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Special Reviews

DTA AND DSC STUDIES ON POLYMERS CONTAINING FIRE RETARDANTS

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This publication surveys the results obtained by means of thermal analysis particularly with DTA and DSC methods in the field of synthetic and natural polymers treated with various flame retardant additives.

The 167 references citated cover the most important territories of the up to date problems.

For several years, differential thermal analysis (DTA and DSC) have been widely used as a screening test and for quality control purposes. The most convenient method for studying polymer oxidation by DTA or DSC is to use the instrument in isothermal mode. Typically, thermal equilibrium is established with nitrogen flowing over the sample and the gas is then changed to oxygen or air.

In the instruments, a Perkin–Elmer model DSC-2 Calorimeter and SETARAM-DSC III are well known. The capability of the DSC III for doing a gas sweeping of the sample allows the study of solid-gas reactions. The quantitative measurements obtained with different gases are reproducible and can be compared because the sensitivity of the calorimeter is not modified by the nature and the flow-rate of the gas.

In the Perkin–Elmer Model DSC-2, the sample weighing between 1 and 20 mg is placed in an open pan in the DSC head, the sample cup closed with a perforated cover and the head closed. At this stage, Billingham et al. found that the temperature was 320 K and an oxygen flow of 30 ml min^{-1} was maintained in the head. The sample was heated to the required temperature at 320 K min^{-1} and the recorder and data logger started at the point where thermal equilibrium was indicated. There was a small thermal lag involved due to the sample melting, but this took less than 1 minute and they found this method easier than attempting to change the flowing gas, because of the long gas flow path of the DSC head.

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Billingham et al. [1] have pointed out that several thermoplastics are susceptible to degradation reactions, occurring during processing or use. The single most important factor in causing instability in polymers is the presence of oxygen. Oxidation occurring at the high temperatures and sheer rates involved in processing reduces the molecular weight of the polymer and can lead to deterioration in mechanical and electrical properties. At the same time oxygen-containing functional groups are produced in the polymer and act as centres for the initiation of further oxidation during use.

Thus, studies can be based upon weight loss but degradation processes may occur in a polymer which are not associated with the loss of volatiles. It is here that both DTA and DSC techniques are useful as they show whether any reactions are occurring which involve either heat evolution or absorption. Their value in degradation studies is limited, however, to an indication of the start of reaction [2].

In polymer work, studies have been made of phase transitions, crystallization, polymerization, curing, crosslinking, thermal degradation, and thermo-oxidative stability. The effect and rate of curing of a resin can be studied by DTA as shown in Fig. 1 [3].

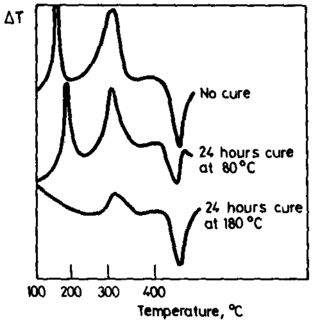

Fig. 1 Curing study of a commercial resin

This study surveys the thermal analysis work from 1967 to 1982. There are hundreds of work in this direction but the following have been selected due to proximity with our type of research and most of these studies were used in Chemical Abstracts.

Cullis and Smith [4] pointed out that the studies of the thermal degradation and oxidation of polyethylene at about 400° showed that the rates of both reactions and the nature and distribution of the products were influenced by the composition of the surrounding gaseous atmosphere. The rate of degradation of the polymer was the same in helium as in nitrogen and was unaffected by the presence of volatile hydrocarbons. On the other hand, the addition of hydrogen bromide substantially reduced the rate of weight loss but caused considerable fragmentation of the initial gaseous products. Investigations of the effect of some simple organic bromine compounds showed that such compounds retard the degradation of polyethylene only if they underwent prior decomposition to hydrogen bromide. Generally similar results were obtained for the oxidation of the polymer. Addition of hydrogen bromide decreased the rate of weight loss but accelerated the further oxidation of the primary degradation products of polyethylene.

It must be pointed out that the introduction of bromine into certain polymers decreases their flammability. At the relatively high temperatures involved during combustion, however, much of the halogen is released into the atmosphere surrounding the polymer and the presence of the resulting gaseous bromine compounds might well influence the course of the subsequent reactions of the polymers.

The course of the oxidation of polyethylene was followed in some cases by means of the accompanying over-all pressure change, which was shown in a separate series of experiments to be approximately proportional to the uptake of oxygen. Figure 2 shows the pressure increase taking place after given time intervals when both the weight of the initial polymer sample and the partial pressure of oxygen were separately varied. The pressure increase varies linearly with the weight of the sample (up to a weight of about 7—8 mg) and with the initial oxygen concentration (over the whole range investigated). Experiments were also carried out in which varying amounts of hydrogen bromide were introduced into the oxygen-containing atmosphere. Some typical pressure/time curves are shown in Fig. 3 and from these it can be seen that

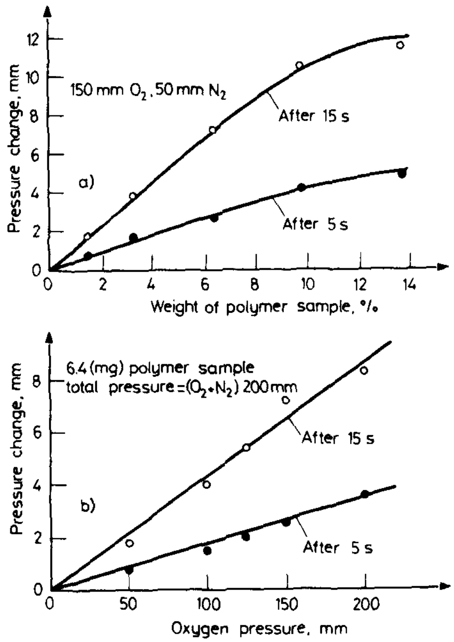

Fig. 2 Influence of sample size (a) and oxygen pressure (b) on the pressure change accompanying the oxidation of polymer at 430°C

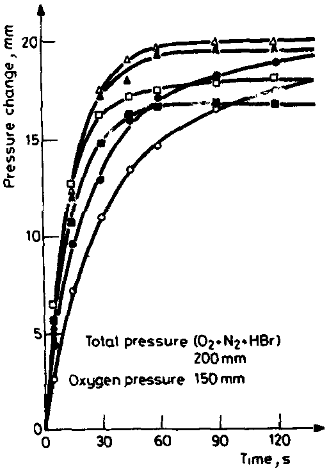

Fig. 3 Influence of the concentration of hydrogen bromide on the pressure change accompanying the oxidation of a 6.4 – mg polymer sample at 430°C; HBr (mm); ○ – 0; ● – 0.1; △ – 1; ▲ – 2; □ – 5; ■ – 10

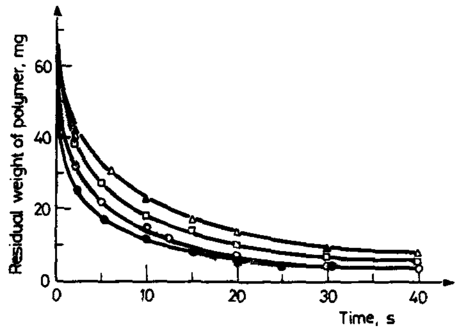

Fig. 4 Influence of the concentration of hydrogen bromide on loss of weight accompanying the oxidation of a 6.4 – mg polymer sample at 430°C; ● 200 mm O_2; ○ 150 mm O_2, 50 mm N_2; □ 150 mm O_2, 48 mm N_2, 2 mm HBr; ▲ 150 mm O_2, 45 mm N_2, 5 mm HBr; △ 150 mm O_2, 40 mm N_2, 10 mm HBr

hydrogen bromide markedly increases the initial rate of pressure change. Small amounts of the additive increase but larger quantities decrease the accompanying over-all pressure change.

Measurements were also made of the loss of weight of the polyethylene during oxidation in the presence and absence of hydrogen bromide. The loss of weight of the polymer is a function of time, as shown in Fig. 4, and it can be seen that hydrogen bromide caused a marked decrease in the rate of volatilization of the sample. At least in the intermediate stages of oxidation, the rate of loss of weight was directly proportional to the weight of polymer remaining, *w*. First-order velocity constants, k', could therefore be calculated, for this part of the reaction, from the slope of plots of $\log_{10} w$ against time (Figs 2–4). The resulting values for k' are shown in Table 1. It is thus clear that, although the presence of hydrogen bromide in the surrounding atmosphere increases the total number of molecules of volatile products (probably owing to the generally promoting effects of this additive on the slow oxidation of volatile organic compounds), the halogen compound nevertheless in some way retards decomposition of the solid polymer.

Table 1 Influence of hydrogen bromide on the first-order rate constants for the intermediate stages of the oxidation of a 6.4 mg sample of polyethylene at 430°C

Atmosphere, mm	k', s^{-1}
200 O_2	0.75
150 O_2 50 N_2	0.70
150 O_2 48 N_2 2 HBr	0.64
150 O_2 45 N_2 5 HBr	0.56
150 O_2 40 N_2 10 HBr	0.56

In 1970, a review on calorimetry, DTA, and thermogravimetric analysis of coatings (with 18 references) was described by Garn [5] and Mihaila et al. [6] published the DTA of polymers such as PVC, polyethylene, and polyesters. In the same years, Blair [7] studied polymers blends by thermal analysis.

There were two interesting works on combustion of polymers and effects of bromine compounds on the oxidative degradation by Cullis [8] and Carabine, Cullis and Croome [9]. The reference [8] is a detailed review on the combustion of polyolefins and covers degradation of polyethylene, polypropylene, etc. and the fire retardants. The introduction of bromine into certain olefinic polymers decreases the flammability [10]. As we have stated earlier that the addition of hydrogen bromide substantially reduces the weight loss but causes considerable fragmentation of the initially formed gaseous products (Table 2). Investigations of the effect of some simple organic bromine compounds show that such compounds retard the degradation of polyethylene only if the conditions are such that they undergo prior decomposition to hydrogen bromide [8, 11–13], which is therefore assumed to be the active species responsible for the observed inhibition, as appears to be the case also with other

Table 2 Influence of hydrogen bromide of the yields of volatile products formed on pyrolysis of 5 mg samples of polyethylene

Product	Yield per mg of polymer volatilized: Average value for experiments in absence of HBr, moles × 10^8	Yield per mg of polymer volatilized: Average value for experiments in presence of HBr, moles × 10^8	Ratio col 3/col 2
Propane	7.5	23.9	3.2
n-Butane	5.6	25.2	4.5
n-Pentane	1.8	11.5	6.6
Propylene	16.6	16.6	1.0
But-1-ene	11.8	6.6	0.6
But-2-ene (trans)	1.0	6.8	6.8
But-2-2n2 (cis)	0.9	2.8	3.1

polymers [14]. It is well known that at higher temperatures most organic polymers start to undergo thermal degradation, a process which is accompanied by extensive cleavage of C—C and C—H bonds. The reaction which takes place in the presence of oxygen at these higher temperatures is thus essentially an oxidative degradation, the free radicals formed by bond fission reacting rapidly with oxygen, although direct attack of oxygen on the polymer may also occur [8]. It certainly seems likely that the oxidation processes occurring at these higher temperatures are much more relevant to the mechanism of burning of polymers. Nevertheless it seems to be generally agreed that the thermal degradation of polyolefine at temperatures in the range 200—400° is quite markedly catalyzed by oxygen in the surrounding atmosphere [15]. The oxidation of polyethylene at 430° in a static system is accompanied by a considerable pressure increase which varies linearly with the weight of the polymer and the initial oxygen pressure. If the surrounding atmosphere also contains a small concentration of hydrogen bromide (0.1 to 10%), the rate of weight loss of the polymer is decreased although the accompanying overall pressure change is generally increased.

Thus in fire retardancy, this result suggests that, although the hydrogen bromide in some way retards decomposition of the solid polymer (as it does in the absence of oxygen), the presence of the halogen compound increases the total number of molecules of volatile products by promoting further oxidation of intermediate organic products [16]. This conclusion was supported by analysis of the gaseous products formed which contained a smaller proportion of intermediate products and a larger proportion of final products (e.g. CO_2) when hydrogen bromide was present (Fig. 5, reference [8]). Bromine also appears to decrease the rate of weight loss accompanying the oxidative degradation of polystyrene [14].

Fenimore and Jones [17] attempted to obtain evidence as to whether inhibitors affected the rate of pyrolysis of the condensed phase or the rate of the subsequent gas-phase combustion of the pyrolysis products, by studying the burning of polyethylene (and other polymers) in different oxidant gases. It was argued that an in-

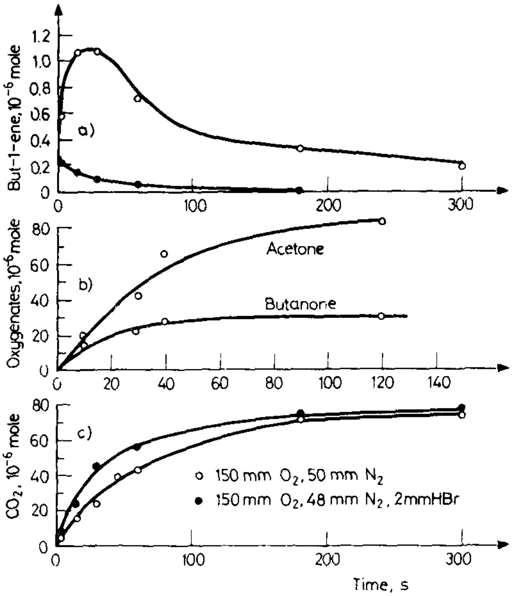

Fig. 5 Formation of volatile products during the oxidation of a 10 mg sample of polyethylene at 430°C and the influence of hydrogen bromide thereon

hibitor which interferes with the thermal degradation of the solid polymer should work independently of the nature of the flame reactions and still have the same effect if the polymer is burnt in an oxidant other than oxygen, its effect would nevertheless probably depend on polymer structure. On the other hand, an additive which inhibits the flame reactions, might, for example, be largely specific to the burning of the polymer in oxygen and not have the same effect when combustion takes place in another oxidant, such an inhibitor should act, however, more or less independently of the structure of the solid polymer.

Thus, for example, it was shown that chlorine incorporated into polyethylene inhibits the burning of this polymer in nitrous oxide as effectively as it does its combustion in oxygen (Fig. 6). On the other hand, bromine (added as tetrabromobisphenol) is more effective than the equivalent amount of chlorine when polyethylene burns in oxygen but has much the same effect when the gas supporting combustion is nitrous oxide. These results strongly suggest that, whereas chlorine inhibits the burning of polyethylene by retarding the thermal degradation of the solid polymer, bromine (which reduces the flammability of many hydrocarbon polymers) also has an effect on the oxygen-supported flame, this is consistent with the fact that bromine compounds inhibit premixed hydrocarbon-air flames much more effectively than do chlorine compounds.

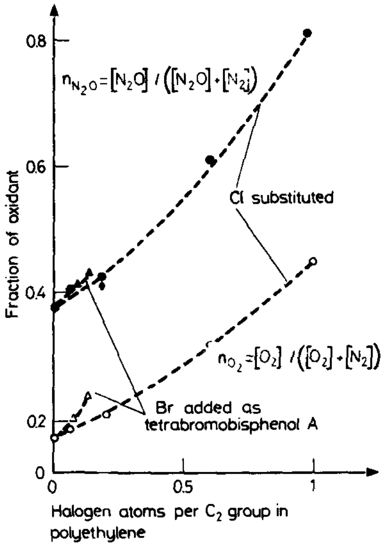

Fig. 6 Effect of halogen incorporation into polyethylene on critical indices for burning in oxygen and in nitrous oxide

Similarly, Carabine et al. [9] studied the thermal degradation of polyethylene and polypropylene in atmospheres containing oxygen and special attention was paid to the influence of bromine on the various reactions concerned.

Measurements in a static system showed that neither bromine incorporated into the polymer nor hydrogen bromide in the surrounding gaseous atmosphere had any appreciable influence on the rate of mass loss, although the presence of the halogen compound did affect the nature of the volatile products formed during oxidation. Detailed chemical analysis was carried out in a flow system in which molten polymer was injected into a flowing gas mixture of known oxygen content. The results obtained made it possible to determine the extents to which oxidation took place in both the liquid and gaseous phases and elucidated the action of hydrogen bromide on the reactions in the two phases. It was shown that with polypropylene and polyethylene considerable uptake of oxygen occurred in the liquid phase but some further oxidation generally took place in the gas phase. With both the polymers, hydrogen bromide decreased the overall oxygen uptake. However, with polyethylene the halogen compound promoted oxidation in the liquid phase but acted as a powerful inhibitor of subsequent oxidation in the gas phase. In contrast, with polypropylene, as little as 1% of hydrogen bromide suppressed almost completely uptake of oxygen by the liquid but might have promoted oxidation in the gas phase to such an extent that ignition took place above the molten polymer.

Another interesting study on thermal decomposition products was made by Vandersall [18]. It dealt with the functional component e.g. a halogenated organic material in the conventional intumescent system. This component may be a resin or a non-resin e.g. chlorinated paraffin, chlorinated aromatics or polyvinyl chloride. These materials release non-flammable gases, usually HCl, forming bubbles which result in the characteristic puff or foam of an intumescent system. Water vapour or/and probably carbon oxides are released during dehydration and thermal decomposition of the polyol. These gases function as blowing agents, also, if they are released at the proper time, i.e. after the polyol-phosphate melt is formed and before solidification occurs. In order to achieve voluminous gas release at the proper point in the reaction, blowing agents with predetermined decomposition temperatures are employed. The most common blowing agent is a 70% chlorine-containing paraffin. This material melts at about 100° and then releases HCl over a temperature range of 160 to 350°. Melamine is also used as a blowing agent. It decomposes releasing ammonia, and probably low molecular weight hydrocarbons and carbon oxides between 300 and 350°. The following TG curves (Fig. 7) illustrate these decomposition temperatures. In 1972, Chaigneau et al. [19] studied the pyrolysis of plastic materials. Rigid and flexible polyurethane foams were pyrolyzed at $\leqslant 500°$ in air or oxygen. Formed were CO, CO_2, H, N, C_{1-4}, aliphatic C_{2-4}, olefins and traces of C_6H_6. Hydrocyanic acid was detected in variable but sometimes large amounts, leading to suggestion that fire retardant foams be examined from a toxicological viewpoint during flammability tests.

Use of DTA as applied to coatings was reviewed by Berger [20] and use of thermal analysis in the paint industry was described by Kovács et al. [21]. By using the thermogravimetric, DTA, and rate of weight loss curves data were obtained for alkyd resins, cellulose nitrate, dolomite and butyl methacrylate.

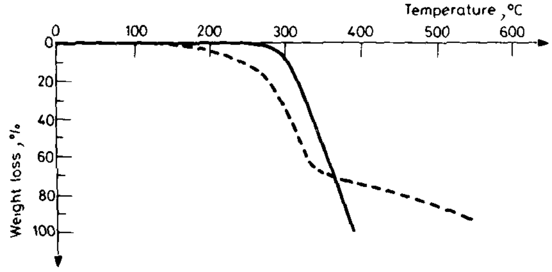

Fig. 7 TG curves of chloronated paraffin (— — —) and melamine (———)

Pyrolysis of tetrabrominated epoxy resin and its fire retardant mechanism were studied by Nara et al. [22]. Pyrolysis of DER 542 (epoxy resin-brominated) and Epikote 1001 (non-brominated epoxy resin) was investigated by DTA and TG. Fire retardancy was explained by lower temperature decomposition and generation of HBr which catalyzed condensation of the resin to carbonized material.

Ohuchi and his co-workers [23] reported the effect of fire retardants on the pyrolysis of wood. Birchwood treated with 2% diammonium hydrogen phosphate started to lose weight at 157° and had 19.5% residual charcoal at 450° compared with 204° and 8.4% respectively for similar untreated wood. The results of thermogravimetric and differential thermal analyses of birchwood treated or untreated with fire retardants in the air were also recorded.

The applications of DTA, DSC, thermogravimetric analysis, thermal volatilization analysis, etc. to the characterization of fibers and polymers were reviewed (51 references) by Rangarajan and Francis [24]. There were some earlier interesting studies too [25–35] and also works of Learmonth et al. [36–41] and Alaminov et al. [42]. TG work was done by Alaminov et al. on the degradation of phenol HCHO resins modified with cyanuric acid, while Learmonth et al. [37] studied the flammability of plastics especially relation between pyrolysis and burning. They reviewed the mechanism of pyrolysis of polymers, the relation between pyrolysis and burning, polymer degradation reactions, and pyrolysis in the solid state. The effects of halogenated additives on the pyrolytic decomposition of polyesters were also given. The polyesters were stabilized with a halogenated additive selected from Dechlorane, Cereclor 70, pentabromotoluene, tetrakis(pentabromophenoxy)silane, Cereclor 70 L, Cereclor 65 L, Cereclor S 52, and/or Timonox (Sb_2O_3). The polyesters were subjected to a candle burning test, ignition tests (ASTM D-1929-62T), and DTA and thermogravimetric analysis. The thermal curves indicated 5 separate zones. The use of an additive decreased the total loss in weight and this difference occurred by the end of the 2nd stage of pyrolysis. The addition of flameproofing material produced an increase in ignition temperature above that of the standard resin in every case. The flame retardant effect was attributed to inhibition in the vapor phase.

In the other work [38], Learmonth et al. used Setchkin ignition tests and candle burning tests to provide a numerical index of the effect of fire retardant agents in polyesters. A polyester resin based on maleic and phthalic anhydrides and propylene glycol crosslinked with styrene was used. The resin was dissolved in styrene monomer, retardants were added, 2 weight % Bz_2O_2 was added, and the samples were cured 1 hour at 70° and post-cured 24 hours at 70°. Additives used to reduce flammability of resins were Cereclor 70 (I) . . . solid chlorinated paraffin 70% Cl; Cereclor 70 L . . . liquid chlorinated paraffin containing 70% Cl; Cereclor 65 L . . . liquid chlorinated paraffin containing 65% Cl; Cereclor S 52 . . . liquid chlorinated paraffin containing 52% Cl; Timonox (Sb_2O_3), Dechlorane 4070 . . . perchloropentacyclodecane, 65% Cl; FireMaster T23P . . . tris(2,3-dibromopropyl)phosphate(II); Tris(2,3-dichloropropyl) phosphate(III); TTP (Tritolylphosphate); TXP (trixylyl phosphate); Flammex 4BS [Tetrakis(pentabromophenoxy)silane]; Flammex 5BT (pentabromotoluene); Flammex 5AE (pentabromophenyl allyl ether); Flammex 3AE (tribromophenyl allyl ether); zinc borate 9506 [$Zn(BO_2)_2 \cdot 2\,H_2O$], and calcium borate 9578 [$Ca(BO_2)_2 \cdot$ $\cdot\ 2.5\,H_2O$]. The oxygen index, spontaneous ignition temperature, rate of burning (according to British Standard 2782 method 508A), and Vickers pyramid hardness number were determined for each material. Polyesters containing halogenated additives tended to glow after ignition eased. The effectiveness of I was greater than the 3 liquid chlorinated paraffin, III was more effective as fire retardant than II.

In further studies [40], Learmonth et al. described reaction between antimony trioxide and organic halogenated fire retardants with reference to their performance in a crosslinked polyester resin. The isothermal weight loss of Cereclor (I), perchloropentacyclodecane (Dechlorane 4070) (II), Tetrakis(pentabromophenoxy)silane (Flammex 4BS) (III), and pentabromotoluene (Flammex 5BT) (IV), and other mixtures with Sb_2O_3 at 300–500° was determined. IV did not react with Sb_2O_3 and IV–Sb_2O_3 mixtures showed no flame retardancy synergism. The weight loss vs. time plots for mixtures of I, II and III with Sb_2O_3 indicated that a reaction took place. Weight loss was more rapid in the presence of Sb_2O_3. The quantitative analysis of the volatile reaction products from I–Sb_2O_3 and Sb_2O_3-poly(vynil chloride) (Corvic P65-50) mixtures showed $SbCl_3$ to be the main product in both cases. The synergism between the halogenated compounds and Sb_2O_3 resulted from the flame-inhibiting action of the volatile reaction products.

In a later investigation [41], Learmonth et al. described the thermal degradation of polyester resin compositions. A thermal volatilization analysis of maleic anhydride-phthalic anhydride-propylene glycol-styrene copolymer showed that decomposition on strong heating occurred in 2-stages and that inclusion of fire retardant e.g. Flammex 5BT (pentabromotoluene) has little effect on this. The results were in accord with previously proposed mechanisms, namely, the first stage was due to cleavage of the crosslinking bridge, perhaps by peroxidation to yield benzaldehyde and other fragments, and the 2nd stage was due to bond rupture in the main ester cleavage and decarboxylation and other minor competing processes.

Passalenti and co-workers [43] studied the factors affecting surface characteristics of films based on unsaturated polyester resins. Thermal analysis of coatings based on maleic anhydride-phthalic anhydride-propylene glycol polymer confirmed that the most reactive resins and the systems which has a lower quantity of residual reactive sites, also showed a lower sinking after application on wood.

Benbow and Cullis [44] studied the mechanisms of flame retardance by bromine compounds. The thermal degradation experiments were carried out using a Mettler Thermoanalyser 2 thermobalance. The samples, films of thickness less than 0.2 mm, were prepared by evaporation of dichloromethane solutions containing polymer and additive. It was suggested that the hydrogen bromide is formed almost exclusively in the gas phase. Thermal degradation experiments were carried out in air on larger samples of additives-containing polymers which had been produced initially for the burning experiments. These experiments were stopped and the reaction quenched as soon as the additive weight loss step was complete. The residual polymer was analysed for phosphorus using both wet analysis and spectroscopic techniques. No phosphorus was found up to the limit of detection (in the latter case better than 1 part in 10^5). It was found that the initial stages of the degradation of additive-containing films were very similar in both air and nitrogen. The similarity between the reactions in air and nitrogen suggests that the additive is being volatilized as complete, unchanged molecules.

Benbow and Cullis [45] studied the influence of halogen compounds on the burning of polymers and especially how chlorine and bromine alter the mode of action of phosphorus esters on the thermal degradation and burning of polystyrenes. The thermal degradation of the polymer was studied using a Mettler Thermoanalyser 2 thermobalance. All samples were heated at a linear rate of 5° $\min^{-1}$ to a temperature of 1020°. Some results for the thermal degradation of additive-containing polystyrene are shown in Fig. 8 and Table 3.

In Table 3, the column headed first stage provides a measure of the ease with which the various additives are lost from the polymer, and the other three columns show the effect of the remaining additive on the later stages of degradation. The residue is the amount of material which is involatile at 1000° and probably consists mainly of phosphoric acid. The activation energies were calculated by an integral method [46].

Figure 8 shows the first 20% of the degradation process. For tris-phosphates (Fig. 8a), more than 95% of the additive originally present in the polymer is volatilized, in both air and nitrogen, before polymer degradation begins. With these compounds, no residue remains at the end of the experiment and the amount of carbon formed is the same as for the degradation of pure polystyrene. Table 3 and Fig. 8b show that the reaction is much more complicated for polymers containing many of the other compounds studied. Three main types of behaviour were observed:

(i) For mono- and bis-halophosphates, about 40–60% of the additive originally present was lost in the first stage, carbon formation was slightly increased, and a

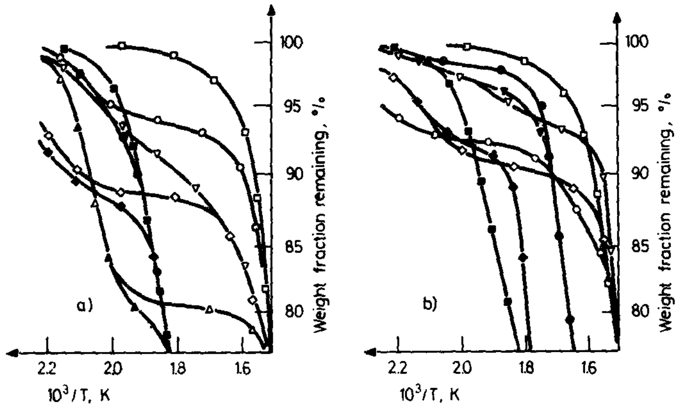

Fig. 8 Weight fraction remaining for the first 20% of degradation of additive containing polystyrenes heated at 5°C $\min^{-1}$. Open symbols, – N_2; closed symbols, – air. (a) Phosphates: □, ■; no additive: ○, ●; + 5% Tris(2,3-dibromopropyl)phosphate: △, ▲; + 20% Tris(2,3-dibromopropyl)phosphate: ⌑; + 20% Tris(2,3-dichloropropyl)phosphate: ◇, ◆; + 10% Tris(n-propyl)phosphate; (b) Phosphites and other compounds: □, ■; no additive: ◇, ◆; + 20% Tris (2,3-dibromopropyl)phosphite: ○, ●: + 20% Tris-(ethyl)phosphite: ⌑, ⌘; + 20% Vinyl phosphonic dichloride

Table 3 Weight fraction lost (%) and activation energy (kcal • mol^{-1}) for the reaction stages during thermal degradation of polystyrene containing *X*% of various flame-retardants

Additive	*X*	First-stage		Carbon	Residue	Activation energy of polymer degn. reaction (air)
	%	(N_2)	(air)	(air)	(air)	
None	–	–	–	3.2	0.0	28(±2)
A	5	5.0	4.8	3.2	0.0	22
	10	9.5	9.4	3.2	0.0	16
	20	20.0	19.7	3.2	0.0	11
B	20	18.3	18.4	3.3	0.0	22
C	10	9.3	9.1	3.2	0.3	25
D	20	16.1	14.3	4.2	2.7	29
E	20	8.4	5.7	4.0	1.9	30
F	20	6.9	2.0	5.7	1.4	41
G	20	5.8	2.8	8.0	ca. 10.0	37

A = tris(2,3-dibromopropyl) phosphate
B = tris(2,3-dichloropropyl) phosphate
C = tris(*n*-propyl) phosphate
D = bis(2,3-dibromopropyl) phosphate
E = tris(2,3-dibromopropyl) phosphite
F = tris(ethyl) phosphite
G = vinyl phosphonic dichloride

residue corresponding to the remaining additive was left at the end of the experiments. The first stage of degradation was similar in nitrogen and air.

(ii) For many of the phosphites studied, the amount of additive lost is only about 20–40% of that expected for full volatilization, but the later stages of degradation were not greatly effected. The explanation of this was the prior loss of additive during preparation of the polymer films, the phosphites being more volatile than the corresponding phosphates.

(iii) Atlhough only 10–20% of the vinyl phosphonate compounds originally present in the polymer was lost in the first stage, the later stages were significantly affected when these compounds were present. As much as 60% of the additive might have remained at the end of the experiment. When these compounds were copolymerized with styrene, the degradation of the resultant polymer was completely different from that of pure or additive-containing polystyrene.

It may be of interest to give in this work thermal analysis curves of KR Sb_2O_3 and NH_4BF_4:Sb_2O_3. It was published in Harshaw Chemical Company Bulletin on Antimony Oxide [47]. The chemical company is well known for supplying fire retardant chemicals.

In 1973, Carroll-Porczynski [48] described the applications of simultaneous TG and DTA and DTA/MS analysis for predicting the flame of composite textile fabrics and polymers. Chiu [49] reviewed the polymer thermal analysis. Sokdova et al. [50]

studied the polyurethane foams and stated that the application of Cl-containing simple polyethers increased the decomposition temperature of foams from 170° to 210° and 220° for polyurethane compositions containing tolylene diisocyanate(I) and 4,4′-diphenylmethane diisocyanate as prepolymers, respectively. The optimum polyurethane formulations were containing 24% NCO groups. Thermogravimetric curves indicated a thermal degradation of foams at 228 and 240°, respectively.

Some DSC studies [51], and thermal analysis of polymers were described in 1974 [52]. Chiu [53] published the polymer characterization by thermal methods of analysis. Ivanov and co-workers [54] described some studies on the determination of polymers during melting of substances capable of polymerization. The formation of a polymer at temperatures close to its melting point was verified by the presence of an endo-exo transfer on the DTA curve. Pompowski et al. [55] described the products of decomposition of six anticorrosive paints used in the ship building industry at 200–1000° and at air flow rates up to 2 m/second. Roth et al. [56] examined the use of thermal analysis to screen binders for intumescent fire retardant coatings. Differential scanning calorimetry and thermogravimetry were used to match the thermal behaviour of several conventional binders with that of two intimescent compounds, predicted behaviour was compared with experimentally determined flame spread ratings for the formulated coatings. Charalambouks et al. [57] determined the film weight variance of epoxy and vinyl beer can coatings by differential scanning calorym-

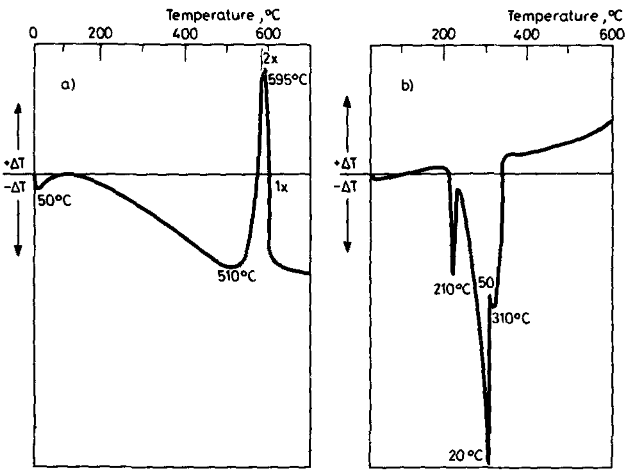

Fig. 9 Curve a, sample: KR Sb_2O_3; weight: 0.0010 g; heating rate: 10°C/min; max. temp.: 700°C; gas: air; flow rate: ambient; axis scale: 10 μv/0.43″. Curve b, sample: 3 NH_4BF_4:1 Sb_2O_3 (by wt.); weight: 0.0010 g; heating rate: 5°C/min; max. temp.: 600°C; gas: air; flow rate: ambient; axis scale: 20/50 μv/0.43″. Interpretation: a, 50°C, adsorbed water loss; to 510°C, sublimation of Sb_2O_3; 595°C, oxidation of Sb_2O_3 to Sb_4O_4; b, 210°C, NH_4BF_4 undergoes phase transition, rhombic to cubic; 310°C, volatilization of NH_4BF_4 and reaction of the two components with each other

etry. The physical characterization of coatings in aging changes in physical properties of several commercial alkyd, acrylic and vinyl based coatings on accelerated aging in an Atlas Weather-Ometer were given on a basis for DSC, thermal analysis, and water vapour permeability and compared to mechanical property data [58] e.g. from the Sward Rocker, torsion pendulum, and Instron Tensile Tester. Surface morphology as a function of aging was determined by electron scanning microscopy.

Reftery [59] studied smoke and toxicity hazards of plastics in fires. The pyrolysis and hazards of its degradation were reviewed. The thermogravimetric and differential thermal analysis of the thermal degradation of polyurethanes was described by Stepanova et al. [60].

Thermal analysis for the investigation of paints, coatings, and plastics has been reported by Sickfeld and Heinze [61]. Applications of DTA and thermogravimetric analysis to polymer and coating technology were illustrated by the study of the crosslinking of bisphenol-A-epichlorohydrin polymer, the resistance of polyethylene to thermal oxidation, the activation energy of thermal dehydrochlorination of PVC, solvent retention by coatings, desolvation of reactive epoxy coatings, and determination of the film thickness of very thin coatings. Talas [62] described the qualitative and quantitative composition of paints by DTA. DTA of coatings was discussed in relation to binder composition (epoxy resins, nitrocellulose, alkyd resins, chlorinated rubber) and pigment content, and an improved sample holder for DTA of coatings was pointed out.

Donaldson et al. [63] described thermal studies on fire retardant polyester/cotton textile blends. Thermal analysis techniques were applied to a series of polyester-cotton blends fireproofed by tetrakis(hydroxymethyl phosphonium chloride)-urea-poly(vinyl bromide), and attempts were made to correlate data obtained from thermogravimetric analysis, differential scanning calorimetry, and thermochemical analysis with the fabric properties.

Agrawal and coworkers [64] reported the thermal analysis of antimony(II)oxide in air, nitrogen and argon. Thermogravimetry, DTA and X-ray diffraction studies of Sb_2O_3 in air, N_2 and Ar atmospheres were made. In air Sb_2O_3 was oxidized to Sb_2O_4 at $>510°$. The oxidation reaction proceeds in two stages as revealed by the TG and DTA curves. The behaviour of Sb_2O_3 was similar in N_2 and Ar. Sb_2O_3 remained unaffected up to 430° above which there was a slow and continuous mass loss up to 550°. Above 550°, Sb_2O_3 volatilized, resulted in an enormous weight loss. X-ray studies of the sublimate and the residue indicated the former to be the cubic form of Sb_2O_3 (senarmontite), the residue had orthorhombic (valentinite) structure. From the DTA curves in air, N_2 and Ar, the transition temperatures for the cubic to the orthorhombic modification was established to be about 610°.

In 1975, two reviews [65, 66] dealt with the thermal analysis of polymers, and coatings and plastics materials.

Benbow and Cullis [67] described experiments of the decomposition of halogen-containing polymers. Decabromobiphenyl and decabromobiphenylether which are thermally stable flame retardants were used. The thermal degradation studies were carried out using a Mettler Thermoanalyser 2 thermobalance. Samples of flame retardant, both alone and mixed with polymer, were heated at linear rates to 650°. The weight of sample and its temperature, as well as the rate of weight loss, were recorded continuously. Figure 10 shows the path of the carrier gas through the thermobalance, a flow rate of 40 cm^3 min^{-1} (nitrogen or air) was used to prevent back-diffusion of corrosive gases into the balance housing.

Figures 11—13 show the variation with temperature of the weight of material volatilized and of the rate of weight loss for various additive and polymer systems. Figures 11a and c show how increasing sample size can significantly increase the apparent stability of the flame retardant, which is also influenced by heating rate and crucible size. The temperature of maximum rate of weight loss indeed provides a useful measure of the thermal stability of flame retardant additives, some "stability temperatures" determined in this way are shown in Table 4.

Some technical data sheets quote thermal stability in terms either of the initial weight-fraction volatilized in a given time at a constant temperature [68] or of the temperature needed for the volatilization of a given weight-fraction during thermal analysis [69]. In view of the fact that many commercial flame retardants contain considerable amounts of impurity, however, the temperature of maximum rate of the main degradation reaction appears to be a better criterion of thermal stability. Plots of weight against temperature for the various additives studied in this work [67] (Fig. 12), indicate the high purity of these materials, the order of thermal stability is thus the same as that in Table 4.

Benbow and Cullis [70] also investigated the mechanisms and evaluation of flame retardance by studying the combustion of flexible polyurethane foams. Thermal degradation studies indicated that at least a part of these flame retardant additives

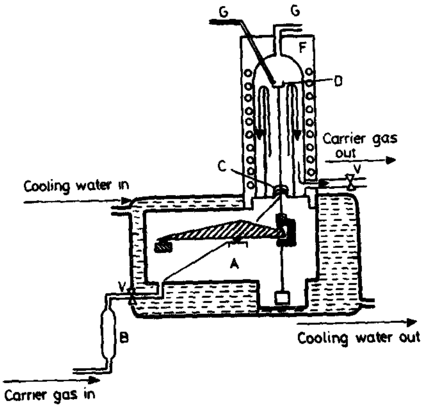

Fig. 10 The interior of the balance housing and furnace of the Mettler thermobalance. A, Balance arm in gas-tight housing; B, rotameter; C, protective baffles; D, platinum crucible; F, bifilar wound furnace and protective heat shield; G, gas exist to traps for analysis of volatile products; V, control valves for carrier-gas flow

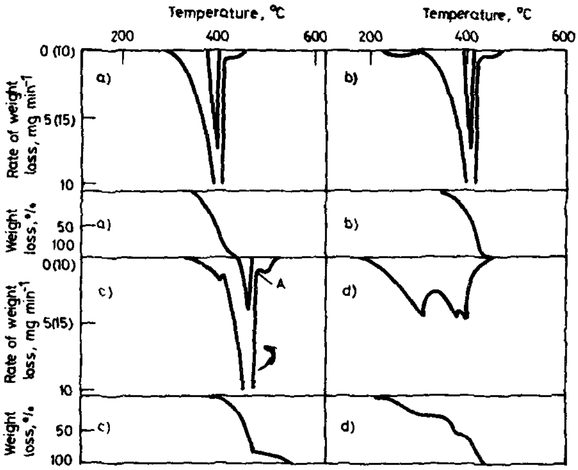

Fig. 11 Rate of weight loss and weight fraction of material volatilized at various temperature for: (a) decabromobiphenyl (10 mg); (b) decabromobiphenyl ether (10 mg); (c) decabromobiphenyl (100 mg); and (d) a 1:1:1 mixture of decabromobiphenyl, octabromobiphenyl and hexabromobiphenyl (10 mg total sample weight)

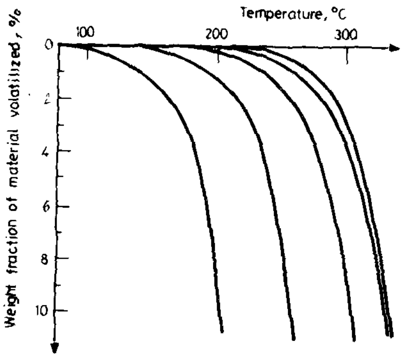

Fig. 12 Initial stages of the thermal degradation of various flame-retardants studied. Curve 1, decabromobiphenyl ether; curve 2, decabromobiphenyl; curve 3, octabromobiphenyl; curve 4, hexabromobiphenyl; curve 5, tetrabromobiphenyl ether

e.g. tris(2,3-dibromopropyl)phosphate and tris(2-chloroethyl)phosphate was incorporated into the polyurethane structure.

In the degradation studies, cubes of foam (1 cm X 1 cm X 1 cm) were cut from the interior of the large foam leaves and heated at linear rates of 3 deg min^{-1} or 5 deg min^{-1}, both in air and in nitrogen, in a Mettler Thermoanalyser 2 thermo-

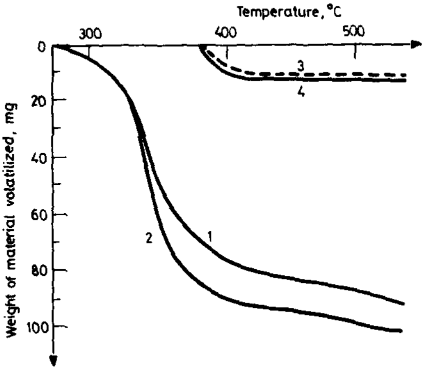

Fig. 13 The effect of a polymer matrix on the volatilization of decabromobiphenyl. Curve 1, polystyrene alone; curve 2, polystyrene containing ca. 12.5% w/w decabromobiphenyl; curve 3, decabromobiphenyl alone; curve 4, decabromobiphenyl in polymer by subtraction

Table 4 The temperature of maximum rate of reaction for samples of various halogenated biphenyls and biphenyl ethers heated, in air, at 5° min^{-1}

Compund	100 mg sample	10 mg sample (V)	10 mg sample (R)
Decabromobiphenyl	442	397	401
Octabromobiphenyl	422	392	390
Hexabromobiphenyl	362	325	322
Octabromodichlorobiphenyl	413	370	370
Tetrabromohexachlorobiphenyl	383	343	*
Decachlorobiphenyl	343	310	313
Decabromobiphenyl ether	446	418	412
Tetrabromobiphenyl ether	319	280	*

V virgin material, heated for the first time; R residue from experiment with 100 mg sample; * material decomposes, so that residue is very impure

balance. This gives a continuous record of the weight of the sample, the rate of weight change and the sample temperature. The rate of flow of the gas mixture through the balance housing and over the sample was 40 cm^3 min^{-1}.

Rates of thermal degradation, in nitrogen, of pure and additive containing polyurethane foams are plotted against temperature in Figs 14–15. The temperature at which the various reactions occur and the weight-fractions volatilized at each stage are shown in Table 5.

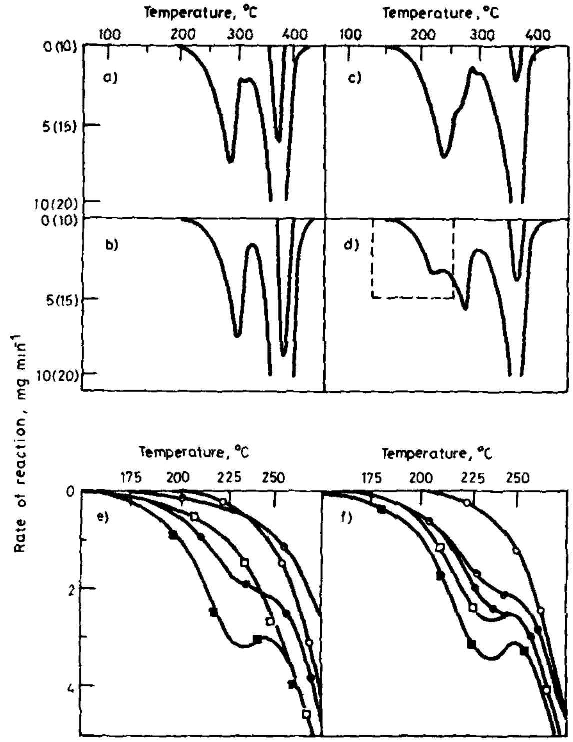

Fig. 14 The variation of the rate of reaction with temperature for the degradation in nitrogen of various polyuerthane foams. (a) untretaed foam; (b) untreated foam (aged for 16 h at 140°C); (c) foam + 40% w/w tris(2,3-dibromopropyl)phosphate; (d) foam + 16.5% w/w tris(2,3-dibromopropyl)phosphate; (e), (f) expansions of early stages of degradation as shown in (d) for 16.5% w/w tris(2,3-dibromopropyl)phosphate (■) and for other concentrations: ○, untreated foam; ●, foam + 9% w/w additive; ◉, foam + 9% w/w additive (aged); ▣, foam + 16.5% w/w additive (aged). (e) additive incorporated during preparation of foam; (f) additive incorporated by acetone-solution method. (Points shown in this and subsequent Figures are included for identification purposes only)

Edwards [71] used DTA in the flexible packaging converting industry. Gömöry [72] gave an analysis of papers published during 1965–74 in terms of three basic methods: DTA, DSC and TG. Pielichowski [73] described quantitative thermal analysis in polymer studies.

Some quantitative investigations on the curing behaviour of phenoplasts by means of DSC measurements were carried out by Schindbauer et al. [74]. They described a DTA method for examination of the crosslinking degree of phenol-formaldehyde polymer (I) using a dynamic-static test. The degree of crosslinking of I was determined as a function of cure time and temperature and the heating rate. The temperature and time of curing for a desired crosslinking degree of I could also be determined. The data

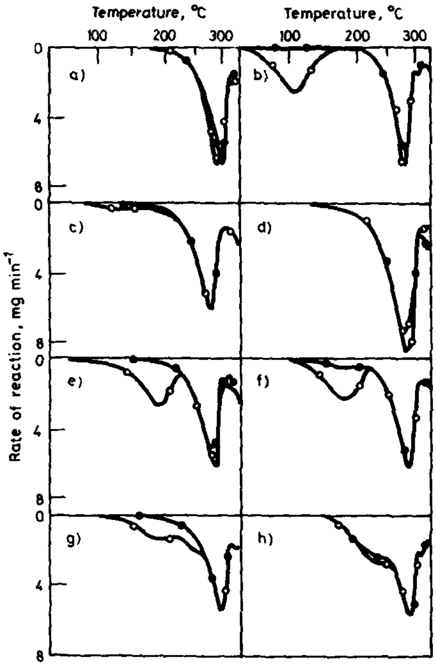

Fig. 15 The variation of the rate of reaction with temperature for the degradation in nitrogen of various polyurethane foams. (a) untreated foam; (b) foam + dibromopropanol; (c) foam + tris(allyl)phosphate; (d) foam + tris(xylyl)phosphate; (e) foam + tris(2-chloroethyl)phosphate; (f) foam + tris(2,3-dichloropropyl)phosphate; (g) foam + 8.2% w/w tris(2,3-dichloropropyl)phosphate + 8.2% w/w tris(2,3-dibromopropyl)phosphate; (h) foam + pentabromotoluene. All additives present in concentration of 16.5% w/w, unless otherwise stated. ○, foam not aged; ●, foam aged (16 h at 140°C)

showed a significant increase in the activation entropy of crosslinking with increasing crosslinking degree.

Elder [75] reported the application of DTA to polymers and Seemann et al. [76] studied the formation of toxic isocyanate vapors from the thermal decomposition of polyurethane lacquers and their polyfunctional hardeners.

Hassel [77] evaluated the polymer flammability by thermal analysis. The versatility of thermal analysis in evaluating fire retardant textiles was demonstrated using three different polyester fibers. DSC, thermogravimetric analysis, thermal evolution analysis, moisture evolution analysis, thermomechanical analysis, and dynamic mechanical analysis were evaluated, with regard to the type of information that could be obtained by each technique.

Ennis [78] studied DTA curves of four Cl-containing fibers. Saran, Cordelan, Teklan and Kanekalon, and their blends were influenced by experimental conditions, although not to be the same extent as those of poly(vinyl chloride) resin in powder form. The

Table 5 Temperature of the maximum rate of weight-loss (T_{max}) and the weight-fraction of material volatilised (W. F.) at each stage during the thermal degradation, in nitrogen, of polyurethane foam containing various flame-retardant additives[a]

Additive	Additive weight-loss stage			Polymer degradation stages				Residue
				First		Second		
	T_{max}, °C	W. F., %	W. F. lost on ageing, %	T_{max}, °C	W. F., %	T_{max}, °C	W. F., %	W. F. remaining, %
None	(x)	(—)	0.0	292	29.5	380	66.7	3.9
None (aged)	(x)	(—)		296	29.4	378	66.3	4.3
1. Tris(2,3-dibromopropyl) phosphate (T23p)(9.0%)	240 (sh)	6.7	5.9	278	25.3	376	63.3	3.5
Tris(2,3-dibromopropyl) phosphate (9.0%) (aged)	(x)	(—)		277	30.4	373	64.4	4.0
Tris(2,3-dibromopropyl) phosphate	230	13.6	7.5	278	23.7	370	55.3	6.5
Tris(2,3-dibromopropyl) phosphate (aged)	227	6.9		270	20.6	374	63.4	6.9
Tris(2,3-dibromopropyl) phosphate (a)	230	14.9	3.6	275	25.8	377	52.0	6.6
Tris(2,3-dibromopropyl) phosphate (a) (aged)	227	10.2		270	20.8	370	58.2	7.3
Tris(2,3-dibromopropyl) phosphate (a) (40%)	233	(*)	(—)	259 (sh)	42.6 (*)	369	50.2	6.7
2. Dibromopropanol (a)	117	17.1	17.1	294	25.0	376	54.5	1.7
Dibromopropanol (a) (aged)	(x)	0.0		296	30.0	378	63.5	1.9
3. Tris(allyl) phosphate	139	1.9	2.1	283	31.0	370	62.4	4.8
Tris(allyl) phosphate (aged)	(x)	0.0		285	29.5	378	65.2	4.3
4. Tris(xylyl) phosphate	(x)	0.0	0.0	287	43.1	384	51.0	5.7
Tris(xylyl) phosphate (aged)	(x)	0.0		284	43.1	377	50.5	5.8
5. Tris(2-chloroethyl) phosphate	191	16.2	15.2	277	24.5	371	53.3	6.0
Tris(2-chloroethyl) phosphate (aged)	(x)	0.0		293	24.6	381	70.0	5.2
6. Tris(2,3-dichloropropyl) phosphate (TCPP)	182	16.5	14.0	284	26.9	375	54.3	1.5
Tris(2,3-dichloropropyl)·phosphate (aged)	185	2.0		298	28.7	380	65.6	0.5
8.2% T23P + 8.2% TCPP	182, 243 (sh)	10.2	7.4	291	27.9	377	58.5	2.7
8.2% T23P + 8.2% TCPP (aged)	(x), 240 (sh)	3.4		286	29.3	378	64.5	5.5
7. Tris(2,4,6-tribromophenyl) phosphate	209	(—)	0.2	283	41.4	374	55.9	1.9
Tris(2,4,6-tribromophenyl) phosphate (aged)	(x)	0.0		286	38.4	376	57.4	3.2
8. Tris(2,4-dibromophenyl) phosphate	140	1.5	2.2	278	31.5	369	64.7	2.0
Tris(2,4-dibromophenyl) phosphate (aged)	(x)	0.0		282	30.2	372	65.5	2.2
9. Pentabromotoluene	234	13.8	3.4	290	26.4	377	56.0	2.1
Pentabromotoluene (aged)	234 (sh)	12.4		289	27.9	376	55.8	2.5
10. Decabromobiphenyl	(x)	0.0	0.2	290	25.3	335	68.2	5.7
Decabromobiphenyl (aged)	(x)	0.0		293	25.3	344	67.8	6.4

[a] Concentration (unless otherwise stated) pf 16.5% (w/w of foam). Heating rate, 5°C min^{-1}.

Notation. (aged), foam aged 16 h at 140°C; (a), foam produced by acetone-solution method; (x), stage does not exist; (—), could not be measured; (sh), a shoulder, rather than a well-defined peak, occurs on DTG trace, hence temperature was difficult to measure; (*), additive weight-loss stage and polymer degradation stage could not be separated (see Fig. 14).

importance of procedural variables in "fingerprint" application of thermal analysis for routine fiber identification was re-emphasized. Einhorn et al. [79] reviewed a strategy for analysis of thermal decomposition of polymeric materials, while Cassel [80] and Slusarski et al. [81] described thermal analysis on polymers and an apparatus for the thermomechanical analysis of polymers, respectively.

In 1978, Cullis and Laver [82] made detailed studies of the successive stages in the thermal degradation in air and nitrogen of carboxy-terminated polybutadiene (CTPB). During oxidation at high temperatures, a protective surface film was formed, this film ruptured at temperatures where pyrolysis lead to the formation of volatile products in the bulk of the polymer. Thermogravimetric curves for the degradation of CTPB in nitrogen were complex in shape, it appeared that the free-radical crosslinking and cyclisation reactions caused an increase in the thermal stability of the polymer during degradation.

It is of interest to point out that when CTPB is exposed to air at 250°, a jet-black skin is formed on the surface; it is completely effective in protecting the interior of the polymer against oxidation [83]. This skin is tough and owes its strength to peroxidic crosslinks formed during oxidation. Bevilacqua [84] has reported that at high temperatures thermal degradation experiments [82] were carried out using a Mettler Thermoanalyser 2 thermobalance. DTA studies were also made with the thermoanalyser using a special sample holder and two identical crucibles, 8 mm in diameter, one of which was left empty as a reference.

Supplementary visual information relating to the oxidation of CTPB was obtained by hot-stage microscopy. This technique greatly facilitated the interpretation of the TG curves and provided information unobtainable by other means.

Figure 16 shows the TG and DTG curves as well as the separately obtained DTA curves for CTPB heated in air. From these it can be seen that there are four distinct stages in the oxidative degradation process. Thus the first stage ends at T_1 (Fig. 16,

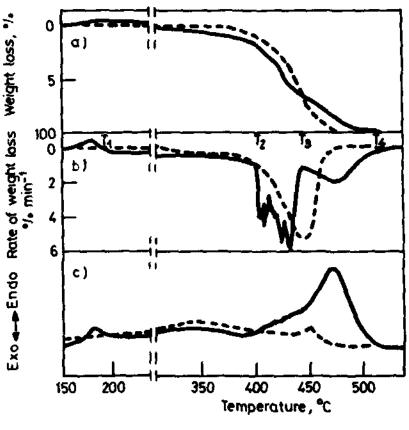

Fig. 16 The TG, DTG and DTA curves for CTPB heated in air (———) and in nitrogen (– – –)

Table 6 The weight losses incurred in each stage of the oxidation of CTPB in air

Sample size, mg	Heating rate, °C min^{-1}	Wt loss in 2nd stage (from T_1 to T_2), %	Wt loss in 3rd stage (from T_2 to T_3), %	Wt loss in 4th stage (from T_3 to T_4), %
9.11	5	14.4	59.4	26.2
8.68	3	16.5	51.3	32.2
8.11	3	19.0	48.3	32.7
6.06	5	22.3	40.6	37.1
8.28	5	23.3	41.0	35.7
9.29	1	26.6	34.9	38.5
9.54	1	30.0	29.0	41.0
7.22	1	36.8	21.0	42.2

part b), the second at T_2, and so on. Typical values of T_1, T_2, T_3 and T_4 are 189, 405, 447 and 500°, respectively. The weight losses incurred in each stage of the oxidation of CTPB in air are shown in Table 6.

The TG, DTG and DTA curves for CTPB, heated in flowing nitrogen, are also shown in Fig. 16. Although the TG curve appears to be of a simple S-shape, the DTG curve clearly exhibits a slight but well-defined shoulder on the low temperature side of the main weight loss stage (Fig. 16b). The weight lost in this first stage (or shoulder) was found to be independent on the heating rate and accounts for approximately 8% of the total, at a heating rate of 5° min^{-1}. An identical DTG curve was obtained when a high molecular weight polybutadiene rubber was heated. Thus the shoulder was evidently not due to the volatilization of low molecular weight CTPB chains, which had escaped crosslinking.

A device for differential thermal analysis was reported by Uryash et al. [85] and Komazawa et al. [86] studied the toxic gases evolved from fire retardant plywoods. In the latter work, the powders prepared from plywood containing 50% fire retardant were decomposed thermogravimetrically, and the amount of evolved gases were simultaneously measured by gas chromatography. Acrylic fibers, polyurethane, and PVC were similarly examined, to compare the amount of toxic gases evolved during thermal decomposition with that evolved from urea-formaldehyde resin and urea-formaldehyde resin (I) adhesives. The amounts of CO, CO_2 and HCN evolved during thermal decomposition and the temperature for evolution of toxic gases and CO_2 varied with the various fire retardants. CO evolution from plywoods treated with $(NH_4)_2HPO_4$, $(NH_4)_2SO_4$, and minalith increased with increasing temperature, whereas CO evolution for plywood treated with NH_4Br decreased with increasing temperature. Evolution of HCN from fireproofed plywoods was very slight, except for plywood bonded with I.

Hawkins [87] described the testing for oxidative stability against thermal oxidation. Accelerated tests for evaluating the resistance of polymers to thermal oxidation and the possible errors in extrapolating the accelerated test data down to service conditions were discussed.

Zapunnaya [88] described the possibilities for studying the syntheses and degradation of polymers according to the data of derivatographic measurements. Shalaby [89] published thermal methods in polymer analysis.

Lesiak et al. [90] described furfural as a new raw material for the synthesis of self-extinguishing polyurethane intermediate products. 1,4-hexanediol (I) and 1,4-heptanediol (II) and their halogen derivatives obtained from furfural, and TDI were used for preparation of fire retardant polyurethanes. Thermal stability of polyurethanes containing halogen-substituted diols was higher than that of I and II containing resins.

There were several interesting studies in this field in 1979 [91–99]. Polykova et al. [92] described studies of solid lubricating coatings with tribopolymer-forming filler by pyrolysis-mass spectrometry. Products obtained from a solid lubricant containing hexamethylene diisocyanate tribopolymer-forming filler 57, poly(vinyl alcohol) binder 28, and di-Buphthalate plasticizer 15% during friction between steel elements were pyrolized at 200–400° and the pyrolysis products were studied by mass spectrometry. The product obtained from the solid lubricant during friction was a highly crosslinked urethane polymer.

Chaigneau et al. [93] described some results on the study of polymers and plastic materials pyrolysis especially urea-formaldehyde resins. In the absence of oxygen the pyrolysis of urea-formaldehyde resins (I) produces CO, CO_2, H, CH_4 and HCN besides MeCN, EtCN, etc. In the presence of oxygen, I liberates HCHO at 5°. At 400° 1.37 g HCHO were formed per 100 g of I in 1.5 hour. The oxidation pyrolysis at 800° produced HCN 8.50, NH_3 4.0 and N oxides 1.50 g/100 g of I.

Andejs et al. [100] stated that differential scanning calorimetry, thermomechanical determinations and thermogravimetric analysis give information on coating properties e.g. curing conditions, elasticity, degree of crosslinking, and degree of degradation.

Antimony oxides were investigated [101] by combining TG and Raman spectroscopy. Residues and condensates produced from the TG analysis of Sb_2O_3 (senarmontite and valentinite), Sb_2O_4 (α and β forms), $Sb_2O_5 \cdot x\, H_2O$ and Sb_6O_{13} were identified by X-ray diffraction, Raman and infrared spectroscopy. The formation of β-Sb_2O_4 was accomplished by heating α-Sb_2O_4 or Sb_6O_{13} in closed quartz capillaries at 960°. Heating the two polymorphs of Sb_2O_3 in air revealed that both senarmontite and valentinite exhibited simultaneous volatilization and oxidation. However, senarmontite displayed a net weight loss of 21.26% whereas valentinite gained 0.8–2.4%. TG experiments of $Sb_2O_5 \cdot x\, H_2O$ heated in air indicated that the 650–850° plateau was Sb_6O_{13} and the 890–970° plateau was α-Sb_2O_4. Infrared and Raman spectra of all the above mentioned antimony oxides were recorded, with the Raman spectra of α-Sb_2O_4, β-Sb_2O_4 and Sb_6O_{13} being reported for the first time.

Application of thermal analysis for the investigation of coating deficiencies was reported by Sickfeld and Heinze [102]. Defects in coatings and sealants were examined by DTA, TG, DTG and thermomechanical analysis (TMA), combined with conventional testing as required. Defective curing of acrylic resins was examined by isothermal DTA, resin-hardener mixing errors by determination of thermal stability by TG–DTG, solvent retention by PVC coatings by determination of the glass temperature and defective cohesion of epoxy powder coatings on tank interiors by determination of the glass temperature via TMA. Anomalous swelling of inadequately resistant reactive-coatings was examined by isothermal TMA.

Recent methods for characterization of thermosetting resin prepolymers were described by Fukuda [103]. The methods included DSC for determining relations between hardening conditions and degree of hardening of polyesters, phenolic resins, epoxy resins and urea resins as well as other thermal analytical methods, infrared and NMR.

Laser degradation of polymer coatings on reflective heat sinks was reported by Cozzens and Fox [104]. The volatilization rate constants kJ of 10.6 μ laser induced degradation of thin non-char forming coatings of Et acrylate–ethylene copolymer, polystyrene, poly(Et-methacrylate), poly(Me methacrylate) and nitrocellulose on Al heat sinks were 0.30, 0.85, 1.6, 2.1 and 3.1, respectively at 110 W/cm^3. Degradation resulted from exposure to the thermal environment provided by the heat sink as well as direct absorption of laser radiation. Relative polymer stabilities at this laser irradiation level and by conventional heating methods were in agreement.

A method of different equations was used to determine the kinetic parameters of the degradation of polymers by isothermal thermogravimetry [105]. The method was simple and applicable to degradation processes for all reaction orders. The kinetic parameters determined for two styrene polymers agreed with parameters obtained by other methods.

Generalization of Reich's method was reported by Agherghinei [106]. Kinetic parameters were determined by a generalization of Reich's method. The method involves a knowledge of the values of the weight loss, temperature, rate of weight loss and derivative of the rate of weight loss, corresponding to a certain point in the thermogravimetric curve. Kinetic parameters determined by the method agreed with those determined by Reich's method.

Egyed and Simon [107, 108] reported recent investigations on the flame retardation of cellulosic fibrous materials. Derivatography and quantitative DTA methods for untreated cotton and fabric treated with P- and N-containing flame retardants were found suitable for determining the efficiency of flame retardants and provided data that correlated with oxygen index values. The temperature characteristic of the thermal stability of the sample could be read directly and the complete process of decomposition, including the formation of incombustible residues, could be followed. The weight losses corresponding to the end-points of the main decomposition processes of untreated and treated fabrics were characteristic of the flammability, whereas the difference between these weight losses characterized flame retardation.

Thermal investigation of the dehydration process was then followed [108]. Thermal analysis showed that treatment of cotton with Pyrovatex (di-Me phosphorpropionic amide) affected the thermal decomposition of cellulose by decreasing the amount of water vapour formed in the main decomposition, presumably by inhibiting the dehydration process. Since levoglycosan is a product of this process, the result supported the inhibition theory according to which Pyrovatex CP inhibits the formation of the flammable intermediate in the solid phase.

The capability of the DSC III (Differential Scanning Calorimeter, SETARAM, Lyon, France) for doing a gas sweeping of the sample allows the study of the solid-gas reactions [109]. In this report the thermal study of cellulose-influence of a fire retardant treatment was reported. Two samples of cellulose were studied, the first one called "O" (original) and the other "FR" which was fire retarded. The two samples were studied under oxygen and argon sweeping in order to investigate the effect of fire retardant treatment.

The SETARAM DSC-III was used with its cooling system in order to decrease the time between two runs. The samples were weighed with the SETARAM γ-21 N4 Analytical Microbalance and then analyzed in an alumina cell. The samples were scanned under oxygen at 5 deg min^{-1} up to 520°. The sample "O" (Fig. 17) shows two exothermic effects with their maxima at 313° and 427°. The heats of these two effects measured as shown in Fig. 17 are 6330 J/g and 3390 J/g.

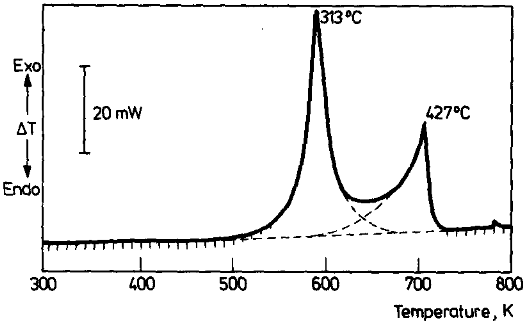

Fig. 17 DSC curve of cellulose tissue. $m = 3.46$ mg; Crucible or cell: alumina; atmosphere: oxygen; heating rate: 5°C • min^{-1}; Recorder $\begin{cases}\text{Sensitivity: 1 mV full scale}\\ \text{Chart speed: 2.5 mm • min}^{-1}\end{cases}$

The sample "FR" in the same conditions (Fig. 18) shows also two exothermic effects with two maxima at 290° and 478°. The heats of these two effects measured as shown in Fig. 18 are 4940 J/g and 3240 J/g.

The same samples were also scanned at 5 deg min^{-1} under argon (Figs 19, 20). The obtained curves did not show any significant thermal effect. Only a small wave at about 320° could be noticed. This weak phenomenon could be certainly amplified because a small sensitivity (1 mV full scale) was employed.

The gas analysis could not be performed as DSC was not, at the time of these experiments, connected to a gas chromatograph.

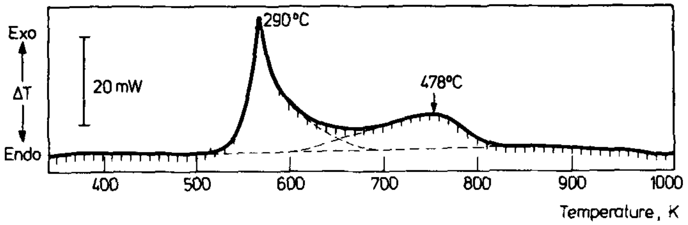

Fig. 18 DSC curve of cellulose FR. $m = 3.39$ mg; Crucible or sell: alumina; atmosphere: oxygen; heating rate: 5°C • min^{-1}; Recorder $\begin{cases}\text{Sensitivity: 1 mV full scale}\\ \text{Chart speed: 2.5 mm} \cdot \text{min}^{-1}\end{cases}$

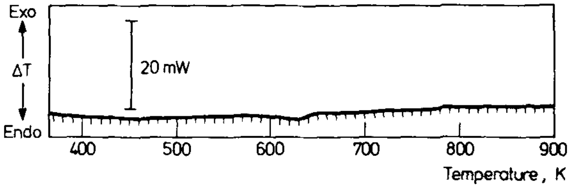

Fig. 19 DSC curve of cellulose "0". $m = 3.04$ mg; Crucible or cell: alumina; atmosphere: argon; heating rate: 5°C • min^{-1}; Recorder $\begin{cases}\text{Sensitivity: 1 mV full scale}\\ \text{Chart speed: 2.5 mm} \cdot \text{min}^{-1}\end{cases}$

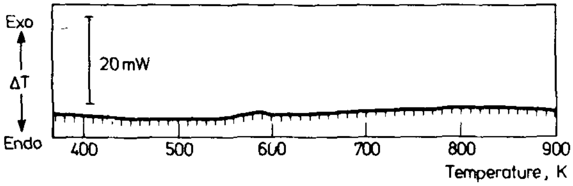

Fig. 20 DSC curve of cellulose FR. $m = 3.77$ mg; Crucible or cell: alumina; atmosphere: argon; heating rate: 5°C • min^{-1}; Recorder $\begin{cases}\text{Sensitivity: 1 mV full scale}\\ \text{Chart speed: 2.5 mm} \cdot \text{min}^{-1}\end{cases}$

A correction δT was applied to the temperature, which was a function of scanning rate and temperature of program.

$$\delta T = b_0 + b_1 \cdot T_p + b_2 V$$

where T_p = temperature of program, °, V = scanning rate, deg min^{-1}, with $b_0 = 0.35°$, $b_1 = 0.0019$, $b_2 = 0.54$ min.

The capability of gas sweeping the sample allowed the study of decomposition of cellulose under oxygen and argon, as for a fire proofed cellulose. It was shown that the decomposition under oxygen occurred in two stages.

Thermal decomposition of polymers was also reviewed by Margossian [110]. Brennan [111] described thermal analysis for quality control. DSC, thermogravimetry and thermomechanical analysis were reviewed for polymers quality control.

Camino et al. [112] studied the effect of chlorinated fire retardant additives on the thermal degradation of polypropylene. This paper reported some preliminary results of a project in which a comprehensive study would be made of the thermal degradation of mixtures of polyolefins and halogenated fire retardant additives. The system studied was a mixture of polypropylene (PP), a chlorinated paraffin (Cereclor 70) (CP), 9% (10 phr), and basic bismuth carbonate, 9% (10 phr).

The TVA traces of pure PP and the mixture are compared in Fig. 21.

The volatilization began at a lower temperature in the mixture and occurred over a wider temperature range. The maximum rate of volatilization occurred about 50° lower than in pure polymer. Figure 22 compares TG curves for bismuth carbonate (1), and the chloro-paraffin (2) with the theoretical curve for a 50/50 mixtures (3) assuming no interaction. The experimental TG (4) and DTA curves for the mixture indicated that an exothermic reaction occurred, with production of volatiles, at a lower temperature and in a total amount larger than expected. It seemed likely that bismuth chloride was present amongst these volatiles.

Simpon et al. [113] applied a derivatograph in flame retardation research in determining ignition temperature. The study was aimed at modifying the derivatograph for the measurement of the flash ignition and self-ignition temperature of various materials and to combine these characteristic data with the simultaneously measured TG, DTG and DTA curves. Figure 23a shows the thermal curves of polystyrene foam using a 5 deg $\min^{-1}$ heating rate. Thermal decomposition of the sample took place between 300° to 400° according to the DTG curve. The curves of the same sample obtained by sparking are demonstrated on Fig. 23b. The flash ignition temperature is indicated on curve T_1 at 345°.

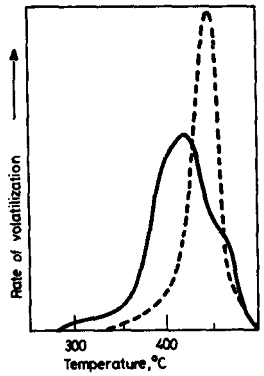

Fig. 21 TVA curve of PP (dashed line) and a mixture of PP, CP, 9% (10 phr) and basic bismuth carbonate, 9% (10 phr) (solid line). Traces for total rate of evolution of volatiles non-condensable at 25°C. Heating rate: 10°C/min; sample size: 60 mg

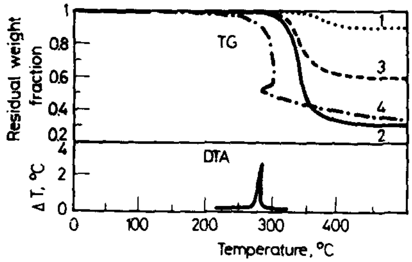

Fig. 22 Thermal analysis of CP (———), basic bismuth carbonate (·········) and a 1 : 1 w/w mixture, calculated (— — —), experimental (—·—·—). Heating rate: 10°C/min; sample size: TG, 10 mg, DTA, 3 mg; atmosphere: N_2, 90 cm^3/min; instrument: DuPont 990 Thermal Analyser

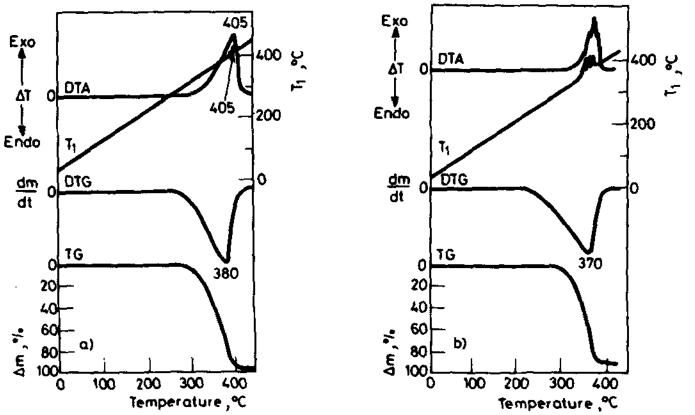

Fig. 23 Thermal curves and ignition temperature of (a) polystyrene sample (without sparking); (b) polystyrene sample (with sparking)

Simon et al. [114] also reported the advantage of thermo-analytical techniques in flame retardation research from theoretical and practical point of view. The reaction between cellulose and the FR was seen in the DTG curve at 180°. The thermal stability was slightly decreased, but at higher temperature the TG curve of the treated sample always was above that of the non-treated sample. The treatment decreased the amount of potentially flammable gases. When compared at a characteristic point, the end of the main decomposition process, there was a 25% difference in weight loss. The change in enthalpy relating to the main decomposition was smaller by 23% and this amount of heat was released at a lower rate than in case of the untreated sample as measured with a SETARAM DSC. Antimony(III) oxide combined with a halogen-containing compound was found to be a good fire retardant. The evaporation of

$SbCl_3$ was an extremely rapid endothermic process and occurred within a narrow temperature range. In the thermal curves studied for a powdered PVC sample, the HCl content was around 60%. Increasing amounts of Sb_2O_3 were added to the PVC and the $SbCl_3$ formation was observed. The higher the Sb_2O_3 content of the mixture, the larger was the peak at 280° in the DTG curves due to the formation of antimony halides.

In the thermal curves of PVC foam and of PVC foam retarded with a P-containing compound, HCl formation was independent of the atmosphere, and the weight loss was 28% in all cases.

Runt et al. [115] reviewed thermal analysis of polymers, in particular differential scanning calorimetry and DTA. Bredereck [116] reviewed the effect of thermal degradation on the general properties of unplasticized PVC.

Some limiting aspects of the thermogravimetry of polymers was reported by Schneider [117]. The effect of volatility of degradation products and the influence of reaction heat on thermogravimetry of polymers were demonstrated for polyisoprene (I) and polyethylene (II). The weight loss in I with predominantly cis-1,4-configuration was much faster than in I with about 50% vinyl sequences where the probability of network formation due to double bonds in the pendant groups increased. The network formation retarded the formation and elimination of volatile products and consequently the weight loss. At lower heating rates the TG curves of II clearly exhibited a jump in weight loss as if a modification of the reaction mechanism had occurred. These results were explained in terms of the volatility of the fragments. It was recommended that higher heating rates should be used to assure for elimination of the larger fragments formed during thermal degradation.

Hilado et al. [118, 119] studied some toxicity results. A rising temperature program to integrate fixed temperature off-gas toxicity was used [118] to determine polymer off-gas toxicity in experiments using no forced air and forced air. Without forced air flow the deviation of the experimental survival time value from the calculated value averaged 6% for 6 synthetic polymers for which CO was the principal toxicant and with a 1 l/minute air flow the deviation averaged 12.4% for the polymers.

Increased thermal stability, as indicated by reduced weight loss heating appeared to be accompanied by decreased relative toxicity in the case of polymer groups from which CO was the principal toxicant evolved [119]. For polymers containing N decreasing weight loss appeared to be accompanied by decreasing toxicity within a certain range, and by increasing toxicity within another range. For polymers containing S, decreasing weight loss appeared to be accompanied by increasing toxicity over the entire range studied. Thus, the increase in relative toxicity observed with decreasing weight loss for the N- and S-containing polymers, contrary to the trend observed for other groups of polymers, indicated that volatile compounds containing these elements might be significant toxicants.

Brennan et al. [120], Hill [121] and Peppas et al. [122] also reported some work on thermal analysis of polymer foams, small scale fire tests for PVC, and migration of potentially toxic compounds from plasticized polymers, respectively.

Self-heating in coating resins and the occurrence of fires were discussed by Schmitz [123], and a model was derived giving the optimum conditions for self-heating and for its measurement. A DTA apparatus developed for determining the heat of reaction was reported, which gave results identical with the trends of published data.

Zapunnaya et al. [124] recently made studies of the thermal stability of organosilicon polyurethanes. The oxidative thermal degradation (20–700°) of phenylglycoxysiloxane oligomer (I) with hexamethylene diisocyanate biuret (II), or of I with a trimethylolpropane-tolylene diisocyanate (1:3) adduct (III), or of I with II and III (II/III ratios were 1:1 and 3:2) was studied by DTA, DTG and IR spectroscopy. The films from a I–II–III (II/III ratio 1:1) copolymer exhibited the lowest weight loss (7%) at the initial degradation stage (170–260°), as well as other favorable thermal properties, due to the presence of electron-acceptor and -donor substituents on N atoms, which resulted in an increased recombination of the radical formed.

Some relationships between relative toxicity and total and lethal weight loss of polymers was reported by Hilado et al. [125], while Ilichkin et al. [126] described studies of the composition and toxicity of volatile products of the thermal degradation of polymer products. All the polymers investigated showed very high quantities of CO_2 and CO during their thermal degradation [350, 600 and 800°]. CO_2 increased with increasing temperature. Vilares showed an invers relation between the evolution of CO and the temperature of decomposition. It also showed an unusual amount of CO evolution at 350 and 800°. Other O-containing decomposition products were negligible. A high amount of aliphatic hydrocarbons were liberated from PPU-306, vilares and linoleum TTN. HCN was formed from PPU-306 and a product made from PhOH–HCOH and melamine–HCOH resins. In toxicology experiments, animals subjected to degradation product vapors died < 1 day except in case of linoleum TTN. Based on equal weight decomposition, TTN was the safest material. Vilares was the most toxic. Some of the products which liberated HCl gas caused irritation.

Camino et al. [127] described the thermal degradation of a highly chlorinated paraffin used as a fire retardant additive for polymers. Thus in thermal analysis of chlorinated paraffin (70% Cl) used as a flame retardant, the main volatile degradation product was HCl, which was eliminated in two steps: On heating above 250°, the chlorinated paraffin eliminates 60–70% of its Cl in an apparent 0 order reaction, forming a charred residue containing about 30% Cl. This more stable form degrades above 300° giving mostly HCl. The activation energy of the process between 250° and 350° was 167.2 kJ/mol.

Dynamic and isothermal gravimetric analysis and DTA were carried out on the 951 thermogravimetric analyser and DTA modules of a DuPont 990 Thermal Analyser instrument, under nitrogen flow of 90 cm^3 min^{-1}. The TG curve in Fig. 24 shows that the thermal degradation of chlorinated paraffin (CP) is a two stage process. The DTA curve shows that the process is endothermic at first but becomes exothermic as the temperature increases and degradation proceeded.

The second stage occurred over a broader temperature range, starting above 450°. At 800°, a further 10% of weight had been lost but the residue was still volatilising

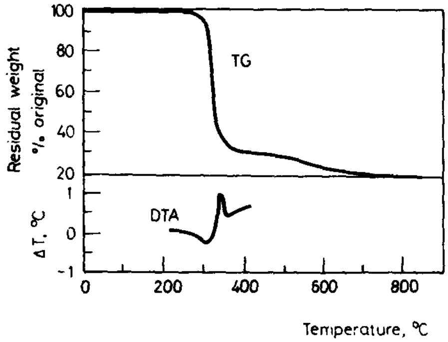

Fig. 24 Thermal analysis of CP. Heating rate: 10°C/min; atmosphere: nitrogen, 90 cm^3/min; sample size: TG, 10 mg, DTA, 3 mg

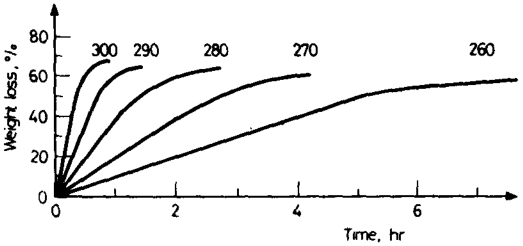

Fig. 25 Isothermal TG of CP. Atmosphere: nitrogen, 90 cm^3/min; sample size: 10 mg

though at a very low rate. The main product of degradation was HCl as measured by titration, 70% w/w of the CP was evolved at 800° compared with the theoretical value of 72% calculated for complete elimination of the chlorine in the chlorinated paraffin.

The results of isothermal TG on CP between 260 and 300° are shown in Fig. 25. A constant rate of weight loss, increasing with temperature, was shown up to about 40–50% of the original weight, this value was independent of the temperature. The rate of weight loss then decreased, the total weight loss tending to a 70% limit as in the first stage of dynamic TG.

Thermal degradation of polymer-fire retardant mixtures e.g. polypropylene-chlorinated paraffin and evidence of interaction were reported by Camino and Costa [128]. It was shown that the thermal behaviour of polypropylene and chlorinated paraffin (Cl 70%) was not the sum of their individual behaviours. An interaction was shown to take place in the degrading mixtures which was related to the low temperature dehydrochlorination step of the chloro-paraffin. This occurred at temperatures at which pure polypropylene was stable and lead to an increase in the overall rate of volatilization of the mixtures compared with that of the separate components. A partial overlapping of volatilization of polymer and additive, which otherwise degraded in two well separated temperature ranges when heated alone, was observed. Results are shown in Figs 26, 27.

Russo et al. [129] reported the effect of polyurethane and polyimide thermal decomposition products on shock escape and avoidance behaviour. Decomposition products were generated by placing 1 g samples of the foams on a conductive plate heated in either 435, 605 or 775°. The decomposition products of the two foams varied differentially with test temperature. At the two lower temperatures, the decomposition products of polyurethane proved to be more behaviourly disruptive than those of polyimide, while at 775°, the reverse was true.

The kinetics of the thermal dissociation of urethane and other polymers was described by Kordomenos et al. [130] and thermal degradation of bromine-containing polymers by Grassie et al. [131]. The oxidative stability of polyethylene was given by DTA [132]. Developments in Polymer degradation are also reported in a book edited by Grassie [133]. Childress and Barker [134] described studies on brominated phosphite and phosphate flame retardants. The thermal behaviour of these was

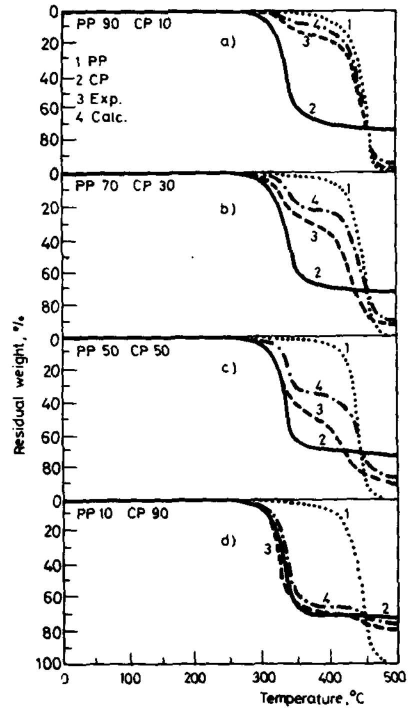

Fig. 26 Thermogravimetric curves of: polypropylene (PP) (1); chloroparaffin (CP) (2); mixtures: experimental (3); calculated assuming additive behaviour (4); compositions w/w. Sample, 10 mg; heating rate: 5°C/min; atmosphere: nitrogen, 90 ml/min

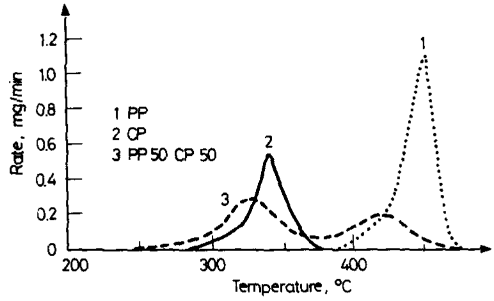

Fig. 27 Derivative thermogravimetric curves of: polypropylene (PP) (1); chloroparaffin (CP) (2); and a 1 : 1 w/w mixture of polypropylene and choroparaffin (3). Sample, 10 mg; heating rate: 10°C/min; atmosphere: nitrogen, 90 ml/min

evaluated by DTA, DSC and TG. Those derived from 2,3-dibromopropanol and 2,2,2-tribromoethanol appeared to undergo dehydrohalogenation between 260–300°. The other esters appeared to decompose at much higher temperatures. These results suggested that the various esters could show a range of flame retardant efficiencies depending upon the polymer substrates involved.

Metal compounds as flame retardants for organic polymers have been described by Cullis [135] and several degradation and thermal analysis results are included. In order to compare the likely flame retardant action of metal oxides with that of antimony oxide, thermogravimetric studies have been made of a whole range of such oxides mixed with a chlorinated wax and Table 7 shows the extents of their volatilization as metal oxides. Inert oxides are not volatilized and do not affect the decomposition of the chlorinated wax. The main limitation of thermogravimetric studies is of course that, while they show the occurrence of interactions in the condensed phase leading to the formation of volatile products (which may or may not influence the flame reactions), they give little information about reactions resulting in the production of new species which may exert an inhibiting action on the combustion of the organic polymers by virtue of reactions occurring purely in the condensed phase.

A considerable number of metal oxides have been investigated as partial replacements for antimony oxide in flexible polyurethane foams containing some chlorine. Thermogravimetric studies of polyurethane foams containing some metal oxides as partial substitutes for antimony oxide showed very little change in behaviour. Fe_2O_3 and CuO both of which improve the flame retardant influence of Sb_2O_3, lower the initial decomposition temperature of SbOCl. In contrast, CaO and ZnO, which have an antagonistic effect on the action of antimony oxide, apparently inhibit the breakdown of the oxychloride. This strongly suggests that SbOCl is the first product formed in systems containing Sb_2O_3 and a halogen compound and that this then undergoes thermal decomposition to yield antimony trichloride as the actual species responsible for flame retardance.

Table 7 Extents of volatilization of metal oxides when heated with a chlorinated wax (Cl:metal = 3:1)

Metal oxide	Percentage of metal oxide volatilized	
	873 K	1273 K
Inert oxides		
Al_2O_3	0	0
Cr_2O_3	0	0
NiO	0	0
TiO_2	0	0
ZrO_2	0	0
Catalytic oxides		
CoO	0	0
Fe_2O_3	6	6
Reactive oxide forming involatile chloride		
Ag_2O	0	0
Reactive oxide forming probably volatile chloride		
SnO_2	16	16
Reactive oxides forming easily volatile chloride		
Sb_2O_3	90	90
Bi_2O_3	100	100
CdO	0	100
CuO	60	94
PbO	3	81
MoO_3	38	79
ZnO	88	88

There is no definite thermogravimetric evidence for chemical interaction between any of the aluminium oxides and the antimony-halogen system, although the partial replacement of Sb_2O_3 by $Al_2O_3 \cdot H_2O$ cases some decrease in the endothermicity of the overall combustion reaction. This is of interest inasmuch as a 1:1 mixture of Sb_2O_3 and Al_2O_3.

Zinc borate is quite widely used in conjunction with halogen compounds either as a partial replacement for antimony oxide or with chlorinated polyester resins or poly(vinyl chloride) as a total replacement. Comparative studies have been made of the DTA curves in oxygen of poly(vinyl chloride) containing zinc borate alone, Sb_2O_3 alone, and a mixture of the two compounds ([136], Fig. 28). This shows that the thermal behaviour of the polymer containing antimony oxide is almost the same as that of the polymer on its own but that samples containing zinc borate react at temperatures 100°; this reaction is little affected by the presence of antimony oxide. Essentially similar results have been obtained with a chlorinated polyester, suggesting that the mechanisms of flame-retardant action must be different for the two compounds and that zinc borate probably acts mainly in the condensed phase.

Cobalt ammines have been shown to be very good flame retardants for flexible polyurethane foams [137]. The results obtained with $Co(NH_3)_6Cl_3$ could probably

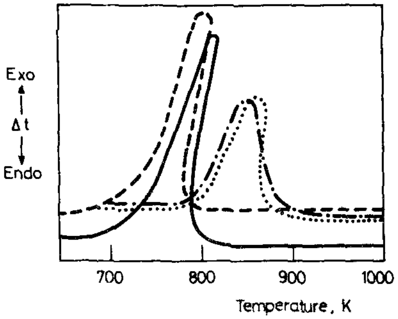

Fig. 28 The effect of antimony oxide and zinc borate on the oxidative degradation of poly(vinyl chloride). (———), PVC alone; (— — —), PVC containing 10 phr Sb_2O_3; (·········), PVC containing 10 phr zinc borate; (—·—·—), PVC containing 5 phr Sb_2O_3 + 5 phr zinc borate

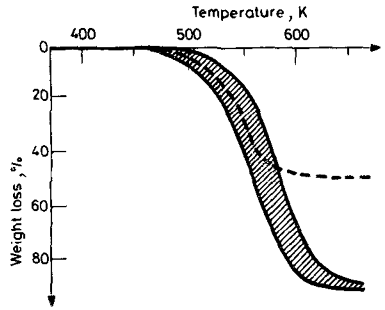

Fig. 29 Thermogravimetric curves for the thermal degradation of polyurethane foam containing 3.7–4.0 wt% H_2O and $Co(NH_3)_6Cl_3$. (———), polyurethane; (— — —), cobalt amine

be ascribed to the fact that it breaks down in precisely the same temperature region as the polymer (Fig. 29), according to the overall equation:

$$6\,Co(NH_3)_6Cl_3 \rightarrow 6\,CoCl_2 + 6\,NH_4Cl + N_2\uparrow + 28\,NH_3\uparrow$$

In other words, 6 moles of the complex yield, on decomposition some 35 moles of non-combustible volatile products. Similar encouraging results had been obtained with other cobalt-ammine complexes e.g. $Co(NH_3)_6Br_3$ and $[Co(NH_3)_5Cl]Cl_2$.

Starnes [138] has also reported on fire retardance of polymers by metal oxides. A detailed work on the application of thermal analysis methods to oxidation and stabilization of polymers is given by Billingham, Bott and Manke [1]. They reviewed previous work on DTA and DSC in the study of polymers. A simple isothermal DTA apparatus designed for the study of polymers was also described.

Irwin [139] has published a detailed bibliography on analytical and pyrolysis techniques in polymers. The following references may be of interest [140–163] but

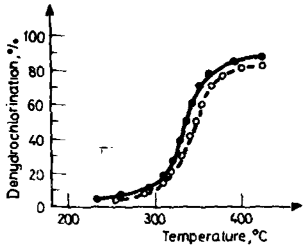

Fig. 30 Dynamic dehydrochlorination curves: •, CP; ○, mixture of PP 70 and CP 30. Composition w/w. Heating rate: 5°C/min; atmosphere: nitrogen, 60 cm^3/min

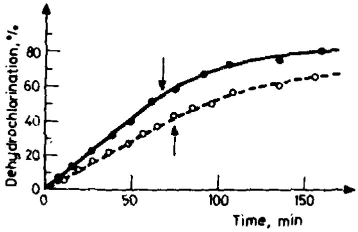

Fig. 31 Isothermal dehydrochlorination at 280°C: •, CP; ○, mixture of PP 70 and CP 30. Composition w/w. Atmosphere: nitrogen, 60 cm^3/min

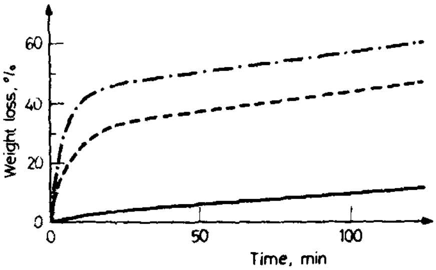

Fig. 32 Isothermal mass change curves at 350°C; (———), PP; (— — —), mixture of PP 70 and CP 30; (—·—·—), mixture of PP 90 and CP 10. Composition w/w. Atmosphere: nitrogen, 90 cm^3/min

for more references on synthetic polymers, pages 11–17 of reference [139] should be consulted.

Allan and Struszczyk [164] recently reported thermal properties of chitosan-phosphazene polymers. The chitosan-phosphazene polymers have lower temperatures of the maximum of the exothermic effect and of maximum mass-loss rate as compared with those of chitosan. This paper reported thermal properties in the temperature range 20–500°. The thermal investigations were made with a derivatograph type OD-102. In the case of DTA and TG, experiments were carried out with 100 mg samples. The investigations were performed in an atmosphere of air in the range of temperature 20–500° and at a heating rate of 5 deg/min. The degradation of this type of fire retardant polymers was observed at relatively low temperature, yielding volatile, non-flammable, flame-inhibiting products.

Camino et al. [165, 166] described the mechanism of interaction in polypropylene-chlorinated paraffin mixtures [165] and degradation products of the same [166]. The dehydrochlorination behaviours of the chlorinated paraffin (70% Cl) pure and in a mixture with polypropylene are compared in Fig. 30. The shapes of the curves are substantially similar, but the curve referring to the mixture was displaced by 10–20° to higher temperatures indicating a lower rate of HCl elimination as compared with the pure chlorinated paraffin.

Isothermal experiments were carried out at relatively low temperatures 260–290° at which the reaction rate was low and the effect of heat transfer was eliminated. The mechanism proposed accounted for the attack of the chlorine atoms which propagated the dehydrochlorination reaction on the tertiary hydrogen atoms of polypropylene with the formation of HCl. The kinetic chain length of the dehydrochlorination was decreased and the rate of evolution of HCl was lowered while the radicals formed on the polypropylene chain lead to its scission and volatilization.

Isothermal dehydrochlorination and isothermal mass change curves are shown in Figs 31 and 32.

In the other work [166], Camino et al. reported that when polypropylene is thermally degraded in mixtures with a highly chlorinated fire retardant paraffin, a smaller amount of the lighter hydrocarbon fraction, which is also modified in composition, is evolved compared with that evolved from pure polypropylene. A corresponding increase in the amount of high boiling chain fragments was obtained from the mixtures. This effect was explained in terms of the interactions which occurred between degrading polymer and the additive. Camino et al. [166] pointed out that in the presence of chlorinated paraffin, the thermal degradation of polypropylene gave a relatively larger amount of hydrocarbons which, burned alone, are characterized by higher oxygen index. For example, among the C_1–C_4 hydrocarbons evolved in the thermal degradation of polypropylene, a considerable increase in the proportion of methane, which is characterized by the highest oxygen index, was observed in the case of a mixture of polypropylene with 30% chlorinated paraffin, as compared with pure polypropylene.

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Zusammenfassung — Die durch thermische Analyse, insbesondere durch DTA und DSC auf dem Gebiet der mit verschiedenen entzündungsretardierenden Zusatzstoffen behandelten synthetischen und natürlichen Polymeren erhaltenen Ergebnisse werden in einer Übersicht zusammengefasst. Die zitierten 166 Publikationen betreffen die wichtigsten aktuellen Problem.

Резюме — Статья касается обозрения результатов исследования синтетических и природных полимеров, обработанных различными замедлителями пламени, с помощью термического анализа и в особенности, методами ДТА и ДСК. Приводится 166 литературных ссылок на все важные области данной проблемы.