Char formation in polymer blends

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A quantitative study on the formation of carbonaceous char at 350, 500, 650 and 800°C in unplasticized poly(vinyl chloride), acrylonitrile–butadiene–styrene and especially in blends of the two polymers has been carried out. Incorporating iron compounds at varying levels into the polymer blends dramatically increases char formation even at 800°C. Flammability and smoke data are also presented and the relationship between char formation and levels of iron present are discussed. Crosslinking/char-forming schemes are proposed in an attempt to explain the action of iron compounds in these polymer formulations.

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

INTRODUCTION

Investigations into the formation of carbonaceous char during polymer degradation have been considered unexciting work and of little real value in the elucidation of mechanisms of polymer flammability and decomposition. Over the years many hundreds of papers have been published on polymer degradation and the great majority of these have been aimed at gaining an understanding of polymer degradation processes and/or the chemical composition of the volatile organic compounds which are produced when polymers degrade thermally. It is of course these volatile organic compounds which act as fuels in real fires and the fire gases themselves are the cause of death in many fire victims. There have been many mechanistic studies[1–5] carried out on the chemical action of flame-retarding/smoke-suppressing additives for polymers, especially poly(vinyl chloride) (PVC); however, little work has been aimed at examining 'what is left' after pyrolysis.

We have recently looked at char formation in unplasticized poly(vinyl chloride) (UPVC), acrylonitrile–butadiene–styrene terpolymer (ABS) and in blends of ABS and PVC. Using some active iron compounds we have found that char-forming reactions are very significant in these polymer systems and we are reporting our findings in this paper.

EXPERIMENTAL

The determination of residual char after polymer pyrolysis has generally been the end point of differential thermal analysis/thermogravimetric analysis/differential scanning calorimetry (d.t.a./t.g.a./d.s.c.) work when mass/energy changes during thermal decomposition have been the major aims of the research. Samples used in this work are usually on the milligram scale, and although many excellent data have been obtained by these methods, the residue remaining after pyrolysis in air or in nitrogen is usually recorded to round off the experimental data and is not normally considered to be a prime goal of the work. Some workers have, however, used much larger sample sizes and determined residual char by different methods[6–8].

We have determined residual char using a vertical tube furnace which has a sensitive microprocessor control system*. The temperature of the furnace can be adjusted anywhere in the range 110 to 1100°C with an accuracy of ±2°C. Samples of polymer were placed in a preweighed, specially designed platinum crucible which was then carefully lowered into the tube furnace, the crucible being supported in a stainless steel frame which positions the crucible accurately in the controlled temperature zone of the furnace. After 10 min at the chosen temperature the whole assembly was removed from the furnace, and the crucible was cooled in a desiccator and then reweighed. We have found this method gives extremely accurate and reproducible results. In all the experiments carried out so far (now more than 300 runs), char values for each formulation have never varied by more than 0.5%.

DISCUSSION

UPVC is not, like many other plastic materials, an inherently flammable material. Its high limiting oxygen index (*LOI*) value (49.8) is indicative of its inability to burn freely in air. A sustained high heat flux on the polymer is required to maintain burning. Plasticized PVC is, however, much more flammable (see *Table 1* taken from ref. 9).

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ABS is very different from PVC. It is a very flammable material; indeed, its low *LOI* value (18.3) ensures that it readily burns in air. ABS, unlike UPVC, is easily ignited, it burns with a hot flame[10] and produces large quantities of thick black smoke (see *Figure 1*). It is of course not the polymer itself which burns but the volatile organic compounds (VOCs) which are produced when ABS is thermally decomposed. Literature in the public domain on ABS in terms of its flammability and smoke-producing properties is not very extensive. Early work reported by Madorsky and others[11] on the thermal decomposition of copolymers of polybutadiene with styrene and acrylonitrile clearly showed that the butadiene part of the polymer system produces a wide range of unsaturated compounds including linear alkenes, conjugated alkenes, cyclic alkenes, etc. Styrene and acrylonitrile similarly produce significant quantities of unsaturated alkenes during pyrolysis and it is these volatile fuels which ignite and burn when ABS is exposed to a source of ignition. Mechanistic studies on the thermal decomposition of ABS are very 'thin on the ground'[12].

The understanding of PVC decomposition behaviour is much more advanced. Workers in the field have published extensively and hundreds of papers are available in the literature. We have recently reviewed the current level of understanding of the role of iron compounds acting in the PVC system[13]. However, the debate about the mechanism of action of flame retardants and smoke suppressants in PVC continues[14,15].

A formulation containing 70 ABS/30 PVC is only slightly less flammable than 100% ABS. Having 30 phr of PVC in the blend raises the *LOI* by only 3.5 '*LOI* units', and this blend cannot be classed as a flame-retardant material. A calculated *LOI* value for this material (based on values obtained from the 'pure' polymers) is 27.8, and this high value is not reflected in the experimental value of 21.8. Even a formulation containing 70 PVC/30 ABS has an *LOI* value of 31.2, a value considerably lower than the calculated value (40.35).

Hence, we can conclude that the PVC in blends with ABS is not exerting its full potential to act as a flame retardant and the PVC needs to be activated in some way to become more effective. In a series of recent papers we have highlighted the quite dramatic effects which occur when a few parts per hundred of a range of iron compounds (including some organometallics) are added to semi-regid PVC and ABS/PVC blends[16–21]. Adding 1, 2.5 and 5 phr of some quite simple inorganic iron compounds dramatically raises the *LOI* of the blend and at the same time smoke production is reduced considerably. We have attempted to explain the smoke-suppressing effect of these iron compounds but we have so far been unable to account for the high *LOI* values of the iron-containing blends. In this paper we would like to offer a slightly different explanation, based on new experimental evidence, of the effects which certain iron compounds have on the flammability of these blends of ABS and PVC. Our original suggestion was that the excellent flame-retarding effect of iron compounds in the

Table 1 *LOI* and smoke data for rigid and plasticized PVC

DOP[a] in PVC[b] (phr)	*LOI*	Smoke density D_{max} (g^{-1})
0	49.8	25.7
10	38.7	44.3
20	31.5	55.7
30	28.0	64.3
40	25.0	74.3
50	23.9	85.7

[a] Dioctyl phthalate (di(2-ethylhexyl)phthalate)
[b] 100 phr Corvic S67/111, PVC polymer; 5 phr tribasic lead sulfate, stabilizer; 1 phr calcium stearate, lubricant

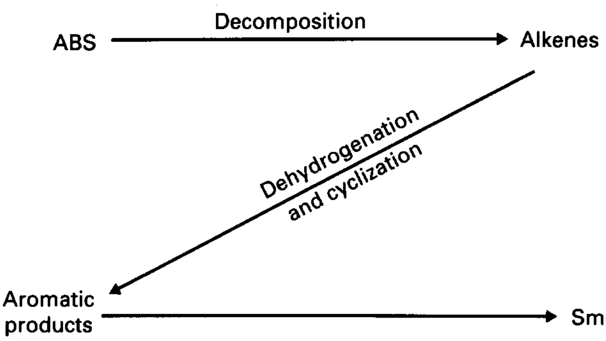


Figure 1 Combustion of ABS

Table 2 ABS/PVC/FeOOH blend compositions and char values

Formulation (phr)	Char (%)				Fe (mol)	Cl (mol)	Fe/Cl ratio	Smoke D_{max} (g^{-1})	*LOI*
	350°C	500°C	650°C	800°C					
100 UPVC	41.42	21.97	13.70	10.82	–	0.016	–	62.4	49.8
100 ABS	96.51	2.6	<0.2	0	–	–	–	111	18.3
70 ABS/30 PVC	78.60	10.21	6.42	3.87	–	0.482	–	104	21.8
70 ABS/30 PVC/1 FeOOH	79.58	17.22	9.74	7.14	0.011	0.477	1/43	85	33.6
70 ABS/30 PVC/2.5 FeOOH	79.17	22.43	13.94	10.08	0.027	0.470	1/17	80	33.6
70 ABS/30 PVC/5 FeOOH	79.67	27.46	19.05	14.36	0.053	0.459	1/9	63	33.4
70 ABS/30 PVC/7.5 FeOOH	80.50	33.30	24.89	18.25	0.078	0.448	1/6	61	33.4
70 ABS/30 PVC/10 FeOOH	81.14	34.07	26.97	19.71	0.102	0.438	1/4	54	33.8
70 PVC/30 ABS	57.68	17.10	11.14	9.63	–	1.124		92	31.2
70 PVC/30 ABS/1 FeOOH	61.48	24.28	18.94	14.69	0.011	1.113	1/101	56	37.3
70 PVC/30 ABS/2.5 FeOOH	62.86	27.38	21.38	16.02	0.027	1.097	1/40	50	40.8
70 PVC/30 ABS/5 FeOOH	63.44	31.40	23.60	17.21	0.054	1.070	1/20	45	44.2
70 PVC/30 ABS/7.5 FeOOH	65.73	33.73	27.13	19.53	0.078	1.046	1/13	41	42.8
70 PVC/30 ABS/10 FeOOH	66.36	37.60	30.79	22.38	0.102	1.022	1/10	39	39.8

blends was a result of the formation of 'active' carbonaceous char removing the free radicals which promote burning. This could still be an important factor, but we are now of the opinion that char formation itself is the key to both the high *LOI* values of the blends and why smoke reductions are very significant.

All the experimental data we have obtained are shown in *Table 2*, which includes char formation across a range of formulations at four different temperatures. The first of these, 350°C, would represent conditions in the early stages of a fire; 500°C and 650°C represent temperatures reached during pre-'flashover' and post-'flashover' periods of fire growth; and 850°C is a temperature typical of a fully developed fire. Also included in *Table 2* are two flammability parameters, namely *LOI* and D_{max} values, and information on the molar amounts of iron and chlorine present and the molar ratios of Fe/Cl in the formulations.

In terms of char formation, two points are very obvious in the 70 ABS/30 PVC and 70 PVC/30 ABS blends, namely that char values increase with increasing iron content and decrease with increasing temperature. Smaller amounts of char forming at high temperatures are possibly the result of high temperature cracking reactions occurring, a phenomenon well documented in molybdenum work[22].

At 350°C, 100% ABS is not decomposed to any great extent and 96.51% of the original material remains after pyrolysis. However, at 500°C and above, ABS forms very little char; indeed, at 800°C there is no char. ABS is thus quite stable below 350°C but it is rapidly and totally decomposed and volatilized at temperatures in excess of 500°C. UPVC is much less thermally stable than ABS below 500°C. Indeed, at all temperatures it rapidly forms char: at 500°C the value is 21.97%, and even at 800°C, a temperature normally referred to as an 'ashing temperature', UPVC forms 10.82% char.

Using data obtained from the separate polymers, alloying the two polymers in a blend of 70 ABS/30 PVC should give 8.4% char. The experimental value is 10.21% at 500°C, and even at 800°C the calculated value of 3.25% is again not reflected in the actual value obtained (3.87%), although the agreement between the theoretical and experimental values here is reasonable. In the 70 PVC/30 ABS system, higher char values are to be expected and at 500°C the calculated value of 16.16% is less than the experimental value (17.10%). At 800°C 70 PVC/30 ABS should give, in theory, 7.57% char and the experimental value is 9.63%, a value considerably higher than the estimated value. Adding iron to the formulations has quite dramatic effects on char formation, even at 800°C. At 500°C a 70 ABS/30 PVC blend containing only 1 phr of iron shows increased char formation by about 7%, and as more iron is added these char values increase further. The data are graphically shown in *Figures 2* and *3*. Although these plots are not quite linear, they do clearly show that, apart from an initial large increase in char formation, adding iron causes char formation to increase in an almost uniform way. In both the 70 ABS/30 PVC and 70 PVC/30 ABS systems, char formation seems to be very dependent on the amount of iron present.

In the absence of PVC, ABS forms very little char at temperatures in excess of 500°C. ABS is known[23] to be one of the smokiest polymers when it burns because all the polymer is converted into smoke. No crosslinking occurs at all in 100% ABS when it burns. Adding PVC to ABS increases char formation slightly, e.g. for 70 ABS/30 PVC the char at 650°C is 6.42%. This char is not all derived from the PVC in the blend as a calculated value for 70 ABS/30 PVC at 650°C would be 4.11%, so the PVC plays some role in promoting char formation in the ABS/PVC blend even in the absence of iron. In the 70 PVC/30 ABS system at 650°C, 11.14% of char is formed. The calculated value is 9.59%, so again PVC is promoting char formation in the blend. On its own, UPVC forms 21.97% char at 500°C, 13.70% char at 650°C, and even at 800°C 10.82% char is formed.

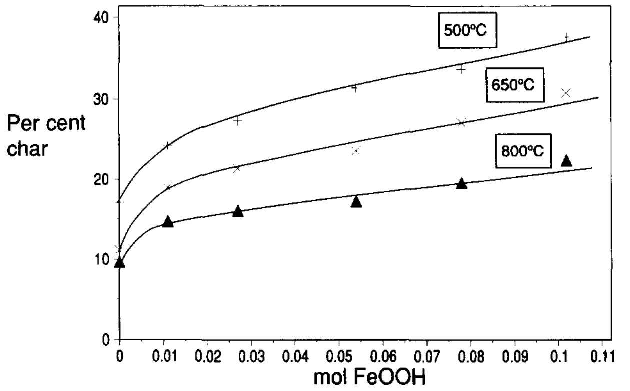


Figure 2 Per cent char against amount of FeOOH for 70 PVC/30 ABS

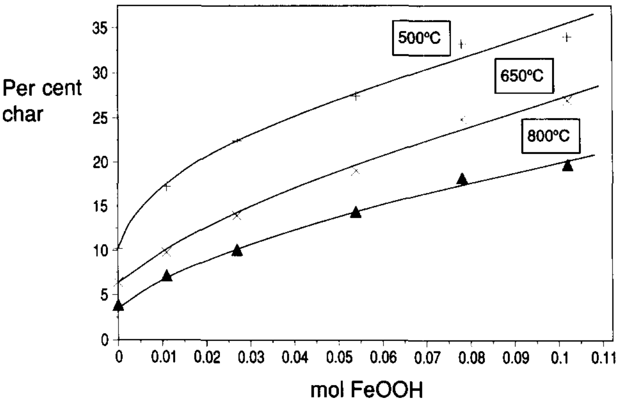
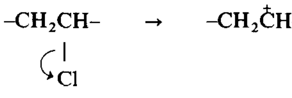


Figure 3 Per cent char against amount of FeOOH for 70 ABS/30 PVC

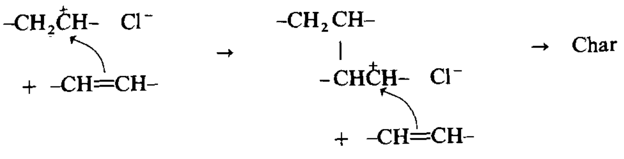
We can attempt to explain these effects by looking at possible decomposition routes for PVC. Very detailed work by Starnes *et al.*[24] has established a general pattern for PVC decomposition and the following argument does not alter this general pattern of behaviour to any great extent. PVC both as UPVC and in blends with ABS may promote crosslinking and char formation by forming reactive carbonium ion centres in the polymer (see *Scheme 1*).



$$-CH_2\underset{Cl}{CH}- \rightarrow -CH_2\overset{+}{C}H- \ Cl^-$$

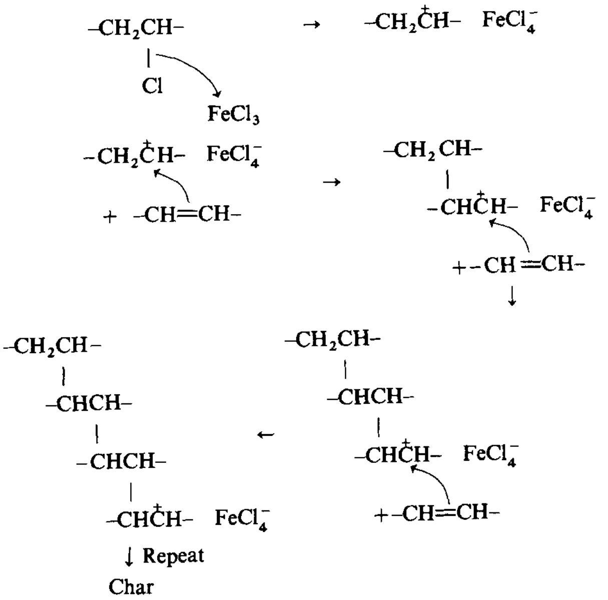
Scheme 1

The carbonium ion species then acts as an active centre for building char either in UPVC itself or in blends of PVC with ABS (see *Scheme 2*).



Scheme 2

Any chemical species present which promotes the formation of these positive centres in the polymer will therefore increase the rate of char formation, and we believe that $FeCl_3$ derived from the iron compound does this. Iron(III) chloride is a very powerful Lewis acid, it is stable, molecular and involatile[25]. As $FeCl_3$ is formed in the PVC, carbonium ion centres are produced and it is these centres which promote crosslinking and char formation (see *Scheme 3*). We have thus explained char formation in UPVC and we can extend this idea to explain the high levels of char formed in ABS/PVC blends, even though ABS is a very poor char former on its own. Madorsky unequivocally found a wide range of alkenes (simple and conjugated) when copolymers of butadiene, styrene and acrylonitrile are pyrolysed[26], and we can use these experimental data to explain why ABS/PVC blends containing iron additives are high char formers, produce less smoke and are much more difficult to ignite and burn.



Scheme 3

On its own, ABS produces large quantities of smoke (see *Figure 1*); however, in the presence of PVC/$FeCl_3$ it produces much less smoke, does not ignite and burn so easily and forms large amounts of carbonaceous char. The decomposition products from both PVC and ABS contain high proportions of unsaturated organic compounds which in the absence of iron provide the fuel and smoke precursors. However, in the presence of $FeCl_3$ (or some other derived iron compound which is a strong Lewis acid) the alkenes produced from the decomposing ABS and PVC react with the active char-forming centres in the PVC to produce more char. Thus, these carbon compounds are converted into char and are not available to act as fuels or promote smoke formation. There is still some residual smoke, however, and the material is not totally resistant to burning because in the decomposition of ABS and PVC some alkanes are produced which are unreactive towards char formation.

A typical formulation of 70 ABS/30 PVC/10 FeOOH has an *LOI* value of 33.8 and a D_{max} value of 54 g^{-1} (70 ABS/30 PVC has an *LOI* of 21.8 and a D_{max} of 104 g^{-1}). These figures speak for themselves. The iron-containing formulation is much less flammable (V-O in the UL94 test)[27] and produces less than half the smoke produced from an iron-free formulation.

A rather important feature of this work relates to the production of HCl. Free HCl is known to promote further PVC decomposition[28] and some argue that HCl is itself a toxic hazard in fires where PVC is decomposed[29,30]. In the specific case of Lepidocrocite, HCl produced from the decomposing PVC reacts with the basic iron(III) oxide

$$FeOOH + HCl \rightarrow FeOCl + H_2O$$

$$FeOCl + 2HCl \rightarrow FeCl_3 + H_2O$$

Thus the reaction of HCl with the iron compound has three beneficial effects: it forms active $FeCl_3$, it indirectly promotes char formation and it removes HCl from the fire gases. We have confirmed experimentally that HCl produced from a 70 ABS/30 PVC/10 FeOOH blend produces 25% less HCl than that from a control formulation containing no iron. In addition we have examined FeOCl as a smoke suppressant in its own right in this system, and although the work is still incomplete, we have evidence that iron(III) oxychloride is itself a good char former.

In conclusion, two other pertinent points are worth making. Other workers have found that high metal/halogen ratios give consistently good flame-retardant performance in commercial formulations[31]. We have also seen in this work that high *LOI* values are obtained when Fe/Cl ratios are much higher than the stoichiometric 1/3.

We have very recently had some heat release work carried out on several of our ABS/PVC/Fe formulations and we will report on this in full at a later date. However, a 70 ABS/30 PVC/10 FeOOH formulation produces about 70% less maximum heat release than an iron-free formulation when examined using the Ohio State Heat Release (OSU RHR) Calorimeter at a heat flux of 25 kW m^{-2}.

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