STRESSES AROUND A POLYMER CRAZE

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INTRODUCTION

The understanding of stress crazing of polymeric solids has come a long way since its earlier studies. Just before 1950 [1] the craze mechanism was for the first time associated with molecular orientation. Subsequently various physical and chemical methods have been utilized to determine and confirm this molecular orientation behaviour in a tensile stress field [2]. Essentially under stress certain polymers deform from sites where large stress concentrations are present. Because of geometrical constraints the polymeric long chain molecules orient themselves in bundles as domains [1] in the direction of stressing like many tensile specimens distributed between the craze boundaries. As a result voids are created and the density of the medium in the crazed region is reduced. These domains containing oriented molecules act as elastic springs forming an elastic foundation and are bounded by a similar layer of oriented molecules as a continuous membrane which eventually form distributed domains in the region of craze.

The general shape of several horizontal crazes in an oriented polystyrene sheet specimen subjected to a vertical stress is shown in Figure 1. The horizontal dimension of the photograph is about 300μ which is comparable to the diameter of the laser beam used. The specimen is illuminated by laser from behind. The crazes are seen to be bounded with fine parallel horizontal interference lines in between. The boundary at each central section has zero slope in contrast with an inclined one at the tips. The similarities of individual crazes suggest the local nature of each craze. Consequently a realistic model for stress analysis would likely be restricted to the immediate neighbourhood of a craze. Using a membrane anology model with varying elastic foundation, attempts have been made to evaluate the stresses along a linear craze [3]. This report examines further the justification and extension of the linear membrane model to a three dimensional one for analyzing the stresses around a circular craze.

MODEL AND GOVERNING EQUATION

The formation of a craze comes about from a physical transformation in the deformation processes of the polymer molecules from one configurational state to another depending upon the applied tensile load, time, temperature, homogeneity of the polymer, and possibly the chemical environments surrounding the polymer medium. The oriented polymer bundles or domains behave as elastic springs under tensile loads. The interface layers are considered thin membranes formed by intermediately oriented long polymeric molecules without much bending stiffness. They are simply bounds but are capable of further deformation and transformation into highly oriented molecular domain structures found in the craze. The molecular domains possess high strength with voids among them, however. The net result is a

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reduction of the density of the medium in the craze and a redistribution of local stresses around the boundaries of the craze.

Referring to a rectangular coordinate system Oxyz as shown in Figure 2, the cross-section of a craze is set in the xz-plane with the z-axis as its displacement direction. An applied constant tensile stress field σ_o is parallel to the z-axis. First consider that the craze is linear or rectangular in shape with a unit depth and a total length 2c. At an arbitrary point (x,z) an infinitesimal element of length ds is subjected to forces S and S + dS as shown with force equilibrium as:

$$(S+dS)\cos(\theta+d\theta) - S\cos\theta = 0, \tag{1}$$

$$(S+dS)\sin(\theta+d\theta) - S\sin\theta + \sigma_o dx - \sigma(x)ds = 0, \tag{2}$$

where $\sigma(x)ds = k(x)z(x)ds$ is the force exerted by the distributed spring function $k(x)$ along the arc length of the membrane whereas the applied force is $\sigma_o dx$.

Utilizing proper trigonometric relations and limit fundamentals, equations (1) and (2) can be reduced to give:

$$(S\cos\theta)_x = 0, \tag{3}$$

$$(S\sin\theta)_x = - \sigma_o + \sigma/\cos\theta, \tag{4}$$

where the subscript x represents the differentiation with respect to x. These equations can further be reduced to:

$$S\theta_x = - \sigma_o \cos\theta + \sigma. \tag{5}$$

In terms of the x, z coordinates, it appears as:

$$\left(1+z_x^2\right)^{-1/2} Sz_{xx} = - \sigma_o + \sigma\left(1+z_x^2\right)^{1/2} \tag{6}$$

where the double subscripts xx represent the second order derivative. From this governing differential equation both the displacement field $z(x)$ and stress field $\sigma(x)$ are obtainable with the boundary conditions $z_x(0) = 0$, $z(c) = 0$ provided for a homogeneous medium. Remember that σ is a linear function of z. Thus equation (6) is nonlinear with no apparent analytical solution. Numerical solutions indicate that, it is, however, possible to simplify equation (6) by assuming small deformations for which the slope of the craze displacement field is very small. Then equation (6) can be reduced to:

$$Sz_{xx} = - \sigma_o + \sigma. \tag{7}$$

This applies to the study of a linear craze occurring often on the surface of a brittle polymer. An analysis of this type of craze has been made earlier [3].

For a circular craze occurring usually in the interior of a homogeneous polymer under stress, the above formulation may be extended. Consider polar symmetry and introduce the forces in the y direction in an infinitesimal elemental plate dxdy of thickness h. If the tensile forces in the

y-direction are similar as those in the x-direction, then the governing differential equation becomes:

$$S\left(z_{xx} + z_{yy}\right) = - \sigma_o + \sigma. \tag{8}$$

In polar coordinates the above differential equation transforms to:

$$S\left(z_{rr} + z_r/r\right) = - \sigma_o + \sigma, \tag{9}$$

where r is the radial coordinate and $\sigma(r) = k(r)z(r)$.

Equation (9) can be solved if k/S is a constant. Physically k is the modulus function of the oriented craze medium at position (r,z) in units of force per unit length per unit area; and S is the tensile force in the membrane per unit length in the neighbourhood of the same position (r,z). They both describe the tensile behaviour of the oriented polymer molecular domains but at slightly different stages or orientation [4]. Therefore it is reasonable to assume that their ratio does not change. That is we can let $\alpha^2 = k/S$ where α is a constant. Now substitute $\gamma = \alpha r$ in equation (9) as a new variable, then one gets:

$$z_{\gamma\gamma} + z_\gamma/\gamma - z = - \sigma_o/k(\gamma), \tag{10}$$

This equation has the solution:

$$z(\gamma) = \left[C_1+\phi_1(\gamma)\right]I_o(\gamma) + \left[C_2+\phi_2(\gamma)\right]K_o(\gamma), \tag{11}$$

where C_1 and C_2 are two constants to be determined by boundary conditions, and

$$\phi_1(\gamma) = - \sigma_o \int K_o(\gamma)d\gamma/k(\gamma), \tag{12}$$

$$\phi_2(\gamma) = \sigma_o \int I_o(\gamma)d\gamma/k(\gamma). \tag{13}$$

Depending upon the form of the modulus function $k(\gamma)$, analytical solutions may or may not be obtained. If

$$k(\gamma) = fk_o e^{-\gamma}, \tag{14}$$

where k_o is the original modulus constant and f is a fraction which varies between 0 to 1, then analytical results are obtainable [5]. However, they are not totally desirable as the stress distribution at the centre of craze does not satisfy the boundary condition that the slope of the stress at the central position must be zero. To correct this let us employ an adequate modulus function:

$$k(\gamma) = k_o \frac{f(e^{\alpha c}+e^{-\alpha c}) - 2 + (1-f)(e^{\gamma}+e^{-\gamma})}{e^{\alpha c} + e^{-\alpha c} - 2} \tag{15}$$

With this modulus function, analytical solutions were not found. However, results could be obtained numerically for the displacement field $z(\gamma)$ as well as for the stress field $\sigma(\gamma)$.

RESULTS AND DISCUSSION

Based upon the model used a series of displacement fields and stress distributions for different values of f have been numerically obtained and plotted as shown in Figures 3-10. In general it is seen that the craze displacement field is length dependent. As f decreases from 0.5, 0.25, 0.125 to 0.01, Figures 3, 5, 7 and 9 show respectively the corresponding increase in the displacements. For the same craze length, the displacement field for the circular craze is always smaller than that of the linear rectangular one [3]. As observed earlier experimentally [6], it is interesting to note that the slope of the craze boundary does increase progressively at the craze tip as craze length increases. It is also seen that the craze displacement is progessively increasing as f reduces.

Similarly Figures 4, 6, 8 and 10 show respectively the variation of the stress distribution corresponding to the decrease of f from 0.5, 0.25, 0.125 to 0.01. However, a closer examination of the curves indicates that the stress distribution is very much dependent upon f for $f < 0.5$. When $f > 0.5$, the stresses were found to be monotomically decreasing similar to those shown in Figure 4 for which $f = 0.5$. When $f < 0.5$ stress fluctuations develop as shown in Figure 6 for $f = 0.25$ and Figure 8 for $f = 0.125$. This phenomenon is especially true as f gets smaller and smaller. As shown in Figure 10 stresses for any craze length have humps. A similar trend was also observed for the linear case [3] with an exception that negative stresses could develop after reaching certain craze length. Whereas no such stress behaviour was found for the circular craze.

Overlooking some of the differences in the production of craze, the current results of stress distribution are qualitatively similar to those measured experimentally [7]. For small values of f with proper craze length given a maximum stress was found to occur always behind the craze tip. As crazes get larger, the maximum stress shifts closer to the craze tip. Further experiments are needed for verification of this and other calculated behaviours. There has been one previous attempt [8] in calculating stresses around a polymer craze. The model used did not seem to match with the problem and was unrealistic. Consequently there was little or no experimental evidence available to support it.

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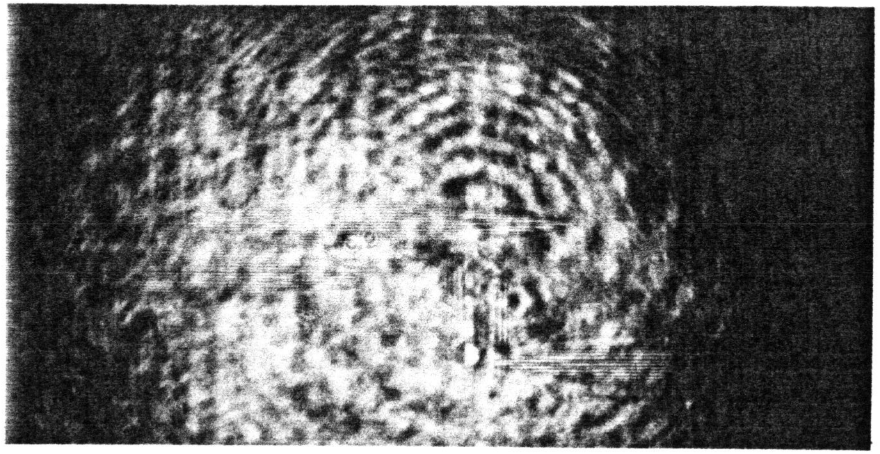

Figure 1 Laset Transmission Micrograph of Crazed Polystyrene

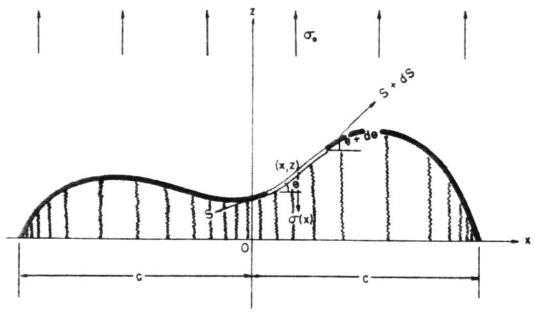

Figure 2 Upper Cross-Section of a Craze in Tension

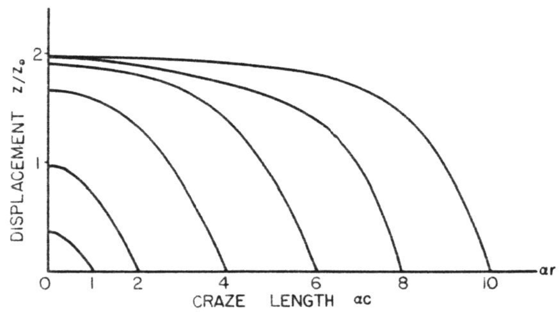

Figure 3 Craze Length versus Displacement for $f = 0.5$

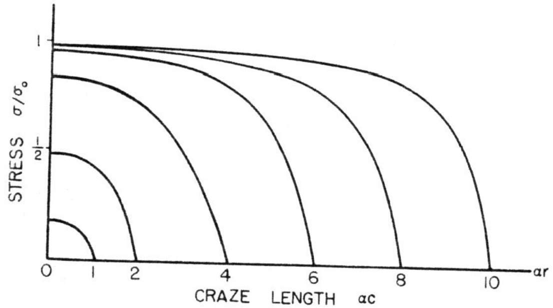

Figure 4 Craze Length versus Stress for f = 0.5

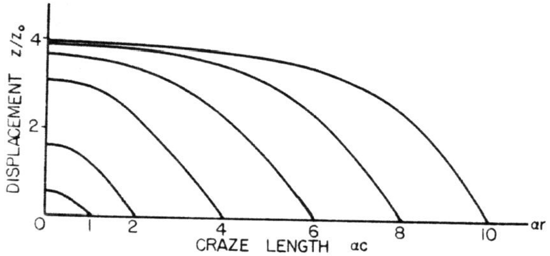

Figure 5 Craze Length versus Displacement for f = 0.25

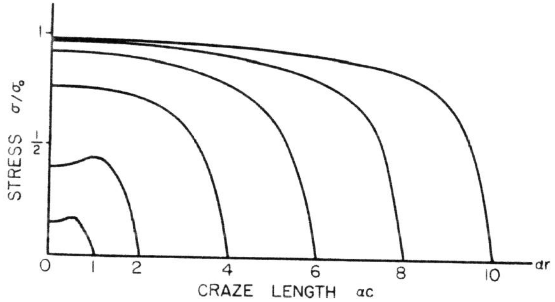

Figure 6 Craze Length versus Stress for f = 0.25

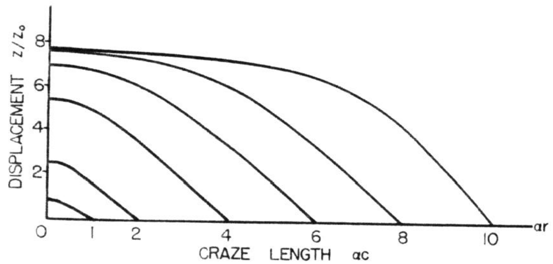

Figure 7 Craze Length versus Displacement for f = 0.125

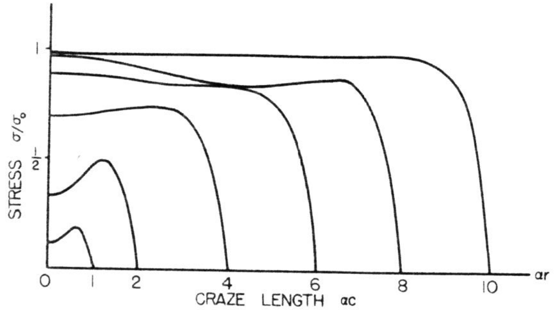

Figure 8 Craze Length versus Stress for f = 0.125

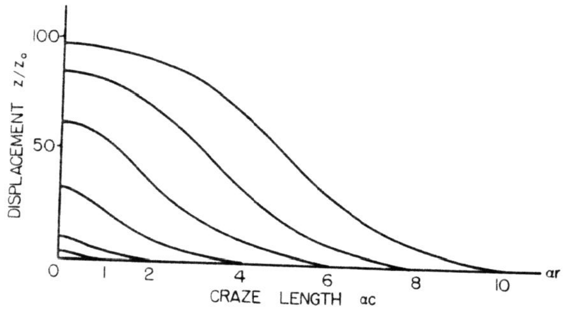

Figure 9 Craze Length versus Displacement for f = 0.01

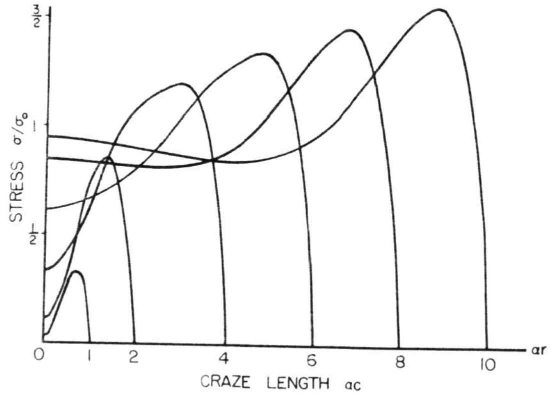

Figure 10 Craze Length versus Stress for f = 0.01