Effect of stress and temperature on dry craze growth kinetics during low-stress creep of polycarbonate

Part 2 Theoretical model

NICOLE VERHEULPEN-HEYMANS, J.C. BAUWENS Physique des Matériaux de Synthèse, Université Libre de Bruxelles, 1050 Bruxelles, Belgium

A model for craze growth is presented, based on stress and strain analysis around a craze and on rheological properties of craze matter. This model is shown to account quantitatively for observed growth rates, and to be in agreement with the variation of the delay time for crazing in polycarbonate with stress and temperature.

1. Introduction

Critical conditions for craze growth have been analysed previously using methods derived from fracture mechanics [1-4]. However, these studies concerned craze growth in an active environment. According to a model put forward by Gent, which is also applicable to dry crazing, craze initiation occurs under the influence of a local stress concentration, by transformation of the region at the tip of a chance flaw to a rubbery state, and subsequent cavitation of the rubbery phase. The craze propagation mechanism is identical, except that the stress concentration is now due to the craze itself [5, 6]. This model is unsatisfactory, among other reasons, in that it implies stress concentration factors of order 20 or 30 [5]. Under a moderate applied stress of, say, 3 kg mm⁻², the craze- or flawtip stress would be 60 kg mm^{-2} , and such a stress must lead to immediate fracture. Also, in order to obtain agreement of the predicted strain-rate dependence of crazing stress with experiment, the stressconcentration factor of a given flaw must depend on strain-rate, which is an unrealistic assumption.

Our attempts to derive a law for craze growth from conditions for craze tip yielding were unsuccessful, as this assumption implied accelerated craze growth, in contrast with the observed decelerated growth [7]. It was then thought that craze growth might be attributed to release of strain energy due to relaxation of the modulus of

© 1976 Chapman and Hall Ltd. Printed in Great Britain.

the matrix. This assumption led to a decelerated growth law which, however, was not linear in log time. Also, theoretical propagation rates were one to two orders of magnitude smaller than experimental rates [7].

The model for craze growth, given below, is based on the stress field along a craze and on the rheological properties of the craze material itself. This model leads to a law for craze growth in agreement with the most frequently observed experimental law, and can account for various other kinds of behaviour. Also, the observed variation of delay time for crazing with stress and temperature is compatible with the predictions of the model.

2. Stress analysis around a craze

A Fourier transform method was previously used by Knight for analysis of the stress field along a craze. Knight's results were not used here for the following reasons.

(1) The above method is valid only if there are no stresses acting parallel to the craze edge. It was felt that a more complete analysis might be needed, in case this condition were not satisfied.

(2) According to Knight's results, given the shape of the craze body (Fig. 1), there is only one possible craze tip shape, and only one possible stress field, compatible with stress equilibrium in the matrix. In particular, this implies a stress field independent of the stress—strain relationship in the



Figure 1 Craze geometry for analysis of stress field due to a craze.

plastically-deforming craze tip region and, therefore, identical whatever the material under observation. It was found that Knight's conclusion was due to an oversight in his derivation, and that in fact an infinity of craze tip shapes are possible. This point is fully discussed elsewhere [8].

For these reasons, it was preferred to use Muskhelishvili's method for stress and strain analysis in a plate in which there are displacement discontinuities; this method also has the advantage of giving the solution for the entire plate. A single craze of half-length *a* embedded in an infinite sheet is considered, and suitable boundary conditions must be given along the craze-matrix interface. The stress field in the matrix can then be computed from two potentials, $\phi(x + iy)$ and $\psi(x + iy)$ (see Appendix).

It is presumed that the thickness of the unstressed craze is negligible with respect to its length. Two parts of the craze are defined on Fig. 1: the tip of length r, in which transformation to craze material takes place, and the body of length 2(a-r), in which craze material has welldefined, though unknown, rheological characteristics. Transformation is presumed complete at the base of the tip.

As a first approximation, the stress acting perpendicular to the craze is considered constant along the craze tip. This assumption is based on the fact that for a given craze propagation rate, strain-rate cannot vary by orders of magnitude from one part of the craze tip to another. As strainrate at yield of glassy polymers is extremely sensitive to small variations in stress, it appears reasonable to assume that stress is constant (equal to σ_e) in the craze tip.

Along the craze body, two different simple assumptions can be made, allowing an explicit solution to be found: either the displacement δ_0 or the stress σ_e perpendicular to the craze edge can be constant. In the first case (stress field I) there is a stress singularity at the base of the tip, indicating incompatibility between constant displacement along the craze body and constant stress along the tip. In the second case (stress field II), which can be looked on as a modified Dugdale problem [9], there is no such singularity. Variation of normal stress σ_y and displacement δ along the craze is given in Fig. 2 for stress-field I and on Fig. 3 for stress field II.

These solutions are based solely on conditions for stress equilibrium in the Hookean matrix. If craze properties were also taken into account, it is probable that the resulting stress field would much resemble that which is schematically represented on Fig. 4, from which it can be seen that both stress and displacement must be approximately constant under stress along the craze body, and therefore either stress field I or II can be considered as a good first approximation of the real stress field. In computations (Section 3) stress field II was used, as it does not present any stress singularities along the craze.



Figure 2 Distribution of normal stress and displacement along a craze using Muskhelishvili's method of analysis $(\delta_0 \text{ and } \sigma_e \text{ are given}).$



Figure 3 As Fig. 2 but σ_c and σ_e are given.



Figure 4 Probable stress and displacement field surrounding a craze.

The stresses and displacements at a point P(x, y) are given by Equations A24 to A28, which reduce to the following along the craze alignment. In these equations, σ_a is average applied stress, u and v are displacements respectively parallel to Ox and Oy, and κ is a constant defined in the Appendix.

(a) Craze body: $|x| \le a - r, y = 0$

$$\sigma_{\mathbf{x}} = -(\sigma_{\mathbf{a}} - \sigma_{\mathbf{c}}) \tag{1}$$

$$\sigma_{y} = \sigma_{c} \tag{2}$$

$$\tau_{xy} = 0 \tag{3}$$

$$2Gu = \left\{-\frac{\sigma_{a}}{4}(\kappa+1) + \frac{\sigma_{c}}{2}(\kappa-1)\right\}x \quad (4)$$

$$2Gv = \frac{\sigma_{\rm e} - \sigma_{\rm c}}{2\pi} (\kappa + 1) \\ \left\{ x \ln \frac{(a-r)\sqrt{(a^2 - x^2)} - x\sqrt{[r(2a-r)]}}{(a-r)\sqrt{(a^2 - x^2)} + x\sqrt{[r(2a-r)]}} \right\}$$
(5)
+ $(a-r) \ln \frac{\sqrt{(a^2 - x^2)} + \sqrt{[r(a-r)]}}{\sqrt{(a^2 - x^2)} - \sqrt{[r(a-r)]}}$

(b) Craze tip: $a - r \le |x| \le a, y = 0$

7

$$\sigma_x = \sigma_e - \sigma_a \tag{6}$$

$$\sigma_{y} = \sigma_{e} \tag{7}$$

$$x_{xy} = 0 \tag{8}$$

$$2Gu = \left\{-\frac{\sigma_{\mathbf{a}}}{4}(\kappa+1) + \frac{\sigma_{\mathbf{c}}}{2}(\kappa-1)\right\}x + \frac{\sigma_{\mathbf{e}} - \sigma_{\mathbf{c}}}{2}(\kappa-1)(x-a+r) \quad (9)$$

$$2Gv = \frac{\sigma_{\rm e} - \sigma_{\rm c}}{2\pi} (\kappa + 1)$$

$$\begin{cases} x \ln \frac{x\sqrt{[r(2a-r)]} - (a-r)\sqrt{(a^2 - x^2)}}{x\sqrt{[r(2a-r)]} + (a-r)\sqrt{(a^2 - x^2)}} (10) \\ + (a-r) \ln \frac{\sqrt{[r(a-r)]} + \sqrt{(a^2 - x^2)}}{\sqrt{[r(a-r)]} - \sqrt{(a^2 - x^2)}} \end{cases}$$

(c) Beyond craze tip: $x \ge a, y = 0$

$$\sigma_x = \frac{\sigma_e - \sigma_c}{\pi/2} \tan^{-1} \frac{(a-r)\sqrt{[r(2a-r)]}}{x[x + \sqrt{(x^2 - a^2)}] - (a-r)^2}$$
(11)

$$\sigma_{y} = \sigma_{a} + \frac{\sigma_{e} - \sigma_{c}}{\pi/2} \tan^{-1} \frac{(a - r)\sqrt{[r(2a - r)]}}{x[x + \sqrt{(x^{2} - a^{2})] - (a - r)^{2}}}$$
(12)

$$\tau_{xy} = 0 \tag{13}$$

$$2Gu = \frac{\sigma_a}{4} (\kappa - 3)x + \frac{\sigma_e - \sigma_c}{\pi} (\kappa - 1)$$

$$\left\{ x \tan^{-1} \frac{(a - r)\sqrt{[r(2a - r)]}}{x[x + \sqrt{(x^2 - a^2)}] - (a - r)^2} \quad (14) - (a - r) \tan^{-1} \sqrt{\left[\frac{r(2a - r)}{x^2 - a^2}\right]} \right\}$$

$$2Gv = 0 \quad (15)$$

It can be seen not only that there is a stress concentration at the craze tip, but also that the normal stress parallel to the craze, σ_x , is tensile there, raising the hydrostatic component of the local stress and aiding cavitation and, therefore, craze propagation. On the contrary, along the craze body, σ_x is compressive, lowering the hydrostatic component, and as σ_{e} is lower than the applied stress, there is no tendency for the craze to propagate towards the matrix. Therefore, the thickness of the layer of material from which the craze is formed must remain practically constant during craze propagation. This has been confirmed by electron microscopy of surfaces of crazed polycarbonate specimens: thicknesses of unstressed crazes do not vary significantly with length nor with testing conditions [7, 10].

The stress distribution is such that the local stress σ_c is practically constant at any time along the craze body. We shall now consider variation during craze growth of σ_c , which depends on the ratio of craze width to length by Equation 5. As a first approximation, when $r \ll a$ and putting x = 0,

Equation 5 can be expressed as:

$$\sigma_{\mathbf{a}} - \sigma_{\mathbf{c}} = \frac{4G}{\kappa - 1} \frac{\delta_0}{a} \tag{16}$$

where δ_0 is the displacement at x = 0. According to Bessonov and Kuvshinskii's observations on plasticized PMMA, the ratio of total craze thickness to craze length remains practically constant during propagation, decreasing slowly during the early stages of growth [11]. As total thickness is equal to unstrained thickness plus displacement, these observations would seem to indicate that displacement is roughly proportional to length. Then, by Equation 16, craze stress σ_c is constant during growth, which proceeds under stationary conditions, and craze material is subjected to creep loading.

It is implicit in the above statement that craze deformation can take place at low stresses at which propagation of plastic deformation does not occur in the matrix, since it has been supposed that no material is drawn into the craze during growth.

3. Model for creep of craze material

The rheological characteristics of craze material are unknown. It appears however from work by Kambour and Kopp [12] and by Hoare and Hull [13] that craze material is non-linear viscoelastic, with a yield stress at moderate strain-rates somewhat lower than that of uncrazed material. Variation of craze yield stress with temperature and strain-rate was not measured. Taking account of these observations, it seems reasonable to represent craze material by a rheological model similar to the one proposed by Haward and Thackray for glassy polymers [14]. In our model (Fig. 5), η_c is an Eyring dashpot representing yield behaviour of craze material, and E_{c} represents rubbery elasticity of craze material. E_{c} is considered constant as a first approximation. The high-modulus Hookean spring, present in Haward and Thackray's model, is not considered here as the resulting strain is small with respect to total strain.

From this model, the law of deformation of



Figure 5 Rheological model representing behaviour of craze matter.

craze material is:

$$\sigma_{\mathbf{c}} = E_{\mathbf{c}}\epsilon_{\mathbf{c}} + A_{\mathbf{c}}T\left(\frac{Q_{\mathbf{c}}}{RT} + \ln 2C_{\mathbf{c}} + \ln \dot{\epsilon}_{\mathbf{c}}\right).$$
(17)

If the craze was formed from a layer of material of thickness e prior to deformation, the craze strain is

$$\epsilon_{\rm c} = \frac{2\delta_0}{e} \tag{18}$$

Putting $\Delta = \delta_0/a$, constant by hypothesis during growth of a given craze, and making use of Equation 18, Equation 17 becomes:

$$\sigma_{\mathbf{c}} = \frac{E_{\mathbf{c}}\Delta l}{e} + A_{\mathbf{c}}T\left(\frac{Q_{\mathbf{c}}}{RT} + \ln 2C_{\mathbf{c}}\frac{\Delta}{e} + \ln \dot{l}\right)$$
(19)

where the total craze length l has been introduced instead of half-length a.

Supposing that Δ and *e* are constant during the entire propagation phase, integration of Equation 19 from time t_i at which l = 0 gives:

$$l = l_0 \ln \frac{t - t_i + t^*}{t^*}$$
(20)

where

$$l_0 = \frac{eA_cT}{E_c\Delta} \tag{21}$$

$$t^* = \frac{2C_{\rm c}E_{\rm c}}{A_{\rm c}T} \exp\left(\frac{Q_{\rm c}}{RT} - \frac{\sigma_{\rm c}}{A_{\rm c}T}\right) \qquad (22)$$

and t_i is the craze initiation time.

4. Discussion

4.1. Craze propagation law

Observations of craze propagation in polycarbonate have been presented previously and results will only be recalled briefly here. Growth of individual crazes was generally linear with log time (Fig. 6a) although occasionally deviations from a linear plot were observed immediately after initiation (Fig. 6b). Less simple plots were sometimes observed (Fig. 6c and d); such cases were, however, extremely infrequent. Craze growth can thus be defined by two parameters: the slope l_0 of the plot of length against log time, and the abscissa intercept t^* .

The law for propagation derived from our model is identical with the experimental law of Fig. 6a if $t_i = t^*$. It is to be stressed that craze



Figure 6 Various cases of craze growth in polycarbonate: (a) $\sigma = 2.69 \text{ kg mm}^{-2}$, $T = 60^{\circ}$ C; (b) $\sigma = 2.24 \text{ kg mm}^{-2}$, $T = 80^{\circ}$ C; (c) $\sigma = 2.77 \text{ kg mm}^{-2}$, $T = 80^{\circ}$ C; (d) $\sigma = 2.58 \text{ kg mm}^{-2}$, $T = 80^{\circ}$ C.



Figure 7 Electron micrograph of a replica of a crazed polycarbonate specimen showing sudden variations of craze thickness.

propagation was frequently followed over several decades of time.

If craze initiation time t_i is different from t^* , logarithmic propagation is only observed if time under load is much greater than $(t_i - t^*)$. In this case, t_i is the abscissa intercept of the plot of length against log time and t^* is the intercept of the linear section of the plot (Fig. 6b).

Anomalous behaviour (Fig. 6c and d) can be explained if sudden growth of craze thickness e and displacement δ_0 occur. The rise of δ_0/a then causes σ_c to drop (Equation 16) and propagation continues with higher values of t^* and of l_0 (Fig. 6c). On the other hand, if growth in length is nearly simultaneous with growth in thickness, both δ_0/a and σ_c will remain almost unchanged, and growth will be of the kind shown on Fig. 6d. Sudden variations of craze thickness have on a few occasions been observed in electron microscopy (Fig. 7) and therefore even anomalous behaviour is compatible with the model.

4.2. Time constant for craze growth

It appears from Equation 20 that t^* is the time constant for craze growth, and also for retarded deformation of craze material. This parameter is a function only of the rheological characteristics of craze material, and of the stress transmitted to it (Equation 22). It can be seen from Equation 20 that t^* is the time axis intercept of the linear part of plots of craze length against log time.

A point is to be noted here, in connection with various studies of craze initiation kinetics. As shown in a previous paper, variation of craze length in polycarbonate with log time was generally linear since the craze appeared [10], and it would seem, therefore, that in this material craze initiation and propagation kinetics are determined by quite similar parameters. However, in other materials such may not be the case, and if l_0 is sufficiently small, a considerable difference between initiation time and propagation time constant could have very little effect on the experimentally observed growth pattern, since very short crazes are not easily detected. In other words, the time necessary for detection of crazing, generally thought of as a good approximation of initiation time [15-17], could very well be close to the time constant for propagation, t^* , and in fact depend very little on initiation time.

Experimental variation with applied stress and temperature of the time constant for craze propagation in polycarbonate was studied in a previous paper [10]. Equation 22 is not expressed as a function of applied stress σ_a but of local stress σ_c . However, as shown above, the hypothesis of constant σ_c during growth under creep conditions is compatible with experiment, and thus

$$\sigma_{\mathbf{a}} = s\sigma_{\mathbf{c}} \tag{23}$$

where σ_a is applied stress and s is constant during growth of each craze, although it may vary from one craze to another. The multiplying factor s depends on craze geometry by Equation 16, and an exact value could be found if the shape of the stressed craze were known. Past efforts at replicating crazed surfaces of specimens under stress have on the whole been unsuccessful, due to limitation in the choice of a replicating agent suitable for stressed polycarbonate [7]. Work along this line is currently in progress. Approximate limiting values of s can be found from considerations of the stress field near a craze. As craze stress is lower than applied stress, s must be greater than unity. Also, it seems unlikely that craze stress could drop much lower than half the applied stress, since craze behaviour would then be crack-like. It is shown below that with s = 1.1, $\sigma_{\rm a}-\sigma_{\rm c}$ can be evaluated from experimental values of l_0 as 0.47 kg mm⁻², which is quite a reasonable value, indicating self-consistency of the model.

Finally, Equation 22 can be expressed as:

$$\frac{\sigma_{a}}{T} = sA_{c} \left[\frac{Q_{c}}{RT} + \ln \frac{2C_{c}E_{c}}{A_{c}T} - \ln t^{*} \right] \quad (24)$$

$$1 < s < 2.$$

is Fig. 8 represents theoretical plots of σ_a/T against t^* derived from Equation 24, together with

experimental points representing average values.



with

Figure 8 Plot of ratio of applied stress to temperature o/T against time constant for craze growth t^* . Straight lines are from Equation 24.

Variations of craze geometry at initiation would lead to variations of s; this could be a possible cause of data scatter.

The following parameters may be derived from the best fit of Equation 24 to the data:

$$A = 7.34 \times 10^{-4} \text{ kg mm}^{-2} \text{ K}^{-1} \text{ at all } T$$

$$Q = 22.35 \text{ kcal mol}^{-1}$$

$$C = 10^{-8} \text{ sec}$$

$$T \le 60^{\circ} \text{ C}$$

$$Q = 51.4 \text{ kcal mol}^{-1}$$

$$C = 10^{-27} \text{ sec}$$

$$T \ge 60^{\circ} \text{ C}.$$

Variation of activation energy as a function of temperature could be partly due to chance fluctuations between specimens, but there does seem to be a definite tendency towards a rise in activation energy above about 60° C, possibly connected with structural modifications which occur in polycarbonate during annealing at temperatures higher than 80° C [18, 19]. Several workers have, in fact, shown that mechanical behaviour is influenced by annealing [20, 21].

It is to be noted that these parameters are quite different from those for yielding of macroscopic specimens [10], and therefore that craze material cannot be thought of as a collection of scaled-down tensile specimens. In fact, for ingernal consistency of the proposed model, the deformation mechanism of craze material must necessarily be different from that of the matrix, in order that deformation of craze material be possible at stresses which do not cause appreciable creep of the matrix.

As a consequence of the high value of A and the

low value of activation energy, low strain-rate viscosity of craze material is much smaller than that of undeformed material. The cause of this difference could be the small dimensions of craze filaments; as pointed out by Kambour and Kopp [12], below a critical dimension, viscosity is proportional to $1/d^2$ where d is the filament diameter.

To confirm internal consistency of the model, an approximate value of the craze stress may be derived from Equations 16 and 21.

A value of E_c was found from a stress-strain curve of polycarbonate under conditions such that deformation was homogeneous at yield; in this case the lower yield point is immediately followed by a rise in stress which can be attributed to rubbery elasticity of the yielded material (Fig. 9). The slope of the near-linear part of the curve was 500 g mm⁻² at 130° C, using initial cross-section and gauge length to enable comparison with the model of Fig. 5.

Craze thicknesses were measured in transmission or scanning electron microscopy (Fig. 10). The ratio of craze thickness to width of the associated surface groove was supposed equal to 0.75 and the residual strain in the unstressed craze was taken as 70%, from work by Kambour and Kopp [12]. Scatter of craze thickness was in a ratio of over 1:2 and an average value of $0.6 \,\mu\text{m}$ was taken, giving $e = 0.35 \,\mu\text{m}$.

From analysis of variation of time constant t^* using Equation 24 and taking s = 1.1, $A_c = 6.7 \times 10^{-4}$ kg mm⁻²K⁻¹; an average value of l_0 , which also presented quite a wide scatter, was 200 μ m. Finally, from Equation 21, $\delta_0/a = 9.4 \times 10^{-4}$. This



Figure 9 Tensile stress-strain curve of polycarbonate. $T = 130^{\circ}$ C, $\dot{\epsilon} = 2 \times 10^{-4}$ sec⁻¹.



Figure 10 Scanning electron micrographs of a craze for determination of thickness-to-length ratio.

value is introduced into Equation 16 with $G = 100 \text{ kg mm}^{-2}$; in plane strain, if Poisson's ratio is 0.3, $\kappa = 1.8$ and $\sigma_a - \sigma_c = 0.47 \text{ kg mm}^2$. This value is compatible with the proposed value of s with $\sigma_a = 5.2 \text{ kg mm}^2$. It is to be noted that as s is close to unity, small changes of s greatly affect the ratio of applied stress to the difference between applied stress and craze stress, whereas this difference itself is left almost unchanged. This means that it is difficult to distinguish experimentally whether s or $\sigma_a - \sigma_c$ is independent of testing conditions.

It appears from the above that although craze material viscosity is quite different from that of a macroscopic specimen, rubbery elastic effects are similar in the two forms of material.

5. Conclusions

A model for craze growth has been presented, whereby propagation is due to creep of craze material under a local stress which is lower than the average applied stress. The variation with applied stress and temperature of the time constant for propagation, as well as experimental scatter, are compatible with results derived from the proposed model. According to this model, craze growth is linear with log time, in agreement with experiment. Quantitative agreement for craze growth in polycarbonate implies a similar rubbery-elastic modulus for craze material as for cold-drawn specimens, but different parameters of the rate-process responsible for viscosity. The cause of this difference could be that craze filaments are extremely thin.

The proposed model is thus consistent with several aspects of craze propagation in glassy polymers, and also leads to quite reasonable values of the rheological parameters of craze material.

Appendix

By Muskhelishvili's method of analysis [22], the stresses and displacements in a plane sheet can be derived from two potentials, $\phi(z)$ and $\psi(z)$, as:

$$\sigma_x + \sigma_y = 4 \operatorname{Re} \phi'(z), \qquad (A1)$$

$$\sigma_y - \sigma_x + 2i\tau_{xy} = 2[\bar{z}\phi''(z) + \psi'(z)]$$
 (A2)

$$2G(u+iv) = \kappa\phi(z) - z\overline{\phi'}(z) - \psi(z) \quad (A3)$$

where z = x + iy, x and y being cartesian coordinates; $\kappa = 3 - 4v$ in plane strain; $\kappa = (3 - v)/(1 + v)$ in plane stress; G and v are the shear modulus and Poisson's ratio of the matrix; u and v are displacements parallel to Ox and Oy. If a displacement discontinuity exists along an ellipse L of major axis 2a along Ox and minor axis 2b along Oy, the following conformal transformation is used to map the ellipse onto the unit circle $\gamma([22] p.$ 333):

$$z = R\left(\zeta + \frac{m}{\zeta}\right) \tag{A4}$$

where a = R(1 + m) b = R(1 - m). (A5)

In the case of symmetrical loading along L, and if the external load is a stress σ_a normal to Ox, the potentials reduce to ([22], p. 184)

$$\phi(\zeta) = \frac{\sigma_a a}{8} \zeta - \frac{1}{2\pi i} \oint_{\gamma} \frac{f(\eta) \mathrm{d}\eta}{\eta - \zeta}$$
(A6)

$$\psi(\zeta) = -\frac{\sigma_{a}a}{4}\zeta - \frac{1}{2\pi i}\oint_{\gamma}\frac{\overline{f(\eta)}d\eta}{\eta - \zeta}$$
$$-\zeta \frac{1+m\zeta^{2}}{\zeta^{2}-m}\frac{d}{d\zeta}\left(\phi(\zeta) - \frac{\sigma_{a}a}{8}\zeta\right) \quad (A7)$$

where

$$f = i \int_{0}^{\pi} (X_n + iY_n) \,\mathrm{d}s$$
$$-\frac{\sigma_a a}{8} \left(\eta + \frac{\eta^2 + m}{\eta(1 - m\eta^2)} \right) - \frac{\sigma_a a}{4} \cdot \frac{1}{\eta} \qquad (A8)$$

In this equation, X_n and Y_n are stresses given along L, s is a linear co-ordinate along L, and η is the value taken by ζ along the unit circle γ .

s

The thickness of a well-developed craze is negligible with respect to its length and therefore m = 1. Only external stresses parallel to Oy are considered:

$$Y_n = \pm \sigma_e \quad |x| < a - r, \quad y = O^+ \text{ or } O^-$$

$$Y_n = \pm \sigma_e \quad a - r < |x| < a, \quad y = O^+ \text{ or } O^-.$$
(A9)

The load can be divided into three parts, as potentials for partial loads are additive: potentials are then derived separately for the external load σ_a ; the craze stress σ_e acting along the whole of the craze; the excess stress $\sigma_e - \sigma_e$ acting along the craze tips.

For the excess stress:

$$Y_{n} = \sigma_{e} - \sigma_{c} \qquad a - r < |x| < a \quad y = O^{*}$$
$$Y_{n} = -(\sigma_{e} - \sigma_{c}) \qquad a - r < |x| < a \quad y = O^{-}$$
(A10)

and

$$f(\eta) = -(\sigma_{e} - \sigma_{c}) \left\{ \frac{a}{2} \left(\eta + \frac{1}{\eta} \right) + a - r \right\}$$
$$-a \leqslant x \leqslant -a + r$$
$$f(\eta) = -(\sigma_{e} - \sigma_{c}) \left\{ \frac{a}{2} \left(\eta + \frac{1}{\eta} \right) - a + r \right\}$$
$$a - r \leqslant x \leqslant a \qquad (A11)$$
$$f(\eta) = 0 \quad |x| \leqslant a - r$$

1

Therefore

$$\phi_{1}(\zeta) = (\sigma_{e} - \sigma_{c}) \frac{a}{4i\pi} \left\{ -\frac{4i\beta}{\zeta} + \left(\zeta + \frac{1}{\zeta} \right) \ln \frac{\zeta^{2} - e^{2i\beta}}{\zeta^{2} - e^{-2i\beta}} + 2\cos\beta \ln \frac{\zeta^{2} - 1 + 2i\zeta\sin\beta}{\zeta^{2} - 1 - 2i\zeta\sin\beta} \right\}$$
and
$$\psi_{1}(\zeta) = (\sigma_{e} - \sigma_{c}) \frac{a}{4i\pi} \left\{ \frac{8i\beta}{\zeta - (1/\zeta)} + 2\cos\beta \ln \frac{\zeta^{2} - 1 + 2i\zeta\sin\beta}{\zeta^{2} - 1 - 2i\zeta\sin\beta} \right\}$$
(A12)
(A13)

where

$$\cos\beta = 1 - (r/a).$$

The potentials resulting from the craze stress $\sigma_{\rm c}$ are found by replacing $\sigma_{\rm e} - \sigma_{\rm c}$ by $\sigma_{\rm e}$ and putting $\beta = \pi/2$ in Equations A10 to A13:

$$\phi_2(\zeta) = -\sigma_c \, \frac{a}{2} \frac{1}{\zeta} \tag{A14}$$

$$\psi_2(\zeta) = -\sigma_c \frac{a}{\zeta - (1/\zeta)}.$$
 (A15)

For the external load σ_{a} ,

$$f(\eta) = -\frac{\sigma_{a}a}{8} \left[\eta + \frac{\eta^{2} + 1}{\eta(1 - \eta^{2})} \right] - \frac{\sigma_{a}a}{4} \frac{1}{\eta}$$
(A16)

and by integrating Equations A6 and A7, one obtains:

$$\phi_{3}(\zeta) = -\frac{\sigma_{a}a}{8} \left(\zeta - \frac{3}{\zeta}\right)$$
(A17)

$$\psi_{3}(\zeta) = \frac{\sigma_{a}a}{\zeta - (1/\zeta)}.$$
 (A18)

A relation between β (or r/a) and the external stresses can be found in the hydrostatic component of the stress at the leading edge of the craze is to be bounded. This component is:

$$\sigma_{x} + \sigma_{y} = 4 \operatorname{Re} \frac{\mathrm{d}\phi}{\mathrm{d}z}$$

$$= 4 \operatorname{Re} \left(\frac{\mathrm{d}\phi}{\mathrm{d}\zeta} \frac{2\zeta^{2}}{a(\zeta^{2} - 1)} \right)$$
(A19)

where $\phi = \phi_1 + \phi_2 + \phi_3$

and the required condition is

$$\frac{\sigma_{\mathbf{a}} - \sigma_{\mathbf{c}}}{\sigma_{\mathbf{e}} - \sigma_{\mathbf{c}}} = \frac{\cos^{-1} \left[1 - (r/a)\right]}{\pi/2}.$$
 (A21)

This condition reduces to the Dugdale condition if $\sigma_c = 0$, that is, for a crack or a crack-like craze [9].

Making use of Condition A21, the potentials can be expressed as:

$$\phi(\zeta) = \frac{\sigma_{a}a}{8} \left(\zeta + \frac{1}{\zeta}\right)$$
$$-\frac{\sigma_{e} - \sigma_{c}}{4i\pi} a \left\{ \left(\zeta + \frac{1}{\zeta}\right) \ln \frac{\zeta^{2} - e^{2i\beta}}{\zeta^{2} - e^{-2i\beta}} \right. (A22)$$
$$+ 2\cos\beta \ln \frac{\zeta^{2} - 1 + 2i\zeta\sin\beta}{\zeta^{2} - 1 - 2i\zeta\sin\beta} \right\}$$

(A20)

$$\psi(\zeta) = \frac{\sigma_{a}a}{4} \left(\zeta + \frac{1}{\zeta}\right)$$
$$-\frac{\sigma_{e} - \sigma_{e}}{2i\pi} a \cos\beta \ln \frac{\zeta^{2} - 1 + 2i\zeta\sin\beta}{\zeta^{2} - 1 - 2i\zeta\sin\beta}$$
(A23)

giving the following expressions for stresses and displacements:

$$\sigma_{x} = -\frac{\sigma_{e} - \sigma_{c}}{2\pi} \left\{ 2 \arg \frac{\zeta^{2} - e^{2i\beta}}{\zeta^{2} - e^{-2i\beta}} \right\}$$
(A24)
$$-\operatorname{Im} \frac{16y \sin 2\beta}{a\left(\zeta - \frac{1}{\zeta}\right) \left[\left(\zeta - \frac{1}{\zeta}\right)^{2} + 4 \sin^{2}\beta \right]}$$
(A24)
$$\sigma_{y} = \sigma_{a} - \frac{\sigma_{e} - \sigma_{c}}{2\pi} \left\{ 2 \arg \frac{\zeta^{2} - e^{2i\beta}}{\zeta^{2} - e^{-2i\beta}} \right\}$$
(A25)
$$-\operatorname{Im} \frac{16y \sin 2\beta}{a\left(\zeta - \frac{1}{\zeta}\right) \left[\left(\zeta - \frac{1}{\zeta}\right)^{2} + 4 \sin^{2}\beta \right]}$$

$$\tau_{xy} = -\frac{\sigma_{\rm e} - \sigma_{\rm c}}{2\pi} \times$$

Re
$$\frac{16y \sin 2\beta}{a\left(\zeta - \frac{1}{\zeta}\right)\left[\left(\zeta - \frac{1}{\zeta}\right)^2 + 4\sin^2\beta\right]}$$

$$2Gu = \frac{\sigma_a}{4}(\kappa - 3)x$$
(A26)

$$-\frac{\sigma_{e} - \sigma_{e}}{2\pi} \left\{ y(\kappa+1) \ln \left| \frac{\zeta^{2} - e^{2i\beta}}{\zeta^{2} - e^{-2i\beta}} \right|$$
(A27)
$$+ x(\kappa-1) \arg \frac{\zeta^{2} - e^{2i\beta}}{\epsilon^{2} - e^{-2i\beta}} \right\}$$

)

$$2Gv = \frac{\sigma_{\mathbf{a}}}{4}(\kappa+1)y$$

$$+ \frac{\sigma_{e} - \sigma_{c}}{2\pi} \left(x(\kappa+1) \ln \left| \frac{\zeta^{2} - e^{2i\beta}}{\zeta^{2} - e^{-2i\beta}} \right| \right.$$

$$\left. - y(\kappa-1) \arg \frac{\zeta^{2} - e^{2i\beta}}{\zeta^{2} - e^{-2i\beta}} \right|$$
(A28)

+
$$(a-r)(\kappa+1) \ln \left| \frac{\zeta^2 - 1 + 2i\zeta \sin \beta}{\zeta^2 - 1 - 2i\zeta \sin \beta} \right|$$

References

- 1. E. H. ANDREWS and L. BEVAN, *Polymer* 13 (1972) 337.
- E. H. ANDREWS, G. M. LEVY and J. WILLIS, J. Mater. Sci. 8 (1973) 1000.
- G. P. MARSHALL, L. E. CULVER and J. G. WILLIAMS, Proc. Roy. Soc. Lond. A319 (1970) 165.
- 4. G. P. MARSHALL and J. G. WILLIAMS, J. Appl. Polymer Sci. 17 (1973) 987.
- 5. A. N. GENT, J. Mater. Sci. 5 (1970) 925.
- 6. Idem, J. Macromol. Sci. B8 (1973) 597.
- 7. N. VERHEULPEN-HEYMANS, Thèse de doctorat, Université Libre de Bruxelles (1975).
- 8. idem, J. Polymer Sci-Polymer Phys. 13 (December 1975).
- 9. D. S. DUGDALE, J. Mech. Phys. Solids 8 (1960) 100.
- 10. N. VERHEULPEN-HEYMANS and J. C. BAUWENS, J. Mater. Sci. 11 (1976) 1.
- 11. M. I. BESSONOV and E. V. KUVSHINSKII, Sov. Phys.-Solid State 3 (1961) 950.
- R. P. KAMBOUR and R. W. KOPP, J. Polymer Sci. A-2 7 (1969) 183.
- 13. J. HOARE and D. HULL, Phil. Mag. 26 (1972) 443.
- 14. R. N. HAWARD and G. THACKRAY, Proc. Roy. Soc. A302 (1968) 453.
- 15. V. R. REGEL, Sov. Phys. Tech., Phys. 1 (1956) 353.
- R. N. HAWARD, B. M. MURPHY and E. F. T. WHITE, "Fracture 1969, Proceedings of the 2nd International Conference on Fracture", Brighton (Chapman and Hall, London, 1969) pp. 519-30.
- 17. I. NARISAWA, J. Polymer Sci. A-2 10 (1972) 1789.
- W. FRANK, H. GODDAR and H. A. STUART, Polymer Letters 5 (1970) 1711.
- K. NEKI and P. H. GEIL, J. Macromol. Sci.-Phys. B8 (1973) 295.
- J. H. GOLDEN, B. L. HAMMANT and E. A. HAZELL, J. Appl. Polymer Sci. 11 (1967) 1571.
- 21. T. E. BRADY and G. S. Y. YEH, J. Appl. Phys. 42 (1971) 4622.
- 22. N. I. MUSKHELISHVILI, "Some basic problems of the mathematical theory of elasticity" (Noordhoff, Groningen, 1953).

Received 16 June and accepted 27 June 1975.