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Optimal control of accelerator concentration for resin transfer molding process

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Abstract

Resin cure following mold filling is an essential element in resin transfer molding. To fabricate a composite part with high dimensional stability and minimize residual stress, uniform resin cure should be achieved. This study considers a three-part resin system composed of epoxy, hardener and accelerator. The cure kinetics can be controlled by the accelerator concentration at the injection gate. A numerical method that can predict degree of cure distribution based on accelerator concentration at the gate was proposed. The degree of cure distribution is obtained by solving the resin flow, heat transfer, accelerator concentration and cure problems sequentially. Utilizing this numerical method, an optimal variation of accelerator concentration during mold filling was sought by solving a constrained optimization problem. The effect of accelerator control on degree of cure distribution was investigated and its validity was examined for two different geometries.

Keywords: Resin transfer molding; Degree of cure; Accelerator concentration

1. Introduction

The resin transfer molding (RTM) is one of the most studied manufacturing processes of thermoset polymer composite materials because of its wide applicability. The process consists of preform placement, resin injection and mold filling and curing. One of the most important issues in RTM is what is optimization of processing conditions. In order to estimate the optimum processing window and curing conditions, it is necessary to predict the filling pattern of the resin and degree of cure distribution of the composite part throughout the entire process. To date many researchers have investigated numerical techniques for mold filling simulation [1–5]. In order to determine the optimum processing cycle, however, it is essential to establish a combined model, which describes not only the mold filling stage but also the curing process. A comprehensive review of filling and cure phenomena in RTM can be found in [6].

When manufacturing large composite structures or high fiber volume ratio composites, the mold filling time can be very long and nonuniform curing can occur. The filling and curing times could be shortened by heating the mold moderately. Preheating the mold, however, there are differences in degree of cure. The degree of cure near the vents is higher than that near the injection gate. This difference can introduce residual stresses and deformation of the final part [7–9]. Recently, Antonucci et al. proposed varying the mold wall temperature to control the cure reaction [10]. In this study, cure reaction is controlled in order to achieve uniform cure by changing the cure kinetics. Some RTM machines allow resin injection with varying accelerator concentration. This approach in manufacturing requires a model to analyze the distribution of accelerator concentration

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during mold filling. The resulting degree of cure distribution depends on the variation of accelerator concentration at the injection gate. This work intends to determine its optimal variation that renders uniform cure for a given geometry, cure cycle, preform and resin system. A combined model for RTM process involving flow analysis, heat transfer analysis, accelerator distribution analysis and cure analysis is established. A numerical scheme based on the control volume finite element method (CVFEM) and fixed grid method is employed to solve the governing equations for the models. This study proposes to use an objective function, which represents the uniformity of the degree of cure over the whole domain. A constrained optimization problem is solved to minimize the objective function for a given total amount of accelerator to be injected. The proposed method was implemented and tested on two different geometries.

2. Model formulation

2.1. Flow

The resin flow in an RTM mold can be described by Darcy's law of flow phenomena through porous media [11]:

$$\mathbf{v} = -\frac{\mathbf{K}}{\mu}\nabla \cdot p \tag{1}$$

where $\mathbf{v}$, μ, p and $\mathbf{K}$ denote the velocity vector, viscosity and pressure of the resin and the permeability tensor of the preform [12,13], respectively. The mass conservation of resin can be expressed as

$$\nabla \cdot \mathbf{v} = 0 \tag{2}$$

Combining Eqs. (1) and (2), we obtain the following equation for pressure distribution:

$$\nabla \cdot \left(\frac{\mathbf{K}}{\mu}\nabla p\right) = 0 \tag{3}$$

The boundary conditions are

$$\int_S \rho \mathbf{v} \cdot \mathbf{n}\,\mathrm{d}S = \rho Q = \dot{m} \text{ at the injection gate} \tag{4a}$$

$$\frac{\partial p}{\partial n} = 0 \text{ at the mold wall} \tag{4b}$$

$$p = p_{\mathrm{atm}} \text{ at the flow front} \tag{4c}$$

Here, S, Q, $\dot{m}$ and p_{atm} denote the surface surrounding the injection gate, volumetric flow rate, mass flow rate and atmospheric pressure, respectively.

2.2. Energy

The temperature distribution inside the composite during cure is determined by the corresponding energy equation. The temperature of the fiber and the resin can be taken to be identical except at the area near the flow front since heat transfer area per unit volume between the fiber and resin is very large. Based upon this assumption, we have the following energy equation [14]:

$$\rho C\frac{\partial T}{\partial t} + \rho_{\mathrm{r}}C_{\mathrm{r}}\mathbf{v}\cdot\nabla T = \nabla\cdot(\mathbf{k}\nabla T) + \dot{H} \tag{5}$$

where ρ, C and T denote the density, heat capacitance and temperature of the resin and fiber mixture, respectively. The subscript 'r' denotes resin. Note that the convective term, $\rho_{\mathrm{r}}C_{\mathrm{r}}\mathbf{v}\cdot\nabla T$, is described only for resin. Besides, $\mathbf{k}$ is the thermal conductivity tensor and $\dot{H}$ denotes the rate of heat produced by the exothermic curing reaction of the resin per unit volume. It is related to the rate of degree of cure as

$$\dot{H} = H_{\mathrm{T}}\frac{\mathrm{d}\alpha}{\mathrm{d}t} \tag{6}$$

where H_{T} and α denote total reaction heat of resin and degree of cure, respectively. The boundary conditions for the energy equation are

$$T = T_{\mathrm{inj}} \text{ at the injection gate} \tag{7a}$$

$$T = T_{\mathrm{mold}} \text{ at the flow front} \tag{7b}$$

$$(\mathbf{k}\nabla T)\cdot\mathbf{n} = h_{\mathrm{w}}(T_{\mathrm{mold}} - T) \text{ at the mold wall} \tag{7c}$$

where $\mathbf{n}$ and h_{w} denote normal vector to the mold surface and heat transfer coefficient at mold wall, respectively.

2.3. Cure

The degree of cure distribution can be calculated from the law of conservation of species as follows:

$$\frac{\partial\alpha}{\partial t} + \frac{1}{\phi}\mathbf{v}\cdot\nabla\alpha = \dot{s} \tag{8}$$

where ϕ is the porosity of the preform. Since the mobility of cured epoxy is very low, the diffusion of cured epoxy was neglected [15,16]. Here, $\dot{s}$ is a rate of species generation by the curing reaction which generally depends on degree of cure and temperature of the resin. Um and Daniel proposed a model for cure kinetics of a Ciba-Geigy epoxy resin system based on differential scanning calorimetry (DSC) [17]. This model was adopted in the present study. In the model the rate of generation of cured epoxy can be expressed as a certain function of degree of cure, temperature and accelerator concentration:

$$\dot{s} = f(\alpha, T, C_{\mathrm{A}}) \tag{9}$$

where C_{A} denotes the accelerator concentration. The precise functional form of Eq. (9) can be found in the above mentioned reference [17]. The boundary condition for degree of cure equation is

$$\alpha = \alpha_{inj} \text{ at the injection gate} \tag{10}$$

where α_{inj} is the degree of cure at the injection gate.

2.4. Accelerator

When the accelerator concentration in the resin is changed at the injection gate, the distribution of C_A should be known before calculating the degree of cure. Fig. 1(a) shows a schematic of the reaction regime and Fig. 1(a) shows the shift of this regime with varying accelerator concentration for the resin system considered. The distribution of accelerator concentration should be also calculated from the conservation of species principle. Since the accelerator moves with the bulk resin flow, the convection term should be included. A certain amount of accelerator could be transferred by molecular diffusion and there would be microscopic movement between the fiber to microstructure and the channel. Several investigations were reported on the diffusivity of some chemicals in polymeric materials [18,19]. The effect of diffusion might be much lower than that of convection of the resin. In this study, the effects of diffusion and microscopic movement were neglected.

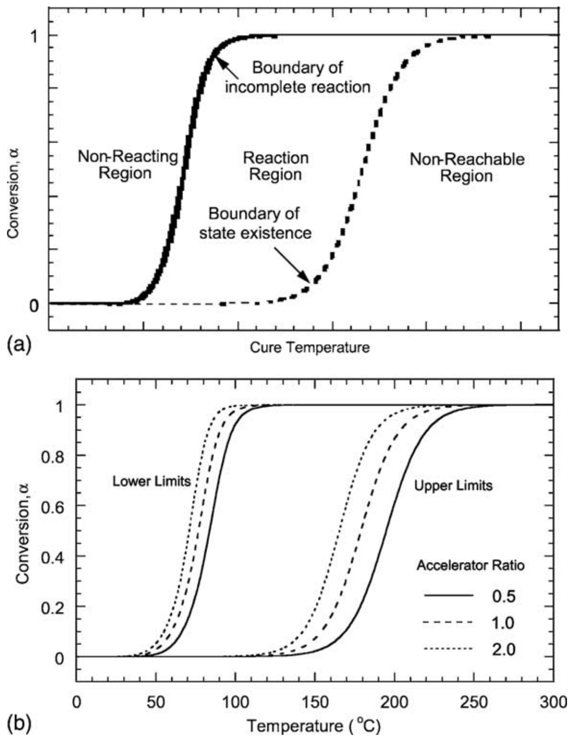


Fig. 1. (a) Reaction regions observed for three-part epoxy resin studied and (b) boundaries of reaction regions for various accelerator concentration ratios.

Then, the conservation of accelerator mass can be expressed as

$$\frac{\partial C_A}{\partial t} + \frac{1}{\phi}\mathbf{v} \cdot \nabla C_A = 0 \tag{11}$$

The boundary condition for accelerator concentration is

$$C_A = g(t) \text{ at the injection gate} \tag{12}$$

where $g(t)$ is the time varying accelerator concentration at the injection gate.

As mentioned before, the accelerator concentration at the injection gate can be varied with time if necessary. The governing equations are also applicable after mold filling. Solving Eqs. (3)–(12) at each time step, the mold filling and curing of the composite parts after mold filling can be simulated and the degree of cure distribution can be determined.

3. Optimal control

3.1. Objective function

The velocity, temperature, degree of cure and accelerator concentration are variables involved in this problem. For a given accelerator concentration C_A, the temperature T and degree of cure α can be determined. The nonuniformity of cure over a certain time interval $t_o < t < t_l$, is expressed as

$$S(g) = \frac{\int_{t_o}^{t_l}\int_\Omega \left[\frac{\alpha(x,y,t;g)-\bar{\alpha}(t;g)}{\bar{\alpha}(t;g)}\right]^2 \mathrm{d}\Omega\,\mathrm{d}t}{\int_{t_o}^{t_l}\int_\Omega \mathrm{d}\Omega\,\mathrm{d}t} \tag{13}$$

where

$$\bar{\alpha}(t;g) = \int_\Omega \alpha(x,y,t;g)\,\mathrm{d}\Omega \Big/ \int_\Omega \mathrm{d}\Omega \tag{14}$$

An optimal accelerator concentration at the gate $g(t)$ can be sought by minimizing $S(g)$. A combination of the optimization code and the simulation code provides the desired accelerator variation. The time interval is related to specific degrees of cure, that is, t_o and t_l correspond to $\alpha = 45\%$ and $\alpha = 55\%$, respectively, since nonuniformity of cure in this range of degrees of cure can produce residual stresses and warpage, due to high likelihood of gellation occurring in this interval.

3.2. Optimization

The optimization problem is stated as follows:

$$\text{Minimize} \quad S(g)$$

$$\text{Subject to} \quad g_{min} \leqslant g(t) \leqslant g_{max} \quad \text{and} \quad \int_0^{t_f} \dot{m}g(t)\,\mathrm{d}t = G \tag{15}$$

where t_f is the filling time and G is the total amount of accelerator to be injected. The problem becomes a simple optimization problem with a linear constraint. However, one evaluation of the objective function $S(g)$ involves solutions of four transient partial differential equations. Thus, an efficient as well as reliable method is essential in this optimization. A piecewise linear model is utilized to represent $g(t)$. The accelerator concentration at the injection gate $g(t)$ can be represented by a vector $\mathbf{g}$ as follows:

$$\mathbf{g} = \{g_1, \ldots, g_k, \ldots, g_N\} \tag{16}$$

where $N-1$ is the number of piecewise linear time intervals.

4. Implementation

4.1. Discretization of governing equations

The computational domain is discretized by the CVFEM [1,20]. This method has been widely employed to simulate various kinds of transport phenomena thanks to its advantages of applicability to arbitrary geometries and proven accuracy. Because the CVFEM automatically satisfies flux conservation, it provides an accurate solution of the described equations. Since most of the RTM products have small thicknesses compared to other dimensions, two-dimensional geometry is assumed. Once the analysis is proven, however, it can be easily extended to three-dimensional cases [4].

4.2. Mold filling

As mentioned before, since the mold filling process is a moving boundary problem where the calculation domain varies with time, flow front advancing technique is needed. The volume of fluid based technique was adopted in this study [21]. At each time step the fill fraction of the element was calculated from the mass flux through the control surface. Calculations were performed within the flow region, which was determined from the resin fill fraction.

4.3. Degree of cure calculation

Once the flow domain is defined, the pressure distribution is calculated and then the velocity of the resin is determined. The distributions of temperature and accelerator concentration are calculated. The degree of cure can be calculated using the accelerator concentration and velocity profile of the resin. After mold filling, the temperature and degree of cure calculation is continued to the complete cure of the part. A flow chart of the solution procedure is shown in Fig. 2.

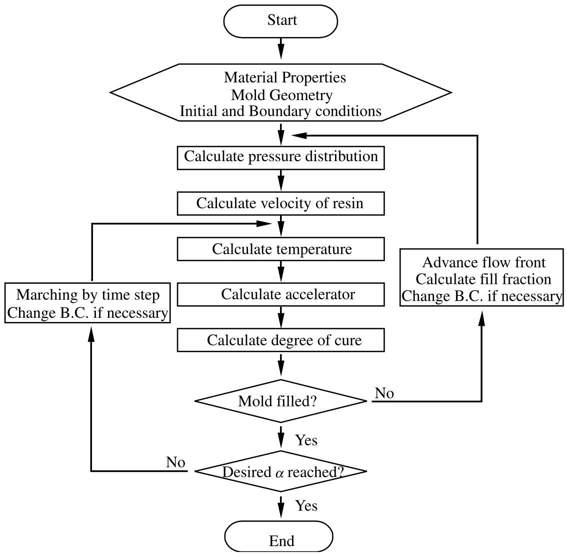


Fig. 2. Procedure for degree of cure calculation.

4.4. Optimization

The constraint $\int_0^{t_f} \dot{m}g(t)\,dt = G$ is converted to a linear constraint $\sum_{i=1}^{N} a_i g_i = G$, where the coefficients a_i's are determined by the trapezoidal rule. The nonlinear optimization problem with a linear constraint is solved by an existing IMSL optimization code LCONF [22].

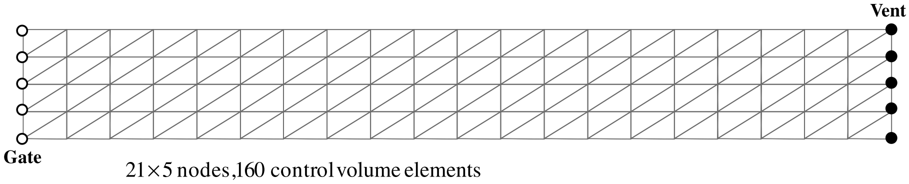
5. Results and discussions

5.1. Test specification

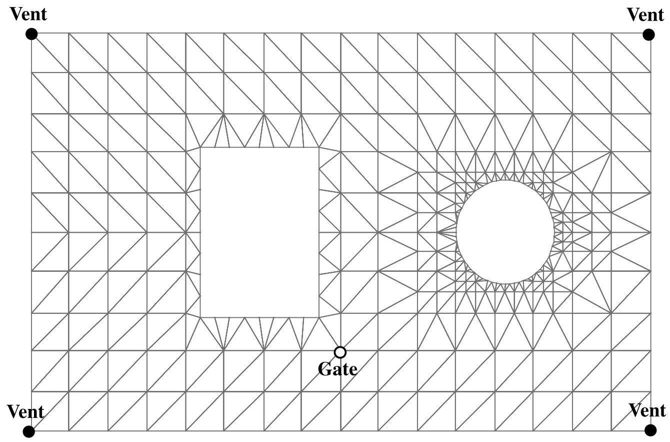
The simulation was applied to a case with glass fabric preform (Hexel 7500) and a three-part epoxy resin (Ciba-Geigy). The viscosity of the resin is strongly dependent on the temperature and degree of cure. The kinetic model for curing reaction and the viscosity of the previously mentioned resin as a function of temperature and degree of cure are obtained from the result of a previous study [17]. The permeability of the glass fabric is obtained from Um et al. [23] and the results were adopted in this study. The density, heat capacitance and thermal conductivity of the composite material can be expressed as functions of the fiber volume fraction [15]. All relevant material properties of the glass preform and resin system used in the simulation are shown in Table 1. The fiber volume fraction of the glass preform was 41.9%. The simulations were performed for two different cases, A and B. Fig. 3 shows computational meshes of the geometries considered. Case A considers one-dimensional domain of dimensions $2032 \times 254 \times 3.56$ mm with a line gate (Fig. 3(a)). In case B, a more complex

Table 1
Material properties of glass fiber perform and resin used in the simulations [17,23]

	Resin	Fiber
Density (kg/m^3)	1030	2540
Heat capacitance (J/kg K)	1900	835
Thermal conductivity (W/m K)	0.198	0.76
Viscosity (Pa s)	$1.44 \times 10^{-9} \exp(6037/T + 33.4\alpha^{1.60})$	–
Permeability (m^2)	–	$K_{11} = 2.53 \times 10^{-10}$ $K_{22} = 8.45 \times 10^{-11}$



(a)



(b)

Fig. 3. Computational mesh: (a) case A and (b) case B.

geometry is considered as shown in Fig. 3(b). A rectangular domain of dimensions 768×482×3.56 mm with a rectangular hole of dimensions 127×178 mm and a circular hole of 51 mm radius was analyzed. Resin flow rates at the gate were $Q = 4.27$ cm^3/min and $Q = 21.4$ cm^3/min, respectively for cases A and B (see Eq. (4a)). The same cure cycle was applied to both cases. The mold temperature was maintained at 80 °C during mold filling and it was elevated to 130 °C after mold filling with a ramping rate of 0.5 °C/s for both cases.

5.2. Result for Case A

In Case A, the prediction of the filling pattern is straightforward due to the simple geometry and constant flow rate condition. Fig. 4 shows the accelerator concentration at the gate as a function of time, $g(t)$, for different N values of piecewise linear intervals. The dimensionless time in the figure is defined by $t^+ \equiv t/t_f$, where t_f is the filling time. With the linear scheme ($N = 2$), the measure of cure nonuniformity, $S^{0.5}$ is drastically reduced in comparison with that for constant accelerator injection. For $N = 5$, $S^{0.5}$ is further reduced noticeably. However, increasing N from 5 to 9 gave negligible improvement. It is noted that the computational times were 4310 s for $N = 5$ and 15,780 s for $N = 9$. The increase of $g(t)$ for $N = 5$ and $N = 9$ near the end of filling time is attributed to the nonlinear behavior of the cure kinetics including the exothermic reaction. The filling time was estimated as 3019 s and an

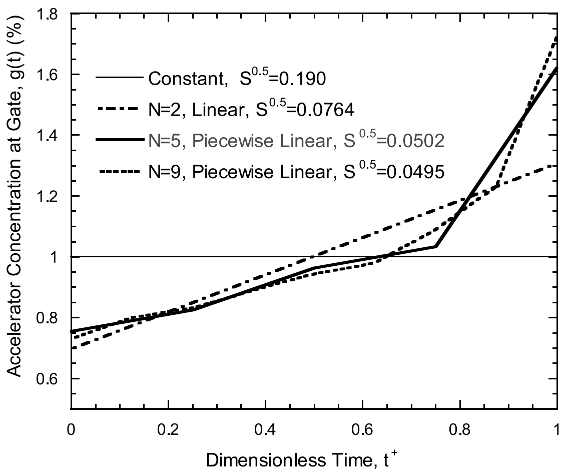


Fig. 4. Optimal accelerator concentration at injection gate for case A.

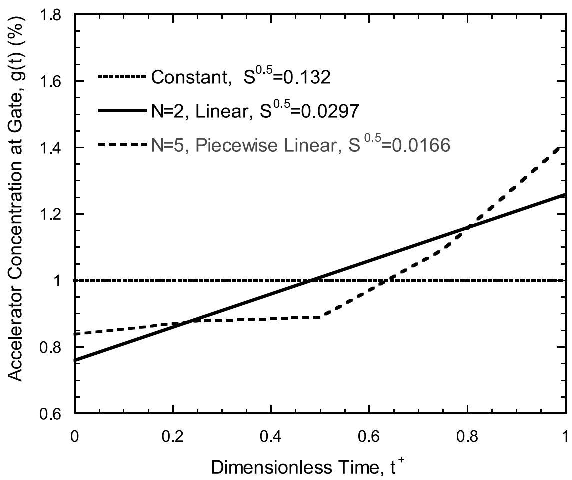


Fig. 5. Optimal accelerator concentration at injection gate for case B.

average degree of cure of $\bar{\alpha} = 0.5$ was accomplished in 3423 s. Both times were almost invariant (within ±4 s) with changing $g(t)$ for a given total amount of accelerator G. It was also found from numerical simulation that the time required for $\bar{\alpha} = 0.5$ depends on G. Increasing G accelerates the cure process remarkably. When the average accelerator concentration at the gate was 1.2% (20% increase from G of the present result), the time

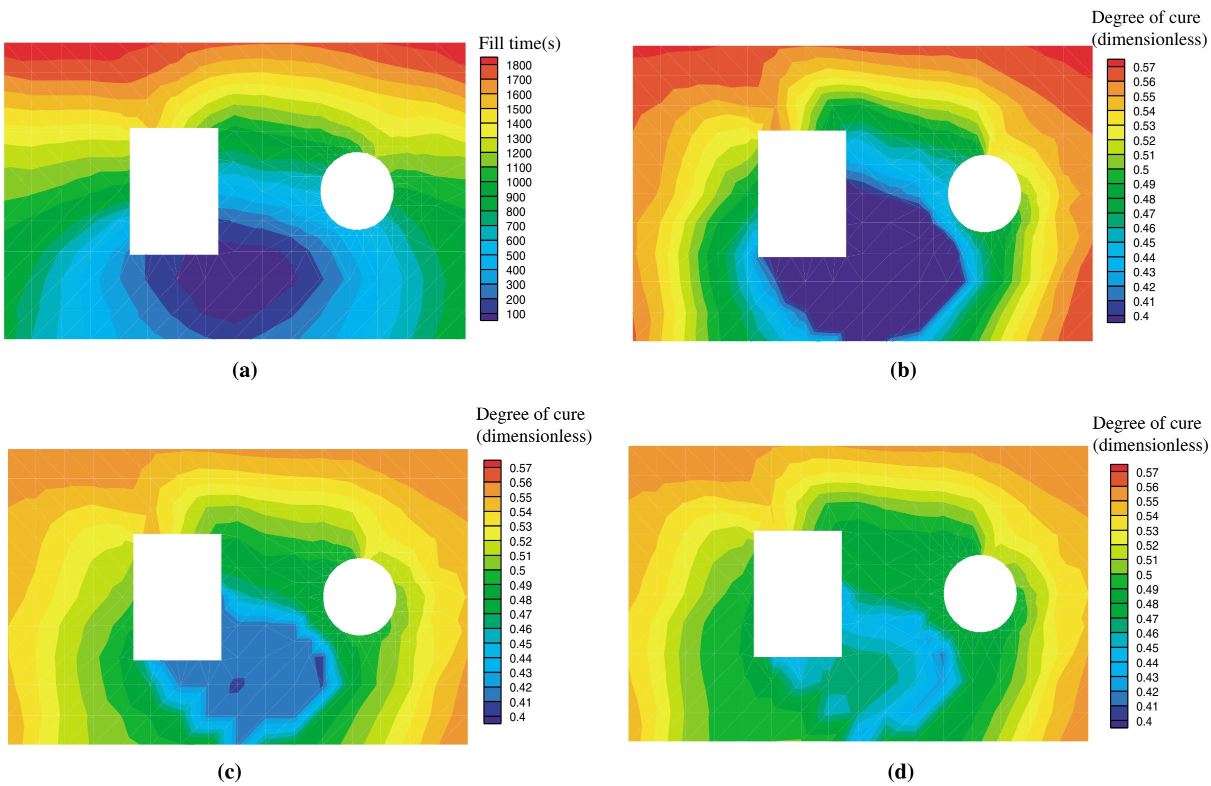


Fig. 6. (a) Flow front movement with time. Degree of cure distribution when $\bar{\alpha} = 0.5$ for (b) constant accelerator concentration, (c) linearly varying accelerator concentration ($N = 2$) and (d) piecewise linearly varying accelerator concentration ($N = 5$).

required to reach $\bar{\alpha} = 0.5$ was 3317 s. However, such cure acceleration also increases nonuniformity. As shown in the result, such adverse effects of acceleration can be alleviated by optimal control of accelerator injection.

5.3. Result for Case B

Fig. 5 shows results for case B. Based on the previous result, it is concluded that the number of segments does not have to be greater than 4 ($N = 5$). Results are shown for $N = 2$ and $N = 5$. The shape of $g(t)$ for $N = 5$ in cases A and B are considerably different because of different filling pattern. Fig. 6(a) shows flow front movement with time. Fig. 6(b)–(d) show the degree of cure distribution for constant $g(t)$, $N = 2$ and $N = 5$ when $\bar{\alpha} = 0.5$ was reached. As expected from the values of $S^{0.5}$ shown in Fig. 5, more uniform distribution is obtained with the piecewise linear scheme. It is noteworthy that the linear scheme ($N = 2$) always reveals considerable alleviation of nonuniformity, especially when cure simulation takes a long computational time owing to large number of nodal points in the mesh. The linear scheme is recommended for a rapid estimation.

6. Conclusions

The RTM process of composite materials was modeled including the mold filling and curing stages. A numerical method that can predict degree of cure distribution as a function of accelerator concentration at the gate was used. The degree of cure distribution is obtained by analyzing the resin flow, heat transfer, mass transfer and cure phenomena, sequentially. Utilizing this numerical method, an optimal variation of accelerator concentration during mold filling was determined by solving a constrained optimization problem. The effect of accelerator control on degree of cure distribution was investigated and its validity was examined. Three different schemes for the accelerator variation, i.e., constant, linear and piecewise linear schemes were compared. It was found that the linear scheme could alleviate the cure nonuniformity considerably and the piecewise linear scheme reduced it further. However, increasing the number of segments in the piecewise linear scheme resulted in a dramatic increase of computational time and negligible reduction of cure nonuniformity.

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