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Inorganic tin compounds as flame retardants and smoke suppressants for polyester thermosets

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Abstract

The fire retardant action of inorganic tin additives in polyester resin thermosets cross-linked with styrene has been investigated. Thermal methods were used to analyse the degradation and oxidation index and smoke measurements were also carried out on the resins with and without tin additives. The interaction between the tin compounds and the halogens introduced into the polymer structure using halogen-containing reactive monomers affects the degradation, fire retardant and smoke suppressant properties. The changes are described and the nature of the fire retardant action is discussed.
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1. Introduction

Polyester resins have many applications with some 75% of the annual production being used in glass reinforced polyester for engineering, electronic, marine and construction purposes. The high flammability of any polymeric system presents a considerable hazard, for example a general purpose polyester resin containing styrene has a limiting oxygen index (LOI) value of 19, that is, the resin will burn readily in an atmosphere containing 19% oxygen or more. Many methods have been used to combat this [1–3]. The polymer itself may be modified by using an alternative fire retarding monomer during synthesis. Another widely used method is the incorporation of an additive which will impart fire retardant properties. This additive may be a filler whose decomposition suppresses burning, or a compound which reacts with the polymer during combustion to produce products which quench the flame or which are less flammable. These modifications and additions affect the decomposition by interaction on a molecular level [4–6] and raise the LOI to values well above the percentage of oxygen in air (ca. 21% by volume). For example, a resin containing bromine and 10% of a suitable metal oxide additive could have an LOI of 48.

Generally, the mechanism of action is classified as "vapour phase" if species are produced which interfere with the flame propagation mechanism, and "condensed phase" if the interaction before vaporisation changes the nature of the products of degradation and combustion, making the mixture less flammable. The distinction between the various modes of action is often not clear-cut.

Some fillers have undesirable effects. For example, high loadings of alumina trihydrate can alter the

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physical properties of the material, while antimony trioxide is toxic and can increase smoke production. The inclusion of halogenated compounds can produce corrosive acidic products.

Tin compounds have been shown to be most effective fire retardants and smoke suppressants for natural materials such as wool [7] and cotton [8] and for synthetics like poly(vinyl chloride) [9,10], chlorosulphonated polyethylene [11], polyester resins [12] and paints [13]. They are effective at low incorporation levels and so have a small effect on the physical properties of the polymer. They are white, of low toxicity and do not discolour the polymer and are safe to use because they produce less undesirable by-products than other additives.

Touval [14] investigated the effects of anhydrous and hydrated tin oxides, $SnO_2 \cdot xH_2O$ (where x is 0, 1 or 2), and Cusack and co-workers [15–18] at the International Tin Research Institute and elsewhere have tested tin oxide in various forms as well as metal stannates, $MSnO_3$ and hydroxystannates, $MSn(OH)_6$ and also combinations of tin oxide with other fire retardant additives such as molybdenum trioxide, MoO_3, or alumina trihydrate.

These compounds have also been shown to reduce the production of smoke and of carbon monoxide during combustion, and hence to reduce toxicity of the degradation products.

The presence of halogen in the polymer system can also greatly increase the fire retardancy of the materials. They may be put in either as separate polyhalogenated compounds like a halogenated wax, or a reactive halogenated monomer may be used in producing the polymer. For example, tetrabromophthalic anhydride is used in polyester resin synthesis, and vinyl chloride in making PVC. The combined effect of the two additives may be much greater than the sum of either used separately. This is referred to as "synergism" and is very noticeable where some metal oxides (Sb_2O_3 or MoO_3) are added to halogen-containing polymers [19].

The mechanism of action of tin compounds and the way in which the halogen enhances the fire retardant effects has been investigated [20–22], but no definite conclusions reached.

Bulewicz and Padley [23] claimed that tin acts by catalysing the recombination of hydrogen radicals via reactions such as

$$SnO_2 + H_2 \rightarrow SnO + H_2O$$

$$SnO + H\cdot \rightarrow SnOH^*$$

$$SnOH^* + H\cdot \rightarrow SnO + H_2$$

Work at the International Tin Research Institute suggests that the mode of action is more complex, involving a combination of radical scavenging, char promotion and catalysis for soot oxidation on the flame [24]. Since zinc compounds are themselves useful fire retardants [25,26], the possibility of improving fire suppression performance by using both tin and zinc encouraged the manufacture and testing of zinc stannate $ZnSnO_3$ (ZS) and zinc hydroxystannate $ZnSn(OH)_6$ (ZHS).

2. Experimental

2.1. Preparation of the polyester resin

The resins used in this study were produced by reacting together a glycol, maleic anhydride and a second dibasic acid anhydride, such as phthalic anhydride. The method used has been described in full in previous papers [19,27].

In order to introduce halogen into the resin, a reactive halogenated monomer was used in place of the normal reagent. The glycol, 1,2-propanediol (PG) was replaced by dibromoneopentyl glycol (DBNPG), or the phthalic anhydride (PA) by tetrabromophthalic anhydride (TBPA) or by chlorendic anhydride (HET).

The components used are shown in Table 1. The resins were cross-linked with styrene using methyl ethyl ketone peroxide catalyst (2% (w/w)) with a cobalt naphthenate accelerator (1% (w/w)) and a cure cycle of room temperature overnight followed by 3 h at 80°C. Test strips were moulded using silicone rubber moulds of various sizes.

2.2. Additives

The tin additives were all used as received. Tin(IV) oxide and β-stannic acid were supplied by Keeling and Walker, Stoke on Trent. ZS and ZHS were synthesised at the International Tin Research Institute, Uxbridge, according to previously reported procedures [28,29].

All additives were white, free-flowing powders of negligible volatility, low toxicity and with low levels

Table 1
Resin components used[a]

Glycol	Unsaturated anhydride	Other dibasic anhydride	Resin code
1,2-Propanediol	Maleic anhydride	Phthalic anhydride	GPR
1,2-Propanediol	Maleic anhydride	HET anhydride[b]	HET
Dibromoneopentyl glycol (DBNPG)[c]	Maleic anhydride	Phthalic anhydride	DBNPG
1,2-Propanediol	Maleic anhydride	TBPA[d]	TBPA

[a] All resins were cross-linked with styrene.
[b] Chlorendic acid anhydride.
[c] 1,3-Dibromo-2,2-bis(hydroxymethyl) propane.
[d] Tetrabromophthalic anhydride.

of impurities. They were added to the mix before the catalyst and accelerator and a homogeneous mix obtained using a high-shear mixer.

2.3. *Thermal analysis*

2.3.1. *Thermogravimetry*

This was carried out using the Stanton Redcroft TG770 thermobalance system. Each cured resin was ground and sieved to ensure a particle diameter of less than 125 μm. Samples of 10–11 mg were placed in a platinum pan and heated at 15°C/min from room temperature to 600°C in a gas atmosphere of nitrogen or air with a flow rate of 3 cm^3/min. The derivative thermogravimetric curve (DTG) was obtained electronically. Each determination was carried out in duplicate.

2.3.2. *Differential scanning calorimetry*

The samples were analysed in duplicate on a Mettler-Toledo DSC 20 system, using samples of about 10 mg in unsealed aluminium pans heated at 10°C/min from 50 to 600°C.

2.4. *Flammability tests*

2.4.1. *Oxidation index tests*

Three separate tests were performed to determine the room temperature and high temperature oxygen indices and the nitrous oxide index (NOI).

2.4.1.1. Room temperature limiting oxygen index. The Stanton Redcroft FTA module was used according to the recommendations of ASTM D2863-70. After calibration with pure oxygen and oxygen-free nitrogen, the flow rates of nitrogen and oxygen were adjusted to give about 25% oxygen at a total flow of 17–18 l/min. The sample was ignited and the time to self-extinguish recorded. The oxygen content was then adjusted to obtain a reproducible result for the sample to self-extinguish in 3 min.

2.4.1.2. High temperature oxygen index. The Stanton Redcroft HFTA module was used and set to a temperature of 100°C and allowed to equilibrate. The procedure employed with the room temperature system was followed except that a flow rate of 10.6 l/min was used. The samples, having equilibrated at 100°C for at least 2 min were tested as before.

2.4.1.3. Nitrous oxide index. The Stanton Redcroft FTA unit was used again, but with nitrous oxide, N_2O in place of oxygen. The calibration was carried out with oxygen and the flow rates of the nitrous oxide or oxygen adjusted to be the same.

2.4.2. *Smoke tests*

The hazard due to smoke production during burning must be considered. The amount of smoke may be measured gravimetrically [30] or optically [31]. These tests operate under different conditions and the results may not agree. Any additive which increases char production removes carbonaceous material from the flame zone and normally lowers the amount of smoke produced. It is important to measure both smoke and char values for a more complete understanding of the action of the additives upon the burning processes.

2.4.2.1. Arapahoe smoke chamber [30]. This was used to determine gravimetrically the amount of smoke produced, the amount of sample burnt and the amount of char residue. Samples were weighed and placed in the apparatus. A sheet of glass fibre filter paper (GF/C) was also weighed and fitted in the holder and attached at the top of the combustion chamber. The sample was lit with a propane gas micro-burner and the air flow turned on. After 30 s the flame was extinguished by cutting the air flow, or using nitrogen and the filter paper removed and re-weighed. The charred sample was also re-weighed and then decharred for 45 min in a small sand mill running at 60 rpm. The clean, decharred sample was then weighed again. The results given are the mean of five determinations.

2.4.2.2. NBS smoke test. Using the Stanton Redcroft NBS smoke box in accordance with ASTM E622-1983 [31], samples were wrapped in aluminium foil so that only a central area was exposed. Having backed the sample with a non-combustible board and secured it in the chamber, the burner was lit and the sample moved into the flame. Smoke density was monitored by the light sources and photo-detectors for about 10 min.

2.5. X-ray diffraction studies (XRD)

Using a Phillips 1730/10 X-ray diffractometer with Cu Kα radiation, powdered samples were scanned at 1°/min with a slit size of 0.1 or 0.25°.

3. Results and discussion

3.1. The resins and additives

All of the cured resins were light-coloured, fairly hard, brittle materials, and when the tin additives were incorporated, they had a uniform, opaque white colour. In this study, inorganic tin compounds have been studied in polyester resin systems containing 0–28% halogen.

Anhydrous tin oxide is an amphoteric oxide and simple to manufacture. Several metal stannates and hydroxystannates have been studied as potential fire retardants [29]. $ZnSnO_3$ (ZS) and $ZnSn(OH)_6$ (ZHS) were found to be the most effective.

ZHS may be precipitated from an aqueous solution of zinc chloride by the addition of sodium hydroxystannate. On heating ZHS above 180°C, it loses all the water and forms amorphous ZS. This dehydration, taking place over the temperature range at which the most rapid degradation of some polymeric systems occurs, must contribute to its effectiveness as a fire retardant. ZHS has been shown to have fire retardant properties, in the presence of halogens, comparable to antimony oxide Sb_2O_3 [17,18]. ZS is stable up to about 600°C when it starts to disproportionate to Zn_2SnO_4 and SnO_2.

3.2. Thermal analysis

Thermal methods have been widely used for the measurement and comparison of the stages of degradation of the polyester resins alone, of the additives alone and of the additive-containing resins. The stability of the resins may be assessed by the temperature range of their mass losses measured by thermogravimetry (TG), while the effects of additives on the heat changes during decomposition can be studied using differential scanning calorimetry (DSC) and differential thermal analysis (DTA). The interaction of the additives with the halogen-containing monomers may also be studied by DSC [19].

3.2.1. Thermogravimetry

A new batch of resin was prepared for each additive, and although mixing was thorough, the mixtures could show some differences. There will therefore be a small inter-batch variation between results for different batches of resin which nominally have the same composition.

The degradation takes place in several overlapping stages, without any clear plateau separating them. The DTG curve does not return to the baseline and the normal practice has been to measure the weight loss corresponding to the minimum between DTG peaks. When an additive causes a change in the shape or breadth of a DTG peak, the minima may become less distinct. In addition, where the additive itself decomposes, as happens with ZHS, the TG curve becomes most complex. The combination of these effects may cause a variation in the measured temperature of between 10 and 20°C, but the trends in values observed are still valid. It should be noted that these variations will cause some difficulties in reproducibility and in quantifying the thermogravimetric curves obtained.

Table 2
Thermogravimetric results for representative systems in air

Resin	Additive (phr)	Stage 1 (%)	Stage 2 (%)	Stage 3 (%)	Residue at 600°C (%)
GPR	(0)	190 (8.8)	321 (78.2)	530 (12.2)	(0)
	SnO_2 (10)	196 (9.0)	323 (73.0)	519 (8.0)	(10)
	ZHS (10)	183 (5.2)	304 (73.2)	505 (13.4)	(8.2)
	ZS (10)	191 (7.0)	324 (69.0)	554 (14.0)	(10)
HET	(0)	135 (2.3)	330 (78.7)	532 (18.5)	(0)
	SnO_2 (10)	125 (2.0)	328 (77.0)	513 (11.0)	(10)
	ZHS (10)	126 (2.0)	322 (68.7)	548 (24.2)	(5.1)
	ZS (10)	–	304 (63.0)	540/576 (26.0)	(11.0)
DBNPG	(0)	214 (14.2)	339 (70.0)	533 (16.0)	(0)
	SnO_2 (10)	204 (10.0)	349 (68.0)	543 (13.0)	(9.0)
	ZHS (10)	198 (17.5) 278 (38.0)	409 (9.0)	539 (28.0)	(2.0)
	ZS (10)	192/250 (49.0)	409 (34.0)	546 (16.0)	(1.0)
TBPA	(0)	–	336 (88.7)	513 (11.3)	(0)
	SnO_2 (10)	–	351 (80.0)	562 (11.0)	(9.0)
	ZHS (10)	128 (3.0)	328 (67.0)	562 (22.0)	(8.0)
	ZS (10)	128 (3.0)	310/328 (69.0)	562 (20.0)	(8.0)

The results in Table 2 show the temperatures of the DTG peak maximum together with the percentage mass loss for each stage and the residue remaining at the highest temperature of 600°C.

3.2.1.1. Resins. TG of the resins alone showed that a general purpose resin made from a glycol, phthalic anhydride and maleic anhydride decomposes in air in three stages. The first stage, occurring around 200°C is due to the elimination of phthalic anhydride. The second stage, around 350°C. is due to the release of styrene and a complex mixture of other materials, while the third stage above 500°C is the loss of high-boiling tars and the oxidation of any char formed [32]. The GPR and DBNPG resins show these stages illustrated in Fig. 1a. However, the HET resin cannot produce phthalic anhydride, so the first stage is minimal. The decomposition of HET resins has been most thoroughly investigated by Fink and co-workers [33]. Similarly, the TBPA resin shows only two stages.

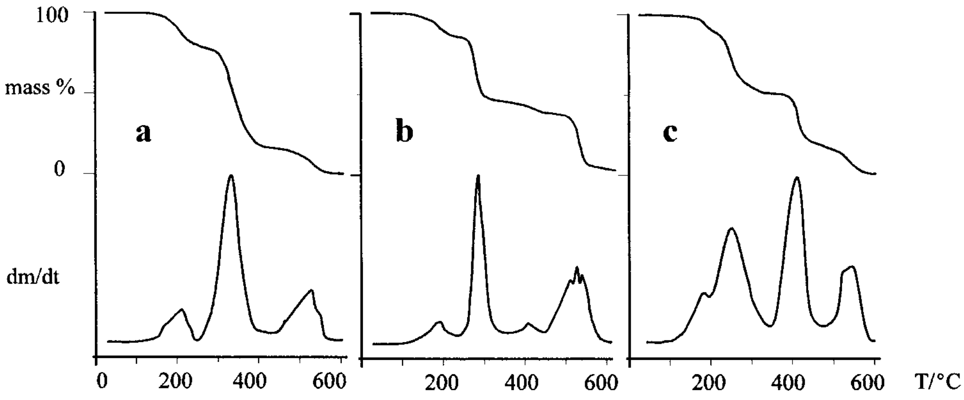

Fig. 1. TG and DTG curves for: (a) DBNPG resin alone; (b) DBNPG resin+10 phr ZHS; (c) DBNPG resin+10 phr ZS.

3.2.1.2. Additives. TG of the tin additives alone showed that the anhydrous tin(IV) oxide, SnO_2 and the zinc stannate $ZnSnO_3$ did not lose any weight over the temperature range up to 600°C, whereas the hydrated tin oxide $SnO_2{\cdot}xH_2O$ lost up to 19% and ZHS lost 18.9% in two stages when heated to 300°C.

3.2.1.3. Resins plus additives. Table 2 shows the mean DTG peak maximum temperatures for the unfilled resins and for representative samples filled with 10 phr of tin oxide, ZHS and ZS.

GPR resin. Tin oxide has little effect on any of the three stages, although the temperature of stage 3 is lowered slightly. ZHS lowers all three temperatures by about 10°C, while ZS only affects the third stage, raising its peak temperature by about 20°C. It is also worthy to note that lower amounts of ZS (e.g. 2 phr) also raise the temperature of stage 2. The fillers remained, quantitatively within experimental error, at the highest temperature of 600°C, although the ZHS had lost water and thus the 10% added was reduced to 8.2%.

HET resin. This resin shows a small loss of about 2% around 120–140°C, possibly due to water entrained during processing or to the loss of solvent used with the cross-linking catalyst. This loss is little affected by any of the additives. The major loss of 78% at 330°C is hardly affected by SnO_2, but is reduced by ZHS and greatly reduced by ZS to 63% at 304°C. Even after correction for filler, this loss is too small. The third stage shows a complex behaviour, being reduced by tin oxide, raised by ZHS and split into two parts by ZS. The amount of ZHS retained at 600°C is reduced, but the other two fillers remain largely unchanged. If the third stage is attributed largely to char oxidation, ZS and ZHS appear to increase the char significantly.

DBNPG resin. All the additives affected the degradation of this resin. Tin oxide had the least effect, lowering the temperature of the first stage and raising the second and third stages by about 10°C, and losing only a small amount of tin by 600°C.

ZHS presents a complex pattern, as shown in Fig. 1b, where the decomposition of ZHS, the degradation of the resin, and probably the interaction of filler and resin produce some 5 or 6 DTG peaks. Only about 2% (out of 10%) of the filler remains at the highest temperature, which is far less than the amount of dehydrated product expected. Clearly, some interaction has taken place.

The amount remaining lost in stage 3 is greater, suggesting increased char formation. ZS presents a similar complex pattern, as shown in Fig. 1c, suggesting that the interaction shown with ZHS owes more to the reactions between filler and resin than to dehydration. At 600°C, 1% (out of 10%) of filler remained.

TBPA resin. This resin also contains bromine, and shows some similarities to the DBNPG resin. Tin oxide raised the temperatures of the two stages considerably but remained almost completely at the end of the run. ZHS altered the TG behaviour and losses and ZS showed a complex pattern of DTG peaks and a loss of 2% (from 10%).

For the resins containing ZS and ZHS, the TG curves are more complex, showing both the effects of the additives on the resin degradation and also the decomposition of the additive itself. The third stage loss is increased and the amount of additive remaining is lowered. These results strongly suggest interaction between the additives and the halogen-containing resins. The effects are greatest with the DBNPG resin and ZHS. Increases in the amount lost in stage 3 and the temperature of that stage suggest promotion of a more stable char due to a change in the mechanism of degradation caused by the additive. This is in accord with the findings by other workers [11,12]. It has also been shown that there is a synergism between ZHS and ZS and halogen-containing materials such as cerechlor used as additive fire retardants [21].

Thus, although the TG results show that ZHS and ZS promote char formation, and act by a condensed phase mechanism, the volatilisation of the additives when halogen-containing materials are present suggests that a vapour phase mechanism may also be operating.

3.2.2. Differential scanning calorimetry

In order to study possible interactions between the halogenated monomers and the tin additives, mixtures of equal amounts of monomer and additive were run on the DSC.

For the additives alone, tin oxide gave no peaks, and ZS a small endotherm at around 190°C, probably due to moisture loss. ZHS gave three major endothermic peaks at 184, 225 and 285°C, showing the dehydration to ZS.

Table 3
DSC peak temperatures for representative monomers alone and as 1:1 mixtures with additives

Monomer	Additive	Peaks			
None	SnO_2	None			
	ZHS	184, endo	225, endo	285, endo	
	ZS	190, endo			
HET[a]	None	208, endo	213, endo	243, endo	
	SnO_2	199, endo	211, 216, endo	238, endo	
	ZHS	165, 193, endo	214, endo	240, 274, endo	**424, exo**
	ZS	165, 193, endo	214, endo	**324, exo**	**580, exo**
DBNPG	None	115, endo			
	SnO_2	109, endo			
	ZHS	100, endo	198, 233, endo	**240, 243, exo**	
	ZS	102, endo	**218, exo**		
TBPA[b]	None		272–275, endo		
	SnO_2	238, endo	277, endo		
	ZHS	200, endo	260, 276, endo	290, 363, endo	
	ZS		272, endo	**400, 443, exo**	

[a] The peaks for HET are complex due to decomposition to HEX.

[b] The peaks for TBPA monomer are doublets.

For the monomers alone, only endothermic peaks were observed, corresponding to melting in the case of DBNPG and TBPA and to decomposition of HET to hexachlorocyclopentadiene (HEX). In the mixtures of equal masses of additives and monomers, tin oxide did not produce any new peaks or change their temperature but reduced the enthalpy change, measured by the peak area to approximately half, as would be expected. This suggests that there is little or no interaction between tin oxide and any of the monomers.

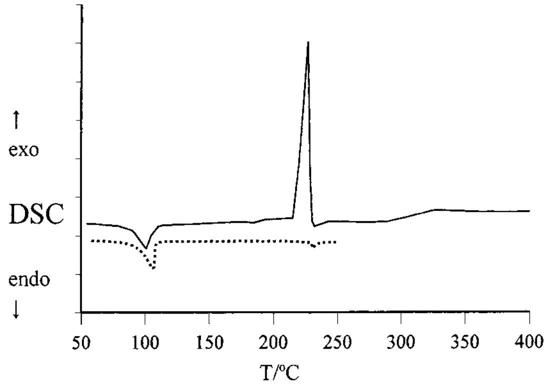

Fig. 2. DSC curves for DBNPG monomer (dotted) and for a 1:1 mixture of DBNPG monomer and ZS (full line).

However, as Table 3 shows, mixtures of ZHS and ZS with the halogenated monomers gave large exothermic peaks which must be due to strong interaction between the ZSs and the halogenated monomers.

Fig. 2 illustrates the changes brought about by the addition of ZS to DBNPG monomer. For DBNPG alone, the melting endotherm near 100°C is followed by a small endotherm at 230°C. With ZS present a very large exotherm occurs at 218°C, due to interaction. This confirms the distinction between the mode of action of tin oxide and that of the ZSs which was observed by TG.

3.3. Oxidation index measurements

3.3.1. Limiting oxygen index

Table 4 shows the LOI results for representative resins with and without fillers and these are compared in Fig. 3 for the zinc stannate additive, ZS.

In the GPR, each of the fillers raised the LOI by very small amounts only, ZHS being most effective. This confirms that none of these additives is an effective flame retardant in the absence of halogen. However in the resins containing halogen the effects were much greater especially with DBNPG where the LOI was raised from around 39 to over 50. Another noteworthy feature is the low amount of filler needed to attain the

Table 4
Limiting oxygen index at room temperature (LOI)

Resin	Additive (phr)	LOI
GPR	None	20.1
	SnO_2 (10)	20.8
	ZHS (10)	22.7
	ZS (10)	20.4
HET	None	26.5
	SnO_2 (10)	32.8
	ZHS (10)	29.3
	ZS (10)	34.0
DBNPG	None	38.9
	SnO_2 (10)	49.9
	ZHS (10)	54.3
	ZS (10)	58.8
TBPA	None	37.2
	SnO_2 (10)	48.7
	ZHS (10)	41.7
	ZS (10)	41.6

Table 5
Limiting oxygen indices at 100°C (HTOI)

Resin	Additive (phr)	HTOI
GPR	None	15.0
	SnO_2 (10)	16.0
HET	None	27.0
	SnO_2 (10)	40.7
DBNPG	None	53.1
	SnO_2 (10)	78.4
TBPA	None	45.0
	SnO_2 (10)	61.7

"plateau" of the LOI-Filler plot. Even 2% of ZHS and ZS will increase the LOI nearly to the highest value measured here.

The LOI results obtained in this work are within 1–2 units of literature values for comparable resin and additive systems. This is within the probable experimental error for the LOI determination, allowing some variation for different batches of the same resin.

3.3.2. High temperature oxygen index

The initial work performed at room temperature may not indicate fully what occurs at the higher temperatures which apply near to a burning material. A better correlation to real fire behaviour has been shown to be obtained by running the test at a higher temperature [34].

Literature results for ethylene–acrylic rubbers containing tin additives and alumina trihydrate show a very considerable reduction in the LOI when the temperature is raised [24]. The room temperature value is approximately halved at 100°C. With these polyester resins, Table 5 shows the oxygen index results carried out at 100°C. Interestingly, although the value for the unfilled GPR is lower than the room temperature value by about 4 at 100°C, those for all the halogenated resins are higher by 3–14 at 100°C. This continues to apply for the resins containing tin oxide. With 5% tin oxide, the high temperature oxygen index (HTOI) value for GPR is around 4 lower than at room temperature, but TBPA is raised by

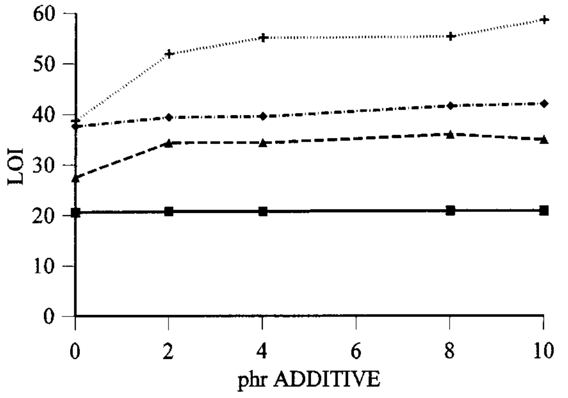

Fig. 3. LOI values for each resin with ZS additive. Legend: (■) GPR; (▲) HET; (◆) DBNPG; (+) TBPA.

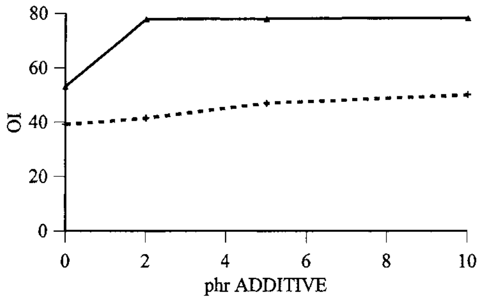

Fig. 4. Variation of oxygen index with temperature for DBNPG resins with tin oxide additive. Legend: (▲) 100°C; (+) room temperature.

Table 6
Limiting oxygen indices for HET resins with 10% chlorine

Additive (phr)	LOI (room temperature)	HTOI (100°C)
0	21.9	18.4
1	22.6	19.1
3	25.1	22.0
7	25.8	26.0
10	26.5	26.2

nearly 8, DBNPG by 30, and HET by 7. The effect of temperature is shown for a DBNPG resin in Fig. 4.

The effect of halogen concentration is demonstrated by the HTOI results with a HET resin containing 10% halogen in Table 6. With no additive, the HTOI at 100°C is lower than at room temperature by 2.5. This effect persists with 1 and 3% tin oxide present, although at 7 and 10% levels the difference is quite small.

The results from LOI and HTOI strongly suggest that the tin oxide is acting with the halogen to promote fire retardance and that raising the temperature allows the mechanism to act more effectively. Clearly, the amount of additive, the stoichiometric ratio of tin to halogen and the temperature of testing all play a part.

3.3.3. Nitrous oxide index

Measuring the oxidation index in nitrous oxide enables a distinction to be drawn between a vapour phase mechanism, which would occur in oxygen, but not in nitrous oxide, and a condensed phase mechanism, which would be unaffected by the atmosphere [35].

Table 7 shows the results for the room temperature NOI. For the GPR, all three additives raise the NOI, but for the HET resin, the value is either lowered or little changed. All values for the TBPA resin are around 66, irrespective of filler content, but for the DBNPG resin, the NOI is lowered by tin oxide, and raised by ZHS and ZS to very high values indeed. The NOI results are shown in Fig. 5 for the ZHS additive.

The above oxidation index results suggest that there are different mechanisms operating with each of these additives. For the GPR, the mechanism appears to be condensed phase, whereas for the HET and TBPA resins, vapour phase mechanisms seem to be operating. A complex situation occurs with the DBNPG resin, since tin oxide lowers the index suggesting vapour phase, whereas ZS and ZHS raise the index greatly, favouring a condensed phase mechanism.

Table 7
Nitrous oxide indices (NOI)

Resin	Additive (phr)	NOI
GPR	None	35.0
	SnO_2 (5)	55.0
	ZHS (10)	47.0
	ZS (10)	47.5
HET	None	67.0
	SnO_2 (5)	62.0
	ZHS (10)	67.7
	ZS (10)	55.0
DBNPG	None	65.8
	SnO_2 (10)	58.5
	ZHS (10)	77.4
	ZS (10)	85.3
TBPA	None	65.4
	ZHS (10)	66.5
	ZS (10)	66.9

3.4. Smoke and char

3.4.1. Arapahoe smoke chamber

Representative mean values of the smoke measurements for these systems using this gravimetric system are given in Table 8.

For the GPR, all three additives lowered smoke levels from around 15–10% by weight. For the HET

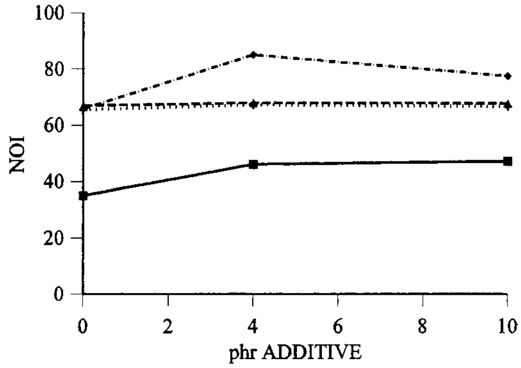

Fig. 5. NOI for resins with ZHS additive. Legend: (■) GPR; (▲) HET; (◆) DBNPG; (+) TBPA.

Table 8
Arapahoe smoke and char measurements

Resin	Additive (phr)	Smoke (%)	Char (%)
GPR	None	16.5	0
	SnO_2 (10)	7.9	7.6
	ZHS (10)	9.3	6.0
	ZS (10)	10.4	11.8
HET	None	8.5	14.5
	SnO_2 (10)	8.6	19.1
	ZHS (10)	12.0	24.9
	ZS (10)	12.8	23.1
DBNPG	None	17.8	6.1
	SnO_2 (10)	18.6	11.9
	ZHS (10)	20.3	17.0
	ZS (10)	26.8	18.6
TBPA	None	17.3	6.1
	SnO_2 (10)	13.6	16.2
	ZHS (10)	16.7	20.9
	ZS (10)	16.5	24.6

resin tin oxide produced little change, while ZS and ZHS increased the smoke significantly. For the TBPA resin, although tin oxide reduced the smoke by 21%, ZS and ZHS were less effective with a 3–5% reduction. DBNPG resins generally showed an increase in smoke with one clear exception. A loading of 2% ZHS in DBNPG lowered the smoke from 17.8 to 9.5%. Representative values for the three additives in a DBNPG resin are shown in Fig. 6.

Char values with the GPR alone were negligible, but were raised considerably by each filler. For all the halogenated resins the percentage of char was raised by the fillers, most notably from 6% to more than 20% for ZS in TBPA. The values for the three additives are shown in Fig. 7.

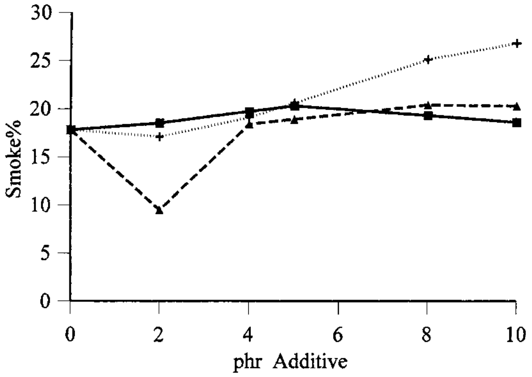

Fig. 6. Smoke values for DBNPG resin with additives. Legend: (■) SnO_2; (▲) ZHS; (+) ZS.

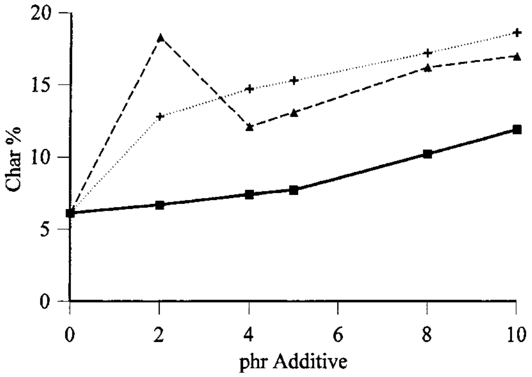

Fig. 7. Char percentage for DBNPG resins with additives. Legend: (■) SnO_2; (▲) ZHS; (+) ZS.

3.4.2. NBS smoke box

DBNPG resins containing ZSs were tested using the NBS system. The results are shown in Table 9 and conflict somewhat with the findings with the Arapahoe system. At loadings of 10 phr, ZHS reduced the maximum value of the smoke density by 41%, and ZS reduced it by 53%.

Several workers have shown that the tin additives lower smoke production in polymer systems [15,16]. However, comparison of results of the Arapahoe test with literature work is difficult, since the majority of the tests were conducted with the NBS system. The reasons for these conflicting results may lie in the nature of the test methods. The NBS chamber has no air flow from outside, and may thus be self-

Table 9
NBS smoke measurements

Resin	Additive (phr)	Maximum smoke density D_S (g)
DBNPG	None[a]	42
	ZHS (2)	30
	ZHS (10)	26
	None[b]	55
	ZS (2)	46
	ZS (10)	25

[a] Batch 1.
[b] Batch 2.

smothering. The collection method of the Arapahoe requires an air flow which would enhance burning and smouldering. Additionally, the Arapahoe system should collect smoke particles of all sizes, even large agglomerates, whereas the NBS chamber design allows them to sink to the bottom out of the light beams. These differences have been reported by Hilado and Scharf [36].

3.5. X-ray powder diffraction

The powder diffraction patterns of the original additives and of their products when heated alone were determined. Tin oxide showed the characteristic cassiterite pattern, and the patterns of the original ZHS and ZS corresponded to those in the literature. When heated to 300°C, the product from ZHS gave a featureless pattern with no peaks, showing that the ZS formed was in an amorphous state. Further heating to 1000°C gave a product showing the peaks due to Zn_2SnO_4 and SnO_2.

The residues obtained from heating SnO_2 with any of the resins still gave the same peaks as the original tin oxide suggesting that there had been no reaction between the additive and resin. Heating ZS with the resins up to 1000°C yielded a mixture of Zn_2SnO_4 and SnO_2, the most abundant product being tin oxide, suggesting that zinc is preferentially volatilised during the degradation. The products from ZHS and the resins gave evidence of both zinc oxide, and with DBNPG a single small peak corresponding to the largest diffraction peak of $SnBr_2$.

4. Conclusions

The effectiveness of tin oxide, ZS and ZHS as fire retardants and smoke suppressants for polyester resins has been demonstrated. The stannates are more effective than the tin oxide and are especially effective in resins containing halogens. The additives reduce flammability, but smoke production was affected to a smaller extent than expected, although the production of char was enhanced.

The thermal analysis evidence, the oxidation index measurements and the X-ray product analysis indicate that the ZSs in the presence of halogenated materials interact and are volatilised, and that this has a most significant effect on the fire retardant performance.

Differences between the resins were noteworthy. While the additives in the general purpose resin were shown to be acting by a condensed phase mechanism, the HET and TBPA resins gave evidence of vapour phase action. The DBNPG resin appeared to be showing a condensed phase behaviour.

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