Table 1 Spacings from most significant crystalline peaks

d spacing Å	Comparative Intensity
5.02	Weak
4.50	Strong
3.93	Medium
3.63	Medium
3.32	Medium–strong
2.98	Weak
2.45	Weak

methane. The solution was cooled to 5°C and held at that temperature overnight, the result being a whitened solid mass. The solid lost solvent gradually over a period of one month at room temperature but about 21 wt % of solvent was still present when the X-ray analysis was performed. Reasonably rapid removal of this solvent requires heating under vacuum and such treatment appears to destroy the X-ray crystallinity if the temperature exceeds 150°C. (The glass transition temperature of PES is 220°C.) In an attempt to orient the sample the X-ray crystallinity was also destroyed by cold rolling.

A remarkable property of samples of PES which have been crystallized and then stripped of solvent is shown by their resistance to dissolution when they encounter the solvent a second time. This appears to be because recrystallization occurs so rapidly that it forestalls dissolution at any temperature up to the boiling point of the solvent. The recrystallization has been confirmed by X-ray diffraction and it is now proposed that polymer exhibiting this property should be known as 'susceptible polymer'. This susceptibility to rapid recrystallization is obliterated only by heating to the glass transition temperature.

The possibility that crystallinity is due to a stoichiometric adduct of polymer and solvent is attractive but not yet established.

Thanks are due to Dr D. A. Barr of ICI Plastics Division who provided advice in addition to the PES samples, and also to Mr B. D. Seymour of Cambridge University for technical assistance with the X-ray diffraction experiment.

D. A. Blackadder and H. Ghavamikia
Department of Chemical Engineering
and A. H. Windle
Department of Metallurgy and Materials Science,
University of Cambridge,
Cambridge, UK

References

1 Rebenfeld, L., Makarewicz, P. J., Weigmann, H. -D., and Wilkes, G.L *J. Macromol. Sci. (C)* 1976, 15, 279
2 Blackadder, D. A. and Ghavamikia, H. *Polymer* 1979, **20**, 523
3 Blackadder, D. A. and Ghavamikia, H. to be published

Volume strain measurement during the creep of polymers in liquid environments

In the course of a detailed study on the engineering properties of unfilled polyamide-6,6 (PA 66) and short glass fibre reinforced polyamide-6,6 (GFPA 66) injection mouldings, all three orthogonal strains were measured during uniaxial tensile creep on specimens tested in air or in distilled water. This permitted the calculation of the variation of volume strain with time during tensile creep. The purpose of this Letter is to summarize some of the very interesting trends observed.

If $\Delta V/V$, $\Delta l/l$, $\Delta t/t$ and $\Delta w/w$ are the volume, axial, thickness and width strains respectively, then:

$$\frac{\Delta V}{V} = \left(1 + \frac{\Delta l}{l}\right)\left(1 + \frac{\Delta t}{t}\right)\left(1 + \frac{\Delta w}{w}\right) - 1 \qquad (1)$$

with all strains measured at any one creep time.

Figure 1 plots volume strain against log(creep time) and axial strain against log(creep time). The data from these two graphs may be combined to produce a linear plot of volume strain against axial creep strain where both strains are measured at the same creep time (and stress).

Bucknall[1] has shown that this linear volume strain versus axial strain plot can provide valuable indications of the mechanism of deformation during tensile creep. In mechanisms which involve crazing, a slope of one on this plot indicates that all deformation is due to volume processes, whereas a horizontal line (i.e. a slope of zero) indicates that deformation arises from shear effects.

Observations of volume strain behaviour during creep in air of short glass fibre reinforced thermoplastics have also been undertaken and it has been found that an upturn in the volume strain–axial strain plot for these materials may provide an indication of the onset of permanent damage during creep[2]. Thus it would seem that evaluation of volume strain during tensile creep *in liquids* may also provide insight into the underlying mechanisms of deformation and absorption.

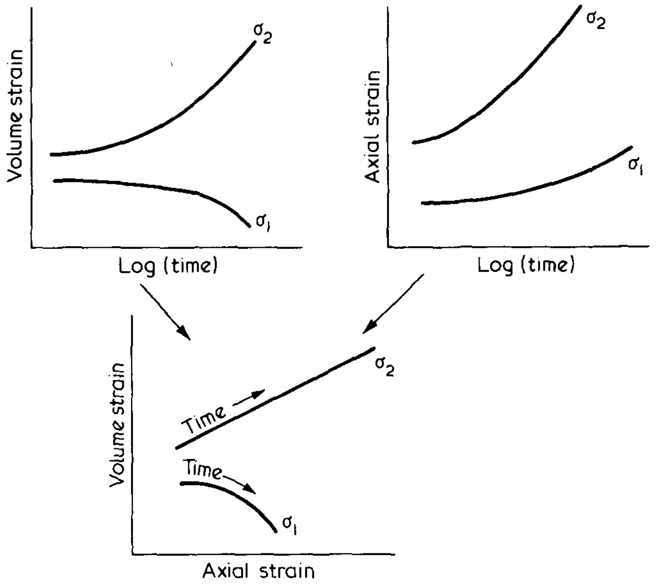

Figure 1 Derivation of volume strain–axial strain plot. σ is the applied tensile stress and $\sigma_2 > \sigma_1$

0032–3861/79/060782–02$02.00

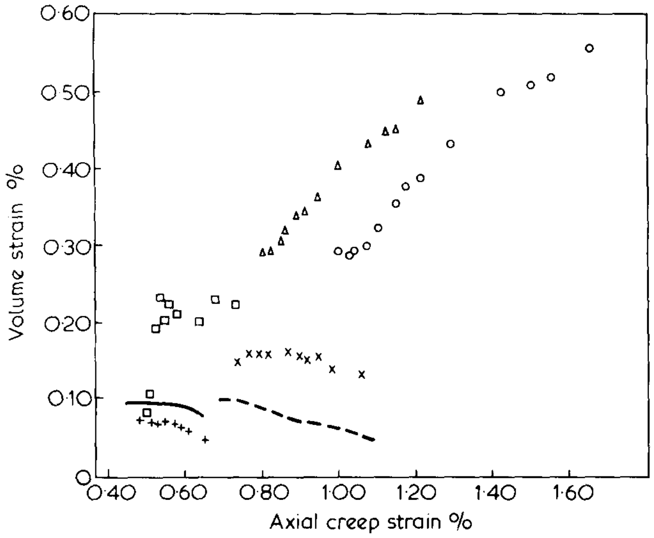

Figure 2 Corrected volume strain versus axial strain for the creep at 23°C of GFPA 66 specimens machined from ASTM bars. Dry into distilled water: ○, 88.7 MN/m^2; △, 70.1 MN/m^2; □, 46.0 MN/m^2. Dry into air at 50% r.h.: x, 70.1 MN/m^2; +, 46.0 MN/m^2. Equilibrated to and tested in air at 50% r.h.: — — —, 42.7 MN/m^2; ——, 29.2 MN/m^2

Figure 2 plots volume strain against axial strain for the tensile creep of GFPA 66 specimens machined from ASTM bar injection mouldings. Data are presented for initially dry specimens creep tested in distilled water at 23°C at three stress levels using apparatus and materials described elsewhere[3]. The data have been corrected for the strain responses of a specimen immersed in water under zero load. These data are compared with zero load corrected volume strain results for similar specimens tested at two other environmental conditions. Details are given in the Figure caption. (It should be noted that corrected volume strains are the algebraic sum of six independently measured strains; i.e. the uncorrected creep and the zero load swelling strains in the axial, thickness and width directions.)

The creep tests in the air environments all show a gradual decrease in the volume strain (corrected for swelling and/or ageing effects) with increasing axial strain (and creep time). This may be associated with some structural re-ordering of the polymer matrix during creep as has been described elsewhere for polypropylene[4].

During creep of initially dry GFPA 66 specimens in distilled water, the *corrected* volume strains show a different behaviour, with a large increase in volume strain occurring with increasing axial strain. Similar results have also been noted for unfilled PA 66 specimens from ASTM bars and for GFPA 66 specimens from edge-gated disc injection mouldings[5].

One possible explanation for this behaviour is that the diffusion coefficient for initially dry GFPA 66 and PA 66 in distilled water may be stress dependent. Thus the *corrected* volume strain, which has been corrected on the basis of swelling strains measured under zero load, may still reflect an enhanced swelling due to an increased water absorption with applied tensile stress. However, some work on polyamide-6 in humid (rather than aqueous) environments has not revealed any marked stress dependence of the diffusion rate[6].

In conclusion, the measurement of volume strains during tensile creep in liquid environments may provide an intriguing means of gaining further insight into the mechanism of deformation of polymers in liquid environments. This approach would seem to merit further investigation.

G. R. Smith and M. W. Darlington
Department of Materials,
Cranfield Institute of Technology,
Cranfield, Bedford, MK43 0AL, England

References

1 Bucknall, C. B. 'Toughened Plastics' Applied Science Publishers, London, 1977
2 Darlington, M. W. and Clayton, D. 31st Antec SPE, Montreal, 1973
3 Smith, G. R. and Darlington, M. W. Paper submitted to Plastics and Rubbers: Materials and Applications
4 Benham, P. P. and Mallon, P. J. *J. Strain Analysis* 1973, **8**, 277
5 Smith, G. R. Ph. D. Thesis, Cranfield Institute of Technology, 1976
6 Hunt, D. G. *PhD Thesis* Polytechnic of the South Bank, (C. N. A. A.) 1977

Thermal decomposition of flame retardants. Chlorine–bromine antagonism in mixtures of halogenated polymers with Sb_2O_3

The interaction of antimony oxide with halogenated polymers, or polymers containing halogenated additives, constitutes the classic case of flame-retardant synergism. The evidence points to the formation of volatile flame-retardant $SbCl_3$ or $SbBr_3$[1,2] as the basis of the antimony–halogen synergism.

In fact, when HCl or HBr are evolved from the pyrolysing halogenated materials, they react steadily with Sb_2O_3 to form $SbCl_3$ or $SbBr_3$[1–5].

Synergism between chlorine and bromine in presence of Sb_2O_3 has also been investigated[3,6] and, surprisingly, the results obtained showed that when bromine is present, the chlorine–antimony combinations become ineffectual. This unexpected antagonism between the two halogens suggested[3,6] that a different extinction mechanism may operate; that chlorine and bromine may differ *qualitatively* in respect to flame-retardancy performance, and that it may be misleading to generalize about 'halogens'[3].

We have previously[7,8] found that direct pyrolysis in the ion source of a mass spectrometer can provide useful information on the volatile species evolved during the thermal decomposition of polymeric materials permitting determination of the decomposition mechanism.

Therefore, we have used this technique in order to detect the volatile decomposition products formed heating mixtures of poly(vinyl bromide) (PVB) with Sb_2O_3 and poly(vinyl chloride) (PVC) or poly(vinylidene chloride) (PVC_2).

The PVC and PVC_2 samples used in this study were pure homopolymer resins ($\bar{M}_n$ = 37 000 and 18 000, respectively) supplied by Borden Chem. Co. PVB was obtained by suspen-

0032-3861/79/060783-02$02.00