	57 ± 6	57	56	64 ± 3	70	80	90	94	105 ± 4

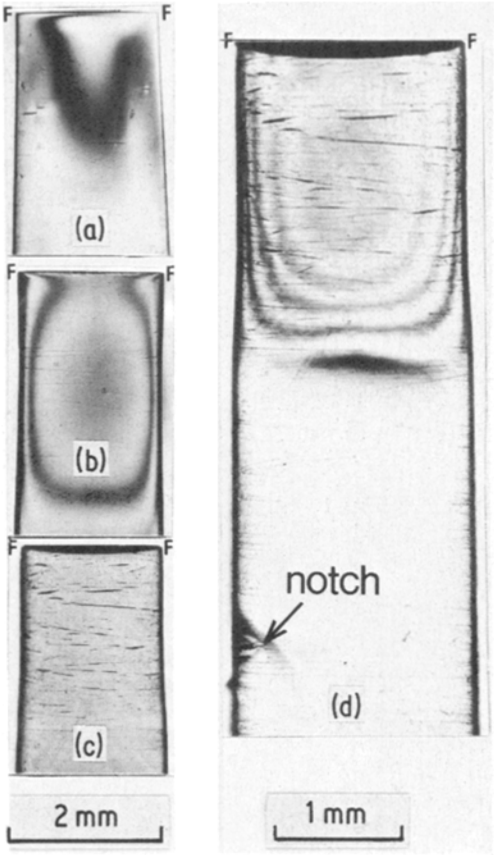

Figure 4 Longitudinal sections through failed specimens: (a) tested under 25 MN m^{-2} superposed pressure, showing fracture, F–F, within the drawn region (taken using polarized light); (b) tested under 300 MN m^{-2} superposed pressure, showing fracture outside the drawn region (taken using polarized light); (c) tested under 310 MN m^{-2} superposed pressure, showing surface non-propagating microcracks in the drawn region; and (d) tested, following notching and coating, under 310 MN m^{-2} superposed pressure, showing the artificial crack, necked region and path of failure, F–F, (taken using polarized light).

growth regions seen, for example, in PMMA [8] and polysulfone [7].

Some specimens were observed using optical (including polarizing) microscopy during straining at atmospheric pressure, and no evidence of slow crack-growth prior to catastrophic failure was obtained. When an artificial crack, about 0.2 mm deep, was introduced into a tensile specimen, no change in behaviour was detected. Zones I and II were subsequently found, associated with the crack nucleus on the fracture surface.

Artificial crack nuclei, approximately of atmospheric Zone I size, were also introduced into specimens prior to rubber coating and testing under 300 MN m^{-2} superposed pressure. In these samples failure did not necessarily take place from these origins. Fig. 4d illustrates a specimen where the artificial crack, necking (drawing) and failure were in three different cross-sections.

Fractographic features of specimens tested under pressure fall into two main groups. The first comprises all the uncoated samples and those coated and tested below 100 MN m^{-2} superposed pressure; the second comprises the coated specimens tested in a tri-axial (but unequal) compressive system.

The appearance of the first group resembled the atmospheric behaviour of the material except that, for the coated specimens, the size of Zone I appeared to increase with pressure. The effect of increasing pressure (for this group) was qualitatively similar to the effect of increasing temperature at ambient pressure and, additionally, Zone IV was not observed in these specimens. Some specimens were tested in water at 30, 40 and 50° C and the stress–strain curve for the 50° C test is presented in Fig. 1e.

For the second group Zones II and III were absent, but more than one of the Zone I nuclei were generally observed on the failure surface (e.g., Fig. 5a). The direction of cracking was outwards from one of these nuclei, the "pole", and, the crack having reached the "equator", the rib markings changed direction, approximately as lines of longitude on a map, see, for example, Fig. 5b. In addition to, or instead of, the "ribs" there were "plume" markings (e.g., Fig. 5c) resembling "fingers", previously reported for a fatigued epoxy resin [9].

Examination of the surfaces of failed specimens sometimes revealed, more frequently in the coated specimens than in the uncoated specimens, cracks remote from the failure surface. These cracks tended to be confined to the drawn region, as illustrated in Fig. 4c. They were also examined using reflection and transmission optical microscopy (through the failure surface), and it was seen that the nonpropagating surface cracks resembled Zone I regions (e.g., Fig. 6).

K_{Ic} was evaluated at atmospheric pressure using specimens of the single-edge notch geometry loaded in three-point bending. A value of 1.0 ± 0.2 MN m$^{-3/2}$ was obtained from specimens with cracks sharpened with a razor blade. The experiment was repeated (using a round sample) on material which had formed part of a coated

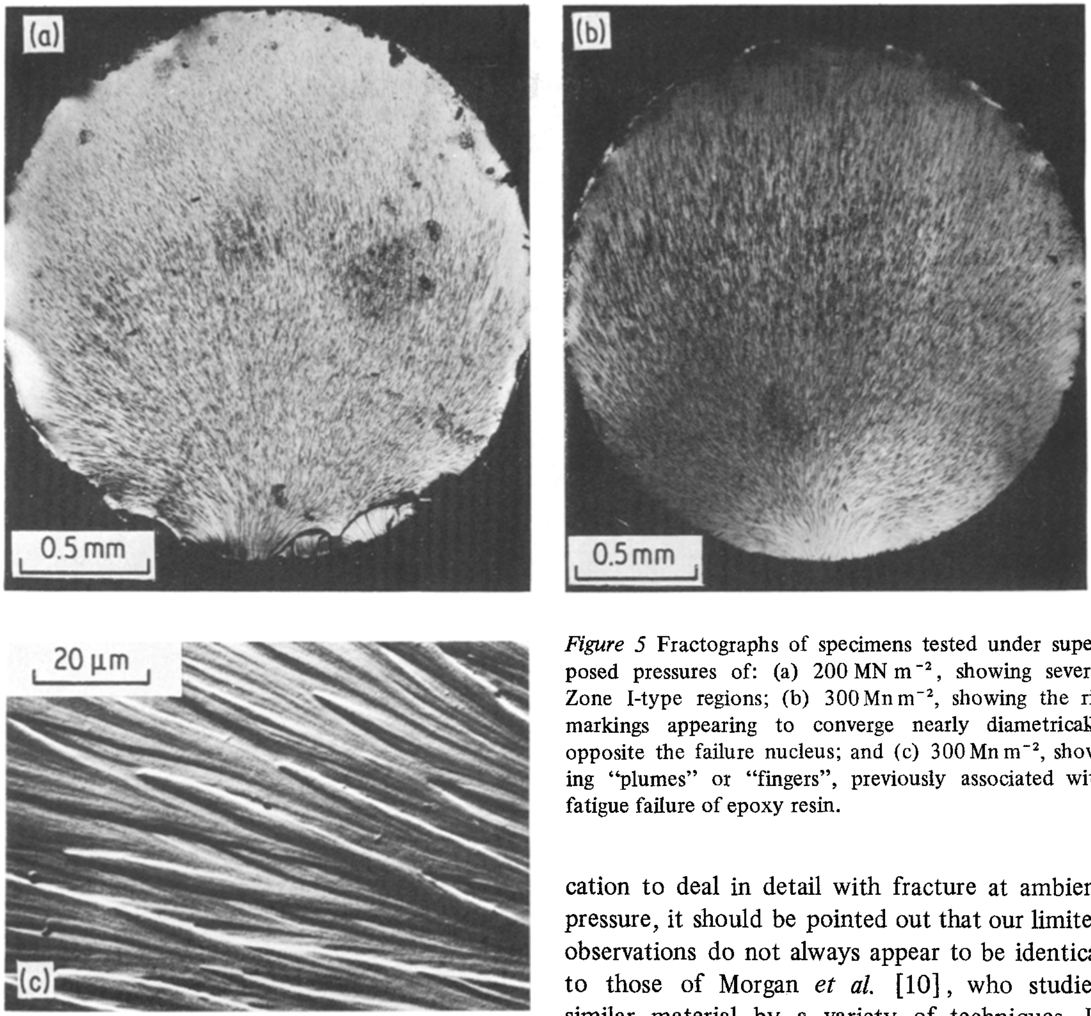

Figure 5 Fractographs of specimens tested under superposed pressures of: (a) 200 MN m^{-2}, showing several Zone I-type regions; (b) 300 Mn m^{-2}, showing the rib markings appearing to converge nearly diametrically opposite the failure nucleus; and (c) 300 Mn m^{-2}, showing "plumes" or "fingers", previously associated with fatigue failure of epoxy resin.

specimen which was loaded to about 90% of its failure strain at 300 MN m^{-2}. A value of about 1.9 MN m$^{-3/2}$ for K_{Ic} of the strained material was obtained.

4. Discussion

The fracture of these epoxide specimens took place by the propagation of deformation-induced cracks and not by the extension of inherent flaws, as Duckett's model [1] requires. Fracture mechanics analysis of atmospheric data is consistent with the "failure initiating site" being the size of Zone I. It is tempting, therefore, to suggest that this region is one of sub-critical slow crack-growth [7]. It seems that attainment of critical size and catastrophic propagation, Zone II, resulted principally in a change of cracking speed and direction, delineated by the "rib" markings.

Though it is not the purpose of this communication to deal in detail with fracture at ambient pressure, it should be pointed out that our limited observations do not always appear to be identical to those of Morgan *et al.* [10], who studied similar material by a variety of techniques. In particular, consistent with the majority of reports on epoxides [5], we found no evidence of crazing.

It is suggested that, not unlike yielding, crack nucleation and initial crack growth, Zone I, are associated with shear-stress operated mechanisms. Whereas atmospheric data are consistent with crack propagation taking place under the action of a tensile stress according to a Griffith or fracture-mechanics model, this simple interpretation must be questioned, at least for tests on coated specimens, when all the principal stresses were compressive and fractographic examination indicated the existence of Zone I only.

It has been proposed [11] that the principle of superposition is applicable to fracture mechanics analyses and this hypothesis has been discussed for the case of Mode I cracking under superposed hydrostatic pressure [12]. If it is considered that the stress singularity is not affected by hydrostatic pressure, then there should be a constant, or perhaps slightly increasing with pressure, K_{Ic} value, derived from the superposed tensile stress. This has been reported for a number of ceramics [13]. Table II lists K_{Ic} values evaluated from the superposed tensile stress and Zone I size data. It is seen that for all specimens tested below 100 MN m^{-2}, and also the uncoated specimens tested above it, the interpretation is tenable, but K_{Ic} increases with pressure. A test at atmospheric pressure on a specimen deformed at pressure and then notched indicates an irreversible increase in K_{Ic} due to the straining, consistent with this interpretation.

The data on tests with coated specimens when all the principal stresses were compressive are not susceptible to such simple interpretation. Of relevance also is the test (see Fig. 4d) where an artificial crack under pressure did not propagate, but a fresh nucleus was initiated elsewhere and grew. In general, no interpretation involving concentration of local tensile stress should be invoked, as there was no macroscopic tensile stress to concentrate. It is suggested that tensile or devi-

Figure 6 Transmission optical micrograph of (a) the surface adjoining the fracture surface of a coated specimen which failed at a superposed pressure of 150 MN m^{-2} and (b and c) non-propagating cracks, resembling Zone I regions, found below the failure surface and photographed using (b) transmission and (c) reflection optical microscopy.

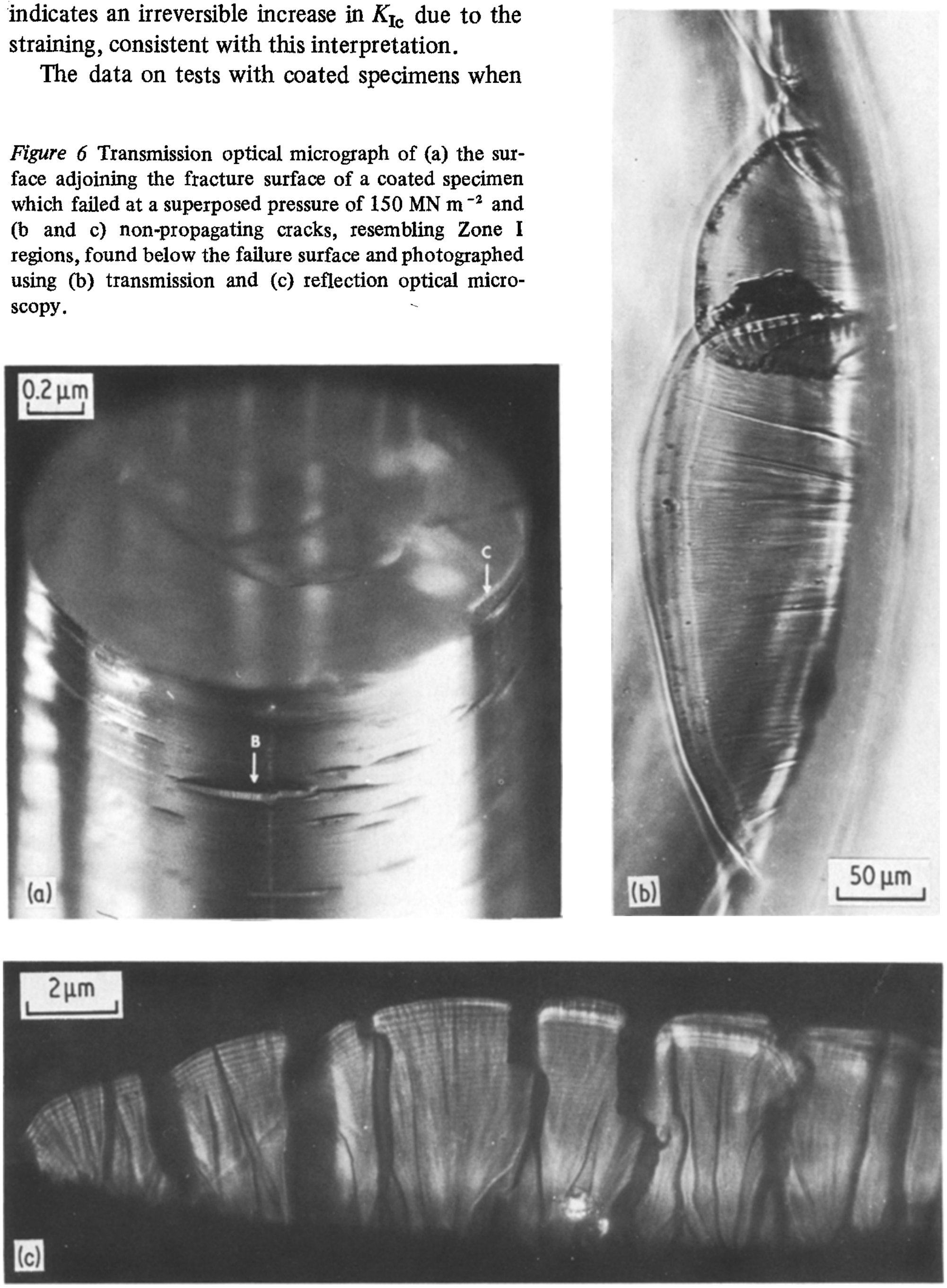

TABLE II Fracture toughness, K_{Ic}, calculated from the Zone I size and shape and the *superposed* tensile stress for the uncoated and some coated specimens.

Sample	Pressure (MN m^{-2})	Superposed tensile stress (MN m^{-2})	Major ($2a$) and minor (c) axes of semi-elipse		K_{Ic} (MN m$^{-3/2}$)
			$2a$ (mm)	c (mm)	
Uncoated	ATM	47	0.84	0.34	1.02
	25	57	0.77	0.29	1.31
	50	56	0.68	0.31	1.36
	75	67	0.49	0.30	1.42
	100	70	0.6	0.25	1.41
	150	80	0.37	0.15	1.51
	200	90	0.40	0.25	1.49
	250	94	0.37	0.15	1.50
	300	105	0.38	0.16	1.68
Coated	25	54	1.31	0.61	1.58
	50	63	0.91	0.46	1.54
	75	64	1.1	0.54	1.75

atioric strain may be a more relevant parameter. Although all the principal stresses at yield and failure were compressive, there was always an axial tensile strain. Fractographic observations support the suggestion that a criterion different from that at atmospheric pressure then operates. There is no Zone II, which has been associated with attainment of K_{Ic}. It seems that, in a stress system little different from that causing yielding, but with increasing tensile strain, the mechanism responsible for Mode I crack growth continues to operate. The criterion for the operation of this mechanism could be similar to that for crazing, but crazing itself has not been detected. It is noteworthy that this mechanism operates in the absence of a tensile stress and, therefore, in terms of fracture mechanics analyses, is another type of sub-critical crack growth.

Acknowledgements

The authors acknowledge the provision of laboratory facilities by Professor D. Bijl, discussions with and assistance with fractography by Dr M. Rebbeck and the support of the SERC.

References

1. R. A. DUCKETT, *J. Mater. Sci.* **15** (1980) 2471.
2. A. S. WRONSKI and M. PICK, *ibid.* **12** (1977) 28.
3. A. J. KINLOCH, *Metal Sci.* **14** (1980) 305.
4. A. S. ARGON and J. G. HANNOOSH, *Phil. Mag.* **36** (1977) 1195.
5. R. J. YOUNG, in "Developments in Polymer Fracture: I" edited by E. H. Andrews (Applied Science Publishers, London, 1979) p. 183.
6. E. ENGEL, H. KLINGELE, G. W. EHRENSTEIN and H. SCHAPER, in "An Atlas of Polymer Science" (Wolfe Publishing, Munich, 1981) p. 197.
7. R. D. R. GALES and N. J. MILLS, *Eng. Fract. Mech.* **6** (1974) 93.
8. J. P. BERRY, in "Fracture Processes in Polymeric Solids" edited by B. Rosen (John Wiley and Sons, New York, 1964).
9. S. A. SUTTON, *Eng. Fract. Mech.* **6** (1974) 587.
10. R. J. MORGAN, J. E. O'NEAL and D. B. MILLER, *J. Mater. Sci.* **14** (1979) 109.
11. B. AAMODT and P. G. BERGAN, *Eng. Fract. Mech.* **8** (1976) 437.
12. A. S. WRONSKI, *Int. J. Fract.* **17** (1981) R17.
13. M. S. STUCKE and A. S. WRONSKI, *Proc. Brit. Ceram. Soc.* **25** (1975) 109.

Received 21 September
and accepted 30 November 1981