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Modeling of Conventional Autoclave Curing of Unsaturated Polyester Based Composite Materials as Production Process Guide

Adefemi Adeodu[1, *], Christopher Anyaeche[1], Oluleke Oluwole[2], Samuel Afolabi[3]

[1]Department of Industrial and Production Engineering, University of Ibadan, Ibadan, Nigeria

[2]Department of Mechanical Engineering, University of Ibadan, Ibadan, Nigeria

[3]Department of Mechanical and Mechatronics Engineering, Afe Babalola University, Ado-Ekiti, Nigeria

Email address:

femi2001ng@yahoo.com (A. Adeodu), osita.anyaeche@ui.edu.ng (C. Anyaeche), oluwoleo2@asme.org (O. Oluwole), afowolesam@yahoo.com (S. Afolabi)

Abstract: Modeling of composite curing process is required prior to composite production as this would help in establishing correct production parameters thereby eliminating costly trial and error runs. Determining curing profile temperatures from experiment is a huge challenge which in itself is like re-inventing the wheel of trial and error, when mathematical models of physical, chemical and kinetic properties of the constituent materials could be used in modeling the cure situation to some degree of trust. This work has modeled two types of polymer based composite materials (Aluminum filled polyester and carbon-black filled polyester) representing polymer-metal and polymer-organic composites in order to predict the possible trends during conventional autoclave heating with regards to effect of heating rate on degree of cure of the composites. The numerical models were constructed by taking into account the heat transferred by conduction through the resin/filler mixture, as well as kinetic heat generated by cure reaction. The numerical solution of the mathematical models presented were discretized using forward finite differences of the Runge Kuta Method and finally solved using MATLAB® C programming language. It was observed that Aluminum filled polyester composite responded faster to heat input- induced curing and as such was able to cure faster than polyester –carbon black composite which had much slower cure –heat input response. This implies that in the production process of polymer-organic composites, faster heating rate was necessary to input heat into the process as there was no heat of reaction released during the cure process whereas, polymer-metal composites release heat of reaction contributing to the quick transfer of heat into the metal components causing the metal components to behave as points of adhesion to the polymer matrix thereby necessitating a slower heating rate.

Keywords: Modeling, Polymer- Matrix Composites, Autoclave Curing, MATLAB®

1. Introduction

Thermosetting matrix composites structures are manufactured by subjecting a reinforce matrix to a prescribed temperature cycle, which initiates and maintains an exothermic, cross linking chemical reaction called the cure. The cure process irreversibly transforms the reinforce matrix to a hard structure component, which is a critical step in that the temperature cure histories, and the matrix spatial arrangement during the process directly influence the final quality of composites.

At the initiation of a typical process, the outer layers of the laminate, which are subjected to the external heating, cure faster than the inner layers. As the cure progresses, temperature of the inner layers may exceed 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 such as voids, bubbles and debonded broken reinforcement, in the network structure of

the matrix phase [1] [2]

Processing of polymeric composites is based on thermoset matrices, 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 [3].

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, heat generated by the chemical reaction, heat of conduction in the material and the dissipation at the composite skin [4]. The energy balance equation is couple with a suitable expression for kinetic behavior of the chemical reaction accounting for diffusion control effects [4]. The solution of the complete mathematical system gives the temperature and degree of reaction as function of time. One of the main advantages of this model is the ability to predict the profile temperature and state of cure within the laminate. Modeling of the curing process is required to predict the variation of different properties of the material and control the process better. One of the main advantages of the mathematical model is to obtain information about the profiles of temperature and the state of curing developed through the laminate during curing. It is possible but difficult to determine the profile temperature from experiments, and it is more difficult to measure the profile of state of cure within the sample. 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 [5]. These facts may lead to cracking or crazing [5]. 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. Conventional autoclave curing is the one in which thermal energy is delivered to the surface of the material by radiant or convection heating that is transferred to the bulk of the material via conduction. Many composite materials require a low oxygen curing environment; such an environment is expensive to provide with the conventional methods [6]. These conventional curing methods involve exposing the out surface of the part to an external source of heat. Heat transport to the interior of the part occurs by conduction. This process requires that surface temperature exceed interior temperature for some or all of the production cycle. The rate of heating is dependent on this temperature gradient (i.e., the greater the temperature gradient, the faster the part will be fully heated). Since the polymeric matrix will be damaged if exposed to excessive temperature, the heating rate must be restrained (thus lengthening cycle time) so that no portion of the part exceeds the temperature limit [6].

In addition, some polymers undergo condensation type chemical reactions during curing which produce volatile reactants. The higher exterior temperatures of conventional heating techniques tends to advance curing at the surface of the parts, sometimes forming a hard impermeable skin on the part surface which can trap the volatiles given off during the condensation type reaction. Trapped volatiles usually result in excessive voids and delaminations, essentially rendering the finished part useless [6]. Therefore, it is necessary to develop simplified mathematical models from which the occurrence of such phenomena can be predicted. The aim of the research is developed a simplified mathematical model for curing of polyester based composites using conventional autoclave heating system, so as to be able to predict possible trends during heating with regards to heating rate effect on degree of cure.

2. Literature Review

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 [7] 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 caused high thermal gradients across the thickness, the flexural and inter-laminar shear strengths are strongly dependent on the mold cycle time [7]. Barone and Caulk [8] 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 [9] 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 [10] developed three dimensional flow and one-dimensional consolidation models of the composite.

3. Materials and Method

3.1. Material Composition

The proposed models involve evaluating the processing of laminates based on two different polyester mixtures composites A and B. System A consists of an othophthalic type, thermosetting (M3903) polyester resin. The composite based on slurry with the following typical parts by weight [5] 25% propylene glycol, 25% phthatic anhydride, 16% malic anhydride, 38% styrene monomer and 2% additive making 100% unsaturated polyester resin, inert and reinforcing fillers with 30% of aluminum powder material.

In system B, same composition as in system A is maintained with the exception of aluminum which is totally replaced by N762 carbon –black of same composition as in system A.

The following are the set of sequential steps that would be used for making Aluminum and Carbon black- Polyester resin composites.

i. The fabricated moulds are properly prepared and clean.

ii. Correct amount of fillers (Aluminum and Carbon black) are weighed into containers.

iii. Correct amount of polyester resin, hardener and other additives are weighed and mixed together.

iv. Resin and filler are evenly and slowly mixed with the aid of mechanical blender inside a fume cabinet (for safety) in order to ensure a homogeneous composite mixture.

v. Each mixture is poured into moulds and transferred into the oven. Note, before pouring the mixture into the mould, plate surface would be covered with a glossy paper to facilitate easy removal of the final product after solidification [1] [2] [11].

3.2. Process Model

The schematic diagram of an autoclave process of fabricating the thermosetting matrix composites is described in the figure 1. The process is a laminate consisting of many layers of the filler-resin mixture, which is placed on 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 systems are placed into an autoclave, vacuum is applied to the bag and the temperature is increased at constant rate in order to promote the resin flow and polymerization
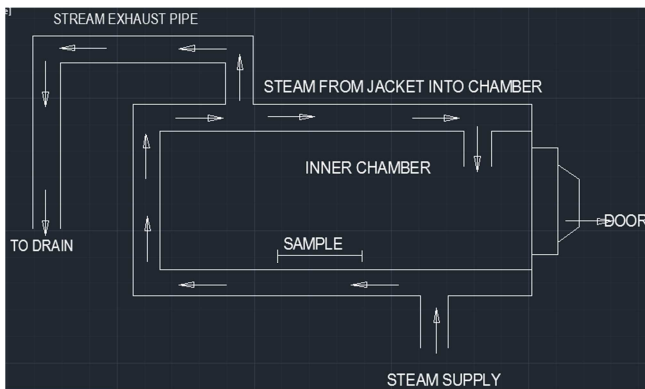

Figure 1. A Schematic Diagram of an Autoclave

3.3. Kinetic Model for Curing

Unsaturated polyester resins are commonly used matrix for particulate 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 literature [12] [13]. 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 and Trivisano [14] and Barton [15] have studied the kinetic 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 [16]. It is the most widely used and describes free radical polymerization [4] [17-18]. It is expressed as;

$$\frac{d\alpha}{dt} = K\alpha n^m (1-\alpha)^n \qquad (1)$$

Kamal [19] and Han et al [20] proposed a slightly complex kinetic model given by

$$\frac{d\alpha}{dt} = K_1 + K_2 \alpha^m (1-\alpha)^n \qquad (2)$$

Where K_1 and K_2 are rate constants given by

$$K_i = A_i Exp^{\left(\frac{E}{RT}\right)}$$
$$i = 1, 2, 3, 4 \ldots \ldots \qquad (3)$$

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

3.4. Thermal Model for Conventional Heating

In order to build up a model for the cure in autoclave, the following assumptions are made [4] [12]
1. Negligible temperature change during flow
2. Homogeneous and well mixed reaction
3. One dimensional heat conduction, the laminate thickness is small compared to the other dimensions
4. Constant mould temperature through the entire cure
5. The density and the specific temperature are computed as proper average of single resin and filler property values

$$\rho_c = (1-\varphi)\rho_r + \rho_f \qquad (4)$$

$$Cp_c = \left\{ \left(\frac{\rho_r}{\rho(1-\varphi)} Cp_r + \frac{\rho_f}{\rho\varphi} Cp_f \right) \right\} \qquad (5)$$

Where φ is the volume fraction of fillers and subscripts r and f refer to the resin and filler respectively.
1. The composite thermal conductivity K in the direction perpendicular to the planes of the laminate is computed using Halpin-Tasi equation [2]

$$K = K_r \left\{ \frac{(1-B_1 B_2 \varphi)}{(1-B_1 \varphi)} \right\} \qquad (6)$$

Where

$$B_1 = \left\{ \frac{(K_f / K_r - 1)}{(K_f / K_r + B_2)} \right\} \qquad (7)$$

$$B_2 = \left\{ \frac{1}{(4-3)(1-\varphi)} \right\} \tag{8}$$

2. The experimental evidence, more over suggested that there is no variation in these properties with the temperature or degree of cure

With these assumptions, the thermal model consists of solving the energy equation in Cartesian coordinates, for the temperature distributions in the laminate cross section. The governing equation for one dimensional heat transfer, also account for the heat generation due to the exothermic cure reaction in the composites may be written in the form developed by Bejan [21]

$$\rho C_p \frac{\partial T}{\partial t} = K \frac{\partial^2 T}{\partial x^2} + \rho \frac{\partial H}{\partial t} \tag{9}$$

Where $\frac{dH}{dt}$ the rate of heat is generated by the chemical reaction and is defined as follows, Kim [22]

$$\frac{dH}{dt} = RH_r \tag{10}$$

Where R is given by the equation described by (11) and Hr is the total heat of reaction during the cure

$$R = \frac{d\alpha}{dt} = K(1-\alpha)^n \alpha^m \tag{11}$$

Where α is the degree of cure, t is time, K is the kinetic rate constant, n and m are the order of reaction. In equation (11), the kinetic rate constant is given by

$$K = A\exp(\frac{-Ea}{RT}) \tag{12}$$

Where A is the pre-exponential factor and Ea is the activation energy.

Numerical Analysis

For the numerical solution of the mathematical model presented equations (9) and (11), the structure of the models can be summarized as follows:

1. Equation (9) is discretized using forward finite differences, summarized by Mathew and Fink [23]
2. At each time interval, the value of R is computed from equation (11) by using Runge Kutta method. These models are solved by buildup computer program in Matlab version 10.1.

The following initial and boundary conditions respectively are used in the model

$$\begin{aligned} \theta(0,x) &= 1 \\ \alpha(0,x) &= 10^{-8} \end{aligned} \tag{13}$$

$$\begin{aligned} \theta(t,1) &= \theta_m = \frac{T_m}{T_0} \\ \tfrac{\partial \theta}{\partial t} &= 0, \; for\, x = 0 \end{aligned} \tag{14}$$

Table 1. Assumed Physico-Chemical parameters used as input data for the model

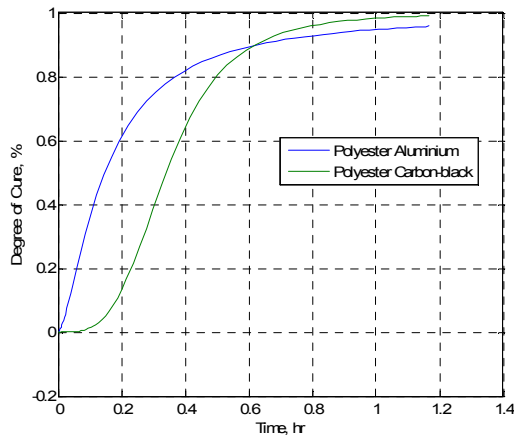| PROPERTY	UNIT	Polyester-Aluminum composite	Polyester-Carbon black
Density (ρ)	kg/m^3	1860	1650
Weight fraction (*wt*)	%	30	30
Specific Heat capacity (C_p)	J/kg. K	1460	1400
Thermal Conductivity (λ)	W/m.K	0.169	0.172
Heat of reaction (ΔH_r)	J/g	285.7	283.8
Activation Energy (E_a)	kJ/mol	42.5	54.2
Arrhenius Constant (Ar)	s^{-1}	2991.4	5995
Kinetic Constant (k)	s^{-1}	2950	
Reaction Order (n)		1.66	1.23
Reaction Order (m)		0.34	0.71
Maximum temperature of the reaction (T_{max})	^{0c}	95	95

4. Discussion of Results

4.1. Determination of Cure Characteristics of Polyester-Aluminum and Polyester-Carbon Black Composites

Cure characteristic measures the cure response of the samples to increasing heat input through the cure cycle [24]. It is the measurement that is usually contrasted with a reference sample. It essentially provides data about the exothermic and endothermic reactions taking place by monitoring the amount of heat added or extracted from the samples to maintain a cure temperature. Points of measureable heat flows indicate the phase transitions of the material.

It was observed that, system A(Polyester-Aluminum composite) was fast curing and increased heat input helped drive the curing process forward, whereas system B (Polyester-Carbon black composite) was slow rising with increased heat input. For instant, 60% of system A had cure within 0.19 hrs, while that of system B at 0.39 hrs. This initial variation in the degree of cure can be traced to the specific heat capacity of the two systems, 1460J/kg. K and 1400J/kg.K respectively which invariably impacted their heat

of reaction as the two systems are heat diffusion controlled process.

Figure 2. *Degree of Cure as a function of curing time for (A) Polyester-Aluminum composite (B) Polyester- Carbon black composite.*

It is observed from the graph that there was overlapping of the two systems at about 0.63 hrs that correspond to about 90% cure for both systems. This was as a result of system A almost set, whereas, system B still undergoing curing. These observations agree with the literatures that material with low dielectric loss factor can only absorb limited amount of heat. Therefore, it was difficult to heat from room temperature to the required temperature [25]. The figure also reveals varying ultimate degree of cure for the two systems. System A ultimate cure of 95% at 0.97 hrs. While system B ultimate cure of 98% at 1.11 hrs. Another reason for the long time of the composites to reach the ultimate cure is that, in conventional heating, heat transfer is very slow because of poor thermal conductivity of the resin.

The cure cycles for the systems are tabulated in the table below.

Table 2. *Cure cycles for autoclave method for (A) Polyester-Aluminum composite (B) Polyester- Carbon black composite.*

material	Tmax (^{0}C)	Actual cure cycle time (hrs)	Ultimate cure (%)
Polyester-Aluminum composite	95	0.97hrs	95
Polyester-Carbon black composite	95	1.11 hrs	98

4.2. Determination of Temperature profiles for Polyester-Aluminum and Polyester-Carbon Black Composites

Temperature control and heating rate show the responses of the systems in the curing process to heat as a function of time. It also determines the achievement of temperature stability and uniformity of heating with composites samples.

Figure 3 shows the heating rate profile of the systems during the curing. The curing in both systems was monitored at the centers of the samples. From this figure, the temperature profile of system A shows much higher heating rate, thus reached curing temperature faster than system B in less than 0.63 hrs. As for system B curing, the average time required to attain the cure temperature was 0.83 hrs. The vast difference between the two cured systems was due to the differences in the specific heat capacity and thermal conductivity of the two systems, which invariably impacted on the heat of reaction of the two systems. The higher specific heat capacity of 1460 J/kg. K and lower thermal conductivity of 0.167 W/m. K of system A compared to system B give rise to high enthalpy of cure associated with system A. Thus a higher temperature at the center of the system is responsible for higher temperature gradient, which in turn increases the rate of cure [26-28].

The figure also shows that there was gradual and proportional increase in temperature as a function of time from the onset of the curing in system A, compared to system B which does not exhibit any rise in temperature until after 0.14 hrs. For system A curing, the temperature was also maintained at 95^{0}C after the cure temperature was reached unlike system B that overshot by +5^{0}C. All these indicated that the process control developed in system A was able to

achieve temperature stability and uniformity in heating of the composite sample. At the end of the curing cycle, as the samples become cured, the temperature profiles gradually decreased. These decreases were most likely due to the formation of thick impermeable skin layer at the surfaces of the samples thus preventing further penetration of heat into the samples thus bringing down the exothermic heat of reaction within the systems [25].
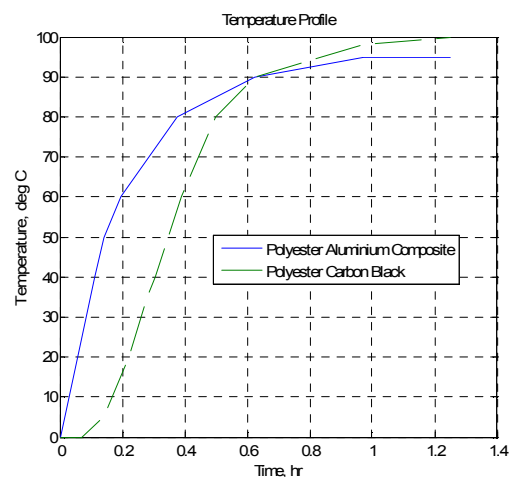
Figure 3. *Temperature Profile during curing of system (A) Polyester-Aluminum composite (B) Polyester- Carbon black composite at different cure temperature under convectional heating*

5. Conclusions

1. Varying ultimate degree of cure (α) was obtained from both composite systems using conventional method of heating

2. Polyester- Aluminum composite reached ultimate cure faster than Polyester-Carbon black composite showing that rigid temperature control procedures must be developed for the production of both composites to suit their cure characteristics.

3. Better control of temperature was observed during the conventional curing of Polyester-Aluminum composite as compared to polyester- Carbon black composite

Symbol

A_r – Arrhenius number, s–1
C_p – Specific heat capacity, at constant pressure, J kg–1 K–1
E_a – Activation energy, kJ mol–1
H_r – Heat of reaction, kJ kg–1
k – Rate coefficient, s–1
R – Gas constant, 8.314 J mol–1 K–1
$r_A = d\alpha/dt$ – rate of reaction, s–1
t – Time, s
T – Temperature, K
T_0 – Initial temperature, 298 K
T_m – Mould temperature, K
T_{max} – Maximum temperature of reaction, K
Greek Symbol
ρ - Density, kg m–3

λ - Heat conductivity, J m–1s–1K–1

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