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NUMERICAL STUDY OF THE PULTRUSION PROCESS WITH VARIABLE THERMAL PROPERTIES

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Abstract: Pultrusion process has gained significance as a composite manufacturing method over the past few years. It is a continuous process for composite materials with constant cross-sections with a high productivity and cost-effective. Pultrusion of thermosetting matrices consists of two phases, namely impregnation and curing. At first, a fiber creel passes through a resin bath. The fiber impregnated with liquid resin enters a heated die where the elevated temperature induces the curing resin process. Then, the pultruded bar is pulled through the die with a constant speed. The pulling speed, the die temperature, the fiber volume fraction and the thermal properties are important parameters that must be set carefully to obtain a high quality of the final product. At the present work, the carbon/Epoxy system has been simulated with a three-dimensional parabolic model employing the finite element method using thermal properties as a function both of temperature and degree of cure distributions inside the pultruded rectangular bar and making comparison with the assumption of to use constants average thermal properties. The evaluating the degree of cure and temperature profiles in different conditions for die-wall set-point temperature was also performed. Results showed that the degree of cure development is delayed for the variables properties case, requiring a larger die length to reach a suitable design value of the degree of cure and cure and temperature's positions in the die is important for to increase the rate degree of cure.

***Keywords**. Pultrusion, Finite Element Method, Thermal Simulation, carbon/Epoxy system.*

1. Introduction

The last decade has seen an intense interest in processes using composite materials. The potential product improvements related to damage tolerance, toughness, corrosion resistance and reparability, have been the main reasons for this growing interest. Pultrusion is one of several manufacturing processes for composite materials. A schematic representation of the pultrusion is shown in Fig. 1, initially the fiber reinforcements are impregnated with a resin formulation and continuously pulled firstly through a perform fixture which gives the desirable shapes to the resin/fiber combination and extracts the excess of resin. After that, the reformed material passes through a heated die where the resin cures and consolidates into a profile with the same cross-section as the die cavity. The profile is extracted at a uniform speed by a set of pullers and cut to the desired length by a synchronized cutoff saw.

As in the case of any other manufacturing process, it is important for pultrusion, although the process appears to be simple, to understand and optimize the processing parameters that can influence the properties of the finished parts such as pull speed die temperature, quality of fiber/resin wet-out, thermal properties and die temperature and fiber volume profile can affect the pultruded product final quality. Among all, the die temperature is closely related to the final state of cure of the product and the uniformity of cure can be improved significantly by optimizing the die-heating environment Li et al (2002).

During recent years, a great deal of work has been published concerning the optimization of the process parameters by means of thermochemical and physical model: Many previous works have analyzed the pultrusion process simulation: Loss and Springer (1983) developed a one-dimensional model to simulate the cure process of a flat-plate by solving the governing equation using an implicit finite difference method. Han and Lee (1986) applied an empirical kinetic model with a prescribed wall temperature profile in the simulation. Pultrusion characteristics were studied with variables such as resin type, fiber type and the pulling speed. Wu and Joseph (1990) developed an unsteady-state model to describe transient conditions for start-up or change of operation conditions, which includes the degree of cure and temperature distributions in the material and die.

Ma and Chen (1993) developed a kinetic model for heat transfer to predict profiles of temperature and degree of cure in a pultruded glass-fiber composite of rectangular cross-section for a block-polyurethane resin by using a finite-difference method.

Batch and Macosko (1993) studied the effect of die temperature, pull speed, resin properties and initiator concentration on part temperature profile and cure using a one-dimensional model in traditional pultrusion.

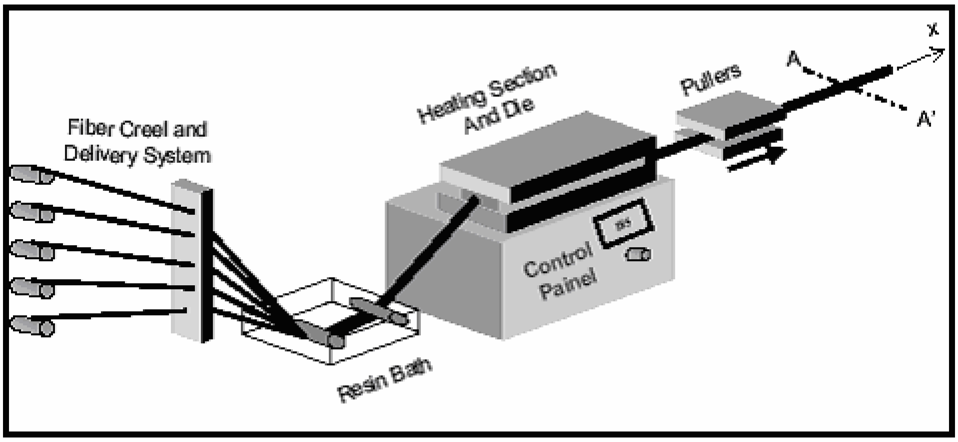

Figure 1. Schematic representation of the pultrusion process.

Their studies indicate that, prior knowledge of the die temperatures, resin physical properties and reaction kinetics can be used to predict the part temperature and cure profile.

Gorthala et al. (1994) extended this approach using a comprehensive two-dimensional model in cylindrical coordinates for resin flow, cure and heat transfer associated with the traditional pultrusion process. Different types of viscosity and velocity models were developed and experimentally validated to predict the temperature and cure profiles in the radial and axial direction. Their work provides some insights into the basic processing science.

Chachad et al. (1995) used an unsteady three-dimensional model for the pultrusion of irregular shaped glass composites using a finite difference scheme; no comparison of predicted results and experimental dada was provided.

Amazouz and Gauvin (1997) analyzed the thermal conductivity increase of polymer matrix composites replacing a small amount of glass fibers by carbon fibers, resulting in a decrease in the composite material temperature. The authors employed a finite element technique and showed that the distribution of the anisotropic conductive fibers in the composite has an important effect on its thermal efficiency.

In this context, the objective of the present work is to study numerically the pultrusion process using a three–dimensional parabolic approach to simulate the carbon/Epoxy composite materials, employing the assumption of to use constants average thermal properties and evaluating the degree of cure and temperature profiles in different conditions for die-wall set-point temperature. Results showed that the use thermal properties constants overestimate the degree of cure and temperature's positions in the die is important for to increase the rate degree of cure.

2. Mathematical formulation

With the assumption that a fibrous medium impregnated with incompressible resin forms a macroscopically homogeneous material system for heat transfer analysis, the three-dimensional energy equation for a moving composites lay-up in a pultrusion die may be written as:

$$u\rho_C Cp_C \frac{\partial T}{\partial x} - \nabla \cdot \left[k_C \nabla T \right] - \frac{\partial}{\partial x}\left(k_C \frac{\partial T}{\partial x} \right) = \dot{q} \tag{1}$$

with the boundary conditions, as is shown in Fig 2.:

at x = 0 (die entry) → $T = T_0$ (ambient temperature)
at bar/die interface → $T = T_{wi}$, i = 1, 2, 3 (control set point temperature)

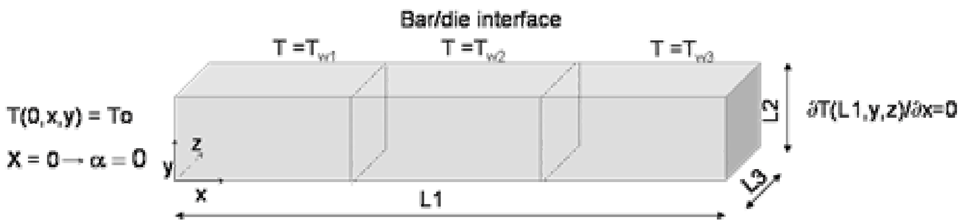

Figure 2 – Schematic representation of the composite material with boundary conditions this problem.

Where T is the temperature, u the velocity vector in pull (x) direction, ρ the density, Cp the specific heat, k the thermal conductivity , $\dot{q}$ the heat of reaction. The subscript *c* denotes the composites and ∇ denotes diferential operator. The values of the thermal properties are given in Tab. 1.

Table 1. The thermal properties of carbon/Epoxy composite materials (Scott and Beck, 1992)

Material	Density (kg m^{-3})	Thermal conductivity (W m^{-1}ºC^{-1})	Specific heat (MJm^{-3} ºC^{-1})
carbon/Epoxy	1850	$0.668 + 0.000902T + 0.0742\alpha$	$1.251 + 0.0045T + 0.139\alpha$

The volumetric heat rate (q) due to the resin-cure reaction is related to the degree of cure (α) by the Eq. (2):

$$\dot{q} = \rho r(1 - FV)\Delta H \frac{D\alpha}{Dt} \tag{2}$$

with ΔH = total heat of reaction per unit mass of resin.

The degree of cure is defined as the ratio between the energy liberated by the reaction until an instant of time (t) and the total energy liberated in whole cure reaction. The degree of cure variation with the time dα/dt, is obtained form the appropriate kinetic models and kinetic parameters for the composite under study. In this case, the models for $\alpha \le 0.5$ and $\alpha > 0.5$ presented by Scott (1989) for a carbon/epoxy system were used. The model for $\alpha(t) \le 0.5$ is:

$$\frac{d\alpha}{dt} = \left(c_1 + c_2\alpha^m\right)\left(1 - \alpha\right)^{2-m} \qquad 0 < \alpha \le 0.5 \tag{3}$$

and, the model for $\alpha(t) > 0.5$ is:

$$\frac{d\alpha}{dt} = \left.\frac{d\alpha}{dt}\right|_{\alpha = 0.5} + c_3\left(0.5 + \alpha\right)\exp\left(-D\left(0.5 - \alpha\right)\right) \qquad \alpha > 0.5 \tag{4}$$

where m=0.98-0.0023T, D=13.4-0.177T, and T is in ºC. The rate constants, c_1, c_2 and c_3, are assumed to follow Arrhenius relationships with temperature, that is

$$c_i = A_i \exp\left\{- E_i / \left[R\left(T + 273.15\right)\right]\right\} \qquad i = 1,2,3 \tag{5}$$

where R is the gas constant, the $E_i^{'}s$ are the activation energy constants, and the $A_i^{'}s$ are the pre-exponential factors. The values used for kinetic parameters are: E_1=55.8 kJ/mole, E_2=49.2 kJ/mole and E_3 = 56.9 kJ/mole, $A_1 = A_2 = 12100$ s^{-1}, and $A_3 = 2.75\times10^7$ s^{-1}.

$$\frac{D(\ )}{Dt} = u\frac{\partial(\ )}{\partial x} = \text{Steady-state one-dimensional substantial derivative.} \tag{6}$$

3. Solution methodology

For the convective-diffusive problems simulated by Eq. (1) the Peclet number is defined as:

$$Pe = (\ \rho C_p / k\ )\ u\ R \tag{7}$$

When the Peclet number is high, the pultrusion process shown in Fig. 1 can be solved using a parabolic model and the Eq. (1) is simplified by neglecting the axial conduction term, as follow:

$$u\ C_p\ \partial T/\partial x - \ \nabla \cdot \left[\ k\nabla T\right] = \dot{q} \tag{8}$$

In this parabolic approximation, Eq. (2), to Eq. (5) and Eq. (8) were discretized in the pultruded bar cross-section (Fig. 2) by the Galerkin finite element and the axial direction (pulling axis) was evaluated by a similar time marching technique. A computational grid in the intermediate process solution is shown in Fig. 2, where represent one forth of material.

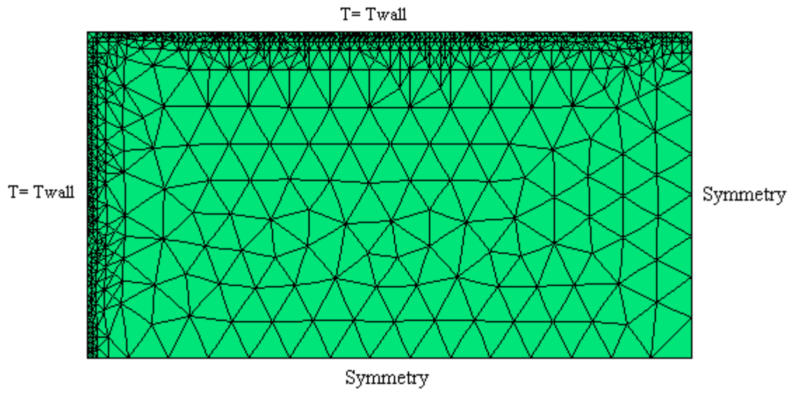

Figure 2. Computational grid in the intermediate process solution, 12x6mm, 1549 cells.

The heat transfer process and the resin cure kinetics equations in this parabolic approach are solved by a commercial code named PDEase2D. At the present work the Galerkin Finite Element Method of weighted residuals with quadratic basis to convert continuous partial differential equations into discrete nodal equations is used. This method insures highly accurate results and rapid convergence. An adaptive scheme was used with successive mesh refinement in the more intense gradient regions, using an unstructured mesh with triangular elements of six nodes and second-degree interpolation polynomials. The algebraic equations were solved by Conjugated Gradient and Newton-Raphson iterative methods.

The solution in the axial direction is obtained applying a Crank-Nicolson scheme where the cubic term in the Taylor series expansion is determined by a three-step approach. The z-axis step was controlled imposing this cubic term less than a pre-determined error limit.

4. Results

4.1. Parabolic Approach Validation

Pantaleão et al. (2000) presented a comparison between the elliptic Taylor-Galerkin and the parabolic results for the pultrusion process of thermosetting composite with circular cross-section. Both methodologies showed a good agreement for the pultrusion pulling speed typical values. Authors also reported a comparison with the experimental data provided by Suratno et al. (1998) and their numerical results are illustrated in Fig. 3a and Fig. 3b for the temperature and degree of cure profiles at the bar cross-section centerline. It was concluded that the parabolic scheme has some advantages: it requires smaller computational time processing and is easier to be implemented than the elliptic model.

Based on these previous results, at the present work a parabolic approach, Eq.(8), was used to study the effect of different controlling parameters in the pultrusion process of a bar with rectangular circular cross-section. The pultruded material aspect ratio (L2/L3, Fig 2) was maintained constant for all numerical simulations and the carbon/Epoxy composite materials properties were presented in Tab1.

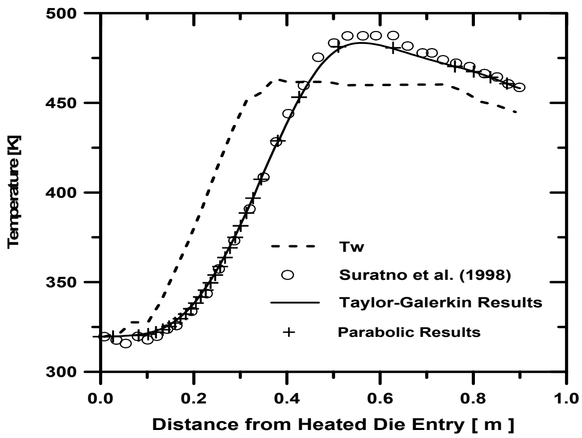

Figure 3a. Results for the axial temperature profile (u = 0.1/60 m·s-1and FV = 0.7)

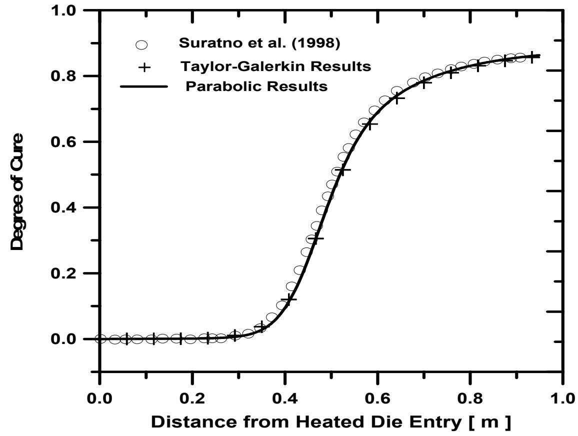

Figure 3b. Results for the axial degree of cure profile (u = 0.1/60 m·s-1 and FV = 0.7)

4.2. Parabolic approach with variables thermal properties.

The effect of the constant properties material assumption was employed using an volumetric average thermal conductivity (k_{av}) and specific heat (Cp_{av}) values, defined as:

$$Cp_{av} = \frac{1}{V}\int_0^V Cp dV \qquad\qquad k_{av} = \frac{1}{V}\int_0^V k dV \tag{9}$$

Figure 4 shows the variation of the thermal properties (as function of both temperature and degree of cure) along the rectangular bar centerline and its respective average values.

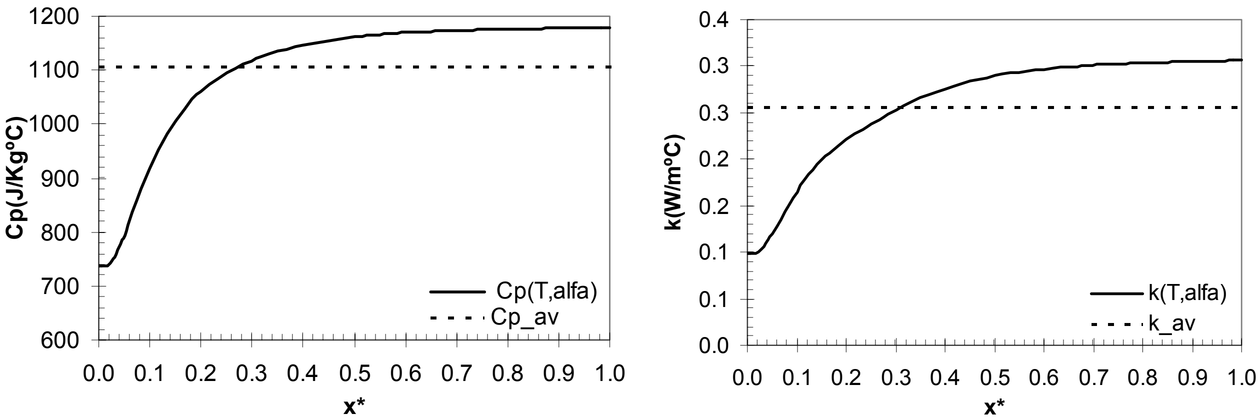

Figure 4: Variation of the thermal properties along the dimensionless rectangular bar centerline (x^*=x/L).

The profiles in Fig. 4 showed that the heat specific and thermal conductivity values increase during the pultrusion process. This fact induced significant differences on the process simulation, as depicted in Fig. 5 which compares the temperature and the degree of cure profiles for average and variable properties cases. These results show that the increase in the thermal mass (due to the increase in the specific heat capacity of the resin with the degree of cure) contributed most to the fall in the temperatures (Fig 5a) of the pultruded material in the region where the cure reaction rate was higher (Fig. 5b).

The higher the thermal mass of the resin, the more the heat energy required to raise the temperature of the bar composite. This shows that ignoring the temperature-dependence of the material properties leads to higher estimations of temperatures and degree of cure of the pultruded bar. This same conclusion was also met by Joshi and Lam (2001), working with a cylindrical rod epoxy resin system and 1% fiber volume.

It must be noted that temperature and degree of cure evolution presented in Fig. 5 were obtained imposing a constant die-wall temperature as boundary condition. The influence of the die-wall set-point temperature in the pultrusion process is described in the following section of this work.

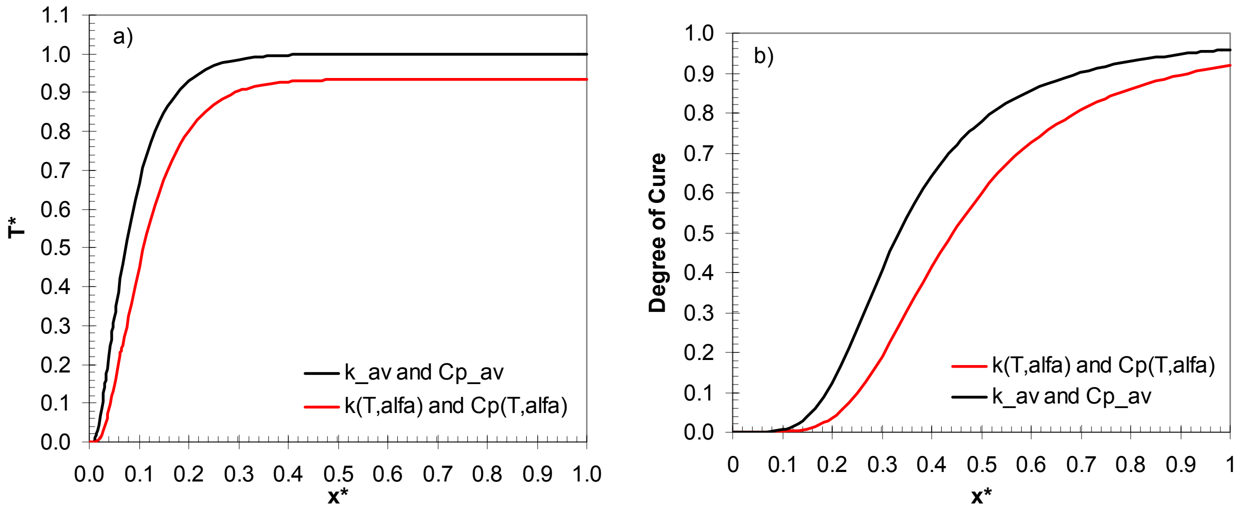

Figure 5 - Predicted center line temperature and degree of cure profiles for the rectangular bar and their comparison using average values of the thermal properties. $T^* = (T-T_0)/(T_w - T_0)$

4.3. Influence of the Die-Wall Set-Point Temperature.

Firstly, the die extension was divided in three same parts. After, three values of die-wall set-point temperature were imposed as boundary condition at each part (Fig. 2). Simulations were performed both decreasing and increasing the imposed temperature values, as illustrated in Tab.2. The non-dimensional temperature's values are calculated by: $T^* = (T-T_0) / (T_w-T_0)$.

Table 2 – Temperature boundary condition and validity region.

Region distance from heat die entry	$T^*w_{increasing}$ Case 1	$T^*w_{decreasing}$ Case 2	$T^*_{average}$ Case 3
$0 \le x \le L_1/3$	$T^*_{w1} = 0.868$	$T^*_{w1} = 1.000$	$T^*_{w1} = 0.868$
$L_1/3 < x \le 2L_1/3$	$T^*_{w2} = 0.934$	$T^*_{w2} = 0.934$	$T^*_{w2} = 0.868$
$2L_1/3 < x \le L_1$	$T^*_{w3} = 1.000$	$T^*_{w3} = 0.868$	$T^*_{w3} = 0.868$

Results using parabolic approach model with temperature-dependent thermal properties are given in figs 6, 7 and 8. The predicted rectangular bar centerline temperature with different die-wall set-point temperature are shown.

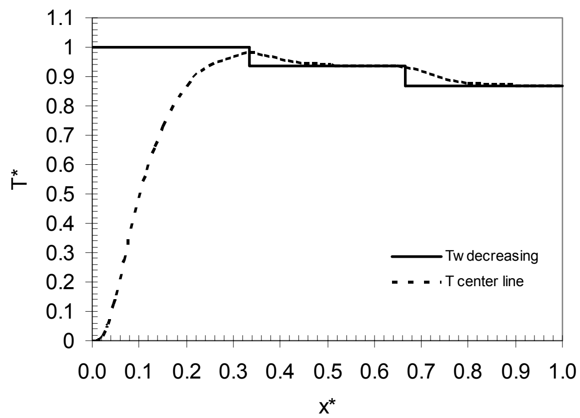

Figure 6 - Predicted center line temperature profiles for the rectangular bar with die-wall set-point temperature decreasing.

At the beginning of the resin cure process, the centerline temperature elevates independent of the boundary condition variation. When the die-wall set-point temperature increases (Fig.6) or decreases (Fig.7), the centerline temperature follows the same tendency along the dimensionless die extension. At the final portion of the heated die, the centerline temperature value for the constant die-wall set-point temperature (case 3, Fig. 8) is located at the average level between the cases 1 and 2.

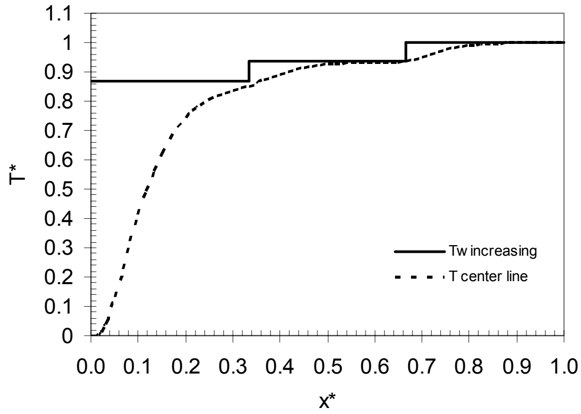

Figure 7 - Predicted center line temperature profiles for the rectangular bar with die-wall set-point temperature increasing.

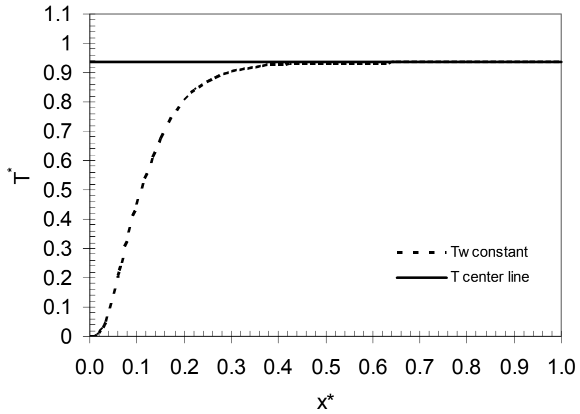

Figure 8 - Predicted center line temperature profiles for the rectangular bar with die-wall set-point temperature constant.

Numerical simulation results for the degree of cure are given in Fig. 9 for the three boundary conditions depicted in Tab. 2. The thermal properties (*Cp* and *k*) were calculated using the temperature and degree of cure dependence expressed in Tab.1.

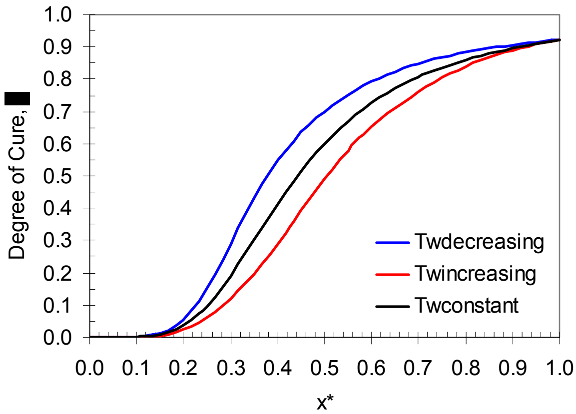

Figure 9 - Predicted degree of cure at center line for the rectangular bar for different conditions of wall temperature.

As it was expected, the die-wall temperature decrease (case 1) along the die-extension was favorable to accelerate the resin cure reaction rate due to higher temperature values at the die entry region. On the other hand, the case 2 (temperature increasing along the die-extension) induces a slower degree of cure evolution. So, the temperature boundary condition were only interchanged (the total thermal energy supply was the same) between the three cases, but the effect it was a variable performance in the temporal evolution of the pultrusion process.

4. Conclusions

At the present work a three-dimensional parabolic approach model was employed to numerically simulate the pultrusion process of a composite material composed Epon 828/mPDA epoxy system using finite element method. The constant/variable thermal properties and the influence of the die-wall set-point temperature were analyzed. Results showed that the use of constant specific heat and thermal conductivity values overestimates the degree of cure and temperature evolutions. The imposed temperature boundary condition also affects the pultrusion process, once the higher temperature values at the die entry accelerates the resin cure reaction rate.

5. Acknowledges

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