Tikrit Journal of Eng. Sciences/Vol.17/No.1/March 2010, (1-9)

Mathematical Model For Autoclave Curing Of Unsaturated Polyester Based Composite Materials

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Abstract

Heat transfer process involved in the autoclave curing of fiber-reinforced thermosetting composites is investigated numerically. A model for the prediction of the temperature and the extent of the reaction across the laminate thickness during curing process in the autoclave of unsaturated polyester based composite has been developed. 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. It was found that the temperature at the central of the laminate 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.

Key words: Mathematical model, Autoclave, Curing, Composite, Unsaturated poly ester.

نمذجة رياضية للانضاج بالاوتوكليف لراتنج البولي استر لمواد متراكبة

الخلاصة

تم دراسة عملية انتقال الحرارة في جهاز الاتوكليف لإنضاج المواد المتراكبة باستخدام راتنج البولي أستر الغير المشبع حيث تم أيجاد نموذج رياضي يقوم بحساب درجات الحرارة و درجة الإنضاج كدالة من الزمن و الموضع لعمليه إنضاج البولي استر غير المشبع في جهاز الاوتوكليف ويشمل هذا النموذج على حل معادلة الطاقة (unsteady state energy equation) مع إضافة حدود تمثل الحرارة المتولدة (generated heat) نتيجة تصلب البولي أستر غير المشبع. لقد وجد ان درجه الحرارة في منتصف طبقات المادة المتراكبة تزداد حتى تصل إلى درجه حرارة الإنضاج . ونتيجة للحرارة المتولدة من تفاعل الإنضاج الباعث للحرارة ، و لكون الموصلية الحرارية للراتنج والليف واطئة ولايمكن إزالة الحرارة بصوره جيده لذلك سوف ترتفع الحرارة في منتصف الطبقات والذي سوف يولد المزيد من الحرارة .

Nomenclature

A	Pre-exponential factor,
C_f	Specific heat, J/g ^oC Specific heat, J/ ^oC
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 ^oC
m&n	Empirical exponents in the cure kinetic model
p	Intercept in Eq. (15)
q	The heat generated by the curing resin, j/g sec

R	Gas constant, j/mol K
S	Slop in Eq. (15)
T	Time, sec
T	Temperature, ^{o}C
x,y,z	Rectangular coordinates

Greek Letters

α	Degree of cure
ρ	Density, Kg/m^3
φ_f	Volume fraction of fibers.

Introduction

Autoclave curing is a process used to produce fiber-reinforced polymeric parts in final shape. The simulation and optimization of autoclave processing have seen widespread application in industry as a mean to understand and improve product quality.

During processing, the autoclave is heated according to a predetermined temperature cycle and, at the same time, pressurized according to a predetermined pressure cycle. The applied heat increases the temperature in the composite, resulting in changes in the molecular structure of the resin and, correspondingly, in resin viscosity. When the resin viscosity has become sufficiently low, the applied pressure squeezes excess resin from the composite into a bleeder ply as the laminate consolidates. The resin then cures and cross-links, producing a rigid finished part.

Modeling of the curing process is required to predict the variation of different properties of the material and help control the process better .One of the main advantages of the mathematical model is to be able to give information about the profiles of temperature and the state of curing developed through the laminate during curing process. It is possible but difficult to determine the profile of temperature from experiments, and it is quite impossible to measure the profile of state of cure within the sample [1].

Δ_{Tmax}	Maximum temperature difference between the surface and center of the laminate.

Subscripts

C	composite
F	fiber
r	resin
$\circ$	initial

Process Model

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.[2,3] .

The entire system is placed into an autoclave; the process consists of exposing the assemblage above to a prescribed cure temperature cycle, which transforms the soft fiber- resin mixture to a structurally hard product. The magnitudes of the imposed temperature variation and the duration constitute important design parameters affecting the product quality and the process productivity.

The dominant physical phenomena involved in the cure process are: (a) the chemical reactions affecting the curing process, and (b) the heat transfer associated with the heating of the fiber/resin mixture, including the heat of the exothermic cure reaction.

Kinetics Model

Unsaturated polyester resins are commonly used a matrix for fiber reinforced composites. Commercial systems are generally supplied as relatively low molecular, unsaturated linear polyesters dissolved in a polymerizable monomer such as styrene, providing cross-linking units by reacting with unsaturation of the resin in a radical addition reaction. The complex chemistry of the unsaturated polyester reactions has been reported in the literature[4]. First, the initiator is decomposed leading to the formation of free radicals which progressively reduce the inhibitor concentration .The cure reaction are activated only when the inhibitor is exhausted (induction time); polyester and styrene radicals are first formed and then larger sized active molecules are generated. Finally, the termination reactions progressively reduce the active radical concentration and consequently the polymerization rate. Kenny[5] and Barton[6] have studied the kinetics of the curing reactions of thermosetting polyester by means of differential scanning calorimetry (DSC), the degree of cure can be modeled simply as an autocatalytic reaction described by the (Gonzalez-Romero) relationship [7]

$$\frac{d\alpha}{dt} = k\alpha^{m}(1-\alpha)^{n} \quad \text{………………. (1)}$$

Kamal[8] and Han [9] proposed a slightly more complex kinetic model

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^{m})(1-\alpha)^{n} \quad \text{………. (2)}$$

in which k_1 and k_2 are rate constant given by:

$$k_i = A_i.\exp(\frac{-E_i}{RT}) \quad \text{i=1, 2 ……..(3)}$$

Where A is the pre-exponential factor, E is the activation energy, and R is the gas constant, and m and n are constant which are independent of temperature.

Thermal Model

The thermal model consists of solving the energy equation in Cartesian coordinates for the temperature distribution in the lay-up cross section.

Assumptions

In order to build up a model for the cure in autoclave the following assumptions are made: [10, 11]

1. Negligible temperature change during flow.
2. Homogenous and well mixed reaction system.
3. Temperature and degree of cure are functions only of time and direction normal to the part surface. The composite is an infinite medium and can therefore be assumed to be one dimensional. The geometry of the system is shown in Fig.(2).
4. Constant mould wall temperature through the entire cure.
5. The density ρ_c and the specific heat C_{pc} are computed as proper average of single resin and fiber property values.

$$\rho_c = (1-\psi)\rho_r + \psi\rho_f \quad \text{………….. (4)}$$

$$C_{pc} = \rho_r / \rho(1-\psi)C_{pr} + \rho_{f/}\rho\psi C_{pf} \quad \text{.. (5)}$$

Where ψ 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_c in the direction perpendicular to the plane of the laminate is computed using Halpin-Tasi equation [12]

$$K_c = K_r(1-B_1B_2\psi)/(1-B_1\psi) \quad \text{…... (6)}$$

Where

$$B_1 = (K_f / K_r - 1)/(K_f / K_r + B_2) \quad \text{…..(7)}$$

$$B_2 = 1/(4-3(1-\psi)) \quad \text{……………….(8)}$$

7. All material properties (specific heat, density, thermal conductivity) are constant during the curing process.

8. Deformation of the material is negligible.

9. There is no convection heat transfer.

Mathematical Treatment

The governing equation for transient heat conduction, including internal heat generation due to the exothermic cure reaction, may be written as: [13]

$$\rho_c c_{p_c} \frac{dT}{dt} = K_c \frac{d^2T}{dx^2} + \frac{dq}{dt} \quad \text{........(9)}$$

The heat generated by the curing resin, dq/dt, is calculated within the simulation according to Eq. (9), which assumes that the heat released by the resin is proportional to the change in the resin's degree of cure, dα/dt The fractional change in degree of cure is multiplied by the resin's total heat of reaction, H_r. The result is then weighted by the mass fraction of the resin within the composite, φ_f.

$$\frac{dq}{dt} = \varphi_f H_r \frac{d\alpha}{dt} \quad \text{................(10)}$$

The cure rate of the resin, as shown in Eq. (10). is modeled according to the empirical autocatalytic model used by Kamal [8] and popularized by many other researchers [14, 15] to describe free-radical polymerization.

Numerical Analysis

For the numerical solution of the mathematical model presented Eqs.(9, 10) the structure of the model can be summarized as follows:

1. Eq. (9). is discretized using forward finite differences [16]

2. At each time interval the value of dq/dt is computed from Eq. (10) by using Runge Kutta method.

The following initial and boundary conditions are used in the model

$$t = 0 \quad x \ge 0 \quad \alpha = 0 \quad T = T_0 \quad \text{.......(11)}$$

$$t > 0 \quad x = 0 \quad T = T_c \quad \text{...........(12)}$$

$$t > 0 \quad x = \frac{h}{2} \quad T = T(t) \quad \text{..........(13)}$$

Where T_0 is the initial temperature, T_c curing temperature, (h/2) the center of the laminate.

The model is solved by build up computer program in Mat lab version 5.3

Results and Discussion

The proposed model was applied to evaluate processing of laminates based of two different polyester mixtures composite:

1. System (A) consist of : Commercial grade thermoset DSM produced by DSM Italia based on mixtures of relatively low molecular weight unsaturated linear polyester dissolved in a polymerizable monomer such as styrene, thickening agents, low profile additives, inert and reinforcing fillers with 25% of Glass Mat Fibers [4] and

2. System (B): The composite based on slurry with the following typical parts by weight [17] : Polyester resin (100), Catalyst (1.2), Zinc stearate (4.0), Calcium carbonates (190), and Magnesium hydroxide (3.5) On this slurry were deposited 25 mm of hopped glass strand to make a final glass content of 30% by weight.

For system (A) the curing temperature is 60 °C, but for system B the curing temperature is 150 ° C (as recommended by suppliers).

In order to develop a master model for the simulation of cure process of Unsaturated Polyester based composite, a kinetic sub-model must be provided to described the polymerization and cross linking reactions.

For system (A) the degree of the cure as a function of time obtained from isothermal DSC experiments carried out at four different temperatures. 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 [18] and Denils [19] accounting for diffusion control effects:

$$d\alpha / dt = K\alpha^{m}(\alpha_{m} - \alpha)^{n} \quad \ldots\ldots\ldots\ldots.(14)$$

In Eq. (14).α_m denotes the final degree of cure in isothermal DSC scans.

$$\alpha_{m} = p + sT \quad \ldots\ldots\ldots\ldots\ldots\ldots(15)$$

For system (B), Eqs. (2) and (3) had been used as a kinetic model to describe the polymerization and cross linking reactions.

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

The variation of the temperature as a function of processing time, on the surface and center of the laminate, for the two systems A and B are showing in Figs. (3 and 4) respectively.

In general for the thermosetting based composites system, due to the contribution of the thermal conductivity of the fibers, the temperature at the center of the laminate rapidly reaches the external imposed temperature and increase as a consequence of the imbalance between the rates of heat generation (due to exothermic polymerization reaction) and the thermal diffusivity of the composite (composite had low thermal conductivity), when this two quantities are comparable, the temperature profile reaches a maximum.

The resulting peak temperature is set up across the laminate, This behavior agrees with the results obtained by Kenny [4], Nixon [17] and Kosar. [11]

A laminate prepared using a system (A) resin shows a more intense temperature at the center, comparable to the system (B), due to the higher value of the resin reactivity as a consequence of the sudden acceleration of the reaction. System (A) shows a higher value of the temperature peak ($\Delta T_{\max}$ =95 ^{o}C), while for system (B) ($\Delta T_{\max}$ =18 ^{o}C), the smaller area under the curve relative to system (B) reflects the lower activation energy for the reaction of polymerization of this system.

The results of the degree of cure as a function of the process time are shown in Figs 5 and 6, for the material at the center and at the external surface also in this case the effect of the different values of the reaction kinetics are evident.. 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.

It is interesting to note that the value and the position of the maximum temperature reached in the laminate during the isothermal cure does not only depend on the heat of reaction but is also strongly influenced by the value of the kinetic parameters and the thermal diffusivity of the system.

Conclusions

1. A general model for prediction the temperature and the extent of the reaction across the laminate thickness during curing process of unsaturated polyester based composite has been developed.
2. Thermal characterization of the reacting systems and kinetic model

gives the input data necessary for the mathematical model.

3. It was found that the temperature at the central of the laminate, 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 increase 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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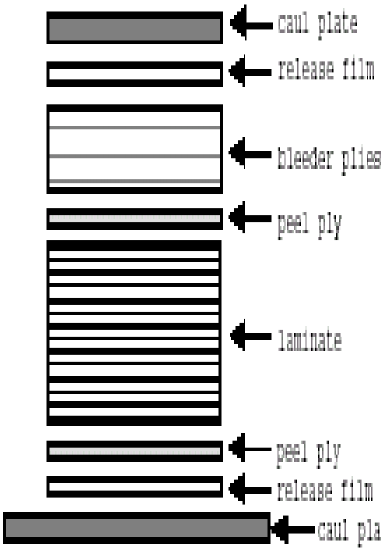

Fig.(1) A schematic of an autoclave

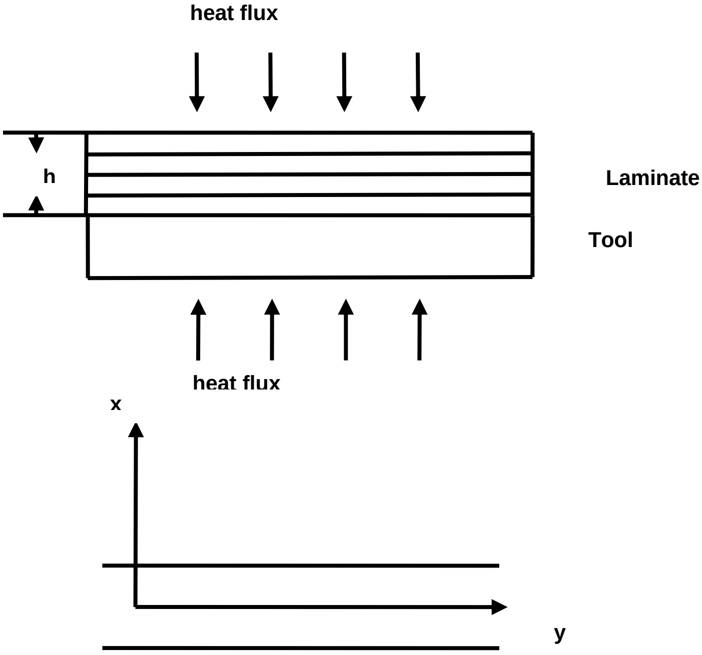

Fig. (2)   Sketch of laminate geometry

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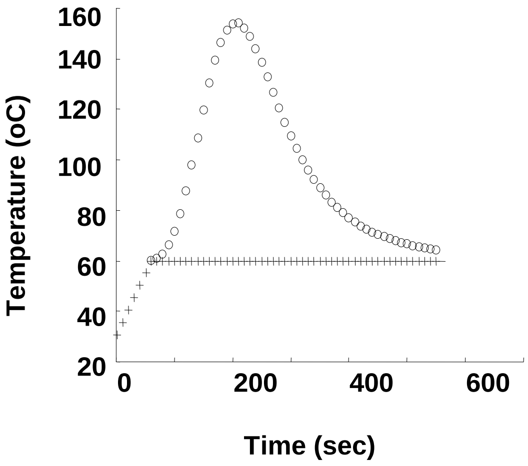

Fig. (3) The temperature versus time at the center of composite and on the surface, curing temperature is 60 ^oC for system A.

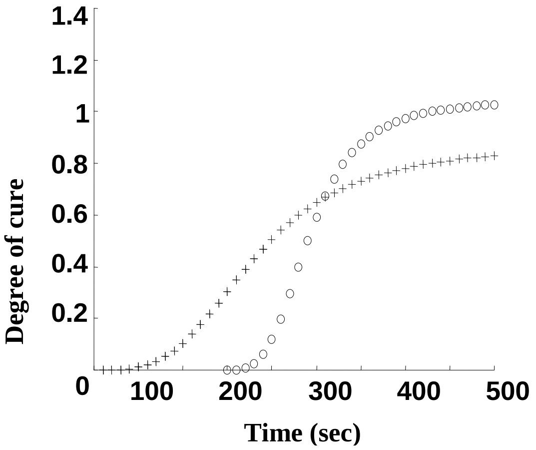

Fig. (5) Degree of cure versus time at the center and on the surface of the composite cured at 60 ^oC for system A

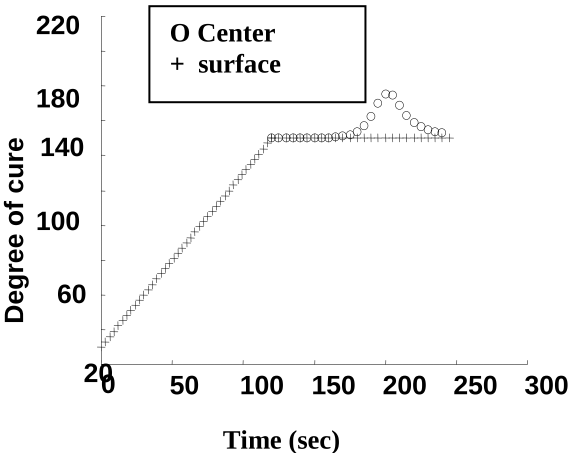

Fig. (4) The temperature versus time at the center of composite and on the surface, curing temperature is 150 ^oC for system B.

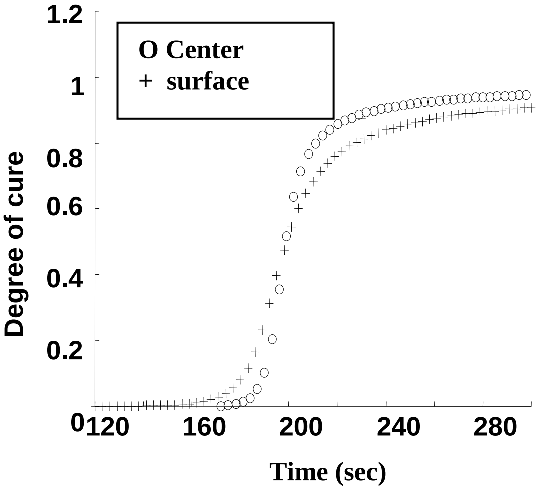

Fig. (6) Degree of cure versus time at the center and on the surface of the composite cured at 150 ^oC for system B

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

Property	**Unit**	**Values of systems**	
		A	**B**
Density ρ_c	g/cm^3	1.35	1.84
Thermal conductivity K_c	W/m ^{o}C	0.2	0.63
Weight fraction of fibers φ_f	%	30%	25%
Specific heat c_{pc}	J/g ^{o}C	1.72	1.35
Result of the calorimetric characterization			
Heat of reaction H_r	J/g	330.7	75
Activation Energy E	Kj/mol	35.3	
Kinetic constant k	Ln (1/s)	8.9	
System A Reaction order: n=1.35 Reaction order: m=0.65 Coefficient of eqn (15): p= -3 Coefficient of eqn (15) (K^{-1}): s=0.01164 System B Eqs. (2 and 3) A_1 (s^{-1})*10^{14} = 1.22 A_2 (s^{-1})*10^5 = 25.9 E_1 (Kj/mol) = 140 E_2 (Kj/mol) =55 Reaction order: n=1.3 Reaction order: m=2.7			