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KINETIC MEASUREMENTS ON POLYMERS – APPLICATIONS AND LIMITS

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A modern kinetic evaluation method for nonisothermal reactions measured with TG or DSC is presented. The obtained kinetic data are the basis for computation of a reaction process under any condition, e.g. isothermal or adiabatic.

The measurements were performed on a Mettler TA3000 system with built-in evaluation software. Mainly the following reactions are discussed: polyaddition of an epoxy premix and pyrolysis of polystyrene.

To judge the reliability of the results, 4 check procedures are recommended.

Thermoanalytical measurements on polymeric materials mainly comprise physical phenomena such as glass transition, melting and crystallization, as well as chemical reactions such as polymerization /including polyaddition, polycondensation, vulcanization/ and thermal decomposition in an inert or oxidative atmosphere. In contrast to physical transitions, chemical reactions are not characterized by simple temperatures such as onset or peak temperature, but by their kinetic data. These data allow the computation of the rate of reaction under any given conditions.

Due to the fact that the basic equations developed for reactions in gases or dilute solutions are often not valid for the complex reactions in polymers, a tool is required to judge the reliability of the results.

The purpose of this paper is to present a modern evaluation method for nonisothermal reactions, some applications of the obtained kinetic data, and last but not least a judgement of the reliability of the data.

Evaluation principle

The mathematical model used to describe the kinetics is:

$$d\alpha/dt = k\ (1-\alpha)^{n} \qquad \text{(Equation 1)}$$

$d\alpha/d\underline{t}$: rate of reaction, in s^{-1}
$\underline{k}$: reaction rate constant, in s^{-1}
α : fraction reacted /growing from 0 to 1/
$\underline{n}$: order of reaction

The Arrhenius equation gives the temperature-dependence of the reaction rate constant:

$$k = k_o \exp(-E_A/RT) \qquad \text{(Equation 2)}$$

$\underline{k}_o$: preexponential factor
$\underline{E}_A$: activation energy in J mol^{-1}
$\underline{R}$: gas constant: 8.31 J mol^{-1} K^{-1}

On substituting the Arrhenius equation into Eq. 1 we arrive at the multiple linear equation, written out in logarithmic form:

$$\ln(d\alpha/dt) = \underline{\ln k_o} + \underline{E}_A\ (1/-RT) + \underline{n}\ \ln(1-\alpha)$$

of the type: $\underline{z}_i = \underline{a} + \underline{b}\quad \underline{x}_i \quad + \quad \underline{c}\quad \underline{y}_i$

Multiple linear regression analysis [1] provides the wanted kinetic data /underlined/ using $\underline{i}$ triples of measured values $(d\alpha/d\underline{t})_i$. $\underline{T}_i$ and α_i from the thermoanalytical curve /Fig. 1/. In addition, the deviations of the measured points from the least square fit plane allow the computation of the confidence limits for 95% probability. Reactions that exactly follow Eqs 1 and 2 result in very low confidence limits of

$$\underline{n} \leq 0.05 \quad \underline{E}_A \leq 5\ \text{kJ mol}^{-1} \text{ and } \ln \underline{k}_o \leq 1.$$

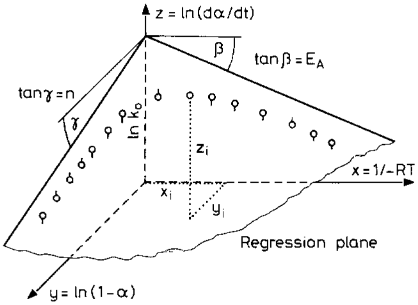

Fig. 1. Regression plane /least square fit/ of a number of triples of measured values i /i = 20 to 40/ in 3-dimensional space.

Generally, the best /lowest/ confidence limits are obtained using a range of evaluation of 10 to 80% conversion /0.1= α= =0.8/. Obviously, the very beginning and end of a reaction do not behave as well as the major part of the reaction /start-up, catalytic effects; steric problems/.

Very often, the specific heat changes during reaction. In such cases, the integral baseline, where this change is considered proportional to the fraction reacted, leads to lower confidence limits than the straight baseline.

The required properties $d\alpha/dt$ and α easily follow from the basic assumption that a fraction reacted $d\alpha$ corresponds to a proportional enthalpy change dH (DSC) or a proportional mass change dm (TG).

DSC: $\alpha = \Delta H_{part} / \Delta H_{tot}$ TG: $\alpha = \Delta m_{part} / \Delta m_{tot}$

$d\alpha/dt = dH/dt / \Delta H_{tot}$ $d\alpha/dt = dm/dt / \Delta m_{tot}$

ΔH_{part} : partial area of DSC curve, in mJ, up to the point to be evaluated

ΔH_{tot} : total peak area, in mJ

dH/dt : rate of enthalpy change of the sample or heat flow, in mW

Δm_{part} : partial mass change of TG curve in mg, up to the point to be evaluated

$\Delta \underline{m}_{tot}$: total mass change, in mg

$d\underline{m}/d\underline{t}$: rate of mass change, in gm/s (DTG)

Applied kinetics

Experience has shown that in most cases the kinetic data are not the actual aim of an analysis. They are, however, the basis for computation of a reaction process under any condition, e.g. isothermal, constant heating rate or adiabatic. The respective equations are available on request.

EXPERIMENTAL

The DSC and TG measurements were performed on a Mettler TA3000 system with the respective DSC20 and TG50 measuring modules and a Print Swiss Matrix printer/plotter. Exceptionally, the built-in evaluation software was used.

Two almost ideal chemical reactions were measured, namely the polyaddition of a liquid epoxy premix consisting of 100 g epoxidized bisphenol A, 90 g methyltetrahydrophthalic anhydride and 0.5 g benzyldimethylamine /the Ciba-Geigy products Araldit F, curing agent HV917 and catalyst DY 062/ with DSC /Fig. 2, Table 1/ and the thermal depolymerization of standard polystyrene in nitrogen /Fig. 3/. Both reactions show excellent confidence limits.

Less ideal is the reaction of a dicyandiamide cured epoxy powder, Araldit KU600 /Table 2/. Examples of unsuitable autocatalytic reactions that do not follow Eq. 1 are the polymerization of ethyl acrylate and the oxidation of stabilized polyethylene /Fig. 4, isothermal reaction/. The confidence limits of the kinetic data of a dynamic measurement attain the order of magnitude of the kinetic data themselves.

RESULTS AND DISCUSSION

Equation 1 is valid for "normal chemical reactions only:

- no autoaccelerating /or autocatalytic/ reactions;
- no overlapping physical transitions and competitive or consecutive reactions;

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K I N E T I C   A N A L Y S I S
      9-JUNE-1982   13.54

KINETIC ANALYSIS
START TEMP. °C          70
END TEMP.   °C          200
BASELINE TYPE           8
ALPHA START             0.1
ALPHA END               0.8
PLOT        CM          15
PLOT MODE               101
SINGLE ALPHA            0
APPLIED KINETICS
ΔT TABLE      K         10
START TEMP. °C          150
END TEMP.   °C          200
ALPHA END               0.9
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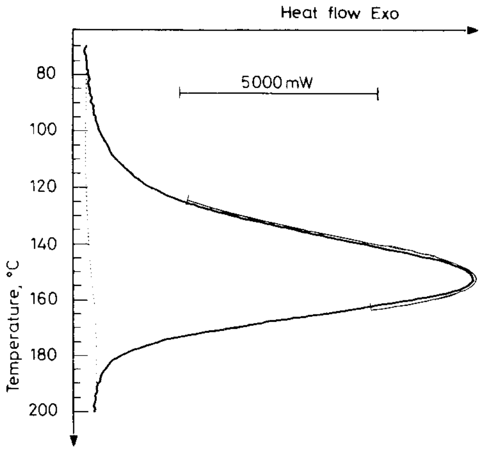

Fig. 2. DSC kinetics of the curing reaction of the epoxy premix. Sample weight: 16.457 mg, heating rate: 5 degree/min, sealed crucible. The chosen integral baseline considers the c_p change during reaction. The evaluated range /α= 0.1 to 0.8/ is marked by a double line on the automatically scaled DSC curve. The table of applied kinetics gives the computed isothermal behaviour: ln k, initial /maximum/ power released by the reaction in W kg^{-1} and the time required to attain the selected fraction reacted of 90% /~isothermal curing time/.

```
ΔH EXO     mJ           4221.3
ΔH        J/G           256.50

REACT. ORDER              1.13
CONF. LIMIT                 00
E A    KJ/MOL           113.24
CONF. LIMIT                .36
LN Ko                    26.92
CONF. LIMIT                .10

 T °C       LN K    P W/KG    + MIN

 150.0  -  5.27    1310.9    8.8498
 160.0  -  4.53    2757.5    4.2072
 170.0  -  3.82    5607.7    2.0688
 180.0  -  3.14    11054     1.0494
 190.0  -  2.49    21161     .54825
 200.0  -  1.87    39415     .29434


K I N E T I C   A N A L Y S I S

    28-May-82      9:47

    SCAN PARAMETERS
    START TEMP. °C          300
    RATE   K/MIN.           1
    END TEMP.    °C         430
    TIME ISO. MIN.          0
    PLOT         CM         10
    RANGE FS     mG         10
    OFFSET        %         90
    VALVE T6+ 1/2           0
    KINETIC ANALYSIS
    AUTOLIMIT 0/1           0
    START TEMP. °C          300
    END TEMP.    °C         429
    BASELINE TYPE           1
    ALPHA START             0.1
    ALPHA END               0.8
    PLOT         CM         0
    SINGLE ALPHA            0
    APPLIED KINETICS
    ISO/ADI 1/2             1
    PLOT         CM         9
    TIME MIN.               60
    PLOT T1                 360
    PLOT T2                 380
    PLOT T3                 400

    IDENT. NO.
    WEIGHT       mG         8.5400
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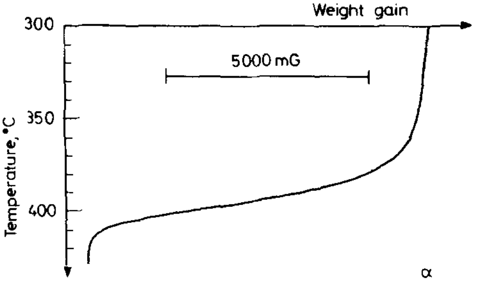

STEP	
START TEMP. °C	300.0
END TEMP. °C	429.0
Δm mG	- 8.464
Δm %	-99.117
REACT. ORDER	.77
CONF. LIMIT	.08
E A KJ/MOL	326.43
CONF. LIMIT	15.22
LN Ko	51.87
CONF. LIMIT	2.81

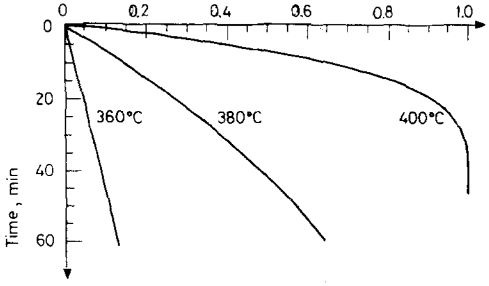

Fig. 3. TG kinetics of the thermal depolymerization of polystyrene. Sample weight: 8.54 mg, heating rate: 1 degree/min, atmosphere: N_2. The experimental and evaluation parameters are listed on top. Here the applied kinetics furnish a graph of the fraction reacted as a function of time for up to 3 selected isothermal reaction temperatures.

Table 1

Kinetic data evaluated in various ranges of conversion. The well-behaved polyaddition of the epoxy premix results in practically range-independent kinetic data with excellent confidence limits and a constant computed isothermal reaction time for 90% conversion. The oxidation of a stabilized polyethylene in pure oxygen is an example of a reaction that is unsuitable for kinetic evaluation.

Sample substance	Range of evaluation in fraction reacted	n	E_A,	ln k_0	$t_{90\%}$, min
			kJ/mol		
16.45 mg	0.1...0.8	1.13±0.00	113.2±0.36	26.92±0.10	8.8 at 150°
epoxy	0.1...0.5	1.22±0.01	116.2±2.85	27.81±0.85	9.3 at 150°
premix	0.4...0.8	1.05±0.03	104.2±4.09	24.30±1.19	8.5 at 150°
5 degree/min					
2.54 mg PE	0.1...0.8	2.68±0.17	792.4±57.6	187.11±13.96	5.1 at 230°
5 degree/min	0.1...0.5	2.11±0.18	644.8±40.6	156.12± 9.58	3.2 at 230°
	0.4...0.8	4.60±1.08	1612 ±470	385.2±113.6	26.1 at 230°

- no influence of thermal history [2], i.e. the single reaction coordinate, α, should be sufficient to describe the state of the sample.

Superimposed thermal effects can often be separated from the reaction under investigation by the selection of an appropriate heating rate or, in the case of gas or vapor evolution, using pressure-resistant sealed crucibles to suppress the heat of evaporation.

On the other hand, the Arrhenius equation also has its limited range of validity: extrapolation of more than 20 to 50 K out of the investigated temperature range should be avoided.

Table 2

Kinetic data from experiments performed with different heating rates. The well-behaved premix requires 10 min curing for a 90% conversion in a real isothermal experiment /Fig. 4/. The corresponding figure for the less ideal powder is 20 min at 170°. As a general rule, the highest accuracy of the computed isothermal course is obtained with a dynamic measurement in which the peak temperature coincides with the isothermal temperature of interest.

Sample substance	Rate degree/ /min	Peak temp. °C	n	E_A,	ln k_o	$t^{90\%}$, min
				kJ/ mol		
Epoxy	2	138	1.15±0.02	107.2±1.61	25.42±0.49	7.2 at 150°
premix	5	153	1.13±0.00	113.2±0.36	26.92±0.10	8.8 at 150°
	10	165	1.12±0.02	119.2±1.45	28.36±0.42	11.1 at 150°
Epoxy	2	177	1.27±0.06	165.9±5.27	38.63±1.46	32.5 at 170°
powder	5	190	1.40±0.02	167.1±2.04	38.53±0.55	58.8 at 170°
KU600	10	200	1.68±0.07	171.1±6.43	39.22±1.69	130.6 at 170°

To judge the validity of Eqs 1 and 2 and thereby the accuracy of the kinetic data and applied kinetics, the following procedures are recommended:

1/ - The confidence limits should be smaller than 10% of the respective value. Comparison of the measured TG or DSC traces with a computer-generated curve based on the kinetic data /a simple BASIC program for the HP85 that synthesizes TG and DTG or DSC curves is available on request/ permits a visual check of the fit.

2/ - Kinetic data evaluated in the range α= 0.1 to 0.5 should not deviate from those computed in the range α= 0.4 to 0.8 by more than 10% /Table 1/.

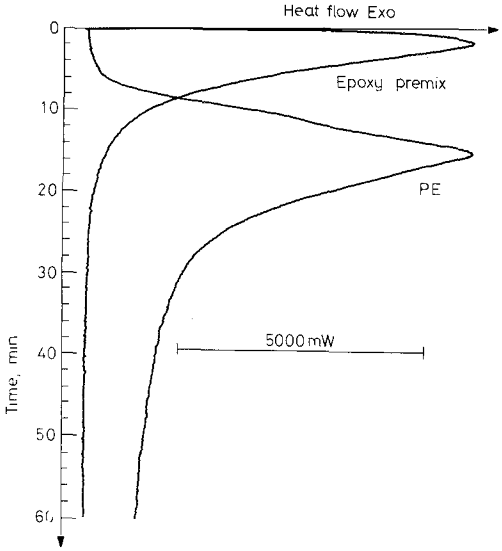

Fig. 4. Isothermal DSC curves.
The curing of the epoxy premix /9.93 mg, 170°/ follows Eq. 1. The time to attain a fraction reacted of 90% is 10 min. Another type of reaction is the autocatalytic oxidation of stabilized polyethylene /4.27 mg, 200°/, showing an induction period of about 6 min.

3/ - Kinetic data from experiments performed with different heating rates should not deviate significantly [3] /Table 2/.

4/ - An isothermal experiment must lead to a "normal kinetic curve shape /Fig. 4/. The time required for a certain conversion, α, of the isothermal measurement should correspond to the computer time, $\underline{t}$, using the kinetic data of the dynamic measurement [4] /Fig. 4/:

$$t = (1 - \alpha)^{1-n} - 1 \ / \ k(n-1) \qquad \text{valid for } n \neq 1$$

$$t = \ln(1 - \alpha) \ / \ -k \qquad \text{valid for } n = 1$$

In other words, the kinetic data of the dynamic experiment should allow the description of the isothermal course of the reaction.

All the above shows that the reliability of kinetic results can be judged. Well-behaved reactions allow the computation of their course under any condition. With the others, the obtained data may be used for comparison at least.

REFERENCES

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ZUSAMMENFASSUNG - Es wird eine moderne kinetische Auswertungsmethode für durch TG oder DSC verfolgte nichtisotherme Reaktionen vorgestellt. Die erhaltenen kinetischen Daten stellen die Basis der Berechnung der Reaktionsprozesse unter jeder, z.B. isothermer oder isobarer Bedienung dar. Die Messungen wurden mit dem Mettler-System TA3000 mit Auswertungs-software ausgeführt. In erster Linie werden die folgenden Reaktionen diskutiert: Polyaddition eines Epoxy-Vorgemisches, Pyrolyse von Polystyrol. Zur Beurteilung der Zuverlässigkeit der Ergebnisse werden 4 Testverfahren empfohlen.

Резюме - Представлен современный метод оценки кинетики неизотермических реакций, измеренной методами ТГ и ДСК. Полученные кинетические данные являются основой для компьютеризации реакционного процесса в каком-либо режиме, как например, изотермическом или адиабатическом. Измерения были проведены на Меттлер ТА 3000 системе с математическим обеспечением для проведения такой оценки. Обсуждены главным образом реакции полиприсоединения какого-либо начального эпоксида и пиролиз полистирола. Для оценки надежности получаемых результатов рекомендуется четыре способа проверки.