Alpha-T-T and T-T-alpha-T diagrams as a new element in comprehensive modelling of thermoset processing*

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The majority of existing models for processing of thermoset matrix composites concentrate nearly exclusively on heat and mass transfer problems and account for material-related aspects in a very simplified manner. The objective of this work is to provide that missing element by proposing a clearly defined system which yields all the information of Gillham's T-T-T diagram but can be used for non-isothermal curing cycles. To build the system, three elements are needed: the gelation and vitrification curves, expressed as functions of degree of conversion; the kinetic model of conversion; and a diagram combining all complex information provided by the system. The proposed system for Narmco resins incorporates Cole's recently developed mechanistic model for the kinetics of conversion. The algorithm calculates and graphically presents the progress of thermoset processing using the developed diagrams which reintroduce time as an independent variable. The diagrams and the system may be applied to any processing cycle. Results obtained from the system are positively verified by experiments conducted on the Rheometrics dynamic analyser.

(Keywords: alpha-T-T diagram; conversion; processing; thick composites)

INTRODUCTION

There is a tendency in mathematical modelling of composite processing to concentrate nearly exclusively on heat and mass transfer problems and account for the material-related aspects in a very simplified manner[1]. However, the reaction of the conversion and consequent generation of heat are not the only phenomena taking place in a material during processing, which are of importance either to the process itself or to the final properties of the product. The phenomenon of gelation marks the end of flow of a resin, while knowledge of the point of gelation is useful for toughened resin processing from the point of view of precipitation of an additional phase. Vitrification causes the diffusion-controlled slow-down of the conversion reaction and determines the final degree of conversion obtained in the product. It also creates changes in the specific volume of a material contributing to stress generation.

In order to fill the existing gap in process modelling, an additional model element must be developed to represent material behaviour within the overall model of processing. An algorithm based on Gillham's T-T-T diagram would be the obvious choice for the element; for any specific time and temperature of processing the diagram determines the point representing the state of the material, providing information on the phase of the thermoset as well as the distance to the curves of phase change[2-4]. Unfortunately, the diagram is built for, and can be applied to, isothermal curing only, while in industrial practice the processing cycles are usually non-isothermal. The concept of an algorithm that could be applied to any processing cycle stems from the fact that the point of gelation and the point of final vitrification for a resin system, can be quite easily expressed as a function of degree of conversion and temperature[5]. Gelation is expected to occur at a constant value of conversion, while the point of vitrification is conveniently described by the DiBenedetto equation[6]. Both curves may be plotted on the grid of degree of conversion *versus* temperature of processing. In order to place the point of processing in the same figure, its coordinates, the momentary temperature of processing and degree of conversion, must be determined. The latter can be calculated only if the model of kinetics of conversion is available. The method does not require isothermal conditions of processing, but the display it produces is inferior to Gillham's diagram. Due to the system of coordinates used in the method, the time of processing cannot be read directly from the produced graph, and the curve of upper devitrification from Gillham's diagram cannot be easily incorporated into the graph.

The objective of this work was to create an algorithm based on the presented concept, while looking for improved forms to display comprehensively the complex information produced. The research effort resulted in the development of a system that calculates and presents graphically the progress of thermoset processing. The system can be applied to non-isothermal processing and accounts for the degree of conversion as well as phase

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changes in a material. The new proposed diagrams reintroduce time into their system of coordinates.

STRUCTURE AND OPERATION OF THE DEVELOPED SYSTEM

In order to build the presented system for a new material, three elements are needed: the gelation and vitrification curves, expressed as a function of degree of conversion, alpha; the kinetic model of conversion; and diagrams displaying the information of the two previously mentioned elements in a clear and efficient fashion. All these elements and their interaction are presented in *Figure 1.* For any specific time and temperature history, the kinetic model employing numerical integration calculates the momentary degree of conversion. The momentary temperature of processing, T, provides the remaining coordinate of the point representing the state of processing in the alpha-T coordinate system.

The system presented here is developed for Narmco resins. For this material, there exists an excellent mathematical model of kinetics of conversion, developed by Cole, based on a mechanistic approach, which was incorporated into the system[7,8]. The value of conversion at gelation was adopted from the work of Bidstrup, and the parameters of the DiBenedetto vitrification curve were assumed on the basis of various literature sources[9]. Both gelation and vitrification parameters were further verified experimentally

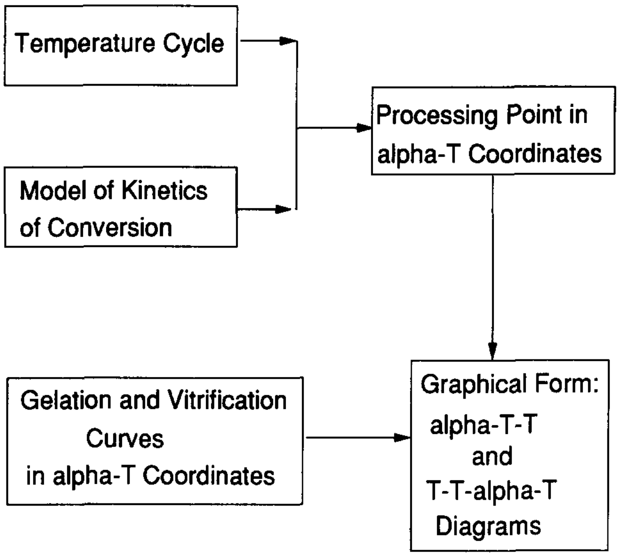

Figure 1 Structure of the system

INTERACTION OF THE PROPOSED SYSTEM WITH COMPOSITE PROCESSING MODEL

In a curing process, a material is exposed to an elevated temperature and pressure for a specified length of time. The modelling of composite processing consists of at least two main models: heat transfer and resin flow. It is assumed, however, that the effect of flow-related phenomena on thermal variables is negligible. In a typical processing arrangement, the temperature is applied to a heating tool adjacent to one side of a composite, while the other side is insulated by a bleeder and a vacuum bag. Due to low thermal conductivity of the material and strong exothermic effect of chemical reactions, the temperature in the material differs from location to location. The most pronounced difference is that between the temperature in the material adjacent to the heating tool and the temperature of far-side location, and it depends on the overall thickness of the composite. The difference is visible even for a composite a few millimetres thick, and becomes serious for a thicker one, thereby creating a need for modelling this thermal phenomenon. Any thermal model requires information on the exothermic reaction of conversion and in this way depends on material-related information. The interaction of a thermal model of composite processing and the system presented here is shown in *Figure 2.* The temperature cycle applied to a heating tool provides boundary conditions for a heat transfer model, which in turn calculates the temperature distribution in other locations in a material. A conversion kinetics model, interacting with other elements of the system, utilizes the temperature distribution to calculate local rates of conversion, which are used by a heat transfer model and treated as heat sources. The conversion model numerically integrates the rates of conversion to calculate the momentary degree of conversion for different locations in the composite.

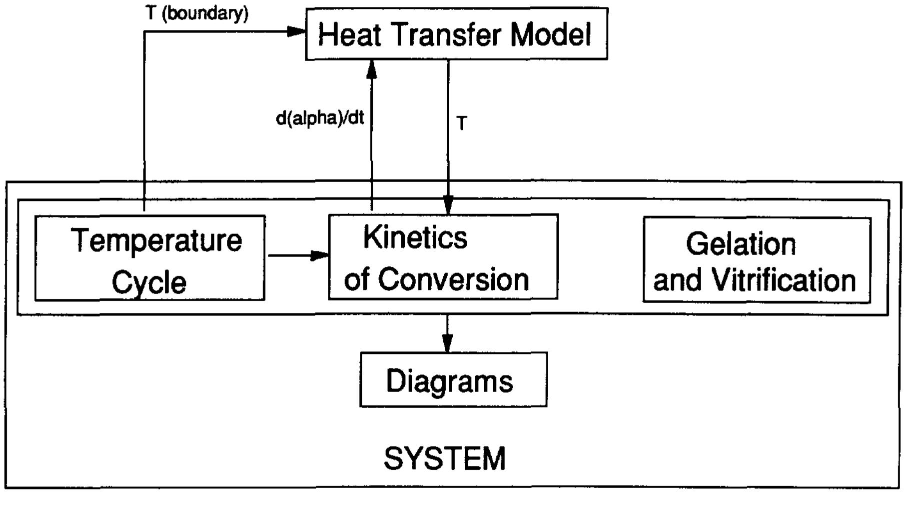

Figure 2 Interaction of the proposed system with composite processing model

CONVERSION KINETICS MODEL

In Cole's model, the progress of polymerization is described in terms of two parameters: α, the overall degree of conversion as expressed in terms of the fraction of epoxide groups reacted; and β, the fraction of amine N–H bonds which have reacted. These two quantities are closely interrelated and their evolution with time is given by the following equation:

$$\frac{d\beta}{dt} = [(K_1 + BK_2\beta)(1-\beta)](1-\alpha)f(\alpha, T) \quad (1)$$

$$\frac{d\alpha}{dt} = [B(K_1 + BK_2\beta)(1-\beta) + K_3\beta^3](1-\alpha)f(\alpha, T) \quad (2)$$

where K_1, K_2 and K_3 are reaction rate constants depending only on temperature, B is the ratio of amine. N–H bonds to epoxide rings in the initial mixture and the diffusion control factor $f(\alpha, T)$ is given by:

$$f(\alpha,T) = [1 + \exp(30.1\alpha + 4.06 - 0.1617T)]^{-1} \quad (3)$$

On the basis of Cole's kinetic model, a computer code was developed which numerically integrates the rate of conversion as a function of time for the given temperature history. Then, a sample of Narmco resin provided by Canadair Inc. was tested, using a d.s.c. as a primary tool. The experiment included dynamic heating as well as isothermal tests. Examples of the experimental results, plotted against those predicted from the model, are presented in *Figures 3* and *4*. An excellent agreement between results predicted from Cole's model (smooth lines), and the experimental data (lines with circles) is found. In the case of dynamic heating at 5°C min^{-1} (*Figure 3*) there is virtually no difference between the predicted curve and the experimental data up to 210°C. Since the diffusion factor from Cole's model was not included at this stage in the computer code, there is a difference for the time of processing above 100 min for isothermal curing at 170°C (*Figure 4*).

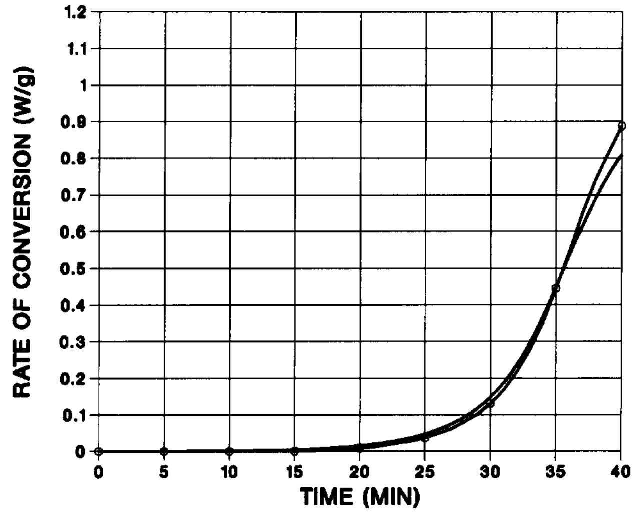

Figure 3 Verification of conversion kinetic model for dynamic heating: ——, Cole's model; —○—, experimental data

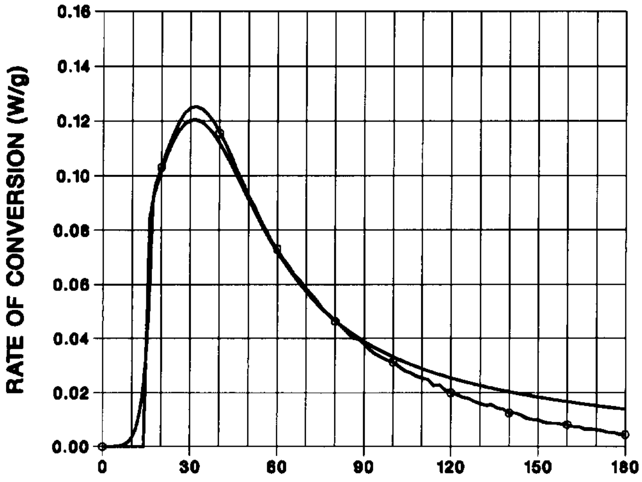

Figure 4 Verification of conversion kinetic model for isothermal heating: ——, Cole's model; —○—, experimental data

VERIFICATION OF THE GELATION AND VITRIFICATION CURVES

A Rheometrics system II dynamic analyser with parallel plate geometry was used to determine the extent to which the results of the system apply to real processing. In the experiments, the gap between the plates was fixed at the beginning of runs, not allowing for the expansion or contraction of the material. Typical records from the instrument are shown in *Figure 5*. In agreement with other researchers, it was assumed that a moment of gelation takes place when curves of storage modulus G′ and loss modulus G″ cross each other[9,10]. The moment of final vitrification could only be approximately recognized as a moment when, due to rapid contraction of a material and the resulting stress, a material brakes partially (the rapid decrease in G′).

Good agreement was found for the gelation point and satisfactory agreement was found for vitrification points, except for the extreme case when the material was processed at 190°C for 3 h.

ALPHA-T-T AND T-T-ALPHA-T DIAGRAMS — THE GRAPHICAL OUTPUT OF THE SYSTEM

In *Figure 6* the results of the system, obtained for a temperature cycle similar to that suggested by the producer, are displayed. The diagram consists of three parts. Part 1 displays an assumed temperature cycle. In part 2 this temperature history is used by a kinetic model of conversion to obtain the degree of conversion as a function of time. Part 3 presents the alpha-T-T diagram, which contains the curve of gelation (G), the curve of vitrification (V), the line of full cure, and the curve of processing (P). The curve of processing is marked with small circles. The marks are drawn for approximately 10 min time intervals, as a way to introduce time into the graph, which uses an alpha-T system of coordinates. The three-part diagram not only contains complete information about a material under specific processing conditions but the configuration of the graphs also provides an additional advantage. It allows for the determination of the time of processing for any point on the processing curve. This can be done either by drawing a vertical line from the point to the curve of conversion below and then reading the time horizontally, or by drawing a horizontal line from the point to the processing curve and then reading time vertically. Usually only one of these two ways is practical.

It should be noted that even if the temperature cycle

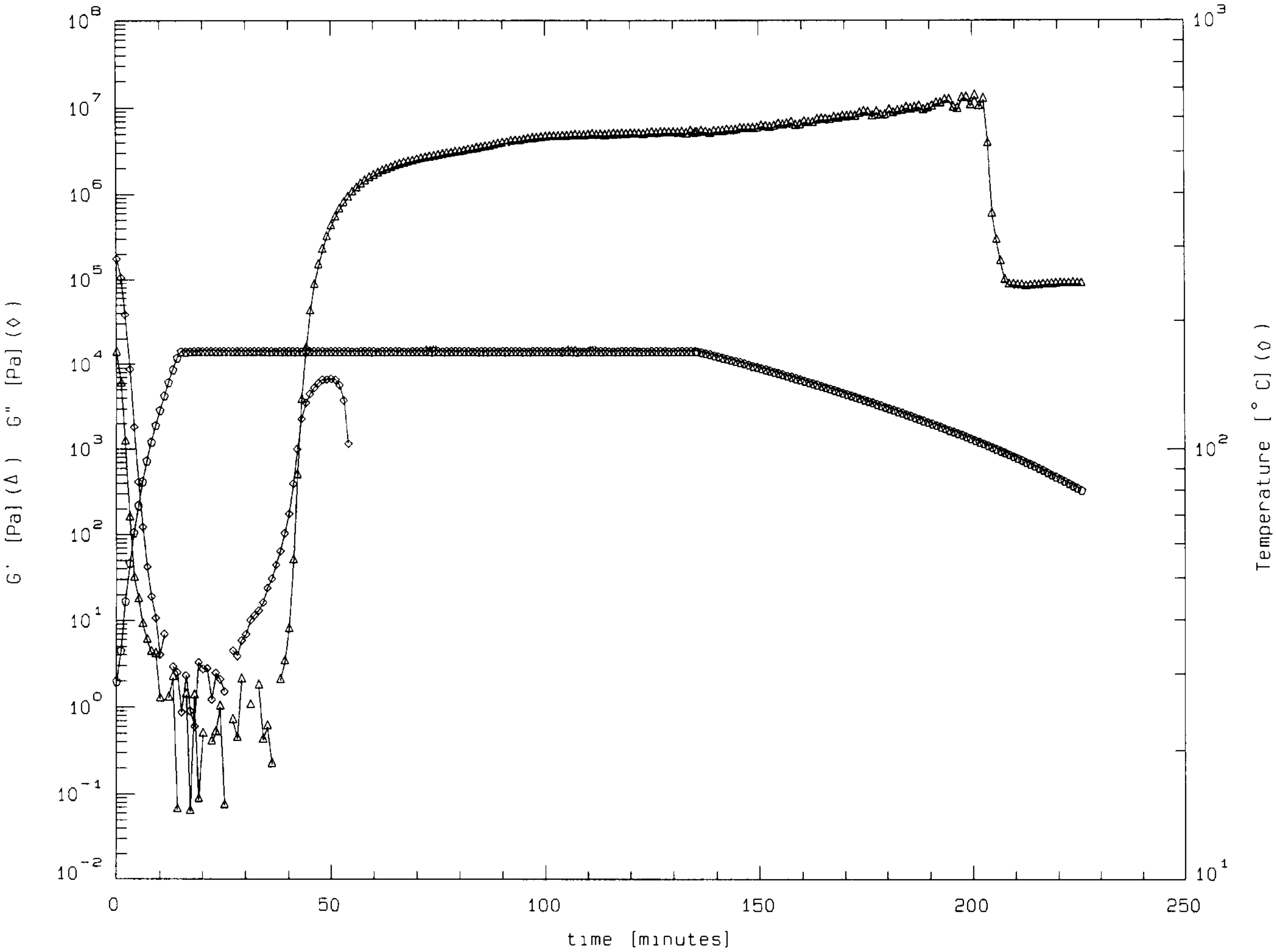

Figure 5 Verification of curves using Rheometrics dynamic analyser

is fixed, there are still three parameters of processing in the diagram: time, temperature and degree of conversion. This is the reason why a complex alpha-T-T diagram consists of three different figures. Another option for representing an equivalent amount of information is to develop a three-dimensional image, presented in *Figure 7*. The x and y coordinates are time and temperature, so that the thermal cycle of processing can be drawn in the base of the graph. The z coordinate is the degree of conversion. The curves of gelation and vitrification take the form of surfaces. The thermal cycle of processing shown in *Figure 7* is the same as that of *Figure 6*. Since surfaces of gelation and vitrification sometimes obstruct the view of the processing curve, the same graph can be shown without the mentioned surfaces. This is done in *Figure 8* where the curve of processing is produced exclusively. The non-continuities of the curve mark the points of its cross-section with the gelation and vitrification surfaces.

ALPHA-T-T DIAGRAM IN PROCESSING OF THICK COMPOSITES

In thick materials, different locations usually have a different temperature history and therefore a different degree of conversion, different glass transition temperature, and a different moment of vitrification. All these differences result in different structures of a material and creation of stresses. The alpha-T-T diagram provides information on which point vitrifies first and on the temperature of vitrification. *Figure 9* shows a diagram which was generated by combining the computer code of the presented system (*Figure 1*) with a thermal model as shown in *Figure 2*. The presented calculations were conducted for Narmco resins 4.5 mm thick. In each part of the diagram two curves are present: one for the location in the processed material adjacent to the heating tool (circles) and the other for the location most distant from the heating tool (triangles). Part 1 of the diagram shows the assumed curing temperature cycles at the tool, and the resulting temperature cycle at the other side of material with a high temperature peak, due to the exothermic reaction of conversion. This peak is responsible for the high degree of conversion observed for the location distant from the tool, as shown in part 2. Finally, in part 3 there are two curves of processing. The lines connecting the curves are drawn to connect processing points of the same processing time. When the temperature of processing starts dropping, the temperature in both mentioned locations is nearly the same; however, the far-side location obtains a higher degree of conversion, and therefore vitrifies first at a temperature of 170°C. The location at the tool vitrifies more than 10 min later at a temperature of 150°C. As a result of the applied processing cycle, the structure and degree of shrinkage of a material differ from location to location. The presented diagram can be used to look for alternative temperature cycles which would eliminate the unwanted effects.

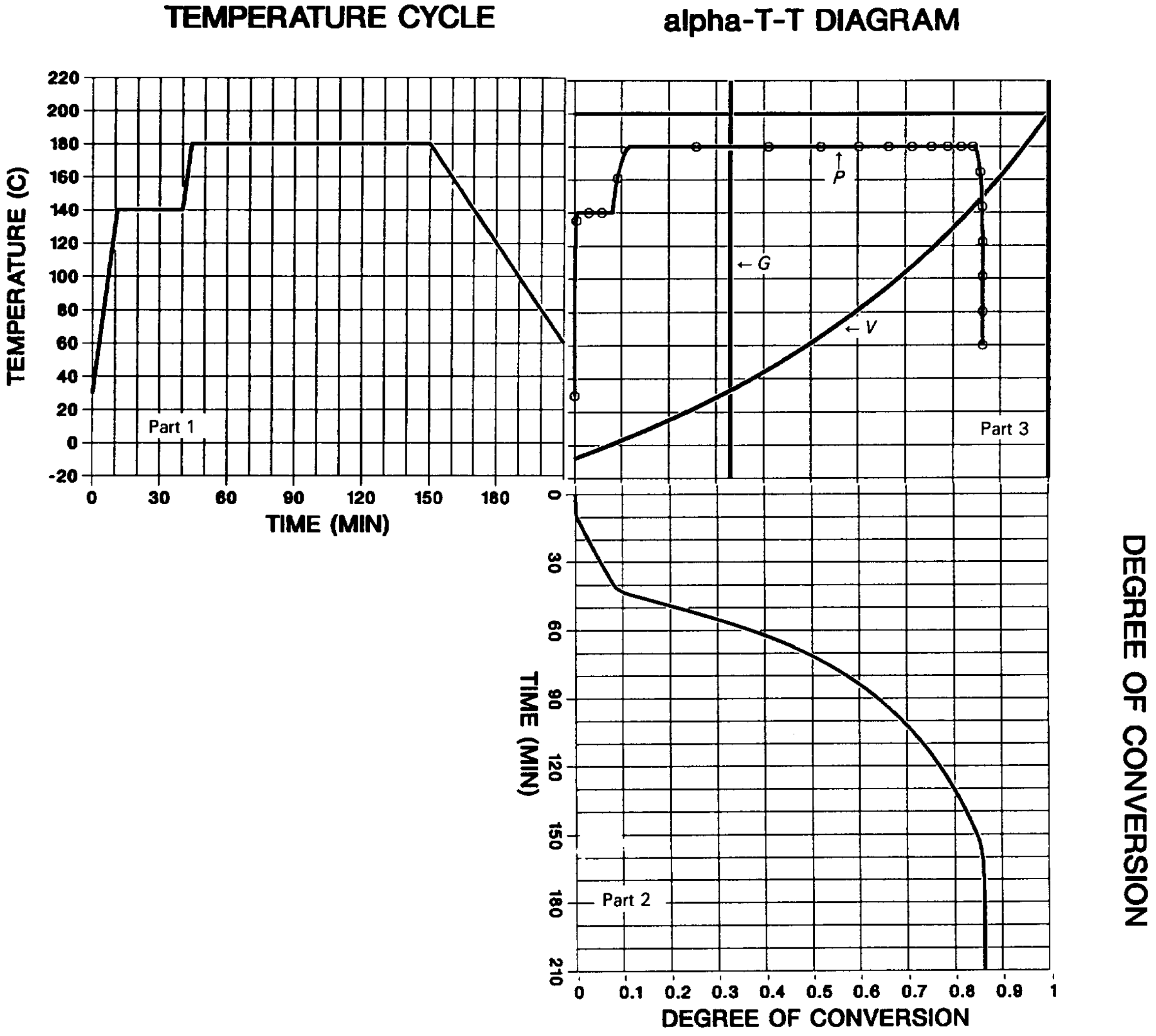

Figure 6 Three-part alpha-T-T diagram

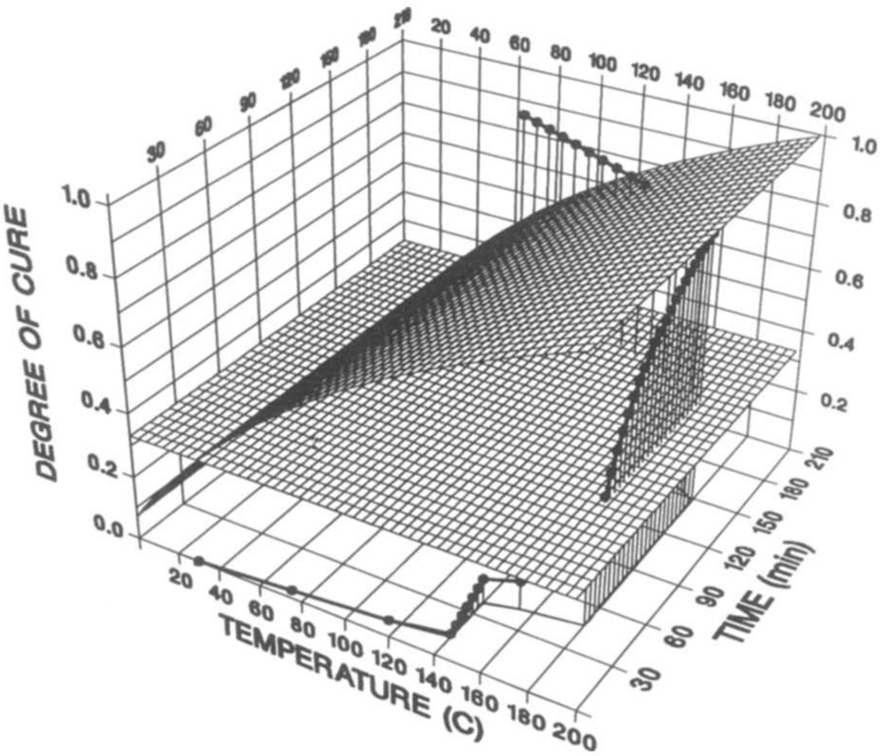

Figure 7 Three-dimensional T-T-alpha-T diagram

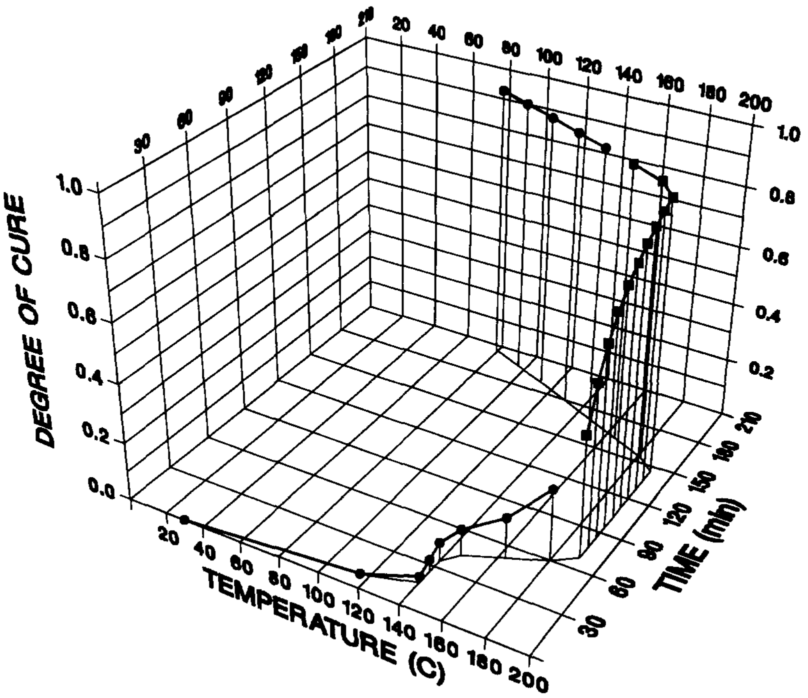

Figure 8 Three-dimensional T-T-alpha-T diagram without curves of gelation and vitrification

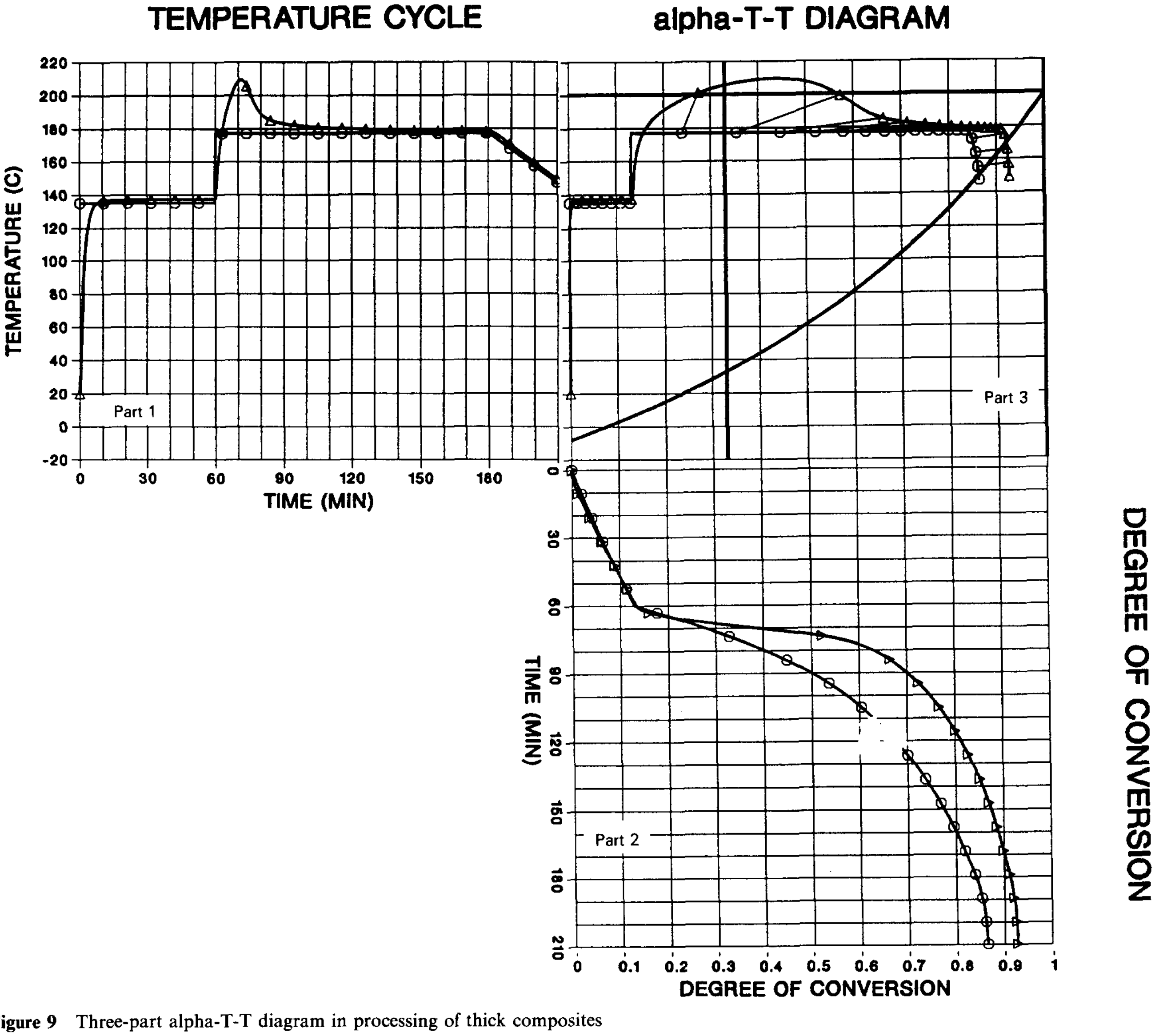

Figure 9 Three-part alpha-T-T diagram in processing of thick composites

CONCLUSIONS

Two types of diagram are presented as a general method of displaying the complex information produced in modelling of composite processing. Although both convey identical content, the three-dimensional diagram provides a better general orientation in the process, while the three-part diagram allows for a more quantitative approach. In order to demonstrate their capabilities, the diagrams have to be incorporated into the larger modelling structure, or system. The proposed system can calculate the progress of thermosetting resin processing and can display information about a material comprehensively. The system that incorporates Cole's advanced model of kinetics of conversion may be applied to isothermal, as well as non-isothermal processing. The simulation of the processing cycle for the system, using a temperature cycle as suggested by the producer, has shown the comprehensive nature of information provided by the diagrams. However, the full advantages that the diagrams offer in modelling thermoset processing become obvious when they are used in the simulation of thick composite parts. In order to conduct such a simulation, the previously developed system had to be coupled with the thermal model of processing.

The diagrams presented, used in a mathematical model of processing for simulation of alternative processing cycles, provide the following information:

moment of gelation;
moment of diffusion slow-down caused by vitrification;
final temperature of vitrification as a local property of a material;
final degree of conversion;
moment of vitrification, including sequence of vitrification.

The information creates a sufficient basis for the reasonable selection of a technologically correct processing cycle.

REFERENCES

1 Loos, A. C. and Springer, G. S. *J. Composite Mater.* 1983, **17**, 135
2 Enns, J. B. and Gillham, J. K. *J. Appl. Polym. Sci.* 1983, **28**, 2567
3 Pens, X. and Gillham, J. K. *J. Appl. Polym. Sci.* 1985, **30**, 4685
4 Wisanrakkit, G. PhD Thesis, Princeton University, 1990
5 Williams, R. J., Benavente, M. A. and Ruseckaite, R. A. *Polym. Eng. Sci.* 1990, **30**, 1140
6 Pascault, J. P. and Williams, R. J. *J. Polym. Sci., Polym. Phys. Edn* 1990, **28**, 85
7 Cole, K. C. *Macromolecules* 1991, **24**, 3093
8 Cole, K. C., Hechler, J. J. and Noel, D. *Macromolecules* 1991, **24**, 3098
9 Bidstrup, S. A. PhD Thesis, University of Minnesota, 1986
10 Serrano, D., Peyrelasse, J., Boned, C., Harran, D. and Monge, P. *J. Appl. Polym. Sci.* 1990, **39**, 679