TG AND FLAMMABILITY STUDIES ON POLYMER BLENDS CONTAINING ACRYLONITRILE–BUTADIENE–STYRENE AND CHLORINATED POLY(VINYL CHLORIDE)

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Abstract

The effects which an iron(III) based smoke suppressing compound have on the thermal stability of some acrylonitrile–butadiene–styrene/chlorinated poly(vinyl chloride) (*ABS/CPVC*) polymer blends have been investigated. Thermogravimetric analysis (TG) experiments have shown that there are three distinctive stages occurring during the thermal breakdown of these blends both when the iron compound is absent and present in the polymer formulations. The most important effect which the iron compound has when it is present in these blends is to modify the decomposition chemistry which takes place and the effect becomes more pronounced as the concentration of *CPVC* present in the blends increases. Other important effects are that the iron compound stabilises the blends so that mass loss is significantly reduced (by up to 50% in some cases) and the onset temperature of decomposition is raised. Flammability data generated during earlier work is supported by the TG results obtained in this work especially in the important area of smoke formation and suppression.

Keywords: changes in decomposition chemistry, flammability data, iron(III) smoke suppressant, polymer blend (*ABS/CPVC*), TG results

Introduction

The flammability of polymers and the smoke produced when they burn still present a major hazard in the developed world. Every year, fires in the UK kill about 800 people and cause non-fatal injuries to 15 000. Annually, on average, the direct material loss is £1200 million and the indirect loss is £120 million. The direct and indirect losses in the UK represent about 0.21 per cent of the Gross Domestic Product [1]. About half of the reported deaths in fires are the result of asphyxiation caused mainly by carbon monoxide and smoke/soot produced during combustion of the multiplicity of polymeric materials found in most buildings. In recent years the additional fire and smoke hazards from communication cables routed through underfloor and/or over-

head spaces coupled with the rapidly rising demands for IT systems have added to the problem. The hazards are often exacerbated by the fact that it is usual practice to add new cables without removing the old and also that the hidden voids may also be part of the heating and ventilation/air-conditioning system with potential to spread fire and smoke to all parts of buildings [2]. Troitzsch has also recently voiced concern about the fire safety of TV sets and PC monitors in Europe [3]. The recent train crash and subsequent fire at Paddington, West London has once again brought the whole issue of fire safety/fire casualties to the attention of the public in the UK.

As part of a research programme to evaluate the flammability properties of some new mixed polymer systems, we have examined a wide range of blends containing acrylonitrile–butadiene–styrene (*ABS*) and chlorinated poly(vinyl chloride) (*CPVC*-65% Cl) containing smoke suppressing and flame retarding additives. The most effective smoke suppressant among the range of compounds studied was found to be an iron(III) compound (basic iron(III) oxide–FeOOH) which in some blends of the two polymers, as well as reducing smoke production by up to 50% in some systems, had the additional benefit of significantly improving the flame retardant performance of some the blends. Table 1 shows some of the flammability data which we obtained and examination of the data shows that the most significant improvements in these flammability properties occurred at quite different blend compositions. It was therefore decided to carry out a TG study concentrating specifically on those blends which have particularly significant char forming, flame retarding or smoke suppressing properties in order to clarify why some particular compositions of *ABS*/*CPVC*, containing a fixed quantity of the iron compound, were so very active. Thus we examined six blends; 99*ABS*/1*CPVC*, 80*ABS*/20*CPVC* and 70*ABS*/30*CPVC* with and without 5 phr (parts per hundred of polymer) of FeOOH present in the formulations.

Table 1 Flammability properties of *ABS*/*CPVC*/FeOOH blends. Maximum values are in italics

Formulation	Fe:Cl ratio	Increase in char/%[*]	δ LOI[**]	δ smoke $(D_{MAX} g^{-1})$/%[***]
99.5*ABS*/0.5*CPVC*/5FeOOH	6.5:1	502	+3.3	0
99*ABS*/1*CPVC*/5FeOOH	3.3:1	*600*	+3.5	0
98*ABS*/2*CPVC*/5FeOOH	1.6:1	529	+3.8	0
96*ABS*/4*CPVC*/5FeOOH	1:1.2	474	+5.2	0
91.5*ABS*/8.5*CPVC*/5FeOOH	1:2.6	404	+6.6	–5
88*ABS*/12*CPVC*/5FeOOH	1:3.7	220	+8.2	–12
80*ABS*/20*CPVC*/5FeOOH	1:6.1	167	*+9.3*	–21
75*ABS*/25*CPVC*/5FeOOH	1:7.7	129	+6.3	–48
70*ABS*/30*CPVC*/5FeOOH	1:9.2	31	+2.9	*–51*
60*ABS*/40*CPVC*/5FeOOH	1:12.9	16	0	–18

[*]Percentage increase in char yield for iron-free to iron-containing blends
[**]Change in LOI for iron-free to iron-containing blends
[***]Percentage decrease in smoke density for iron-free to iron-containing blend

It is the major purpose of this paper to present the TG results which we have obtained, discuss the implications of the results with respect to the thermal decomposition of *ABS*/*CPVC* blends in the absence and presence of an iron-based smoke suppressant and to attempt to relate the results to the previously determined flammability properties of this polymer system.

Experimental

Preparation of the polymer blends used and the evaluation of their flammability properties (including details of the flammability tests used and the implications of the results obtained) have been recently described and published in some detail elsewhere [4]. The TG experiments were carried out using a Stanton Redcroft TG-760 thermobalance with approximately 2–3 milligram samples (platinum crucible) in flowing air (10 cm^3 min^{-1}) at a heating rate of 20°C min^{-1} from ambient temperature to 850°C. The use of thermal analysis (TG/DTA/DSC) in conjunction with flammability experiments as a way of helping to clarify polymer degradation mechanisms and fire chemistry was proposed many years ago [5].

Results

The TG data obtained for the six polymer blends are comprehensively summarised in Table 2. Both sets of polymer formulations showed three distinctive, well-characterised decomposition stages. The incorporation of the iron compound into these *ABS*/*CPVC* formulations resulted in significant changes occurring during the thermal decomposition of the blends. The most important changes which occurred were during the first decomposition stage especially as the concentration of *CPVC* in the blends increased. The iron compound appeared to have minimal effects on the second stage of decomposition but it did affect the pattern of decomposition during the third/final stage.

Iron-free blends

The TG traces for these three blends showed three decomposition stages occurring over the temperature ranges 200–450, 450–580 and 580–700°C. Increasing mass losses of 10% for the 99*ABS*/1*CPVC* blend, 20% for the 80*ABS*/20*CPVC* blend and 24% for the 70*ABS*/30*CPVC* blend were recorded during the first decomposition stage. From these results it is obvious that as the *CPVC* content of the blend increased the mass loss also increased. *CPVC* is known to be less thermally stable than *ABS* [6] so in blends, as the *CPVC* content increased, there was a corresponding increase in mass loss. In the second stage of decomposition the 99*ABS*/1*CPVC* blend lost significantly more mass (about two times as much) than the other two iron-free formulations indicating that this stage is probably a result of the decomposition of the *ABS* present. The third and final stage of decomposition, possibly resulting from high-temperature char oxidation or char cracking reactions taking place, showed a mass

Table 2 TG data for ABS/CPVC blends

Mass loss and temperature range	Blend					
	99*ABS*/1*CPVC*	80*ABS*/20*CPVC*	70*ABS*/30*CPVC*	99*ABS*/1*CPVC*/ 5FeOOH	80*ABS*/20*CPVC*/ 5FeOOH	70*ABS*/30*CPVC*/ 5FeOOH
1st mass loss/%	10	20	24	4	8	12
Temp. range/°C	200–460	200–400	240–400	250–420	290–340	300–330
2nd mass loss/%	75	45	48	74	47	39
Temp. range/°C	460–590	440–560	450–570	460–560	440–570	450–600
3rd mass loss/%	8	31	26	15	38	39
Temp. range/°C	600–650	590–650	610–650	600–680	600–720	620–710

The iron-containing blends had a 5% residue (Fe_2O_3)

loss of 8% for the 99*ABS*/1*CPVC* blend, a 31% loss for the 80*ABS*/20*CPVC* system and a 26% mass loss for the 70*ABS*/30*CPVC* blend.

Iron-containing blends

These blends also showed three distinctive decomposition stages occurring and, as happened in the iron-free blends, during the first stage of decomposition the mass loss gradually increased as the *CPVC* content of the blend increased. Thus in the 70*ABS*/30*CPVC*/5FeOOH blend 12% of the mass was lost over a 30°C temperature range (300–330°C), in the 80*ABS*/20*CPVC*/5FeOOH blend the mass loss was 8% in the range 290–340°C and in the 99*ABS*/1*CPVC*/5FeOOH blend only 4% of the mass was lost and it occurred over a much wider range of temperature (250–420°C). However the iron-containing blends lost significantly less mass overall (24%) during the first decomposition stage (i.e. up to a temperature of about 350°C) compared with the mass loss which occurred during the same decomposition stage in the iron-free blends (54%). These results clearly indicate that FeOOH strongly interacts with the blend (almost certainly with the *CPVC* component) and modifies the path of decomposition especially during the early stages. Thus the presence of the iron-based smoke suppressant has the twin effects of stabilising the blend quite significantly (mass loss is reduced to almost 50% less than in the iron-free blends) and the temperature of the onset of the first decomposition stage is raised by as much as 60°C. Less mass lost from the blend during decomposition must therefore result in a greater proportion of the polymer being retained in the solid state (probably as char) and consequently the amount of smoke and volatiles produced when thermal decomposition occurs is reduced. These results the support of the flammability data shown in Table 1 which clearly shows that this iron compound increases char yield, suppresses the formation of smoke and in some cases reduces flammability.

The second decomposition stage occurred between 450–590°C and the mass loss data was similar for both the iron-free and the iron-containing blends. As mentioned above, this second stage is probably a result of the slow decomposition of the *ABS* in the blends and it follows the decomposition of *CPVC* during the first stage. The fact that the mass loss data and temperature ranges over which the decomposition occurred were almost the same for the iron-free and the iron-containing blends suggests that during this stage of the thermal decomposition of *ABS*/*CPVC* blends the iron additive was having minimal effects on the decomposition pathway. However one blend, 70*ABS*/30*CPVC*/5FeOOH, did have a 39% mass loss in contrast with a 48% mass loss in the iron-free 70*ABS*/30*CPVC* blend. It can therefore tentatively be assumed that the major smoke-precursor species are produced from decomposing *ABS* during this second stage of decomposition of the blends. This hypothesis is further substantiated by the fact that the mass loss decreased when going from the 99*ABS*/1*CPVC* blends to the 70*ABS*/30*CPVC* blends both in the iron-free and in the iron-containing blends. It is not surprising therefore that the smoke density values similarly fell with decreasing amounts of *ABS* being present in the blends.

The final stage of decomposition of these blends occurred between 600–650°C for the iron-free blends and over a slightly wider temperature range (600–710°C) for the iron-containing systems. There was a quite marked increase in the mass lost from the iron-containing blends when the results are compared with those obtained for the iron-free blends during this final decomposition stage. For the 99*ABS*/1*CPVC*/5FeOOH blend, there was a 7% increase in mass loss, in the 80*ABS*/20*CPVC*/5FeOOH blend an 8% increase and in the 70*ABS*/30*CPVC*/5FeOOH blend a 13% increase in mass loss. The implications of this will be discussed in the next section.

Discussion

When polymers ignite and burn the smoke and fire gases produced (mainly carbon monoxide) are the major cause of death in fires. It is still not really clear how smoke is formed during burning but a reduction in the amount of smoke produced in fires will unquestionably save lives. Chemical additives are known to suppress the formation of smoke and soot but the detailed chemistry of how they do this is not fully understood.

Earlier flammability work carried out on these polymer blends was the major reason why this study was initiated and the results which we have obtained so far are generally very supportive of the flammability data. It is not the purpose of this paper to explain in detail all the flammability properties of these blends. However, these TG results have helped to clarify how the thermal decomposition of the polymers involved takes place and it is now possible to speculate on the nature and scale of the chemical reactions which are taking place during the decomposition and subsequent combustion of *ABS*/*CPVC* blends.

In these polymer blends the three decomposition stages which we have identified can be related directly to what happens when these polymers burn in air. The first decomposition stage for both the iron-free and the iron-containing blends is most likely the result of dehydrochlorination of *CPVC* polymer with the subsequent formation of char. This loss of HCl and formation of char is the most important reaction which occurs in the overall decomposition of *CPVC*. We have unequivocally shown in our flammability work that FeOOH interacts strongly with thermally decomposing chlorinated polymers to produce large amounts of carbonaceous char and as a consequence smoke formation during burning is reduced [7, 8]. The mass loss data and temperatures at which the mass loss occurs in these blends during the first and second decomposition stages have essentially confirmed our smoke density findings. The greater the amount of *CPVC* present in the blend, and more especially when the iron compound is also present, the greater is the reduction in the amount of smoke which is formed. Hence the 70*ABS*/30*CPVC*/5FeOOH blend has the lowest smoke value of all the blends investigated and this equates with it having the lowest mass loss during the first and second thermal decomposition stages. Conversely the 99*ABS*/1*CPVC* and the 99*ABS*/1*CPVC*/5FeOOH blends have the highest smoke values and not surprisingly they have the highest mass loss in the first two decomposition stages. Thus

the evidence obtained from these TG experiments very strongly supports the flammability data especially in this important area of smoke formation and suppression.

Two other important flammability results were identified during the flammability testing programme. The most significant improvement in limiting oxygen index (LOI) values were associated with the 80*ABS*/20*CPVC*-80*ABS*/20*CPVC*/5FeOOH blends while the greatest increase in char yield with the 99*ABS*/1*CPVC*-99*ABS*/1*CPVC*/5FeOOH pair of blends. These parameters were calculated by comparing data obtained from the iron-free and the iron-containing blends (Table 1). We cannot draw any definite conclusions or comment in detail on these two important sets of data on the basis of the results obtained in this work. However the formation of large amounts of char catalysed we believe, by the presence of the smoke suppressant FeOOH in these blends, cannot in itself explain the very significant improvements in the flammability behaviour which we found in the 80*ABS*/20*CPVC*-80*ABS*/20*CPVC*/5FeOOH systems (an increase of 9.3 LOI units). Increased amounts of char being retained in the residue will reduce the fuel load (less material is available for burning) and the quite dramatic improvement in LOI values for the 99*ABS*/1*CPVC*- 99*ABS*/1*CPVC*/5FeOOH blends (an increase of 3.5 LOI units) is evidence for this. However the 70*ABS*/30*CPVC*-70*ABS*/30*CPVC*/5FeOOH blends contained more *CPVC* and yet the improvements in LOI values were not as significant as they were in the 80*ABS*/20*CPVC*-80*ABS*/ 20*CPVC*/5FeOOH blends. We are still at a loss to explain these LOI data.

A comment on the significance of the final decomposition stage is relevant to the overall flammability performance of smoke suppressants such as FeOOH which are thought to function via Lewis acid intermediates. Starnes has frequently stated that Lewis-acid based smoke suppressants are problematical when high-enthalpy conditions prevail such as those encountered in real fires [9]. The problem of char-cracking reactions producing significant quantities of low molecular mass products which increases the fuel load has been used to explain the failure of some Mo-based smoke suppressants in large-scale experiments. Price has also detected similar low-molecular mass products in his work [10]. It may be the case in this work that char-cracking reactions were the source of the mass losses occurring in the final decomposition stages for both the iron-containing and the iron-free blends and we did record higher mass losses occurring during the final decomposition stage of all three of the iron-containing blends than in the iron-free blends. Thus the 99*ABS*/1*CPVC*/5FeOOH blend lost 15% of the total mass loss compared with only 8% for the 99*ABS*/1*CPVC* blend similarly in the 80*ABS*/20*CPVC* blends, the iron-free system lost only 31 compared with 38% for the iron-containing blend and the 70*ABS*/30*CPVC*/5FeOOH blend lost 39 compared with 26% in the iron-free blend during this stage of the thermal decomposition. We have shown many times in many different chlorinated polymers and chlorinated polymer blends that the major effect of this iron compound is to dramatically improve char yields and subsequently to reduce smoke formation very significantly. It is an interesting point but the 99*ABS*/1*CPVC*/5FeOOH blend produced more than 600% more char than the 99*ABS*/1*CPVC* blend,

and its mass loss almost doubled from 8 in the iron-free blend to 15% in the iron-containing blend. Whether this massive increase in char yield is reflected in the high mass loss which we found in the final decomposition stage for the 99*ABS*/1*CPVC* blend is a matter of conjecture; certainly the other iron-containing blends also had some high values for the final mass loss stage. Also the 70*ABS*/30*CPVC*/5FeOOH blend lost as much mass during the final decomposition stage as it did during the second mass loss stage (39%). The possibility that char oxidation may be the cause of the mass losses occurring in the final stage must also be borne in mind and the way to resolve this anomaly would be to repeat all the TG experiments in a nitrogen atmosphere.

Finally, we firmly believe that iron:chlorine ratios affect the decomposition chemistry and consequently the flammability properties of these systems whether it is in reducing smoke, increasing char yield or modifying the burning performance of the blend. Maximum increase in char yield in these systems is associated with an iron:chlorine ratio of about 3:1, maximum improvement in flammability is associated with an iron:chlorine ratio of about 1:6 and maximum reduction in smoke yield is associated with an iron:chlorine ratio of about 1:9. Why these Fe:Cl ratios occur in multiples of three at these very important flammability points and at these particular blend compositions it is still very much a mystery! Much more work needs to be done.

Conclusions

- Blends of *ABS*/*CPVC* with and without the smoke suppressing compound FeOOH present show three distinctive decomposition stages occurring between 200–700°C.
- FeOOH markedly modifies the decomposition pattern of the blends, mass loss is considerably reduced, and the temperature at which the onset of decomposition begins is raised.
- Flammability data, especially in the important area of smoke formation and suppression, correlates well with the thermal decomposition patterns shown by the blends.

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