The density of the craze layer on the fracture surface of polystyrene

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The refractive index and the density of the craze layer on the fracture surface of polystyrene have been measured directly from interferometric measurement of level differences on the fracture surface. The experimental results are in approximate agreement with the values calculated from either the Lorenz-Lorentz equation or Rayleigh's equation for parallel rods.

1. Introduction

A crack propagating in polystyrene is usually preceded by a layer of "craze", an expanded form of the polymer of lower density. When the crack propagates at low velocities (below about 1 cm sec^{-1} at room temperature), the craze ruptures close to its median plane by a mechanism having the approximate characteristics of viscous flow; each fracture surface is then covered by a thin layer of craze. At higher crack velocities, however, failure tends to occur along the boundaries between the craze and the adjacent bulk polymer by a mechanism of practically brittle fracture [1]. The change in fracture mechanism is shown schematically in Fig. 1.

Kambour has determined the refractive index of crazes in polystyrene by measuring the critical angle for total internal reflection of light at the craze-bulk boundary; the refractive index of unbroken, unstressed crazes embedded in the
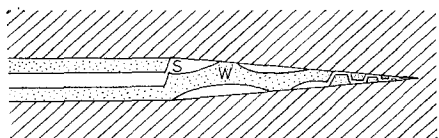
Figure 1 To show how the craze wedge, W, is detached by fracture along the craze-bulk boundary; to the left the crack has propagated along the median plane of the craze and on one fracture surface the craze layer is terminated by a steep scarp, S.

bulk polymer has been found to be 1.33 [2], and that of the craze layer on cleavage fracture surfaces at 70°C has been measured as 1.31 [3]. Using the same method in the present work, in cleavage fracture of polystyrene (viscosity average molecular wight 2.1 × 10⁵) at 70°C, I have obtained values of the refractive index ranging from 1.21 to 1.30 as the crack velocity increased from about 0.1 to 1 cm sec^{-1}. At room temperature I have found the refractive index of fracture surface craze layers to be usually in the range between 1.12 and 1.17.

The density of the craze layer has been calculated by Kambour [4] from the Lorenz-Lorentz equation

$$\frac{n^2 - 1}{n^2 + 2} \times \frac{1}{d} = \frac{4}{3}\frac{N_a\,\alpha}{M} = \text{constant} \qquad (1)$$

where n is the refractive index, d the density, α the molecular polarizability, M the molecular weight and N_a is Avogadro's number. Strictly speaking, the equation applies only for dipoles arranged in a cubic lattice; it can be used for isotropic materials as an approximation [5]. For the few substances for which sufficient data are available, the constant in Equation 1 varies by only a few per cent over the range of densities from the gaseous state to the liquid state [6].

The electron micrographs of Kambour [7, 8] and more recently by others [9, 10] suggest that under some conditions at least, the craze layer consists of more or less parallel and continuous

fibrils of molecule bundles, about 200 Å in diameter, perpendicular to the plane of the layer. For the fibrillar craze the Lorenz-Lorentz equation cannot be expected to apply; where the fibril diameter is considerably smaller than the wavelength of light, the appropriate equation would be that for parallel rods, which Rayleigh called "Newton's Law" [11]:

$$n_c{}^2 = 1 + (n_b{}^2 - 1) v \qquad (2)$$

where v is the volume fraction of polymer in the craze and n_b the refractive index of the fibrils, which is probably close to that of the bulk polymer. In view of the uncertainties of the applicability of Equations 1 and 2, it was of interest to measure the density and the refractive index of the craze layer directly.

2. Experimental

As seen in Fig. 1, there is a scarp, S, terminating the craze layer on one of the fracture surfaces along the front, RR, beyond which the entire craze wedge, W, separates from the bulk. By heating the craze layer, it can be collapsed nearly to bulk density, and from the thickness of the original craze layer and that of the collapsed layer, the void content of the craze layer can be calculated. The process is easily carried out by covering half of the craze layer on the fracture surface with a thin copper foil, as indicated in Fig. 2, and holding the
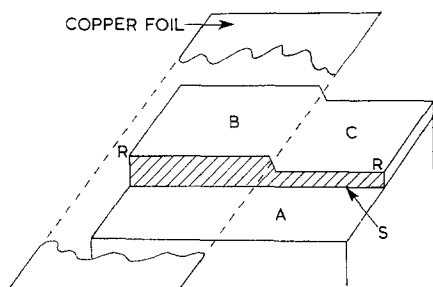

Figure 2 Sketch to show the level differences along the scarp S after part of the craze layer has been thermally collapsed. The area A is the naked bulk; after heating, the quadrant B is uncollapsed craze and quadrant C is collapsed craze.

fracture surface in the hot air over a Bunsen flame for a few seconds. In Fig. 2, the area, A, of the fracture surface is the naked bulk; after heating, the remainder contains a quadrant, B, of uncollapsed craze and a quandrant, C, of

collapsed craze. The entire fracture surface is then silvered by evaporation, and the level differences between the naked bulk, the collapsed and the uncollapsed craze measured by a Zeiss double-beam interferometer. For correct comparison of these level differences, points along RR were selected which had the same initial craze thickness before the heat-treatment. This could be done by referring to a photomicrograph of the original fracture surface, taken in reflected monochromatic light, before collapsing the craze. Light reflected from the surface of fracture interferes with light reflected from the craze-bulk boundary, and small variations in the thickness of the craze layer gives rise to a pattern of interference fringes. On this reference micrograph points along RR were selected on the same interference fringe where, therefore, the craze layer had the same thickness (provided that the refractive index was constant). From the original thickness of the craze layer and the thickness after thermal collapse, the void content of the craze was calculated. Lednicky and Pelzbauer [13] have measured the geometric thickness of polymethyl methacrylate (PMMA) fracture surface craze layers by observation of microtomed sections from the fracture surface in the electron microscope; the present method, applied to polystyrene, avoids the possibility of deformation of the craze layer which may occur in the preparation of the microtomed section.

For the calculation of the refractive index of the craze it was necessary to determine the order of the optical interference at the points where the thickness of the layer had been measured. Where the craze layer ruptures along its median plane, before peeling off the bulk, "fracture parabolas" are seen; their foci are sites at which initiation of advance fractures occurs. After the main crack intersects the advance fracture on the "upstream" side, the "downstream" side continues to run abreast with the main fracture front, and the two fronts intersect in a parabola-like curve. The mechanism of their formation has been explained in a previous paper [1]. Near the focus of some of the parabolas the craze layer is very thin, often showing $\frac{1}{4}\lambda$ destructive interference: away from the focus the craze layer gradually increases in thickness, and where it intersects the main fracture surface the craze layer reaches its full thickness. A section through a parabola is sketched in Fig. 3. Viewed in reflected monochromatic light a continuous
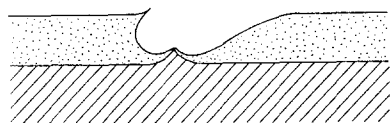
Figure 3 Cross section of a "fracture parabola"; the craze layer increases in thickness away from the focus.

series of interference fringes surrounds the focus of the parabola, and the interference order of the main fracture surface can be determined by counting the number of these fringes. Another method has been described by Pelzbauer and Lednicky [14] who determined the optical thickness of the craze layers on the fracture surface of PMMA by measuring the shift of the position of the interference fringes with a change in wavelength; the method used in the present work appeared to be quite satisfactory and unambiguous in the case of polystyrene fracture surface layers.

3. Results and discussion

Along the front RR, the craze layer usually showed 10th to 13th order interference; from the interferometrically measured thickness (*d*) of the craze layer and the interference equation

$$2n_c d = (k + \tfrac{1}{2})\lambda \quad (\lambda = 5460\text{Å}) \qquad (3)$$

the refractive index was found to be in the range between 1.16 and 1.20 ± 0.02. The void content calculated directly from the interferometric measurements was then in the range between 69 and 75 ± 2%. Points measured on three different specimens, together with the curves corresponding to Equations 1 and 2 are shown in Fig. 4. It is seen that the differences between Equations 1 and 2 are small relative to the scatter of the measured points.

The refractive index of the craze layer as measured by the above method is in each case slightly higher than that found by Kambour's total reflection method; the difference is slightly greater than the margin of error. The interferometric method gives average values of the refractive index and the mean density of the whole layer; the total reflection method would be expected to give a result closer to the lowest value of the refractive index within the craze layer [12]. This would account for the small difference mentioned; even so the results are in good agreement.
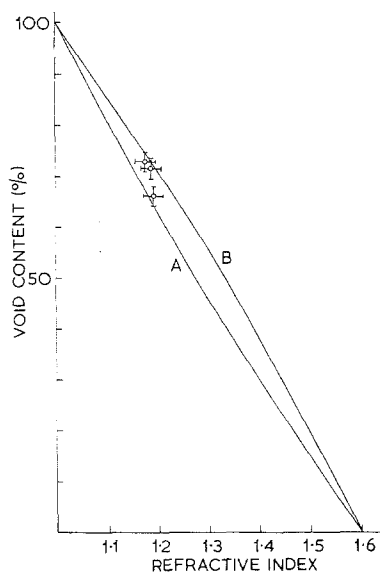
The craze layer can also be collapsed by

Figure 4 Refractive index of the fracture surface craze layer of polystyrene versus void content. Curve A: the Lorenz-Lorentz equation; curve B: the equation derived by Rayleigh for parallel rods.

mechanical pressure or by placing a small drop of a suitable solvent such as toluene on the fracture surface, e.g. from an atomizer spray. The mechanical pressure was applied by a Vickers microhardness indenter; in both cases a series of interference fringes was observed around the central area where the craze layer had been completely compressed or collapsed. When the initial craze layer had the same thickness, the number of fringes was the same whether the craze was collapsed by heating, by a solvent or mechanically.

Fig. 5 shows an indentation from the microhardness indenter; the fringes decrease in order towards the centre as the layer is increasingly compressed. Under its own weight the indenter formed a large impression involving considerable plastic deformation of the underlying bulk polymer; the indentation in Fig. 5 was, therefore, made with the indenter resting against its stop and by lowering the microscope tube to which it is attached so that the craze layer was completely compressed only at the very centre of the indentation. After silvering the surface, the depth of the indentation at the point where the interference fringes disappear (that is, the level difference between the collapsed and uncollapsed layers) was measured with the interferometer. The thickness of the compressed layer could not
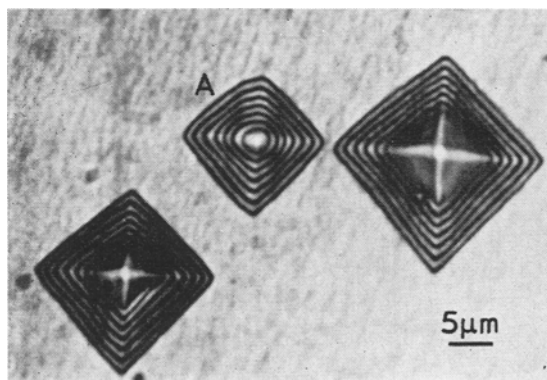
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Figure 5 Indentations in the craze layer made by a Vickers microhardness indenter. In the indentation A the craze layer has been completely compressed only in the small area at the centre; reflected monochromatic light ($\lambda = 5460$ Å).

be measured directly but was estimated in the following way. The innermost interference fringe corresponds to a layer of compressed craze of almost the same refractive index and density as the bulk polymer; its order of interference was obtained by counting back from the known order of the unchanged craze layer (see above) surrounding the indentation. If this value is introduced into the interference equation and the refractive index of the bulk polymer is assumed to be 1.60, the thickness of the fully compressed craze layer is obtained. The void content calculated by this method was 65%, roughly in agreement with the previous results.

The void content of unbroken, unstressed crazes embedded in bulk polystyrene has been calculated by Kambour [2] as 40%; the density of the craze layer on the fracture surfaces of polystyrene is considerably lower. This is not surprising since the disruption of the craze requires more stretching than the formation of an undisrupted craze layer; this results in a permanently lower density of the fracture surface craze layer. The void content (40 to 50%) of the craze layer formed by fracture at 70°C seems to result from a partial thermal collapse at the higher temperature; a fracture surface formed at room temperature and placed in an oven at 70°C for a few minutes showed a craze density of about this magnitude.

Acknowledgements

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