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Slip band formation in polycarbonate under tension

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The effect of thermal history on slip band formation in glassy polymers has been studied extensively. Bowden and Raha[1] discovered that in both polystyrene and poly(methyl methacrylate) under plane strain compression two distinct deformation modes were possible. Yielding took place either along well-defined slip bands or in diffuse yielded zones. As the strain rate decreased the slip bands gradually disappeared. However, it was noticed that it was much easier to form slip bands in thermally aged specimens than in quenched material. Wu and Li[2] obtained similar results in notched compression samples of polystyrene and also found that the diffuse zones were aggregates of fine slip bands around 0.1 μm thick. Various other authors[3-5] have also studied slip band formation in polystyrene under compresion but little work has been done in tension or on other polymers.

During tensile experiments on a 1 mm thick commerical polycarbonate sheet (Makrolon) it was noticed that the propagating neck often appeared to contain an irregular texture. After concluding that the texture was produced by a collection of discrete slip bands, it was decided to investigate the effect of thermal history and neck velocity on the formation of these slip bands.

Firstly, the orientation in the sheet was removed by drying at 120°C for 18 h and then holding at 160°C for 4 h between glass plates. The sheet was then air-cooled and d.s.c. traces showed that it had been effectively quenched. Conventional dumb-bell specimens (narrow section 12.7 × 60 mm) were cut from the sheet. Half of the specimens were then aged by holding at 130°C for 48 h. This treatment provides the maximum degree of aging obtainable in polycarbonate. The specimens were then extended on an Instron Mechanical Testing Machine at crosshead speeds in the range 0.0008 to 0.833 mm s^{-1}. In all experiments the draw ratio was close to 1.7 and therefore the neck velocities lay in the range 0.002 to 2.02 mm s^{-1}.

The appearance of the necks in the aged specimens can be seen in *Figure* 1. When describing the visible features it is convenient to define an orthogonal set of axes xyz with the y axis coincident with the tensile axis and the xy plane lying in the plane of the specimen. The z direction is then normal to the specimen surface. The texture in the necks is easily seen but becomes less pronounced as the neck velocity is decreased. As the neck propagates, 'ripples' are left on the surface of the drawn material. Also visible are groups of slip bands in the xy plane. Evidently the slip bands form at the edge of the specimen and run towards the centre of the specimen as the neck propagates. The specimens in the micrograph are unloaded and elastic relaxation may affect the orientation of the slip bands. However, since they are close to 45° to the tensile axis it is reasonable to assume that they are propagating along the direction of maximum shear stress. The tips of the slip bands remain at a constant distance above the top of the necked region and clearly the presence of the neck is necessary to generate these slip bands. As the neck velocity is reduced the extent of the slip bands increases until at the lowest neck velocity the two sets of slip bands overlap. Possibly a small degree of thermal softening occurring ahead of the neck hinders the formation of the slip bands at the higher neck velocities. Infra-red photography[6] has shown that a neck velocity of 2.02 mm s^{-1} produces a temperature rise of around 15°C. The temperature decreases when moving from the centre of the neck to the edges and perhaps the extent of the slip bands corresponds to some limiting temperature above which they are not produced. At the lowest neck velocity the temperature increase is less than 0.2°C and no significant thermal softening occurs.

In order to learn more about the texture in the necks, sections were taken in the yz plane by cutting with a diamond impregnated slitting wheel. *Figure* 2 shows that the texture is produced by a system of slip bands operating in the yz plane. Again the specimen is unloaded and elastic strains would tend to make the slip bands intersect at angles closer to 90°. Nevertheless, it is reasonable to

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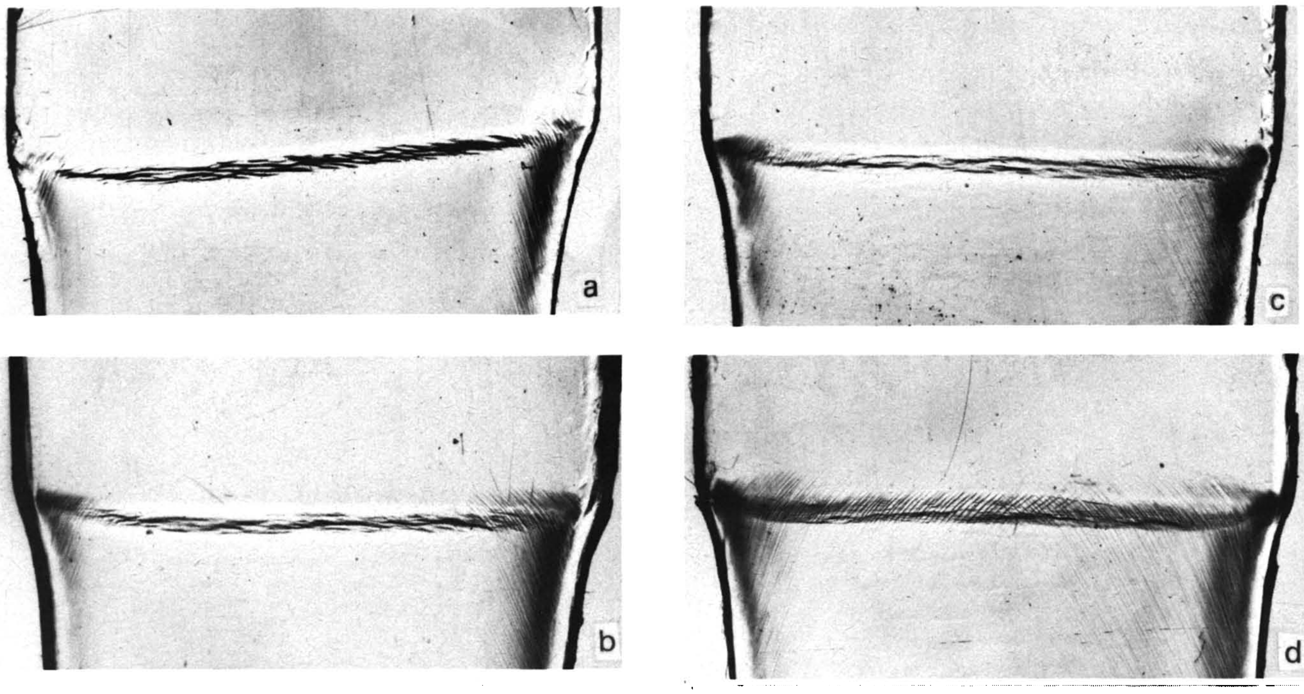

Figure 1 Configuration of necks in thermally aged polycarbonate with velocities (a) 2.023, (b) 0.202, (c) 0.020, (d) 0.002 mm s^{-1}

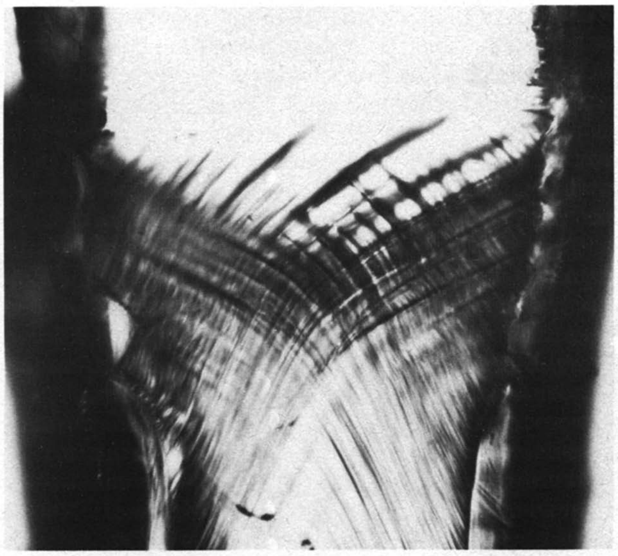

Figure 2 Section through the central region of a neck in thermally aged polycarbonate. Neck velocity = 0.081 mm s^{-1}

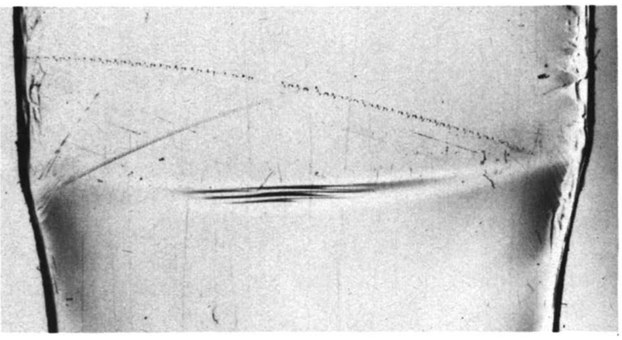

Figure 3 Neck in quenched polycarbonate. Neck velocity = 0.202 mm s^{-1}

assume that the deformation is close to pure shear yielding, which suggests that plane strain conditions applies. The large width/thickness ratio of the specimen hinders distortion in the x direction and a tension is developed along this axis. Assuming plane strain deformation and that the stress in the z direction is small, this tension is required to be one half of the applied tensile stress. It is surprising therefore that slip bands occur in the xy plane since the maximum shear stress in that plane will be one half of that in the yz plane.

Usually no texture or slips bands were observed in the quenched samples, but occasionally a few slip bands occurred in the yz plane (*Figure* 3). It is not clear why aged specimens produce a greater number of slip bands than quenched material. The increase in yield stress obtained by aging cannot account for the difference since the range of yield stresses produced by varying the crosshead speed in the quenched (56–72 MPa) and aged (67–81 MPa) specimens overlap. Possibly a combination of yield stress and deformation rate is required to produce slip bands, but it is more likely that some structural changes in the aged specimens favour their production.

The shear strain associated with slip bands in polystyrene has been estimated to lie in the range 1 to 2.15[1-3]. However, the slip bands observed here in the xy plane appear to have a small shear strain. *Figure* 4 is a scanning electronmicrograph which shows a region ahead of the neck where slip bands and scratches intersect. Little displacement of the intersection points on either side of the slip band can be seen. The *SEM* was also used to investigate whether the diffuse necks were aggregates of fine slip bands as found in polystyrene by Wu and Li[2]. No fine structure could be observed at similar magnifications to those used by Wu and Li.

In summary, it is evident that aging can produce heterogeneous yielding in polycarbonate under tension.

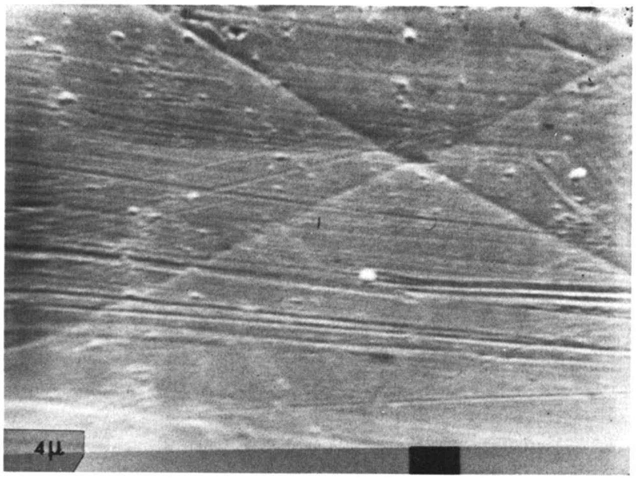

Figure 4 Intersections of shear bands and scratches in aged polycarbonate. Neck velocity = 0.002 mm s^{-1}. The micron marker refers to the length of the black band

However, in common with other papers in this field, no explanation for this phenomenon can be readily provided.

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An approach to the mechanism of environmental stress cracking by theoretical kinetics

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Environmental stress cracking (*ESC*) in polyethylene (PE) has been studied both from scientific and technological viewpoints. A study based on the fracture mechanics of a continuum body was reported by Williams *et al.*[1]. Two different molecular mechanisms have been proposed. One was based on a surface energy reduction by *ESC* active liquids[2] and the other[3,4] attributed *ESC* to stress-induced plasticization. A study of PE *ESC* growth rate in our laboratory[5] has indicated that the thermal motion of PE segments at crack tips is enhanced by active liquids. Although the two theories of Brown[3] and Gent[6] for treating stress-induced plasticization are adequate, they are equilibrium theories. Because cracking is not a thermodynamically reversible process, a sound approach to the problem should take irreversibility into account. The theory presented here, which represents the role of stress as a promotion of the compatability of active liquids with polymers, is developed from irreversible statistical mechanics. The results seem to give us a deeper insight into *ESC* in PE and other polymers. The *ESC* growth rate is assumed to be so slow that the flow of liquids is not rate-controlling.

We consider a system composed of phases I and II. Phase I, representing a polymer crack tip region, is a mixture of n_r r-mers and n_s s-mers. The former are polymer molecules and the latter are *ESC* active molecules and phase II represents an *ESC* active liquid. Phases I and II are in contact and s-mer molecules can migrate between the both phases. Phase I is subjected to a dilative stress P_1 due to the stress concentration at the crack tip and II to P_2 (negative) due to atmospheric pressure. The whole system is maintained at a temperature T. Assuming local equilibrium and using the Flory–Huggins lattice theory, the Gibbs free energy of the system is given by:

$$G/kT = n_r \ln(1-\varphi_s) + n_s \ln\varphi_s + \chi_{r,s} r n_r \varphi_s - s n_s (p_1 - p_2)/kT + \text{constant} \qquad (1)$$

where φ_s is the volume fraction of the s-mer in phase I and $\chi_{r,s}$ is the interaction parameter defined for a pair of segments, one r-mer and one s-mer.

The free energy G *versus* φ_s, calculated for a system of 100-mers and 3-mers with $\chi_{r,s}=1$ and various effective dilative stresses $\Delta p=(p_1-p_2)/kT$ are shown in *Figure* 1. For Δp positive or zero, the free energy has a minimum near $\varphi_s=0$, i.e., the r-mers and the s-mers are almost incompatible. As Δp becomes more positive G exhibits a minimum and a maximum and tends to $-\infty$ as $\varphi_s \to 1$. With further increase in Δp, it decreases monotonically, When Δp is positive, the most stable state of phase I is thus the state $\varphi_s=1$. At the moment when the loading by p_1 on phase I and the contact of phase I and II starts, the system is at the state $\varphi_s=0$ and then is shifted towards the stable state $\varphi_s=1$ by the thermodynamical force. The shift rate will be slowed down in the interval between the two free energy extremes. When the concentration of the s-mer in phase I reaches a value, say φ_s^* phase I will not support the dilative stress and will collapse, which is regarded here as

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