Effect of 1-substituted imidazole derivatives for the curing process of epoxy--isocyanate composition

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The kinetics of the curing process of isocyanate-epoxy materials hardened in the presence of 1- substituted imidazole derivatives was studied by the Coast-Redfern method. The extent of a conversion parameter of the curing process in two ways was calculated: DSC (peak area integration) and rheology (viscosity changes). The activation energy values were determined for epoxy-isocyanate cured in the presence of 0.5; 1.0 and 2.0 phr 1-substituted imidazole derivatives respectively. Increasing of accelerators amount results in decreasing the activation energy and other kinetic parameters.

Keywords: curing process, DSC investigation, rheometric curves, Coats-Redfern method, autocatalytic curing process, Sesták-Berggren model.

INTRODUCTION

Epoxy resins are 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, composites. One possibility of obtaining materials with high thermal resistance is mixing epoxy resin with isocyanate derivatives[2–16]. The described reagents are known to react to 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 diisocyanate kind.

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 and isocyanate trimerizations as well as formulation of biuret and allophanate compound.

The isocyanate-epoxy compositions without accelerator exhibited a relatively long pot life at room temperature, especially with aliphatic and cycloaliphatic diizocyanate derivatives. The curing process could be accelerated by introducing the selected catalyst(s) or catalyst system into the isocyanate-epoxy composition.

The conventional catalysts of epoxy resin/diisocyanates crosslinking reactions could be divided into two groups: (i) tertiary amine e.g. diazabicyclo-[2.2.2]-octane or Girard reagent[2, 3] and (ii) the halogen derivatives of zinc salts[16].

THEORY AND CALCULATIONS

Activation energy

All kinetic studies can start with the basic equation relating to the rate of the weight loss at a constant temperature to the decomposition conversion[17–21]

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

where k is the rate constant and α is the decomposition conversion at a given time.

The differential conversion function $f(\alpha)$ may present various functional forms with the most common one, applicable for solid-state reactions, being the reaction of the n-order kinetic model, namely:

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

where n is the reaction order, assumed to remain constant during the reaction. The rate constant dependent on the reaction temperature is normally expressed by the Arrhenius formula:

$$k = Aexp(\frac{-E_d}{RT}) \tag{3}$$

where E_d is the activation energy (in this case the curing process activation energy), A is a pre-exponential factor, R is the universal gas constant (8.314 J/(mol K)) and T is the absolute temperature of the reaction. Eqs. (1–3) may be combined to obtain the function:

$$\frac{d\alpha}{dt} = A(1 - \alpha)^n exp(\frac{-E_d}{RT}) \tag{4}$$

The use of the non-isothermal analytics method requires the need to transform Eq. (4) with Eq. (5), whose reaction rate is as a function of the temperature at a constant heating rate by using the relationship:

$$\frac{d\alpha}{dt} = \frac{d\alpha}{dT} \cdot \frac{dT}{dt} \tag{5}$$

where $d\alpha/dT$ is the non-isothermal reaction rate, $d\alpha/dt$ is the isothermal reaction rate, and dT/dt is the heating rate (β) (K/min). Combination Eq. (2) and Eq. (4) with Eq. (5) leads to:

$$\int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta} \int_{T_0}^T exp(\frac{-E_d}{RT}) dT \tag{6}$$

Integration of Eq.6 from the initial temperature T_0, and the degree of reaction of α_0 to the maximum temperature T_p, where $\alpha = \alpha_p$, leads to the Eq. 7:

$$\int_{\alpha_0}^{\alpha_p} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^{T_p} exp \frac{-E_d}{RT} dT \tag{7}$$

If T_0 is low, it can be assumed that $\alpha_0 = 0$ from 0 to T_0, there is no reaction in the temperature range of 0 to T_0, then the obtained Eq. (8)

$$g(\alpha) = \int_{\alpha_0}^{\alpha_p} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^{T_p} exp(\frac{-E_d}{RT}) dT \tag{8}$$

where $g(\alpha)$ is the integral reaction model defined by the function of conversion[21–23].

The temperature dependent Eq. (8) cannot be solved analytically there but exist many good approximation methods e.g. the classical Coats-Redfern method[23, 24], which has been widely applied to analyze the DSC data under the constant heating rate and non-isothermal conditions. The Coats-Redfern correlation is described by the following expression Eq. 9:

$$ln\frac{g(\alpha)}{T^2} = ln\left(\frac{AR}{\beta E_d}\right) - \frac{E}{RT} \tag{9}$$

For n=1 Eq. 9 leads to form

$$ln\left[\frac{-ln(1-\alpha)}{T^2}\right] = ln\frac{AR}{\beta E}\left[1 - \frac{2RT}{E_d}\right] - \frac{E_d}{RT} \; for \, n = 1 \tag{10}$$

For n≠1 Eq. 9 leads to form:

$$ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = ln\frac{AR}{\beta E}\left[1 - \frac{2RT}{E_d}\right] - \frac{E_d}{RT} \; for \, n \neq 1 \tag{11}$$

A plot of $ln[1-(1-\alpha)^{1-n}/(T^2(1-n)]$ or $ln[(1-\alpha)/(T^2)]$ versus $1/T$ should result in a straight line of slope being equal to $-E_d/R$ for the correct value of the reaction order n and a set of kinetic parameters such as E_d and A can be obtained.

Model fitting kinetics

After obtaining the value of E_d, there could be used a statistic method to analyze the non-isothermal experiment data for a thermal stimulated physical or chemical process, by constructing two functions with special $y(\alpha)$ and $z(\alpha)$ for guiding to determine an appropriate kinetic model[24, 25]. The functions $y(\alpha)$ and $z(\alpha)$ could be expressed in terms of Eqs. 12 and 13.

$$y(\alpha) = (\frac{d\alpha}{dt})\exp(x) \tag{12}$$

$$z(\alpha) = \pi(x)(\frac{d\alpha}{dt})\frac{T}{\beta} \tag{13}$$

where x is the reduced activation energy, $(-E_d/RT)$, and β is the heating rate, $\pi(x)$ is the expression related to the temperature integral which can be well approximated using the equation of Senum and Yang[27] Eq. 14 .

$$\pi(x) = \frac{x^3 + 18x^2 + 86x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \tag{14}$$

From the maximum of the curves $y(\alpha)$ and $z(\alpha)$ or $(d\alpha/td)$ vs α suitable α_M, α_p^∞ and α_p could be assigned, respectively.

An examination of α_M, α_p^∞ and α_p shows that their values satisfy the following conditions simultaneously: $0<\alpha_M<\alpha_p^\infty$ and $\alpha_p^\infty \neq 0.632$, which leads to the conclusion that the two parameter Sesták-Berggren model (SB (m, n))[27, 28], (Eq. 15).

$$\left(\frac{d\alpha}{dt}\right) = A\exp\left(-\frac{E_d}{RT}\right)\alpha^m(1-\alpha)^n \tag{15}$$

where m and n are the reaction orders, and the other parameters else have the same meaning as the above equations. Note here that the ratio of m and n, p, can be replaced by $\alpha_M/(1 - \alpha_M)$ according to Málek[25]. Thus, Eq. 15 can be transformed into the following Eq. 16.:

$$ln\left[\left(\frac{d\alpha}{dt}\right)exp(-\frac{E_d}{RT})\right] = lnA + nln[\alpha^{(\alpha_M/1-\alpha_M)}(1-\alpha)] \tag{16}$$

From Eq. 16 there could be constructed a series of the plots of $ln(d\alpha/dt)exp(x)$ vs. $ln(\alpha^p(1 - \alpha)$ with good linearity for each curing process, and consequently the values of m, n and ln A could be calculated from the intercept and slope of these fitting straight lines.

EXPERIMENTAL

Materials

The compositions were prepared by mixing Bisphenol A epoxy resin Epidian 6 (E6, epoxy equivalent 185, viscosity 18 000 mPa·s at 23°C) from Organika Sarzyna S.A. (Poland) with isophorone diisocyanate (IPDI, purity 99%) from Sigma-Aldrich in a molar ratio of epoxy group:isocyanate group 1:1 and 1:2. The accelerators were: 1-methylimidazole (1MI, purity 98%) and 1-butylimidazole (1BI, purity 98%) from Sigma-Aldrich. The catalyst was introduced in the amount of 0.5; 1.0 and 2.0 phr of epoxy resin. The epoxy-isocyanate materials content were collected in Table 1.

Methods

The curing process of the epoxy-isocyanate composition was characterized by using a differential scanning calorimeter DSC Q-100 by TA Instruments (USA), at the heating rates of 10K/min in the temperature range of 273–653 K and an ARES Rheometer (from Rheometrics Scientific) at a heating rate of 10°C/min in the temperature range of 313–573K, in 40 mm parallel-plate configuration with a gap of 1 mm.

RESULTS AND DISCUSSION

The increasing of 1-substituted imidazole derivatives content causes decreasing of the beginning, maximum temperature (Fig. 1) and the gel point (Fig. 2) of the curing process.

DSC curves could be divided into two areas: in the temperature range from 100 to 200–275°C, in which undesired reactions could be observed and urethane bonds and allophanate formulations are formed and the range from 200–275°C to 310–340°C, which are accounted for

Table 1. Exemplary epoxy-isocyanate compositions content

| Acronim	Epoxy: Isocyanate molar ratio [-]	Epoxy resin content [wt.%]	Isophorone diisocyanate content [wt.%]	Accelarator content per epoxy resin [wt.%]	Accelerator content [wt.%]
E6_IPDI	1:1	63.5	36.5	–	–
E6_IPDI_1MI_05	1:1	63.3	36.4	0.5	0.3
E6_IPDI_1MI_10	1:1	63.1	36.3	1.0	0.6
E6_IPDI_1MI_20	1:1	62.7	36.1	2.0	1.2
E6_2IPDI	1:2	46.5	53.5	–	–
E6_2IPDI_1MI_05	1:2	46.4	53.4	0.5	0.2
E6_2IPDI_1MI_10	1:2	46.2	53.3	1.0	0.5
E6_2IPDI_1MI_20	1:2	46.1	53.0	2.0	0.9
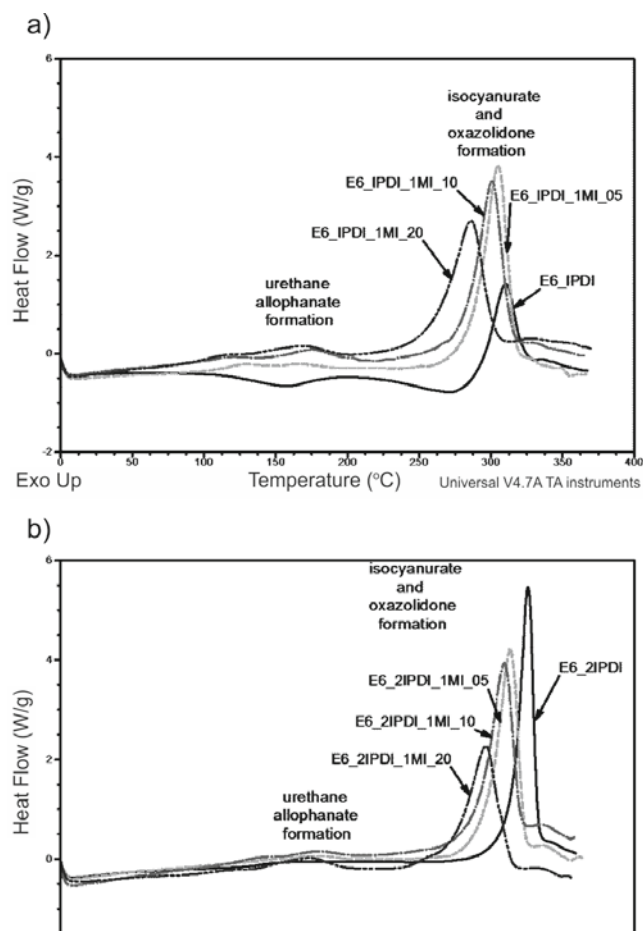
Figure 1. DSC curves of epoxy-isocyanate compositions curing process catalyzed with 1MI, (a – molar ratio of epoxy group: NCO 1:1, b – molar ratio of epoxy group: NCO 1:2)

the main reactions: the obtaining of isocyanurate and oxazolidone ring. In further analyses we are based on the description of the second peak, which described two main crosslinking processes.

Independently of the epoxy-isocyanate kind composites and accelerator content rheometric curves could be divided into several ranges: (i) from 40 to 120°C where slight viscosity changes might be observed, (ii) from 120 to 200–250°C with decreasing viscosity caused by minor reactions (similarly to DSC curves) and (iii) above 200–250°C with high viscosity increase assigned to major reaction (the initial temperature of this range is related to the amount of the catalyst). Independently of the isocyanate content the highest viscosity changes might be observed for epoxy-isocyanate composition with the highest amount of 1-ethylimidazole. The lowest viscosity increase is noticed
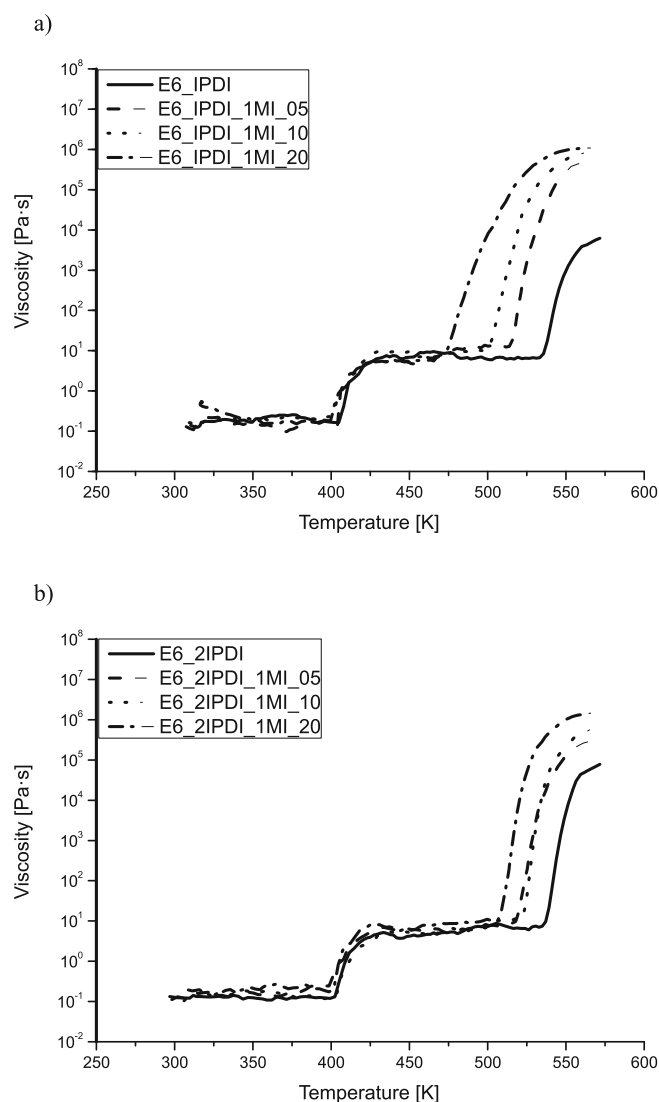

Figure 2. Rheometric curves of epoxy-isocyanate compositions curing process catalyzed with 1MI, (a – molar ratio of epoxy group: NCO 1:1, b – molar ratio of epoxy group: NCO 1:2)

for the composition without accelerator with the epoxy: isocyanate group molar ratio equal 1:1.

The degree of conversion is calculated by integrating the area of the second peak on the DSC curve, or as a result of comparison of the viscosity at current temperature to the maximum viscosity, which is read off the rheological curve. The designated data are allowed to calculate the activation energy with the Coast-Redfern method for the first order reaction (Table 2).

The crosslinking process of the composition with a higher diisocyanate isophorone content requires much higher energy (the activation energy for neat mixture

Table 2. Activation energies of epoxy-isocyanate compositions curing process

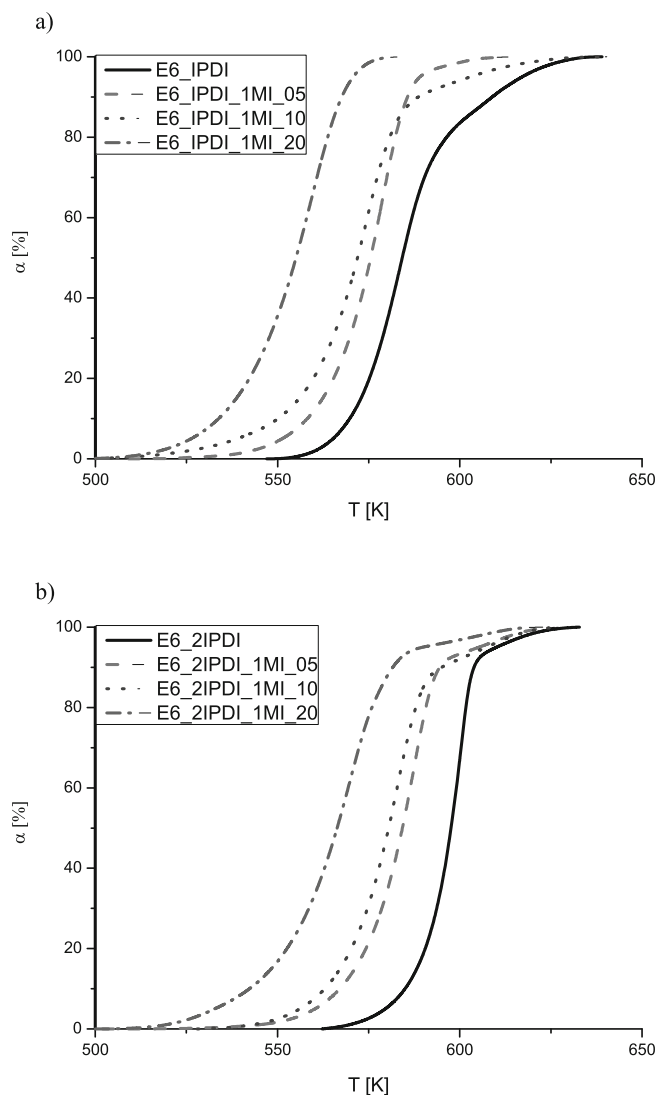|		Activation energy [kJ/mol]			
Acronim	Accelerator content [% wt.]	DSC		ARES	
		1MI	1BI	1MI	1BI
E6_IPDI	–	68.18		70.88	
E6_IPDI	0.5	73.69	85.12	79.33	99.26
E6_IPDI	1.0	64.11	69.87	54.64	76.36
E6_IPDI	2.0	54.52	47.69	41.40	54.19
E6_2IPDI	–	145.02		133.58	
E6_2IPDI	0.5	89.06	99.13	101.39	115.29
E6_2IPDI	1.0	79.38	86.12	91.92	111.69
E6_2IPDI	2.0	59.00	83.24	71.12	97.59

a)

b)

Figure 3. Plots conversion vs. the temperature of the epoxy-isocyanate compositions curing process catalyzed with 1MI, (a – molar ratio of epoxy group: NCO 1:1, b – molar ratio of epoxy group: NCO 1:2)

a)

b)

Figure 4. The reaction rate vs. conversion (calculated αp) of the epoxy-isocyanate compositions curing process catalyzed with 1MI, (a – molar ratio of epoxy group: NCO 1:1, b – molar ratio of epoxy group: NCO 1:2)

E6_2IPDI is more than twice higher than the value obtained for the material with lower IPDI content (E6_IPDI).

The increasing of 1-substituted imidazole derivative content causes decreasing of activation energy and larger changes are observed in the case of 1-methylimidazole using, with exception of the values, which are calculated for the type E6_IPDI mixtures (ratio of-NCO to epoxy groups of 1:1) with the smallest 1-butylimidazole content.

The activation energy obtained by two methods is slightly different, usually greater (from about 4 to 20) are the values calculated on the rheological curves basis.

In order to determine precisely the effect of the curing accelerators, mixtures of epoxy resin and IPDI used
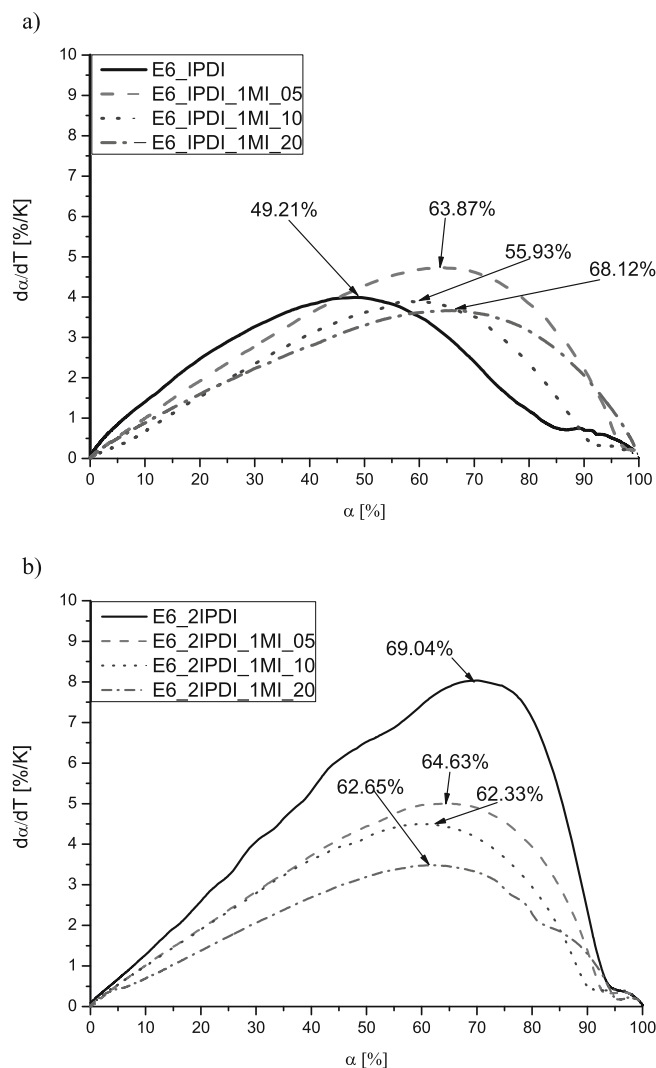
fitting kinetics model. Differentiation of the fractional conversion relative to reaction temperature (Fig. 3) followed by a certain transformation gives rise to the reaction rate $d\alpha/dt$ as a function of conversion α, as displayed in Figure 4.

Noticeably, as the accelerator content is increased, $d\alpha/dt$ increases steadily, but the peak reaction rate appears at essentially constant α_p of 0.49–0.69 (Figs. 5 and 6, Table 3).

After obtaining the value of E_d, we can construct the normalized function curves of $y(\alpha)$ and $z(\alpha)$ (Eqs. 12 and 13). As illustrated in Figure 4, the $y(\alpha)$ curves exhibit a sigmoidal profile with essentially the same peak values

Table 3. Characteristic peak conversion values α_p, α_M and α_p^∞ for epoxy-isocyanate compositions curing process with different accelerator content

| Acronim	Accelerator content [% wt.]	α_p [-]		α_M [-]		α_p^∞ [-]	
		1MI	1BI	1MI	1BI	1MI	1BI
E6_IPDI	–	0.4921		0.4413		0.4882	
E6_IPDI	0.5	0.6387	0.6398	0.5971	0.6477	0.6202	0.6523
E6_IPDI	1.0	0.5593	0.5622	0.5943	0.5687	0.6054	0.5998
E6_IPDI	2.0	0.6812	0.6852	0.5882	0.5997	0.6502	0.6658
E6_2IPDI	–	0.6904		0.6652		0.6979	
E6_2IPDI	0.5	0.6463	0.6495	0.5861	0,5921	0.6399	0.6428
E6_2IPDI	1.0	0.6233	0.6286	0.5858	0.5987	0.6233	0.6386
E6_2IPDI	2.0	0.6265	0.6605	0.5868	0.5914	0.6095	0.6145
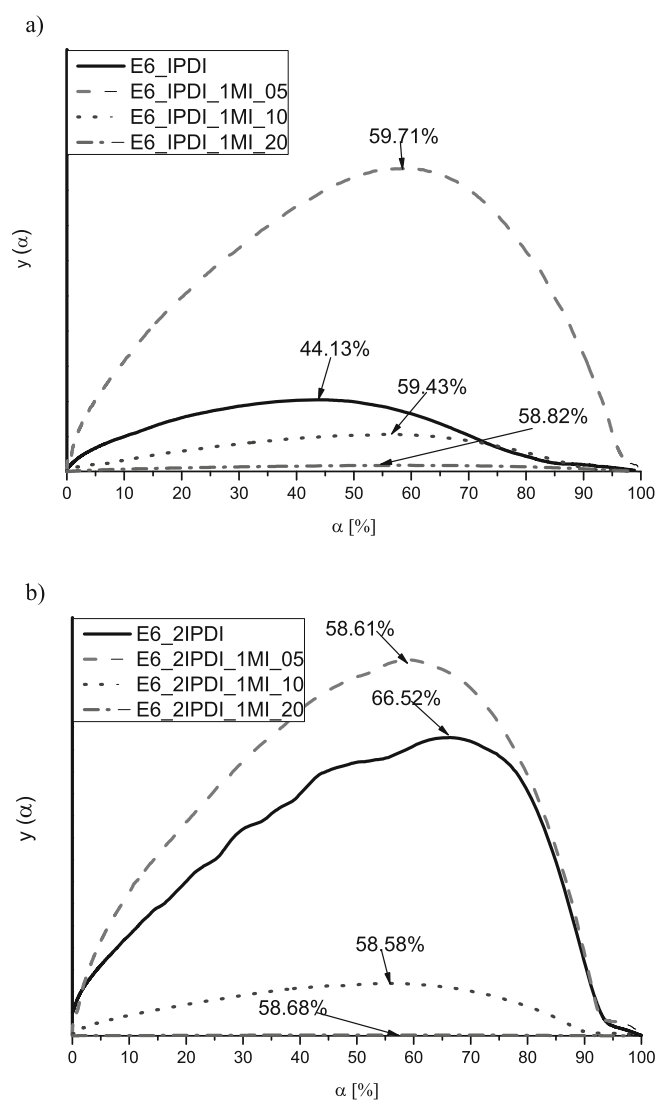
a)

b)

Figure 5. Selected y(α) master plots (calculated αM) of the epoxy-isocyanate compositions curing process catalyzed with 1MI, (a – molar ratio of epoxy group: NCO 1:1, b – molar ratio of epoxy group: NCO 1:2)

a)

b)

Figure 6. Selected z(α) master plots (calculated αp∞) of the epoxy-isocyanate compositions curing process catalyzed with 1MI, (a – molar ratio of epoxy group: NCO 1:1, b – molar ratio of epoxy group: NCO 1:2)

conversion α_M being in 0.44–0.67, while the z(α) curves show α_p^∞, within 0.49–0.70, dependent of accelerator content and kind. The greatest differences are noted for the composition without accelerator with a different IPDI content. The use of accelerators decrease the differences in the values, which are located in the range for α_M from 0.58 to 0.64.

A further examination of α_M and α_p^∞ shows that their values satisfy the following conditions simultaneously: $0 < \alpha_M < \alpha_p^\infty$ and $\alpha_p^\infty \neq 0.632$, which leads to the conclusion that the two parameter Sesták–Berggren model (SB (m, n) – Table 4) is suitable for the kinetic modeling of the studied reactions according to the criteria of the
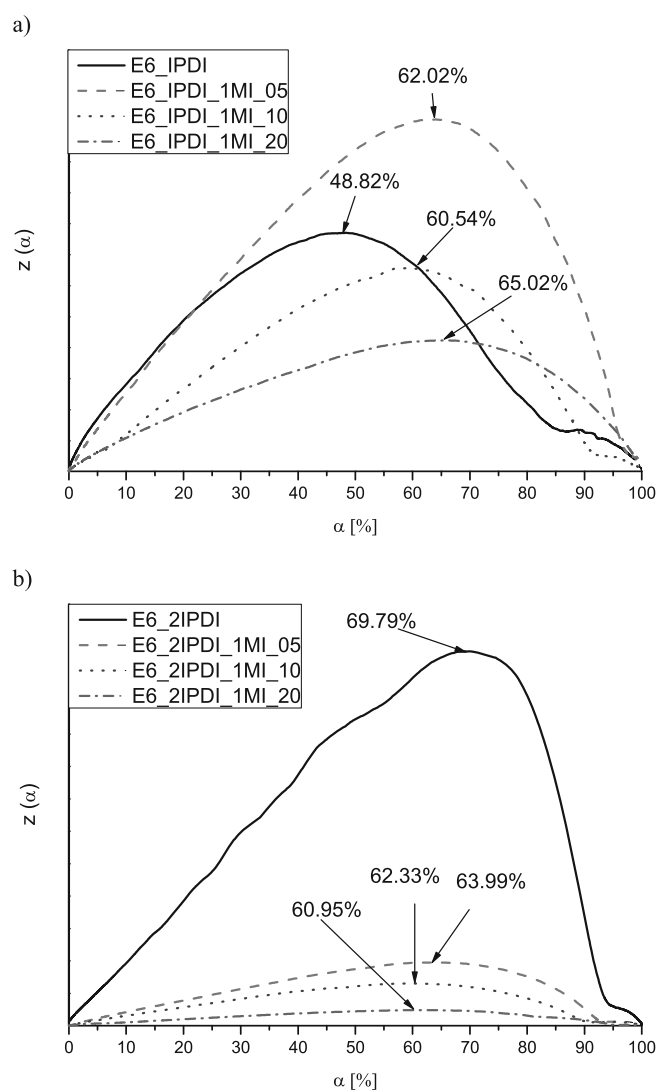
Málek method. Notice that as the demonstrated α_M could serve as a probe for reflecting the autocatalytic tendency of the reaction; i.e., the smaller α_M value, the less apparent tendency of the autocatalytic reaction.

As can be found, kinetic parameters for the composition with accelerator very slightly depends on their content, but exceeding 10% of their mean values (m, n) can be observed.

The greatest differences are observed for A factor, especially in the case of the composition with a higher content of isocyanate component. The introduction of the accelerator (especially 1-methylimidazole) reduces

Table 4. Calculated kinetic parameter m, n and ln A for SB (m, n) model for isocyanate-epoxy compositions curing process with different accelerator content

Acronim	Accelerator content [% wt.]	m [-]		n [-]		ln A [min⁻¹]	
		1MI	1BI	1MI	1BI	1MI	1BI
E6_IPDI	–	1.314		0.765		13.387	
E6_IPDI	0.5	1.310	1.365	0.352	0.354	14.401	15.630
E6_IPDI	1.0	1.303	1.237	0.235	0.332	11.488	12.951
E6_IPDI	2.0	1.172	1.234	0.409	0.392	11.077	9.536
E6_2IPDI	–	0.660		0.296		29.897	
E6_2IPDI	0.5	1.290	1.166	0.325	0.303	16.849	20.714
E6_2IPDI	1.0	1.262	1.241	0.290	0.271	14.781	17.347
E6_2IPDI	2.0	1.242	1.414	0.299	0.384	10.880	17.115

the A value of more than 100% (E6_IPDI mixture with the largest 1MI content).

CONCLUSIONS

Introducing catalysts to epoxy-isocyanate material accelerates its curing process independently of the isocyanate content. The effect of using 1-imidazole derivatives, such as: 1-methylimidazole and 1-butylimidazole is similar and kinetic parameters are comparable for mixtures with the same 1-imidazole derivatives content. The further advantage of using 1-imidazole derivatives is their excellent solubility in epoxy resin.

The biggest differences for the crosslinking process are observed for mixtures without accelerators, especially in the case of the activation energy and other kinetic parameters (especially α_M). The greater autocatalytic tendency of a crosslinking process is observed for the composition with a higher IPDI content.

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