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Theory and practice in the thermoanalytical kinetics of complex processes: Application for the isothermal and non-isothermal thermal degradation of HDPE

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ABSTRACT

The criterion according to which the best mechanism of a complex process and the associated kinetic parameters correspond to the best fitting of TG and DTG curves recorded at several heating rates is discussed. The main problem is if the application of such a criterion for a complex process will lead to the mechanism and corresponding kinetic parameters to be used for predictions. To this end, the thermal degradation of HDPE has been investigated by TG/DTG + DSC simultaneous analysis performed in Ar flow, at five heating rates as well as in four quasi-isothermal conditions. An algorithm for correct determination of the mechanism and the corresponding kinetic parameters of a complex process from non-isothermal and quasi-isothermal data was suggested.

1. Introduction

Experimental data for kinetic analysis of heterogeneous reactions are often obtained in non-isothermal conditions, under linear temperature increase conditions over time ($\beta = \mathrm{d}T/\mathrm{d}t = \text{const.}$, where β is the heating rate, T is the temperature and t is the time). Under such conditions, the assessing methods for kinetic parameters in a single step reaction are based on the rate equation [1]:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \beta\frac{\mathrm{d}\alpha}{\mathrm{d}T} = Af(\alpha)\exp\left(-\frac{E}{RT}\right) \tag{1}$$

or its integral form:

$$g(\alpha) \equiv \int_0^{\alpha} \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{A}{\beta}\int_0^{T}\left[\exp\left(-\frac{E}{RT}\right)\right]\mathrm{d}T \tag{2}$$

where α is the conversion degree, A—the pre-exponential factor, E—the activation energy, $f(\alpha)$—the differential conversion function, $g(\alpha)$—the integral conversion function, and R—the gas constant.

According to the above equations, a kinetic triplet (E, A, $f(\alpha)$ or $g(\alpha)$) describes the progress of a physical or chemical change over time. Obviously, a complex process is described properly by a set of kinetic triplets.

The correct determination of non-isothermal kinetic parameters involves the use of experimental data recorded at several heating rates, as has resulted from some relative critical analyses of the assessing methods for the kinetic parameters from non-isothermal data [2–18].

The following software packages only available for commercial use were drawn up particularly for kinetic analysis of non-isothermal data corresponding to a complex process: TA-KIN for Windows v. 1.6 (Anderson et al.) [19]; NETZSCH Thermokinetics software (Opfermann) [20]; KINETICS for Windows 95/98/NT (Burnham and Braun) [21]; ATKS for Windows 95-98 (Roduit) [22]. The best lie of TG, DTG, DTA or DSC experimental points on the corresponding calculated curves corresponds to the true mechanism and kinetic triplets. The accuracy of such procedures will be critically analyzed in the present paper. To this end, the kinetic analysis of the experimental non-isothermal and quasi-isothermal data corresponding to the complex process of thermal degradation of a sort of ultra high density polyethylene (HDPE) was performed. Based on the obtained results, the "algorithm for the kinetic parameter assessment from the non-isothermal data" suggested in a previous paper [13] is to be completed with a final step that will have to be performed at the kinetic analysis of a complex process.

2. Some remarks on the kinetic analysis of non-isothermal data

Criado and Morales [23,24] pointed out that a single α vs. T curve recorded at a certain heating rate can be satisfactory described by some different kinetic triplets. The inherent experimental errors determine the impossibility to discriminate the correct kinetic triplet by applying a statistical criterion. This state-

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ment has led to the main conclusion from some recent papers [2–18], especially of ICTAC 2000 Project [3] and the Workshop at ICTAC 13 [15], according to which the correct kinetic analysis of non-isothermal data corresponding to a heterogeneous process can be only performed by making use of the experimental data recorded at several heating rates. These data have allowed to apply the model-free methods in assessing the activation energy dependence on the conversion degree, that can be correlated with the investigated process mechanism. Therefore, the kinetic analysis of the non-isothermal data is to be started with the application of model-free methods, the most used being those suggested by Friedman [25] (FR method) and Ozawa, Flynn and Wall [26,27] (OFW method). There are the following two cases: (1) E is independent on α; (2) E values are changed with α.

In the first case, with high probability, the investigated process is simple and it is described from the kinetic point of view by a unique kinetic triplet. In such a case, among the procedures for $f(\alpha)$ or $g(\alpha)$ (kinetic model) asssessment from a pre-established set [28–41], we have focused ourselves to the DTG fitting method [34,38,39], as according to it the true values of kinetic parameters correspond to the best lie of DTG experimental points on the calculated DTG curves. The correlations between the shape parameters of DTG curves and the expression of $f(\alpha)$ pointed out by Dollimore et al. [32,33] have supported this criterion. Obviously, checking such a criterion involves a good agreement of experimental and calculated TG curves. The DTG curve shape is revealed to be more sensitive with the kinetic model and therefore, in some cases, a satisfactory agreement of the experimental and calculated TG curves has not always involved the check of the DTG curve fitting criterion.

In the second case (E values are changed with α), the investigated process is complex (successive, parallel, reversible reactions), and, consequently, it is described by a set of kinetic triplets. In such a case, the differential isoconversional FR method based on the logarithmic form of Eq. (1) is recommended as the results obtained by integral isoconversional OFW method are dependent on the history of the system in the 0–α range [42]. The isoconversional methods are revealed to be based on Eqs. (1) and (2), which are forced applied for a complex process, and, therefore, in the cases of very complex processes, a high scattering of the E values assessed by an isoconversional method has been revealed [43,44].

For a complete kinetic description of the investigated process, all members of a kinetic triplet for a single step process or triplets for a multi-steps process should be determined. The final test of every kinetic analysis should involve the parameter determination to construct the calculated curves for comparison with the experimental results over a wide and representative range [15]. Some procedures for the kinetic parameter assessment from non-isothermal data, like the above mentioned software packages [19–22] and DTG fitting method [34,38,39] are based on this last necessary condition.

The application of isoconversional methods allows the direct determination of the activation energy but not the whole kinetic triplet. According to the relationships underlying the linear isoconversional methods, the pre-exponential factor could be only assessed by choosing the reaction model. For the single step process, Vyazovkin [45] has suggested an original procedure for assessing the pre-exponential factor and reaction model based on the data obtained by an isoconversional method and the apparent compensation effect (linear relationship between $\ln A$ and E) due to the analytical form of the conversion function.

For a complex process (consecutive, parallel and/or reversible reactions), the TG and DTG experimental points are expected to have a satisfactory lying-out around corresponding to the calculated curves for some different mechanisms and kinetic triplets. Therefore, there are doubts on the results obtained by above mentioned software packages [19–22] applied in the kinetic analysis of complex processes. Such a case was revealed in a recent paper [46] dealing with the kinetic analysis of the poly(vinyl alcohol) thermo-oxidation. In such a case, the spreading of experimental data resulting from quasi-isothermal experiment on the calculated curve was obtained for the second mechanism in the order of decreasing of the first F-test on fit-quality for non-isothermal TG data. As in the cases of the single step processes, the mechanism and corresponding kinetic parameters of a complex process have resulted not to be assessed accurately from the non-isothermal data when applying a statistical criterion. This statement could be explained by the impossibility of the rigorous application of the statistical tests to TG and DTG experimental data because of the inherent measurement errors. Other reasons could be the relative high number of adjustable kinetic parameters characteristic for a complex process, the compensation effect between the activation parameters and the fact that the formal kinetic models in the considered set are too simple to account for all features of the actual process.

The application of the non-isothermal techniques, such as TG, DTA and DSC, for rapid prediction of thermal lifetime requires extrapolation of the test results over a large temperature range. Consequently, it appears the question if there is a similar degradation mechanism in both non-isothermal and isothermal conditions. This problem could be solved by comparing the activation energy values obtained by isoconversional (model-free) methods for non-isothermal data recorded at several heating rates and for isothermal data recorded at several temperatures.

According to the above mentioned software packages [19–22], the quick prediction of thermal lifetime outside the temperature range in experimental measurements requires the knowledge on the thermal degradation mechanism and the corresponding kinetic triplets. Another possibility for “isothermal predictions” from non-isothermal data was suggested by Vyazovkin [47,48] (“model-free prediction”), and it is based on the following equation:

$$t_\alpha = \frac{\int_0^{T_\alpha} [\exp(-(E/RT))]\, dT}{\beta \exp(-(E/RT_{iso}))} \quad (3)$$

where t_α is the time required to reach a given conversion (α) and T_{iso} is the isothermal simulation temperature.

The application of this method for a single step process only requires the activation energy value determined by an isoconversional method, and the use of $\alpha = \alpha(T)$ curve recorded at a given heating rate. The form of Eq. (3) was also modified to employ data from arbitrary heating programmes [47]. When E varies with α, the assumption of constant activation energy only for small segments leads to the following relation [49,50]:

$$t_\alpha = \frac{\sum_0^\alpha \int_{t_{\alpha-\Delta\alpha}}^{t_\alpha} [\exp(-(E_\alpha/RT))]dt}{\exp(-(E/RT_{iso}))} \quad (4)$$

The application of this last procedure for isothermal simulations raises the following problems: (a) the validity of integral rate Eq. (2) that grounds this method, even for a small segment of t or T; (b) the high scattering of E values determined by an isoconversional method, obtained for some complex processes [43,44].