A STUDY OF FLAME RETARDED POLYMERS BY THERMAL METHODS

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ABSTRACT

The use of molybdenum trioxide as a flame retardant in halogen-containing polyester resins has been studied. Although oxygen index measurements showed that Sb_2O_3 is more effective as a flame retardant, MoO_3 formulations produce far less smoke. The thermal degradation of these polyesters has been investigated by TG, DTA and by hot-stage microscopy, and the changes in the decomposition curves caused by the MoO_3 studied in both nitrogen and air atmospheres. MoO_3 has been shown to act predominantly by a condensed phase mechanism, to increase the number of decomposition steps, to produce more char, and to alter the structure of the char. Analysis of the volatiles and solid products has given no evidence for any molybdenum–halogen compound.

INTRODUCTION

The need for more effective flame retardants and for the suppression of smoke during burning is always present. Smoke and toxic gases account for many of the fire fatalities, especially in buildings and in aircraft fires [1,2]. The tendency for synthetic polymers to replace traditional building materials is often quoted as being responsible for an increase in the smoke hazard.

Polyester resins are widely used for structural and decorative purposes and if untreated constitute a hazard by both fire and smoke. The addition of antimony oxide, Sb_2O_3, particularly in the presence of polymers containing halogen or a halogen additive, has been shown to be very effective as a fire retardant but to produce a greater amount of smoke during burning [3–6]. This work has studied the action of molybdenum trioxide, MoO_3, in polyesters containing bromine. The incorporation of molybdenum compounds into polymers has been shown to reduce the smoke evolved during burning and to show a synergistic effect if halogen is present in the polymer itself or as a halogen-containing fire retardant additive. Church and Moore [7] studied

PVC and polyester resins, and Skinner et al. [8] showed the synergism with halogenated additives.

The methods used to test fire retardants have been reviewed [2] and include small-scale ignition tests, critical oxygen index, flame spread tests on small specimens or whole structures, smoke production and toxicity tests. Thermal analysis has been used extensively to study the polymer decomposition reactions and to test polymer stability.

Learmonth and Thwaite [9] also used thermal analysis to study the interaction between Sb_2O_3 and various halogen sources. Pitts and co-workers [5a,b] showed that, after TG and DTA studies, the mode of decomposition of an antimony fire retardant could be matched to the polymer decomposition. Brauman and Brolly [6a] used thermogravimetry and differential scanning calorimetry with pyrolysis to study the Sb_2O_3–halogen fire retardance in several polymers. Their work showed how TG and DSC could demonstrate the differences in decomposition caused by additives, and the reactions between additives. For example, the endothermic degradation of a chlorinated wax was altered by the addition of Sb_2O_3 into a highly exothermic event. They were also able to analyse volatile species and show that the effective flame retarding species was a volatile antimony trihalide.

EXPERIMENTAL

The polymers used in these experiments were all prepared by reacting maleic anhydride, phthalic anhydride and either neopentyl glycol [2,2, dimethyl propane diol, NPG, (I)] or dibromoneopentyl glycol [2,2, (bromomethyl) propane diol, DBNPG, (II)] in the ratio 1:1:2.2. The slight excess of glycol is lost during the reaction. This reaction was allowed to complete before mixing with about 35% styrene.

Analysis for bromine was carried out by oxygen flask combustion followed by potentiometric titration with silver nitrate. Resins containing known concentrations of bromine were then prepared by mixing thoroughly appropriate quantities of resins from (I) and (II). Commercial, undensified molybdenum trioxide was mixed in at this stage and the resin finally degassed and cured at 90°C to complete the crosslinking of the chains by the styrene.

The final resins were transparent, slightly yellow solids, unless molybdenum was present when they were opaque blue-grey solids. The MoO_3 did not alter the mechanical properties of the resin.

Thermogravimetry was performed on the Stanton-Redcroft TG 770 thermobalance using 10 mg samples heated in flowing air or nitrogen, generally at a heating rate of 10°C min^{-1}, although heating rate was shown to have little effect on the mode of decomposition. The DTG curves were obtained electronically. The reproducibility of the mass losses was within ±1% and of temperatures ±5°.

Differential thermal analysis was carried out on a Stanton-Redcroft DTA 673-4 using samples of about 40 mg and heating rates of 10 or 15°C min^{-1} in flowing air or nitrogen, with Al_2O_3 as reference. The larger samples and different geometry of the apparatus may give slightly less control of the gaseous environment over the samples in DTA than in TG.

Critical oxygen index studies were conducted on a Stanton-Redcroft oxygen index apparatus and smoke and char studies on an Arapahoe smoke chamber, using the standard manufacturers' sample size.

The appearance of the samples at each stage of the decomposition was noted and photographs taken using either the Stanton-Redcroft hot-stage microscope unit or by photographing the stage of a Perkin-Elmer DSC 1-B through a low power microscope.

Analyses of volatile and solid products were carried out by several techniques. Volatiles from samples heated in a furnace were trapped in a tube cooled in solid CO_2–acetone, and subsequently analysed by GC mass spectrometry. Sublimates and other solids were studied as nujol mulls or KBr discs by IR, although the opacity of the residues often required considerable processing of the spectra. Solid samples were also examined by laser Raman spectroscopy, and residues characterised by X-ray diffraction.

RESULTS

Interaction between additives

The effect of molybdenum trioxide on the decomposition of pure DBNPG (II) in air was investigated using DTA. Figure 1a shows the pure DBNPG melting at 98°C, giving a shallow endotherm peaking at 280°C followed by large, complex exotherms ending at 550°C.

Incorporation of MoO_3 did not affect the melting, but lowered the temperatures of the exotherms (Fig. 1b). This effect was more noticeable with "undensified" than with "Analar" MoO_3. An additional peak at 790°C corresponds to the sublimation of MoO_3 in accord with the literature.

Mixtures of an "inert" filler, Al_2O_3, and DBNPG also showed the same behaviour (Fig. 1c), suggesting that the surface of the powders facilitates the decomposition of the glycol. Infrared spectra of the solid products of decomposition at comparable stages were similar with and without MoO_3 present, and the residue at 550°C in Fig. 1b gave an X-ray diffraction pattern showing all the lines of MoO_3, although they were slightly broadened.

Fire retardance studies

The effect of MoO_3 on the critical oxygen index (COI) of these polyester resins is shown in Fig. 2, with the results obtained using Sb_2O_3 given for
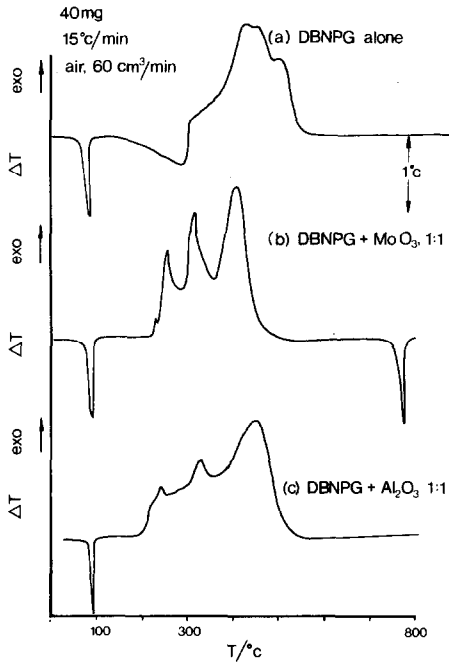
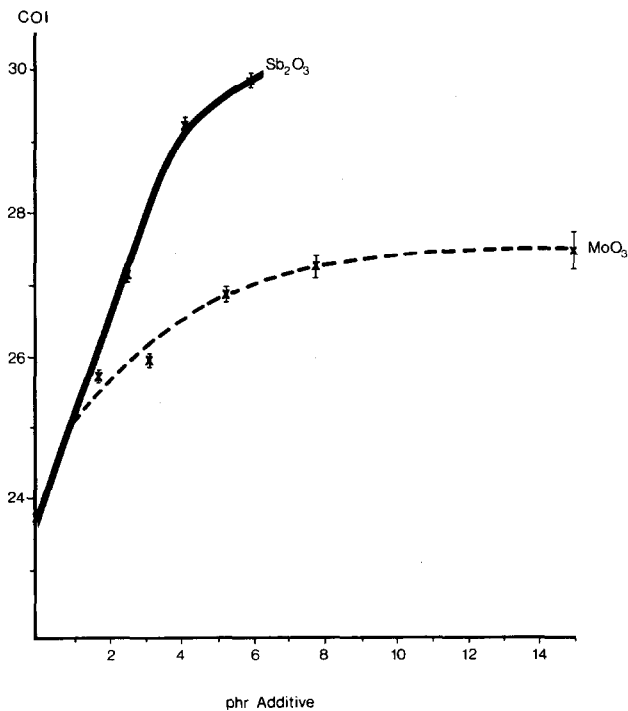Fig. 1. DTA of dibromoneopentyl glycol mixtures.

Fig. 2. Critical oxygen index values for polymers containing 10% Br (w/w) as DBNPG.

comparison [10]. These results show that the Sb_2O_3 has a greater effect on the oxygen index than a comparable weight of MoO_3. The difference between the two oxides may be seen most clearly by considering the nitrous oxide index (NOI) and the smoke produced by resins with these additives (Fig. 3). If a flame retardant acts as a gas phase inhibitor, its activity should be confined to an oxygen atmosphere, with no activity in N_2O since the flame chemistry is different. Conversely, if the flame retardant works by a condensed phase mechanism, it should be unaffected by the change in oxidant [11].

Figure 3a shows that Sb_2O_3 has little effect in N_2O while MoO_3 retains enhancement of the oxidant index. The levels of smoke produced by the burning polymer are shown in Fig. 3b and the deleterious effect of Sb_2O_3 may be contrasted with the considerable smoke suppression given by MoO_3.
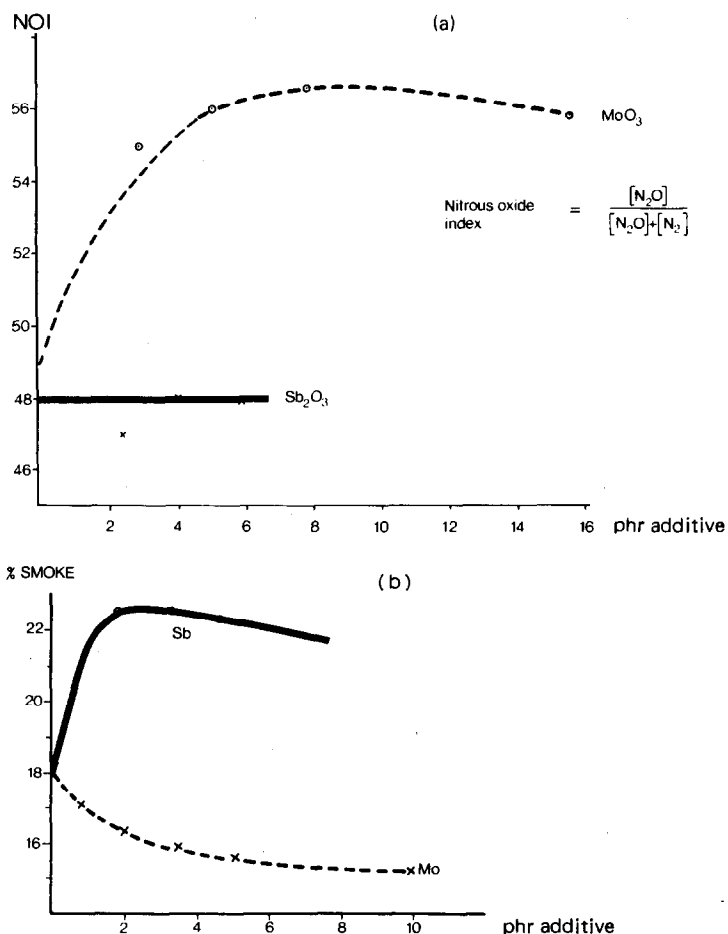

Fig. 3. (a) Nitrous oxide index; (b) smoke levels for polymers containing 10% Br (w/w) as DBNPG.

TABLE 1

Oxidant indices, smoke and char levels for 10% bromine resins

	M : Br (w/w)	COI	NOI	Smoke	Char
	0	23.7	47	18.1	6.0
Mo	1:5	26.0	54	16.3	6.3
	1:3	27.5	55	16.1	7.8
	1:2	28.0	55.5	15.8	9.3
	1:1	28.5	55	15.2	13.5
Sb	1:5	28.0	46	23.0	1.5
	1:3	31.5	47	22.5	3.0
	1:2	32.0	47	22.2	3.0

The numerical values of the oxidant indices, the smoke and char levels are given in Table 1.

Thermal analysis of polymers

The polyester resin samples were run both as single small pieces of about 10 mg and as sieved powders of evenly sized particles, but only very small changes were caused by particle size.

Thermogravimetric curves and the corresponding DTG traces show the differences brought about by incorporating MoO_3 into a bromine-containing polyester and the difference that the atmosphere can make. Figure 4 shows that in nitrogen the resin with 10% Br but no MoO_3 commences decomposition at 200°C and loses 90% of its mass in two stages by 400°C and the remainder soon after that. A resin containing MoO_3 starts to degrade at the same temperature, but breaks down more rapidly to lose 85% by 380°C and to leave a residue which does not sublime at 790°C but reacts between 860 and 950°C to give a black powder. Analysis by X-ray diffraction showed that at 550°C it was mainly MoO_2, and above 900°C the residue was chiefly Mo_2C (Fig. 5).

The reactions of the polymer in air are more relevant to flame retardance and gave the TG traces of Fig. 6 and the data in Table 2. These showed three stages of decomposition of the original bromine-containing polyester, all of which were affected by adding MoO_3. The first step was moved to slightly higher temperatures with similar mass loss. The second step was shifted to lower temperatures with less mass loss when MoO_3 was present. A third stage was very evident in air and MoO_3 enhanced this stage and lowered the temperatures of the DTG peaks, besides altering their shape. The residue at 600°C was shown by X-ray diffraction to be MoO_3, and the TG showed that it remained in almost quantitative yield from the original polyester mixture. The MoO_3 sublimed around 770°C.
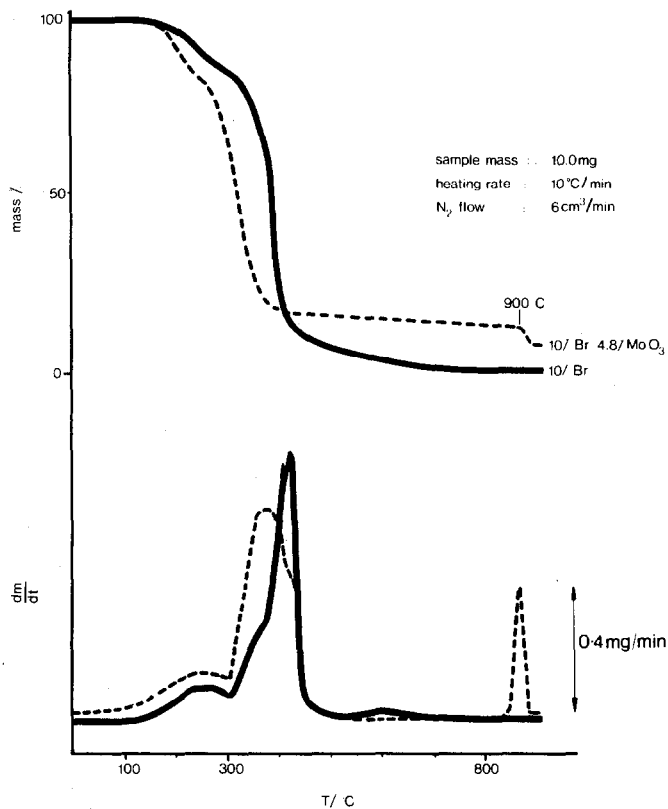
sample mass : 10.0mg
heating rate : 10 °C/min
N₂ flow : 6 cm³/min

900 C

10/ Br 4.8/ MoO₃
10/ Br

0·4 mg/min

Fig. 4. Thermogravimetric curves for 10% Br polymers in flowing nitrogen.

(a) Residue in air above 550°c

MoO₃

(b) Residue in N₂ above 550°c
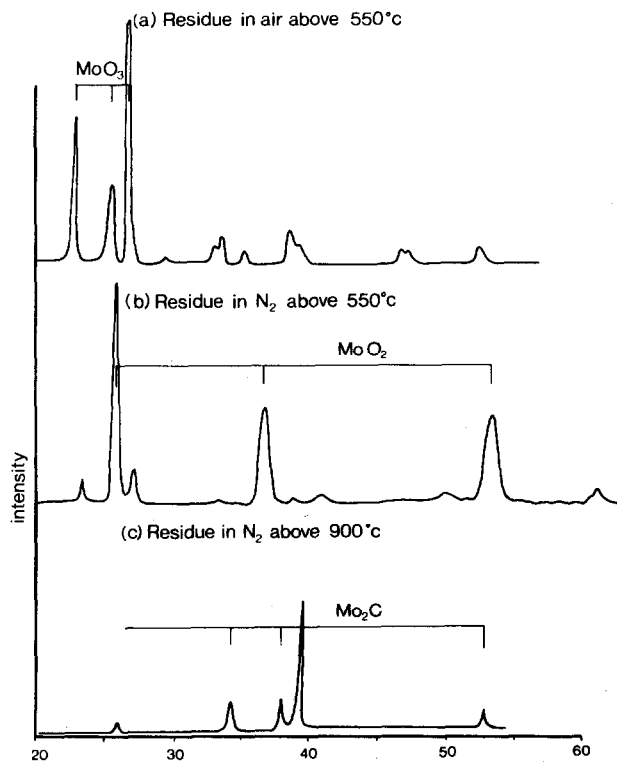
MoO₂

(c) Residue in N₂ above 900°c

Mo₂C

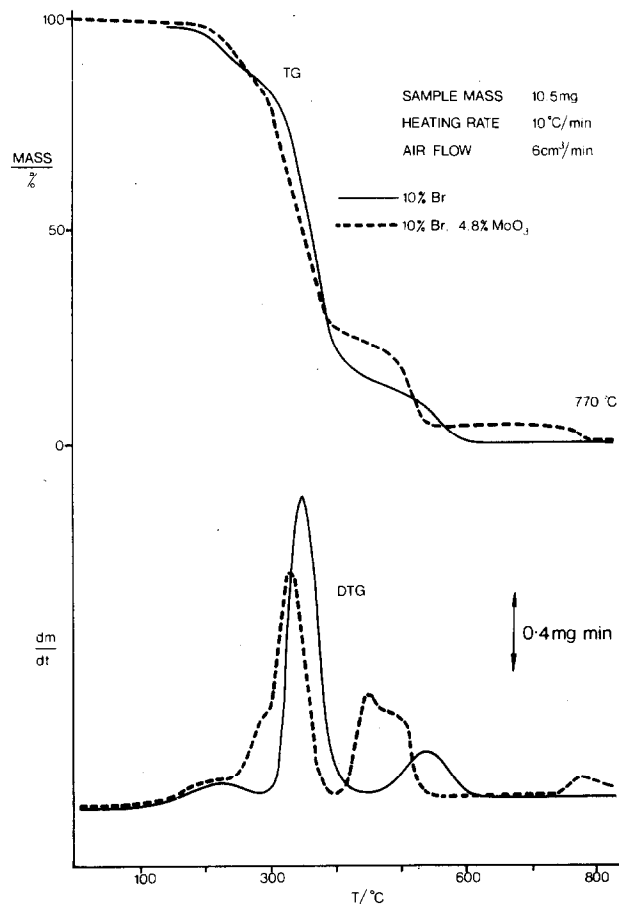Fig. 5. X-Ray diffraction of residues from thermal analysis of polymers.

Fig. 6. Thermogravimetric curves for 10% Br polymers in air.

TABLE 2

Thermogravimetric data for 10% Br polyester

phr MoO$_3$ [a]	First		Second		Third		% Original MoO$_3$ left at 570°C
	T(°C) [b]	Loss (%)	T(°C) [b]	Loss (%)	T(°C) [b]	Loss (%)	
0	217	16.3	345	69.7	530	13.9	
1.5	226	15.6	330	63.1	487	20.2	
3.0	232	16.1	328	63.7	485	20.2	
5.0	232	15.4	327	63.1	472	21.3	97
7.5	232	16.1	337	62.3	471	21.8	96
15.0	226	16.2	327	62.0	461	21.9	99

[a] phr = Parts by weight of MoO$_3$ to 100 parts of resin.
[b] Temperature of DTG peak maximum.

Differential thermal analysis traces (Fig. 7) for the polymers in air show the effect of MoO_3 on the thermicity of these stages. The first stage shown by TG exhibits a very small DTA effect, while the second stage gives an exotherm peaking at around 330°C. In both the polymer containing no added bromine or molybdenum and the 10% Br polymer a broad endotherm shows at 400–450°C. A large, irregular exotherm then extends to over 600°C.

The polymer with both bromine and MoO_3 present gives a different DTA trace. The first exotherm around 300°C is more complex and smaller, the endotherm at 400°C has disappeared and the exotherm at 500°C is broader and larger. As expected, an endothermic peak at 780°C shows the sublimation of MoO_3.

Hot-stage microscopy (HSM) was employed to observe the stages and to see the effect which MoO_3 had on the physical nature of the degrading polymer in air. The first stage loss around 200°C caused no large change in the appearance of the sample which retained its shape and colour. Slight sublimation was noted. The second stage around 350°C showed the development of a yellow-brown colouration, with the polymers containing bromine colouring at lower temperatures. This darkening continued with some bub-
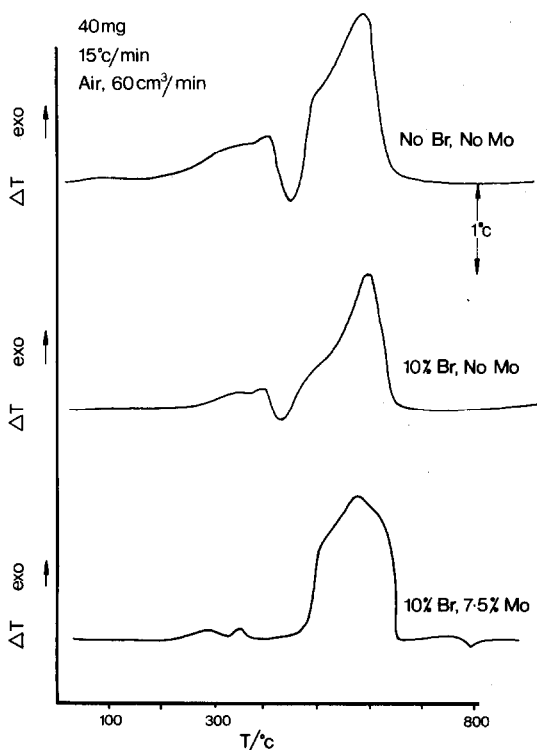

Fig. 7. DTA curves for polymers in air.

bling and sublimation, but no loss of shape, until well over 400°C. Polymers containing no MoO_3 then showed evidence of melting, losing shape and forming a tar. The polymers with MoO_3 retained their shape and structure to higher temperatures. The final stage above 500°C corresponded to the gradual disappearance of the char, leaving an insignificant residue except where MoO_3 was present when a yellow crystalline powder remained.

The IR spectra of the sublimate at 200°C showed that it contained phthalic anhydride but the sublimate around 350°C gave a very complex IR spectrum. Laser Raman spectra of the residues showed the characteristic strong spectrum of MoO_3, plus an increasing fluorescent background as the polymer became more conjugated at higher temperatures. X-Ray diffraction of the residues in air showed lines due to MoO_3 and MoO_2, but none for any molybdenum bromides.

DISCUSSION

The structure of the polyester resins examined in this study consists of chains of glycol and dibasic acid units joined by ester links, and then linked between chains by styrene to give the structure shown in Fig. 8.

The bromine is thus part of the molecular structure, while the additives such as MoO_3 are held as solid particles in the polymer cage. When such a polyester, with no bromine or molybdenum oxide added, is ignited it burns vigorously producing considerable smoke and little char. With the large aromatic content, this would be expected, and any additives should increase the char if they are to reduce smoke. Flame retardants often reduce the temperatures of decomposition so that different, less flammable volatiles are formed.

The COI, NOI, smoke and char measurements show that the incorporation of molybdenum trioxide into polyester formulations containing bromine
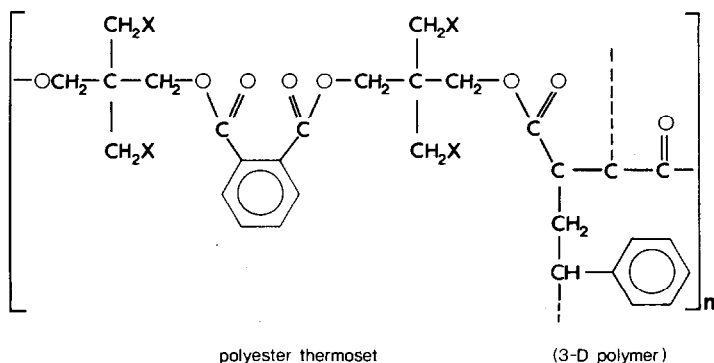

polyester thermoset   (3-D polymer)

Fig. 8. Partial structure of polyester resin.

reduces flammability and suppresses the smoke. The evidence is that MoO_3 acts in the condensed phase to reduce the evolution of flammable, smoke producing volatiles, in contrast to Sb_2O_3 which acts as a flame retardant by a vapour phase mechanism but actually increases smoke.

TG, DTA and HSM show that the decomposition of the brominated polyester resin in air occurs in at least three overlapping stages, all of which are affected by the addition of MoO_3. The first stage initiating the decomposition at around 150°C is due to a loss of material, probably phthalic anhydride as reported by Brauman [6b], without any great effect on the polymer structure. This is a low energy process.

The second stage produces an increasingly coloured material, indicating that there is an increase in conjugation probably accompanying loss of styrene and HBr.

The elimination of material eventually gives a less rigid structure which melts over a temperature range near 440°C, giving the DTA endotherm observed. The final exothermic oxidation of char around 500°C accounts for the third stage.

The observation of the effects of MoO_3 in air show that it makes only a small change in the initial decomposition, slightly raising its temperature, but lowers the second decomposition temperature, as it does for the DBNPG. The product after the second stage with MoO_3 present has more char and a more rigid char which means that melting does not occur, and the solid structure is retained. This appears to depend on the surface of the MoO_3 which may be reduced partially to molybdenum blue or even MoO_2. The greater amount of char reduces the smoke and the flammable volatiles. The char is oxidized exothermically to CO and CO_2 on the "molybdenum blue" surface, giving a larger DTA exotherm with molybdenum present. Any reduced molybdenum is eventually re-oxidized to produce MoO_3. A full analysis of the very large number of volatile products has not proved possible, but some evidence shows that smaller amounts of aromatics are evolved with MoO_3 present.

The synergistic effect of molybdenum compounds and halogens might be due to the formation of a Mo–Br species as has been demonstrated for Sb_2O_3–halogen synergism [5]. The residues from decomposition in air were examined by X-ray diffraction and by laser Raman. No evidence was found in the Raman of the characteristic Mo–Br stretching observed at 255 cm^{-1}, but only of the strong Mo–O stretching bands at 300, 830 cm^{-1} and 1000 cm^{-1} [12].

It is possible that any Mo–Br species produced is extremely labile and does not last until the analysis. The X-ray patterns showed mostly MoO_3 below 400°C, with a little MoO_2 above this temperature.

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