# THERMOOXIDATIVE DEGRADATION OF AN UNSATURATED POLYESTER RESIN
## The effect of oxygen pressure on the kinetics

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## Abstract

The results of non-isothermal kinetic analysis of the thermooxidative degradation in air and oxygen of an unsaturated polyester resin are presented. It has been shown that the thermooxidative degradation in oxygen occurs at lower temperatures than the thermooxidative degradation in air. The kinetic parameters of the thermooxidative degradation depend on the heating rate and the oxygen pressure. Two straight lines of $\ln A$ vs. $E$ ($A$ is the preexponential factor and $E$ is the activation energy), characteristic for the compensation effect, have been obtained for the thermooxidative degradation in air and in oxygen respectively. The difference between the intercepts of these straight lines can be explained by dependence of the pre-exponential factor on the oxygen pressure.

Keywords: kinetics, thermooxidative degradation

## Introduction

The wide use of the polymeric materials requires the knowledge of their behaviour under environmental conditions (heat, light, humidity, nuclear radiation, etc.). In order to obtain these informations one has to investigate the accelerated aging of these materials by following the change in their mechanical properties (elongation at break, resistance to traction, resistance to compression, flexural strength, etc.) and their electrical properties (dielectric rigidity, dielectric losses, resistivity, etc.) due to degradation.

For thermal or thermooxidative degradation, the acceleration factor has to be chosen in such a way that the mechanism of the accelerated degradation of the material should be the same as that of its degradation under the conditions of its practical use.

Thermal analysis methods (TG, DTG, DTA or DSC) are very useful in the solution of such problems as they permit the estimation of the temperature range of thermal stability [1–6], the values of the non-isothermal kinetic parameters of degradation [6–18] and the changes undergone as a consequence of the accelerated aging [2, 19, 20].

In our previous papers [21–23] we have shown that the increase of oxygen pressure determines the acceleration of the isothermal thermomechanical degradation of

ethylene+propylene rubber (elongation at break), glass-reinforced epoxy resin (flexural strength), and nitrile-butadiene rubber (elongation at break).

This, work aims to present the results of an investigation by help of thermal analysis concerning the influence of oxygen pressure on the rate of thermooxidative degradation of an unsaturated polyester resin. From the kinetic analysis in non-isothermal conditions in air and oxygen atmosphere, the dependence of the pre-exponential factor on the pressure of oxygen is established.

## Experimental

The styrenated unsaturated polyester resin was obtained using, as starting material, the unsaturated reactive resin NESTRAPOL-450, which was manufactured by Policolor-Bucharest-Romania, using a procedure described in an earlier paper [24]. NESTRAPOL-450 contains 65 wt% of unsaturated polyester from maleic anhydride, phthalic anhydride and propylene glycol and 35% styrene (1.72 mol styrene/gram-equivalent double bonds in polyester). The resin NESTRAPOL-450 was diluted with styrene (22.8 g styrene/100 g resin). In presence of 1% $t$-butyl perbenzoate the resin was subjected to block-copolymerization (16 h at 80°C+1 h at 90°C+2 h at 100°C). The rigid thermoset was characterized by density of 1.185 g cm$^{-3}$ and Martens thermal stability of 59°C.

The heating curves of powdered samples have been recorded by help of Q-1500 D MOM-Budapest type Paulik-Paulik-Erdey derivatograph in the temperature range 20–500°C, at heating rates in the range 0.70–13.50 K min$^{-1}$.

The resin degradation was investigated in air static atmosphere, air flow (10 l h$^{-1}$) and oxygen flow (10 l h$^{-1}$).

## Results and discussions

Figure 1 shows the thermal curves (TG, DTG, DTA) obtained in air atmosphere at a heating rate of 11.90 K min$^{-1}$. Similar curves have been obtained for other heating rates as well as in air flow and oxygen flow.
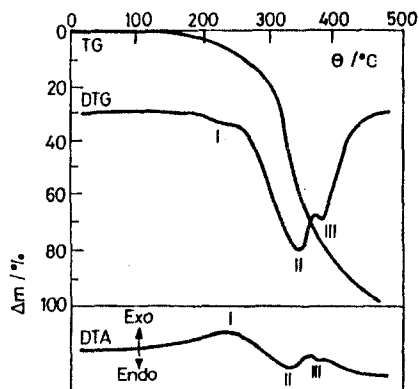


Fig. 1 The TG, DTG and DTA curves of styrenated polyester resin in static air atmosphere at 11.90 K min$^{-1}$

Inspecting the curves we noticed three temperature regions, I, II and III, in which weight loss occurs. The total mass loss, 82–86%, is in good agreement with that obtained isothermally at 220°C [24]. These results are similar to those obtained by Anderson and Freeman [25] who investigated the degradation in argon and air of styrenated phthalic acid-maleic acid-propylene glycol polyester. The authors noted that in the first exothermic change, molecular oxygen reacts with tertiary carbon atoms from the styryl groups generating hydroperoxide which decomposes to benzaldehyde and unsaturated hydroxyesters. In steps II and III of degradation, strong scission of the macromolecular chains with the generation of phthalic acid, phthalic anhydride, esters of propylene glycol, carbon dioxide, methane, hydrogen and propylene occurs [25].

Figure 2 shows the TG curves obtained for the same heating rate ($\cong 2.85$ K min$^{-1}$) for the degradations in static air atmosphere, air and in oxygen flows. As one can see, for the same degree of degradation, the lowest temperature is recorded for oxygen flow and the highest temperature is recorded for static air atmosphere. Similar results have been obtained for other heating rates.
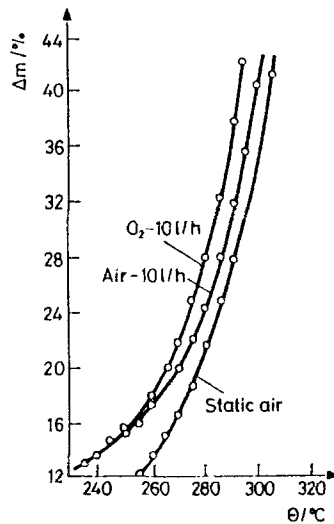


**Fig. 2** The TG curves for the thermooxidative degradation of the styrenated polyester resin in: static air atmosphere, air flow (10 1 h$^{-1}$) and oxygen flow (10 1 h$^{-1}$)

In a previous paper [24] it has been shown that the isothermal degradation of the resin in air for mass losses $\%\Delta m$ located in the range $15 \leq \%\Delta m \leq 44$ (change II) occurs according to the rate equation:

$$\frac{d\alpha}{dt} = k\alpha^{-1} \tag{1}$$

where $\alpha$ is the degree of conversion.

The rate Eq. (1) is characteristic for a diffusion limited reaction (parabolic law) [26].

The rate constant depends on temperature according to Arrhenius equation:

$$k = A \, \exp\left(-\frac{E}{RT}\right) \qquad (2)$$

where $A$ is the pre-exponential factor, $E$ – the activation energy, $T$ – the temperature (K), $R$ – the gas constant.

By definition, the degree of conversion is related to $\Delta m$, i.e.

$$\alpha = \frac{\Delta m}{\Delta m_{max}} \qquad (3)$$

where $\Delta m_{max}$ is the total mass loss in the change II ($\Delta m_{max}$ cannot be exactly determined from our experimental data).

From the experimental data obtained for the isothermal degradation, it has been obtained:

$$E = 159 \text{ kJ mol}^{-1} \text{ and } \ln A(\Delta m_{max})^2 = 336 \ (A \text{ expressed in s}^{-1})$$

In order to evaluate the non-isothermal kinetic parameters we should admit that the non-isothermal degradation of the investigated resin occurs according to
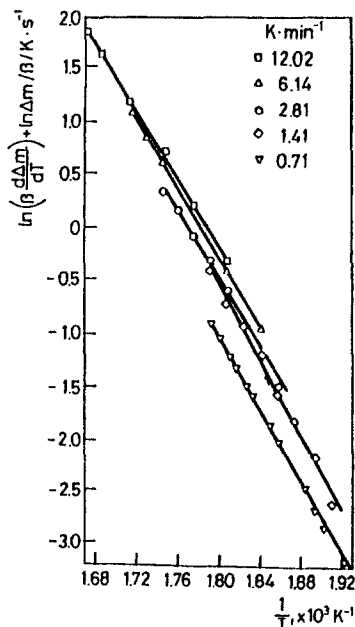


Fig. 3 The straight lines [ln($\beta$(d$\Delta m$/d$T$))+ln$\Delta m$] vs. (1/$T$) for the non-isothermal thermal degradation of the resin in static air atmosphere
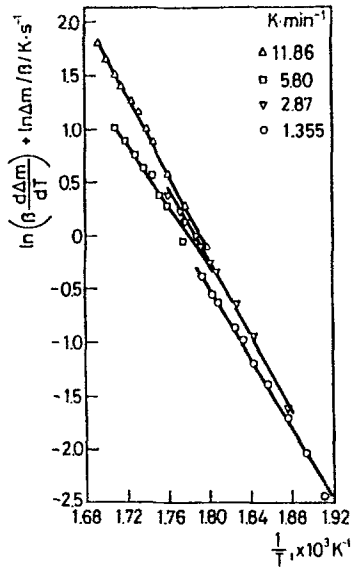
**Fig. 4** The straight lines [ln($\beta$(d$\Delta m$/d$T$))+ln$\Delta m$] *vs.*(1/$T$) for the non-isothermal thermal degradation of the resin in air flow

Eq. (1). Taking into account that the heating rate is kept at a constant value ($\beta$=const.), from relationships (1)–(3) one obtains:

$$\ln\left(\beta\frac{d\Delta m}{dT}\right) + \ln\Delta m = \ln A(\Delta m_{max})^2 - \frac{E}{RT} \qquad (4)$$

Thus, the plot [ln($\beta$(d$\Delta m$/d$T$))+ln$\Delta m$] *vs.* (1/$T$) should be a straight line from which the intercept and slope result in $A(\Delta m_{max})^2$ and $E$. Actually this procedure is a variant of isoconversional Friedman's method for evaluating the non-isothermal kinetic parameters [27]. In order to evaluate d$\Delta m$/d$T$, rather than using DTG curves, as shown in a previous work [28], a better precision is obtained by approximating the TG curve as a power series of $T$. For 15≤%$\Delta m$≤35, the truncation of the series at the term with $T^4$ leads to a high correlation coefficient ($r$ >0.997).

Figures 3–5 show the straight lines [ln($\beta$(d$\Delta m$/d$T$))+ln$\Delta m$] *vs.*(1/$T$), for various heating rates in the three media in which the derivatograms have been recorded. The parameters of these straight lines and corresponding the values of the non-isothermal kinetic parameters of the degradation depend on the heating rate as well as of the atmosphere in which the thermal degradation is recorded. As shown in Fig. 6 the non-isothermal kinetic parameters of the degradation in static air atmosphere and in air flow together with the corresponding isothermal kinetic parameters are correlated through the compensation effect [29, 30] characterized by the relationship:

$$\ln A(\Delta m_{max})^2 = aE + b \qquad (5)$$

where $a$ and $b$ are constants specific for the given series of related reactions.

Figure 6 shows that the kinetic parameters of the degradation in oxygen flow are also correlated through relationship (5).

As shown in our previous review articles [29, 30], the validity of relationship (5) shows that the change of an operational parameter as the heating rate or the atmosphere in which the degradation occurs determines the change of the non-isothermal kinetic parameters. The parallelism of the straight lines in Fig. 6 suggests the following factorization of the preexponential factor [31]:

$$A = A_0 g(P) \tag{6}$$

where $P$ is the partial pressure of oxygen.

As shown previously [21–23] the thermomechanic degradation of some polymeric materials is described by Eq. (6) in which:

$$g(P) = P^{\delta} \tag{7}$$

where $\delta$ is a parameter whose value depends on the material as well as on the chosen mechanical property.
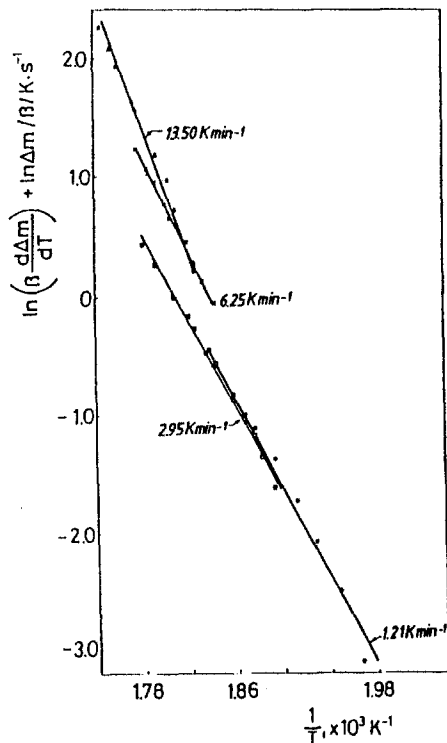


Fig. 5 The straight lines $[\ln(\beta(d\Delta m/dT)) + \ln\Delta m]$ vs. $(1/T)$ for the non-isothermal thermal degradation of the resin in oxygen flow
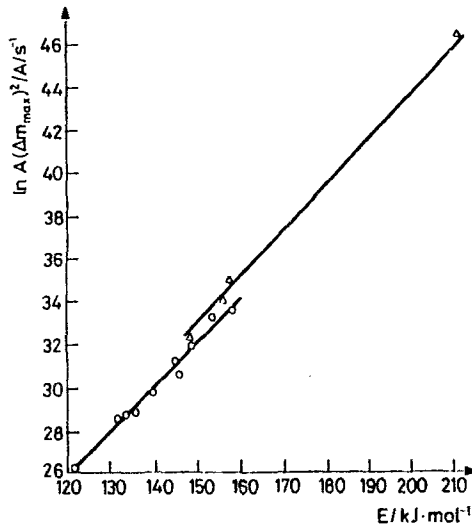
**Fig. 6** Compensation effect straight lines ($\ln A(\Delta m_{max})^2$ *vs.* $E$) for the thermooxidative degradation of the resin. o isothermal degradation, degradation in static air atmosphere, degradation in air flow; $\triangle$ degradation in oxygen flow

Considering that for the thermal degradation of the investigated resin relationships (6) and (7) are valid one obtains:

$$\ln A_0(\Delta m_{max})^2 = \ln A(\Delta m_{max})^2 - \delta \ln P \qquad (8)$$

where: $P = 0.2$ barr for the degradation in air (either static or flow) and $P = 1.0$ barr for the degradation in oxygen flow.

Obviously, the plots $\ln A_0(\Delta m_{max})^2$ *vs.* $E$ should be straight lines for the kinetic parameters of the degradation in air as well as in oxygen.

In order to evaluate $\delta$, the correlation coefficient of the linear regression of the straight lines $\ln A_0(\Delta m_{max})^2$ *vs.* $E$, for $0 \leq \delta \leq 1.00$ (with the step 0.05) have been calculated. Figure 7 shows the change of the correlation coefficient, $r$, with $\delta$. The
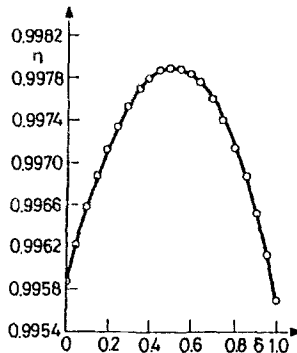


**Fig. 7** $r$ values of the linear regression $A_0(\Delta m_{max})^2$ *vs.* $E$ for various values of $\delta$
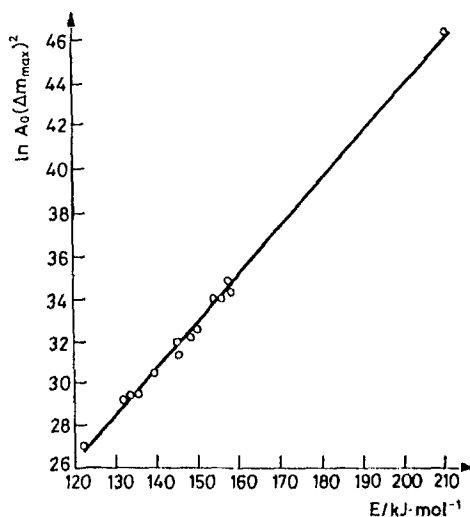
**Fig. 8** The straight line $\ln A_0 (\Delta m_{max})^2$ vs. $E$ for $\delta'=0.50$

maximum value of $r$ corresponds to $\delta = 0.50$. This optimal value of the parameter $\delta$ described most probably the dependence of the kinetic constant characteristic for the thermooxidative degradation of the investigated resin on oxygen pressure.

The straight line $\ln A_0(\Delta m_{max})^2$ vs. $E$ corresponding to $\delta = 0.50$ is shown in Fig. 8. The values of the corresponding compensation parameters are:

$$a = 0.221 \ (\pm 0.004) \ \text{mol kJ}^{-1}$$

$$b = - 0.277 \ (\pm 0.626) \ (A \text{ expressed in s}^{-1})$$

$$r = 0.9979$$

The presented results illustrate Agrawal's idea [32] according to which the compensation effect is a useful tool for chemical research directed towards identifying the reaction mechanism as well as for predicting the effect of various parameters of reaction and correlation of the experimental data.

## Conclusions

1. The investigation of the thermooxidative degradation of a styrenated phthalic acid-maleic acid propylene glycol polyester showed that this change occurs at lower temperatures in oxygen atmosphere than in air atmosphere.

2. Three successive steps of the degradation are evident.

3. Kinetic parameters for the second step of degradation using Friedman's non-isothermal method have been determined. It has been shown that the kinetic parameters depend on the heating rate as well as the gaseous atmosphere in which the degradation occurs.

4. The activation parameters for the degradation in air as well as in oxygen are correlated through the compensation effect.

5. It has been shown that the pre-exponential factor of the degradation depends on the partial pressure of oxygen according to the relationship: $A = A_0 P^\delta$.

# References

1 O. Vogl, I. Ivan Sung, H. G. Miller and H. W. Williams, J. Macromol. Sci., A2 (1968) 1975.
2 V. V. Korshak, S. V. Viragradova, G. V. Danilov, L. A. Beribze and S. N. Salazkin, Vysokomol. Soedin., 12 (1970) 129.
3. A. A. Berlin, S. G. Gherasimov and A. A. Ivanov, J. Polym. Sci., C-41 (1973) 183.
4 T. J. Gademer, J. Macromol. Sci., A-8 (1974) 105.
5 S. Ciutacu, D. Fatu and E. Segal, Thermochim. Acta., 131 (1988) 279.
6 P. Budrugeac and E. Segal, Thermochim. Acta, 211 (1992) 131.
7 J. H. Flynn and L. A. Wall, J. Res. Bur. Stand., Sect., A, Physics and Chemistry, 70A (1966) 487.
8 J. H. Flynn, in 'Thermal Methods in Polymer Analysis' (S. W. Shlaby, Ed.), the Franklin Inst. Press, Philadelphia PA, USA, 1977, p. 163.
9 J. H. Flynn and B. Dickens, in 'Durability of Macromolecular Materials' (R. Eby, Ed.), ASC Symp. Ser., 95 (1979) 97.
10 J. H. Flynn, Polym. Eng. Sci., 20 (1980) 675.
11 D. Fatu, G. Geambasu, E. Segal, P. Budrugeac and S. Ciutacu, Thermochim. Acta, 149 (1989) 181.
12 P. Budrugeac, E. Segal and S. Ciutacu, J. Thermal Anal., 37 (1991) 1179.
13 P. Budrugeac and E. Segal, Thermochim. Acta, 184 (1991) 33.
14 P. Budrugeac and S. Ciutacu, Polym. Degrad. Stabil., 33 (1991) 377.
15 P. Budrugeac, Thermochim. Acta, 221 (1993) 229.
16 P. Budrugeac and E. Segal, Thermochim. Acta, 221 (1993) 221.
17 P. Budrugeac, Rev. Roumaine Chim., 39 (1994) 229.
18 G. Mares and P. Budrugeac, in 'Handbook of Elastomer Technology' (Nicholas P. Cheremisinoff Ed.), CRC Press, Boca Raton, Ann Arbor, London, Tokyo 1993, Ch. 10.
19 E. Segal, P. Budrugeac and S. Ciutacu, Thermochim. Acta, 164 (1990) 171.
20 P. Budrugeac and E. Segal, Thermochim. Acta, 184 (1991) 25.
21 S. Ciutacu, P. Budrugeac, G. Mares and I. Boconcios, Polym. Degrad, Stabil., 29 (1990) 321.
22 S. Ciutacu, P. Budrugeac and I. Niculae, Polym. Degrad, Stabil., 31 (1991) 365.
23 P. Budrugeac, Polym. Degrad. Stabil., 47 (1995) 129.
24 P. Budrugeac, E. Segal, E. Stere and Alice Luminita Petre, J. Thermal Anal., 46 (1996) 1313.
25 D. A. Anderson and E. S. Freeman, J. Appl. Polym. Sci., 1 (1959) 192.
26 E. Segal and D. Fatu, 'Introduction to Non-isothermal Kinetics' (in Romanian), Ed., Academiei Romane, Bucharest 1983, p. 68.
27 H. L. Friedman, J. Polym. Sci., 6C (1965) 183.
28 P. Budrugeac, Alice Luminita Petre and E. Segal, Thermochim. Acta, 275 (1996) 193.
29 P. Budrugeac and E. Segal, J. Thermal Anal., 39 (1993) 1199.
30 P. Budrugeac and E. Segal, ICTAC-News, 28 (1995) 33.
31 J. Šesták, Thermophysical Properties of Solids', Elsevier Sci. Publishers B. V. Amsterdam 1982, p. 240.
32 R. K. Agrawal, J. Thermal Anal., 35 (1989) 909.