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CHAR FORMATION FROM POLYOLEFINS

CORRELATIONS WITH LOW-TEMPERATURE OXYGEN UPTAKE AND WITH FLAMMABILITY IN THE PRESENCE OF METAL–HALOGEN SYSTEMS

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Abstract—The oxidative degradation and combustion of polypropylene were investigated by simultaneous thermal analysis (STA) and by flammability measurements. STA shows that, while halogen compounds and metal oxides invariably increase char formation from the polymeric substrate, metal chelates can act both as inhibitors and as promoters of carbonisation. In general, however, there appears to be a direct correlation between the effect of an additive on oxygen uptake and that on char formation. Pro-oxidants which catalyse char formation are effective condensed-phase flame retardants, as a result of their producing fewer volatile species from the polymer.

INTRODUCTION

One very important method of reducing the hazards associated with the degradation and burning of organic polymers consists in the promotion of carbonisation of the polymeric material. Perhaps the greatest benefit to be obtained in this way is a dramatic decrease in the heat generated, since the exothermic combustion of the polymer is replaced, at least in the first instance, by its normally endothermic dehydrogenation. Other advantages include the conservation of the structural integrity of the polymeric material as a result of the retention of substantial amounts of solid carbon and a decrease in the extent of formation of flammable or toxic gaseous products.

Thermoanalytical measurements can, in suitable circumstances, serve as useful indicators of polymer flammability [1, 2]. Although such measurements cannot accurately reflect the very complex reactions involved in the combustion of organic polymers, they can nevertheless be helpful in the elucidation of some of the constituent processes. For example, halogenated additives often change the pattern of thermal degradation of a polymeric substrate by altering either the number of different stages or the temperatures at which these occur [1, 3, 4]; such additives are known, *inter alia*, to catalyse the dehydrogenation of polymeric materials. Metal-containing compounds have been shown to have a useful synergistic flame-retardant action when they are used in conjunction with halogen compounds [3, 5–14]. On the other hand, certain metal chelates are known to affect the initial stages of polymer degradation and especially the oxygen uptake reaction [15–24].

The present paper describes investigations of the correlations between the effects of metal compounds, in particular metal chelates, and halogen compounds on oxygen uptake and on carbonisation. The polymeric substrate chosen for this work was polypropylene, because hydrocarbon polymers do not undergo extensive carbonisation on their own.

EXPERIMENTAL

Materials

Polypropylene (Profax 6301) was kindly supplied by Hercules Incorporated. The halogen compounds used, all high-purity commercial samples, were: bis(2,3-di-chloropropyl phosphite) (46.7 wt% Cl); chloranil (57.7 wt% Cl); pentachloronitrobenzene (60.1 wt% Cl); pentachlorothiophenol (62.8 wt% Cl); Dechlorane-515 plus (Hooker $[(C_5Cl_6)_2 \cdot C_8H_{12}]$: two hexachlorocyclopentadiene molecules joined by a cyclooctane molecule (65 wt% Cl)); hexachloro-*p*-xylene (68.1 wt% Cl); Dechlorane 602 (Hooker $[(C_5Cl_6)_2 \cdot C_4H_4O]$: two hexachlorocyclopentadiene molecules joined by a furan molecule (69 wt% Cl)); Cereclor 70 (ICI, wax grade, mixture of normal alkanes between C_{20} and C_{28}, mainly C_{24}, formula probably near to $[C_{23}H_{28}Cl_{20}]$ (70 wt% Cl)); pentachlorobenzene (70.9 wt% Cl); hexachlorobenzene (74.7 wt% Cl); Dechlorane 4070 (Hooker, $[C_{10}Cl_{12}]$ perchloropentacyclodecane, (78 wt% Cl)) and Dechlorane 604 (Hooker $[(C_5Cl_6)\ C_8Br_4H_4]$: a molecule of tetrabromobenzene joined to one of hexachlorocyclopentadiene via two additional carbon atoms (31 wt% Cl and 46 wt% Br)).

The metal chelates used included compounds of

(a) cobalt, *viz.* (i) Co(III) acetylacetonate (CoAcAc); (ii) tris-*N*-butyl salicylaldimino Co(III) (CoBuSal); (iii) Co(II) bis salicylaldehyde dihydrate (CoSalAl); (iv) ethylene diamine Co(III) (CoED); (v) Co(II) diisopropylsalicylate (CoDIPS); (vi) bis-*N*-phenylsalicylaldimino Co(II) (CoPheSal).

(b) copper, *viz.* (i) *N*-*n*-butylsalicylaldimino Cu(II) (CuNBS); (ii) Cu(II) salicylate (CuSal); (iii) Cu(II) stearate (CuSte); (iv) Cu(II) diisopropylsalicylate (CuDIPS).

(c) Nickel, *viz.* (i) Ni(II) diisopropylsalicylate (NiDIPS); (ii) Ni(II) acetylacetonate (NiAcAc); (iii) bis-*N*-phenylsalicylaldimino Ni(II) (NiPheSal).

(d) Zinc, *viz.* Zn(II) acetylacetonate (ZnAcAc).

The metal oxides were all high-purity commercial samples.

Sample preparation

Polypropylene films, for thermal analysis and for flammability determinations by ASTM D635, were prepared (both when additives were incorporated and when they were not) by mixing the constituents in a Brabender

Plastograph for 15 min at 443 K under N_2. After the mixture had cooled, films of the required thickness (0.5 mm) were prepared by pressing the polymeric crepe at 473 K and 20.7×10^3 kPa pressure. When determinations of the limiting oxygen index (LOI) were to be carried out, samples were prepared by milling the constituents (which contained 2 phr of stearic acid as a lubricant) on a Ruth Schwabenthan two-roll mill (front roller at 443 K, back roller at 453 K) and then pressing the polymeric crepe by heating it for 150 sec at 443 K and finally applying a pressure of 5.5×10^3 kPa for 90 sec, using the procedure described previously [12].

Procedure

Simultaneous thermal analyses [thermogravimetric analysis (TGA), differential thermogravimetric analysis (DTG) and differential thermal analysis (DTA)] were carried out as described previously [25] on a Mettler Thermoanalyser II thermobalance. The samples weighed *ca* 10 mg and the flow rate of the carrier gas (air) was 60 cm^3 min^{-1}.

Flammability was determined by following the procedure recommended for the standard ASTM D635 test and by measuring the LOI on Stanton–Redcroft equipment designed to meet ASTM D2863 test requirements.

RESULTS AND DISCUSSION

Thermoanalytical measurements in the absence of metal chelates

Simultaneous thermal analyses were carried out on polypropylene in the absence and presence of various additives. Table 1 shows some results for pure polypropylene and for the same polymer containing 10 wt% Dechlorane 602, Dechlorane 604 and Cereclor 70 respectively; DTG and DTA traces are shown in Fig. 1. In all cases, there were quite well-defined stages during the thermal degradation of the polymer samples. Melting of pure polypropylene (at 425–35 K) was followed by uptake of oxygen (at 450–70 K) which manifested itself as a weight gain; during the main degradation stage (at 470–670 K) over 90% of the initial weight of the polymer was lost and finally a carbon burn-off stage was observed at 670–720 K. DTA measurements showed that not only the melting process but also unexpectedly the carbon burn-off reaction were endothermic. Kinetic analysis of the apparently single main degradation

Table 1. Simultaneous thermal analysis of polypropylene in the presence of halogen-containing additives*

	No additive	Cereclor 70	Dechlorane 602	Dechlorane 604
Melting				
T (K)	425–35	428–35	—	—
DTA (μV)	−1.8	−1.2	—	—
Oxygen uptake				
Wt%	0.304	0.176	0.146	0.120
T range (K)	450–70	435–40	425–40	390–408
DTA max.	—	—	—	4.5 μV–407 K
First weight loss				
Wt%	1.4	4.8	6.1	6.6
T range (K)	470–95	440–86	440–74	408–61
T max. rate (K)	491	474	462	450
Max. rate (mg min^{-1})	0.11	0.07	0.11	0.10
T DTA max. (K)	405	471	462	—
DTA max. (μV)	1.5	5.0	9.5	—
Second weight loss				
Wt%	95.2	60.2	56.2	73.4
T range (K)	495–673	486–668	474–632	461–637
T max. rate (K)	554	638	509	549
Max. rate (mg min^{-1})	0.62	0.41	0.23	0.30
T DTA max. (K)	547	636	587	574
DTA max. (μV)	23.7	6.5	9.0	10.0
Third weight loss				
Wt%	—	27.4	32.0	12.2
T range (K)	—	668–700	632–701	637–710
T max. rate (K)	—	685	669	668
Max. rate (mg min^{-1})	—	0.48	0.29	0.11
T DTA max. (K)	—	690	694	670
DTA max. (μV)	—	25.0	15.0	2.0
Carbon burn-off				
Wt%	1.45	6.60	3.86	2.75
T range (K)	673–717	700–46	701–65	710–52
T max. rate (K)	685	721	749	739
Max. rate (mg min^{-1})	0.05	0.15	0.15	0.07
T DTA max. (K)	693	711	—	746
DTA max. (μV)	−7.0	1.0	—	−4.0
Total weight loss				
Wt%	98.4	94.4	92.2	88.5
T_D (K)†	470	435	440	408
$T_{1\%}$ (K)‡	486	462	457	438

*10 wt% additives, heating rate: 5 deg min^{-1}.
†Minimum decomposition temperature.
‡Temperature for 1 wt% decomposition.

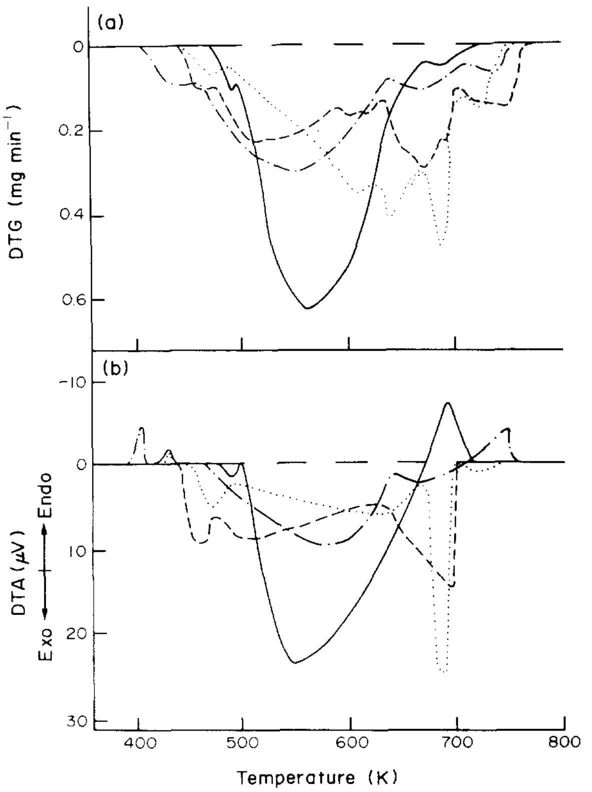

Fig. 1. Simultaneous thermal analysis of polypropylene containing 10 wt% of halogenated additives. (——) polypropylene; (----) polypropylene + Dechlorane 602; (-·-·-·-) polypropylene + Cereclor 70; (·····) polypropylene + Dechlorane 604; (—) background. (a) DTG; (b) DTA.

stage (by determination of weight loss, rate of weight loss and temperature at a large number of points) [25] showed that two separate stages were in fact involved, *viz.* (i) a small initial stage corresponding to decomposition of the peroxidised substrate and (ii) further breakdown of the products of peroxide decomposition to leave a carbonaceous residue.

When the polymer contained 10 wt% of a chlorinated additive, the changes included the introduction of an extra weight-loss stage. These additives invariably increased the amount of char formed from the polymer, even if allowance was made for the char derived from the additives themselves; in other words they produced "excess carbon", which may be defined as:

$$\text{Excess carbon} = \text{Total carbon} - \left[\frac{(\text{Polymer carbon} \times \text{wt\% substrate})}{100} + \sum\frac{(\text{Additive carbon} \times \text{wt\% additive})}{100}\right].$$

The extent of carbonisation, i.e. the amount of char formed, can be estimated from the weight lost in the carbon burn-off stage.

All the chlorinated additives delayed to higher temperatures the burn-off of the carbon formed from the polymer; this stage then tended to occur at a temperature closer to that at which the char derived from the additive itself was oxidised (Table 2). It is perhaps surprising that the amount of excess carbon formed bears no direct relationship to the chlorine content of the additive.

The amounts of total carbon and of excess carbon formed from polymer samples containing 10 wt% Cereclor 70 and 5 wt% of various metal oxides are shown in Table 3. The extent of formation of excess carbon was invariably further increased by the presence of the metal oxides, although the temperature of maximum rate was sometime higher and sometimes lower than that found in the absence of the oxides.

Varying proportions of four chlorinated additives, *viz.* Dechlorane-515 plus, Dechlorane 4070, Dechlorane 604 (which contains bromine and chlorine) and Cereclor 70, all of which gave intrinsically more carbon than the polymer substrate, were incorporated into polypropylene and the carbon burn-off stage was then studied. In all cases, the amounts of carbon burnt off (and thus of excess carbon formed) increased with additive concentration: the temperature of the maximum rate of carbon burn-off also

Table 2. Carbon formation from polypropylene containing 10 wt% of a halogenated additive*

	C additive		C mixture		
Additive	Wt%	*T* max. rate (K)	Wt%	*T* max. rate (K)	Excess carbon (wt%)
None	—	—	1.45	685	—
2,3-DCP†	19.30	713	6.50	793	3.27
Chloranil	1.00	713	1.90	747	0.50
Pentachloronitrobenzene	3.25	698	2.40	717	0.77
Pentachlorothiophenol	17.00	692	6.10	758	3.10
Dechlorane-515 plus	3.35	743	8.05	758	6.41
Hexachloro-*p*-xylene	—	—	3.15	743	1.85
Dechlorane 602	2.80	747	5.44	749	3.86
Cereclor 70	25.70	698	6.60	721	2.73
Pentachlorobenzene	1.35	698	3.30	702	1.86
Hexachlorobenzene	—	—	8.70	749	7.40
Dechlorane 4070	3.73	758	9.25	758	7.57
Dechlorane 604	13.13	766	2.75	739	0.13

*Heating rate: 5 deg min^{-1}.
†2,3-DCP: bis(2,3-dichloropropyl phosphite).

Table 3. Effect of metal oxides on carbon formation from polypropylene*

Metal oxide	Total carbon: T max. rate (K)	Total carbon: Wt%	Excess carbon (wt%)
None	741	6.60	2.73
MoO_3	766	6.81	2.94
NiO	763	7.08	3.21
Ag_2O	773	8.52	4.65
SnO_2	786	8.61	4.74
Sb_2O_3	762	9.33	5.46
CuO	747	9.75	5.88
Cr_2O_3	762	10.10	6.23
PbO_2	762	10.90	7.03
ZnO	747	11.32	7.45
CrO_3	731	11.60	7.73
CdO	731	12.60	8.73
MgO	758	13.80	9.93
Bi_2O_3	710	14.20	10.33

*85 wt% polypropylene, 10 wt% Cereclor 70, 5 wt% metal oxide.

increased with loading of the halogen compound except with Dechlorane 604 (Table 4). A small proportion of this compound raised the temperature of carbon burn-off by *ca* 100 K, although larger amounts lowered the temperature of maximum rate of reaction. The amount of excess carbon formed was smallest for Cereclor 70 and largest for Dechlorane 4070 but the specific effectiveness of the additives in producing such carbon, e, as defined by the equation

$$e = \frac{\text{Excess carbon (wt\%)}}{\text{Additive loading (wt\%)}},$$

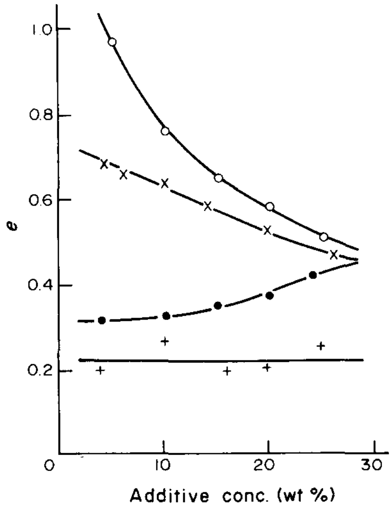

Fig. 2. Effectiveness, e, of halogenated additives as promoters of the formation of excess carbon from polypropylene. (○) Dechlorane 4070; (●) Dechlorane 604; (×) Dechlorane-515 plus; (+) Cereclor 70.

progressively decreased in the case of the two purely chlorinated Dechloranes.

However, the effectiveness of Dechlorane 604 increased with its concentration, so that, at very high loadings, the relative differences in the amounts of excess carbon formed between this and the other Dechloranes is much smaller than that at low loadings. The results in Fig. 2 show that, at the limit, the value of e for all the additives except Cereclor 70 is *ca* 0.45. The difference between the excess carbon (which in practice is that produced by the interaction

Table 4. Carbon formation from polypropylene containing increasing amounts of halogenated additives*

Additive	Conc. (wt%)	Total carbon (wt%)	Excess carbon (wt%)	Component carbon (wt%)	e	T max. rate (K)
None	—	1.45	—	—	—	685
Dechlorane-515 plus	4	4.25	2.72	1.53	0.68	745
Dechlorane-515 plus	6	5.50	3.94	1.56	0.66	747
Dechlorane-515 plus	10	8.05	6.41	1.64	0.64	758
Dechlorane-515 plus	14	9.90	8.18	1.72	0.58	765
Dechlorane-515 plus	20	12.45	10.62	1.83	0.53	769
Dechlorane-515 plus	26	14.10	12.16	1.94	0.47	773
Dechlorane 4070	5	6.40	4.84	1.56	0.97	748
Dechlorane 4070	10	9.25	7.57	1.68	0.76	758
Dechlorane 4070	15	11.60	9.81	1.79	0.65	768
Dechlorane 4070	20	13.65	11.74	1.91	0.59	773
Dechlorane 4070	25	14.90	12.88	2.02	0.52	778
Cereclor 70	4	3.21	0.79	2.42	0.20	732
Cereclor 70	10	6.60	2.73	3.87	0.27	741
Cereclor 70	16	8.60	3.24	5.36	0.20	750
Cereclor 70	20	10.55	4.25	6.30	0.21	754
Cereclor 70	25	14.10	6.49	7.51	0.26	762
Dechlorane 604	4	2.75	1.27	1.48	0.32	783
Dechlorane 604	10	4.75	3.23	1.52	0.33	779
Dechlorane 604	15	6.90	5.35	1.55	0.36	771
Dechlorane 604	20	9.00	7.41	1.59	0.37	766
Dechlorane 604	25	12.20	10.58	1.62	0.42	753

*Heating rate: 5 deg min^{-1}.

Table 5. Activation energy for thermal decomposition of hydroperoxide*

Additive	Conc. (wt%)	Activation energy (kJ mol^{-1})
None	—	39.8
Cereclor 70	10	41.2
Dechlorane 4070	10	40.1
Dechlorane 604	10	40.5
Dechlorane-515 plus	10	40.7
Dechlorane-515 plus	4	41.4
Dechlorane-515 plus	20	40.9
Dechlorane-515 plus	26	40.6

*Heating rate: 5 deg min^{-1}.

of polypropylene with the additives) and the amount of carbon that would be formed separately from the various components (component carbon) is generally positive for all three Dechloranes but negative for Cereclor (Table 4). This reinforces the previous evidence that, while all the halogenated additives promote char formation, Cereclor is the least effective in this respect. Table 5 gives the activation energies for the main decomposition stage for polypropylene alone and for the polymer containing 10 wt% of each of the four halogenated additives. These were calculated by plotting a function of residual weight and temperature against the reciprocal temperature for different orders of reaction in polymer [26] and were found to be almost independent of the presence of the additive. Similarly the value of the activation energy was not appreciably affected by the concentration of Dechlorane-515 plus (Table 5). In contrast, the activation energy for the carbon burn-off reaction increased monotonously, albeit rather slowly, with additive concentration (Table 6). The increase in the amount of char produced in the presence of Dechlorane-515 plus is accompanied by an increase in oxygen uptake, and indeed the amount of oxygen reacting per unit weight of polymer varies linearly with the concentration of this additive (Fig. 3).

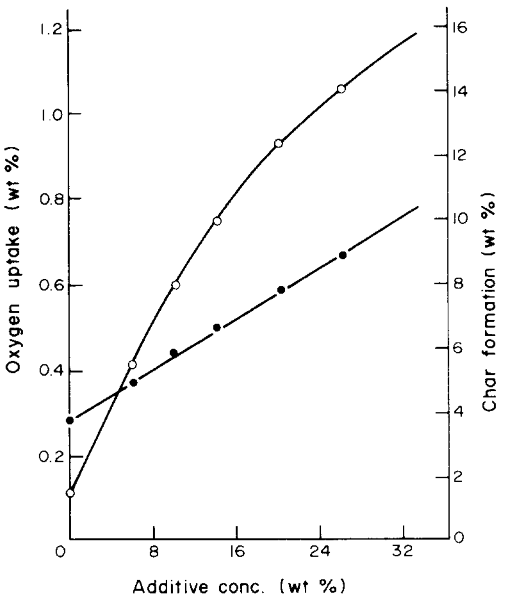

Fig. 3. Oxygen uptake by and carbon formation from polypropylene containing increasing proportions of Dechlorane-515 plus. (●) oxygen uptake; (○) carbon formation.

Thermoanalytical measurements in the presence of metal chelates

Metal chelates are known to be particularly effective in altering the oxygen uptake by polyolefins [15, 24]. These compounds may act as pro-oxidants in which case they increase the amount of oxygen absorbed by the polymer in the initial stages of degradation. On the other hand, certain metal chelates are anti-oxidants, i.e. they inhibit oxidation of the associated polymeric substrate. Table 7 shows the extents of carbonisation of and of oxygen uptake by polypropylene containing Dechlorane-515 plus and various metal chelates.

Table 6. Activation energies for carbon burn-off reaction*

Dechlorane-515 plus (wt%)	Activation energy (kJ mol^{-1})
0.0	228.8
4.0	240.1
6.0	242.0
10.0	244.0
14.0	245.0
20.0	249.0
26.0	251.0

*Heating rate: 5 deg min^{-1}.

The large majority of the chelates studied did not increase the amount of char formed from polymer–halogen systems; they were in fact both anti-oxidants and inhibitors of char formation. However a few of the metal chelates investigated (CoAcAc, CuNBS and ZnAcAc) were pro-oxidants and at the same time promoters of char formation, while some others (NiAcAc, NiPheSal and CuSte)

Table 7. Effect of metal chelates on oxygen uptake and carbon formation*

Additive	Oxygen uptake (wt%)	Total carbon (wt%)
None	0.200	5.13
CoAcAc	0.278	6.92
CoBuSal	0.100	3.67
CoSalAl	0.122	2.81
CoED	0.189	5.08
CoDIPS	0.189	3.89
CoPheSal	0.122	3.85
CuNBS	0.205	7.18
CuSal	0.167	2.81
CuSte	0.100	5.76
CuDIPS	0.078	4.34
NiDIPS	0.167	3.90
NiAcAc	0.100	5.87
NiPheSal	0.110	6.55
ZnAcAc	0.211	7.64

*90 wt% polypropylene, 9 wt% Dechlorane-515 plus; 1 wt% metal chelate; heating rate: 10 deg min^{-1}.

Table 8. Effect of metal chelates on the thermal decomposition of polypropylene*

	Oxygen uptake		Hydroperoxide breakdown			Carbon burn-off		
Metal chelate	Gain (wt%)	T max. rate (K)	Loss (wt%)	T max. rate (K)	Activation energy (kJ mol^{-1})	Loss (wt%)	T max. rate (K)	Activation energy (kJ mol^{-1})
None	0.240	473	0.32	479	48.7	2.85	704	115.7
None†	0.271	480	0.92	486	50.3	18.81	747	187.0
NiAcAc	0.140	460	1.12	479	43.4	4.18	704	75.7
NiAcAc†	0.143	473	1.30	479	46.4	16.68	731	200.3
CuSte	0.120	460	1.17	473	39.5	4.97	691	123.4
CuSte†	0.143	467	1.32	479	45.9	19.05	742	118.0
CoAcAc	0.270	436	1.48	454	29.3	5.40	691	198.6
CoAcAc†	0.414	429	2.39	448	35.7	26.65	742	132.5
ZnAcAc	0.260	447	1.43	468	40.1	4.79	726	68.6
ZnAcAc†	0.400	436	2.09	454	35.9	23.83	731	234.5

*70 wt% or 99 wt% polypropylene; 1 wt% metal chelate; halogen compound: Dechlorane-515 plus, heating rate: 10 deg min^{-1}.

†Contains 29 wt% Dechlorane-515 plus.

were anti-oxidants but nevertheless catalysed the formation of char. There thus appears to be in general a direct relationship between oxygen uptake and carbonisation; an increase in one is normally accompanied by an increase in the other, and vice-versa, but this behaviour is not observed with all metal chelates. It has been proposed [17, 22] that metal chelates function initially as anti-oxidants by converting alkylperoxy radicals to more stable species. Once the chelate has reacted, rapid oxidation of such species occurs due to metal-catalysed decomposition of hydroperoxides. The present results suggest, however, that not all metal chelates operate by a single mechanism.

Four of the metal chelates, selected from the two different classes of char promoters and each containing a different metal, were subjected to thermal analysis; some results are shown in Table 8. All of these compounds affected the extent of oxygen uptake by polypropylene. The effects observed with the anti-oxidants were independent of the presence of Dechlorane; with the pro-oxidants there was little influence on oxygen uptake when the polymer contained no Dechlorane. The temperature of maximum rate of oxygen uptake was decreased by all the metal chelates and this reduction was naturally most pronounced with the pro-oxidants. Other features were:

(a) all metal chelates tended to increase the weight loss during the carbon burn-off and hydroperoxide breakdown stages;

(b) the temperatures of maximum rate of reaction for the different stages were never greatly altered by the anti-oxidants or by the pro-oxidants in the absence of chlorine;

(c) the activation energies for hydroperoxide breakdown were decreased by the pro-oxidants but scarcely affected by the anti-oxidants;

(d) the activation energies for carbon burn-off were tremendously, and somewhat erratically, affected by all the metal chelates.

These results suggest that, while the pro-oxidants do not alter the basic mechanism of decomposition of the polymeric substrate, the anti-oxidants cause clear mechanistic changes. All the additive systems used appear to act primarily in the condensed phase.

Flammability measurements

Tables 9 and 10 show the results of burning experiments on polypropylene–additive mixtures carried out by ASTM D635; Table 11 gives results obtained according to ASTM D2863. At least 20 wt% of Dechlorane-515 plus was needed before extensive carbonisation and slight dripping were observed during the combustion of a sample which could be classified by ASTM D635 as "self-extinguishing"; the same effect could be achieved with only 1 wt% of the pro-oxidants studied (Table 9). This is a very important result because it shows that flame-retardant activity can arise from the action of compounds

Table 9. Effect of increasing amounts of Dechlorane-515 plus and of 1 wt% of various metal chelates on the flammability of polypropylene, by ASTM D635

Metal chelate	Dec. (wt%)	Carbonisation	Dripping	Test result	Extent of burn	Ignition time (sec)
—	0	Very slight	Extensive	Burning	12.7 cm min^{-1}	5
—	10	Slight	Extensive	Burning	10.9 cm min^{-1}	5
—	20	Extensive	Slight	Self-ext.	3.2 cm	15
—	25	Extensive	Slight	Non-burning	—	20
—	30	Extensive	Slight	Non-burning	—	>30
CoSalAl	0	None	Extensive	Burning	16.5 cm min^{-1}	<5
NiAcAc	0	Slight	Extensive	Burning	11.2 cm min^{-1}	5
CuSte	0	Slight	Extensive	Burning	11.4 cm min^{-1}	5
CoAcAc	0	Extensive	Slight	Self-ext.	5.1 cm	10
ZnAcAc	0	Extensive	Slight	Self-ext.	5.1 cm	10

Table 10. Combined effects of Dechlorane-515 plus and metal chelates on the flammability of polypropylene, by ASTM D635

Metal chelate*	Dec. (wt%)	Carbonisation	Dripping	Test result	Extent of burn	Ignition time (sec)
CoSalAl	9	Slight	Extensive	Burning	12.7 cm min^{-1}	5
CoSalAl	29	Extensive	Slight	Non-burning	—	30
NiAcAc	9	Slight	Extensive	Burning	10.7 cm min^{-1}	5
NiAcAc	29	Extensive	None	Non-burning	—	30
CuSte	9	Slight	Extensive	Burning	10.8 cm min^{-1}	5
CuSte	29	Extensive	None	Non-burning	—	30
CoAcAc	9	Extensive	Slight	Self-ext.	3.8 cm	10
CoAcAc	29	Extensive	None	Non-burning	—	>30
ZnAcAc	9	Extensive	Slight	Self-ext.	4.1 cm	10
ZnAcAc	29	Extensive	None	Non-burning	—	>30

*1 wt%.

which significantly decrease the thermal stability of the polymer. The anti-oxidants used did not significantly alter, on their own, either the extent of carbonisation or any of the other burning parameters.

When the system contained 9 wt% Dechlorane-515 plus and 1 wt% metal chelate (Table 10), the results were remarkably similar to those found in the absence of chlorine, except that a slightly more thermally stable polymeric system was obtained. When the system contained 29 wt% of the chlorinated additive, however, the burning characteristics of the polymer were improved, even in the presence of the anti-oxidants.

Determinations of LOI (Table 11) showed that the chlorinated additives decreased polymer flammability but that 10 wt% of these compounds was not sufficient to produce a flame-retardant system, since in general an LOI of at least 26 is needed for a realistic degree of flame retardance. 30 wt% of Cereclor 70 was already sufficient to produce a system which burned only with great difficulty. When an inhibitor of char formation, e.g. CoSalAl, was added to a polypropylene–Cereclor system, the flammability was increased. As regards promoters of char formation, NiAcAc had little effect on either the 90/10 or 70/30 polymer–additive systems, while CuSte decreased the flammability of a sample containing little chlorine but did not affect the combustion behaviour of highly chlorinated systems. Finally, the pro-oxidants which also promoted char formation, *viz.* ZnAcAc, lowered the flammability of both systems but again the effect was most pronounced with low chlorine contents.

CONCLUSION

Metal chelates strongly affect the extent of carbon formation from, and of oxygen uptake by, polypropylene, as a result of reactions occurring mainly in the condensed phase. The chlorinated additives, which produce increased oxygen uptake, appear to do so by dehydrogenating larger proportions of the side chains, i.e. the methyl groups attached to the tertiary carbon atoms in polypropylene, which subsequently undergo peroxidation. These peroxidised side chains then appear to cross-link to leave a carbon skeleton and this increases the extent of carbonisation. All the metal chelates used, both in the presence and absence of halogen compounds, tend to destabilise the polymer which thus undergoes thermal reactions at lower temperatures. This effect can be brought about by catalysing the decomposition of hydroperoxides, by causing the scission of increasing proportions of C—C bonds or both. The pro-oxidants catalyse mainly the cleavage of bonds between the main polymer chain and the side chains; the latter then cross-link so that the structure remaining contains a higher proportion of charry residue. The anti-oxidants, on the other hand, probably cause

Table 11. Effect of halogen compounds and metal chelates on LOI of polypropylene

Polypropylene (wt%)	Halogen compound	Concn (wt%)	Metal chelate	Concn (wt%)	LOI
100	—	—	—	—	18.4
90	Dechlorane 602	10	—	—	21.1
90	Cereclor 70	10	—	—	23.4
90	Dechlorane 604	10	—	—	24.9
70	Cereclor 70	30	—	—	26.7
90	Cereclor 70	9	CoSalAl	1	21.1
90	Cereclor 70	9	NiAcAc	1	22.8
90	Cereclor 70	9	CuSte	1	25.4
90	Cereclor 70	9	ZnAcAc	1	26.9
70	Cereclor 70	29	CoSalAl	1	24.4
70	Cereclor 70	29	NiAcAc	1	26.8
70	Cereclor 70	29	CuSte	1	26.8
70	Cereclor 70	29	ZnAcAc	1	27.2

principally increased main-chain scission. If these scissions occur at positions which are relatively close to one another, there will be volatilisation of the decomposition products, so that less char is formed. The anti-oxidant char promoters cause, however, main-chain scissions at positions very distant from one another so that volatilisation is impossible and the increased charring must be a consequence of the cross-linking which eventually occurs.

These results emphasise once more the value of thermoanalytical measurements in the elucidation of factors governing the flammability of organic polymers [1]. It is clear however that any extrapolations from one type of measurement to the other cannot be carried out in an entirely straightforward fashion but must take into account the complexities of the processes involved in polymer combustion.

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REFERENCES

1. C. F. Cullis and M. M. Hirschler, *Polymer* **24,** 834 (1983).
2. M. M. Hirschler, *Eur. Polym. J.* **19,** 121 (1983).
3. J. D. Donaldson, J. Donbavand and M. M. Hirschler, *Eur. Polym. J.* **19,** 33 (1983).
4. M. M. Hirschler and O. Tsika, *Eur. Polym. J.* **19,** 375 (1983).
5. S. Coppick, *Flameproofing Textile Fabrics—Am. chem. Soc. Monogr. Ser. No. 104* (Edited by R. W. Little), p. 239. Reinhold, New York (1947).
6. R. W. Little (Ed). *Flameproofing Textile Fabrics—Am. chem. Soc. Monogr. Ser. No. 104,* p. 248. Reinhold, New York (1947).
7. G. S. Learmonth, A. Nesbitt and D. G. Thwaite, *Br. Polym. J.* **1,** 149 (1969).
8. J. J. Pitts, *Flame Retardancy of Polymeric Materials* (Edited by W. C. Kuryla and A. J. Papa), Vol. 1, p. 133. Dekker, New York (1973).
9. C. F. Cullis and M. M. Hirschler, *The Combustion of Organic Polymers.* Oxford University Press, Oxford (1981).
10. C. F. Cullis, *Developments in Polymers Degradation* (Edited by N. Grassie), Vol. 3, p. 283. Applied Science, London (1981).
11. M. M. Hirschler, *Developments in Polymer Stabilisation* (Edited by G. Scott), Vol. 5, p. 107. Applied Science, London (1982).
12. F. K. Antia, C. F. Cullis and M. M. Hirschler, *Eur. Polym. J.* **17,** 451 (1981).
13. F. K. Antia, C. F. Cullis and M. M. Hirschler, *Eur. Polym. J.* **18,** 95 (1982).
14. F. K. Antia, P. J. Baldry and M. M. Hirschler, *Eur. Polym. J.* **18,** 167 (1982).
15. G. Scott, *Atmospheric Oxidation and Antioxidants.* Elsevier, London (1965).
16. N. Uri, *Chem. Ind.* 2060 (1967).
17. R. P. R. Ranaweera and G. Scott, *Chem. Ind.* 774 (1974).
18. A. Tkac, *Int. J. Radiat. Phys. Chem.* **7,** 457 (1975).
19. N. Uri, *Chem. Ind.* 199 (1975).
20. R. P. R. Ranaweera and G. Scott, *Eur. Polym. J.* **12,** 825 (1976).
21. G. Scott, *Am. chem. Soc., Symp. Ser.* **25,** 340 (1976).
22. A. W. Benbow, C. F. Cullis and H. S. Laver, *Polymer* **19,** 824 (1978).
23. J. Holcik, M. Kosik, A. W. Benbow and C. F. Cullis, *Eur. Polym. J.* **14,** 769 (1978).
24. H. S. Laver, *Developments in Polymer Stabilisation* (Edited by G. Scott), Vol. 1, p. 167. Applied Science, London (1979).
25. M. M. Hirschler, *Eur. Polym. J.* **18,** 462 (1982).
26. A. W. Coats and J. P. Redfern, *Nature* **201,** 68 (1964).