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The thermoxidative decomposition of low density polyethylene in non-isothermal conditions

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Abstract

The results of the thermogravimetric study of the non-isothermal thermoxidative degradation of low density polyethylene (LDPE) are analysed. The observed changes in the weight-loss rate during the programmed heating suggest the complex degradation mechanism of LDPE. This is confirmed by the specific changes with conversion of the apparent kinetic parameters of the weight-loss process.

INTRODUCTION

The thermoxidative decomposition of polyethylene (PE) has been investigated extensively. Both isothermal and non-isothermal studies have been performed in order to determine the reaction products, both qualitatively and quantitatively, to investigate changes in structure, and the molecular weight and its distribution, as well as to evaluate the kinetic parameters of the decomposition process. The values of the kinetic parameters are controversial as they vary between large limits, even under isothermal reaction conditions.

The aim of the present study is to examine the dependence of the non-isothermal thermoxidative behaviour of low density polyethylene (LDPE) on the reaction conditions (especially the heating rate) and the conversion. The changes in the kinetic parameters during the decomposition of LDPE are analysed.

EXPERIMENTAL

The LDPE used was synthesised in the research laboratories of the Petrochemical Company Brazi (Romania). The purity of the LDPE was assessed by IR and its characteristics are: MW = 30 500, $T_m = 105\,°C$,

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density 0.915 g cm^{-3} and 8.5 CH_3-branches per 100 C atoms. The thermoxidative behaviour of this LDPE was investigated in the temperature range 20–600 °C on a Paulik–Paulik–Erdey-type Derivatograph thermobalance, MOM, Budapest. The sample weight was 50 mg, the flow rate of the air was 30 ml min^{-1} and heating rates of 5.2, 14.8 and 22.4 °C min^{-1} were used. The kinetic parameters were estimated as previously described [1,2] by using several methods of evaluation because it has been shown that for complex decomposition processes in non-isothermal conditions, a single method (especially if applied to a single thermogravimetric curve obtained at only one heating rate) is inappropriate for the determination of the kinetic parameters of such reactions [1–4].

RESULTS AND DISCUSSION

The thermoxidative decomposition of LDPE is a complex exothermic process accompanied by weight losses which occur, depending on the heating rate, in the temperature range between 220 and 590 °C. At least three weight-loss stages were observed; unfortunately it was not possible to separate these with the range of heating rates employed. The different weight-loss stages can be seen in the changes in slope of the weight-loss curves, TG, and in the more or less well developed maxima of the complex DTG curves (see Fig. 1). The corresponding temperatures of these DTG maxima depend on the heating rate used. It seems, however, that the initial temperature of decomposition is not affected by the heating rate. As a result of the superposition of the decomposition stages, any kinetic analysis of the weight-loss curves will be affected by more or less pronounced uncertainties. Consequently, the computed kinetic parameters will be influenced both by the conversion degree and by the heating rate.

As shown in Fig. 2, the global activation energy (E_{CR}) and the pre-exponential factor ($\ln A_{CR}$), computed according to the Coats–Redfern equation [5], increase with the heating rate used. A probable explanation is that larger chain fragments are already present at lower temperatures of decomposition; they accumulate and are volatile only at higher temperatures. This retarded volatilisation of decomposition products which are already formed, results in increasing weight-loss rates at higher temperatures. Thus higher temperature coefficients of the reaction and, consequently, higher activation energies are suggested by the weight loss data [6]. In addition, this effect of increasing activation energy during decomposition will be amplified because the volatilisation of larger and larger chain fragments implies higher and higher volatilisation energies [7].

The accumulation and volatilisation of the decomposition products depends on the heating rate used, the probability of accumulation being higher the lower the heating rate because, at lower heating rates, the sample is

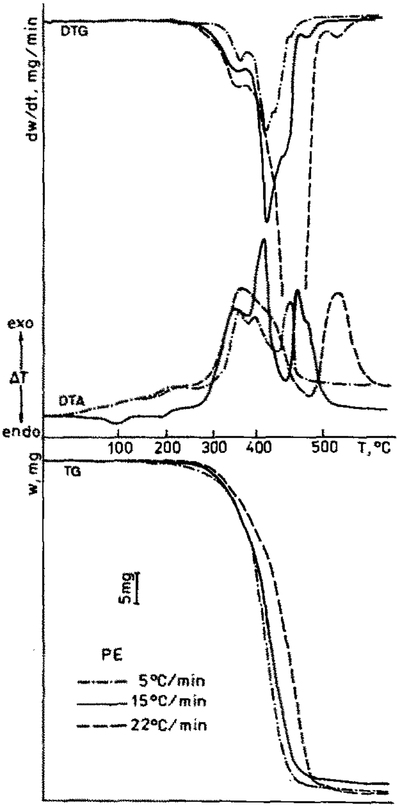

Fig. 1. Thermogravimetric (TG), derivative thermogravimetric (DTG) and differential analytical (DTA) curves of the non-isothermal decomposition of LDPE for different heating rates.

maintained for a longer time at the lower decomposition temperatures where the larger fragments are formed and accumulated. In addition, the temperatures of volatilisation of these fragments will be retarded, i.e. reached at higher conversion degrees. Thus, the kinetic parameters obtained are valid

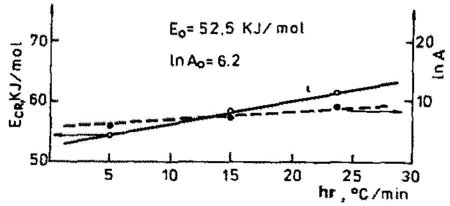

Fig. 2. Influence of the heating rate (hr) on the overall activation energy (E_{CR}) and pre-exponential factor (ln A_{CR}) of the thermoxidative decomposition of LDPE computed according to Coats and Redfern [5]. Values of the kinetic parameters extrapolated for zero heating rate are shown on the figure.

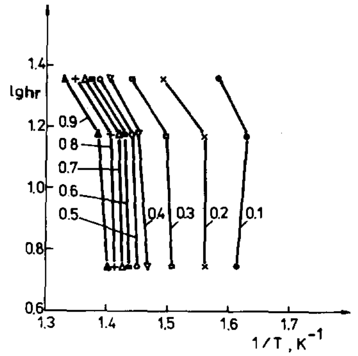

Fig. 3. Flynn–Wall–Ozawa plot [8] for the thermoxidative decomposition of LDPE. The numbers on the curves refer to the respective conversion degrees (α).

only for the observed weight loss, and not necessarily for the decomposition reaction itself.

Changes in the weight-loss mechanism due to modifications of the reaction mechanism with the conversion degree and the temperature range, respectively, are supported by the non-linearity of the curves plotted in Fig. 3 according to the Flynn–Wall–Ozawa method [8].

The difference between the shapes of these curves for LDPE and those observed in the decomposition of linear PE [4] can be explained by the increased susceptibility to oxidation of the LDPE. The prevailing oxygen attack will occur on the energetic weak points represented by the hydrogen attached to the tertiary carbon atoms of the chain supporting the chain branches. The number of such branches is much higher in the LDPE.

The dependence of the kinetic parameters on the conversion degree expressed but the weight losses at a given temperature (time) of transformation and at the end of the decomposition process ($\alpha = w_T/w_\infty$) has been evaluated using the computing methods of Swaminathan and Madhavan [9], Friedman [10] and Reich and Levi [11], respectively. The results obtained are illustrated in Fig. 4.

The dependence is very unusual: all the curves show two maxima, one in the conversion range of about $\alpha = 0.3$–0.45 and the second at 0.55 or 0.77, depending on the method of calculation used.

The increase in the kinetic parameters with the conversion and/or the temperature range of the decomposition of PE was first mentioned by Jellinek [12] and confirmed later by other authors [13–15]. The presence of the two maxima in the kinetic parameter versus conversion degree curves, however, has never been emphasised.

Taking into account the extremely large number of different products evolved during the decomposition of PE [16,17], the process can be compared with the pyrolysis of complex fuels for which either a Gaussian or a discrete distribution of the activation energy has been suggested [18,19].

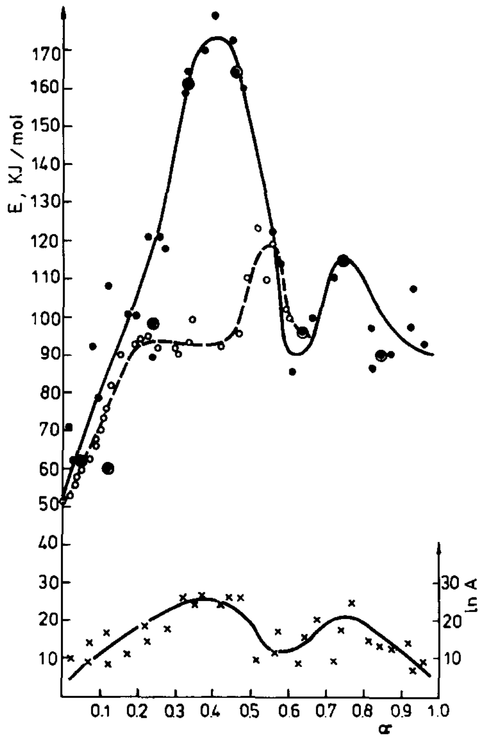

Fig. 4. Influence of the conversion degree (α) on the activation energy (E) and the pre-exponential factor (ln A) of the weight-loss process during the thermoxidative decomposition of LDPE. Values of E computed according to Friedman [10] for conversion intervals subdivided in respective 10 (●) and 20 (●) equidistant segments, and according to Reich and Levi [11] (○).

It is remarkable that the overall thermogravimetric curves can be described only by using different weight-loss rate equations for the different conversion ranges of the decomposition process of LDPE. These rate equations are of the form $f(\alpha) = (1-\alpha)^n$, for the range $\alpha = 0$–0.35; $f(\alpha) = \alpha^{\mathrm{m}}$ and/or $(-\ln(1-\alpha))^p$, for 0.35–0.74; and $f(\alpha) = \alpha^m(1-\alpha)^n(-\ln(1-\alpha))^p$, for 0.74–0.95. The most probable average values of the exponents of the rate equations are $m = 0.5$, $n = 0.65$ and $p = -1.4$. They are, however, valid for only a restricted domain of the respective conversion ranges because of the continuous transition between the corresponding rate equations.

It is further remarkable that the ranges of the conversion degrees in which the change in the rate equations occurs coincide more or less with the positions of the maxima observed in the E versus α curves in Fig. 4.

These specific behaviours observed in the analysis of the thermoxidative decomposition of LDPE under non-isothermal reaction conditions suggest a continuous modification of the reaction mechanism due to competition between the different processes involved (various decomposition paths,

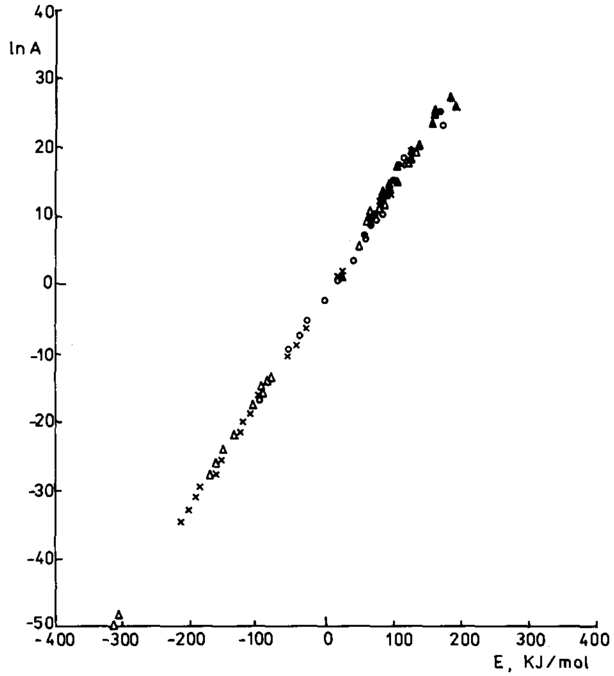

Fig. 5. Compensation effect illustrated by the ln A vs. E dependence of the thermoxidative decomposition of LDPE. Different signs refer to kinetic parameters computed using different rate equations for the conversion domains up to $\alpha = 0.74$ (▲, ●) and, respectively, 20 (△) or 40 (×) equidistant reading points on the TG curves obtained at the different heating rates (○).

diffusion and volatilisation) which are all influenced differently by the temperature change during the heating.

The correlation between the computed activation energies, E, and the pre-exponential coefficients, ln A, is shown in Fig. 5 which indicates an apparent compensation effect for the whole decomposition range independent of the form of the equation used for kinetic computation. This correlation is not affected by the heating rate or by the number of equidistant weight-loss points read from the TG curves (reading points) and employed for the evaluation of the kinetic parameters.

The resulting isokinetic equation is of the form $\ln A = -1.05 + 0.1536E$, deduced by the least-squares method. The corresponding isokinetic temperature, $T_{\mathrm{iso}} = 580\,°\mathrm{C}$, is quite different from the temperatures of the DTG maxima. This suggests, once more, the complex mechanism of weight loss during the oxidative decomposition of LDPE in non-isothermal conditions.

Owing to the complexity of the decomposition process, any attempt to extrapolate the data to other decomposition conditions is questionable. This conclusion is also confirmed by the results reported recently for the decomposition of polyethylene in iso-thermal conditions [20].

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