Letters

Discontinuous shape changes associated with Case II transport of methanol in thin sheets of PMMA

As part of an ongoing study of Case II transport in glassy polymers, we have observed changes in specimen shape during swelling which can be related to the stress state associated with the characteristically sharp diffusion front. We consider that observation of such dimension changes can further the understanding of the Case II transport mechanism, and hence take this opportunity of bringing these effects to general notice.

The term Case II transport was introduced by Alfrey *et al.*[1] to describe transport of non-solvents in glassy polymers well below their T_g when the sharp boundary separating the inner glassy core from the outer swollen layer advances at constant velocity into the polymer. Such systems are also characterized by linear absorption with time and their behaviour is well documented[2,3].

The results reported are part of a detailed study of the kinetics of methanol transport in PMMA sheet[4], although here we shall confine our remarks to shape changes in 40 x 20 x 1mm sheet specimens swollen at 24°C. The parameters measured are shown schematically in *Figure 1*. The sharp fronts however, are normally observable only after the specimens are sectioned, since it is virtually impossible to prevent methanol diffusion into the edges as well as the faces of the specimen.

Figure 2 shows the data plotted against a common time axis. Weight increase (*Figure 2a*) is linear with time up to the moment when the fronts meet and absorption is complete. The plot of volume increment *versus* time (*Figure 2b*) has the same shape as that of the weight gain, and the ratio of these two parameters is constant.

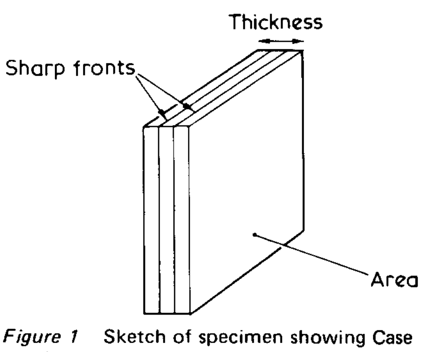

Figure 1 Sketch of specimen showing Case II diffusion fronts

There is, however, a discontinuity in the relationship between thickness increase and time (*Figure 2c*). This discontinuity represents a reduction in specimen thickness which occurs after the fronts have met, and is reflected in a corresponding increase in specimen area (*Figure 2d*) which is hardly surprising in view of the lack of any discontinuous change in volume.

Changes in specimen dimension have been reported for other systems[5,6] where they were thought to be indicative of a stress–strain mechanism of penetrant transport. Indeed, since shape changes give direct evidence of internal stresses on swelling, their consideration must play an important part in any understanding of 'anomalous diffusion' in polymers[7,8].

We consider these effects to be a direct result of the stress state which controls Case II transport. The swollen polymer at the advancing front is constrained by the glassy material in the unpenetrated core. Thus the polymer can only increase in volume by changing its shape, as it must maintain a nearly constant area parallel to the front. Shape change occurs by a process of creep which is essentially the rate controlling mechanism for front advance. The PMMA used in this work had a molecular weight $M_w = 3 \times 10^6$, and hence the creep deformation can be considered as an example of retarded rubber elasticity, and is recoverable on removal of the stress.

When the fronts meet, the constraint of the glassy core is lost and hence the shape change imposed upon the swollen material is able to relax. This relaxation, which occurs at constant volume, accounts for the observed increase in area and corresponding reduction in thickness. The fact that it does not take place immediately the fronts meet is seen as being the result of the viscous component of retarded elastic behaviour.

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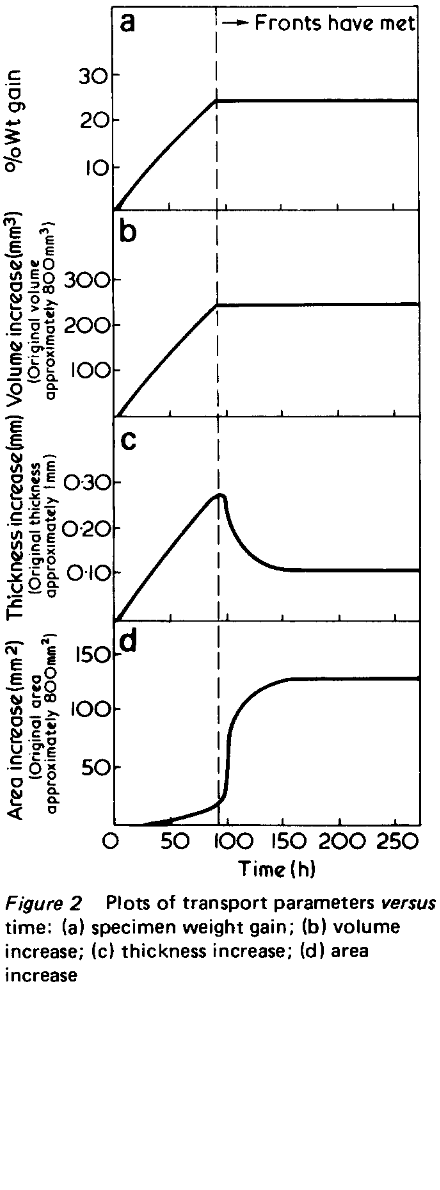

Figure 2 Plots of transport parameters *versus* time: (a) specimen weight gain; (b) volume increase; (c) thickness increase; (d) area increase

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