MODELING OF THE CURE OF EPOXY BASED COMPOSITE, HEATED AT CONSTANT TEMPERATURE IN CYLINDERICAL MOULD

Adnan A. Abdul Razak[*], Ali M. Hameed[**], Saad R. Sultan[***]
Chemical Engineering Department, University of Technology
*E-mail: adnansss2002@yahoo.com
**E-mail: ali2alganabi@yahoo.com
***E-mail:saadraheemsultan@yahoo.com

ABSTRACT:- The heat transfer process involved in the curing of fiber-reinforced thermosetting composites is investigated numerically. This composite is made of woven fiber and resin and placed in a cylindrical mould. The governing equation for one dimensional heat transfer, and accounting for the heat generation due to the exothermic cure reaction in the composites had been used. A finite element method is developed to solve the mathematical model problems for composites manufacturing. The solution of the complete mathematical system gives, both, the temperature and the degree of reaction as functions of time and position. It was found that the temperature at the central of the sample increases up to the external imposed temperature, because of the thermal conductivity of the resin and fiber. The heat generated by the exothermic reaction of the resin is not adequately removed; the increase in the temperature at the center increases the resins rate reaction, which in turn generates more heat.

Keywords:- Mathematical model, curing, epoxy resin, cylindrical mould

1. INTRODUCTION

In the last decade, the use of composite materials has increased considerably, due to their light-weight and high-performance features. Composites have found many widespread applications in modern industry. This increased demand for composites has led researcher in pursuit of better and faster methods of manufacturing composites. Thermosetting-matrix composites fabrication is well served by many continuous and batch process, all of which share the common and critical step of cure.

Cure refers to an irreversible exothermic chemical reaction by which the composite lay-up is transformed from a soft, multi-layered mixture of fibers and resin, to a hard structural component.

The high exothermicity of curing reaction associated with the low thermal conductivity of the material is a feature of fundamental importance. As a result, the curing reaction gives rise to high temperature within the resin especially at the center, and high temperature gradients are developed through the sample(Progelhof et al., 1975; Pusatcioglu et al., 1980). These facts may lead to cracking or crazing (Nixon et al., 1985; Hutchinson et al., 1985) . 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 optimize the operational conditions.

The purpose of the work described in this series of papers (Adnan et al., 2007; Adnan., 2010) was to build mathematical models to describe the process of cure taking place in a composite resin. This composite is made of woven fiber and resin and placed in a cylindrical mould. 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.

Although the model is perfectly general, in part (1) (Adnan et al., 2007) of this series of papers, the development of the model is described and the predictions of the model was used for a sample of laminate epoxy based composite. In part (2) (Adnan 2010) unsaturated polyester based composite had been used as a matrix of the laminate composite.

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 n the material, and the heat dissipation at the composite skin. The energy balance equation is coupled with a suitable expression for kinetic behavior of the chemical reactions accounting for diffusion control effects.

2. PROCESS MODEL

The equations describing the cure process are (1) the kinetic model for the reaction rate in terms of the temperature and degree of cure (2) the energy equation in cylindrical coordinates for one dimensional cross section of the product

2-1 Kinetic Model

The cure kinetic model chosen for this study is described by an empirical Arrhenius-type equation given below, which has been shown to be effective in representing the cure behavior of a variety of epoxy and polyester resins system (Prime, 1981)

$$\frac{d\alpha}{dt} = k \exp \frac{-\Delta E}{RT} (1-\alpha)^n \qquad (1)$$

In above equation, α is the degree of cure, t is the time, k is the Arrhenins frequency factor, E is the activation energy, R is the universal gas constant, T temperature, and n is the reaction rate. The degree of the cure α is defined as the instantaneous fraction of the cured polymer in the reaction mixture, and increase from 0 to 1 as cure progresses. The kinetic parameters, k, E, and n for a given resin catalyst system are determined usually experimentally using differential scanning calorimetry (DSC).(Kamal et al., 1973; Stevenson,1986)

2-2 Thermal Model

The thermal model consists of solving the energy equation in cylindrical coordinates for the temperature distribution in the cross section. The governing equation for the one dimensional heat transfer through the thickness of the two-material formed the laminate and the heating source, and accounting for the internal heat generation is due to the exothermic cure reaction in the composite which may be written as (Bejan ,1990)

$$\rho C_p \frac{dT}{dt} = \frac{1}{r}\frac{dT}{dr}(rK\frac{dT}{dr}) + H_r \rho \frac{d\alpha}{dt} \qquad (2)$$

Where ρ is density, CP is specific heat capacity, K is heat conductivity, Hr is heat of reaction and r is radius. Contribution to the increase in temperature due to heat conduction and heat evolved from the cure reaction can be seen in the second term of equation "(2)".

2-3 Finite Element Analysis

The forward finite element difference method approximation has adopted, in which the curing part is divided into a number of zones and the heat balances is determined for each zone for successive time step (Mathews. et al., 1999) .The system is separated into a series of small units or element; each element is described by nodes which are at the corners and in some cases along the faces of the element.

Assume that the rectangle

Rr = [(r, t) : 0 ≤ r ≥ a,0 ≤ t ≥ b] is subdivided into (n-1) by (m-1) rectangles with sides Δr =hr and Δt=kt, as shown in figure 1, start at bottom row, where t=t1=0, and the solution is T(ri,t1)=T(ri). A method for computing the approximation to T(r,t) at grid points in successive rows

[T (ri,tj):i=1,2,…..n] , for j=2,3,….m, could be rewritten for equations (1) and (2)

$$T_{i,j+1} = (1-2r_d)T_{i,j} + r_d(T_{i-1,j} + T_{i+1,j}) + H_r \frac{1}{C_p} \frac{d\alpha}{dt} \Delta t \qquad (3)$$

Where the dimensionless number is expressed as a function of the increments of space Δr and time Δt. For the resin

$$r_d = \frac{(\Delta r)^2}{(\Delta t)} \frac{1}{\alpha_r} \qquad (4)$$

Where αr is the thermal diffusivity

$$\alpha_r = \frac{K}{C_p \rho} \qquad (5)$$

3. MATHEMATICAL MODEL

3-1 Assumptions

The following assumptions, useful for simplifying the study, were made (Suhli, et al., 1996; Plesu et al., 1994).

As a long cylindrical mould and sample were used, only radial heat through the circular cross section was considered.

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

3-2 Boundary Conditions

Solutions to "(3)" and "(1)" can be obtained once the initial and boundary conditions are specified. The initial conditions require that the temperature and degree of cure inside the composite be given before the start of the cure (time < 0). The boundary conditions require that the temperature on the top and bottom surfaces of the composite be known as a function

of time during cure (time > 0). Accordingly, the initial and boundary conditions corresponding to "(3)" and "(1)" are:

Initial Conditions

$$T = T_i(r) \qquad 0 \le r \ge a \qquad\qquad (6)$$

T_i is the initial temperature distribution in the composite and L its total thickness.

Boundary Conditions

$$T = T_o(t) \quad \text{at} \quad r = 0 \qquad\qquad (7)$$

$$T = T_t(t) \quad \text{at} \quad r = a \qquad\qquad (8)$$

Where T_o and T_t are the temperatures on the bottom and top surfaces of the composite, respectively, (a) is the radius of the cylinder.

4. RESULTS AND DISCUSSION

The proposed model was applied to the evaluation of the processing of two different epoxy resin mixtures composite. The composites material introduced into a glass test type, cylindrical in shape, playing the role of a mould, as shown in figure 2

1. System A consists of: Epoxy resin (Lopox 200; CDF-Chimie). Hardener D 2605 (CDF-Chimice) containing metyl nadic anhydride and an accelerator with 0.75 of aromatic amine type A 105 (CDF-Chimice). The mixture was prepared at room temperature by adding the hardener with continuous stirring. The mixture was then dropped into the cylindrical glass mould. The composition was as follows (wt %), Epoxy resin: 55.6, Hardener: 44.4 .The mould and resin sample were put in a heated air oven at constant temperature (150 ^{o}C). (Chater et al., 1987)

2. System B: The composite material used was a woven glass fiber impregnated by an epoxide resin (Vicotex 1454) with 49% resin by mass. The mould was introduced into silicone oil in circulation and kept at constant temperature (150 ^{O}C). (El Brouzi et al., 1989).

4-1 Method of Solution

"Equations (3) and (1)" were solved simultaneously, subject to the boundary conditions, by a numerical technique, an iterative procedure were followed. The basic numerical scheme involved the utilization of the explicit forward difference method for the

solution of the heat conduction equation "(3)" and Runge Kute method for the solution of the reaction rate equation" (1)".

The simplicity of formula (3) makes it appealing to use, however, it is important to use numerical techniques that are stable. If any error made at one stage of forward difference equation "(3)" is stable if and only r_d is restricted to the interval $0 \leq r_d \geq 0.5$.

Formula (3) is stable for $r_d=0.5$ and can be used successfully to generate reasonably accurate approximations to T(r,t), for our solution we use the step sizes $\Delta x = h_r = 0.02439, 0.02$ and $\Delta = k_t = 0.2, 0.333$ for system (A) and (B) respectively, the grid will be n=42 columns wide by m=6 rows high for system (A) and n=50 by m=4 for system (B), so that the ratio $r_d = 0.4874, 0.5017$ for these systems, the formula (3) becomes

$$T_{i,j+1} = 0.0252 \times T_{i,j} + 0.4874 \times (T_{i-1,j} + T_{i+1,j}) + H_r \frac{1}{C_p} \frac{d\alpha}{dt} \Delta t \qquad (9)$$

$$T_{i,j+1} = -0.0034 \times T_{i,j} + 0.5017 \times (T_{i-1,j} + T_{i+1,j}) + H_r \frac{1}{C_p} \frac{d\alpha}{dt} \Delta t \qquad (10)$$

The parameters needed as input data for the model are given in table (1).

The results of the model are given considering on the one hand the temperature – time history in various parts of the moulds, and on the other hand the state of cure obtained as a function of time in various parts of the moulds.

4-2 Temperature- Profile and   Temperature- Time History

The temperature profiles are illustrated in Figures 3 and 4, which show the temperature time history calculated at various places of the moulds.
There steps could be distinguished during the cure process;

1. The heating of the sample when the temperature of the sample was lower than the heating source. In this case the temperature at the interface is higher than the temperature at the middle.

2. The heating of the sample due to the heat of reaction. When the temperature reached (150) ^{0}C for sample (A) and about (140) ^{0}C for sample (B), a very high increase in the slope of the temperature-time curves was seen. The temperature at the middle rose to a maximum of about 225 ^{o}C.

3. The cooling period which occurred after the temperature had risen to the maximum value.

The resulting 'exotherm' occurs because composite has a low thermal conductivity and heat transfer through a composite is therefore low. The low thermal conductivity also causes a build-up of heat in the areas in which there is substantial thickness of reacting material, resulting in an accelerated rate of reaction very high peak exotherm temperature can be achieved, the value of these peak temperature being dependent on the thickness of the molding and on the kinetics parameters of the resins.

4-3 State of Cure- Time History

One of the advantages of the present model is that it can give information on the state of cure as well as on the temperature, because it is possible to determine the profile of temperature from experiments and it is quite impossible to measure the profiles of state of cure within the sample.

The state of cure- time history is illustrated in Figures 5 and 6, three stages can be distinguished in both case (A) and (B)

1. The cure reaction is shown to start at about (600) sec. for sample (A), and (330) sec. for sample (B), when the temperature on the interface was about (150) ^{0}C for sample (A) and about (140) ^{0}C for sample (B), of course the reaction started first at the interface where the temperature was highest, the rate of cure increased regularly as the temperature was increased.

2. The maximum value of the rate of cure was obtained when the temperature had risen to maximum value. In this case, the state of cure is higher at the middle of the resin, than the resin-mould interface.

3. After the maximum temperature had been attained, the cure reaction was shown to progress, for several minute (about (200) sec. for sample (A) and (360) sec. for sample (B)). The rate of cure reaction was very low, because of the low amount of unreacted resin.

5. CONCLUSIONS

This paper is essentially devoted to the development of a model able to predict not only the temperature but also the profile of the degree of reaction. Cylindrical mould was used, heated by circulation air. Two problems were examined in this paper using the mathematical model. One is concerned with the cure of composite made of woven fiber composite and epoxy resin, the other is concerned with the cure of pure epoxy resin.

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Table (1): Physico-Chemical parameters used as input data for the model.

Property	Unit	Values of systems	
		A	B
Density ρ_c	g/cm³	1.48	1.48
Thermal conductivity K_c	W/m °C	0.418	0.418
Weight fraction of fibers φ_f	%	49%	49%
Specific heat c_{pc}	J/g °C	0.998	1.128
Result of the calorimetric characterization			
Heat of reaction H_r	J/g	317.68	121.22
Activation Energy E	Kj/mol	113.45	181.203
Kinetic constant k	Ln (1/s)	26.71	45.25
Reaction order n		1.5	2.3
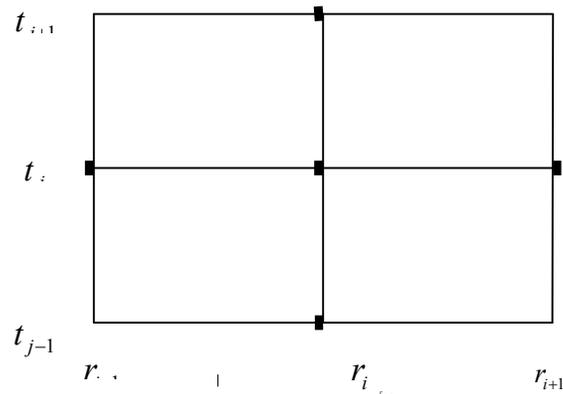
Fig. (1) The grid for solving equation (2) over R.
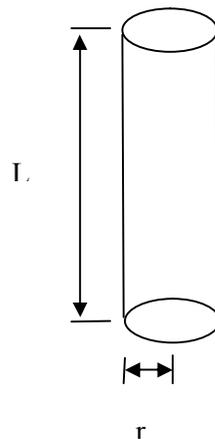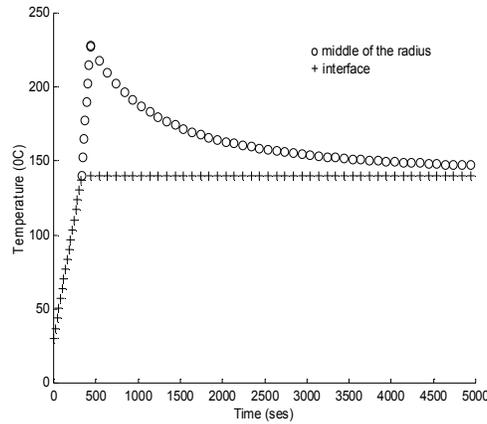

Fig. (2): Scheme of the mould.

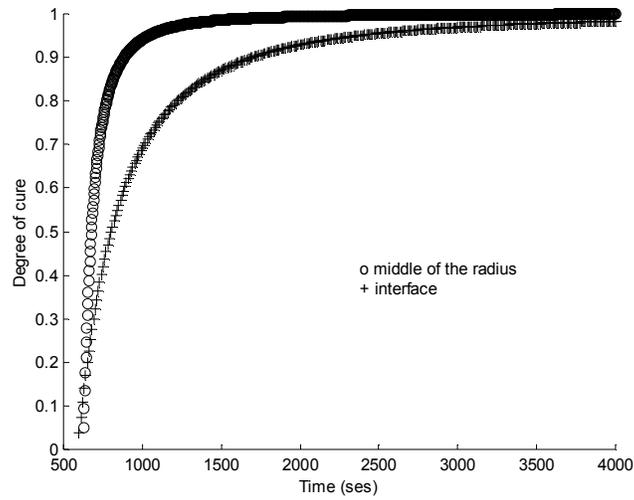**Fig.(4):** Temperature-time history at the interface and the middle of the sample (B).

Fig.(5): State of cure-time history at the interface and the middle of the sample (A).
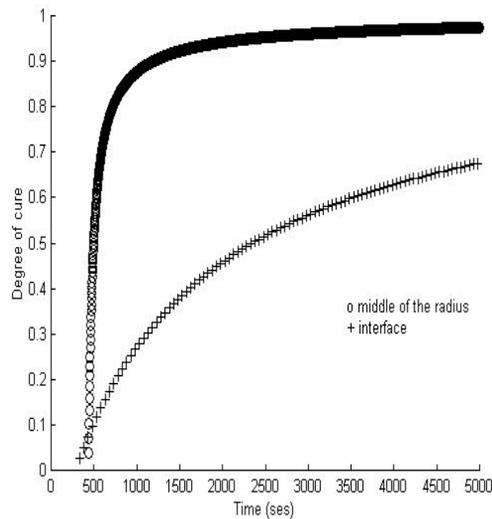

Fig.(6): State of cure-time history at the interface and the middle of the sample (B).

الموديل الرياضي لعملية تقسية متراكبات الايبوكسي في قوالب اسطوانية تحت ظروف ثبوت درجات الحرارة

سعد رحيم سلطان   علي محمد حميد   د.عدنان عبد الجبار عبد الرزاق

مدرس مساعد   مدرس مساعد   مدرس

قسم الهندية الكيمياوية _ الجامعة التكنولوجية

الخلاصة

في هذا البحث تم ايجاد موديل رياضي لعملية انتقال الحرارة المصاحبة لتقية المواد المتراكبة المتكونة من الاليف المدعمة بالراتنجات المطاوعة للحرارة والموضوعة في قالب اسطواني مع تثبيت درجة حرارة التقسية . يشمل هذا الموديل على حل معادلة الطاقة (Unsteady state energy equation) مع اضافة حدود تمثل الحرارة المتولدة(Generated heat) نتيجة تصلب الراتنج الباعث للحرارة تم حل الموديل الرياضي بطريقة (finite element) . نتيجة حل الموديل الرياضي تم حساب درجات الحرارة ودرجة التقسية كدالة من الزمن والموضع.لقد وجد ان درجة الحرارة في منتصف طبقات المادة المتراكبة تزداد حتى تصل الى درجة حرارة التقسية. ونتيجة للحرارة المتولدة من تفاعل التقسية الباعث للحرارة ولكون الموصلية الحرارية للراتنج واليف واطئة ولا يمكن ازالة الحرارة بصورة جيدة لذلك سوف ترتفع الحرارة في منتصف الطبقات والذي سوف يولد المزيد من الحرارة .

الكلمات الدالة : الموديل الرياضي , التقسية , متراكبات , راتنج الايبوكسي , قالب اسطواني.