

The effect of oxygen pressure on the rate of non-isothermal thermo-oxidation of low density polyethylene

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The results of non-isothermal kinetic analysis of the thermo-oxidative degradation in air and in oxygen of the low density polyethylene (LDPE) are presented. It was observed that similar processes take place at thermo-oxidative degradation in air and in oxygen. The first process, which leads to solid products, is followed by thermo-oxidative degradation with generation of volatile products. It was shown that the first process of thermo-oxidation occurs at lower temperatures in oxygen than in air. The kinetic analysis of this process, performed using Kissinger method, shows that the pre-exponential factor (A) depends on the partial pressure of oxygen (P) according to the relationship: $A = A_0 P^\delta$, where A_0 and δ are material constants. © 2001 Kluwer Academic Publishers

1. Introduction

In some recent articles [1, 2], the effect of oxygen pressure on the rate of the thermo-oxidative degradation of an unsaturated polyester resin, copolymer EVA and a nitrile-butadiene rubber (NBR) was put in evidence by thermal analysis methods.

Another recent studies [3–6] of the dependence of elongation at break for EPR (ethylene-propylene rubber), LDPE, and NBR and of flexural strength for glass reinforced epoxy resin on temperature and air or oxygen pressure reveal the importance of the oxygen pressure as an accelerator in thermo-oxidative degradation of the polymeric materials.

This work aims to present the results of an investigation by help of thermal analysis (TG, DTG and DTA) concerning the influence of oxygen pressure on the rate of thermo-oxidative degradation of the low density polyethylene (LDPE). Special emphasis is given to the thermo-oxidation leading to solid products. From the kinetic analysis of DTA data obtained in air and in oxygen atmosphere, the dependence of the pre-exponential factor on the oxygen pressure is established.

2. Experimental

The LDPE produced by Petrochemical Company Brazi-Romania was used.

The heating curves (TG, DTG and DTA) 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, and heating rates in the range 0.59–7.90 K · min⁻¹.

The thermal degradation of all materials was investigated in air flow (6.5 L · h⁻¹). and oxygen flow (6.5 L · h⁻¹).

3. Results and discussion

Fig. 1 depicts TG, DTG and DTA curves for LDPE, obtained in air flow, at a heating rate of 3.20 K · min⁻¹. Similar curves have been obtained for other heating rates, as well as, in air flow and oxygen flow.

The DTA curve displays a first-order phase change (melting or softening) through the minimum I at $\cong 105^\circ\text{C}$. At higher temperatures, the melted LDPE undergoes an exothermic change (peak II in the DTA curve), accompanied by a slight increase in weight. In order to account for this, a DTA curve of LDPE was recorded in argon. This curves no longer exhibit peak II. Thus, the exothermic peak corresponds to the thermo-oxidation of LDPE with the generation of solid products, probably hydroperoxides, due to the attack of oxygen on the active carbon atoms from the macromolecular chain [7]. At higher temperatures, thermo-oxidative degradation with generation of volatile products occurs.

Such a thermo-oxidative degradation characterized by two kinds of oxidation processes, one accompanied by weight increase, and the other by release of volatile products was earlier reported in connection with the thermo-oxidative degradation of polymeric materials [7–13].

The kinetic parameters of the first degradation process observed in thermogram could be correlated with the thermal lifetime of the polymeric material [14, 15]. Therefore, we will focus to the thermo-oxidation process designated in DTA curve by the exothermal peak II and in TG curve by the maximum II.

Figs 2 and 3 shows that, for the investigated polymeric material, the temperatures corresponding to the beginning and to the maximum of peak II from DTA

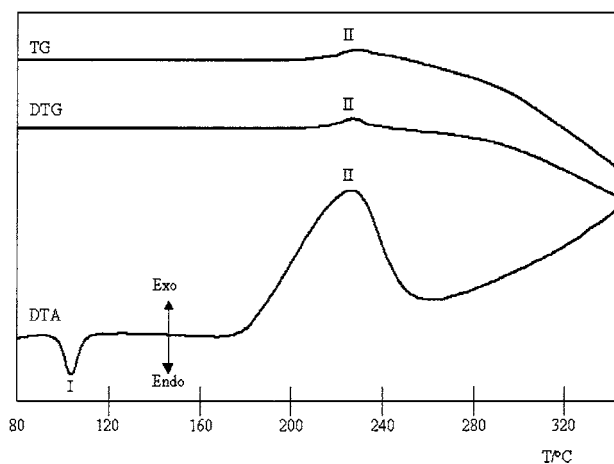


Figure 1 TG, DTG and DTA curves of LDPE in air flow ($6.5 \text{ L} \cdot \text{h}^{-1}$) at heating rate $3.20 \text{ K} \cdot \text{min}^{-1}$.

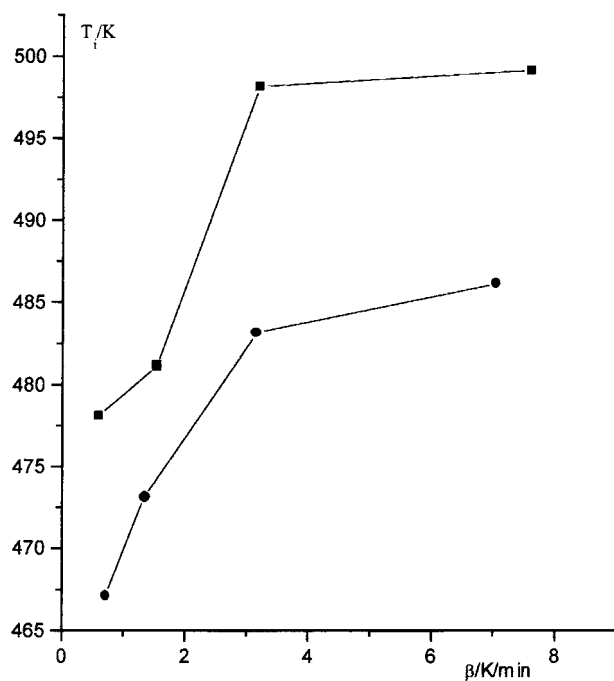


Figure 2 The plot of T_i vs. β (heating rate) for the thermo-oxidation of LDPE with the generation of solid products. ■ air flow; ● oxygen flow.

curve (T_i and T_{\max} , respectively) depend on the heating rate, as well as the atmosphere in which the non-isothermal degradation takes place.

The non-isothermal kinetic analysis of the process II (Fig. 1) was carried out using the Kissinger method [16] which is grounded on the following relationship:

$$\ln \frac{\beta}{T_{\max}^2} = \ln \frac{RA}{E} - \frac{E}{RT_{\max}} \equiv a - \frac{E}{RT_{\max}} \quad (1)$$

where: β is the heating rate, E is the activation energy, A is the pre-exponential factor, R is the gas constant and $a \equiv \ln \frac{RA}{E}$.

The plots ($\ln \frac{\beta}{T_{\max}^2}$) vs. ($\frac{1}{T_{\max}}$) corresponding to the thermo-oxidation of LDPE in air flow and in oxygen flow are shown in Fig. 4.

For degradation in air flow at the heating rates $7.60 \text{ K} \cdot \text{min}^{-1}$ and $7.86 \text{ K} \cdot \text{min}^{-1}$ (higher than the maximum heating rate of degradation in oxygen flow),

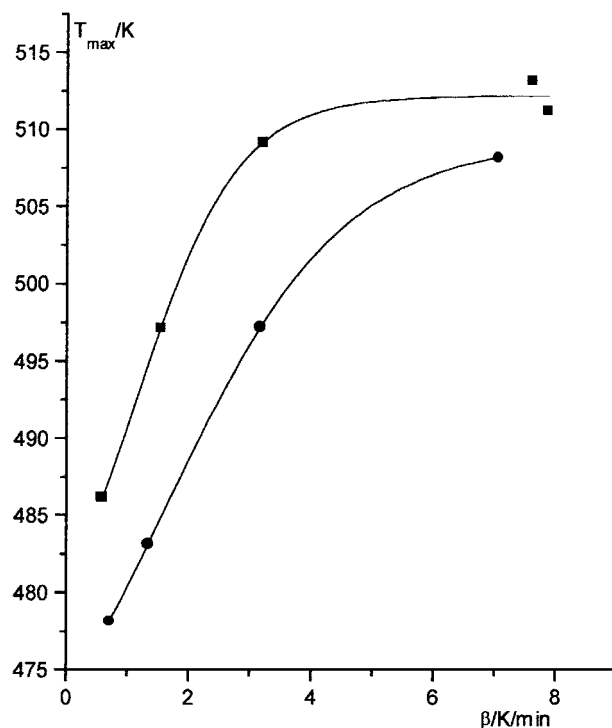


Figure 3 The plot of T_{\max} vs. β (heating rate) for the thermo-oxidation of LDPE with the generation of solid products. ■ air flow; ● oxygen flow.

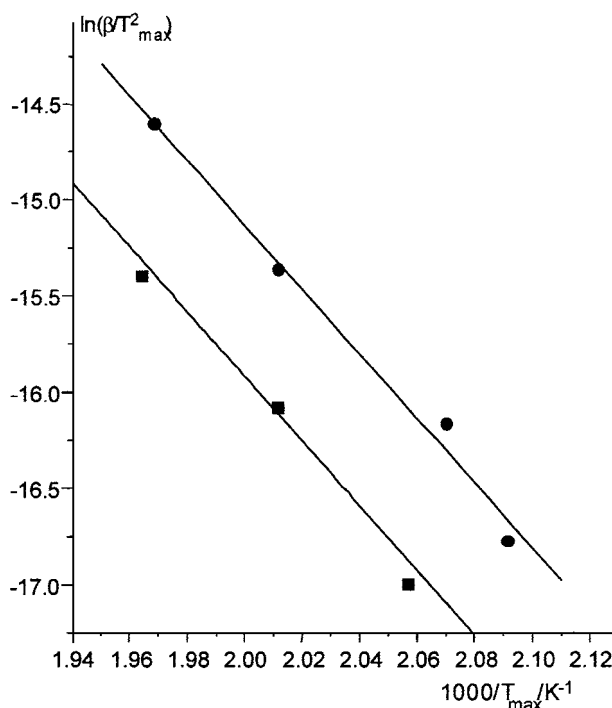


Figure 4 The straight lines ($\ln \frac{\beta}{T_{\max}^2}$) vs. ($\frac{1}{T_{\max}}$) for the thermo-oxidation of LDPE with the generation of solid products. ■ air flow; ● oxygen flow.

the thermo-oxidation leading to solid compounds, and the process with generation of volatile compounds take place practically simultaneously (the DTA maximum is accompanied by a sudden weight loss of the analyzed sample). Therefore, for the degradation in air, the plots ($\ln \frac{\beta}{T_{\max}^2}$) vs. ($\frac{1}{T_{\max}}$) were drawn only for the heating rates in the range $0.59\text{--}3.20 \text{ K} \cdot \text{min}^{-1}$. A similar case was previously put in evidence at the thermal degradation

of NBR in oxygen flow at heating rates higher than $3.20 \text{ K} \cdot \text{min}^{-1}$ [2].

The parallelism of the straight lines in Fig. 4 shows that the investigated material has the same value of the activation energy in air and in oxygen. In addition, this suggests the following factorization of the pre-exponential factor [17]:

$$A = A_0 g(P) \quad (2)$$

where P is the partial pressure of oxygen.

As shown previously, the thermo-mechanic degradation of some polymeric materials [3–6] and the non-isothermal degradation of an unsaturated polyester resin [1], the copolymer EVA and a nitrile-butadiene rubber [2] are described by Equation 2 in which:

$$g(P) = P^\delta \quad (3)$$

where δ is a parameter whose depends on the material.

Considering that for the thermo-oxidative degradation of LDPE relationships (2) and (3) are valid, the value of δ can be calculated using the following relationship:

$$a_{\text{air}} = a_{\text{O}_2} + \delta \ln P \quad (4)$$

where: a_{air} and a_{O_2} are the values of the intercepts of the straight lines shown in Fig. 4, and $P = 0.2$ barr (the partial pressure of oxygen in air).

The values of the kinetic parameters of the investigated thermo-oxidative process, evaluated from the parameters of the Kissinger's straight lines, are: $E = 139.3 \text{ kJ} \cdot \text{mol}^{-1}$; $\ln A_0 = 28.11$ (time is expressed in s and P in barr); $\delta = 0.49$. The ratio between the rate of degradation in oxygen at 1 barr and the rate of degradation in air at 1 barr is 2.20.

Assuming that, both in air and in oxygen, the activation energy has the same value, from Equations 1–3 it results that, for a given value of T_{max} :

$$\delta = \frac{\ln \frac{\beta_{\text{air}}}{\beta_{\text{O}_2}}}{\ln P} \quad (5)$$

where β_{air} and β_{O_2} are the heating rates corresponding to the degradation in air and in oxygen, respectively.

β_{air} and β_{O_2} can be evaluated from the curves shown in Fig. 3. Table I lists the values of δ evaluated by this method. One can note a satisfactory agreement among the values of δ evaluated using Equation 5 and the value

TABLE I The values of parameter δ evaluated using Equation 5

| T_{max} K | β_{air} K · min ⁻¹ | β_{O_2} K · min ⁻¹ | δ |
|--------------------|--|--|----------|
| 488 | 0.75 | 1.90 | 0.58 |
| 493 | 1.20 | 2.60 | 0.48 |
| 498 | 1.70 | 3.45 | 0.44 |
| 503 | 2.10 | 4.95 | 0.49 |
| 508 | 3.00 | 7.02 | 0.53 |

of this parameter obtained from the intercepts of the straight lines shown in Fig. 4.

The Equation 5 was used also to evaluate the δ parameter for copolymer EVA and NBR, using the data reported in the previous paper [2]. It was obtained δ values in a satisfactory agreement with those resulted from the intercepts of the straight lines ($\ln \frac{\beta}{T_{\text{max}}^2}$) vs. ($\frac{1}{T_{\text{max}}}$), too.

The results obtained for LDPE, as well as those obtained in our previous works [1–6] reveal the importance of the oxygen pressure as an accelerator in thermo-oxidation of the polymeric materials.

4. Conclusions

1. The thermal analysis (TG, DTG and DTA) of LDPE showed that, on progressive heating of this material, two kinds of thermo-oxidative processes take place: one accompanied by a slight weight increase, and other by release of volatile products.

2. It was shown that the process accompanied by a slight weight increase occurs at lower temperatures in oxygen than in air.

3. The non-isothermal kinetic analysis of the process accompanied by a slight weight increase was carried out using the Kissinger method. It has been shown that the pre-exponential factor depends on the oxygen pressure and it was suggested a relationship which describes this dependence. The parameters that characterize the dependence of thermo-oxidative rate of LDPE on the oxygen pressure were evaluated.

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