



The potential of metal oxalates as novel flame retardants and synergists for engineering polymers



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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 (ZnO_x) offers both possible flame retardant activity in terms of enhanced residue formation ≥ 500 °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/ ZnO_x /flame retardant blends but UL94 test ratings were disappointingly low and more likely than not, “fails”. PA66/ ZnO_x blends with ALPi and ALPi/MPP gave poor plaques suggesting that thermal interactions were occurring during compounding.

The bromine-containing blends had better processability and both TGA and cone calorimetric studies showed that the PA66/poly(pentabromobenzyl acrylate)/ ZnO_x 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.

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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 (e.g. 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 or synergistic activity, they were impregnated on to cotton for simple flammability

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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

2.1.1. 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).

2.1.2. 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.

2.1.3. 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 (aluminium 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 h 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 Omnian analytical suite and AA analysis was undertaken using a Perkin Elmer AAnalyst 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 × 50 mm) followed by drying at 80 °C for 1 h. 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 NH₄Br, AB) and phosphorus (as (NH₄)₂HPO₄, 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 × 170 × 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 × 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) 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. Oxalate samples 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

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