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THERMOGRAVIMETRIC STUDY OF TETRAFUNCTIONAL PHENOL NOVOLAC EPOXY MIXTURES CURED WITH A DIAMINE*

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One of the problems met last time in the field of non-isothermal kinetics consists in the apparently unusual dependence of the activation parameters on the degree of conversion α. Such a dependence has been put in evidence in many cases [1–9], the activation parameters (the pre-exponential factor (A) and the activation energy (E)) being correlated through the compensation effect relation:

$$\ln A=a+bE \tag{1}$$

where a and b are constant coefficients.

Under such conditions, one has to be very careful when choosing an appropriate procedure to estimate the values of the kinetic parameters. Such thoughts described in the paper of a group of Spanish researchers have inspired paper [10]. Some comments concerning the mentioned paper are going to be presented in the following.

1. The authors applied the Flynn–Wall–Ozawa method [11, 12] for the values of the conversion degree located in the range $0.05<\alpha<0.20$. As shown in Table 1 of the commented paper [10], the E values increase from 140.4 to 167.6 kJ mol^{-1}. The authors mention neither the standard deviations of E values nor the correlation coefficient values of the linear regressions $\log q$ *vs.* $(1/T)$ (q is the heating rate and T is the temperature). For $\alpha=0.20$, the E value is by 19.4% higher than for $\alpha=0.05$. In a recent paper [13], Flynn noticed that some dependencies of E on α could be assigned to the use of Doyle's approximation [14] for $E/RT>20$ which leads to the relation:

$$\log q=\log\frac{AE}{g(\alpha)R}-2.315-0.457\frac{E}{RT} \tag{2}$$

where $g(\alpha)$ is the integral conversion function.

Flynn [13] considers that the factor 0.457 depends on (E/RT) value. Nevertheless, a difference of 19.4% between E value for $\alpha=0.20$ and E value for $\alpha=0.05$ can-

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[*] Comments on the paper by L. Barral, J. Cano, J. Lopez-Bueno, P. Nogueira, C. Ramirez and M. J. Abad, J. Therm. Anal. Cal., 51 (1998) 489.

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not be removed through the change of this factor. As a matter of fact, as seen in Fig. 7 [10], for the isothermal degradation too, E depends on α.

In a recent previous paper [15] we showed if E depends on α, the integration of the equation:

$$q\frac{\mathrm{d}\alpha}{\mathrm{d}T}=Af(\alpha)\exp\left(-\frac{E}{RT}\right) \tag{3}$$

cannot be performed by the separation of a temperature integral and a conversion integral. Under such conditions the use of Friedman's method [16], which does not require the integration of Eq. (3), is recommended.

A dependence of E on α shows either a complex thermal degradation process (parallel or/and consecutive reactions) or the existence of a process with a compensation effect characterized by the relationship (1). From the data listed in Table 1 [10] it is difficult to conclude which out of the mentioned factors is actually responsible for the dependence of E on α.

2. The authors [10] used other integral methods (Coats and Redfern [17] Horowitz and Metzger [18] and van Krevelen *et al.* [19]). Their proper use supposes that the thermal degradation of the investigated material is described kinetically only by one conversion function, (Table 2 [10] shows the expression considered for $g(\alpha)=\int_0^\alpha\frac{\mathrm{d}\alpha}{f(\alpha)}$). The authors [10] do not explain why only experimental data in the range of conversion $0.05<\alpha<0.20$ were considered. Generally, the integral methods are applied for much larger range of α values. Besides, the authors give neither the values of the pre-exponential factor nor the correlation factor for the linear regressions. The use of the integral methods requires the integration of the rate equation. Such an operation cannot be performed for $E=E(\alpha)$.

As seen from Table 3 [10], E values are strongly dependent on the heating rate. The reason for such a dependence consists probably in the complex character of the thermal degradation process. Through the analysis of some curves simulated for a system in which two parallel reactions occur [20], we showed that the apparent activation parameters, evaluated in the hypothesis that the process could be described by a single overall reaction, depend on q and, consequently, on temperature.

3. The analysis of the thermal degradation data has been performed [10] considering the integral form of the equation:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=Af(\alpha)\exp\left(-\frac{E}{RT}\right) \tag{4}$$

Considering that E and A do not depend on α, it was obtained [10]:

$$\ln t=\ln\left(\frac{g(\alpha)}{A}\right)+\frac{E}{RT} \tag{5}$$

As one can see in Fig. 7 [10], the straight lines ln$t$ *vs*. $(1/T)$ for α=const., are not parallel. Thus even for the isothermal degradation $E=E(\alpha)$, although the authors [10] consider only the average value of E. In this case the integration of the rate equation is not correctly performed. Under such conditions (dependence of the activation parameters on α), in order to evaluate the kinetic parameters, the differential method, which result directly from the relationship (4) in its logarithmic form, should be recommended.

4. Finally, in order to estimate the half-life using the relation:

$$g(\alpha)=\int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)}=k(T)t \tag{6}$$

($k/(T)$ is the rate constant) considering that the investigated system obeys a first order degradation mechanism, the authors [10] do not mention the used values of the activation parameters.

In order to conclude our criticism we list some suggestions which could be of some help for the authors:

1. For activation parameters which depend on the degree of conversion, in order to determine their values, the differential methods (like Friedman's method [16]) should be used.
2. It would be interesting to compare the curves $E=E(\alpha)$ obtained under isothermal as well as non-isothermal conditions.
3. It is necessary to evaluate the pre-exponential factor for various forms of $f(\alpha)$ and for each kinetic model to verify the existence of the compensation effect.
4. Finally, it would be interesting to compare the values of the compensation effect parameters obtained under isothermal as well as non-isothermal conditions.

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