The Effect of Oxygen Pressure on the Kinetics of Thermo-oxidative Degradation of the Copolymer EVA and Nitrile–Butadiene Rubber

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ABSTRACT: The results of nonisothermal kinetic analysis of the thermo-oxidative degradation in air and in oxygen of the copolymer EVA and nitrile–butadiene rubber (NBR) are presented. It was observed that similar processes take place at thermo-oxidative degradation in air as well as in oxygen of both investigated polymeric materials. The first process, which leads to solid products, is followed by thermo-oxidative degradation with the generation of volatile products. It has been shown that the first process of thermo-oxidation occurs at lower temperatures in oxygen than in air. For this process, the nonisothermal kinetic analysis was carried out using the Kissinger method. The obtained results revealed the importance of the oxygen pressure as an accelerator in the thermo-oxidative degradation of copolymer EVA and NBR. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 1453–1457, 2000

Key words: thermo-oxidative degradation; nonisothermal kinetics; polymeric materials

INTRODUCTION

Some recent studies[1–4] of the dependence of elongation at break for EPR, 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. The results reported in these studies show that thermal aging in air or oxygen, under pressure, can be the basis for the rapid evaluation of the thermal lifetime of the solid polymeric materials.

In another recent article,[5] the effect of oxygen pressure on the rate of the thermo-oxidative degradation of an unsaturated polyester resin was put in evidence by thermogravimetric analysis (TG).

This work aims to present the results of an investigation by help of thermal analysis (TG, DTA) concerning the influence of oxygen pressure on the rate of thermo-oxidative degradation of the copolymer EVA and nitrile–butadiene rubber (NBR). 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 preexponential factor on the oxygen pressure is established.

EXPERIMENTAL

The ELVAX 260 (copolymer EVA containing 28% vinyl polyacetate) produced by DuPont, USA, and a vulcanized nitrile–butadiene rubber (NBR) produced by CATC, Jilava, Romania, were used.

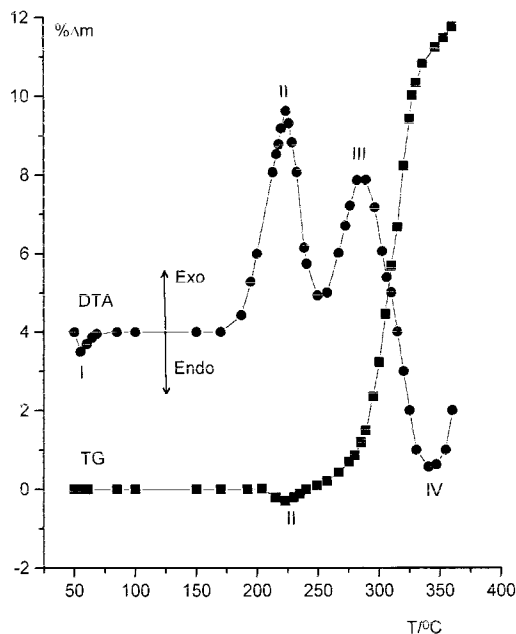The heating curves of powdered samples have been recorded with the help of a Q-1500D MOM,

Figure 1 The TG and DTA curves of copolymer EVA in air flow ($6.5 \text{ L} \cdot \text{h}^{-1}$) at $1.125 \cdot 10^{-1} \text{ K} \cdot \text{s}^1$.

Budapest-type Paulik-Paulik-Erdey derivatograph in the temperature range of 20–500°C, and heating rates in the range of $1.17 \cdot 10^{-2}$–$2.5 \cdot 10^{-1} \text{ K} \cdot \text{s}^{-1}$.

The thermal degradation of both materials was investigated in air flow ($6.5 \text{ L} \cdot \text{h}^{-1}$) and oxygen flow (6.5 L/h^{-1}).

RESULTS AND DISCUSSION

Figure 1 shows the thermal curves (TG and DTA) of copolymer EVA obtained in air flow, at a heating rate of $1.125 \cdot 10^{-1} \text{ K} \cdot \text{s}^{-1}$. Similar curves have been obtained for other heating rates in both air and oxygen flow.

The analysis of thermogram shows that on progressive heating of copolymer EVA, the following processes take place: (a) a first-order phase transition (I), which corresponds to the soaking of the copolymer; (b) an exothermic thermo-oxidation accompanied by a slight weight increase (II); (c) two oxidation and/or decomposition processes accompanied by the release of volatile products (III and IV).

The thermograms obtained for NBR are similar with that obtained for copolymer EVA, excepting the absence of the endothermic peak corresponding to the soaking.

Such a thermo-oxidative degradation characterized by two kinds of oxidation processes (one accompanied by a weight increase, and the other by release of volatile products) was earlier reported in connection with the thermo-oxidations of polymeric materials.[6–13]

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 minimum II. This process consists of the thermo-oxidation of polymeric material with the generation of solid products, probably hydroperoxides, due to the attack of singlet oxygen ($^1O_2$, $^1\Delta_g$) on the active carbon atoms from the macromolecular chain.[9]

Figures 2 and 3 show that for both investigated polymeric materials, the temperature corresponding to the maximum of peak II from DTA curve (T_{max}) depends on the heating rate, as well as the atmosphere in which the nonisothermal degradation takes place. One can note that, for each polymeric material and the same heating rate, the T_{max} value corresponding to the degradation in oxygen is lower than in air.
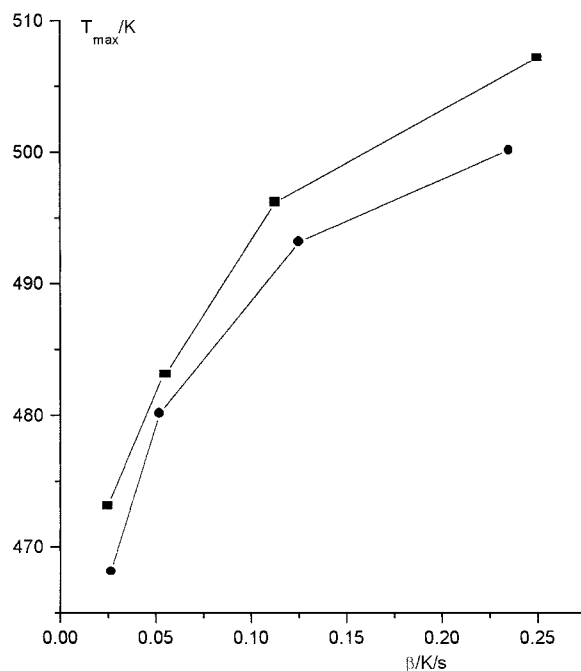

Figure 2 The plot of T_{max} vs. β (heating rate) for the thermo-oxidation of copolymer EVA with the generation of solid products. ■ air flow; ● oxygen flow.
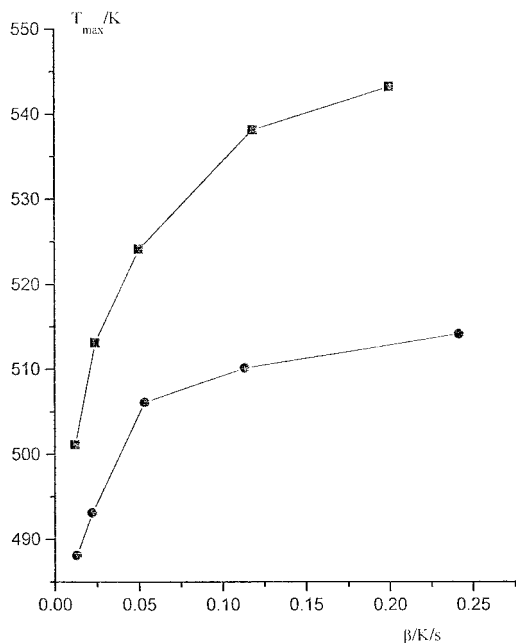
Figure 3 The plot of T_{max} vs. β (heating rate) for the thermo-oxidation of NBR with the generation of solid products. ■ air flow; ● oxygen flow.

The kinetic analysis of process II 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 preexponential factor, R is the gas constant, and

$$a \equiv \ln \frac{RA}{E}.$$

The plots

$$\left(\ln \frac{\beta}{T_{max}^2} \right) \text{ vs. } \left(\frac{1}{T_{max}} \right)$$

corresponding to the thermo-oxidation of the copolymer EVA and NBR are shown in Figures 4 and 5.

For NBR, in the oxygen flow, at heating rates higher than $5.33 \cdot 10^{-2}$ K $\cdot$ s^{-1}, the thermo-oxidation leading to solid compounds, and the first 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 of NBR in oxygen, the plots

$$\left(\ln \frac{\beta}{T_{max}^2} \right) \text{ vs. } \left(\frac{1}{T_{max}} \right)$$

were drawn only for the heating rates in the range $1.28 \cdot 10^{-2}$ K $\cdot$ s^{-1}–$5.33 \cdot 10^{-2}$ K $\cdot$ s^{-1}.

The parallelism of the straght lines in Figures 4 and 5 shows that each investigated material has the same value of the activation energy in air and in oxygen. In addition, this suggests the following factorization of the preexponential factor:[17]

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

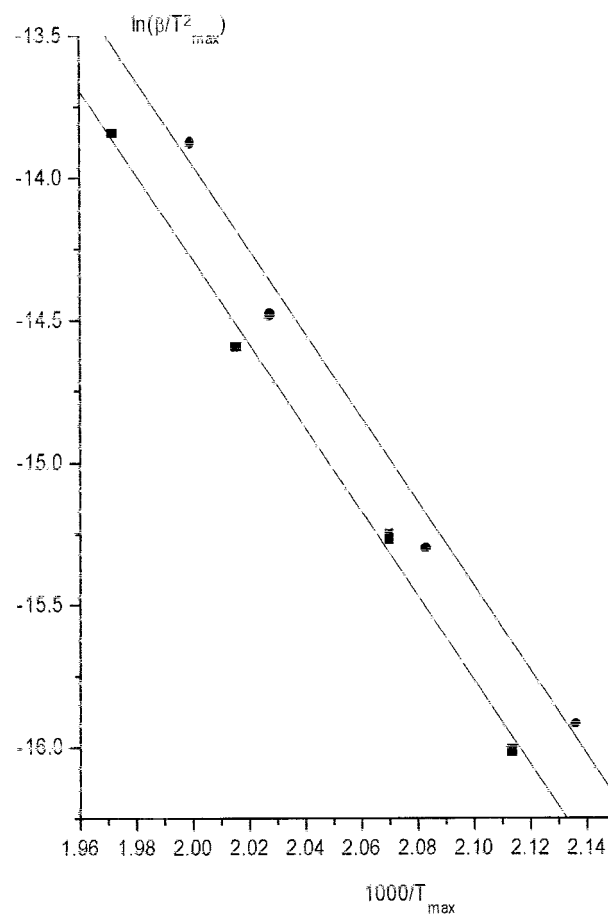where P is the partial pressure of oxygen.

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

As shown previously, the thermo-mechanic degradation of some polymeric materials[1–5] and the nonisothermal degradation of an unsaturated polyester resin[7] are described by eq. (2) in which:

$$g(P) = P^{\delta} \qquad (3)$$

where δ is a parameter that depends on the material.

Assuming that for the thermo-oxidative degradation of copolymer EVA and NBR, the relationships (2) and (3) are valid, δ can be evaluated using the following relationship:

$$a_{air} = a_{O_2} - \delta \ln P \qquad (4)$$

where a_{air} and a_{O2} are the values of the intercepts of the straight lines shown in Figure 4, respectively, Figure 5, and $P = 0.2$ barr (the oxygen pressure of oxygen in air).

The kinetic parameters, E, A_0, and δ for the investigated polymeric materials are listed in Table I. Also, Table I lists the values of the ratio between the rate of degradation in oxygen at 1
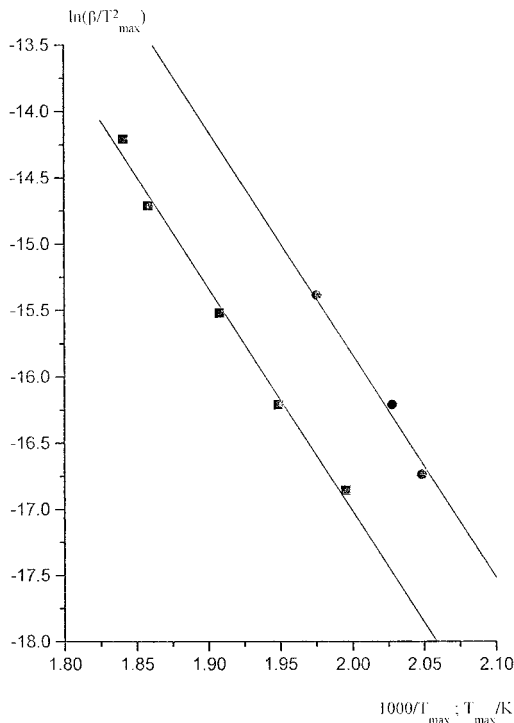
Table I   The Kinetic Parameters of the Thermo-oxidation of Investigated Materials

Material	E kJ · mol^{-1}	$\ln A_0$	δ	$\dfrac{r_1}{r_{0.2}}$
Copolymer EVA	122	25.24	0.205	1.39
NBR	140	27.61	0.730	3.24

r_1 is the rate of thermo-oxidation in oxygen, at $P_{O_2} = 1$ barr.
$r_{0.2}$ is the rate of thermo-oxidation in air, at $P_{air} = 1$ barr. Time is expressed in s and pressure—in barr.

barr and the rate of degradation in air where the partial pressure of oxygen is 0.2 barr. The obtained results reveals the importance of the oxygen pressure as an accelerator in thermo-oxidation of the investigated materials.

CONCLUSIONS

1. The thermal analysis (TG and DTA) of the copolymer EVA and NBR showed that, on progressive heating of both materials, 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 nonisothermal kinetic analysis of the first process of thermo-oxidation was carried out using the Kissinger method. It has been shown that the preexponential factor depends on the oxygen pressure, and it a relationship was suggested that describes this dependence.

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Figure 5 The straight lines $\left(\ln \dfrac{\beta}{T_{max}^2}\right)$ vs. $\left(\dfrac{1}{T_{max}}\right)$ for the thermo-oxidation of NBR with the generation of solid products. ■ air flow; ● oxygen flow.

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