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Mathematical Model of Autoclave Curing of Epoxy Resin Based Composite Materials

Adnan A. Abdul Razak * **Najat J. Salah** * **Hassen Sh. Majdi** **

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Abstract

Polymer matrix composites using thermosetting resins as the matrix are increasingly finding use in several applications. Process modeling describing the governing curing has played an important role, in improving the fundamental understanding and development of composite fabrication techniques. In present work, the thermokinetic involved in the autoclave curing of fiber-reinforced epoxy has been studied by means of a computer program, using the transient heat conduction equation coupled with kinetic equation, and the initial and boundary conditions. In the analysis the cure assembly is assumed to consist of a tool plate, composite laminate. The temperature distribution and the degree of reaction are obtained as a function of position and time.

Keywords: Mathematical model, curing, epoxy resin

الموديل الرياضي لعملية إنضاج متراكبات الأيبوكسي في جهاز الاوتوكليف

الخلاصة

يشهد استخدام المواد المتراكبة الايبوكسية تطورا كبيرا. ويلعب الموديل الرياضي لعملية الإنضاج دورا كبيرا في فهم هذه العملية وتحسينها وتطويرها .
تم أيجاد مود يل رياضي يقوم بحساب درجات الحرارة و درجة الإنضاج كدالة من الزمن و الموضع ويشمل هذا الموديل على حل معادلة الطاقة (un steady state energy equation) مع إضافة حدود تمثل الحرارة المتولـــدة (generated heat) نتيجـــة تصلب الايبوكسي . ويعتمد الموديل الرئيسي على موديل ديناميكية التفاعل الأيبوكســـي والذي تم دراسته باستخدام جهاز المسح التفاضلي .

* Chem. Eng. Dep., University of Technology, Baghdad -Iraq
** Ministry of Science and Technology, Baghdad -Iraq

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2412-0758/University of Technology-Iraq, Baghdad, Iraq

Nomenclature

A	pre-exponential factor,
C_p	specific heat, J/g ^{o}C
E	activation energy, Kj/mole
h	thickness of laminate, mm
H_r	total heat of reaction, j/g
k	reaction rate constant, s^{-1}
K	thermal conductivity, Kcal/h ^{o}C
m&n	empirical exponents in the cure kinetic model
q	the heat generated by the curing resin, j/g sec
R	gas constant, j/mol K
t	time, sec
T	temperature, ^{o}C
x,y,z	rectangular coordinates
	Greek Letters
α	degree of cure
a_m	maximum degree of cure.
r	density, Kg/m^3
j	volume fraction of fibers.
	Subscripts
c	curing
f	fiber
m	Matrix
r	resin
o	Initial

1. Introduction

Thermosetting-matrix composite structures are manufactured by subjecting a fiber/resin lay up to a prescribed temperature cycle, which initiates and sustains an exothermic, crosslinking, chemical reaction, called the cure.

The cure process irreversibly transforms the soft fiber/resin matrix to a hard structure component, it is a critical step in that the temperature and cure histories, and their spatial variation with in the lay up cross section, during the process directly influence the final quality of composite products.[1] At the initiation of a typical process, the outer layers of the laminate, which are subjected to the external heating, cure more rapidly, than the inner layers, whereas, as the cure progress, temperature of the inner layers may exceed these of the outer layers due to the exothermic cure reaction and low thermal conductivity of the composite.

Uncontrolled polymerization may cause undesired and excessive thermal variation that could induce microscopic defects in the network structure of the matrix phase, and macroscopic defects such as voids, bubbles and debonded broken fibers.[2,3]. Processing of polymeric composites is based on thermoset matrixes therefore requires optimization of the cure cycle parameters as well as adequate formation of the reacting system as a function of the geometry of the parts.

The main structure of the master model is formed by an energy balance which takes into account the accumulation of the heat in the composite, the heat generated by the chemical reaction, the heat conduction in the material and the dissipation at the composite skin. The energy balance equation is coupled with a suitable expression for the kinetic behavior of the chemical reactions accounting for diffusion control effects. The solution of the complete mathematical system gives the temperature and degree of reaction as function of time and position. One of the main advantages of this mathematical model is one is able to give this information, because it is possible but difficult to determine the profile of temperature from experiments and it is quite impossible to measure the profiles of state of cure within laminate.

2. Theory

2.1 Physical Aspects

Fig. (1) shows a schematic of an autoclave process for fabricating thermosetting matrix composites. In this process, a laminate lay-up consisting of multiple layers of the fiber-resin is placed upon a smooth tool surface and covered with successive layers of an absorbent material (glass bleeder fabric), a fluorinated film to prevent sticking, and, finally, with a vacuum bag. The entire system is placed into an autoclave, vacuum is applied to the bag, and the temperature is increased at a constant rate in promote the resin flow and polymerization.

The principal physical events occurring during a cure cycle are illustrated in Fig. (2) [3]. The viscosity

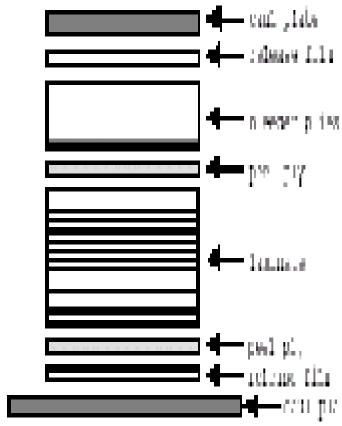

Figure (1): A schematic of an autoclave

initially decreases with time as the temperature is increased, but

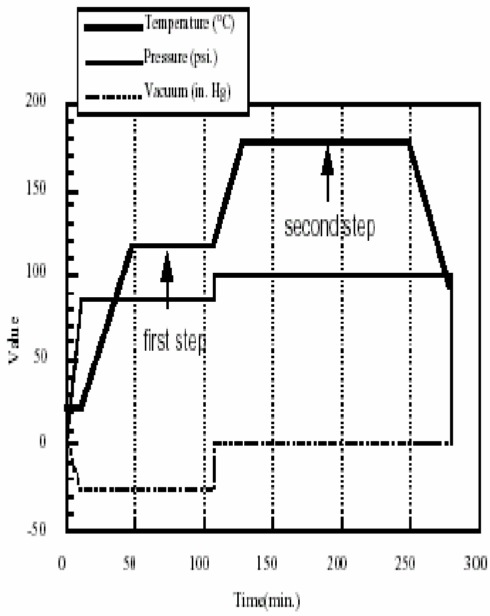

Figure (2): A diagram of cure

the reaction is still not activated. During this first stage, sorbet volatilize should start to diffuse out of the resin. When the viscosity reaches its minimum and then begins to increase, due to the occurrence of the thermosetting reactions, trapped bubble must be allowed to leave the composite. Pressure, which drives the resin flow, should be correctly applied to remove the excess resin and trapped bubbles. [2, 4]

2-3 Previous Work

Most of the research efforts have been directed towards proposing/ improving process models and assessing the effects of the process parameters on the cure.

Mallick has studied the effect of cure cycle time, temperature, preheating and post-cooling on mechanical properties of continuous as well as chopped glass fiber reinforced polyester and vinyl ester systems. Internal heat generation due to curing reaction causes high thermal gradients across the thickness, the flexural and interlaminer shear strengths are strongly dependent on the mold cycle time.[7]

Barone and Caulk studied the influence of the applied heat on the curing process of epoxy resin and proposed a thermo chemical model based on a two-dimensional heat conduction equation with internal heat generated by the exothermic chemical reaction.[8]

Loos and Springer developed resin flow and void model of the curing process of the epoxy resin. The resin velocity was related to the pressure gradient, fiber permeability, and resin viscosity through Darcy's law. [9]

Gutowski, Morigaki, and Cai developed three dimensional flow and one-dimensional consolidation models of the composite. [10]

3. Mathematical Model

3.1 Assumptions

In order to build up a model for the cure in autoclave the following assumptions are made [3, 11]

1. Negligible temperature change during flow.
2. Homogenous and well mixed reaction system.
3. One dimensional heat conduction, the laminate thickness is small compared to the other dimensions.
4. Constant mould wall temperature through the entire cure.
5. The density r and the specific heat C_p are computed as proper average of single resin and fiber property values.

$$r = (1 - y) r_r + y r_f \quad (1)$$

$$C_p = r_r / r (1 - y) C_{pr} + r_f / r y C_{pf} \quad (2)$$

where y is the volume fraction of fibers and the subscripts "r" and "f" refer to the resin and fiber respectively?

6. The composite thermal conductivity K in the direction perpendicular to the plane of the laminate is computed using Halpin Tasi equation. [12]

$$K = K_r (1 - B_1 B_2 y)/(1 - B_1 y) \quad (3)$$

where

$$B_1 = (K_f / K_r - 1)/(K_f / K_r + B_2) \quad (4)$$

$$B_2 = 1/(4 - 3(1 - y)) \quad (5)$$

7. The experimental evidence, moreover, suggested that there is no variation in these properties with the temperature and/or degree of cure should be considered.

3.2 Mathematical Treatment

With these assumptions, the thermal model consists of solving the energy equation in Cartesian coordinates, for the temperature distributions in the lay-up cross-section. The governing equation for one dimensional heat transfer, and accounting for the heat generation due to the exothermic cure reaction in the composites may be written in the form developed by Bejan: [13]

$$r c_p \frac{dT}{dt} = K \frac{d^2T}{dx^2} + r \frac{dH}{dt} \qquad (6)$$

where $\frac{dH}{dt}$ is the rate of heat generated by the chemical reaction and is defined as follows; Kim [14]

$$\frac{dH}{dt} = R \; H_r \qquad (7)$$

where R is given by the following eq. and H_r is the total heat of reaction during cure.

$$R = \frac{da}{dt} = k(1-a)^n a^m \qquad (8)$$

where a is the degree of cure, t is time, k is the kinetic rate constant, n & m are the reaction order.

A model for the dependence of the cure rate on the temperature and on the degree of cure reaction should then be specified. Experimentally, one of the simplest ways of found kinetics model is using differential scanning calorimetry (DSC). [3]

In equation (8) a kinetic rate constant is given by:

$$k = A \exp\left(\frac{-E_a}{RT}\right) \qquad (9)$$

where A is frequency factor or pre-exponential factor and E_a is the activation energy.

3.3 Numerical Analysis

For the numerical solution of the mathematical model presented equations (6, 8), the structure of the model can be summarized as follows:

1. Equation (6) is disretized using forward finite differences. Mathews and Fink [15] have summarized this method.
2. At each time interval the value of R is computed from equation (8) by using Runge kutta method.

Our own model is solved by build up computer program in Matlab version 5.1.

The following initial and boundary conditions are used in the model

$$t = 0 \qquad x \;^3\; 0 \qquad a = 0 \quad T = T_0 \qquad (10)$$

$$t > 0 \quad x = 0 \qquad T = T_c \qquad (11)$$

$$t > 0 \quad x = \frac{h}{2} \qquad T = T(t) \qquad (12)$$

where T_0 is the initial temperature, T_c curing temperature, $\frac{h}{2}$ the center of the laminate.

4. Results and Discussion

In order to develop a master model for the simulation of cure process of epoxy based composite, a kinetic sub-model must be provided to described the polymerization and cross linking reactions. The degree of the cure as a function of time obtained from isothermal DSC experiments carried out at four different temperatures is shown in Fig (3) has been given in previous paper. [16] Since, in isothermal processes at low temperature, the polymerization reactions are not completed, the kinetic analysis of the isothermal DSC scans has been performed by modifying the model used by Pusatcioglu, et. al. [17] and O'Brien, and White [18] accounting for diffusion control effects:

$$da / dt = K a^m (a_m - a)^n \qquad (13)$$

In equation (13) a_m denotes the final degree of reaction in isothermal DSC scans. O'Brien and White [17] obtained relationships between temperature of cure and final degree of reaction as shown in fig (4)

The proposed model was applied to the evaluation of the processing of laminate based on Epon828-TETA, which have been given in previous paper.[16] Unidirectional XA-S carbon fiber, woven tape (340 g/m^2), 100 mm width was selected as the reinforcing component of the composite system.

The DSC therogram has been used to evaluate the overall heat of reaction and kinetic parameter of the cure reaction reported in Table (1).

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

Property	unit	value
Density of carbon fiber r_f	g/cm^3	1.8
Density of epoxy resin r_r	g/cm^3	1.1
Volume fraction of fibers j_f		0.3
Thermal conductivity of the matrix K_r	Kcal/h m ^{o}C	0.348
Thermal conductivity of the fiber K_f	Kcal/h m ^{o}C	17.43
Specific heat of matrix C_{pr}	J/g ^{o}C	1.2
Specific heat of fiber C_{pf}	J/g ^{o}C	0.712
Result of the calorimetric characterization		
Heat of reaction H_r	*J/g*	275
Activation Energy ΔE	*Kj/mol*	19441
Kinetic constant k	1/s	6.25
Reaction order: $m = 0.417 + 0.010552T - 0.000141T^2$ $n = 0.520 + 0.024408T - 0.000137T^2$		

Generally, the laminate is placed in the autoclave at room temperature and the system is heated at a controlled rate Vt, in this case the external temperature is given by:

$$T_e = T_o + V_t t \qquad (14)$$

where T_o is the room temperature.

Fig.(5) shows the variation of the temperature as a function of the processing both on the surface and on the center of the laminate at the four different curing temperatures (50, 60, 70, and 80 o C).

Due to the contribution of the thermal conductivity of the fiber the temperature at the center of the laminate rapidly reaches the external imposed temperature, and increases as a consequence of the imbalance between the rate of heat generation by exothermic reaction of the resin and the heat removed by the composite, because of the low thermal conductivity of the resin and fiber.

The increase in the temperature at the center increases the resin reaction rate, which in turn generates more heat. The resulting 'exotherm' can cause severe damage to the part if not controlled properly.
This behavior agrees with the results obtained by Kenny et. al. [3, 19] and El Brouzi, Bouzon, and Vergnaud,. [20]

The results of the degree of cure as a function of the process time are shown in Fig (6), for the material at the center and at the external surface. The resin placed on the surface follows kinetics governed by the isothermal imposed temperature, while the resin at the center, the reaction starts later, the temperature rapidly reaches the external temperature and increase (as discussed in previous section), so kinetics are accelerated because of higher temperature reached at the center.

5. Conclusion

A general model for prediction the temperature and the extent of the reaction across the laminate thickness during curing process of epoxy based composite has been developed.
Thermal characterization of the reacting systems and kinetic model gives the input data necessary for the mathematical model.

It was found that the temperature at the central of the laminate increases up to the external imposed temperature, because of the low 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. The resulting 'exotherm' can cause severe damage to the part if not controlled properly.

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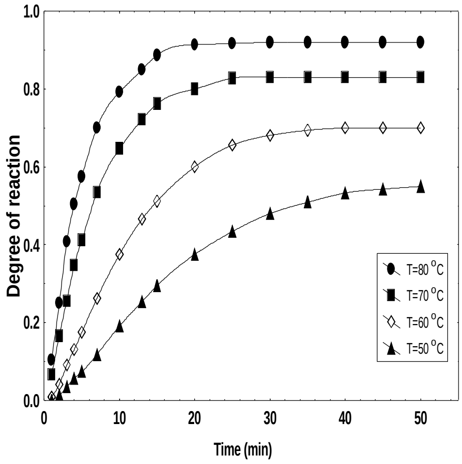

Figure (3): Degree of cure as a function of time from isothermal DSC experiments at four different temperatures. (16)

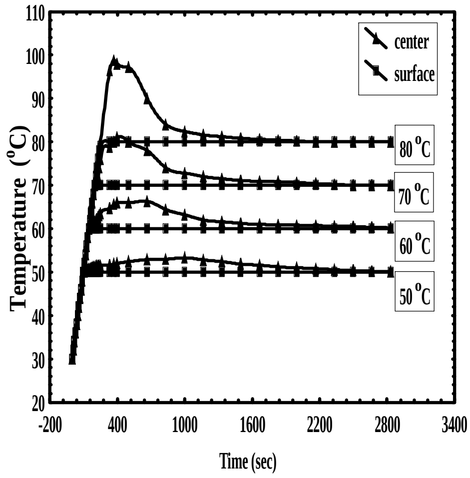

Figure (5): The temperature versus time at the center of composite and on the surface curing temperatures are (50, 60, 70 and 80 °C).

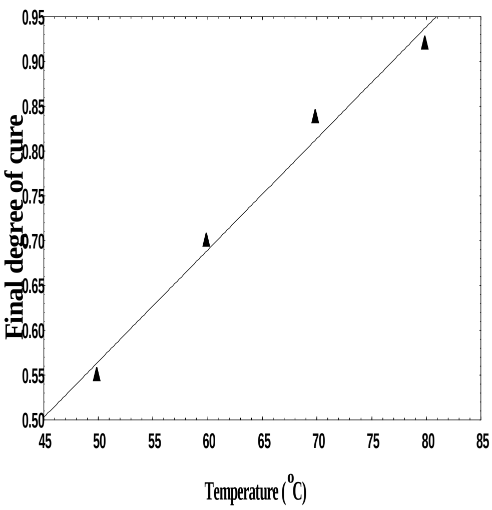

Figure (4): Final degree of cure obtained in isothermal DSC experiments as a function of test temperature. (16)

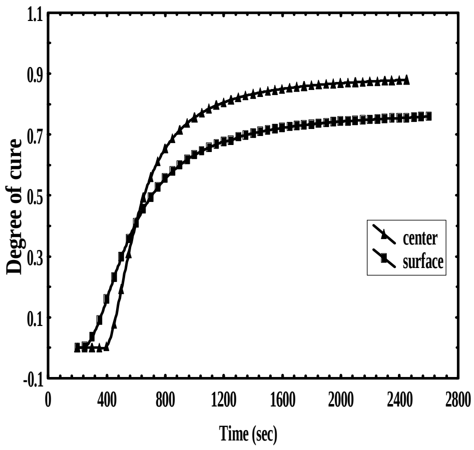

Figure (6): Degree of cure versus time at the center and on the surface of the composite cured at 70 °C.