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# A RAPID METHOD FOR THE EVALUATION OF CURE KINETICS OF THERMOSETTING POLYMERS

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Thermo-analytical methods are widely used in the characterization of various materials. Among them, DSC is especially important for polymer analysis, since it enables determination of basic thermodynamic and kinetic parameters of crystallization, melting, crosslinking, etc. In this study we report the results of a rapid method used for the evaluation of the data obtained by DSC measurements of a cure reaction for thermosetting resins. The method was based on the Borchardt and Daniels kinetic model and enables determination of basic parameters that are important for product and process development, as well as for optimization of cure cycles for a variety of thermosets. The method described in this work will help university students and engineers in the fields of polymer science and engineering to simplify the analysis process for data collected during cure measurements with DSC.

**Keywords:** polymer engineering; thermoanalytical methods; DSC; thermosetting resins; curing reaction; kinetic models; kinetics parameters

## БРЗ МЕТОД ЗА АНАЛИЗА НА КИНЕТИКАТА НА ВМРЕЖУВАЊЕ НА ТЕРМОРЕАКТИВНИТЕ СМОЛИ

Термоаналитичките методи наоѓаат широка примена во карактеризацијата на материјалите. Меѓу нив од особено значење за анализа на полимерите е диференцијалната скенирачка калориметрија (DSC), која овозможува определување на основните термодинамички и кинетички параметри на кристализацијата, топењето, вмрежувањето и др. Во трудот се презентирани резултати од примената на брз метод применет за обработка на резултатите добиени од анализа на реакцијата на вмрежување на термореактивни смоли со DSC. Методот е базиран на Borchardt-Daniels-овиот кинетички модел и овозможува определување на основните параметри важни за развој на производ и процес, но исто така и за оптимизација на реакционите циклуси кај различни термореактанти. Опишаниот метод ќе им помогне на студентите и на инженерите од подрачјето на полимерната наука и инженерство да ја поедноставнат обработката на податоците добиени при процесот на вмрежување следен со DSC.

**Клучни зборови:** полимерно инженерство; термоаналитички методи; DSC; термореактивни смоли; реакција на вмрежување; кинетички параметри

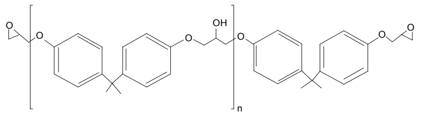
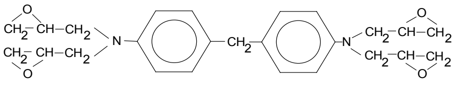
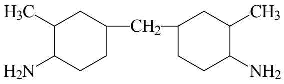
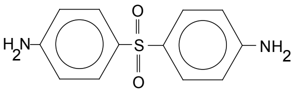
# 1. INTRODUCTION

## 1.1. *Thermosetting polymers and cure reaction*

Thermosetting polymers represent a large group of commercially valuable products that are used in many different industries as surface coatings, adhesives, textile finishing agents, matrices for composite materials, etc. The family of thermosetting polymers includes a variety of polyester resins, epoxy resins (Table 1), polyuretanes, silicones, polyamides, and melamine resins. Many of the thermosets are inexpensive and can be reinforced with fillers or fibers to provide physical and mechanical properties for a wide variety of applications. On the other hand, specially designed, extreme temperature-resistant thermosets have been developed with properties that seem unlikely to be matched by any now-foreseen thermoplastic polymer [1, 2].

Table 1

*General formulas of epoxy resins and amino-curing agents*

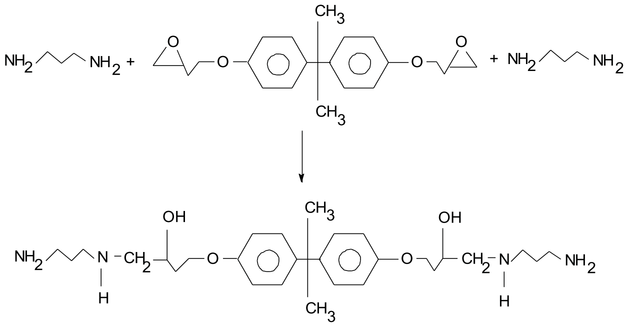
| Epoxy resins | Abbreviations | Chemical formulas |
|---|---|---|
| Bisphenol A diglycidyl ether | **DGEBA** |  |
| Tetraglycidyl-4,4´ -diaminodiphenylmethane | **TGDDM** |  |
| Epoxy curing agents | | |
| Aliphatic polyamine | **APA** | $H_2N\text{–}(CH_2)_3\text{–}NH\text{–}(CH_2)_3\text{–}NH_2$ |
| Cyclohexanamine, 4,4´-methyllenebis-2-methyl | **CHAM** |  |
| 4-(4-aminophenyl) sulfonylaniline | **DDS** |  |

Thermosetting polymers are usually produced as oligomers with linear macromolecules and of moderately low molecular mass. During this first stage of the production process, most of these oligomers, known also as prepolymers, represent solid or liquid (low viscosity) products that are soluble in polar or nonpolar (mostly organic) solvents. In general, the state of a thermosetting polymer at various stages of its processing can be classified into one of three categories:

- stage A: uncured polymer (resin; characterized by low viscosity at room temperature and low molecular mass);
- stage B: partially cured polymer (characterized by gel-time, increased viscosity due to partial crosslinking, and partial solubility/swelling in certain solvents);
- stage C: completely cured (crosslinked) resin.

The third stage, which occurs during the transformation into the final products, involves conversion of the polymer into insoluble, highly crosslinked materials. In contrast to thermoplastic polymers, thermosets harden irreversibly in a reaction that usually requires heat, and cannot be resoftened. This reaction, known as curing or cure, proceeds via crosslinking and interlinking of the oligomeric chain molecules, resulting in the formation of a two- or three-dimensional network that has infinite molecular mass.

A curing reaction that starts in stage B involves the presence of a second component, as well as sometimes a third with catalytic activity, in the system. The curing agent is, most often, a low molecular mass compound with functional groups capable of reacting with certain groups/reactive sites in the oligomeric molecule. For instance, the common curing agents for epoxides (Table 1) are primary or tertiary amines and anhydrides, and the reaction of crosslinking proceeds as shown, in a simplified form, in Scheme 1.



**Scheme 1.** Curing reaction of epoxy-resins with amines

Stage B is characterized by a rapid increase of molecular weight resulting from the progress of the linking reaction between the chains, which marks the beginning of a network formation. The onset of this irreversible transformation from a viscous liquid to elastic gel is called the gel point. Beyond this point, the cross-link density increases rapidly to give a rigid network with a glass transition temperature, $T_g$, that is incomparably higher than that of the starting resin system (stage A) and the resin in stage B.

The glass transition temperature is a measure of cross-link density and the potential mobility of the molecular segments, which, in turn, governs the capability of the system to undergo changes in volume. The smaller this capability, the higher the $T_g$, and many of the ultimate physical and mechanical properties of the cured resin are increased [3].

Generally, there are low- and high-temperature thermosetting systems, depending on the most appropriate cure temperature. Regardless of the type of thermoset, if the cure temperature is approaching the $T_g$ of the system at a certain point of the cure reaction, the product is becoming a glass, a process known as vitrification, and the resulting high viscosity limits further reaction between the components in the system (diffusion is hindered). Above the $T_g$, segmental mobility is increased and, thus continuing the cure at temperatures higher than the $T_g$, the cross-linking process to continue as a result of promoted diffusion of all of the molecules that take part in the reaction [4].

### 1.2. *Cure reaction kinetics and DSC measurements*

For thermoplastic and thermoset polymers, differential scanning calorimetry (DSC) has been widely used over the years for different purposes, such as determination of glass transition temperature ($T_g$), melting temperature ($T_m$), enthalpy of melting or crystallization ($\Delta H_m$ and $\Delta H_c$, respectively; for thermoplastics), heat of curing reaction ($\Delta H_r$; for thermosets), etc. In general, DSC measures the heat flow associated with changes in the structure of materials as a function of time and temperature in a controlled, most often inert, atmosphere.

For thermosets, DSC allows for the monitoring of cure reactions, degree of cure, and detection of the glass transition temperature. The rate of reaction between the components (resin, curing agents, and possibly a catalyst) is a function of time and temperature for a given formulation. Data from DSC experiments can be applied to reaction models to predict reaction rates, overall reaction kinetics, and required processing conditions. Kinetics calculations based on a DSC heating run that is performed either in isothermal or in nonisothermal conditions, provide valuable guidance, not only for product and process development, but also for optimization of cure cycles for a variety of thermosetting resins. The Borchardt-Daniels calculation method is the most rapid means of modeling a cure reaction [5], and it allows for fast interpretation of the experimental results derived for the cure exotherm recorded by DSC. This method provides the activation energy, the frequency factor, and the order of reaction from a single DSC thermogram.

### 1.3. *Theoretical background and Borchardt-Daniels method*

There are several models that have been proposed in the literature to describe the cure kinetics of thermosets [5, 6, 7]. The most simple of these is the $n^{\text{th}}$ order reaction model (given by equation (1)), which was developed for systems showing no autocatalytic phenomena:

$$d\alpha / dt = k(1-\alpha)^n. \tag{1}$$

For systems that exhibit autocatalytic effects, this model is modified and appears as:

$$d\alpha / dt = k\alpha^m (1-\alpha)^n, \tag{2}$$

where $d\alpha / dt$ = reaction rate, $m$ and $n$ = reaction orders.

The equation describing an overall $n^{\text{th}}$ order reaction with autocatalytic effect is given by:

$$d\alpha / dt = (k_1 + k_2\alpha^m)(1-\alpha)^n. \tag{3}$$

For a complex reaction systems consisting of independent reactions, further modification of the equation (3) leads to a general complex reaction model (4):

$$(d\alpha / dt)_{overall} = \sum g_i A_i e^{-E_i/RT} f_i(\alpha)_i \tag{4}$$

where $A_i$ = pre-exponential factor of the $i^{\text{th}}$ reaction, $i$ = number of independent reactions, $E_i$ = activation energy of the $i^{\text{th}}$ reaction, $f_i(\alpha)_i$ = reaction function of $i^{\text{th}}$ reaction, and $g_i$ is normalized weighting factor of the $i^{\text{th}}$ reaction.

Arrhenius dependence of the rate constant is given by (5):

$$k_i(T) = Ae^{-E/RT} \tag{5}$$

Application of all of these models does not always leads to unique conclusions for the same thermoset system [8]. On the other hand, the methods developed from the work of Ozawa and Duswalt [6, 7] required a series of DSC scans of a sample run at different heating rates for determination of the above-mentioned kinetics parameters.

The method reported by Borchardt and Daniels [5] allows for the calculation of activation energy, pre-exponential factor, heat of reaction, and reaction order from a single DSC scan, assuming that the reaction follows $n^{\text{th}}$ order kinetics and that the temperature dependence of the reaction rate follows the Arrhenius expression. Thus, the DSC exotherm obtained as a result of a cure reaction is used to measure the two basic parameters required to solve these equations. There are two basic assumptions made in the analysis: (i) the reaction rate $d\alpha / dt$ as a function of time is given by the ratio of the heat output rate at time $t$, $dH_t / dt$, to the overall heat of reaction $\Delta H_{total}$; and (ii) the heating rate can be considered constant. Then, the reaction rate $d\alpha / dT$ can be calculated as a function of temperature for a given heating rate.

## 2. EXPERIMENTAL

DGEBA based epoxy/polyester resins cured with amines were used in our experiments. The resin system was prepared by mixing appropriate amounts of epoxide and amines immediately before the DSC experiments. The cure reaction proceeded upon heating directly in a DSC pan. DSC was performed using a Perkin-Elmer DSC-7 under nitrogen atmosphere to determine the progress of the cure of the resins. The enthalpy of cure ($\Delta H$) and peak reaction temperature ($T_p$) were determined from the first heating run, performed in the temperature range 20–300 ºC with a heating rate of 10 ºC·min$^{-1}$. The first heating run was followed by rapid cooling, and then a second heating run (10 ºC·min$^{-1}$) was made on the same sample to obtain the glass transition temperature ($T_g$) of the network. The apparatus was calibrated regularly using indium and zinc. Reproducibility of the obtained results was in the range of 3±5%. The enthalpy was calculated by:

$$\Delta H = \int (dQ/dt)_{p=const}\,\beta^{-1}dT ,$$

where $\beta$ = scanning rate; because $p$ = const., $dQ/dt = dH/dt$.

A schematic presentation of a heating run recorded by DSC and the methods used to determine $T_g$ and $\Delta H$ is shown in Figure 1. (first heating run (Figure 1.a); second curve (Figure 1.b) represents value of $T_g$ as a result of post-curing of a resin during the heating scan performed after the first one.

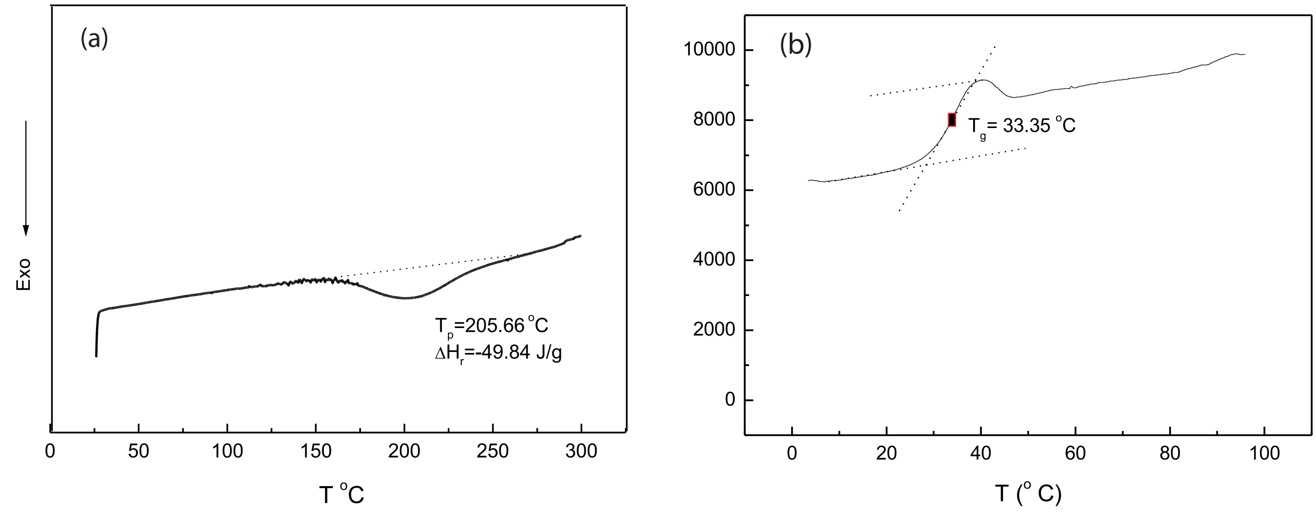


**Fig. 1.** Schematic presentation of a DSC run for determination of $\Delta H$ (a) and $T_g$ (b)

## 3. RESULTS AND DISCUSSION

### 3.1. *Epoxy resin thermosetting system* (*laboratory synthesized*)

DSC is a useful analytical technique for the characterization of thermosetting materials. By applying this technique, several valuable parameters can be identified, such as $T_g$, the onset temperature ($T_{onset}$) at which the cure reaction begins to progress, heat of reaction ($\Delta H_r$) as well as end temperature ($T_{end}$) of curing. These parameters give information that is useful for the optimization of processing conditions of thermosetting resins.

Figure 2 represents a typical DSC thermogram of a nonisothermal curing reaction of epoxy resin mixed with an appropriate amount of catalyst, previously synthesized to test its activity in the curing process. The glass transition observed at 82 ºC, detected before the curing process, was determined from the half width midpoint between the onset and the end temperatures of the transition.

The presence of $T_g$ could indicate that the epoxy resin was partly cured during the mixing

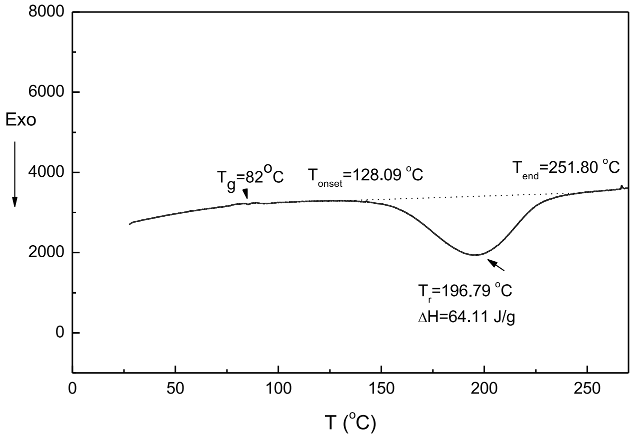


**Fig. 2.** Non-isothermal DSC scan for an epoxy resin mixture with a scanning rate of 10 ºC/min

process with the certain amount of catalyst. The changes in $T_g$ could also be used for quantification of the degree of cure of the resin material [9]. From the Figure 2 it could be seen that the curing process of the epoxy resin was followed by a considerable exothermic effect. The enthalpy of reaction was determined as $\Delta H_r$= -64.1 J/g by integration of the peak area. The heat of cure can be used to quantitatively determine the extent of cure of resin material. In fact, the degree of cure is defined as the ratio of the released heat up to the current time by the total heat of the reaction. It ranges from 0, for uncured resin, to 1, for completely cured resin. The typical conversion curve (α) versus temperature ($T$) is shown in Figure 3.

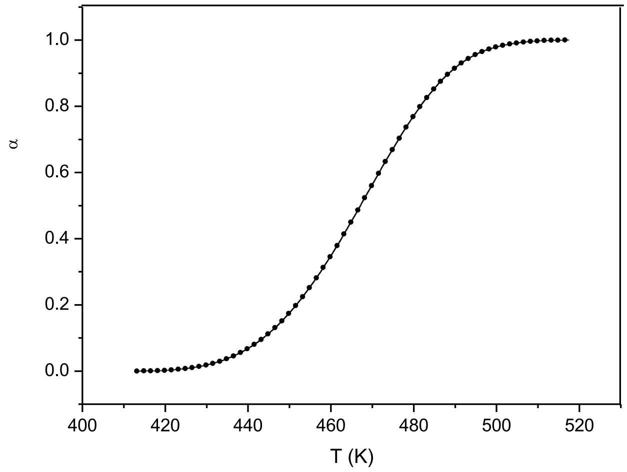


**Fig. 3.** Conversion curve as a function of temperature for the investigated epoxy resin

In non-isothermal conditions, when the temperature rises at a constant heating rate $\beta = dT / dt$, the conversion curve, $\alpha = f(T)$, could be transformed to $\alpha = f(t)$ (Figure 4), and further used for the kinetic analysis. For kinetic analysis of the resin, Borchardt and Daniels method as the simplest one was used.

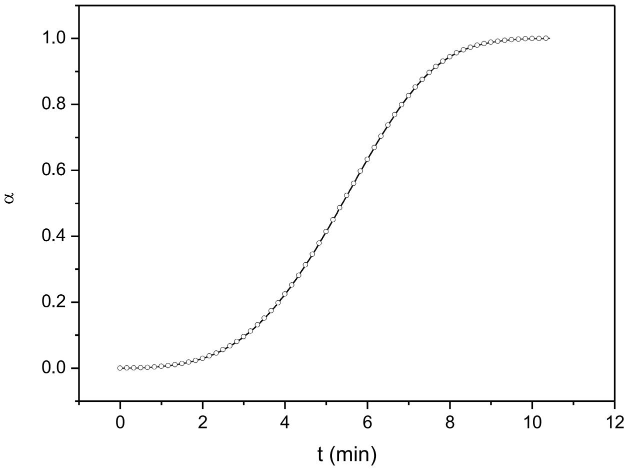


**Fig. 4.** Conversion curve as a function of time for the epoxy resin

In Figure 5, $\ln d\alpha / dt$ versus reciprocal values of $1/T$ are displayed. The best fit to linear allowed to determine the activation energy, $E_a$ = 112.52 kJ/mol, and the average reaction order, $n$ = 1.2. The pre-exponential factor, $\ln k_0$, was determined to be 24.2 $s^{-1}$.

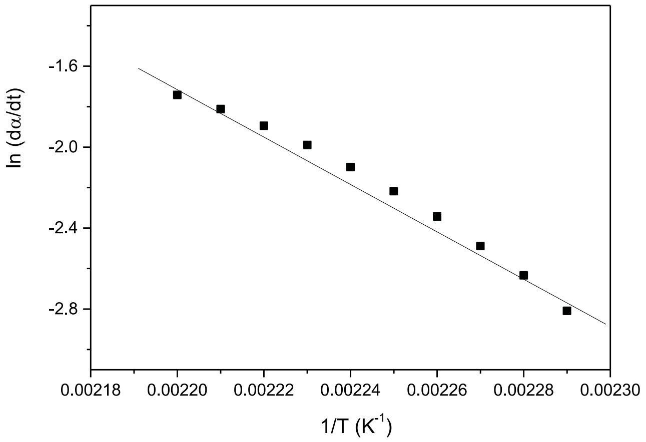


**Fig. 5.** Reaction rate versus inverse temperature kinetics plot for epoxy resin

### 3.2. *Commercial epoxy resin: comparison of Borchardt-Daniels' with ASTM-method*

The overall cure behavior of DGEBA-based epoxy resin cured with 3,3-dimetil-4,4-diaminodicyclometan was studied by isothermal DSC. The isothermal DSC curve, obtained by heating the resin mixture at 80 ºC (200 min) is shown in Figure 6. At 80 ºC, the maximum reaction rate was reached for 6.9 min, and the overall exothermic reaction effect was 370 J·g$^{-1}$.

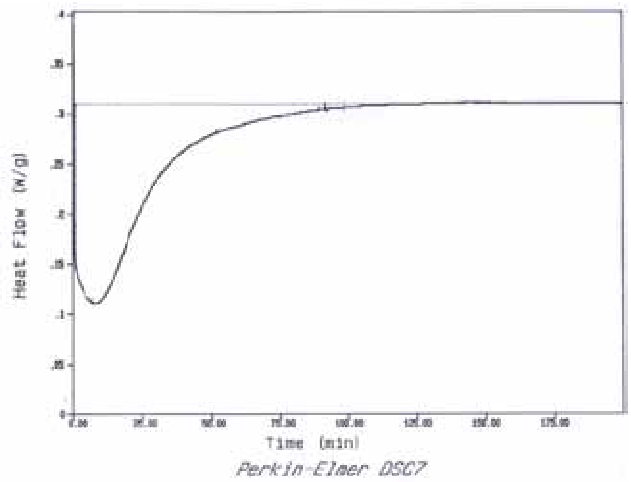


**Fig. 6.** Isothermal DSC scan for DGEBA-based epoxy resin mixture with amino-hardener (1:0.32 *w*/*w*) at $T = 80$ ºC

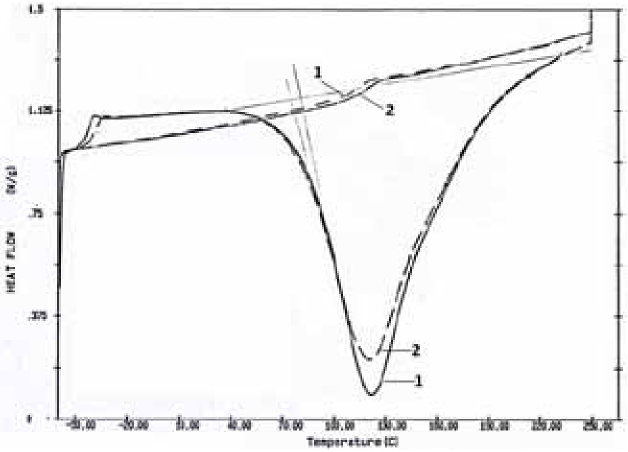


**Fig. 7.** Dynamic DSC scan for a DGEBA-based epoxy resin mixture with amino-hardener (1:0.32 *w*/*w*) with a heating rate of 10 ºC·min$^{-1}$

The peak reaction temperature, $T_p$, determined from non-isothermal heating experiments carried out from 10 to 260 ºC with a heating rate of 10 ºC·min$^{-1}$, was 121 ºC. The corresponding $T_g$ of the network formed during the heating run was 119 ºC ($\Delta C_p$ = 0.11 J·g$^{-1}$grad$^{-1}$; Figure 7). From the area under the exotherm, a total reaction enthalpy of 350 J·g$^{-1}$ was calculated. To determine the activation energy of the crosslinking reaction taking place during the cure, additional dynamic runs were performed at heating rates of 5 ºC·min$^{-1}$ and 15 ºC·min$^{-1}$.

For the purposes of comparison and in order to simplify the analysis, we assumed that there are no other enthalpic events than the chemical reaction of curing that contributes to the heat flow and that the reaction follows a first-order kinetics.

From the $\ln\dfrac{d\alpha/dt}{(1-\alpha)^n}$ *versus* $1/T$ plot, the apparent activation energy was calculated as 107 kJ·mol$^{-1}$, and $n$ = 0.8–1. The corresponding value for the activation energy was determined by application of the Borchardt-Daniels method (as described in methods section) was 115 kJ·mol$^{-1}$, which is very close, if not identical, to the value obtained by systematic kinetics measurements performed in accordance with ASTM method [4] for this system. The difference of 8 kJ·mol$^{-1}$ could be ascribed to the peculiarities of the methods used to determine the activation energy [10].

## 4. CONCLUSION

The optimization and modeling of the processing conditions for various thermosettings require a fast and simple method for the determination of curing parameters. Such a method, based on the Borchardt and Daniels kinetic approach, was described in this paper and was proven for certain laboratory synthesized and commercially applied resin/catalyst systems.

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