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THERMOGRAVIMETRIC ANALYSIS OF POLY(ETHYLENE TEREPHTHALATE) TREATED WITH POLYMERIC BROMINE COMPOUNDS *

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ABSTRACT

The thermal oxidative degradation of poly(ethylene terephthalate) (PET) both topically treated and radiation grafted with poly(bromostyrene) (PBS), poly(vinyl bromide) (PVB) and poly(vinylidene bromide) (PVDB) has been studied by non-isothermal thermogravimetry. Activation energies were calculated from the data according to the isoconversional method of Flynn, along with regression coefficients of the compensation effect plots. It is shown that these bromo polymers have only marginal effects upon the condensed-phase fuel producing reactions and are dependent upon the structure of the brominated polymer and its method of incorporation into PET.

INTRODUCTION

Non-isothermal methods of thermal analysis have been widely used [1] to obtain kinetic data for the thermal degradation of polymeric systems based upon the Arrhenius form of the rate law:

$$\mathrm{d}\alpha/\mathrm{d}t = Af(\alpha)\exp(-E/RT) \tag{1}$$

In this equation, A and E are the Arrhenius pre-exponential factor and activation energy, respectively, α is the extent of reaction, T the absolute temperature and $f(\alpha)$ a function of α dependent upon the reaction mechanism. In the majority of practical cases, the activation energy, E, is the principal focus of kinetic studies and is obtained from a study of the thermal decomposition as a function of heating rate, β, via the following expression:

$$\mathrm{d}\alpha/\mathrm{d}T = Af(\alpha)/\beta\exp(-E/RT) \tag{2}$$

When the variables are separated and the expression integrated to fixed values of α, eqn. (2) becomes:

$$F(\alpha) = \int_0^{\alpha}\frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{A}{\beta}\int_0^{T}\exp(-E/RT)\,\mathrm{d}T \tag{3}$$

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By the use of Doyle's method [2] which approximates the logarithm of the temperature integral to a straight line, the following expression can be obtained:

$$\log F(\alpha) \simeq \log(AE/R) - \log \beta - 2.315 - 0.4567E/RT \qquad (4)$$

This expression allows E to be obtained from the variation of the temperature for a constant α, as a function of β [3].

This report contains the results of the kinetic investigation of the thermal oxidative degradation of poly(ethylene terephthalate) (PET) treated with poly(4-bromostyrene) (PBS), poly(vinyl bromide) (PVB) and poly(vinylidene bromide) (PVDB), when analysed by the above procedure. These materials were examined in our studies as potential flame retardants for PET. The polymeric nature of these compounds offers advantages with respect to being less susceptible to loss during fabrication or utilisation. PET fabrics topically treated with these polymers are reported in this study along with results obtained with the same polymers chemically grafted to the PET by the use of a γ-radiation grafting procedure.

EXPERIMENTAL

Materials

The PET fabric used in this study was commercial Dacron T54 (126 g m^{-2}) obtained from Testfabrics Inc., Middlesex, NJ (Style 767). All solvents were general purpose reagent grade and used as received.

The PBS, PVB and PVDB were obtained from Polyscience Inc., and used as received. Chemical analysis for bromine revealed the following information: PBS = 35.0% (expected 43.7%); PVB = 66.4% (expected 74.8%); PVDB = 76.0% (expected 85.9%).

The monomers, 4-bromostyrene and vinylidene bromide, were obtained from Polyscience Inc., while the vinyl bromide was obtained from Matheson Inc. Grafting to PET was accomplished by γ-irradiation of fabric samples in liquid monomer or its solution under vacuum. Topically treated fabrics were obtained by the application of polymer solution in methylene chloride. The content of bromo polymer in the PET fabrics was determined from bromine analysis. The actual samples examined in this study are listed in Table 1.

Apparatus and Procedure

A Du Pont 951 thermobalance coupled to a Du Pont 1090 thermal analyzer was used. Thermal oxidative degradations were carried out in air (50 cm^3 min^{-1}) at constant heating rates of 1, 2, 5, 10, 20, 30 and 50°C min^{-1} using sample sizes 16–20 mg. Data reduction was performed accord-

TABLE 1

PET treated samples examined in this study

Sample designation	Polymer	Treatment	Analysis for Br (%)	Weight add-on (%)
PBSG	Bromo styrene	Graft	6.3	14.5
PBST	Bromo styrene	Topical	5.6	12.9
PVBG	Vinyl bromide	Graft	3.4	4.5
PVBT	Vinyl bromide	Topical	3.9	5.3
PVDBG	Vinylidene bromide	Graft	7.5	8.7
PVDBT	Vinylidene bromide	Topical	8.1	9.4

ing to the isoconversional method [3] employing the setup we have described previously [4].

RESULTS AND DISCUSSION

The TG and DTG curves for PET, PBS, PVB and PVDB are presented in Fig. 1 for samples heated at a rate of 10°C min^{-1}. The data presented in this figure clearly indicate the differences in thermal stability of the bromo polymers when compared to PET. PET at this heating rate (10° min^{-1}) appears to start decomposing around 360°C, reaching a peak rate of decomposition at 434°C. PBS, is not quite as thermally stable as PET, commencing its major weight loss around 340°C, reaching a peak rate at 404°C. It should be noted, however, that whilst the degradation of PBS may not be very fast up to about 340°C, it does gradually start to lose weight at lower temperatures and at 340°C it has already lost over 10% of its initial weight. Although the major decomposition reaction of PBS is depolymerisation to give bromostyrene as the main product [5,6], HBr has been detected in the pyrolysate [6,7].

In the case of PVB and PVDB, the onset of thermal degradation is occurring at temperatures of 160 and 140°C with peak rates of weight loss at 202 and 195°C, respectively, and with HBr being the major product [8]. The polyenes formed as a result of these dehydrobromination reactions then undergo further fragmentation and oxidation at higher temperatures (500–600°C) in the same region that the PET residues undergo oxidative decomposition.

Some of the results of the kinetic analysis of the thermal decomposition of these polymers are shown in Fig. 2 which presents the calculated apparent activation energies as a function of fractional weight loss (α). This figure clearly indicates that the polymers PET, PBS, PVB and PVDB do not have a single value for the apparent activation energy, but a range of values,

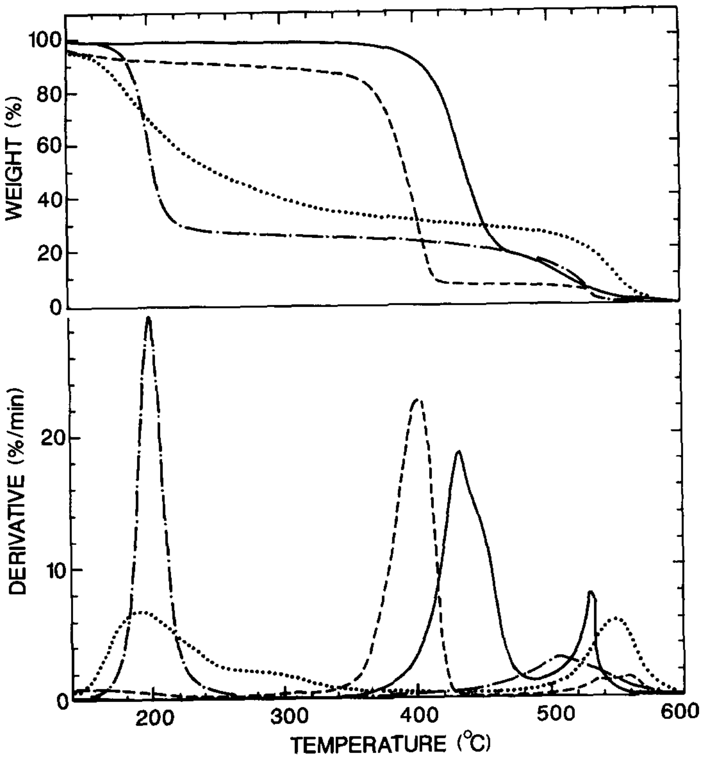

Fig. 1. Weight loss and derivative thermogravimetric curves in air at 10°C min^{-1} for: (———) PET; (— — —) PBS; (·—·—·) PVB; (······) PVDB.

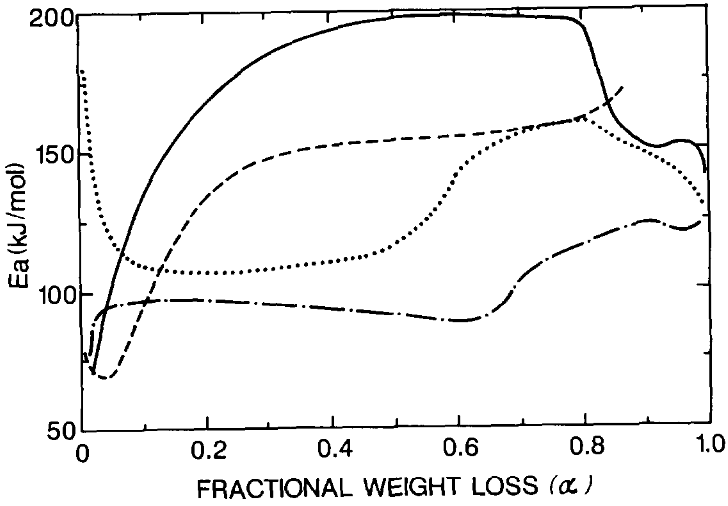

Fig. 2. Calculated activation energies as a function of fractional weight loss for: (———) PET; (— — —) PBS; (·—·—·) PVB; (······) PVDB.

dependent to some extent on the degree of reaction. In the case of untreated PET, the main degradation in the α range 0.02–0.75 has an E_a value of 191 ± 6 kJ mol^{-1}, in good agreement with the data that we reported and reviewed in an earlier publication [9]. The E_a for PBS meanwhile is lower than that for PET, i.e., 150 ± 3 kJ mol^{-1} for its major degradation step. The dehydrobromination reactions for PVB and PVDB are very similar with values of 93 ± 2 and 113 ± 7 kJ mol^{-1}, respectively, for the major weight loss zones. These values appear to be reasonable in comparison with the E_a values for HBr elimination for the model compound ethyl bromide with a value of 130 kJ mol^{-1}, and 1,2-dibromoethane, where C–Br bond fission rather than molecular elimination occurs, with a value of 84 kJ mol^{-1} [10]. The value for PVB is slightly less than the E_a value of 124 kJ mol^{-1} reported by Mazon-Arechederra et al. [11] for random dehydrobromination and much less than the E_a of 170 kJ mol^{-1} for the "autocatalytic" process reported by the same authors. However, it should be noted that the above data were reported for vacuum or inert nitrogen atmosphere studies, while our work has been conducted in an oxidative air atmosphere.

The influence of PBS on the main degradative weight loss of PET is illustrated in Fig. 3 for a heating rate of 10°C min^{-1}. The presence of PBS, in combination with PET, has an effect upon the PET curve merely because of the overlap of the individual weight loss curves. The resultant effect of this overlap of the two curves can be computed using the DuPont File Modification Utility program. Thus, the simulated curves presented in this and subsequent graphs were obtained from the individual weight loss data for each polymer added together in the correct ratio to give a simulation of the add-on utilised in the topically treated samples. The direct comparison of this simulated curve with the grafted and topically treated curves gives, therefore, a greater indication of actual interactions between the two polymers. If no interactions were occurring between the PET and the PBS polymers during the weight loss processes, the simulated curve should coincide with the grafted or topically treated curves. Examination of Fig. 3, however, clearly indicates that the weight losses for the grafted and topically treated PETs are not identical to that of the simulated curve. Grafting of PBS to PET appears to be responsible for an earlier onset of degradation and associated weight loss. However, it will be noted that although the weight loss rate is faster at lower temperatures, the actual maximum rate is less than that of untreated PET and occurs at a slightly higher temperature. Although grafting PBS to PET does not appear to increase the char residue (in effect there appears to be a slight reduction) the residue from the graft does have a slightly greater thermal stability, degrading at temperatures slightly higher than those observed with the untreated PET and the topically treated sample.

The topically treated PBS on PET, meanwhile appears to behave very similarly to the simulated PET curve. The actual weight loss curves for the

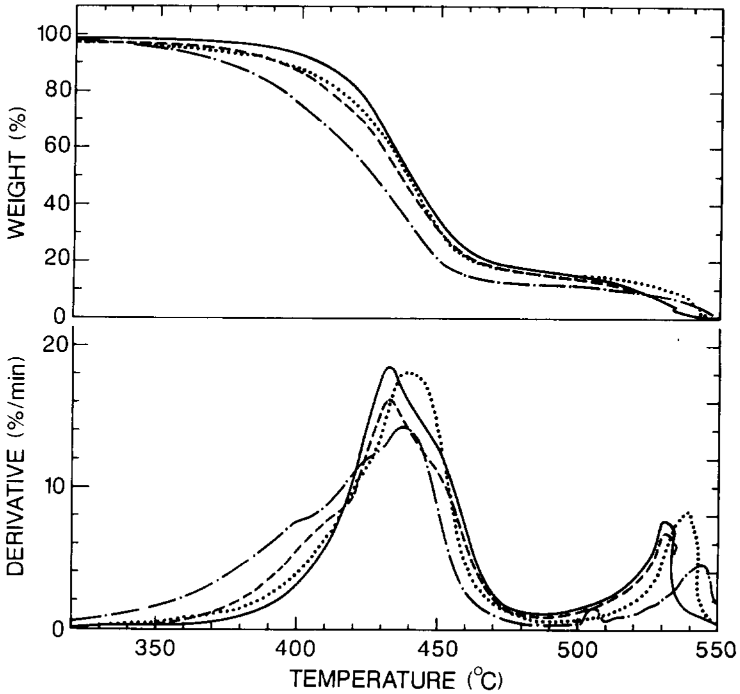

Fig. 3. Weight loss and derivative thermogravimetric curves in air at 10°C min^{-1} for: (———) PET; (· · · · · ·) PBST;(· — · — ·) PBSG; (— — —) simulated curve calculated from the addition of PBS and PET curves.

simulated experiment and the topically treated sample differ only slightly in the actual onset temperature and rate. Meanwhile, the peak temperatures corresponding to the maximum rate for the topical treatment are slightly higher than the simulated values and in close agreement with results obtained for the grafted samples.

The calculated E_a values for these samples, according to the isoconversional technique, are presented in Fig. 4 as a function of α, the degree of conversion. From these data it can be seen that the topical treatment and grafting of PBS to PET is not responsible for any major changes in the activation energy, E_a, of the major degradation stage of PET, although both treatments are responsible for some slight reductions in E_a with the largest reductions being observed when the PBS is grafted.

The weight loss data for the PVB treated PET samples heated at 10°C min^{-1}, are presented in Fig. 5. Once again, the trends observed for PBS are noted for PVB, although not as large especially for the grafted sample. The reason for this decreased effect is probably associated with the lower magnitude of the treatment level rather than reduced effectiveness. However, attempts to achieve PET with a higher graft concentration of PVB were unsuccessful. Once again the grafted and topically treated samples give peak

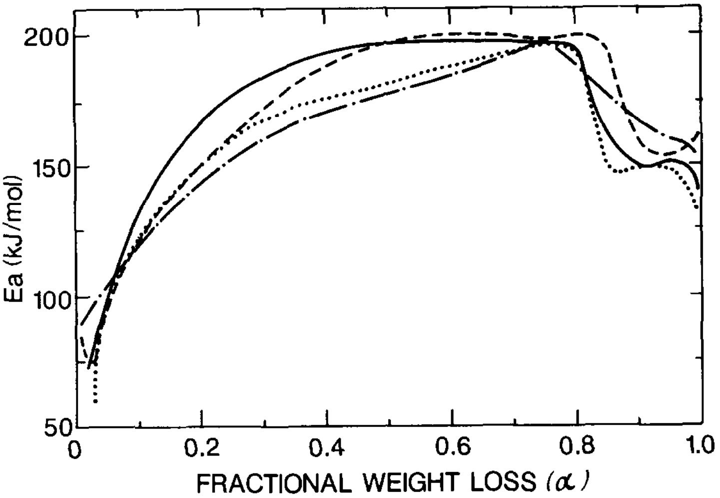

Fig. 4. Calculated activation energies as a function of fractional weight loss for: (———) PET; (······) PBST; (·—·—·) PBSG; (— — —) simulated curves for a PBS/PET combination.

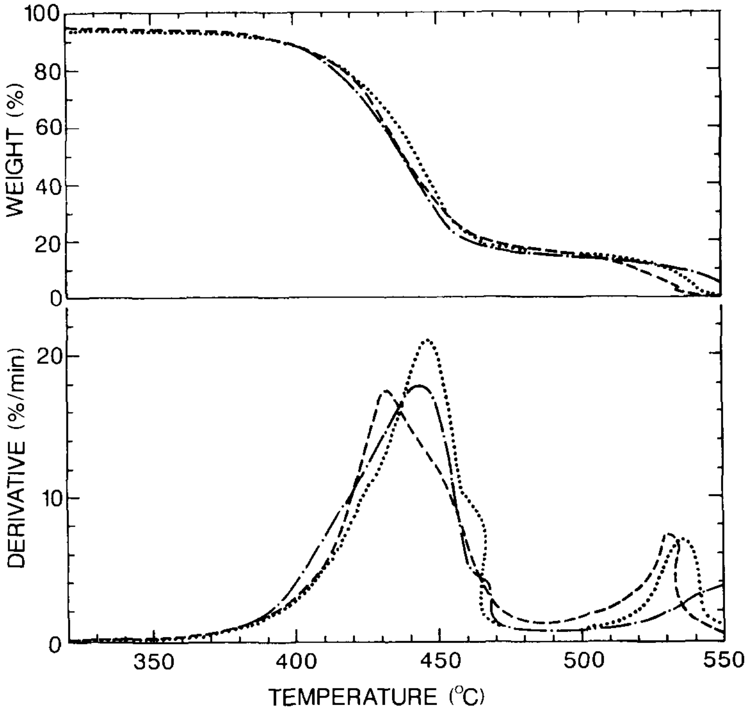

Fig. 5. Weight loss and derivative thermogravimetric curves in air at 10°C min^{-1} for: (······) PVBT; (·—·—·) PVBG; (— — —) simulated curve calculated from the addition of PVB and PET curves.

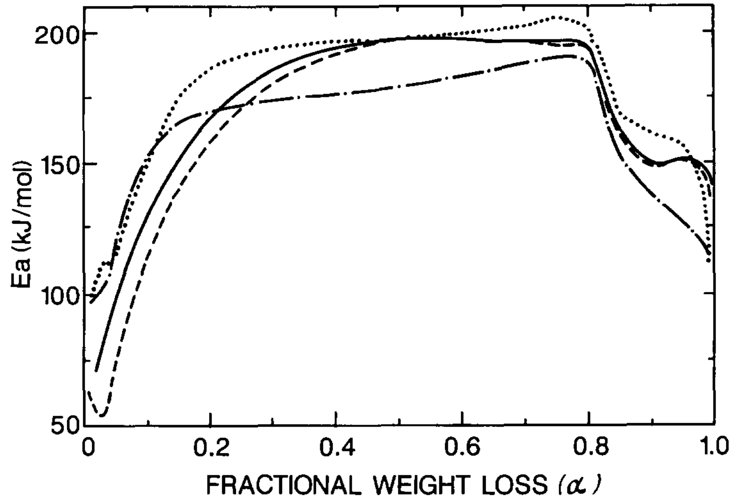

Fig. 6. Calculated activation energies as a function of fractional weight loss for: (———) PET; (······) PVBT; (·–·–·)PVBG; (— — —) simulated curves for a PVB/PET combination.

rate temperatures slightly higher than those observed with the simulated data. The residual material in the PVB grafted PET also appears to be stabilised, degrading at higher temperatures. The topical PVB treatment appears to be responsible for a slight reduction in the degradation rate of PET in that the weight loss process is retarded. This stabilisation seems to be reflected in E_a values (Fig. 6), which appear to be slightly higher than those observed with the simulated experiments. The grafted PVB samples, meanwhile, seem to be responsible for reduced E_a values during the main PET degradation process, in much the same way as was observed for the PBS grafted samples.

In the case of PVDB (Fig. 7), both the grafted and the topically treated samples appear to be responsible for a destabilisation of PET causing an increase in the rate of weight loss at lower temperatures. However, as was noted with both PBS and PVB, the temperature of maximum rate of weight loss has been moved to slightly higher temperatures. Meanwhile, evaluation of E_a values for PET degradation (Fig. 8) once again reveals that in the major region of weight loss the topical treatment is responsible for a slight increase in E_a while grafting causes a reduction in E_a.

In terms of evaluating complicated solid-phase decomposition kinetics, it has been suggested that an investigation of the kinetic compensation effect (CE) is capable of providing mechanistic information on the degradation processes [12] provided the investigator ensures that other variables are kept constant. In our studies, we have attempted to keep all the experimental variables constant and made comparisons of untreated samples with treated

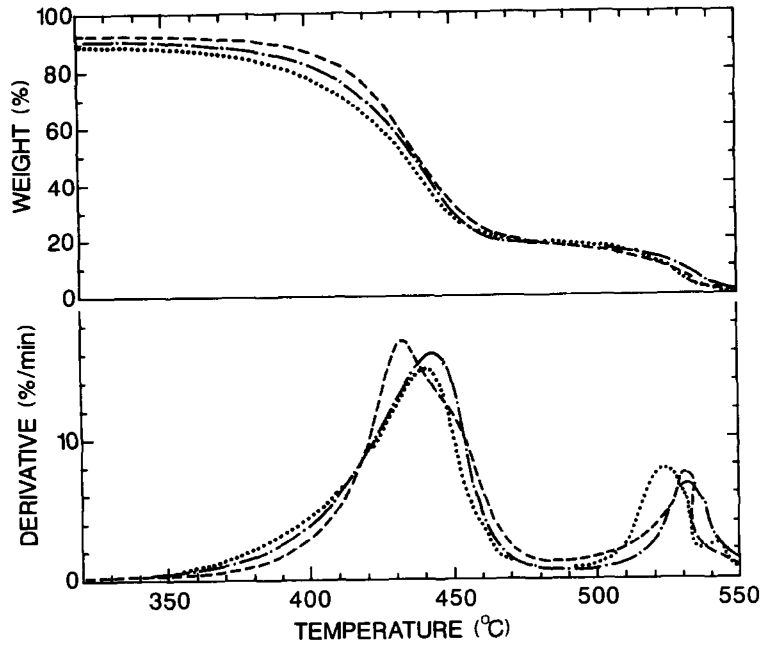

Fig. 7. Weight loss and derivative thermogravimetric curves in air at 10°C min^{-1} for: (······) PVDBT; (·–·–·) PVDBG; (— — —) simulated curve calculated from the addition of PVDB and PET curves.

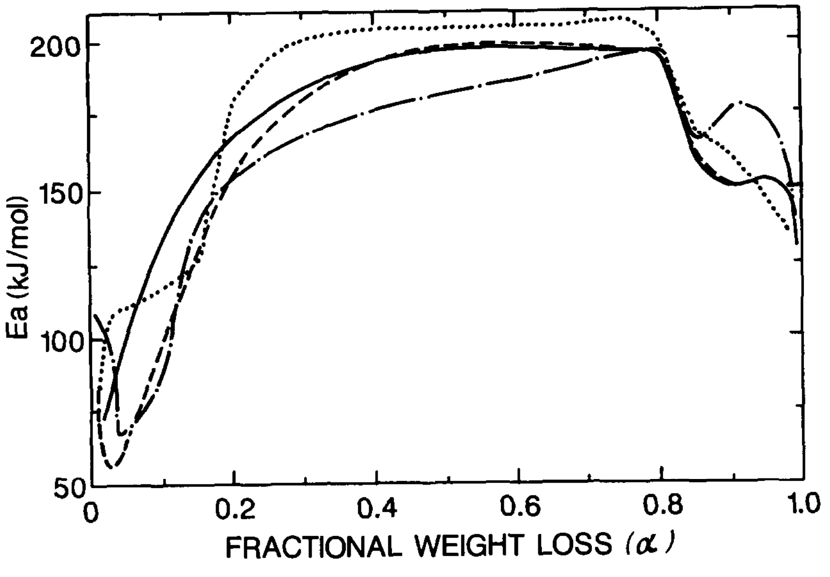

Fig. 8. Calculated activation energies as a function of fractional weight loss for: (———) PET; (······) PVDBT; (·–·–·) PVDBG; (— — —) simulated curves for a PVDB/PET combination.

TABLE 2

Regression coefficients of the compensation effect plots for the data $\alpha = 0.2$–0.75 inclusive

	a_0	a_1	r [a]
Untreated PET	0.0781	1.338	0.9997
Simulated PBS treatment	0.0745	2.116	0.9997
Topical PBS treatment	0.0738	2.204	1.0000
Grafted PBS on PET	0.0733	2.395	0.9999
Simulated PVB treatment	0.0763	1.702	0.9996
Topical PVB treatment	0.0723	2.426	0.9996
Grafted PVB on PET	0.0752	1.863	0.9985
Simulated PVDB treatment	0.0752	1.925	0.9995
Topical PVDB treatment	0.0704	3.031	0.9976
Grafted PVDB on PET	0.0733	2.236	0.9999

[a] Correlation coefficient.

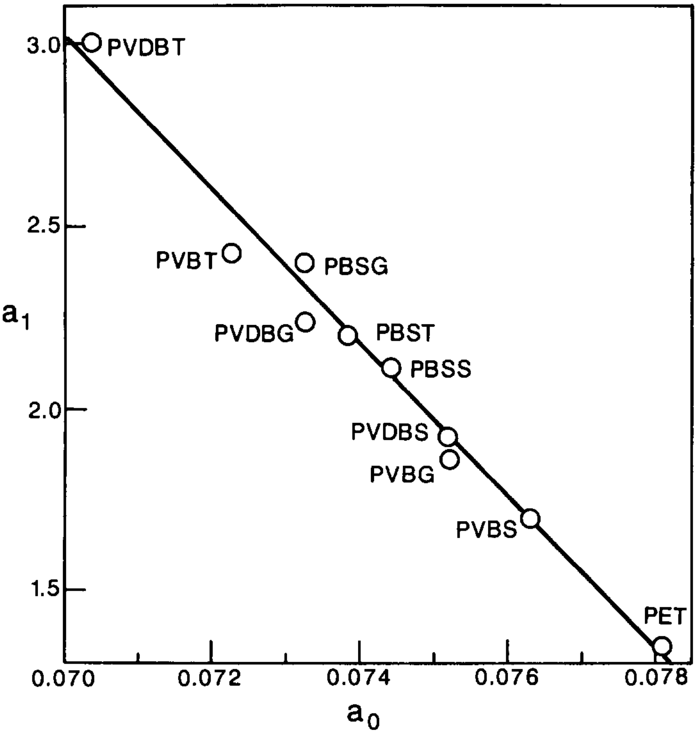

Fig. 9. Correlation of regression coefficients for data with simulated experiments denoted PBSS, PVBS and PVDBS.

samples in a sequential manner in order to ensure, as near as possible, that the CE is a formal consequence of the decomposition process, and not an artifact of some secondary effect. The regression coefficients, a_0 and a_1, determined using the expression log $A = a_0E + a_1$ are presented in Table 2, for the major PET weight-loss zone of each sample (i.e., $\alpha = 0.2$–0.75), and plotted graphically in Fig. 9 using the approach suggested by Lesnikovich et al. [13].

In the case of the simulated experiments, the values for a_0 and a_1 should be close to those for PET but not identical due to the additive overlap of the curves used in their elucidation. This is indeed found to be the case with the simulated PBS showing the largest deviation from the PET, presumably due to the greater overlap of the PBS and PET weight loss curves (see Fig. 1). If the polymer treatments had no influence on the condensed-phase mechanism of degradation, the topically treated and grafted samples would be anticipated to have similar, if not identical regression coefficients a_0 and a_1 to those observed with the simulated experiments. Examination of Table 2 reveals that this is not the case, although the PBS grafted and topically treated samples gave regression coefficients very similar to those observed for the simulated samples. It therefore appears likely that PBS has little or no effect on the kinetics of PET degradation.

In the case of PVB and PVDB meanwhile, both topical treatments appear to be responsible for the largest changes in the regression coefficients while the grafted samples are close to the simulated values. It is interesting to note that all treatments appear to be responsible for an increase in a_1 and a decrease in a_0, a change which has been interpreted to be beneficial in terms of flame retardation [14]. This result is initially a little surprising in view of the recognised potential of these materials as flame retardants [15]. However, studies in our laboratories have indicated that whilst these bromo polymers may offer advantages as combustion inhibitors for the gas-phase reactions, they have a negative effect as condensed-phase active species [7], in terms of the generation of gaseous pyrolysates.

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