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Thermochimica Acta 388 (2002) 313–325

thermochimica acta

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Validation in process-like conditions of the kinetic and thermophysical modeling of a dicyanate ester/glass fibers composite

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Received 21 June 2001; received in revised form 11 July 2001; accepted 18 July 2001

Abstract

In a previous paper, the kinetic behavior of a cyanate ester trimerization was studied. In this paper, the thermophysical properties (heat capacity, thermal conductivity) are measured and modeled (as a function of temperature and conversion) for the neat resin and for a glass fibers composite. These models (thermophysical and kinetics) are used to simulate the thermal transfers in an instrumented heated mold. The calculated local temperatures and surface heat fluxes appear to be in very good agreement with measurements, for both the neat resin and the composite.

Keywords: Kinetics; Thermosets; Process simulation; Calorimetry; Thermophysical properties

1. Introduction

Over the last decades, considerable effort has been done by both academic and industrial research groups to model composite reactive manufacturing processes in order to develop simulation and optimization tools [1,2].

For resin transfer molding process, for example, this leads to an increasing number of commercial software. Unfortunately, the reliability of these simulations is still limited by the ability of their users to properly characterize and model each material property needed by the computer code.

One important problem is the determination of the reaction kinetic model parameters which affects with a huge sensitivity the predicted evolution of the conversion degree and temperature fields during the process [3,4]. This particularly stands for thermosets that present high exothermal reaction heat (epoxies, cyanate esters, bismaleimides,. . .) which coupled to their low thermal conductivity can generate high temperature gradients within thick pieces, leading to locally non-homogenous properties of the final network, or even to degradation caused by overheating.

Traditionally, thermoset chemistry specialists tend to characterize kinetics from isothermal experiments using chemical group specific detection techniques such as SEC [5], FT-IR [6] or ^{13}C NMR [7], their main objective being to establish a detailed reaction mechanism.

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0040-6031/02/$ – see front matter
PII: S0040-6031(02)00040-0

This first step generally allows to define a simplified kinetic model that can be introduced in process simulation software. Nevertheless, in order to estimate with a good accuracy the kinetic parameters (activation energies, etc.) of this model, it is often more interesting to perform a new kinetic study using calorimetry experiments.

Indeed, such measurements being based on the hypothesis of proportionality between the heat flow due to the reaction (that is the source term of the heat equation solved by software) and the overall rate of reaction, they provide an useful link between the knowledge of thermoset chemistry and its application to process simulation.

In a previous paper [8], we described how anisothermal DSC, when used with adapted data analysis and parameter estimation methods, could be used to identify with a very good accuracy the kinetic parameters of a thermoset following the widely used Kamal and Sourour kinetic model.

The present work focuses on a method useful for validating the reaction kinetics in process like conditions, that is to say for macroscopic samples (as an opposition to DSC, where samples of only a few milligrams are used) and in the presence of fibers.

Because the modeling of the process (especially heat transfer) is very sensitive to the accuracy of the kinetic model and parameters of the reactive system, the simulation, in process like conditions, of the reaction appears to be a convenient way to validate the kinetic characterization of the reaction.

Another aspect is that it is very difficult to characterize the kinetic behavior of composite systems. It is impossible to use DSC because of the very little mass of the samples needed, composites are usually opaque to infrared light, etc. Once more, it has been shown that the fibers may change the kinetic behavior of the matrix [4,9] (presence of water, effect of the coating, etc.). After the validation of the neat resin kinetic behavior, the simulation of the cure of a composite, using the kinetic model and parameters of the neat resin, will point out an eventual effect of the fibers (if the simulation is not similar to the experiment).

In this case, the macrocalorimetry and its simulation might be used as an inverse method to correct the kinetic model and parameter in order to take into account the effect of the fibers.

2. Macrocalorimetry

2.1. Principle

A 1-D macrocalorimeter was developed: it consists in a metallic cylindrical mold (equipped with thermocouples and heat flux sensors) which can receive 100 mm-diameter and 6 mm-thick samples (Fig. 1), with an aspect ratio:

$$r = \frac{\text{diameter}}{\text{thickness}} \geq 10$$

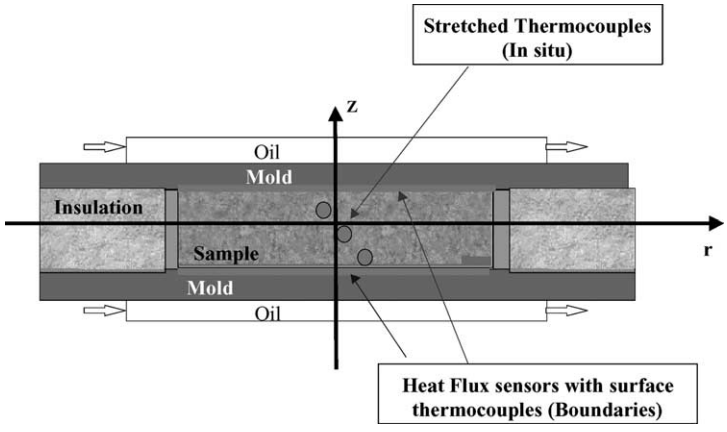

Fig. 1. Instrumented mold.

The mold temperature being regulated by oil circulation, the unreacted sample (introduced at room temperature) can be heated up to a defined temperature. The highly exothermic reaction (about 800 J g^{-1}) combined with the low thermal conductivity of the sample (about 0.25 W m^{-1} K^{-1} for most thermosets) gives birth to non-uniform temperature and conversion degree fields.

Unidirectional heat transfers are obtained by limiting heat exchanges through the lateral parts of the mold, thanks to thermal insulation. Moreover, the small thickness of the sample allows to avoid convection into the thermoset or composite sample during the cure. As a matter of fact, the Rayleigh number is <1700.

Two thin foil heat flux sensors equipped with type K thermocouples (RDF Corp.), glued inside the mold (on the upper and lower surfaces), allow to measure the surface temperatures and heat flux. In order to protect the sensors and to reduce demolding problems, they are covered with (20 μm-thick) Teflon coated adhesive tissue. This adhesive layer also provides a better thermal contact between the mold and the thermoset. The thermal conductivities of flux sensors, Teflon and resin being similar, the flux sensors do not disturb the heat transfer. Consequently, temperatures measured by these surface thermocouples will be considered as boundary conditions to predict the temperature field within the resin.

In situ temperature measurements are performed using three type K 80 μm thermocouples that are stretched in the mold. Their exact locations is measured after the piece has been demolded.

2.2. Modeling

Assuming pure conductive heat transfer conditions it becomes easy to model heat transfers within the sample during cure by using the transient heat diffusion equation with a source term:

$$\frac{C_p}{V}\frac{\partial T}{\partial t} = \frac{\partial}{\partial z}\left(\lambda\frac{\partial T}{\partial z}\right) - \frac{\Delta H}{V}\frac{\mathrm{d}\alpha}{\mathrm{d}t} \tag{1}$$

where α is the degree of conversion, T the temperature, C_p the specific heat, λ the thermal conductivity, V the specific volume and ΔH is the exothermic heat of the reaction.

This equation is coupled with a kinetic model of the following form:

$$\frac{\partial\alpha}{\partial t} = \sum K_i(T) f_i(\alpha) \tag{2}$$

where $f_i(\alpha)$ are called kinetic functions corresponding to single reactions or groups of reactions and $K_i(T)$ are Arrhenius constants:

$$K_i = A_i \exp\left(-\frac{E_i}{RT}\right) \tag{3}$$

where E_i is the activation energy and A_i is the frequency factor of the reaction or group of reactions considered.

After measuring the evolution of the sample surface temperatures (used as boundary conditions), one can calculate the unidirectional temperature field evolution and, therefore, temperature at each in situ thermocouple position.

Simultaneously, one can calculate the temperature gradients at the surfaces, and deduct the heat flux Φ (with $\lambda(T)$ the thermal conductivity at temperature T):

$$\Phi = \lambda(T_{\text{surface}})\left(\frac{\mathrm{d}T}{\mathrm{d}z}\right)_{\text{surface}} \tag{4}$$

Comparison of experimental and simulated temperatures and heat fluxes finally leads to the validation (or invalidation) in process like conditions of the kinetic previously established using DSC.

3. Application to a thermoset system

Practically, one now needs to characterize and model not only reaction kinetics, but also thermophysical properties changes such as heat capacity C_p, thermal conductivity λ and specific volume V. A cyanate ester system which reaction kinetics was previously [8] studied and modeled using TM-DSC will be used.

Cyanate ester monomers received considerable attention for aerospace structural composite applications [10] thanks to their desirable properties (high fracture toughness, high service temperature). Our motivations for choosing this system were double. First, the model of Kamal and Sourour can be applied to model its kinetic behavior: this model, which is widely used to simulate reaction kinetics of a large

variety of thermosets, is generally the one available in software packages that simulate heat transfers in materials during reactive molding processes. Second, an interesting property of cyanate esters is that their reaction is supposed to be sensitive to moisture [10]. Therefore, by introducing glass fibers (which tend to retain water at their surface) in our macrocalorimeter, we could expect to observe if it exists some significant deviation from the kinetic model determined from TM-DSC measurements.

In the following sections we will describe the characterization of the different thermophysical properties of cyanate ester system and of a model glass fiber composite, discuss their modeling and finally try to simulate macrocalorimetry experiments performed on these two systems.

4. Experimental and computations

4.1. Model system used

The dicyanate ester monomer used, 1,1-bis(4-cyanatophenol) ethane, is a liquid. It combines a low initial viscosity with an high reaction rate when catalyzed by metal ions, which make it suitable for liquid molding processes. It was supplied by Vantico under the trade name LECY and contains about 1% impurities (monophenol–monocyanate and *ortho–para* substituted isomers). An analysis by SEC shows that the initial cyanate group conversion is 5% (essentially leading to the triazine tricyanate molecule).

The composite is realized by introducing 1 layer per mm of glass mat (Vetrotex UNIFILLO) which results in a fiber volume fraction of 20%.

A catalytic agent consisting of copper acetyl acetonate (from Jansen Chemica) dissolved in nonyl phenol (from Aldrich) is used. Catalytic solutions are prepared by dissolving copper acetyl acetonate powder (4.118 g) into nonyl phenol (100 g) at 60 °C for 4 h. Two phr of this solution is added to LECY at ambient temperature, so that resulting catalyst concentration is 200 ppm of copper ions.

In such conditions, even if the reaction mechanism remains very complex, it appears that the major reaction pathway is a thermally activated step-growth polycyclotrimerization that gives birth to a highly crosslinked polycyanurate network (Fig. 2).

The overall kinetics is supposed to be described by a simple third-order differential kinetic model [11]:

$$\frac{\partial\alpha}{\partial t} = A_1 \exp\left(-\frac{E_1}{RT}\right)(1-\alpha)^2 + A_2 \exp\left(-\frac{E_2}{RT}\right)\alpha(1-\alpha)^2 \quad (5)$$

where

$$K_i = A_i \exp\left(-\frac{E_i}{RT}\right)$$

are Arrhenian rate constants, referring, respectively, to reaction catalyzed by metallic ions ($i = 1$) and autocatalyzed reaction ($i = 2$).

A precise kinetic study using TM-DSC experiments and *iso*-conversional analysis effectively showed that such a model can describe very well the overall cure kinetic behavior (conversion and reaction rate), except at the early stages of the reactions [11].

The following kinetic parameters were identified in our previous work [8] using an original estimation

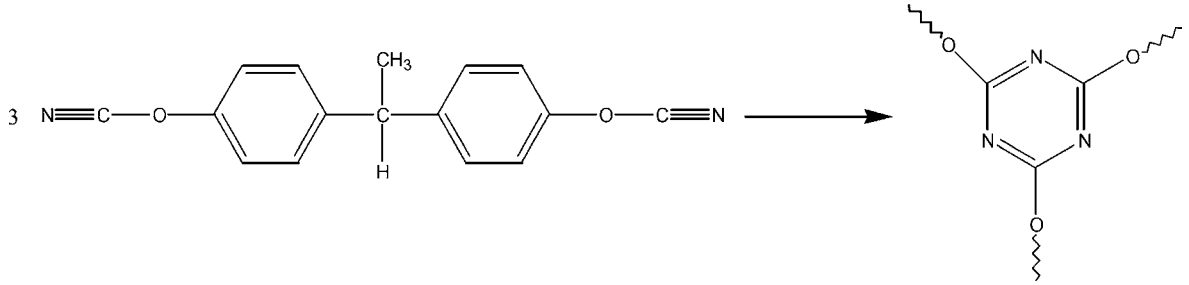

Fig. 2. Scheme of the cyanate ester reaction.

procedure based on the modeling of both apparent activation energy and reaction rate evolution during TM-DSC scans.

$A_1 = 5.05 \times 10^3\,s^{-1}, \quad A_2 = 9.96 \times 10^5\,s^{-1}$

$E_1 = 54\,kJ\,mol^{-1} \quad E_2 = 71\,kJ\,mol^{-1}$

5. Heat capacity

The evolution of the heat capacity of the cyanate ester monomer during reaction was studied using a temperature modulated DSC apparatus as already described in our previous paper.

Nevertheless, due to a lot of discussions about the validity of heat capacity measurements by such a technique [12], some complementary experiments are also performed:

- In order to verify TM-DSC apparatus heat capacity calibration, a 28 mg standard sapphire sample from Perkin-Elmer is tested in the same conditions.
- A second verification consists in measuring cyanate ester monomer and totally reacted cyanate ester network heat capacities by macrocalorimetry, using a Calvet C80 heat flux calorimeter. This technique, based on the measurement of the heat necessary to raise the temperature of the material of 1 K, allows us to use much bigger samples than DSC (typically 5 g) and can be considered as a reliable and accurate technique for heat capacity measurements.

A Perkin-Elmer DSC 7 apparatus, with temperature modulation option under nitrogen atmosphere, is used for all experiments. Perkin-Elmer interface and Pyris software enable online PC control of the measurements. The Pyris software is also used for the processing of TM-DSC curve de-convolution. Apparatus calibration is performed with indium and zinc standards for temperature and indium for heat. Sampling rate is 1 point per second.

Typical sample mass is about 10 mg. Experiments are performed with aluminum pans. For each temperature program, two measurements are made: one with the sample and one with an empty pan (this signal is then subtracted from the other one).

Uncatalyzed and catalyzed cyanate ester samples and sapphire standard are submitted to temperature scans from ambient temperature up to 340 °C. Two different mean heating rates are used (1 and 4 °C min^{-1}). The modulation is a saw tooth with an amplitude of 0.75 °C and a period of 60 s. Complementary runs are performed with totally reacted cyanate ester in the same conditions.

A parallel investigation concerned the heat capacity of the glass fiber mat and of the reacted (cyanate ester/glass mat) composite, which are measured from ambient temperature to 280 °C, using the Calvet macrocalorimeter, due to an evident need of large samples for these non-homogenous materials.

Cyanate ester network and composite samples are obtained from molded plates, submitted to an adapted cure cycle (1 h at 100,150, 200 °C, respectively, and 2 h at 280 °C).

5.1. Specific volume

This second thermophysical property is much more difficult to measure and to model during reaction. It can explain why, in most studies, it is considered as a constant for thermal transfers simulation. Nevertheless, as it is evident that a thermoset undergoes specific volume variations during reaction, we will try to evaluate the error due to this assumption.

Specific volume of liquid monomer is studied as a function of temperature (from 293 to 343 K, with 5 K increment) by weighting a known volume of liquid. The specific volume of the totally reacted cyanate ester network is measured at ambient temperature by Archimede's method.

5.2. Thermal conductivity

The method, which has been already fully described [13], is based on inverse heat conduction calculus and allows to determine thermal conductivity of non reactive plane samples.

The sample, equipped with a core thermocouple, is placed between the two plates of a specifically designed experimental press. Both plates, thermally controlled, are submitted to programmed heat cycles, while the temperatures of the plates and the core of the sample are recorded.

An inverse conduction algorithm developed by Jurkowski [14] is used to obtain the thermal conductivity from the core temperature evolution, the plates temperatures being used as boundary conditions.

The identification method consists in computing the unidirectional temperature field throughout the sample, and, therefore, at the core thermocouple position, and in comparing the computed temperatures with those measured experimentally. To complete the calculation, the material is assumed to be homogenous and its specific heat $[\rho C_p]$ is supposed to have been determined previously. No reaction is considered.

One can, thus, express the following deviation criterion, whose minimization leads to thermal conductivity evolution in the temperature range considered:

$$\mathrm{OLS}(\lambda) = \int_{t_0}^{t_f} [T_{\mathrm{simulation}}(t;\lambda) - T_{\mathrm{experimetal}}(t)]^2 \mathrm{d}t \tag{6}$$

Neat cyanate ester networks and cyanate ester/glass fibers composite samples are tested. For the later, thermal conductivity is determined in the direction perpendicular to the fiber layers.

Practically, due to the ''no reaction'' condition and to temperature limitations of the press, measurements are only performed on unreacted samples (without catalyst and at temperatures below 80 °C) and on totally reacted samples in the glassy state ($T < 200$ °C).

For unreacted samples, in which cyanate ester matrix is a low viscosity liquid, a device (as shown in Fig. 3) was specially designed, in order to control both sample thickness and core thermocouple position. This little mold plays the role of a measurement cell and is placed directly between the press plates.

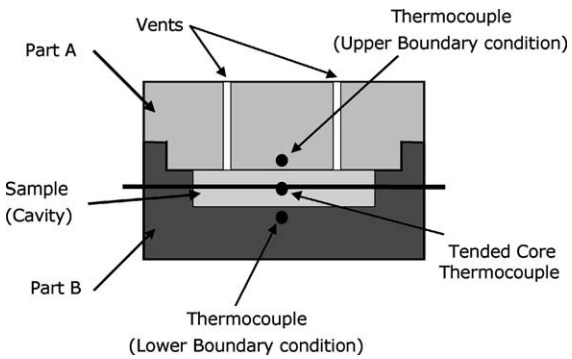

Fig. 3. Special device for conductivity measurements of unreacted samples.

Two 4 mm-thick samples are molded and totally reacted (conditions already described in the heat capacity measurements part). They are glued by a conductive silicone grease, after a 80 μm thermocouple has been introduced between them, and then placed directly into the experimental press.

5.3. Macrocalorimetry experiments

Two experiments (one with catalyzed cyanate ester containing 20% glass fibers in volume, and the other one without glass fibers) are performed, in our instrumented mold (Fig. 1).

After the in situ thermocouples were stretched, and eventually the fiber layers pre-placed, the mold is closed and the catalyzed cyanate ester system is injected through one of two top vents at room temperature. Circulating oil is then heated up to 130 °C in approximately 25 min and maintained at this temperature until the measured temperatures are constant. A typical experiment lasts about 90 min. The temperature and heat flux measurements frequency is 1 Hz.

5.4. Simulation of thermal transfers

The two coupled non-linear differential equations are solved using a numerical method. The finite difference method with an explicit scheme was chosen. The thickness of the piece is divided into control volumes. The temperature and conversion are calculated at the nodes placed at the center of these control volumes. The stability of the solution requires that the time step for the calculation is small. Thus, the calculation time is longer but the accuracy of the solution of the non-linear problem is guarantied.

The mesh size is varied so that a node coincides with each thermocouple location. The solution algorithm is quite straightforward. For each time step, the discrete kinetic equation is solved first to obtain the reaction velocity and the local degree of cure:

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_i^j = \frac{\alpha_i^{j+1} - \alpha_i^j}{\Delta t} = A_1 \exp\left(-\frac{E_1}{RT_i^j}\right)(1-\alpha_i^j)^2 + A_2 \exp\left(-\frac{E_2}{RT_i^j}\right)\alpha_i^j(1-\alpha_i^j)^2,$$
$$i = 1, \ldots, N \tag{7}$$

Afterwards, this reaction rate is used in the discrete heat diffusion equation to calculate the temperature at each node:

$$\frac{C_{pi}^j}{V_i^j}\frac{T_i^{j+1}-T_i^j}{\Delta t} = \frac{2}{\Delta z_{i-1,i}+\Delta z_{i,i+1}} \times \left(\lambda_{i+(1/2)}^j \frac{T_{i+1}^j - T_i^j}{\Delta z_{i,i+1}} - \lambda_{i-(1/2)}^j \frac{T_i^j - T_{i-1}^j}{\Delta z_{i-1,i}}\right) + \frac{\Delta H}{V_i^j}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_i^j, \quad i = 1,\ldots,N \tag{8}$$

where superscript j refers to time calculation steps and subscript i to node locations.

The thickness of the piece is usually divided into 20–30 intervals and the time step guaranteeing calculation stability is about 30 ms.

6. Results and discussions

6.1. Heat capacity

6.1.1. Cyanate ester heat capacity

As previously explained in the Section 4, a great attention was paid to the reliability of TM-DSC measurements. Fig. 4 shows that for cyanate ester monomer and totally reacted cyanate ester network, as for sapphire standard sample, this technique clearly gives an accurate measurement. As a matter of fact, the values obtained are in agreement with macrocalorimetry measurements and standard tables.

The evolution of the heat capacity during cure for both catalyzed and uncatalyzed cyanate ester obtained by TM-DSC can, thus, be used for modeling. Eq. (9), derived from thermodynamical considerations [13], is fitted to experiments by considering simple linear temperature dependence of the heat capacities of cyanate monomer C_{p0} and totally reacted cyanate ester network $C_{p\infty}$ in the rubbery state. Corresponding simulation of C_p evolution during cure can be seen in Fig. 5.

$$C_p(\alpha,T) = \alpha C_{p_\infty}(T) + (1-\alpha)C_{p_0}(T) \tag{9}$$

Estimated values of C_{p0} and $C_{p\infty}$ (Eqs. (10) and (11)), are used to estimate theoretical variation of total isothermal enthalpy of reaction [15] during a TM-DSC scan, using Kirchhoff's law. This leads to a variation of only 30 $\mathrm{Jg^{-1}}$ from ambient temperature to 350 °C which tends to justify the assumption we made (constant enthalpy of reaction) in the cure kinetic study.

Estimated values:

$$C_{p0} = 1.5784 + 0.0021T(^\circ\mathrm{C})\,\mathrm{Jg^{-1}K^{-1}} \tag{10}$$

$$C_{p\infty} = 1.8335 + 0.0012T(^\circ\mathrm{C})\,\mathrm{Jg^{-1}K^{-1}} \tag{11}$$

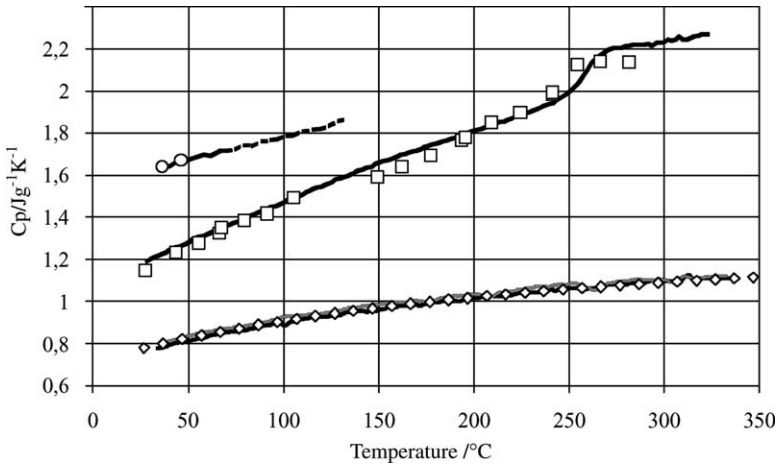

Fig. 4. Validity of TM-DSC heat capacity measurements: (○) cyantate ester monomer heat capacity measured by macrocalorimetry; (□) reacted cyanate ester heat capacity measured by macrocalorimetry; (◇) sapphire heat capacity standard values; (—) TM-DSC measurements at 1 °C $\mathrm{min^{-1}}$ mean heating rate (for sapphire and reacted cyanate ester); (–) TM-DSC measurements at 4 °C $\mathrm{min^{-1}}$ mean heating rate (for sapphire only).

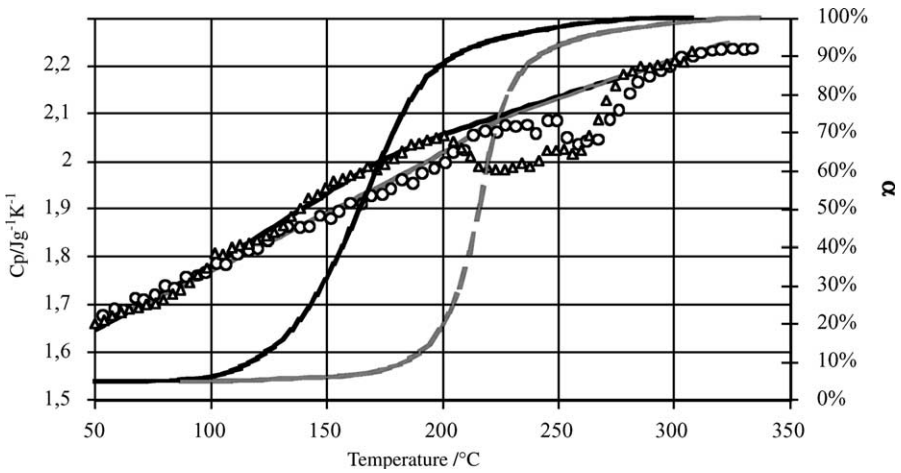

Fig. 5. Cyanate ester heat capacity modelization: (△) catalysed system (experimental); (○) uncatalysed system (experimental); (—) calculated heat capacities; (- - –) degree of conversion (experimental).

6.1.2. Glass mat and composite heat capacities

The measurements are shown in Fig. 6. Composite heat capacity is successfully described by the following mixing law (V_f being the fiber volume ratio), which will be used for heat transfers modeling:

$$C_p\text{composite} = \frac{V_f \rho_{\text{fibers}} C_{p\text{fibers}} + (1 - V_f)\rho_{\text{matrice}} C_{p\text{matrice}}}{V_f \rho_{\text{fibers}} + (1 - V_f)\rho_{\text{matrice}}} \tag{12}$$

Glass mat heat capacity is found to vary linearly with temperature up to 220 °C were the fusion of thermoplastic polyester sizing leads to a slight step.

Estimated value:

$$C_{p\text{fibers}} = 0.901 + 0.00118T(^\circ\text{C})\,\text{Jg}^{-1}\text{K}^{-1} \tag{13}$$

6.2. Specific volume

As expected, the specific volume of monomer (at $T > T_g = -50$ °C) clearly increases linearly with temperature. The one of totally reacted cyanate ester network was found to be equal to 8.14×10^{-4} m^3kg^{-1} at 20 °C. Despite its variation with temperature was not studied, its volumetric expansion coefficient can be estimated around $1.6 \times 10^{-4}\,\text{K}^{-1}$ according to

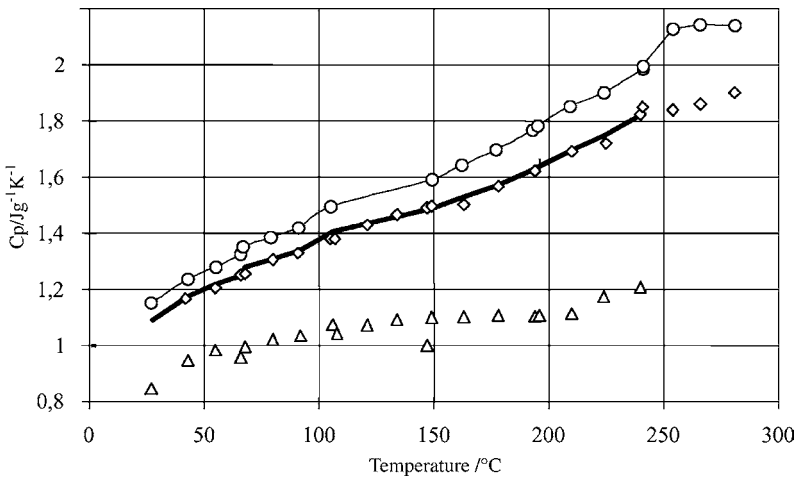

Fig. 6. Heat capacity of totally reacted (○) cyanate ester; (△) glass mat; model composite ((◇) experiments and (—) simulation, using Eq. (12)).

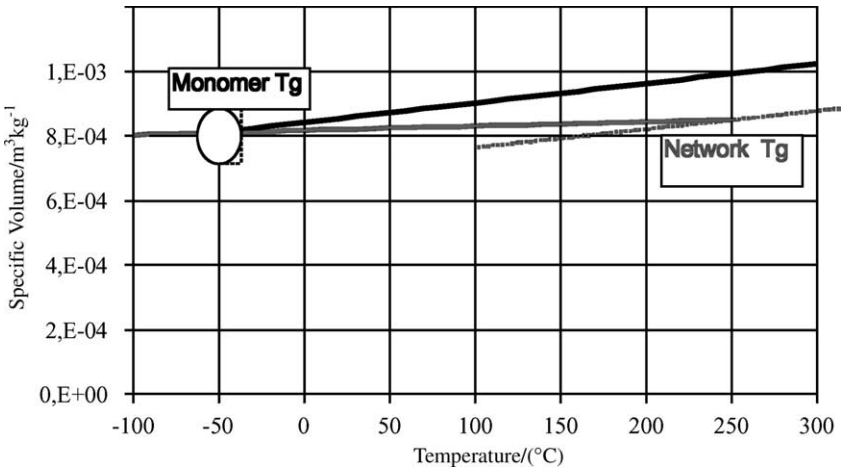

Fig. 7. Specific volume of the monomer and the reacted cyanate ester as a function of temperature.

previous works in our laboratory [16]. That leads to the following expressions are illustrated in Fig. 7 (extrapolation):

$$V_0 = 8.413E\text{-}04 + 6.08007E\text{-}07 \quad T(^\circ\text{C}) \tag{14}$$

$$V_\infty = 8.170E\text{-}04 + 1.31E\text{-}07 \quad T(^\circ\text{C}) \tag{15}$$

The lower slope for the network is due to the fact that it is in the glassy state. Above its T_g which is around 250 °C, the slope should be higher.

In order to evaluate the variation of specific volume with reaction during one of our macrocalorimetry experiments, let us have a look at the only empirical model that has been proposed in the literature to describe the variation of volumetric mass with conversion [17]:

$$\rho = \rho_1(T) + B\alpha \quad \text{for } \alpha < \alpha_{gel} \tag{16}$$

$$\rho = \rho_2(T) \quad \text{for } \alpha > \alpha_{gel} \tag{17}$$

where α_{gel} is the conversion degree at gelation, and B is a constant.

Practically, this model shows that the specific volume will increase with temperature until reaction starts, after that it will decrease, its lowest values being that of the network. Consequently, if we suppose that reaction starts at 100 °C, the amplitude of the variation of specific volume during one experiment can be estimated as <5% (which is the approximate difference, at 100 °C, between monomer and network, as shown in Fig. 7). Therefore, due to the impossibility for us to estimate parameter B, it seems acceptable to consider specific volume as constant for further computations.

6.3. Thermal conductivity

Heat conductivities obtained respectively for neat cyanate ester and cyanate ester/glass fibers composite are shown in Figs. 8 and 9.

Experimental dispersion of measurements being important (about 10%), we will describe the temperature dependence of the conductivity using the following interpolations obtained by simple linear regressions.

6.3.1. Neat cyanate ester

$$\text{Monomer} \quad \lambda_0 = 0.155\,\text{Wm}^{-1}\text{K}^{-1} \tag{18}$$

$$\text{Network} \quad \lambda_\infty = (0.0003T + 0.2236)\,\text{Wm}^{-1}\text{K}^{-1} \tag{19}$$

6.3.2. Cyanate ester/glass fiber composite

$$\text{Unreacted} \quad \lambda_{\perp 0} = 0.183\,\text{Wm}^{-1}\text{K}^{-1} \tag{20}$$

$$\text{Reacted} \quad \lambda_{\perp\infty} = (0.0004T + 0.2705)\,\text{Wm}^{-1}\text{K}^{-1} \tag{21}$$

Despite we can consider that these expressions will predict initial and final thermal conductivity with an

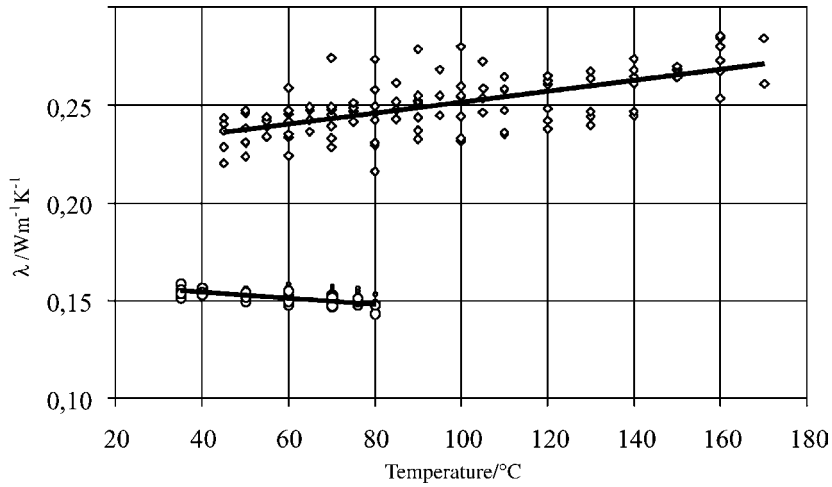

Fig. 8. Heat conductivity of neat cyanate ester: (○) unreacted samples; (◇) totally reacted samples.

acceptable accuracy for this thermophysical property, the problem still stands for the interpolation of materials behavior during cure.

This problem being particularly complex, we will use the following empirical approximations for further heat transfer simulations, by analogy with heat capacity:

$$\lambda_{\text{matrix}}(\alpha, T) = \alpha\lambda_{\infty}(T) + (1-\alpha)\lambda_0(T) \quad (22)$$

$$\lambda_{\perp\text{composite}}(\alpha, T) = \alpha\lambda_{\perp\infty}(T) + (1-\alpha)\lambda_{\perp 0}(T) \quad (23)$$

7. Macrocalorimetry

Figs. 10 and 11 shows the evolution of experimental temperatures and surface heat fluxes measured and simulated for the neat cyanate ester sample (the surface temperatures are used as boundary conditions for simulation). For easier reading, only one core temperature, corresponding to the higher gradient is represented. One can see that the exothermic reaction coupled with the low thermal conductivity of the resin

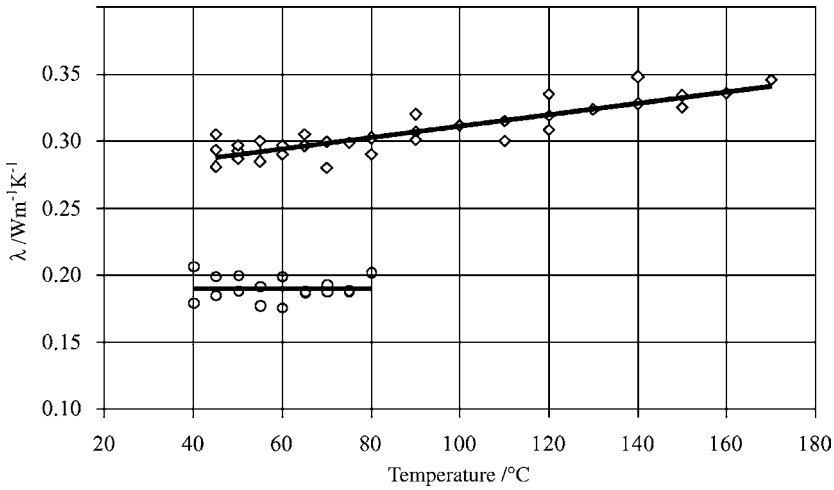

Fig. 9. Heat conductivity cyanate ester/glass fiber composite: (○) unreacted samples; (◇) totally reacted samples.

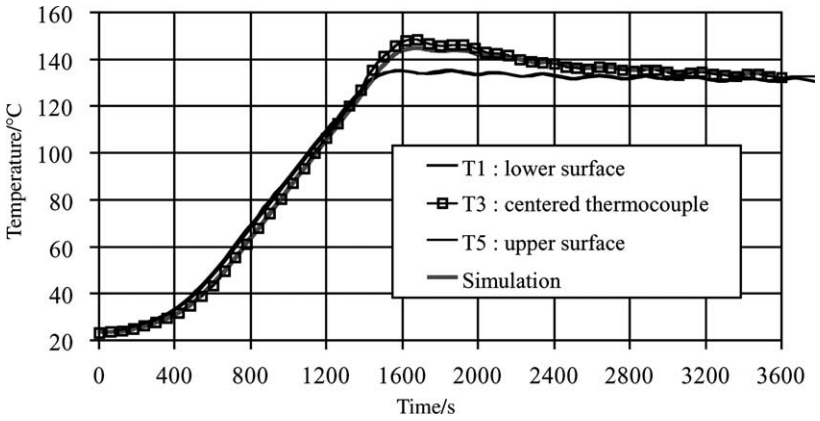

Fig. 10. Measured and simulated temperatures during the neat cyanate ester reaction.

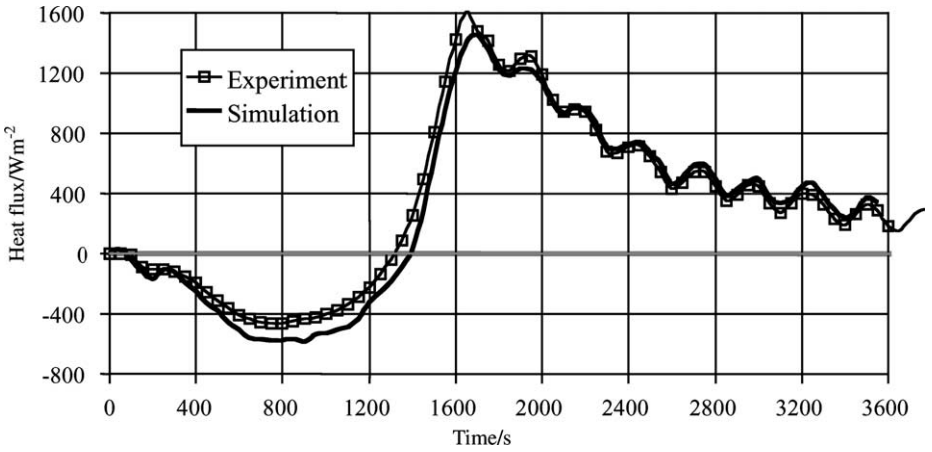

Fig. 11. Measured and simulated surface heat fluxes during the neat cyanate ester reaction.

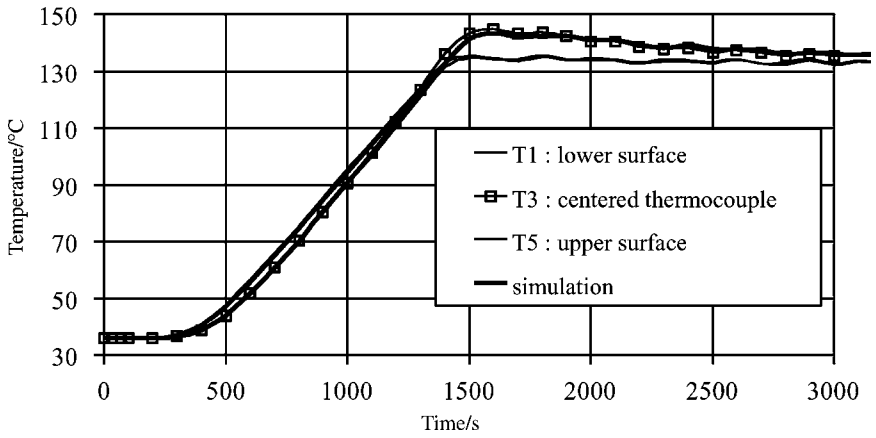

Fig. 12. Measured and simulated temperatures during the composite reaction (20% glass fibers).

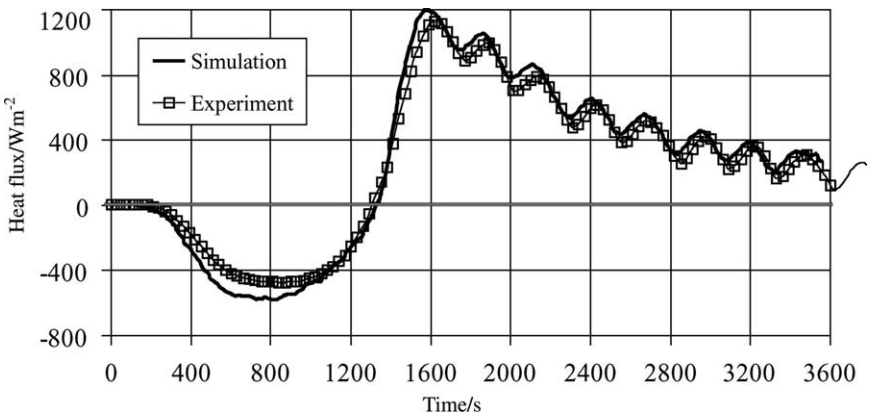

Fig. 13. Measured and simulated surface heat fluxes the composite reaction (20% glass fibers).

conducts to a 15 °C difference between the surface and the center temperature, for a 6 mm-thick sample. As expected, the mold behaves as a heater (negative heat flux until 1400 s) until the sample temperature reaches the desired temperature (about 130 °C). Then, the mold behave as a cooler (positive heat flux) until the reaction is practically finished (the heat flux tend to zero when the internal heat source is nearly zero). The oscillations that can be observed (Figs. 10–13) for long times are due to the bad thermal regulation of the oil heater. But this ''defect'' clearly points out that our model is able to fit such oscillations.

The agreement between experiment and simulation is very good for both temperature and heat flux. At maximum temperature, one can see that the difference between experiment and simulation does not exceed 2 °C.

Similar observations can be made for the composite sample (Figs. 12 and 13), with the same kinetic model and kinetic parameter. The very good agreement between simulation and experiment clearly shows that, in this case, the fiber glass does not change the kinetic behavior of the resin.

8. Conclusion and perspectives

A methodology for validating thermoset cure kinetic and thermophysical studies in reactive molding process like conditions has been described: this validation is based on the resolution of the heat equation in a 1 D heated mold, using kinetic and thermophysical models to model the resin behavior during cure.

In the future, we will try to use this method as an inverse method to determine (or to modify) the kinetic parameters and/or the thermophysical behavior ($C_p(x, T)$, $\lambda(x, T)$, ...) of others thermosets. This would be particularly convenient in the case of composites if the kinetic behavior is modified by the presence of fibers because very few methods are available to study the kinetic behavior of composites.

Acknowledgements

Authors would like to thank Dr. Jean Marie Létoffé (Laboratoire de Thermodynamique Appliquée (LTA) de l'INSA de Lyon, France) for his helpful collaboration for all Calvet 80 macrocalorimetry measurements. Drs. J.-L. Bailleul, T. Jurkowski and D. Delaunay (Laboratoire de Thermocinétique, Ecole Polytechnique de Nantes, France), for the measurements of the thermal conductivities.

References

[1] A.A. Skordos, I.K. Partridge, in: Proceedings of the Polymer Composites'99, Canada, 1999, p. 225.
[2] D.R. Calhoun, S. Yalvac, D.G. Wetters, C.H. Wu, T.J. Wang, J.S. Tsai, L.J. Lee, Polym. Comp. 17 (1996) 251.
[3] E. Bournez, M. Raynaud, J. Dupuy, P. Nicolle, Therm. Conduct. 24 (1998) 695.

[4] A. Yousefi, P.G. Lafleur, R. Gauvin, Polym. Eng. Sci. 37 (1997) 757.
[5] E. Girard-Reydet, C.C. Riccardi, H. Sautereau, J.P. Pascault, Macromolecules 28 (1995) 7599.
[6] T. Scherzer, U. Decker, Polymer 41 (2000) 7681.
[7] M.I. Tavares, J.R. D'Almeida, S.N. Monteiro, J. Appl. Polym. Sci. 78 (2000) 2358.
[8] E. Leroy, J. Dupuy, A. Maazouz, Macromol. Chem. Phys. 202 (2001) 465.
[9] S.H. Mc Gee, Polym. Eng. Sci. 22 (1982) 484.
[10] A.W. Snow, in: I. Hamerton (Ed.), Chemistry and Technology of Cyanate Ester Resins, London, 1994, Chapter 2, p. 7.
[11] S.L. Simon, J.K. Gilham, J. Appl. Polym. Sci. 47 (1993) 461.
[12] R. Androsch, I. Moon, S. Kreitmeier, B. Wunderlich, Thermochim. Acta 357/358 (2000) 267.
[13] J.L. Bailleul, D. Delaunay, Y. Jarny, J. Reinf. Plast. Comp. 15 (1996) 479.
[14] T. Jurkowski, Ph.D. thesis, Mise en œuvre d'une méthode et réalisation d'un appareillage de mesure de la conductivité thermique d'un polymère, Université de Nantes, France, 1993, p. 150.
[15] J. Dupuy, E. Leroy, A. Maazouz, J. Appl. Polym. Sci. 78 (2000) 2262.
[16] O. Georgeon, Ph.D. thesis, Relation entre la structure et les propriétés de réseaux polymers synthétisés à partir d'un monomère cyanate, INSA de Lyon, France, 1994, p. 255.
[17] J. Mijovic, H.T. Wang, SAMPE J. March–April (1988) 42.