

The Potential of Metal Oxalates as Novel Flame Retardants and Synergists for Engineering Polymers

A. F. Holdsworth, A. R. Horrocks¹, B. K. Kandola and D. Price².

*Institute for Materials Research and Innovation (IMRI), University of Bolton, Deane Road,
Bolton, BL3 5AB, UK*

Abstract

Based on their known decomposition to carbon dioxide, carbon monoxide and the respective oxide, six metal (calcium, manganese (II), iron (II), copper (II), tin (II) and zinc) were synthesised and assessed for their potential flame retardant activity in the absence and presence of selected flame retardants. Initially they were assessed when impregnated on cotton as a screening process and then selectively compounded with polyamide 6.6 (PA66), as a typical engineering polymer. Only manganese (II) and iron (II) oxalates alone reduced the burning rate of cotton, whereas together with ammonium bromide, calcium and iron (II) oxalates showed an apparent additional burning rate reducing effect. Derived synergistic effectivity (E_s) values fall within the limits $0 < E_s < 1$ indicating a less than additive interaction.

TGA/DTA analysis of oxalate/PA66 blends suggested that only zinc oxalate (ZnOx) offers both possible flame retardant activity in terms of enhanced residue formation $\geq 500^\circ\text{C}$, coupled with acceptable stability in molten PA66. When compounded with PA66, in the presence and absence of either aluminium diethyl phosphinate (AlPi)-based or selected polymeric bromine-containing flame retardants, LOI values increased in most PA66/ZnOx/flame retardant blends but UL94 test ratings were disappointingly low and more likely than not, “fails”. PA66/ZnOx blends with AlPi and AlPi/MPP gave poor plaques suggesting that thermal interactions were occurring during compounding.

The bromine-containing blends had better processibility and both TGA and cone calorimetric studies showed that the PA66/poly(bromopentabromobenzyl acrylate)/ZnOx sample not only yielded the highest residues in air and nitrogen at 500 and 580°C, but also the lowest peak heat release rate value of 398 compared with 1276 kW/m² for pure PA66. The derived E_s value for this blend is 1.17 suggesting a small level of synergy between the zinc oxalate and poly(pentabromobenzyl acrylate) flame retardant. The possible role of zinc bromide is discussed.

Keywords: metal oxalates, cotton, polyamide 6.6, phosphorus, bromine, synergism

Note 1. Corresponding author

Note 2: Deceased December 2013

1. Introduction

Many metal oxides, including those of zinc, tin and iron are known to possess inherent flame retardant behaviour in some polymers [1, 2], while some, such as antimony (III) oxide or zinc stannate, can act synergistically with flame retardants containing halogens [2-7] (Br and Cl in particular) and others, such as zinc borate, with some phosphorus-containing species [8-12]. Due to recent concerns regarding the potential toxicity and environmental accumulation of the antimony-bromine flame retardant systems, alternatives are being sought, including the development of both inorganic and non-halogenated replacements.

Metal oxalate salts are often used as precursors in the preparation of high-purity oxides [1, 13-20]. They decompose with the loss of carbon oxides at similar temperatures to many polymers (eg 200-400 °C) [1, 14-19], are water insoluble[13] and have received little recent attention in this field [1, 21-28], thus making them an interesting starting point for an investigation into potential new flame retardant compounds either in their own right or as synergists.

In this paper we report the synthesis of six divalent metal oxalates followed by an assessment of their potential flame retardant behaviour, both alone and in combination with selected phosphorus- and bromine-containing flame retardants. Initially, as a screening process for potential flame retardant activity, they were impregnated on to cotton for simple flammability testing from which selected oxalates were studied initially as mixtures to determine the most suitable candidates and then the most melt-compatible examples as compounded blends with polyamide 6.6 (PA66) as a typical engineering polymer.

2. Materials and experimental

2.1 Materials

Polymer substrates

The cotton used was a commercially bleached, woven fabric with an area density of 114 g/m².

The polyamide 6.6 was provided by Invista Engineering Polymers (compounding grade, 100% PA66, MPt 260 °C, MFI 19.56 g/min @ 280 °C).

Oxalate Precursors

The metal salts and oxalic acid dihydrate used for the synthesis of oxalates were supplied by VWR (UK), and were of reagent grade (98%+ purity) and used as purchased with no further purification undertaken. All synthesis reactions were conducted using deionised water.

Flame Retardants

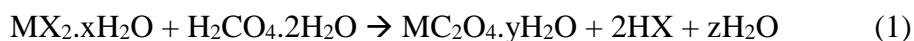
Ammonium bromide and diammonium phosphate were supplied by Sigma Aldrich (UK) and were of reagent grade (98%+ purity), requiring no further purification before use.

The organophosphorus flame retardants used were acquired from Clariant (Germany), as Exolit 1230 (aluminium diethylphosphinate (AlPi)) and Exolit 1311 (aluminum diethyl phosphinate/melamine polyphosphate (AlPi/MPP) as a 2:1 blend). The polymeric brominated flame retardants were acquired from ICL (Israel) as FR803P (brominated polystyrene (BrPS)) and FR1025 (poly(pentabromobenzyl acrylate (BrPBz))). These polybrominated flame retardants were selected because they are known to be relatively stable during melt processing of PA66 and are effective in this polymer in the presence of synergists like

antimony (III) oxide and zinc stannate [5]. All materials used for compounding were dried at 80 °C for at least 24 hours before use.

2.2 Synthesis of metal oxalates

Six divalent metal oxalates (MO_x, of general formula MC₂O₄.nH₂O where M = Ca, Mn, Fe, Cu, Zn, or Sn and n = 0, 1, 2) were synthesised using an aqueous route (see Eq. 1, where M = Ca, Mn, Fe, Cu, Zn, or Sn; X = Cl or NO₃ and x, y and z are variable integer waters of hydration) using equimolar amounts of 1 mol/dm³ solutions of the required reagents scaled to give 100 g of dried product. The exact syntheses were based on a proprietary method used by William Blythe Ltd for the synthesis of tin (II) oxalate but similar methods are reported in the literature.[14-17, 19]



The oxalates were characterised initially using TGA/DTA, as described in Section 2.5 below, followed by the determination of metals content by atomic absorption (AA), inductively coupled plasma (ICP) spectrometry and x-ray fluorescence spectroscopy (XRF). ICP analysis was conducted using a Thermo Scientific ICAP6000, XRF analysis was conducted using a Panalytical Axios analyser, using internal elemental standards with the Omnia analytical suite and AA analysis was undertaken using a Perkin Elmer Analyst 300 analyser. Determination of the oxalate content was undertaken by redox titration with potassium permanganate. [29, 30]

2.3 Preparation of impregnated cotton samples

Cotton was chosen as one of the model polymer substrates for this study to initially screen each oxalate for any char-forming and hence potential flame retardant activity. Furthermore, sample preparation via impregnation and drying is a simple procedure to carry out. All samples were prepared (in triplicate) by brush application of a suspension of each oxalate in water to a cotton sample (170 x 50 mm) followed by drying at 80 °C for 1h. Oxalate impregnation levels (determined gravimetrically) were selected to be approximately 3 wt%, at which any flame retardant effect would demonstrate itself as a change in sample burning rate. Further oxalate samples containing water-soluble sources of bromine (as NH_4Br , AB) and phosphorus (as $(\text{NH}_4)_2\text{HPO}_4$, DAP), were also prepared at concentrations that yielded M:Br and M:P molar ratios of 1:2 and 3:2 respectively, where M is the metal ion present in each oxalate. The levels of AB and DAP were maintained at 2.5 wt% in total, with the amount of oxalate in each suspension being adjusted accordingly in an attempt to achieve these ratios. These levels were chosen because they were sufficient to promote a marginal level of flame retardancy in terms of modifying burning rate rather than promoting complete extinction. For example, higher levels (ca 5 wt% add-on) of DAP render the cotton samples completely resistant to ignition. Thus any positive or negative influence of any additional metal oxalate could be more easily observed using the lower concentration of 2.5 wt%.

2.4 Compounding of PA66 samples

Compounding of all PA66 formulations was undertaken using a laboratory-scale, Thermo-Scientific twin-screw extruder, with six heating elements set at 250, 255, 260, 265, 270 and 275 °C respectively and a screw speed of 350 rpm. All PA66 polymer pellets and flame retardant powders were dried at 80 °C for at least 36 h before processing. The produced pellets were pressed into plaques (170 x 170 x 3 mm) using a hot press at 260 °C with a

pressure of 20 kg/cm², followed by cutting into strips 12.7 mm wide for UL94 and LOI testing and 75 x 75 mm plaques for cone calorimetry analysis where appropriate.

Both commercial phosphorus-containing flame retardants based on aluminium diethylphosphinate (AlPi) and the 2:1 blend of AlPi and melamine polyphosphate (AlPi/MPP) were compounded with PA66 for at levels of 7.5, 10, 12.5 and 15 wt% to determine a minimum effective concentration of each in the first instance. Once these values had been established for each flame retardant (see Section 3.4), formulations containing these respective levels plus 5 wt% of the metal oxalate that showed the greatest char-promoting trend and appropriate thermal stability from TGA studies were prepared. In fact, only zinc oxalate was selected and this was calcined at 150°C to ensure that it was anhydrous prior to compounding (see Section 3.3). The 5wt% level was selected because this is a typical maximum value used by metal salt synergists in commercial polymer formulations.

Both brominated polystyrene (BrPS) and poly(pentabromobenzyl acrylate) (BrPBz) FR1025) were introduced at bromine levels of 10 wt% [7], corresponding to 15.2 wt% BrPS and 14.1 wt% BrPBz, with a zinc oxalate concentration of 5 wt%, where again, the oxalate selected was that shown to have the best char-promoting properties from TGA. Respective bromine-containing controls were prepared at the same 10 wt% Br concentrations. Oxalates were calcined to 150 °C before use to ensure dehydration.

2.5 TGA/DTA analysis

TGA/DTA analyses were performed using a TA Instruments SDT 2960 analyser, under 100 ml/min flow of air or nitrogen, with a heating rate of 20 °C/min from ambient temperature to 600 °C, with a sample size of approximately 10 mg. The activity of each PA66 formulation

was determined by analysing a finely powdered, intimately mixed composition of each oxalate and PA66 using TGA/DTA in a 1:3 ratio by mass, a level chosen because favourable interactions would be more apparent than if a lower oxalate concentration were used. The powdered PA66 was prepared from polymer pellets cooled to -196 °C using liquid nitrogen and subsequently processed several times using a simple coffee grinder. The resulting powder was passed through a 100 µm sieve to remove larger particles.

Additional TGA/DTA analyses were performed on each oxalate and pure PA66 powder under the same conditions, allowing for calculation of theoretical decomposition curves for assessment of possible interactions between oxalate and polymer between 300 and 580 °C, representing the primary degradation range of PA66. The difference between the theoretical interaction-less degradation and the observed result TGA versus temperature responses were then plotted against temperature, with each 20 °C data point represented by Eq. 2:

$$M_{\text{diff}} = M_{\text{obs}} - (0.75.M_{\text{poly}} + 0.25.M_{\text{oxalate}}) \quad (2)$$

where M_{obs} is the observed mass loss at that temperature and M_{poly} and M_{oxalate} are the observed mass losses at that temperature for PA66 and each oxalate powder respectively.

2.6 Flammability testing

The dried, metal-oxalate impregnated cotton samples were tested in triplicate following a 10 s application of a Bunsen burner, by timing the horizontal burn rate of the sample, which was held in a U-shaped frame, over a measured distance (150 mm). The results were averaged over the three replicates tested.

Compounded PA66 samples were assessed for Limiting Oxygen Index (LOI) according to ASTM 2863, and UL-94 in the vertical orientation, according to ISO 1210 [31]. Cone calorimetry was also performed on samples which produced viable plaques, using a 50 kW/m² heat flux (FTT cone calorimeter, Fire Testing Technology, UK) according to ISO 5660. A number of parameters were determined, including: times to ignition, peak heat release rate and extinction, peak heat release rate, total heat release, effective heat of combustion and total smoke release.

3.0 Results and discussion

3.1 Synthesis and characterisation

TGA/DTA analysis was used to characterise the oxalates, which decompose at elevated temperatures according to the reactions listed in Table 1. These reactions are stepwise for the majority of oxalates, with water being lost first for hydrated salts, followed by CO and CO₂ in a second step which latter occurs between 250 and 400 °C for the majority of oxalates. The mass losses for each compound correspond to the expected values for the species lost, which are summarised in Table 1 along with the theoretical mass losses, and displayed graphically in Figure 1 for one set of each sample TGA curves.

The results of wet chemical (by AA, ICP and KMnO₄ titration methods) and XRF analyses are summarised in Table 2. The observed values match the theoretical contents of the compounds within an acceptable margin, excepting several of the permanganate titrative analyses which give erroneous results due to the poor solubility of the compounds in the dilute aqueous acidic medium required for the analysis. Where appropriate, the observed results have been adjusted to account for the oxidation of redox-active metal centres. However, these permanganate-derived results determine only the oxalate ion and any redox-

active metal centres such as iron (II) or tin (II) and confirm the presence of the former in each salt (see Section 2.2).

From the TGA/DTA and XRF/wet chemical analysis, it can be concluded that the desired products had been formed.

3.2 Effect of burning rate on cotton

The burning rate tests yielded variable results depending upon the oxalate and synergist present and are displayed in Table 3 and graphically in Figure 2. Alone, none of the metal oxalates promoted extinction of the cotton substrate and only manganese (MnOx) and iron (FeOx) oxalates showed reduced burning rates relative to the control, with stannous oxalate (SnOx) greatly increasing the burn rate. In the presence of ammonium bromide, AB, all oxalates reduced the burn rate relative to the control, with calcium (CaOx) and iron (FeOx) oxalates providing the greatest reductions.

Alone, when applied to cotton, the relatively low concentrations (approx 2.5 wt% each) of AB and DAP applied have significantly differing effects. Only two oxalates (CaOx and MnOx) were tested with diammonium phosphate due to highly variable loadings obtained after impregnation compared with the control and only CaOx displayed any appreciable reduction in burning rate compared to the control. Addition of ammonium bromide, however, reduced the burning rate with all oxalates. Both flame retardant/oxalate combinations promoted the formation of charred residue although none of the oxalates alone on cotton displayed any inherent char promotion and the SnOx-containing samples were observed qualitatively to produce a greater degree of smoke than the other oxalates.

It is possible that the oxalates are functioning as potential synergists and the synergistic effectivity (E_s) values for each oxalate may be calculated using Eq.3 [7]

$$E_s = [X_{(FR+S)} - X_{cotton}] / [(X_{FR} - X_{cotton}) + (X_S - X_{cotton})] \quad (3)$$

where E_s is the synergistic efficiency of the oxalate, X is a typical flammability parameter such as burning rate and so X_{cotton} , X_{FR} , X_S and $X_{(FR+S)}$ are the respective burning rates of cotton alone and impregnated with the flame retardant, oxalate (synergist) and both together. If $0 < E_s < 1$, then the interaction between the oxalate and flame retardant is less than additive (ie $E_s = 1$). Calculated values are included in Table 3 for the ammonium bromide/oxalate-impregnated (AB) samples only from which it is seen that there is no obvious synergy evident since E_s values are all less than 1.

3.3 Thermogravimetric analysis of PA66/oxalate mixtures

The effect of each of the six oxalates at 25 wt% on the TGA/DTA degradation curves under flowing air conditions of PA66 are shown below in Figure 3. Data extracted from these curves is collated in Table 4 below includes the TGA-derived mass loss temperatures at 5% ($T_{5\%}$), 10% ($T_{10\%}$) and 50% ($T_{50\%}$) mass losses, respective residues remaining at 580 °C and both the DTG-derived and DTA-derived peak temperatures. Figure 3 shows that each oxalate has significantly modified the control PA66 TGA response with a general reduction in the onset of degradation temperatures and increases in residues above 550 °C for each PA66/oxalate mixture. However, the curve shapes in Figure 3 do not simply reflect the respective oxalate decomposition curves in Figure 1. For instance, while the multistage decomposition of zinc oxalate is reflected in a two-stage decomposition of the PA66/ZnOx mixture up to 400 °C, the multistage decompositions of calcium oxalate and manganese oxalate are not reflected in their respective PA66 mixture TGA responses. Conversely, the

single stage decompositions of copper and tin oxalates yield multistage decompositions in mixtures with PA66. In these latter two cases, this is not perhaps surprising since both iron and copper ions are known to sensitise PA66 thermal degradation [32, 33].

In order to examine whether interactions are occurring which may indicate possible flame retardant interactions with PA66 via increased char formation, differential mass values, M_{diff} , for each formulation at 20 °C temperature intervals (see Eq. 2) were calculated for those PA66/oxalate formulations that demonstrated a number of characteristics that suggest both char promotion and PA66 melt stability. These are that at least 10% residue at 580 °C remained, no DTG/DTA peaks occurred at temperatures <300 °C, which would indicate that degradation of the polymer was occurring close to the PA66 melting point at (~260 °C), and $T_{5\%}$ and $T_{10\%}$ mass loss temperatures were greater than 200 °C and 300 °C respectively excluding peaks resulting from loss of water from hydrated samples. Only the three oxalates, CaOx, ZnOx and SnOx, fulfilled these criteria and so plots of M_{diff} versus temperature were constructed for these as shown in Figure 4. As mentioned above, the sensitisation of thermal degradation by FeOx and CuOx was responsible for their rejection while MnOx fails to produce the required level of residue when present in PA66.

As can be seen from Figure 4, the PA66/ZnOx mixture displays a significantly higher char yield between 480 and 540 °C than would be expected if no interaction occurred between the two compounds. CaOx has the lowest effect on the degradation of PA66 compared with the other two oxalates tested, but promotes little char above 500 °C. While SnOx has the greatest effect on the degradation of PA66 in terms of its yielding the most intense negative curve within the 350 to 450 °C region, it also promotes the lowest amount of char amongst all the oxalates tested via this methodology. These observations suggested, therefore, that ZnOx was

the only oxalate suitable for larger scale synthesis and fire testing with compounded PA66 samples.

3.4 Compounded PA66/zinc oxalate samples

Based on the results in Section 3.3 above, only zinc oxalate fitted the criteria defined for acceptable PA66 melt stability and char promotion and so formulations with the selected flame retardants were compounded in the absence and presence of 5 wt% anhydrous ZnOx as a reasonable maximum concentration for an inorganic species in an engineering polymer (see Section 2.4). Formulated samples were then prepared as plaques having the required dimensions for larger scale fire testing as described in Section 2.6.

3.4.1 Phosphorus-containing PA66/zinc oxalate formulations

The LOI values and UL94 test ratings for formulations containing either AlPi or AlP/MPP at 7.5, 10, 12.5 and 15 wt% respectively in PA66 compounded samples are shown in Table 5.

From these results above it can be seen that for AlPi at 7.5 wt% in PA66 yields a UL94 “fail” rating with an elevated LOI value of 28.2 vol% compared with the control PA66 sample. Higher AlPi concentrations all give UL94 V-0 ratings with LOI values maximising at 33.9 vol%. However, while AlPi/MPP present at 7.5 wt% also raised the LOI (=26.6 vol%), the variable “V-2/fail” rating remained unchanged relative to that for pure PA66. This variability continued when the AlPi concentration was raised to 10 wt%, although V-0 ratings were observed at higher concentrations and LOI values stabilised at 28.5 vol%.

A second matrix of six samples was prepared as above but with the addition of 5 wt% zinc oxalate. However, for the PA66/ZnOx/AlPi sample, acceptable plaques could not be produced for LOI, UL94 or cone calorimetric testing and for the PA66/ZnOx/AlPi/MPP

sample, plaques of acceptable quality (although containing voids) were obtained for UL94 and LOI testing but not for cone calorimetry. This was a consequence of changed melt rheology most likely resulting from interactions ZnOx/flame retardant/PA66 encountered during compounding. All formulated samples were subjected to TGA/DTA under both air and nitrogen and the results of these experiments are shown below in Table 6 together with the LOI results, UL94 ratings and the cone calorimetric parameters of time-to-ignite (t_{ig}), time-to-peak (t_{PHR}), time-to-flame-out (t_{fo}), peak heat release rate (PHRR) and total smoke release (THR).

The TGA results confirm that thermal interactions were indeed occurring in the PA66/ZnOx/AlPi and PA66/ZnOx/AlPi/MPP samples by the reductions in the values of $T_{5\%}$ in air to 322 and 325 °C respectively, much lower than when zinc oxalate only is present ($T_{5\%} = 345^{\circ}\text{C}$). The voids observed in plaques from the latter sample probably influenced the variability of the UL94 results and prevented its being of a quality acceptable for cone calorimetric studies.

With respect to the control TGA results under air, while each single additive has a reduced $T_{5\%}$ value, residue levels are significantly greater than for PA66 at 500 °C as expected and also at 580 °C, apart from the PA66/ZnOx sample. This suggests that the presence of ZnOx has reduced the normal PA66 char residue and/or some residual zinc oxide has volatilised. However, TGA residues under both air and nitrogen conditions suggest that the presence of ZnOx and flame retardant has increased their formation at 500 and 580°C, although whether or not these comprise increased char is not clear at this stage since the residues will also comprise zinc oxide. Under nitrogen, residues from the PA66/ZnOx sample at both

temperatures are higher than for PA66 suggesting that loss of zinc oxide at 580 °C is not occurring as initially proposed above.

When AlPi only is present, residues under nitrogen at both 500 and 580 °C are less than from pure PA66 presumably because of the formation of and volatilisation of diethyl phosphinic acid [8]. Generally, the residues in air are greater than those formed under nitrogen because of recent evidence that in pure PA66 alone, formation of oxidatively-derived char is a significant reaction which increases the residues at 500 °C from 3.8% under nitrogen to 11.2% in air although at the higher temperature of 580°C, this increase is less marked [34]. Residues formed under air conditions of formulations containing AlPi are enhanced by the formation of aluminium phosphate [8] as well as by the presence of zinc oxide in those containing ZnOx.

With regard to flammability testing, the LOI and UL94 results in Table 6 suggest from the outset that zinc oxalate displays, if anything, antagonistic behaviour with the selected phosphorus-containing flame retardants as well as creating the observed difficulties with compounding and processing. The antagonistic effects are similar to those observed for the cotton fabrics impregnated with both oxalate and diammonium phosphate (see Table 3). Thus while LOI values reduce following the addition of ZnOx to the PA66/AlPi/MPP formulation from 28.2 to 24.9 vol% respectively, UL94 testing shows consistent failures for both.

Cone calorimetric results show that while all compounded formulations examined have lower T_{ig} values than pure PA66, the presence of ZnOx, AlPi and AlPi/MPP individually all had reduced PHRR values with only the last sample showing significant smoke reduction.

3.4.2 Bromine-containing PA66/zinc oxalate formulations

The selected BrFRs, namely brominated polystyrene (BrPS) and poly(pentabromobenzacrylate) (BrPBz) were each compounded at levels equivalent to 10 wt% bromine, both in the absence and presence of 5 wt% zinc oxalate, to yield pellets capable of being pressed into plaques for UL94, LOI and cone calorimetric testing. The collated results are shown in Table 7.

In the control samples, it can be seen that both ZnOx and each brominated flame retardant have little effect on LOI value and a marginal effect on UL94 rating. Again, the very low TGA residue at 580 °C under air observed for the PA66/ZnOx sample is also similarly low when BrPS alone is present at 580 °C. However, the addition of zinc oxalate to both flame retardant formulations increases respective LOI values while having negligible effect on UL94 ratings, which is paralleled by increased respective residue values under both air and nitrogen conditions at 500 and 580 °C. For example, residues of PA66/BrPS/ZnOx and PA66/BrPBz/ZnOx samples at 500°C are considerably higher in air and nitrogen conditions than the sums of their respective residues of the PA66/ZnOx and PA66/BrFR samples.

The heat release calorimetric curves are shown in Figure 5 and the final residues from each formulation are shown in Figure 6. The heat release curves show a shift towards shorter times-to-ignition for each formulated sample relative to pure PA66 with a similar shift in the times-to-peak heat release rate. These shifts accompany the general reduction in the intensity of the curve although the time-to-flame-out has increased only for the PA66/PrBz/ZnOx sample, which also has the lowest PHRR value at 398 kW/m². The presence of each brominated flame retardant has significantly increased smoke generation with addition of ZnOx further exacerbating this effect only for the BrPS-containing sample. The cone

calorimetric residues in Figure 6 suggest show that only both PA66/BrPS/ZnOx and PA66/BrPBz/ZnOx have measurable char forming character. This especially true for the latter compound, which produced a thick, resilient char, reflected in the TGA residue data in Table 7. E_s values were calculated for each PA66/BrFR/ZnOx formulation using a modification of Eq 3 [7], where the cone calorimetry peak heat release rate as the metric for analysis, X. These are listed in Table 7 and indicate that the BrPS/ZnOx interaction is less than additive ($E_s < 1$), whereas that for BrPBz/ZnOx suggests there to be synergy ($E_s > 1$) between the components reflecting also the higher residue and perhaps char promotion under both air and nitrogen conditions observed during thermogravimetric analysis.

3.5 Mass differential study of mixtures of zinc oxalate with brominated and phosphorus flame retardants

The results in Sections 3.4.1 suggest that the combined effects of zinc oxalate and both AlPi and AlPi present in PA66 has a marginal effect increasing residues above 500°C in both air and nitrogen although no effect on overall flammability was observed in terms of LOI or UL94 results. However, the combined effects of zinc oxalate and both brominated flame retardants, and especially BrPBz (see Section 3.4.2), showed evidence of increased TGA residues and LOI values as well as reduced PHRR values. The E_s value (= 1.17) for ZnOx and BrPBz suggests some level of synergistic activity, although how this is divided between possible condensed and vapour phase mechanisms is not clear.

In order to determine whether ZnOx and any of the flame retardants (both PFRs and BrFRs) used are indeed interactive, several additional TGA/DTA experiments were performed under flowing air, using analogue mixture equivalents of the flame retardant content of each

compounded sample without the presence of PA66 to plot mass differential versus temperature curves (see Equation 2 and Section 2.5) as shown in Figure 7.

In the case of ZnOx with both PFRs, increased mass is observed at higher temperatures (>400 °C), suggesting some level of condensed-phase interactions possibly due to both the ZnO produced during ZnOx decomposition and to the phosphorus (as phosphate [8]) contained in AlPi and AlP/MPP. The opposite is true of ZnOx with both BrFRs, with volatilisation indicated at higher temperatures in contrast to the high residue levels recorded in Table 7 when present in PA66, especially for the PA66/BrPBz/ZnOx sample at 500 °C in air and in nitrogen. This suggests that ZnOx is increasing the volatilisation and possibly the potential vapour phase activity of poly(pentabromobenzyl acrylate). If vapour phase flame retardant activity is enhanced, then it could be via formation of the relatively volatile ZnBr₂ (b.p. 697 °C) with some sublimation from 450 °C onwards. However, the high residues recorded in Table 7 could also be partly due to some condensed phase activity of ZnBr₂ acting as a Lewis acid, promoting the formation of cross links between PA66 chains and hence char. However, to show that ZnBr₂ is indeed active in the vapour phase as a flame retardant, in a similar manner to SbBr₃, further research would be required and is the subject of current interest within this research group.

4.0 Conclusions

Of the six metal oxalates synthesised, only two (MnOx and FeOx) alone reduced the burning rate of cotton, whereas together with ammonium bromide, calcium and iron (II) oxalates show an apparent possible additional effect in the reduction of burning rate, although derived synergistic effectivity values fall within the limits $0 < E_s < 1$ indicating a less than additive effect.

When metal oxalates are mixed with PA66, as a representative engineering polymer, TGA/DTA analysis suggests that only zinc oxalate offers both possible flame retardant activity in terms of enhanced residue formation at 500°C and above, coupled with acceptable stability in molten PA66. When compounded with PA66, in the presence and absence of selected phosphorus-(AlPi and AlPi/MPP)- and bromine (BrPS and BrPBz)- containing flame retardants, LOI values increased in most PA66/ZnOx/flame retardant blends but UL94 ratings were disappointingly low and more likely than not “fails”. PA66/ZnOx blends with AlPi and AlPi/MPP gave poor plaques suggesting that thermal interactions were occurring during compounding.

The bromine-containing blends showed better processibility and both TGA and cone calorimetric studies showed that the PA66/BrPBz/ZnOx sample not only yielded the highest residues in air and nitrogen at 500 and 580°C, but also the lowest peak heat release rate value of 398 compared with 1276 kW/m² for pure PA66. The derived E_s value for this blend is 1.17 suggesting a small level of synergy between the zinc oxalate and poly(pentabromobenzyl acrylate) flame retardant. Whether or not this synergy arises from enhanced condensed phase or vapour phase activity or both is not clear but evidence is presented to suggest that formation of ZnBr₂ may be formed as an intermediate, although further work would be required to confirm this.

Acknowledgements

One of us (AH) wishes to thank both the UK Engineering and Physical Science Council and William Blythe Chemicals Ltd, UK for their support via a CASE Studentship. Analytical work was carried out using facilities kindly provided by William Blythe Chemicals Ltd.

References

- 1) Rault F, Pleyber E, Campagne C, Rochery M, Giraud S, Bourbigot S, Devaux E. Effect of manganese nanoparticles on the mechanical, thermal and fire properties of propylene multifilament yarn. *Polym Degrad Stab* 2009;94:955-964.
- 2) Laoutid F, Bonnaud M, Alexandre M, Lopez-Cuesta J M, Dubois, P. New prospects in flame retardant polymer materials: from fundamentals to nanocomposites. *Mater Sci Eng* 2009;63:100-125.
- 3) Hastie J W. "Molecular basis of flame inhibition. *J Nat Res Bureau Stds* 1973;77A:773.
- 4) Petsom A, Roengsumran S, Ariyaphatanakul A, Sangvanich P. An oxygen index evaluation of flammability for zinc stannate as synergistic flame retardants for acrylonitrile-butadiene-styrene copolymer. *Polym Degrad Stab* 2003;80(1):17-22.
- 5) Horrocks A R, Smart G, Kandola B, Holdsworth A, Price D. Zinc stannate interactions with flame retardants in polyamides; Part 1: Synergies with organobromine-containing flame retardants in polyamides 6 (PA6) and 6.6 (PA6.6). *Polym Degrad Stab* 2012;97(12):2503-2510.
- 6) Cusack P, Hornsby P. Zinc stannate-coated fillers: novel flame retardants and smoke suppressants for polymeric materials. *J Vinyl Addit Tech* 1999;5(1):21-30.
- 7) Horrocks A R, Smart G, Price D, Kandola B K. Zinc stannates as alternative synergists in selected flame retardant systems. *J Fire Sci* 2009;27:495-521
- 8) Braun U, Schartel B, Fichera M A, Jager C. Flame retardancy mechanisms of aluminium phosphinate in combination with melamine polyphosphate and zinc borate in glass-fibre reinforced polyamide 6,6. *Polym Degrad Stab* 2007;92:1528-1545.
- 9) Karrasch A, Wawrzyn E, Schartel B, Jager C. Solid-State NMR on thermal and fire residues of bisphenol a polycarbonate/silicone acrylate rubber/bisphenyl a bis (dipheyl-

phosphate)/(PC/SiR/BDP) and PC/SiR/BDP/ZnB) – Part I: PC Charring and the impact of BDP and ZnB. *Polym Degrad Stab* 2010;95:2525-2533.

10) Samyn F, Bourbigot S, Duquesne S, Delobel R. Effect of zinc borate on the thermal degradation of ammonium polyphosphate. *Thermochim Acta* 2007;546:134-144.

11) Pawlowski K H, Schartel B, Ficher M A, Jager C. Flame retardancy mechanisms of bisphenol a bis (diphenyl phosphate) in combination with zinc borate in bisphenol a polycarbonate/acrylonitrile-butadiene-styrene blends. *Thermochim Acta* 2010;498:92-99.

12) Fontaine G, Bourbigot S, Duquesne S. Neutralised flame retardant phosphorus agent: facile synthesis, reaction to fire in polypropylene and synergy with zinc borate. *Polym Degrad Stab* 2008;93:68;76.

13) Frackowiak A, Skibinski P, Gawel W, Zaczynska E, Czarny A, Gancarz R. Synthesis of glycoside derivatives of hydroxyanthraquinone with ability to dissolve and inhibit formation of crystals of calcium oxalate. Potential compounds for kidney stone therapy. *Euro J Med Chem* 2010;45(3):1001-1007.

14) Malecka B, Drozd-Ciesla E, Malecki A. Mechanism and kinetics of the thermal decomposition of zinc oxalate. *Thermochim Acta* 2004;423(1-2);13-18.

15) Mujumdar R, Sarkar P, Ray U, Mukhopadhyay R. Secondary catalytic reactions during the thermal decomposition of oxalates of zinc, nickel and iron (II). *Thermochim Acta* 1999;335(1-2):43-53.

16) Gabal M A, El-Bellihi A A, El-Bahnasawy H H. Non isothermal decomposition of zinc oxalate-iron (II) oxalate mixture. *Mat Chem Phys* 2003;81(1):174-182.

17) Mohamed M A, Galwey A K, Halawy S A. A comparative study of the thermal reactivities of some transition metal oxalates in selected atmospheres. *Thermochim Acta*, 2005;429(1):57-72.

- 18) Vlaev L, Nedelchev N, Gyurova K, Zagorcheva M. A comparative study of non-isothermal kinetics of decomposition of calcium oxalate monohydrate. *J Anal Appl Pyrol* 2008;81(2):253-262.
- 19) Donkova B, Mehandjiev D. Mechanism of decomposition of manganese (II) oxalate dehydrate and manganese (II) oxalate trihydrate. *Thermochim Acta* 2004;421(1-2):141-149.
- 20) Echigo T, Kimata M. Re-investigation of the crystal structure of whewellite ($\text{Ca}(\text{C}_2\text{O}_4)\cdot\text{H}_2\text{O}$) and the dehydration mechanism of caoxite ($\text{CaC}_2\text{O}_4\cdot 3\text{H}_2\text{O}$). *Physic Chem Mat* 2008;35(8):467-475.
- 21) US Patent 3965068, Dickens E D Jr, B. F. Goodrich Co. smoke retardant vinyl chloride and vinylidene chloride polymer compositions. 1976.
- 22) US Patent 4079033A, Oswitch S, Barr T F, Ferro Corp. Iron and zinc salts as smoke suppressants for chlorine-containing resinous organic materials. 1978.
- 23) US Patent 3382209, George D W, American Cyanamid Co. Flame retardant systems. 1968.
- 24) US Patent 5036121A, Coaker A W M, Vyvoda J C, B. F. Goodrich Co. Flame and smoke retardant cable insulation and jacketing compositions. 1988.
- 25) US Patent 4053453, McRowe A W, Kroenke W J. Vinyl halide polymers having improved resistance to burning and smoke formation. 1977.
- 26) US Patent 4216139, McRowe A W, B. F. Goodrich Co. Fireproofing, smokeless, 1980.
- 27) US Patent 4593060, Batdorf V H, H. B. Fuller Co. Smoke retardant polyvinyl halide compositions. 1990.
- 28) Weil E D, Levchik S, Moy P. Flame and smoke retardants in vinyl chloride polymers – commercial usage and current developments. *J Fire Sci* 2006;24:211-236.
- 29) Kovacs K. A., Grof P., Burai L and Reidel M, Revising the Mechanism of the Permanganate/Oxalate Reaction, *J. Phys. Chem. A*, 2004, 108 (50), 11026-11031

- 30) McBride R. S., The Standardisation of Potassium Permanganate Solution by Sodium Oxalate, *J. Am. Chem. Soc.*, 1912, 34 (4), 393-416.
- 31) J. Troitzsch International Plastics Flammability Handbook. Germany, Hanser 2nd Ed., 1990, 346-348.
- 32) Cerruti P, Rychly J, Matisova-Rychla L, Carfagna C. Chemiluminescence from oxidation of polyamide 6,6 II: The effect of metal salts. *Polym Degrad Stab* 2004;84:199-206
- 33) Cerruti P, Carfagna C. Thermal-oxidative degradation of polyamide 6,6 containing metal salts. *Polym Degrad Stab* 2010;95:2405-2412.
- 34) Seefedt H, Duemichen E, Braun U. Flame retardancy of glass fibre reinforced high temperature polyamide by use of aluminium diethylphosphinate: thermal and thermo-oxidative effects. *Polym Int* 2013;62:1608-1616.

Legends to Figures:

Figure 1: TGA mass loss curves for metal oxalates heated in air.

Figure 2: Graphical representation of burning rates of cotton fabric impregnated with metal oxalates and oxalate/flame retardant mixtures. Ox = metal oxalate alone; Ox +AB = metal oxalate plus ammonium bromide; Ox + P = metal oxalate plus diammonium phosphate

Figure 3: TGA responses under flowing air of the 3:1 mass ratio PA66:MOx samples including the PA66 control.

Figure 4: Mass differential analyses of CaOx, ZnOx and SnOx mixtures with PA66 in 1:3 mass ratio.

Figure 5: Rate of heat release curves for PA66/ZnOx formulations with each brominated flame retardant and respective controls.

Figure 6: Images of the cone calorimetry-exposed sample residues.

Figure 7: Mass differential versus temperature plots under air for PA66 mixtures with ZnOx with AlPi, AlPi/MPP, BrPS and BrPBz as analogues of compounded formulations in Tables 6 and 7.

Table 1: Summary of TGA/DTA characterisation of oxalates.

Oxalate	Reaction	Mass Loss (%)	Temp (°C)	Reaction Occurring	Observed Residue (%)	Theoretical Residue (%)
Calcium	3a	15	100-185	$\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O} \rightarrow \text{CaC}_2\text{O}_4 + \text{H}_2\text{O}$	85	87
	3b	19	375-500	$\text{CaC}_2\text{O}_4 \rightarrow \text{CaCO}_3 + \text{CO}$	67	68
	3c	29	595-745	$\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$	38	38
Manganese (II)	4a	18	120-175	$\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{MnC}_2\text{O}_4 + 2\text{H}_2\text{O}$	82	81
	4b	29	275-465	$\text{MnC}_2\text{O}_4 \rightarrow \text{MnO}_2 + 2\text{CO}$	53	48
Iron (II)	5	55	140-290	$\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O} \rightarrow 0.5\text{Fe}_2\text{O}_3 + 0.5\text{CO}_2 + 1.5\text{CO} + 2\text{H}_2\text{O}$	45	44
Copper (II)	6	51	260-310	$\text{CuC}_2\text{O}_4 \rightarrow \text{CuO} + \text{CO} + \text{CO}_2$	49	49
Zinc	7a	18	90-180	$\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{ZnC}_2\text{O}_4 + 2\text{H}_2\text{O}$	82	81
	7b	38	310-410	$\text{ZnC}_2\text{O}_4 \rightarrow \text{ZnO} + \text{CO} + \text{CO}_2$	44	43
Tin (II)	8	32	280-380	$\text{SnC}_2\text{O}_4 \rightarrow \text{SnO} + \text{CO} + \text{CO}_2$	68	66

Table 2: Summary of elemental and wet chemical analysis of oxalates (AA/ICP/XRF). All values are expressed as wt% of total.

Compound	Expected Metal	XRF	AA	ICP	Expected Oxalate	KMnO₄ Titration value
CaOx	27.4 (monohydrate)	28.5	27.4	-	60.2	55.1
MnOx	38.4 (anhydrous)	39.1	38.5	-	49.2	50.0
FeOx	38.8 (anhydrous)	41.9	42.3	-	48.9	49.3*
CuOx	41.9 (anhydrous)	42.2	40.2	-	46.9	49.0
ZnOx	42.6 (anhydrous)	42.9	40.2	40.7	46.5	52.1
SnOx	57.4 (anhydrous)	58.7	-	58.7	42.6	40.1*

Note * These figures are adjusted to account for the oxidation of Fe(II) to Fe(III) and Sn(II) to Sn(IV).

Table 3: Burning rates (mm/s) of each metal oxalate alone and in the presence of either ammonium bromide or diammonium phosphate applied to cotton.

Oxalate	Control	AB	DAP	E_s (AB/oxalate)
Control	2.66	2.50	3.02	
CaOx	2.90	1.59	2.18	0.907
MnOx	2.49	2.22	2.78	0.741
FeOx	2.46	2.08	-	0.801
CuOx	2.73	2.56	-	0.360
ZnOx	2.83	2.15	-	0.774
SnOx	3.04	2.41	-	0.600

Table 4: TGA/DTA data extracted from the TGA responses in Figure 3, derived DTG curves and concurrent DTA responses. DTA peaks in **bold** are endothermic.

Sample	TGA data				DTG peak temperatures, °C					DTA peak temperatures, °C			
	T _{5%}	T _{10%}	T _{50%}	Residue at 580°C, %	1	2	3	4	5	1	2	3	4
Control	387	411	454	1.1	458	546				257	453	468	534
CaOx	265	382	452	19.1	155	443	470	498		160	258	479	496
MnOx	140	369	396	8.0	132	392				132	392	410	441
FeOx	196	258	422	10.6	190	262	430	484		196	271	323	483
CuOx	285	297	422	11.0	295	415	447	502		258	322	414	503
ZnOx	147	351	404	10.7	144	369	425	465	550	150	260	374	545
SnOx	302	333	418	11.1	406	461	552			259	548		

Key: T_{5%}, T_{10%}, T_{50%} are temperatures (°C) at which 5, 10 and 50% mass loss respectively occurs

Table 5: LOI and UL94 results of AIPi and AIPi/MPP in PA66

[FR], wt%	UL94 rating		LOI, vol%	
	AIPi	AIPi/MPP	AIPi	AIPi/MPP
0% (Control)	V-2/Fail	V-2/Fail	22.5	22.5
7.5%	Fail	V-2/Fail	28.2	26.4
10%	V-0	V-0/V-1/Fail	31.5	28.2
12.5%	V-0	V-0	33.3	28.5
15%	V-0	V-0	33.9	28.5

Table 6: Flammability testing and thermal analytical results for ZnOx in combination with AlPi and AlPi/MPP and related control samples.

Sample	Composition, wt%				TGA/DTA (Air)				TGA/DTA (N ₂)				LOI vol%	UL94 Rating	Cone Calorimetry at 50 kW/m ²				
	PA66	ZnOx	AlP	AlP/ MPP	T _{5%}	DTG peak °C	Residue, % 500 °C 580 °C		T _{5%}	DTG peak °C	500 °C	580 °C			t _{ig} , s	t _{PHR} s	t _{fo} s	PHRR kW/m ²	TSR, m ² /m ²
Control	100				386	461	11.2	3.9	402	453	3.8	3.5	22.5	Fail/Fail/V- 2	63	143	169	1276	732
ZnOx	95	5			345	382	16.1	2.6	343	369	11.0	9.9	22.2	Fail	38	142	180	745	746
AlP	92.5		7.5		368	437	14.0	7.8	373	419	2.2	1.9	28.2	Fail	40	115	143	766	1755
AlP/MPP	90			10	338	433	21.5	11.5	344	420	4.8	4.3	28.2	V-0/V- 1/Fail	55	130	181	498	1678
AlP /ZnOx	87.5	5	7.5		322	396	24.1	20.3	332	395	9.4	8.2	-	-	-	-	-	-	-
AlP/MPP/ ZnOx	85	5		10	325	413	23.2	18.5	333	396	11.0	9.4	24.9	Fail	-	-	-	-	-

Notes: T_{5%} is the temperature to 5% mass loss, °C

Table 7: Flammability testing and thermal analytical results for ZnOx in combination with BrPS and BrPBz and related control samples.

Sample	Composition, wt%				TGA/DTA (Air)				TGA/DTA (N ₂)				LOI	UL94	Cone Calorimetry					
	PA66	ZnOx	BrPS	BrPBz	T _{5%}	DTG peak °C	Residue, %		T _{5%}	DTG peak °C	500 °C	580 °C	vol, %	Rating	t _{ig} s	t _{PHR} s	t _{fo} s	PHRR kW/m ²	TSR m ² /m ²	E _s
Control	100				386	461	11.2	3.9	402	453	3.8	3.5	22.8	Fail	63	143	169	1276	732	
ZnOx	95	5			345	382	16.1	2.6	343	369	11.0	9.9	22.2	Fail	38	142	180	745	746	
BrPS	84.8		15.2		397	424	9.6	2.3	399	429	2.3	2.0	23.0	V-2/Fail	56	118	153	874	1686	
BrPBz	85.9			14.1	360	403	11.5	4.7	367	404	5.4	4.8	22.2	Fail/V-2	58	123	160	1056	1394	
BrPS/ZnOx	79.8	5	15.2		349	367	20.5	13.3	351	366	10.6	9.3	26.8	Fail/V-2	39	103	152	570	2531	0.76
BrPBz/ZnOx	80.9	5		14.1	345	374	31.6	27.0	352	373	25.3	22.9	25.6	Fail	39	73	418	398	1344	1.17

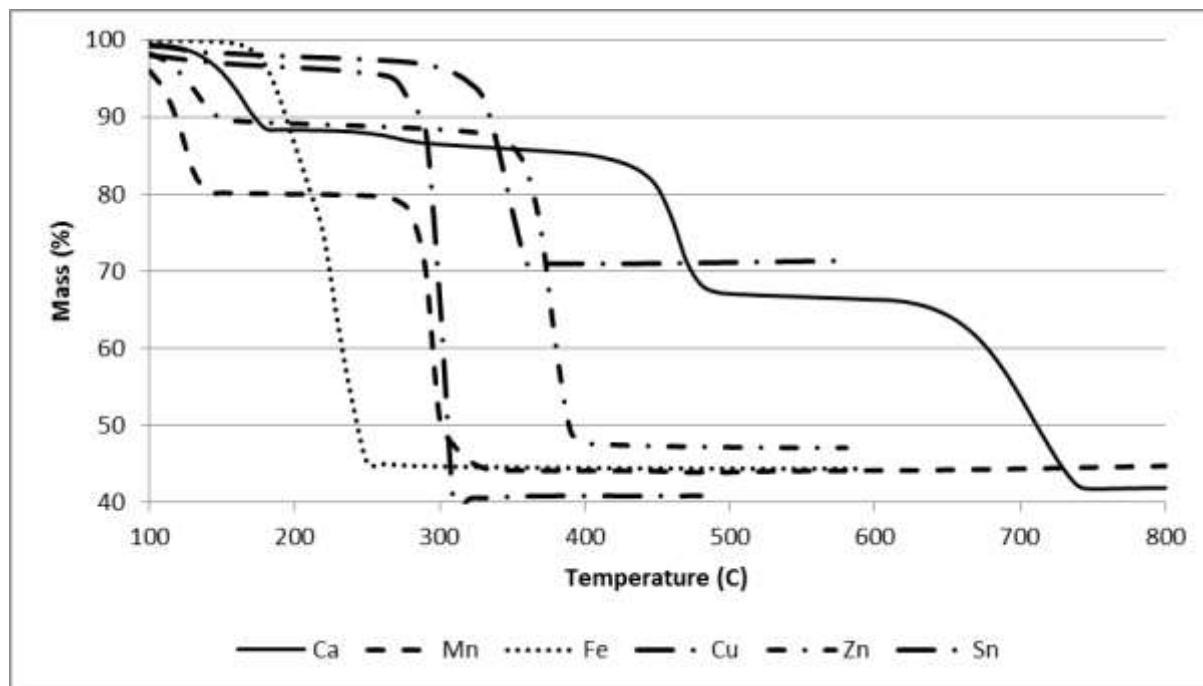


Figure 1: TGA mass loss curves for metal oxalates heated in air.

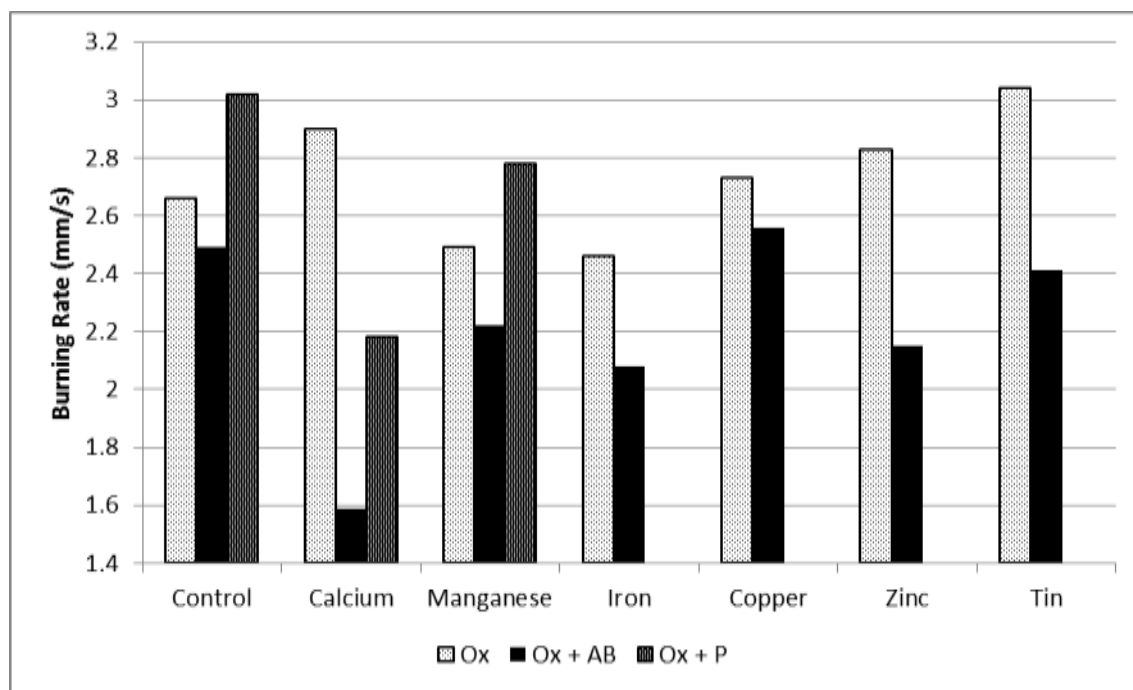


Figure 2: Graphical representation of burning rates of cotton fabric impregnated with metal oxalates and oxalate/flame retardant mixtures. Ox = metal oxalate alone; Ox +AB = metal oxalate plus ammonium bromide; Ox + P = metal oxalate plus diammonium phosphate

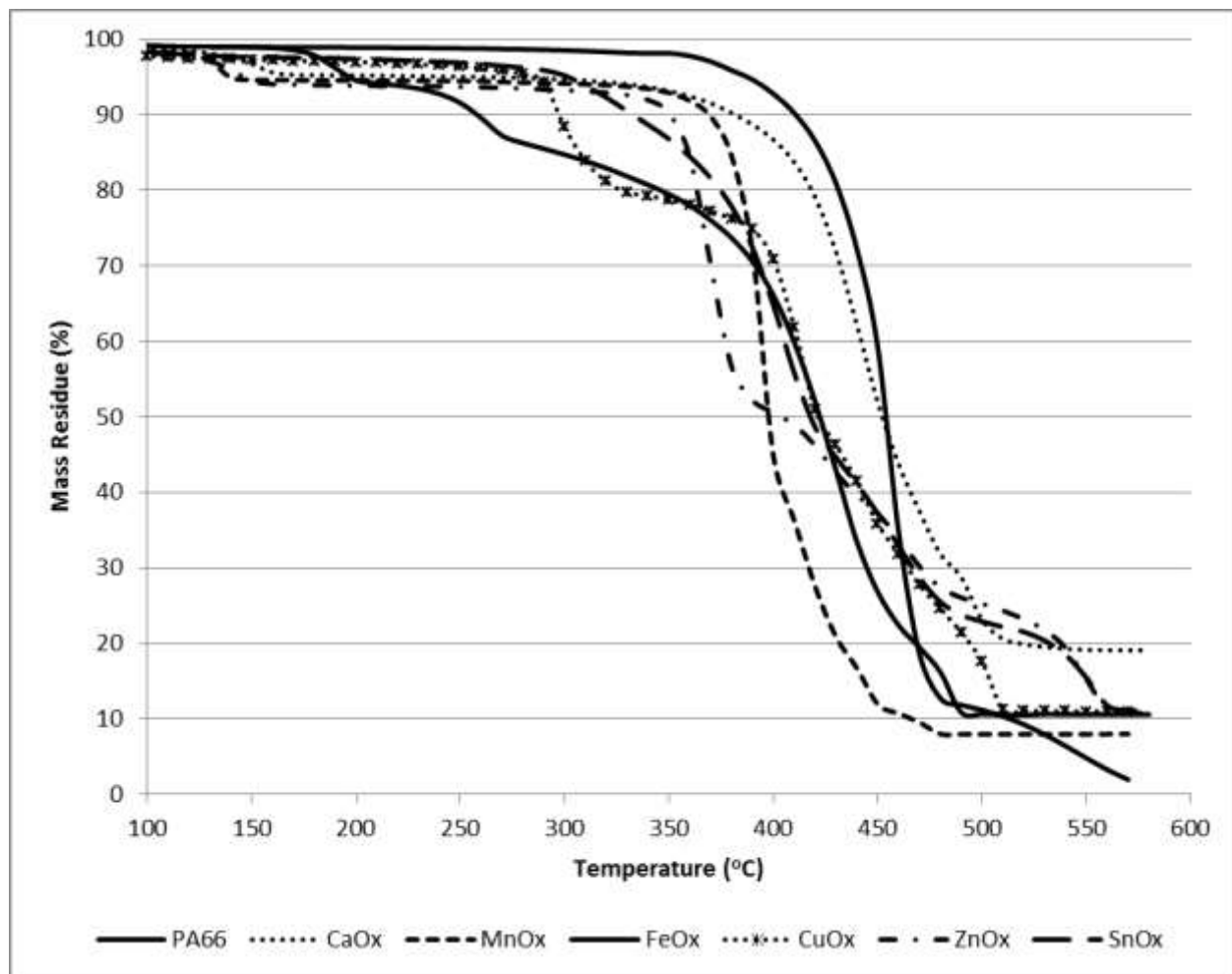


Figure 3: TGA responses under flowing air of the 3:1 mass ratio PA66:MOx samples including the PA66 control.

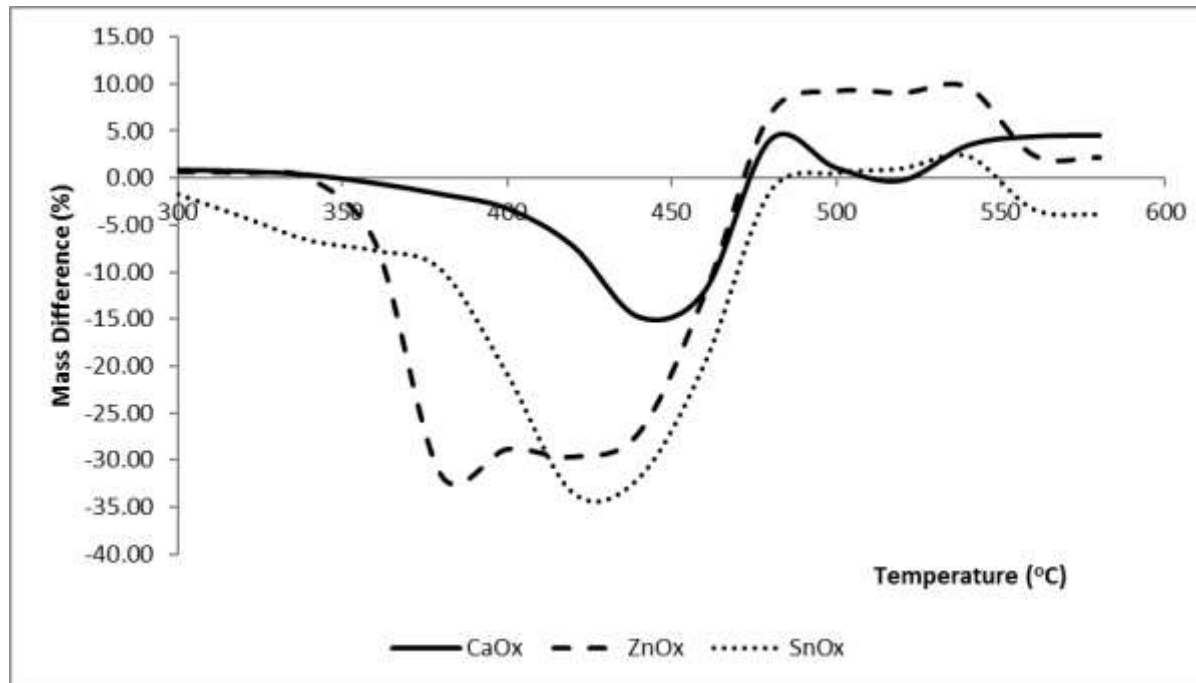


Figure 4: Mass differential analyses of CaOx, ZnOx and SnOx mixtures with PA66 in 1:3 mass ratio.

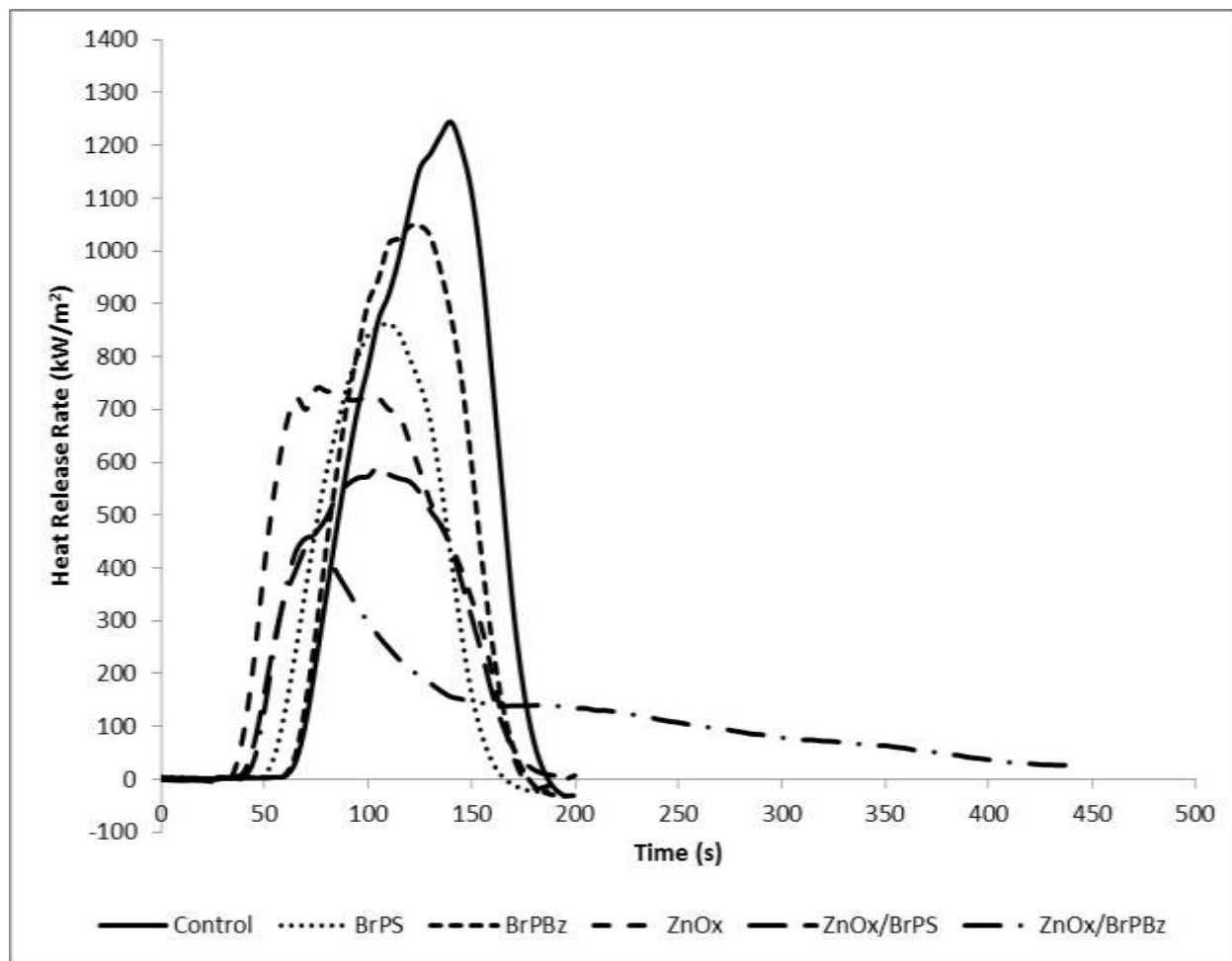


Figure 5: Rate of heat release curves for PA66/ZnOx formulations with each brominated flame retardant and respective controls.



Figure 6: Images of the cone calorimetry-exposed sample residues.

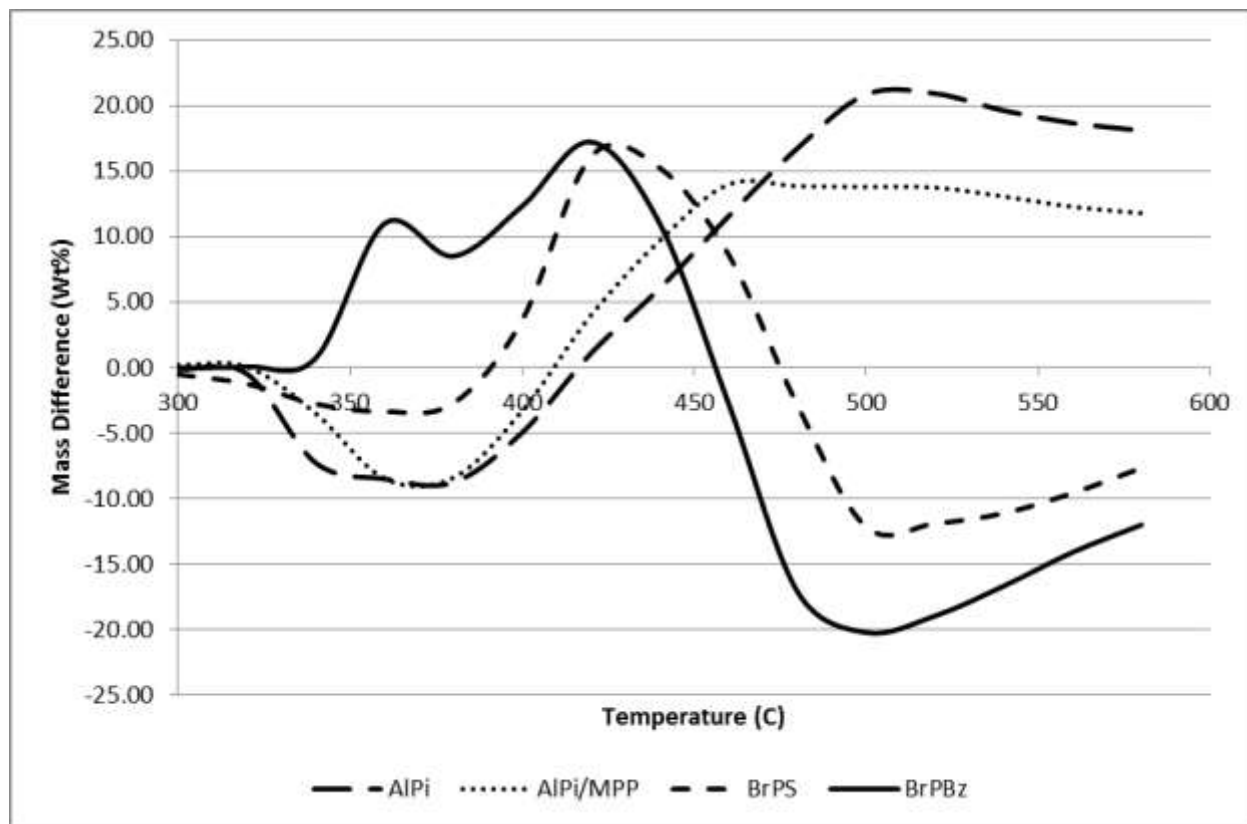


Figure 7: Mass differential versus temperature plots under air for PA66 mixtures with ZnOx with AlPi, AlPi/MPP, BrPS and BrPBz as analogues of compounded formulations in Tables 6 and 7.