polymer reports

# Stress modified Case II diffusion in poly(methyl methacrylate)

**A. P. More, A. M. Donald and A. Henderson**
*Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, UK*
*(Received 24 December 1991; revised 11 March 1992)*

The penetration of iodine-stained methanol into poly(methyl methacrylate) has been monitored as a function of externally applied stress. Both the induction time for first penetration and the total distance penetrated by the solvent depend strongly on the magnitude of the applied stress. These observations support implicit assumptions made in the literature.

(**Keywords: Case II; diffusion; stress; solvent; PMMA; induction time**)

## INTRODUCTION

The diffusion of small molecule solvents in glassy polymers has been extensively studied and a mechanism describing the observed non-Fickian (Case II) diffusion developed[1–3]. This model explains the sharp front characteristics of Case II diffusion in terms of a coupling between the swelling due to solvent ingress and the standard diffusion equations. It is suggested that initially swelling of the glassy polymer occurs, and this process sets up an osmotic pressure and a consequent change in the local chemical potential. Case II diffusion can only take place after a critical surface volume fraction of penetrant has been achieved[4], after which the viscosity of the matrix has dropped sufficiently and the diffusivity increased to a point that the Case II diffusion front can be established. This means that there is a finite time delay between first exposure to the solvent and penetration; this leads to the appearance of an induction time[4,5]. Once the diffusion front is established the surface concentration continues to rise towards its equilibrium value, the osmotic pressure tends to zero and a steady state is achieved. The boundary between the swollen polymer and the glassy core into which the solvent has not yet pentrated is sharp with only a small Fickian precursor preceding the front, which moves with time.

This model suggests the coupling between mechanical stress and diffusion. This same idea is implicit in models of solvent induced crazing that are >10 years old[6], as well as more recent ones[7]. However, experimental data to support the idea that the presence of an applied stress may alter the diffusion coefficient of small organic molecules have not been forthcoming, although there is indirect evidence to suggest that in regions of a glassy polymer that have already yielded, diffusion may be enhanced[8–11]. In this paper, preliminary results are presented showing directly how an external stress may lead to a change in both the rate of propagation of a diffusion front and in the preceding induction time. The system studied is the same as that studied by Thomas and Windle[1,12], namely iodine-stained methanol diffusing into poly(methyl methacrylate) (PMMA). The advantage of using this same system is that its behaviour in the absence of stress is well known from the earlier studies, in which it was shown that the iodine stain faithfully followed the methanol penetration. In this study, as previously, the iodine lends itself as a convenient strain for optical microscopy measurements of the location of the diffusion front. We now make the assumption that the equivalence of the methanol penetration and the iodine stain still holds.

## EXPERIMENTAL

Samples of PMMA (ICI Perspex$^{\mathrm{TM}}$, $T_g \sim 110$°C) measuring 60 mm × 20 mm were milled from a 1 mm thick sheet. Residual stresses and water were removed by vacuum annealing the PMMA strips at 125°C for 1 h. The experimental set-up is schematically shown in *Figure 1*. The PMMA strip, enclosed in a polyethylene jacket, is clamped at either end, with the lower clamp fixed and the upper clamp attached to a suspended load. Loads

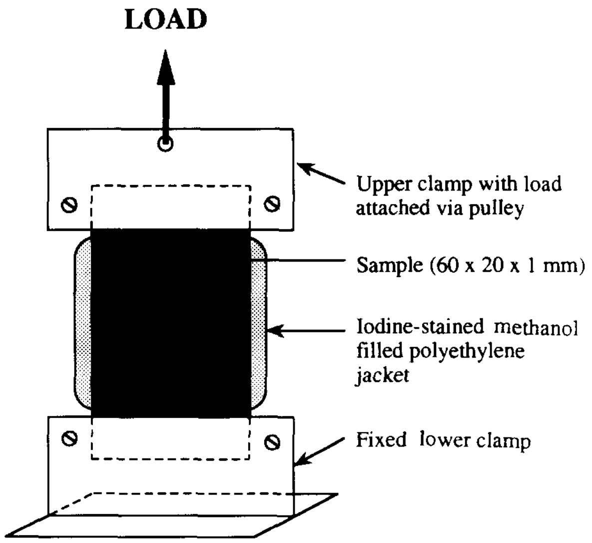

**Figure 1** Schematic diagram of the experimental test rig. The sample sits in a polyethylene jacket filled with iodine-stained methanol

0032-3861/92/173759-03

up to 2.5 kg (equivalent to an applied tensile stress of ~1.25 MPa) were used. These stresses are well below the yield point of PMMA. Under the simple experimental set-up described here the strain was compressive arising from a Poisson's ratio contraction. Assuming a Poisson's ratio of ~0.4 for PMMA[13] each kg of applied load represents a compressive force of ~3.9 N acting over ~$20 \times 10^{-6}$ $m^2$, i.e. equivalent to a compressive stress of ~0.196 MPa. The polyethylene jacket is then filled with a 30 mg $l^{-1}$ solution of iodine in methanol, and a known load applied. Sample areas ~30 mm × 20 mm are exposed to the iodine/methanol solution, at a temperature of ~20°C (±2°C).

After each run the PMMA strip is briefly rinsed in distilled water, dried and immediately sectioned with a sledge microtome. Sections ~20 $\mu$m thick, taken from the centre of the strip, were mounted on a glass microscope slide in oil of refractive index 1.48. Oil mounting minimizes opacity due to microtome-induced crazing[11]. The iodine propagation distance is then measured by photography of the sections with a Carl Zeiss Jenapol optical photomicroscope and subsequent comparison of the micrographs with a series of calibrated standards. Previous studies show iodine to be a good indicator of the diffusion front[1,12]; the same is assumed to be true in the presence of stress. Diffusion front penetration distances of < ~5 $\mu$m could not be reliably measured by this method, and are recorded only as trace. Significant swelling of the film was not measured even for the 16 h runs. However swelling is anticipated to be problematical for very long run times[1,12].

## RESULTS

*Figure 2* shows the results for the propagation of the diffusion front as a function of time for an unloaded sample together with data for the lowest two loads applied. As expected for Case II diffusion, the front propagates with a linear dependence on time (note that the position of the front is measured with respect to the surface of the swollen polymer, and not with respect to the original unswollen polymer). The lowest stressed samples would still appear to undergo Case II diffusion without a detectable induction time, but the third curve in *Figure 2* suggests an induction time of ~0.5 h may be present, from the line of best fit through the data points.

*Figures 3* and *4* show solvent diffusion data for 2, 4, 8 and 16 h as a function of the compressive stress. It can be seen that for the highest loads diffusion is almost entirely suppressed within the time-scale of the experiment. In *Figure 3* after 4 h there has been no detectable penetration of the solvent under the highest two loads, and this is still true for the highest load after 8 and 16 h. In other words, the induction time is clearly a function of load/stress.

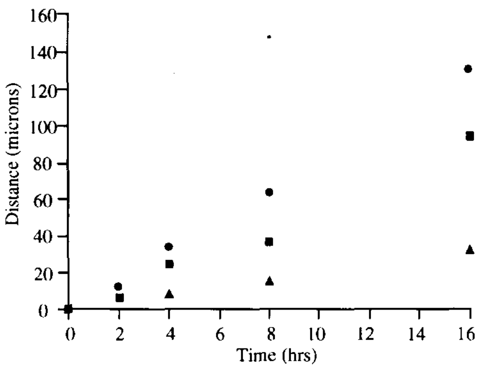

**Figure 2** Variation of diffusion distances with time for unstressed and lightly stressed PMMA samples: (●) 0.1 MPa; (■) 0.2 MPa; (▲) 0.3 MPa

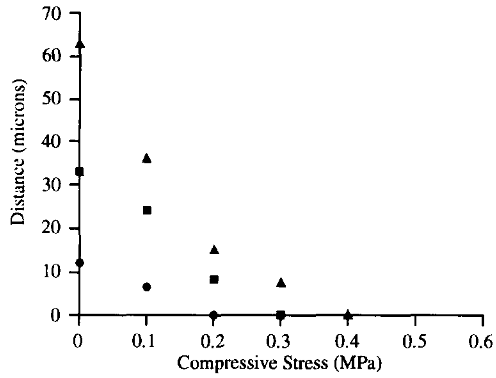

**Figure 3** Variation of diffusion distance with load for 2 (●), 4 (■) and 8 h (▲) run times. Compressive stresses of ~0.3 MPa (1.5 kg applied load) and greater would appear to be sufficient to suppress diffusion for the duration of the 4 h run, and compressive stresses of ~0.4 MPa (2.0 kg applied load) and greater for the 8 h run

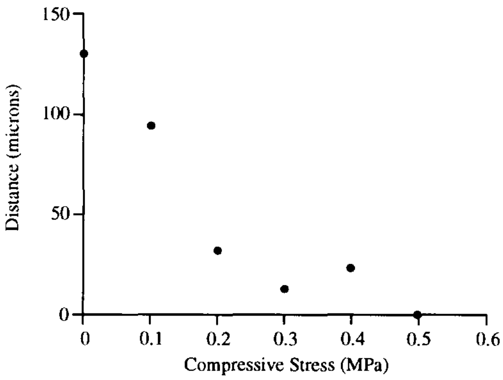

**Figure 4** Variation of diffusion distance with tensile stress for 16 h (●) run times. Compressive stresses of ~0.5 MPa (2.5 kg applied load) and greater would appear to be sufficient to suppress diffusion for the duration of the 16 h runs

## DISCUSSION

The first and most important result is that there *is* a marked effect of externally applied stress on the penetration of the iodine-stained methanol. This supports the implicit assumptions already present in the literature. The loads applied were chosen to be well below the (unplasticized) yield stress of PMMA, and observation showed no sign of inhomogeneous deformation having taken place, so this change in rate is not related to the effect of shear banding. The propagation front was always sharp and parallel to the original edge of the specimen also supporting the view that local inhomogeneities were not contributing to the effect.

A modest compressive stress of only ~0.2 MPa is sufficient to give rise to a significant induction time, and at longer times a four-fold reduction in penetration distance. Higher stresses have even more dramatic effects.

It is therefore apparent that this is not a particularly minor effect, but one that may give rise to appreciable changes in response under rather low levels of load. The corollary of the data presented here is that tensile stresses will accelerate solvent penetration – precisely the result assumed in the models of environmental craze growth[6,7], although the companion experiments to check this have still to be completed. In addition further experiments are planned to look at the changes in sorption with stress, and to examine the validity of assumptions previously made regarding diffusion of the iodine-stained methanol under stress. Concentration profiling of iodine and methanol will provide information as to the diffusivity of the two components through stressed PMMA.

## ACKNOWLEDGEMENTS

The authors would like to acknowledge the help of David Salmon in development of the experimental rig. APM would like to acknowledge financial support from the SERC.

## REFERENCES

1 Thomas, N. L. and Windle, A. H. *Polymer* 1981, **22**, 627; 1982, **23**, 529

2 Hui, C. Y., Wu, K. C., Lasky, R. C. and Kramer, E. J. *J. Appl. Phys.* 1987, **61**, 5129, 5137

3 Gall, T. P., Lasky, R. C. and Kramer, E. J. *Polymer* 1990, **31**, 1491

4 Lasky, R. C., Kramer, E. J. and Hui, C. Y. *Polymer* 1988, **29**, 673

5 Windle, A. H. in 'Polymer Permeability' (Ed. J. Comyn), Elsevier, London, 1985, p. 65

6 Brown, H. R. *Polymer* 1978, **19**, 1187

7 Brown, H. R. *J. Polym. Sci., Polym. Phys. Edn* 1989, **27**, 1273

8 Chau, C. C. and Li, J. C. M. *Phil. Mag.* 1981, **44A**, 493

9 Harmon, J. P., Lee, S. and Li, J. C. M. *J. Polym. Sci., Polym. Chem. Edn* 1987, **25**, 3215

10 Miller, P. and Kramer, E. J. *J. Mater. Sci.* 1990, **25**, 1751

11 Windle, A. H. *J. Membr. Sci.* 1984, **18**, 87

12 Thomas, N. L. and Windle, A. H. *Polymer* 1978, **19**, 255

13 Stadler, B. and Kausch, H. H. *J. Mater. Sci.* 1982, **17**, 2481