

Combustion and Pyrolysis of Poly(ethylene Terephthalate). II. A Study of the Gas-Phase Inhibition Reactions of Flame Retardant Systems*

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Synopsis

A device to measure the flammability limits of the gaseous pyrolysis products of polymeric materials has been developed and applied to a study of untreated and flame-retarded poly(ethylene terephthalate). The results indicate that phosphorus-containing compounds, like bromine-containing compounds, are capable of inhibiting the gas-phase free radical combustion reactions of the pyrolysis products obtained from poly(ethylene terephthalate).

INTRODUCTION

The mechanism by which flame retardant systems reduce the flammability of poly(ethylene terephthalate) (PET) has been the subject of several investigations. The action of the halogenated systems is usually attributed to the gas phase. In this phase, it is generally thought that the inhibiting action of the halogens is attributable to the hydrogen halides which remove some of the radicals produced in the free radical chain propagation reactions associated with the combustion process.¹ Although some condensed-phase activity between PET and brominated retardants have been observed by McNeill² and Avondo,³ both concluded that the gas-phase activity was the major factor in reducing the flammability of the polyester.

The mode of action of phosphorus systems on the flammability of PET is still a subject of much debate. One simple physical mode that should not be overlooked is the possibility of the enhancement of the melt drip phenomenon⁴ (i.e., the flame retardant causes the PET fabric to melt and drip more readily than an untreated material). Consequently, the burning fabric may extinguish as the burning molten fabric falls away from the rest of the material. Chemical action in both the solid and gas phases has, however, been observed in PET phosphorus systems. Hastie,⁵ who studied the triphenylphosphine oxide-PET system established the existence of gas-phase retardation with this system in which phosphorus radicals such as PO· were scavenging H· radicals. Bostic,⁶ who studied the same system, found no significant solid phase activity based on analysis of the decomposition reaction products.

Deshpande⁷ has compared PET with phosphorus incorporated in the polymer backbone to that containing triphenylphosphine oxide as an additive and concluded that the solid-phase mechanism operative with the polymer reactive system was more effective than the gas-phase process associated with the additive. Solid-phase activity with a series of *N*-sulphonyl phosphoramidates has

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also been shown to be marginal in reducing the flammability of PET.⁸ The red phosphorus/PET systems are, however, a different picture. Although some gas-phase inhibition may occur, the major mode of action in reducing the flammability of the polyester is a solid-phase mechanism.^{9,10} Likewise, polymer-modified PET containing phosphorus in the polymeric chain retards the flammability by a solid-phase process.^{3,7}

The mechanistic action of phosphorus can therefore be seen to be greatly dependent upon the nature of the phosphorus in the complete system. This finding was clearly illustrated by Einsele,¹¹ who studied a whole range of phosphorus compounds. Like Deshpande,⁷ he concluded that the desired phosphorus compounds for flame retardation were those that showed the greatest effect on the solid-phase pyrolysis. These compounds were usually found to be associated with the chemical species which had phosphorus in the 3+ oxidation state, a high phosphorus-to-organic ratio, and low volatility.

In view of the effectiveness of both phosphorus and halogens in flame retarding PET, it is not surprising that numerous attempts have been made to combine the two elements into one flame retardant chemical. With these haloalkyl phosphorus compounds, however, the problem of determining the mode of action becomes more complex. According to Avondo,³ the halogen is released on degradation into the gas phase to inhibit the flame, while the phosphorus remains behind in the solid phase to promote char formation. The generation of phosphorus oxyhalides upon pyrolysis is, however, an example of gas-phase inhibition.^{12,13} In this situation, the phosphorus is acting as a carrier for the flame-inhibiting halogen species. Meanwhile, Inagaki,¹⁴ who studied PET treated with a series of haloalkyl phosphates, concluded that these species altered the solid-phase pyrolysis reactions by catalyzing the aldol condensation reactions.

Pyrolysis experiments in our laboratories with PET containing several commercial flame retardants¹⁵ have revealed that the phosphorus-only species have little effect on the solid-phase pyrolysis reactions and that the bromine-only species have only a marginal effect. The phosphorus- and bromine-containing compound tris(2,3-dibromopropyl) phosphate (Tris), however, was observed to have a significant effect on the pyrolysis product distribution. In view of these findings, it was decided to investigate the role of several commercial flame retardants on the gas-phase combustion reactions.

The approach taken in this gas-phase evaluation was to pyrolyze standard weights of PET and flame-retarded PET in a defined closed system and determine the flammability limits of the gaseous products produced as a function of weight loss on pyrolysis. In the case of a single-component gas such as methane mixed with air, the propagation of a flame through the gas mixture is dependent upon one or more of the following parameters: (1) the temperature of the mixture, (2) the pressure of the mixture, (3) the characteristics of the ignition source, (4) the geometry, nature, and size of the reaction vessel, (5) the ratio of the gas to air, and (6) the presence of another inert, reacting, or inhibiting gas.

Experimentally, for comparison purposes, all of the above parameters are normally kept constant, with the exception of (5). This value is the experimentally variable parameter which is the basis for the determination of the flammability limits of the gas being investigated. It should be realized, however, that the experimentally determined flammability limits for a particular gas are not a fundamental property of the gas because of the dependence of the data upon

the experimental technique. Despite this, it has been shown^{16,17} that the flammability limits of numerous gases and vapors can be fairly well defined for a particular experimental setup, and the data obtained have proved to be invaluable in such areas as the safe use and transportation of fuels.

The purpose of this investigation was to determine the flammability limits of the pyrolysis products from PET and PET treated with flame retardants. From a comparison of these experimentally determined limits and a knowledge of the solid-phase pyrolysis products, the extent of gas-phase chemical inhibition of the flame retardants studied could be determined.

EXPERIMENTAL

Materials

The five commercial PET fabrics investigated are listed in Table I. These materials correspond to those used in our previous investigation¹⁵ on the solid-phase pyrolysis reactions. The concentrations of phosphorus and bromine present in these materials were determined by appropriate analytical procedures.¹⁸

Apparatus

Figure 1 is a scale drawing of the actual reaction vessel used to determine the flammability limits of the pyrolysis gases. Essentially, it is a brass cylinder 75 mm high and 50 mm in diameter insulated with Marinite X-LS* (g) to reduce heat losses during pyrolysis. Access to the interior for cleaning and loading purposes is either via the top or side flange (d), both of which are sealed with O-rings. The top flange has a mica window (f) transparent to the infrared radiation used to pyrolyze the samples under test. Two 20-gauge platinum electrodes (a) with a 3-mm gap provide the spark. The temperature and pressure within the vessel are monitored by a platinum/platinum 10% rhodium 50 gauge thermocouple (b) and ICP model 111A21[†] dynamic pressure transducer (c), respectively.

The supplementary equipment used in conjunction with the reaction vessel is shown schematically in Figure 2. The spark for the ignition is derived from a 12-V power supply linked to an ignition coil (h) and controlled by a push-button switch (i). The heat for pyrolysis is supplied by an infrared spot heater (k)[‡] focused on the test sample contained in the crucible (e). The temperature and pressure monitored by the thermocouple (b) and pressure transducer (c) are continually recorded on a strip chart recorder (l) during pyrolysis and by the storage oscilloscope (m) during ignition.

* Marinite X-LS is an asbestos-free material consisting of calcium silicate with inert fillers and reinforcing agents and coated with a sodium silicate impregnant. This material is available from Johns-Manville Co. Ltd., 565 Lakeshore Rd. E., Mississauga, Ont., Canada.

[†] Available from PCB Piezotronics, Inc., P.O. Box 33, Buffalo, NY, U.S.A.

[‡] A model 4085 high-intensity infrared spot heater from Research Inc., Box 24064, Minneapolis, MN, U.S.A.

TABLE I
 Polyester Materials Tested

Fabric designation	Source	Nature of flame retardant	Structure	% Flame retarding element on fabric, w/w	
				Br	P
Standard Tris	Test fabrics Michigan Chemical	none tris(2,3-dibromopropyl) phosphate	— $(\text{CH}_2\text{BrCHBrCH}_2\text{O})_3\text{P}=\text{O}$	— 6.6	— 0.43
AB19	Mobil Chemical	mixture of cyclic phosphonate esters	$\begin{array}{c} \text{O} \\ \parallel \\ (\text{CH}_3\text{O})\text{P} \\ \\ \text{CH}_3 \end{array} \left(\begin{array}{c} \text{CH}_2\text{O} \\ \diagup \\ \text{OCH}_2\text{CH} \\ \diagdown \\ \text{CH}_2\text{O} \end{array} \right)_{1-2}$	—	0.28
900F	E.I. duPont	PET with ethoxylated tetrabromobisphenol A units	$\begin{array}{c} \text{Br} \\ \\ \text{—O—CH}_2\text{—CH}_2\text{—O—} \\ \\ \text{Br} \end{array} \text{—C—} \begin{array}{c} \text{CH}_3 \\ \\ \text{—C—} \\ \\ \text{CH}_3 \end{array} \text{—C—} \begin{array}{c} \text{Br} \\ \\ \text{—C—} \\ \\ \text{CH}_3 \end{array} \text{—C—} \begin{array}{c} \text{OCH}_2\text{CH}_2\text{O—} \\ \\ \text{Br} \end{array}$	4.3	—
T.271	Hoechst	PET copolymer with a derivative of phosphinic acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{HO—P—X—COOH} \\ \\ \text{Y} \end{array}$	—	0.20

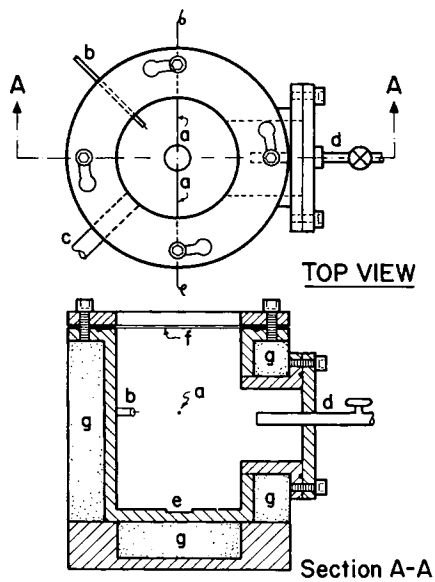


Fig. 1. Plan and cross section of reaction vessel.

Test Procedure

200 mg of the PET fabric under test is accurately weighed into a 5-ml porcelain crucible and introduced into the reaction vessel. The reaction vessel is then closed and the recording system activated. The spot heater is then switched on, and after a predetermined time a spark is discharged at the electrode and the resulting temperature and pressure pulse associated with the ignition of the pyrolysis gases (if it occurred) are noted. The heater was immediately switched off and the system allowed to cool before the crucible was removed and reweighed to determine the percentage weight loss due to pyrolysis. Depending upon the behavior in the preceding experiment, the test was repeated using a new specimen but with a different heating period in order to alter the percentage weight loss and hence the concentration of pyrolysis gases mixed with the air in the reaction vessel. This process is repeated for a whole range of heating times in order to obtain a full range of percentage weight losses sufficient to enable the flammability limits to be determined.

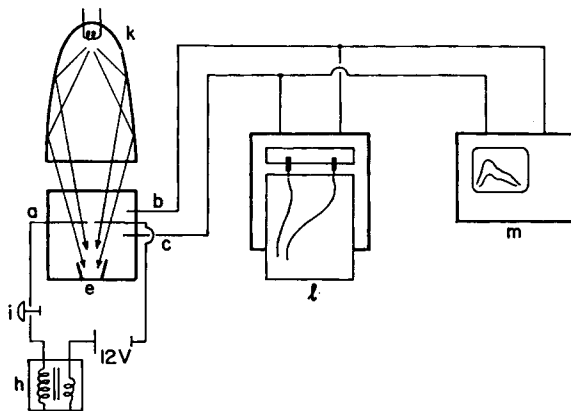


Fig. 2. Schematic of pyrolysis and recording equipment.

RESULTS AND DISCUSSION

The results obtained for the standard untreated PET fabric are shown in Figure 3. In this figure, the pressure rise observed as a result of the ignition of the pyrolyzed gases has been plotted against the percentage weight loss due to pyrolysis. It will be noted that there is a reasonably sharp demarcation between the percentage weight loss which gave a flammable gas-air mixture and those that were nonflammable. The results obtained with the flame-retarded PET systems are given in Figures 4-7. It will be noted that the shapes of all these graphs are very similar in that relatively weak pressure pulses are observed close to the flammability limits, while the strongest responses are recorded at the midpoint between the limits.

The flammability limits determined by this method based on the data in Figures 3-7 are summarized in Table II. It will be noted that in all cases that the lower flammability limits, as expressed as a percentage of the weight loss on pyrolysis, are increased by the presence of a flame retardant in the system. This increase in the lower flammability limit due to the presence of the flame retardant chemical would indicate that for a given percentage weight loss on pyrolysis, a less flammable gaseous mixture is produced. For example, if the 19.5% weight loss point is chosen, the only system to give a flammable gas-air mixture in our study was the standard untreated material. All the flame-retarded PET systems produced nonflammable gas-air mixtures at this percentage weight loss. The values for the upper flammability limits also appear to be dependent upon the presence of the flame retardant in the system. For example, it will be noted that in all cases, with the exception of the 900F material, the upper flammability limit is reduced by the presence of the flame retardant. It can be clearly seen that the flame retardants examined in this study all caused a reduction in the range

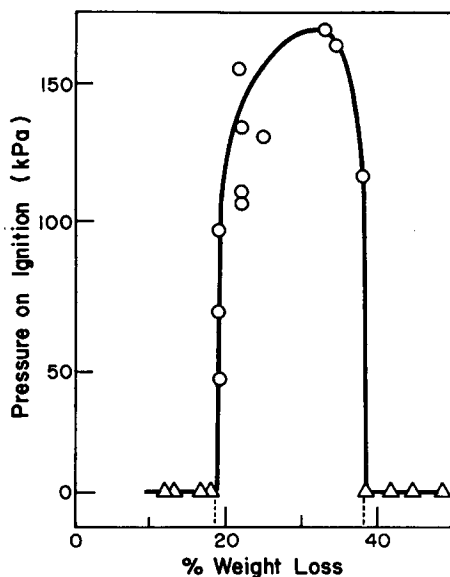


Fig. 3. Variation of pressure pulse as function of percentage weight loss due to pyrolysis for the combustible gas mixtures obtained with the standard untreated PET: (O) indicates the flammable gas mixtures; (Δ) indicates the nonflammable gas mixtures; flammability limits are indicated by (---).

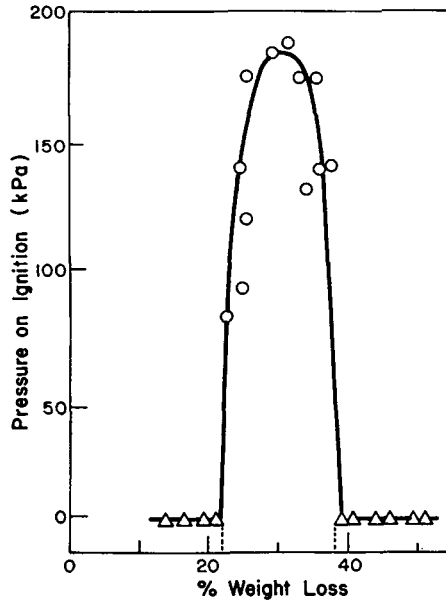


Fig. 4. Variation of pressure pulse as function of percentage weight loss due to pyrolysis for the combustible gas mixtures obtained with the AB19 PET: (O) indicates the flammable gas mixtures; (Δ) indicates the nonflammable gas mixtures; flammability limits are indicated by (---).

of percentage weight loss on pyrolysis required to give flammable gas-air mixtures. This reduction in the flammability range was least for the AB19 and 900F systems and largest for the Tris system, yet all the systems examined were responsible for a 25–32% reduction in the flammability range when compared to the untreated material. Thus, it may be concluded that the pyrolysis gases produced from the flame-retarded fabrics are less flammable (i.e., they have a

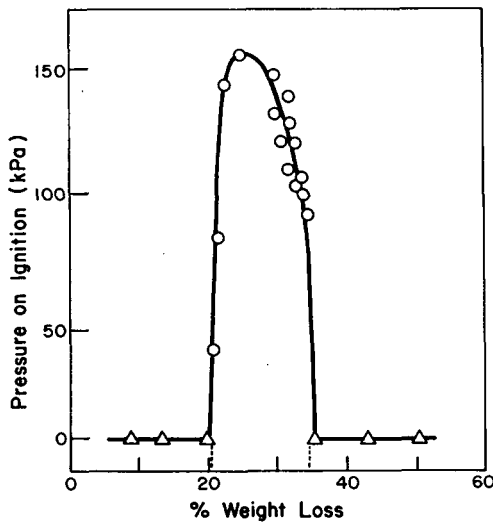


Fig. 5. Variation of pressure pulse as function of percentage weight loss due to pyrolysis for the combustible gas mixtures obtained with the T271 PET: (O) indicates the flammable gas mixtures; (Δ) indicates the nonflammable gas mixtures; flammability limits are indicated by (---).

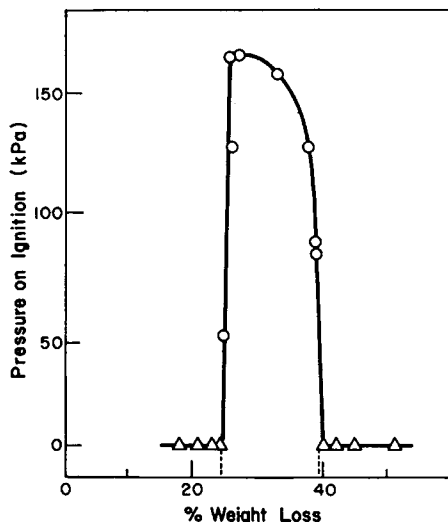


Fig. 6. Variation of pressure pulse as function of percentage weight loss due to pyrolysis for the combustible gas mixtures obtained with the 900F PET: (O) indicates the flammable gas mixtures; (Δ) indicates the nonflammable gas mixtures; flammability limits are indicated by (---).

higher lower limit of flammability) and have reduced combustibility (i.e., smaller flammability range) than the gases produced on the pyrolysis of standard untreated PET.

This reduced combustibility can be attributed either to the composition of gases evolved on pyrolysis or to inhibition of the gaseous combustion reactions. Since the composition of the pyrolysis products have been shown to be only slightly dependent upon the presence of flame retardants,¹⁵ it thus appears likely

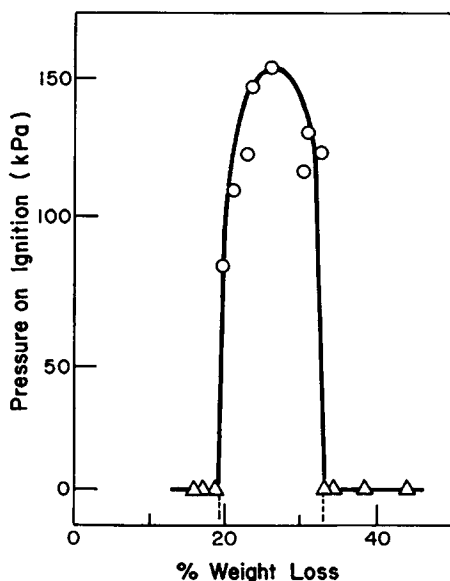


Fig. 7. Variation of pressure pulse as function of percentage weight loss due to pyrolysis for the combustible gas mixtures obtained with the Tris PET: (O) indicates the flammable gas mixtures; (Δ) indicates the nonflammable gas mixtures; flammability limits are indicated by (---).

TABLE II
Flammability Limits of Pyrolyzed Gases Expressed as Percentage of Weight Loss on Pyrolysis

Fabric	% Weight loss on pyrolysis		Flammability range	% Reduction in range
	Lower limit	Upper limit		
Standard	18.5	38.5	20.0	—
AB19	22.5	37.5	15.0	25.0
T271	20.5	35.0	14.5	27.5
900F	24.5	39.5	15.0	25.0
Tris	19.5	33.0	13.5	32.5

that the reduced combustibility can be attributed to gas-phase inhibition of the combustion process.

The flammability limits derived in Figures 3–7 and summarized in Table II are based upon the percentage weight loss on pyrolysis not on the gas–air composition in the reaction vessel. However, since pyrolysis data have been determined in our laboratory on the same fabrics used in this study, it is possible to calculate not only the approximate gas composition but also volume percentage of the gaseous products in air at the lower and upper flammability limits. These calculations, however, can only be made by assuming that the composition determined at in our previous solid phase studies¹⁵ can be applied at the percentage weight loss required to give the lower and upper flammability limits in this study. Although it is realized that this assumption will not be absolutely correct, as a first approximation it will give a good indication of the gas–air volume percentage at the flammability limits. Using the data contained in Ref. 15, the compositions of the pyrolysis gas mixtures at the lower and upper flammability limits have been calculated and presented in Tables III and IV, respectively. Since the

TABLE III
Calculated Volume Composition of Pyrolysis Products at Lower Flammability Limit^a

Pyrolysis product	Std. (18.5) ^b	AB19 (22.5)	T271 (20.5)	900F (24.5)	Tris (19.5)
Carbon monoxide	1.59	1.20	1.50	1.12	3.02
Carbon dioxide	2.00	2.14	1.81	1.65	3.51
Acetylene	0.48	0.51	0.50	0.39	0.78
Acetaldehyde	1.36	1.01	1.51	0.31	2.68
Ethanol	0.12	0.13	0.17	0.06	0.26
Benzene	0.12	0.19	0.26	0.22	0.26
Styrene	0.02	0.06	0.05	0.02	0.13
Vinyl benzoate	0.52	0.77	0.58	0.59	0.29
Benzoic acid	0.82	0.68	0.70	0.65	0.37
<i>p</i> -Ethyl vinyl benzoate	0.08	0.06	0.05	0.06	0.02
<i>p</i> -Vinylvinyl benzoate	0.19	0.15	0.19	0.20	0.05
<i>p</i> -Acetylvinyl benzoate	0.02	0.02	0.02	0.51	0.42
Divinyl terephthalate	0.59	0.86	0.79	0.74	0.34
<i>p</i> -Acetylbenzoic acid	0.02	0.02	0.02	0.20	0.08
Methyl 1-hydroxyethyl terephthalate	0.03	0.06	0.05	0.39	0.23
Ethylene dibenzoate	0.43	0.66	0.62	0.35	0.16
Total	8.39	8.52	8.81	7.46	12.60
Total less CO ₂	6.39	6.38	7.00	5.81	9.09
Vol % Flammable gas	3.69	3.68	4.03	3.37	5.12

^a Milliliters of product per 200 mg sample heated, calculated at S.T.P. Data from Ref. 15.

^b Percent weight loss at lower limit.

TABLE IV
Calculated Volume Composition of Pyrolysis Products at Upper Flammability Limit^a

Pyrolysis product	Std. (38.5) ^b	AB19 (37.5)	T271 (35.0)	900F (39.5)	Tris (33.0)
Carbon monoxide	3.30	2.00	2.57	1.81	5.12
Carbon dioxide	4.17	3.56	3.09	2.67	5.94
Acetylene	0.99	0.84	0.85	0.63	1.32
Acetaldehyde	2.82	1.69	2.57	0.49	4.54
Ethanol	0.26	0.22	0.29	0.10	0.44
Benzene	0.26	0.31	0.44	0.36	0.44
Styrene	0.03	0.09	0.09	0.03	0.22
Vinyl benzoate	1.09	1.28	0.99	0.95	0.49
Benzoic acid	1.70	1.13	1.20	1.05	0.63
<i>p</i> -Ethylvinyl benzoate	0.16	0.09	0.09	0.10	0.03
<i>p</i> -Vinylvinyl benzoate	0.39	0.25	0.32	0.33	0.08
<i>p</i> -Acetylvinyl benzoate	0.03	0.03	0.03	0.82	0.71
Divinyl terephthalate	1.22	1.44	1.34	1.19	0.58
<i>p</i> -Acetylbenzoic acid	0.03	0.03	0.03	0.33	0.14
Methyl 1-hydroxyethyl terephthalate	0.06	0.09	0.09	0.63	0.38
Ethylene dibenzoate	0.90	1.09	1.05	0.56	0.27
Total	17.41	14.14	15.04	12.05	21.33
Total less CO ₂	13.24	10.58	11.95	9.38	15.39
Vol % Flammable gas	7.26	5.90	6.63	5.30	8.26

^a Milliliters of product per 200 g sample heated, calculated at S.T.P. Calculated from Ref. 15.

^b Percent weight loss at lower limit.

volume of air in the reaction vessel (165 mm) is also known, it is possible to calculate the actual flammable gas/air volume percentage at these limits. (Note: Since CO₂ is a nonflammable gas, its contribution to the total pyrolysis gases has to be corrected for.) The results of these calculations are summarized at the bottom of Tables III and IV.

In addition to determining the flammability limits from the observed percentage weight loss required to produce flammable gas-air mixtures, it is possible to estimate these values provided the composition of the flammable gas mixture is known along with flammability limits for the individual gaseous components making up the mixture. These calculations are based upon the use of a simple formula advanced by Le Chatelier,¹⁹ namely:

$$L = \frac{100}{(V_1/L_1) + (V_2/L_2) + (V_3/L_3) + \dots}$$

In this formula, $V_1, V_2, V_3 \dots$ are the volume percentages of each flammable gas present in the mixture free from air and the inert gas carbon dioxide such that $V_1 + V_2 + V_3 + \dots = 100$. $L_1, L_2, L_3 \dots$ are the lower flammability limits in air for each gas separately. The above formula can, of course, be equally applied to the upper flammability limit mixtures by the appropriate replacement of $L_1, L_2, L_3 \dots$ by $U_1, U_2, U_3 \dots$, the upper flammability limits for the individual gaseous species. Unfortunately, although the values of $V_1, V_2, V_3 \dots$ can be readily obtained from Table III or IV, a knowledge of the flammability limits of each pyrolysis product listed in these tables is also required. With the lower-molecular-weight species up to styrene, these limits can be readily obtained from the literature.¹⁶ However, for the higher-molecular-species, the technique developed by Hilado²⁰ was employed to estimate the flammability limits. This

empirical method involves multiplying the stoichiometric concentration (C_s) by a factor (A) characteristic of the particular class of compound.²¹ The value for C_s was calculated using the formula

$$C_s = \frac{100}{1 + 4.773[n + (m - 2p)/4]}$$

where n , m , and p are the number of carbon, hydrogen, and oxygen atoms, respectively, in the organic species $C_nH_mO_p$. The flammability limits of the individual gaseous species required for our investigation are listed in Table V along with the values for C_s and A used in these calculations where appropriate. These flammability limits of the individual products were then used in conjunction with their volume percentages in the pyrolysis gases to predict the flammability limits of the gas mixtures using Le Chatelier's formula.

The results of these calculations are given in Table VI under the predicted flammability limit column. Also included in this table are the values determined from the percentage weight loss experiments. These data indicate that in all cases the predicted values for the lower flammability limits were smaller and the

TABLE V
Flammability Limits of Major Pyrolysis Products and Values Used in Their Calculation

	C_s	A_{lower}	A_{upper}	Flammability limit, % volume in air	
				Lower	Upper
Carbon monoxide	—	—	—	12.5 ^a	74 ^a
Acetylene	—	—	—	2.5 ^a	81 ^a
Acetaldehyde	—	—	—	4.1 ^a	55 ^a
Ethanol	—	—	—	4.3 ^a	19 ^a
Benzene	—	—	—	1.4 ^a	7.1 ^a
Styrene	—	—	—	1.1 ^a	6.1 ^a
Vinyl benzoate	2.05	0.54	3.02	1.1	6.2
Benzoic acid	2.72	0.55	3.02	1.5	8.2
<i>p</i> -Ethylvinyl benzoate	1.59	0.54	3.02	0.9	4.8
<i>p</i> -Vinylvinyl benzoate	1.65	0.54	3.02	0.9	5.0
<i>p</i> -Acetylvinyl benzoate	1.72	0.54	3.02	0.9	5.2
Divinyl terephthalate	1.65	0.54	3.02	0.9	5.0
<i>p</i> -Acetylbenzoic acid	2.16	0.54	3.02	1.2	6.5
Methyl 1-hydroxyethyl terephthalate	1.79	0.54	3.02	1.0	5.4
Ethylene dibenzoate	1.18	0.54	3.02	0.6	3.6

^a Experimental values from Ref. 16.

TABLE VI
Flammability Limits of Pyrolyzed PET Samples

PET system	Experimentally determined limits				Predicted Limits, % volume in air	
	% Weight loss on pyrolysis values		% Volume in air of flammable gas		Lower	Upper
	Lower	Upper	Lower	Upper		
Std.	18.5	38.5	3.69	7.26	1.81	11.31
AB19	22.5	37.5	3.68	5.90	1.48	9.02
T271	20.5	35.0	4.03	6.63	1.66	10.25
900F	24.5	39.5	3.37	5.30	1.35	7.89
Tris	19.5	33.0	5.12	8.26	2.54	17.28

upper flammability limits higher than those actually observed experimentally. Although this would be anticipated in terms of gas-phase retardation associated with inhibition of the combustion processes, the fact that the same phenomenon is observed with the standard untreated PET suggests that part of the differences must be due to the calculations involved. However, despite the limitations in the calculations, it is possible to get some general information based upon the data presented in this table.

Consider first the flammability range predicted (last two columns in Table VI) on the basis of the solid-phase pyrolysis reactions. Since these predictions are based solely upon the concentration distribution of the gaseous products produced, it can be taken as some indication of the effectiveness of the flame retardant system in reducing the flammability of gaseous products because of solid-phase activity. With the AB19 and T271 flame-retarded system, it can be seen that the predicted flammability ranges are reduced by 21 and 10%, respectively, from those obtained with the standard untreated material. Thus, although it was reported in our earlier study¹⁵ that these flame retardant systems have no effect on the solid-phase pyrolysis, it can be seen that some activity, undoubtedly small, may be occurring. The predicted flammability range for the 900F is reduced 31% from that obtained with the standard untreated material. This would indicate that some solid-phase retardation is being achieved with this material as well. In terms of mode of action, it would appear to be linked to the reduced acetaldehyde formation observed with the 900F system. With the Tris-treated material, the situation is completely different. The predicted range is now larger than that obtained with the standard untreated material, indicating greater flammability of the gaseous products produced from the pyrolysis of Tris-treated PET. This apparent increase (55% greater than that obtained with the standard PET) is obviously due to the low-molecular-weight species of greater flammability being produced when the flame retardant Tris is present. Thus, it appears that the Tris is having a negative effect upon reducing the flammability of PET in terms of its ability to influence the pyrolysis reactions.

The apparent effectiveness of the flame retardant systems in reducing the flammability of PET by gas phase inhibition can be obtained from the experimentally determined flammability ranges expressed as the percentage flammable gases in air (Table VI, middle two columns). The reduction in this range caused by the AB19 and T271 from that obtained with the standard PET are found to be 38 and 27%, respectively. Since it has been estimated that 21 and 10% of this activity, respectively, can be attributed to solid-phase activity, it must be assumed that the remaining 17% in both cases can be attributed to the gas-phase combustion reactions. With the 900F flame retardant system, a 46% reduction in the experimentally observed range is observed compared with the standard PET. However, with this system, it was noted that 31% of this reduction could be accounted for on the basis of solid-phase activity, leaving only 15% to be explained on the basis of gas-phase inhibition. The experimentally determined flammability range for the Tris-treated PET is also reduced such that it is now 12% of the range observed with the standard untreated PET. Although this reduction is small in comparison with the percentage reductions obtained with the other three systems, it must be remembered that based upon the solid-phase pyrolysis and the gaseous products produced, an increase in the range of 55% had been

expected. Hence, it can be estimated that the Tris system is a very effective gas phase-retarding system in that it is capable of producing chemical species which are very efficient inhibitors of the combustion reactions (67% effective as a gas-phase inhibitor).

CONCLUSIONS

If it is assumed that the measured flammability limits of the pyrolysis products from a polymer are a measure of the flammability of that polymer, we have devised a simple experimental procedure for their determination. Applying the technique to PET and PET flame-retarded systems, we have been able to demonstrate the effectiveness of these systems in retarding the flammability of the PET. Provided information is available concerning the composition of the gaseous pyrolysis products, it is possible to estimate the relative effectiveness of the flame retardants as solid-phase retardants or gas-phase inhibitors of the burning process. Based upon the data presented in this report, it would appear that the two phosphorus-only systems, AB19 and T271, are both capable of reducing the flammability of PET by a combination of solid-phase and gas-phase activity. The bromine-only species, 900F, also appears to be capable of dual activity in retarding the burning of PET, although its solid-phase activity appears to be principally related to a reduction in the acetaldehyde produced. On the other hand, the Tris system appears to be having a nonbeneficial effect upon the solid-phase pyrolysis reactions, since it is causing more flammable pyrolysis products to be formed than are produced from the standard untreated PET. However, the gas-phase activity of Tris is sufficiently high that it is capable of reducing the combustion such that the overall flammability of the system is less than that of the untreated standard polyester.

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