Journal of Thermal Analysis, Vol. 46 (1996) 1313-1324

THERMAL DEGRADATION OF A STYRENATED UNSATURED POLYESTER RESIN

P. Budrugeac[*], *E. Segal*[**], *E. Stere*[*] *and Alice Luminita Petre*[**]

[*]ICPE – Research and Development Institute for Electrical Engineering, Splaiul Unirii,
Nr. 313, Sector 3, Bucharest 74204, Romania
[**]Department of Physical Chemistry, Faculty of Chemistry, University of Bucharest,
Bd. Republicii 13, Bucharest, Romania

(Received March 12, 1995)

Abstract

The isothermal and non-isothermal degradation of a typical styrenated phthalic acid-maleic acid-propylene glycol polyester were measured. Non-isothermal and isothermal kinetic analyses were performed on the various degradation steps observed. The values of the non-isothermal and the isothermal kinetic parameters are in good agreement.

Keywords: kinetics, polyester resin

Introduction

The thermal stabilities of polymeric electrical insulating materials are usually evaluated by using tests of accelerated ageing under isothermal conditions, with determination of the time necessary for the chosen property to reach the established failure criterion [1]. For each failure criterion, the temperature index for a lifetime of 20.000 h is inferred. The use of this methodology [1] is correct only for constancy of the degradation activation energy for temperatures located in the range between the utilization temperature and the maximum accelerated thermal ageing temperature. In order to be able to choose the temperatures of accelerated thermal ageing, one has to know the range of chemical stability of the material, i.e. the temperature range in which no chemical changes are detected in the material during a relatively short time of several hours [2]. One also has to know the mechanism of thermal degradation of the polymeric material. For the performance of such analysis, thermal analysis methods have proved their efficiency [2–14].

The present paper reports results obtained from an investigation of the thermal degradation (isothermal and non-isothermal) of a typical styrenated phthalic acid-maleic acid-propylene glycol polyester.

0368–4466/96/ $ 5.00

John Wiley & Sons, Limited
Chichester

Experimental

Materials

To obtain the styrenated unsaturated polyester resin, the highly reactive unsaturated polyester resin Nestrapol 450, manufactured by Policolor-Bucharest (Romania), was used as starting material. This resin contains 65% by mass of unsaturated polyester from maleic anhydride, phthalic anhydride and propylene glycol, and 35% styrene (0.51 moles styrene/100 g unsaturated polyester; 1.72 moles styrene/gram-equivalent double bonds in the polyester). The main properties of the Nestrapol 450 resin are: density 1.135 g cm^{-3}; acidity index 30.7 mg KOH/g; hydroxyl index 16.0 mg KOH/g.

The Nestrapol 450 resin was diluted with styrene (22.8 g styrene/100 g resin), the unsaturated polyester and styrene contents thereby becoming 53.3% and 46.7% (0.84 moles styrene/100 g polyester) respectively. In the presence of 1% *t*-butyl perbenzoate, the resin was submitted to block-copolymerization (16 h at 80°C+1 h at 90°C+2 h at 100°C). The rigid thermoset was characterized by a density of 1.185 g cm^{-3} and a Martens thermal stability of 59°C.

Isothermal degradation

The isothermal degradation of the resin samples was investigated in WSU-200 ovens in which the temperature was kept constant with an accuracy of ±2°C. The change in mass due to thermal degradation was followed in time.

Thermal analysis

The heating curves of the powdered samples were recorded with a Paulik-Paulik-Erdey Q-1500D (MOM, Budapest) derivatograph in static air atmosphere in the temperature range 20–500°C at heating rates of 1.4, 2.8, 6.1, 11.9 and 25.1 K min^{-1}.

Results and discussion

Mass loss *vs.* time isotherms

Figure 1 shows isothermal mass loss (as a percentage of the initial mass) *vs.* time plots at 191, 200, 210 and 220°C.

Inspection of the curves in Fig. 1 shows that at all these temperatures, after an initial period characterized by a fast mass loss ($t<3$ h), there was a relatively slow change in mass with time.

We assumed that the kinetics of the isothermal mass loss can be described by the classical rate equation:

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{1}$$

where k is the overall rate constant, α is the degree of conversion and $f(\alpha)$ is the differential conversion function.

The degree of conversion is related to the mass loss Δm as follows:

$$\alpha = \frac{\Delta m}{\Delta m_{\max}} \tag{2}$$

The dependence of the overall rate constant on temperature is given by the Arrhenius equation:

$$k = A \exp\left(-\frac{E}{RT}\right) \tag{3}$$

where A is the pre-exponential factor and E is the activation energy.

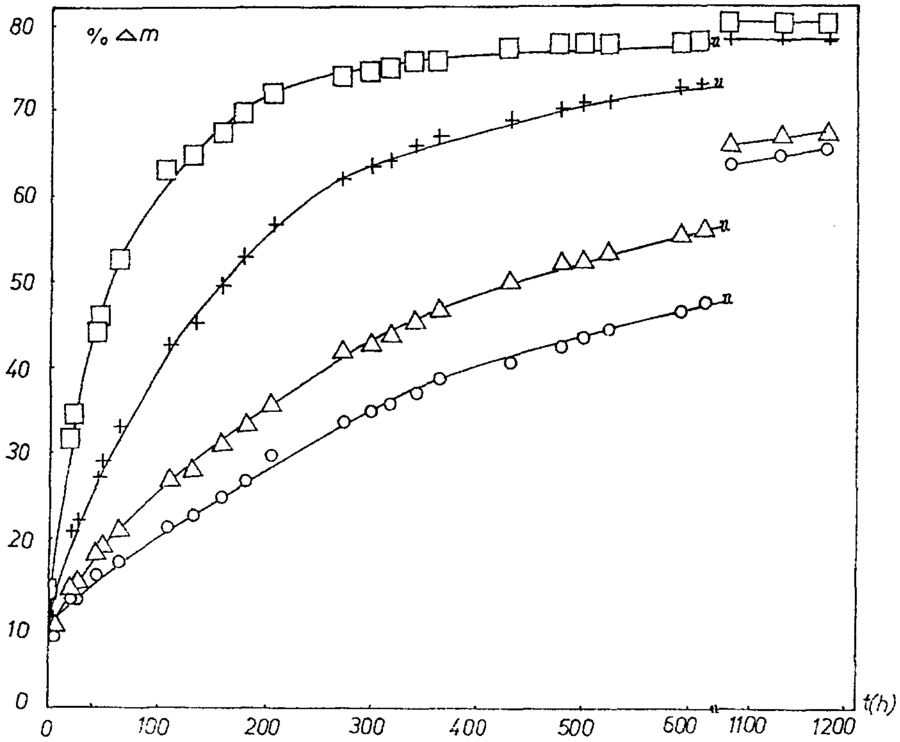

Fig. 1 Isotherms of mass loss of the styrenated polyester resin during its thermal degradation; o 191°C; Δ 200°C; + 210°C; □ 220°C

With utilization of relationship (2), the integrated form of Eq. (1) is:

$$\ln t = \ln F\,(\Delta m) - \ln A + \frac{E}{RT} \qquad (4)$$

where

$$F(\Delta m) = \frac{1}{\Delta m_{\max}} \int_{\Delta m_0}^{\Delta m} \frac{d(\Delta m)}{f\left(\dfrac{\Delta m}{\Delta m_{\max}}\right)}$$

Thus, for Δm=const., a plot of ln *t* *vs.* $1/T$ should be a straight line with a slope which relates to the activation energy. Figure 2 shows such straight lines for $17.5 \leq \%\Delta m \leq 50$. In this range of $\%\Delta m$, the values of the activation energy, located in the range 155.3–164.0 kJ mol^{-1} ($r>0.989$; the accuracy of the determined values of the activation energy is 10%) can be considered to be practically constant.

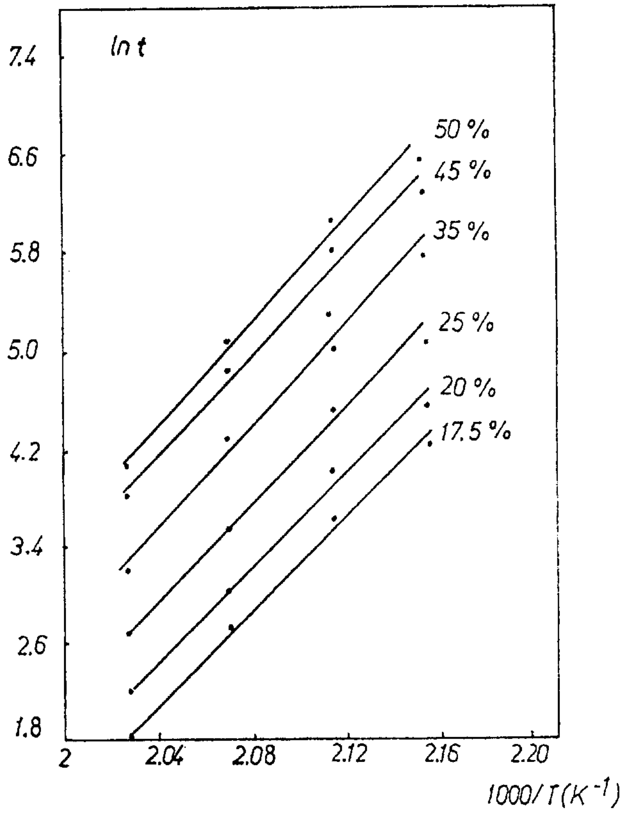

Fig. 2 The straight lines ln *t* *vs.* $1/T$ for isothermal degradation of the styrenated polyester resin

The degradation of the resin in the range $15 < \%\Delta m \leq 44$ followed the rate equation:

$$\frac{d\alpha}{dt} = k\,\alpha^{-1} \qquad (5)$$

characteristic of a diffusion-limited reaction (parabolic law) [15].

A consideration of relationship (2) and the initial mass loss (Δm_o), with integration of Eq. (5), leads to

$$(\Delta m)^2 = (\Delta m_o)^2 - 2k(\Delta m_{max})^2 t_o + 2k(\Delta m_{max})^2 t \qquad (6)$$

Figure 3 shows the straight lines $(\Delta m)^2$ *vs.* t for the data depicted in Fig. 1 (r>0.998).

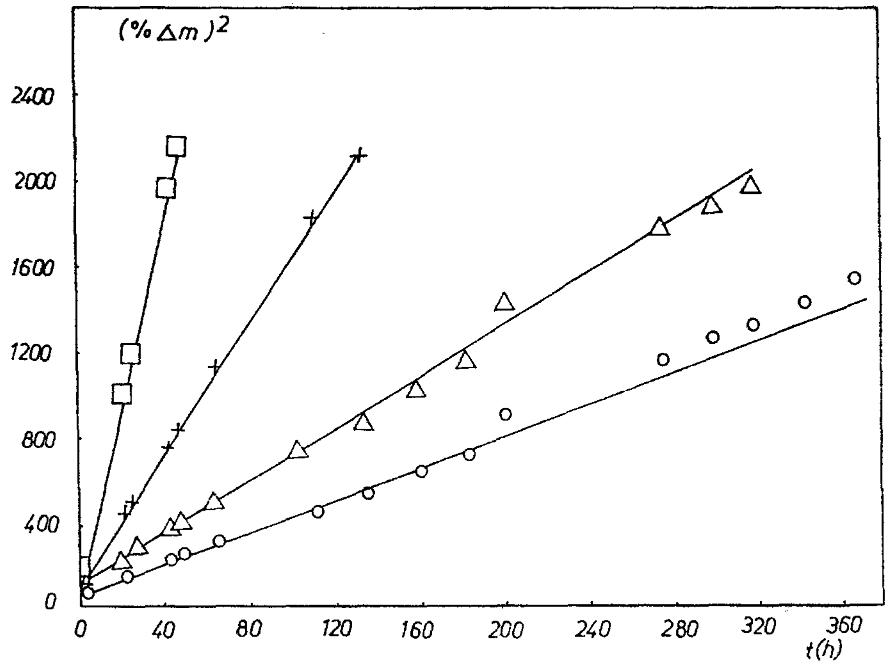

Fig. 3 Verification of Eq. (6) for isothermal degradation of the styrenated polyester resin; ○ 191°C; △ 200°C; + 210°C; □ 220°C

The slopes of these straight lines given by $2k(\Delta m_{max})^2$. With the assumption of Arrhenius dependences with temperature for k, a plot of $\{\ln 2k(\Delta m_{max})^2\}$ *vs.* $1/T$ is shown in Fig. 4. From the slope and intercept of this straight line, the following values were obtained for E and $2A(\Delta m_{max})^2$:

$$E = 159.0\ \text{kJ·mol}^{-1};\ 2A(\Delta m_{max})^2 = 7.93\cdot 10^{14}\ \text{s}^{-1}.$$

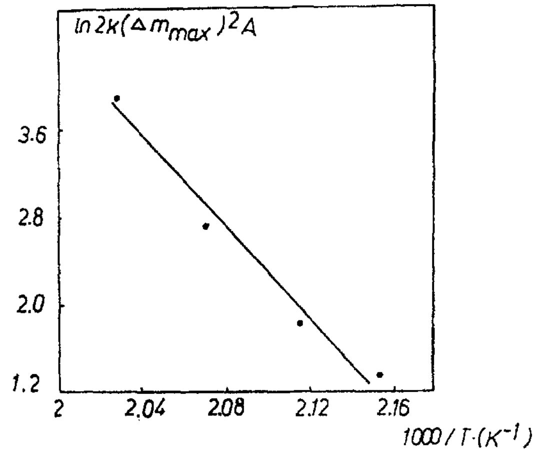

Fig. 4 The Arrhenius straight line for isothermal degradation of the styrenated polyester resin

In order to evaluate Δm_o from the parameters of the straight lines $(\Delta m)^2$ *vs.* t, the values of t_o corresponding to the four temperatures of the isotherms and for $9\leq\%\Delta m\leq 15$ were calculated. These values were compared with those determined experimentally (Fig. 1). The best agreement between the calculated and experimental t_o values was found with $\Delta m_o=12\%$.

Thermoanalytical data

Figure 5 shows the TG, DTG and DTA curves obtained at a heating rate of 11.9 K min^{-1}. Similar curves were observed at other heating rates.

Inspection of the curves reveals three temperature regions (I, II and III) in which mass loss occurs. The first, low-temperature change, I, is exothermic, whereas the following ones, II and III, are endothermic. The total mass loss, 82–86%, is in good agreement with the total mass loss observed isothermally at 220°C (Fig. 1). These results are similar to those obtained by Anderson and Freeman [16], who investigated the degradation of a styrenated phthalic acid-maleic acid-propylene glycol polyester in argon and air. They reported that, in the first exothermic change, molecular oxygen reacts with the tertiary carbon atoms from the styryl groups, generating a hydroperoxide which decomposes to benzaldehyde and unsaturated hydroxyesters. Steps II and III of the degradation involve strong scission of the macromolecular chains, with the generation of phthalic acid, phthalic anhydride, esters of propylene glycol, carbon dioxide, methane, hydrogen and propylene [16].

For $5<\%\Delta m<70$, the Flynn-Wall isoconversion diagram [17, 18] was plotted (Fig. 6), with a consideration of local heating rates, evaluated around the considered experimental points ($10\ \mathrm{K}<\Delta T<15\ \mathrm{K}$).

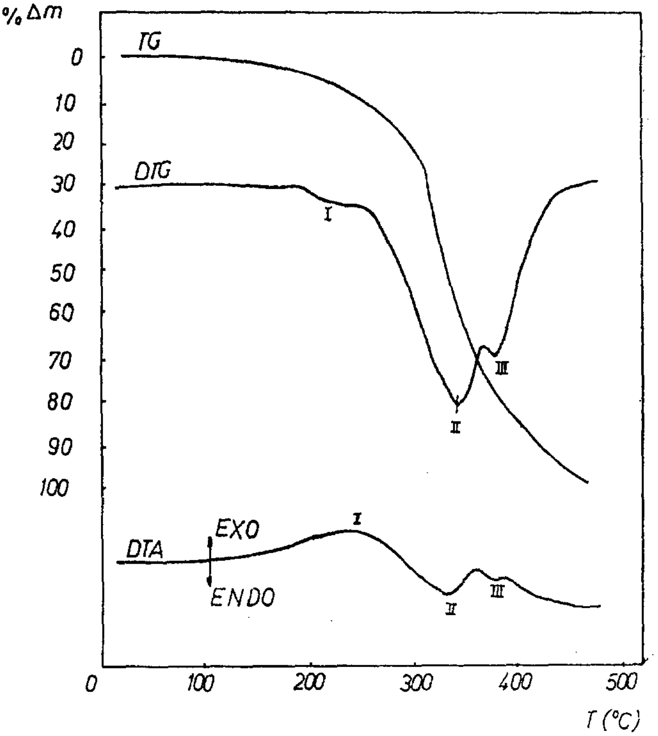

Fig. 5 TG, DTG and DTA curves of the styrenated polyester resin in static air atmosphere at a=11.9 K min^{-1}

The results show that:

(a) for 5<%Δm<15 (change I), the plot of ln a *vs.* $1/T$ is not linear;

(b) for 15<%Δm<70 (changes II and III), the plots ln a *vs.* $1/T$ are linear for heating rates in the range 1.4–11.9 K min^{-1}.

The dependence of the non-isothermal kinetic parameters on the heating rate is due to the heat transfer limitation, which can be important mainly at high values of this experimental parameter.

For change I, the activation energy cannot be evaluated by means of the Flynn-Wall isoconversion method. For this change, the non-isothermal kinetic parameters were evaluated by three integral methods: the Coats-Redfern method [19], the Coats-Redfern method as modified by Urbanovici and Segal [20], and the Flynn-Wall method for a=const. [17, 18]. A program written in BASIC language [21, 22] was used to analyse the experimental data. The values of the non-isothermal kinetic parameters for change I are listed in Table 1.

As expected, the values of the non-isothermal kinetic parameters depend on the heating rates. The relatively low values of the activation energy are located

Table 1 Values of the isothermal kinetic parameters of the process I of degradation

	Methods											
	Coats-Redfern				Modified Coats-Redfern				Flynn-Wall, a=const.			
Heating rate/ K min^{-1}	E/ kJ mol^{-1}	n	A/ s^{-1}	r	E/ kJ mol^{-1}	n	A/ s^{-1}	r	E/ kJ mol^{-1}	n	A/ s^{-1}	r
1.4	24.3	0.1	$9.79\cdot10^{-2}$	0.9982	27.2	0.2	$3.1\cdot10^{-1}$	0.9987	30.1	0.1	$2.83\cdot10^{-1}$	0.9990
2.8	31.0	0.1	$8.03\cdot10^{-1}$	0.9984	32.6	0.1	1.574	0.9990	35.8	0.0	$1.28\cdot10$	0.9989
6.1	30.5	0.3	1.40	0.9893	33.5	0.4	3.81	0.9910	35.1	0.1	$1.91\cdot10$	0.9931
11.9	29.3	0.3	1.805	0.9811	31.4	0.4	4.14	0.9846	34.3	0.2	$3.23\cdot10$	0.9846

E is the activation energy; n is the apparent reaction order; A is the pre-exponential factor and r is the correlation coefficient of the linear regression

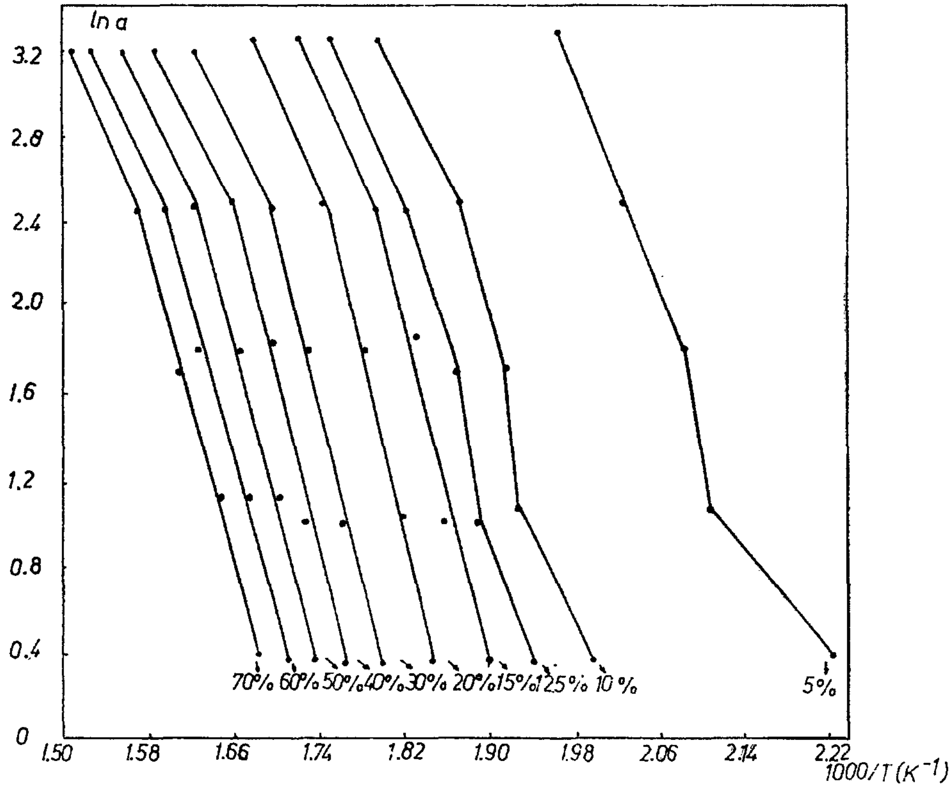

Fig. 6 Flynn-Wall isoconversion diagram for thermal degradation of the styrenated polyester resin

in the range 24–30 kJ mol^{-1}. Correspondingly, the reaction order values are located in the range 0–0.4. Thus, change I corresponds to an initial fast mass loss observed in the isotherms (Fig. 1).

For changes II and III, at heating rates in the range 1.4 K $min^{-1} \leq a \leq$ 11.9 K min^{-1}, the activation energy values were obtained by means of the Flynn-Wall isoconversion method [17, 18]. Thus:

(a) for $15 \leq \% \Delta m \leq 45$, 160.7 kJ $mol^{-1} \leq E \leq 174.9$ kJ mol^{-1}, with $r \geq 0.99$;

(b) for $45 < \% \Delta m \leq 70$, the values of E decrease gradually from 160.7 kJ mol^{-1} to 140.6 kJ mol^{-1} ($r > 0.99$).

For $15 \leq \% \Delta m \leq 45$, the values of the activation energy are close to those found under isothermal conditions. For this change, the non-isothermal kinetic parameters were obtained by using the Coats-Redfern method [19] and the Flynn-Wall method for a=const. [17, 18]. From a consideration of the differential conversion function found for isothermal degradation, $f(\alpha) = \alpha^{-1}$, the following working equations were derived:

(a) for the Coats-Redfern method:

$$\ln\frac{(\Delta m)^2-(\Delta m_o)^2}{T^2}=\ln\frac{2(\Delta m_{max})^2AR}{aE}-\frac{E}{RT} \tag{7}$$

(b) for the Flynn-Wall method with a=const.:

$$\log[(\Delta m)^2-(\Delta m_o)^2]=\log\frac{2(\Delta m_{max})^2AE}{aR}-2.315-0.457\frac{E}{RT} \tag{8}$$

As in the case of isothermal degradation, $\Delta m_o=12\%$. The verifications of Eqs (7) and (8) for $16<\%\Delta m<45$ are shown in Figs 7 and 8.

From the slopes and the intercepts of these straight lines, the values of E and $2A\ (\Delta m_{max})^2$ were calculated. The results are listed in Table 2 and reveal values

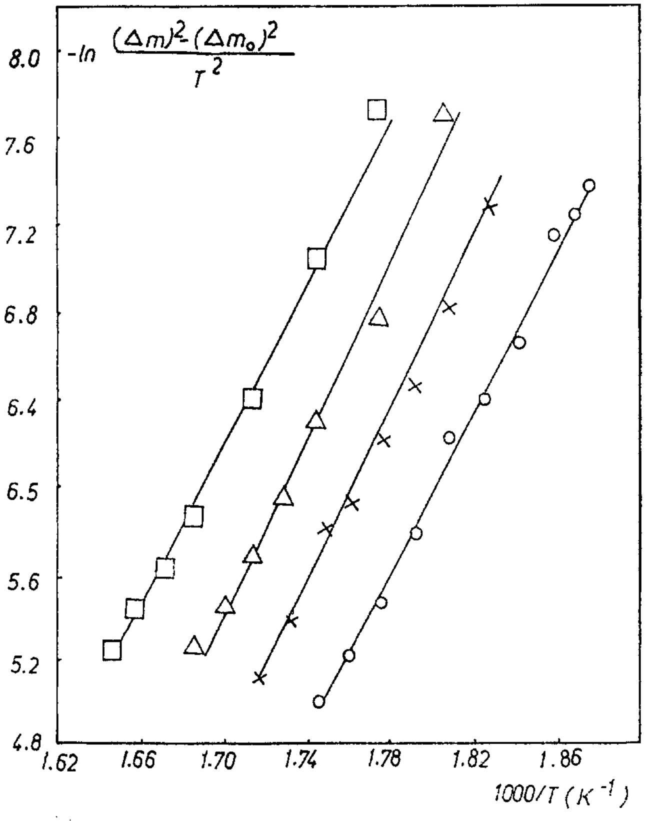

Fig. 7 Coats-Redfern straight lines for $16\leq\%\Delta m\leq45$; o a=1.4 K min^{-1}; x a=2.8 K min^{-1}; Δ a=6.1 K min^{-1}; □ a=11.9 K min^{-1}

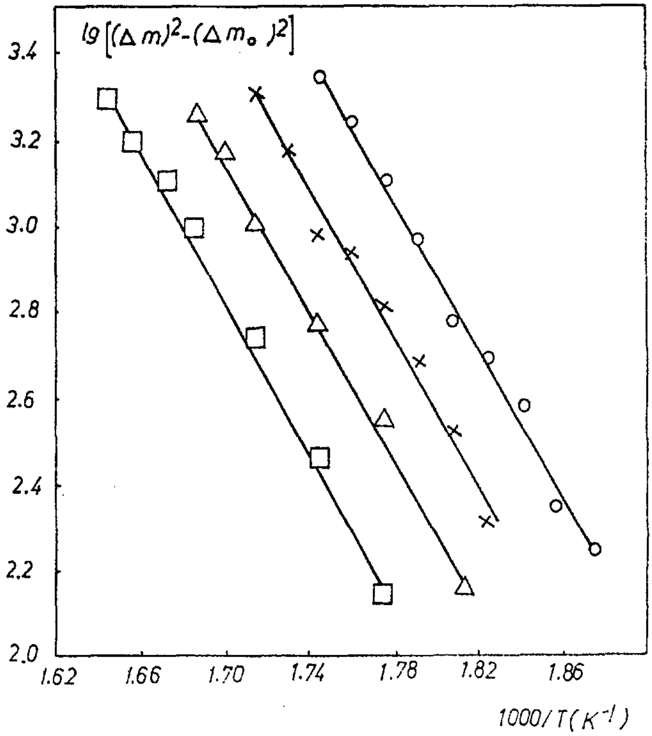

Fig. 8 Flynn-Wall (a=const.) straight lines for $16 \leq \%\Delta m \leq 45$; o $a=1.4$ K min^{-1}; x $a=2.8$ K min^{-1}; Δ $a=6.1$ K min^{-1}; □ $a=11.9$ K min^{-1};

of E and $2A\ (\Delta m_{\max})^2$ in satisfactory agreement with the corresponding isothermal data.

For change III, the activation energy was evaluated by means of Kissinger's method [23], applied to the third peak of the DTG curve. The resulting value, $E=147.7$ kJ mol^{-1}, lies in the range of values obtained by the Flynn-Wall isoconversion method for $\%\Delta m>45$.

Table 2 Nonisothermal kinetic parameters for $16 \leq \%\Delta m \leq 45$ obtained by using integral methods

	Method					
	Coats–Redfern			Flynn–Wall, a=const.		
a/ K mol^{-1}	E/ kJ mol^{-1}	$2A(\Delta m_{\max})^2$ / s^{-1}	r	E/ kJ mol^{-1}	$2A(\Delta m_{\max})^2$ / s^{-1}	r
1.4	156.5	$6.1380 \cdot 10^{14}$	0.9955	155.7	$5.1030 \cdot 10^{14}$	0.9969
2.8	155.3	$4.4497 \cdot 10^{14}$	0.9936	156.5	$6.1894 \cdot 10^{14}$	0.9943
6.1	164.3	$3.4830 \cdot 10^{15}$	0.9935	165.1	$4.4381 \cdot 10^{15}$	0.9942
11.9	157.8	$7.6864 \cdot 10^{14}$	0.9966	159.4	$1.1724 \cdot 10^{15}$	0.9975

Conclusions

Both isothermal and non-isothermal mass loss curves for a styrenated phthalic acid-maleic acid-propylene glycol polyester indicated three successive changes on progressive heating of the sample. A kinetic analysis of these changes was carried out. Fairly good agreement was observed between the values of the non-isothermal and the isothermal kinetic parameters.

References

1 IEEE 101/1972 – Guide for the Statistical Analysis of Thermal Life Test Data, Institute of Electrical and Electronic Engineers, New York, 1972.
2 P. Budrugeac and E. Segal, Thermochim Acta, 211 (1992) 131.
3 O. Vogl, I. Ivandung, H. C. Miller and H. W. Williams, J. Macromol. Sci., A, 2 (1968) 175.
4 V. V. Korshak, S. V. Viragradova, G. V. Danilov, L. A. Beribze and S. N. Salazkin, Visokomol. Soedin., 12 (1970) 129.
5 A. A. Berlin, B. G. Gherasimov and A. A. Ivanov, J. Polym. Sci., C, 41 (1973) 183.
6 T. T. Gademer, J. Macromol. Sci., A, 8 (1974) 15, 105.
7 S. Ciutacu, D. Fătu and E. Segal, Thermochim. Acta, 131 (1988) 279.
8 D. Fătu, G. Geambaşu, P. Budrugeac and E. Segal, Thermochim. Acta, 149 (1989) 181.
9 J. H. Flynn, in "Thermal Methods in Polymer Analyses" (S. W. Shalaby, Ed.), The Franklin Inst. Press, Philadelphia PA, USA, 1977, p. 163.
10 J. H. Flynn and B. Dickens, in "Durability of Macromolecular Materials" (R. Eby, Ed.), ASC Symp. Ser., 95 (1979) 97.
11 J. H. Flynn, Polym. Eng. Sci., 20 (1980) 675.
12 E. Segal, P. Budrugeac, S. Ciutacu and G. Mareş, Thermochim. Acta, 164 (1990) 161.
13 S. Ciutacu, P. Budrugeac and I. Niculae, Polym. Degrad. Stabil., 31 (1991) 365.
14 G. Mareş and P. Budrugeac, in "Handbook of Elastomer Technology" (Nicolas P. Cheremisinoff Ed.), CRC Press, Boca Raton, Ann Arbor, London, Tokyo, 1993, Ch. 10.
15 E. Segal and D. Fătu, "Introduction to Nonisothermal Kinetics", (in Romanian), Ed. Academiei R. S. Romania, 1983, p. 68.
16 D. A. Anderson and E. S. Freeman, J. Appl. Polymer Sci., 1 (1959) 192.
17 J. H. Flynn and L. A. Wall, Polym. Lett., 4 (1966) 323.
18 J. H. Flynn and L. A. Wall, J. Res. Natl. Bur. Stand., Sect. A, 70 (1966) 487.
19 A. W. Coats and J. P. Redfern, Nature, 201 (1964) 68.
20 E. Urbanovici and E. Segal, Thermochim. Acta, 80 (1984) 379.
21 E. Segal and T. Coseac, Rev. Roumaine Chim., 34 (1989) 287.
22 N. Dragoe and E. Segal, Thermochim. Acta, 185 (1991) 129.
23 H. A. Kissinger, Anal. Chem., 29 (1959) 1702.