



The kinetic analysis of isothermal curing reaction of an unsaturated polyester resin: Estimation of the density distribution function of the apparent activation energy

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ABSTRACT

The kinetic process of isothermal curing of an unsaturated polyester resin samples has been studied. The differential isoconversional method is used to yield dependency of the apparent activation energy, E_a , on the degree of cure. It was found that the dependence of E_a on α is complex, but in the conversion range $\alpha = 0.10$ – 0.50 , E_a is practically constant. It was found that the gelling stage of curing process is mainly controlled chemically which can be best described by two-parameter autocatalytic model. At higher values of α , when vitrification point is reached, the change in rate-limiting step was observed. As the consequence of shifting effect from the kinetics to diffusion control, the kinetic law equation is modified with additional diffusion term. It was found that the experimentally obtained density distribution function of the apparent activation energy can be approximate by unbalanced modified Gaussian distribution function with quite satisfactory precision.

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1. Introduction

Unsaturated polyester resins (UPR) were first commercially developed in the 1940s and have grown to be one of the most versatile, globally used, thermoset polymer systems. This versatility allows manufacturing of many useful products common in modern society. In recent years, thermosetting resins have received increasing attention from industry. Unsaturated polyester resins were frequently used as matrix materials in polymer composites such as fiber-reinforced plastic and polymer concretes [1]. Unsaturated polyester resins were widely used in a host of applications where advantage may be taken of their good range of mechanical properties, low cost, good corrosion resistance and low weight [2].

Unsaturated polyesters were broadly defined as condensation products of organic diacids and glycols. Unsaturation was incorporated in a variety of ways to produce terminal, pendant and internal double bonds. Of these types, internal unsaturation provided by maleic anhydride is most common [2]. It can be pointed out, that the unsaturated polyesters are usually prepared by polycondensation of maleic anhydride, propylene glycol and dicyclopentadiene (DCPD). During this, the double bonds of the maleic acid isomerize to a large extent from the *cis*- into the *trans*-structure, so that the unsaturated polyester contains primarily fumaric acid units.

Commercial unsaturated polyester resins (UPR) consist mainly of a linear polyester with different amount of unsaturated units, a cross-linking monomer (usually 33–45% depending on the resin viscosity and processing conditions) and inhibitors that are used to prevent any cross-linking reaction before the resin is processed. The most frequently used cross-linking monomer is styrene [3].

Unsaturated polyester resins (UPR) cure by a free-radical mechanism. The high free-radical flux needed to cure the thermoset resins can be generated under many conditions: room temperature, heat, UV light, or visible light, provided the appropriate free-radical initiator is used. Room temperature cure is one of the key reasons UPR have enjoyed such widespread use [4]. Room temperature cure involves generating the high free-radical flux using an organic peroxide such as methyl ethyl ketone peroxide (MEKP). MEKP is a stable organic peroxide that decomposes rapidly in the presence of certain metallic carboxylate salts.

The transformation of a reactive thermosetting liquid to a glassy solid generally involves two distinct macroscopic transitions: molecular gelation and vitrification. Molecular gelation is defined as the time or temperature at which covalent bonds connect across the network form an infinite three-dimensional which gives rise to long range elastic behavior in the macroscopic fluid. Vitrification is when the glass-transition temperature of the system rises to the cure temperature and when further reaction is prohibited or is dramatically reduced [5].

The curing kinetics of UPR system was investigated in recent years by different authors [6–13]. Yun et al. [6] investigated the

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curing kinetics of unsaturated polyester resin under isothermal (static) and non-isothermal (dynamic) conditions. They established the two model elementary rate equations which describe the free-radical polymerization of the considered system. The power law was adopted to express the conversion dependence function of the initiation efficiency and the monomer reaction rate. Lu et al. [7] investigated the isothermal cure behavior of an unsaturated polyester resin system using the differential scanning calorimetry. The same authors were evaluated the various kinetic parameters and details connected with investigated process they explained through the application of the Avrami theory. In addition, Vilas et al. [8] studied the unsaturated polyester networks with various structures built from an orthophthalic polyester, with methyl ethyl ketone peroxide as an initiator and cobalt octoate as a promoter. For investigation, they used the dynamic mechanical thermal analysis in the range from -50 to 200 °C in order to characterize changes in the mechanical properties as a function of the temperature. From these measurements, the glass-transition temperatures of the different networks were determined and their dependence on conversion being fitted to an equation related to the Couchman and DiBenedetto equations. Salla and Ramis [9] performed the comparative study of cure kinetics of UPR using different methods. They established that the chemical kinetics of curing of polyester resins is complex, since many reactive processes are involved.

The aim of this work is to re-investigate the curing kinetics of UPR under isothermal conditions and compared the obtained results (estimation of full kinetic 'triplet' (the apparent activation energy (E_a), the pre-exponential factor (A) and function of curing mechanism $f(\alpha)$, where α is the degree of cure)) with previously reported results. For determination of kinetic parameters, the different kinetic methods were used. Based on the complexity of investigated curing process, the density distribution function of the apparent activation energy was evaluated. The experimentally evaluated density distribution function of the apparent activation energies was approximated with corresponding numerical function with quite satisfactory precision.

2. Experimental

2.1. Materials and methods

The unsaturated polyester resin used in this study was a 1, 1.15, 1.14 and 1.44 m/m mixture of maleic anhydride, orthophthalic acid, propylene glycol and diethylene glycol, respectively, containing 33% by weight styrene (STYRENE S4650, Sigma–Aldrich Co.), with an average of 5.88 vinylene groups per unsaturated polyester molecules. The *cis*-maleate units in a polyester molecule have lower reaction rates with styrene because of the steric hindrances that often remain unreacted within a cross-linked copolymer. The average molecular weight of the unsaturated polyester resin is 2750 g mol^{-1} and the equivalent molecular weight/(mol C=C) is 468 g mol^{-1} . The molar ratio of styrene/unsaturated polyester resin is 2.5. In order to cure the resin, methyl ethyl ketone peroxide (MEKP, 0.5 wt.% of the resin) (MEKP 1338-23-4, Sigma Aldrich Co.) with 9.0% active-oxygen solution of MEKP was added as an initiator. MEKP was added right before the measurement. The unsaturated polyester resin used in this study was not accelerated.

A Towson and Mercer model 9-300 conventional oven was used for the isothermal curing process. The oven temperatures were set at 80, 100, 120 and 140 °C. These temperatures were selected after studying a DSC (differential scanning calorimetry) dynamic scan for the uncured sample which showed that curing took place at temperature above 75 °C. When conducting isothermal tests, the oven was preheated to the predetermined isothermal temperature, and then the sample was installed quickly and held at the consid-

ered cure temperature. A sol–gel method [14–18] to evaluate the corresponding conversion through the reaction was used.

3. Theoretical background

The fundamental rate equation which describes the reaction rate as a function of time and temperature is

$$\frac{d\alpha}{dt} = kf(\alpha) = A \exp\left(\frac{-E_a}{RT}\right) f(\alpha) \quad (1)$$

where α is the degree of cure (DOC), t is the time, $(d\alpha/dt)$ is the curing rate, k is the rate constant as a function of temperature, generally given by an Arrhenius relation in which E_a is the apparent activation energy, A is the pre-exponential (frequency) factor, R is the gas constant, and T is the absolute temperature; and $f(\alpha)$ is the reaction model, which is related to the reaction mechanism. The form of $f(\alpha)$ is usually phenomenological. The simplest empirical model used is the n -th order (RON) rate equation:

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \quad (2)$$

where n is the reaction order. The n -th order kinetics model predicts a maximum of reaction rate at the beginning of the curing and does not account for any autocatalytic effects. It has been applied to the curing of epoxy resins [19,20] and maleic polyester resins [21]. More often used as the reaction model is the autocatalytic model [22] shown as:

$$\frac{d\alpha}{dt} = k\alpha^m(1 - \alpha)^n \quad (3)$$

where m and n are reaction orders by similarity with the n -th order model. The autocatalytic reaction attains a maximum reaction rate at about 10–40% of conversion. It has been applied to the cure of vinyl ester resins [23].

One drawback of these models is its incapability to deal with diffusion-controlled reaction at the later stage of curing. As the reaction system approaches vitrification, the local viscosity becomes so high that the reaction rate virtually drops to zero. It is possible to modify the autocatalytic model in Eq. (3) to provoke mathematically the prediction of zero reaction rate at the vitrification point by using a maximum DOC [24]:

$$\frac{d\alpha}{dt} = k\alpha^m(\alpha_{\max} - \alpha)^n \quad (4)$$

where α_{\max} is the maximum DOC of the reaction system can achieve at a given temperature. Using the above kinetic equations, the isothermal conversion data can be fitted to obtain the model parameters at a given temperature. From the reaction constants at the different temperatures, the apparent activation energy and the pre-exponential factor can be obtained. The reaction orders and the maximum DOC can be modeled as the functions of temperature to give accurate description to the curing behavior. This represents one of the methods for adding a rate-limiting diffusion term to the cure rate equation. The method represents a modification of the definition for the final degree of curing in the rate equation. The widely accepted Rabinowitch model [25] requires an expression for the diffusion rate based on the free volume theory. Another method to account for diffusion modifies the definition of the extent of cure in order to achieve the lower reaction rate. Sbirrazzuoli and Vyazovkin [26] used a relative degree of cure, instead of actual degree of cure. This method was also followed by Gonzalez-Romero and Cassilas [27], using the DiBenedetto [28] equation to describe the relationship between maximum conversion and temperature.

In the recent years, the model-free analysis has gained acknowledgment as an approach to analyze the isothermal data. The isoconversional method proposed by Friedman allows evaluation of the apparent activation energy unattached to the reaction model

[29]. Writing Eq. (1) in the logarithmic form for different isothermal temperatures, and considering it at a constant conversion, the following equation can be obtained as the basis of the isothermal isoconversional method:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln[Af(\alpha)] - \frac{E_a}{RT} \quad (5)$$

According to Eq. (5), the apparent activation energy, E_a , and the constant $\ln[Af(\alpha)]$ can be obtained, respectively, from the slope and the intercept of the linear relationship of $\ln(d\alpha/dt)$ against $1/T$ for a constant conversion.

Assuming the simple additive superposition of the individual reactions of a possible multi-step mechanism, the isoconversional method can be used to predict the curing behavior under isothermal conditions. Kinetic modeling procedure in isothermal condition is somewhat similar to that in non-isothermal condition. By integration of Eq. (1) in isothermal conditions, the following equation is obtained:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \int_0^t A \exp\left(\frac{-E_a}{RT}\right) dt = A \exp\left(\frac{-E_a}{RT}\right) t \quad (6)$$

where $g(\alpha)$ is the integral form of the reaction model.

Once the apparent activation energy has been determined, we can find the appropriate kinetic model which best describes a measured set of curing data. For this purpose it is useful to define the two special functions, $Y(\alpha)$ and $Z(\alpha)$, which can easily be obtained by simple transformation of the experimental data.

Following the Málek et al. [30], $Z(\alpha)$ function applied to the isothermal condition is defined by combination of Eqs. (1) and (6) as:

$$Z(\alpha) = \left(\frac{d\alpha}{dt}\right) t = f(\alpha)g(\alpha) \quad (7)$$

Similar to the normalization procedure, this function is usually plotted within the (0,1) interval for practical reasons. The maximum of this function, labeled α_p^∞ , has characteristic values for basic kinetic models. This value is useful for basic classification of possible kinetic models, but it is not sufficient for an unambiguous determination of true kinetic model function $f(\alpha)$. Another defined function $Y(\alpha)$ is proportional to $f(\alpha)$ in isothermal conditions because $A \exp(-E_a/RT)$ is constant:

$$Y(\alpha) = \left(\frac{d\alpha}{dt}\right) \approx f(\alpha) \quad (8)$$

Therefore, if the reaction rate is plotted as a function of α its shape corresponds to the $f(\alpha)$ function. It is convenient to normalize the $Y(\alpha)$ function within (0,1) interval. The parameter α_m corresponds to the maximum of $Y(\alpha)$ function, which represents an important parameter in the kinetic model determination of the investigated process. The shape of $Y(\alpha)$ vs. α plot is characteristic for each kinetic model, and it can be used as a diagnostic tool for the kinetic model determination using the rules demonstrated by Málek et al. [30,31].

4. Results and discussion

Fig. 1 shows the isothermal curing curves for the unsaturated polyester resins obtained at the different operating temperatures (80, 100, 120 and 140 °C). The experimental data (the discrete values), was fitted using a sigmoidal (logistic) equation, because due to the vitrification and diffusion limitations over the curing kinetics, the experimental conversion curve typically shows a characteristic sigmoidal shape (Fig. 1).

The continuous values obtained by the sigmoidal equation enable us to determine the kinetic parameters for modeling the cure behavior of the investigated resin.

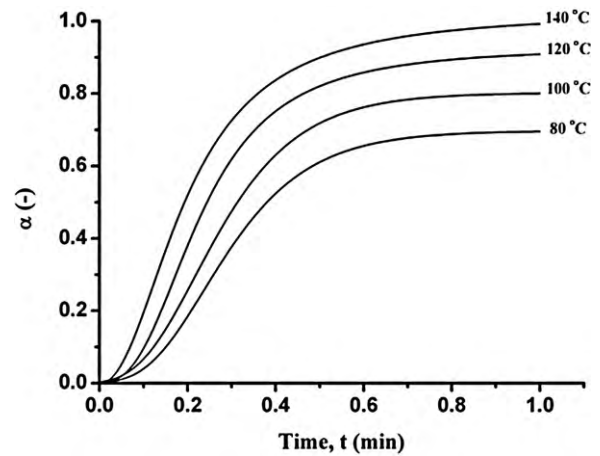


Fig. 1. The experimentally obtained conversion curves (α vs. t) for isothermal curing reaction of an unsaturated polyester resin samples containing methyl ethyl ketone peroxide at different operating temperatures ($T = 80, 100, 120$ and 140 °C).

From the shapes of curing curves (Fig. 1), we can see that after an induced period, the conversion rate increases rapidly (acceleration period), followed by a progressive slowing down (deceleration period) until the curing curve reaches approximately a plateau corresponding to the maximum value of the degree of cure at all temperatures. As expected, the maximum degree of cure increases with the increase of temperature. Yousefi et al. [32] proposed that the temperature dependency of the maximum degree of cure could be presented in the form of a third-order polynomial expression. This equation was valid only in the range of temperature studied [32]. For our investigated curing process, with methyl ethyl ketone peroxide as initiator, the following polynomial equation was found: $\alpha_{\max} = 0.87609 - 0.01299 \times T + 1.81102 \times 10^{-4} \times T^2 - 5.88766 \times 10^{-7} \times T^3$ (in the temperature range 80 °C $\leq T \leq 140$ °C). The observed progressive slowing down is due to the diffusion limitations on the mobility of the reacting species as the cross-link density increases. It can be seen, that under isothermal conditions the degree of cure (α) is less than 1 (Fig. 1) due to the presence of unreacted monomer in the resin [33]. However, the results obtained from Fig. 1 indicate that the temperature increase (from 80 to 140 °C) is responsible for the higher conversion and better cure of the investigated resin.

Fig. 2 shows the differential reaction rate curves obtained for the isothermal curing process of the unsaturated polyester resins at the different operating temperatures.

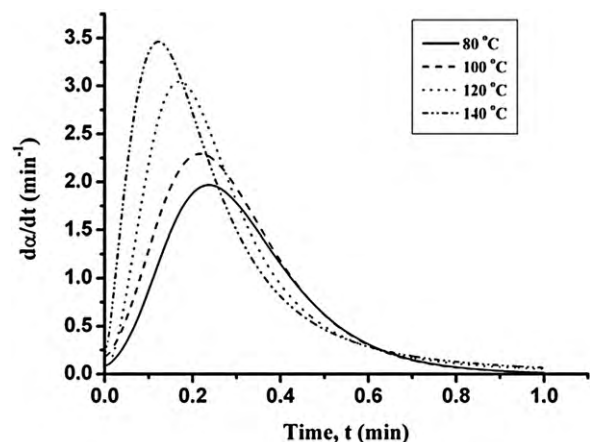


Fig. 2. The differential reaction rate curves ($d\alpha/dt$ vs. t) obtained for the isothermal curing process of an unsaturated polyester resin at different operating temperatures.

Table 1

The values of $(d\alpha/dt)_{\max}$, t_{\max} , $t_{m/2}$ and $t_{m/2}^*$ for the experimental reaction rate-time ($d\alpha/dt$ against t) curves at the different operating temperatures (T): $T = 80, 100, 120$ and 140 °C.

Temperature, T (°C)	$(d\alpha/dt)_{\max}$ (min ⁻¹)	t_{\max} (min)	$t_{m/2}$ (min)	$t_{m/2}^*$ (min)
80	1.968	0.232	0.113	0.420
100	2.293	0.212	0.095	0.396
120	3.050	0.172	0.073	0.325
140	3.470	0.121	0.043	0.270

Fig. 2 shows the kinetic effect of the temperature. Namely, at the higher temperatures, the curing times are lower and the reaction rates are higher. All reaction rate curves are the asymmetrical bell-shaped with long right-tails on the side of higher curing times (Fig. 2). It can be pointed out that in the isothermal process the cure takes place below the glass-transition temperature (T_g) [9] and the investigated material does not cure totally due to the vitrification, especially at the lower operating temperatures (Fig. 1). This is confirmed recently, by the existence of a residual heat after the isothermal cures [9], so at the experimental conditions the cures are not completed. In fact, the curing of the resin must have been incomplete even after post cure as the curing was a highly diffusion-controlled reaction.

The reaction rate curves at 80, 100, 120 and 140 °C shows that the maximum rate of process, $(d\alpha/dt)_{\max}$, existed for $t_{\max} > 0$. The values of $(d\alpha/dt)_{\max}$, t_{\max} , $t_{m/2}$ ($t_{m/2}$ is the time taken for the rate to drop to the half of its maximum value (i.e., $(d\alpha/dt)_{\max}/2$) – characteristic time value for $(d\alpha/dt)$ – t rate curves) and $t_{m/2}^*$ ($t_{m/2}^*$ is the time on the descent for $(d\alpha/dt)$ – t rate curves) for the reaction rate curves of the curing process of the unsaturated polyester resin at four different operating temperatures are presented in Table 1.

From Table 1, it can be seen that the values of t_{\max} , $t_{m/2}$ and $t_{m/2}^*$ decreased with increasing operating temperature from 80 to 140 °C. On the other hand, the values of $(d\alpha/dt)_{\max}$ increases with increasing temperatures. The results presented in Table 1 and the shapes of the reaction rate curves (Fig. 2) are useful for the basic classification of kinetic models [34]. From the results given above, we can conclude that the investigated isothermal curing reaction of the unsaturated polyester resin can be probably described by the sigmoid group of kinetic models [34].

For the cure modeling, the Friedman isoconversional (model-free) method (Eq. (5)) has been used to compute the apparent activation energy at the different constant conversion values.

Fig. 3 shows the variation of the apparent activation energy (E_a) and the isoconversional intercepts (constants $\ln[Af(\alpha)]$) as a function of the degree of cure (α).

This figure shows that the apparent activation energy remains almost constant during the initial stage of the polymerization reaction up to $\alpha = 0.50$, and starts to increase ($\alpha > 0.50$) due to the diffusion limitations for higher values of the degree of cure (α), where attendant that the curing is a complex process. Namely, this behavior can be attributed to the autocatalytic effect of the curing process once the reaction has begun (with slightly decreasing of E_a value at the beginning of reaction, Fig. 3) and to the phenomena of gelling, vitrification, and high viscosity in the reaction medium, when α increases. The autocatalytic effect of the process can cause an additional production of free radicals, which would be in agreement with detected acceleration in reaction rate (Fig. 2) and decrease in the apparent activation energy that is observed in the range of $0.05 \leq \alpha \leq 0.10$ (Fig. 3). On the other hand, due to the phenomenon of vitrification, or to the process of completion of the reaction, the curing rate decreases and the apparent activation energy increases.

From Fig. 3, it can be observed that the apparent activation energy is practically constant in the range of $0.10 \leq \alpha \leq 0.50$ and

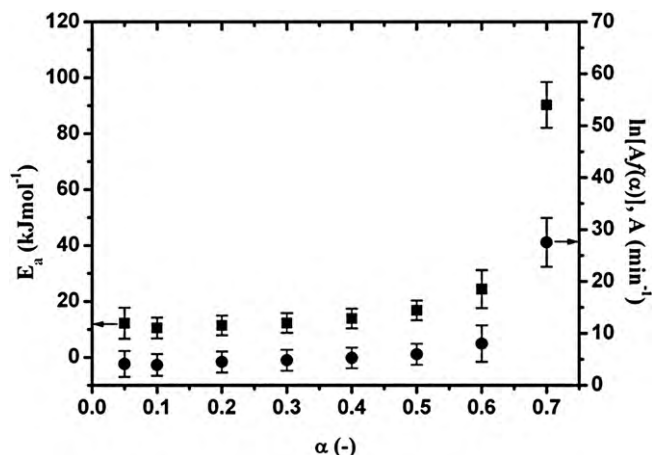


Fig. 3. The dependence of the apparent activation energy (E_a) and the isoconversional intercepts (constant $\ln[Af(\alpha)]$) on the curing degree (α) obtained by differential isoconversional (model-free) method for the curing reaction of an unsaturated polyester resin.

the average value of E_a was found to be $E_a = 12.9 \text{ kJ mol}^{-1}$. Alternatively, $\ln[Af(\alpha)]$ – α plot associated with isoconversional method demonstrates an identical manner (Fig. 3), which it may suggest that the apparent activation energy (E_a) and the pre-exponential factor (A) both depend in the same way on the degree of cure.

For predictive purposes, it is possible to create an isothermal reduced-time curve by simply scaling the raw data with time [35]. This is accomplished by dividing the cure time on the x axis by $t_{0.50}$, the cure time required for α to reach 0.50, resulting in a collapsing of all curing curves (Fig. 1) onto a single curve as seen in Fig. 4.

Isokinetic data from a number of experimental runs should line on a single curve. It can be seen that the data are isokinetic from $\alpha = 0.00$ to 0.50 at all considered operating temperatures. However, it can be observed that the data for $\alpha > 0.50$ is not isokinetic for all temperatures. These deviations of the experimental data from a single curve at higher values of α can be a consequence of varying at least one component in kinetic 'triplet' with operating temperature. Values of $t_{0.50}$ estimated at the several different operating temperatures were used in the Arrhenius-type plot, $[\ln(1/t_{0.50})$ against $1/T$], to evaluate the apparent activation energy of the investigated curing process, without the necessity for identifying the kinetic model. The apparent activation energy (E_a) can be calculated from the slope of the observed straight line (Fig. 5).

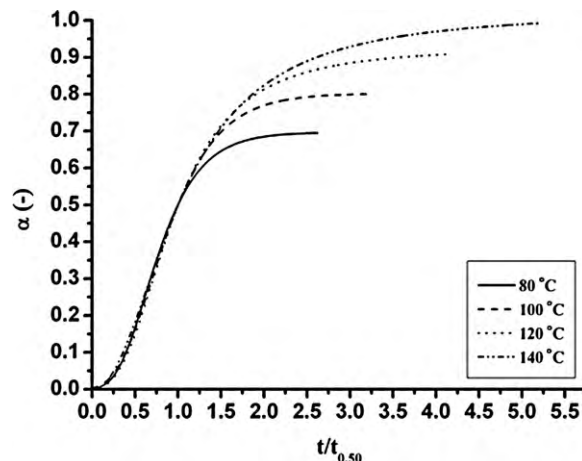


Fig. 4. The experimental reduced-time plots (α vs. $t/t_{0.50}$) for the curing reaction of an unsaturated polyester resin at different operating temperatures.

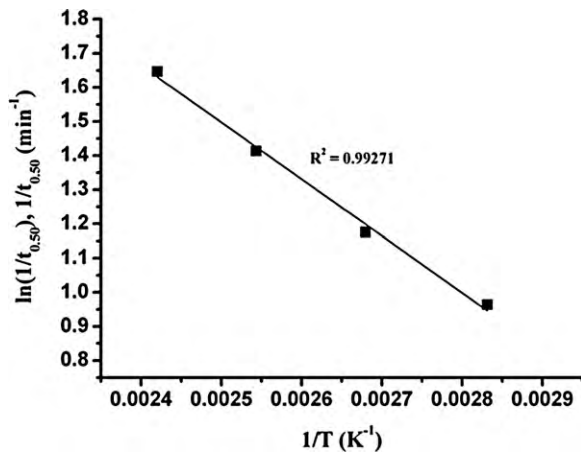


Fig. 5. The Arrhenius-type plot ($\ln(1/t_{0.50})$ vs. $1/T$) evaluated for the curing reaction of an unsaturated polyester resin under isothermal conditions.

The intercept includes $\ln[g(\alpha)]$ and does not directly yield the pre-exponential factor. The calculated values for E_a and $\ln[g(\alpha)]$ of the investigated isothermal curing process of the unsaturated polyester resin are the following: $E_a = 13.8 \text{ kJ mol}^{-1}$ and $\ln[g(\alpha)] = 5.65$. The obtained value of E_a is a little higher than value of E_a calculated by differential (Friedman) isoconversional method. However, this value of E_a is in very good agreement with value of E_a calculated by the isoconversional analysis, because the difference between these two values are less than 1 kJ mol^{-1} ($\Delta E_a = 0.9 \text{ kJ mol}^{-1}$).

4.1. Determination of the reaction model and the pre-exponential factor for curing process

The variation of $Y(\alpha)$ and $Z(\alpha)$ functions with the degree of cure are indicated in Figs. 6 and 7, calculated using Eqs. (8) and (7), respectively. The values of both $Y(\alpha)$ and $Z(\alpha)$ functions were normalized within (0,1) interval for all considered operating temperatures.

The conversions, in which the $Y(\alpha)$ and $Z(\alpha)$ functions and also the reaction rate curves exhibit the maximum values (α_m , α_p^∞ and α_p , respectively) for the different temperatures are listed in Table 2.

As was noted, the data in Table 2 which has been extracted from Figs. 6 and 7, show that the α_m , α_p^∞ and α_p values depend on the operating temperature. The maxima of $Y(\alpha)$ and $Z(\alpha)$ func-

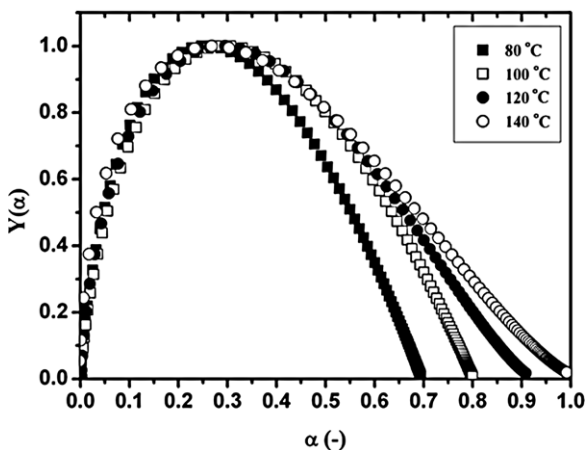


Fig. 6. Normalized $Y(\alpha)$ functions obtained by transformation of isothermal data for the curing reaction of an unsaturated polyester resin at different operating temperatures.

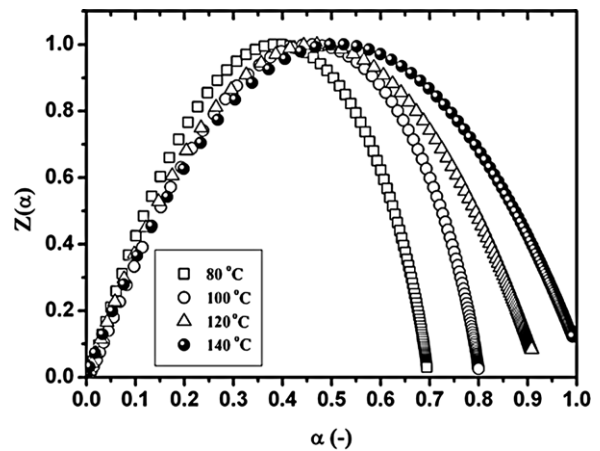


Fig. 7. Normalized $Z(\alpha)$ functions obtained by transformation of isothermal data for the curing reaction of an unsaturated polyester resin at different operating temperatures.

tions fall into range of $0.247 \leq \alpha_m \leq 0.295$, $0.399 \leq \alpha_p^\infty \leq 0.525$ and $0.247 \leq \alpha_p \leq 0.295$, respectively. These variances probably corresponded to the variances in at least one component in the kinetic 'triplet' for considered isothermal curing process.

It can be pointed out that both $Y(\alpha)$ and $Z(\alpha)$ functions exhibit the concave shapes where α_m values, at all temperatures, satisfy the condition $0 \leq \alpha_m \leq \alpha_p$ (Table 2 and the Fig. 6). The validity of the Johnson–Mehl–Avrami (JMA) kinetic model can easily be verified by checking the maximum α_p^∞ that falls in the $0.610 \leq \alpha_p^\infty \leq 0.650$ [31]. For curing process of unsaturated polyester resin, at all considered operating temperatures, α_p^∞ is shifted to the lower values, and this does not correspond to the JMA kinetic model [30,31]. Therefore, the $Y(\alpha)$ and $Z(\alpha)$ functions, at all operating temperatures, satisfy the condition for the two-parameter autocatalytic (Šesták–Berggren (SB)) model, which for the reaction with zero initial rate can be expressed as [22]:

$$f(\alpha) = \alpha^m(1 - \alpha)^n \quad (9)$$

where m and n represents the reaction orders for initiation and propagation stages, respectively. The autocatalytic reaction assumes that the step reaction products are involved in the chain growth reaction.

The reaction order n and the logarithm of the pre-exponential factor ($\ln A$) can be calculated from the logarithmic form of Eq. (1) considering $f(\alpha) = \alpha^m(1 - \alpha)^n$ after rearrangement yields [31]:

$$\ln \left[\left(\frac{d\alpha}{dt} \right) \exp \left(\frac{E_a}{RT} \right) \right] = \ln A + n \ln [\alpha^P(1 - \alpha)] \quad (10)$$

where the kinetic parameter ratio P is equal

$$P = \frac{m}{n} = \frac{\alpha_m}{1 - \alpha_m} \quad (11)$$

From the slope and intercept of the linear relationship $\ln[(d\alpha/dt) \exp(E_a/RT)]$ vs. $\ln[\alpha^P(1 - \alpha)]$ we can obtain the reaction order n and the value of $\ln A$, respectively. The value of reaction order m can be obtained from relation $m = P \times n$. Table 3 lists the

Table 2

The conversions, in which the $Y(\alpha)$, $Z(\alpha)$ and the reaction rate-time peaks exhibit the maximum values (α_m , α_p^∞ and α_p , respectively) for the different operating temperatures (80, 100, 120 and 140 °C).

Temperature, T (°C)	α_m	α_p^∞	α_p
80	0.247	0.399	0.247
100	0.284	0.461	0.284
120	0.295	0.470	0.295
140	0.268	0.525	0.268

Table 3
The autocatalytic model reaction orders (m , n , $m+n$) as well as the $\ln A$ and A values, resulting from Eqs. (10) and (11) for the isothermal curing process of an unsaturated polyester resin at four different operating temperature.

T (°C)	m	n	$m+n$	$\ln A$	A (min ⁻¹)	R^2 ^a	RSS ^b
80	0.76	2.33	3.09	6.80	8.98×10^2	0.997	3.02×10^{-3}
100	0.74	1.86	2.60	6.54	6.92×10^2	0.995	3.51×10^{-3}
120	0.62	1.48	2.10	6.33	5.61×10^2	0.996	1.54×10^{-3}
140	0.52	1.42	1.94	6.13	4.59×10^2	0.999	1.80×10^{-4}
Average	0.66	1.77	2.43	6.45	6.53×10^2		

^a Adj. R -squares.

^b Residual sum of squares.

values of reaction orders (m , n and $m+n$), the logarithm of the pre-exponential factor ($\ln A$), the pre-exponential factor (A), as well as the values of Adj. R -Squares (R^2) and residual sum of squares (RSS) of linear relationship presented by Eq. (10) at all considered operating temperatures.

For the calculation of the autocatalytic kinetic parameters presented in Table 3, the apparent activation energy (E_a) ($E_a = 12.9 \text{ kJ mol}^{-1}$; $0.10 \leq \alpha \leq 0.50$) evaluated from differential (Friedman) isoconversional method was used.

It can be observed from Table 3, that both reaction orders, m and n , decrease with the increase of the operating temperature. Both parameters exhibit the dependency on the operating temperature. The curing temperature has the influence on the complexity of considered process, especially through the value of n parameter. Namely, because the curing reaction is a free-radical chain growth polymerization, with the three stages of initiation, propagation and termination, the decreasing behavior of parameter n with the increase in operating temperature (Table 3), indicates decreasing complexity in propagation stage of curing reaction. These results show that the complexity of the investigated process has the dominant role in the propagation stage at the lowest temperature (at $T=80^\circ\text{C}$, $n=2.33$, Table 3), while at the highest temperature, the mentioned complexity of considered process is not enough expressive (at $T=140^\circ\text{C}$, $n=1.42$, Table 3). In accordance with above results, it can be pointed out that the curing rate curve which has the highest reaction rate (Fig. 2) is the one that has the lowest value of n reaction order (Table 3). On the other hand, the decrease in the value of the reaction order m (Table 3) with the increase in the operating temperature (T), indicates a less important role of the polymerization product on the overall curing kinetics with an autocatalytic behavior. In that sense, at the lower operating temperatures we may expect the raising amount of the styrene residuals. The average values of reaction orders, m and n (Table 3), are in good agreement with values of m and n reported by Shin et al. [13]. On the other hand, the obtained values of m are lower, while the values of n are higher (Table 3) then corresponding values of m and n reported by Salla and Ramis for Method A [9]. The observed variations probably lies in the different type of catalysts which were used in the investigations, and also in different curing temperature regions [9].

In addition, taking into account the values of reaction orders, $m+n$, we can assign a value of $m+n=3.09$ at $T=80^\circ\text{C}$ (Table 3) when a mechanistic model is valid ($m+n=3.00$) [36], while the value of $m+n=1.94$ at $T=140^\circ\text{C}$, corresponds to the condition when the empirical model ($m+n=2.00$) [37,38] can be used. Taking into account the average value of the reaction orders, $m+n$, ($m+n=2.43$), the phenomenological (empirical) modeling of the investigated isothermal curing process is a most appropriate ($m+n=2.43$ (Table 3) is closer to the $m+n=2.00$ value).

By summarizing the results, we can conclude that the higher operating temperatures lead to the increase of the time to reach

the gelled glass state. This is due to the favorable steric association for propagation of the resin due to the decrease in viscosity and the increase in the reaction rates as a function of temperature. At the highest operating temperature the time to vitrification obtains a minimum value due to the competing effects between the reaction rates and the consumption of the reactants.

Fig. 8 shows the comparison between the experimentally obtained reaction rate curves and calculated reaction rate curves using the two-parameter autocatalytic model (Eqs. (1) and (9)) with values of reaction orders, m and n , presented in Table 3.

It can be seen from Fig. 8, that the quite good agreement between the experimental and calculated reaction rate curves exists in the earlier stages of the curing process, while in the later stages the some deviations can be observed (except at $T=140^\circ\text{C}$). The deviations from the autocatalytic kinetic model start at approximately $\alpha=0.50$ – 0.55 for all observed operating temperatures (except at $T=140^\circ\text{C}$) (Fig. 8), which indicates that the isothermal curing of the unsaturated polyester resin does not follow the autocatalytic model in the whole range of the degree of cure.

These deviations can be attached to the interaction of the chemical kinetics with certain physical processes that take place during the curing, such as the phenomena of gelling and vitrification. When the investigated system reaches the gel-point (gelation), it may be considered as a high-molecular weight network and consequently, the viscosity reaches infinity. As the reaction progresses the material continues to react and the glass-transition temperature (T_g) increases creating a solid rigid structure after which the final conversion occurs as a diffusion-controlled process. As the consequence of the change from the chemical kinetic control to the control by diffusion, the basic rate equation for investigated curing process must be modified, which includes beside the autocatalytic term and also the diffusion term.

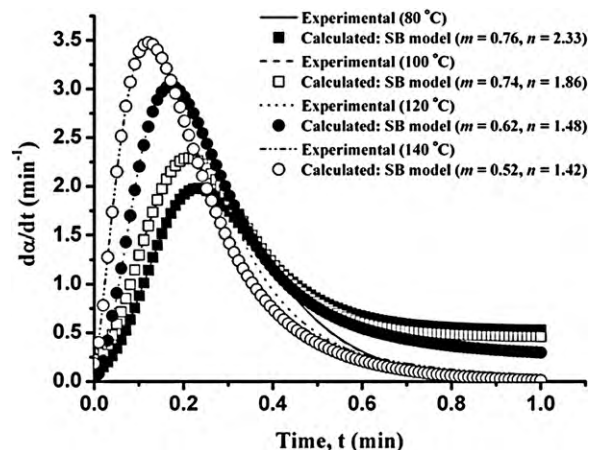


Fig. 8. The comparison between the experimentally obtained reaction rate curves and calculated reaction rate curves using the two-parameter autocatalytic model, with values of reaction orders (m and n) listed in Table 3.

Table 4

The numerically evaluated parameters of Eq. (12) using the Levenberg–Marquardt method for the isothermal curing of an unsaturated polyester resin.

Temperature, T (°C)	C	α_{C_0}	α_{CT} (K ⁻¹)	χ^2 ^a
80	45	-1.685	6.605×10^{-3}	2.39×10^{-6}
100	43	-1.690	6.580×10^{-3}	7.86×10^{-6}
120	41	-1.695	6.500×10^{-3}	8.66×10^{-6}
140	40	-1.699	6.470×10^{-3}	2.32×10^{-5}

^a The reduced chi-square function.

4.2. Modeling of isothermal curing process

The basic rate equation (Eq. (1)) is modified by adding a term to explicitly account for the shift from the kinetics to diffusion control in an autocatalytic unsaturated polyester resin system, and the modified rate equation has the following form:

$$\frac{d\alpha}{dt} = \frac{1}{1 + \exp[C(\alpha - (\alpha_{C_0} + \alpha_{CT}T))]} A \exp\left(\frac{-E_a}{RT}\right) \alpha^m (1 - \alpha)^n \quad (12)$$

where C is the diffusion constant, α_{C_0} is the critical degree of cure at the absolute zero temperature, and T is the operating (isothermal) temperature in [K]. The constant α_{CT} accounts for an increase in the critical degree of cure with operating temperature. A , E_a , m and n have the same definitions as in the previous equations. For modeling procedure of the investigated curing process, the kinetic parameters (A , E_a , m and n) evaluated in previous section were used. To determine the constants described in the above equation, a non-linear regression fit based on the Levenberg–Marquardt method is used [39–41]. The Levenberg–Marquardt method is a method which varies smoothly between the inverse-Hessian method and the steepest descent method and has become the standard of non-linear least-squares routines.

It can be pointed out that the modified rate equation in the form of Eq. (12) is the only applied in the case of HexPly® 8552 epoxy resin curing [42]. However, by the author's knowledge, the modified rate equation presented through Eq. (12) does not live to see application in the complex curing process of an unsaturated polyester resin.

Table 4 lists the values of numerical constants (C , α_{C_0} and α_{CT}) computed using Eq. (12), as well as the values of reduced chi-square function (χ^2), at the different operating (isothermal) temperatures.

It can be seen from Table 4, that the diffusion constant values vary in quite small range, $40 \leq C \leq 45$ and exhibits slightly decreasing behavior. The isothermal reaction rate profiles of an unsaturated polyester resin measured at four different isothermal temperatures, is shown in Fig. 9.

Such good agreement between the lines, which indicate the results from the model prediction (Eq. (12) and Table 4) and the symbols (symbol \circ), which indicate the experimental results, is observed. Results from the model indicate that at a high activation temperatures the reaction develops much faster than when the activation temperature is at a low temperature. Moreover, the model describes very well the initial stages of the curing reaction, which correspond to a chemically controlled regime at the different activation temperatures. If we compare the results presented in Figs. 8 and 9, we can conclude that the reaction model expressed through Eq. (12) with parameters listed in Table 4, enable us to describe the isothermal curing process of unsaturated polyester resin in the whole range of conversions (α). This is confirmed by a good correlation between experimental and predicted values when the proposed model is used. However, we must point out one important fact. If we put that

$$(\alpha_{C_0} + \alpha_{CT}T) = \alpha_c \quad (13)$$

the first term in Eq. (12) is transformed into the Chern and Poehlein equation for the diffusion control factor (f_d) [43]. The aforementioned

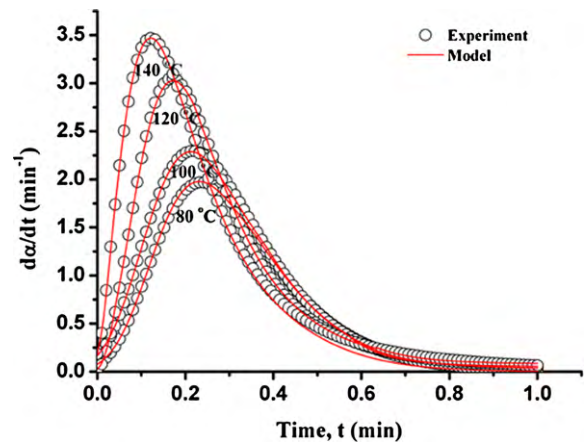


Fig. 9. Comparison of the model prediction (Eq. (12)) (lines –) and experimental data (symbol \circ) for the reaction rate curves of isothermal curing of an unsaturated polyester resin.

mentioned authors have introduced a semi-empirical approach to modeling diffusion control which was modified by Cole et al. [44]. The equation for diffusion control factor (f_d) in the present-day form is follows [45–51]:

$$f_d = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \quad (14)$$

where α_c is the critical degree of cure at the onset of diffusion control. As noted by Cole et al. [44], the onset to diffusion is generally a gradual transition from chemical to diffusion control, rather than abrupt transition at α_c . In accordance with Eq. (13), for the curing reaction of an unsaturated polyester resin, the critical degree of cure (α_c) was obtained, with values of 0.648, 0.765, 0.861, 0.974 at 80, 100, 120 and 140 °C, respectively. It was found that α_c linearly depends on temperature according to Eq. (13). For $\alpha \ll \alpha_c$, f_d approximately equals unity and the effect of diffusion is negligible, so that the reaction is kinetically controlled. As α approaches α_c , f_d begins to decrease and approaches 0.50 when $\alpha = \alpha_c$. Beyond this point, it continues to decrease and approaches zero, which means that the reaction becomes very slow and effectively stops. In this study, f_d was determined as the ratio of the experimental reaction rate to the reaction rate predicted on the basis of the Šesták–Berggren autocatalytic kinetic model [52]. The values of diffusion control factor (f_d) as a function of the degree of cure (α) at the different operating temperatures are shown in Fig. 10.

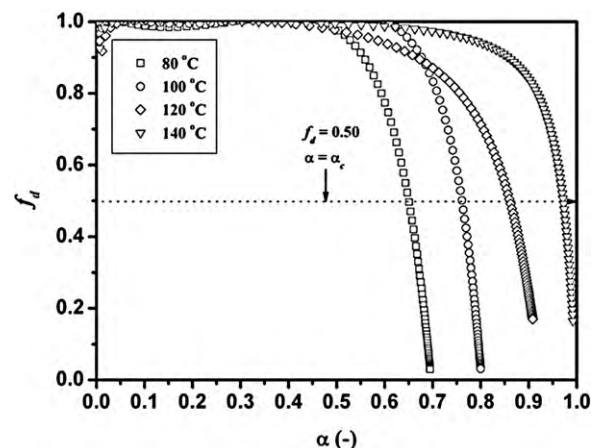


Fig. 10. Diffusion control factor vs. the degree of cure for the isothermal curing of an unsaturated polyester resin at 80, 100, 120 and 140 °C.

In the combined model, the diffusion effects are negligible when the values of the diffusion control factors stay near 1.00. The critical degree of cure increases with increasing the operating temperature, indicating that the temperature has an important role in describing the kinetics of investigated curing process. In that sense, the curing behavior under isothermal conditions is very important in industrial practice.

It can be pointed out that the diffusion control factor for the proposed model in Eq. (12) and the same factor in Eq. (14) which belongs to the Chern–Poehlein model, represent the type of Williams–Landel–Ferry function [53,54]. These two factors are different only in the number of empirical parameters. In the first case, for the proposed model (Eq. (12)), we have three parameters (C , α_{Co} and α_{CT}), while in the latter case (Eq. (14)) we have only two parameters (C and α_c). From a mathematical point of view, the increasing degrees of freedom (increase in the number of empirical parameters) of the considered function leads to increased flexibility of function, in the sense that it increases the possibility of describing a wide variety of curing data, expressed through the differential reaction rate curves (Fig. 2). Because of this fact, the proposed reaction model represented by Eq. (12) is much more accurate than the Chern–Poehlein model with two empirical parameters (Eq. (14)).

4.3. Evaluation of the density distribution function of the apparent activation energy (DDFE_a) for the isothermal curing process

In this paper, the Miura's [55] computational procedure was used to estimate the distribution function $f(E_a)$, which is obtained by the differentiation of the $\alpha(E_a)$ function with respect to the apparent activation energy:

$$f(E_a) = \frac{d\alpha(E_a)}{dE_a} \quad (15)$$

because the following relation holds approximately [55]:

$$\alpha = 1 - \int_{E_a}^{\infty} f(E_a) dE_a = \int_0^{E_a} f(E_a) dE_a \quad (16)$$

The $\alpha(E_a)$ function, that relates the degree of cure with the apparent activation energy, is calculated from the experimental data of α vs. t (Fig. 1). It can be pointed out, that the Braun and Burnham [56] clarified that the conversion-dependent E_a values obtained by Friedman isoconversional method (Eq. (5)) result from the distribution of the apparent activation energy. This is the correct interpretation because conversion-dependent E_a values actually are obtained by Friedman's method when E_a is assumed to be a function of α (Fig. 3). The experimentally evaluated density distribution function of the apparent activation energy $f(E_a)$, using Eq. (13) and results from Fig. 3 is presented in Fig. 11 (the experimental DDFE_a is shown in Fig. 11 by the full line).

It can be observed that the experimentally evaluated DDFE_a exhibits the strong asymmetrical character (unison shape factor SF=0.437) with long right-tail on the side of higher values of the apparent activation energy. The observed distribution function is a narrow with $E_{a,max} = 11.5 \text{ kJ mol}^{-1}$ ($E_{a,max}$ is value at the maximum of distribution function). The obtained value of $E_{a,max}$ is in good

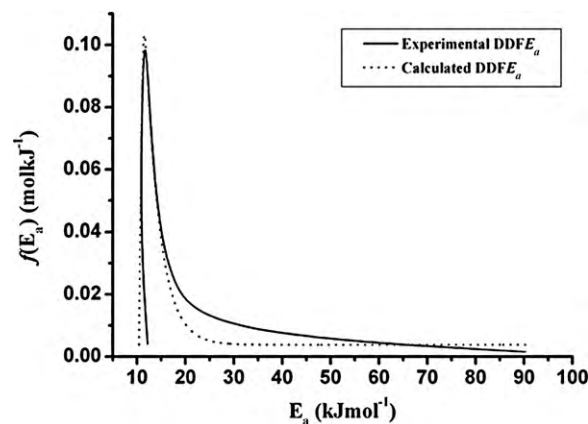


Fig. 11. The comparison of the experimentally obtained DDFE_a (full line) and the numerically evaluated DDFE_a (unbalanced modified Gaussian distribution function, Eq. (17)) (the dot line) for the isothermal curing of an unsaturated polyester resin.

agreement with average value of E_a calculated by the differential isoconversional method ($E_a = 12.9 \text{ kJ mol}^{-1}$).

The observed deviation of DDFE_a from a symmetric distribution curve (SF = 1.000) is the measure of the complexity of investigated process. In our case, the DDFE_a deviates on the side with higher values of conversion and higher values of E_a , which is typical for the curing process complicated with diffusion.

However, for this complex process, the experimentally evaluated DDFE_a ($f(E_a)_{exp}$) can not be approximated by simple symmetric Gaussian or Gaussian-type distribution [57–60]. Using the numerical non-linear curve fitting (NLCF), it was found that the experimentally obtained DDFE_a can be best approximated by the asymmetric (unbalanced) modified Gaussian distribution function (MGDF), in the form:

$$f(E_a) = f(E_a)_o + \frac{A^*}{t_o^*} \times \exp \left[\frac{1}{2} \times \left(\frac{w}{t_o^*} \right)^2 - \frac{E_a - E_{a,c}}{t_o^*} \right] \times \int_{-\infty}^z \frac{1}{(2\pi)^{1/2}} \times \exp \left(-\frac{y^2}{2} \right) dy \quad (17)$$

and

$$z = \frac{E_a - E_{a,c}}{w} - \frac{w}{t_o^*} \quad (18)$$

where $f(E_a)_o$ is the lowest value of $f(E_a)$, A^* is the constant, w is the width of distribution, $E_{a,c}$ is the centered value of the apparent activation energy and t_o^* is the peak correction coefficient. Table 5 lists the values of MGDF parameters calculated for the isothermal curing process of unsaturated polyester resin. In the same table, the corresponding values of reduced chi-square function (χ^2) and residual sum of squares (RSS) are also given.

It can be seen from Table 5 that the value of $E_{a,c}$ are in good agreement with established values of $E_{a,max}$ (11.5 kJ mol^{-1}), which confirms that the MGDF can approximate the experimentally evaluated DDFE_a with quite satisfactory precision.

Table 5
The parameter values of unbalanced modified Gaussian distribution function (MGDF) calculated using the numerical non-linear curve fitting (NLCF) for the complex curing process of an unsaturated polyester resin under isothermal conditions.

MGDF parameters						
$f(E_a)_o$ (mol kJ ⁻¹)	A^* (kJ mol ⁻¹)	t_o^* (kJ mol ⁻¹)	w (kJ mol ⁻¹)	$E_{a,c}$ (kJ mol ⁻¹)	χ^2 ^a	RSS ^b
0.00374	0.44341	3.06601	0.01218	10.5	9.15×10^{-6}	2.75×10^{-5}

^a The reduced chi-square function.

^b Residual sum of squares.

This fact can be easily detected from Fig. 11, which shows the comparison of the experimentally obtained $DDFE_a$ (full line) and the numerically evaluated MGDF (the dot line) for the investigated curing process.

These results show that the experimentally obtained $DDFE_a$ can be best described with quite complex asymmetric Gaussian distribution function, which follows from the complex dependence of E_a on α .

From the established results we can conclude that the empirical two-parameter autocatalytic model cannot describes the investigated curing process in the whole range of conversions, already only up to $\alpha = 0.50$. After vitrification the reaction is very slow as it becomes diffusion controlled at the higher values of α . In that case, the kinetic law equation for curing process must be modified with additional term which properly describes the diffusion-controlled process. The shape and basic characteristics of the experimentally obtained density distribution function of the apparent activation energy ($DDFE_a$) unambiguously show that the curing of unsaturated polyester resin is complex, because the many reactive processes occur simultaneously.

5. Conclusions

The kinetic process of isothermal curing of an unsaturated polyester resin has been studied. The differential isoconversional method is used to yield dependency of the apparent activation energy on the degree of cure. It was found that the dependence of E_a on α is complex, but in the conversion range of $0.10 \leq \alpha \leq 0.50$, the apparent activation energy (E_a) is practically constant and was found to be $E_a = 12.9 \text{ kJ mol}^{-1}$. It was established that the gelling stage of curing process is mainly controlled chemically which can be best described by two-parameter autocatalytic model (in the conversion range of $0.10 \leq \alpha \leq 0.50$). It was found that the autocatalytic adjustment cannot be applied in the whole range of conversion values. At the higher values of α ($\alpha > 0.50$), when the vitrification point is reached, the change in the rate-limiting step was observed (from the chemical controlled to diffusion-controlled curing process).

As the consequence of shifting effect from the kinetics to diffusion control in an autocatalytic unsaturated polyester resin system, the kinetic law equation is modified with additional diffusion term. The experimental reaction rate curves were fitted by the model prediction with a high degree of accuracy at all considered isothermal temperatures. It was found that the experimentally obtained density distribution function of the apparent activation energy ($DDFE_a$) can be approximate by the unbalanced modified Gaussian distribution function (MGDF) with quite satisfactory precision. It was established that the observed deviation of $DDFE_a$ on the side with higher values of α and higher values of E_a is a typical for complex curing process complicated with diffusion.

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