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ESTIMATION OF ACTIVATION ENERGIES FOR THERMO-OXIDATIVE DEGRADATIONS OF LDPE AND NBR FROM NON-ISOTHERMAL AND ISOTHERMAL DTA DATA

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Abstract

Results obtained on the thermooxidative degradations of LDPE (low-density polyethylene) and NBR (nitrile-butadiene rubber) are presented. The activation energies for the thermooxidations leading to solid products were estimated. For LDPE, the activation energies obtained from non-isothermal data are in satisfactory agreement with those obtained from isothermal data. For NBR, the isothermal activation energy is ≈16% higher than the non-isothermal one. This difference is due to the morphological changes undergone by NBR during its heating at the rather high temperatures at which isothermal measurements were performed.

Keywords: activation energy, isothermal kinetics, non-isothermal kinetics, thermooxidative degradation

Introduction

The procedures for evaluation of the non-isothermal kinetic parameters of solid-gas reactions have been submitted to various criticism [1–5] for example, since the Maxwell-Boltzmann distribution of energy is not established instantaneously, use of the well-known Arrhenius equation is questionable; further various experimental factors, such as the mass of the sample, the heating rate, the thermal history of the sample, the gaseous environment, etc., influence the rate of the investigated change.

In order to overcome certain difficulties in the estimation of the kinetic parameters, Flynn [2] recommended a set of general rules for the kinetic analysis of non-isothermal data.

Some successes and failures of non-isothermal kinetics have been reported. A survey of this topic is given in [3].

In many cases, the disagreement between the isothermal and non-isothermal kinetic parameters is due to the complexity of the investigated changes. As

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shown by Schneider [4], the use of thermogravimetric kinetics in investigations of the thermal degradations of polymers, which are in fact complex processes, leads to kinetic parameters which cannot be assigned to a given reaction mechanism and consequently used to predict the course of the reaction under other conditions.

We have recently shown [6] that the proper choice of the conversion function for the thermooxidative degradation of a styrenated unsatured polyester resin leads to non-isothermal kinetic parameter values in fairly good agreement with those obtained from isothermal data.

The present paper reports results of an investigation of the thermooxidative degradations of LDPE and NBR by means TG, DTG and DTA. Special emphasis is given to the thermooxidations leading to solid products, for which the activation energies obtained from DTA curves recorded under non-isothermal and isothermal conditions have been estimated. The non-isothermal values of activation energy are compared with the isothermal ones.

Experimental

Materials

The LDPE used was synthesized in the research laboratories of the Petrochemical Company Brazi (Romania). Its characteristics are: MW=30500; T_m=105°C; density 0.915 g cm^{-3}.

The NBR used in these investigations was a CATC (Jilava, Romania) product.

Thermal analysis

The heating curves (TG, DTG and DTA) of the powdered samples were recorded with a Q-1500 D Derivatograph (MOM, Budapest), in static air atmosphere, in the temperature range 20–500°C, at heating rates of 0.75, 1.65, 2.80, 6.40 and 12.50 K min^{-1}.

The derivatograph was also used to record the isothermal DTA curves. The polymeric material was heated in argon atmosphere up to the programmed constant temperature. As soon as this temperature was reached, the argon atmosphere was switched over to oxygen. The DTA isothermal curve was recorded under these conditions. This procedure was applied mainly to determine the oxidative induction time at elevated temperatures [7–10].

Results and discussion

The DTA curves (isothermal and non-isothermal) were used to evaluate the activation energy of the induction period (for LDPE) and that of the thermooxidation leading to solid products which follows the induction period (for LDPE and NBR). Previous experience [11] indicated that the activation energy does not depend on the oxygen pressure or on the conditions of degradation (static of flow). Consequently, comparison of the activation energies obtained from isothermal and non-isothermal data is justified.

Thermooxidative degradation of LDPE

Non-isothermal data

Figure 1 shows heating curves obtained at a heating rate of β=2.80 K min^{-1}; for other heating rates, the recorded curves were similar.

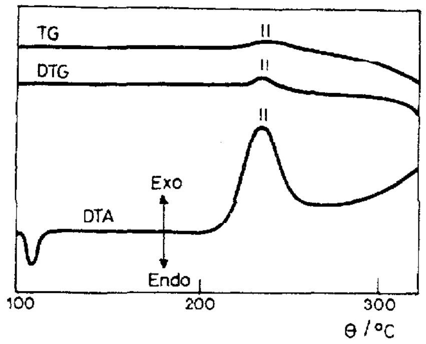

Fig. 1 Derivatogram of LDPE in static air atmosphere at a heating rate of 2.80 K min^{-1}

The DTA curve exhibited a first-order phase change (melting or softening), evidenced through minimum I, at 100–110°C. At higher temperatures, the melted polyethylene underwent an exothermic change (peak II in the DTA curve), accompanied by a slight increase in mass. In order to account for this, a thermogram of LDPE in argon was recorded. This thermogram no longer exhibited peak II. Thus, the exothermic peak corresponds to the thermooxidation of LDPE with the generation of solid products, probably hydroperoxides due to attack by the oxygen singlet ($^1O_2$, $^1\Delta_g$) on the methylene groups of the monomeric units [12]. At higher temperatures, thermooxidative degradation with the generation of volatile products occurred. Such a thermooxidative degradation, characterized by two oxidation processes (one accompanied by a mass increase and the other by the release of volatile products) was earlier reported in connection with the thermooxidations of polymeric materials [12–18].

For the oxidation with solid product generation, the activation energy was estimated by Kissinger's method [19] applied to the DTA peaks (the experimental data were automatically processed by a program written in BASIC language [20]). The value E=98.3 kJ mol^{-1} (r=0.995) was obtained.

The existence of an induction period for the thermooxidation of polyolefines is a well-known fact [7–10, 21]. It has been shown [7–10] that a plot of $\ln t_i$ *vs.* $(1/T)$ (t_i is the induction period and T the temperature) is linear. From the slope of this straight line, the activation energy for the induction period can be obtained.

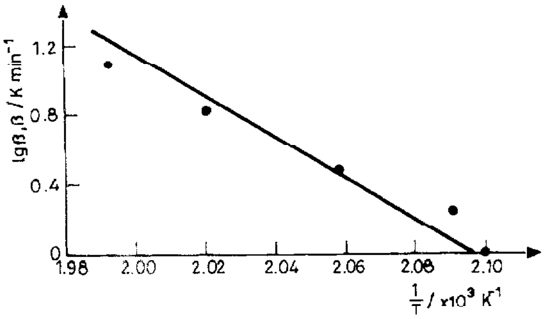

Fig. 2 Flynn-Wall isoconversion line for the beginning of the DTA exothermic peaks obtained for the non-isothermal thermooxidation of LDPE

In all reported results, this value of the activation energy is higher than that for the following fast reaction leading to solid products. There is controversy as regards the explanation of the difference [12–24]. Some authors are quite reserved concerning use of the suggested liquid-phase kinetic model to describe the oxidation of polymers [22]. Nevertheless, as step II in the DTA curve (Fig. 1) corresponds to the liquid-phase oxidation of LDPE, it can be considered that a given concentration of peroxides and hydroperoxides is reached after the induction period. The beginning of the exothermic peak in the DTA curve (Fig. 1) therefore corresponds to the temperature at which such a concentration is reached. The activation energy of the induction period could be determined by using the isoconversional Flynn-Wall method [25] applied to the beginning of the DTA exothermic peak for several heating rates. The corresponding Flynn-Wall straight line is shown in Fig. 2. From the slope of this straight line, the activation energy of the induction period was E_{ind}=189 kJ mol^{-1} (r=0.980).

This value is in the range obtained by other authors [8, 10, 26] who investigated the thermooxidation of LDPE that was either pure or doped with various antioxidants.

Isothermal DTA

The isothermal DTA curves of LDPE were recorded for temperatures in the range 168–198°C. Some of these curves are shown in Fig. 3. The thermooxidation of LDPE can be seen to exhibit an induction period, which decreases with temperature increase.

Figure 4 depicts the straight line $\ln t_i$ *vs.* $(1/T)$. Its slope gives E_{ind}= 194 kJ mol^{-1} (r=0.993). This value is close to that obtained from the non-isothermal data.

In order to evaluate the activation energy of the autocatalytic reaction with the corresponding DTA-iso peak, the method of Dharwadkar *et.al.* [27] was applied. In this method, the activation energy is estimated from the slope of the straight line $\ln h_{max}$ *vs.* $(1/T)$, where h_{max} is the maximum height of the DTA peak. This straight line is shown in Fig. 5.

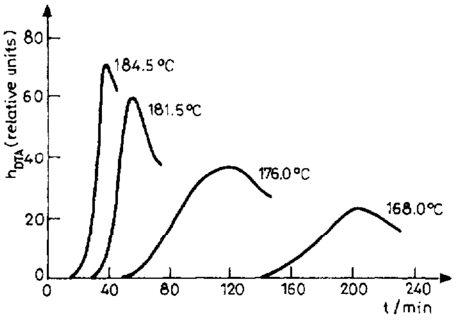

Fig. 3 DTA-iso curves for LDPE thermooxidation

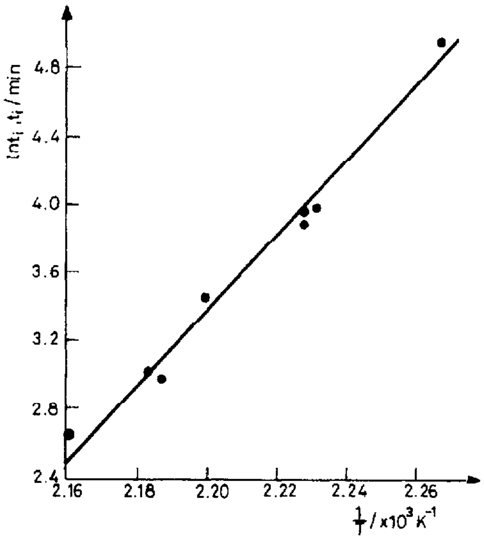

Fig. 4 Arrhenius line for the induction period of LDPE thermooxidation

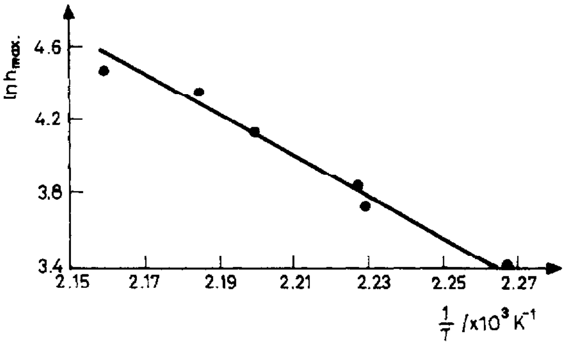

Fig. 5 $\ln h_{max}$ *vs.* $(1/T)$ for the isothermal thermooxidation of LDPE

The value obtained for the activation energy is E=95.0 kJ mol^{-1} (r=0.996). The agreement with the non-isothermal activation energy is fairly good.

Thermooxidative degradation of NBR

Non-isothermal data

Figure 6 shows the TG, DTG and DTA curves of NBR in static air atmosphere at a heating rate of 2.98 K min^{-1}; similar curves were obtained at other heating rates.

Inspection of these curves reveals two changes, I and III, accompanied by mass loss. Exothermic peak II corresponds to a change between changes I and III and is accompanied by a slight increase in mass.

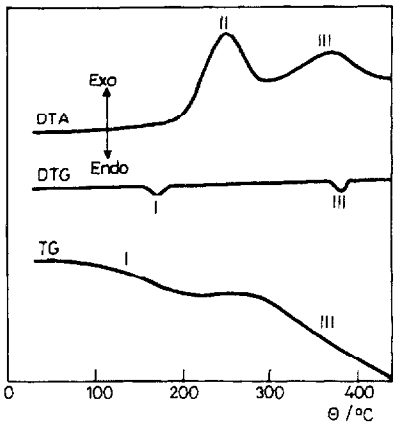

Fig. 6 Derivatogram of NBR in static air atmosphere at a heating rate of 2.98 K min^{-1}

The results obtained by the thermal analysis of NBR can be correlated with those obtained previously [28] concerning the change in the elongation at break of NBR due to its thermal degradation in air. The relatively fast decrease in the elongation at break in air at 80, 90 and 100°C is due to change I in the curve in Fig. 6. This corresponds to the loss of plastifier and other ingredients. In previous work [28], change II (Fig. 6) was assigned to the formation of solid products (probably hydroperoxides). This change is responsible for the mechanical degradation of NBR which follows the volatilization of plastifier and other ingredients. For change II, Kissinger's method [19] applied to the DTA peaks gave E=88.2 kJ mol^{-1} (r=0.992). This is close to the value obtained in the earlier investigation [28] of the change in the elongation at break due to thermal degradation.

Isothermal DTA

Initially, NBR samples were heated up to the chosen temperature in argon at a heating rate of 10 K min^{-1}. The samples were then heated isothermally in argon until constant mass was attained. The total mass decrease was 7–8%, corresponding to the loss of plastifier and other ingredients. In the temperature range chosen for the determinations, 190–206°C; the time of sample heating until constant mass was achieved 105–112 min. After this, the argon was replaced by oxygen and the DTA curve was recorded. Some of these curves are shown in Fig. 7.

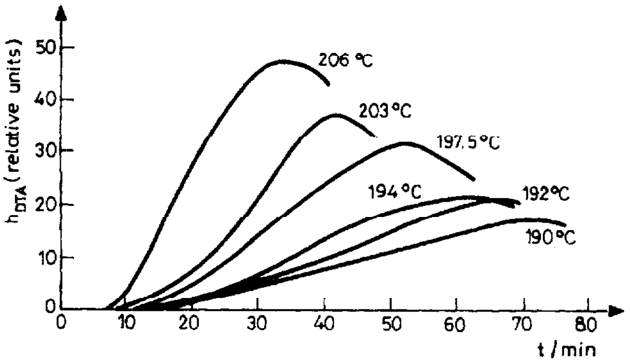

Fig. 7 DTA-iso curves for NBR thermooxidation

The curves are similar to those obtained for LDPE (Fig. 3). With regard to the complex character of the change undergone by NBR before the thermooxidation, it is difficult to evaluate the apparent activation energy of the induction period. For this material, only the activation energy for the fast oxidation to which the DTA-iso peak corresponds was evaluated by the method of Dharwadkar *et al.* [27]. The corresponding plot of $\ln h_{max}$ *vs.* ($1/T$) is shown in Fig. 8.

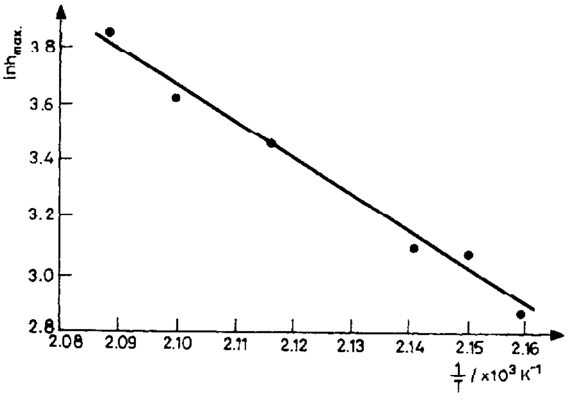

Fig. 8 $\ln h_{max}$ *vs.* ($1/T$) for the isothermal thermooxidation of NBR

The slope of this straight line yielded E=104 kJ mol^{-1} (r=0.990). This is higher than the value obtained from the isotherms of the elongation at break change [28]. The explanation may be related to the comparatively long time (t>100 min) of pretreatment of NBR in argon at a rather high temperature

(T>190°C) to produce the DTA-iso curves. In response to this treatment, NBR changes its morphology, turning into another material with different values for the kinetic parameters of the thermooxidation with respect to those of the initial material. Such a change does not occur in the relatively short time necessary either to record a non-isothermal thermogram or at the temperatures of accelerated thermal aging (80–100°C) at which the isotherms corresponding to the change in the elongation at break were recorded [28].

Table 1 Values of activation energy of LPDE and NBR thermooxidation

Material	Experimental data	Process	Method for activation energy evaluation	E/ kJ mol^{-1}	r
LPDE	non-isothermal DTA	induction period	Flynn-Wall isoconversion	189	0.980
	isothermal DTA	induction period	slope of lnt_i *vs.* (1/T)	194	0.993
	non-isothermal DTA	fast oxidation	Kissinger	98.3	0.995
	isothermal DTA	fast oxidation	Dharwadkar *et al.*	95.0	0.996
NBR	non-isothermal DTA	fast oxidation	Kissinger	88.2	0.992
	isothermal DTA	fast oxidation	Dharwadkar *et al.*	104	0.990
	isotherms of variation of the elongation at break*	thermooxidative degradation	verification of kinetic equation	87.5	–

*Results in previous work [28]

The results obtained for the isothermal and non-isothermal thermooxidative degradations of LDPE and NBR leading to solid products are given in Table 1.

Conclusions

1. For the thermooxidative degradation of LDPE, satisfactory agreement was observed between the activation energies obtained under isothermal and non-isothermal conditions. This agreement could be explained by taking into account the fact that the investigated LDPE sample does not contain ingredients (antioxidants, plastifier, etc.) and consequently the thermooxidation is not accompanied by secondary phenomena such as the volatilization or oxidation of these ingredients. Further, the liquid-phase oxidation of LDPE is simpler than the interaction of the solid polymeric material with oxygen.

2. For the thermooxidative degradation of NBR, a difference was observed between the activation energies obtained from the isothermal and non-isother-

mal data. This difference can be explained in terms of the complexity of this material. Its heating for over 100 min at high temperatures corresponding to DTA-iso leads not only to a loss of the ingredients, but also to morphological changes.

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