Control of Thermal Gradients in Thin Resin Transfer Molding Parts

Aouatif Saad [1,*] 🆔

[1]   Laboratory of Engineering Research in Advanced Systems. National School of applied sciences, Ibn Tofail University, Kenitra, Morocco

*   Correspondence: saad_aouatif@yahoo.fr (A.S.), saad.aouatif@uit.ac.ma (A.S.);

Abstract: Resin transfer is a manufacturing process of composite materials where a thermodurcisable resin is injected in a closed mold containing dry fibrous reinforcement. After the entire mold has been filled, a curing reaction is initiated to bind the resin to the solid reinforcement. A rise in the mold temperature accompanies this exothermic curing reaction. The heat released gives rise to a temperature gradient in the composite. This thermal gradient causes residual stresses that are treated as undesirable since they cause deformations and affect the quality of the final product. In our numerical analysis by using the finite difference method for the composite laminate, we have first highlighted the thermal gradient by presenting the evolution of the temperature and the degree of cure during the resin curing; we then investigated the effect in the thermal gradient of the first the resin and fiber nature, second the reinforcement structure and last the temperature cycle choice. The validity of our model is evaluated by comparing numerical and experimental results in the existing literature, and a good agreement was observed.

Keywords: RTM; thermal gradients; finite difference method; residual stresses; cure.

1. Introduction

Resin transfer molding (RTM) is a process for manufacturing composites in which a thermosetting resin (polyester, epoxy, etc.), with relatively low viscosity, is injected at low pressure (1 to 10 bars) or a low flow rate (a liter per minute), through a dry reinforcement placed in a heated closed mold. Once the injection step is complete, the polymerization process begins, and finally, the demoulding and finishing of the final piece [1,2]. This released heat generates a thermal gradient in the composite, which is as pronounced as the thermal conductivity of organic matrices decreases. This undesirable thermal gradient is detrimental to the final composite [3,4].

By managing the temperature of mold walls, we can manage the curing reaction and then minimize the temperature gradient in the composite. Many studies in the literature were interested in optimizing the curing process of composites. The results of Choi *et al*. [5], Yang *et al*. [6], and Cheung *et al*. [7] allow for highlighting the existence of a thermal gradient that appears during the heating reaction and is strongly pronounced at the center of the mold. Szarski *et al*. [8] presented a methodology to control the heat resulting from the chemical reaction. Kawagoe *et al*. [9] proposed a curing simulation technique in thermoset resin combined with carbon fiber for good materials properties. Reichanadter *et al*. [10] developed

a new rapid cure epoxy resins to achieve a complete cycle time, Zhang *et al.* [11] developed an optimization method for the curing thick composite, Hoshino *et al.* [12] proposed a heterogeneous dynamics method for the curing process of epoxy resins which helps to optimize the curing conditions of different materials to ameliorate their properties.

In this paper, we have presented a methodology to control the heat reaction, which minimizes the temperature gradients in the composite laminates. The method efficiency is proved with a highly reactive resin injected into various fiber reinforcements in a mold of rectangular shape.

2. Materials and Methods

2.1. Mathematical equations.

2.1.1. Heat Transfer model.

The heat transfer in the composite laminate is governed by the following equation [13-15]:

$$\rho C_p \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial z^2} + \rho_r.(1 - v_f).\Delta H_r . \frac{d\alpha}{dt} \tag{1}$$

The expressions of the thermal properties k, ρ and C_p are defined as follows [5]:

$$\frac{1}{\rho} = \frac{w_r}{\rho_r} + \frac{w_p}{\rho_r} + \frac{w_f}{\rho_f} \tag{2}$$

$$C_p = w_r.C_{p,r} + w_p.C_{p,p} + w_f.C_{p,f} \tag{3}$$

$$lnk = V_{rp}.lnk_{rp} + V_f.lnk_f \tag{4}$$

The mass fractions wr, wp, and wf are respectively given by the following expressions [5,16]:

$$w_r = w_{r0}.(1 - \alpha) \tag{5a}$$

$$w_p = w_{r0} . \alpha \tag{5b}$$

$$w_f = w_{f0} \tag{5c}$$

The volume fractions v_r, v_p and v_f are given respectively by [5,17]:

$$v_r = w_r \frac{\rho}{\rho_r} \tag{6a}$$

$$v_p = w_p \frac{\rho}{\rho_p} \tag{6b}$$

$$v_f = \frac{\rho}{\rho_f} \tag{6c}$$

2.1.2. Kinetic equation.

The curing rate reactions used in our simulation is given by the following equation [5,7]:

$$\frac{d\alpha}{dt} = (K_1 + K_2\alpha^m)(1 - \alpha)^n \tag{7}$$

With [18,19]: $K_i = A_i.\exp\left(-\frac{E_i}{RT}\right)$ i=1, 2, 3….

2.2. Boundary conditions.

At (t=0): $T = T_0$
The mold wall: $T = T_w(t)$
The wall center: $\frac{\partial T}{\partial n} = 0$

The initial condition of curing reaction [7]: $\alpha = \alpha_0$ at $t=t_0$.

As a time-dependent analysis was conducted, it was necessary to define the initial condition for both the heat transfer and the conversion rate models. A room temperature equal to 25°C, and a value of 0 degrees of cure were the imposed condition at the time zero.

2.3. Numerical methods.

In our numerical calculation we have chosen the explicit finite difference method to approximate the two equations (1) and (7). The distribution in all the domain of temperature and degree of cure is calculated at each time step as a function of the temperature of the imposed curing cycle [15]. The discretization results of the curing equation by means of finite difference method is presented as [20-22]:

$$\alpha_j^{t+\Delta t} = \left(\frac{d\alpha}{dt}_j^{t+\Delta t} + \alpha_j^t\right). \Delta t \tag{8}$$

The stability condition used in this work is expressed as follows:

$$\Delta t \leq \Delta z^2/(2. a) \tag{9}$$

The discretization of the heat equation by the finite difference method is given as follows [20-22]:

$$\frac{T_j^{i+1}-T_j^i}{\Delta t} = \frac{k}{\Delta z^2}(T_{j+1}^i - 2T_j^i + T_{j-1}^i) + \rho_r. (1-v_f). \Delta H_r \left(\frac{d\alpha}{dt}\right)_j^{t+\Delta t} \tag{10}$$

This gives:

$$T_j^{i+1} = T_j^i + a * \frac{\Delta t}{\Delta z^2 (T_{j-1}^i - 2T_j^i + T_{j+1}^i)} + \rho r. (1-v_f). \Delta H_r .* \Delta t/\Delta z^2. \left(\frac{d\alpha}{dt}\right)_j^t \tag{11}$$

3. Results and Discussion

3.1. Validation of the numerical method.

The mold used in our simulation is of a rectangular shape with (10 cm x1 cm) (figure 1). With a fiber Glass preforms saturated with the Polyester resin, the curing reaction is then initiated by heating the mold wall. For the resin/fiber parameters, we opted in our work for the kinetic parameters used by Choi *et al.* [5] as listed in Table 1, and the thermo-physical properties presented in Table 2.
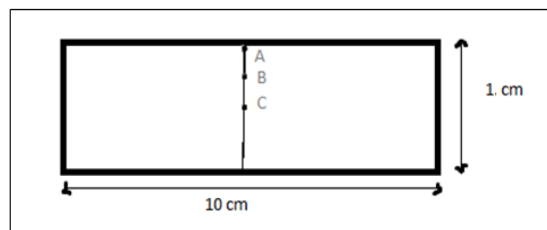

Figure 1. Mold configuration with the studied point: A, B, and C.

Table 1. Glass/polyester cure kinetics parameters [5].

Parameters	Values
$k_1(1/s)$	$5{,}68667 \ 10^{12}$
$k_2(1/s)$	$8{,}61167 \ 10^{8}$
E_1(cal/mol)	25570
E_2(cal/mol)	17930
n	1.42
m	0.58
ΔH (cal/mol)	47.8

Table 2. Thermo-physical properties of fibers used in our simulation.

	ρ (kg/m^3)	Cp (J/kg)	k (W/m.K)
Fiber 1	1000	1000	0.31
Fiber 2	1900	1000	0.31
Fiber 3	1000	1500	0.31
Fiber 4	1000	1000	1.9

We have resolved the couped heat equation and the curing kinetic equation in our numerical approach. This allows us to calculate at each time step and point in the thickness of the laminate both the temperature T and the degree of cure α [17]; this makes it possible to understand the evolution of the resin during curing. We can observe from figures 2 and 3 that the temperature and the degree of cure increase very quickly at the center of the composite; consequently, this gives rise to an exothermic peak, which is in good agreement with the results of Choi *et al*. [5].

The temperature reached a maximum of 400.27 K, while the temperature of the boundary condition in the mold wall didn't exceed 378 K.
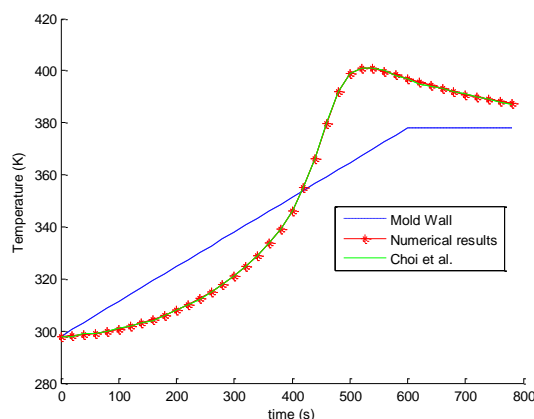

Figure 2. The temperature profile of the central node for the polyester/glass laminate.
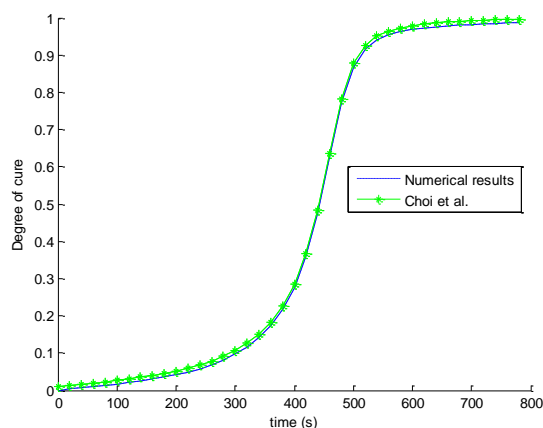

Figure 3. Degree of cure of the central node for polyester/glass laminate.

3.2. Procedure to reduce thermal gradients.

3.2.1. Effect of the fiber choice.

One can deduce from our simulation results (Table 3) that the more the density and the thermal capacity, and the thermal conductivity of fiber are greater, the more the thermal gradient generated is reduced.

Table 3. The maximum temperature reached in the four fibers used.

	Maximum temperature (K)
Fiber 1	400.2749
Fiber 2	399.1394
Fiber 3	400.2357
Fiber 4	396.2129

3.2.2. Effect of the fiber volume fraction.

Here we have kept constant all the Thermo-physical properties of fiber and matrix, and we have taken different values of fiber volume fraction. Figure 4 shows the evolution of thermal gradient with fiber volume fraction; we can conclude that the maximum temperature at the center of the laminate decrease by increasing the volume fraction of the fiber, for a $V_f = 0.7$, there is no thermal gradient appeared since the maximum temperature reached is 377.9 K while it was 378 k in the mold wall, we can deduce from these results that the more the volume fraction is higher, the less the is the thermal gradient.
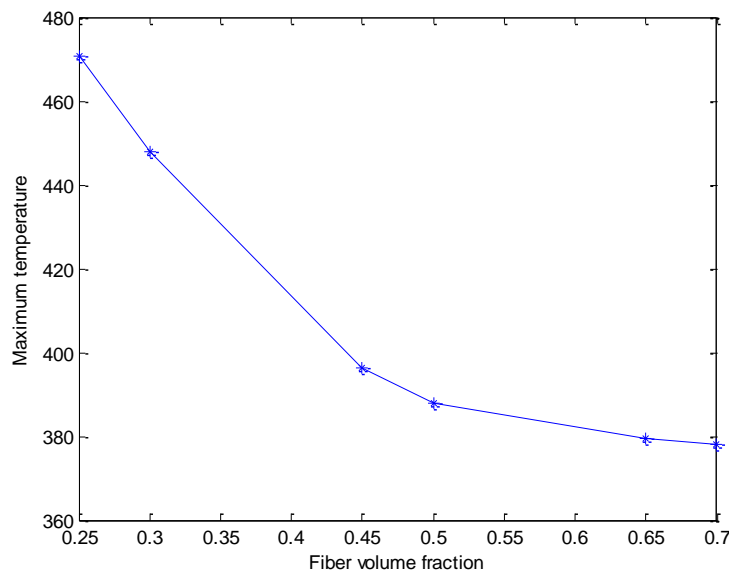

Figure 4. Evolution of maximum composite temperature versus the fiber volume fraction.

3.2.3. Multiple plies reinforcement.

In almost all of the applications, we use only one ply of reinforcement with uniform properties, but in the case of low thermal conductivity, the thermal gradient is highly pronounced. To resolve this situation, one can increase the conductivity of the whole reinforcement, which is not practical since it increases the cost of the final product. To overcome this restriction, we have suggested using multiple plies of reinforcement (Three plies) (figure 5), and we then choose a high conductivity for only the middle ply because the thermal gradient is higher at the center of the composite, according to Choi *et al*. [5].

Table 4 below presents the thermo-physical properties of the reinforcement used in our simulation.

In our numerical study, we have used the fiberglass in the three plies with the fiber volume fraction is higher at the center. Figure 4 shows the temperature profiles at the three points A, B, C) in the laminates, we can note that a big margin reduces the thermal gradient. In fact, by using the mold wall temperature of 378K, the maximum temperature is 378.28 K. While it was 399.1 K in the case of simple reinforcement with low fiber fraction.
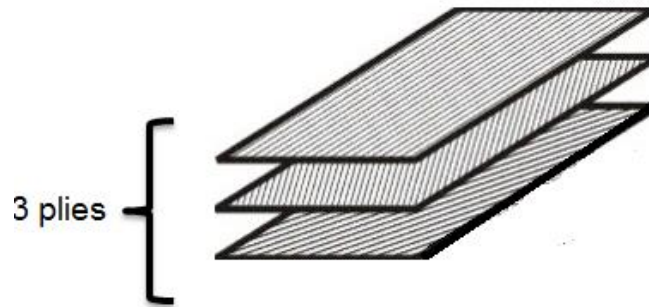

Figure 5. Three plies reinforcement used in our simulation.

Table 4. Thermo-physical properties of the material used in our simulation [23].

	ρ (kg/m^3)	Cp (J/kg)	k (W/m.K)
Fiberglass	1900	1500	0.31

The profile of the degree of cure at the central section is presented in figure 6. At the initial stage of curing, a lower degree of cure was observed at the midpoint of the central section due to the low temperature; however, the degree of cure increased abruptly due to the internal exothermic reaction as the autoclave temperature increased, but it is reached only 0.94 (figure 7).
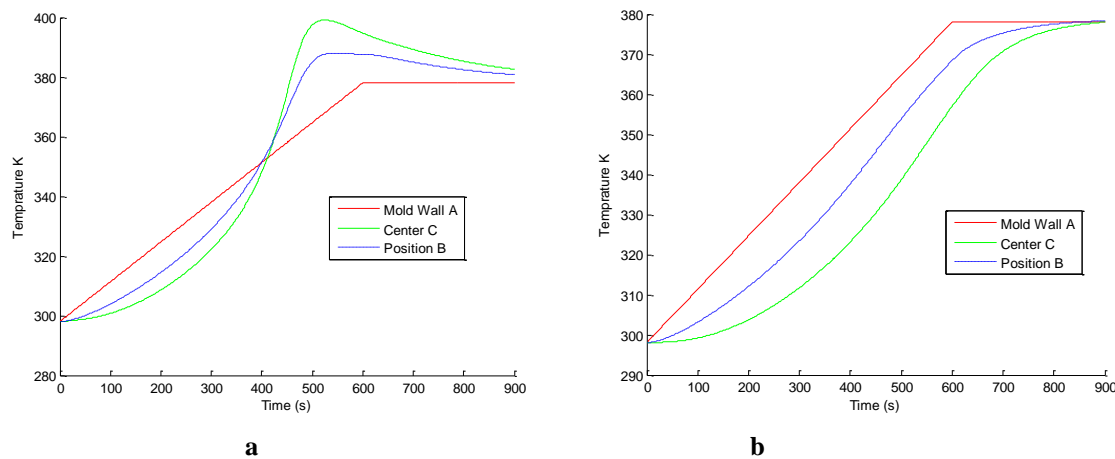

a

b

Figure 6. Temperature profile at different mold positions for the polyester/glass: a. one reinforcement, b. three plies of the laminate.

To increase more the degree of cure to ensure a complete resin polymerisationpolymerization, we have increased the mold wall temperature from 378K to 400K. Consequently, the degree of cure moved to 0.98 (figure 8). Furthermore, it appears clearly from the comparison between figure 7 and 8 that the cure speed is high, and thus the rate of cure is typically enhanced in the case of 400K for mold wall temperature.
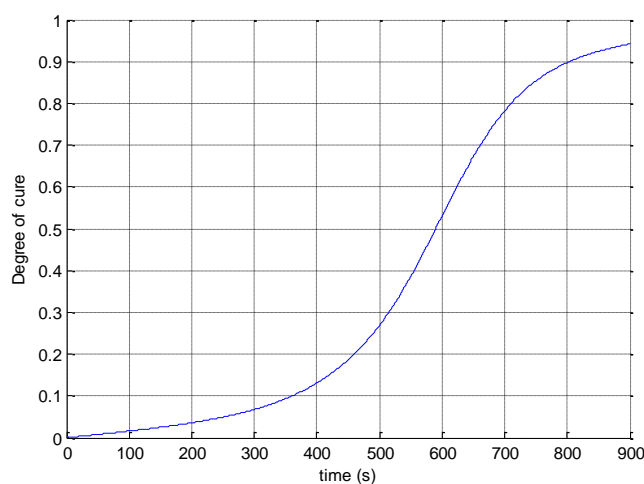
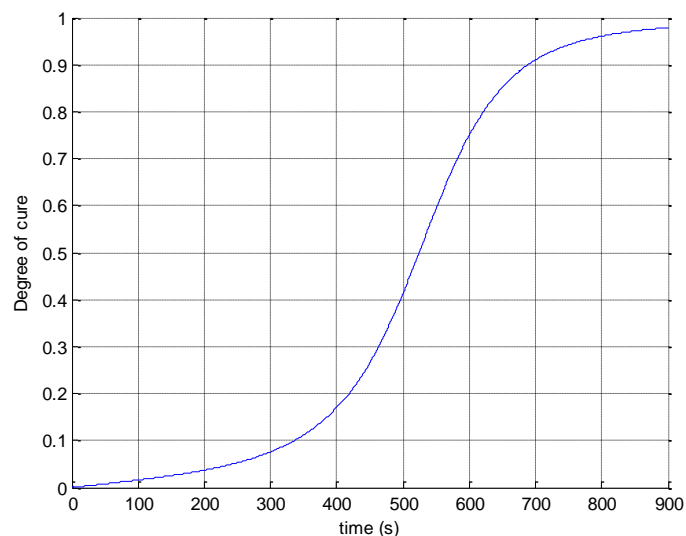**Figure 7.** Degree of cure of the central node for polyester/glass laminate.

Figure 8. Degree of cure of the central node for polyester/glass laminate with the mold wall temperature of 400K.
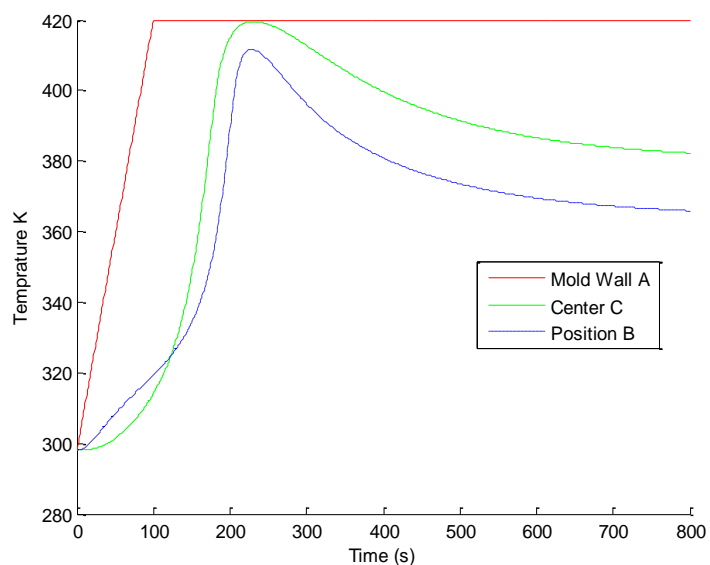

Figure 9. The temperature profile in different positions of the reinforcement for the polyester/glass.

3.2.4. Effect of the temperature cycle.

The influence of variables like resin type, fiber type control the temperature distribution and could if they were carefully chosen, reduce the thermal gradient, as is shown in the study of Saad *et al*. [22].

It was proved by many studies [5,23] that the temperature history has more influence on the curing optimization.

The main problem deals with finding an optimum cycle for the wall temperature to allow a full or almost full resin cure. In our numerical analysis and among different choices, we have opted for a particular temperature cycle (figure 9); this allows a minimum gradient and a good resin cure, as shown in figure 10.
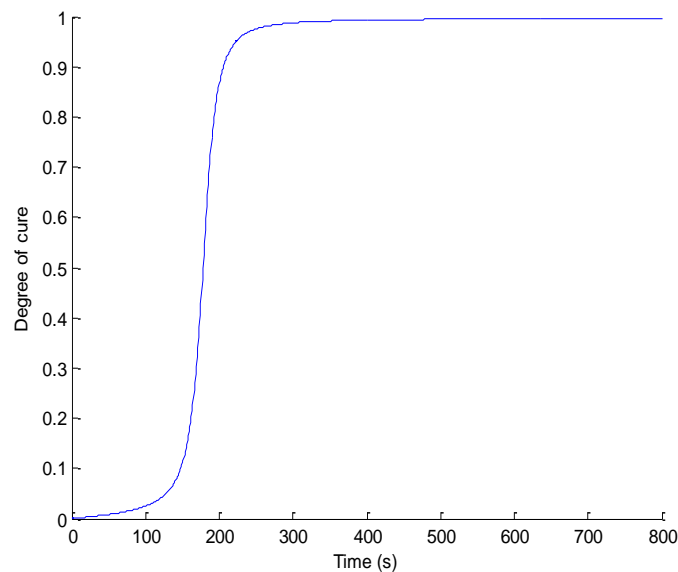

Figure 10. The temperature profile in different reinforcement positions for the polyester/glass.

The maximum temperature doesn't exceed 420.1745 K, while the temperature of the mold wall was fixed to 420 K. The degree of curing is 0.9988 in almost all parts of the composite; this allows a good and complete polymerization of the whole composite.

3.2.5. Effect of the resin choice.

In this study, we have kept the same fiber, but we have changed the resin nature. The polyester resin was replaced by the one used in Yang *et al*. [24]. The thermal properties of the resin used in this study are respectively ρ (kg/m^3)=1202 and Cp(J/kg)=2800.

The impact of resin choice has a considerable effect on the temperature profile during filling. As shown in Figure 11, there is a large difference in temperature in the laminate center between the two resins. We can conclude from figure 11 that resin with ρ (kg/m^3)=1202 and Cp(J/kg)=2800 has a minimal thermal gradient (maximum temperature is 380.26 K) by comparison with resin ρ (kg/m^3)=1890 and Cp(J/kg)=1260 (maximum temperature is 399.1 K), thus is more recommended.

Table 5 below summarizes the evolution of the thermal gradient with the resin parameters; one can conclude from these results that a resin with high density gives a maximum thermal gradient, while the gradient is as lower as the specific heat is higher.
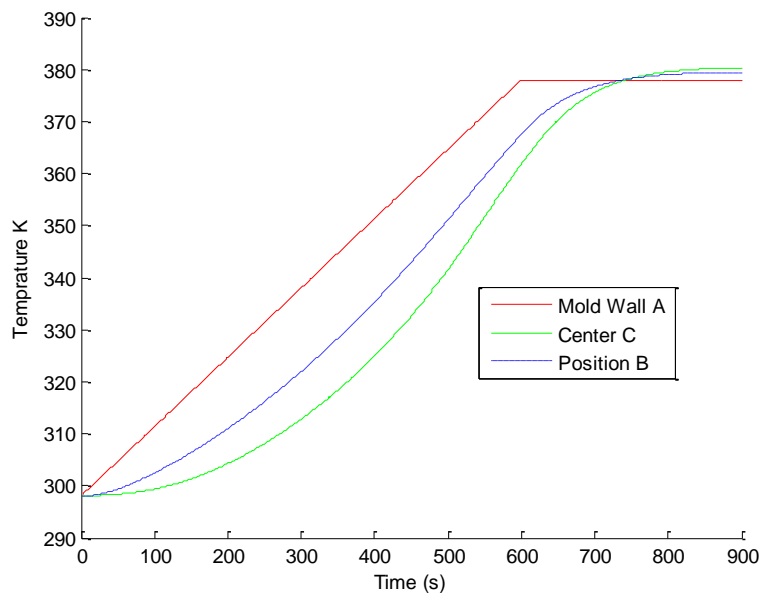
Figure 11. The temperature profile in different reinforcement positions for the polyester/glass.

Table 5. Results for mold temperature T=378K.

	ρ (kg/m^3)	Cp(J/kg)	Maximun temperature	Degree of cure
Resin 1	1000	1000	386.5	0.98
Resin 2	2000	1000	415.69	0.99
Resin 3	1000	2000	382.16	0.97

4. Conclusions

In this work, we are interested in studying the resin transfer molding process, especially the polymerization stage, which is characterized by a thermal gradient problem; this latter causes residual stresses that damage the quality of the final product. We have based on the finite difference method to develop a calculation program; this latter allows us to understand the evolution of the curing procedure in the resin transfer molding process. In this macroscopic approach, we are able to calculate the temperature and the degree of cure variation during curing. We have proved that the problem of a thermal gradient can be minimized by considering a series of preventive strategies, namely: the choice of fiber and the resin nature, the optimization of the temperature cycle in the mold, and the reinforcement structure. The obtained results present good conformity with some results in the literature.

The results show that our approach effectively reduces the thermal gradients during composite parts manufacturing by resin transfer molding process. This numerical study can considerably help engineers in RTM heating process in order to produce safe and healthy composite materials with good quality.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Yang, W.; Lu, S.; Liu, W. Numerical Simulation of Edge Effect in Resin Transfer Molding for Plain-weave Fabric. *Fibers and Polymers* **2020**, *21*, 2068-2075, https://doi.org/10.1007/s12221-020-9991-8.
2. Zaldua, N.; Maiz, J.; de la Calle, A.; García-Arrieta, S.; Elizetxea, C.; Harismendy, I.; Tercjak, A.; Müller, A.J. Nucleation and crystallization of PA6 composites prepared by T-RTM: Effects of carbon and glass fiber loading. *Polymers* **2019**, *11*, https://doi.org/10.3390/polym11101680.
3. Mueller, J.; Müller-Pabel, M.; Lorenz, N.; Gröger, B.; Gerritzen, J.; Gude, M.; Hopmann, C. Visco-thermo-elastic Simulation Approach For Prediction of Cure-induced Residual Stresses in Fiber Reinforced Composites. *ESAFORM 2021* **2021**, https://doi.org/10.25518/esaform21.4266.
4. Müller, M.; Gerritzen, J.; Gröger, B.; Gude, M. Thermomechanical Characterization of a Fast Curing Epoxy Resin for Simulation of Surface Waviness. *Procedia Manufacturing* **2020**, *47*, 129-133, https://doi.org/10.1016/j.promfg.2020.04.152.
5. Choi, M.; Lee, M.; Lee, S. Numerical Studies During Cure in the Resin Transfer Molding Process. *Korea polymer journal* **1998**, *6*, 211-218.
6. Yang, W.; Lu, S.; Liu, W. Optimization method to reduce three-dimensional thermal gradients in resin transfer molding. *Journal of Applied Polymer Science* **2020**, *137*, https://doi.org/10.1002/app.48948.
7. Cheung, A.; Yu, Y.; Pochiraju, K. Three-dimensional finite element simulation of curing of polymer composites. *Finite Elements in Analysis and Design* **2004**, *40*, 895-912, https://doi.org/10.1016/S0168-874X(03)00119-7.
8. Szarski, M.; Chauhan, S. Composite temperature profile and tooling optimization via Deep Reinforcement Learning. *Composites Part A: Applied Science and Manufacturing* **2021**, *142*, https://doi.org/10.1016/j.compositesa.2020.106235.
9. Kawagoe, Y.; Kikugawa, G.; Shirasu, K.; Okabe, T. Thermoset resin curing simulation using quantum-chemical reaction path calculation and dissipative particle dynamics. *Soft Matter* **2021**, *17,* 6707-6717, https://doi.org/10.1039/D1SM00600B.
10. Reichanadter, A.; Bank, D.; Mansson, J.A.E. A novel rapid cure epoxy resin with internal mold release. *Polymer Engineering & Science* **2021**, *61*, 1819-1828, https://doi.org/10.1002/pen.25703.
11. Zhang, W.; Xu, Y.; Hui, X.; Zhang, W. A multi-dwell temperature profile design for the cure of thick CFRP composite laminates. *The International Journal of Advanced Manufacturing Technology* **2021**, *117*, 1133-1146, https://doi.org/10.1007/s00170-021-07765-1.
12. Hoshino, T.; Okamoto, Y.; Yamamoto, A.; Masunaga, H. Heterogeneous dynamics in the curing process of epoxy resins. *Scientific reports* **2021**, *11*, 1-12, https://doi.org/10.1038/s41598-021-89155-x.
13. Bogetti, T.A.; Gillespie Jr, J.W. Process-induced stress and deformation in thick-section thermoset composite laminates. *Journal of composite materials* **1992**, *26*, 626-660, https://doi.org/10.1177/002199839202600502.
14. Kim, J.S.; Lee, D.G. Development of an autoclave cure cycle with cooling and reheating steps for thick thermoset composite laminates. *Journal of composite materials* **1997**, *31*, 2264-2282, https://doi.org/10.1177/002199839703102203.
15. Zade, A.; Shyamprasad, P.; Kuppusamy, R.R.P. Finite element modelling of non-isothermal curing kinetics for resin transfer moulding process. *Materials Today: Proceedings* **2021**, *47*, 5281-5288, https://doi.org/10.1016/j.matpr.2021.05.695.
16. Han, C.D.; Lee, D.S.; Chin, H.B. Development of a mathematical model for the pultrusion process. *Polymer Engineering & Science* **1986**, *26*, 393-404, https://doi.org/10.1002/pen.760260604.
17. Bogetti, T.A.; Gillespie Jr, J.W. Two-dimensional cure simulation of thick thermosetting composites. *Journal of composite materials* **1991**, *25*, 239-273, https://doi.org/10.1177/002199839102500302.
18. Palmieri, B.; Petriccione, A.; De Tommaso, G.; Giordano, M.; Martone, A. An Efficient Thermal Cure Profile for Thick Parts Made by Reactive Processing of Acrylic Thermoplastic Composites. *Journal of Composites Science* **2021**, *5*, https://doi.org/10.3390/jcs5090229.
19. Zhu, L.; Wang, Z.; Rahman, M.B.; Shen, W.; Zhu, C. The Curing Kinetics of E-Glass Fiber/Epoxy Resin Prepreg and the Bending Properties of Its Products. *Materials* **2021**, *14*, https://doi.org/10.3390/ma14164673.
20. Ghadle, K.P.; Mohammed, M.A.; Ghadle, A.K. Usage of the finite difference method for solving one-dimensional heat equations. *Bull. Pure Appl. Sci. Sect. E Math. Stat* **2021**, *40*, 87-98, http://dx.doi.org/10.5958/2320-3226.2021.00009.6.
21. Nolasco, C.; Garcia, N.A.; Garcia, G.G. Finite difference method applied to heat transfer in polymers. *Proceedings of the Journal of Physics: Conference Series* **2020**.
22. Saad, A.; Echchelh, A.; Hattabi, M.; El Ganaoui, M. Optimization of the cycle time in resin transfer molding process by numerical simulation. *Journal of reinforced plastics and composites* **2012**, *31*, 1388-1399, https://doi.org/10.1177/0731684412458166.
23. Kamal, M.; Sourour, S. Kinetics and thermal characterization of thermoset cure. *Polymer Engineering & Science* **1973**, *13*, 59-64, https://doi.org/10.1002/pen.760130110.
24. Yang, W.; Lu, S.; Xiang, L.; Liu, W. Simulation of non-isothermal resin transfer molding process cycle and optimization of temperature system. *Journal of Reinforced Plastics and Composites* **2019**, *38*, 3-14, https://doi.org/10.1177/0731684418800599.