

NUMERICAL SIMULATION AND OPTIMIZATION OF RESIN TRANSFER MOLDING CYCLE WITH DUAL- INITIATOR SYSTEMS

H. Farrahinia¹, A. Shojaei^{1,2}, and M. R. Pishvaie¹

¹ *Department of Chemical and Petroleum Engineering, Sharif University of Technology,
Tehran 11365-9465, Iran*

² *Corresponding author's Email: akbar.shojaei@sharif.edu*

SUMMARY: In the non-isothermal resin transfer molding (RTM) process, the resin is injected into the preheated mold containing the fiber perform. In such cases, the process cycle is strongly governed by the temperature distribution of the resin along the flow length at the end of mold filling stage and the overall process cycle time is significantly controlled by heating and curing of the resin near the injection gate. In the present work, the role of initiators with different reactivities to overcome the above mentioned problems is examined using the numerical simulation developed in this study. The model comprises flow, heat and mass transfer equations combined with an appropriate mechanistic kinetics model which elucidates the functions of the initiators. The model developed allows us to investigate the role of the initiator systems on the process cycle of the non-isothermal RTM process. The numerical simulations performed for various initiator systems indicated that the cycle time reduction depends on the type and concentration of initiators as well as the injection methodology of dual-initiator. Nelder-Mead optimization technique is used to obtain the optimum policy for injecting two different initiators into the mold. The numerical simulation under the optimized condition shows a significant improvement in uniformity of cure and a considerable reduction in cycle time.

KEYWORDS: Resin Transfer Molding (RTM), optimization, numerical simulation, mechanistic cure model, initiator

INTRODUCTION

RTM process cycle consists of two sequent stages including mold filling and curing. In the non-isothermal Resin Transfer Molding (RTM) process, the resin injection is performed into the preheated mold containing the fiber perform. In such cases, the process cycle is strongly governed by the temperature distribution of the resin along the flow length at the end of mold filling stage and the overall process cycle time is significantly controlled by heating and curing of the resin near the injection gate [1]. To compensate the role of thermal quench at the injection gate, a series of process developments based on the additional heat sources during

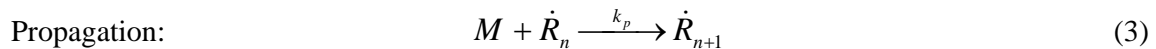
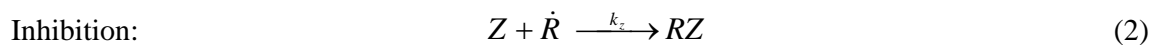
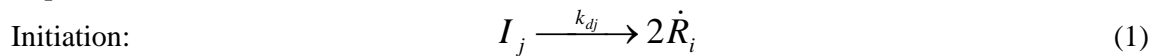
the mold filling has been suggested [2-3]. These involve zone heated molds, batch and continuous in-line microwave preheating the resin before entering to the mold. However, most of these methods have their own drawbacks. For instance, batch preheating is found to be lengthy and microwave preheating may lead to resin gelation in the injection line. An alternative method can be the modification of resin reactivity by changing the initiator system during the resin injection. Blanchard and Rudd [5] developed an injection system based on this approach in which the resin reactivity is modified by on-line modification of the catalyst system during the resin injection. Experimental trials carried out using this machine showed a considerable reduction in resin cure time at the injection gate resulting in overall cycle time reduction.

In the present work, the role of initiators (curing agents of unsaturated polyester and vinylester resins) with different reactivities in curing of unsaturated polyester resin to overcome the above mentioned problems is examined using the numerical simulation developed in this study. The model comprises flow, heat and mass transfer equations combined with an appropriate mechanistic kinetic model which elucidates the functions of the initiators. The model developed allows us to investigate and optimize the role of dual-initiator systems on the process cycle of the non-isothermal RTM process.

THEORY

Mechanistic Kinetics Model

Cure kinetics model based on mechanistic approach involves a series of stoichiometric balances of reactive species during the course of curing process according to elementary reactions of cure reaction mechanisms. Therefore, such model can provide detailed information concerning the role of reactive ingredients taking part in the curing reaction. For such resins as unsaturated polyester and vinyl ester, cure mechanisms are based on the generally accepted free radical polymerization and this enables one to develop appropriate mechanistic models for curing of those resins [6]. The mechanism includes the following steps:



in which I , Z , M , R and \dot{R}_i represent initiator, inhibitor, monomer, radical and primary radical, respectively, and subscript j denotes the j -th initiator.

According to Eqn. 1, dissociation rate of each initiator in the resin can be expressed by the following equations:

$$\frac{d[I_j]}{dt} = -k_{d_j}[I_j] \quad (4)$$

where k_{d_j} is the dissociation rate constant for j -th initiator. When the inhibitor is present in the resin compound, no radicals can react with monomer and consequently, the crosslinking rate is assumed to be zero during this period, called induction period. In this study, we assume that there is no inhibitor in the system and therefore, the induction period due to the presence of inhibitor is neglected.

The rate of curing reaction or propagation reaction may be written based on the above mentioned elementary reaction, i.e., Eqn. 3, by inserting the monomer conversion α instead of concentration $[M]$ as:

$$\frac{d\alpha}{dt} = k_p (1 - \alpha) [\dot{R}_n] \quad (5)$$

where k_p is the overall propagation rate constant and $[\dot{R}_n]$ represents the concentration of radicals. In Eqn. 5, it is assumed that α is the total conversion of all carbon double bonds, either vinylene groups in the resin or vinyl groups in the reactive diluent, and the reactivity of both types of double bounds with radicals is the same so as to only one propagation rate constant is appeared in Eqn. 5. Since the termination reactions are ignored during the curing process, the rate of radical production can be expressed as:

$$\frac{d[\dot{R}_n]}{dt} = 2f \sum_{j=1}^N k_{d_j} [I_j] \quad (6)$$

Since the propagation rate slows down due to diffusion limitations of polymeric segments and monomer molecules, the propagation rate constant should be modified with an appropriate relation such as [7]:

$$k_p = k_{p_0} (1 - \alpha)^n \quad (7)$$

where k_{p_0} is the temperature dependent propagation rate constant and n is a constant. It is assumed that temperature dependence of all the rate constants presented here is expressed by an Arrhenius relationship.

Governing Equations for Filling and Curing Stages of RTM

Mold filling stage of RTM includes the resin flow inside the mold preplaced with fiber reinforcement. Darcy's law is often used to describe the resin flow through fibrous porous media during the mold filling stage of the RTM process:

$$\vec{v} = -\frac{[K]}{\mu} \nabla P \quad (8)$$

where $[K]$, μ , P and \vec{v} represent the permeability of the fiber reinforcement, resin viscosity, resin pressure and velocity vector, respectively. Darcy's law can be combined with an appropriate resin mass conservation equation to obtain the resin pressure distribution within the mold. The mass conservation model utilized in this study is based on the concept of partial saturation at the flow front [8] based on the following conservation equation:

$$\phi \frac{\partial s}{\partial t} + \nabla \cdot \vec{v} = 0 \quad (9)$$

where s is the saturation level ranging between 0 and 1, and ϕ is the porosity.

The temperature distribution inside the mold during the mold filling stage can be determined by an appropriate energy equation for porous media. Thermal equilibrium model is known to be reasonable for the RTM process and has been widely used by researchers to simulate the non-isothermal RTM [1, 9, 10]. In the thermal equilibrium model, it is assumed that the

temperatures of the resin and fiber are the identical at each location, and consequently the energy balance can be described by a single equation as:

$$\rho C \frac{\partial T}{\partial t} + \rho_r C_r \vec{v} \cdot \nabla T = \nabla \cdot (k \nabla T) + \phi H_T \dot{m} \quad (10)$$

where ρ , C , k and ∇T denote the density, specific heat, thermal conductivity and temperature gradient, respectively. The subscript "r" stands for the resin, H_T is the total heat of reaction and $\dot{m} = d\alpha / dt$ represents the rate of cure.

During the filling stage, the distribution of degree of cure can be obtained by the mass conservation of chemical species, representing the conversion of monomer to polymer as:

$$\phi \frac{\partial \alpha}{\partial t} + \vec{v} \cdot \nabla \alpha = \phi \dot{m} \quad (11)$$

Based on the mechanistic kinetic modeling, \dot{m} can be obtained using Eqn. 5, in which the rate equation is expressed as a function of reactive ingredients of the resin system. In Eqn. 11, it is assumed that the molecular diffusion of macromolecules is negligible and conversion is dominated by the convection of fluid and chemical reaction. In order to complete the set of governing equations in the filling stage of the RTM process, it is required to obtain the mass conservation model for reactive species including initiators and radicals. For the initiators, we get:

$$\phi \frac{\partial I_j}{\partial t} + \vec{v} \cdot \nabla I_j = \phi \dot{m}_{I_j} \quad (12)$$

in which \dot{m}_{I_j} is the dissociate rate of j -th initiator expressed by Eqn. 4. The same equation can be written for radical concentration. The possible boundary conditions at injection gate are: $P = P_0$ for constant pressure injection or $Q = Q_0$ for constant flow rate injection; $T = T_0$; $\alpha = 0$; $[Z] = [Z]_0$; $[R_n] = 0$; $[I_j] = I_{j,0}(t)$, at the mold wall $\frac{\partial P}{\partial n} = 0$; $T = T_w$ and at the flow front $P = 0$, $T = T_f$ where T_f denotes the fiber temperature.

The governing equations in the curing stage include the heat and chemical species balances. These equations are identical with those of filling stage without convection terms in the relevant equations, due to the motionless feature of the resin.

Numerical Implementation

The control volume/finite element method (CVFEM) is used to discretize the governing equations of both filling and curing stages. Using the CVFEM, the momentum (Darcy's law), heat and mass balance models are converted to equation sets from which pressure, temperature and conversion distribution can be obtained subject to appropriate boundary and initial conditions. Details of the numerical formulation can be found elsewhere [1, 8].

NUMERICAL RESULTS AND DISCUSSION

Fig. 1 exhibits the flow front progression predicted by numerical simulation inside a rectangular mold. The dimensions of the mold are 0.4 m in length, 0.2 m in width and 0.01 m in thickness. As can be seen, the resin flows unidirectionally inside the mold, in particular at the end of mold filling stage.

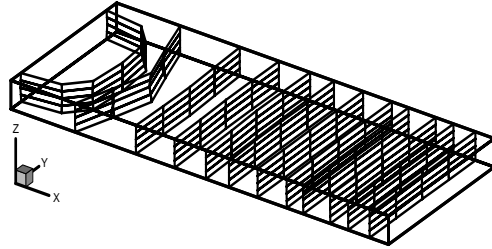


Fig. 1 Flow front progression during the injection stage.

Fig. 2 displays the simulated temperature history of different points located along the length of a rectangular mold as a reference system. Reference molding condition includes injection pressure of 100 kPa, mold wall temperature of 90 °C, fiber permeability of $2 \times 10^{-9} \text{ m}^2$, fiber volume fraction of 0.3, initial fiber and the inlet temperatures of 25 °C. TBPB (*tert*-butyl perbenzoate) is used as initiator whose dissociation rate constants can be found in [11]. The concentration of this initiator is 30 mol/m^3 . Other thermophysical and rheological properties required for the numerical simulations are taken from Ref. [9]. The constant n in Eqn. 7 is 0.65 and propagation rate constant is given as [7]:

$$k_{p_0} (\text{m}^3 / \text{mol} \cdot \text{sec}) = 5.73 \times 10^9 (-9993/T) \quad (13)$$

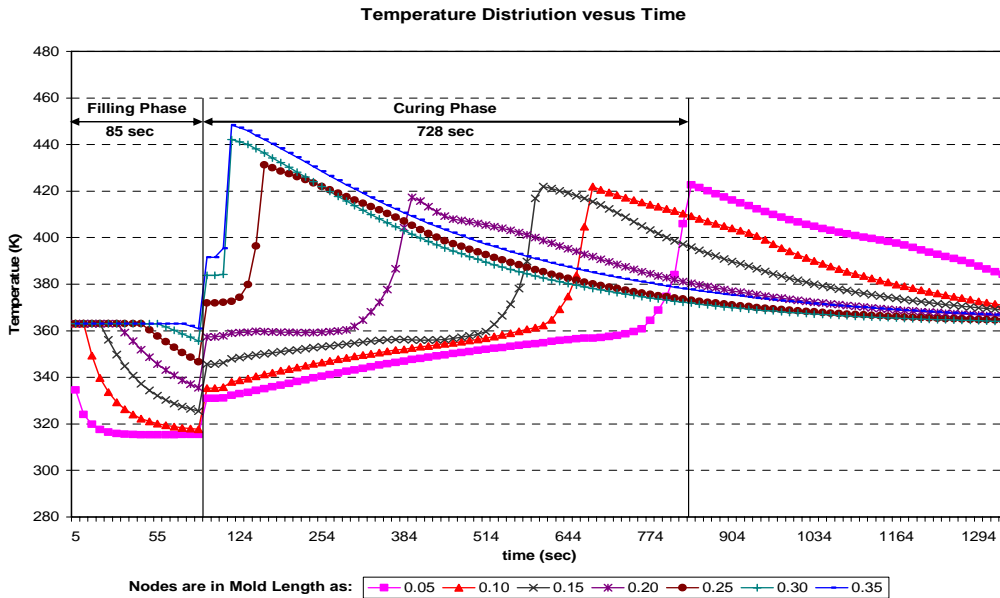


Fig. 2 Predicted temperature history for various points located along the length of the mold for a reference molding condition.

As can be seen in Fig. 2, the locations near the injection gate are cured last due to lower temperature of the resin in those regions. Moreover, the major part of the cycle time belongs to the curing stage. In this condition, the predicted cycle time including filling and curing stage is 813 s.

In order to examine the role of fast initiator on the cycle time, benzoyl peroxide (BPO) is used in the numerical simulations. The dissociation rate constant of BPO is taken from Ref. [11]. The numerical simulations showed that replacing the BPO with TBPB at the same molding condition results in premature resin gelation before complete mold filling due to high reactivity of this initiator. In order to reduce the cycle time without resin gelation during mold filling, the use of mixture of the initiators with a suitable manner can be helpful. To do this effectively, it is wise to enter the initiator with low reactivity at first stage of the mold filling followed by entering the high reactivity initiator. The task of determining the best (optimal) policy for combination/injection of two different initiators in this non-lumped system belongs to the dynamic optimization problem for distributed systems. The approach to analyze and solve the problem is a much difficult task unless; some engineering assumptions and convenient methodology are taken to get the sub-optimal solution in a much simpler manner and less computational load. More precise speaking, we have used a pre-determined injection pattern, i.e., soak-ramp methodology of two different initiators. Injection methodology of two different initiators, i.e. ter-Butyl perbenzoate (TBPB, initiator 1) and Benzoyl peroxide (BPO, initiator 2), used in this study is presented in Fig. 3. As shown in Fig. 3, mixture of both initiators is injected into the mold, so that $I_1(t)+I_2(t) = 30 \text{ mol/m}^3$. At the early stage of mold filling, only TBPB is injected into the mold so that $I_{01} = 30 \text{ mol/m}^3$. However, after a certain cavity filled fraction, i.e., V_0 , concentration of initiator 1 starts to decrease and initiator 2 increases, accordingly. Certainly, by decreasing the V_0 , cycle time reduction will be increased, however, the risk of resin gelation before complete mold filling increases. In addition to injection methodology, the concentration of initiators, i.e., I_{01} , and the rate of initiator injection, i.e., the slopes a and b represented in Fig. 2, can also influence the cycle time reduction and the uniformity of the cure cycle.

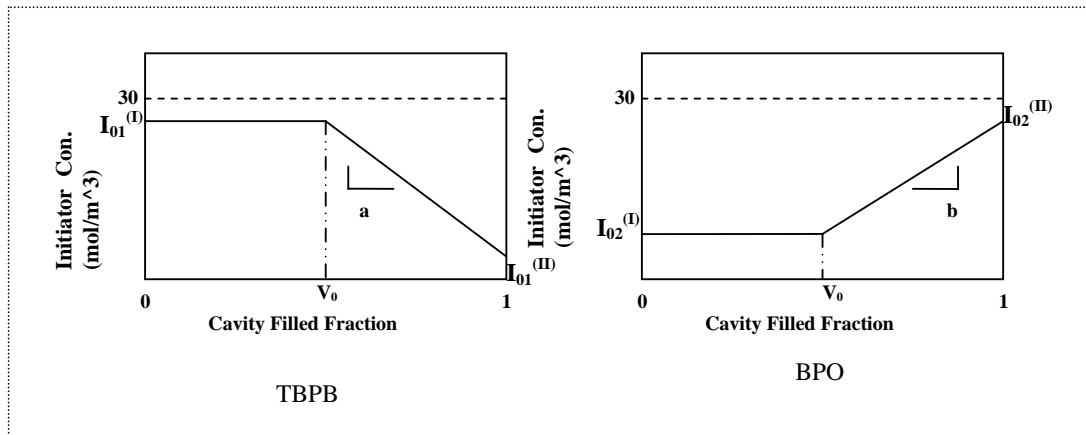


Fig. 3 Injection methodology of initiators BPO and TBPB.

It seems that by selecting appropriate values for parameters $I_{01}^{(I)}$, a and V_0 , the uniform cure with reduced cycle time without incomplete filling can be achieved. In this study, this is done by the use of an optimization technique called Nelder-Mead. This relatively wise algorithm

belongs to direct search (optimization) methods which do not need gradient information of objective function and works well for low dimension systems. It should be added that the static (algebraic) objective function has been defined as operational/engineering performance index of uniformity of the cure cycle. In the other words, the optimizer tries to find the best values of (I_{01} , a , b and V_0) to minimize the difference between cure times of the injection gate and the vent. According to this method, the optimized values for the parameters are: $I_{01}=12.5$ mol/m³, $a = -b= 27.5$, $V_0 =0.72$. The numerical simulation under the optimized condition is shown in Fig. 4. As can be seen, the uniformity of the cure cycle (the difference between cure times of the injection gate and the vent) and the total cycle time show significant improvement when the mixture of two initiators is used. In the case of dual-initiator systems, cycle time reduces from 813 s to 254 s showing around 60% reduction.

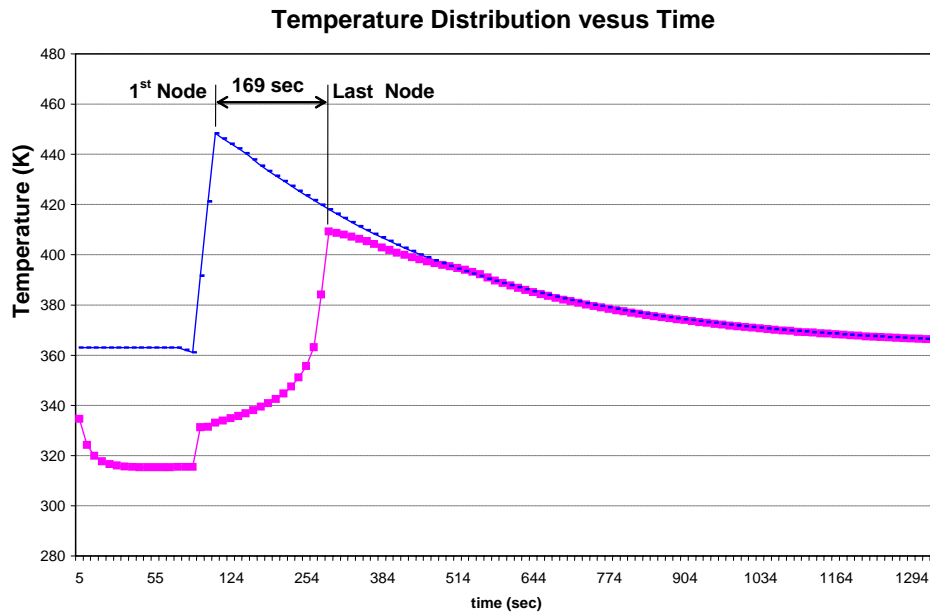


Fig. 4 Temperature history for the locations near the injection gate under optimized conditions.

CONCLUSIONS

This paper is focused on the modeling and simulation of the non-isothermal RTM process based on the mechanistic kinetics models. A mechanistic model based on general free radical copolymerization concept is developed in this study. The free radical copolymerization mechanism has been accepted for curing of such resins as unsaturated polyester and vinyl ester resins. The mechanistic kinetic model used in this study is combined with the heat and mass conservation equations for filling and curing stages. Numerical simulation based on the developed models enables us to investigate the role of type and concentration of initiators as well as dual initiator systems on the cycle time. The numerical simulation performed on a simple rectangular mold showed that by injecting two initiators with different reactivities in a suitable manner, a considerable reduction in cycle time can be achieved. It is shown that the optimum condition for injection of initiators can be achieved by combining the numerical simulation with a suitable optimization technique.

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