The American Society of Mechanical Engineers

Reprinted From
HTD-Vol. 241, Advanced Computations in Material Processing
Editors: V. Prasad, and R. V. Arimilli
Book No. G00798 — 1993

OPTIMAL CURE CYCLES FOR THERMOSET COMPOSITES MANUFACTURE

Urmila M. Diwekar
Department of Engineering and Public Policy
Carnegie Mellon University
Pittsburgh, Pennsylvania

Rangarajan Pitchumani
Center for Composite Materials
University of Delaware
Newark, Delaware

ABSTRACT

This paper addresses the problem of determining time-optimal cure cycles for the manufacture of thermoset composites. The cure cycle is considered to be a series of heating and cooling zones, and the optimal values of the end-point temperature and duration of each zone are obtained using numerical optimization techniques, combined with a process model to simulate the cure. The optimal cure schedules incorporate constraints on the maximum material temperatures, the maximum heating and cooling rates, and the maximum difference in the temperatures across the composite cross section. The optimization results are shown to improve significantly upon the cure cycles recommended in the literature and by the manufacturers. Parametric studies are presented in terms of dimensionless groups in order to assess the effects of the product and process variables on the optimal cure cycles.

NOMENCLATURE

B_o dimensionless parameter, defined in Eq. (3)
C_A resin concentration at any time 't' and spatial location (x,y) $[kg/m^3]$
C_{A0} initial concentration of the resin, $[kg/m^3]$
E_1, E_2 activation energies in the kinetics model (Eq. (1)), $[kJ/mol]$
$\overline{E}_1, \overline{E}_2$ dimensionless activation energies defined in Eq. (3)
ΔH_R heat of the cure reaction, $[kJ/kg]$
k thermal conductivity, $[W/m\ K]$
$\overline{k}$ dimensionless thermal conductivity $= k/k_{ey}$
K_1, K_2 frequency factors in the kinetics model (Eq. (1)), $[s^{-1}]$
$\overline{K}_1, \overline{K}_2$ Damköhler numbers, defined in Eq. (3)
L thickness of the composite cross section (Fig. 1), $[m]$
m empirical exponent in the cure kinetics model (Eq. (1))
t time, $[s]$
T temperature in the composite at any time 't' and spatial location (x,y) $[K]$
T_o initial temperature of the composite, $[K]$
v_f fiber volume fraction
W width of the composite cross section (Fig. 1), $[m]$
$\overline{W}$ dimensionless width of the composite cross section $= W/L$
x, y, z coordinate axes
$\overline{x}$ dimensionless spatial coordinate, x/L, measured with the center of the composite cross section as the origin
$\overline{y}$ dimensionless spatial coordinate, y/L, measured with the center of the composite cross section as the origin

Greek Symbols

α thermal diffusivity $= k/(\rho c)$ $[m^2/s]$
ϵ degree of cure $= (C_A - C_{A0})/C_{A0}$
θ dimensionless temperature $= (T - T_o)/T_o$
(ρc) volumetric specific heat, $[J/m^3 K]$
τ dimensionless time $= \alpha_{ey} t/L^2$

Subscripts

$cure$ cure cycle
$crit$ critical value
e effective value
ey effective value along the y- (thickness) direction
i index for cure cycle stage i
max maximum value
min minimum value
x along the width of the cross section (x-direction)
y along the thickness of the cross section (y-direction)

INTRODUCTION

Manufacturing a reinforced thermoset composite involves many steps, of which the cure is the most critical. The cure step involves 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 magnitude and the duration of the temperature variations (referred to as the cure temperature cycles) during the manufacturing process are important parameters influencing the cure and the product quality.

State-of-the-art manufacturing is based on a trial-and-error procedure where numerical models are used to simulate the fabrication process for several candidate cure cycles. Most of the research efforts have been directed towards proposing/improving process models and assessing the effects of process variables on the cure (Broyer and Macosko, 1976; Loos and Springer, 1983; Han et al., 1986; Batch and Macosko, 1988; Han and Chin, 1988; Walsh and Charmchi, 1988; Bogetti and Gillespie, 1991). However, the trial-and-error approaches, even if aided by accurate process models, do not ensure the best possible process parameters, as a result of which processing is carried out under suboptimal conditions that lead to increased manufacturing times and costs.

To overcome these problems, rigorous process optimization strategies are a very useful and a logical step which improves productivity, and thereby reduces costs. Attempts towards generating *rapid* cure cycles for advanced composite materials using various rule-based strategies have been initiated in recent years (Pillai et al., 1992; Ciriscioli et. al., 1991; Abrams et al., 1987). Martinez (1991) obtained cure cycles for a graphite/epoxy system, which yielded centerline temperatures matching an arbitrary profile, chosen by trial-and-error so as to reduce, but not necessarily minimize, the cure time.

Recently, Pitchumani and Yao (1992a) presented optimal cure cycles in the absence of constraints, for the minimum-time manufacture of partially cured prepregs. Since constraints such as the maximum heating/cooling rates and the maximum allowable temperature difference in the composite were not considered, the best possible temperature profile was argued to be a constant temperature imposed throughout the cure process. The corresponding cure cycle duration was then reported as the minimum possible manufacturing time. With the objective of achieving a homogeneous partial cure of 50±5% across the prepreg cross section, the magnitudes and duration of the constant cure temperature were obtained by means of extensive numerical simulations. However, owing to the unconstrained nature of the problem solved, their solution serves only as a guideline for selecting cure cycles in practice.

Although the aforementioned approaches yield faster-than-conventional cure cycles, a systematic optimization of the processes accounting for practical constraints is still lacking, and it is the intent of the present research to fill this void. The problem considered here is that of determining optimal cure cycles for the manufacture of thermoset composite materials, using a rigorous optimization procedure. The objective is to minimize the cycle time while simultaneously satisfying practical constraints on the maximum material temperature, the maximum heating rate and the maximum temperature variation across the composite cross section. From an optimization perspective, the problem was posed as a differential-algebraic optimization problem, referred to as a DAOP (Biegler and Cuthrell, 1985; Vasantharajan and Biegler, 1988). The complexity of the problem formulation renders the solution of DAOPs — which generally involve decisions about (a) optimal control profile and/or (b) scalar variables — a computationally challenging task. In the absence of scalar decision variables, a DAOP is equivalent to an optimal control problem (Diwekar, 1992).

The Maximum Principle (Pontryagin, 1956, 57; Boltyanskii et al., 1956) is one of the popular solution techniques, for solving optimal control problems, without involving transformations and/or discretization of the governing equations. Application of the Maximum Principle involves addition of adjoint variables (one adjoint variable per state variable), the corresponding adjoint equations, and a Hamiltonian in the model. The optimal decision vector (i. e., the optimal cure cycle in the present problem) can be obtained directly by extremizing the Hamiltonian. This approach, although elegant, is computationally intensive since it necessitates an iterative solution of a two-point boundary value problem and the equality constraints. Besides, the method can not handle constraints on the control variables. Moreover, in the context of composite manufacturing processes, the complex nature of the problem, coupled with its large dimensionality, renders the Maximum Principle computationally inefficient.

Recent advances in nonlinear programming (NLP) techniques offer a viable alternative tool for solving optimization problems. One such technique is Successive Quadratic Programming (Lang and Biegler, 1987), which has been used widely in the optimization of steady state chemical processes. In this approach, the continuous control profile is discretized into a finite set of scalar decision variables which are supplied to the process model for the evaluation of the objective function and the constraints. In the context of the present problem, the control profile is the cure temperature cycle, which is discretized into a series of five heating and cooling zones resulting in ten scalar decision variables namely, the five zone end-point temperatures and the five zone durations. Furthermore, the objective function is the cure cycle time, while the constraints include practical limits on the material temperatures and the heating/cooling rates. Note that in this approach, the process model is regarded as a black box by the optimizer and hence the solution methodology remains unaltered regardless of the dynamic or steady state nature of the model. This eliminates the need for transformation of a dynamic model into a set of algebraic equations, which may be required in other techniques (Diwekar, 1992).

From the process modeling point of view, the cure kinetics is expressed using the empirical correlation of Han et al. (1986), which was shown to work well for both unsaturated polyester and

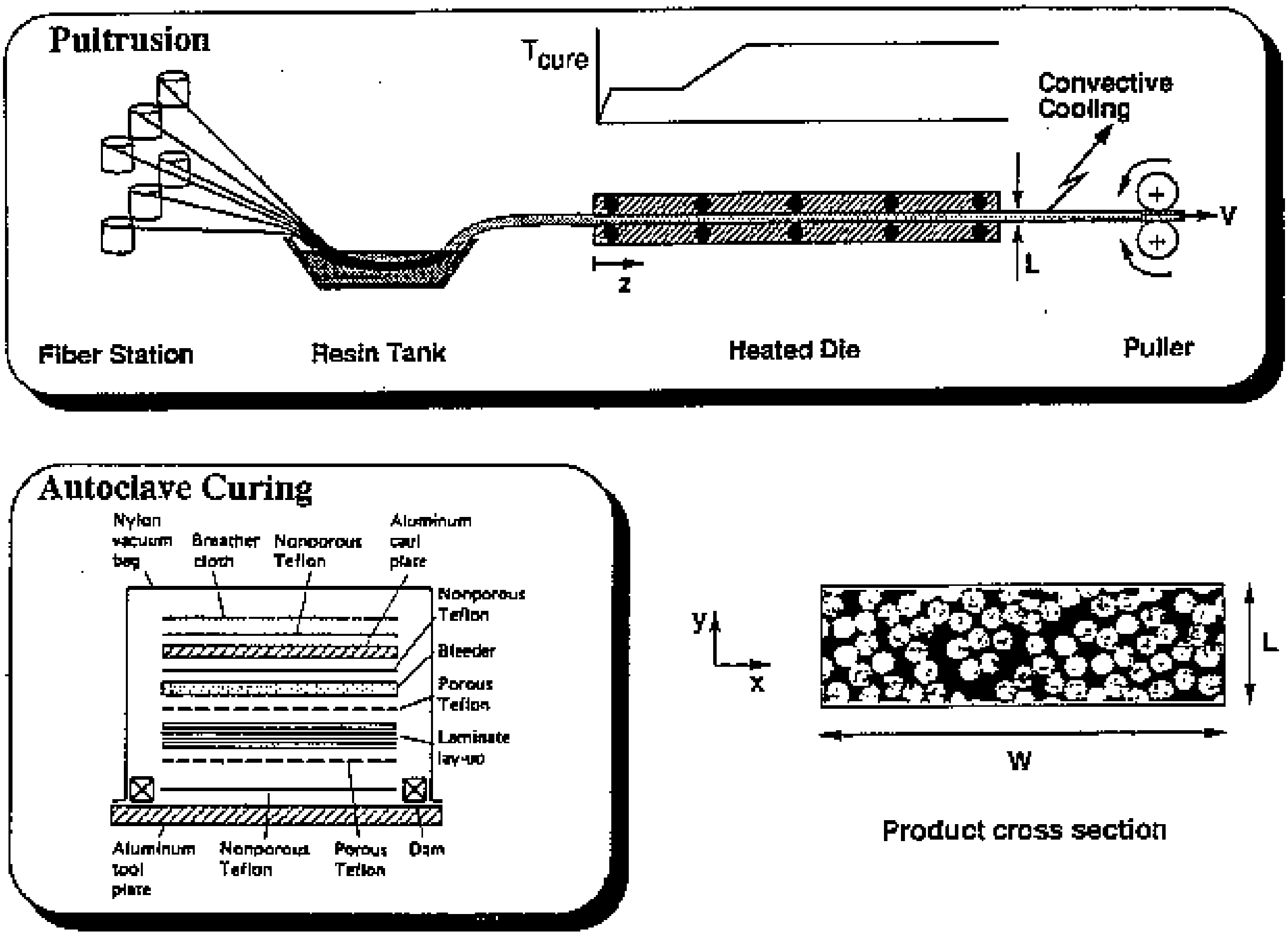

Figure 1: SCHEMATIC OF CONTINUOUS (PULTRUSION) AND BATCH (AUTOCLAVE) PROCESSES FOR MANUFACTURING THERMOSET COMPOSITES. ALSO SHOWN IS THE CROSS SECTION OF A TYPICAL PRODUCT

epoxy systems. The thermochemical process model is formulated in a Lagrangian sense, and is therefore applicable to both batch processes, such as autoclave curing, and continuous processes, exemplified by pultrusion, alike. Furthermore, the analysis is carried out in a dimensionless form for a generalized applicability of the results (Pitchumani and Yao, 1992a; Walsh and Charmchi, 1988).

Only the results for polyester systems are presented in this paper, although the analysis is readily applicable to epoxy systems as well. The optimal cure schedules are compared with some of the recent results in the literature and are demonstrated to offer significant savings in the manufacturing time. Parametric plots of the optimal cure cycles as a function of dimensionless groups formed of the process and product variables, are also presented and discussed.

PROCESS MODEL

Figure 1 shows the schematic of a continuous and a batch process for manufacturing thermoset composites, along with the cross section of a typical product of width, W, and thickness, L. The key step in the manufacturing process is the cure, which involves exposing the resin-impregnated fibers to elevated temperatures for a predetermined length of time. This initiates and sustains a cross-linking chemical reaction which transforms the soft fiber-resin mixture to a structurally hard product. The imposed temperature variations and their duration, together constitute a cure (temperature) cycle, which is an important design parameter in the manufacture of thermoset composites. A cure cycle is illustrated schematically in the pultrusion inset in Fig. 1, where the form of the temperature profile corresponds to a typical conventional cure cycle.

The equations describing the cure process are *(a)* the kinetics model for the reaction rate, in terms of the temperature and the degree of cure, and *(b)* the energy equation in cartesian coordinates for the two-dimensional cross section of the composite. In modeling the cure process, we employ the following assumptions: (1) the process is at steady state, (2) the axial heat conduction is small compared to that in the transverse thickness direction, (3) the velocity profile in the case of pultrusion is flat, and (4) the diffusion and local motion of resin during cure is are negligible. It must be mentioned that while axial conduction of heat may be neglected in the modeling of an autoclave curing process, in the case of pultrusion, it may not be small and must be taken into account for an accurate analysis. However, since the main objective of the paper is to demonstrate a rigorous optimization approach to composites curing, rather than to present a detailed process model, the axial heat conduction effects are neglected. They will be incorporated in a future study.

The governing equations for the cure kinetics and the energy equation are presented here in a non-dimensional form employing the dimensionless groups suggested by Pitchumani and Yao (1992a). The non-dimensional analysis allows for a generalized assessment of the effects of the process and product parameters simultaneously. The kinetics model for the cure reaction, including the effects of initiators, is typically described in terms of an Arrhenius type rate equation (Loos and Springer, 1983; Han et al., 1986). This study employs a two-activation energy kinetics model which has been reported to be reasonably accurate in describing the experimentally observed cure rates (Han et al., 1986). The kinetics equation, given below, is also quite general in its applicability to a wide range of polyester, polyimide and epoxy systems,

$$\frac{d\epsilon}{d\tau} = \left(\overline{K}_1 e^{\frac{-\overline{E}_1}{1+\theta}} + \overline{K}_2 e^{\frac{-\overline{E}_2}{1+\theta}} \epsilon^m\right)(1 - \epsilon)^{1-m} \qquad (1)$$

In the above equation, m is an empirical exponent, which is approximately equal to unity for epoxy systems and about 0.5 for polyester systems. The other terms in the equation are explained in connection with Eq. (3) and are also listed in the nomenclature.

The energy equation with the reaction source term is formulated in the Lagrangian sense, which allows for a unified modeling of batch and continuous processes. A non-dimensional form of the equation may be written as follows:

$$\frac{\partial\theta}{\partial\tau} = \frac{\partial}{\partial\overline{x}}\left(\overline{k}_x\frac{\partial\theta}{\partial\overline{x}}\right) + \frac{\partial}{\partial\overline{y}}\left(\overline{k}_y\frac{\partial\theta}{\partial\overline{y}}\right) + B_o\left(\frac{d\epsilon}{d\tau}\right) \qquad (2)$$

Equations (1) and (2) employ the following important dimensionless groups

$$B_o = \frac{C_{A0}\Delta H_R}{T_o(\rho c)_e}\left(1 - v_f\right); \overline{K}_1 = \frac{K_1 L^2}{\alpha_{ey}}; \overline{K}_2 = \frac{K_2 L^2}{\alpha_{ey}}$$
$$\overline{E}_1 = \frac{E_1}{RT_o}; \overline{E}_2 = \frac{E_2}{RT_o} \qquad (3)$$

where K_1, K_2 and E_1, E_2 are respectively the pre-exponential (frequency) factors and the activation energies characterizing the cure reaction, R is the universal gas constant, and v_f is the fiber volume fraction. All the other terms appearing in the above equations are defined in the nomenclature.

The quantities k_{ey}, α_{ey} and $(\rho c)_e$ which are used in Eqs. (1) and (2) refer to the effective thermal conductivity and the effective thermal diffusivity along the thickness (y-) direction, and the effective volumetric specific heat of the composite material, respectively. The effective conductivity (k_{ey}) and diffusivity (α_{ey}) may be obtained from studies in the literature on structure-property relationships (for e.g., Pitchumani, 1992; Pitchumani and Yao, 1991, 1992b). The effective volumetric specific heat $(\rho c)_e$, is the volume average of the volumetric specific heats of the fibers and the matrix, $(\rho c)_f$ and $(\rho c)_m$, respectively.

$\overline{k}_x$ and $\overline{k}_y$ in Eq. (2) are the thermal conductivities along the x- and y-directions, k_x and k_y respectively, scaled with respect to the effective thermal conductivity k_{ey}, along the y- (thickness) direction. In a general case, the conductivities k_x and k_y are functions of the location within the composite and can not be removed from inside the gradient operator. However, if the composite were treated as an equivalent homogeneous medium having the effective properties, k_y equals k_{ey}, and $\overline{k}_y$ equals unity. Homogenization of composite media for transient thermal analysis is generally justified in most practical situations except in the manufacture of very thin laminates where the composite thickness is on the order of heterogeneity dimension (Pitchumani and Yao, 1992b). In this paper, we consider composite thicknesses where homogenization is valid, and accordingly, $\overline{k}_y$ is set to unity. Furthermore, in practice, composite microstructures exhibit a uniform random arrangement of fibers (Fig. 1), in which case, the properties are transversely isotropic. In other words, the effective conductivities, k_{ex} and k_{ey} are equal. The isotropic effective properties, i.e., $k_{ex} = k_{ey}$, combined with homogenization of the composite medium, i.e., $k_x = k_{ex}$, implies that $\overline{k}_x$ $(= k_x/k_{ey})$ is also unity in Eq. (2).

The key non-dimensional groups appearing in the cure model are, $\overline{K}_1$, $\overline{K}_2$, $\overline{E}_1$, $\overline{E}_2$ and B_o. $\overline{K}_1$ and $\overline{K}_2$ are the Damköhler numbers which provide a measure of how fast the reaction takes place relative to the conduction of heat from the outer layers of the composite to the central core. $\overline{E}_1$ and $\overline{E}_2$ are dimensionless activation energies, and B_o has the physical meaning of the non-dimensional temperature rise potential due to the heat of the reaction, ΔH_R.

The initial and boundary conditions associated with Eqs. (1) and (2) are as follows

$$\theta(\overline{x},\overline{y},0) = \epsilon(\overline{x},\overline{y},0) = 0$$
$$\theta\left(\overline{x},-1/2,\tau\right) = \theta\left(\overline{x},1/2,\tau\right) = \theta\left(-\overline{W}/2,\overline{y},\tau\right)$$
$$= \theta\left(\overline{W}/2,\overline{y},\tau\right) = \theta_{cure}(\tau) \qquad (4)$$

where $\theta_{cure}(\tau)$ is the dimensionless cure temperature cycle, and τ_{cure} is the dimensionless cure cycle duration.

The governing equations, Eqs. (1) and (2), and the associated conditions, Eq. (4), were solved using an Alternating Direction Implicit (ADI) finite difference scheme (Patankar, 1980). The source term was treated implicitly, and was linearized with respect to the previous time step. The two-dimensional domain

$-\overline{W}/2 \leq \overline{x} \leq \overline{W}/2$ and $-1/2 \leq \overline{y} \leq 1/2$, representing the transformed composite cross section, was discretized using 31 grid points along both the $\overline{x}$ and $\overline{y}$ directions. The values of the dimensionless time step, $\Delta\tau$, varied in the range 10^{-3}–10^{-5}, where the smaller values correspond to faster reacting systems, i.e., systems with high Damköhler numbers and/or low dimensionless activation energies. The spatial and temporal discretization was arrived at based on the fact that further refinements resulted in a change of at most 0.01% in the dimensionless temperature and cure profiles.

THE OPTIMIZATION PROBLEM

As previously stated, the goal of optimization is to determine temperature schedules, $\theta_{cure}(\tau)$, for curing composite laminates in the shortest possible time. The objective function is therefore the cure cycle time, τ_{cure}, and the optimization problem may be written as

$$\underset{\theta_{cure}(\tau)}{\text{Minimize}} \quad \tau_{cure} \tag{5}$$

where the above notation, used widely in the formulation of optimization problems, is read as "minimize the objective function, τ_{cure}, with respect to the control profile, $\theta_{cure}(\tau)$."

Equation (5) is subject to the physical inequality constraints as described below.

- The temperature inside the material must not exceed the maximum material limit, θ_{crit}, for the composite.

$$\theta(\overline{x}, \overline{y}, \tau) - \theta_{crit} \leq 0 \tag{6}$$

- The temperature difference across the cross section must not exceed a preset maximum value, $\Delta\theta_{crit}$.

$$\Delta\theta(\tau) - \Delta\theta_{crit} \leq 0 \tag{7}$$

- The heating and cooling rates during the cure process must be within allowable limits, to prevent undue thermal stresses and cracking.

$$\left|\frac{d\theta_{cure}}{d\tau}\right| - \dot{\theta}_{crit} \leq 0 \tag{8}$$

  This constraint may also serve to limit the residual stresses which often result from a rapid curing of the composite.

- At the end of the cure, the minimum cure in the composite must be greater than a critical value, ϵ_{crit}.

$$\epsilon_{crit} - \epsilon_{min} \leq 0 \tag{9}$$

In Eqs. (6)-(9), the subscripts min, max, and $crit$ refer to minimum, maximum and critical values, respectively. The dimensionless critical values used in the study are summarized in Table 1,

Table 1: CRITICAL VALUES OF THE CONSTRAINTS USED IN THE STUDY

Figure	θ_{crit}	T_{crit} [°C]	$\Delta\theta_{crit}$	ΔT_{crit} [°C]	$\dot{\theta}_{crit}$	$\dot{T}_{crit}$ [°C/s]
4	0.386	140	0.134	40	1.6	0.067
5	0.240	140	0.180	60	20.7	4.0
6,7	0.377		0.200		11.3	
ϵ_{crit} = 0.95 in all the cases studied						

which also lists the physical values of the constraints used in the case studies presented in the next section (Figs. 4 and 5).

The cure temperature cycle, $\theta_{cure}(\tau)$, is represented as a series of five piecewise linear segments, as shown schematically in Fig. 2. This representation combines the simplicity of linear functions with the flexibility of describing complex cure schedules by increasing the number of stages. In this study, we have chosen five stages, which seems to be the typical number employed in practical cure cycles (Pillai et al., 1992; Han et al., 1986; Davè, 1990). The number of stages may be increased in later studies for more accurate descriptions of the cure cycle. Figure 2 also shows the ten decision variables, $\{(\theta_i, \tau_i), i = 1, \ldots, 5\}$, defining the cure schedule, where θ_i is the end point temperature of stage i, while τ_i is the stage duration.

Since the composite laminate is required to be cured completely at the end of the cure cycle, the cure time, τ_{cure}, must identically equal the sum of the five stage durations, $\tau_i, i = 1, \ldots, 5$. This introduces the following equality constraint.

$$\tau_{cure} - \sum_{i=1}^{5} \tau_i = 0 \tag{10}$$

The optimization problem described by Eqs. (5)-(10) is solved using a nonlinear programming technique, specifically, the tool of successive quadratic programming (Vasantharajan and Biegler, 1988; Lang and Biegler, 1987; Biegler and Cuthrell, 1985; Powell, 1978; Han, 1977; Wilson, 1963). The underlying concept in the optimization scheme is presented below. A more elaborate discussion on the successive quadratic programming algorithm is beyond the scope of this paper, but can be found in the above-cited references.

The application of the nonlinear programming technique to the composite manufacturing process model is illustrated schematically in Fig. 3. As seen in the figure, the optimizer invokes the process model with the values of the ten decision variables, $\{(\theta_i, \tau_i), i = 1, \ldots, 5\}$. The process model simulates the cure for temperature schedule provided by the optimizer and feeds back the values of the cure time, τ_{cure}, (the objective function), and the left hand side of the constraint equations, Eqs. (6)-(10). This information, together with the partial derivatives of the objective function (Eq. (5)) and the constraints with respect to the decision variables, is utilized by the optimizer to update the values of the decision variables.

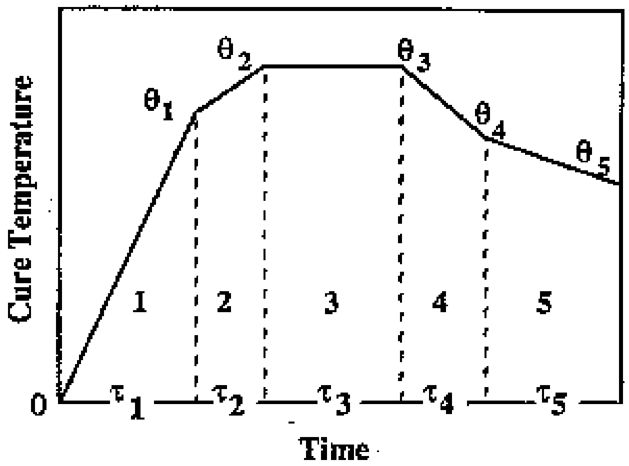

Figure 2: REPRESENTATION OF THE CURE CYCLE AS A SERIES OF FIVE HEATING AND COOLING STAGES. THE TEMPERATURE VARIATION WITHIN EACH STAGE IS LINEAR.

The optimizer calculates the partial derivatives by perturbing the values of the decision variables and observing the corresponding changes in the objective function and the constraints. The iterative sequence shown in Fig. 3 is carried out until the optimality conditions described below are satisfied. At convergence, the values of the decision variables constitute the time-optimal cure temperature schedule.

The optimality conditions include satisfying the constraints in Eqs. (6)-(10) in addition to a "zero-gradient" condition which, using Lagrange multipliers, incorporates the equality and inequality constraints. For mathematical ease of representing these conditions, we introduce the terms, **b** to denote the set of decision variables $\{(\theta_i, \tau_i),\ i = 1,\ldots,5\}$, h(**b**) to denote the left hand side of the equality constraint, Eq. (10), and $g_j(\mathbf{b})$, $j = 1,\ldots,4$, to denote the four inequality constraints, Eqs. (6)-(9), respectively. Using this notation, the optimality conditions may be written as follows.

$$\nabla_{T_{cure}}(\mathbf{b}) + \lambda \nabla h(\mathbf{b}) + \sum_{j=1}^{4} \mu_j \nabla g_j(\mathbf{b}) = 0 \qquad (11)$$

$$h(\mathbf{b}) = 0 \qquad (12)$$

$$\mu_j g_j(\mathbf{b}) = 0, \quad j = 1,\ldots,4 \qquad (13)$$

$$\text{where } \mu_j = 0 \text{ if } g_j(\mathbf{b}) < 0$$

$$\mu_j \geq 0 \text{ if } g_j(\mathbf{b}) = 0$$

Equation (11) is the "zero-gradient" condition, or the Kuhn-Tucker condition, where λ and $\mu_j, j = 1,\ldots,4$, are the Lagrange multipliers for the equality and the inequality constraints, respectively. The left hand side of Eq. (11) is also referred to as the Kuhn-Tucker error. Equation (12) represents the equality constraint feasibility condition at optimum, and likewise, Eq. (13) is the inequality constraint feasibility condition at optimum.

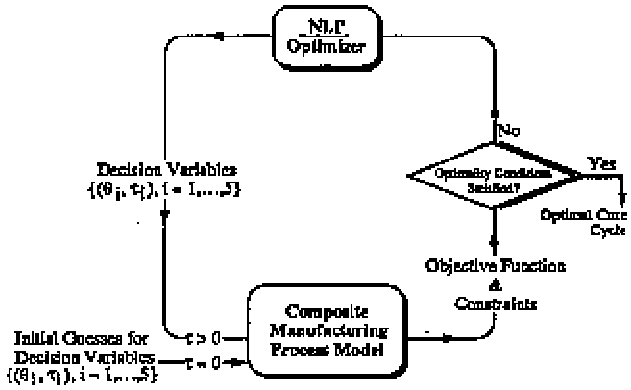

Figure 3: SCHEMATIC DESCRIPTION OF THE OPTIMIZATION PROCEDURE.

RESULTS AND DISCUSSION

Before starting the optimization runs, the accuracy of the numerical process model was confirmed by comparing the model results with the data of Han et al. (1986) and Pillai et al. (1992). The results of the validation are not presented here for the sake of brevity. The optimization runs were initiated by supplying a trial temperature profile, i.e., the set of decision variables, $\{(\theta_i, \tau_i), i = 1,\ldots,5\}$, and the optimization procedure described earlier, was numerically executed until the optimal solution was found. All calculations were performed on a Microvax-3200 workstation. The CPU times required for convergence varied, depending upon the kinetic parameters as well as the Kuhn-Tucker error specification. For a Kuhn-Tucker error equal to 1% of value of the objective function, the typical CPU times were on the order of 1-2 hrs.

As an illustration of the application of the optimization strategy in practical systems, consider the cure of the polyester system, CYCOM 4102, supplied by the American Cyanamid Company. The kinetic parameters for this system are given in Pillai et al. (1992). Figure 4 shows the optimal cure cycle obtained from the present analysis, for the cure of a 1 inch thick laminate. The constraints for this case are given in Table 1. The constraint of 0.067 °C/s (4 °C/min.) on the temperature gradient corresponds to the typical maximum heating rate of autoclave ovens. The constraint on the maximum temperature difference, given in Table 1, was chosen to be equal to the maximum temperature difference which results from the cure schedule of Pillai et al. (1992).

For the purpose of comparison, the cure cycle obtained by Pillai et al. (1992) using a heuristic optimization approach, as well as the manufacturer recommended cure schedule are also included in

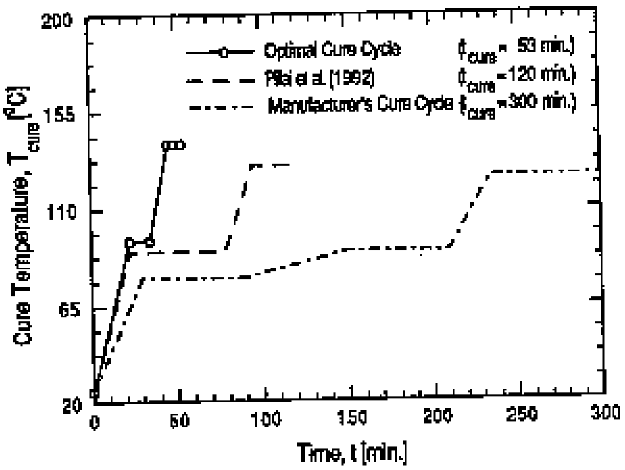

Figure 4: COMPARISON BETWEEN THE OPTIMAL CURE CYCLE AND THE CURE CYCLE OBTAINED BY PILLAI et al. (1992) USING A HEURISTIC OPTIMIZATION TECHNIQUE, FOR A 1 IN. THICK AMERICAN CYANAMID CYCOM 4102 LAMINATE.

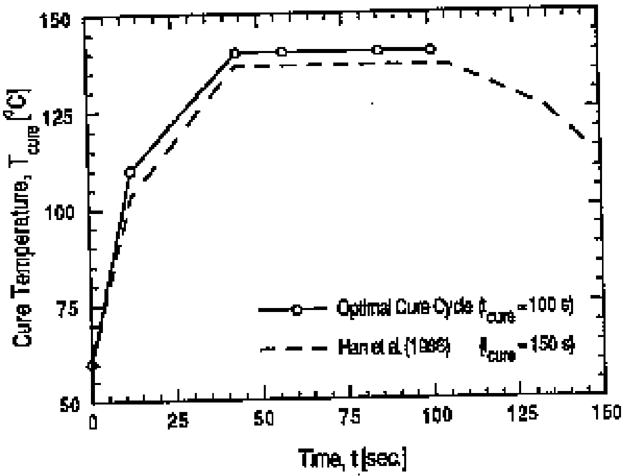

Figure 5: COMPARISON BETWEEN THE OPTIMAL CURE CYCLE AND THE CURE CYCLE USED BY HAN et al. (1986) FOR AN OWENS-CORNING POLYESTER/FIBER GLASS SYSTEM.

Fig. 4. It may be noted that the optimal cure cycle results in a considerably reduced cycle time of 53 min., in contrast to the cure cycle times of 120 min. in the case of the heuristic optimization results, and 300 min. for the manufacturer's cure cycle. This represents a saving of about 82% with respect to the manufacturer's cycle and about 56% relative to the cure cycle of Pillai et al. (1992).

Figure 5 shows the optimal cure temperatures for an Owens-Corning polyester (OC-E701)/fiber glass composite system, mixed with initiators for rapid curing. The material properties and the kinetics data may be obtained from Han et al. (1986). For comparison, the cure cycle used by Han et al. (1986) in their study are also plotted in Fig. 5. To ensure a fair comparison, the constraints on the maximum temperature gradient, $\hat{T}_{crit}$ in Table 1, and the maximum temperature difference, ΔT_{crit}, were taken to be equal to their respective maximum values in the results of Han et al. (1986). It is evident from Fig. 5, that the optimal cure cycle yields a shorter cure time relative to the cure cycle used by Han et al. (1986). Nevertheless, it is interesting to note that the cure schedule used by Han et al. (1986) is actually very close to the optimal cycle. Since an explanation on the choice of their cure cycle was not provided, further discussion on its similarity with the optimal cycle is not possible.

The two examples presented above demonstrate that a systematic optimization approach offers significant savings in the processing time than both the trial-and-error and the heuristic approaches. The illustrations above correspond to two specific cases of product and kinetic parameters. For an enhanced value, the results must be generalized to a wide range of kinetic and product parameters. Towards this end, and further, to assess the influence of these parameters on the optimization results, parametric studies were carried out in terms of the non-dimensional groups $\overline{K_1}$, $\overline{K_2}$, $\overline{E_1}$, $\overline{E_2}$ and B_o. The adiabatic reaction temperature, B_o, was kept constant at 0.06, which corresponds to a typical polyester system with a fiber volume fraction of 60%. The dimensionless values of the constraints used in the parametric studies are given in Table 1. The exponent, m, in the kinetics expression (Eq. (1)) was kept constant, at a value of 0.56.

Figure 6 shows the dimensionless optimal cure temperature cycle, as a function of the first Damköhler number-dimensionless activation energy pair, $\overline{K_1}$-$\overline{E_1}$. It may be seen that as the Damköhler number increases, the cure cycle time decreases. An increase in the Damköhler number implies a quicker reaction (high cure rate), and hence a shorter processing time. Similarly, a decrease in the value of the dimensionless activation energy corresponds to an enhanced reaction rate, and therefore a shorter cycle time. Also noteworthy in the figure is the high sensitivity of the cure time to the Damköhler number and the dimensionless activation energy. An increase in the value of $\overline{K_1}$ by three orders of magnitude reduces the processing time by 67%, and a 10% decrease in the value of $\overline{E_1}$ lowers the cycle time by nearly 50%.

Figure 7 presents the effect of the second Damköhler number-dimensionless activation energy pair, $\overline{K_2}$-$\overline{E_2}$, on the optimal cure schedule. The qualitative response of the cure cycle to the changes in $\overline{K_2}$ and $\overline{E_2}$ are similar to those seen in Fig. 6. However, the quantitative effects are much more pronounced than in Fig. 6. An increase in the value of $\overline{K_2}$ by merely two orders of magnitude leads to the cure time being one-fourth of its original value. A similar reduction is also seen when the dimensionless activation energy is reduced by about 15%. This suggests that the $\overline{K_2}$-$\overline{E_2}$ pair plays a

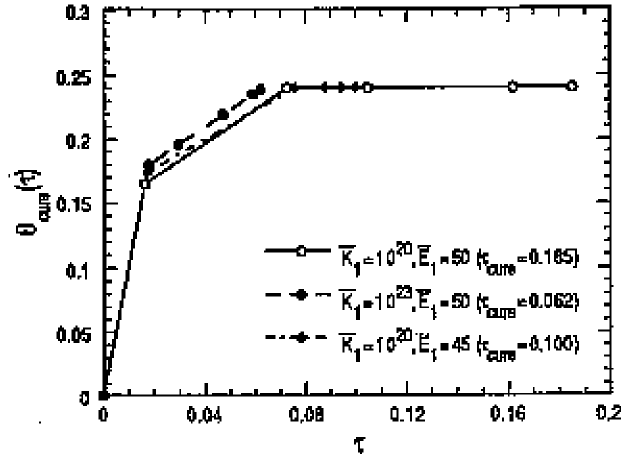

Figure 6: EFFECT OF $\overline{K}_1$ AND $\overline{E}_1$ ON THE OPTIMAL CURE CYCLE, FOR $\overline{K}_2 = 10^{13}$ AND $\overline{E}_2 = 30$.

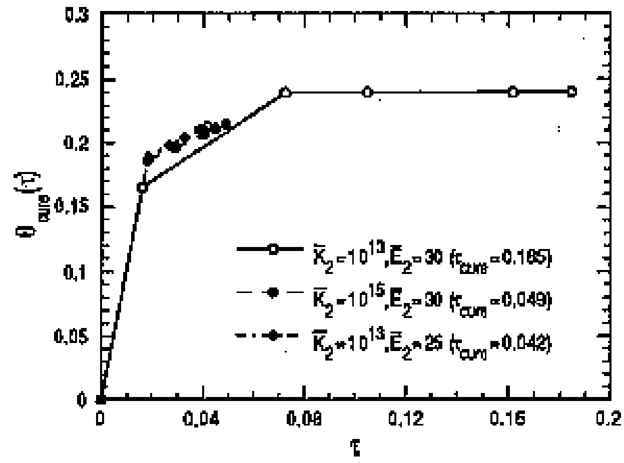

Figure 7: EFFECT OF $\overline{K}_2$ AND $\overline{E}_2$ ON THE OPTIMAL CURE CYCLE, FOR $\overline{K}_1 = 10^{20}$ AND $\overline{E}_1 = 50$.

dominant role in the cure process.

It is important to note that the parametric effects presented in Figs. 6-7 include not only the kinetic parameters but also the thermal properties and the product specifications of the composite. For example, it may be recalled that the Damköhler number is a ratio of the conduction to reaction time scales. Therefore, an increase in the Damköhler number could be due to either an increase in the kinetic frequency factor or poor thermal properties of the composite.

The process model used in this paper concerns only on the thermochemical aspect of the manufacturing process. In an autoclave however, externally applied pressures, referred to as the cure pressure, are used in conjunction with the cure temperature cycle, in order to squeeze out the excess resin and voids. Although the void dynamics and resin flow are not modeled here, the magnitude of the cure pressure required may be calculated by using the optimal cure cycles in the following void stability equation (reproduced from Davè (1990)), as per the guidelines given in Davè (1990).

$$P_{min} \geq 4962\, exp\left(\frac{-4892}{T_{cure}}\right) (RH)_o \qquad (14)$$

where T_{cure} is the optimal cure temperature in degrees K as a function of time, $(RH)_o$ is the % relative humidity to which the composite layup is equilibriated prior to processing, and P_{min} is the minimum cure pressure (in atm.) required to prevent water vapor void growth by moisture diffusion.

It must be mentioned that the parametric studies reported here constitute only the preliminary results of the work. A more exhaustive analysis spanning a wide range of values will be of added practical interest, and will be presented in a later work. Furthermore, this study focused on polyester systems, for which the heats of the cure reaction are relatively small in comparison to epoxy systems. It will be interesting to see the nature of the optimization results for epoxy systems, in view of the increased heat generation. From an optimization point of view, the issue of global versus local optimality of the solution also needs to be examined. These topics will be addressed in future studies.

CONCLUSIONS

A systematic process optimization was carried out for the cure of thermoset composite systems, with the goal of determining the time-optimal cure schedules. The cure cycle was modeled as a series of five heating and cooling zones and the optimal temperature schedule was determined using the successive quadratic programming optimization technique. The optimization approach is independent of the process model, and is therefore valid for both polyester and epoxy systems. Focusing on polyester systems, optimal cure temperature cycles were obtained and compared with the heuristic optimization results in the literature, and the manufacturer recommended cure cycle. It was shown that the rigorous optimization optimization approach yields cure cycles which are considerably shorter in duration than both the heuristic optimization results (by about 56%) and the manufacturer's cure schedule (by over 80%).

Parametric studies were carried out to assess the effects of the product and process variables on the optimal cure cycles. In the range of parameters studied, the $\overline{K}_2$-$\overline{E}_2$ pair in the kinetics model was found to have a more pronounced effect on the optimization results, in comparison to the $\overline{K}_1$-$\overline{E}_1$ pair.

ACKNOWLEDGMENTS

The authors thank Professor Lorenz T. Biegler who provided the computer program for the SQP algorithm. The discussions with him concerning the optimization problem are also gratefully acknowledged.

REFERENCES

Abrams, F., *et al.*, 1987, "Qualitative Process Automation of Autoclave Curing of Composites," *Air Force Materials Laboratory Report AFWAL-TR-87-4083*, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Dayton, OH.

Batch, G. L., and Macosko, C. W., 1988, "Pultrusion Modeling," in *The Manufacturing Science of Composites*, T. Gutowski ed., Vol. 4, pp. 57-62.

Biegler, L., T., and Cuthrell, J. E., 1985, "Improved Infeasible Path Optimization for Sequential Modular Simulators-II. The Optimization Algorithm," *Comput. chem. Engng.*, Vol. 9, pp. 257-267.

Bogetti, T. A., and Gillespie, J. W., 1991, "Two-dimensional Cure Simulation of Thick Thermosetting Composites," *Journal of Composite Materials*, Vol. 25(3), pp. 239-273.

Boltyanskii V. G., Gamkrelidze, R. V., and Pontryagin, L. S., 1956, "On the Theory of Optimum Processes," (in Russian) *Doklady Akad. Nauk SSSR*, Vol. 110(1).

Broyer, E. and Macosko, C. W., 1976, "Heat Transfer and Curing in Polymer Reaction Molding," *AIChE Journal*, Vol. 22(2), pp. 268-276.

Ciriscioli, P. R., Springer, G. S., and Lee, W. I., 1991, "An Expert System for Autoclave Curing of Composites," *Journal of Composite Materials*, Vol. 25, pp. 1542-1587.

Davè, R. S., 1990, "Autoclave Processing," in *International Encyclopedia of Composites*, Vol. 1, VCH Publishers, NY, pp. 67-99.

Diwekar, U. M., 1992, "Unified Approach to Solving Optimal Design-Control Problems in Batch Distillation," *AIChE Journal*, Vol. 38, p. 1551.

Han, S. P., 1977, "A Globally Convergent Method for Nonlinear Programming," *J. Optimization Theory and Application*, Vol. 1977(7), pp. 144-157.

Han, C. D., and Chin, H. B., 1988, "Development of a Mathematical Model for the Pultrusion of Unsaturated Polyester Resin," *Polymer Science and Engineering*, 28(5), pp. 321-332.

Han, C. D., Lee, D. S., and Chin, H. B.,1986, "Development of a Mathematical Model for the Pultrusion Process," *Polymer Science and Engineering*, 26(6), pp. 393-404.

Lang, Y. D, and Biegler, L. T., 1987, "A Unified Algorithm for Flowsheet Optimization," *Comput. chem. Engng.*, Vol. 11, p. 143.

Loos, A. C., and Springer, G. S., 1983, "Curing of Epoxy Matrix Composites," *Journal of Composite Materials*, 17, pp. 135-169.

Martinez, G. M., 1991, "Fast Cures for Thick Laminated Organic Matrix Composites," *Chemical Engineering Science*, 46(2), pp. 439-450.

Patankar, S. V., 1980, *Numerical Heat Transfer and Fluid Flow*, Hemisphere, Washington D.C.

Pillai, V., Beris, A., and Dhurjati, P., 1992, "Local Methods for Optimization of Batch Processes," *Computers and Chemical Engineering*, Submitted.

Pitchumani, R., 1992, *Modeling the Thermal Properties and Processing of Composite Materials*, Ph. D. Dissertation, Department of Mechanical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania.

Pitchumani, R., and Yao, S. C., 1991, "Correlation of Thermal Conductivities of Unidirectional Fibrous Composites Using Local Fractal Techniques," *Trans. ASME Journal of Heat Transfer*, Vol. 113(4), pp. 788-796.

Pitchumani, R., and Yao, S. C., 1992a, "Non-dimensional Analysis of an Idealized Thermoset Composites Manufacture," *Journal of Composite Materials*, Vol. 27(10).

Pitchumani, R., and Yao, S. C., 1992b, "Evaluation of Transient Thermal Diffusivity of Unidirectional Fiber-reinforced Composites," *International Journal of Heat and Mass Transfer*, Vol. 35(9), pp. 2185-2194.

Pontryagin, L. S., 1956, "Some Mathematical Problems Arising in Connection With the Theory of Automatic Control System," (in Russian) *Session of the Academic Sciences of the USSR on Scientific Problems of Automatic Industry*, October 15-20.

Pontryagin, L. S., 1957, "Basic Problems of Automatic Regulation and Control," (in Russian) *Izd-vo Akad Nauk SSSR*.

Powell, M., J., D., 1978, "A Fast Algorithm for Nonlinear Constrained Optimization Calculations," *Numerical Analysis, Dundee, 1977, Lecture Notes in Mathematics 630*, G. A. Watson ed., Springer-Verlag, Berlin, pp. 144-157.

Vasantharajan, S., and Biegler, L. T., 1988, "Large Scale Decomposition Strategies for Successive Quadratic Programming," *Comput. chem. Engng.*, Vol. 12, p. 1087.

Walsh, S. M., and Charmchi, M., 1988, "Heat Transfer Characteristics of a Pultrusion Process," *Proceedings of the ASME National Heat Transfer Conference, Houston, TX*, pp. 23-28.

Wilson, R. B., 1963, *A Simple Algorithm For Concave Programming*, Ph. D. Dissertation, Harvard University.