



Synthesis and thermal analytical screening of metal complexes as potential novel fire retardants in polyamide 6.6



Alistair F. Holdsworth^{a, b}, A. Richard Horrocks^{a, *}, Baljinder K. Kandola^a

^a School of Engineering, University of Bolton, Deane Road, Bolton, BL3 5AB, UK

^b Now at School of Physical Sciences and Computing, University of Central Lancashire, Preston, UK

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ABSTRACT

The development of new flame retardants is of ever increasing importance because of ecotoxicity concerns over existing systems and related regulatory pressures. From a range of low-toxicity, water-insoluble reagents, a total of 151 metal complexes were assessed for their potential to impart flame retardant behaviour in polymer matrices. These were successfully synthesised on a small scale and possible interactions were explored with a model engineering polymer, namely polyamide 6.6 (PA66). Powder mixtures of each complex with PA66 in a 1:3 mass ratio were analysed under air using TGA/DTA. Based on the stability of each at the typical processing temperature of 290 °C and its char forming potential (the final residue requirement at 580 °C being > 25%), selected mixtures were then analysed further using a differential mass loss technique. Metal complex/PA66 mixtures in which the differential residual mass above 470 °C was >10% with respect to the theoretical value were considered to have a positive char forming interaction. Only eight of the metal complexes passed this last criterion including aluminium, tin (II) and zinc tungstates, three tin (II) phosphorus oxyanion complexes, iron (II) aluminate and iron (III) hypophosphite. These selected compounds were synthesised on a larger scale (c.a. 100 g), characterised and compounded into PA66 at 5 wt% for flammability assessment using LOI, UL94 and cone calorimetry. Of these, only aluminium tungstate and iron (II) aluminate showed some degree of FR behaviour with LOI values ≥ 23.0 vol% compared with PA66 (LOI = 22.9 vol%) and the former almost achieved a UL94 V-2 rating. However, while up to 32% reductions in total heat releases and up to 49% reduction in PHRR in cone calorimetric tests were observed for the metal complex/PA66 composites generally, those for $\text{Al}_2(\text{WO}_4)_3$ were 6 and 29% respectively and for $\text{Fe}(\text{AlO}_2)_2$ were 18 and 45% respectively.

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1. Introduction

The fire hazard posed by many polymeric materials often necessitates the incorporation of flame retardant compounds in order to meet stringent regulatory factors which increase safety with respect to ignition resistance or burning intensity [1,2]. Recently, the replacement of potentially toxic flame retardant compounds and synergists such as certain monomeric polybrominated flame retardant/antimony trioxide (ATO) formulations is of increasing importance and a significant amount of research continues to be devoted to this end [3–6].

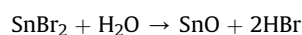
Many metal oxides possess a degree of flame retardant activity

either on their own or in combination with other, primary flame retardants (FRs), the mechanism of action being dependent on the nature of metal centre present, the host polymer, and the interactions with any primary FRs present [1,7,8]. Metal hydroxides such as $\text{Al}(\text{OH})_3$ and $\text{Mg}(\text{OH})_2$ are known to have such a retardant effect through endothermic decomposition, releasing water into the vapour phase which subsequently dilutes the fire gases, and through the physical replacement of flammable material, although they are often required in high loadings (c.a. 50 wt%) [1,2,9,10]. Many metal oxides such as ZnO, Fe_2O_3 and SnO can provide an inherent degree of flame retardancy in some polymers [7,9,11], while others, such as antimony trioxide, Sb_2O_3 (ATO), zinc hydroxystannate, (ZHS) and zinc stannate (ZnSnO_3 , or $\text{ZnSn}(\text{OH})_6$ (ZS)) can act in concert with phosphorus or halogen flame retardants [8,9,12–19], and, in the case of the last example, can additionally display smoke suppression activity [14,15].

* Corresponding author.

E-mail address: a.r.horrocks@bolton.ac.uk (A.R. Horrocks).

Many inorganic synergists, however, display little or no interaction with their host polymer due to their chemical inertness, lack of viable reaction pathway with their host polymer or specific reaction mechanism with any primary flame retardant present [16,20]. Neither ATO nor ZnS alone has any significant effect on the thermal degradation or flame retardant behaviour of most polymers, but in combination with an appropriate primary halogen-containing FR, a significant increase in performance is observed relative to a halogen-only control [9,14,21]. Both these synergists are understood to react with the hydrohalic acids (either HCl or HBr) produced by halogenated flame retardants during their thermal degradation to form volatile metal halides which serve to mediate the release of halogen radicals in the vapour phase [9,14,21]. For ATO, this process is understood to take place via the gradual volatilisation of SbX_3 (where X is Cl or Br) from a range of antimony oxyhalides, whereas for ZnS, the process is less well understood, as either Zn or Sn could potentially be released to the vapour phase in the form of Zn (II), Sn (IV) or Sn (II) chlorides or bromides. With regard to zinc hydroxystannate in particular, Kicko-Walczak [22] has proposed that SnO, formed from the degradation of ZnS or interaction with BrFRs, has a role in the flame retarding activity via the reaction:



It has been suggested by Cusack and coworkers [23] that SnO demonstrates vapour phase activity via hydrogen radical scavenging reactions such as:



In contrast, we have recently demonstrated the potential of ZnO (formed from the thermal decomposition of ZnC_2O_4) to act as a condensed-phase char promoter in PA66 and as a promising synergist with bromine-containing retardants (BrFRs) [7].

In combination with phosphorus-containing flame retardants (PFRs), metal oxides generally act in the condensed-phase to form more coherent (glassy) barriers through their interaction with released H_3PO_4 to form metal phosphates, although this is by no means exclusive [24]. Synergists known to act with polymeric flame retardants include zinc borate and nitrogen-containing moieties, with the former forming phosphates and the latter reacting with these phosphates to form so-called P-O-N glasses [9].

In this work and based on our previous study [7], we demonstrate the methodology behind the selection, synthesis, screening and testing of more than 240 inorganic complexes for assessment as potential flame retardants and/or synergists for engineering polymers, exemplified by polyamide 6.6 (PA66). PA66 was selected for this study because of its use in electrical components requiring the combination of mechanical and flame retardant properties and is of interest to our sponsor. The overall screening process developed may be summarised in Scheme 1 below:

In this scheme metal complex candidates are synthesised at a small scale to allow their screening for possible char-forming behaviour in mixtures with PA66 by TGA/DTA and differential TG mass analysis. The best forming candidates are synthesised at a larger scale, characterised and compounded in PA66, which samples are then subjected to flammability testing and then final

selection.

Complexes were selected for their potential low toxicity and water insolubility, based on their general chemical properties. A 1:3 mass ratio of complex to PA66 was used for screening purposes as this represents the highest level of FR that would be incorporated into an engineering polymer, and the normally low-levels of flame retardant activity imparted by oxides would be amplified by the higher loadings. The potential of the produced complexes for introducing a degree of inherent condensed-phase FR activity into PA66 (in the form of char promotion) is also reported.

2. Experimental

2.1. Materials

The selection of metal cations and complex metal-containing anions was based on the observation that oxy-compounds (often as mixed metal oxides) can act in a number of possible ways when heated in polymer matrices [7,8]. Such reactions may include condensed-phase Lewis-acidic characteristics acting to cross-link oxygen- or nitrogen-containing polymers and/or as synergists with other primary phosphorus and/or bromine flame retardants [2,9]. Some nitrogen-containing complex anions were also selected because it was postulated that they might release NO_x radicals that might act in a similar manner to the PO^\bullet radical in the vapour phase as a radical quenching agent [9,20]. In a similar manner, P-containing compounds were chosen for the potential ability to release radical-quenching PO^\bullet radicals during polymer degradation as well as acting as Lewis acids to cross-link degrading polymers [9,20,25].

As a consequence, the following compounds as metal salts were acquired as cation sources: $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, FeCl_3 , $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, ZnCl_2 , SnCl_2 , and $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$. The following anionic species were obtained as sodium, potassium or ammonium salts, or as free acids which were deprotonated to the required level later stoichiometrically with sodium carbonate: $\text{B}(\text{OH})_4^-$, CO_3^{2-} , $\text{C}_2\text{O}_4^{2-}$, NO_2^- , HO^- , $\text{Al}(\text{OH})_4^-$, $\text{Si}(\text{OH})_4^{2-}$, H_2PO_4^- , H_2PO_3^- , HPO_3^- , PO_4^{3-} , $\text{P}_2\text{O}_7^{4-}$, $\text{P}_3\text{O}_{10}^{5-}$, PhPO_3^{2-} , MoO_4^{2-} , SnO_3^{2-} , WO_4^{2-} , dimethylglyoxime (dmg), salicylaldehyde (sal) and 2-nitrophenol.

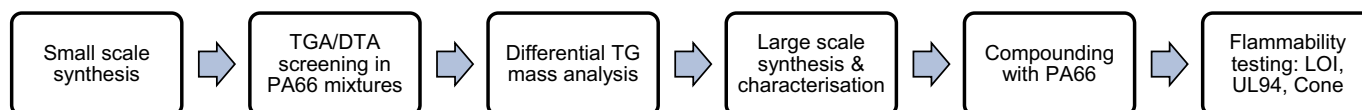
Based on the above simple and complex salts, Table 1 shows the cations and anions with the latter sub-divided into a number of groups based upon functionality (and likely mechanisms of action), namely oxides/oxyanions and N-containing and P-containing anions. These sub-groupings are used throughout the rest of this publication. All reagents were of reagent grade ($\geq 98\%$) and procured from a range of suppliers including Sigma Aldrich, VWR International and Fisher.

100% polyamide 6.6 (PA66) was acquired from Invista Engineering polymers and used as procured (compounding grade, 100% PA66, MPt 260 °C, MFI 19.56 g/min @ 280 °C).

2.2. Synthesis of metal complexes

2.2.1. Small-scale syntheses

In order to undertake a potentially large (>200) number of syntheses based on cations and anions in Table 1, a series of experimental matrices was prepared, whereby each cation would be reacted with each anion to determine whether the desired



Scheme 1. A representation of the overall screening process.

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