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KINETIC METHOD BY USING CALORIMETRY TO MECHANISM OF EPOXY-AMINE CURE REACTION
Part I. Mangelsdorf's approach

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Abstract

A Mangelsdorf's approach to modeling the epoxy-amine cure kinetics has been developed. Analysis of the data by means of Mangelsdorf's approach makes it possible not only to determine the reaction rate constant and the heat of epoxy ring opening, but also to elucidate the reaction mechanism. However, to model the kinetic curves obtained by the calorimetric method for the complicated reaction should be derived an equation expressing the rate of change of the heat with time, as a function of the reaction rate and the extent of conversion. In a detailed examination the thermokinetic data, we found that glassy state transition is kinetically feasible. Using data available in literature, the kinetic model for epoxy-amine cure reaction was developed. Our treatment of glass formation is based on the picture of the reaction system as a miscible mixture of two structurally different liquids. This approach is similar to that presented by Bendler and Shlesinger as a Two-Fluid model. In the application of this model to reaction kinetics, we believe the explanation of glass structure formation lies in the splitting of the homogeneous mixture into two liquid phases.

Keywords: cure reaction, epoxy-amine, isothermal calorimetry, kinetic model, Mangelsdorf's approach, thermokinetics, vitrification

Introduction

Epoxy are one of the most developed high-temperature polymers in use today. Considerable effort has been devoted to studies of the reactions involved in the synthesis of these materials, but due to the infusibility of the products formed at vitrification, their chemistry – and especially the reaction mechanism – still escapes complete elucidation.

The kinetic method by using calorimetry appears to provide a solution to this problem. Calorimetric method to mechanism of epoxy-amine cure reaction, of course, not a new note. This subject has an extensive literature. Today there is rarely a publication in which this approach is not used for investigation of the reaction between epoxide and amine molecules.

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Kinetic method by using calorimetry to mechanism of epoxy-amine cure reaction requires knowledge of the molar heat of the epoxy ring opening during the cure reaction. As a rule, kinetic parameters are determined with the assumption that the heat evolved at any time during the cure reactions directly proportional to the extent of conversion. The ratio of the heat produced at given time to the heat produced at infinite time is a measure of the extent of conversion.

$$\alpha = \frac{Q_t}{Q_p} \tag{1}$$

where Q_t is the heat evolved to a given time; Q_t is commonly determined by measuring the partial area under isothermal curve up to the point of interest; Q_p is the total heat (the enthalpy) of cure.

The main limitation of these approaches is the oversimplified notion of the cure kinetics, which, for example, takes no account the occurrence of a slow secondary reaction, the precipitation of a product or simply a reaction so slow that it is inconvenient to wait for its completion. However, this assumption is rigorously valid only when a single reaction is responsible for the advancement of the process.

A survey of the literature shows that the calculation of the total heat of cure is based on the assumption leveling effect during the late stages of the cure process. Then the total heat of cure reaction is determined by integrating the area under kinetic curve and adding to this integral the heat evolved during the first scan. This heat is assumed to be further reaction that occurs on heating during the first scan.

The controversial details of these methods of analysis can be revealed by examination of the dynamic DSC curves recorded after isothermal run. A notable example is shown in Fig. 1 where two exothermic processes are seen clearly along the first DSC scan. The question which arises at this point is indeed, what is the manner of the determination of the total heat of cure reaction when the origin these exothermic processes is unknown.

In some studies of the amine cured epoxide system, as a molar heat of the epoxy ring opening the enthalpy found for the model reactions was applied in thermokinetic experiments [1–3]. It was turned out, for instance, that is almost impossible to obtain

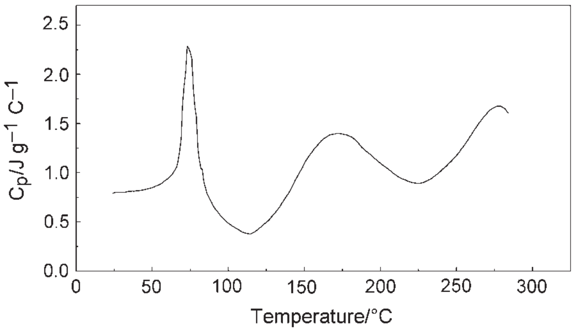


Fig. 1 Isothermal heat release rate *vs.* time for the reaction between phenyl glycidyl ether and *m*-phenylenediamine at 97°C. (Data are from [4])

accurate quantitative data for the model system composed by phenyl glycidyl ether and *m*-phenylenediamine using the total heat outlined above [4]. This reaction demonstrates the precipitation process. It was being shown that the contribution of the precipitation process to the total heat is found to be dependent on the reaction temperature. The above clearly shows that the total heat, measured from the areas enclosed by the rate of heat on a time axis, may easily lead to erroneous results.

In most cases, it is impossible to avoid inaccuracies associated with the superposition of the heat efficiencies. This uncertainty obscure the application of calorimetric method to mechanism of epoxy-amine curing reactions as well as underlines the need for caution in interpreting the results obtained from the use of this treatment.

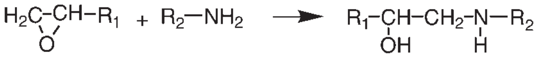
In this situation the Mangelsdorf's method available at present of tacking the problem of how to describe the kinetic curves obtained by the calorimetric method [5]. The Mangelsdorf's method makes it possible to obtain both kinetic rate constants and the molar heat of the reaction, even if the final instrument reading cannot be accurately measured [5]. The total heat plays no role in Mangelsdorf's approach. In essence the method consists of kinetic describing the curves obtained by the calorimetric method. However, in order to apply this method, the order of reaction must be known. In other words, to model the kinetic curves obtained by the calorimetric method for the complicated reaction should be derived an equation expressing the rate of change of the heat with time, as a function of the reaction rate and the extent of conversion. This method was adopted in study of isothermal cure kinetics of a polyurethane-forming system [6]. In one’s time, examples of the application of this method to the reaction kinetics has been discussed in Russian chemical literature [7, 8]. Thus, a similar approach has been successfully applied to study of the polycondensation reaction between terephthalyl chloride and ethyleneglycol in dioxane solution [7].

As is well known, in order to analyze the kinetics by using ‘kinetic investigation’ approach to epoxy-amine curing mechanism, the curves must be expressed in terms of the extent of conversion. Then kinetic curves obtained by the calorimetric method allow to determine the extent of conversion at each moment of the reaction if the molar heat of epoxy ring opening is known. Analysis of the data by means of Mangelsdorf's approach makes it possible not only to determine the reaction rate constant and the heat of epoxy ring opening, but also to elucidate the reaction mechanism. However, in order to apply this method, the order of reaction must be known. In other words, to model the kinetic curves obtained by the calorimetric method for the complicated reaction, it should be derived an equation expressing the rate of change of the heat with time, as a function of the reaction rate and the extent of conversion.

We are writing this paper to correct serious inaccuracies and ambiguities on the subject of the thermokinetic analyses that occurs in the studies of epoxy-amine reactions. Thus the object of the present paper is a ‘kinetic investigation’ approach to curing mechanism. A full description of cure kinetics for the epoxy-amine reaction system prior to and after vitrification is the focus of interest in this paper.

Model

The epoxy-amine cure reaction consists mainly of epoxy ring opening, which are thought to take place as in Scheme 1, involving a two-step process:



$$H_2\underset{\diagdown O \diagup}{C-CH}-R_1 + R_2-NH_2 \longrightarrow R_1-\underset{OH}{CH}-CH_2-\underset{H}{N}-R_2 \qquad (1)$$

Scheme I

In schematic form: $E+A$=product (OH groups), where A is NH-group; E is epoxy group and OH-group is reaction product.

At present, the kinetic method is the main approach to the detail reaction mechanism since by using the direct physical methods we can hardly establish the reaction mechanism under vitrification.

On the assumption of Scheme 1, earlier investigators applied termolecular interaction mechanism first proposed by Smith [9]. Today a termolecular interaction mechanism is still conventional and there is rarely a publication in which this approach, most notable being that of Horie *et al*. model [1], is not used for investigation of the reaction between epoxide and amine molecules by using calorimetry. In all details analysis of Horie model is given in [10].

At the functional group level, simple autocatalytic interaction of an amino group with an epoxy ring is generally used to describe this Scheme 1:

$$W = k_{\mathrm{ef}}(C_{\mathrm{A}}-C_{\mathrm{x}})(C_{\mathrm{E}}-C_{\mathrm{x}})C_{\mathrm{x}} \qquad (2)$$

where W is the reaction rate being measured during the kinetic experiment; C_{x} (mol L^{-1}) is the total concentration of the reaction product; C_{E} is the initial concentration of functional group of epoxide in mol L^{-1}; C_{A} is the initial concentration of amine group in mol L^{-1}; k_{ef} is a rate constant.

However, it is well known that a termolecular collision is very improbable [11]. In [12] the reaction was followed by measuring the concentration of unreacted epoxy groups by a titrimetric analysis. In a detailed examination of the applicability of Eq. (2) to solvent-free epoxy-amine thermokinetic data the epoxy-amine reaction, under consideration, have been shown to be first order with respect to concentration of the deficient reagent.

In actual practice, to describe the kinetic experiment in the terms of the reaction rate, the current reagent concentrations are used [11]. With this is mind the fact that the part of the reagents can be bounded into the complex. Therefore ($C_{\mathrm{A}}-C_{\mathrm{x}}$) and ($C_{\mathrm{E}}-C_{\mathrm{x}}$) are current (observed) reagent concentrations respectively in mol L^{-1}.

In comprehensive studies on the mechanism of epoxide reactions [13–15], it has shown that there must be no great selectivity of primary amine successively from secondary to tertiary amines in the epoxy ring opening reactions.

It has been shown the absence of substitution effect in system under study (curing conditions: 70ºC, abundant amount of amine) [16].

We found that the set of Eqs (3) and (4) is easily obtained from Eq. (2) on the condition that during the catalytic reaction the functional groups of amine and epoxy molecules almost completely bound into a complex by means of H-bonds. In other words, the interaction between an epoxy group and an amine progresses in strongly structured melts. For the sake of comparison, according to the phenomenological model used in Eq. (2), the reaction medium is treated as a structureless continuum.

Taking into account the curing reaction occurs by two mechanisms: one is a non-catalytic mechanism, and the other is a catalytic interaction [1, 17] as well as equal reactivity of primary and secondary amine groups in terms of the observed concentration cure kinetics can be described up to the onset of the vitrification by using the following equations:

$$\frac{\mathrm{d}C_{\mathrm{x1}}}{\mathrm{d}t}=k_{\mathrm{ef1}}(C_{\mathrm{A}}-C_{\mathrm{x}})(C_{\mathrm{E}}-C_{\mathrm{x}}) \tag{3}$$

$$\frac{\mathrm{d}C_{\mathrm{x2}}}{\mathrm{d}t}=k_{\mathrm{ef2}}(C_0-C_{\mathrm{x}})C_{\mathrm{x}} \tag{4}$$

where $\mathrm{d}C_{\mathrm{x1}}/\mathrm{d}t$ and $\mathrm{d}C_{\mathrm{x2}}/\mathrm{d}t$ are the reaction rates in 'uncatalyzed' and autocatalyzed reactions, respectively; C_{x} is the total concentration of OH groups for both reactions; C_{E} is the initial concentration of functional groups of epoxy resin in mol/l; C_{A} is the initial concentration of amine groups in mol L^{-1}, k_{ef1} is a rate constant for 'uncatalyzed reaction, k_{ef2} is a rate constant for the same reaction catalyzed by OH groups formed in the reaction C_0 is the initial concentration of the deficient reagent. $(C_0–C_{\mathrm{x}})$ is the concentration of the complex consisted of the molecules amine and epoxide in mol L^{-1}.

According to the foregoing Scheme 1, the kinetics of epoxy-amine cure reaction must be presented by the equation:

$$\frac{\mathrm{d}C_{\mathrm{x}}}{\mathrm{d}t}=k_{\mathrm{ef1}}(C_{\mathrm{A}}-C_{\mathrm{x}})(C_{\mathrm{E}}-C_{\mathrm{x}})+k_{\mathrm{ef2}}(C_{\mathrm{A}}-C_{\mathrm{x}})(C_{\mathrm{E}}-C_{\mathrm{x}})C_{\mathrm{x}} \tag{5}$$

The kinetic analysis of cure reaction should allow not only for chemical interactions of functional groups but also for formation a rigid network of the vitrified system. It is therefore preferable to speak of the combination of reaction of epoxy ring opening (Scheme 1) plus vitrification. To establish, in a quantitative manner, how do the over-all kinetics for cure reaction vary from liquid mixture to glassy system, it is desirable to include the vitrification phenomenon into the full rate expression. Since a general theory of the glass transition is still missing, the difficulty lies in finding model which will unambiguously resolve this question.

If we review some facts about glass formation, it can be found that the viscosity is not the sole major factor determining glass-forming ability of aqueous solutions work [18]. However, we should also mention the [19] which has demonstrated that association between the components of a mixture has been shown to increase the viscosity and thereby the glass transition temperature.

Faced with these conflicting data, in our view, it can be misleading to focus on the viscosity of the reaction system in 'kinetic investigation' approach to reaction mechanism. The physical idea behind our treatment of glass formation is based on the picture of the reaction system as a miscible mixture of two structurally different liquids. This approach is similar to that presented by Bendler and Shlesinger as a Two-Fluid Model [20, 21].

This model suggests the presence of small amounts of more mobile material below the glass transition. In the application of this model to reaction kinetics, we believe the explanation of glass structure formation lies in the splitting of the homogeneous mixture into two liquid phases when the rate of network formation is faster than the demixing rate. In other words, the reaction mixture ‘freezes’ in non-equilibrium demixing state. Two–Fluid Model allows to describe the kinetic features of epoxy-amine cure reaction in the late stages.

The experimental evidence for this interpretation can be found, for instance, in [22] where it was demonstrated with the use of an electron spin resonance investigation (EPR) that the dynamics of small and large molecules decouple while T_g is approached from higher temperature. Also the decoupling of mobility of small molecules from the matrix mobility has been observed before in a glassy matrix in [23].

Supposing that at the conditions of the vitrification the reaction proceeds in liquid holes, present among the solid matrix, it is necessary to postulate that a feature of this reacting medium is the saturation with OH groups. In saturated solution, the OH concentration, from here on denoted by C_x^{sat}, remains constant. By this is meant that the newly formed OH groups leave the reaction medium. This approach allows for the coupling between the reaction and the collective mobility of the particles composing the solid matrix. This scenario is valid at the vitrified system where the reaction is accompanied by diffusion of the reaction products rather than the reagents. To describe this diffusion process we introduced equation:

$$\frac{dC_{x3}}{dt}=k_{ef3}[(C_x-C_x^{sat})-C_{x3}](C_xC_x^{sat}) \tag{6}$$

where C_{x3} is the concentration of OH groups which escape from the reaction medium. C_x^{sat} is the saturated concentration OH groups in the reaction volume. k_{ef3} is a rate constant for process under consideration.

In many reports in the literature, the studies of the epoxy-amine cure kinetics have dealt with the phenomenology of chemical kinetics, that is the observation and description of kinetic phenomena. We now turn to kinetic theory with which one can interpret our kinetic data.

According to absolute reaction rate theory the rate of reaction the rate equation is defined by the decay rate of the activated complex; this formulation of transition state theory has been defined in terms of transition state concentrations [24]:

$$a^{\neq}=\frac{a_A a_E}{K_p} \tag{7}$$

where K_p – an equilibrium constant of the activated complex formation is defined in terms of activities; a_A and a_E – activities of amine and epoxide, respectively.

Because the epoxy-amine reaction is exothermic, then in accordance with the Hammond postulate, the activated complex must be reactantlike [25].

It is reasonable, epoxy groups can form several complexes with amine in the ratio 1:1. These complexes have different structure, and very some of them are reactive $(AE)_{\mathrm{ir}}$. The equilibrium constant of the complex formation:

$$A+E \leftrightarrow (AE)_{\mathrm{ir}} \tag{8}$$

The equilibrium constant of complex formation defined in terms of concentrations is:

$$K_{\mathrm{ir}}=\frac{C_{(\mathrm{AE})_{\mathrm{ir}}}}{C_{\mathrm{A}}C_{\mathrm{E}}} \tag{9}$$

$(AE)_{\mathrm{ir}}$ is one in epoxy-amine complexes which, upon addition of an OH group (denoted by X) transforms into a reactive AEX complex:

$$(AE)_{\mathrm{ir}}+X \leftrightarrow AEX \tag{10}$$

where K_{x} is the equilibrium constant of AEX formation.

For a reaction Scheme 1, application of transition state theory gives the following rate equation:

$$\frac{\mathrm{d}C_{\mathrm{x}}}{\mathrm{d}t}=W=k\frac{a^{*}}{f^{*}}=k\frac{a_{\mathrm{AEX}}}{f^{*}}=\frac{k}{K_{(\mathrm{X})}}\frac{a_{(\mathrm{AE})_{\mathrm{ir}}}a_{(\mathrm{X})}}{f^{*}}=\frac{kC_{(\mathrm{AE})_{\mathrm{ir}}}C_{\mathrm{x}}f_{(\mathrm{AE})_{\mathrm{ir}}}f_{(\mathrm{X})}}{K_{(\mathrm{X})}f^{*}} \tag{11}$$

where a^{*} and f^{*} are the activity and activity coefficients of the activated complex, and a_{AEX} is the activity of the reactive complex composed of A, E and X. Concentrations of species are denoted by C, and their activity coefficients, by f; k – the true rate constant.

According to our assumption,

$$(C_0-C_{\mathrm{x}})=\sum C_{(\mathrm{AE})_{\mathrm{i}}}+C_{(\mathrm{AE})_{\mathrm{ir}}} \tag{12}$$

where $C_{(\mathrm{AE})\mathrm{i}}$, is the concentration of reactive complexes. The equilibrium constant of formation of these complexes equals

$$\sum K_{\mathrm{i}}=\sum\frac{C_{(\mathrm{AE})_{\mathrm{i}}}}{C_{\mathrm{A}}E_{\mathrm{E}}} \tag{13}$$

From the literature data on activation energy values for a given reaction follows that:

$$C_{(\mathrm{AE})_{\mathrm{ir}}}<<\sum C_{(\mathrm{AE})_{\mathrm{i}}} \tag{14}$$

Hence,

$$(C_0-C_{\mathrm{x}})=\sum C_{(\mathrm{AE})_{\mathrm{i}}} \tag{15}$$

Combining the expressions (9) and (13) yields

$$\frac{C_{(\mathrm{AE})_{\mathrm{ip}}}}{\sum C_{(\mathrm{AE})_{\mathrm{i}}}}=\frac{K_{\mathrm{ir}}}{\sum K_{\mathrm{i}}} \tag{16}$$

As is shown in [26], applied to the kinetic situation of Scheme 1, the ratio $(f_{(\mathrm{AE})_{\mathrm{ip}}} f_{\mathrm{x}})/f^{*}$ in Eq. (11) can be set equal to unity. Then using Eqs (15) and (16) in (11) gives the rate equation:

$$W=\frac{\mathrm{d}C_x}{\mathrm{d}t}=\frac{kK_{\mathrm{ir}}}{K_{(\mathrm{x})}\sum K_{\mathrm{i}}}(C_0-C_{\mathrm{x}})C_{\mathrm{x}} \tag{17}$$

in which

$$\frac{kK_{\mathrm{ir}}}{K_{(\mathrm{x})}\sum K_{\mathrm{i}}}=k_{\mathrm{ef}} \tag{18}$$

Thus the complex formation between the reagents leads to Eq. (4).

Expressed in termed of the observed concentration of OH-groups formed by the reaction (C_x) and the initial concentration of functional groups of the deficient reagent (C_0) the extent of conversion (α) is as follows:

$$\alpha = C_{\mathrm{x}}/C_0 \tag{19}$$

Through isothermal calorimetry the extent of conversion reaction is commonly determined by measuring the total heat evolved to a given time Q_{t} (kJ L^{-1}) of reaction as follows:

$$\alpha=\frac{Q_{\mathrm{t}}}{Q_{\mathrm{mol}}C_0} \tag{20}$$

In the course of the kinetic experiment we measure the heat release rate. The later implies that the rate enhancement must be described in the terms of the heat release rate rather than the rate of conversion *vs*. time profiles. In contrast to this, extensive and careful studies were carried out by many other workers using calorimetric method with the aim of fitting equations to the rate of conversion *vs*. time profiles. We must point out that this 'kinetic investigation' approach is seriously flawed and misleading. It seems extremely unlikely that the conclusion drown from this experiment can be correct.

The relation between the heat release rate, W (J L^{-1} s^{-1}) and the reaction rate, $\mathrm{d}C_{\mathrm{x}}/\mathrm{d}t$ (mol L^{-1} s^{-1}) may be written in the form:

$$W=Q_{\mathrm{mol}}\frac{\mathrm{d}C_{\mathrm{x}}}{\mathrm{d}t} \tag{21}$$

This is a simple expression relating the heat releasing rate W to the reaction rate, $\mathrm{d}C_{\mathrm{x}}/\mathrm{d}t$ where Q_{mol} is the molar heat of epoxy ring opening (kJ mol^{-1}).

With Eq. (5) the heat releasing rate can be written in the following form:

$$W=W_1+W_2=Q_{\mathrm{mol1}}k_{\mathrm{ef1}}(C_{\mathrm{A}}-C_{\mathrm{x}})(C_{\mathrm{E}}-C_{\mathrm{x}})+Q_{\mathrm{mol2}}k_{\mathrm{ef2}}(C_0-C_{\mathrm{x}})C_{\mathrm{x}} \tag{22}$$

where Q_{mol1} and Q_{mol2} are the molar heat of epoxy ring opening for 'uncatalyzed' and autocatalyzed reactions.

To allow for the heat of the third process (Eq. 6), the molar heat (Q_{mol3}) has been introduced. Under consideration the rate of this process determined by using calorimetric method is equal to multiplied by Q_{mol3}:

$$W_3 = Q_{\mathrm{mol3}} \frac{\mathrm{d}C_{\mathrm{x3}}}{\mathrm{d}t} \tag{23}$$

Combining Eqs (22) and (23) give the net rate of heat evolution:

$$W = W_1 + W_2 + W_3 \tag{24}$$

Eq. (24) was solved with initial condition $C_{\mathrm{x3}}=0$ at $C_{\mathrm{x}} < C_{\mathrm{x}}^{\mathrm{sat}}$.

Deviation of the calculated dependence W from its measured counterpart W_{i} was estimated by the R-factor defined as:

$$R = \sqrt{\frac{\sum (W - W_{\mathrm{i}})^2}{\sum W_{\mathrm{i}}^2}} 100\% \tag{25}$$

It should be noted that R-factor does not exceed 1.5%.

Finally, to illustrate the reliability of the data obtained by Mangelsdorf's method we examined the cure reaction of resorcinol diglycidyl ether (RDGE) with *m*-phenylenediamine (MPDA) described in [2] which was erroneously calculated and interpreted at that time. Figure 2 shows the kinetics curves of the rate of evolving of the heat comparing the data obtained by the calculation with the experimental curves. Apparently, the approximation between the calculation and the experimental results over the entire conversion range is very close.

In support of this, there is data of the titrimetric analysis: $k_{\mathrm{ef2}}=15.8 \cdot 10^{-5}$ L mol^{-1} s^{-1} (70ºC) [13]. The value obtained as results of our calculation is $15.7 \cdot 10^{-5}$ L mol^{-1} s^{-1} respectively. The latter clearly rule out the doubt upon a physical meaning of the above treatment.

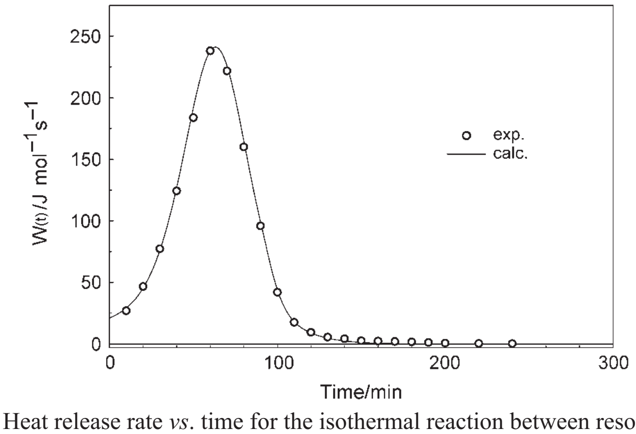


Fig. 2 Heat release rate *vs*. time for the isothermal reaction between resorcinol diglycidyl ether and *m*-phenylenediamine: experimental points (o), the result of computer treatment (line). The cure temperature is 70°C and the ratio of functional groups amine/epoxy equals 1.05

Conclusions

A Mangelsdorf's approach to modeling the epoxy-amine cure kinetics has been developed. Since the object of deriving kinetic equations and fitting them into kinetic data is to obtain evidence about the molecular processes that control the rate of reactions, it may be noted that the aim of the presented work was not to ‘fit’ the experimental data, but rather to provide an insight into the origin of the reaction mechanism.

The important point which we want to emphasize in the scope of this work is that the rate enhancement is described in the terms of the heat release rate rather than the rate of conversion *vs*. time profiles.

The kinetics of epoxy-amine cure reaction has clearly shown that interaction between epoxy and amine groups follows the second-order rate law. This finding is important evidence in favour of conception of strongly structured reactive medium during epoxy-amine cure reaction.

The model we used was based on a picture of the cold liquid as a miscible mixture of two structurally different liquids.

Upon vitrification, kinetics of epoxy-amine cure reaction was calculated using the Two-Fluid concept. Our explanation of glass structure formation lies in the splitting of the homogeneous mixture into two liquid phases when the reaction rate is faster than the demixing rate. In other words, the reaction mixture ‘freezes’ in non-equilibrium demixing state.

Certain features of the reaction at the later stages, such as the changes in kinetic order, could be accounted for by assuming that reaction occurs only in the decreasing liquid phase. The presence of liquid regions in completely vitrificated samples and the possible occurrence of the reactions in these regions was considered.

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