The Effect of Elemental Red Phosphorus on the Thermal Degradation of Poly(ethylene Terephthalate)

A. GRANZOW, R. G. FERRILLO, and A. WILSON, *Chemical Research Division, American Cyanamid Company, Bound Brook, New Jersey 08805*

Synopsis

The influence of elemental red phosphorus on the rate of thermal degradation of poly(ethylene terephthalate) has been studied in the temperature range of 400° to 500°C in inert and oxidizing atmospheres by means of isothermal thermogravimetric analysis. Addition of red phosphorus is found to reduce the rates of both the pyrolytic and the thermo-oxidative degradation and to increase the amount of residual char. A correlation of pyrolysis rates with oxygen index data has been attempted.

INTRODUCTION

As we have reported previously, addition of elemental red phosphorus to poly(ethylene terephthalate), PET, significantly decreases the flammability of that polymer.[1] Elemental phosphorus can, therefore, be considered as a model for practically useful phosphorus organic flame retardants. Our earlier results indicate that although some gas phase flame-retardant activity by red phosphorus is likely to occur, the major part of its effectiveness is evidently due to inhibition in the condensed phase. This assumption is based on the following observations: The flame-retardant activity of elemental phosphorus is strongly dependent on the nature of the matrix polymer. The effectiveness of red phosphorus in PET is reduced but not eliminated if the combustion is carried out in an atmosphere which contains N_2O instead of O_2 as the oxidant. The rate of thermal degradation of PET is affected by the presence of elemental phosphorus.

In this study, we have attempted to determine quantitatively the effect of red elemental phosphorus on the rate of thermal degradation of PET by means of thermogravimetric analysis, TG. To assess the relative importance of the pyrolytic and thermo-oxidative pathways of degradation, the weight loss curves were measured in both an inert argon and a reactive oxygen atmosphere. The effects of phosphorus concentration on the pyrolysis and the flammability of PET, respectively, were compared in order to obtain a correlation between the two parameters.

EXPERIMENTAL

Materials used and the method of incorporation of red phosphorus in PET have already been described.[1] The TG experiments were performed on a Per-
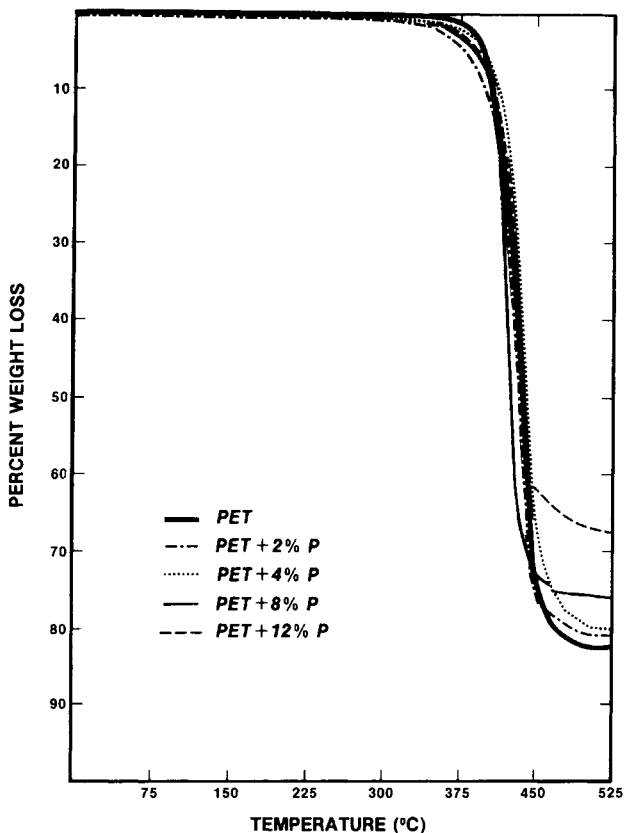
Fig. 1. Dynamic TG runs for PET containing different amounts of elemental red phosphorus, in argon atmosphere.

kin–Elmer TGS-1, which incorporates a Cahn RG Electrobalance. The sample size was 5 mg; the inert gas atmosphere was maintained by a stream of 30 ml/min of purified argon, while the reactive atmosphere was established by a stream of pure oxygen at identical flow rate. The samples were dried over phosphorus pentoxide. All experiments were carried out in gold pans in order to minimize possible reactions with the pan material. In the case of the dynamic TG runs, the heating rate was 10°C/min.

In the isothermal experiments, the weighed sample was melted at 280°C in the TG pan and subsequently cooled in order to produce a thin sample film providing optimum heat transfer and, thus, minimizing errors in the heat-up time. The furnace was then heated to the desired temperature and the sample introduced. The recorder drive was started simultaneously.

RESULTS AND DISCUSSION

Effect of Elemental Phosphorus on the Pyrolytic Degradation of PET

A series of dynamic TG curves of PET in the presence of different amounts of elemental red phosphorus is depicted in Figure 1. One recognizes that the addition of elemental red phosphorus results in an increase in the amount of
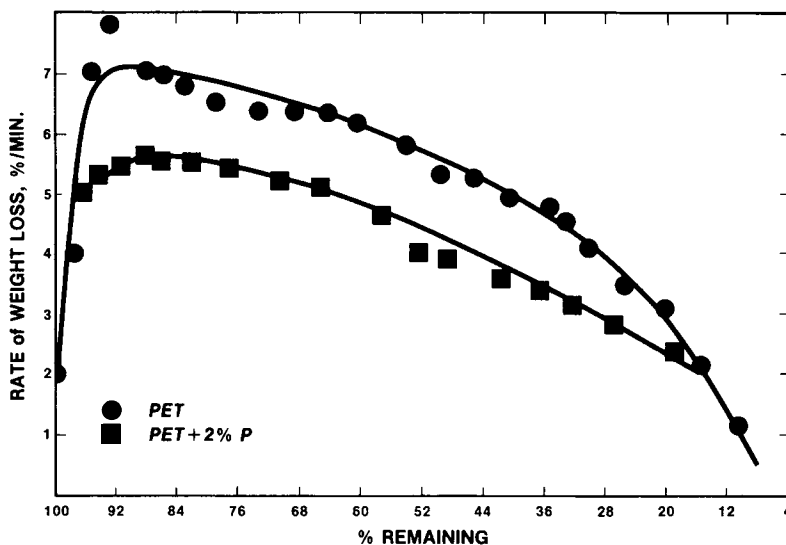
Fig. 2. Plot of rate of weight loss vs. conversion for PET and PET + 2% phosphorus in argon atmosphere at 402°C.

residual char. Since the TG curve of pure red phosphorus indicates that complete volatilization occurs at temperatures below 550°C,[1] the increased char yield must be caused by a condensed phase reaction between the phosphorus and the pyrolyzing PET. The shapes of the dynamic TG curves show minor variations for different phosphorus concentrations. However, a quantitative evaluation of this effect from temperature-programmed TG curves is not feasible. Consequently, all further TG experiments are performed in the isothermal mode.

The pyrolysis of PET is known to occur by a random scission mechanism with an initial breaking of the ester linkage via a beta hydrogen-type alkyl-oxygen fission. This reaction is believed to involve a concerted cyclic transition state.[2] Polymers which decompose by a random cleavage mechanism are known to exhibit a maximum in their rate of weight loss-versus-conversion curves,[3] which, in the case of PET, occurs at about 10% conversion instead of 26% conversion as expected on the basis of theoretical considerations.[4]

The maximum rate of volatilization, v_{max}, is independent of the initial molecular weight of the PET and is related to the rate constant of chain breaking, k, by eq. (1), with L being the smallest number of basic units in the chain fragment for which gasification without prior decomposition is possible:

$$v_{max} = kL/2.7 \tag{1}$$

In the case of PET, a value of $L = 5$ is assumed.[5] It is, therefore, possible to obtain nontrivial activation energies for the decomposition of PET by determining the maximum rate of weight loss for a series of TG runs carried out at different isothermal temperatures.

The surface temperature of burning PET samples amounts to $T_s \approx 380°C$, while for PET + 2% phosphorus, $T_s \approx 450°C$ was measured.[1] Consequently, TG runs were carried out in the range of 350° to 500°C in order to simulate pyrolysis conditions at the surface of the burning polymer. Figure 2 shows repre-

TABLE I
Effect of Elemental Phosphorus on the Rate of Weight Loss of PET
in an Argon Atmosphere

Temperature, °C	PET		PET + 2% phosphorus	
	v_{max}, %/min	Residue, %	v_{max}, %/min	Residue, %
402	6.9	17.8	5.5	21.2
427	21.5	—	15.0	—
467	87	12.1	75	18.2
510	325	4.4	284	17.6

sentative weight loss curves for pure PET and PET + 2% elemental phosphorus at $T = 402°C$. One sees that neither the shape of the weight loss curve nor the position of the maximum is significantly altered by the addition of phosphorus; the composition of the pyrolysis gases remains likewise unchanged with acetaldehyde being the major gaseous constituent.[6] Hence, the only effect of phosphorus appears to be a reduction of the maximum rate of pyrolysis accompanied by a broadening of the rate maximum and a higher fraction of nonvolatile residue. We would like to point out that the concentration of the added phosphorus in the sample is, by far, too low to contribute significantly to the overall rate of weight loss. The change in pyrolysis rate has, therefore, to be attributed to an inhibition of the rate of volatilization of PET by the added phosphorus.

We have no reason to doubt that the effect of phosphorus organic flame retardants on the thermal degradation of PET is essentially the same as in the case of elemental phosphorus, although an experimental confirmation based on TG measurements is difficult due to the much higher add-on levels that are required for phosphorus organic compounds to produce a comparable degree of flame retardancy. In these cases, the TG curves, therefore, reflect the volatilization behavior of the system PET + flame retardant, rather than that of the pure polymer, which makes the interpretation of the TG results quite ambiguous.

Table I summarizes the maximum rates of weight loss for both pure PET and PET + 2% phosphorus at different temperatures, as well as the amount of nonvolatile residue which is formed during the pyrolysis. One sees that at all temperatures, the maximum rates are reduced in the presence of phosphorus, while the amount of residue is increased.

The rate data of Table I can be accommodated by the Arrhenius equation according to Figure 3, yielding activation energies of $\Delta E = 37$ kcal/mole for PET and of $\Delta E = 39$ kcal/mole for PET + 2% phosphorus. The former value is in good agreement with $\Delta E = 38$ kcal/mole, which has been reported for pure PET over the temperature range between 275° and 305°C.[7]

One sees that in an inert atmosphere, the activation energy for the decomposition of PET is only slightly increased in the presence of phosphorus; therefore, the reduction of the maximum volatilization rate has to be due to a decrease of the overall frequency factor of the pyrolytic decomposition.

The pyrolysis of PET can be visualized to occur in two different stages according to eq. (2):
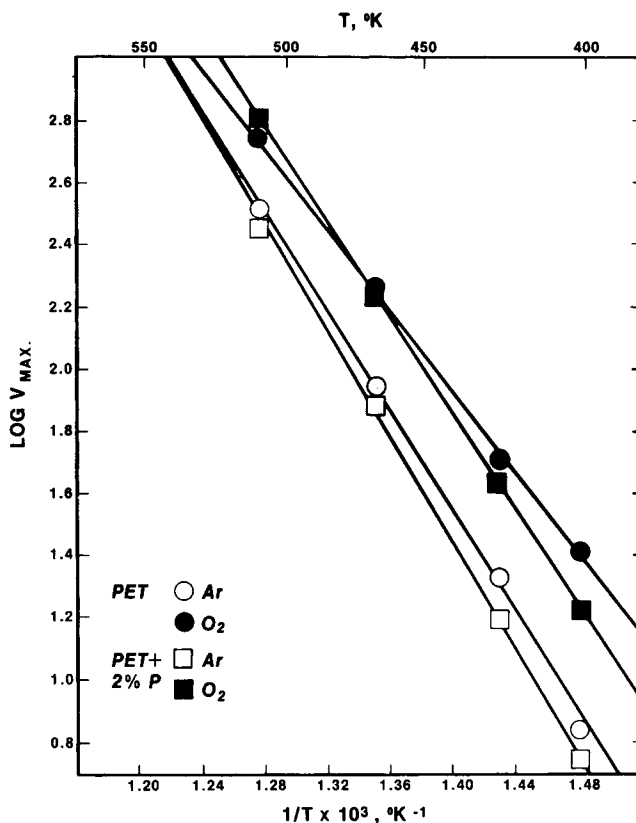
$$\text{polymer} \xrightarrow{v_1} \text{nonvolatile products} \xrightarrow{v_2} \text{volatile products} \qquad (2)$$
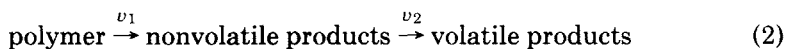
Fig. 3. Arrhenius plots derived from maximum decomposition rates for PET and PET + 2% phosphorus in argon and oxygen atmospheres.

The first step, v_1, involves the primary bond breaking of the polymer chain, while the second step, v_2, represents the further decomposition of the primary degradation products into volatile species. In the case of pure PET, the first step becomes rate limiting once the maximum volatilization rate has been attained; after this point, the sample weight decreases exponentially with time, giving rise to an apparent first-order decomposition process.

The presence of phosphorus may affect the velocity of either of the two steps. A decision in favor of one of the two pathways of inhibition may be derived from the apparent kinetic type of the weight loss curve in the presence of phosphorus. If the rate of bond breaking is affected by phosphorus, the weight loss-versus-time curve should still be exponential, but the apparent first-order rate constant should be different. On the other hand, if the second step is inhibited and thus becomes rate limiting, the kinetics of weight loss are expected to change to an apparent zero-order law.

To resolve the question of the mechanism of inhibition, the isothermal TG curves of pure PET and PET + 12% phosphorus are compared, as shown in Figure 4. The high phosphorus concentration of 12% was selected in order to amplify the effect on the weight loss curve; similar results are obtained at lower phosphorus concentrations. According to Figure 4, the weight loss for the pure PET sample follows a first-order time dependence with an apparent rate constant
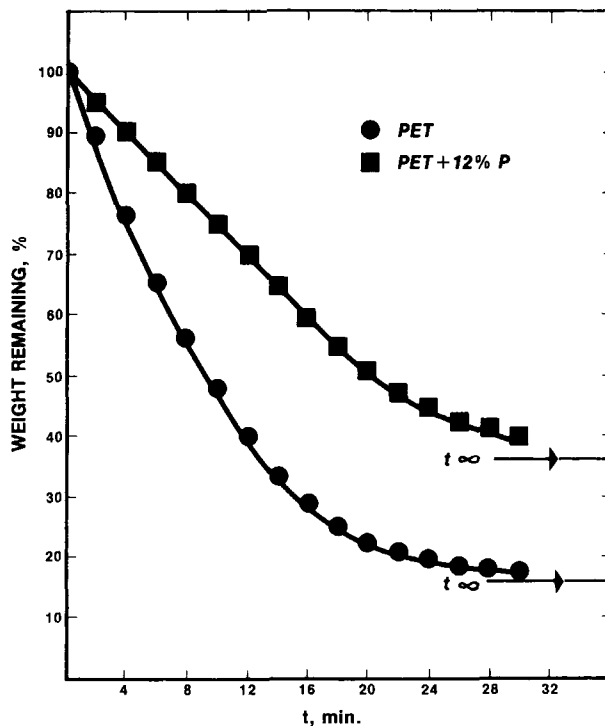
Fig. 4. Isothermal TG curves for PET and PET + 12% phosphorus in argon atmosphere at 400°C.

of k = 0.131 min^{-1} over about 90% of the curve. Addition of 12% phosphorus changes the weight loss curve to an apparent zero-order process over about 80% of the decomposition; the last part is again exponential with k = 0.151 min^{-1}. The close agreement of the two first-order rate constants indicates that no inhibition of the initial chain cleavage does occur. Therefore, we have to assume that the inhibition by phosphorus is exclusively due to the decrease of the velocity of the second step.

The effect of phosphorus on the generation of low molecular products is possibly due to the formation of thermally stable phosphorus–oxygen bonds in the pyrolyzing PET, thus preventing the formation of gaseous pyrolysis products.

This explanation is supported by the fact that elemental phosphorus has been shown to be an inefficient flame retardant for oxygen-free polymers, such as polystyrene or polypropylene, while being highly effective in oxygen-containing systems like PET, nylons, and polyurethanes.[1]

Effect of Elemental Phosphorus on the Thermo-Oxidative Degradation of PET

An important question in relation to the mechanism of polymer burning is the relative contributions of pyrolytic and thermo-oxidative pathways to the overall degradation of the polymer. The effect of a change from an inert argon to a reactive oxygen atmosphere on the isothermal TG curves can be used to estimate the relative importance of the two degradation routes.
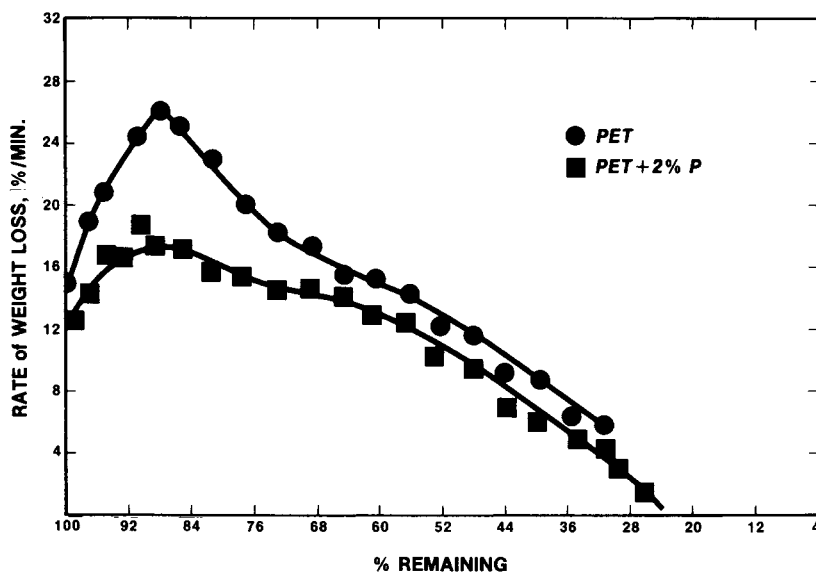
Fig. 5. Plot of rate of weight loss vs. conversion for PET and PET + 2% phosphorus in oxygen atmosphere at 402°C.

Figure 5 shows a typical TG experiment carried out in an oxygen atmosphere. Again, addition of phosphorus reduces the maximum rate of volatilization without affecting the general shape of the TG curve. Comparison with Figure 2 indicates that the rates in an oxygen atmosphere are higher than in an argon atmosphere; this indicates that the thermo-oxidative mechanism is indeed important in the temperature range under consideration.

The maximum weight loss rates in oxygen for PET and PET + 2% phosphorus for a series of temperatures are listed in Table II, and the corresponding Arrhenius plots are depicted in Figure 3; from their slopes, activation energies of $\Delta E = 30$ kcal/mole for pure PET and of $\Delta E = 36$ kcal/mole for PET + 2% phosphorus are obtained.

Contrary to the results obtained in an inert atmosphere, the activation energy for decomposition in an oxygen atmosphere is strongly increased in the presence of phosphorus. According to Figure 3, the Arrhenius plots for decomposition in an oxygen atmosphere intersect at $T = 470°C$, indicating that above this temperature, the thermo-oxidation is accelerated in the presence of phosphorus.

TABLE II
Effect of Elemental Phosphorus on the Rate of Weight Loss of PET
in an Oxygen Atmosphere

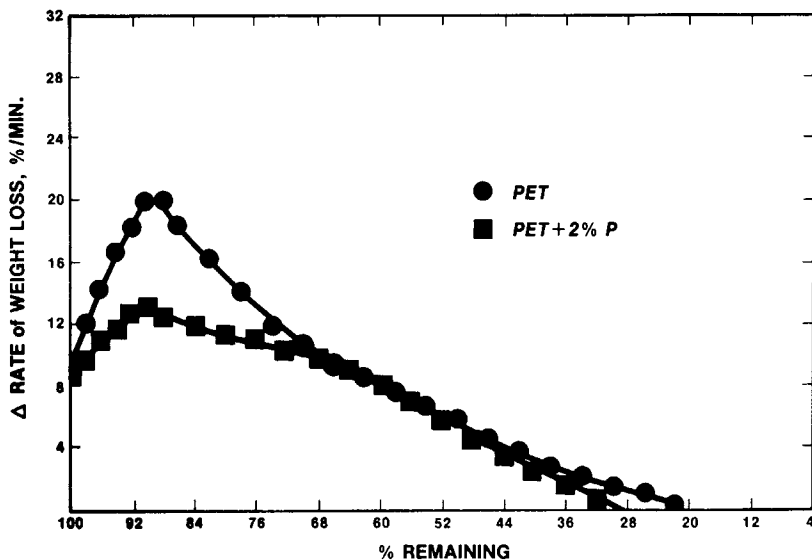| Temperature, °C	PET v_{max}, %/min	PET + 2% phosphorus v_{max}, %/min
402	26.2	17.0
427	52.0	43.1
467	225	175
510	550	655

Fig. 6. Plot of difference of weight loss rates in oxygen and argon vs. conversion for PET and PET + 2% phosphorus at 402°C.

Therefore, it is expected that in a highly oxidizing atmosphere, phosphorus should lose its flame-retardant properties if the temperature of the PET sample approaches the point at which the Arrhenius plots intersect. This assumption is supported by the observation that, in a pure oxygen atmosphere, the autoignition temperature for PET + 2% phosphorus is lower than for pure PET.

Following from the principle of the independent coexistence of reactions,[8] the rate that is measured in an oxygen atmosphere corresponds to the sums of the rates of the pyrolytic and the thermo-oxidative degradation pathways. Therefore, the rate-versus-conversion plot for purely thermo-oxidative degradation is obtained as the difference between the Figure 4 and the Figure 2 plots, as shown in Figure 6. Table III lists the differences between the maximum rates of weight loss for TG runs in oxygen and argon atmospheres, respectively, for different temperatures.

Comparison of the data listed in Tables I and III, respectively, indicate that at 400°C in a pure oxygen atmosphere, the thermo-oxidative degradation rate is about three times as large as the rate of pyrolysis. However, since the oxygen

TABLE III
Effect of Elemental Phosphorus on the Rate of Thermo-oxidative Degradation of PET

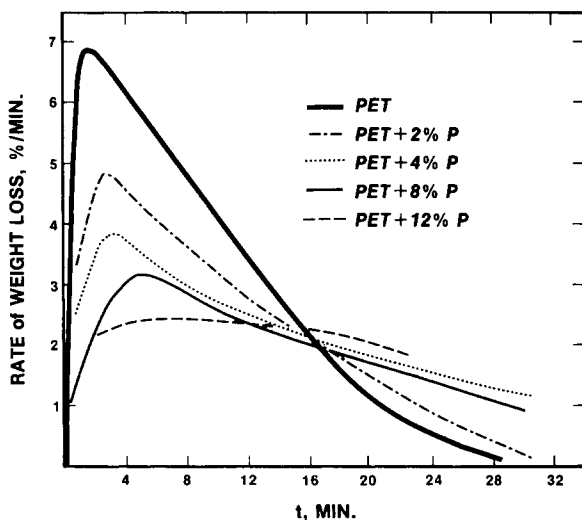| Temperature, °C	PET $(v_{max\ O_2} - v_{max\ Ar})$, %/min	PET + 2% phosphorus $(v_{max\ O_2} - v_{max\ Ar})$, %/min
402	19.3	11.5
427	30.5	28.0
467	138	100
510	225	371

Fig. 7. Rate of weight loss vs. time plots for PET containing different amounts of phosphorus, in argon atmosphere, $T = 400°C$.

mole fraction at the surface of a burning polymer is usually in the range of 0.01 to 0.05, the thermo-oxidative pathway is likely to be negligible, although the possibility of a catalytic action by small amounts of oxygen cannot be discounted.[9]

Correlation of TG Curves with Oxygen Indices for the System PET–Elemental Phosphorus

If the flame retardancy imparted to PET by the addition of elemental red phosphorus is indeed caused by the inhibition of the condensed phase reactions leading to the formation of combustible gases, it should be possible to quantitatively correlate the degree of flame retardancy as expressed by the oxygen index with the reduction of the rate of fuel generation measured under TG conditions. Assuming that the degradation of PET occurs predominantly by pyrolysis rather than by thermo-oxidation, the comparison is made on the basis of isothermal TG curves obtained in an argon atmosphere. The isothermal weight loss curves at $T = 400°C$ for a series of PET samples containing different amounts of

TABLE IV
Effect of Elemental Phosphorus on the Maximum Volatilization Rate and on Oxygen Index of PET[a]

Sample composition	Max. rate, %/min	Max. rate rel. to PET	Oxygen index	Oxygen index rel. to PET
PET, pure	6.90	1.00	20.4	1.00
PET, 2% phosphorus	4.80	0.70	25.1	1.23
PET, 4% phosphorus	3.85	0.56	27.5	1.35
PET, 8% phosphorus	3.30	0.48	30.4	1.49
PET, 12% phosphorus	2.45	0.36	32.6	1.60

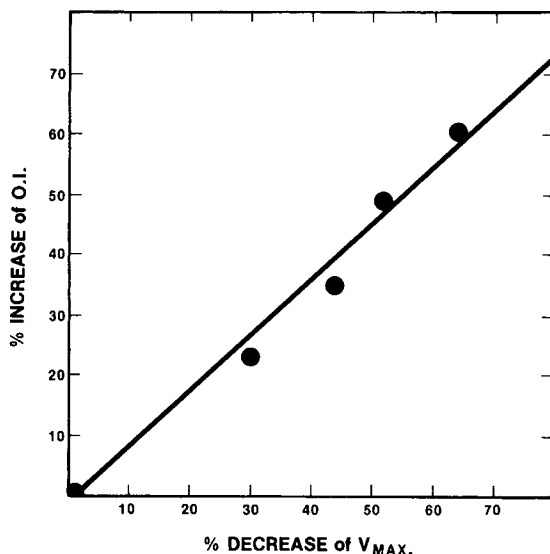[a] The oxygen index values are taken from ref. 1.

Fig. 8. Plot of relative increase of oxygen index vs. relative decrease of maximum pyrolysis rate at different phosphorus concentrations.

phosphorus are shown in Figure 7. One sees that, in all cases, the weight loss curves exhibit a maximum, indicating that the basic random scission mechanism is not changed in the presence of phosphorus. The only effect, therefore, appears to be a reduction of the maximum volatilization rate accompanied by a broadening of the rate maximum at high phosphorus concentrations.

In Table IV, the effect of phosphorus on the maximum weight loss rates is compared to its effect on the oxygen index.

One recognizes that the relative increase of the oxygen index does indeed correlate with the relative decrease of the maximum volatilization rate at corresponding phosphorus concentrations. According to the graphic representation in Figure 8 of the data of Table IV, a linear relationship is obtained. The correlation is rather good as indicated by a value of $r = 0.991$.

This linear correlation of flammability with TG data is only understandable if the flame retardant action of elemental phosphorus is predominantly caused by a condensed rather than a gas phase mechanism. Moreoover, since the correlation is obtained by considering only the pyrolytic mode of decomposition, one has to assume that in the case of PET, the contribution of the thermo-oxidative pathway of degradation is negligible under burning conditions.

CONCLUSIONS

1. In the temperature range of 400° to 500°C, addition of phosphorus at the 2% level reduces the rate of thermal decomposition of PET and increases the amount of residual char. The observed change of the pyrolysis kinetics suggests that the addition of phosphorus inhibits the secondary reactions that lead to the formation of volatile pyrolysis products rather than the initial cleavage of the polymer chain.

2. If the thermal decomposition is carried out in a reactive oxygen atmosphere,

the degradation is found to occur at a faster rate. However, owing to the low oxygen concentration at the polymer surface under actual combustion conditions, the contribution of the thermo-oxidative pathway is assumed to be negligible.

3. We have been able to arrive at a correlation between the increase of the oxygen index and the decrease of the pyrolysis rate of PET in the presence of phosphorus. This may be considered additional evidence for condensed-phase flame-retardant action of phosphorus in PET.

References

1. A. Granzow and J. F. Cannelongo, *J. Appl. Polym. Sci.,* **20,** 689 (1976).
2. E. P. Goodings, in *Monograph No. 13, Soc. Chem. Ind.,* London, 1961, pp. 211–228.
3. R. Simha and L. A. Wall, *J. Phys. Chem.,* **56,** 707 (1952).
4. L. A. Wall, in *Monograph No. 13,* Soc. Chem. Ind., London, 1961, pp. 146–162.
5. R. Simha and L. A. Wall, *J. Polym. Sci.,* **6,** 39 (1951).
6. A. Granzow and D. L. Zabel, unpublished results.
7. S. Straus and L. A. Wall, *J. Res. Nat. Bur. Stand.,* **60,** 39 (1958).
8. L. P. Hammett, *Physical Organic Chemistry,* 2nd ed., McGraw-Hill, New York, 1970, p. 95.
9. D. E. Stuetz, A. H. DiEdwardo, F. Zitomer, and B. P. Barnes, *J. Polym. Sci.,* **13,** 585 (1975).