# Thermal Effects of Cure Reaction for an Unsaturated Polyester in Cylindrical Moulds

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*Im memory of Prof. Emeritus Vera Johanides*

The cure of unsaturated polyester was studied by using experiments and a model of the process. The kinetic parameters were calculated from the heat flow rate – time curves obtained by differential scanning calorimetry (DSC, Netzsch – Simultaneous Thermal Analyser DSC 200), working in DC (isothermal) and DSC (dynamic) mode. The temperature – time histories were studied in moulds of cylindrical shape.

The numerical model was constructed by taking into account the heat transferred by conduction through the resin, as well as the kinetics of heat, generated by cure reaction. The contributions to the rise in temperature from heat conduction and chemical reaction are different in different parts of the composite, and can explain the temperature, or conversion – time histories.

By considering the reaction-cure – time, temperature – time and heat flow rate – time histories developed within the sample, more extensive knowledge of the process can be obtained. The effect of the conduction heat transfer through the composite, as well as the internal heat generated by the cure reaction, is clearly shown, despite the complexity of the process.

Finally, the good agreement between experimental data and predicted mathematical model of the curing process in cylindrical mould, was shown.

*Keywords:*
DSC, curing, polyester resin, mould, kinetic model

## Introduction

Unsaturated polyester resins are commonly used as matrices for fiber-reinforced composites. Commercial systems are generally supplied as relatively low molecular mass, unsaturated linear polyesters, dissolved in a polymerizable monomer such as styrene, providing crosslinking units by reacting with the unsaturated resin in a radical addition reaction. In addition, thickening agents, low profile additives, inert and reinforcing fillers, are added to the compound in order to modify the performance of the product. Finally, initiators, inhibitors, and other additives are added to control the reaction kinetics.[1]

The process of cure of thermosets consists of two main stages: the heating period of the liquid resin (either pure or in the form of composites with fillers) and the cure reaction in the mould.[2]

The cure behaviour of unsaturated polyester resins is characterized by a complex mechanism involving copolymerisation of the polyester and styrene molecules induced by the decomposition of an initiator. In order to optimise and control exothermic cure process, resin thermokinetic and rheological models can be used in a computer simulation. The main structure of the master model is formed by the energy balance, which takes into account several factors: the accumulation of heat in the composite, the heat generated by the chemical reaction, the heat conduction in the material, and the heat dissipation at the composite skin. The energy balance equation is coupled with a suitable expression for kinetic behaviour of the chemical reactions accounting for diffusion control effects. The solution of the complete mathematical system gives, both, the temperature and the degree of reaction as functions of time and position, from experimental results obtained by the thermo-calorimetric and rheological characterization of the resin as input data.[3]

In calorimetry techniques, the enthalpy changes accompanying chemical events in the sample are monitored as a function of temperature or time. The result is a profile of the rate of enthalpy change either as a function of temperature when the sample is heated at a known linear rate, in differential scanning calorimetry (DSC), or as a function of time,

the calorimeter being held at constant temperature, in differential calorimetry (DC). High accuracy is needed for the determination of the kinetic parameters, as they strongly influence the process.[4]

Simulation of the process of cure is of great importance from a theoretical point of view, in order to gain a fuller insight into the nature of the process, and from a practical point of view to optimise the operational conditions.

## Experimental

### Materials

*Polyester Resin.* General-purpose polyester resin (A100) was selected and used in this research. It was supplied by Chromos d.d., Zagreb, Croatia. The base polyester resin was prepared using phthalic anhydride, maleic anhydride, and propylene glycol in different amount ratios ($r_1 = 2/1$, $r_2 = 5/4$). As a crosslinking agent, styrene monomer was added to the resin by the supplier ($w = 30$ %).

*Initiator.* A j = 50% solution of methyl ethyl ketone peroxide (MEKP) in dymethil phthalate supplied by Chromos d.d., Zagreb, Croatia, was used.

j = volume fraction $V_A/V_0$

y = volume ratio $V_A/V_B$

s = volume concentration $V_A/V$

### Kinetic measurements

The calorimetric measurements were conducted in a Netzsch thermal analyser DSC 200 differential scanning calorimeter, operating in the range of temperatures between –170 and 530 °C, equipped with a liquid nitrogen cooling system. The tests were performed both in isothermal and dynamic condition on samples of 1–5 mg of resin.

A resin sample was catalysed by mixing it with MEKP (cca. $w = 1.0$ %) for about 1 min, and the required amount of sample was weighted (about 3 mg) into a previously weighted sample pan for each isothermal run.

After the instrument was prepared for the isothermal operation at the desired temperature, the sample was introduced into the DSC cell, and the recording of the $\Delta H$ output immediately started. Records of the $\Delta H$ output in time were taken until the exothermal curve levelled off to a baseline, which was not far from the original baseline. The total area under the exothermal curve was the total heat generated isothermally at a temperature $T$[5].

Isothermal experiments were performed at the temperatures varying between 95 and 115 °C, Figure 1. At higher temperatures the cure time was of the order of minutes so that the heat absorbed as the
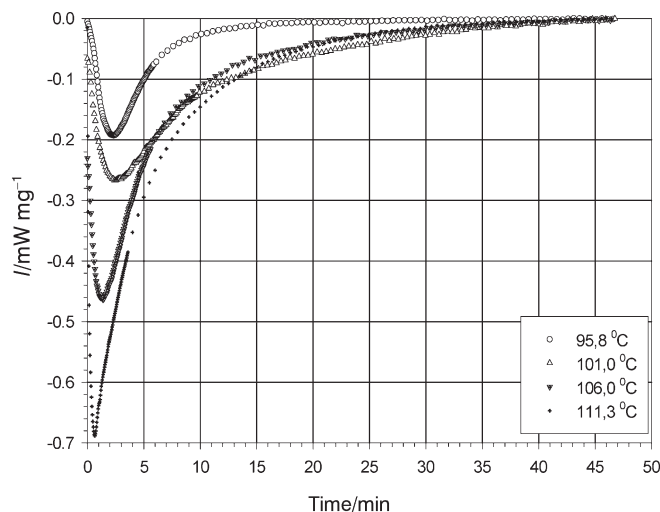


F i g . 1 – *Rate of heat evolved from the cure reaction as a function of time in DC mode*

sample equilibrated to the cure temperature partially cancelled out the exotherm. At the end of each isothermal run, samples were cooled rapidly and rescanned using 10 °C min$^{-1}$ heating rate. Scanning of samples above the temperatures of their isothermal cure was necessary for determination of their residual reactivity.[6] Thus, the total amount of heat generated by the curing reaction is the sum of the heat generated during the isothermal cure and the residual heat.

The dynamic DSC analysis was performed at three heating rates: 1, 3 and 5 °C min$^{-1}$. The sample was heated from the room temperature to 250 °C, Figure 2.
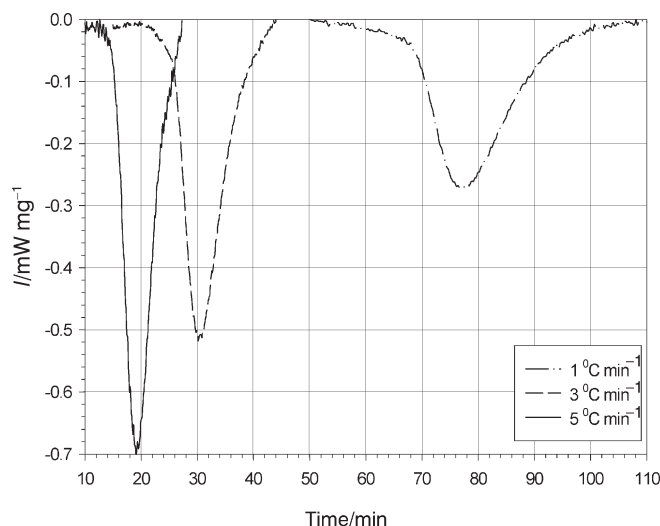


F i g . 2 – *Rate of heat evolved from the cure reaction as a function of time in DSC mode*

The heat of reaction was estimated by drawing a straight line connecting the base line before and after the peak, and integrating the area under the peak.

## Moulding and heating system

The moulds, cylindrical in shape, were made of glass and of copper, of the length much longer than the diameter, Table 1. Because of this fact only the radial heat was considered, especially in the middle of the mould where the thermocouple was placed.

T a b l e  1  – *Dimensions of moulds*

| Mould material | Height/mm | Diameter (inner/outer)/mm | Thickness/mm |
|---|---|---|---|
| Copper | 112.0 | 10.0/12.0 | 1.00 |
| Glass | 107.0 | 10.0/12.5 | 1.25 |

The mould with the sample was then immersed into the oil heated at a constant temperature. The temperature at the centre of the resin was constantly recorded during the process, Figure 3.
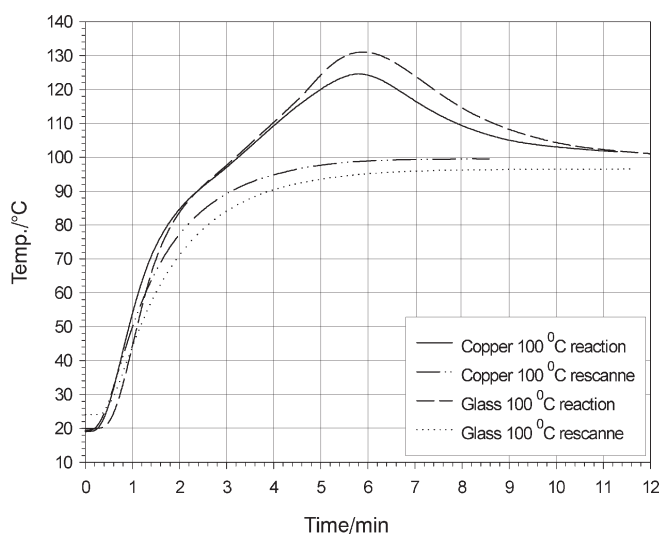


F i g .  3  – *Temperature – time histories in moulds at 100 °C*

After every measurement the mould was rapidly cooled and immersed again in the heated oil of the same temperature like before. As we expected no residual reactivity was observed, Figure 3.

The accessories for data acquisition were supplied by National instruments. NI4351 card has 16 differential analogue inputs. Each instruments has a 24-bit ADC and six possible reading rates – 10, 50, 60 readings s$^{-1}$ in single channel acquisition mode and 2.8, 8.8, and 9.7 total reading s$^{-1}$ in multiple channel acquisition mode (for channel speed, divide the total readings/s by the number of channel acquired), Figure 4.
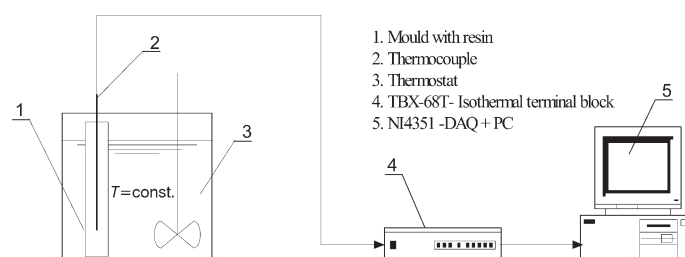


F i g .  4  – *Scheme of the measurement system*

## Results and discussion

### Heat of reaction

The heats of reaction were calculated from the areas under heat flow rate – time plots, both, for isothermal and dynamic scans. It was noticed that the reaction heat increases with higher temperatures, because of the diffusion control instead of chemically controlled mechanism of reaction.[8] So, after every isothermal scan, the residual heat was estimated, as was described in the experimental part.

The total heat of reaction is a sum of the heat of reaction at a given temperature and a residual heat, Table 2, Figure 5; that heat is comparable with the heat of reaction estimated from dynamic scans,[4,8] Table 3.

T a b l e  2  – *Heat generated by curing reaction at various isothermal cure temperatures*

| Temperature, °C | $\Delta H_t$, J g$^{-1}$ | $\Delta H_{res}$, J g$^{-1}$ | $\Delta H_{tot}$, J g$^{-1}$ | |
|---|---|---|---|---|
| 95.8 | –97.1 | –185.3 | –282.4 | |
| 101.0 | –173.1 | –113.8 | –286.9 | $\Delta H_r = \dfrac{\sum \Delta H_{tot}}{4} 285.7$ J g$^{-1}$ |
| 106.0 | –223.8 | –60.0 | –283.8 | |
| 111.3 | –277.2 | –12.5 | –289.7 | |

T a b l e  3 – *Heat generated by curing reaction at various heating rate*

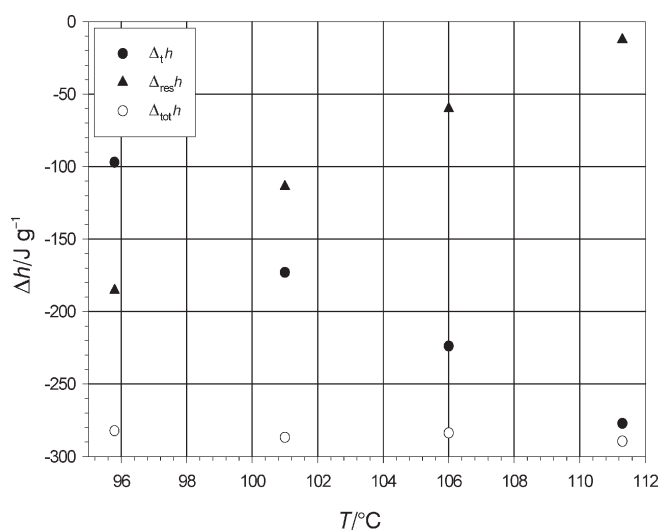| Heating rate/ °C min$^{-1}$ | $\Delta H_{din}$/ J g$^{-1}$ |
|---|---|
| 1 | 279.5 |
| 3 | 283.8 |
| 5 | 288.0 |

$$\Delta H_r = \frac{\sum \Delta H_{din}}{3} = 283.8 \text{ J g}^{-1}$$



F i g .  5 – *Heat generated by curing reaction at various isothermal cure temperatures*

So, as a mean value for a total heat of reaction, $\Delta H_r$ was chosen in experimental calculation of conversion and the reaction rate Equations (1) and (2).
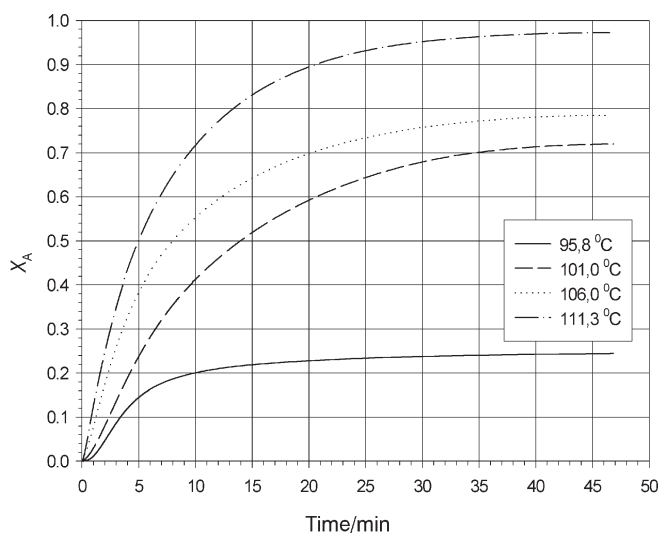


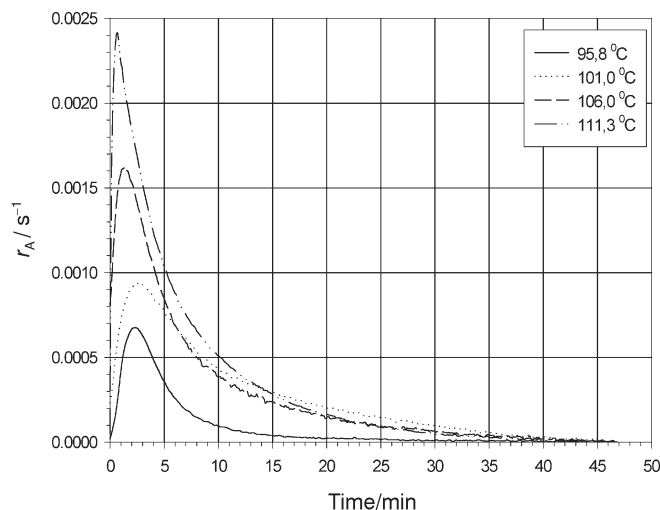F i g .  6 – *Conversion of monomer A measured in isothermal tests as function of time*



F i g .  7 – *Rate of reaction measured in isothermal tests as a function of time*

## Kinetics

A basic assumption in DSC kinetics is that the heat flow rate, relative to the instrumental baseline, is proportional to the reaction rate:[5]

$$r_A = \frac{dX_A}{dt} = \frac{1}{\Delta H_r} \frac{dH}{dt} \qquad (1)$$

Conversion was calculated as partial fraction under the d$h$/d$t$ – $t$ curve (Fig. 2.):

$$X_A = \frac{1}{\Delta H_r} \int_0^t \frac{dH}{dt} dt \qquad (2)$$

A mathematical expression for the curing reaction that could fit all the experimental data has been developed from previous studies of various proposed kinetic models.[10,11] In previous studies it was difficult to predict the kinetics beyond the gel point because of the lack of experimental data.[4,6,12] Those studies included only qualitative analysis of the results or suggested some models based on the n-th order kinetics. However, it has been recently reported that such models were not satisfactory because they could not predict the maximum temperature observed experimentally in the isothermal experiments.[13,14,15]

On this account, a kinetic equation of the following form was used to fit the isothermal experimental data, Figure 8:

$$r_A = \frac{dX_A}{dt} = k X_A^n (X_{max} - X_A)^m \qquad (3)$$

Dependence of the rate constant upon temperature is represented with an Arrhenius relation:

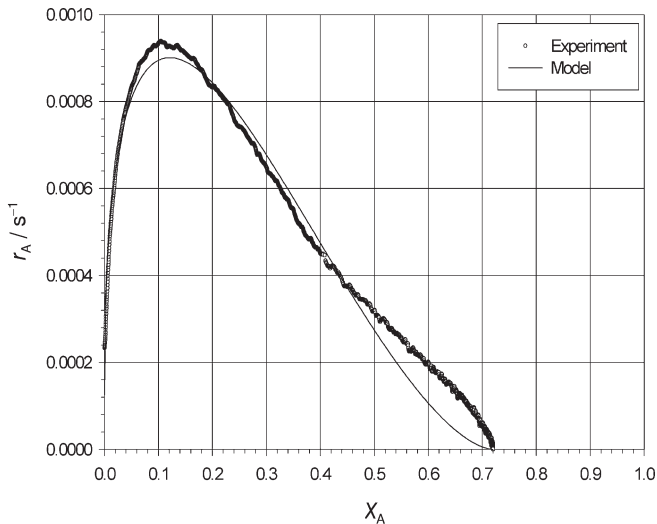$$k = A_r \exp\left(-\frac{E_a}{RT}\right) \qquad (4)$$

F i g . 8  – *Experimental and predicted values for reaction rate vs. conversion at 101 °C*

From the linear least-square fit of ln$k$ versus $1/T$ data the Arrhenius number $A_r$ and the activation energy $E_a$ were determined, Figure 9. The estimated kinetic quantities from isothermal experiments are presented in table 4.
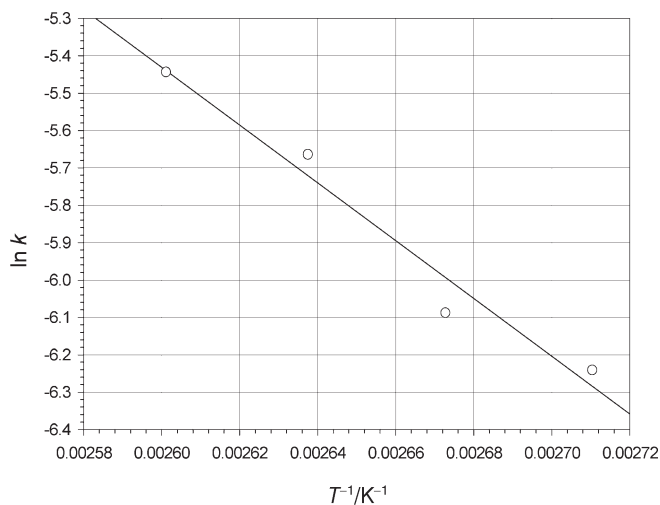


F i g . 9  – *Arrhenius relation for the kinetic model, Equation (4)*

Table 4  – *Kinetic quantities from isothermal experiments*

| Temperature, °C | $m$ | $n$ | $k \cdot 10^3$, s$^{-1}$ | |
|---|---|---|---|---|
| 95.8 | 0.34 | 1.66 | 2.95 | |
| 101.0 | 0.30 | 1.70 | 3.01 | $E_a = 42.5$ kJ mol$^{-1}$ |
| 106.0 | 0.29 | 1.71 | 4.07 | $A_r = 2991.4$ s$^{-1}$ |
| 111.3 | 0.32 | 1.68 | 5.12 | |

It is seen from Table 4 that over the range of isothermal curing temperatures investigated (i.e., 95 –115 °C), the values of $m$ and $n$ are relatively insensitive to temperature, and the values of $k$ increases with temperature, following Arrhenius relation.

Dynamic experiments for kinetics of the system were measured in higher temperature range (25 – 250 °C) and the kinetic model represents the average of kinetic behaviour. So, it was supposed that the reaction was going to its end, and the final conversion was 1.

$$r_A = \frac{dX_A}{dt} = A_r \exp\left(-\frac{E_a}{RT}\right) X_A^n (1 - X_A)^m \quad (5)$$

It is seen from Figure 2 that higher reaction rates were observed at higher heating rates. So, increase of activation energy and Arrhenius number, were observed, Table 5. The reason for much higher values of kinetic parameters can be explained by the less accuracy in measurements at 5 K min$^{-1}$ that ones at 1 and 3 K min$^{-1}$.

In further calculations we will use kinetic quantities estimated from dynamic measurement, Table 5, because of the more reliable experimental output.

T a b l e 5  – *Kinetic quantities from dynamic experiments*

| Heating rate/ °C min$^{-1}$ | $m$ | $n$ | $E_a$/ kJ mol$^{-1}$ | $A_r$/ s$^{-1}$ |
|---|---|---|---|---|
| 1 | 0.71 | 1.23 | 43.2 | 3675 |
| 3 | 0.67 | 1.25 | 43.4 | 4547 |
| 5 | 0.74 | 1.21 | 76.0 | 9763 |

## Mould modelling

In order to build up a model for the cure process in a mould, the following assumptions are made:[3,16]

1. Negligible temperature change during flow.
2. Homogeneous and well-mixed reaction system.
3. One-dimensional heat conduction.
4. Constant density $\rho$, specific heat capacity $c_p$ and heat conductivity $\lambda$.
5. Constant mould wall temperature through the entire cure.

The most general equation for heat transferred through a material is obtained by considering not only heat conduction through the solid but also internal heat generated by cure reaction.[2,7] The rate of change in temperature in a sample is thus given by

$$\rho c_p \frac{\partial T}{\partial t} = \lambda \nabla^2 T + r_A \rho \Delta H_r \qquad (6)$$

Generally $\lambda$ and $c_p$ are assumed to be constant and Equation (6) then changes into the Fourier classical heat-conduction equation

$$\frac{\partial T}{\partial t} = \alpha \nabla^2 T + r_A \frac{\Delta H_r}{c_p} \qquad (7)$$

where $\alpha = \dfrac{\lambda}{\rho c_p}$

Based on the above assumptions, the complex model of heat transfer and reaction in moulds of different shapes can be written as:

$$\rho c_p \frac{\partial T}{\partial t} = \lambda \frac{1}{r^s} \frac{\partial}{\partial r}\left(r^s \frac{\partial T}{\partial t}\right) - r_A \Delta H_r \rho \qquad (8)$$

$$r_A = \frac{\partial X_A}{\partial t} = k X_A^n (1 - X_A)^m \qquad (9)$$

With variable exponent $s$, Equation (8), we got solutions for different geometry of mould (for $s = 0$ plane sheet, for $s = 1$ cylinder and for $s = 2$ sphere).

Introducing dimensionless variables, the number of variables in the solution of heat-conduction problems[3,16] may be reduced:

– dimensionless temperature, $\theta$: $\theta = \dfrac{T}{T_0}$

– dimensionless time, $\tau$: $\tau = \dfrac{\alpha}{d^2} t$

– dimensionless length, $x$: $x = \dfrac{z}{d}$

– and: $\quad B = \dfrac{\Delta H_r}{c_p T_0}; \quad C = \dfrac{A_r d^2}{\alpha}; \quad D = \dfrac{E_a}{RT}$

So, for $s = 1$ heat equation for cylindrical mould Equation (8) in dimensionless form became

$$\frac{\partial \theta}{\partial \tau} = \frac{\partial^2 \theta}{\partial x^2} + \frac{1}{x} \frac{\partial \theta}{\partial x} + B \frac{\partial \alpha}{\partial \tau} \qquad (10)$$

After substituting the Arrhenius relation, Equation (4) in kinetic model, and using dimensionless variables Equation (9), became:

$$\frac{\partial X_A}{\partial \tau} = C \exp\left(-\frac{D}{\theta}\right) X_A^n (1 - X_A)^m \qquad (11)$$

For this kind of numerical problem boundary and initial conditions were defined as follows:

Boundary conditions:

$$\theta(\tau, 1) = \theta_m = \frac{T_m}{T_0}$$
$$\frac{\partial \theta}{\partial \tau} = 0, \text{ for } x = 0 \qquad (12)$$

Initial conditions:

$$\theta(0, x) = 1$$
$$X_A(0, x) = 10^{-8} \qquad (13)$$

Equations (10) and (11) were solved simultaneously, subject to the boundary and initial conditions, Equations (12) and (13), by numerical techniques. Since the two partial differential equations were coupled, an iterative procedure was followed. The basic numerical scheme involved the utilization of the method of lines for the solution of parabolic partial differential equation.[17]

Thermal parameters were taken from literature and they were supposed to be constant through the entire temperature range,[2] Table 6.

T a b l e  6  – *Thermal quantities*

| Material | $\rho$ / kg m$^{-3}$ | $c_p$ / J kg$^{-1}$ K$^{-1}$ | $\lambda$ / W m$^{-1}$ K$^{-1}$ |
|---|---|---|---|
| Resin | 1830 | 1100 | 0.169 |
| Copper | 8900 | 390 | 393 |
| Glass | 2210 | 1254 | 0.76 |

In numeric procedure the heat of reaction, $\Delta H_r$, was estimated, with the initial value according to the heats from isothermal measurements, Table 2. As we expected, the final values for $\Delta H_r$, Table 7,

T a b l e  7  – *Estimated heats of reaction at different mould temperatures*

| Mould material | $T$ / °C | $\Delta H_r$ / J g$^{-1}$ |
|---|---|---|
| Copper | 95.0 | 144.8 |
| | 100.0 | 185.0 |
| | 105.0 | 224.0 |
| | 110.0 | 232.6 |
| Glass | 95.0 | 125.3 |
| | 100.0 | 203.1 |
| | 105.0 | 227.2 |
| | 110.0 | 228.0 |

were higher than the ones from isothermal measurements because of more heat generated at higher temperature (for example, $T_m = 95$ °C, and $T_{max} = 107$ °C).

Good agreements for temperature vs. time plots in centre of the composite were observed between experimental and estimated data, Figure 10 and 11. Both for copper and glass moulds, higher exothermic peaks were reached at higher temperatures. That was reasonable, because of more heat generated in the centre of the composite that should be taken away from the system. Heat conductivity of glass is smaller than the conductivity of copper, and more time was needed to remove the reaction heat from the system. As the result, at the same mould temperatures higher temperatures were observed in the centre of the
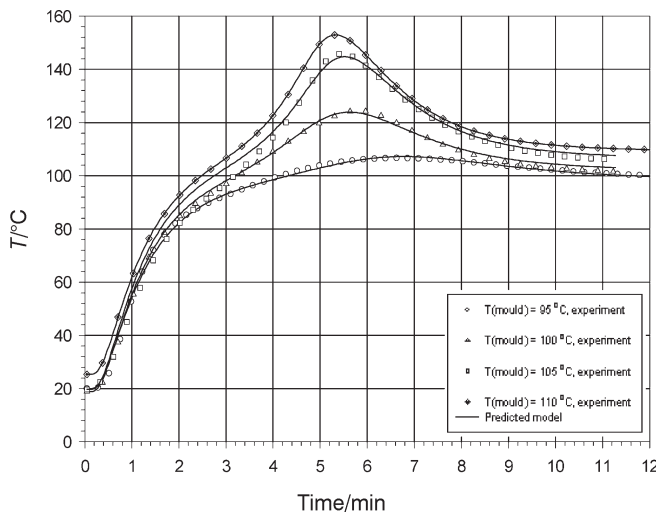


F i g . 1 2 – *Exothermic peaks reached in centre of the mould for different mould temperature*



F i g . 1 0 – *Comparison between model and experimental data for copper mould*
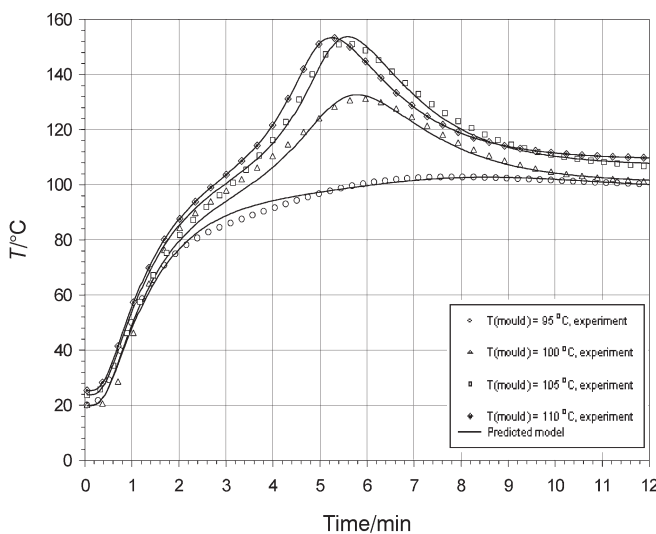


F i g . 1 1 – *Comparison between model and experimental data in glass mould*
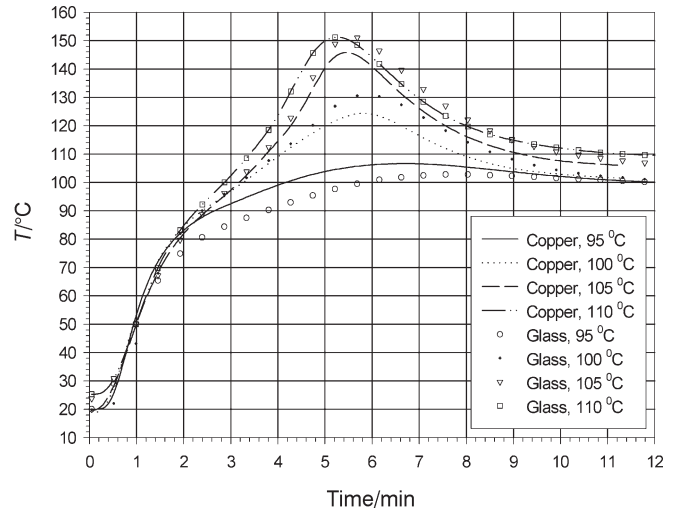
resin in the glass mould than in the copper mould[2], Figure 12.

This high enthalpy of cure associated with a rather low thermal conductivity can give rise to an excessively high temperature, which may cause discoloration and degradation of the material, and also to substantial temperature gradients. The material is thus heterogeneous during the process of cure, and these temperature-time histories in the resin may have same effects on the properties of the final material.

Thus a higher temperature in the mould is responsible for higher temperature gradients and a higher increases in temperature, which in turn increases the rate of cure reaction.[1,2,7]

The only observed distinction from this behaviour was at the mould temperature of 95 °C. At that temperature smaller value of heat is generated and system has enough time to remove the heat overflow away.

Building a model requires a precise view and knowledge of the process by the researcher or the engineer, as the various stages of the process must be set forth. But, once the model is established, the process can be simulated with the help of computer, and the comparisons made between the experimental and calculated results are able to test not only the validity of the model but also the accuracy of the various data which are used, such as thermal and kinetic parameters. Finally, the model is able to offer further insight into the nature of the curing process. Simulation provides the user with more information than experiments do: for instance, the profiles of temperature as well as the profiles of the state of cure developed within the sample at any time.[2,18]

## Conclusions

First of all, calorimetric measurements were necessary to describe kinetic behaviour of the curing system. Kinetic parameters were estimated, both, from dynamic and isothermal experiments, and good agreement was established between this two experimental technique (in terms of presented kinetic parameters and reaction heat).

Secondly, heat generated from the cure reaction was measured in moulds of cylindrical shape. The difference between glass and copper in heat conductivity was the main reason for more heat generated in the glass mould.

Finally, model of heat and mass transfer was established. Good agreement between the predicted model and the experimental data, was shown.

In further works we will represent the influence of an inert filler (carbon based) on curing reaction, as well as a more detailed mathematical treatment of the presented model of cure reaction.

## Symbols

$A_r$    – Arrhenius number, $s^{-1}$

$c_p$    – specific heat capacity, at constant pressure, $J\ kg^{-1}\ K^{-1}$

$E_a$    – activation energy, $kJ\ mol^{-1}$

$I$    – enthalpy flow rate, $mW\ mg^{-1}$

$\Delta H_r$ – heat of reaction, $kJ\ kg^{-1}$

$\Delta H_t$    – heat of reaction on given isothermal temperature, $kJ\ kg^{-1}$

$\Delta H_{res}$– residual heat of reaction, $kJ\ kg^{-1}$

$\Delta H_{tot}$– total heat of reaction, $kJ\ kg^{-1}$

$\Delta H_{din}$– heat of reaction in dynamic scans, $kJ\ kg^{-1}$

$k$    – rate coeficient, $s^{-1}$

$d$    – mould diameter, 0.01 m

$R$    – gas constant, 8.314 $J\ mol^{-1}\ K^{-1}$

$r$    – radius, m

$r_{1,2}$    – amount ratio

$r_A = dX_A/dt$ – rate of reaction, $s^{-1}$

$t$    – time, s

$T$    – temperature, K

$T_0$    – initial temperature, 298 K

$T_m$    – mould temperature, K

$T_{max}$    – maximum temperature of reaction, K

$X_A$    – conversion of monomer A

$w$    – mass fraction

$z$    – length, m

## Greek symbols

$\rho$    – density, $kg\ m^{-3}$

$\lambda$    – heat conductivity, $J\ m^{-1}s^{-1}K^{-1}$

$\alpha$    – thermal diffusivity, $m^2\ s^{-1}$

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