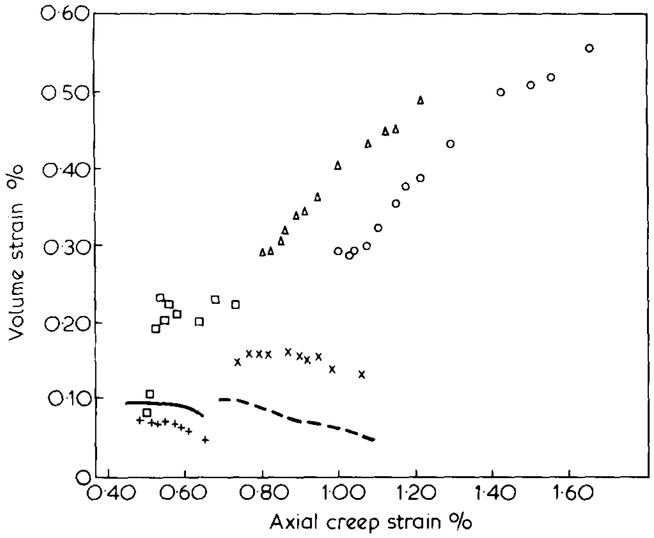

Figure 2 Corrected volume strain versus axial strain for the creep at 23°C of GFPA 66 specimens machined from ASTM bars. Dry into distilled water: ○, 88.7 MN/m²; △, 70.1 MN/m²; □, 46.0 MN/m². Dry into air at 50% r.h.: x, 70.1 MN/m²; +, 46.0 MN/m². Equilibrated to and tested in air at 50% r.h.: — — —, 42.7 MN/m²; ——, 29.2 MN/m²

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.

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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

Table 1 Maximum temperature (°C) of the volatilization rate profiles for relevant species and for the total ion current (*TIC*)

Mixture	Composition[a] (molar ratio)	HCl	HBr	$SbCl_3$	$SbBr_3$	Sb_4	*TIC*
PVB/PVC_2	1:1	210	160	–	–	–	200
$PVB/PVC_2/Sb_2O_3$	1:1	190	180	170	180	160	180
PVB/PVC	1:4	250	170	–	–	–	250
$PVB/PVC/Sb_2O_3$	1:4	230	230	215	210	200	230
PVB	–	–	140	–	–	–	140
PVB/Sb_2O_3	–	–	185	–	170	165	180

[a] 5% (w/w) Sb_2O_3 is the amount added to the polymers in all cases

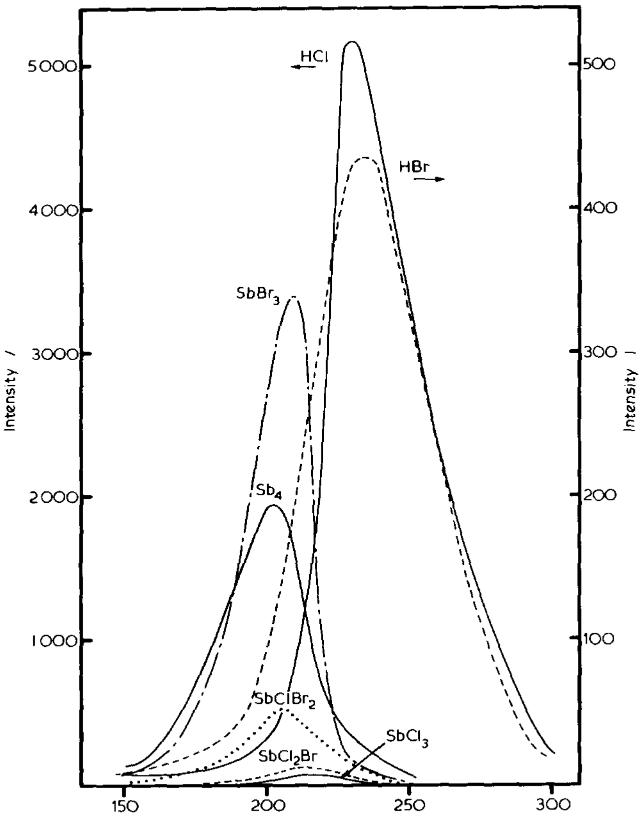

Figure 1 Intensity of relevant mass peaks as a function of temperature for $PVB/PVC/Sb_2O_3$

sion polymerization of vinyl bromide (EGA Chemie); intrinsic viscosity (cyclohexanone, 30°C), 0.3 dl/g. Sb_2O_3 (Timonox White Star) was obtained from Associated Lead. Mixtures were prepared by mixing the polymers mechanically with finely ground Sb_2O_3; their composition is given in *Table 1*.

Pyrolyses were carried out in quartz probes using the direct insertion inlet of an electron impact mass spectrometer LKB-9000S following the technique described elsewhere[4,7,8]; the heating rate was about 10°C/min.

The mass spectra of the pyrolysate of Sb_2O_3–PVB mixture were recorded up to about 400°C. In the temperature range of 150°–250°C, HBr appears as the most intense peak, while the presence of $SbBr_3$ is indicated by the appearance of the peaks corresponding to Sb^+, $SbBr^+$, $SbBr_2^+$ and $SbBr_3^+$. In addition, there is a peak at *m/e* 484, accompanied by the characteristic isotopic pattern, corresponding to the Sb_4^+ species[4]. At temperatures as high as 350°C peaks generated by the thermal degradation of PIB appear. These are clearly aromatic fragments and are essentially those observed in previous m.s. reports for PVC[4,5]. The mass spectra relating to the pyrolysate of Sb_2O_3–PVB–PVC mixture show the simultaneous formation of $SbBr_3$, $SbBr_2Cl$, $SbBrCl_2$ and $SbCl_3$ species. Except[4,5] for $SbCl_3$, this is the first direct evidence for the presence of these species in the gas-phase. However, the intensity of the chlorinated fragments is much lower than the corresponding brominated species, as shown by their volatilization profiles in *Figure 1*, despite the fact that the molar ratio HCl/HBr is four to one in favour of HCl in this mixture (*Table 1*). Essentially the same results were obtained in the case of the Sb_2O_3–PVB–PVC_2 mixture (*Table 1*).

Our data indicate that both HBr and HCl, evolved during the pyrolysis of PVB, PVC, and PVC_2, react steadily with Sb_2O_3 to form $SbBr_3$ and $SbCl_3$, respectively. However, when both acids are present, although they are evolved simultaneously, HBr reacts so quickly with Sb_2O_3 that only small amounts of $SbCl_3$ are formed. This explains the apparently puzzling observation[6] that the chlorine–antimony synergism becomes ineffective in the presence of bromine.

Although it is well recognized[9] that HBr is about five times more effective than HCl as a flame retardant, the higher reactivity of HBr towards antimony had passed unnoticed up to now.

Therefore, we can conclude that a uniform mechanism of flame-retardancy applies to the halogens, and that the observed chlorine–bromine antagonism towards antimony is consistent with this mechanism.

ACKNOWLEDGEMENT

Financial support from the Consiglio Nazionale delle Ricerche, Rome, is gratefully acknowledged.

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(Received 28 December 1978)

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