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Thermal degradation of glass reinforced epoxy resin and polychloroprene rubber: the correlation of kinetic parameters of isothermal accelerated aging with those obtained from non-isothermal data

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Abstract

The results of a kinetic investigation of the non-isothermal and isothermal degradation of a mechanical property for glass reinforced epoxy resin (GRER) and polychloroprene rubber (PCL-R) are presented. For each of the materials investigated, similar dependences of the activation energy on the degree of conversion were obtained from non-isothermal data and from the thermal accelerated aging of the mechanical property (flexural strength, for GRER; residual deformation under constant deflection, for PCL-R). The obtained results are arguments for the quasichemical approximation according to which the degradation of a mechanical property of a polymeric material is due to a chemical reaction that can be described by equations from chemical kinetics. In the particular case of GRER, in which E is constant in the range $0.05 \leqslant \alpha \leqslant 0.40$, the value of the activation energy obtained from non-isothermal data can be used for rapid prediction of the thermal lifetime. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The practical use of polymeric materials requires a knowledge of their thermal lifetime corresponding to a certain end-point criterion and the operating temperature. According to the procedure recommended by IEC 216 Standard [1], to predict the thermal lifetime, the material is submitted to accelerated aging by following the changes in time of a property of interest [mechanical property (elongation at break, elastic modulus, flexural strength, residual deformation under constant deflection, etc.), electrical property (dielectric strength, resistivity, etc.), mass loss]. Through kinetic analysis of the results, the thermal lifetime under the condition of use can be obtained. This procedure requires 8–10 months of gathering experimental data for a given material and a given property. As is suggested by IEC 1026 Standard [2], the test duration needed for thermal lifetime prediction can be shortened by using some analytical techniques (gas chromatography, mass spectrometry, and isothermal differential calorimetry). This Standard does not recommend the use of the rapid non-isothermal techniques, such TG, DTA and DSC, since these methods require extrapolation of test results over a large temperature span, which may lead to erroneous conclusions. However, the results reported by some investigators [3–12] show that a careful analysis of the non-isothermal data leads to the values of activation energy that can be used for rapid prediction of the thermal lifetime. In recent papers [13,14], it was pointed out that a cause of poor performance in the thermal lifetime prediction from non-isothermal data is the use of imprecise values of activation energy obtained by some improper procedures. In relation with the last remark, we note that most papers concerning the kinetic analysis of non-isothermal data report results obtained by means of a limited set of methods. There is the suspicion that, in every analyzed case, the use of other method could lead to different results. This is the source of the doubt expressed by various authors in the methods of non-isothermal kinetics.

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In this paper, the results obtained in the study of accelerated thermal aging and thermal analysis (TG, DTA) of glass reinforced epoxy resin (GRER) and polychloroprene rubber (PCL-R) are presented. A relative high number of non-isothermal kinetic methods will be used and a procedure of kinetic analysis of non-isothermal data will be suggested too. The values of the activation energy of the isothermal accelerated aging will be compared with those obtained by some different methods from non-isothermal data.

2. Kinetics of isothermal accelerated thermal aging of GRER and PCL-R

2.1. GRER

A previous paper [15] presented the isotherms of degradation of the flexural strength of GRER in air, at atmospheric pressure, and in oxygen at various pressures ($P > 1$ atm). Based on the experimental results, the following kinetic equation of thermo-oxidative degradation was derived:

$$\frac{\varepsilon}{\varepsilon_0} = a\exp\left[-A_0 P^m t\exp\left(-\frac{E}{RT}\right)\right] \tag{1}$$

where ε is the property value at a certain moment; ε_0 is the initial property value; $a = 1.370$ is a material constant; t is the time expressed in hours; $A_0 = 6.805.10^5$ is the pre-exponential factor; P is the oxygen pressure expressed in atm; $E = 69.4$ kJ mol^{-1} is the activation energy; T is the temperature; $m = 1.314$ is a material constant and R is the gas constant.

2.2. PCL-R

The results obtained for thermal degradation of the residual deformation under constant deflection of PCL-R have been presented previously [16]. In another previous paper [17], it has been shown that:

- the activation energy evaluated by means of the differential isoconversional method increases with the degree of degradation from ≈ 80 kJ mol^{-1}, for $\frac{\varepsilon}{\varepsilon_0} = 0.85$, to ≈ 135 kJ mol^{-1}, for $\frac{\varepsilon}{\varepsilon_0} = 0.65$; this change is well approximated by the equation:

  $$E = E_0 + E_1 \ln\frac{\varepsilon}{\varepsilon_0} \tag{2}$$

  where $E_0 = 45.5$ kJ mol^{-1} and $E_1 = -201.9$ kJ mol^{-1} are empirical parameters.
- the activation parameters [E and A (pre-exponential factor)] are correlated through the compensation effect relationship:

  $$\ln A = \alpha^* + \beta^* E \tag{3}$$

  where $\alpha^* = -2.5337$ (A expressed in h^{-1}) and $\beta^* = 0.3117$ mol kJ^{-1}.
- the dependence of relative property on time and temperature is:

  $$\frac{\varepsilon}{\varepsilon_0} = \left(\frac{1}{nA_0 t + 1}\right)^{1/n} \tag{4}$$

  where $n = \beta^* E_1 - \frac{E_1}{RT}$ and $A_0 = \exp(\alpha^* + \beta^* E_0 - \frac{E_0}{RT})$.

3. Kinetics of non-isothermal degradation of GRER and PCL-R

3.1. The methods used to evaluate the non-isothermal kinetic parameters

All kinetic analyses of non-isothermal data (TG, DTA, DSC) are based on the rate equation (see, e.g. [18]):

$$\frac{d\alpha}{dt} \equiv \beta\frac{d\alpha}{dT} = Af(\alpha)\exp\left(-\frac{E}{RT}\right) \tag{5}$$

where α is the conversion; $f(\alpha)$ is the differential conversion function and $\beta = \frac{dT}{dt} =$ const. is the linear heating rate.

The use of Eq. (5) supposes that the overall (apparent) kinetic triplet [E, A, $f(\alpha)$] describe a chemical or physical change, no matter its complexity. Obviously, such a forced description is perhaps one of the reason for obtaining activation parameters dependent on the degree of conversion.

3.1.1. Isoconversional methods

These methods are known to allow for model-independent estimates of activation energy. Their use allows the investigation of the dependence of activation energy on conversion degree.

3.1.1.1. Friedman method [19] (FR method). The differential isoconversional method suggested by Friedman [19] (FR method) is based on Eq. (5) that leads to:

$$\ln\beta\frac{d\alpha}{dT} = \ln A + \ln f(\alpha) - \frac{E}{RT} \tag{6}$$

For $\alpha =$ const., the plot $\ln\left(\beta\frac{d\alpha}{dT}\right)$ vs. $(1/T)$, obtained from thermograms recorded at several heating rates, should be a straight line whose slope allows evaluation of the activation energy.

3.1.1.2. Flynn–Wall–Ozawa method [20,21] (FWO method). The isoconversional integral method suggested independently by Flynn and Wall [20] and Ozawa [21] uses Doyle's approximation [22] of the temperature integral. This method is based on the equation:

$$\ln\beta = \ln\frac{AE}{Rg(\alpha)} - 5.331 - 1.052\frac{E}{RT} \tag{7}$$

where

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)}$$

is the integral conversion function.

Thus, for $\alpha=$const., the plot ln β vs.$(1/T)$, obtained from thermograms recorded at several heating rates, should be a straight line whose slope allows evaluation of the activation energy.

3.1.1.3. Kissinger–Akahira–Sunose method [23,24] (KAS method). This isoconversional integral method is based on the Coats–Redfern approximation [25] of the temperature integral. It was shown that:

$$\ln\frac{\beta}{T^2} = \ln\frac{AR}{Eg(\alpha)} - \frac{E}{RT} \tag{8}$$

Thus, for $\alpha=$const., the plot $\ln\frac{\beta}{T^2}$ vs. $(1/T)$, obtained from thermograms recorded at several heating rates, should be a straight line whose slope can be used to evaluate the activation energy.

3.1.1.4. Li–Tang method [26–28] (LT method). This is based on the following equation that results from Eq. (5) by taking the logarithm, multiplying by dα and integrating:

$$\int_{\alpha_0}^{\alpha}\left(\ln\beta\frac{d\alpha}{dT}\right)d\alpha = -\frac{E}{R}\int_{\alpha_0}^{\alpha}\left(\frac{1}{T}\right)d\alpha + G(\alpha,\alpha_0) \tag{9}$$

where $G(\alpha,\alpha_0) = (\alpha-\alpha_0)\ln A + \int_{\alpha_0}^{\alpha}(\ln f(\alpha))d\alpha$.

The plot of $I_2 \equiv \int_{\alpha_0}^{\alpha}\left(\ln\beta\frac{d\alpha}{dT}\right)d\alpha$ vs. $I_1 \equiv \int_{\alpha_0}^{\alpha}\left(\frac{1}{T}\right)d\alpha$, at a given α, for a set of β, should be a straight line whose slope is $\left(-\frac{E}{R}\right)$.

3.1.1.5. Vyazovkin nonlinear procedure [29–31] (V nonlinear method). This integral method is based on the following condition of minimum that is obtained from the integral form of Eq. (5):

$$\sum_{i}^{n}\sum_{j\neq i}^{n}\left[\frac{I(E_\alpha, T_{\alpha,i})\beta_j}{I(E_\alpha, T_{\alpha,j})\beta_i}\right] = \min, \tag{10}$$

where: $I(E,T) = \frac{E}{R}p(x)$ [$p(x)$ is the temperature integral and n is the number of the heating rates for which the $\alpha=\alpha(T)$ curves were determined].

A range of E with a given step is considered. The value E_α corresponds to the minimum value of the double sum (10).

Unlike the FWO and KAS integral methods, Vyazovkin integral method permits the use of more exact approximations of the temperature integral. In this paper we will use the fourth rational expression of Senum and Yang [32].

3.1.2. Methods which use a single $\alpha = \alpha(T)$ curve for only one linear heating rate

These methods consider the values E and A that correspond to the function of conversion with the lowest deviation of the $\alpha=\alpha(T)$ calculated curve with respect to the experimental one. Table 1 [33] lists the differential $f(\alpha)$ and integral $g(\alpha)$ functions in current use.

3.1.2.1. The differential method (D method). The method is based on Eq. (1) written in the form:

$$\ln\beta\frac{d\alpha}{dT} - \ln f(\alpha) = \ln A - \frac{E}{RT} \tag{11}$$

The plot $\left(\ln\beta\frac{d\alpha}{dT} - \ln f(\alpha)\right)$ vs. $\left(\frac{1}{T}\right)$, for a given analytical form of $f(\alpha)$, should be a straight line whose parameters are ln$A$ and $\left(-\frac{E}{R}\right)$.

3.1.2.2. Coats–Redfern method [25] (CR method). This integral method uses the equation:

$$\ln\frac{g(\alpha)}{T^2} = \ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \cong \ln\frac{AR}{\beta E} - \frac{E}{RT} \tag{12}$$

The left-hand side of Eq. (12), for various values of α, is plotted as a function of the reciprocal values of the temperature to give a straight line whose slope and intercept allow to obtain the values of the activation energy and the pre-exponential factor. It was shown [34] that for $\frac{E}{R} > 5$, this method leads to values of E with an error less than 4%.

3.1.2.3. The invariant kinetic parameter method [35,36] (IKP method). The IKP method is based on the observation [37–47] that the same experimental curve $\alpha=\alpha(T)$ can be described relatively correctly by several functions of conversion and, for a single TG curve, the values of the activation parameters, obtained for various analytical forms of $f(\alpha)$, are correlated through the relation of the compensation effect [Eq. (3)]. In order to apply this method for a given heterogeneous reaction,

Table 1
Expressions for $f(\alpha)$ and $g(\alpha)$ functions for the most common mechanisms operating in the solid state reactions

Mechanism	Symbol	$f(\alpha)$	$g(\alpha)$
Reaction order model	Fn	$(1-\alpha)^n$	$-ln(1-\alpha)$, for $n=1$ $\frac{1-(1-\alpha)^{(-n+1)}}{-n+1}$, for $n \neq 1$
Random nucleation and growth of nuclei (Avrami–Erofeev equation)	An	$n(1-\alpha)[-\ln(1-\alpha)]^{(1-1/n)}$	$[-\ln(1-\alpha)]^{1/n}$
One-dimensional diffusion (parabolic law)	D1	$\frac{1}{2\alpha}$	α^2
Two-dimensional diffusion (bidimensional particle shape)	D2	$\frac{1}{[-\ln(1-\alpha)]}$	$(1-\alpha)\ln(1-\alpha)+\alpha$
Three-dimensional diffusion (tridimensional particle shape) (Jander equation)	D3	$3(1-\alpha)^{2/3}/2\left[1-(1-\alpha)^{1/3}\right]$	$\left[1-(1-\alpha)^{1/3}\right]^2$
Three-dimensional diffusion (tridimensional particle shape) (Ginstein–Brouhnstein equation)	D4	$\frac{3}{2\left[(1-\alpha)^{-1/3}-1\right]}$	$\left(1-\frac{2\alpha}{3}\right)-(1-\alpha)^{2/3}$
Prout–Tompkins	B1	$\alpha(1-\alpha)$	$\ln\frac{\alpha}{1-\alpha}$
Power law	Pn	$n(\alpha)^{(n-1)/n}$	$\alpha^{1/n}$
Exponential law	E1	α	$\ln\alpha$

$\alpha=\alpha(T)$ curves for several heating rates (β_v, $v=1,2,3,\ldots$) should be recorded. Also, a set of conversion functions, f_j, $j=1,2,3\ldots$, is considered. For each heating rate, β_v, using an integral or differential method, the pairs (A_{vj}, E_{vj}), characteristic for each conversion function, are determined. Using the relation of the compensation effect, for each heating rate the compensation parameters (α_v*, β_v*) are determined. The straight lines $\ln A_v$ vs. E_v for several heating rates should intersect in a point which corresponds to the true values of A and E. These were called by Lesnikovich and Levchik [35,36], invariant activation parameters (A_{inv}, E_{inv}). Variations of the experimental conditions actually cause a region of intersection in the space (A, E). For this reason the evaluation of the invariant activation parameters is performed using the relation:

$$\ln A_{\text{inv}} = \alpha_v^* + \beta_v^* E_{\text{inv}} \tag{13}$$

which leads to the *supercorrelation* relation:

$$\alpha_v^* = \ln A_{\text{inv}} - \beta_v^* E_{\text{inv}} \tag{14}$$

Thus, the plot α_v* vs. β_v* is actually a straight line whose parameters allow evaluating the invariant activation parameters.

3.2. Kinetics of non-isothermal degradation of GRER

The TG curves corresponding to the thermal degradation of GRER in static air atmosphere at the heating rates of 0.72; 2.97; 6.08 and 12.46 K min^{-1} were reported in a previous paper [48]. The investigated material exhibits an exothermic process, with formation of volatile products.

The results obtained by isoconversional methods are listed in Table 2. One has to notice that for $0.05 \leqslant \alpha \leqslant 0.40$, E does not depend on α as well as the applied method. For $0.40 < \alpha \leqslant 0.65$, E increases with α and for a given value of α, E value depends on the applied isoconversional method. FR method uses the point values of the overall rate, while the integral isoconversional methods use integrals, which describe the history of the system in the range 0–α. This is why one expects that for an increase of E with α, E_{FR} is higher than E evaluated by means of integral isoconversional methods (E_{int}) and for decrease of E with α, $E_{\text{FR}} < E_{\text{int}}$.

In order to apply the IKP method we focus on the range $0.05 \leqslant \alpha \leqslant 0.40$ where E values are practically constant. The kinetic models F0.7, F1, F1.2, F1.5, F1.7, F2, A0.5 and A0.8, for which the straight lines corresponding to the method of kinetic parameter evaluation (D method and CR method) are characterized by r close to 1, were considered. The values of the activation parameters depend on the kinetic model as well as on the heating rate, as shown in Tables 3 and 4 which list the results obtained by D and CR methods. Some high differences among the values of the activation parameters corresponding to different kinetic models can be noted, although the correlation coefficients have appropriate values. For D method, the maximum value of $|r|$ was obtained for A0.5 model, although the activation energy corresponding to this model is much higher than that obtained by isoconversional methods. On the other

Table 2
Values of the activation energy obtained by means of isoconversional methods for GRER

	$0.05 \leqslant \alpha \leqslant 0.40$		$0.40 < \alpha \leqslant 0.65$	
Method	E (kJ mol^{-1})	r[a]	E (kJ mol^{-1})	r
FR	65.7 (±4.6)	$\geqslant$0.991	increases from 65.7 to 81.0	$\geqslant$0.991
FWO	69.2 (±1.5)	$\geqslant$0.993	increases from 70.3 to 77.8	$\geqslant$0.997
KAS	65.0 (±1.6)	$\geqslant$0.991	increases from 65.7 to 73.2	$\geqslant$0.995
LT(α_0=0.025)	64.5 (±1.4)	$\geqslant$0.994	increases from 65.5 to 69.8	$\geqslant$0.996
V	65.3 (±1.6)	–	increases from 66.1 to 73.6	–

[a] r is the correlation coefficient of the linear regression corresponding to the used method.

Table 3
Kinetic parameters evaluated from TG curves for thermal degradation of GRER using D method

	β=0.72 K min^{-1}			β=2.97 K min^{-1}		
Model	E (kJ mol^{-1})	ln$A$ A/s^{-1}	$-r$	E (kJ mol^{-1})	ln$A$ A/s^{-1}	$-r$
F0.7	42.0	2.3209	0.98405	48.9	4.6531	0.97737
F1	46.1	3.5213	0.98852	54.3	5.8455	0.98367
F1.2	48.8	4.3233	0.99063	57.2	6.6404	0.98683
F1.5	52.9	5.5248	0.99289	61.6	7.8329	0.99043
F1.7	55.6	6.3258	0.99395	64.5	8.6279	0.99224
F2	59.6	7.5272	0.99503	68.9	9.8203	0.99428
A0.5	111.5	20.7303	0.99525	122.2	22.2041	0.99508
A0.8	62.4	7.8682	0.99213	70.7	9.8487	0.98796

	β=6.08 K min^{-1}			β=12.46 K min^{-1}		
Model	E (kJ mol^{-1})	ln$A$ A/s^{-1}	$-r$	E (kJ mol^{-1})	ln$A$ A/s^{-1}	$-r$
F0.7	47.3	4.2959	0.98864	50.0	5.1437	0.98802
F1	51.2	5.3332	0.98976	54.0	6.1615	0.98998
F1.2	53.8	6.0247	0.99015	56.6	6.8402	0.99082
F1.5	57.7	7.0621	0.99034	60.6	7.8580	0.99158
F1.7	60.3	7.7535	0.99024	63.2	8.5366	0.99183
F2	64.2	8.7908	0.99001	67.2	9.5545	0.99193
A0.5	115.0	20.1984	0.99802	119.1	20.7097	0.99781
A0.8	67.2	9.1016	0.99418	70.3	9.8527	0.99401

hand, for CR method, the maximum values of |r| were obtained for Fn models (F2 for β=0.72 K min^{-1} and β=2.97 K min^{-1}; F1.2 for β=6.08 K min^{-1} and F1.5 for β=12.46 K min^{-1}). It follows that the use the statistical criterion assuming that to the maximum value of $|r|$ corresponds to the true kinetic model, leads to a kinetic triplet that depends on the method used for evaluation of the kinetic parameters as well as on the heating rate. Therefore, the small differences among $|r|$ values, which are due mainly to experimental inherent errors, cannot be used to discriminate among the kinetic models. Consequently, the evaluation of the kinetic parameters by using a single $\alpha = \alpha(T)$ curve recorded at a certain heating rate does not lead to reliable results.

As expected, for each heating rate the activation parameters are correlated through the compensation effect relationship [Eq. (3)]. The compensation effect parameters are listen in Table 5. As α^* and β^* are correlated by the supercorrelation relation [Eq. (13)] one obtains:

- D method: $\ln A_{\mathrm{inv}} = 9.3613\ (\pm 2.7028)$ (A_{inv} expressed in s^{-1}); E_{inv}=68.0 (±2.7) kJ mol^{-1}, with r=0.99842;
- CR method: $\ln A_{\mathrm{inv}} = 8.1850\ (\pm 0.5117)$ (A_{inv} expressed in s^{-1}); E_{inv}=63.2 (±2.1) kJ mol^{-1}, with r= 0.99887.

These values of E_{inv} as well as the values of E obtained by isoconversional methods for $0.05 \leqslant \alpha \leqslant 0.40$ are close to that corresponding to isothermal degradation of the flexural strength of GRER. Consequently, the thermal degradation of the investigated mechanical property is a result of the thermo-oxidation process seen in the thermograms. In this case, the thermal lifetime of the material can be predicted by a rapid analytical method consisting in the evaluation of the activation energy from

Table 4
Kinetic parameters evaluated from TG curves for thermal degradation of GRER using CR method

	$\beta = 0.72$ K min^{-1}			$\beta = 2.97$ K min^{-1}		
Model	E (kJ mol^{-1})	ln$A$ A/s^{-1}	$-r$	E (kJ mol^{-1})	ln$A$ A/s^{-1}	$-r$
F0.7	56.2	6.1679	0.99520	59.2	6.9554	0.99805
F1	58.2	6.7960	0.99620	61.3	7.5509	0.99859
F1.2	59.6	7.2232	0.99678	62.7	7.9552	0.99889
F1.5	61.7	7.8765	0.99755	64.9	8.5737	0.99925
F1.7	63.1	8.3204	0.99799	66.3	8.9939	0.99943
F2	65.3	8.9988	0.99854	68.6	9.6357	0.99963
A0.5	123.7	24.0640	0.99670	130.4	24.2665	0.99880
A0.8	74.6	11.1723	0.99641	78.6	11.7891	0.99868

	$\beta = 6.08$ K min^{-1}			$\beta = 12.46$ K min^{-1}		
Model	E (kJ mol^{-1})	ln$A$ A/s^{-1}	$-r$	E (kJ mol^{-1})	ln$A$ A/s^{-1}	$-r$
F0.7	53.9	5.7823	0.99872	54.8	6.1299	0.99918
F1	55.8	6.3295	0.99897	56.7	6.6676	0.99943
F1.2	57.1	6.6831	0.99915	58.0	7.0331	0.99952
F1.5	59.1	7.2698	0.99910	60.1	7.5916	0.99955
F1.7	60.5	7.6558	0.99906	61.5	7.9709	0.99952
F2	62.6	8.2454	0.99892	63.6	8.5502	0.99937
A0.5	119.7	21.2642	0.99912	121.8	21.2867	0.99952
A0.8	71.8	10.1241	0.99903	73.0	10.3835	0.99947

Table 5
Values of the compensation effect parameters obtained for thermal degradation of GRER

	D method			CR method		
β (K min^{-1})	$-\alpha^*$ A/s^{-1}	β^* (mol kJ^{-1})	$-r$	$-\alpha^*$ A/s^{-1}	β^* (mol kJ^{-1})	$-r$
0.72	8.4437	0.2625	0.99948	8.3985	0.2627	0.99972
2.97	7.0759	0.2405	0.99942	7.1010	0.2408	0.99971
6.08	6.4310	0.2323	0.99932	6.5546	0.2328	0.99963
12.46	5.7552	0.2231	0.99929	5.9023	0.2236	0.99962

thermal analysis data and the plotting only one isotherm of accelerated aging, corresponding to the maximum permitted temperature for accelerated aging [11].

3.3. Kinetics of non-isothermal degradation of PCL-R

The TG and DTA curves corresponding to the thermo-oxidative degradation of PCL-R at the heating rates: 0.73, 1.48, 3.08 and 6.20 K min^{-1} were reported in a previous paper [49]. It was showed that the non-isothermal degradation of PCL-R up to 350 °C occurs in a single exothermic step, with the generation of volatile products (mainly hydrogen chloride).

The dependence of the activation energy obtained by means of isoconversional methods on the conversion degree is shown in Fig. 1. As one can see, the activation energy increases with the conversion no matter what the method of evaluation. For a given value of α, E_{FR} is higher than E values evaluated by the integral isoconversional methods, which is in agreement with the reason given in Section 3.2. As is expected, according to the same reason, $E_{\mathrm{LT}}(\alpha_0 = 0.05) < E_{\mathrm{LT}}(\alpha_0 = 0.10)$.

In a recent paper [50], we noted that when E depends on α, the use of the FR method, which does not assume the integration of the rate equation, is recommended. One has to notice that for these cases, the integration of the rate equation is incorrect, as it requires activation parameters that do not depend on α.

Obviously, when E depends on α, the IKP method cannot be applied.

The values of activation energy obtained by FR method are close to those obtained for thermal degradation of the residual deformation under constant deflection (see Section 2.2). The following dependence of E_{FR} on α is found for data given in Fig. 1:

$$E_{\mathrm{FR}} = E'_0 + E'_1 \ln(1-\alpha) \qquad (15)$$

where $E_0' = 56.8$ kJ mol^{-1}; $E_1' = -297.0$ kJ mol^{-1} with $r = -0.99128$.

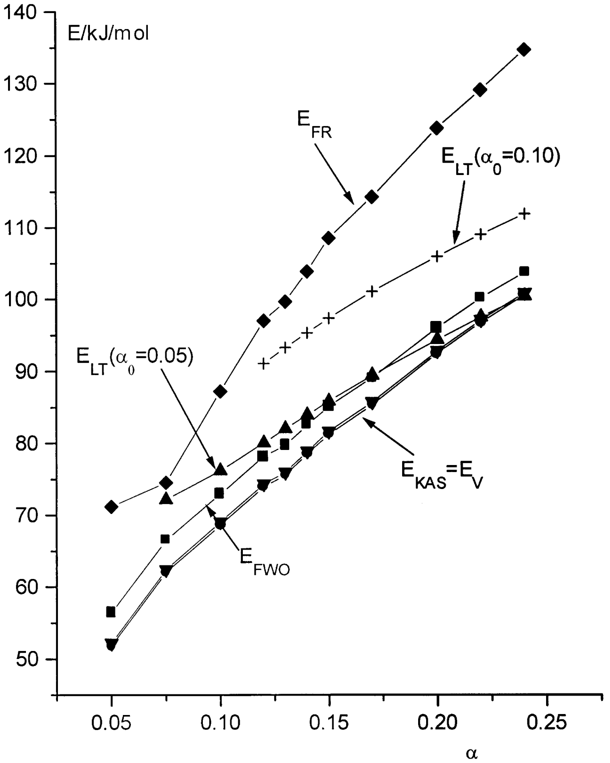

Fig. 1. Dependence of the activation energy evaluated by means of isoconversional methods on the conversion degree for thermal degradation of PCL-R.

Eq. (15) is similar to Eq. (2) obtained for accelerated isothermal aging of PCL-R. It follows that, in this case, a relation between α and $(\varepsilon/\varepsilon_0)$ exists and, consequently, the quasichemical approximation is valid.

4. Conclusions

1. Results relating to the kinetic interpretation of the non-isothermal curves of the mass loss and of the thermal accelerated aging of GRER and PCL-R were presented.

2. The kinetic analysis of non-isothermal data obtained for GRER and PCL-R suggests the necessity to record the $\alpha=\alpha(T)$ curves for several heating rates. This analysis must begin with establishing the dependence of E on α, using isoconversional methods, which do not need a knowledge the kinetic model. If E does not depend on α, either in its whole range of variation, or in the initial portion, the application of IKP method leads to the same activation energy value as that obtained by isoconversional methods. If E depends on α, it means that the investigated change is complex and the IKP method cannot be applied.

3. For GRER, it has been shown that, for non-isothermal degradation, the activation energy evaluated by all considered isoconversional methods is practically constant in the range $0.05\leqslant\alpha\leqslant0.40$. The use of IKP method for this range leads to an appropriate value of the invariant activation energy. The values of the activation energy obtained from non-isothermal data are close to that corresponding to the thermal degradation of the flexural strength.

4. For PCL-R, it has been shown that, for non-isothermal degradation, the apparent activation energy increases with conversion. A similar change of the apparent activation energy with values in the same range was found for the isothermal accelerated aging of the residual deformation under constant deflection.

5. These results are arguments for the quasichemical approximation according to which the degradation of a mechanical property of a polymeric material is due to a chemical reaction that can be described by equations from chemical kinetics. In the particular case of GRER, in which E is constant in the range $0.05\leqslant\alpha\leqslant0.40$, the value of the activation energy obtained from non-isothermal data can be used for rapid prediction of the thermal lifetime.

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