Kinetics of thermal decomposition of isocyanate-epoxy materials crosslinked in the presence of 1-ethylimidazole accelerator [*]

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DOI: dx.doi.org/10.14314/polimery.2014.409

Abstract: The kinetics of thermal decomposition of isocyanate-epoxy materials crosslinked in the presence of 1-ethylimidazole (EMI) as accelerator was analyzed using Ozawa, Kissinger, Friedman, and Coats-Redfern methods. The thermal decomposition parameters of the cured isocyanate-epoxy system were determined by thermogravimetric analysis (TGA) at different heating rates. TG curves showed that the thermal decomposition of the isocyanate-epoxy system occurred in two steps despite EMI content. The thermal stability of the isocyanate-epoxy system increased with increase of EMI content (E_d) 1.2 wt %. The reason could be higher isocyanurate and oxazolidone ring contents, which enhance its thermal resistance properties.

Keywords: isocyanate-epoxy materials, 1-ethylimidazole, thermal decomposition, Ozawa method, Kissinger method, Friedman method, Coast-Redfern method.

Kinetyka procesu rozkładu materiałów izocyjanianowo-epoksydowych sieciowanych w obecności 1-etyloimidazolu

Streszczenie: Badano kinetykę rozkładu termicznego materiałów izocyjanianowo-epoksydowych, sieciowanych w obecności przyspieszacza, którym był 1-etyloimidazol (EMI). Odporność termiczną tych materiałów analizowano za pomocą metod: Ozawy, Kissingera, Friedmana oraz Coasta i Redferna. Parametry rozkładu termicznego wyznaczano na podstawie danych uzyskanych metodą analizy termograwimetrycznej (TGA), stosując różne szybkości ogrzewania. Badano wpływ zawartości przyspieszacza na proces rozkładu. We wszystkich przypadkach rozkład następował w dwóch etapach. Najlepszą odpornością termiczną odznaczała się próbka sieciowana wobec największego dodatku EMI (1,2 % mas.). Obserwowana poprawa odporności termicznej ze wzrostem zawartości EMI jest związana ze zmianami w strukturze utwardzonego kompozytu i zwiększającym się udziałem grup izocyjanurowych i oksazolidonowych.

Słowa kluczowe: materiały izocyjanianowo-epoksydowe, 1-etyloimidazol, rozkład termiczny, metoda Ozawy, metoda Kissingera, metoda Friedmana, metoda Coasta i Redferna.

INTRODUCTION

Epoxy resins belong to the most important industrial reactive oligomers [1]. Mixing epoxy resins with various components allowed to obtain a wide range of materials with different properties, applied e.g. for coatings, adhesives and composites. One possibility to obtain materials with high thermal resistance is reaction of epoxy resin with isocyanate derivatives [2—16]. Epoxy and isocyanate reagents are known to react to form oxazolidones [1—13]: 2-oxazolidone and 4-oxazolidone derivatives. They could be formed in the temperature range of 220—280 °C [12, 13] or 150—250 °C [14], depending on the kind of diisocyanate.

However, it is also known that substantial quantities of undesirable by-products are formed in the temperature range of 80—150 °C [2—11, 15, 16] in the following reactions:

— between epoxy resin and isocyanate forming urethane bond,

— isocyanate trimerizations giving isocyanurate,

— formulation of biuret and allophanate compounds.

The isocyanate-epoxy compositions without accelerator exhibited relatively long pot life at the room temperature. Additionally, in order to obtain the most eligible content of isocyanurate or oxazolidone rings in the crosslinked material — chemical structure control is necessary.

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[*)] Material contained in this article was presented on the Conference "Pomerania — Plast-2013", 4—7 June 2013, Międzyzdroje, Poland.

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The curing process could be accelerated by introducing selected catalyst or catalyst system into the isocyanate-epoxy composition.

The conventional catalysts of epoxy resin/diisocyanates crosslinking reactions could be divided into two groups:

— tertiary amines, e.g. diazabicyclo-[2.2.2]-octane or Girard reagent [2, 3];

— the halogen zinc salts [16].

In that work there was described effect of accelerator amount on thermal resistance of isocyanate-epoxy crosslinked materials and the usefulness of mathematical methods to describe decomposition process.

Thermogravimetric analysis (TGA) was used to measure the weight loss as well as the derivative weight loss as a function of temperature and decomposition time. The methods of Ozawa, Kissinger, Friedman and Coast-Redfern were applied to investigate the kinetics of thermal decomposition.

THEORY AND CALCULATIONS

All the kinetic studies could start with the basic equation that relates the rate of weight loss at a constant temperature to the fractional decomposition:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = kf(\alpha) \tag{1}$$

where: $\mathrm{d}\alpha/\mathrm{d}t$ — the rate of weight loss, α — the fractional decomposition at any time, k — rate constant.

The term $f(\alpha)$ was a function:

$$f(\alpha) = (1 - \alpha)^n \tag{2}$$

The rate constant is dependent on the reaction temperature, according to the Arrhenius expression:

$$k = A\exp\left(\frac{-E_d}{\mathrm{R}T}\right) \tag{3}$$

where: E_d — the activation energy (in this case decomposition activation energy), A — a pre-exponential factor, R — the gas constant, T — the reaction temperature.

Combining equations (1)—(3) we obtain:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A(1-\alpha)^n\exp\left(\frac{-E_d}{\mathrm{R}T}\right) \tag{4}$$

Because $\mathrm{d}\alpha/\mathrm{d}t = (\mathrm{d}\alpha/\mathrm{d}T)(\mathrm{d}T/\mathrm{d}t) = \beta(\mathrm{d}\alpha/\mathrm{d}T)$, the integrated form of eq. (4) could be expressed as:

$$f(\alpha) = \int_0^{\alpha}\frac{\mathrm{d}\alpha}{(1-\alpha)^n} = \frac{A}{\beta}\int_{T_o}^{T}\exp\left(\frac{-E_d}{\mathrm{R}T}\right)\mathrm{d}T \tag{5}$$

where: β — the heating rate.

The temperature dependent term in eq. (5) cannot be solved analytically. A few good approximation methods were proposed using data of thermogravimetric (TG) technique and derivative thermogravimetry (DTG).

The Ozawa method [17—19] essentially assumes that A, $(1-\alpha)^n$ and E_d are independent on T, whereas A and E_d are independent on conversion rate α. By separating and integrating eq. (5), the resulting Ozawa equation is:

$$\log f(\alpha) = \log\frac{AE_d}{\mathrm{R}} - \log\beta + p\frac{E_d}{\mathrm{R}T} \tag{6}$$

Using Doyle's approximation for log ($E_d/\mathrm{R}T$) at $20 < E_d/\mathrm{R}T < 60$, eq. (6) becomes:

$$\log f(\alpha) = \log\frac{AE_d}{\mathrm{R}} - \log\beta - 2.315 - 0.4567\frac{E_d}{\mathrm{R}T} \tag{7}$$

The straight lines of log β against $1/T$ were plotted and E_d values were determined from the slopes ($-0.4567\ E_d/\mathrm{R}$).

The derived E_d could be used to calculate the A value from the coordinates of the y axes intercept. The mean value of A at each heating rate could be calculated from the following expression [20]:

$$\log A = \log\beta + \log E_d + 0.434\frac{E_d}{\mathrm{R}T} - \log R - 2\log T \tag{8}$$

The Friedman method [21] utilizes the following logarithmic differential expression derived from eq. (4):

$$\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) = \ln\left(\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right) = \ln A = n\ln(1-\alpha) - \frac{E_d}{\mathrm{R}T} \tag{9}$$

E_d over a wide range of α could be determined by plotting ln ($\mathrm{d}\alpha/\mathrm{d}t$) against $1/T$ for constant α. Additionally, A could be calculated from the plot of $E_d/\mathrm{R}T_0$ against ln ($1 - \alpha$) [where T_0 is the temperature at which ln ($\beta\mathrm{d}\alpha/\mathrm{d}T$) = 0]. Kissinger [17, 18 and 22] derived a useful expression that allows calculation of the activation energy by the temperature T_m at the maxima of the first derivative of mass loss versus temperature curves at different β values, as shown in Fig. 1. Because the maximum rate occurs when $\mathrm{d}^2\alpha/\mathrm{d}t^2 = 0$, differentiation of eq. (4) gives:

$$\frac{E_d\beta}{\mathrm{R}T_m^2} = An(1-\alpha)_m^{n-1}\exp\left(\frac{E_d}{\mathrm{R}T_m}\right) \tag{10}$$

Kissinger assumes that the product $n(1-\alpha)_m^{n-1}$ is independent of β. So, the following expression is derived:

$$\frac{\mathrm{d}\left[\ln\left(\frac{\beta}{T_m^2}\right)\right]}{\mathrm{d}\left(\frac{1}{T_m}\right)} = -\frac{E_d}{\mathrm{R}} \tag{11}$$

A plot of $\ln(\beta/T_m^2)$ as a function of $1/T$ gives E_d, which could be calculated from the slope.

The values of n are determined from the following expressions, and the pre-exponential factor A can be determined by combining eq. (11) with eq. (10):

$$-\ln(1-\alpha)_m \cong 1 - \frac{2\mathrm{R}T_m}{E_d}\ \text{for}\ n = 1 \tag{12}$$

Integration of eq. (5) from an initial temperature (T_0) corresponding to a initial degree of conversion (α_0) gives:

$$\int_{\alpha_0}^{\alpha_\pi}\frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{A}{\beta}\int_{T_0}^{T_p}\exp\left(\frac{-E_d}{\mathrm{R}T}\right)\mathrm{d}T \tag{13}$$

If T_0 is low, it may be reasonably assumed that $\alpha_0 = 0$, and considering that there is no reaction between 0 and T_0:

$$g(\alpha)\int_{\alpha_0}^{\alpha_\pi}\frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{A}{\beta}\int_{T_0}^{T_p}\exp\left(\frac{-E_d}{\mathrm{R}T}\right)\mathrm{d}T \tag{14}$$

where: $g(\alpha)$ is the integral function of conversion [23].

Coats and Redfern [24] developed an integral method, which could be applied to thermogravimetric data, assuming the order of reaction. The correct order was presumed to achieve the best linear correlation plot, from which E_d was determined. The final form of the equation, which was used for the analysis, took the form [24, 25]:

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right]=\ln\frac{AR}{\beta E}\left[1-\frac{2RT}{E_d}\right]-\frac{E_d}{RT}\ \text{for}\ n=1 \quad (15)$$

In the present study $n = 1$ was assumed in order to compare the results obtained by Kissinger method for isocyanate-epoxy materials with 1-ethylimidazole (EMI).

Thus, a plot of $\ln[-\ln(1-\alpha)/T^2]$ versus $1/T$ should result in a straight line of slope that equals $-E_d/R$ for the correct value of the activation energy.

EXPERIMENTAL PART

Materials

The compositions were obtained using Bisphenol A epoxy resin, i.e. Epidian 6 (E6 with epoxy equivalent 185 g/eq and viscosity 18 Pa · s at 23 °C) from Organika Sarzyna S.A. (Poland), and isophorone diisocyanate (IPDI, purity 99 %) from Sigma-Aldrich. 1-Ethylimidazole (EMI, purity 95 %) from Sigma-Aldrich was applied as accelerator.

Samples preparation

Four kinds of isocyanate-epoxy materials were prepared by mixing of components in appropriate amounts. The compositions and symbols of obtained samples are collected in Table 1.

Table 1. Isocyanate-epoxy composition

Symbol of sample	Epoxy resin content, wt %	Isophorone diisocyanate content, wt %	Accelerator content, wt %
E6/IPDI	63.5	36.5	—
E6/IPDI/EMI03	63.3	36.4	0.3
E6/IPDI/EMI06	63.1	36.3	0.6
E6/IPDI/EMI12	62.7	36.1	1.2

The isocyanate-epoxy compositions were hardened at 200 °C for 4 hours. The reference resin (without accelerator) was post-cured at 240 °C for 4 hours.

Methods of testing

The thermal decomposition of the isocyanate-epoxy systems were investigated using Q-5000 device (TA instrument). The activation energy of decomposition process (only for the first peak) was measured at the heating rate of 5, 10, 20 and 50 °C/min in the temperature range of 0—900 °C. The samples weight varied from about 8 to 12 mg. The air flowed into the furnace at 25 cm^3/min.

RESULTS AND DISCUSSION

Ozawa method

In Fig. 1 the representative TG and DTG curves for E6/IPDI at four different heating rates were shown. It could be observed that despite the heating rate thermal decomposition occurred in two stages.

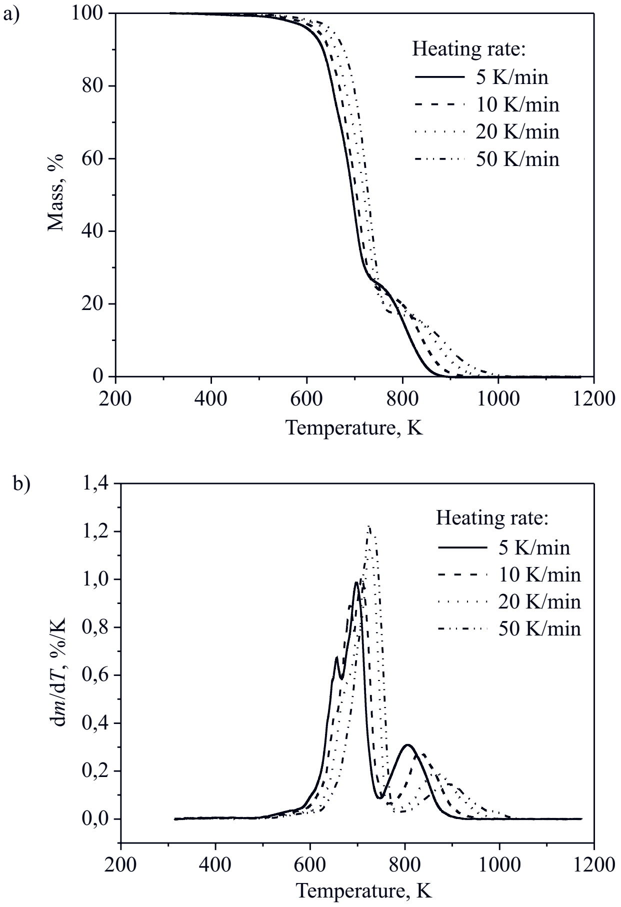

Fig. 1. TG (a) and DTG (b) curves for isocyanate-epoxy system obtained at various heating rates

Moreover, the curves have shifted to the higher temperature range with the heating rate increase. The same trend was found for all the systems, regardless of EMI content. The decomposition temperatures (T_d) were determined from the point where the weight loss abruptly increased (beyond α = 0.05). The obtained values were 608, 624, 641 and 655 K at the heating rates of 5, 10, 20, and 50 K/min, respectively.

The similar slope (decomposition rate) values from the range of α = 0.10—0.50 indicated that the same reaction mechanism influences the decomposition of the crosslinked materials. However, the slope of the line for α = 0.05 line was clearly distinguished from the other ones suggesting that thermal decomposition could be affected by other reaction mechanisms or unreacted isocya-

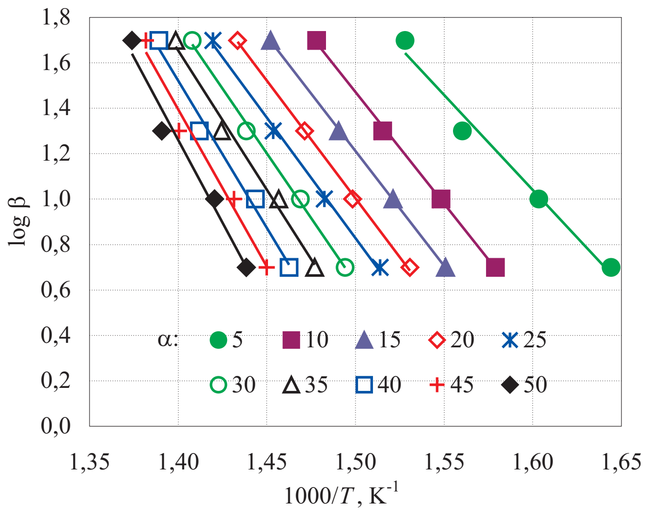

Fig. 2. Plots for determination of activation energy of thermal decomposition by Ozawa method for various decomposition rates of isocyanate-epoxy system without EMI at various heating rates

nate derivative (Fig. 2). The determined activation energy values were listed in Table 2. The average value of E_d at α = 0.05—0.50 was 208 kJ/mol. However, the average E_d for α = 0.05 was 152 kJ/mol, probably because of the volatilization of unreacted reagents, i.e. IPDI. In the case of other systems with accelerator content up to 0.6 wt % similar trends were found (see Table 2). The calculated pre-exponential factors for each conversion value for all the systems were also given in Table 2.

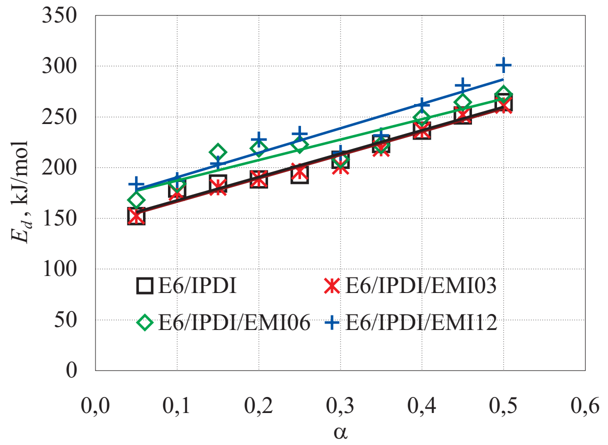

Fig. 3. Activation energies (E_d) determined by Ozawa method versus conversion rate (α) for isocyanate-epoxy system with various EMI content

Generally, E_d and A factors increase with increasing α value. However, some maximum of E_d could be observed for the conversion rate α = 0.25 (Fig. 3). E_d increased by about 60 to 75 % in comparison to the value for isocyanate-epoxy neat material (E6/IPDI) with increasing degree of material decomposition, despite the accelerator content (E6/IPDI/EMI12).

Table 2. Activation energy (E_d) values and pre-exponential factor (A) determined by the Ozawa method

Symbol of sample	α	E_d, kJ · mol^{-1}	A, min^{-1}
E6/IPDI	0.05	152	$2.64 \cdot 10^{12}$
	0.10	179	$1.57 \cdot 10^{14}$
	0.15	184	$2.16 \cdot 10^{14}$
	0.20	188	$2.89 \cdot 10^{14}$
	0.25	193	$4.45 \cdot 10^{14}$
	0.30	208	$4.55 \cdot 10^{15}$
	0.35	223	$5.01 \cdot 10^{16}$
	0.40	236	$3.52 \cdot 10^{17}$
	0.45	252	$3.57 \cdot 10^{18}$
	0.50	265	$2.46 \cdot 10^{19}$
E6/IPDI/EMI03	0.05	152	$3.04 \cdot 10^{12}$
	0.10	176	$1.12 \cdot 10^{14}$
	0.15	181	$1.73 \cdot 10^{14}$
	0.20	189	$5.51 \cdot 10^{14}$
	0.25	197	$1.46 \cdot 10^{15}$
	0.30	202	$2.45 \cdot 10^{15}$
	0.35	219	$3.87 \cdot 10^{16}$
	0.40	237	$6.36 \cdot 10^{17}$
	0.45	252	$6.12 \cdot 10^{18}$
	0.50	261	$2.11 \cdot 10^{19}$
E6/IPDI/EMI06	0.05	168	$2.60 \cdot 10^{13}$
	0.10	184	$1.96 \cdot 10^{14}$
	0.15	215	$3.64 \cdot 10^{16}$
	0.20	219	$4.61 \cdot 10^{16}$
	0.25	223	$5.77 \cdot 10^{16}$
	0.30	208	$3.33 \cdot 10^{15}$
	0.35	222	$2.91 \cdot 10^{16}$
	0.40	250	$2.23 \cdot 10^{18}$
	0.45	265	$2.05 \cdot 10^{19}$
	0.50	272	$4.43 \cdot 10^{19}$
E6/IPDI/EMI12	0.05	184	$1.74 \cdot 10^{15}$
	0.10	188	$1.11 \cdot 10^{15}$
	0.15	204	$1.45 \cdot 10^{16}$
	0.20	228	$7.47 \cdot 10^{17}$
	0.25	233	$1.31 \cdot 10^{18}$
	0.30	215	$2.42 \cdot 10^{16}$
	0.35	232	$3.71 \cdot 10^{17}$
	0.40	261	$4.75 \cdot 10^{19}$
	0.45	281	$9.68 \cdot 10^{20}$
	0.50	301	$1.98 \cdot 10^{22}$

Significantly greater differences were observed for A factor values, especially in the case of isocyanate-epoxy material with the highest EMI content.

There can be seen some maximum of E_d values for α range from 0.15 to 0.30 (Fig. 3), especially for materials with higher accelerator content. This could be explained by oxazolidone and isocyanurate rings content increase.

Friedman method

In order to explain the reason of the above finding further calculations using Friedman method (which is more sensitive for E_d changes) were performed. Similarly as Ozawa method it allows for calculating the E_d values depending on α.

T a b l e 3. Activation energy (E_d) values and pre-exponential factors (*A*) determined by the Friedman method

Symbol of sample	α	E_d, kJ · mol^{-1}	*A*, min^{-1}
E6/IPDI	0.05	178	$7.57 \cdot 10^{14}$
	0.10	187	$2.46 \cdot 10^{15}$
	0.15	190	$1.90 \cdot 10^{15}$
	0.20	202	$8.27 \cdot 10^{15}$
	0.25	216	$5.10 \cdot 10^{16}$
	0.30	208	$7.30 \cdot 10^{15}$
	0.35	268	$8.67 \cdot 10^{19}$
	0.40	290	$1.54 \cdot 10^{21}$
	0.45	299	$2.66 \cdot 10^{21}$
	0.50	303	$2.29 \cdot 10^{21}$
E6/IPDI/EMI03	0.05	174	$4.53 \cdot 10^{14}$
	0.10	188	$5.72 \cdot 10^{15}$
	0.15	194	$8.19 \cdot 10^{15}$
	0.20	211	$8.79 \cdot 10^{16}$
	0.25	206	$1.70 \cdot 10^{16}$
	0.30	201	$3.46 \cdot 10^{15}$
	0.35	270	$2.28 \cdot 10^{20}$
	0.40	284	$1.01 \cdot 10^{21}$
	0.45	286	$5.81 \cdot 10^{20}$
	0.50	281	$8.96 \cdot 10^{19}$
E6/IPDI/EMI06	0.05	198	$1.55 \cdot 10^{16}$
	0.10	208	$7.10 \cdot 10^{16}$
	0.15	245	$2.21 \cdot 10^{19}$
	0.20	250	$2.09 \cdot 10^{19}$
	0.25	263	$9.51 \cdot 10^{19}$
	0.30	218	$1.76 \cdot 10^{16}$
	0.35	286	$8.28 \cdot 10^{20}$
	0.40	295	$1.42 \cdot 10^{21}$
	0.45	306	$3.30 \cdot 10^{21}$
	0.50	312	$2.43 \cdot 10^{21}$
E6/IPDI/EMI12	0.05	222	$7.76 \cdot 10^{18}$
	0.10	229	$1.67 \cdot 10^{19}$
	0.15	234	$3.14 \cdot 10^{19}$
	0.20	262	$2.33 \cdot 10^{21}$
	0.25	248	$1.07 \cdot 10^{20}$
	0.30	219	$2.10 \cdot 10^{20}$
	0.35	287	$3.08 \cdot 10^{22}$
	0.40	328	$7.37 \cdot 10^{24}$
	0.45	331	$5.79 \cdot 10^{24}$
	0.50	329	$6.20 \cdot 10^{24}$

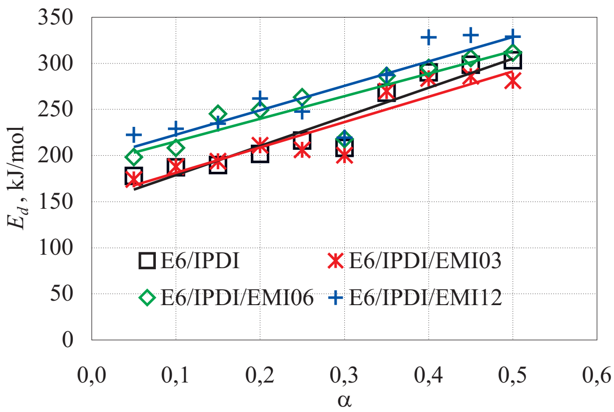

Fig. 4. Activation energy (E_d) values determined by Friedman method versus conversion rate (α) for isocyanate-epoxy system with various EMI content

All the kinetic parameters determined by Friedman method were given in Table 3. Generally, E_d values and *A* factors increased with decomposition rate increase. However, some minimum of these parameters could be observed for conversion rate range from about 0.2 to 0.3 (Fig. 4). E_d values increased by about 58 to 67 %, together with increase in EMI content (from 0 to 1.2 wt %) and with increase in material decomposition degree.

Significantly higher differences were observed for *A* factor values, especially in the case of isocyanate-epoxy material with the highest EMI content. Some maximum of E_d values were observed for α range from 0.10 to 0.35, especially evident in the case of materials with higher accelerator content. This could be explained by the increasing content of isocyanurate rings (they decompose in lower temperature than oxazolidone rings) in isocyanate-epoxy materials.

Kissinger method

To determine the influence of accelerator content on E_d and *A* factor some calculations were performed using the Kissinger and Coast-Redfern methods. Both methods are independent of the conversion rate. Kissinger method seemed more useful than Ozawa one, as more visible differences of E_d values were observed.

T a b l e 4. Activation energy (E_d) values and pre-exponential factors (*A*) determined by the Kissinger method

Symbol of sample	E_d, kJ · mol^{-1}	*A*, min^{-1}
E6/IPDI	235	$1.82 \cdot 10^{17}$
E6/IPDI/EMI03	192	$1.71 \cdot 10^{14}$
E6/IPDI/EMI06	247	$1.39 \cdot 10^{18}$
E6/IPDI/EMI12	279	$3.28 \cdot 10^{20}$

The kinetic parameters for all the systems obtained by Kissinger method were collected in Table 4. The *A* factor of the materials with the lowest EMI content (E6/IPDI/EMI03) was lower than that without accelerator.

However, further increase of the accelerator content caused significant increase in *A* factor value. This difference implied that the thermal stability was improved by the accelerator addition as well as increase in oxazolidone and isocyanurate ring content.

Coats-Redfern method

Next analytical method (Coats-Redfern method) is more universal, and additionally it does not depend on the heating rate. The required data were determined for individual α. Calculated kinetic parameters were presented in Table 5.

Table 5. Activation energy (E_d) values and pre-exponential factor (A) determined by the Coats-Redfern method

Symbol of sample	Heating rate K · min^{-1}	E_d, kJ · mol^{-1}	A, min^{-1}
E6/IPDI	5	96	$1.46 \cdot 10^6$
	10	110	$2.55 \cdot 10^7$
	20	116	$9.54 \cdot 10^7$
	50	131	$2.34 \cdot 10^9$
E6/IPDI/EMI03	5	100	$3.31 \cdot 10^6$
	10	107	$1.07 \cdot 10^7$
	20	126	$2.38 \cdot 10^8$
	50	135	$6.13 \cdot 10^8$
E6/IPDI/EMI06	5	91	$6.15 \cdot 10^5$
	10	103	$4.63 \cdot 10^6$
	20	136	$7.22 \cdot 10^8$
	50	155	$1.20 \cdot 10^{10}$
E6/IPDI/EMI12	5	92	$7.80 \cdot 10^5$
	10	109	$1.50 \cdot 10^7$
	20	122	$1.20 \cdot 10^8$
	50	147	$6.21 \cdot 10^9$

It could be noticed that the values of E_d varied from 91.17 to 154.65 kJ/mol. The values of factor *A* were in a range from $6.15 \cdot 10^5$ to $1.20 \cdot 10^{10}$ min^{-1}. Analyzing the results determined by Coats-Redfern method correlation between kinetic parameters and accelerator content could be noticed. An increase in EMI content resulted in higher thermal stability of cured materials.

General discussion

The calculated average values of E_d (in the case of Ozawa and Friedman methods for all conversions degree and for Coast-Redfern — for four heating rates) and the results of the analytical methods are summarized in Table 6.

The average E_d values determined by Friedman and Kissinger methods gave almost the same value, except for material with the lowest content of accelerator. Average E_d and *A* factors values obtained by Coast-Redfern method were significantly lower than the results calculated by other analytical methods.

Table 6. Comparison of average activation energy (E_d) values and average pre-exponential factors (A) determined by all the applied analytic methods

Symbol of sample	Analytic method	E_d, kJ · mol^{-1}	A, min^{-1}
E6/IPDI	Ozawa	208	$2.86 \cdot 10^{18}$
	Friedmann	234	$6.58 \cdot 10^{20}$
	Kissinger	235	$1.82 \cdot 10^{17}$
	Coast-Redfern	113	$6.16 \cdot 10^8$
E6/IPDI/EMI03	Ozawa	207	$2.79 \cdot 10^{18}$
	Friedmann	229	$1.91 \cdot 10^{20}$
	Kissinger	192	$1.71 \cdot 10^{14}$
	Coast-Redfern	117	$2.16 \cdot 10^8$
E6/IPDI/EMI06	Ozawa	223	$6.72 \cdot 10^{18}$
	Friedmann	258	$8.11 \cdot 10^{20}$
	Kissinger	247	$1.39 \cdot 10^{18}$
	Coast-Redfern	121	$3.18 \cdot 10^9$
E6/IPDI/EMI12	Ozawa	233	$2.08 \cdot 10^{21}$
	Friedmann	269	$1.94 \cdot 10^{24}$
	Kissinger	279	$3.28 \cdot 10^{20}$
	Coast-Redfern	118	$1.59 \cdot 10^9$

The exact physical meaning of the kinetic parameters was not clear. The complete thermoset resins thermal decomposition mechanisms could not be defined. The physical meaning of all the kinetic parameters could be interpreted rather easily, as the apparent weight loss was directly related to the thermal decomposition (emission of gaseous products after the chemical decomposition). However, for network of polymers the decomposition included several processes, each with its own kinetic parameters. Applying various analytical methods affected the kinetic parameters values. The TG curves were proportional to the instant decomposition rate, and the thermal stability increased with increasing IPDI content.

CONCLUSIONS

The kinetics of thermal decomposition was investigated by TGA method. The TG curves showed that the thermal decomposition of isocyanate-epoxy system occurred in two steps, despite the accelerating EMI content. The TG and DTG data were analyzed by four different methods. The apparent E_d values of isocyanate-epoxy system containing 1.2 wt % of EMI determined by Ozawa, Friedman, Kissinger and Coast-Redfern methods were: 233, 269, 279 and 118 kJ/mol, respectively. Thermal stability of the isocyanate-epoxy system increased with the amount of curing process accelerator (increasing isocyanurate and oxazolidone ring content).

Usage of EMI as crosslinking accelerator resulted in thermal strength increase (especially noticeable in E_d values). The increase in E_d was related to isocyanurate rings content (which tend to decompose before oxazolidone ones). The most useful to determine the influence of accelerator amount on the thermal resistance of investigated materials is analytical Friedman's method, which best describes the changes (and differences between particular samples) during heating of isocyanate-epoxy materials. Average enthalpy values of the material decomposition process (Friedman and Ozawa methods) are similar to those calculated by Kissinger method. Kissinger method can be used to predict the decomposition energy, however, it does not provide information regarding the processes (ones E_d value) during heating of samples. The Coast-Redfern approximation is least useful in comparison to other methods as the kinetic parameters are two times smaller than values calculated on the basis of three applied former mathematical equations.

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