BUTTERWORTH HEINEMANN

*Polymer* Vol. 36 No. 5, pp. 1109–1111, 1995

0032-3861/95/$10.00+0.00

# polymer communications

## Iron–chlorine interactions in blends of poly(vinyl chloride) and acrylonitrile–butadiene–styrene containing basic iron (III) oxide

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*(Received 7 October 1994)*

A systematic study of char formation in blends of two thermoplastic polymers, poly(vinyl chloride) and acrylonitrile–butadiene–styrene, containing a char-forming/smoke-suppressing iron compound, suggests that the 'active species' which promotes char-forming reactions in these polymer systems is iron(III) oxychloride (FeOCl).

**(Keywords: poly(vinyl chloride); ABS copolymer; char formation)**

*Introduction*

In a series of publications on the effects of iron compounds on the flammability of acrylonitrile–butadiene–styrene (ABS)/poly(vinyl chloride) (PVC) blends, it has been found that incorporating modest amounts of hydrated iron(III) oxide (FeOOH) increases char formation significantly when compared with equivalent formulations containing no iron[1–5]. The formation of large amounts of char in the presence of basic iron(III) oxide results in a reduction in the amount of smoke produced when the polymer blend burns in air. In addition to the formation of char, it has also been found that the iron(III) compound improves the flame resistance of the blends and also stabilizes the blends against decomposition by both heat and light[6].

About 10 years ago, research carried out by Japanese[7] and French workers[8,9] on iron compounds in rigid and plasticized PVC formulations suggested that iron(III) chloride was the active compound in reducing smoke. It was proposed that the $FeCl_3$ was formed by reaction between the iron compound and HCl produced from the decomposing PVC. Work by Starnes *et al.*[10] using molybdenum(VI) oxide as a smoke suppressant in PVC has further clarified the char-forming, smoke-suppressing effect of $MoO_3$.

Recent work on char formation in ABS/PVC blends carried out in our laboratory suggests that char formation is dependent upon PVC content in iron-free ABS/PVC blends; however, of greater interest is the fact that in the iron-containing polymer blends, char formation depends not only on the PVC content, but also on the Fe/Cl stoichiometry. The main aim of this paper is to present experimental evidence which suggests that the major char-forming compound in these systems is iron(III) oxychloride (FeOCl).

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*Experimental*

Details of the method used to quantitatively determine char yield at 650°C have been published elsewhere[4] and the preparations of the polymer blends have also been described[11].

*Results*

The results are listed in *Table 1* together with other relevant information.

*Discussion*

In earlier work, the authors found that iron compounds present in low concentrations have very significant effects on the limiting oxygen index (a measure of polymer flammability) and smoke density values in ABS/PVC blends. It was assumed that the char-forming/smoke-suppressing effect was the result of the *in situ* formation of the Lewis acid $FeCl_3$, noted earlier. However, when compositions of ABS and PVC were examined across a wide range it became increasingly obvious that although $FeCl_3$ could be the active intermediate, char formation occurred when Fe/Cl ratios were not stoichiometric, i.e. 1:3. Indeed, high char yields have been obtained when Fe/Cl ratios were very much higher than 1:3. The results obtained are shown in *Table 1* and char/PVC relationships and char/PVC/Fe/Cl ratios from the iron-free and iron-containing formulations are shown in *Figures 1*, *2* and *3*.

*Iron-free blends.* There is a very high correlation ($r=0.99$) between char formation and percentage of chlorine in the blend. This suggests that it is the PVC content of the blend which influences the char-forming chemical reactions. Across the range of ABS/PVC iron-free blends studied, even down to formulations containing only 2 phr PVC, *Figure 1* shows that char formation is very dependent on chlorine and therefore PVC content.

**Table 1** Formulations, compositions and char yields

| | Formulation[a] | PVC (%) | Cl (%) | Fe (%) | mol Cl (%) | Fe/Cl molar ratio | Char yield[b] (%) | Char yield Δ/FeOOH | Char yield Δ/FeOOH (%) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 90 PVC/10 ABS | 84.91 | 48.17 | – | 1.357 | – | 16.02 | – | |
| | 90 PVC/10 ABS/5 FeOOH | 80.86 | 45.87 | 2.99 | 1.292 | 1:24.14 | 28.19 | 1.76 | 75.97 |
| 2 | 80 PVC/20 ABS | 75.47 | 42.82 | – | 1.206 | – | 13.06 | – | – |
| | 80 PVC/20 ABS/5 FeOOH | 71.88 | 40.78 | 2.99 | 1.148 | 1:21.46 | 25.86 | 1.98 | 98.01 |
| 3 | 70 PVC/30 ABS | 66.04 | 37.46 | – | 1.055 | – | 11.14 | | – |
| | 70 PVC/30 ABS/5 FeOOH | 62.89 | 35.68 | 2.99 | 1.005 | 1:18.78 | 25.09 | 2.25 | 125.22 |
| 4 | 53 PVC/47 ABS | 50.00 | 28.37 | – | 0.799 | – | 8.96 | – | – |
| | 53 PVC/47 ABS/5 FeOOH | 47.62 | 27.01 | 2.99 | 0.761 | 1:14.25 | 23.44 | 2.62 | 161.61 |
| 5 | 40 PVC/60 ABS | 37.74 | 21.41 | – | 0.603 | – | 6.60 | – | – |
| | 40 PVC/60 ABS/5 FeOOH | 35.94 | 20.39 | 2.99 | 0.574 | 1:10.75 | 21.41 | 3.24 | 224.39 |
| 6 | 30 PVC/70 ABS | 28.30 | 16.06 | – | 0.452 | – | 5.96 | – | – |
| | 30 PVC/70 ABS/5 FeOOH | 26.95 | 15.29 | 2.99 | 0.431 | 1:8.07 | 19.42 | 3.23 | 225.84 |
| 7 | 12 PVC/88 ABS | 11.32 | 6.42 | – | 0.181 | – | 3.18 | – | – |
| | 12 PVC/88 ABS/5 FeOOH | 10.78 | 6.12 | 2.99 | 0.172 | 1:3.20 | 16.63 | 5.23 | 422.96 |
| 8 | 8.5 PVC/91.5 ABS | 8.02 | 4.55 | – | 0.128 | – | 2.41 | – | – |
| | 8.5 PVC/91.5 ABS/5 FeOOH | 7.64 | 4.33 | 2.99 | 0.122 | 1:2.30 | 16.35 | 6.78 | 578.42 |
| 9 | 4 PVC/96 ABS | 3.77 | 2.14 | – | 0.061 | – | 2.16 | – | – |
| | 4 PVC/96 ABS/5 FeOOH | 3.59 | 2.04 | 2.99 | 0.058 | 1:1.1 | 13.17 | 6.09 | 509.70 |
| 10 | 2 PVC/98 ABS | 1.89 | 1.07 | – | 0.0302 | – | 1.82 | – | – |
| | 2 PVC/98 ABS/5 FeOOH | 1.79 | 1.02 | 2.99 | 0.0287 | 1:0.54 | 9.66 | 5.31 | 430.77 |

[a] PVC: 100 phr Corvic S67/111 (PVC resin); 5 phr tribasic lead sulfate (stabilizer); 1 phr calcium stearate (lubricant). ABS: 100 phr Cycolac GSM. FeOOH: Bayferrox 3905, hydrated iron (III) oxide (Bayer UK Ltd)
[b] Char determined at 650°C (see ref. 4)

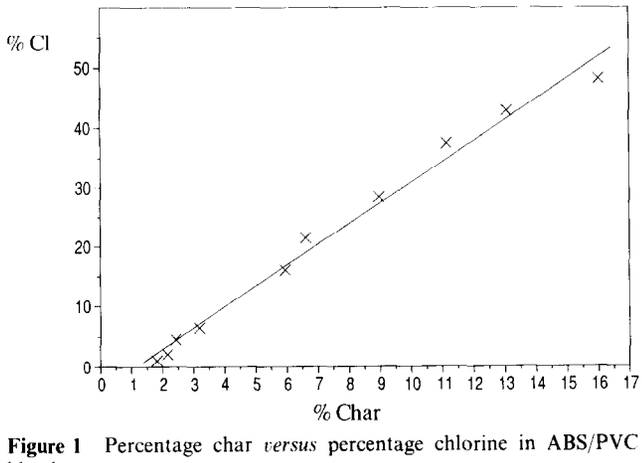



**Figure 1** Percentage char *versus* percentage chlorine in ABS/PVC blends

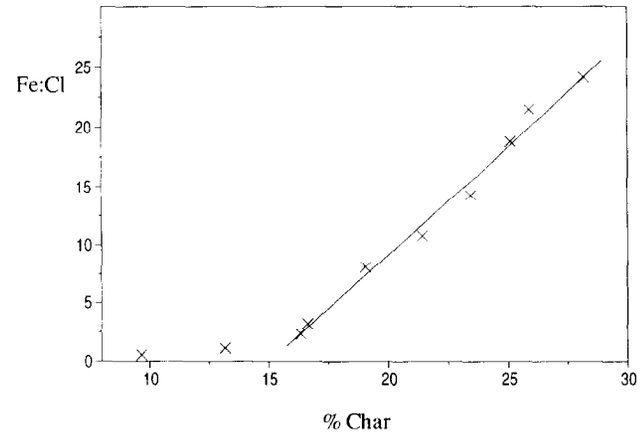



**Figure 2** Fe/Cl ratio *versus* percentage char

*Blends containing FeOOH.* The incorporation of FeOOH into this polymer system has very dramatic effects on char formation, and it can be seen (*Table 1*) that FeOOH increases char yield by more than 550% in some blends. Even with PVC levels of only 2 phr in ABS/PVC in the presence of 5 phr FeOOH, char yield (when measured against an iron-free system) is increased by more than five times.

There is another very strong correlation ($r = 0.99$) between Fe/Cl ratio and char formation in eight out of the 10 systems studied, and it was very obvious that formulations 9 and 10 (see *Table 1* and *Figure 2*) were giving results which differed from the others. When the data were plotted as shown in *Figure 3*, it became clear that $FeCl_3$ could not be the active char-forming species in formulations 9 and 10 since theoretically there is insufficient chlorine available to form $FeCl_3$. Indeed, the formation of $FeCl_3$ in formulations 8, 9 and 10 is rather unlikely, as some HCl will inevitably be 'lost' in other reactions, e.g. with the stabilizer[12], or be carried away from the polymer in the smoke particulates.

The authors are of the opinion that although $FeCl_3$ or $FeCl_2$ (a very weak Lewis acid) could be active in this system, a compound with an Fe/Cl ratio of about 1:1 is more likely. Note that formulation 8 (8.5 PVC/91.5 ABS/8.5 PVC/91.5 ABS/5 FeOOH) gives the greatest increase in char yield. The iron-free system produces 2.41% char at 650°C, while the system containing 5 phr FeOOH gives a char yield of 16.35% – 6.8 times more char than the iron-free system.

In conclusion, the authors propose that the active char-forming/smoke-suppressing compound in this system is likely to be iron(III) oxychloride (FeOCl). A thorough

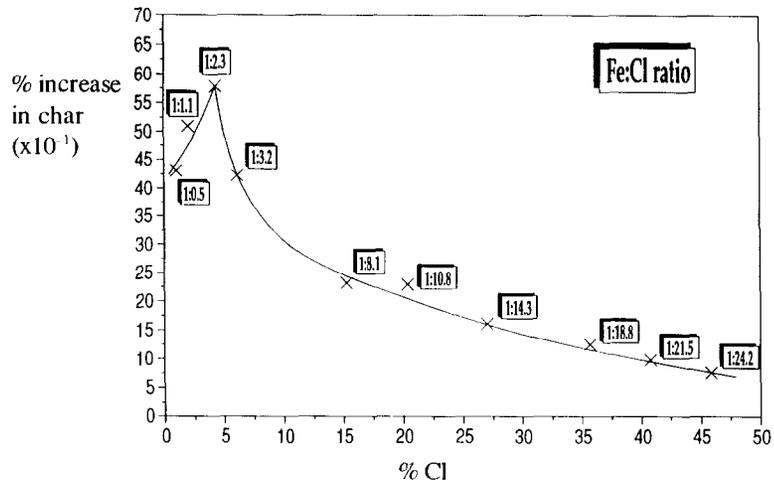
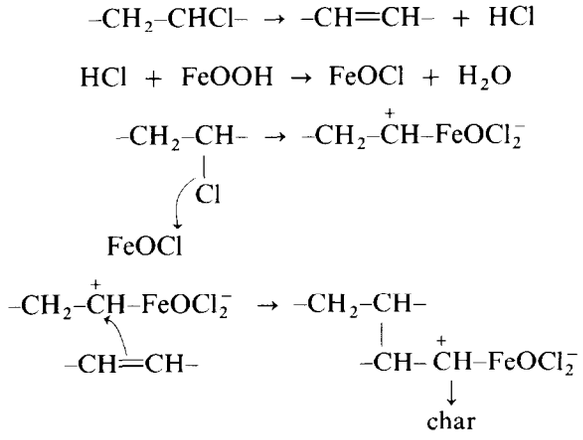



**Figure 3** Percentage increase in char *versus* percentage chlorine

literature search has failed to confirm that FeOCl is a powerful electron acceptor, but we have shown in earlier work[13] that FeOCl does indeed have char-forming/smoke-suppressing effects in some ABS/PVC blends. Several intercalation compounds of iron(III) oxychloride are known[14,15], where Lewis acid/Lewis base interactions have been proposed. Oxy compounds of iron(III) tend to be stable at high temperatures and we can see no reason why FeOCl could not promote char formation in ABS/PVC blends and indeed other polymer systems where iron-based smoke suppressants are active (see *Scheme 1*).




**Scheme 1**

*Acknowledgements*

The authors thank Jan Eastwood (University of Northumbria at Newcastle) who produced the manuscript, Cookson plc who supported this work, and David Adams (University of Northumbria at Newcastle) who helped with the preparation of the figures.

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