

Short-Term Thermal Endurance Evaluation of Thermoplastic Polyesters by Isothermal and Nonisothermal Thermogravimetric Analysis

Andrea Saccani,¹ Antonio Motori,¹ Gian Carlo Montanari²

¹Dipartimento Chimica Applicata e Scienza dei Materiali, University of Bologna, Viale Risorgimento 2, 40316 Bologna, Italy

²Dipartimento di Ingegneria Elettrica University of Bologna, Viale Risorgimento 2, 40316 Bologna, Italy

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ABSTRACT: Thermogravimetric analysis, carried out in a pure oxygen flow both in isothermal and constant-rate heating conditions, is proposed as an analytical technique for the estimation of thermal endurance parameters (the temperature index and halving interval) of polymeric materials, according to the short-term procedure suggested by the IEC 61026 Standard. This technique was applied for the determination of the activation energy of the degradation process of three thermoplastic polyesters used in the electrical and packaging industries: poly(ethylene terephthalate), poly-

(buthylene terephthalate), and poly(ethylene naphthalate). The results obtained are presented and compared with results previously derived by the long-term conventional procedure described in IEC 60216; satisfactory agreement of the thermal endurance parameters was generally observed. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 968–973, 2005

Key words: degradation; polyesters; thermogravimetric analysis (TGA)

INTRODUCTION

The search for fast, reliable, and low-cost techniques for the evaluation of the thermal endurance properties of polymeric materials used in the electrical and packaging industries is a very important topic. The limit of the conventional long-term procedure, which is described in IEC 60216,¹ mainly lies in the remarkable amount of time needed to obtain the thermal endurance parameters: in fact, for the estimation of the temperature index (TI; i.e., the temperature at which the material still maintains a certain amount of one of its original properties after 20,000 h) and the halving interval (HIC; i.e., the temperature rise that halves life), aging tests at three or more temperatures must be performed, and at least 1 year is needed. A remarkable time reduction can be obtained if one resorts to the combined use of an analytical technique, which quickly provides the activation energy (E_a) of the degradation process, and a short-time conventional life test (lasting about 300 h), which provides the location of the thermal endurance line for a selected property and end point² according to the IEC 61026 Standard. This short-term procedure was described in detail in

previous articles.^{3,4} Isothermal differential calorimetry, carried out in a pure oxygen flow, was successfully used as analytical technique for the evaluation of the thermal endurance parameters of several polymeric materials for electrical insulation. The results so obtained were compared with those provided by long-term conventional tests. In particular, the short-term method proved to be very accurate for crosslinked polyethylene and ethylene-propylene rubber;^{5–7} indeed, for polyolefin-based materials, oxidation is largely the prevailing degradation reaction over the investigated temperature range, both in short- and long-term tests. For poly(buthylene terephthalate) (PBT), the results obtained were less accurate,³ whereas for other materials, such as poly(vinyl chloride), the analytical technique did not provide results at all; however, in these materials, other degradation reactions superimpose pure oxidation. In this article, isothermal and nonisothermal thermogravimetric analysis (TGA), both carried out in a pure oxygen flow, are proposed as analytical techniques. Instead of the monitoring of the exothermic reaction taking place during degradation, as in isothermal differential calorimetry, weight changes caused by thermooxidation (and other side reactions) are detected. Although in isothermal differential calorimetry thermograms, the choice of the characteristic points to select at each temperature is limited to the oxidation maximum time or to the oxidation induction time,⁸ the choice of a

Correspondence to: A. Saccani (andrea.saccani@mail.ing.unibo.it).

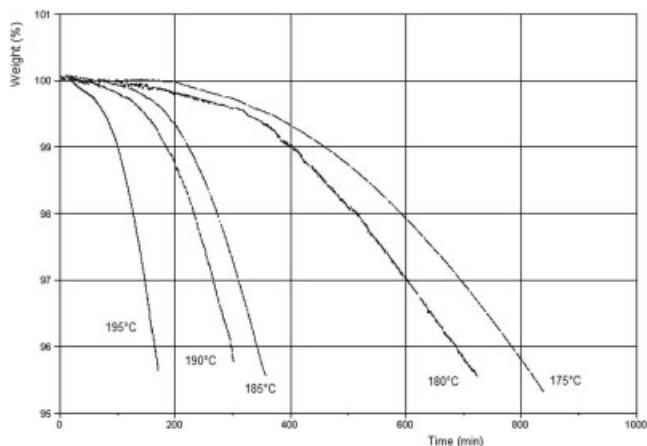


Figure 1 PBT isothermal thermograms for all of the investigated temperatures.

specific characteristic point in isothermal TGA thermograms or of the degree of conversion in nonisothermal TGA can lead to different values of E_a for the degradation process. The data provided by the nonisothermal TGA technique were treated according to the Kissinger,^{9,10} Friedman,¹¹ and Flinn–Wall–Ozawa (FWO)^{12,13} methods, which are the most frequently applied; their limits and accuracy, even in comparison with other methods, have been intensively studied by many authors.^{14–16} The results obtained for three thermoplastic polyesters, poly(ethylene terephthalate) (PET), PBT, and poly(ethylene naphthalate) (PEN), whose thermooxidative degradation has been studied to some extent in literature^{17–18} and in an inert atmosphere,^{19–20} are reported and compared with those derived from both isothermal TGA and long-term conventional tests.

EXPERIMENTAL

The three thermoplastic polyesters investigated had the following characteristics: 1. PBT was laboratory

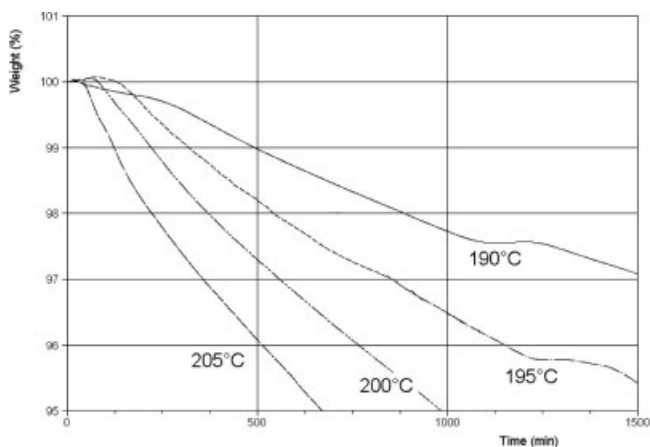


Figure 2 PET isothermal thermograms for all of the investigated temperatures.

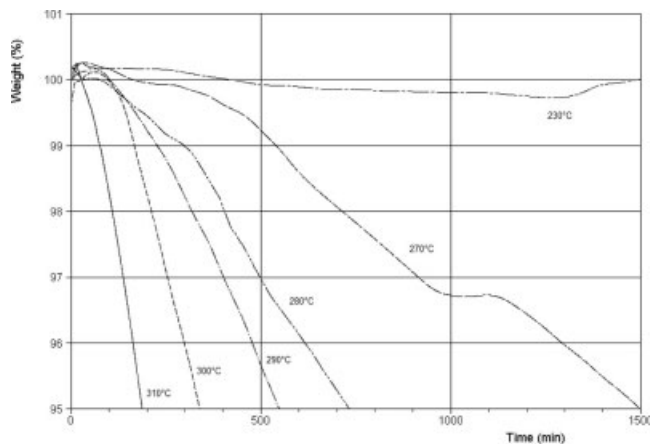


Figure 3 PEN isothermal thermograms for all of the investigated temperatures.

synthesized and had an average numerical molecular weight of 22,000, a melting temperature (T_m) of 222, a glass-transition temperature (T_g) of 28°C, and a 32% degree of crystallinity. 2. PET was laboratory synthesized and had an average numerical molecular weight of 29,700, a T_m of 255, a T_g of 84°C, and a 42% degree of crystallinity. 3. PEN (Teonex, DuPont) had a T_m of 268, a T_g of 126°C, and a 52% degree of crystallinity.

T_m , T_g , and crystallinity values were determined by differential scanning calorimetry (model Q10, Thermal Analysis Instruments, New Castle, Delaware) at a heating rate (β) of 10°C/min.

The isothermal and nonisothermal TGA tests (model Q50, Thermal Analysis Instruments) were performed on samples in the form of films about 100–200 μm thick under a pure oxygen flow of 40 cc/min; until testing, all samples were kept in a dry environment, and no thermal treatment was made on them. β 's of 2, 5, 7, 10, and 20°C/min were used for nonisothermal TGA tests in a temperature range from 40 to 600°C. In

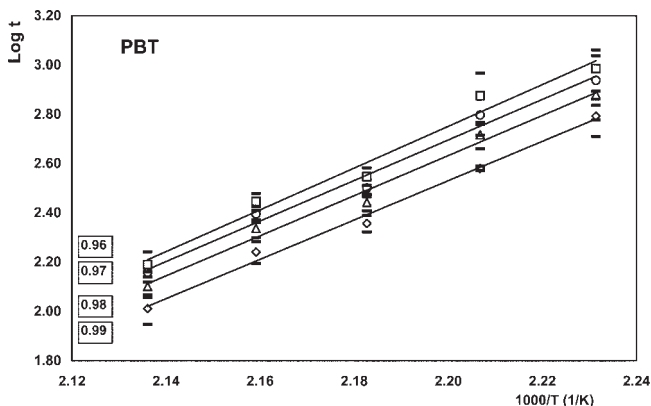


Figure 4 Average times to the selected end point as a function of the reciprocal of the absolute temperature for PBT (confidence interval at 90% probability).

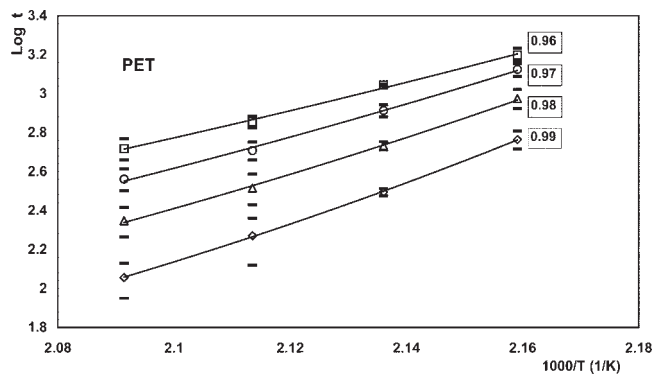


Figure 5 Average times to the selected end point as a function of the reciprocal of the absolute temperature for PET (confidence interval at 90% probability).

isothermal TGA measurements, samples were heated in nitrogen flow at a rate of 30°C/min. When the scheduled temperature was reached, the sample was allowed to stabilize for 1 min; then, the switch from nitrogen to oxygen was made. The isothermal measurements were performed in the following temperature ranges: 175–195°C for PBT, 190–205°C for PET, and 190–300°C for PEN. For each test condition, three measurements were performed.

The thermal endurance parameters TI and HIC of the investigated materials was previously estimated according to the conventional long-term procedure. For PBT, tests had been carried out from 130 to 160°C³ with tensile strength as the diagnostic property. For PET and PEN, tests were performed from 170 to 200°C and from 190 to 220°C, respectively; weight was chosen as the diagnostic property.

RESULTS AND DISCUSSION

Isothermal and constant-rate heating TGA

For the isothermal TGA tests, Figures 1–3 report examples of the thermograms obtained for PBT, PET, and PEN, respectively. For all polymers, the temperature range was just above that of the conventional tests; moreover, whereas for PBT and PET, it was below the T_m , PEN tests were also performed over its T_m . A continuous weight loss with time was observed at all the test temperatures for PBT and PET (Figs. 1 and 2). On the contrary, no significant mass loss was exhibited by PEN below its T_m (Fig. 3) at least for the investigated times (the thermogram at 230°C is reported as an example); at temperatures higher than 270°C (i.e., just over the T_m), a significant weight loss was instead observed. The average times needed to reach a selected mass loss, corresponding to residual fractional mass of 0.99, 0.98, 0.97, and 0.96, respectively, were determined and plotted as a function of the reciprocal absolute temperature (Figs. 4–6). As to

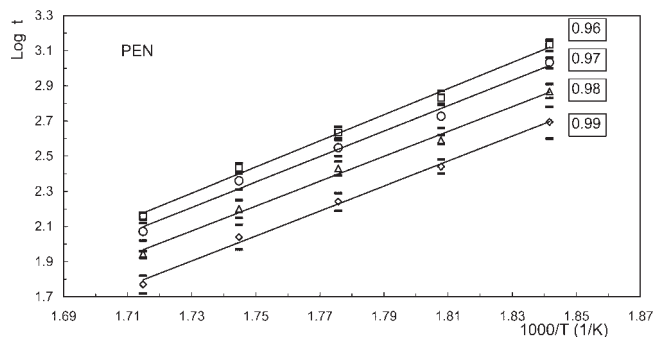


Figure 6 Average times to the selected end point as a function of the reciprocal of the absolute temperature for PEN (confidence interval at 90% probability).

the nonisothermal TGA tests, Figures 7–9 show the thermograms obtained for the three polyesters (PBT, PET, and PEN, respectively) at all the investigated β 's (°C/min).

Determination of E_a

The linear interpolation of the plots reported in Figures 4–6 provides the values of E_a reported in Table I together with their relative correlation coefficients (r 's). PBT and PEN showed a slight dependence of E_a on the selected end point, whereas for PET, a significant decrease in E_a took place as the degradation proceeded. Table II summarizes the data derived from the constant-rate heating tests according to the Kissinger method, which relies on the determination of the temperature (T_{max}) at each of the investigated scanning rates, at which the rate of mass change is highest: the plot of $\log \beta/T_{max}^2$ versus $1/T_{max}$ provides the E_a of the degradation process. Table III shows the data derived according to Friedman analysis at different conversion degrees (α 's), defined as

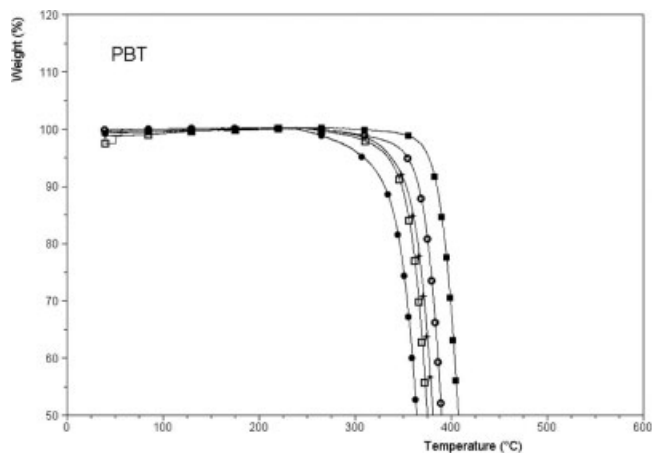


Figure 7 PBT thermograms at different β 's: (■) 2, (○) 5, (◆) 7, (□) 10, and (●) 20°C/min.

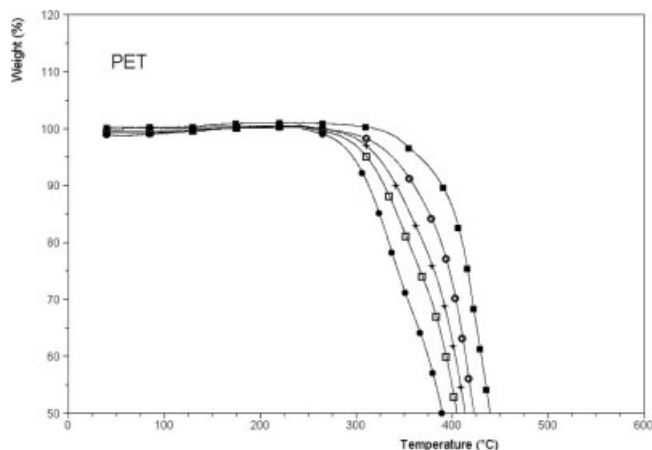


Figure 8 PET thermograms at different β 's: (■) 2, (○) 5, (◆) 7, (□) 10, and (●) 20°C/min.

$$\alpha = (w_i - w_s) / (w_i - w_f)$$

where w_f , w_s , and w_i are the final, instantaneous, and initial weights, respectively, of the sample submitted to a constant β : the energy of activation was thus derived by plotting the values of $d\alpha/dt$ at selected α 's and different β 's as a function of the reciprocal absolute temperature. T is that temperature at which a fixed value of α is reached at a particular β value. Table IV summarizes the data obtained according to the FWO method, that is, by plotting the logarithm of β versus $1/T$ at constant values of α . For the Friedman and FWO methods, the average values of E_a are also reported. The three methods provided almost the same value of E_a for PEN, whereas deviations within 10% of the average value were observed for PBT. The three methods provided quite different E_a 's for PET (particularly those from the FWO one); a strong dependence on α was observed, and lower r 's for the linear regressions in both the Friedmann and FWO

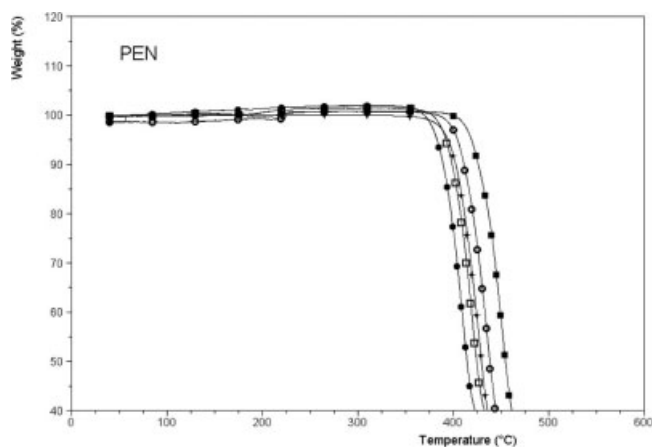


Figure 9 PEN thermograms at different β 's: (■) 2, (○) 5, (◆) 7, (□) 10, and (●) 20°C/min.

TABLE I
 E_a (kJ/mol) and r Values Found by the Isothermal Method

Material	End point	r	E_a
PBT	0.98	0.9942	155.8
	0.97	0.9925	157.2
	0.96	0.9884	162.3
PET	0.98	0.9975	177.1
	0.97	0.9973	161.4
	0.96	0.9983	145.8
PEN	0.98	0.9968	142.3
	0.97	0.9952	138.5
	0.96	0.9973	135.6

methods were found. Indeed, the complexity of the degradation reactions in PET and the differences in E_a derived by isothermal and nonisothermal tests in an inert environment have been previously discussed.²¹ It is thus possible to assume that even in the presence of oxygen, different reactions (e.g., pure thermooxidation, molecular rearrangements or crosslinkings in chain residuals, random chain cleavage, or even low-weight molecular loss) compete during the running steps of the overall degradation reaction; some authors have already disclosed a three-step decomposition of PET in air.²² This feature causes a stronger dependence of E_a on the extent of the reaction than those in PBT and PEN; moreover, the reaction can no more be considered to be a simple first-order one in the conversion ranges investigated. Similar phenomena may have also taken place in PBT and PEN, but in these cases, a prevailing reaction was still seen in the temperature and α ranges investigated, possibly on account of the higher aromatic (or aliphatic) character of PEN (or PBT) in relation to PET.

When the values of E_a provided by the nonisothermal and isothermal thermogravimetric methods were compared, good agreement was found for PBT. On the contrary, for PET, significant differences were observed due to a strong dependence of E_a on the end-point selection in isothermal tests, as well as on the method and the α values used for the data treatment in the nonisothermal tests. For PEN, the values obtained from the nonisothermal data were higher than the isothermal ones; however, this could be ascribed to the temperature range used for the isothermal tests, which was above the T_m of the polymer. It was already

TABLE II
 E_a (kJ/mol) and r Values Found by the Kissinger Method

Material	r	E_a
PBT	0.9985	155.2
PET	0.9973	178.8
PEN	0.9988	176.8

TABLE III
 E_a (kJ/mol) and r Values Found by the Friedman Method

Material	E_a at $\alpha = 0.2$	r	E_a at $\alpha = 0.3$	r	E_a at $\alpha = 0.4$	r	E_a average
PBT	160.5	0.9986	163.0	0.9992	168.8	0.9994	164.1
PET	86.4	0.9524	119.9	0.9451	160.4	0.9928	122.2
PEN	177.3	0.9944	184.2	0.9986	184.0	0.9946	181.7

shown that thermograms obtained for PEN below T_m gave no useful results, probably due to oxygen uptake by the aromatic part of the chain, which counterbalanced the weight loss caused by the formation of gaseous products.

Calculation of the thermal rating indices

The determination of E_a was only the first step toward the calculation of the thermal rating indices: Tables V–VII summarize the TI and HIC values calculated with the E_a 's obtained with the different analytical procedures. For the Friedman and FWO methods, the average values were considered. Two conventional life-test points were taken to draw the thermal endurance graphs; the first referred to a quite long time to end point (ca. 1300–1900 h) and the second to a rela-

tively short one (ca. 400–700 h; that is, just above the minimum time allowed by IEC 61026). The choice of the second conventional point led to a remarkable shortening of the experimental test times, whereas longer times usually ensured a better accuracy in the calculated TI and HIC values. Again, the behavior of the three materials was different. For PBT, all the analytical methods provided values of T that were in good agreement with those derived from the long-term tests, even at the shortest time to end point; this proved the great usefulness of the analytical procedure. Moreover, if compared to values previously provided by isothermal scanning calorimetry,³ the TI values derived from TGA were closer to those resulting from long-term conventional tests. Indeed, calorimetry is sensitive only to strong exothermic reactions and probably neglects the slight effect induced by the for-

TABLE IV
 E_a (kJ/mol) and r Values Found by the FWO Method

Material	E_a at $\alpha = 0.2$	r	E_a at $\alpha = 0.3$	r	E_a at $\alpha = 0.4$	r	E_a average
PBT	134.9	0.9966	140.8	0.9976	146.2	0.9978	140.6
PET	75.1	0.9925	82.7	0.9893	98.5	0.9834	85.4
PEN	182.8	0.9932	182.7	0.9957	184.2	0.9917	183.2

TABLE V
 TI and HIC Values (°C) According to IEC 61026 for PBT for Different Life Tests and E_a Values

T (°C)	Conventional life test		TI and HIC values				
	T_1 (h)	End point	IEC 61026	Isothermal	Kissinger	FWO	Friedman
160	1692	0.3	133 7.7	135 6.6	136 6.2	134 6.8	138 5.9
170	724	0.5	129 7.4	136 6.4	137 6.3	134 6.6	138 6.0

T_1 , time to the selected and end-point in a conventional test.

TABLE VI
 TI and HIC Values (°C) According to IEC 61026 for PEN for Different Life Tests and E_a Values

T (°C)	Conventional life test		TI and HIC values				
	T_1 (h)	End point	IEC 61026	Isothermal	Kissinger	FWO	Friedman
200	1948	0.98	173 7.6	171 8.2	177 6.6	178 6.4	177 6.4
208	343	0.99	170 6.4	157 7.7	168 6.3	169 6.1	169 6.2

TABLE VII
TI and HIC Values (°C) According to IEC 61026 for PET at Different Life Tests and E_a Values

T (°C)	Conventional point		TI and HIC values				
	T_1 (h)	End point	IEC 60126	Isothermal	Kissinger	FWO	Friedman
180	1305	0.96	159	152	155	131	145
			5.1	6.5	6.0	11.0	8.2
180	553	0.98	149	145	148	118	134
			5.6	5.7	5.7	10.3	7.8

mation of low-weight products arising from chemical bond cleavage during polymer degradation. However, this contribution was very small, thus confirming (as previously observed) that thermooxidation was the prevailing degradation mechanism. For PEN, the same considerations held for the comparison between the nonisothermal and conventional test data. On the contrary, isothermal experiments provided lower TI values because of the lower E_a 's derived; as previously stated, isothermal experiments were carried out at temperatures considerably higher than those used for conventional tests. At these temperatures, the destruction of the crystalline phase strongly increased oxygen diffusion in the material, which lowered its thermal stability. For PET, a scattering of TI values was observed because of the remarkable dependence of this parameter on the selected end point, in both conventional long-term tests and isothermal short-term procedures, as well as on the mathematical data treatment in nonisothermal tests. Data derived by the FWO and, to a lesser extent by the Friedman method, were clearly too different from the conventional ones to be significant. In this particular case, the short-term technique could be used for quick comparison of the different grades of PET at equivalent stages of degradation.

These results show that the proposed short-term procedure, which resorted to TGA as analytical technique, proved to be satisfactorily suitable for the evaluation of the thermal endurance parameters for PBT and PEN in place of time-consuming and very expensive conventional tests. For PET, this technique was not able to provide accurate values of the parameters, unless detailed correlations between the different stages of the conventional aging and the accelerated one were previously investigated.

CONCLUSIONS

The thermal endurance parameters of thermoplastic polyesters were estimated by a short-term procedure based on isothermal and nonisothermal TGA as analytical technique; for PBT and PEN, the procedure provided results that were in good agreement with those derived from long-term tests; this allowed a

considerable reduction in the experimental test times and costs. For PET, on the contrary, the results were not so satisfactory, and the main use of the procedure can be a quick comparison of different grades of the polymer, but it cannot be used for the absolute thermal rating of the material.

The obtained results show that a certain analytical procedure cannot be extensively applied to a family of polymeric materials (in this case, linear thermoplastic polyesters) for the evaluation of their thermal endurance, but depending on material under test, the most appropriate technique must be evaluated.

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