The significance of thermoanalytical measurements in the assessment of polymer flammability

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Thermoanalytical techniques have been widely used for the study of polymer decomposition processes, but they cannot accurately represent the very complex process of polymer combustion. The present work discusses some of the advantages and limitations involved in the use of thermoanalytical measurements to elucidate selected aspects of the constituent processes involved during the combustion of an organic polymer. There is no correlation between the flammability of different organic polymers and their thermal stability, even if the latter property is represented by an improved parameter such as the temperature at which 1% of the polymer has decomposed. An attempt has been made to correlate the inverse of the flammability (as measured by the limiting oxygen index) with the ratio of the heats of combustion and of gasification; but the results are not entirely satisfactory. Thermal analysis can, however, be very useful for the study of the effects of additives on a polymeric substrate. The lower heating rates involved, compared with those associated with a fire, allow determinations to be made not only of the ease of decomposition of an organic polymer but also of the thermochemistry of its reactions, of the effects of different atmospheres and of the extent of volatilization of certain species. In particular, thermoanalytical measurements carried out on a polymer–additive system can aid in the prediction of the effectiveness and mode of action of additives as flame retardants.

Keywords Thermoanalytical measurements; flammability; thermal stability; organic polymers; flame retardants; metal oxide–halogen systems

INTRODUCTION

All organic polymers will burn under appropriate experimental conditions and their combustion is invariably a complex process which involves a number of interrelated, although conceptually quite distinct, stages. Thus, in the sustained flaming combustion which occurs with many thermoplastics, the polymer may be envisaged as first suffering decomposition in the condensed phase to give combustible volatile products; these products then enter the flame zone above the decomposing polymer where they burn in the gas phase, yielding the final products (generally carbon oxides and steam) and liberating heat; and finally at least some of this heat is conducted, and to a smaller extent radiated, back to the polymer where it causes evolution of a further supply of volatile products.

The stage in the combustion 'cycle' which might be expected to be of paramount importance in determining polymer flammability is the initial breakdown of the polymer. Thus, if it were possible to design polymers of infinite thermal stability, no volatile combustible products would be formed from them and combustion would not take place. Over the last 50 years or so, a considerable number of very thermally stable and virtually non-flammable polymers[1–4] have in fact been developed for special applications, mainly in connection with the US Space Program and for the manufacture of heat-protective clothing. However, with the very extensive range of polymers which are widely used and of only moderate thermal stability, an important factor controlling flammability is not only the ease of breakdown but also the mechanism of thermal decomposition, which can vary greatly from one polymer to another.

In some cases the breakdown process principally involves ruptures of the main polymer chain with the resulting formation of volatile and generally combustible products. Thus the polymer may either break down by random scission of the main chain or alternatively completely depolymerize or 'unzip' to reform the original monomer fragments of which it was composed; end-chain scission occurs, for example, with poly(methyl methacrylate) and like random-chain scission leads to virtually complete gasification and loss of physical integrity of the polymer. With other polymers, such as poly(vinyl chloride), the breakdown process consists largely in the 'stripping' of the polymer chains with the release of some volatile products but with the 'backbone' remaining intact and continuing to provide some structural integrity. As the other extreme to depolymerization, however, the polymer may suffer crosslinking or simply undergo a molecular rearrangement, with hardly any weight loss or formation of volatile products, to give a polymer with a different structure, as happens, for example, with polyacrylonitrile.

Various types of products may thus be formed when a polymer breaks down and the nature of the decomposition products is clearly a very important factor determining the readiness with which a polymer burns. The evolution of large volumes of highly combustible

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gases will clearly facilitate the flaming combustion of a polymer, unless of course this leads to a gaseous fuel–oxidant mixture too rich to burn. However, even the formation of non-combustible gaseous products tends to break up the polymer structure, so that small fragments of decomposing solid material become entrained in the escaping combustion gases, later appearing in the flame as soot particles. Liquid products are not as readily combustible as gaseous products but liquids tend to spread heat to adjacent parts of the polymer structure. Undoubtedly then a solid residue is the least flammable product, because it helps to preserve structural integrity and thus to protect neighbouring parts of the polymer from decomposition.

The present work attempts to discuss some of the advantages and limitations of the use of thermoanalytical techniques, with the object of elucidating selected aspects of the very complex process of polymer combustion.

THERMAL STABILITY AND FLAMMABILITY OF VARIOUS ORGANIC POLYMERS

The different mechanisms of thermal decomposition and the wide range of types and amounts of products formed certainly constitute one of the main reasons why overall thermal stability, as determined in the laboratory, is not a good criterion of polymer flammability. The absence of any well defined relationship is shown in *Table 1*, which gives the flammability, expressed as the limiting oxygen index (*LOI*), and the thermal stability, taken as the temperature at which decomposition starts to occur (T_D), of a number of organic polymers. In practice, however, it is not always easy to determine T_D from thermogravimetric curves and in many ways a more convenient measure of thermal stability is the temperature at which a given small percentage (e.g. 1%) of the polymer has decomposed (*Figure 1*).

This quantity ($T_{1\%}$) is much less sensitive than T_D to changes in sample size (*Table 2*) and in heating rate (*Table 3*). *Table 4* shows some results for poly(vinylidene fluoride) which indicate that, although, as expected, the value of $T_{1\%}$ changes with the nature of the surrounding atmosphere, it is, for a given atmosphere, largely independent of heating rate. Even so, there is little evidence of any correlation between this improved criterion of thermal stability and polymer flammability (*Table 1*).

Table 1 Comparison of flammabilities and thermal stabilities of some organic polymers

Polymer	*LOI*	T_D (K)*	$T_{1\%}$ (K)*
Polyoxymethylene	15.7	503	548
Poly(methyl methacrylate)	17.3	528	555
Polypropylene	17.4	531	588
Polyethylene (LDPE)	17.4	490	591
Polyethylene (HDPE)	17.4	506	548
Polystyrene	17.8	436	603
ABS copolymer	18.0	440	557
Polybutadiene	18.3	482	507
Polyisoprene	18.5	460	513
Cotton	19.9	379	488
Poly(vinyl alcohol)	22.5	337	379
Wool	25.2	413	463
Nylon-6	25.6	583	
Silicone oil	32.0	418	450
Poly(vinylidene fluoride)	43.7	628	683
Poly(vinyl chloride)	47.0	356	457
Polytetrafluoroethylene	95.0	746	775

* Sample, 10 mg; atmosphere, N_2; heating rate, 10 deg min^{-1}

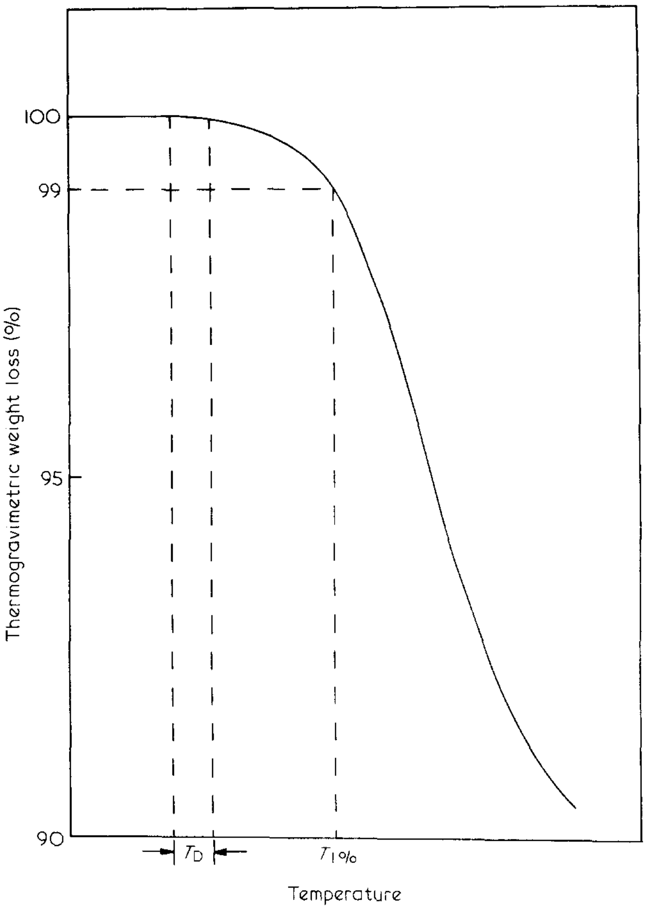

Figure 1 Thermogravimetric behaviour of a polymeric system

Another reason for this lack of correlation is the uncertainty regarding the extent to which oxygen is involved during the decomposition of any given polymer under combustion conditions. Very careful analysis of burning polymer systems shows that, at least in certain cases, some oxygen is present in the immediate vicinity of the polymer surface and even within the polymeric phase[5-7]. Unless the varying extents of oxygen involvement for different polymers are known and can be allowed for, there would not then be expected to be a close correlation between the susceptibility of polymers to purely thermal decomposition and their flammability.

However, another very important factor in the operation of the cycle for the flaming combustion of a polymer must be the heat of combustion of the gaseous decomposition products. The rate of temperature rise of the polymer depends on the rate of flow of heat to it. The heat flux is of course a function of the heat of combustion, although it must also depend on both the heat capacity

Table 2 The effect of sample size on T_D and $T_{1\%}$ for polybutadiene

Mass (mg)	T_D (K)*	$T_{1\%}$ (K)*
9.6	524	564
19.0	521	562
36.5	508	562
78.2	482	567

* Atmosphere, N_2; heating rate, 3 deg min^{-1}

Table 3 The effects of heating rate on T_D and $T_{1\%}$ for different polymers

Polymer	Heating rate (deg min^{-1})	T_D (K)*	$T_{1\%}$ (K)*
Poly(4-vinyl pyridine)	1	298	310
	10	298	308
Silicone oil	1	376	436
	10	418	450
Poly(vinyl chloride)	1	360	455
	10	356	457
Poly(ethylene glycol)	1	413	501
	10	444	507
Polyisoprene	1	289	523
	10	460	513
Polyoxymethylene	1	474	542
	10	503	548
Poly(methyl methacrylate)	1	463	543
	10	528	555
Polyethylene (HDPE)	1	485	548
	5	506	546
	10	506	548
ABS copolymer	5	360	548
	10	440	557
Poly(vinyl acetate)	1	361	559
	10	514	557
Polybutadiene (HTPB)	1	524	564
	3	521	562
	5	508	562
	10	482	567
Ethylene–vinyl acetate copolymer	1	497	570
	10	517	564
Polystyrene (HIPS)	1	425	593
	10	436	603
Polytetrafluoroethylene	1	714	762
	5	705	766
	10	746	775

* Sample, 10 mg; atmosphere, N_2

and the thermal conductivity of the polymer as well as on the latent heat of gasification or of any other change which may occur in the polymer during the heating process. The heat capacities of most organic polymers lie within a relatively narrow range (*Table 5*). Although the thermal conductivities vary rather more widely (*Table 6*), the values for polymers are so low compared with those of other materials, such as metals or even ceramics, that the ability of the polymer to conduct heat away from the source is unlikely to play any appreciable part in the balance which maintains the polymer combustion cycle. Thus the two thermal parameters, the variation of which from one polymer to another is likely to be most significant, are the heat of gasification of the polymer and the heat of combustion of the gaseous decomposition products (*Table 7*). There is in fact little correlation between the heat of combustion and the reciprocal of the limiting oxygen index[8] (*Figure 2*). However, it can be shown that a more significant quantity controlling the ease with which organic polymers undergo sustained combustion should be the ratio of the heat of combustion to the heat of gasification[8] (*Table 7*). Nevertheless the correlation between the flammabilities of different polymers and values of this ratio is still not very good (*Figure 3*).

Table 4 The effects of heating rate on T_D and $T_{1\%}$ for poly(vinylidene fluoride) in different surrounding atmospheres

Heating rate (deg min^{-1})	Atmosphere	T_D (K)*	$T_{1\%}$ (K)*
1	N_2	541	678
5	N_2	604	684
10	N_2	628	683
100	N_2	463	674
5	Air	609	652
25	Air	556	661
100	Air	478	647
5	O_2	588	607
25	O_2	576	605
100	O_2	476	606

* Sample, 10 mg

Table 5 Heat capacities of some organic polymers

Polymer	Heat capacity (J g^{-1} deg^{-1})
Poly(vinyl chloride)	1.01
Polypropylene	1.05
Polytetrafluoroethylene	1.05
Silicone	1.13
Polycarbonate	1.26
Polystyrene	1.34
Poly(vinylidene fluoride)	1.38
ABS copolymer	1.46
Poly(methyl methacrylate)	1.46
Nylon-6	1.58

Table 6 Thermal conductivities of solid materials

Material	Thermal conductivities (J s^{-1} m^{-1} deg^{-1})	Temperature (K)
Copper	10500	293
Aluminium	5650	293
Silver	5100	293
Iron	2997	293
Beryllium oxide	216.3	311
Silicon carbide	90.0	311
Magnesium oxide	36.7	311
Copper(II) oxide	17.7	311
Marble	2.0–2.9	
Glass	0.7–0.9	
Gypsum	0.4–0.5	
Plaster	0.3–0.6	
Polyethylene (LDPE)	0.32–0.34	
Polytetrafluoroethylene	0.24–0.26	
Nylon-6	0.23–0.26	
ABS copolymer	0.21–0.31	
Silicone	0.17–0.29	
Poly(methyl methacrylate)	0.17–0.25	
Polycarbonate	0.17–0.21	
Poly(vinyl chloride)	0.15–0.27	
Oak	0.14–0.15	
Poly(vinylidene fluoride)	0.12–0.13	
Polypropylene	0.11–0.12	
White pine	0.11–0.12	
Polystyrene	0.08–0.14	
Polyurethane	0.06–0.21	

Table 7 Comparison of flammabilities, heats of gasification of organic polymers and heats of combustion of gaseous polymer decomposition products

Polymer*	*LOI*	$10^2/LOI$	Heat of gasification $(\mathrm{J\,g^{-1}})$	Heat of combustion $(\mathrm{J\,g^{-1}})$	Heat of combustion / Heat of gasification
Polyoxymethylene (1)	15.7	6.4	2430	16950	7.0
Polyurethane foam (2)	16.5	6.1	1190	31 400	26.4
Styrene–butadiene rubber (3)	16.9	5.9	2690	44870	16.7
Poly(methyl methacrylate) (4)	17.3	5.8	1630	26650	16.4
Polypropylene (5)	17.4	5.7	2030	46550	22.9
Polyethylene (LDPE) (6)	17.4	5.7	1750	46450	26.6
Polyethylene (HDPE) (7)	17.4	5.7	2320	46450	20.0
Polystyrene (8)	17.8	5.6	1690	41 400	24.4
Wood (9)	23.0	4.4	1250	30950	16.4
Polycarbonate (10)	25.0	4.0	2070	31 400	14.9
Nylon 6 (11)	25.6	3.9	2350	20550	13.4
Poly(vinyl chloride) (12)	47.0	2.1	2470	18150	7.3
Graphite (13)	63.5	1.6	12 330	32220	2.6

* Numbers refer to *Figure 3*

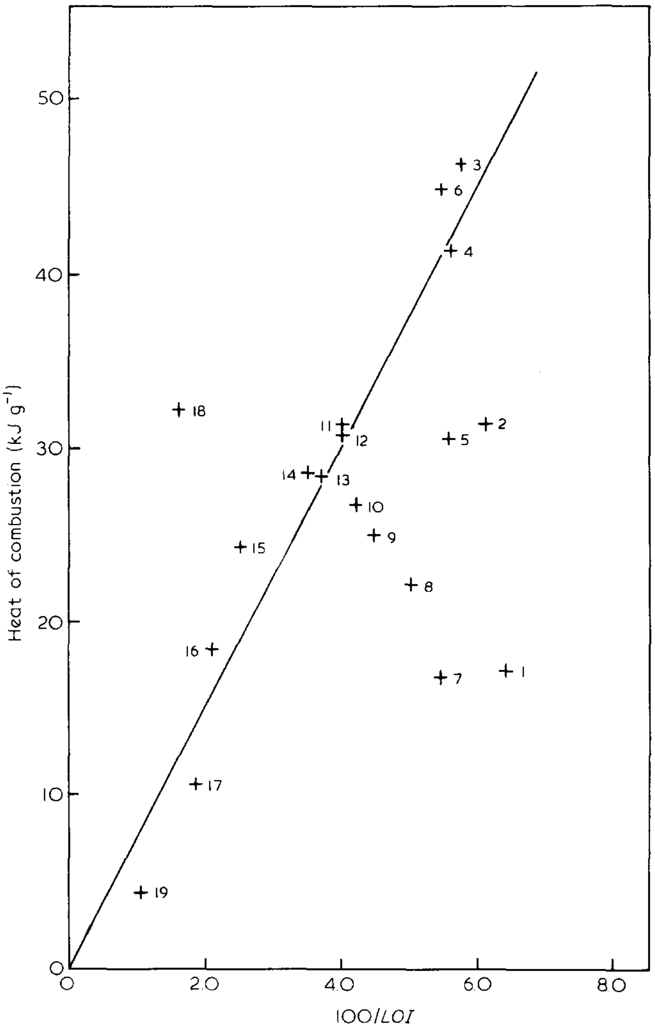

Figure 2 The relation between flammability (expressed as *LOI*) and the heat of combustion of organic polymers
(1) polyoxymethylene; (2) polyurethane foam; (3) polyethylene; (4) polystyrene; (5) polyacrylonitrile; (6) polybutadiene; (7) cotton; (8) poly(ethylene terephthalate); (9) poly(vinyl alcohol); (10) wool; (11) nylon; (12) polycarbonate; (13) Hypalon; (14) Nomex; (15) Neoprene; (16) poly(vinyl chloride); (17) poly(vinylidene chloride); (18) graphite; (19) polytetrafluoroethylene

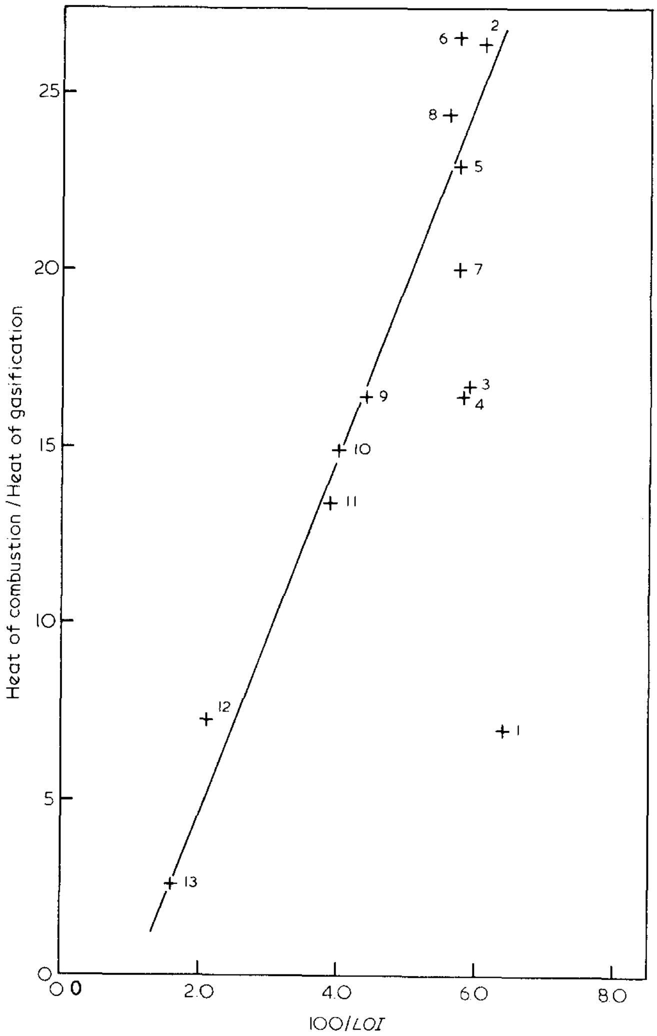

Figure 3 The relation between flammability (expressed as *LOI*) and the ratio of the heat of combustion to the heat of gasification for organic polymers: numbers as in *Table 7*

On this basis, then, it would be expected that the most flammable polymers would be those which not only decompose at relatively low temperatures but also in so doing give large quantities of gaseous products which in turn have a high heat of combustion[9]. In practice, however, it is clear that simple correlations do not exist between polymer flammability and the parameters governing any of the conceptually separate stages of the burning process.

THERMAL ANALYSIS AND FLAMMABILITY: THE EFFECTS OF ADDITIVES ON THE BEHAVIOUR OF A BASIC POLYMER

In a real fire, the amount of heat exchanged is usually very large, surface heating rates often being greater than $10^7 \mathrm{J\,s^{-1}\,m^{-2}}$, whereas heating rates used in thermal analysis are typically $10 \mathrm{deg\,min^{-1}}$ or lower. Thus thermoanalytical measurements cannot accurately represent the massive heat effects present in a full-scale fire but thermal analysis can nevertheless be used to determine the ease with which a polymer decomposes, the thermochemistry of its reactions, the effects of different atmospheres, the extent of volatilization of certain species and, in particular, the influence of additives.

It has already been pointed out that, in the limit, one of the simplest and most certain ways to make an organic polymer non-flammable is to design it initially so that it is very resistant to thermal decomposition. In this case, the first stage of the burning process will be prevented and the combustion cycle will never start. In practice, of course, the problem of polymer flammability is solved, at least to some extent, not primarily by designing new thermally stable polymers but by introducing flame-retardant additives into the commoner high-tonnage polymers. The question then arises as to whether one possible mode of action of flame retardants is to increase the thermal stability of the polymer.

The whole complexity of the combustion of polymers and its inhibition is shown by the behaviour of systems containing halogen compounds and metal oxides. Halogenated additives often change the pattern of thermal decomposition of a polymeric substrate by altering the number or the temperature of the different stages. Most additives of this kind volatilize completely on their own. On thermal analysis of mixed polymer–additive systems, however, the stage of volatilization of the additive alone ceases to exist and is usually replaced by two separate stages, both of which involve the polymer and the additive. *Figure 4* shows the effects of four halogenated hydrocarbons on the differential thermogravimetric curves of various thermoplastic polymers. In contrast, relatively large amounts of metal oxides, such as hydrated alumina, act as heat-sinks to keep down the temperature, and thus alter the temperature of formation of gaseous decomposition products, other than by introducing a dehydration stage (*Figure 5*), and usually without changing the underlying mechanism. Other compounds, such as antimony oxide, which are in general only effective when used in conjunction with a halogen compound, have a more obviously chemical mode of action (*Figure 5*). Studies of the influence of such metal oxide–halogen systems on both the thermal stability and flammability of a thermoplastic polymer (*Table 8*) show that, although the minimum decomposition temperature is of little value as a criterion of the effects of these compounds on the flammability of polymeric systems, measurements of $T_{1\%}$ do indicate correctly the expected direction of change for ABS. Nevertheless there is little or no quantitative correlation between the magnitude of the effects of the various metal–halogen systems on stability and flammability (*Table 8*). Moreover, with certain polymers, such as nylon-6,6, the introduction of halogenated additives may lower the thermal stability of the system and at the same time decrease the flammability.

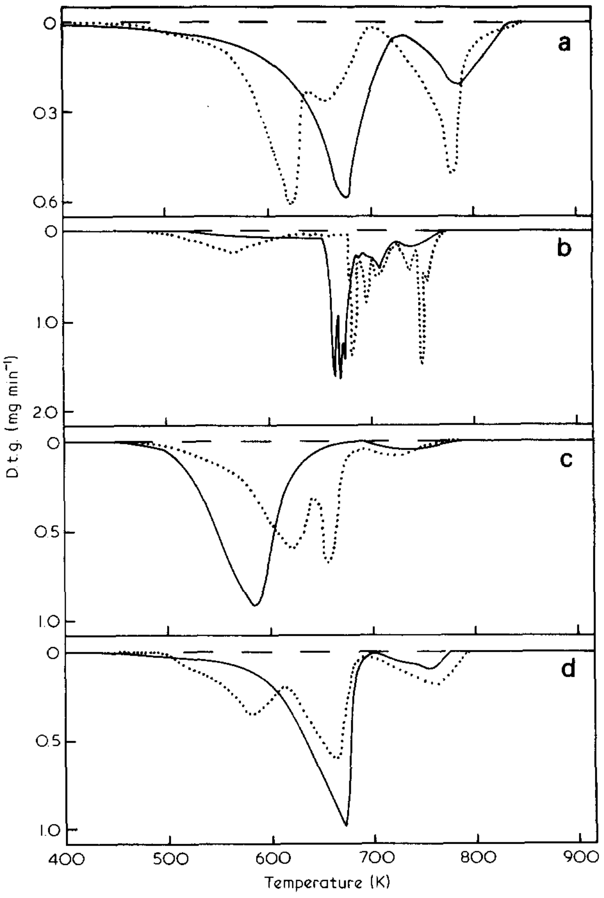

Figure 4 The effect of halogenated additives on differential thermogravimetric analysis (d.t.g.) of polymeric systems: (a) (——), ABS copolymer; (···), ABS (60%)+decabromobiphenyl (DBB) (40%); (b) (——) high-desnity polyethylene (HDPE); (···), HDPE (70%)+Electrofine S70 (chlorinated wax with 70 wt% Cl) (30%); (c) (——), polypropylene (PP); (···), PP+40 phr decabromobiphenyl oxide; (d) (——), polystyrene (PS); (···), PS+40 phr Cereclor 70 (chlorinated wax with 70 wt% Cl). Sample size, 10 mg; atmosphere, air; heating rate, 5 deg $\mathrm{min^{-1}}$

It has until recently been assumed that metal oxides which are chemically effective flame retardants act in the same way as antimony oxide, i.e. they are converted primarily to volatile metal halides which escape into the gas phase and interfere with the flame reactions. Thermal analysis readily identifies those metal oxides which form volatile halides when heated with an organic halogen compound and those which do not[10]. However, volatilization of metal oxides as metal halides frequently does not reach a maximum at stoichiometric ratios, a considerable excess of halogen being required[10–12]. Further, even when volatilization is maximized, complete gasification of the metal as a halide need not result in good flame retardance. Thus, zinc oxide, which readily produces volatile zinc halides, is not very effective as a flame retardant, and is antagonistic when used as a partial substitute for antimony oxide, whereas iron(III) oxide and

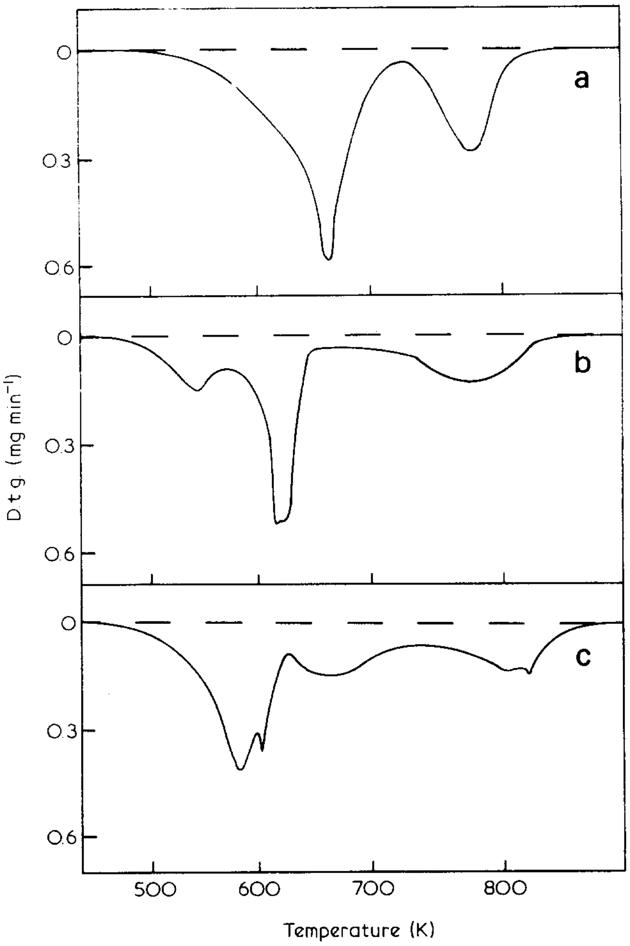

Figure 5 The effect of hydrated alumina and of antimony oxide–decabromobiphenyl on differential thermogravimetric analysis of ABS copolymer: (a) ABS; (b) ABS (60%) + $Al_2O_3 \cdot 3H_2O$ (40%); (c) ABS (70%) + DBB (22.5%) + Sb_2O_3 (7.5%). Conditions as in *Figure 4*

Table 8 The effects of metal oxides on the flammability and thermal stability of ABS copolymer. Polymer: 70 wt% ABS; metal oxides (as shown); decabromobiphenyl (DBB) (to 100 wt%)

Metal oxide(s) (wt%)	ΔT_D (K)	$\Delta T_{1\%}$ (K)	ΔLOI
Values for base polymer	(451)	(513)	(18.6)
None + DBB (23.1)	–6	+35	+5.6
Sb_2O_3 (7.5)	–14	+35	+15.6
SnO(7.5)	–10	+27	+9.2
SnO_2(7.5)	+1	+35	+9.2
ZnO(7.5)	+29	+1	+6.2
Fe_2O_3(7.5)	–28	+18	+11.8
Al_2O_3(7.5)	+16	+31	+9.0
AlOOH(7.5)	–22	+25	+6.2
$Al_2O_3.3H_2O$(7.5)	–38	+42	+5.7
$(NH_4)_6Mo_7O_{24}.4H_2O$(7.5)	–21	+31	+10.1
$Mg_3H_2(SiO_3)_4$(talc)(7.5)	–5	+32	+8.4
Sb_2O_3(2.5); SnO_2 (2.5)	–38	+13	+17.8
Sb_2O_3(10.0); SnO_2(2.5)	–17	+32	+15.0
Sb_2O_3(2.5); ZnO(2.5)	+27	+45	+15.7
Sb_2O_3(2.5); Fe_2O_3(2.5)	–37	+14	+19.5
Sb_2O_3(2.5); Al_2O_3(2.5)	+23	+40	+17.3
Sb_2O_3(2.5); AlOOH(2.5)	–24	+28	+16.1
Sb_2O_3(2.5); $Al_2O_3.3H_2O$(2.5)	–13	+33	+15.5
Sb_2O_3(2.5); $(NH_4)_6Mo_7O_{24}.4H_2O$(2.5)	–13	+26	+16.9
Sb_2O_3(10.0); $Mg_3H_2(SiO_3)_4$(2.5)	+4	+42	+17.0
SnO(2.5); ZnO(2.5)	–24	+29	+9.0
SnO(2.5); Fe_2O_3(2.5)	–38	+7	+13.3
SnO_2(2.5); AlOOH(2.5)	–21	+23	+11.1

aluminium oxide (both in anhydrous and hydrated forms), which do not form volatile halides, have useful flame-retardant action[14,15]. *Table 9* compares the ease of volatilization of some metal oxides as halides with their qualitative effects as replacement materials for antimony oxide. Thermogravimetric studies show that zinc oxide in fact significantly decreases the volatility of the antimony halide. Iron(III) oxide has no appreciable influence on the volatilization of the antimony halide and does not itself

Table 9 Ease of volatilization of metal oxides as their halides, in the absence of polymer, and their effect as flame retardants on thermoplastic polymers

Metal oxide	Maximum volatilized as halide (wt%)	Chlorine/metal atomic ratio for maximum volatilization	Flame-retardant interactive effect of metal oxide with	
			Halogen	Halogen + antimony
ZnO	100	4	none	antagonism
Sb_2O_3	100	7–8	synergism	–
SnO	100	25	synergism	none
$SnO_2.xH_2O$	50	4	synergism	none
AlOOH	20	2–3	synergism	synergism
$Al_2O_3.3H_2O$	5	4	synergism	synergism
Al_2O_3	0	–	synergism	synergism
Fe_2O_3	0	–	synergism	synergism

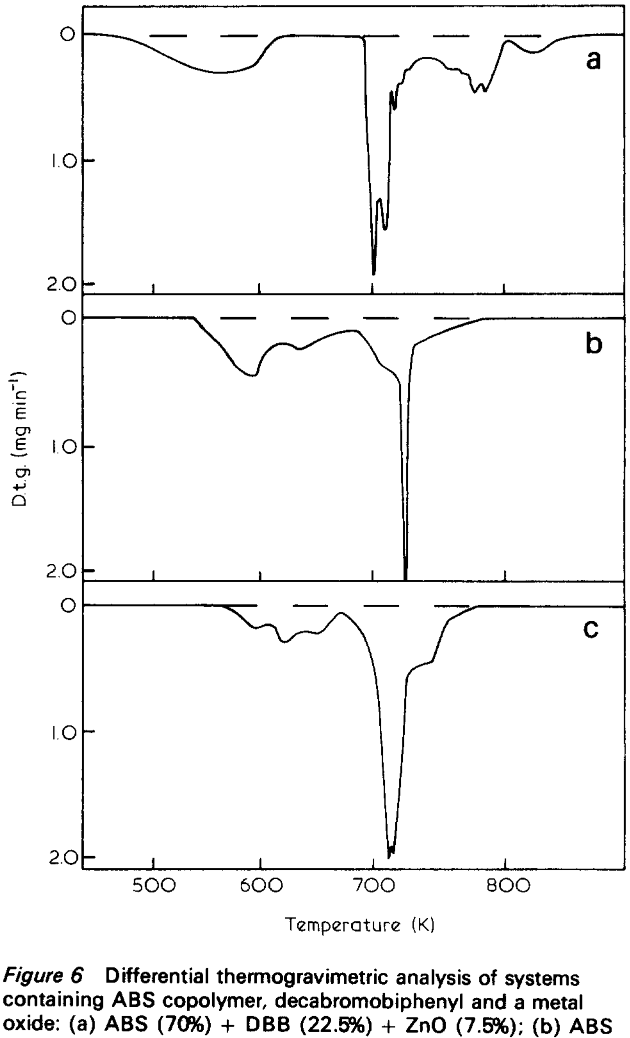

Figure 6 Differential thermogravimetric analysis of systems containing ABS copolymer, decabromobiphenyl and a metal oxide: (a) ABS (70%) + DBB (22.5%) + ZnO (7.5%); (b) ABS (60%) + DBB (20%) + Al_2O_3 (20%); (c) ABS (70%) + DBB (22.5%) + Fe_2O_3 (7.5%). Conditions as in *Figure 4*

form a volatile halide, but it markedly catalyses the decomposition of the halogen compound, causing liberation of the hydrogen halide and charring of the polymer[15]. There is abundant evidence too that, although aluminium is not volatilized as a halide, alumina and organic halogen compounds interact in the condensed phase when present together in a polymeric substrate[13,15,16].

Perhaps the main conclusion which can be drawn from studies of the thermal behaviour of polymer–metal oxide–halogen systems is that, although volatilization of the halogen may be important, it must occur at the right stage of the combustion cycle[15]. With zinc oxide, for example, volatilization occurs too early and the halogen has disappeared from the system before it can become effective. In contrast, with iron(III) oxide and anhydrous alumina, there is thermal activity over a narrow but significant temperature region, so that, even though the metal is not volatilized as the halide, the halogen enters the flame zone at the right time (*Figure 6*).

CONCLUSIONS

In the limiting case, very high thermal stability must make a polymer non-flammable. Nevertheless, there appears to be little correlation between the ease with which polymers decompose and the readiness with which they burn. Similarly flame-retardant additives do not in general act by increasing the thermal stability of polymers. Studies of the thermal behaviour of polymer–additive systems can, however, give useful information regarding the probable mode of action of additives on polymer combustion.

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