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KINETICS OF THE COMPLEX PROCESS OF THERMO-OXIDATIVE DEGRADATION OF POLY(VINYL ALCOHOL)

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The thermo-oxidative degradation of poly(vinyl alcohol) (PVA) has been investigated by TG+DTG+DTA simultaneous analysis performed in static air atmosphere, at four heating rates, namely 3, 5, 10 and 15 K $\min^{-1}$. TG, DTG and DTA curves showed that, in the temperature range 25–700°C, four successive processes occur. The first process consisting in the loss of physical adsorbed water is followed by three processes of thermal and/or thermo-oxidative degradations. The processing of the non-isothermal data corresponding to the second process (the first process of thermo-oxidation) was performed by using Netzsch Thermokinetics – A Software Module for Kinetic Analysis.

The dependence of the activation energy evaluated by Friedman's isoconversional method on the conversion degree shows that the investigated process is complex one. The mechanism of this process and the corresponding kinetic parameters were determined by Multivariate Non-linear Regression Program and checked for quasi-isothermal experimental data. It was pointed out that the first process of thermo-oxidation of PVA consists in three consecutive steps having Avrami–Erofeev kinetic model. The obtained results can be used for prediction of the thermal lifetime of PVA corresponding to a certain temperature of use and an endpoint criterion.

Keywords: *non-isothermal kinetics, poly(vinyl alcohol) (PVA), thermo-oxidative degradation*

Introduction

Poly(vinyl alcohol) (PVA) is a polymer of great interest because of many desirable characteristics (excellent film forming, emulsifying and adhesive properties, resistant to oil and grease, odorless, nontoxic) specifically for various applications (adhesive and thickener material in latex paints, paper coatings, hair sprays, shampoos, glues, carbon dioxide barrier in PET bottles, pharmaceutical and biomedical applications, etc.). Therefore, the properties of PVA and some materials containing this polymer were determined by different methods. Thermal analysis methods (TG, DTG, DTA and DSC) were used for investigation of the thermal and thermo-oxidative stabilities of some sorts of PVA [1–4]. It was pointed out [1–4] that at the progressive heating of PVA in inert atmosphere or in oxidative atmosphere, three or four (depending on both the sort of PVA and atmosphere) complex processes occur successively.

The aim of this paper has been the investigation of the thermo-oxidative destruction of PVA by simultaneous TG+DTG+DTA analysis, and the use of non-isothermal data for evaluation of the kinetic parameters of the first complex process of oxidation put in evidence in thermal curves recorded at several heating rates. Based on the obtained results, a criterion for correct determination of the kinetic parameters characteristic for a complex process consisting in two or more steps will be suggested.

Experimental

Material

The thermal behaviour of pure PVA with $65000 \leq M \leq 87000$, produced by LOBA, was investigated.

Methods

Thermal analysis

The heating curves (TG, DTG and DTA) of PVA were simultaneously recorded with STA 490C apparatus produced by Netzsch–Germany, in static air atmosphere, in the temperature range 25–900°C, and at the following heating rates: 3, 5, 10 and 15 K $\min^{-1}$.

In order to check the mechanism and corresponding kinetic parameters resulting from non-isothermal data, the thermal analysis of PVA was also performed in static air atmosphere and the following temperature program (quasi-isothermal program for T=230°C):

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$$25^\circ\mathrm{C} \xrightarrow{5.1\,\mathrm{K\,min^{-1}}} 190.6^\circ\mathrm{C} \xrightarrow{-0.676\,\mathrm{K\,min^{-1}}} 182.2^\circ\mathrm{C} \xrightarrow{1.86\,\mathrm{K\,min^{-1}}} 233.3^\circ\mathrm{C} \xrightarrow{-0.12\,\mathrm{K\,min^{-1}}}$$

$$230^\circ\mathrm{C} \xrightarrow{330\,\mathrm{min}} 230^\circ\mathrm{C}$$

Processing of the experimental data

'Netzsch Thermokinetics – A Software Module for the Kinetic Analysis of Thermal Measurements' was used for processing of non-isothermal data. The basic concepts of this program have been given in [5].

The isoconversional differential method suggested by Friedman [6] (FR method) and the isoconversional integral method suggested independently by Ozawa [7] and by Flynn and Wall [8] (OFW method) were applied for evaluation of the dependence of the activation energy on the conversion degree.

The complex mechanism of the investigated process and the corresponding kinetic parameters were evaluated using 'Multivariate Non-linear Regression' program.

Results and discussion

Figure 1 shows the TG, DTG and DTA curves for PVA, recorded at 10 K min^{-1}; similar curves were obtained for all heating rates. The thermo-oxidation of PVA occurs through four successive processes with formation of volatile compounds. The first process in endothermic, and consists in the loss of physical absorbed water. This process is followed by three complex processes consisting in [4]:

- process II: partial dehydration of PVA accompanied by polyene formation;
- process III: polyene decomposition in the α position at the tertiary carbon atom to form macroradicals, the destruction of the macroradicals yielding low-mass oxygen-containing products such as acetaldehyde, benzaldehyde, acrolein, and the decomposition of polyene macroradicals to *cis* and *trans* derivates; the latter form polyconjugated aromatic structures as a result of intramolecular cyclization and condensation;
- process IV: thermo-oxidation of carbonized residue.

The results obtained in quasi-isothermal experiment are shown in Fig. 2.

The kinetic analysis was performed for the first process of thermo-oxidation (process II). Figure 3 shows the normalized TG curves corresponding to this process.

Model-free estimation of the activation energy according to Friedman and Ozawa–Flynn–Wall methods

The results obtained by applications of FR and OFW methods are presented in Fig. 4.

As one can see the activation energy (E) increases with the conversion degree (α) no matter the method of evaluation. For a given value of α, E evaluated by FR method (E_{FR}) is higher than E evaluated by OFW method (E_{OFW}). This statement is

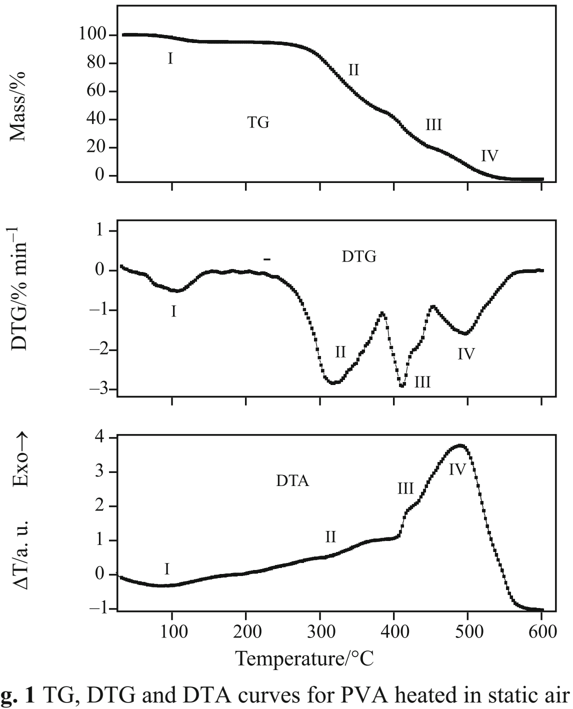

Fig. 1 TG, DTG and DTA curves for PVA heated in static air atmosphere, at the heating rate of 10 K min^{-1}

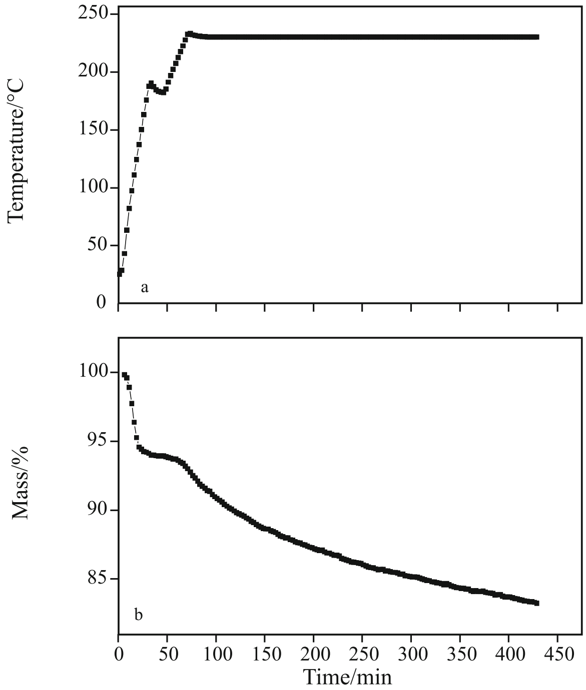

Fig. 2 a – Temperature program and b – TG curve for the quasi-isothermal experiment

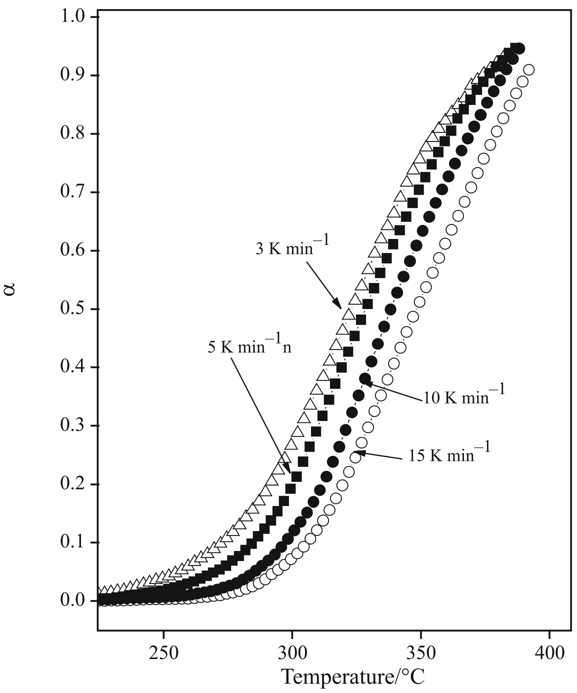

Fig. 3 Normalized TG curves for the first process of thermo-oxidation (process II)

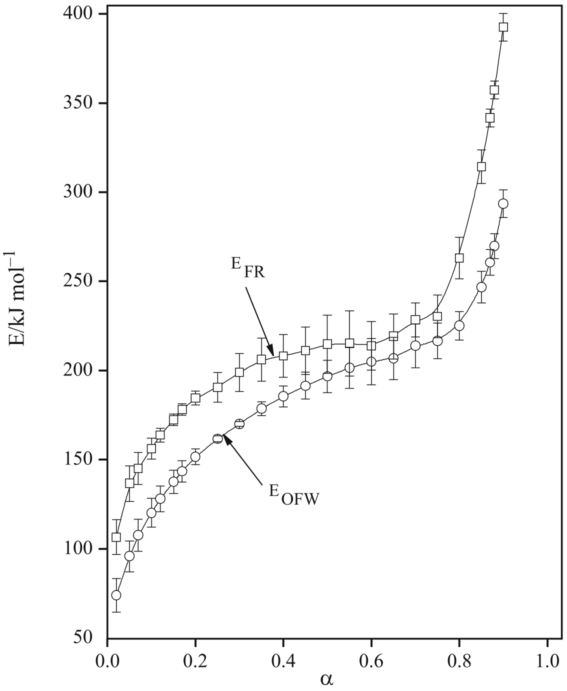

Fig. 4 Dependence of the activation energy evaluated by means of isoconversional methods on the conversion degree, for process II of thermo-oxidation of PVA

explained by the relations that ground the isoconversional methods [9, 10]. The differential FR method uses the point values of the overall rate, while the integral OFW method uses 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 and a certain conversion degree, E_{FR} is higher than E_{OFW}, and for decrease of E with α, $E_{FR}<E_{OFW}$.

Modeling as a single step and multi-step reaction

The dependence of E on α shows that the process II is complex one. Vyazovkin and Lesnikovich [11] suggested that the shape of E *vs.* α curve could be associated with the mechanism of the investigated complex process. However, for very complex processes consisting in more than two steps, there is very difficult to make such correlations. In order to find the mechanism of the process II and the corresponding kinetic parameters, we have been used ‘Netzsch Thermokinetics’ program. The non-isothermal data recorded at the four mentioned heating rates were processed, and some statistical criteria, especially F-test, were applied in order to provide the kinetic scheme and the corresponding kinetic triplets. In principle, this program should be applied for the data recorded at a single heating rate, but the obtained results should be irrelevant because the model-fitting methods that use a single heating rate tend to produce high ambiguous kinetic descriptions. The first demonstration that a single α *vs.* T curve does not allow to discriminate the kinetic model was published by Criado and Morales [12, 13]. Similar conclusion has been found for a large number of authors (some very recent results are given in [14–22]).

The following models (mechanisms) of process II were taken into account:

- model coded by s: A→B
- model coded by t:f,f: A–1→B–2→C–3→D
- model coded by q:f,f,f: A–1→B–2→C; A–3→D–4→E
  A–1→B–2→C
- model coded by q:c,f,c: A–3→D–4→E

the codifications are those used in ‘Netzsch Thermokinetics’ program; A, B, C, D and E are solid compounds; 1; 2; 3; 4 denote the mechanism steps.

For a single step, one of the following two differential conversion functions (kinetic models) was assumed:

- reaction order model, F_n: $f(\alpha)=(1-\alpha)^n$ (n is the reaction rate);
- Avrami–Erofeev model, A_n: $f(\alpha)=n(1-\alpha)[-\ln(1-\alpha)]^{(1-1/n)}$ (n is a constant parameter).

Table 1 lists some of obtained results. The best fit quality, resulted by running of experimental data for $0.02\leq\alpha\leq0.90$, corresponds to the mechanism coded by q:c,f,c (the kinetic triplets are given in Table 2). For this mechanism, the experimental TG

Table 1 F-test for differentiation of the fit quality between some models

No.	Model code	F_{exp}	F_{crit} (0.95)	f-act	Type 1	Type 2	Type 3	Type 4
1	q:c,f,c	1.00	1.29	169	An	An	An	Fn
2	t:f,f	3.04	1.29	175	An	An	An	
3	q:f,f,f	3.99	1.29	170	An	Fn	An	Fn
4	t:f,f	7.06	1.29	175	An	Fn	An	
5	s	13.56	1.29	178	Fn			

Table 2 Non-isothermal kinetic parameters after non-linear regression through the four-step model q:c,f,c and the reaction types An,An,An,Fn

Reaction	Kinetic model	Parameter	Value
1	An	$\log A_1$/s^{-1}	5.00
		E_1/kJ mol^{-1}	85.00
		n_1	1.13
2	An	$\log A_2$/s^{-1}	31.94
		E_2/kJ mol^{-1}	395.50
		n_2	0.37
3	An	$\log A_3$/s^{-1}	6.83
		E_3/kJ mol^{-1}	103.54
		n_3	2.41
4	Fn	$\log A_4$/s^{-1}	31.45
		E_4/kJ mol^{-1}	400.00
		n_4	2.00
		Comp. Tot A>C	1.229
		FollReact.1	0.224
		Comp. Tot A>E	0.687
		FollReact.3	0.133
		Mass loss 1%	0.9300
		Mass loss 2%	0.9470
		Mass loss 3%	0.9458
		Mass loss 4%	0.9097

points lie practically on the regenerated curves (Fig. 5).

The kinetic data listed in Table 2 were also used for calculation of TG curve corresponding to the temperature program in which the quasi-isothermal experiment was performed (Fig. 2). The obtained results are in disagreement with experimental ones (Fig. 6). On the other hand, the isothermal data were calculated using data listed in Table 2, for temperatures 240, 250, 260, 270, 280 and 290°C, and the dependence E_{iso} (E obtained by isoconversional differential metod applied for isothermal data) *vs.* α was determined. As one can see in Fig. 7, for a given conversion degree, E_{iso} and E_{FR} (evaluated from non-isothermal data) have different values. These results show that the mechanism q:c,f,c with the parameters from Table 2 cannot be used for prediction of the thermal behaviour of the investigated system in other conditions than those in which the experiments were performed.

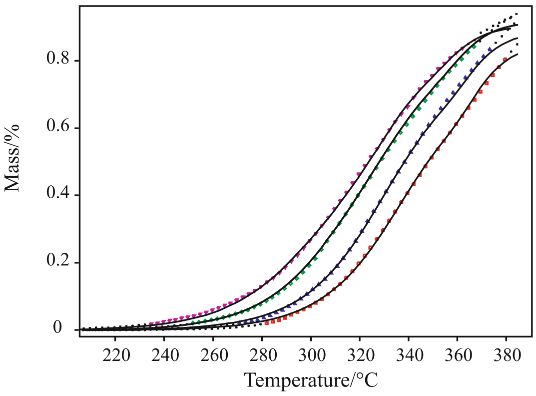

Fig. 5 Fit of the measurements through four-step model q:c,f,c

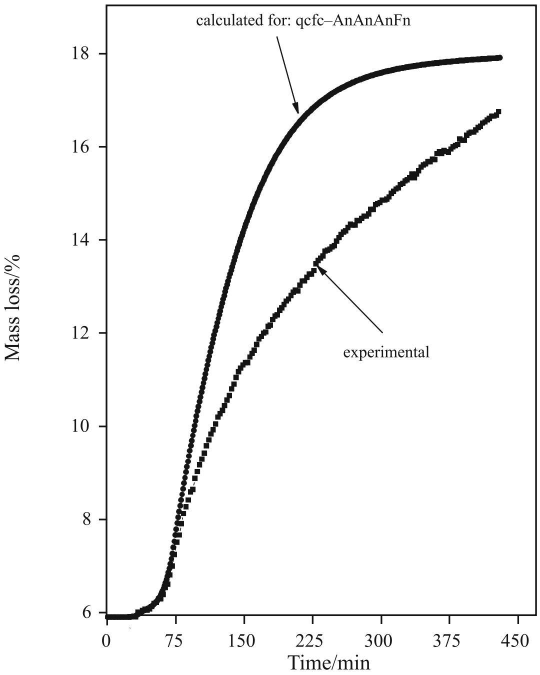

Fig. 6 Calculated (q:c,f,c model) and experimental TG curve for quasi-isothermal data

Therefore, in the following, the second mechanism in the order of F-test quality (t:f,f – A_n, A_n, A_n) will be considered. The corresponding kinetic parameters are listed in Table 3. Applying the same procedure with that are for q:c,f,c mechanism, the results showed in Figs 8–10 are obtained. One can note a good agreement between:

- experimental values of the mass loss in quasi-isothermal condition and those calculated for the same temperature program, using kinetic parameters listed in Table 3;
- values of *E* obtained by differential method from experimental non-isothermal data (E_{FR}) and those obtained isothermal data calculated using the kinetic parameters from Table 3.

These results show that the mechanism t:f,f, with F-test quality lower than mechanism q:c,f,c, can be used for a satisfactory prediction of the thermal behaviour in isothermal and non-isothermal conditions. Thus, using only non-isothermal data and applying a statistical criterion one cannot determine the real mechanism of a complex process. As was firstly pointed out by Criado, Morales and Rives [23], this statement is true even if a single process is involved. However, our results show that a good agreement between experimental quasi-isothermal data and those calculated using the kinetic parameters evaluated from no *n*-isothermal data occurs when there is a good agreement between $E=E(\alpha)$ obtained from non-isothermal experimental data (E_{FR}) and from isothermal data calculated using non-isothermal kinetic parameters (E_{iso}). This agreement associated with a statistical criterion could be a procedure for correct determination of the mechanism and corresponding kinetic parameters of a complex heterogeneous process.

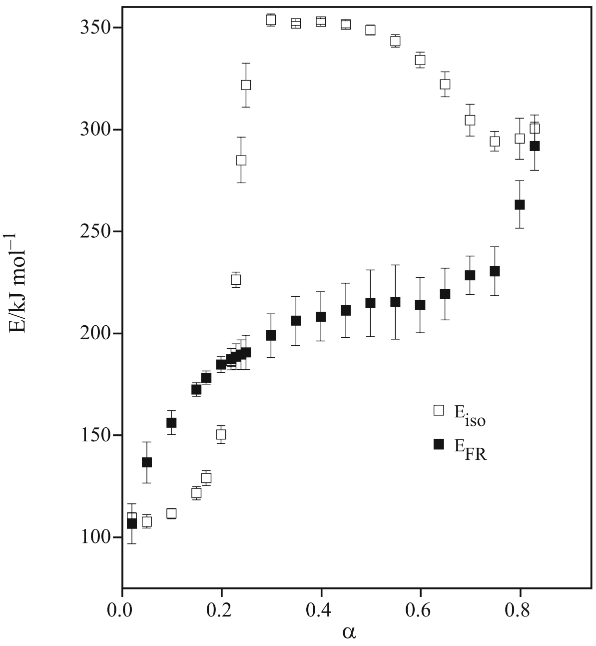

Fig. 7 Comparison between the values of *E* obtained by differential method from experimental non-isothermal data (E_{FR}) and isothermal data calculated using the kinetic parameters from Table 2 (E_{iso}) (T=240, 250, 260, 270, 280, 290°C)

Table 3 Non-isothermal kinetic parameters after non-linear regression through the three-step model t:f,f and the reaction types An,An,An

Reaction	Kinetic model	Parameter	Value
		$\log A_1$/s^{-1}	7.35
1	An	E_1/kJ mol^{-1}	106.60
		n_1	1.24
		$\log A_2$/s^{-1}	14.28
2	An	E_2/kJ mol^{-1}	200.00
		n_2	0.87
		$\log A_3$/s^{-1}	33.48
3	An	E_3/kJ mol^{-1}	400.00
		n_3	0.08
		FollReact.1	0.100
		FollReact.2	0.600
		Mass loss 1%	0.9300
		Mass loss 2%	0.9470
		Mass loss 3%	0.9458
		Mass loss 4%	0.9097

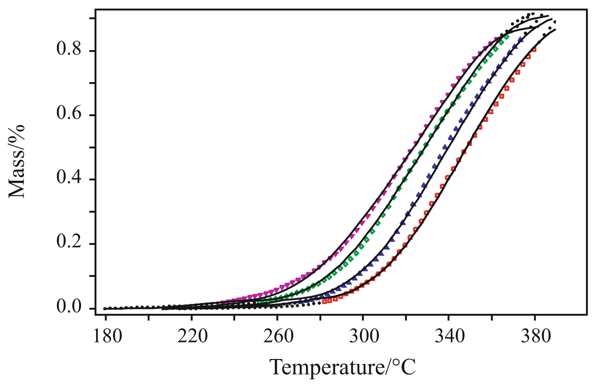

Fig. 8 Fit of the measurements through three-step model t:f,f

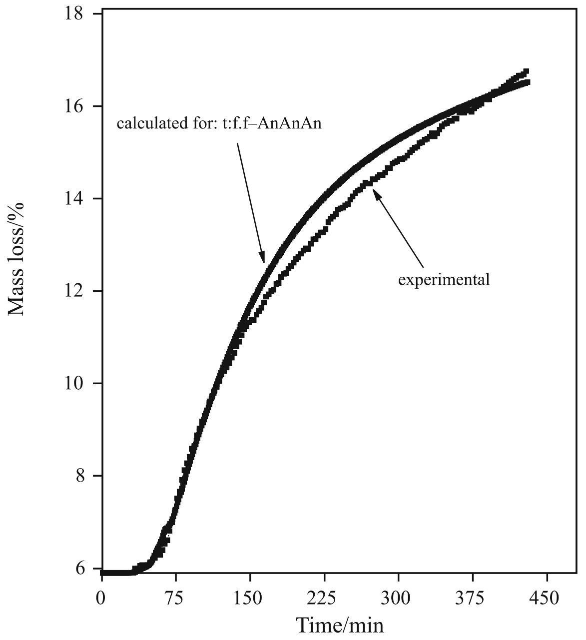

Fig. 9 Calculated (t:f,f model) and experimental TG curve for quasi-isothermal data

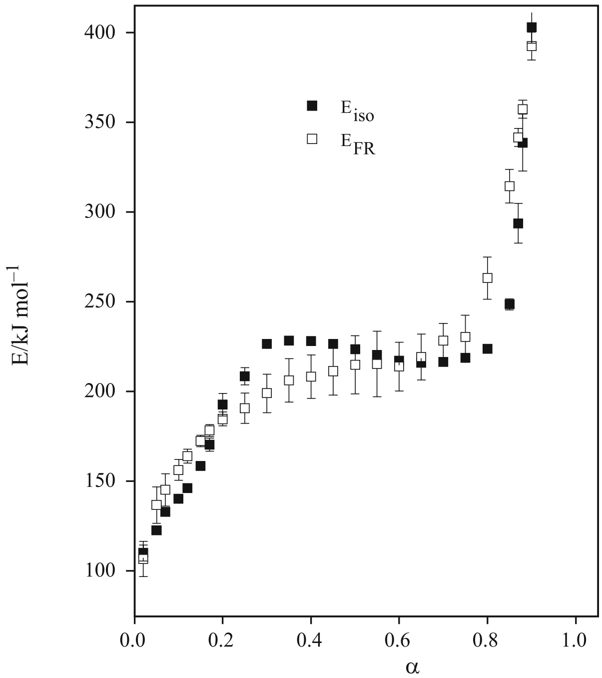

Fig. 10 Comparison between the values of E obtained by differential method from experimental non-isothermal data (E_{FR}) and isothermal data calculated using the kinetic parameters from Table 3 (E_{iso}) (T=230, 240, 250, 260, 270, 280, 290°C)

Conclusions

- By thermal analyses (TG, DTG and DTA), it was obtained that four successive processes occur at the progressive heating in air of PVA.
- The kinetic analysis of the first process of thermo-oxidation was performed by isoconversional methods and a non-linear regression program.
- The correctness of the mechanism and their corresponding kinetic parameters were checked by comparing the calculated and experimental curves for quasi-isothermal data.
- It was pointed out that some mechanisms of the complex analyzed process may relatively corectly describe the α=α(T) curves recorded at several heating rates. Consequently, in such cases, the best fitting of the experimental data, which are affected by experimental errors, cannot be rigorously applied for finding the real mechanism of a complex process.
- A new procedure for correct determination of the mechanism and the corresponding kinetic parameters of a complex process only from non-isothermal data has been suggested.

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