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Kinetics of degradation under non-isothermal conditions of a thermooxidative stabilized polyurethane

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Abstract A flexible polyurethane (PU) foam prepared from a polyol and an isocyanate prepolymer was stabilized against thermooxidation with two types of compounds: 2,6-di-*t*-butyl-4-methyl-phenol (non-reactive) and, respectively, 3,5-di-*t*-butyl-4-hidroxy-benzyl alcohol (reactive). The TG were obtained at different heating rates: $\beta = 5$, 7, 10, and 12 °C min^{-1} and the TG/DTG were processed with the following methods: Freidman, Flynn–Wall–Ozawa, Budrugeac–Segal, and, respectively, Non-Parametric Kinetics. By Freidman and Flynn–Wall–Ozawa methods it was observed a significant (more that 10%) variation of the activation energy, *E*, versus the conversion degree, this being an indication of a complex process. Therefore, the more sophisticated Budrugeac–Segal and NPK methods were used. The Budrugeac–Segal method presents a very good descriptive ability, so it is useful for simulations of the thermal behavior. The NPK method is the less speculative one and in the majority of cases the obtained values of the activation energy were in a rather good agreement with both Friedman and Flynn–Wall–Ozawa kinetic data. The value of the activation energy seems to be an appropriate parameter for the estimation of the thermal stability. In comparison with the unstabilized PU, the one stabilized with the reactive compound presented the best thermal stability

Keywords Polyurethane · Thermal behavior · Stabilisation · Kinetics

Introduction

Polyurethane (PU) is a class of extremely versatile technopolymers. Unfortunately, a prolonged service duration is compulsory connected with the necessity of PU's thermo- and photostabilization due to a rapid self-oxidation [1–3].

In a previous paper [4], it was proved the importance of an elaborated kinetic analysis of the thermooxidative degradation for the selection of an appropriate stabilizer. Also, in a recent paper [5], a synergetic effect by using a mixture of two different stabilizers, one reactive and another non-reactive, was reported.

The potential toxicity of PU is increased due to the content of stabilizers. Therefore, the use of such polymers in a direct contact with the human body is forbidden. But for technical purposes the knowledge of the influence of different stabilizers on the thermal life time (TLT) of PU has a crucial importance.

The topic of this paper is a kinetic analysis of the thermooxidative degradation process of stabilized PU taking place under non-isothermal conditions. The target is to obtain reliable kinetic parameters for TLT prediction.

Experimental

PU synthesis

The PU foam was prepared from an isocyanate prepolymer (MDI-ISO 145/8 from Elastogran, Hungary) and a polyol (Polyesther Elastoflex W5516/115 from Elastogran, Hungary).

Two type of stabilizers were used (see Scheme 1):

- *A01* working as a non-reactive stabilizer is 2,6-di-*t*-butyl-4-methyl-phenol;

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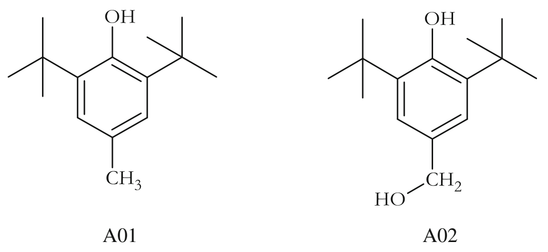

Scheme 1

- *A02* a reactive stabilizer is 3,5-di-*t*-butyl-4-hydroxy-benzyl-alcohol.

The prepared samples are presented in Table 1.

Thermogravimetry

The TG/DTG data were obtained on a Perkin Elmer DIAMOND device, under non-isothermal conditions, i.e. heating rates of 5, 7, 10, and 12 °C min^{-1}, using aluminum crucibles and a dynamic air atmosphere (100 mL min^{-1}).

Results and discussions

Thermoanalytical data

Some representative TG/DTG/DTA curves are depicted in Fig. 1.

By inspecting such diagrams for all the four samples at the four heating rates, the following remarks were taken:

(i) The thermodegradation began around 250 °C, being an exothermic process (thermooxidation); the maximum of DTG corresponds to the DTA ones.

(ii) The mass loss is put in order as follows: MS > 3S ≈ 2S > 4S
This is a first sign about the synergetic effect of a reactive/non-reactive stabilizer mixture.

(iii) In comparison with the unstabilized sample (MS) all the other samples present more complicated curves, with at least two maximum of DTG/DTA diagrams.

Table 1 Stabilizer content of the prepared samples

Sample symbol	Stabilizer content, mass/%	
	AO1/non-reactive	*AO2*/reactive
MS	–	–
2S3	0.9	–
3S3	–	0.9
4S3	0.45	0.45

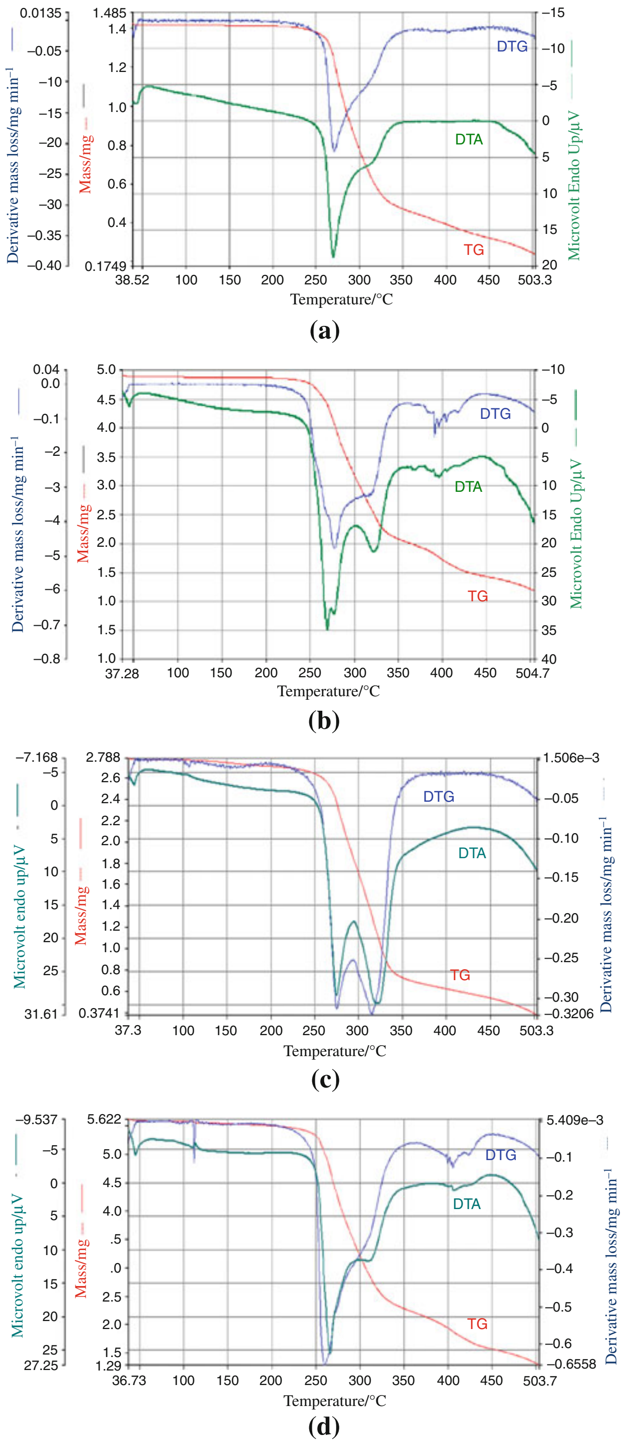

Fig. 1 Thermograms for unstabilized, respectively stabilized polymere: **a** MS; **b** 2S3; **c** 3S3; **d** 4S3 (10 °C min^{-1} in air)

Kinetic analysis

The main idea of the data processing strategy was to use the most simplest, but large used methods, of course taking into account the ICTAC-2000 Protocol [6]. The "model free" methods were preferred, in both differential and integral variants. These methods allow the evaluation of Arrhenius parameters without choosing the reaction model.

An important step in the kinetic analysis is the knowledge of the dependence of activation energy, E, versus the conversion degree, α. This allows the detection of multi-step processes and some conclusions on the reaction mechanism.

(i) Friedman's differential isoconversional method [7]

The generally accepted differential form of the reaction rate under non-isothermal conditions and constant conversion is:

$$\beta \cdot (\mathrm{d}\alpha/\mathrm{d}T)_{\alpha} = f(\alpha) \cdot A \cdot \exp(-E/RT) \tag{1}$$

where β is the heating rate, T is the reaction temperature, and $f(\alpha)$ is the non-explicit conversion function. According to the equivalent form:

$$\beta \cdot (\mathrm{d}\alpha/\mathrm{d}T)_{\alpha} = \ln[f(\alpha) \cdot A] - E/RT \tag{2}$$

the slope of the straight line of $\ln[\beta \cdot (\mathrm{d}\alpha/\mathrm{d}T)]$ vs. $1/T$ gives the activation energy at a certain conversion α.

Due to its simplicity and independence in respect to the kinetic model $f(\alpha)$, the Friedman's method is recommended for obtaining the value of the activation energy. By plotting E versus α the following two situations are relevant:

- an invariance of E in respect of α means a simple single-step process:
- a monotonous variation of E versus α is a sign of complex multi-step process.

According to the data presented in Fig. 2, there is a significant (more than 10%) variation of E versus α. With exception of low conversions ($\alpha < 0.2$), these variations are rather monotonous. Consequently, more sophisticated methods of data processing are necessary (Fig. 2)

(ii) The Budrugeac–Segal method [8–10]

This method is, logical, a continuation of Freidman's method and is based on a particular variation of the activation energy, described by:

$$E = E_0 + E_1 \cdot \ln(1 - \alpha) \tag{3}$$

Considering Eq. 3 together with another two assumptions, namely the existence of a compensation effect:

$$\ln[A \cdot f(\alpha)] = a \cdot E + b \tag{4}$$

and a reaction order type conversion function:

$$f(\alpha) = (1 - \alpha)^n \tag{5}$$

now, Eq. 2 becomes:

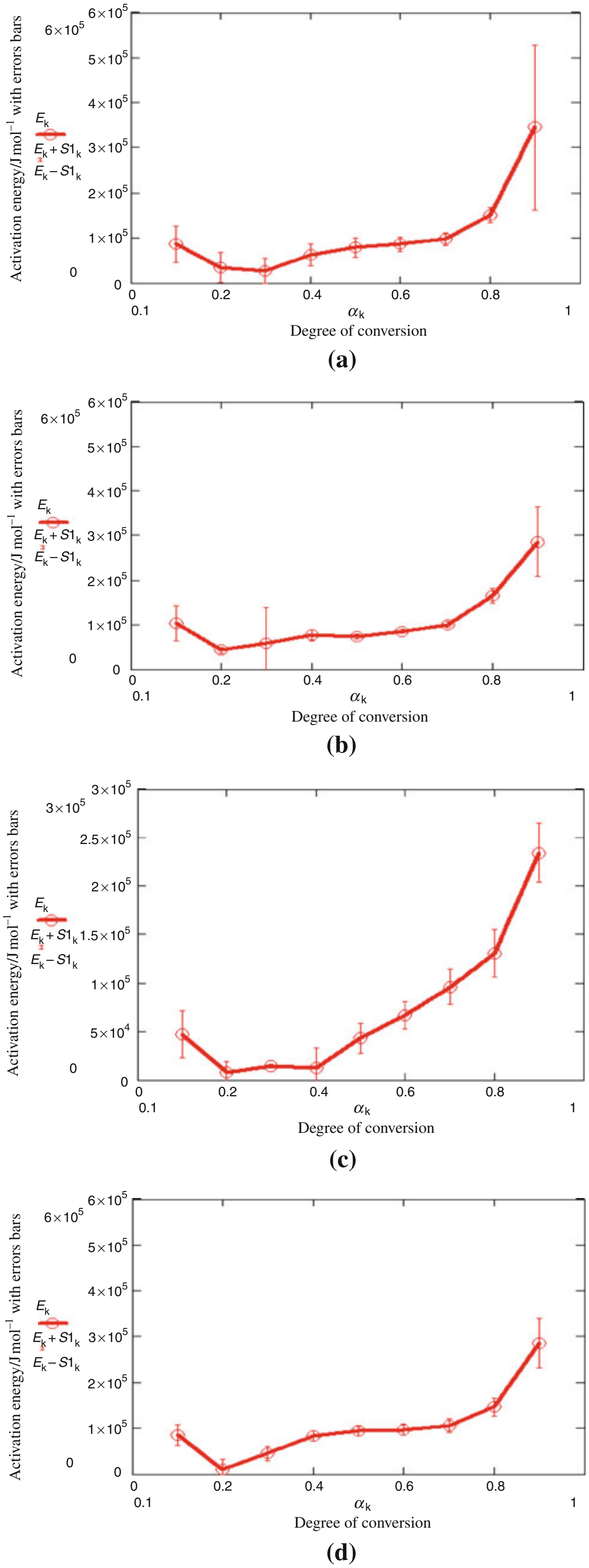

Fig. 2 Activation energy obtained by FR method versus conversion method. **a** MS; **b** 2S3; **c** 3S3; **d** 4S3

Table 2 Activation parameters obtained by Budrugeac–Segal method

Sample	E_0/kJ mol^{-1}	E_1/kJ mol^{-1}	$a \times 10^4$/mol J^{-1}	b	n
MS	11.51 ± 19	−83.05 ± 7.9	2.17 ± 0.01	−0.66 ± 0.25	2
2S3	26.83 ± 22.1	−76.03 ± 9.23	2.077 ± 0.014	−0.525 ± 0.36	1.4
3S3	−21.46	−94.8	2.19 ± 0.024	−1.04 ± 0.44	1.8
4S3	18.65	−81.95	2.18	−0.96	2

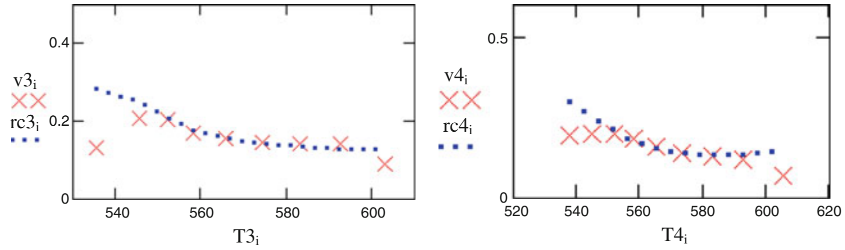

Fig. 3 Simulated (rc_i) and experimental (v_i) values of reaction rate versus temperature—example for 2S3 at heating rate of $\beta3 = 10$ and $\beta4 = 12$ °C min^{-1}

$$\ln\left[\beta \cdot (\mathrm{d}\alpha/\mathrm{d}T)_\alpha\right] = (b + a \cdot E_0 - E_0/RT) + (a \cdot E_1 - E_1/RT + n) \cdot \ln(1 - \alpha) \tag{6}$$

The correct value of n will be the one that gives a correlation coefficient closest to 1 for the straight line represented by ln[β·(dα/dT)] vs. ln(1 − α), the constants E_0, E_1, a and b being obtained from Eqs. 3 and 4, respectively.

The kinetic constants according to Eq. 6 are systematized in Table 2.

The hypothesis according to Eq. 3 being only formal, a discussion on the connections between the sample's history and the values of the invariant part E_0 of the determined activation energy is risky.

The most important characteristic of the B–S method is its descriptive ability, already discussed in some previous papers [11, 12]. This ability was confirmed also for the samples studied here, some examples being presented in Fig. 3. Despite its rather formal character, the simulation using the kinetic parameter obtained by the B–S method leads to very good results.

Regarding the complex character of the degradation process, a kinetic method able to discriminate between two or more steps was necessary.

(iii) The non-parametric kinetic method

The NPK method, elaborated by Nomen and Sempere [13–15] for processing of DSC data was subsequently modified and largely applied in the kinetic analysis [16–20].

The reaction rates, $r = \mathrm{d}\alpha/\mathrm{d}t$, obtained at different heating rates, were represented in a three-dimensional coordinate system (r, T, α) and interpolated by a proper algorithm so that a continuous reaction rate surface was obtained. Based on the assumption that the reaction rate can be expressed as a product of two independent functions, $f(T)$ and $g(\alpha)$, the obtained surface was organized as an $i \times j$ matrix where the rows correspond to different degrees of conversion ($\alpha_1 - \alpha_i$) and the columns correspond to different temperatures ($T_1 - T_j$). Each element i, j of the matrix **M** is:

$$\mathbf{M}_{i,j} = g(\alpha_i) \cdot f\left(T_j\right) \tag{7}$$

Using the singular value decomposition (SVD) algorithm [a] the matrix was decomposed according to:

$$\mathbf{M} = \mathbf{U} \cdot (\mathrm{diag}\ S) \cdot \mathbf{V}^{\mathrm{T}} \tag{8}$$

A vector $\mathbf{u}_1$ (the first column of **U**) was analyzed in respect of dependence on the conversion degree, according to the equation suggested by Śestak and Berggren [b]:

$$g(\alpha) = \alpha^m \cdot (1 - \alpha)^n \tag{9}$$

A similar vector, $\mathbf{v}_1$ (corresponding to matrix **V**) was checked for an Arrhenius type temperature dependence.

If the degradation process is a complex one, for example, with two simultaneous reactions having the rate r_1 and r_2, then the observed reaction rate will be:

$$r = r_1 + r_2 \tag{10}$$

and consequently

$$\mathbf{M} = \mathbf{M}_1 + \mathbf{M}_2 \tag{11}$$

The contribution of each step to the observed process will be expressed by the explained variance λ, so that $\lambda_1 + \lambda_2 = 100\%$.

By applying this data processing strategy, a discrimination between two or more simultaneous processes is possible. Also the SVD algorithm allows a "natural"

Table 3 Kinetic parameters obtained from the kinetic study

Sample	NPK parameters					
	λ/%	E/kJ mol^{-1}	A/s^{-1}	m	n	$\overline{E_a}$/kJ mol^{-1}
2S3	78.1	108.1	3.8×10^9	1	3/2	117.4
	19.6	169.0	9.4×10^{13}	0	3/2	
3S3	47.0	119.4	6.5×10^{10}	1	3/2	130.4
	42.9	168.7	7.5×10^{14}	0	2	
	10.1	19.5	4.6×10	1	1	
4S3	86.8	107.6	7.0×10^9	0	1	122.6
	13.2	145.1	6.3×10^{12}	1/3	2	
MS	82.8	106.3	3.4×10^9	1	3/2	109.3
	15.0	142.0	5.02×10^{11}	0	3/2	

separation of the influences of the temperature, respectively, conversion degree.

The data obtained by applying the modified NPK method on TG/DTG data processing are systematized in Table 3. There is observed a multi-step process (at least two) by all the four samples, but the second one does not exceed a significance of 15–20%. A noticeable exception is sample 3S (with reactive antioxidant) where two simultaneous processes had over 40% contribution.

Another observation is regarding the kinetic homogeneity of the principal process: for all samples the conversion function is $g(\alpha) = \alpha \cdot (1 - \alpha)^{3/2}$, the exception being the sample 4S, i.e. the mixtures of the both reactive and non-reactive stabilizers.

Conclusions

The effect of a thermostabilization on a polyurethane foam can be studied using an adequate kinetic analysis strategy. The strategy suggested here presumes a way from simple to more sophisticated methods, even if the latest one is more formal.

The Friedman's method, excellent for one step processes is useless due to the multistep nature of the thermooxidative degradation of the samples. The NPK method allows at the same time a discrimination between two simultaneous steps and a separation of the temperature, respective conversion dependence of the reaction rate, without any hypothesis.

The use of a mixture of reactive, respectively, non-reactive stabilizers with similar chemical structure leads to a synergetic effect. The major effect in this case is rather on the conversion function.

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