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The sensitisation of thermal decomposition of ammonium polyphosphate by selected metal ions and their potential for improved cotton fabric flame retardancy

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Abstract

A thermal analytical study of a series of metal ion–ammonium polyphosphate (APP) combinations has been undertaken to examine possible interactions that might enhance subsequent flame retardant activity. It is shown that certain metal ions, particularly Mn^{2+} and Zn^{2+}, promote thermal degradation of APP at lower temperatures than in their absence, and that this enables flame retardant activity to commence at lower temperatures in the polymer matrix thereby enhancing flame retardant efficiency. This has significance where flame retardant formulations are required to become active at temperatures well below normal substrate ignition temperatures and especially in the case of back-coated, flame retardant treatments for textiles. Initial experiments show that metal ion-doped APP in the presence of cellulose not only indicates a further sensitisation of cellulose decomposition but also improved flame retardance determined by limiting oxygen index when applied as a back-coating to cotton fabric demonstrates.

Keywords: Ammonium polyphosphate; Metal salts; Manganese; Zinc; Cellulose; Flame retardant; Textiles; Limiting oxygen index

1. Introduction

Certain polymeric applications require that flame retardants should start to function at temperatures low enough for ignition of surrounding polymer matrices to be prevented and yet are high enough to withstand processing temperatures. Applications of relevance to fibres and textiles include back-coating formulations involving phosphorus-based systems where diffusion of active retardant species from the reverse of the fabric to the front face must occur efficiently before front face fibres can ignite [1,2]. Normally, however, most phosphorus-based flame retardants decompose at temperatures well above 300 °C when ignition temperatures of cotton, for example, are close to 350 °C [2]. Any means of reducing flame retardant decomposition temperatures has relevance to improving efficiency in such applications.

Work has been published recently that has demonstrated that the presence of manganese dioxide with ammonium polyphosphate appeared to improve the performance of the flame retardant within polyamide 6 [3]. Following on from this, a more analytical investigation demonstrated that the presence of the manganese dioxide, at loadings of 25% and 12.5% with respect to ammonium polyphosphate, was having an effect on the thermal behaviour of the ammonium polyphosphate. It was evident an interaction between the manganese dioxide and the ammonium polyphosphate was occurring [4]. However, it was interesting to

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note that the decomposition mechanism of the mixture did depend on the percentage loading of the manganese dioxide.

More recently, Lewin and Endo have published work [5,6], which has investigated the addition of small percentages of heavy metal salts to ammonium polyphosphate in combination with pentaerythritol (PER) in polypropylene. They observed that metal salt addition appears to increase the flame retardant performance of the ammonium polyphosphate as part of a flame retardant system with PER in a polypropylene matrix. The loading required was quite specific and an optimum point was observed at loadings of metal ion/salt of 1.5% w/w or less. Loadings above the optimum resulted in a drop off in the performance in the flame retardant as determined by LOI.

It is therefore proposed that this potential enhancement of activity of ammonium polyphosphate may also be exploited within back-coating formulations. Within such systems the potential is generated for the application of an ammonium polyphosphate with a high degree of polymerisation, which also fulfils the durability requirements via a sensitised flame retardant activity.

Lewin and Endo [5,6] have discussed mechanisms of APP–PER-M^{n+} combinations in terms of M^{n+}-accelerated phosphorylation of PER and —OH groups formed on PP molecules following M^{n+} oxidation in parallel with cross-linking. It was suggested that the improved performance may be due to partial cross-linking (effectively increasing the degree of polymerisation) and increased stability of the ammonium polyphosphate, thus reducing the volatility of the phosphorus oxides formed during pyrolysis and making more phosphorus available for phosphorylation and char formation. In the presence of a polypropylene matrix, this cross-linking will also increase the viscosity of the melt thereby diminishing the rate of flow to the flaming surface and improve the barrier effect of the char. However, at higher M^{n+} levels, excessive APP cross-linking may occur with accompanying lower levels of PER phosphorylation and hence reduced char. This hypothesis explains why an optimum level of M^{n+} exists for maximum flame retardant effect.

To date no studies have been undertaken to examine whether the presence of small concentrations of heavy metal ions will destabilise APP and hence reduce its thermal decomposition and liquefaction temperature thereby increasing its general reactivity.

This paper extends our previously reported study [7] of the effect on the thermal behaviour of ammonium polyphosphate of introducing a series of metal salts as a possible means of sensitising flame retardant activity and in improving understanding of the previously reported work of Lewin and Endo [5,6].

2. Experimental

2.1. Ammonium polyphosphate–metal salt combinations

Ammonium polyphosphate (APP) (Antiblaze MCM, supplied by Rhodia Consumer Specialities) having an approximate degree of polymerisation (DP) of 100 was mixed with a series of metal salts. Table 1 lists the heavy metal salts chosen for this study based on the previously reported observations of Lewin and Endo [5,6].

Two sets of experiments were carried out, the first in which a range of simple metal salt-APP mixtures was examined and the second set in which APP crystalline particles were doped with those selected metal salts that appeared to produce greatest effect on thermal decomposition behaviour of APP from the former study. It was considered that surface doping of APP with metal ions would maximise any sensitising effect and so a means of surface-treating ammonium polyphosphate particles was established by ensuring that their dissolution in any metal solution was minimised.

For the preliminary mixture study, a series of dry mixtures was made of ammonium polyphosphate (Antiblaze MCM) with each metal salt at 2% w/w concentration. Ferric sulphate–APP mixtures were also prepared with salt concentrations varying from 1 to 5% w/w.

For the preparation of surface-doped APP, it was considered that its low solubility would enable the soluble metal salts to be added as small quantities of solutions sufficient to wet APP crystallite surfaces. Addition of such small volumes would create a paste, which on drying, would have metal salt ions present only on crystallite surfaces. It was found experimentally that, for the purposes of mixing, a paste could be made from 5 g of APP with 2 g of each salt solution. Based on

Table 1
Metal salts used for mixing with or doping ammonium polyphosphate

Metal salt	Chemical formula
Aluminium sulphate	$Al_2(SO_4)_3{\cdot}xH_2O$ ($x=14$–18)
Copper(II) sulphate	$CuSO_4{\cdot}5H_2O$
Iron(III) (ferric) chloride	$FeCl_3{\cdot}6H_2O$
Iron(III) (ferric) nitrate	$Fe(NO_3)_3{\cdot}9H_2O$
Iron(II) (ferrous) sulphate	$FeSO_4{\cdot}7H_2O$
Magnesium acetate	$Mg(CH_3COO)_2{\cdot}4H_2O$
Magnesium chloride	$MgCl_2{\cdot}6H_2O$
Magnesium sulphate	$MgSO_4{\cdot}7H_2O$
Manganese(II) acetate	$Mn(CH_3COO)_2{\cdot}4H_2O$
Manganese(II) sulphate	$MnSO_4{\cdot}H_2O$
Sodium acetate	$Na\ (CH_3COO)$
Sodium sulphate	$Na_2SO_4{\cdot}10H_2O$
Sodium tungstate	$Na_2WO_4{\cdot}2H_2O$
Zinc acetate	$Zn(CH_3COO)_2{\cdot}2H_2O$
Zinc chloride	$ZnCl_2$
Zinc sulphate	$ZnSO_4{\cdot}7H_2O$