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Anomalous flammability behaviour of CPVC (chlorinated poly vinylchloride) in blends with ABS (acrylonitrile-butadiene-styrene) containing flame-retarding/smoke-suppressing compounds

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Polymer blends are commercially important because producers and users of polymers have increasing access to recycled materials. In addition, polymer blends are capable of providing materials which extend the useful properties beyond the range that can be obtained from single polymer equivalents. The twin problems of high flammability and coping with the hazards associated with the smoke produced during burning are only two of an increasing list of demanding specifications which are required for the commercial application of many plastics. In this paper the results of a systematic study of char formation in blends of CPVC (chlorinated polyvinyl chloride) with ABS (acrylonitrile-butadiene-styrene) containing a char-forming/smoke suppressing iron(III) compound are discussed. Flammability and smoke data are also presented and how the smoke suppressant may interact with the polymer is also proposed. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: polymer blends; CPVC; ABS; char; flammability; smoke suppression)

INTRODUCTION

It is widely believed that the low flammability of halogenated polymers such as uPVC, CPVC, PVDC, and PTFE is related to their halogen content. If LOI (limiting oxygen index) data is examined for a range of halogenated polymers[1], it is clear that the LOI values for these halogen containing polymers do indeed reflect halogen content (*Table 1*).

The very high oxygen index values for these halogen-containing polymers is known to be a consequence of the release of HX from the polymer during thermal decomposition which then acts as a radical chain terminator[2].

We have, in a series of recent papers, highlighted the effects that some inorganic flame-retarding/smoke-suppressing compounds have on the flammability properties of blends of uPVC/ABS, pPVC/ABS and uPVC/ABS/PP[3–11].

There is currently a great deal of interest in halogenated polymer/ABS blends for the computer and business equipment market[12], in 100% CPVC itself for fire sprinkler systems in the United States[13] and for water pipework in general[14].

In early papers, Quinn and Liebman[15,16] established that the chlorine content and structure of the CPVC polymer has a profound effect on thermal stability and on smoke production when CPVC was thermally decomposed in air. Quinn and Liebman found that in 100% CPVC polymer there is an abrupt and significant reduction in smoke production when the chlorine content in CPVC reaches about 64%. This reduction is thought to be related to the structure of the CPVC polymer and to the types of chlorinated aromatic decomposition products formed when CPVC is thermally decomposed. The stability of chlorine atoms attached to aromatic systems is well known[17].

Because of these findings and that CPVC/ABS blends represents a natural progression from PVC/ABS systems, we decided to prepare and study a range of formulations containing CPVC/ABS with the smoke suppressant basic iron(III) oxide (FeOOH), present at a concentration of 5 parts per hundred (phr).

We are presenting some of the early results from this work.

EXPERIMENTAL

Polymer blends

Blends of CPVC and ABS (*Table 2*) were prepared by melt-blending the polymers on a two-roll mill with an oil

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temperature of 170°C. The CPVC was initially stabilized by mixing the polymer resin with tribasic lead sulfate and calcium stearate (details below) in a Hobart Vertical Mixer for 1 h before compounding. The inorganic additive was added to the molten polymer blend on the two-roll mill during the final stages of compounding. The ABS used was Cycolac GSM (Borg-Warner) and the CPVC (containing 65% by weight of chlorine) was RB8065 (Elf-Atochem). The CPVC component of the polymer blends also contained 5 phr of tribasic lead sulfate (stabilizer) and 1 phr of calcium stearate (lubricant). The smoke suppressant used was Bayferrox 3905 (essentially hydrated iron(III) oxide) supplied by Bayer (UK) Ltd.

Flammability parameters

The method used for the determination of carbonaceous char has been fully described in an earlier paper[5]. The method consists of placing the polymer sample in a specially designed, preweighed platinum crucible supported in a stainless steel frame which is then carefully lowered into a vertical tube furnace which is at a controlled temperature of 650°C. After 10 min the platinum crucible and assembly are carefully removed from the furnace, the crucible and its contents cooled in a desiccator for 10 min and then reweighed. Char yields can be calculated from the mass changes that occur.

Table 1 Limiting oxygen index values

Polymer	LOI
PE	17.4
CPE (20 wt% Cl)	24.5
uPVC	45–49
PVDC	60.0
CPVC (65 wt% Cl)	69.4
PTFE	95.0

Taken from Cullis and Hirschler, 1981, with permission

Flammability (as measured by oxygen index ASTM D-2863) was determined according to the standard method. The LOI (limiting oxygen index) test measures the minimum concentration of oxygen in a flowing mixture of oxygen and nitrogen that just supports flaming combustion of a standard sample that burns downwards in a candlelike configuration[18].

The amount of smoke produced during burning was determined using the standard method (ASTM E-662). The values in the Tables are quoted for the flaming mode of the test and are expressed as the maximum smoke density per gram of sample used D_{MAX} (g^{-1})[19].

RESULTS AND DISCUSSION

As mentioned earlier, Liebman and Quinn[15,16] suggested that PVC decomposes thermally via a free radical

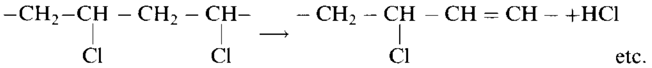
Table 2 Formulations, compositions, char yields and flammability data for CPVC/ABS and CPVC/ABS/FeOOH blends

	Formulation	Cl (wt%)	Fe (wt%)	mol Cl (wt%)	Fe/Cl mol ratio	Char yield (wt%)	Char yield (wt%) (–FeOOH)	Char yield (wt%) (CPVC/ABS/FeOOH CPVC/ABS)	D_{max} (g^{-1})	LOI
1	90 CPVC/10 ABS	55.19	–	1.5546	–	26.36	26.36		23.0	57.2
	90 CPVC/10 ABS/5 FeOOH	52.56	2.99	1.4801	1:27.7	36.06	34.34	7.98	14.0	53.8
2	80 CPVC/20 ABS	49.06	–	1.3819	–	23.58	23.58		32.0	49.3
	80 CPVC/20 ABS/5 FeOOH	46.71	2.99	1.3158	1:24.6	34.02	32.40	8.82	27.0	45.5
3	70 CPVC/30 ABS	42.92	–	1.2091	–	22.75	22.75		39.0	38.8
	70 CPVC/30 ABS/5 FeOOH	40.88	2.99	1.1515	1:21.6	33.88	32.27	9.52	42.0	38.2
4	60 CPVC/40 ABS	39.00	–	1.0986	–	19.00	19.00		45.0	32.0
	60 CPVC/40 ABS/5 FeOOH	37.14	2.99	1.0462	1:19.6	29.47	28.07	9.07	44.0	33.1
5	53 CPVC/47 ABS	32.49	–	0.9152	–	18.46	18.46		51.0	29.0
	53 CPVC/47 ABS/5 FeOOH	30.95	2.99	0.8718	1:16.3	29.45	28.05	10.25	41.0	30.0
6	40 CPVC/60 ABS	24.53	–	0.6909	–	14.61	14.61		51.0	25.0
	40 CPVC/60 ABS/5 FeOOH	23.36	2.99	0.6580	1:12.3	26.03	24.79	10.18	42.0	27.0
7	30 CPVC/70 ABS	18.39	–	0.5180	–	11.21	11.21		76.0	23.2
	30 CPVC/70 ABS/5 FeOOH	17.52	2.99	0.4935	1:9.2	23.90	22.76	11.55	41.0	26.1
8	25 CPVC/75 ABS	15.33	–	0.4318	–	9.06	9.06		87.0	22.4
	25 CPVC/75 ABS/5 FeOOH	14.59	2.99	0.4109	1:7.6	20.75	19.76	11.69	48.0	28.7
9	20 CPVC/80 ABS	12.26	–	0.3454	–	7.79	7.79		94.0	21.7
	20 CPVC/80 ABS/5 FeOOH	11.68	2.99	0.3290	1:6.16	20.78	19.79	12.00	74.0	31.0
10	12 CPVC/88 ABS	7.36	–	0.2073	–	5.59	5.59		105.0	20.4
	12 CPVC/88 ABS/5 FeOOH	7.01	2.99	0.1975	1:3.7	17.89	17.04	11.45	96.0	28.6
11	8.5 CPVC/91.5 ABS	5.21	–	0.1468	–	3.37	3.37		112.0	20.0
	8.5 CPVC/91.5 ABS/5 FeOOH	4.96	2.99	0.1397	1:2.6	16.98	16.17	12.80	105.0	26.6
12	4 CPVC/96 ABSA	2.45	–	0.0690	–	2.47	2.47		110.0	19.1
	4 CPVC/96 ABS/5 FeOOH	2.33	2.99	0.0656	1:1.2	14.19	13.52	11.05	109.0	24.3
13	2 CPVC/98 ABS	1.23	–	0.0346	–	1.84	1.84		109.0	19.0
	2 CPVC/98 ABS/5 FeOOH	1.17	2.99	0.0329	1:0.62	11.58	11.03	9.19	109.0	22.8
14	1 CPVC/99 ABS	0.61	–	0.0172	–	1.59	1.59		112.0	18.6
	1 CPVC/99 ABS/5 FeOOH	0.58	2.99	0.0163	1:0.31	11.14	10.61	9.02	110.0	22.1
15	0.5 CPVC/99.5 ABS	0.31	–	0.0086	–	1.35	1.35		113.0	18.6
	0.5 CPVC/99.5 ABS/5 FeOOH	0.29	2.99	0.0082	1:0.15	8.13	7.74	6.39	114.0	21.9

CPVC: 100 phr CPVC (65% Cl) resin (RB 8065 Elf-Atochem), 5 phr tribasic lead sulfate (Chemson), 1 phr calcium stearate (BDH)
ABS: 100 phr ABS resin (Cycolac GSM Borg-Warner)
Char determined at 650°C (see ref. 5)
FeOOH: Bayferrox 3905, hydrated iron (III) oxide (Bayer UK Ltd)

mechanism. Using mainly spectroscopic and product analysis they proposed that macroradical species were involved in the reactions occurring during thermal breakdown of PVC. However, alternative interpretation of their e.s.r. spectra suggested that the e.s.r. signals could be a result of thermal activation of the Π-electrons present in the formed polyene system[20]. More recent evidence for the presence of stable free radicals being found in 'real fires' involving burning polymers has recently been discussed[6]. Metcalfe and Mitchelson[21,22] have proposed that long-lived free radicals present in the volatile tars and smoke produced during burning may be the cause of the delayed death of some fire victims. The possibility that ionic species are formed during the decomposition of PVC has also been suggested and many authors prefer to describe the thermal decomposition of PVC as an ionic process, possibly involving an elimination mechanism with a cyclic transition state[23,24]. The ionic mechanism is further supported by evidence that the autocatalytic effect of HCl on the rate of dehydrochlorination reactions in PVC can only be understood in terms of an ionic process taking place. A satisfactory mechanism which explains all the experimental data probably does not exist but the debate is still ongoing. A non-radical process appears to be able to explain most of the theoretical and practical studies, but the inert conditions often used in laboratory experiments do not really reflect normal PVC processing and conditions of use.

Virgin PVC decomposes via the elimination of HCl at quite low temperatures (about 100°C)



$$-CH_2-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}- \longrightarrow -CH_2-\underset{Cl}{CH}-CH=CH- + HCl \quad \text{etc.}$$

However, PVC polymer is much less thermally stable than would be expected for a compound which contains saturated chlorocarbon chains. Extensive work using mainly model compounds has shown that unsaturated structures (especially end-chain allylic chlorine groups)[25] are the reason for this low thermal stability of virgin PVC. PVC polymer can contain up to 15 such double bonds for each 1000 carbon atoms present[26]. Chlorination of PVC to form CPVC is very likely to remove these double bonds, and as these double bonds are the main cause of the instability in PVC, the much improved thermal stability of CPVC and high T_g value can be explained on these grounds.

Char formation in CPVC/ABS and in blends of CPVC/ABS containing basic iron oxide

The yield of carbonaceous char for a range of blends containing CPVC/ABS and CPVC/ABS/FeOOH was determined (see Experimental section) and the data is listed in *Table 2* along with some other flammability data. Also shown in *Table 2* is data for char yields from CPVC/ABS/FeOOH blends corrected for the amount (4.76%) of FeOOH present. The FeOOH virtually remains quantitatively in the char as an iron oxide residue[27]. Also tabulated are char values for CPVC/ABS/FeOOH (minus 4.76%—the amount of FeOOH present) minus the char yield for the control formulation, i.e. CPVC/ABS. These values give a measure of the real char-forming effect of FeOOH in these blends. It is clear that for formulations with a chlorine to iron ratio (Cl/Fe) of greater than 1, within experimental error, the iron compound (at 5 phr) generally increases char formation by about 11% in these CPVC systems. This is shown graphically in *Figure 1*. In both the CPVC/ABS and CPVC/ABS/5 FeOOH blends, char formation is directly related to chlorine content. In the iron free blends the correlation coefficient is highly significant ($r = 0.99$) and in the blends containing basic iron oxide the correlation coefficient is again very significant ($r = 0.95$). Comparing this data with our earlier work on PVC/ABS blends, (*Table 3*), it can be seen that PVC/ABS/FeOOH combinations have a similar char-forming dependence on chlorine content.

In these chlorinated polymer systems containing Fe(III), we believe that one of the chemically most active char-forming/smoke-suppressing species formed in the hot decomposing polymer is iron(III) oxychloride, FeOCl[8]. In earlier work with PVC/ABS blends we suggested that FeOCl is the active species and there is further evidence in this research to support this hypothesis. In *Table 2* and *Table 3* and in *Figure 2*, the data clearly show that significant amounts of char are formed even at low Cl/Fe

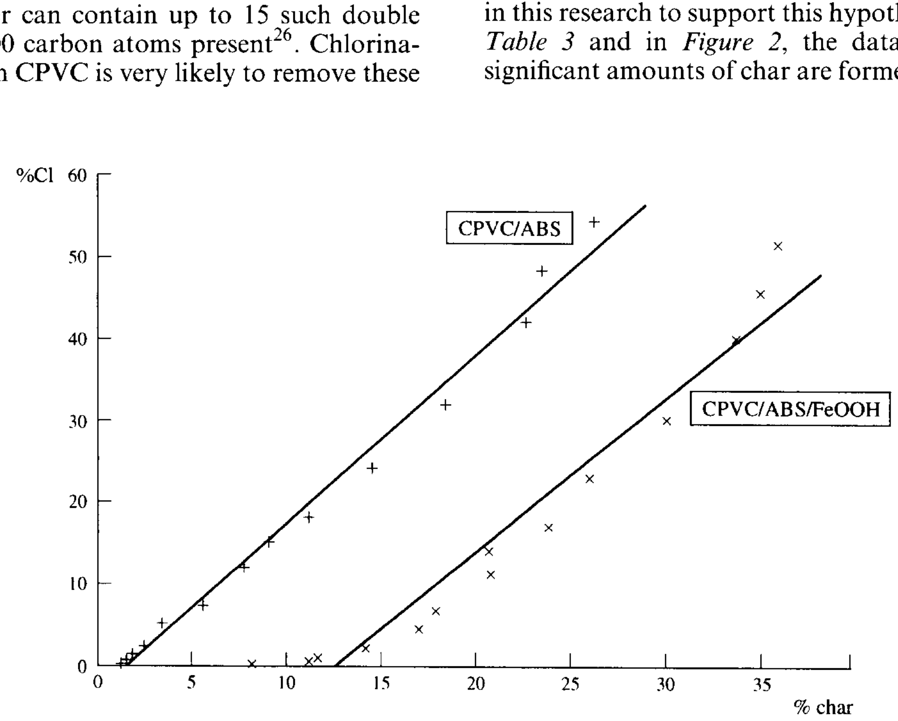


Figure 1 Percentage chlorine against percentage char for CPVC/ABS and CPVC/ABS/FeOOH blends

Table 3 Formulations, compositions, char yields and flammability data for PVC/ABS and PVC/ABS/FeOOH blends

	Formulation	PVC (wt%)	Cl (wt%)	Fe (wt%)	mol Cl (wt%)	Fe/Cl mol ratio	Char yield (wt%)	Char yield (wt%) (–FeOOH)	Char yield (wt%) (PVC/ABS/FeOOH PVC/ABS)	D_{MAX} (g^{-1})	LOI
1	90 PVC/10 ABS	84.91	48.17	–	1.357	–	16.02	–	–	68.0	44.6
	90PVC/10 ABS/5 FeOOH	80.86	45.87	2.99	1.292	1:24.14	28.19	26.85	10.83	38.0	60.5
2	80 PVC/20 ABS	75.47	42.82	–	1.206		13.06	–	–	75.0	35.5
	80 PVC/20 ABS/5 FeOOH	71.88	40.78	2.99	1.148	1:21.46	25.86	24.63	11.57	45.0	54.5
3	70 PVC/30 ABS	66.04	37.46	–	1.055	–	11.14	–	–	82.0	31.2
	70 PVC/30 ABS/5 FeOOH	62.89	35.68	2.99	1.005	1:18.78	25.09	23.90	12.76	45.0	44.2
4	53 PVC/47 ABS	50.00	28.37	–	0.799		8.96	–	–	93.0	24.2
	53 PVC/47 ABS/5 FeOOH	47.62	27.01	2.99	0.761	1:14.25	23.44	22.32	13.36	43.0	33.6
5	40 PVC/60 ABS	37.74	21.41	–	0.603		6.60	–		101.0	23.0
	40 PVC/60 ABS/5 FeOOH	35.94	20.39	2.99	0.574	1:10.75	21.41	20.39	13.79	47.0	35.5
6	30 PVC/70 ABS	28.30	16.06	–	0.452	–	5.96	–	–	104.0	21.8
	30 PVC/70 ABS/5 FeOOH	26.95	15.29	2.99	0.431	1:8.07	19.42	18.50	12.54	63.0	33.4
7	12 PVC/88 ABS	11.32	6.42	–	0.181	–	3.18		–	112.0	20.2
	12 PVC/88 ABS/5 FeOOH	10.78	6.12	2.99	0.172	1:3.20	16.63	15.84	12.66	103.0	27.6
8	8.5 PVC/91.5 ABS	8.02	4.55	–	0.128	–	2.41	–	–	117.0	19.8
	8.5 PVC/91.5 ABS/5 FeOOH	7.64	4.33	2.99	0.122	1:2.30	16.35	15.56	13.15	102.0	25.0
9	4 PVC/96 ABS	3.77	2.14	–	0.061	–	2.16	–		116.0	19.0
	4 PVC/96 ABS/5 FeOOH	3.59	2.04	2.99	0.058	1:1.1	13.17	12.54	10.38	110.0	23.8
10	2 PVC/98 ABS	1.89	1.07	–	0.0302	–	1.82	–	–	115.0	18.8
	2 PVC/98 ABS/5 FeOOH	1.79	1.02	2.99	0.0287	1:0.54	9.66	9.20	7.38	110.0	22.8

PVC: 100 phr Corvic S67/111 (PVC resin) (ICI), 5 phr tribasic lead sulfate (stabilizer) (Chemson), 1 phr calcium stearate (lubricant) (BDH)
ABS: 100 phr Cycolac GSM (Borg-Warner)
Char determined at 650°C (see ref. 5)
FeOOH: Bayferrox 3905-hydrated iron(III) oxide (Bayer UK Ltd)
From Carty and White, 1991[8], with permission.

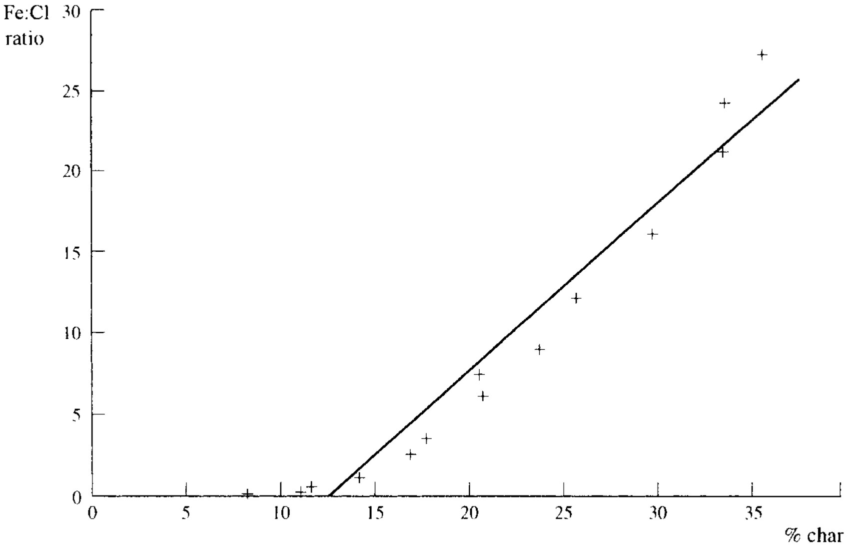


Figure 2 Iron : chlorine ratio against percentage char for CPVC/ABS/FeOOH blends

ratios. Both in PVC and CPVC blends with ABS containing Fe(III), it is highly likely that FeOCl is the active Lewis acid species. For example, in formulation 15 (*Table 2*), 0.5 CPVC/99.5 ABS/5 FeOOH the char yield is markedly higher than that found in the control, iron free system. Indeed, at this very low concentration of CPVC (0.5 phr) the iron containing blend produces more than 5.5 times more char than the control. The char-forming effects of CPVC/FeOOH combinations even at such low chlorine concentrations (0.29%) adds further support to our view that char-forming/cross-linking reactions in the thermally decomposing polymer blend are catalysed by very small amounts of iron (III) oxychloride; as little as *ca* 4.0×10^{-5} mol in this instance. It is also of interest in this context to point out that such small amounts of active material have a significant effect, not just on char formation, but also on flammability. In formulation 14 for example, 0.5 CPVC/99.5 ABS and 0.5 CPVC/99.5 ABS/5 FeOOH, the LOI value of the iron containing formulation is almost 4 LOI units greater than that for the control.

Flammability data for CPVC/ABS and CPVC/ABS/FeOOH blends

For the CPVC/ABS blends there is a gradual increase in LOI as the chlorine content of the blend increases (*Figure 3*).

For the CPVC/ABS blends containing the smoke suppressant there is an initial steep increase in LOI with increasing chlorine content in these iron-containing formulations. The LOI/%Cl curve shows a maximum at an LOI of 31.0 for formulation 9 i.e. 20 CPVC/80 ABS/5 FeOOH (%Cl = 11.7; Fe: Cl = 1/6.2), then, very surprisingly, the LOI values decrease with increasing chlorine content reaching a minimum at an LOI of 26.1 for formulation 7 i.e. 30 PVC/70 ABS/5 FeOOH (%Cl = 17.5; Fe/Cl = 1/9.2). After this point the curve again gradually increases with increasing chlorine content. For formulations containing more than 70 phr CPVC the iron free blends have slightly lower LOI values than the CPVC/ABS/FeOOH blends.

Flammability data for PVC/ABS and PVC/ABS/FeOOH blends

For the PVC/ABS blends there is a gradual increase in LOI as the chlorine content of the blend increases (see *Table 3* and *Figure 4*).

For the PVC/ABS blends containing the smoke suppressant there is a steep increase in LOI with increasing chlorine content, then at an LOI value of 33.4 for the formulation 30 PVC/70 ABS/5 FeOOH (%Cl = 15.3; Fe/Cl = 1/8) the curve reaches a plateau and remains about constant until at an LOI value of 33.6 for the formulation 53 PVC/47 ABS/5 FeOOH (%Cl = 27.0; Fe/Cl = 1/14.3), the LOI again rises as the chlorine content of the blend increases.

Flammability/char relationships

For the CPVC/ABS blends there is a steady increase in LOI with increasing char yield (*Figure 5*). However the relationship is not linear.

For the CPVC/ABS blends containing the smoke suppressant the initial part of the LOI/%char curve for CPVC/ABS/FeOOH is virtually superimposed on the CPVC/ABS curve until at an LOI value of 31 for the formulation 20 CPVC/80 ABS/5 FeOOH (%Cl = 11.7; Fe/Cl = 1/6.2; %Char = 20.78) a maximum value is reached and then the LOI/%char curve falls away as the char yield increases. It reaches a minimum value at an LOI value of 26.1 for the formulation 30 CPVC/70 ABS/5 FeOOH (%Cl = 17.5; Fe/Cl = 1/9.2; %Char= 23.98). Then the curve rises again but in this instance

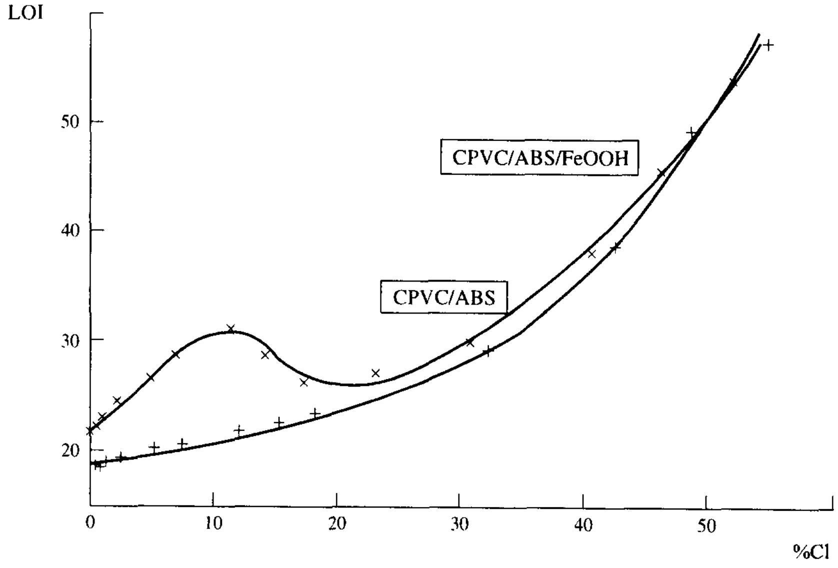


Figure 3 LOI against percentage chlorine for CPVC/ABS and CPVC/ABS/FeOOH blends

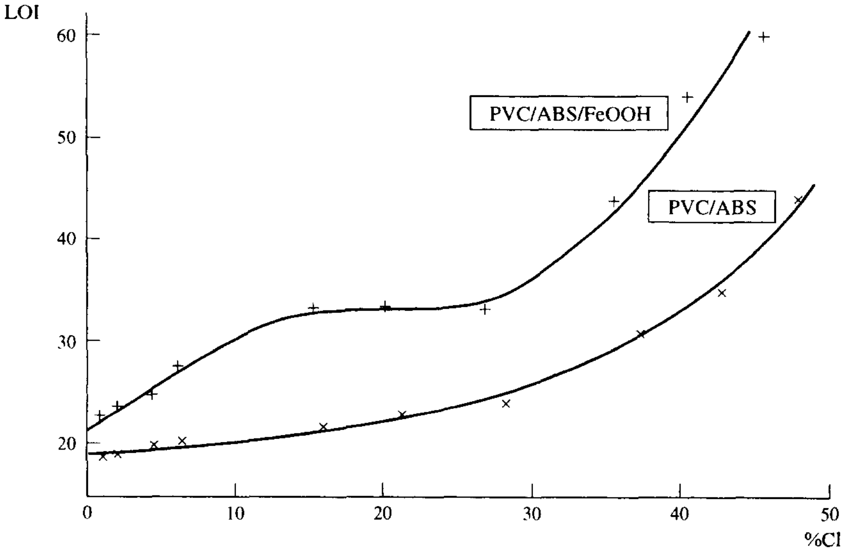


Figure 4 LOI against percentage chlorine for PVC/ABS and PVC/ABS/FeOOH blends

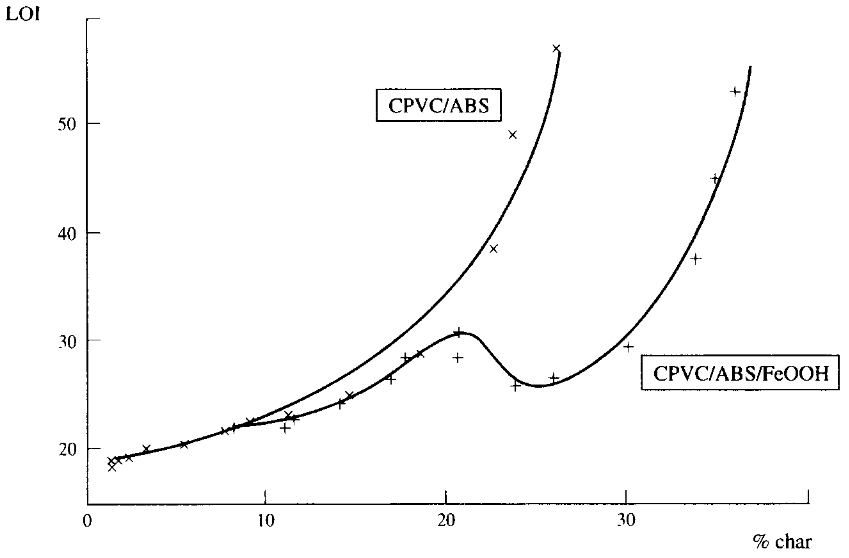


Figure 5 LOI against percentage char for CPVC/ABS and CPVC/ABS/FeOOH blends

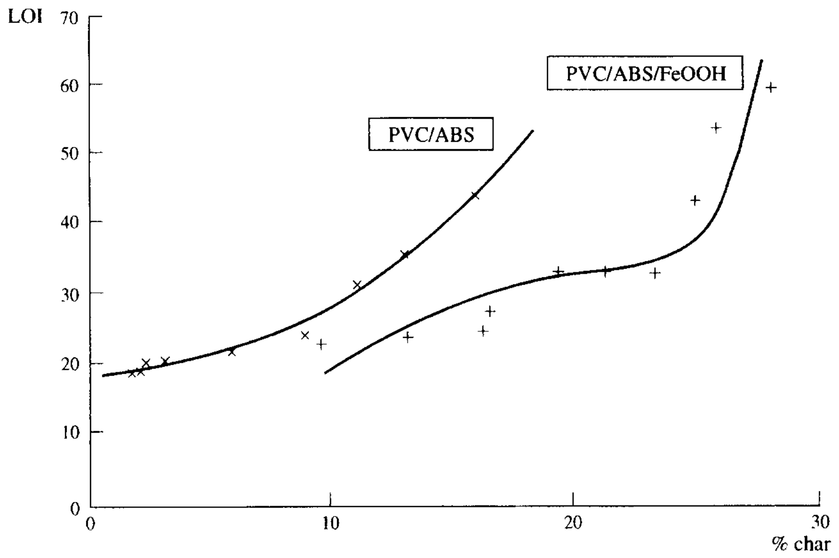


Figure 6 LOI against percentage char for PVC/ABS and PVC/ABS/FeOOH blends

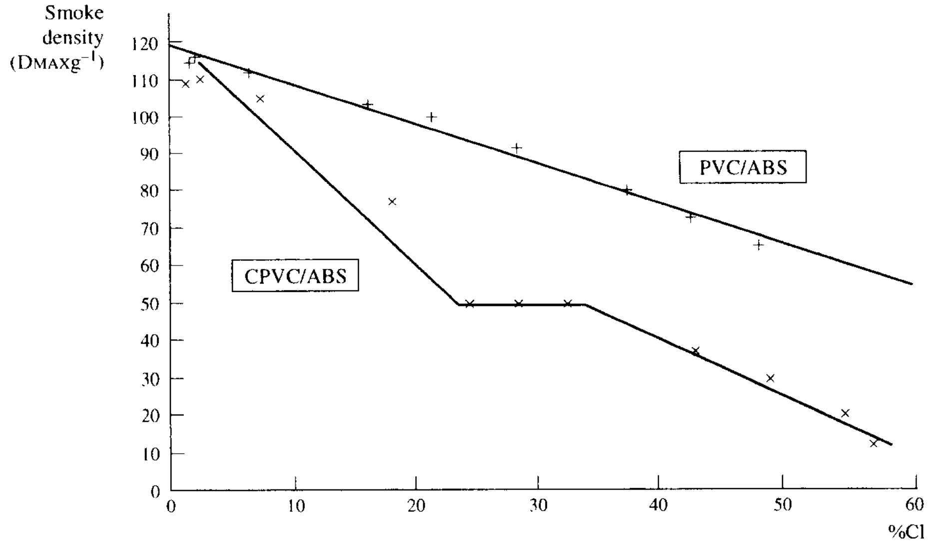


Figure 7 Smoke density (D_{max} g^{-1}) against percentage chlorine for PVC/ABS and CPVC/ABS blends

much higher char values for equivalent LOI values are achieved than those found in the iron-free CPVC/ABS blends.

In the PVC/ABS blends (see *Figure 6*), there is a gradual increase in LOI value with increasing yield of char.

In the same blend containing the smoke suppressant, unlike the CPVC/ABS system, in these blends of PVC and ABS containing basic iron(III) oxide, the initial part of the PVC/ABS/FeOOH curve is not superimposed on the iron-free ABS/PVC curve. At an LOI value of 33.4 for the formulation 30 PVC/70 ABS/5 FeOOH (%Cl = 15.3; Fe/Cl = 1/8; %Char = 19.4) the LOI/percentage char curve reaches a plateau and does not rise until at an LOI value of 33.6 corresponding to the formulation 53 PVC/47 ABS/5 FeOOH (%Cl = 27.0; Fe/Cl = 1/14.3; %Char = 23.44) after this point the curve then gradually rises.

Smoke density measurements

Smoke density measurements were carried out in the flaming mode of the test method ASTM E-662-79 (see ref. 19) for blends of CPVC/ABS and CPVC/ABS/FeOOH (*Table 2*) and for blends of PVC/ABS and PVC/ABS/FeOOH (*Table 3*). When maximum smoke density ($D_{\mathrm{MAX}}\,\mathrm{g}^{-1}$) was plotted against percentage chlorine present in the blend some very interesting results were obtained.

PVC/ABS and CPVC/ABS. As expected, increasing the amount of ABS in a PVC/ABS blend results in a gradual increase in smoke density and indeed the points fall on an almost straight line (*Figure 7*). However the curve for the CPVC/ABS blends is very different. Except for the blends containing high percentages of ABS (>90 phr), the smoke density values are very much smaller than they are for the equivalent PVC/ABS formulations. This is not unexpected[28] but the smoke density/% chlorine curve for the CPVC/ABS system shows the presence of a plateau between 25 and 33% chlorine in the blend. This plateau or a levelling-off in smoke production even though ABS content is increasing, is a real feature because we determined the smoke density value for the formulation 46.5 CPVC/53.5 ABS (i.e. midway between 53 CPVC/47 ABS and 40 CPVC/60 ABS) and the smoke value for this blend falls almost exactly on the plateau region of the curve. We are unsure of reasons for this but we will discuss this point later.

PVC/ABS/FeOOH and CPVC/ABS/FeOOH. The presence of the smoke suppressant has dramatic effects on smoke density values in these systems (*Figure 8*). In the PVC/ABS/FeOOH blends the smoke density/% chlorine curve has, like the CPVC/ABS curve, a plateau between 20 and 40% chlorine present in the blend. A similar effect also occurs in the CPVC/ABS/FeOOH system where the plateau is found on the curve between 17 and 41% chlorine.

We can at present only speculate why there is such a pronounced levelling-off in the production of smoke across this range of chlorine concentrations in these CPVC/ABS/FeOOH and PVC/ABS/FeOOH blends. It was mentioned earlier that the low smoke value for CPVC (chlorine >65%) is thought to be due to a change occurring in the nature of the aromatic decomposition products formed (see *Scheme 1*) when CPVC is thermally decomposed.

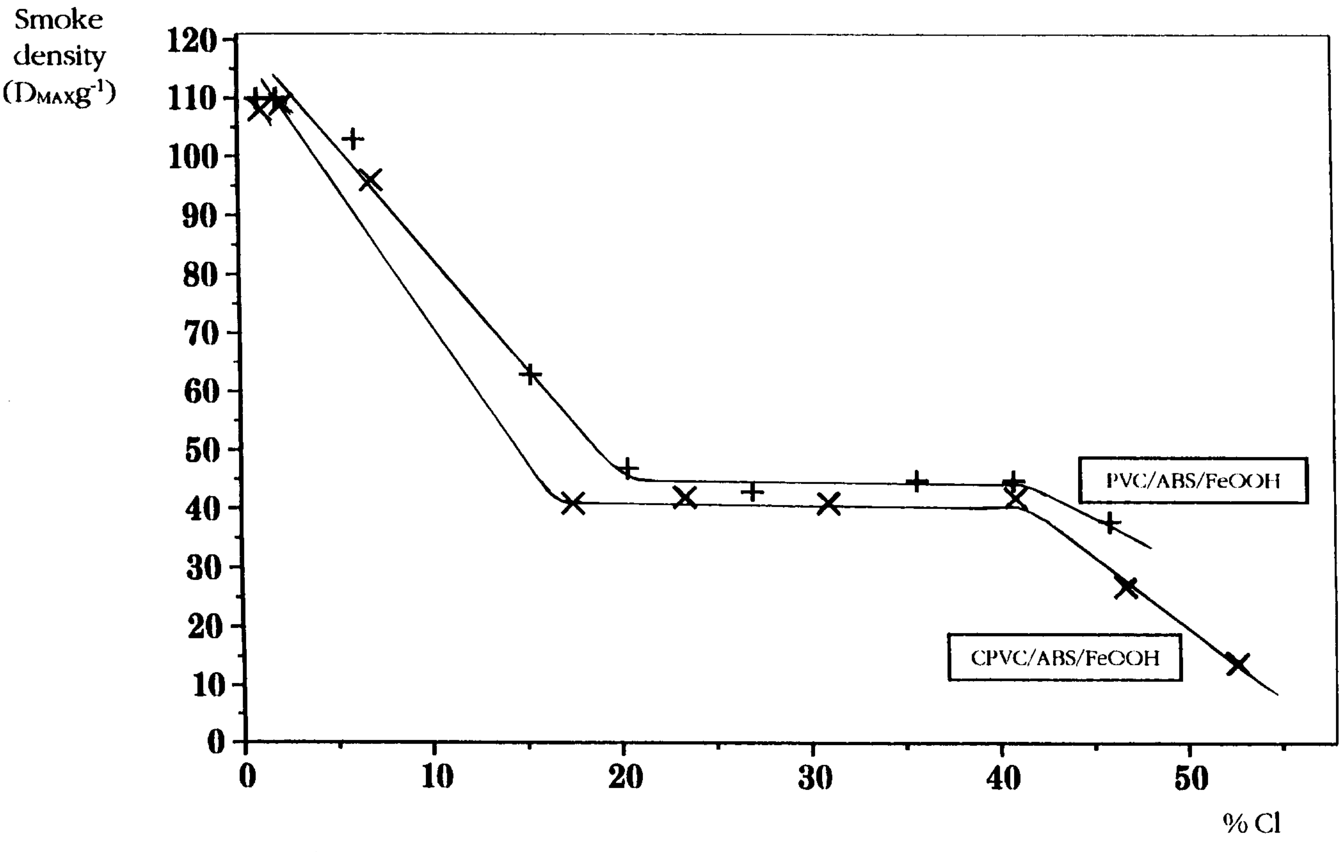
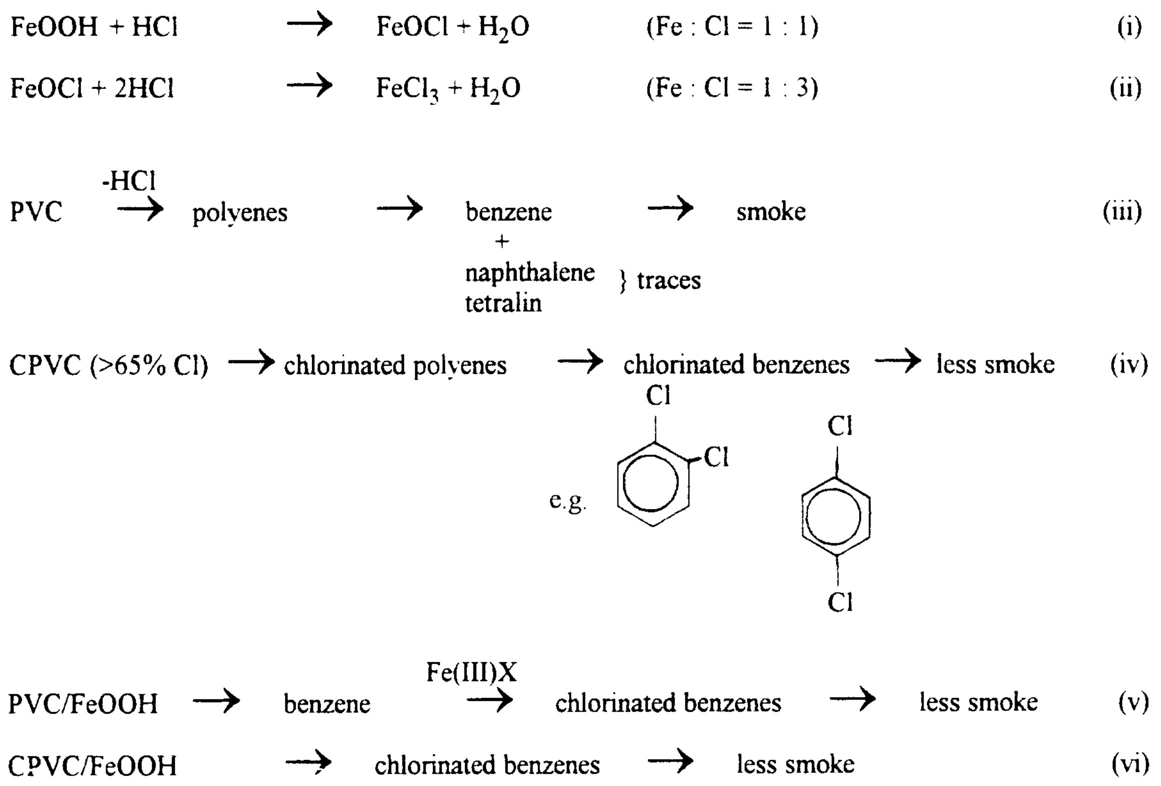


Figure 8 Smoke density ($D_{\max}\,\mathrm{g}^{-1}$) against percentage chlorine for PVC/ABS/FeOOH and CPVC/ABS/FeOOH blends



Scheme 1

Quinn[15] identified dichlorobenzenes in his analysis of the decomposition products formed when CPVC was thermally decomposed. Guyot[29] has also noted the presence of 'chlorinated aromatics' when he examined the pyrolysis of uPVC containing iron(III) oxide. We would like to tentatively suggest that in the CPVC/ABS, CPVC/ABS/FeOOH and also in the PVC/ABS/FeOOH formulations investigated in this study, that the reduction in smoke and indeed the plateau effects mentioned earlier, could be a result of a change occurring in the decomposition products. Iron(III) chloride (and possibly other iron(III) chlorocompounds) is well known to produce high yields of chlorinated benzenes (in the absence of chlorine!) when benzene and chlorobenzene are treated with $FeCl_3$[30]. Kovacic found that chlorobenzene, when allowed to react with $FeCl_3$ at 125–140°C, gives high yields (>80%) of mainly ortho- and *para*-dichlorobenzenes.

It seems highly likely that in these CPVC/ABS, PVC/ABS/FeOOH and CPVC/ABS/FeOOH formulations the production of chlorinated benzenes (formed by reaction with $FeCl_3$ or some other Fe(III) chloro species formed *in situ* from the decomposing PVC/CPVC and FeOOH) is the main reason why smoke density values are so low (see *Scheme 1*). We cannot explain the plateau effect but it would be too much of a coincidence that these three polymer systems produce such similar effects when they are burned in the air.

CONCLUSION

We feel the very effective smoke-suppressing effect of FeOOH in these halogenated polymers is probably the result of a combination of two chemical effects involving FeOOH:

1. Lewis-acid type cross linking catalysed by FeOCl formed *in situ* produces significant amounts of carbonaceous char.
2. The formation of dichlorobenzenes (or polychlorobenzenes) formed by reaction of $FeCl_3$ (or other Fe(III) chloro compound) with the aromatics formed during the decomposition of PVC and CPVC.

Much more work needs to be done to confirm these findings.

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