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Monitoring and Heat Transfer Modelling of the Cure of Thermoset Composites Processed by Resin Transfer Moulding

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Abstract

Experimental studies have demonstrated the existence of significant thermal gradients during the cure stage of Resin Transfer Moulding (RTM). Presence of such thermal gradients can affect the final degree-of-cure distribution and cause the development of residual stresses, leading to a deterioration of the final composite component properties. Therefore the incorporation of heat transfer modelling in the general context of RTM modelling and monitoring of the process is necessary.

The present work focuses on the application of combined monitoring and heat transfer modelling to the process. A finite element heat transfer model incorporating resin cure kinetics has been developed and tested. An inverse solution of the heat diffusion model has been implemented in order to extend the local measurements given by in-situ monitoring to global information about the temperature distribution and the degree-of-cure distribution during the cure.

1.Introduction

Modelling and monitoring of thermoset composites processing have been the subject of extensive study in recent years. Models representing various aspects of processing have been developed and applied to the majority of processing techniques. Heat transfer models have been implemented in order to simulate the curing phenomena in autoclave processing [1-3], resin transfer moulding [4-6], pultrusion [7-9] and filament winding [10-12]. Provided that these models are combined with appropriate cure kinetics subroutines [13,14], they offer the ability to calculate the temperature and the degree-of-cure spatial distributions and their evolution with time during the curing. Alongside with simulation, process monitoring techniques comprising mainly thermal, dielectric, spectroscopic and ultrasonic monitoring have been developed and applied to the cure of thermosets [15-18].

Both approaches are valuable for optimising the curing process. The predictive ability of the simulation can be used as a part of the process design, while monitoring constitutes a potential tool for on line control. However, both approaches present some inherent drawbacks. Correct modelling application requires an extensive knowledge of material properties and process characteristics. This may be impossible in some cases due to limited reproducibility of some of the process conditions, or it can affect negatively the cost effectiveness of the overall manufacturing process. Similarly, monitoring involves insertion of a sensor in some critical area of the component, which composite manufacturers and end users are reluctant to adopt.

A method to overcome these limitations arises from a combination of modelling and monitoring. In the present paper a scheme which combines heat transfer modelling and thermal and dielectric cure monitoring is presented. An inversion of the heat transfer model based on a genetic algorithm is applied to data gathered by monitoring, in order to calculate some of the properties or process characteristics. This way an estimation of those modelling parameters that are most difficult to predefine can be performed, in accordance with the results of monitoring. Subsequently the direct model can be solved in order to obtain the global picture of the cure.

2.Inversion Scheme

The simultaneous modelling-monitoring application is illustrated in Fig. 1. Measurements are fed into the genetic algorithm, which uses the direct model in order to estimate some of the heat transfer parameters. In this particular case the thermal conductivity and the natural air convection coefficient were the unknown parameters. The operation of the genetic algorithm can be outlined as follows:

1. Generation of a random set of parameters values;
2. Application of these values to the direct heat transfer model and calculation of the model result difference from the monitoring results;
3. Sorting of the set members according to their performance (fitness) in the previous stage
4. Encoding of each member of the set as a binary number;
5. Reproduction of a new set with the application of crossover and mutation to the previous set and taking into account their fitness
6. Decoding of the binary members of the new set;
7. Return to step 2.

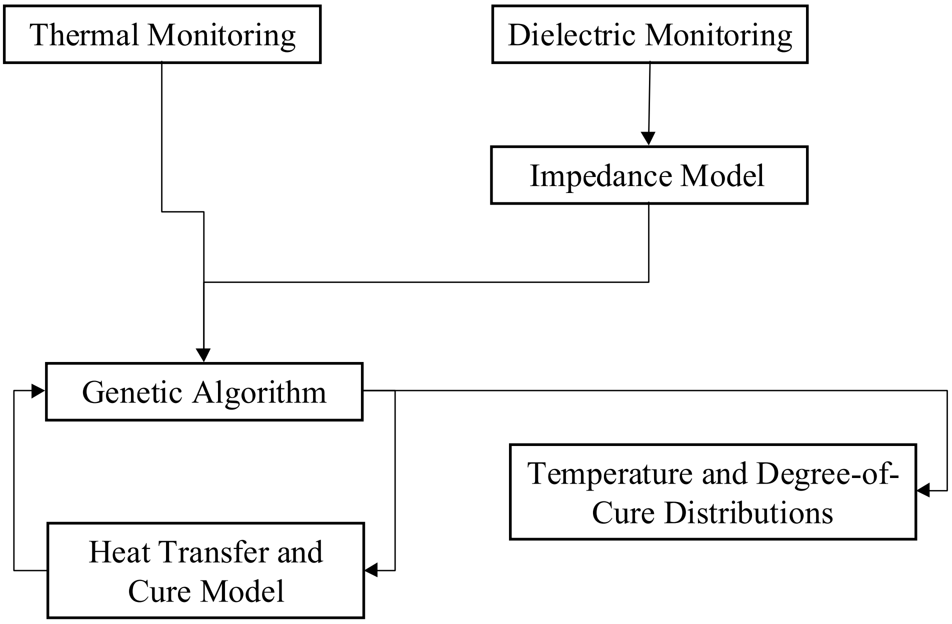

Fig.1: *Inversion scheme*

Although the inversion technique has no rigorous mathematical justification it has the ability to solve globally difficult parameters estimation problems. Its randomness ensures that the solution procedure is not 'trapped' in local optima, but it is time consuming in comparison with conventional parameter estimation techniques.

3.Heat Transfer Model

3.1. Heat transfer mechanisms

Mechanisms of heat transfer, potentially involved in the curing of thermoset based composites are:
- Heat conduction
- Forced convection
- Natural convection

The models presented in the literature [1-12] take into account the heat conduction and forced convention when this is relevant e.g. the filling stage of the RTM process, but they do not consider the natural convection. This mechanism occurs when the density variation due to thermal gradients creates a considerable buoyancy flow, which then contributes considerably to the transfer of heat.

Rayleigh number can be used in order to estimate whether such a mechanism is significant in the curing of composites. For a uniform fluid it is defined by the relation [19]:

$$Ra = \frac{\beta\rho^2 c_p g \Delta T L^3}{\eta K} \tag{1}$$

where β is the volumetric thermal expansion, ρ the density, g the gravitational acceleration, c_p the specific heat capacity, η the viscosity, K the thermal conductivity, L the length scale of the problem and ΔT the thermal gradient.

A similar number, the Rayleigh-Darcy number, can be defined for a porous medium saturated by fluid (20):

$$Ra = \frac{\beta\rho^2 c_p S g \Delta T L^3}{\eta K} \tag{2}$$

where denotes S the permeability of the porous medium.

This number presents high values when convection is dominant and low values when conduction is dominant. It has been demonstrated [20] that a value of 40 is the threshold for domination of the convective mechanism. The Rayleigh and Rayleigh-Darcy numbers have been calculated for a typical curing profile of RTM6 resin. Typical values observed during resin transfer moulding have been used for the permeability, conductivity, thermal gradient and characteristic length. The thermal properties have been calculated as described in the appropriate models presented subsequently and the viscosity according to the model developed by Karkanas [21].

It can be seen in Fig.2 that in the case of the curing of reinforced thermoset the Rayleigh-Darcy number remains low. In contrast, in the case of unreinforced resin the convective contribution can be significant, when the viscosity of the resin is minimised, i.e. at the later stages of heating up and at the beginning of the curing.

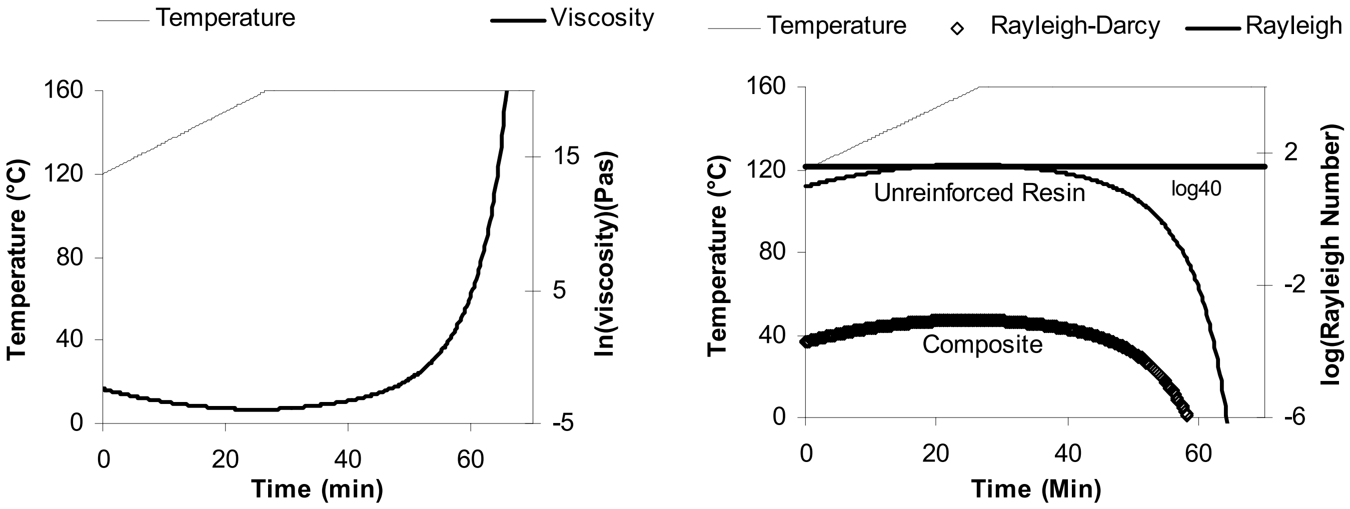

***Fig. :**. Rayleigh number for a typical cure profile*

3.2. General heat transfer model

According to the analysis presented previously, conduction is the dominant heat transfer mechanism during the cure of composites. Consequently phenomena occurring during the cure are represented by the heat conduction equation

$$\rho c_p \frac{\partial T}{\partial t} - \rho H_{tot} \frac{d\alpha}{dt} = \sum_{i,j=x,y,z} \frac{\partial}{\partial i}\left(K_{ij} \frac{\partial T}{\partial j} \right), \quad (x, y, z) \in \Omega \qquad (3)$$

subject to the boundary conditions:

$$T(x, y, z, t) = F(x, y, z, t), \qquad (x, y, z) \in \Gamma_1 \qquad (4)$$

$$q(x, y, z, t) = n(x, y, z, t), \qquad (x, y, z) \in \Gamma_2 \qquad (5)$$

where K_{ij} is the thermal conductivity tensor, α the degree-of-cure and H_{tot} the total heat of the cure reaction per unit mass. Ω denotes the domain of the problem and Γ_1 and Γ_2 the boundaries where the boundary conditions of the first and the second kind are imposed respectively.

Implementation of finite elements, specifically of semi-discrete Galerkin approximation, leads to a system of algebraic equations that approximates the heat transfer behaviour of the curing component.

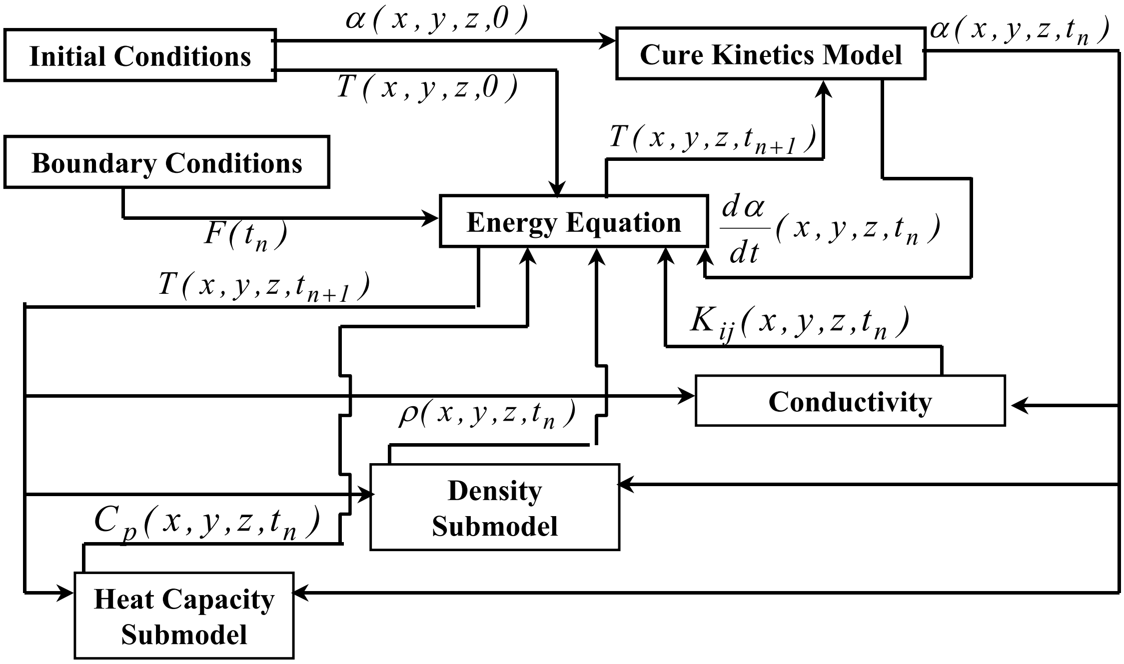

***Fig. 3**: Structure of the heat transfer model*

The structure of the model and the interdependencies of the various submodels are illustrated schematically in Fig. 3

3.3. Cure kinetics, heat capacity and density submodels

The modelling of cure kinetics is based on the essential assumption that the reaction rate is a function of the fractional conversion and of the temperature. This implies that the history of the material does not affect the reaction and consequently the material state is fully characterised by a single fractional conversion.

The validity of this assumption can be demonstrated by analysing the effect of thermal history and the corresponding conversion history in cases where the conversion and the temperature are identical. This analysis is achieved by a comparison of the reaction rate measured at same points of the temperature-conversion phase space, by isothermal and dynamic calorimetry on RTM6 resin. The reaction rate obtained dynamically at the temperatures of the isothermal DSC experiments is illustrated together with the rate-conversion isothermal plots in Fig. 4.

It can be observed that the reaction rate values obtained dynamically are very close to the isothermal curves. Regression analysis applied to the two sets of reaction rate values, showed that they are related with a linear relationship, with a slope of 1.02, and a regression constant of 0.997. Consequently the assumption of reaction rate uniqueness within the conversion-temperature phase space is acceptable, and the reaction rate can be considered as a surface in the space defined by the reaction rate, the conversion and the temperature.

A non-parametric kinetics model, based on this approach is applied directly to the experimental data. The algorithm works in two stages. First the reaction rate at the required conversion is calculated for each of the experimental data sets. This way an 'isoconversional' curve of the reaction rate as a function of temperature is produced. Then linear interpolation is applied to this isoconversional curve and the reaction rate at the required temperature is calculated.

In order to validate this procedure experimental data are compared with modelling results (Fig. 5), where the experimental data of the particular cases are not included in the modelling data. The agreement is excellent and phenomena like vitrification and devitrification can be predicted, something which is impossible with conventional cure kinetics.

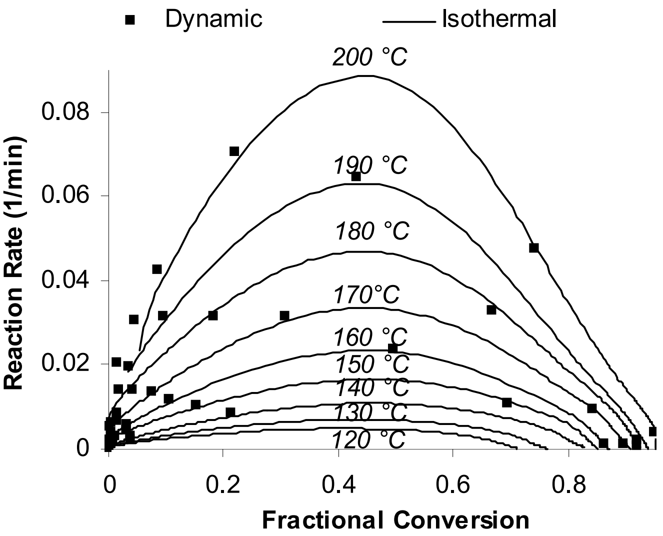

***Fig. 4** : Comparison of reaction rates obtained by isothermal and dynamic calorimetry*

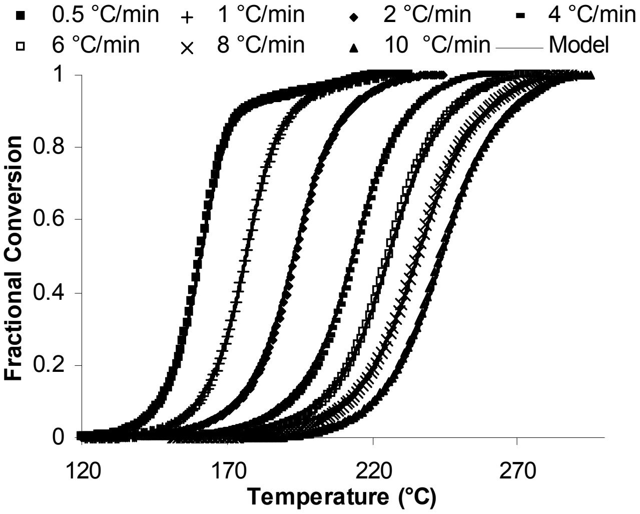

***Fig. 5**: Comparison of model results with experimental data*

The heat capacity submodel is based on the implementation of the same. Interpolation is applied directly to experimental data produced by a series of isothermal temperature modulated DSC experiments.

The model used for density estimation is analytical. Two phenomena are taken into account:-(i) the thermal expansion and (ii) the chemical shrinkage of the resin. The implementation of the model is performed incrementally. At each time step of the heat transfer model the density is calculated as follows:

$$\rho_n = \frac{\rho_{n-1}}{1 + \frac{\Delta V}{V}} \tag{6}$$

where the change in volume is given by the relation:

$$\frac{\Delta V}{V} = 3CTE\Delta T + \gamma\Delta\alpha \tag{7}$$

Here CTE is the linear thermal expansion coefficient and γ the shrinkage.

The thermal expansion coefficient of RTM6 resin is, according to Holmberg [22]:

$$\alpha = \begin{cases} 136\,10^{-6} & ,T \geq T_g \\ 54\,10^{-6} + 0.16\,10^{-6}\,T & ,T < T_g \end{cases} \tag{8}$$

The glass transition temperature is calculated according to Karkanas [21] using the relation:

$$T_g = \frac{93.4\alpha}{1 - 0.565\alpha} - 11 \tag{9}$$

The shrinkage is considered to occur between gelation and vitrification. The total chemical shrinkage reported by Holmberg [22] is 0.046.

4.Correlation between dielectric signal and progress of reaction

In order to utilise monitoring signals in the inversion algorithm their output should be translated into the form of the heat transfer model output. Thermal monitoring results in temperature measurements, therefore modification is not required but in the case dielectric cure monitoring establishment of a correspondence between the dielectric signals and conversion is necessary.

The general shape of the imaginary impedance spectrum and its evolution during cure is illustrated in Fig. 6, as it is measured in a dynamic cure at 1 °C/min.

The impedance depends on both the degree-of-cure and temperature. When the cure is isothermal the temperature dependence vanishes and any characteristic of the spectrum is directly correlated with the degree-of-cure. In the general case, although the process thermal cycles contain an isothermal part during which curing is completed, the reaction does not take place under isothermal conditions due to heat transfer phenomena which alter the temperature within the component. This fact creates a need for temperature

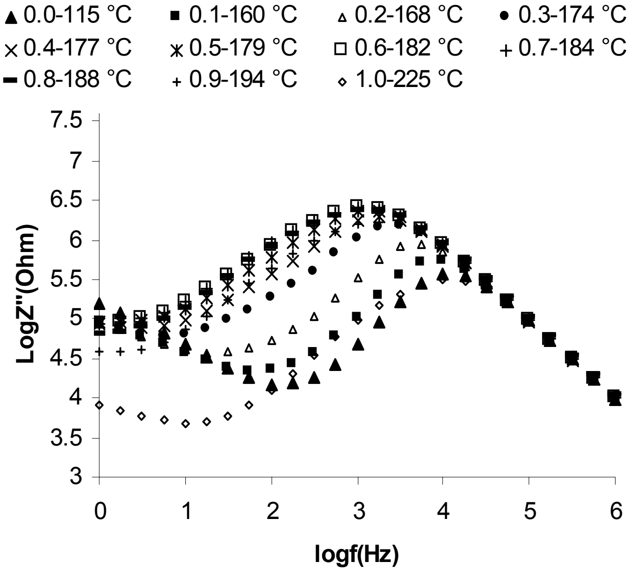

***Fig.6**. General form of the impedance and its changes during the cure*

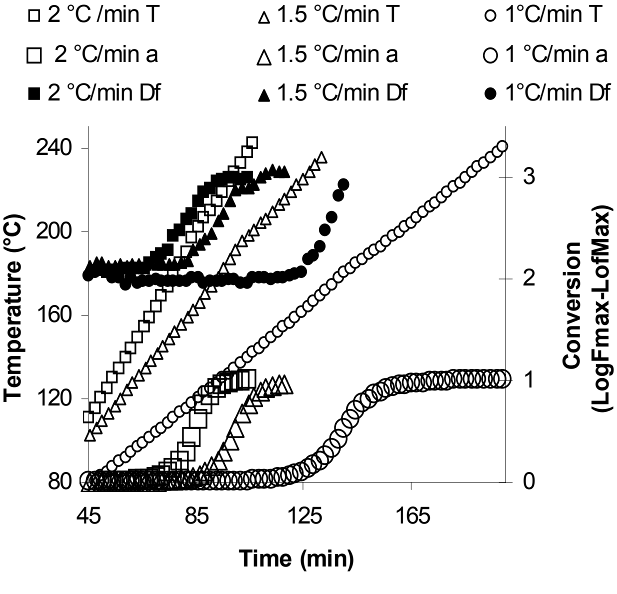

***Fig.** 7. Minimum to maximum frequency difference and conversion for dynamic experiments* measurement at the point of dielectric measurement, so that the temperature effect can be accounted for. This approach limits the applicability of dielectrics to an on line kinetics model validation role, since knowledge of the temperature profile incorporated with a kinetics model can lead to the calculation of the progress of reaction profile, without the use of dielectric sensing. If a direct measurement of the progress of reaction monitoring is desirable, a method to deconvolute the temperature effect is necessary.

It has been found experimentally that the frequency difference between the maximum and the minimum of the imaginary part of impedance depends only on the conversion, for the specific resin system used (RTM6). Thus, this signal can be used in order to estimate the conversion either in isothermal or dynamic curing. This correlation is demonstrated in Fig. 7 where the frequency difference is compared with the conversion as calculated using kinetics modelling, for a series of dynamic cure cycles.

The correlation between conversion and logarithmic frequency difference from minimum to maximum can be quantified according to the following polynomial relation:

$$\Delta log\, f = -1.04\alpha^2 + 1.91\alpha + 2.13 \tag{10}$$

Data from a series of different thermal schedules fit satisfactory this equation with a regression constant of 0.95. Consequently the signal offers the ability to estimate the conversion directly from dielectric data, for the specific resin system.

The applicability of the method is limited by the fact that the minimum of the imaginary impedance is outside the measurement range at low temperatures and high conversions.

5. Inversion procedure application

Results of the application of the inversion technique to the curing of a 10 mm thick flat unreinforced resin plate are given in Fig. 8 and Fig. 9.

The temperature has been recorded at different locations through the thickness. The temperature measurement at 8 mm has been used as the input of the inversion algorithm. The thermal conductivity and the natural air convection coefficient have been calculated

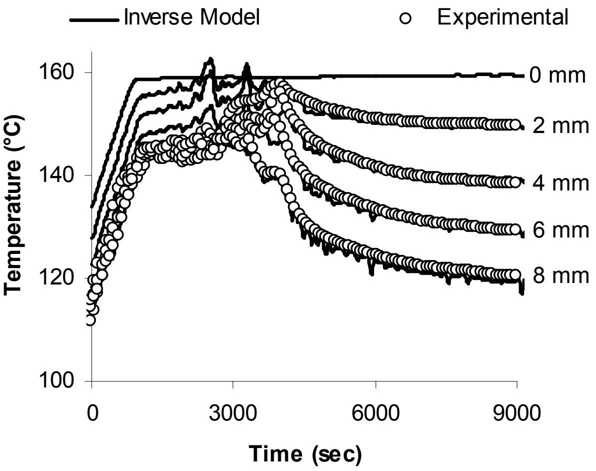

***Fig.8**. Comparison of measured temperature and model results*

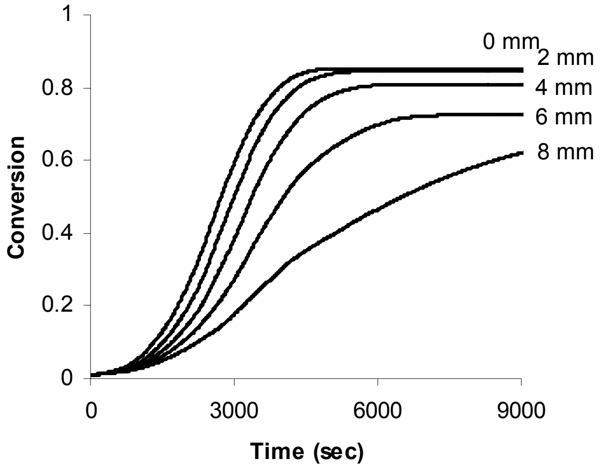

***Fig.9**. Degree-of-cure distribution during the cure*

for each time step using the genetic algorithm and the direct model has been solved in order to calculated the temperature and degree-of-cure distributions.

The model results are in good agreement with the temperature, after the first 4000 sec of the cure. The initial difference can be attributed to the domination of a convective heat transfer mechanism at the beginning of the cure. As mentioned previously the Rayleigh number has high values at the initial stage of the cure. These values are within the region where convection is an active mechanism for an unreinforced thermoset. Consequently a conduction based inverse method cannot represent the situation in the initial stages of the cure.

In the case the inversion is applied to composite cure the convection is impede by the reinforcement, as it has been found using the Raleigh-Darcy number. Therefore the conduction based inversion algorithm would be adequate to express the phenomena in the real application.

6.Conclusions

A modelling-monitoring procedure, that express heat transfer phenomena occurring during the cure using data from measurements, has been developed.

Heat transfer has been modelled using a finite element heat conduction model, combined with a non-parametric cure kinetics model and appropriate thermal properties submodels. An inverse solution procedure of this model based on a genetic algorithm has been developed.

The modelling-monitoring scheme has applied successfully to the curing of unreinforced resin.

The possibility to use cure monitoring alongside with thermal monitoring has been investigated. A technique translating dielectric cure monitoring signals into degree-of-cure has been established for a specific resin system. This enables dielectric cure monitoring results to be used in the inversion procedure as a direct conversion measurement

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