*Journal of Thermal Analysis and Calorimetry, Vol. 59 (2000) 395–408*

*Dedicated to Prof. Edith A. Turi in recognition of her leadership in education*

# STUDIES OF FIRE-RETARDANT POLYESTER THERMOSETS USING THERMAL METHODS

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## Abstract

The use of thermal methods in the study of flammability and fire retardant action is discussed and compared with the standard test methods. This paper provides an overview with examples drawn from continuing studies on polyester resins, especially those containing halogenated monomers. Thermal analysis and cone calorimetry results are complemented by analysis of the gaseous and solid products using a wide range of analytical methods.

**Keywords:** fire retardancy, fire testing, polyester resins, polymers

## Introduction

The increasing use of polymers for industrial and domestic purposes has been a very great boon. However, it must be recognised that it carries with it an increased hazard, since most natural and synthetic polymers are flammable. Plastics materials have worsened the problems of handling fire situations with regard to ignitability, smoke and toxic products [1]. If we consider the materials which first become ignited in the progress of fires, statistics show that food, (especially fats) accounts for 21%, but then textiles and furnishings give 17%, paper and packaging 14%, electrical insulation 12%, and structures and fittings some 6%. Except for fats, all these materials could contain natural or synthetic polymer products. In addition, fires cost in excess of £600 million per year in the UK alone, and cause up to 1000 fatalities [2].

The hazards presented by fires may be considered as follows:

- Heat: producing heat exhaustion and allowing the fire to grow;
- Flame: giving burns and affecting victims psychologically;
- Smoke: obscuring exits, irritating lungs and eyes;
- Toxic gases: poisoning of victims;
- Oxygen depletion: loss of efficiency and judgement
- Structural: loss of mechanical strength in buildings.

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*1418–2874/2000/ $ 5.00*

*Akadémiai Kiadó, Budapest*
*Kluwer Academic Publishers, Dordrecht*

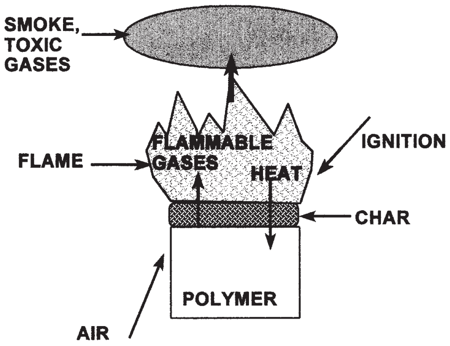


**Fig. 1** Schematic of polymer combustion

The burning of a polymer in air involves four main stages [3] which are illustrated in Fig. 1.

1. Ignition, when some source, usually thermal or electrical, starts the polymer degrading,
2. Pyrolysis, during which the polymer degrades under effect of heat to give products including char, that is solid carbonaceous material and also smoke, which is particulate material in gas phase, together with gases, both toxic ( e.g. CO) and flammable (e.g. benzene),
3. Flame, that is the region where gases ignite and produce heat and more thermally degraded products,
4. Heat, produced by exothermic reactions. The feedback of heat increases the rates of reaction, causes further degradation and polymer melting. It may also alter the mechanisms of burning reactions.

The task of the fire-retardant polymer scientist must be to interfere with or break the burning process at one or more points and to reduce the hazards. One way would be to stop the burning at source, by producing a polymer which is far less flammable. Such polymers are available, for example poly(tetrafluoroethylene) or polyimides, but tend to be too expensive for general use. Frequently they are also more difficult to process or mould than the conventional plastics used in large bulk.

### *Fire testing and thermal methods*

There are many methods of testing materials for their potential fire hazard. Horák [4] pointed out that 'only a few of them have found wide use: oxygen index, flash point determination and measurement of the rate of burning, to mention the most important'. Thermal methods have been shown to provide vital additional information for fire testing [5–7] and these results should be correlated with standard tests. A selection of important standard tests, which are described in the literature [1, 3] and of thermal analysis methods which complement them is given in Table 1.

**Table 1** Fire testing of plastics. Standard and thermal methods

| Stage | Standard tests | Thermal analysis |
|---|---|---|
| Ignition | Setchkin test (ASTM D 1929:1991)<br>Flash point | TG [8]<br>DSC-RLI [9]<br>Cone calorimeter [10, 11] |
| Flammability | Limiting oxygen index (LOI)<br>Nitrous oxide index (NOI)<br>UL94 tests<br>ASTM D 635 | Cone calorimeter [10, 11]<br>TG [12] |
| Smoke | NBS Smoke Chamber<br>Arapahoe Smoke Apparatus<br>Steiner tunnel<br>Ohio State University Release Rate Apparatus | Modified TG [13]<br>Cone calorimeter [10, 11] |
| Thermal degradation | Furnace pyrolysis<br>Pyrolysis-GC and GC-MS | TG and EGA<br>TG-FTIR and TG-MS<br>DTA and DSC<br>TVA [14]<br>TMA [5]<br>Thermomicroscopy [9] |

Thermal analysis has a most significant part to play in the study of thermal degradation of plastics. While pyrolysis-gas chromatography (Py-GC) and Py-GC-MS enable separation and identification of pyrolysis products on a time-resolved basis, thermal volatilisation analysis (TVA) [14] and simultaneous thermal analysis and spectrometric methods such as TG-FTIR [15, 16] and TG-MS [17] allow separation of thermal degradation products on a temperature-resolved basis. Besides the above, changes in mechanical properties [5], measurement of char formation and observations of solid residues [18 ] have all been done using thermoanalytical methods.

### *Flame retardant additives*

In order to change the flammability of a particular polymer without significantly altering the properties which make it useful in its applications, it is necessary to modify the chemistry involved in the burning cycle of that polymer. A method frequently used is to add a substance to the polymer, either by changing the monomer used, called a reactive fire retardant or by including an independent chemical called an additive fire retardant. The mode of action of these fire retardants frequently requires considerable study, but in very general terms, it may be:

- Modification of polymer to render it less liable to ignition or degradation;
- Production of gaseous species which interfere with the radical flame reaction;
- Endothermic decomposition to reduce feedback effect of heat on polymer;

- Changing the solid-state decomposition mechanism of the polymer so that less flammable materials are produced and preferably less smoke and more char.
- Production of a barrier to the feedback of heat, either char, fluid droplets or glassy layer. Intumescent coating systems act in this way [7].

The additives may also have deleterious effects, such as altering the mechanical properties of the polymer system for the worse, changing the colour, making it more difficult to process or actually producing more smoke plus corrosive or toxic products. Consideration of the major fire retardant chemicals with respect to the place their elements occupy in the periodic Table, as shown in Table 2, is a useful exercise, since it suggests possible alternatives or mechanistic similarities. The properties of a wide range of fire retardant chemicals have been reviewed by Cullis and Hirschler [3] and by Bair [19].

**Table 2** Major fire retardant additives according to their periodic table groups

| Group | Element | Compounds |
|---|---|---|
| II | Mg<br>Zn | magnesium hydroxide (MH)<br>zinc compounds (borate, phosphate, stannates) |
| III | B<br>Al | borax, zinc borate<br>aluminium hydroxide (ATH) |
| IV | Ti<br>Sn | titanium compounds<br>tin(IV) oxide, zinc stannates |
| V | N<br>P<br>Sb | ammonium salts, nitrogen-containing polymers<br>phosphorous, phosphate esters including halogenated esters<br>antimony(III) oxide |
| VI | Mo | molybdenum(VI) oxide, ammomium molybdates |
| VII | Cl<br>Br | chlorinated polymers, chlorinated monomers, polychlorinated compounds, chloroparaffins<br>brominated monomers, polybrominated compounds |
| VIII | Fe | ferrocene, iron(III) oxide |

Aluminium hydroxide ('Alumina Tri-Hydrate, ATH') and magnesium hydroxide are materials which decompose endothermically and are incorporated in large quantities, up to 60% w/w in polymers such as polyethylene and polypropylene, as well as in polyesters, polyurethanes and epoxies. The ignitable gases are also diluted by the water vapour evolved.

Antimony oxides together with zinc salts, molybdenum trioxide and others have good effects as fire retardants and give higher oxygen index values when incorporated in quite low concentrations usually with halogens also present. Borax, phosphates and others can work by endothermic decomposition to produce barrier materials. However, phosphates also tend to plasticise many polymers.

Chlorinated additives, whether they be incorporated in the polymer structure, where a good example is polyvinyl chloride (PVC), or added during processing, (e.g. Cerechlor

70, a chlorinated wax) work by producing radicals which interfere with the flame process, especially when used in conjunction with metal compounds such as $Sb_2O_3$.

Other compounds, like ferrocene derivatives are thought to act by providing an alternative pyrolysis route and to produce CO and $CO_2$ instead of smoke by a chemical incandescence mechanism.

It is found that, if two fire retardants are employed together, there may be an effect which is more than the sum of the two separately. This is referred to as a synergistic effect. The reverse, an antagonistic effect would be of little use. The reason for synergy could involve a reaction between the fire retardants, or between the products of their interaction or thermal decomposition.

### *Polyester resins (PER)*

Polyester resin materials, both alone, and fibre reinforced, particularly with glass fibre (GRP) constitute a large proportion of the high volume of composite materials currently in use. They are employed in a wide range of applications such as flooring, surface coatings, vehicle body panels and appliance housings. These uses may bring the polymers into fire situations at any time, adding an urgency to their fire-retardant studies.

The manufacture of a typical polyester resin (PER) involves the condensation of a glycol, an unsaturated acid, usually maleic acid or its anhydride, and a saturated or aromatic acid [18]. This produces a precursor which is then cross-linked most usually with styrene, although methyl methacrylate has also been used. Reinforcement with glass- or carbon-fibre provides excellent structural materials. A typical PER made from neopentyl glycol (NPG), maleic and phthalic anhydrides and styrene is very flammable. However, the glycol may be replaced with one containing bromine, such as dibromoneopentyl glycol (DBNPG) or the phthalic acid moiety with halogenated monomers like HET (1,4,5,6,7,7-hexachloro-5-norbornene-2,3-dicarboxylic acid anhydride), tetrachloro- or tetrabromo-phthalic anhydride shown in Fig. 2b. This has a beneficial effect on fire retardancy and little effect on mechanical properties. Extensive studies of polyesters containing HET acid have been reported by Fink and his co-workers [20]. The manufacturing sequence is shown in Fig. 2a and alternative halogenated monomers are shown in Fig. 2b.

## Experimental

### *The polyester resins*

Polyester resins were synthesised by well-established procedures [18, 21] using maleic anhydride, glycols, or halogenated glycols and saturated or aromatic diacid anhydrides or their halogenated derivatives. The cross-linking agent was usually styrene.

The additives were supplied by the manufacturers as follows: antimony oxide and undensified molybdenum trioxide from Climax Molybdenum Ltd.; alumina trihydrate (in various grades) from Alcan Chemicals Ltd.; tin(IV) oxide, zinc stannate and zinc hydroxystannate from ITRI; and incorporated into the mixture using a high shear mixer prior to the addition of the curing catalyst and accelerator.

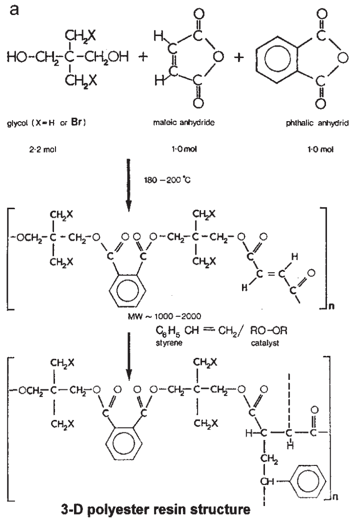
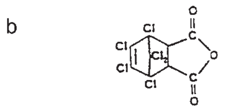
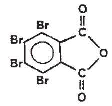


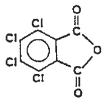
**Fig. 2a** Schematic of the preparation of a PER



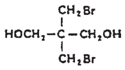
HET anhydride (1,4,5,6,7,7-hexachloro-5-norbornene-2,3-dicarboxylic acid anhydride)



Tetrabromophthalic anhydride



Tetrachlorophthalic anhydride



$$HOCH_2-\overset{\displaystyle CH_2Br}{\underset{\displaystyle CH_2Br}{C}}-CH_2OH$$

DBNPG (dibromoneopentyl glycol)

**Fig. 2b** Alternative halogen-containing monomers

### *Flammability testing*

Room temperature limiting oxygen index (LOI) and nitrous oxide index measurements were made using a Stanton Redcroft FTA Module, as reported earlier [18]. In addition, high temperature oxygen index measurements were made using the Stanton Redcroft HFTA module.

### *Smoke tests*

Smoking tests were carried out using the Arapahoe Smoke Chamber [18] and the Stanton Redcroft NBS Smoke Box. The char was determined by de-charring the sample after the Arapahoe Smoke test in a sand mill.

### *Thermogravimetry*

TG employed the Stanton Redcroft TG770 with samples of approximately 10 mg in a platinum crucible heated at 15°C $\text{min}^{-1}$ in a gas flow rate of 3 mL $\text{min}^{-1}$ from room temperature to about 800°C. The derivative thermogravimetric (DTG) curve was calculated electronically. Early experiments used the Stanton-Redcroft HT-D thermobalance, and a heating rate of 6°C $\text{min}^{-1}$ in static air.

### *Differential scanning calorimetry*

DSC used the Mettler DSC20 system with samples of about 10 mg weighed into aluminium crucibles and heated at 10°C $\text{min}^{-1}$ in a gas flow of 20 mL $\text{min}^{-1}$.

### *Differential thermal analysis*

DTA was carried out using the Stanton Redcroft DTA 673 with samples of up to 30 mg in platinum crucibles, heated at 10°C $\text{min}^{-1}$ in static air.

### *Thermal volatilisation analysis*

TVA was carried out by McNeill at the University of Glasgow. Samples were degraded at temperatures up to 500°C in an oven heated at 10°C $\text{min}^{-1}$ in a continuous evacuation system. The products were then separated by subambient TVA, and the products at each part of the TVA trace were analysed by infrared spectrometry [14].

### *Simultaneous thermogravimetry and FT-IR analysis*

TG-FTIR was performed at Perkin Elmer Ltd. using their TGA7 coupled to a 1720 FTIR spectrometer [16].

### *Cone calorimetry*

Cone calorimetry was done in association with Stanton Redcroft Ltd./Rheometric Scientific using their commercial Cone Calorimetry system [11].

### *Hot stage microscopy*

HSM was done both on the Stanton-Redcroft Hot Stage Microscope and on the combined DSC-RLI system [9].

### *Other analyses*

These included X-ray powder diffraction on the residues, scanning electron microscopy on the charred samples and pyrolysis-gas chromatography of the evolved gases and are reported elsewhere [22]. Acid digestion analysis of the resins containing tin additives was conducted on samples heated to progressively higher temperatures, dissolved in nitric acid and perchloric acid and evaporated to dryness. The metal contents were then determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). The oxygen flask method was used to determine the halogen content of samples [22].

## Results and discussion

Since the primary purpose of any fire retardant additive must be to reduce the flammability of the system, it is important that the oxygen index values (LOI) for the plastic materials with and without additives are compared. Increasing the LOI above 20, corresponding to the oxygen content of air is essential. The reduction of smoke, which is generally paralleled by an increase in char formation, should also be considered. Table 3 shows the results for several polyester systems as a function of bromine and additive concentrations. Resins with neither halogen nor other additives release flammable products, particularly styrene and its decomposition products during the second stage of degradation [21]. The release of bromine-containing moieties from the polymer matrix will inhibit these combustion reactions, but it is essential that they are in the 'right place at the right time' [23].

**Table 3** Limiting oxygen index values, smoke and char for polyester resin systems containing bromine as dibromoneopentyl glycol

| Additive | phr* | Br/% | LOI | Smoke/%[a] | Char/%[b] | Ref. |
|---|---|---|---|---|---|---|
| None | 0.0 | 0.0 | 19.0 | 15.5 | 0.0 | 22 |
| None | 0.0 | 10.0 | 23.7 | 18.0 | 3.1 | 18 |
| None | 0.0 | 28.5 | 39.2 | 17.9 | 6.1 | 22 |
| $Sb_2O_3$ | 5.0 | 10.0 | 32.0 | 22.2 | 3.0 | 18 |
| $MoO_3$ | 5.0 | 10.0 | 26.9 | 15.8 | 9.3 | 18 |
| ATH | 50.0 | 10.0 | 28.5 | 14.3 | 14.8 | 26 |
| ATH | 100.0 | 28.5 | 58.0 | 5.2 | 26.8 | 26 |
| $SnO_2$ | 10.0 | 10.0 | 32.6 | 12.5 | 7.1 | 22 |
| ZHS# | 10.0 | 10.0 | 33.6 | 17.6 | 12.7 | 22 |
| ZS# | 10.0 | 10.0 | 34.7 | 18.0 | 11.1 | 22 |
| $SnO_2$ | 10.0 | 28.5 | 50.2 | 18.6 | 11.9 | 22 |
| ZHS | 10.0 | 28.5 | 54.1 | 20.3 | 17.0 | 22 |
| ZS | 10.0 | 28.5 | 58.6 | 26.8 | 18.6 | 22 |

* phr – parts of additive per hundred parts of resin; # ZHS – zinc hydroxy stannate, ZS – zinc stannate; ATH – alumina trihydrate; [a] smoke % determined by the Arapahoe Smoke Chamber
[b] char % determined by decharring after Arapahoe Smoke test

Table 3 shows that the inclusion of bromine (as dibromoneopentyl glycol, DBNPG) in place of an unbrominated glycol raises the oxygen index, but also increases the smoke level. Addition of the metal-containing fire-retardant additives has a marked effect on both flammability and on smoke. While antimony(III) oxide and molybdenum(VI) oxide have similar effects on the LOI for similar loadings, the smoke is increased with antimony oxide, but reduced with molybdenum oxide. The high loadings of ATH required to produce a similar benefit are offset by the relatively low cost of this additive, but limited by the adverse mechanical effects. Tin(IV) oxide and the zinc stannates produce a complex mixture of effects, increasing the LOI, and producing more char, but making only small changes to the smoke. An additional advantage here is that these additives give less carbon monoxide [24, 25]. Measurements of the nitrous oxide index have been shown to indicate that $MoO_3$ acts in the condensed phase [18] and that, while tin oxide may act in the vapour phase, zinc stannate and zinc hydroxystannate probably act through a condensed phase mechanism [22].

### *Thermal analysis results*

The mass loss commences for all the PER samples, with or without additives, in the temperature range 140–150°C. All the stages of the degradation probably involve losses of several products, as has been demonstrated by careful pyrolysis-gas chromatography [27]. The first stage loss of about 16% is chiefly due to expulsion of phthalic anhydride from the polymer, as reported by Ravey [28] and confirmed by TG-FTIR studies [16, 22]. This loss occurs in the temperature range 190–240°C and is little affected by the additives. The second stage, occurring around 350°C involves the greatest mass loss (50 to 70%) and in this temperature range, brominated products and styrene plus its decomposition products are produced. Also in this temperature range additives such as ATH and ZHS undergo their major endothermic decompositions when heated on their own, as shown by the DTA trace in Fig. 3. They are therefore in the 'right place at the right time' for interaction. The residue remaining at the start of the third stage is mostly carbonaceous material from the polymer, plus any residual products from the additives. Char oxi-

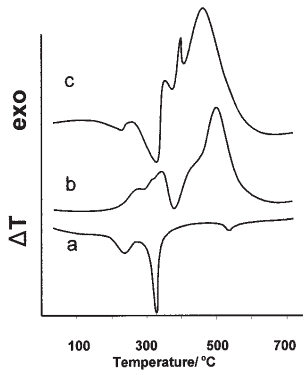


**Fig. 3** DTA curves for ATH and for DBNPG resin with and without ATH 15°C min$^{-1}$ in air

dation is the main reaction in air, and this produces a large exothermic peak in the DTA trace as Fig. 3. With additive present, the exothermic peak is reduced as shown in Fig. 3. If the additive and halogen produce volatile halides [3] loss of the additive may occur and thus the residue is less than would be the case without such reaction.

**Table 4** Thermogravimetry of polyester systems containing bromine as DBNPG in air. (The DTG maximum of each of the three major stages, together with the percentage mass loss in that stage)

| Additive | phr*/% | Stage 1/% | Stage 2/% | Stage 3/% | Residue#/% | Ref. |
|---|---|---|---|---|---|---|
| None | 0 (0.0) | 217 (16.3) | 345 (69.7) | 530 (13.9) | 0.0 | 18 |
| $MoO_3$ | 5 (4.8) | 232 (14.7) | 327 (60.1) | 472 (20.3) | $MoO_3$ (4.7) | 18 |
| $MoO_3$ | 15 (13.0) | 226 (14.1) | 327 (53.9) | 461 (19.0) | $MoO_3$ (12.9) | 18 |
| ATH | 100 (50) | 235 (7.5) | 336 (21.8)<br>391(25.7) | 541 (12.0) | $Al_2O_3$ (32.7) | 26 |
| $SnO_2$ | 5 (4.8) | 204 (10.0) | 331 (69.0) | 553 (17.0) | $SnO_2$ (4.0) | 22 |
| $SnO_2$ | 10 (9.1) | 192 (10.0) | 341 (68.0) | 525 (13.0) | $SnO_2$ (9.0) | 22 |
| ZHS | 10 (9.1) | 198 (18.0) | 278 (39.0)<br>409 (10.0) | 539 (31.0) | ZS (2.0) | 22 |
| ZS | 10 (9.1) | 192 (10.0) | 250 (39.0)<br>409 (34.0) | 553 (16.0) | ZS (1.0) | 22 |

* phr parts of additive per hundred parts of resin
# residue determined as the % mass remaining at 600°C

Thermoanalytical methods demonstrate that additives alter the degradation profile of the polymer. Table 4 illustrates that molybdenum oxide lowers the temperature of the second stage and more char remains. The oxidation of this char occurs at a lower temperature, suggesting a different char structure, and the residue is practically all the original $MoO_3$, which sublimes at 770°C.

Examination of the progress of the reaction using HSM confirmed the stages outlined above and showed the presence of $MoO_3$ after all the polymer had disappeared. Studies also showed that the particle size of the $MoO_3$ used, and of the alumina trihydrate, altered the fire retardant effects considerably. This has important implications also when the mechanical properties of the polymer mix are considered. The high loadings of the alumina trihydrate (ATH) make large changes to the mass losses and to the temperatures. The residue has been shown to contain the alumina expected.

The tin(IV) oxide was recovered with minor loss at the end of the TG run. It also appeared to have little effect on the temperature of the main degradation step, which suggests that the polymer and additive interact little. The temperature for the char oxidation was increased. Zinc hydroxystannate ($ZnSn(OH)_6$, ZHS) behaved in a rather different manner. Although the first stage of the decomposition was little changed, the second stage exhibited two peaks on the DTG trace, and the losses were considerably altered. The final residue was much less than expected, indicating that volatiliza-

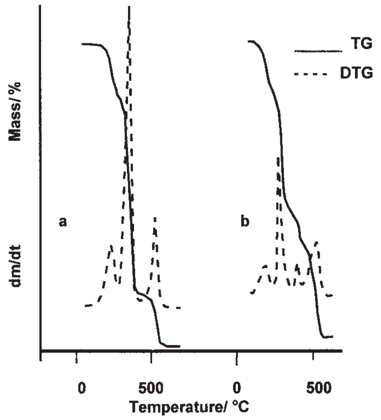


**Fig. 4** Thermogravimetric curves for DBNPG resin with and without ZHS 15°C $\mathrm{min}^{-1}$ in air

tion of the metals had occurred. This is shown in Fig. 4. Zinc stannate ($ZnSnO_3$, ZS) showed similar behaviour, with several overlapping DTG peaks and considerable loss of additive from the residue.

Studies using DSC showed that, while ZS gave a small endotherm at 190°C and ZHS alone gave several endothermic peaks and the DBNPG melted and degraded endothermically, 1:1 mixtures of ZS or ZHS with DBNPG exhibited a clear exothermic peak around 240°C.

### *Studies of evolved gases*

Furnace trapping experiments and Py-GC [27] have demonstrated that the decomposition products of the PER are very similar, whether additives are present or not. Major products from a PER containing phthalic acid moiety and cross-linked with styrene are styrene and its pyrolysis products and phthalic anhydride. No new degradation products were detected with the molybdenum oxide additive, but the level of aromatics was reduced, which corresponds to the decrease in smoke observed. Recent work has shown how the degradation of PER depends upon structure [21].

Samples of the DBNPG resin with and without zinc hydroxystannate additive were studied both by thermal volatilisation analysis and using a simultaneous TG-FTIR system [22]. Library searches confirmed that the products at low temperatures were dominated by phthalic anhydride and carbon dioxide. A clear indication of the production of HBr was given by the spectra of the PER without additive, but this was never observed with the additive present. This would be expected if the interaction produces volatile metal halides.

### *Residue analysis*

The importance of analysing the residues during and after thermal degradation has been demonstrated with molybdenum oxide and ATH [18, 26].

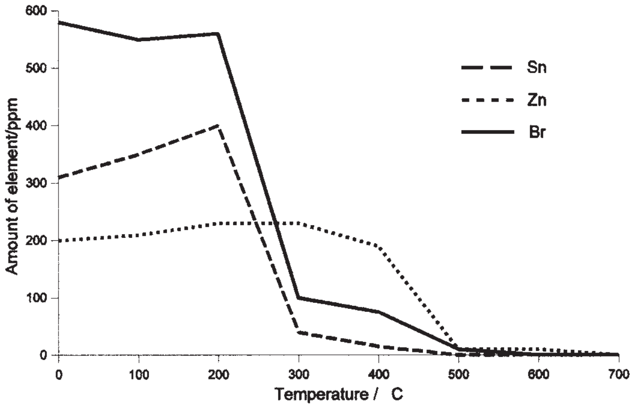


**Fig. 5** Residue analysis for a DBNPG resin containing ZHS

Comparison of the residue analysis for PER containing bromine and tin additives is very supportive of the mechanism suggested for fire retardant behaviour. With no bromine present in the resins, the additives remain behind in the form expected. With brominated resins the bromine content drops sharply to zero between 200 and 500°C, while with the ZHS additive there is an abrupt drop in the tin content around 250°C and of the zinc content between 400 and 500°C. The parallelism between these losses is shown in Fig. 5 and substantiates the interpretation of the gas-phase fire retardant action of the tin additives [22].

*Cone calorimetry*

Samples of the PER with and without bromine and with the ZHS and ZS additives were cast into 100 mm squares, 5 mm thick. They were subjected to a high irradiance,

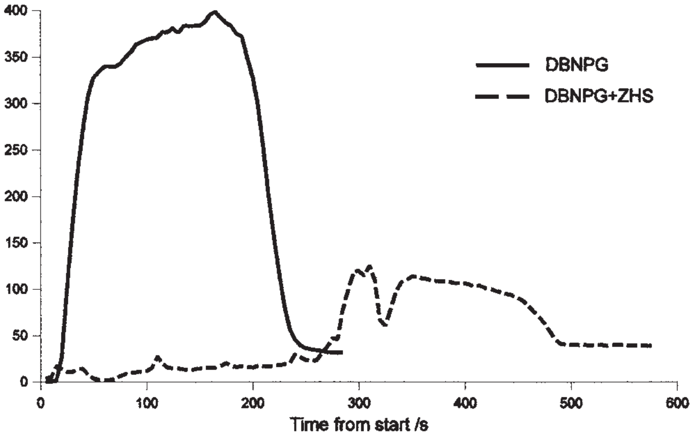


**Fig. 6** Heat release rate curves from cone calorimetry

generally 75 kW m$^{-2}$ and ignition encouraged by a spark igniter above the samples. It was noteworthy that the samples containing additives were difficult to ignite, and that under irradiation swelling took place. This had not been observed using either the thermal analysis or LOI tests. Observations were continued throughout the burning of the polymer and a tendency to smoulder, rather than to flame was noted. Samples of the residues remaining were examined by light and electron microscopy subsequently. Table 5 and Fig. 6 show typical cone calorimeter results for the heat release from DBNPG resins with and without ZHS additive.

**Table 5** Summary results from cone calorimeter experiments on DBNPG resins at an irradiance of 75 kW m$^{-2}$

| Parameter | No additive | 10 phr ZHS |
|---|---|---|
| Ignition time/s | 15 | 180–300 |
| Max. heat release/kW m$^{-2}$ | 394 | 163 |
| Total burn time/s | 230 | 560 |
| Heat of combustion/MJ/kg | 35.1 | 15.3 |
| Max. smoke release rate/s$^{-1}$ | 70 | 30 |
| Average CO/kg/kg | 0.05 | 0.13 |
| Average $CO_2$/kg/kg | 0.33 | 0.75 |

Summarising the findings from cone calorimetry, it is clear that

- the samples with additives were more difficult to ignite;
- they tended to smoulder for longer than they burned;
- the average heat release rate was reduced to one-third;
- smoke levels were lower;
- carbon monoxide levels were slightly higher in some cases;
- the residue remaining showed a ‘honeycomb’ structure suggesting some intumescent effects.

## Conclusions

While there is a lack of international agreement on fire tests and standards, any potential material which might pose a fire hazard should be tested for its flammability and smoke production. Thermal analysis measurements provide a vital link between the degradation temperatures and thermal profiles of the materials, particularly polymers, which should certainly form a part of a full investigation of flammability and fire retardancy testing.

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The authors gratefully acknowledge the generous help and collaboration which they have received over many years from manufacturers, instrument firms and research establishments. In particular, thanks are due to Dr A. Armour and Climax Molybdenum Ltd., Dr J. P. Redfern and Rheometric Scientific Ltd., Dr P. A. Cusack and the International Tin Research Institute, Perkin Elmer Ltd. at

Beaconsfield, Dr K. A. Evans and Alcan Chemicals Ltd., Dr K. Parvin and Scott Bader Co. Ltd., Dr I. McNeill at the University of Glasgow and many project students and technical staff at Kingston University.

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