Kinetics of cross-linking processes of fast-curing polyurethane system

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ABSTRACT

This work focuses on the application of thermal analysis and kinetics investigations to analyze chemical processes during cross-linking of the complex fast-curing polyurethane system. Non-isothermal Differential Scanning Calorimetry (DSC) measurements were performed for both stoichiometric mixtures of polyol and isocyanate component and for mixture with large isocyanate excess. Isoconversional methods were used to calculate initial parameters for the multi-step procedure. Data were fitted according to autocatalytic Sestak-Berggren equation and activation energies and reaction orders were obtained. Those investigations led to the successful identification of three main reactions i.e. polyaddition, isocyanate deblocking and formation allophanate groups.

1. Introduction

Polyurethanes (PUR) are versatile materials applied in almost every branch of industry. Depending on their chemical structure and manufacturing methods and parameters, they can serve as elastomers, rigid or elastic foams, adhesives or coatings [13]. It is well known that the basic method of polyurethanes synthesis is polyaddition reaction between polyol and diisocyanate or polyisocyanate. In order to obtain products with desired properties, addition of various catalysts such as tertiary amines [3] and organotin complexes [4] is essential. The catalytic activity of different catalysts can significantly change the overall kinetics and occurring side reactions. For simple model systems working mechanisms of catalysts are generally well known [6].

However, in many applications commercially available mixtures are used instead of pure polyols and isocyanates and their composition is rather complex. Investigation of kinetic behavior of such system is not an easy task because many processes other than simple polyaddition might occur. Another difficulty is connected with the fact that more than one type of isocyantate is present in such mixture and that they can be fully or partially blocked [17]. This process is most commonly realized by oxymes and its purpose is to prevent reaction with water to stop foaming in room temperature. Besides polyaddition there are several reactions that occur during cross-linking. Depending on catalysts used those might be allophanates and biuret formation or in case of applying excess of isocyanates and special calatysts, dimerisation and trimerisation can also happen. The comprehensive list of different reactions with corresponding mechanisms and catalysts influence is given

in review [5]. Fig. 1 shows the simple diagram of those reactions. All of them have their own enthalpy, therefore they can be investigated by means of thermal analysis. Moreover in temperatures higher than 90 °C the rate of deblocking of isocyanates rapidly grows for most blocking agents, so it must be also taken into account in analysis complex systems. Additionally in case of thermosetting polyurethane resins, a short pot-life is often another difficulty.

Thermal analysis is obviously not the only one method for kinetics investigation. Studying of reacting systems in situ can also be accomplished via FTIR [14], NMR [4], rheological [15] and chromatographic techniques [8]. Mechanisms and properties of novel catalysts can also be estimated by computational chemistry and density functional theory (DFT) calculations [11]. Therefore it exists a wide area for comparison of kinetic models obtained through different methods for particular systems. Such calculations performed for commercial systems can be applied to numerical simulations of various industrial materials processing techniques i.e. Resin Transfer Moulding (RTM), Reactive Injection Moulding (RIM) and Reactive Extrusion (REX) [18].

Keeping in mind that the fast-curing polyurethane systems were used in the construction industry we found it advisable to go into analyses which would make it possible to define more precisely the effect of different NCO : OH ratio on the cross-linking processes of those systems. Kinetic analysis of the observed cross-linking processes of fast-curing polyurethanes turned out useful for that purpose. In some cases, it is only kinetic analysis that may provide additional information on the mechanism of cross-linking processes of polyurethanes. In this work we present a thorough investigation of different chemical processes that
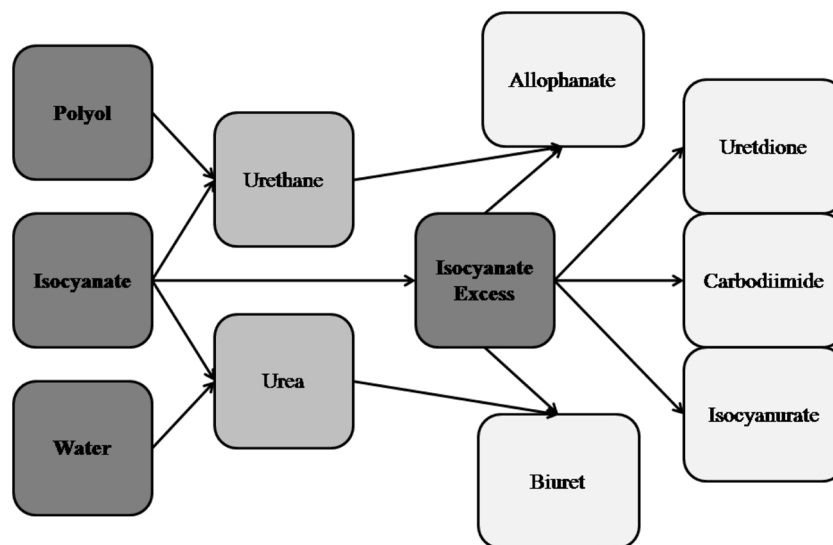
Fig. 1. Schematic representation of reactions that might occur during commercial polyurethane system cross–linking.

occur during cross-linking of complex commercial polyurethane system using non-isothermal differential scanning calorimetry (DSC). Kinetics of those processes are determined by model-free isoconversional method followed by multi-step procedureinvolving autocatalytic model and Sestak-Berggren equation.

2. Experimental

2.1. Materials

Polyurethane system used for kinetics measurements included polyol component Huntsman RenCast®FC 52 and isocyanate component Huntsman RenCast®FC 52/53 ISO. The basic physical properties of components were presented in Table 1.

2.2. Preparation of fast-curing polyurethane system

Fast-curing polyurethanes were obtained by a one-step method from a two-component system in two NCO:OH ratios (1:1 and 1.5:1). Component 1 was polyol mixture with a hydroxyl number L_{OH} = 195 ± 5 mgKOH/g. As component 2, MDI mixture (% NCO = 19.7 ± 0,5%) was used. Both components were mixed together at room temperature and then poured into analuminium pan. Table 2 contains the details of fast-curing polyurethane systems formulations.

2.3. Techniques

2.3.1. Determination of −OH group content
The hydroxyl value of the obtained polyolmixture was determined in accordance with the standard PN-93/C-89052/03. Samples were dissolved in acetylation mixture and then heated in a steam bath. During heating, pyridine and distilled water were added. In the next step, samples were titrated with 0.5 M KOH in the presence of phenolphthalein.

Table 1
Physical properties of polyol and isocyanate components.

Property	Unit	RenCast®FC 52	RenCast® FC 52/53 ISO.
Appearance Colour	visual	Liquid Amber	Liquid Amber
Viscosity at 25 °C	mPa s	250 ± 30	40 ± 5
Density	g/cm³	0.98 ± 0.05	1.12 ± 0.05

Table 2
Formulation of fast-curing polyurethane systems.

	NCO:OH = 1:1	NCO:OH = 1.5:1
RenCast®FC 52, (g)	10.0	10.0
RenCast® FC 52/53 ISO, (g)	7.5	11.3

2.3.2. Determination of–NCO group content
0.5 g of isocyanate component was dissolved in chlorobenzene with addition of 4 cm³ of 0.5 N dibutylamine. Dibutylamine reacts with free NCO groups and urea derivatives are created. Then, excess amine was titrated with the 0.1 M HCl solution, while bromophenol blue was used as a pH indicator (in pH range 3.0–4.6 the color changes form blue to yellow). The volume of HCl used for titration was converted to the amount of unreacted amine and therefore to NCO content [26].

2.3.3. Differential scanning calorimetry analysis (DSC)
Differential Scanning Calorimetry analysis was performed using a NETZSCH DSC 204 F1 Phoenix in the temperature range of 20–200 °C under nitrogen atmosphere. The heating range of 10.0; 12.5; 15.0; 17.5; 20.0; 22.5; 25.0; 27.5 and 30 K/min were used (two curves i.e. 20 and 25 on most figures are omitted for clarity). The measurement conditions were as follows: sample weight: 5–7 mg, gas flow – 40 ml/min, aluminum pan. Data analysis was performed using NETZSCH Proteus Thermal Analysis 10 software. Calculations for isoconversional methods as well as deconvolution and non-linear regression procedures were conducted in Origin software.

3. Theoretical analysis

3.1. Brief description of kinetic modelling

It is well established that in case of solid state processes, the reaction rate v is dependent on the product of two functions, the first one dependent on temperature k(T), and the second one is dependent on a conversion degree α. The overall expression can be written as [19]:

$$v = \frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

Some cases require an additional term that depends on pressure h (P), but in case of most thermal analysis experiments it can be neglected, because the pressure is forced to be constant due to external gas flow [19]. Temperature dependence k(T) is frequently assumed to be
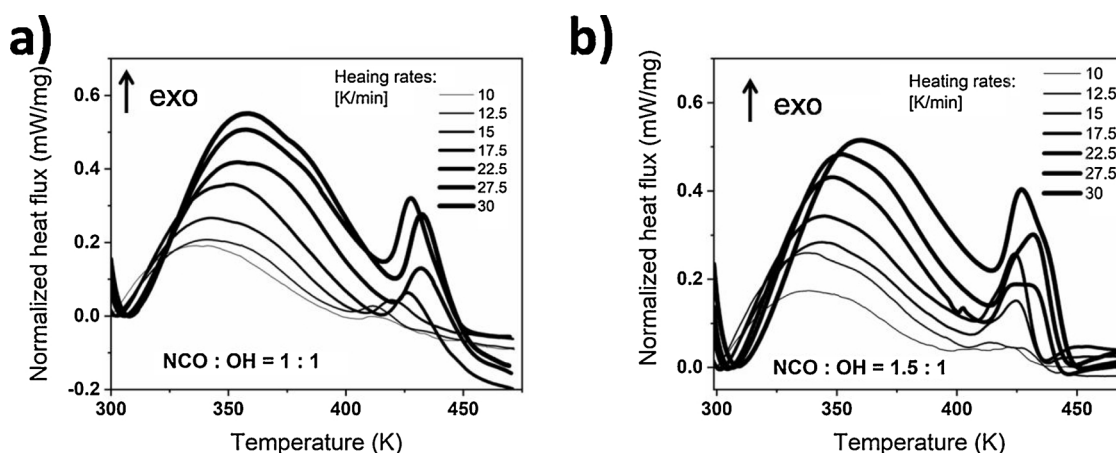
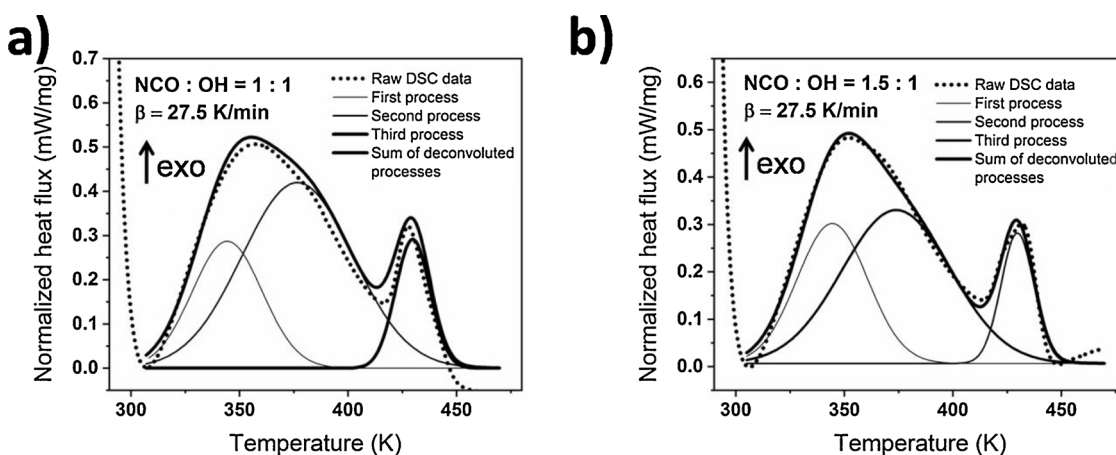**Fig. 2.** DSC raw data for polyurethane curing mixture with NCO:OH ratio equal: a) 1:1 and b) 1.5:1.

Fig. 3. Examples of deconvoluted DSC data for NCO:OH ratio equal: a) 1:1 and b) 1.5:1.

simple Arrhenius-like exponential:

$$k(T) = A exp\left(-\frac{E_a}{RT}\right) \tag{2}$$

E_a is activation energy of particular process, A is pre-exponential factor, which can be interpreted as the intensity of collisions between molecules [25], R is a gas constant equal to $8.314 \, J \, mol^{-1} \, K^{-1}$ and T is absolute temperature. The latter function given in Eq. (1), $f(\alpha)$, is a model function and is strictly related to the mechanism of physical or chemical process. The nature of this function, as well as methods of its determination, will be further exploited in model – based approach section. One of the ways of obtaining kinetic data is to use thermal analysis methods such as DSC. The result of the measurement is the change of enthalpy with respect to time. Typically one can use a standard way of calculating conversion rate based on thermal effects on the basis of Eq. (3).

$$\frac{d\alpha}{dt} = \frac{1}{H_0}\frac{dH}{dt} \tag{3}$$

Where H_0 is the enthalpy of the whole process. Non - isothermal DSC analysis was performed instead of isothermal, because it provides more reliable information than isothermal data according to ICTAC recommendations [16]. Conversion degree α can be further obtained through integration of thermograms with respect to time and used for further analysis.

Traditionally, activation energy can be understood as an energy barrier required for a chemical reaction to occur, however the nature of this quantity is far more complex. For example in case of condensed matter studies it can vary with temperature and/or conversion [19].

This behavior is well known in e.g. electrochemistry, where both Arrhenius parameters varies with temperature [29,30]. Thus a constant E_a cannot be assumed in most studies of polymers. Moreover, in the context of polyurethane systems many processes and chemical reactions can occur at one time and all of them can pursue through different multi – step mechanisms [18]. Furthermore, those mechanisms can change with conversion degree (e.g. autocatalytic effects of urethane groups) [24]. In such scenario the use of isoconversional methods is one of the most reliable solutions.

3.2. Isoconversional methods

Isoconversional methods are commonly used tool for determination of activation energies of complex processes. If certain conditions are satisfied, it is also possible to estimate other Arrhenius parameters i.e. and pre-exponential factor A and model $f(\alpha)$ for each conversion degree (i.e. kinetic triples). A great and deep overview of isoconversional methods one can find in Vyazovkin's book [19]. Breifly, the key isoconversional principle states that for each defined degree of conversion α, the reaction rate $d\alpha/dt$ is only a function of temperature [18]. It can be easily shown by merging Eqs. (1) and (2) and taking logarithm both sides that:

$$ln\left(\frac{d\alpha}{dt}\right) = lnA - \frac{E_a}{RT} + \ln(f(\alpha)) \tag{4}$$

Eq. (4) is a well-known equation for Friedman differential method, usually suitable for analysis on differential data e.g. DSC [21]. Another way to perform isoconversional analysis is to apply integral methods
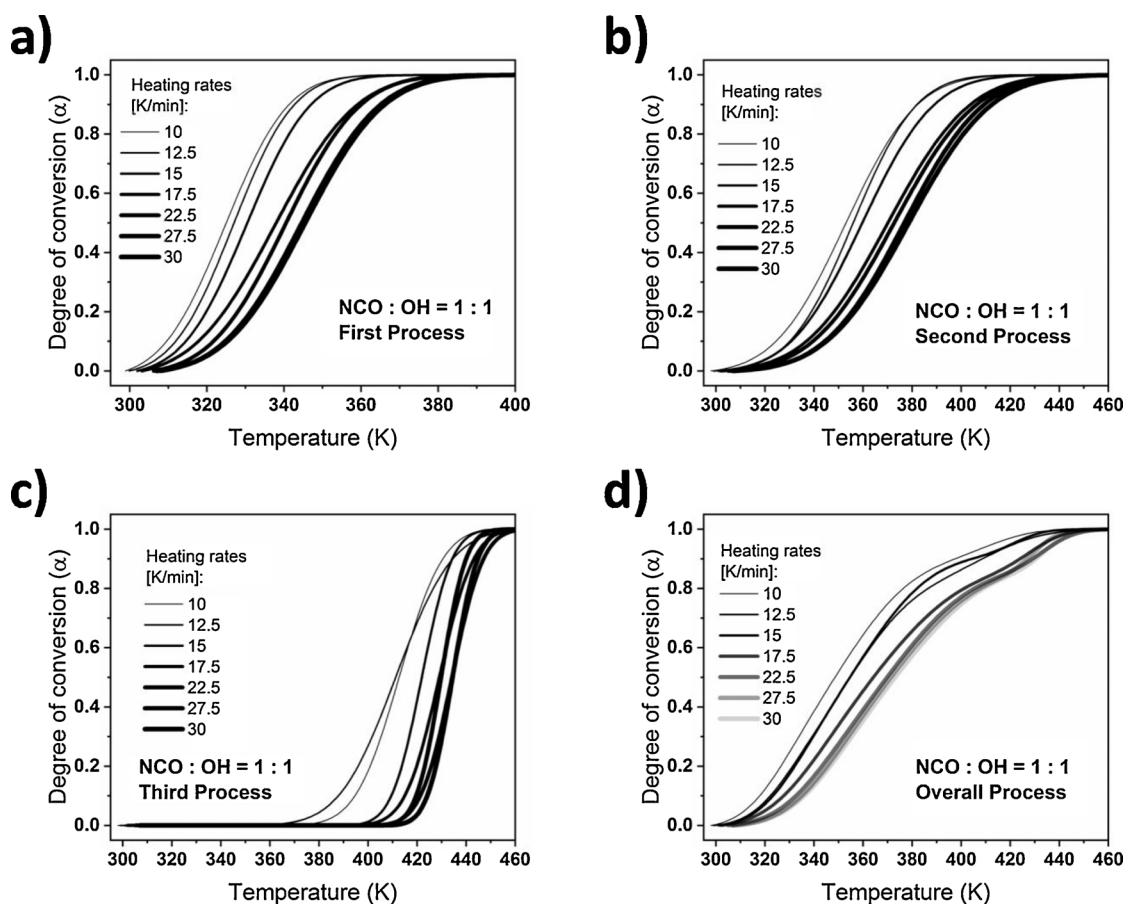
Fig. 4. Conversion as a function of temperature for the ratio NCO:OH = 1:1 a) first process b) second process c) third process d) overall process.

i.e. Kissinger – Akahira – Sunose (KAS) and Ozawa – Flynn – Wall (OFW). Explicitly, the basic Flynn equation is given by Eq. (5) [10]:

$$\ln(\beta) = \ln\left(\frac{AE_a}{R}\right) - \ln(g(\alpha)) + ln\left(\int\limits_{x_1}^{x_0} \frac{exp(-x)}{x^2} dx\right) \tag{5}$$

Where β is heating rate and x = E/RT and g(α) is integrated model function. It is defined according to Eq. (6).

$$g(\alpha) = \int\limits_0^\alpha \frac{d\alpha'}{f(\alpha')} \tag{6}$$

To simplify the integral on the right side and facilitate the analysis, a further step is needed, which is based on Doyle's approximation [9]:

$$ln\left(\int \frac{exp(-x)}{x^2} dx\right) \cong 1.052x - 5,303 + Const. \tag{7}$$

After substitution to Eq. (5) the straightforward relation between heating rate and temperature is obtained. One can estimate the activation energy by plotting logarithm of heating rate with respect to reciprocal temperature (i.e. Arrhenius plots) and performing linear regression for each conversion degree. Another widely applied isoconversional method is named after Kissinger – Akahira – Sunose, and the expression is given in Eq. (8) and is very similar to Eq. (5) [27]:

$$ln\left(\frac{\beta}{T^2}\right) = \frac{-E_a}{RT} + ln\left(\frac{AR}{E_a g(\alpha)}\right) \tag{8}$$

According to Starink however, KAS method gives more reliable results for wider activation energies range and should be superior to OFW [35]. The major drawbacks of isoconversional methods are connected to a limited range of used approximations. This obstacle can be omitted

through modern isoconversional methods involving numerical integration introduced by Vyazovkin [19] or applying certain corrections to existing methods [28]. However in our study, the classic methods gave a sufficient results so that the chemical information about the system was achieved.

3.3. Model – based approach

Sometimes the explicit form of f(α) function in Eq. (1) is known and can be obtained through derivation using certain model. Various existing kinetic models can be found in literature [19,24,25]. The most common model for cross-linking reactions of polymers is described by generalized Prout-Tompkins equation:

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E_a}{RT}\right)\alpha^m (1-\alpha)^n (-\log(1-\alpha)^p) \tag{9}$$

However in case of this study, equation with neglected logarithm term described the system sufficiently well. An expression for this particular case is called Sestak-Berggren. A detailed discussion concerned with advantages and disadvantages of this model can be found in the Sestak work [1]. This approach was also successfully used for investigating epoxy resin curing [7,34]. In the way of our study, the introduction of multi – step approach was essential, because occurring of three different processes during experiment were suspected. Per analogy to Sbirrazzuoli's work [6], an overall expression for conversion rate can be expressed as :

$$\frac{d\alpha}{dt} \approx A_1 exp\left(-\frac{E_{a1}}{RT}\right)\alpha^{m_1} (1-\alpha)^{n_1} + A_2 exp\left(-\frac{E_{a2}}{RT}\right)\alpha^{m_2} (1-\alpha)^{n_2} \tag{10}$$

The third process however was assumed to be consecutive to the previous two and separate fitting was performed using Eq. (9) with
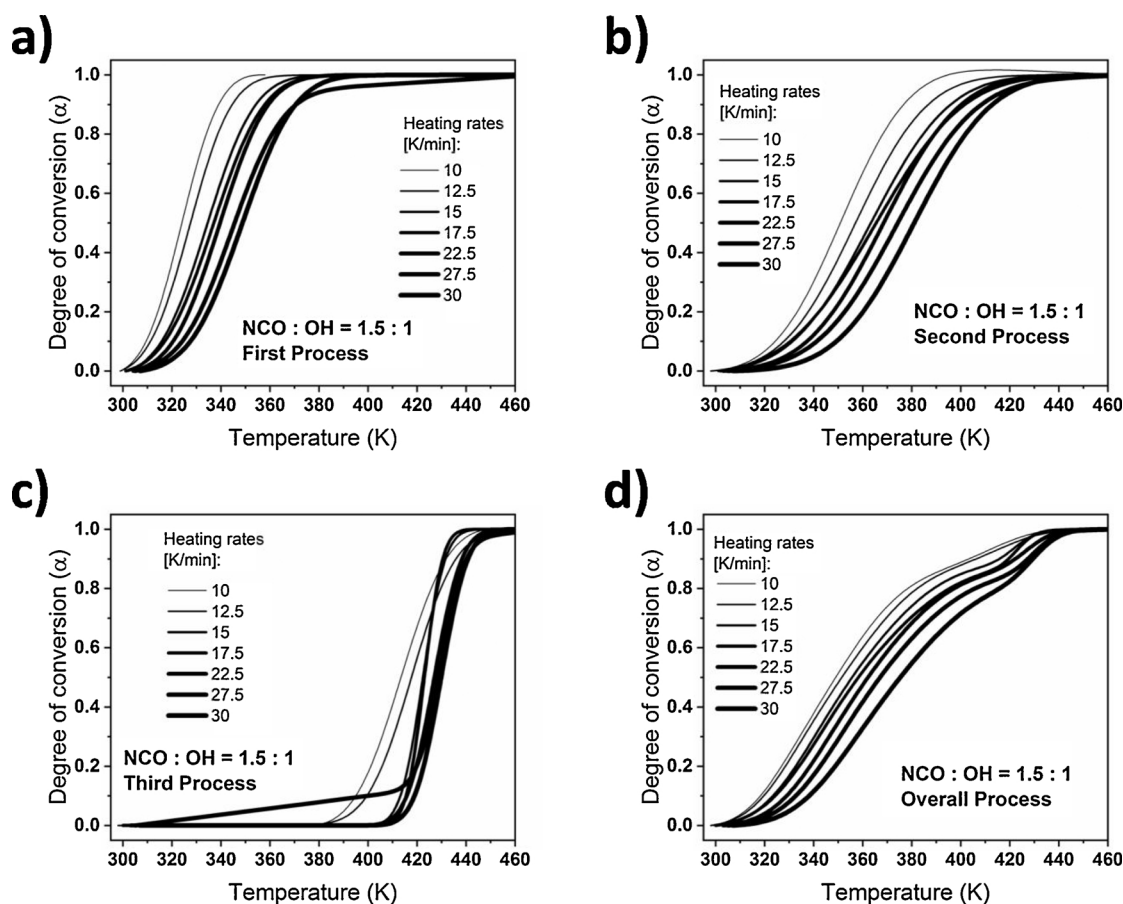
Fig. 5. Conversion as a function of temperature for the ratio NCO:OH = 1:1.5 a) first process b) second process c) third process d) overall process.

neglected logarithm term. Interpretation of constants appearing in Eq. (9) is vague, but intuitively reasoning, n is an analog of simple reaction order and non-zero m measures the intensity of autocatalytic processes [2]. Estimated activation energy values provided by isoconversional methods were used as initial parameters in non-linear regression procedure according to Levenberg-Marquardt algorithm. This data set was very fragile to proper choice of initial parameters and boundaries, so that the fitting procedure was conducted by trial and error until good convergence was accomplished.

4. Results and discussion

4.1. Analysis of thermograms and data deconvolution

DSC thermograms of reacting polyurethane mixtures are presented in Fig. 2. For both NCO : OH ratios two characteristic exothermic maxima can be observed. First of them occurs in temperatures 300 K – 400 K and its values grows almost linearly with increasing heating rate. Second maximum occurs in temperature range of 400 K – 450 K and one cannot give a straightforward peak temperature dependence on heating rate. Degradation of as formed polyurethane chains could also give its contribution to overall heat flow in temperatures close to 460 K [21,22]. It is worthy to note that the range of applied heating rate is unfortunately limited. Experiments with applied heating rates lower than 10 K/min did not result any valuable information i.e. exothermic peaks observed were very small and comparable to signal noise. It is possible that using higher sample masses, the exothermicity would be enhanced, but it was not possible due to equipment limitations. For heating rates higher than 30 K/min however, the signal from temperature lag was so high that too much

information about the first peak was lost. This signal could not be totally avoided even for lower heating rates, because of the nature of fast-curing resin i.e. the beginning of the process starts right after mixing and putting the sample to the aluminum pan.

A closer look on the thermograms reveals that the first peak consists of two different processes, because an additional shoulder right to the maximum can be seen. Therefore we decided to perform a Fourier self-deconvolution procedure and every thermogram was deconvoluted to three separated processes. In order to avoid errors connected to temperature lag at the beginning of experiment, first few data points were not included during deconvolution and baseline was subtracted. Two examples of resulting plots for both NCO : OH ratios are depicted on Fig. 3. Deconvoluted data plots for all of the remaining heating rates, as well as R^2 values for all fits can be viewed in ESI (Fig. S1, Fig. S2 and Tab. S1). Generally, in case of equimollar compositions one can observe that peaks corresponding to the first process have lower area than for the second process, while in case of isocyanate excess composition, those peaks have similar area. It stands for that addition of more isocyanate groups results in increase of the intensity of first process, while the second process is less independent of NCO : OH ratio. Through this analysis one can state the hypothesis that the first process is deblocking of isocyanate groups and second is simple polyaddition of isocyanates and polyols [5]. The nature of the last third process seems to be far more complex, because the shape of the peak is different for lower and higher heating rates. In case of raw data (Fig. 2), one can see that for 10 K/min and 12.5 K/min heating programs it consists of several different small peaks. This suggests than many processes occur in this temperature range. The proposed reactions that could explain this behavior are formation of allophanates and biurets [5]. This idea will be further investigated through isoconverional methods.
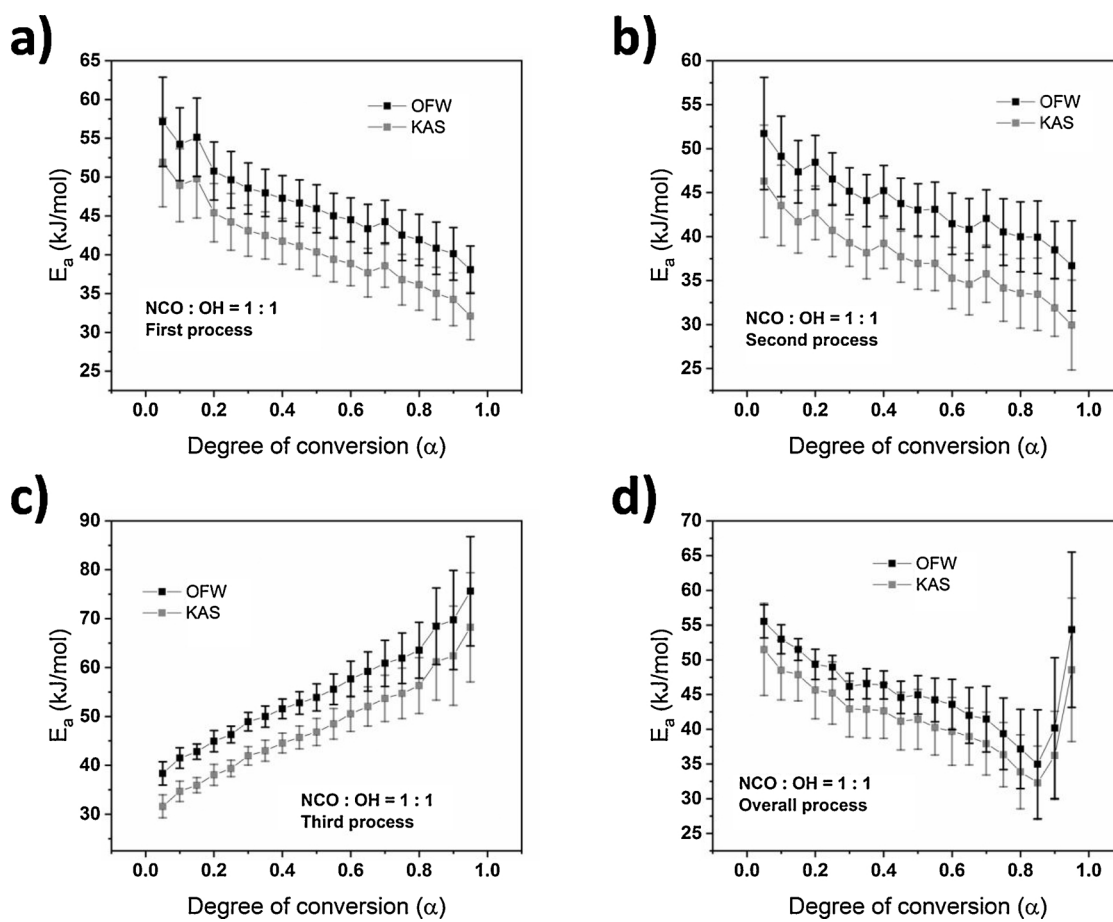
Fig. 6. Activation energy versus of conversion curves for the ratio NCO:OH = 1:1 a) first process b) second process c) third process d) overall process.

Table 3

Averaged activation energies obtained through isoconversional method [kJ/mol].

Method	First process	Second process	Third process	Overall process
NCO : OH = 1 : 1				
OFW	47 ± 5	44 ± 4	55 ± 10	46 ± 6
KAS	41 ± 5	38 ± 4	48 ± 10	42 ± 5
NCO : OH = 1.5 : 1				
OFW	42 ± 6	43 ± 1	–	49 ± 10
KAS	35 ± 5	37 ± 2	–	43 ± 10

4.2. Integration and isconversional methods

Integrated, deconvoluted data of all processes for equimollar and isocyanate excess mixture are given in Figs. 4 and 5respectively. One can see that almost all of the conversion – temperature curves have sigmoidal shapes. It is a commonly met phenomenon in DSC studies of polymer curing [12,18]. In general, the slope of those curves decreases for higher heating rates, however the third process deviates from this relation. The first process is executed in temperature range 300–360 K and is partially parallel with second process (Compare with overlapping peaks on Fig. 3). The offset of the first process occurs in temperature ca. 335 K (α exceeds 80%). In slightly higher temperatures however (340 K), there is an onset of the second process (α exceeds 20%), which means that not full completion of the first process is sufficient to increase the velocity of the second process. This observation supports the hypothesis that the first process might actually be isocyanate de-blocking and the second one the polymerization, because not all of the isocyanates have to be deblocked in order for the cross-linking to start.

Third and second processes also partially overlap, but in a less extent. In case of highest heating rates for example, in temperature 420 K second process is finished (α exceeds 95%) and the third process has not yet started (α less than 1%). This suggests that third process is consecutive with respect to the first and second processes and it is possible that corresponds to allophanate and biuret formation. Similar conclusion can be made by looking at the integrated data for an overall process, that are presented on the Figs. 4d and 5 d. There are no inflection points in temperatures where first and second processes overlaps, whereas in temperature 410 K (highest heating rates) one occurs indicating the transition between processes. It is to be noted, that there are no significant differences in those observations for integrated data of equimolar and isocyanate excess mixtures. The next step involves estimation of Arrhenius parameters and focuses on verifying the proposed hypotheses.

After integration of deconvoluted data, isoconversional methods were applied. Arrhenius plots for corresponding methods, as well as R^2 parameters, are collected in ESI (Figs. S3–S6, Tab. S2–S5). Fig. 6 shows activation energy dependences with respect to conversions, calculated for all processes using and NCO : OH = 1 : 1 mixture. In case of the first and second processes curves are decreasing with conversion and for wide range of conversions values are within 35–50 kJ/mol interval, which is consistent with other studies of similar systems [6,20]. The fact, that those curves decrease might correspond to diffusion control i.e. at higher conversions, the diffusion becomes the rate determining step of the process [31]. This behavior is frequently met during cross-linking of epoxy resins [33] and silicon resins [32] for both isothermal and non-isothermal experiments [34]. The last process however shows an increase of activation energy with respect to conversion form 30 kJ/mol to even 65 kJ/mol at highest conversions. That fact suggests that
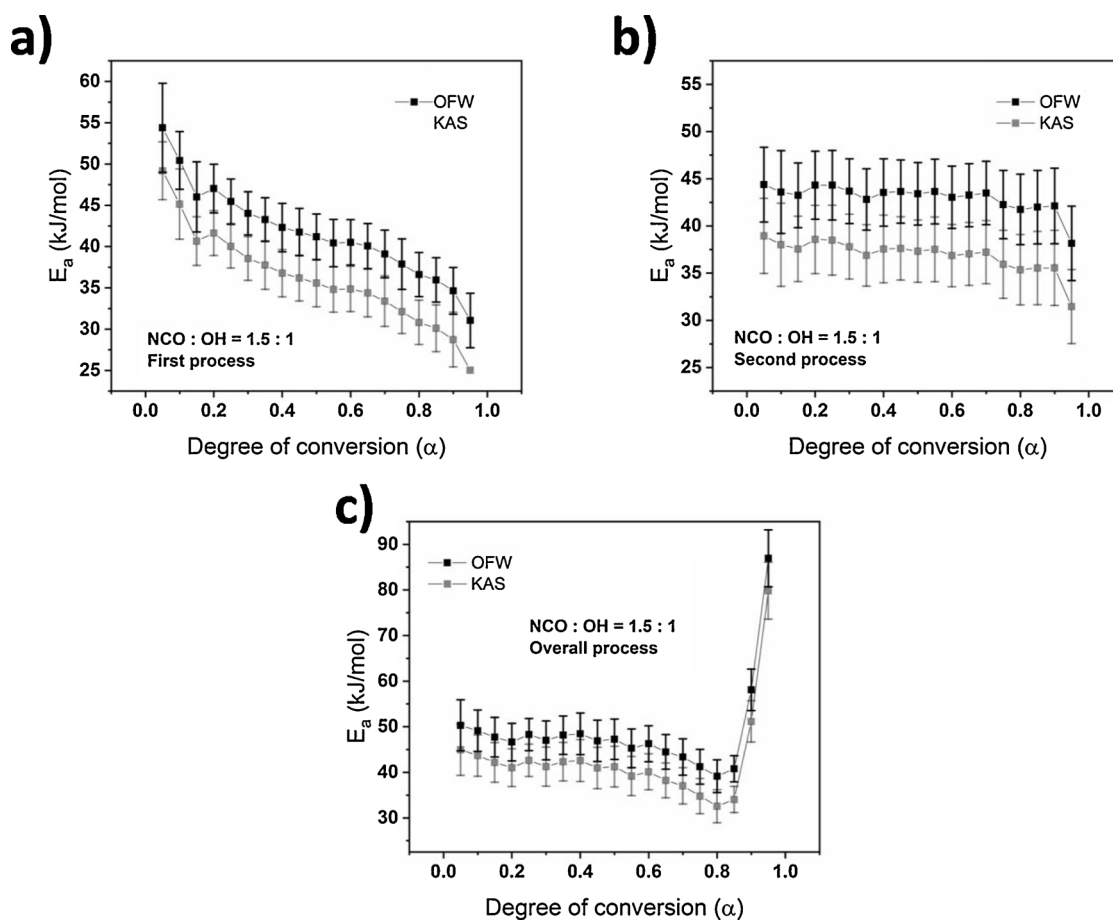
Fig. 7. Activation energy versus of conversion curves for the ratio NCO:OH = 1:1.5 a) first process b) second process c) third process d) overall process.
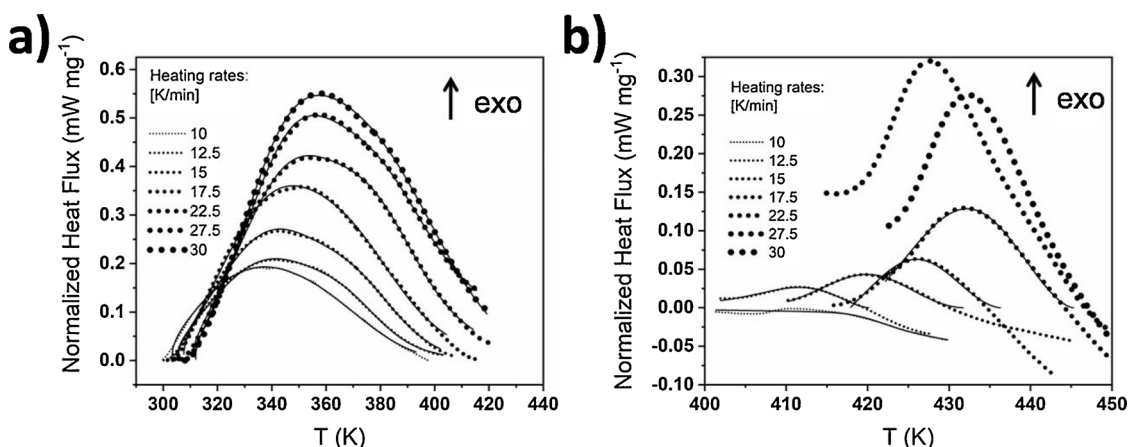

Fig. 8. DSC curves obtained via nonlinear fitting for the equimolar mixture of ingredients (NCO: OH = 1:1): a) first and second processes; b) third process.

the chemistry of this process is possibly different. The similar effect is observed in other studies involving polyurethane cross-linking and is ascribed to side reactions of urethane groups with free isocyanates forming allophanates [18].

For the purpose of comparison, we applied isoconverional methods for all integrated data as a one process. E_a values are very similar to the one obtained for each particular process i.e. for α equal 0.0 – 0.8 the overall curve decreases just like first and second processes do and for 0.8–1.0 increases to the similar values as for third process up to 60 kJ/mol. This observation suggests that even if the complex curing process is treated by isoconversional method as a whole, one can get similar information about particular processes. Averaged values of E_a are

collected in Table 3. Despite OFW and KAS methods resulted a set of activation energies with reasonably small errors, Friedman differential method could not be applied to deconvoluted data, because points on Arrhenius plots deviated significantly from a straight line. Examples of those plots with chaotically distributed data points are presented in ESI (Fig. S7).

Curves corresponding to the first and second processes for ratio NCO : OH = 1.5 : 1, presented on Fig. 7, are similar to the ones obtained for equimollar mixture i.e. activation energy decreases slightly with conversion indicating the diffusion control at highest conversions. However its values are shifted downwards by roughly 5 kJ/mol, which suggests that addition of excess isocyanate groups decrease the energy barrier
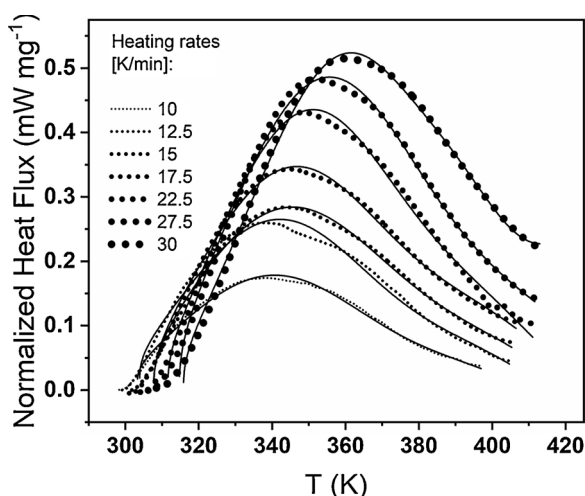
Fig. 9. DSC curves obtained via nonlinear fitting for the isocyanate excess mixture of ingredients (NCO: OH = 1:1.5).

Table 4
Kinetic parameters obtained via model – based approach.

Kinetic parameters	First process	Second process	Third process
NCO : OH = 1 : 1			
Pre – exponential factor [1/s]	5.47 ± 5.15 E5	4.29 ± 1.15 E5	1.1 ± 1.0 E7
Activation energy [kJ/mol]	39.4 ± 0.3	47.1 ± 0.6	61.8 ± 0.7
Reaction order n	4.05 ± 0.05	3.96 ± 0.64	0.94 ± 0.10
Reaction order m	4.44 ± 0.09	0.39 ± 0.10	1.60 ± 0.37
Goodness of fit (χ^2)	1.05 E-5	1.05 E-5	2.46 E-4
NCO : OH = 1.5 : 1			
Pre – exponential factor [1/s]	1.02 ± 0.18 E6	1.46 ± 1.10 E6	–
Activation energy [kJ/mol]	38.4 ± 3.2	43.8 ± 2.9	–
Reaction order n	3.52 ± 2.00	1.83 ± 1.13	–
Reaction order m	0.39 ± 0.25	0.48 ± 0.41	–
Goodness of fit (χ^2)	4.10 E-5	4.10 E-5	–

the surroundings the kinetics of deblocking is facilitated and the polymerization is hampered, because there is an insufficient amount of polyol to react with isocyanate excess. Thus, results of isoconversional methods seem to confirm the hypothesis about the nature of those processes. A little more insight however gives the approach based on nonlinear regression based on Sestak - Berggren model.

4.3. Model – based approach

Although isoconverional method provided a reliable description of kinetics of all three processes, it is worthy to apply the model-based approach also. To verify the hypotheses stated above and identify the chemistry of a system, a nonlinear fitting according to Sestak – Berggren equation was performed (Eq. (10)). Kinetic parameters (i.e. activation energies and pre-exponential factors) calculated through isoconversional method were taken as initial parameters. It is to be noted that the fitting procedure was executed for raw DSC data (not deconvoluted).In case of third process not all of the curves could be fitted according to chosen autocatalytic model. The fact that thermograms registered with highest heating rates (i.e. 27.5 and 30 K/min) could not converge, can be possibly explained by the complexity of secondary curing processes. Due to there is more than one process contributing to the heat flow, parameters of single process (Eq. (9) with neglected logarithm term) could not be fitted properly. Results of nonlinear fitting are presented in Figs. 8 and 9.

In case of curves obtained for fitting thermograms corresponding to excess isocyanate mixture, only the first two processes fits the assumed model. The fitting procedure could not converge for third process regardless of chosen initial parameters and boundary conditions. Therefore, kinetic parameters could not be obtained in this case, similarly as through isoconversional methods. Activation energies, pre-exponential factors and Sestak-Berggren partial orders of reactions n and m, obtained through nonlinear fitting, are presented in Table 4. Study [23] shows that activation energy of deblocking significantly varies with the compound used. In particular for Methyl 3-chloro-4- hydroxybenzoate deblocking temperature is 70 °C and activation energy is roughly 27–32 kJ/mol and for phenol those values are 135 °C and 75–108 kJ/mol correspondingly. In case of our studied system, the blocking component is unknown, but one can certainly conclude that the maximum of the first process indeed occurs in the temperature range of deblocking i.e. 340–350 K (see Figs. S1 and S2 in ESI), suggesting that hypothesis is likely to be true. Activation energy values for second process i.e. 47.1 and 43.8 kJ/mol are in good agreement with results obtained for simpler PUR systems (without blocking agents and with single monomer). Fernandez have shown that if isocyanate HDI is used, activation energy for polyaddition is roughly 45 kJ/mol [20]. Calculations form other studies of P-MDI results 40–42 kJ/mol activation energy [12] and Sbirrazzuoli reports 45–50 kJ/mol for both isoconversional and multi-step methods [6]. Therefore, one can conclude that second process the most probably corresponds to polyaddition reaction. In case of the third process, Tran [12] shows the results of Kamal – Sourour model fitting and they are roughly equal to 60–70 kJ/mol for allophanate side reaction. Sbirazzuoli [6] also reports 60 kJ/mol. By the power of those comparisons, the last exothermic peak (and third process) on thermograms in our study (i.e. 61.8 kJ/mol) is likely to correspond to allophanate formation.

5. Conclusions

A fast-curing complex commercial polyurethane system was investigated by means of non-isothermal DSC. Despite low quality of data connected to intrinsic properties of the commercial polyurethane system i.e. short pot life and cross linking onset in room temperature, three main processes were described kinetically. Based on comparison of activation energies and temperature ranges of peak maxima a mechanistic explanation was developed. Those processes are most likely to

and facilitate kinetics of those processes. Unfortunately, for the third process, isoconversional methods could not be applied, because the fitting of linear Arrhenius curves was impossible. This is a problem analogous to the one met applying Friedman method (See Fig. 7S). The proposed explanation of this phenomenon is that many overlapping processes occur in this temperature regime, so that deconvolution process leads to significant errors. As mentioned earlier, one of those processes are hypothesized to be allophanate formation. However some information on this process can be obtained by analyzing E_a plots of the overall processes. Activation energy grows rapidly in the highest conversions range to even 90 kJ/mol making the third processes for both NCO : OH ratios similar. It is possible that if large excess of isocyanate is introduced also biuret formation occurs. Nevertheless, values of Arrhenius parameters for the third process were still obtained using model-based approach and will be discussed further.

All of the activation energies calculated through isoconversional methods are collected in Table 3. There is a significant difference between results obtained by OFW and KAS methods. It is connected to different limitations of temperature integral approximations. However, activation energies estimated via KAS procedure (Eq. 7) are more reliable, because this method provides less inaccuracies than OFW [35]. An interesting observation is that in case of unity NCO/OH ratio the activation energy of the first process is slightly higher than for the second, but in the latter case it is the opposite. This corresponds well with proposed hypothesis, that the first process is isocyanate deblocking and second is polyaddition. If more NCO groups are present in

be subsequently isocyanate deblocking, polyaddition and allophanate formation. Activation energies obtained through isoconversional methods and nonlinear multi-step fitting procedure agreed very well with other studies in literature made for simpler polyurethane compositions. This shows that thermal analysis methods and kinetic models are suitable to study systems, where many multi-step reactions, and physical processes take place.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.tca.2019.178435.

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