

The kinetics of cure of epoxides and related sulphur compounds studied by dynamic DSC

K. Pielichowski*, P. Czub, J. Pielichowski

Department of Chemistry and Technology of Polymers, Technical University, ul. Warszawska 24, 31-155 Cracow, Poland

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Abstract

Cure kinetics of model epoxides and related sulphur compounds—(1,3-oxothiolane-2-thione)s—by hexahydrophthalic anhydride have been investigated by means of dynamic differential scanning calorimetry (DSC). The apparent activation energy values (E) were determined for the whole conversion range by isoconversional methods of Friedman and Ozawa–Flynn–Wall. For the (1,3-oxothiolane-2-thione)s under investigation E lie in the range of 73.5–281.6 kJ/mol and show some instability regions at either the autoaccelerated initial stages of the cure or the diffusion-controlled final stage. Further kinetic studies confirmed this hypothesis—an advanced approach based on non-linear regression method revealed that model functions possess autocatalytical or n th dimensional nucleation features which give an additional insight into the mechanism of cure process. Nucleation mechanism occurs probably due to sterical arrangements, which strongly influence non-dimensional growth in a cross-linked network during the latter stage of cure, but prior to vitrification, which however governs the nature of post-cure treatments and resulted therefrom deformations of the final network. The obtained kinetic parameters allow a prediction of the cure behaviour in extrapolated range of the degree of conversion, time and temperature. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Epoxides; (1,3-oxothiolane-2-thione)s; Curing behaviour

1. Introduction

A careful survey of existing literature on curing behaviour of epoxides and their sulphur-containing derivatives reveals that in spite of the large amount of work that has been done in polymer chemistry of epoxides, there has been little work on their analogues formed in reaction with carbon disulphide—(1,3-oxothiolane-2-thione)s, although they are of interest as initial compounds which can be further cured to give novel resins with better mechanical properties in subambient temperature [1–3], efficient polyelectrolytes [4], thermal stabilisers for methyl methacrylate and styrene copolymers [5] and metal scavengers in aqueous polymeric dispersions [6]. In a series of papers on thioetherglycidyl resins, which were synthesised by polycondensation of di(mercaptomethyl)naphthalenes with epichlorhydrin, Charnas and Podkościelny proved that the thioderivatives can be cured by means of common curatives used for epoxy resins, such as hexahydrophthalic anhydride [7–9]. For epoxides, the use of di- or poly-carboxylic acid anhydrides is based on the reaction of these materials to produce ester links, in the presence of acidic or basic catalysts. Fisch and Hoffman [10,11] proposed that uncatalysed

cure can occur through reactions involving monoester, diester, and ether formation—Scheme 1

Results of kinetic description of the curing process measured by differential scanning calorimetry (DSC) method for different epoxy systems show that: (i) kinetics of cure may be complicated since it is a multi-step reaction, approaching diffusion-controlled region due to vitrification; and (ii) it is possible to apply kinetic data for controlling cure conditions, provided that a suitable model has been chosen. Barton has reviewed [12] the kinetics of acid anhydride cures of epoxides, listing the kinetic parameters derived using an empirical rate equation

$$\frac{dX}{dt} = - \left. \frac{dC}{dt} \right|_{C_0} = k(1 - X)^n \quad (1)$$

where C_0 is the initial concentration, k is an Arrhenius-type ‘apparent’ rate constant and X is the degree of cure.

The values of n ranged from 0.2 to 2 and the apparent activation energy from 56 to 159 kJ/mol. Some of these results published on the basis of a single-DSC curve data analysis treatment may lead, according to comparative kinetic studies, to false interpretation of the actual mechanism of a thermal process. This may be avoided in isothermal mode, as presented by Khanna and Chanda who have developed a kinetic model on the basis of reaction

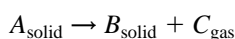
* Corresponding author. Fax: +48-12-6342425.

Table 2
The kinetic models (Ref. [21])

Model	Symbol	$f(\alpha)$
Phase boundary-controlled reaction (contracting area)	R2	$(1 - \alpha)^{1/2}$
Phase boundary-controlled reaction (contracting volume)	R3	$(1 - \alpha)^{2/3}$
Random nucleation. Unimolecular decay law	F1	$(1 - \alpha)$
Reaction n th order	F n	$(1 - \alpha)^n$
Johnson–Mehl–Avrami	JMA	$n(1 - \alpha)[- \ln(1 - \alpha)]^{1-1/n}$
Two-dimensional growth of nuclei (Avrami equation)	A2	$2[- \ln(1 - \alpha)^{1/2}](1 - \alpha)$
Three-dimensional growth of nuclei (Avrami equation)	A3	$3[- \ln(1 - \alpha)^{2/3}](1 - \alpha)$
One-dimensional diffusion	D1	$1/2\alpha$
Two-dimensional diffusion	D2	$1/[- \ln(1 - \alpha)]$
Three-dimensional diffusion (Jander equation)	D3	$3(1 - \alpha)^{2/3}/2[1 - (1 - \alpha)^{1/3}]$
Three-dimensional diffusion (Ginstling–Brounshtein)	D4	$3/2[(1 - \alpha)^{-1/3} - 1]$
n -dimensional nucleation (Avrami–Erofeev equation)	A n	$n[- \ln(1 - \alpha)^n](1 - \alpha)$
Reaction of first order with autocatalysis	C1	$(1 - \alpha)(1 + K_{\text{kat}}\alpha)$
Reaction of n th order with autocatalysis	C n	$(1 - \alpha)^n(1 + K_{\text{kat}}\alpha)$
Prout–Tompkins equation	B n a	$(1 - \alpha)^n\alpha^a$

3. The kinetic equations and models

In general, the thermal process of solids is a very complex phenomenon even in the simple case of the reaction expressed by the stoichiometric equation



The rate of reaction can be described in terms of two functions: $k(T)$ and $f(\alpha)$, thus:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (2)$$

By substitution of the Arrhenius equation, and rearrangement, the following equation results:

$$\frac{d(\alpha)}{f(\alpha)} = \left(\frac{A}{\beta}\right) \exp\left(-\frac{E}{RT}\right) dT \quad (3)$$

where α is the degree of conversion, T the temperature in Kelvin, $f(\alpha)$ the type of reaction, $k(T)$ the rate constant, β the heating rate, E the activation energy, A the pre-exponential factor, and R the gas constant. This equation is given for measurements with a constant heating rate ($T = T_0 + \beta t$).

Using an approximation of the exponential integral in a form proposed by Doyle [16]

$$\ln p(x) = -5.3305 + 1.052x \quad (4)$$

(where $x = E/RT$). It is possible to determine the activation energy of the thermal process by following the specific heat

Table 3
Kinetic analysis results for the cure process of model epoxides

Sample	E (kJ/mol)	Model
1	71.8	D3
2	84.2	F n
3	64.1	R3
4	76.5	F n

flow of a process at several different heating rates [17,18].

$$\ln \beta = \ln\left(\frac{AE}{R}\right) - \ln G(\alpha) - 5.3305 + 1.052x, \quad (5)$$

where $G(\alpha)$ is an integral form of Eq. (3).

Eq. (5) generates a straight line when $\ln(\beta)$ is plotted against $1/T$ for isoconversional fractions, the slope of the line being equal to $-1.052E/R$ during a series of measurements with a heating rate of $\beta_1 \dots \beta_j$ at a fixed degree of conversion of $\alpha = \alpha_k$. The temperatures T_{jk} are those at which the conversion α_k is reached at a heating rate of β_j .

Another isoconversional procedure, introduced by Friedman [19], uses as its basis the following relationship:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln f(\alpha) + \ln A - \frac{E}{RT} \quad (6)$$

which makes it possible to find the activation energy value from the slope of the line ($m = -E/R$) when $\ln(d\alpha/dt)$ is plotted against $1/T$ for isoconversional fractions.

In Eq. (2) the term $f(\alpha)$ represents the mathematical expression of the kinetic model. The most frequently cited basic kinetic models are summarised in Table 2.

Non-isothermal curves of a thermal reaction can satisfy the kinetic equations developed for the kinetic analysis of “ n th order reactions”, even if they follow a quite different mechanism. Results of the comparative studies lead to the conclusion that the actual mechanism of a thermal process cannot be discriminated from the kinetic analysis of a single DSC trace [20]. Besides, both activation energy and pre-exponential factor, given in Eq. (3) may be mutually correlated. As a consequence of this correlation any DSC curve can be described by an apparent kinetic model instead of the appropriate one for a certain value of apparent activation energy. Therefore, the kinetic analysis of DSC data cannot be successful unless the true value of the activation energy is known [21–23].

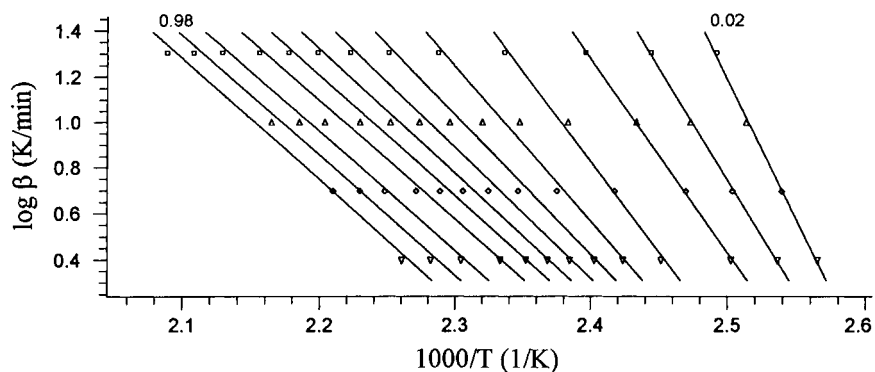


Fig. 1. Ozawa–Flynn–Wall analysis of the cure process of sample 1A.

4. Results and discussion

A comprehensive kinetic analysis of the cure process was first performed for model epoxides—the results obtained are summarised in Table 3.

The apparent activation energy values are in good agreement with literature data [24], whereby kinetic model functions are either of ‘chemical reaction-’ (Fn) or ‘diffusion-controlled’ (D3, R3) types, indicating that different factors limit the extent of reaction kinetically.

Cure of 5-methyl-1,3-oxothiolane-2-thione (1A) is described by an activation energy value approaching ca. 80 kJ/mol for the extent of reaction $\alpha > 0.2$, as found on the basis of Ozawa–Flynn–Wall analysis—Figs. 1 and 2.

Further non-linear regression analysis revealed that best fit (corr. coefficient = 0.99996) was found for kinetic model ‘*n*th order reaction with autocatalysis’ (Cn)—this made it possible to show the modelled conversion vs. time dependency of the cure process (Fig. 3).

Isoconversional kinetic analysis of non-isothermal DSC was adequately interpreted for a model epoxy-amine curing process [25] and it has been found that it is more advantageous than numerous kinetic methods using the variation of peak exotherm with the heating rate, such as well-established ASTM E698-79 [26] which treats the complex

cure as a single-step reaction of the first order. Compared to the results of the isoconversional analysis, the activation energy evaluated by this method is a single point on the dependence of E on α at $\alpha = \alpha_{\max}$.

For sample 5-ethyl-1,3-oxothiolane-2-thione (2A) Friedman analysis yields information concerning the changeability of E vs. α , as shown in Figs. 4 and 5.

Comparison of different kinetic models leads to the conclusion that Cn is the best statistical fit on the basis of the F -test procedure [20]—Table 4.

The resulting kinetic parameters may be applied for prediction of partial reaction extent vs. time at different temperatures (Fig. 6).

Activation energy of the cure process of 5-chloromethyl-1,3-oxothiolane-2-thione (3A) shows a concave route, with its minimal value of ca. 68 kJ/mol—Fig. 7.

As the best fit ‘1st order reaction with autocatalysis’ model (C1) was found which makes it possible to display isoconversional curves of the cure process, as shown in Fig. 8.

The last sample under investigation was 4,5-tetramethylene-1,3-oxothiolane-2-thione (4A), cure process of which runs according to a complex kinetic scheme, as showed in plot of E vs. α —Fig. 9

The dependence of $\ln A$ vs. α shows a similar trend to that

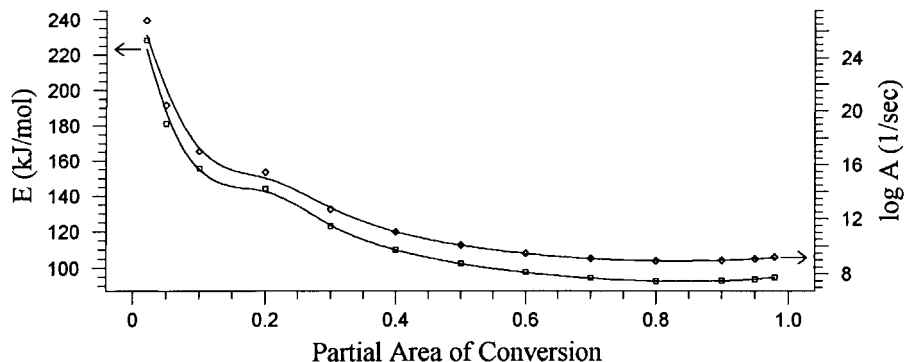


Fig. 2. Energy of activation (E) as a function of degree of conversion for the cure process of sample 1A calculated by Ozawa–Flynn–Wall method.

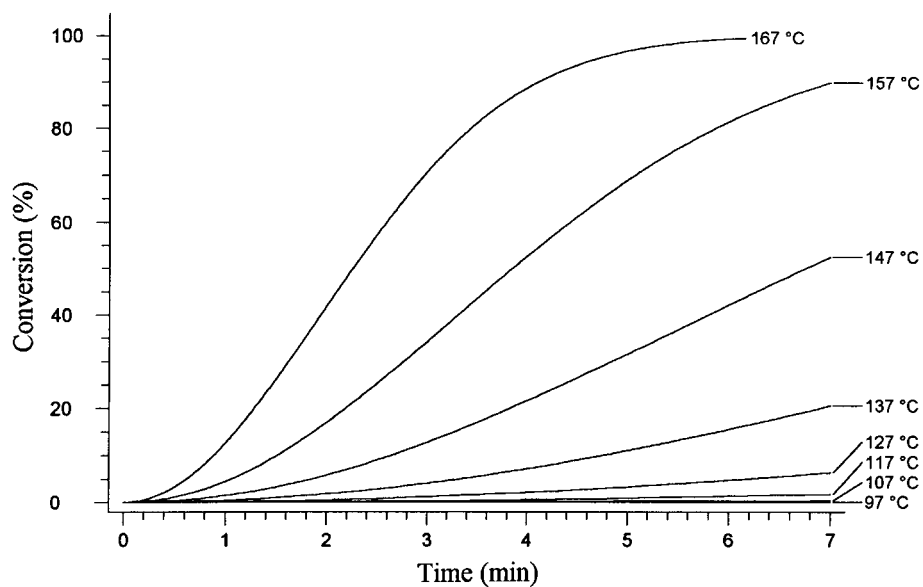


Fig. 3. Degree of conversion vs. time plot for the cure process of sample 1A.

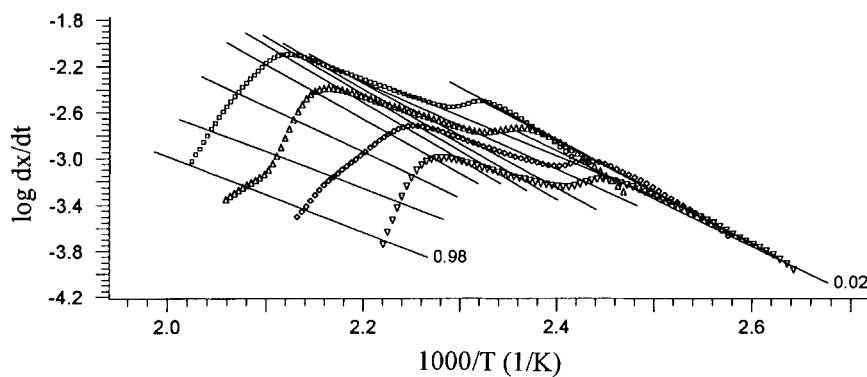


Fig. 4. Friedman analysis of the cure process of sample 2A.

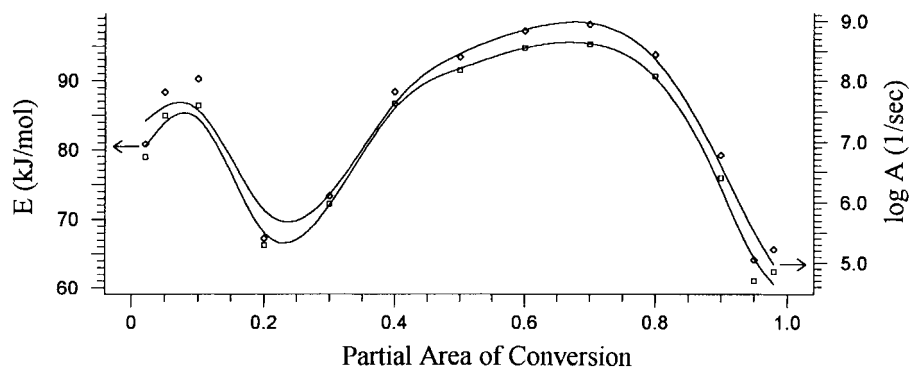


Fig. 5. Energy of activation (E) as a function of degree of conversion for the cure process of sample 2A calculated by Friedman method.

Table 4
Results of *F*-test of the distinctiveness between the models for curing process of sample 2A

Model	<i>Cn</i>	<i>Bna</i>	<i>Fn</i>	F1	<i>An</i>	C1	D2
<i>F</i> exp.	1.00	1.14	1.28	1.31	1.32	1.33	2.05

observed in the apparent activation energy *E*. This effect is a consequence of the correlation between these two kinetic parameters in the form of a linear relationship between $\ln A$ and *E*:

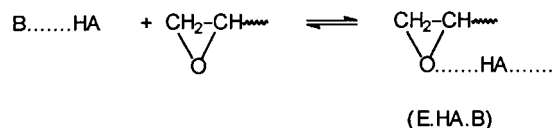
$$\ln A = aE + b$$

where *a* and *b* are constants.

Such a relationship implies a so-called ‘kinetic compensation effect’ (KCA), which has been observed during the cure of catalysed epoxy-anhydride systems with different degrees of crosslinking [27] or in the presence of reactive diluents [28].

Further kinetic analysis revealed the form of model function as ‘*n*-dimensional nucleation–Avrami–Erofeev equation’ (*An*)—Table 5.

All the alkyl derivatives of (1,3-oxathiolane-2-thione)s are kinetically described by autocatalytical model functions which may be interpreted in terms of the stationary state mechanism of Tanaka and Kakiuchi [29] with the reaction:



(where HA and B denote acidic and basic moieties, respectively) as the rate-controlling step.

Additionally, hydroxyl groups from catalyst may contribute to the formation of hydrogen bonds. Both effects cause

Table 5
Results of *F*-test of the distinctiveness between the models for curing process of sample 4A

Model	<i>An</i>	<i>Fn</i>	D3	F2	<i>Bna</i>	<i>Cn</i>	D4
<i>F</i> exp.	1.00	1.06	1.28	1.29	1.35	1.35	1.94

an increase in *E* that can be attributed to the onset of diffusion control prior to gelation.

(4,5-Tetramethylene-1,3-oxathiolane-2-thione)’s curing process is described by a nucleation mechanism probably due to sterical alignments which in turn may induce some topological constraints in a cross-linked network, which strongly influence non-dimensional growth in a cross-linked network during the latter stage of cure. The heat of curing of 4,5-tetramethylene-1,3-oxathiolane-2-thione [14] has the highest value for all the samples under investigation and confirms energetically the Avrami nucleation scheme which depends exponentially on temperature and the growth geometry. The average apparent activation energy values of the cure of (1,3-oxathiolane-2-thione)s are higher than those of parent epoxides, although at final degrees of conversion they may remarkably vary due to architectural and conformational structure—it has been found for several epoxy-anhydride systems that near the gel point vitrification plays an important role due to chemistry of reacting species which have to move toward each other by translational and segmental diffusion and/or rotation [30,31]. For different systems being cured, at vitrification the concentration of reactive units in the epoxy-amine is approximately four times higher compared to the epoxy-anhydride, due to a higher initial concentration and a lower conversion at vitrification. Postulating an equal distribution of non-reacted units, at vitrification the mean distance of the nearest reaction partner, termed the reaction distance, is 8 Å for the

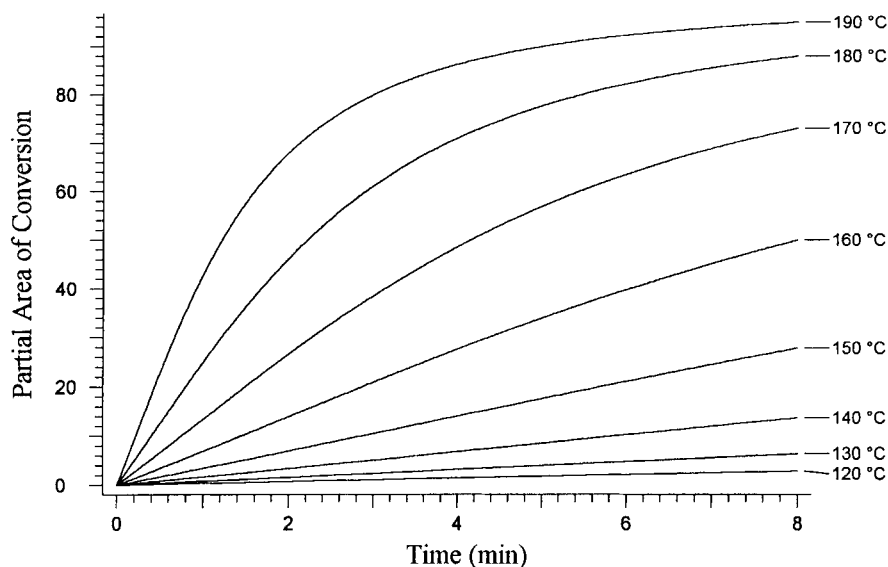


Fig. 6. Partial cure reaction extent vs. time for sample 2A.

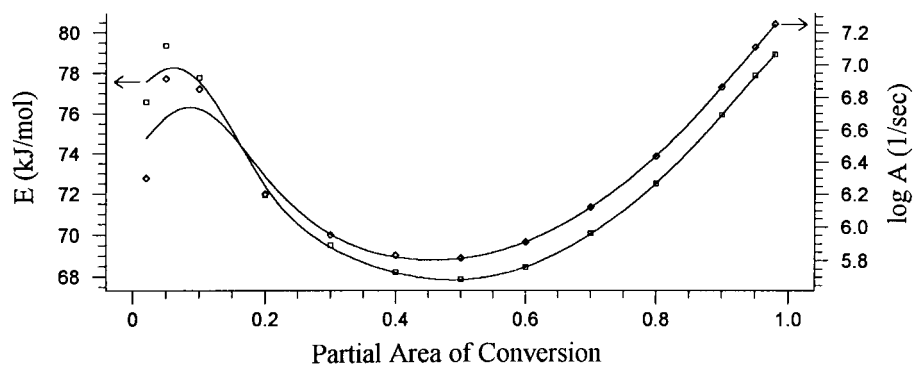


Fig. 7. Energy of activation (E) as a function of degree of conversion for the cure process of sample 3A calculated by Ozawa–Flynn–Wall method.

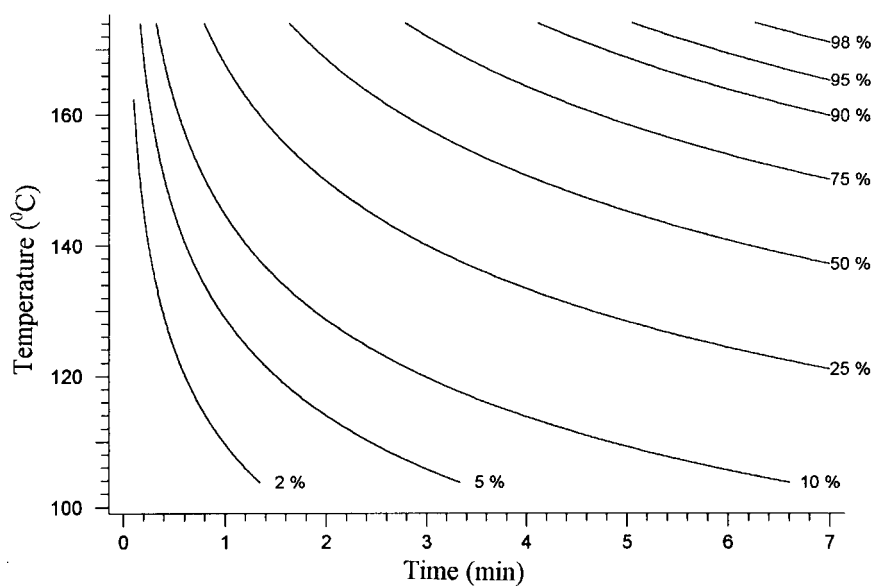


Fig. 8. Isoconversional curves of the curing process of sample 3A.

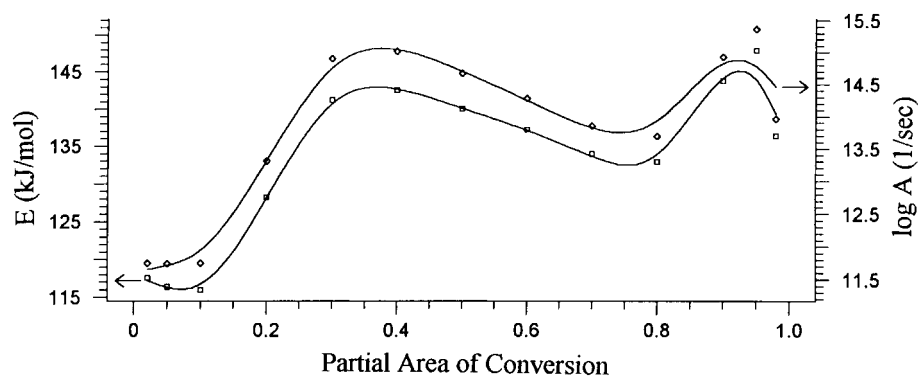


Fig. 9. Energy of activation (E) as a function of degree of conversion for the cure process of sample 4A calculated by Ozawa–Flynn–Wall method.

epoxy-amine and 13 Å for the epoxy-anhydride. In the glass transition region, a mobility of about 30–50% chain segments is available, depending on the specific chemical structure [32], allowing for reaction while the material is vitrifying.

5. Conclusions

Kinetic analysis of the cure process of a series of model epoxides and related sulphur compounds—(1,3-oxothiolane-2-thione)s revealed that there are different kinetic routes present, depending on the structure of initial compounds. The values of apparent activation energy (E), determined by model-free isoconversional methods, were depending on α ; this indicates a complex kinetic scheme. For further analysis an advanced non-linear regression method-based approach was introduced, which made it possible to find statistically best fits of kinetic functions. They were of different types, but autocatalytical processes dominated, indicating that rate-controlling steps are located rather at early stages of cure—well below temperature of vitrification which however governs the nature of post-cure treatments and resulted therefore in deformations of the final network.

Acknowledgements

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