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COMPUTER STUDY OF KINETIC PARAMETER VARIATION IN DEPOLYMERIZATION BY DIGITAL THERMOGRAVIMETRIC INTERPRETATION

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A method for determining the variation of the kinetic parameters A, E and n is proposed, and is exemplified by a study of PVC degradation, with the chlorine partially substituted by benzene. Because of the complexity of the method, a digital computer has been used.

As far back as in 1966, in a paper on the thermal degradation of polyformaldehyde [1], it was shown that the activation energy of a depolymerization process under non-isothermal conditions does not have a constant value, but depends on both the heating rate and the conversion degree. Subsequent researches [2] have demonstrated that the kinetic parameters (and especially the activation energy) of chain depolymerization and degradation or of other complex chemical processes, under non-isothermal conditions, always depend to some extent upon the conversion degree and the heating rate, these two factors being interdependent. The explanation of these dependences is found either in a change of the reaction mechanism of the rate-determining step during the process, or in the non-stationarity of the complex degradation process under non-isothermal conditions. Various computing methods have been suggested for evaluation of the activation energy dependence upon the conversion degree [3–5]. However, these methods more or less neglect possible variations in the other kinetic parameters, i.e. the pre-exponential factor and the reaction order. This stimulated the present study on changes in the kinetic parameters of complex chemical processes under non-isothermal conditions, by a simulating computation of the experimental DTG and TG curves.

First of all we tried to adjust an Arrhenius-type model by the least squares method to describe the overall development of a polymer degradation process, assuming initially that the kinetic parameters are constant. Starting from the simplest rate equation for solid – gas processes:

$$\frac{d\alpha}{dt} = A \cdot \exp(-E/RT) \cdot (1-\alpha)^n \tag{1}$$

we accepted a constant heating rate.

In the above relation

$$\alpha = 1 - \frac{W_t}{W_\infty}$$

is the conversion degree, W_t is the sample weight at a given moment, corrected for the residue weight, and W_∞ is the weight loss at the end of the process.

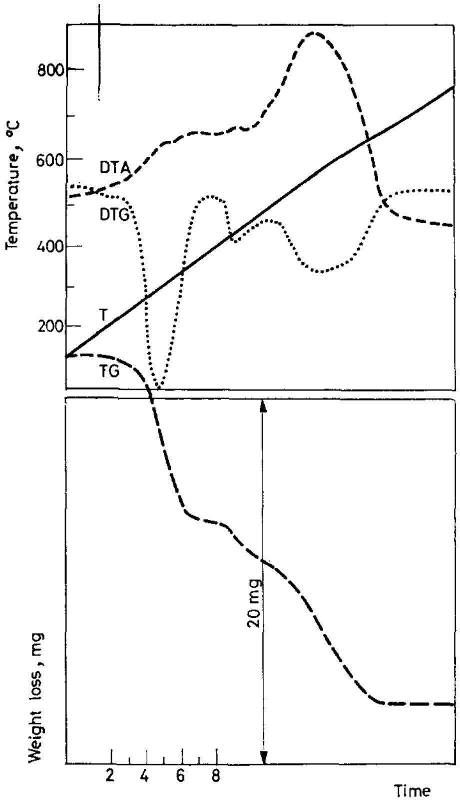

Fig. 1. Thermogravimetric curve of a PVC sample with the chlorine partially substituted by benzene

Experimental

The computations were done using thermogravimetric curves (recorded in air at a heating rate of 12.4 degree/min) relating to a PVC sample with the chlorine partially substituted by benzene by a Friedel-Crafts reaction. The chlorine content was 41.6%, as compared to on a MOM derivatograph (Hungary) is shown in Fig. 1.

Results

The values of the corresponding 20 experimental data, read off the recorded T (in K), TG and DTG curves used in the computational model, are shown in Table 1. The weights and the degradation rates were expressed simply in arbitrary units, due to the fact that the proposed model used the dimensionless conversion degree.

Table 1

Discrete experimental data obtained from the curves shown in Fig. 1

Exp. no.	T, K	W_t, mm (TG)	$-\mathrm{d}W_t/\mathrm{d}t$, mm (DTG)
1	519.7	85.0	12.0
2	526.3	84.0	17.0
3	533.1	81.5	26.0
4	539.7	78.0	37.0
5	546.4	73.0	59.0
6	553.1	67.5	76.0
7	559.7	60.0	93.0
8	566.3	53.0	105.0
9	573.1	45.0	109.0
10	579.5	37.5	105.0
11	586.1	30.0	99.0
12	593.1	23.0	89.0
12	599.7	17.0	80.0
14	606.3	11.0	66.0
15	613.1	7.0	51.0
16	619.5	4.3	41.5
17	626.1	2.5	31.5
18	633.1	0.1	21.0
19	638.8	0.1	11.0
20	644.5	0.1	7.3

The program used, based on the least squares method, gave the following values for the kinetic parameters: $A = 5.85 \cdot 10^7$, $E = 20.00$ kcal/mole, $n = 0.65$.

However, as may be seen from Fig. 2, the experimental and the calculated (using the obtained kinetic parameters) DTG curves do not coincide satisfactorily, one of the probable explanations being the variation of the kinetic parameters during the degradation process. Further no better results could be obtained by adjusting the Arrhenius model with exponential or logarithmic corrections.

With regard to these incongruities, a second Arrhenius-type model with temperature-dependent kinetic parameters was used

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A(T) \cdot \exp\left[-E(T)/RT\right] \cdot (1 - \alpha)^{n(T)}. \tag{2}$$

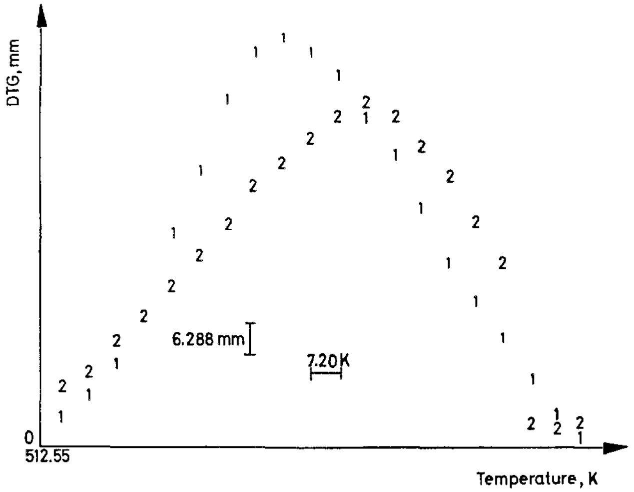

Fig. 2. Comparison between the experimental and the computed DTG curve based on model 1). 1 Experimental DTG curve; 2 DTG curve computed with constant kinetic parameters

This time the TG and DTG curves were also simulated by the least squares method, but on successive sections of 5 points, using the same experimental data as in the first case, the average value of the temperature in the respective interval being included in the obtained values of A, E and n. The correlation was the better, the smaller the temperature interval.

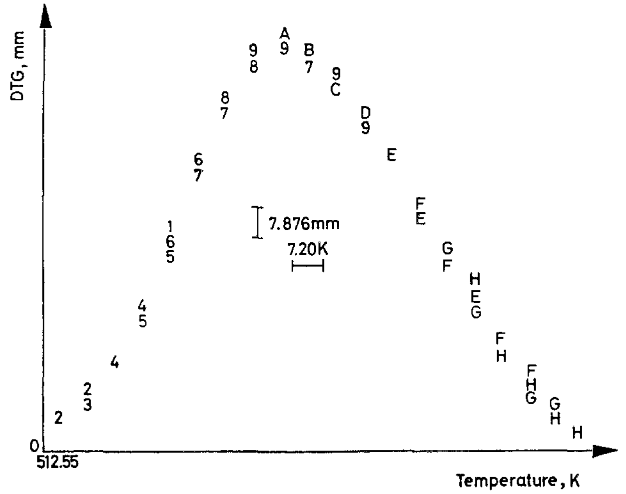

Fig. 3. Comparison between the experimental and the computed DTG curve based on model (2). 1 Experimental DTG curve; 2 DTG curve computed using points 1—5; 3 DTG curve computed using points 2—6; . . . . G DTG curve computed using points 15—19; H DTG curve computed using points 16—20

The results of this computation are presented in Figs 3 and 4. This same time the agreement is much better between the experimental DTG and TG curves and those simulated on the computer. The calculations on the graph were carried out on a Romanian digital computer Felix-C-256.

From Fig. 5 it follows that the kinetic parameters are significantly modified during the process, supporting the well-known compensation effect for simple chemical processes [6, 7] concerning the variation in the same sense of the E and A values.

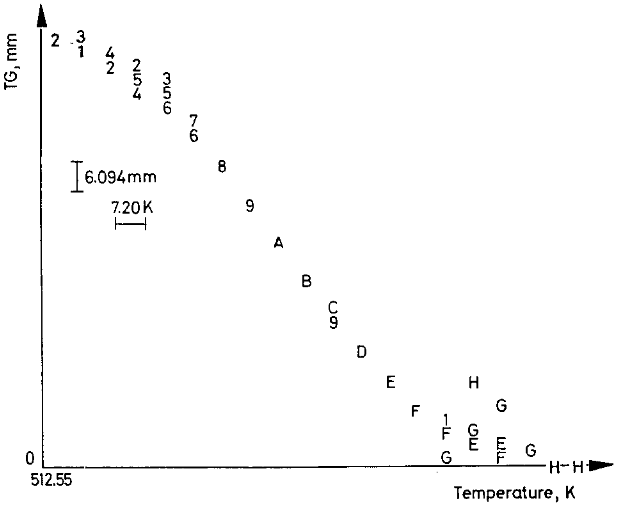

Fig. 4. Comparison between the experimental and the computed TG curve based on model (2) 1 Experimental TG curve; 2 TG curve computed using points 1—5; 3 TG curve computed using points 2—6; . . . .; G TG curve computed using points 15—19; H TG curve computed using points 16—20

In a previous paper, we reported the same dependence on the heating rate of the E and n values for paraformaldehyde depolymerization. This phenomenon was at that time explained by the expressions [8]:

$$E = n^{n/n-1} \cdot R \cdot T_{\max}^2 \cdot \left(\frac{d\alpha}{dt}\right)_{\max} \tag{3}$$

valid for $n > 0, n \neq 1$ and

$$E = n \cdot R \cdot T_{\max}^2 \cdot \left(\frac{d\alpha}{dt}\right)_{\max} \tag{3'}$$

valid for $n = 1$.

The observed variation of the kinetic parameters in the same direction seems to be an indirect function of the conversion degree.

A more careful analysis of these compensation effects would probably allow a deeper insight into the laws of complex degradation processes under non-isothermal

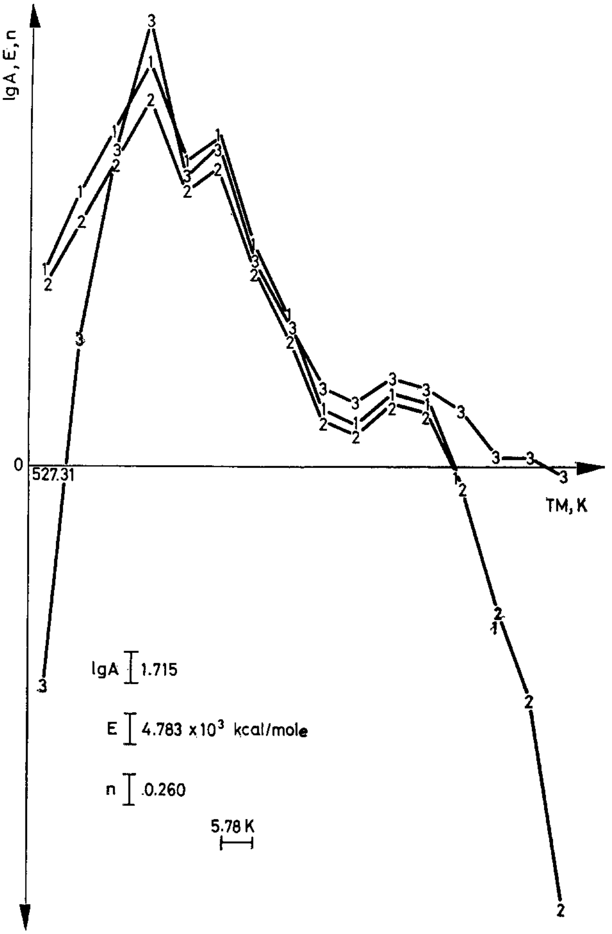

Fig. 5. Variation of kinetic parameters during the process 1 log $A_i=f(TM_i)$; 2 $E_i=g(TM_i)$; 3 $n_i = h(TM_i)$; (TM_i = average temperature in interval i; $i = \overline{1.16}$)

conditions. For the polymer studied in this paper, the increase of the activation energy at the beginning suggests a decisive modification with temperature rise, either of the initiation process or of the rate-determining step (which may also be a physical process) within some possible competitive processes.

As already shown [2], the subsequent decrease of the activation energy is characteristic of certain chain processes under non-isothermal conditions.

Finally, the proposed method for a detailed analysis of the thermogravimetric curves (especially the DTG curves) of complex chemical processes, enables us to confirm the assumed dependence of the kinetic parameters on the conversion degree and provides a better understanding of such processes.

Rereferences

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Zusammenfassung — Eine Methode zur Bestimmung der Variation in den kinetischen Parametern A, E und n wird vorgeschlagen und am Beispiel des Abbaus von PVC mit teilweise durch Benzol substituiertem Chlor veranschaulicht. Wegen der Komplexität der Methode wurde ein Digitalkomputer eingesetzt.

Резюме — Предложен метод определения изменений в кинетических параметрах A, E и n. Метод показан на примере изучения деградации поливинилхлорида, в котором хлор частично замещен бензольными кольцами. Была использована цифровая вычислительная машина, вследствии сложности метода.