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Is the Kamal's model appropriate in the study of the epoxy-amine addition kinetics?

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ABSTRACT

The overall model of the form: $d\alpha/dt = (K' + K\alpha^m)(1-\alpha)^n$, known as Kamal's model, has been analysed in this work. Although it can describe well the isothermal DSC experiment, the statistical criteria does not allow fixing exactly the adjustable power exponents in the model. In turn, the overall "reaction order" varies in a large range at almost identical confidence limits. The model evaluated in isothermal DSC mode at different values of m and n has been tested. The test has not been found out reliable to describe the data at varying temperature.

1. Introduction

The curing reaction of a bulk epoxy system, e.g. epoxy based composite material, occurs in temperature gradient. This is due to the fact that the epoxy ring opening is strongly exothermic. Hence, the heat/mass transfer solutions must be based on models, which reliably predict the reaction advance at varying temperature.

The mechanistic model of the epoxy-amine addition must account for the well-established autocatalysis. We present below the dimension-free form of the classical tri-molecular model of Smith and Horie et al. [1,2] that is further named as SH-model, viz.:

$$-\frac{d\lambda_1}{dt} = 2(K_1' + K_1\alpha)(1-\alpha)\lambda_1 \tag{1a}$$

$$-\frac{d\lambda_2}{dt} = (K_1' + K_1\alpha)(1-\alpha)(r\lambda_2 - \lambda_1) \tag{1b}$$

$$\frac{d\alpha}{dt} = (K_1' + K_1\alpha)(1-\alpha)(\lambda_1 + r\lambda_2) \tag{1c}$$

where α is the mostly important variable called degree of epoxy conversion, λ_1 and λ_2 are normalized concentrations of primary and secondary amine hydrogen atoms, respectively, K'_1 and K_1 dimension-free rate constants, and r amine hydrogen reactivity ratio.

It follows from the mass balance that: $R = (\lambda_1 + \lambda_2)/(1-\alpha)$, where R denotes the currently changing amine to epoxy ratio.

The parameters K_1 and K_1' in Eq. (1) are expressions of the corresponding elemental rate constants, k_1 and k_1'. The latter are supposed to obey the Arrhenius law, viz.:

$$k_1^i = k_0^i \exp\left(-\frac{E_a^i}{RT}\right) \tag{2}$$

where T is the curing temperature, in K; $R = 8.314\,\mathrm{kJ\,kmol^{-1}\,K^{-1}}$ universal gas constant, k_0^i pre-exponential factors having the dimension of k_1^i, and E_a^i activation energies, in $\mathrm{kJ\,mol^{-1}}$.

The rate constant k_1 can be assigned to the tri-molecular autocatalysis, while k_1' denotes the bi-molecular initiation. In the present case, K_1 and K_1' express primary amine reactions.

Flammersheim has recently reported a model based on the assumption that intermediate interactions precede the formation of the transition state complex [3,4]. Other authors have developed this approach and good fit of experiment to model has been established [5–13]. We present below the simplest dimension-free model [10] based on the idea of Flammersheim. It is further named as F-model:

$$K^* = \frac{y}{(1-\alpha-y)(c_0+\alpha-y)} \tag{3a}$$

$$-\frac{d\lambda_1}{dt} = 2[K_1'(1-\alpha-y) + K_1 y]\lambda_1 \tag{3b}$$

$$-\frac{d\lambda_2}{dt} = [K_1'(1-\alpha-y) + K_1 y](r\lambda_2 - \lambda_1) \tag{3c}$$

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$$\frac{d\alpha}{dt}=[K'_1(1-\alpha-y)+K_1y](\lambda_1+r\lambda_2) \tag{3d}$$

where y is normalized concentration of epoxy groups involved in E. . .OH complexes, c_0 initial normalized concentration of hydroxyl groups, and K^* equilibrium constant describing the formation of intermediate E. . .OH complexes prior to the formation of A. . .E. . .OH transition state complexes.

Variations and extensions of Eq. (3) have been applied to account for the discrepancy from SH-model. Hence, the fitting experiments to Eq. (3) are the mechanistic alternative to the formal approach that is analysed in the present study. Another approach for predicting the autoacceleration of the epoxy-amine addition can be also found in the literature [14].

If the reactivity of primary and secondary amine hydrogen is equal, or $r = 1$, then Eq. (1) converge into an overall model of the form [15,16]:

$$\frac{d\alpha}{dt}=(K'+K\alpha)(1-\alpha)(R_0-\alpha)=K(B+\alpha)(1-\alpha)(R_0-\alpha) \tag{4}$$

where $R_0 = a_0/e_0$ is the initial amine to epoxy ratio.

The missing subscript in Eq. (4) means that K and K' have to be considered as overall rate constants. The overall model describing the reaction in stoichiometric proportions, or $R = R_0 = 1$ and $\lambda_1 + \lambda_2 = (1 - \alpha)$, becomes:

$$\frac{d\alpha}{dt}=(K'+K\alpha)(1-\alpha)^2=K(B+\alpha)(1-\alpha)^2 \tag{5}$$

The rate constants K' and K of some epoxy-amine reactions have been determined mainly in stoichiometric quantities of components as the slope and intercept of the plot:

$$\dot{r}=\frac{d\alpha}{dt}\cdot\frac{1}{(1-\alpha)^2}=K'+K\alpha \tag{6}$$

where $\dot{r}$ is an expression in the autocatalytic kinetics known as reduced reaction rate.

The important early research within this approach has been discussed in several books and reviews [16–20]. The analysis of literature shows that experiments sometimes obeyed Eq. (6), at least in limited ranges of conversion and temperature [15,16], but upward deviations from the plot of $\dot{r}$ versus α have been more often observed [2,17–19]. The accepted approximation in Eq. (1), i.e. $r = 1$, cannot explain alone the deviations from the plot of $\dot{r}$ versus α. It has been shown that typical deviations from this plot yield $r > 1$ in terms of Eq. (1) [21]. The calculated best fit value of r has been found out unreliable in some cases, or $r > 2$ [10].

To explain the mentioned discrepancy, Kamal has proposed a modification of Eq. (5) [22]:

$$\frac{d\alpha}{dt}=(K'+K\alpha^m)(1-\alpha)^n=K(B+\alpha^m)(1-\alpha)^n \tag{7}$$

where m and n are experimentally adjustable parameters.

The derivation of power exponents m and n in this model has been carried out using the parameters at the peak maximum of reaction rate curves and accepting the approximation $(m + n) = 2$ [23,24]. K' and K can be iteratively determined from the plot:

$$\dot{r}=\frac{d\alpha}{dt}\cdot\frac{1}{(1-\alpha)^n}=K'+K\alpha^m \tag{8}$$

The comparison of two approaches indicates the advantages of the Kamal's model. It is easy to apply, as well as to adapt to the heat/mass transfer solutions. On the other hand, the Kamal's approach has disadvantages considering the epoxy-amine addition kinetics. They are briefly commented below.

The first disadvantage of the Kamal's approach is well evident from the derivation of the SH-model in dependence of stoichiometry – see Eq. (4). In comparison, the Kamal's model has no physical meaning at varying stoichiometry [2,15,16].

The second disadvantage of the Kamal's model concerns the parameter number. A four-parameter fitting of a single equation model is in principle problematic and it requires special statistics. Having in mind that m and n have been often found out to be temperature dependent, the parameter number makes the model inadequate, especially in non-isothemal DSC regime.

Kamal has introduced his model by analogy with the rate equations describing some auto-accelerating heterogeneous processes [25]. The power exponent m and n in these equations have geometry meaning and their sum was restricted to integer numbers, viz. $m + n = 2$ or $m + n = 3$ [26]. Consequently, the third disadvantage of the Kamal' model relates to the physical meaning of power exponents, as well as their calculated best fit values.

Talbot has reported a mechanistic model [27], which does not confront with the basic idea of the F-model. The author of this study has pointed out that the transform of classical into Kamal's model might be useful but at certain restriction with respect to the power exponents. It appears from the Talbot's consideration that: $1 \le n \le 2$; and $m \le 1$.

The present work is subjected to the advantages and disadvantages of the Kamal's model. Our analysis concerned the very recent research on the epoxy-amine reaction [28–35], where the values of m and n have been found out in agreement with those Talbot predicted. We have restricted intentionally the reference list, but we have to note that one can find some studies in the literature, the "overall reaction order" in which is confusing, viz. $m + n < 1$ or $m + n > 3$. In our opinion, the physical meaning of such values seems doubtful from the point of view of the homogeneous chemical kinetics.

2. Experimental

The epoxy component used in this work was the model epoxy resin DER-332 of Dow Chemical (DGEBA, $M_w = 348\ \mathrm{kg\,kmol^{-1}}$). The amine hardeners for this resin, m-phenylene diamine (mPDA) and diamino diphenyl methane (DDM), were 99% purity grade substances. All reactants were supplied from Fluka. The amine hardeners and DGEBA were melted above their melting temperatures. To minimize the reaction advance during sample preparation, mPDA was mixed with DGEBA at 328 K. The melted DDM was added to DGEBA at 348 K, since DDM tended to crystallize below this temperature. Samples ranging from 10 to 15 mg were prepared in standard Al crucibles. The samples inside a desiccator in plastic bags were frizzed at 253 K. Prior to use, they were allowed to equilibrate with the environment into the bags for 15–20 min. Fresh reactive mixtures were weekly prepared.

The method used in the study was conventional DSC. A DSC-2C instrument of Perkin-Elmer interfaced to 3600 Data Station with the standard data acquisition and analytical software was applied for the system DGEBA with mPDA. The instrument was equipped with an external refrigerating device (Intercooler II) and argon purge gas system (20 mL min^{-1}). It was regularly calibrated using In and Zn standards paying special attention on the final point of the baseline. All data sets for this system were averaged from at least three runs performed at each temperature or heating rate. A detailed description of these experiments can be found in the literature [36,37]. The experiment on the system DGEBA with DDM was carried out at two laboratories using additionally Perkin-Elmer DSC-7 instrument. The measurement conditions were identical to those for the system DGEBA with mPDA.

The experimental data collected in the controlling computers were transferred in an IBM compatible PC and the further analysis was performed using Excel. Both the free version of Berkeley Madonna (ordinary differential equation solver) and self-developed software were applied for the modelling purposes.

Table 1
DSC curing peak characteristics in dependence of heating rate for the reaction of DGEBA with mPDA according to the overall SH-model, see Eq. (5).

Heating rate	Characteristics at T_p		
K min^{-1}	T_p (K)	α_p	$(d\alpha/dT)_p$ (K^{-1})
Experimental data			
10	432.9	0.459	0.02195
5.0	414.7	0.458	0.02380
2.5	398.6	0.454	0.02640
Model simulated data			
10	432.9	0.447	0.02205
5.0	414.9	0.447	0.02405
2.5	398.5	0.447	0.02625
Model parameters $E_a = 50.5$ kJ mol^{-1}; $K_0 = 3.13 \times 10^4$ s^{-1}; $B = 0.025$			

3. Results and discussion

3.1. Kamal's model descriptions based on non-isothermal DSC experiments

We have recently studied the non-isothermal DSC kinetics of the reaction of DGEBA with mPDA applying a four-step kinetic approach. It consisted of: (i) model-free derivation of the dependence E_a versus α; (ii) analysis at the peak maximum temperature; (iii) single curve non-isothermal DSC kinetic methods; and (iv) reaction modeling.

Based on this approach, a single rate constant SH-model has been evaluated [36]. We present in Table 1 the DSC curing peak characteristics at the maximal temperature, T_p, used to control the model simulations. The kinetic parameters of the "best" SH-model derived in non-isothermal DSC regime are given in Table 1.

Applying the same approach on the reaction of DGEBA with DDM, the overall SH-model can be also evaluated. Identical data to those presented in Table 1 are listed in Table 2 for the non-isothermal DSC curing curves of the system DGEBA with DDM.

The comparison of experimental and model predicted data, presented in Table 1, indicate that the overall SH-model can be considered as a good approximation for the system DGEBA with mPDA. On the contrary, the values of α_p in Table 2 imply that the SH-model is probably a rough approximation for the system DGEBA with DDM.

To improve the model description of both data sets, one can accept the Kamal's approach. Assuming $m = 1$, we have optimized the model by varying n. The characteristics at T_p and best fit parameters derived according to Eq. (7) are shown in Table 3 (for the system DGEBA with mPDA) and Table 4 (for the system DGEBA with DDM).

Table 2
DSC curing peak characteristics in dependence of heating rate for the reaction of DGEBA with DDM according to the overall SH-model, see Eq. (5).

Heating rate	Characteristics at T_p		
K min^{-1}	T_p (K)	α_p	$(d\alpha/dT)_p$ (K^{-1})
Experimental data			
10	441.4	0.484	0.02285
5.0	422.9	0.481	0.02500
2.5	407.6	0.478	0.02645
Model simulated data			
10	441.1	0.446	0.02285
5.0	423.6	0.446	0.02465
2.5	407.4	0.446	0.02655
Model parameters $E_a = 54.6$ kJ mol^{-1}; $K_0 = 7.68 \times 10^4$ s^{-1}; and $B = 0.025$			

Table 3
DSC curing peak characteristics in dependence of heating rate for the reaction of DGEBA with mPDA according to the Kamal's model at $m = 1$, see Eq. (7).

Heating rate	Characteristics at T_p		
K min^{-1}	T_p (K)	α_p	$(d\alpha/dT)_p$ (K^{-1})
Experimental data			
10	432.9	0.459	0.02195
5.0	414.7	0.458	0.02380
2.5	398.6	0.454	0.02640
Model simulated data			
10	432.8	0.459	0.02185
5.0	414.9	0.459	0.02380
2.5	398.5	0.456	0.02635
Model parameters: $E_a = 50.5$ kJ mol^{-1}; $K_0 = 2.98 \times 10^4$ s^{-1}; $n = 1.91$; and $B = 0.032$ (at $dT/dt = 10$ K min^{-1}) $B = 0.031$ (at $dT/dt = 5$ K min^{-1}) $B = 0.027$ (at $dT/dt = 2.5$ K min^{-1})			

Table 4
DSC curing peak characteristics in dependence of heating rate for the reaction of DGEBA with DDM according to the Kamal's model at $m = 1$, see Eq. (7).

Heating rate	Characteristics at T_p		
K min^{-1}	T_p (K)	α_p	$(d\alpha/dT)_p$ (K^{-1})
Experimental data			
10	441.4	0.484	0.02285
5.0	422.9	0.481	0.02500
2.5	407.6	0.478	0.02645
Model simulated data			
10	441.1	0.479	0.02285
5.0	423.6	0.479	0.02465
2.5	407.4	0.479	0.02655
Model parameters: $n = 1.78$ $E_a = 54.6$ kJ mol^{-1}; $K_0 = 6.85 \times 10^4$ s^{-1}; and $B = 0.039$			

As one can see from these data, the particular case of the Kamal's model (assuming $m = 1$) can describe the progress of both reactions in linear programmed temperature DSC mode. The simulated curves shown in Figs. 1 and 2 confirm this finding.

Fig. 3 exhibits the model test with respect to isothermal DSC data. The data in this figure show that the evaluated single rate constant Kamal's model predicts reliably the early stage of the reactions

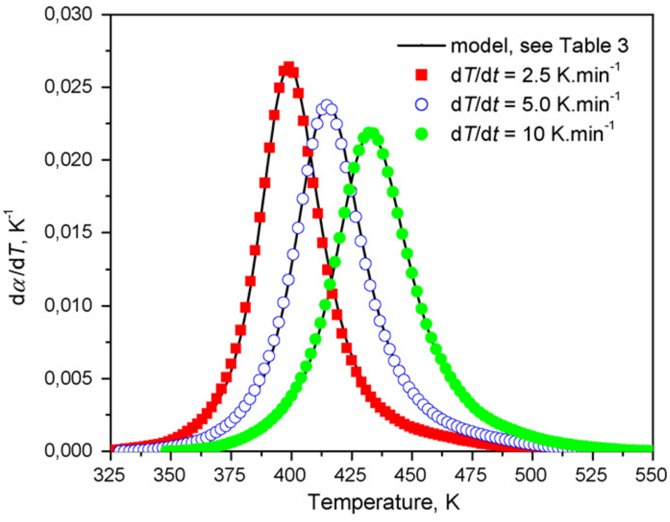

Fig. 1. Comparison between experimental and model simulated data according to the Kamal's model evaluated in non-isothermal DSC regime for the reaction of DGEBA with mPDA, see the kinetic data in Table 3.

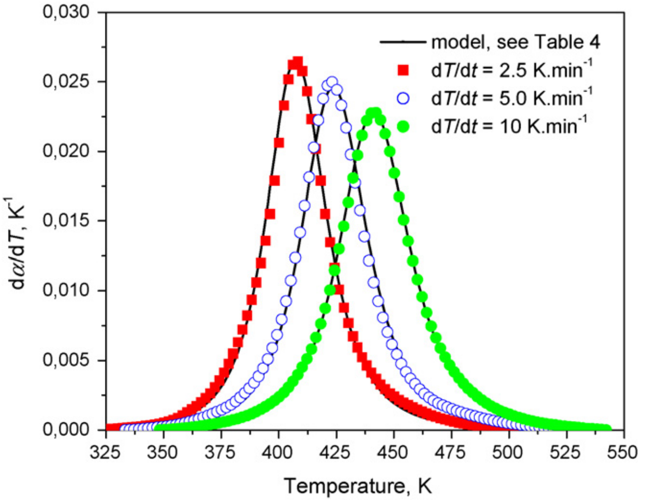

Fig. 2. Comparison between experimental and model simulated data according to the Kamal's model evaluated in non-isothermal DSC regime for the reaction of DGEBA with DDM, see the kinetic data in Table 4.

of DGEBA with mPDA. Hence, it can be accepted as a good approximation for two stage processing descriptions. The model of the second stage can be derived additionally.

As one can find out, the Kamal's model evaluated in non-isothermal DSC regime is not appropriate for single stage processing solution having in mind the deviations of experiment from model at the final stage of the reaction of DGEBA with mPDA.

Such kind of prediction concerning the reaction of DGEBA with DDM is obviously bad.

3.2. Kamal's model descriptions based on isothermal DSC experiments

We have pointed out recently that the model description in isothermal DSC regime is probably different. Assuming $m = 1$, it has been found out that $n \approx 1.6$ for the system DGEBA with mPDA [37]. The present study implies that $n \approx 1.15$ for the system DGEBA with DDM.

We show in Figs. 4 and 5 the Kamal's plots based on isothermal DSC data. The data have been obtained by statistical search of the best fit values of n (at the best fit interval of m). The values of power exponents thus determined, together with statistical criteria of the model fitting, R^2, are labeled in the figures. The Kamal's plots at other curing temperatures, T_c, are even better than those presented in Figs. 4 and 5.

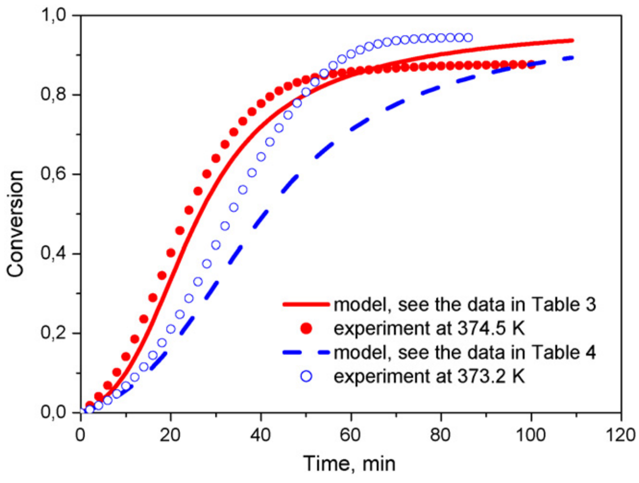

Fig. 3. Tests at T_c = constant of the Kamal's model evaluated in non-isothermal DSC regime, see the kinetic parameters listed in Table 3 for the reaction of DGEBA with mPDA and Table 4 for the reaction of DGEBA with DDM.

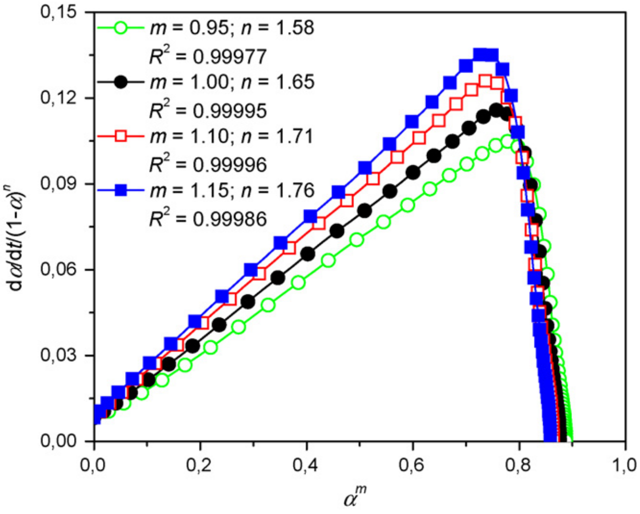

Fig. 4. Kamal's plots at different values of the parameter m for the reaction of DGEBA with mPDA; T_c = 374.5 K.

Several findings can be drown based on the data in these figures:

1. The overall reaction order varies in a large range at nearly identical statistical criteria, i.e. $(m+n) = 2.53–2.92$ (for the system DGEBA with mPDA) and $(m+n) = 1.85–2.13$ (for the system DGEBA with DDM);
2. The value $(m+n)$ and its variance differ for the reactions studied, but $(m+n)$ is less than the value obtained by fitting in non-isothermal DSC mode when accepting $m = 1$;
3. The overall reaction order, as determined in isothermal DSC regime for the reaction of DGEBA with DDM, deviates from the reaction order satisfying the non-isothermal model fitting, which appears to fulfill the original Kamal's restriction, i.e. $(m+n) \approx 2$;
4. The overall reaction order, as determined in isothermal DSC regime for the reaction of DGEBA with mPDA, approaches the

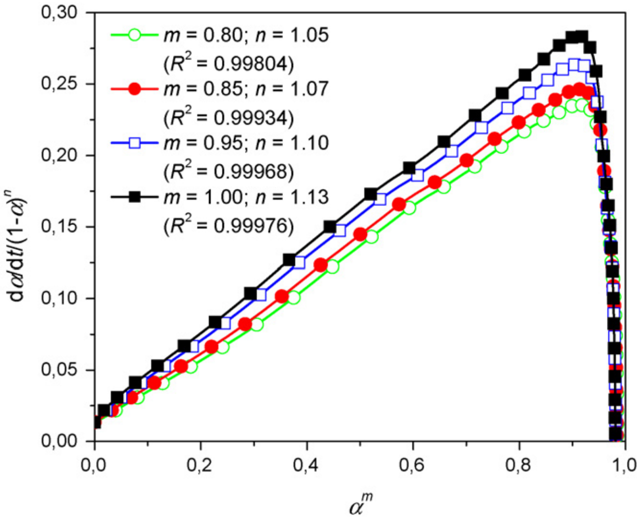

Fig. 5. Kamal's plots at different values of the parameter m for the reaction of DGEBA with DDM; T_c = 403.2 K.

Table 5
Isothermal Kamal's plots in dependence of temperature obtained assuming different values of the power exponent m for the reaction of DGEBA with mPDA.

Temperature	Kamal's model parameters					
	m	n	$m+n$	K	K'	R^2
354.5	0.95	1.58	2.53	0.0525	0.00214	0.99977
364.5				0.0809	0.00395	0.99961
374.5				0.1313	0.00709	0.99982
384.5				0.0201	0.01356	0.99987
	Kinetic parameters of the Kamal's model assuming $m = 0.95$: $E_a = 51.09$ kJ mol^{-1}; $K_0 = 2.87 \times 10^4$ s^{-1}; $E'_a = 69.35$ kJ mol^{-1}; $K'_0 = 5.77 \times 10^5$ s^{-1}					
354.5	1.00	1.63	2.63	0.0559	0.00240	0.99988
364.5				0.0906	0.00390	0.99989
374.5				0.1411	0.00754	0.99989
384.5				0.2180	0.01380	0.99986
	Kinetic parameters of the Kamal's model assuming $m = 1.00$: $E_a = 51.30$ kJ mol^{-1}; $K_0 = 3.37 \times 10^4$ s^{-1}; $E'_a = 66.83$ kJ mol^{-1}; $K'_0 = 2.67 \times 10^5$ V s^{-1}					
354.5	1.10	1.72	2.82	0.0634	0.00286	0.99994
364.5				0.1029	0.00463	0.99991
374.5				0.1615	0.00851	0.99995
384.5				0.2530	0.01464	0.99942
	Kinetic parameters of the Kamal's model assuming $m = 1.10$: $E_a = 52.15$ kJ mol^{-1}; $K_0 = 5.13 \times 10^4$ s^{-1}; $E'_a = 69.35$ kJ mol^{-1}; $K'_0 = 7.07 \times 10^4$ s^{-1}					
354.5	1.15	1.77	2.92	0.0679	0.00306	0.99992
364.5				0.1106	0.00489	0.99981
374.5				0.1745	0.00877	0.99995
384.5				0.2750	0.01469	0.99894
	Kinetic parameters of the Kamal's model assuming $m = 1.15$: $E_a = 52.71$ kJ mol^{-1}; $K_0 = 6.59 \times 10^4$ s^{-1}; $E'_a = 59.89$ kJ mol^{-1}; $K'_0 = 3.30 \times 10^4$ s^{-1}					

reaction order satisfying the non-isothermal model fitting, i.e. $(m+n) \approx 3$.

Table 5 presents an extended test of the Kamal's model at four curing temperatures for the system DGEBA with mPDA. We have to note the small difference between graphical data shown in Fig. 4 and numerical data listed in Table 5. The data in Table 5 are mean values in the investigated temperature range, whereas Fig. 4 exhibits the best fit plots at $T_c = 374.5$ K.

The model fitting test of isothermal data on the reaction of DGEBA with mPDA has been carried out in our previous study [37]. A perfect agreement between model (at $m = 1$ and $n = 1.5$) and experimental data has been observed in the kinetically controlled region. The model fitting tests at all combinations of m and n derived in this study does not differ strongly from those being already published.

The kinetic parameters of the reaction of DGEBA with mPDA according to the Kamal's model at different values of m and n are also given in Table 5. As one can see, E_a of the autocatalytic rate constant (associated with the power exponent m) increases with the increase of m, while E'_a of the non-catalytic rate constant changes strongly in the opposite direction. However, E_a is higher, while E'_a is less, than E_{ap} obtained applying isoconversional shift [37]. From an entirely mathematical point of view, all values of m and n listed in Table 5 appear acceptable.

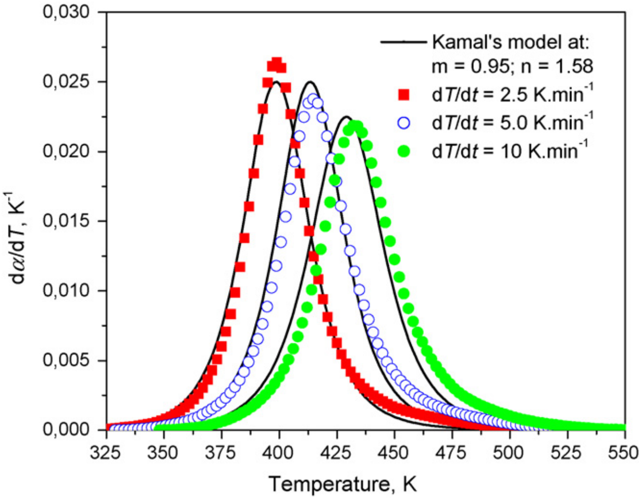

Fig. 6. Comparison between experimental and model simulated data according to the Kamal's model for the reaction of DGEBA with mPDA $(m+n) = 2.53$.

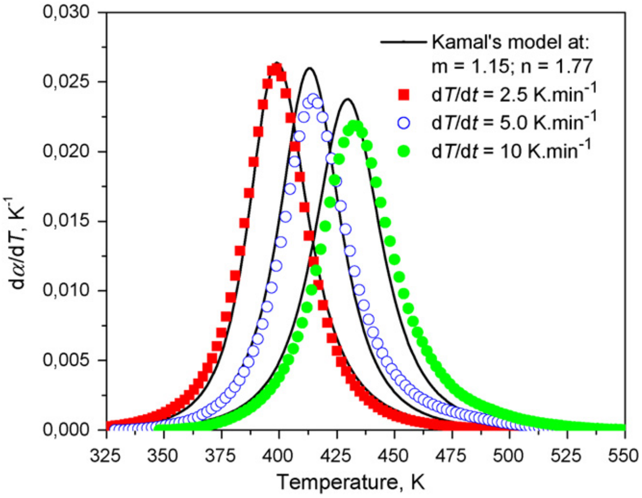

Fig. 7. Comparison between experimental and model simulated data according to the Kamal's model for the reaction of DGEBA with mPDA $(m+n) = 2.92$.

Figs. 6 and 7 show the inverse test of the Kamal's model. The kinetic parameters determined at constant temperatures have been used to simulate the curves at programmed temperature. The boundary solutions in Table 1, at $(m+n) = 2.53$ and $(m+n) = 2.92$, have been simulated at three heating rates. In spite of its mathematical flexibility, the Kamal's model evaluated at constant temperature cannot predict the reaction of DGEEBA with mPDA in programmed temperature DSC mode, as the data in these figures indicate. Therefore, it is not sufficiently reliable for the heat/mass transfer processing solutions. We have to note that such test of the Kamal's model concerning the reaction of DGEBA with DDM is quite worse.

4. Conclusions

As one can establish, we have applied a simple modelling approach to test the validity of the Kamal's model. The test is based on experiments of two reactions, DGEBA with mPDA (reaction (1)) and DGEBA with DDM (reaction (2)), studied in both isothermal and programmed temperature DSC mode.

We have performed two types of data analysis. The mostly probable Kamal's model has been estimated based on non-isothermal DSC data and the evaluated model has been applied to simulate the curves at constant temperatures.

The opposite analysis has been carried out with respect to the isothermal DSC experiment. The Kamal's model has been estimated at constant temperatures. Then, the evaluated model has been applied to simulate the curves in programmed temperature regime.

Assuming $m = 1$, the Kamal's model has been evaluated in non-isothermal DSC regime at the following values: $n = 1.91$ (for reaction (1)) and $n = 1.78$ (for reaction (2)). The data in Figs. 1 and 2, showing an excellent fit of experiment to model, confirm these results.

The Kamal's model evaluated in non-isothermal DSC regime has been tested at $T_c = 374.5$ K for reaction (1), and $T_c = 373.2$ K for reaction (2). The comparison of experimental and model predicted data imply that the experiment significantly deviates from the model for reaction (2). The Kamal's model, thus evaluated, seems acceptable to describe the early stage of reaction (1).

The evaluation of the Kamal's model in isothermal DSC mode infers that it cannot be fixed exactly at a single pair of m and n, their sum exhibiting the overall reaction order. The plots in Figs. 4 and 5 confirm this finding.

The data in Fig. 5 indicate that the overall reaction order in the Kamal's model ($m + n$), as determined in isothermal DSC regime for reaction (2), must be different from that evaluated in non-isothermal DSC mode. Note that $m = 1$ appears in both evaluated models, but ($m + n$) in non-isothermal regime differ dramatically from ($m + n$) in isothermal regime.

The graphical data in Fig. 4 and numerical data in Table 5 imply that the reaction order at $(m + n) = 1.92$ corresponds to the reaction order of the Kamal's model, as estimated in non-isothermal DSC regime. However, the simulated curves at $m = 1.15$ and $n = 1.77$, together with the simulation at $m = 0.95$ and $n = 1.53$, are not sufficiently good to validate the Kamal's model. The data in Figs. 6 and 7 illustrate this conclusion.

Vyazovkin and Sbirrazzuoli have drown similar conclusions concerning the availability of the Kamal's model [38,39]. These authors have proposed that the isoconversional (or model-free) methods are the mostly appropriate methods to describe complex cure kinetics.

Flammersheim [3,4] and Swier et al. [7–9] have performed good description of non-isothermal DSC data based on models similar to Eq. (3). The analysis allows us to suppose that a better description of non-isothermal data can be distinguished applying the mechanistic approach. Moreover, their models describe the epoxy-amine reaction satisfactorily both at stoichiometry and in an excess of amine. The kinetics in an excess of epoxy is a more special case, which has been discussed recently [40].

The mechanistic kinetic models of the epoxy-amine addition must answer two important questions, namely: (i) why the reaction scheme in non-isothermal mode appears so close to the classical scheme describing tri-molecular autocatalysis and (ii) what reasons exist to observe different deviations from the classical model at constant temperature. In our opinion, the Kamal's model cannot answer these questions.

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