Journal of Thermal Analysis, Vol. 33 (1988) 1135–1139

SOME ASPECTS OF THERMAL DESTRUCTION OF POLYURETHANES

Z. Pietrzyk, L. Kulesza and *M. Jasieniak*

INSTITUTE OF SANITARY ENGINEERING AND ENVIRONMENTAL PROTECTION, TECHNICAL UNIVERSITY OF CRACOW, KRAKÓW, POLAND

A number of polyurethane elastomers were investigated by means of non-isothermal thermogravimetry to set a general procedure for numerical estimation of kinetic parameters. The value of an assumed objective function, determining the accuracy of the estimation depends on many factors as: the considered region of a TG-curve, the method of choosing points from the curve, and the initial values of the pre-exponential factor and the reaction order. After the optimal conditions were evaluated, the minimum values of the objective function and the corresponding triplet values of kinetic parameters were obtained. Among these, only the activation energy can be considered as a semiquantitative estimate of thermal stability.

The study of reaction kinetics by thermal analysis is frequently undertaken. In the current work a number of polyurethane elastomers were investigated by means of non-isothermal thermogravimetry. The purpose of this study was to set some principles which should be taken into account in the estimation of kinetic parameters.

Experimental

The investigated polyurethanes were prepared by one-shot synthesis from tolylene diisocyanate (80% of 2,4-isomer + 20% of 2,6-isomer) and diols as follows: ethylene glycol (No.1), 1,4-butanediol (No.2), propylenediol (No.3) and polyoxyisopropylenediol (No.4).

The experiments were carried out in argon and air, respectively, at a heating rate of 5 deg min^{-1}. The experimental data were obtained by using a Mettler thermoanalyzer, model TA-2.

To obtain kinetic data (activation energy, pre-exponential factor reaction order) from the recorded curves, the well known kinetic equation:

$$\beta \cdot \frac{d\alpha}{dT} = A \cdot \exp(-E/RT) \cdot f(\alpha) \qquad (1)$$

was used as a basis for calculations, where:

β – the linear heating rate,

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

A – the pre-exponential factor,
E – the activation energy,
α – the fractional weight loss of the reacted material related to the total weight loss,
R – the gas constant,
T – the absolute temperature,
$f(\alpha)$ – the function of the weight loss.

The values of searched parameters were computed numerically by means of the fourth-order Runge-Kutta method of integration (MERSON). The computer program MINUITS [1] was used to optimize an objective function of three variables. As the objective function to determine the accuracy of estimation – the sum of root-mean-square errors of α was applied.

Results and discussion

1. In order to find the most suitable part of a TG-curve for calculations, each curve was divided into three standardized regions (Fig. 1) and an appropriate form of $f(\alpha)$ either $f(\alpha) = \alpha^n$ or $f(\alpha) = (1-\alpha)^n$, was assigned to them. The best results were obtained for the first region ($T_{1\%}$ + T_d) and $f(\alpha) = \alpha^n$.

2. Points for calculations can be selected in one three ways: the points can lie et equal intervals along the temperature axis; at equal intervals along the mass of sample axis; or at equal intervals along the curve itself. The best

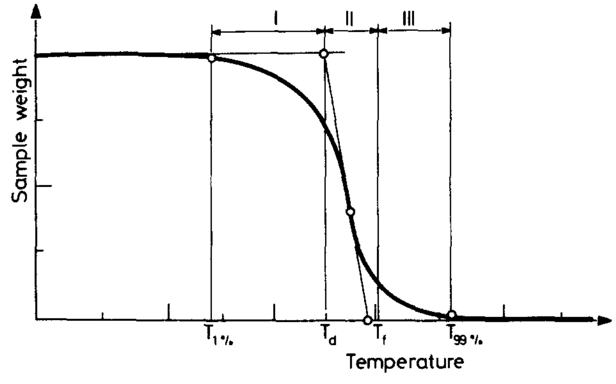

Fig. 1 Standardized division of a TG-curve for calculations

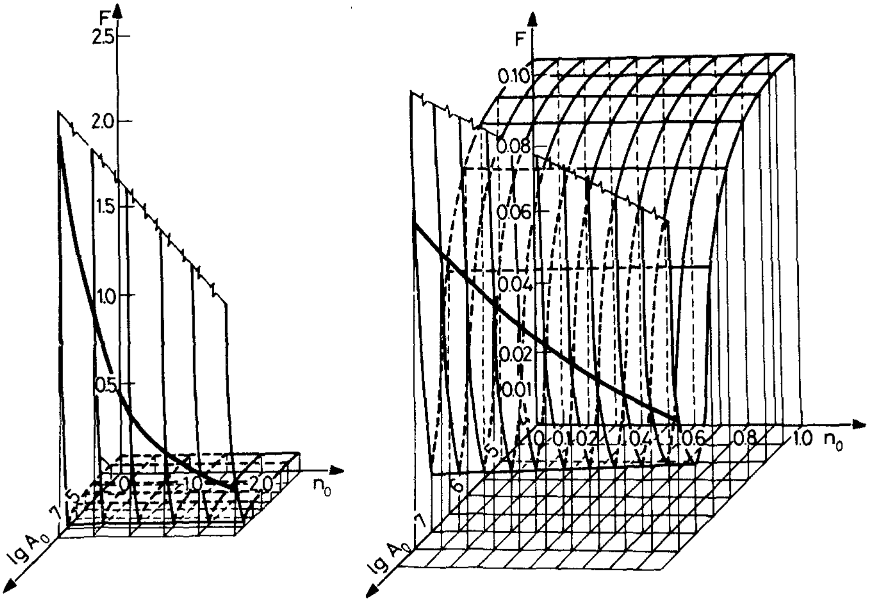

Fig. 2 Pictorial views of the objective function F in relation to the initial values of the pre-exponential factor A_o and the reaction order n_o (sample No.2 — argon)

results i.e. the minimum value of the objective function were achieved for points equally distributed along the curve.

3. The objective function showed numerous local minima depending on the initial values of independent parameters A_o and n_o, but not that of E_o. In order to evaluate the most appropriate initial values of A_o and n_o for numerical estimation – a method of successive approximations was used, in which the optimum value of the objective function was progressively refined (Fig. 2). The initial values for A_o ranged from 10 to 10^{25} s^{-1} and the initial values for n_o extended from 0 to 2.5. The method was applied to every sample and the final results in each case were approximately the same:

$$\begin{aligned} 10^{7} &< (A_o)_{\mathrm{opt}} < 10^{8}\ \mathrm{s}^{-1}, \\ 10^{-3} &\leqslant (n_o)_{\mathrm{opt}} < 10^{-2} \end{aligned}$$

For the evaluated optimum values of A_o and n_o the minimum values of the objective function and the corresponding triplet values of E, A and n were obtained. The calculated values of kinetic parameters are given in Table 1.

Table 1 Values of kinetic parameters for the investigated polyurethanes

No.	Air					Argon				
	$T_{1\%}$, K	T_d, K	n	A, s^{-1}	E, J/mol	$T_{1\%}$, K	T_d, K	n	A, s^{-1}	E, J/mol
1	519	599	0.000	$92 \cdot 10^6$	122 200	509	621	0.023	$53 \cdot 10^6$	125 300
2	499	590	0.000	$101 \cdot 10^6$	121 900	512	625	0.000	$37 \cdot 10^6$	123 800
3	495	594	0.002	$183 \cdot 10^6$	125 300	503	619	0.108	$101 \cdot 10^6$	125 900
4	500	587	0.000	$197 \cdot 10^6$	125 200	508	619	0.000	$34 \cdot 10^6$	123 200

The above method, despite its usefulness, has many drawbacks. The existence of local minima limits the possibility of finding a global minimum. The complexity of the chemical process excludes the correct interpretation of A and n. Only the activation energy can be considered at best as a semiquantitive index of thermal stability.

References

1 Program Library D506, CERN Computer Centre.

Zusammenfassung – Eine Anzahl von Polyurethan-Elastomeren wurde mittels nichtisothermer Thermogravimetrie untersucht, um eine allgemeingültige Verfahrensweise zur numerischen Abschätzung kinetischer Parameter abzuleiten. Der Wert einer angenommenen objektiven Funktion zur Bestimmung der Genauigkeit der Abschätzung hängt von mehreren Faktoren ab: von dem in Betracht gezogenen Teil der TG-Kurve, von der Auswahlmethode für die berücksichtigen Meßpunkte, und von den anfänglichen Werten des Präexponentiellen Faktors und der Reaktionsordnung. Nachdem die optimalen Bedingungen ermittelt waren, wurden die minimalen Werte der objektiven Funktion und die entsprechenden Wertetripel für die kinetischen Parameter erhalten. Von diesen kann nur die Aktivierungsenergie als halbquantitatives Maß für die thermische Stabilität betrachtet werden.

РЕЗЮМЕ — С целью разработки общей методики числовой оценки кинетических параметров разложения ряда полиуретанов, был использован метод неизотермической гравиметрии. Значение какой-либо принятой объективной функции, определяющей точность оценки, зависит от таких факторов, как рассматриваемая область кривой ТГ, метод отбора точек на кривой и исходные значения предэкспоненциального множителя и порядка реакции. После проведения оценки оптимальных условий, были получены минимум значений объективной функции и соответствующих значений трех кинетических параметров. Среди последних, только энергия активации может считаться в качестве полуколичественного параметра оценки термоустойчивости.