MATHEMATICAL MODELLING OF THE PULTRUSION PROCESS OF POLYESTER-GLASS FIBRE COMPOSITES

L. Calabrese[1] and A. Valenza[2]

[1] Department of Industrial Chemistry and Material Engineering, University of Messina, Salita Sperone 31, 98166 Sant'Agata (Messina), Italy
[2] Department of Chemical Process and Material Engineering, University of Palermo, Viale delle Scienze, 90128 Palermo, Italy

ABSTRACT

In this work the rheo-kinetic behaviour of a polyester thermoset system, optimised for the pultrusion technology, was analysed comparing experimental data with mathematical models. Then, to investigate the die temperature, curing degree and viscosity profile of fibreglass composite during the pultrusion process, a numerical model, developed through a numerical code realised with MATLAB, has been used. The realized program is based on the study of the heat transmission and the rheo-kinetic phenomena by a implicit finite difference model. The simulation shows interesting data on the temperature distribution and the curing evolution of the composite structure, within the die. Moreover the effect of temperature profile and pulling speed on the gelation and vitrification transitions within the die is examined to optimise the curing condition of the finished product with the manufacturing conditions.

1. INTRODUCTION

Pultrusion is one of the most used continuous processing techniques for the production of composites with constant cross-section, and it is applicable both for thermoset and thermoplastic matrix composites. In the process continuous fibres or fabrics pass through an orientation system and resin bath within a die, fitted with several heaters located in the die surface. Inside the die, the resin cures and solidifies in a laminate with the same cross-sectional profile of the die. A pulling system continuously exits the solid composite from the die; finally a travelling cut-off saw cuts the profiles to the desired length.

To obtain pultruded laminates with optimal performances in this process it is important to well define and control the pultrusion parameters (i.e. impregnation procedure, reinforcement selection and curing process).

Factors influencing the behaviour of the composite material within the die during the pultrusion process are the temperature, the cure and viscosity evolution [1]. In fact, when the curing reaction occurs, the temperature in the centre of the composite increases rapidly, due to heat of curing reaction;

The cure process is not only related with the significant heat generation, due to exothermic polymerisation reactions of the thermoset resins (that affects i.e. the degree of cure and the temperature profile of the composite within the die), but is also coupled with relevant changes of the material viscosity (that influences i.e. the fibre impregnation, the pulling force and the diffusion effects on the curing evolution) [2].

When the resin enters within the heated die, we observe concurrent phenomena (physical and chemical modifications). To understand the behaviour of the resin-fibre system in the die, during the process, the curing reaction and the viscosity variations, associated at a specific thermal treatment, must be known at the same time. In this way it is possible to improve the simulation and prediction of the cure state evolution of the product as it is pulled through the heated die.

A correct experimental knowledge of the constituent allows to manage efficiently and economically the process parameters.

The aim of this research is to develop a 3-D mathematical model able to describe temperature and curing phenomena that take place in the composite profile during the pultrusion process, establishing the cure and viscosity resin characteristics for a simple geometry of the die.

More researches are executed in the pultrusion process simulation field to predict the temperature, cure degree and viscosity profile. Price [3] was the first to propose a pultrusion heat-transfer and cure model valid in isothermal or adiabatic process conditions. Then other works have developed several models, using finite difference approach [4-5] or finite element model [6-7], which include heat conduction, heat cure and changing thermal properties with temperature and cure degree. Moreover many articles are focused the attention on resins employed for the pultrusion process, particularly on chemo-rheological effect of the thermoset matrix on temperature profile expanding the pultrusion modelling by kinetic analysis [8-9]; few works analysed the gelation and vitrification transition phenomena that take place within the mould during the pultrusion process [10], although they influence heavy finished product quality of the composite profile and process conditions (as pulling force).The knowledge of the position of each transition zone within the die is useful to manage correctly the process parameters selection (as pulling speed or die temperature).

In this work a kinetic and rheological characterization of a polyester thermoset system, optimised for the pultrusion technology, has been carry out, to acquire useful information to solve the problems associated to gelation and vitrification transition within the die and consequently to optimise the curing process by a correct computer design.

Then, all the obtained process parameters have been used to elaborate an algorithm, employing MATLAB language programming, to simulate and optimise, the pultrusion process with a mathematical model based on the study of the heat transmission and the kinetic and rheological phenomena. The implicit finite difference and fourth order Runge-Kutta method are used to solve the heat transfer problem of pultrusion reaction. In this way we can perform and optimise the finished product design.

2. EXPERIMENTAL PROCEDURE

An unsaturated polyester monomer (Exter ES 143 by COIM) was blended with styrene as harder with the weight ratio 2:100. According with a mixture usually used for pultrusion manufacturing process, several additives are added to reduce the product costs, improve the processability and reduce the shrinkage of the resin. The calorimetric measurements are performed using a Shimadzu Thermal Analysis Instruments TA-60. To measure the total heat reaction related with the full resin conversion, dynamic experiments (temperature ramp mode) are carried out at 5°C/min ranging from room temperature to 240°C. Further information of the curing kinetics was obtained executing isothermal curing tests at temperatures ranging 60°C to 110°C.

All the rheological measurements are carried out by means a parallel plate SR5, a stress controlled rheometer supplied by Rheometric Scientific. In order to investigate of the cure reaction contribute to the viscosity variations, dynamic tests at 5°C/min from room temperature to 160°C and isothermal tests are achieved under same isothermal conditions to the calorimetric analysis. The experiments were carried out with a constant stress amplitude (1000 Pa) and angular frequency (1 Hz).

3. PULTRUSION MODEL

A pultrusion process model was developed to accurately simulate the thermal evolution of the resin-fibre system within the die, dividing this procedure in three parts: heat transfer model, kinetic and rheological model.

For the cure and temperature process simulation the inside the rectangular die considered in this study, the following assumptions of the heat transfer model were supposed [2]:

- The process is at steady state; the pultrusion is a continuous process, the transient effects of start up and shutdown machine are excluded.

- The length of the die is much larger than the span wise dimension and therefore the heat conduction in the axial direction, through the resin and fibres is negligible;
- There is perfect contact between composite and wall;
- Longitudinal or transverse flow of the resin with respect to the fibres is negligible. This assumption is valid distant from the entrance taper-die;
- The resin and the fibres have the same local temperature;
- The reaction rate is unaffected by chemical interactions with the fibres and fillers or by internal resin pressure. The reaction kinetic parameters determined by DSC can be used directly in the analysis without modification;
- The effects of heating by friction at the internal die wall is neglected;

In bases these assumptions the temperature inside the composite in a pultrusion die can be expressed by this three-dimensional energy equation:

$$\rho_c C_p V_x \frac{\partial T}{\partial x} = K_y \frac{\partial^2 T}{\partial y^2} + K_z \frac{\partial^2 T}{\partial z^2} + \overset{\bullet}{q} \tag{1}$$

Where $\overset{\bullet}{q} = \Delta H_r \phi_r \rho_r \, \partial\alpha/\partial t$ is the contribute due to resin polymerisation; $\partial\alpha/\partial t$ is the conversion rate of the reactive resin matrix; ΔH is the total heat of reaction per unit mass of the fibre-resin composite. Then T is the temperature, ρ_c and ρ_r are the density respectively of composite and resin, ϕ_r is the weight fraction of the resin C_p is the composite heat capacity and k_i is thermal conductibility of the composite in x or y direction. The temperature distribution of the mould can be expressed by the eq. (1) excluding the resin curing contribute. In the hypothesis that the top and bottom heated faces of the die are at the same temperature, the process is symmetric on the longitudinal and transverse directions. Therefore only a quarter of the composite-die section was modelled. The normal heat flow at the composite-die interface is:

$$-K_{die} \left. \frac{\delta T_{die}}{\delta y} \right|_{y_{die}=0} = -K_C \left. \frac{\delta T_{die}}{\delta y} \right|_{y_C=w_C} \quad and \quad -K_{die} \left. \frac{\delta T_{die}}{\delta z} \right|_{z_{die}=0} = -K_C \left. \frac{\delta T_{die}}{\delta z} \right|_{z_C=l_C} \tag{2}$$

where w_c and b_c are respectively the thickness and the width of the profile.
In Table 1 the necessary parameters for the pultrusion simulation are reported. The heat transfer equations have been considered separately for the die and composite zone.

3.1 Kinetic sub model
To study the cure kinetics by calorimetric analysis it is necessary fitting the reaction rate profiles achieved from isothermal tests to a mathematical model. In this work an autocatalytic model modified by Kenny et al. [11-12] was used to analyse the experimental data:

$$\frac{d\alpha}{dt} = (k_1 + k_2 \alpha^m)(\alpha_{max} - \alpha)^n \tag{3}$$

where α is the degree of cure, α_{max} is the maximum achievable conversion at each temperature, $d\alpha/dt$ is the rate of the degree of cure, m and n are the reaction orders, $k_i(T)$ are the specific reaction rate constants. Multiple regression technique was employed for the analysis of the isothermal tests and to obtain the kinetic parameters. Then the kinetic constant values and the orders of reaction were related to realize a direct conversion-temperature relationship.

3.2 Rheological sub model

In this investigation, the following empirical chemo-rheological model, proposed by Castro and Macosko [15], was found to fit the experimental data, obtained by rheometric analysis.

$$\eta(\alpha,T) = \eta_0 \left(\frac{\alpha_g}{\alpha_g - \alpha} \right)^{f(\alpha)} \tag{4}$$

where μ_0 is the viscosity at t=0, α is the conversion of reaction, α_g is the degree of cure at gel, and $F(\alpha) = A + B\alpha$. As well as in the kinetic model, the rheological constant values are used to obtain a direct relationship with the temperature.

"**Table 1.** Pultrusion simulation input"

Physical properties		Kinetic Parameters	
ρ_r Resin	1100 Kg/m^3	K_1	$\left(2.45057 \cdot 10^{-12} \right) e^{0.219344385 \cdot T}$
ρ_f Fiber	2580 Kg/m^3	K_2	$\left(60.5711 \cdot 10^{-5} \right) e^{0.0470095 \cdot T}$
ρ_d die	7800 Kg/m^3	m	$0.506857 + 0.000743 \cdot T$
C_{pr} Resin	1883 J/Kg K	n	$2.485714 - 0.00971 \cdot T$
C_{pf} Fiber	820 J/Kg K	α_{max}	$0.4576 + \left(0.5021 \big/ \left(1 + \left(T/75.5240 \right)^{-14.9509} \right) \right)$
C_{pd} die	473 J/Kg K	H_r	205479 J/Kg
k_r Resin	0.169 J/m s K	Resin volume fraction	0.5
k_f Fiber	1.04 J/m s K		
k_d Die	43 J/m s K		

Process Conditions		Rheological Parameters	
Pulling velocity	30-50 cm/min	α_{gel}	$0.2316 + \left(0.4357 \big/ \left(1 + \left(T/71.3970 \right)^{-34.2506} \right) \right)$
Die length	120 cm	$\alpha_{vitrification}$	$0.2862 + \left(0.6625 \big/ \left(1 + \left(T/72.7569 \right)^{-13.1946} \right) \right)$
Composite dimension	0. 4 cm x 0.4 cm	η_0	$1.200760 \cdot T^{-0.209255}$
Die cross-section	3.0 cm x 3.0 cm	A	$-3.7380 + 0.0494 \cdot T$
Initial temperature	25°C	B	$3.2900 - 0.037 \cdot T$
Incremental time	0.01 s		

3.3 Numerical technique

The solution to the heat transient diffusion problem can be obtained using an implicit finite difference approach. In this method the temperature at new time step (t+1) is not directly computed from temperature values at the current time step (t), as in the explicit method. In the implicit finite difference method a time derivative is evaluated from unknown temperatures at new time step (t+1), instead of the previous time (t), so that the finite difference scheme is an

implicit equation for the new value of the solution. The method is referred to as implicit time-marching scheme. The implicit form is also known as a backward-difference approximation [16]. The time derivative can be approximated using a Taylor series expansion:

$$\frac{\partial T}{\partial x} = \frac{T_{m,n}^{t+1} - T_{m,n}^{t}}{\Delta t} \tag{5}$$

According to central finite-difference discretisation, a second order partial derivative of T respect x or y can be expressed as:

$$\frac{\partial^2 T}{\partial x^2} = \frac{T_{m-1,n} - 2T_{m,n} + T_{m+1,n}}{(\Delta x)^2} \qquad \frac{\partial^2 T}{\partial y^2} = \frac{T_{m,n-1} - 2T_{m,n} + T_{m,n+1}}{(\Delta y)^2} \tag{6}$$

Evaluating the spatial discretisation at time t+1, it provides the final form of the heat conduction equation:

$$\frac{T_{m,n}^{t+1} - T_{m,n}^{t}}{\Delta t} = \frac{k_x}{\rho_c C_p} \frac{T_{m-1,n}^{t+1} - T_{m,n}^{t+1} + T_{m+1,n}^{t+1}}{(\Delta x)^2} + \frac{k_y}{\rho_c C_p} \frac{T_{m,n-1}^{t+1} - T_{m,n}^{t+1} + T_{m,n+1}^{t+1}}{(\Delta y)^2} + \frac{\dot{q}}{\rho_c C_p} \tag{7}$$
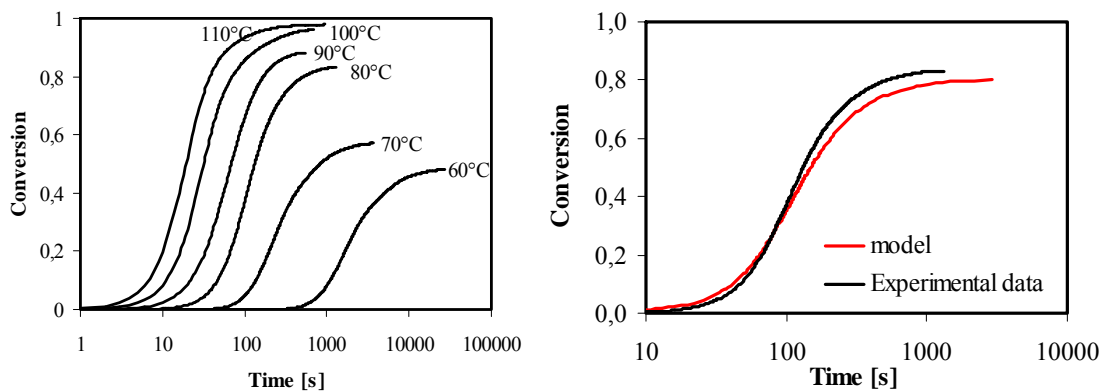
An advantage of the implicit finite difference method is that it is unconditionally stable and consequently unconditionally convergent. But a disadvantageous consequence of the implicit method is that the solution requires solving simultaneously a set of equations. If, in the set of equations, all known terms are located over to the right-hand side of the equation, then the equation system can be written more generally in matrix form as:

$$A \cdot X = B \tag{8}$$

where B is the known terms vector, X is the unknown temperatures vector at new time step (t+1) and A is a tridiagonal matrix of coefficients. Solving this equation system the unknown temperature are calculated.

4. RESULTS & DISCUSSION
4.1 Calorimetric and rheological tests

"**Fig. 1.** Conversion vs time a) calorimetric isothermal tests at different cure temperatures; b) comparison between model and experimental data at 80°C"

In Fig. 1a the degree of conversion versus time at different temperatures is reported. The effect of the temperature is shown in the induction times and in the reaction rates. In fact a reduction of the induction time and an increase of the reaction rate is observed with an increase of the curing temperature.

Moreover it is possible to assert that increasing the temperature of cure the conversion degree, at same reaction time, progressively increases. In particular for the temperature of 110°C the final conversion value of 97,9% is reached, while at lower temperatures the value of the maximum conversion decreases.

This phenomenon can be interpreted considering the molecular and structural modifications of the polymer during the curing. In fact the interaction between molecules to high molecular weight carry to crosslinks formation that limit molecular mobility; at the same time an increase of the viscosity of the resin take place.

The curing process involves an increase of the glass transition temperature. If the curing is carried out at not sufficiently elevated temperature (< 80°C), the glass transition temperature of the resin exceeds the temperature of Tc reaction, when it is not fully cured; the vitrification takes place. In such condition the curing process is controlled by diffusional phenomena that prevent the attainment of 100% of conversion.
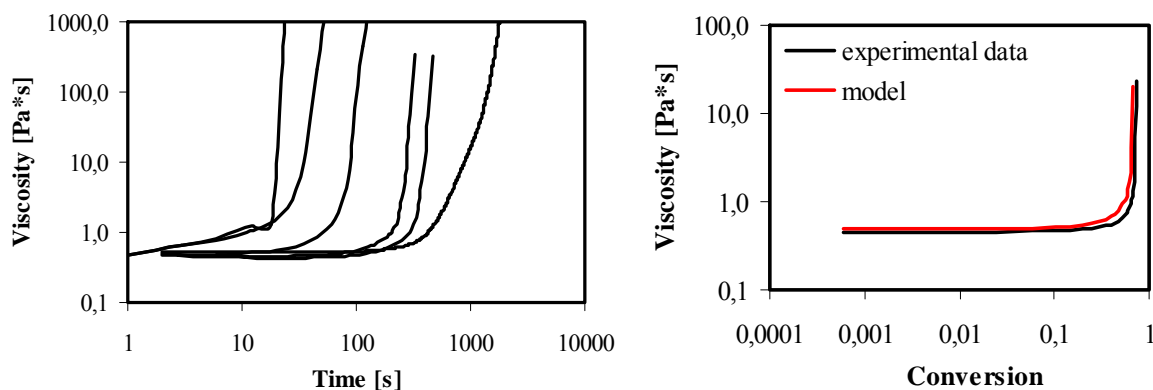
The results obtained by DSC analysis are fitted by application of eq. (3). The kinetic parameters are reported in Table 1. The Fig. 1b give the example at 70°C for degree of conversion versus time, showing that the experimental data are in agreement with the theoretical prediction, finding a good sensibility of the autocatalytic mathematical model.

Fig. 2a gives the comparison of viscosity versus time plot during the curing for several isothermal tests.

During the curing process the resin starts as un un-gelled liquid, but at some time later, it begin to become more viscous until it reaches a rubbery state (gelation) when it has lost its ability to flow. The viscosity increase exponentially. Then the resin continues to harden after it has gelled, until it has obtained its full hardness and properties.

Analysing the curves reported in figure 2a two effects of the temperature are evident: The first trace of the curves evidence that an increase of temperature induces a reduction of the initial viscosity of the un-gelled resin, η_0. Moreover the curves are shifted on the left, because the reaction is thermally activated, and the decrease of the gel time is consequently evidenced.
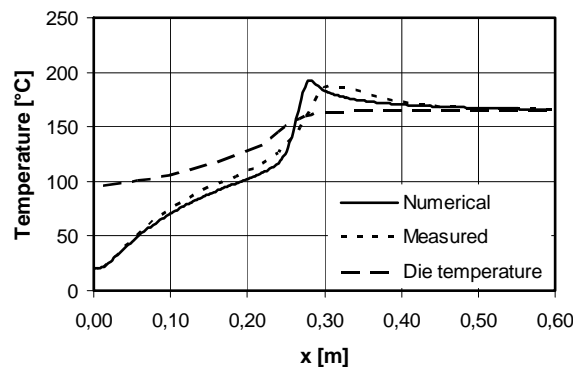
The results, obtained from rheological analysis, are fitted using the eq. (4). The rheological parameters are reported in Table 1. Fig. 2b compares the viscosity versus conversion trend for experimental isothermal data and mathematical model, at the reference temperature of 70°C; It is noticed that the former are very well approximated by the theoretical model.
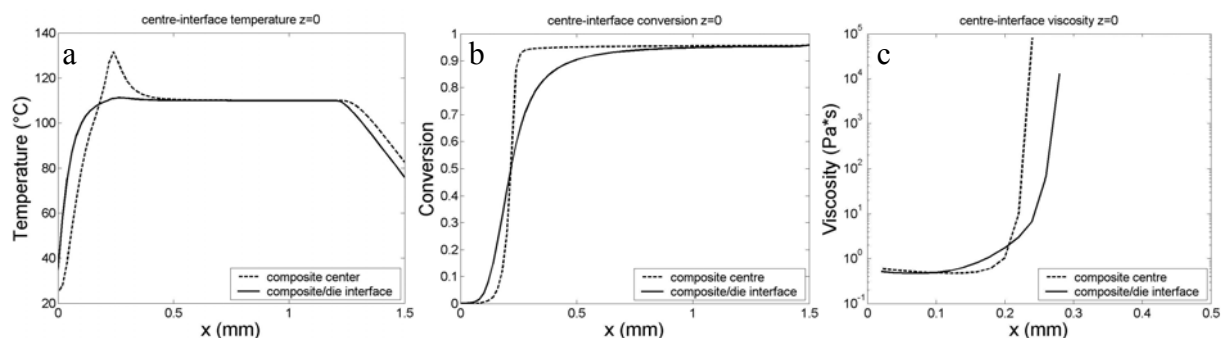
4.2 Model Validation

The comparison between the simulation results and the one reported in [7] is shown in Fig. 3. Kim et al. [7] introduced a thermocouple in the pultrusion die during the pulling procedure of composite. In this way they obtained the temperature evolution of the composite in the thermocouple position during the curing of the resin. The present analysis model is in agreement with the data indicating that the mathematical model is accurate and numerically correct. The differences between the predictive model and the experimental data could be due to the relative displacement of the thermocouple from initial position during the pulling procedure, and to the changing in the conductivity value of the resin during the curing process [17].

"**Fig. 3.** Comparative temperature profile vs die length"
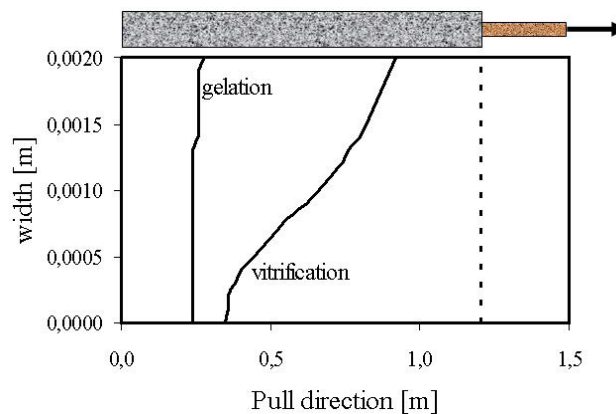
4.3 Numerical simulations

"**Fig. 4.** Temperature (a) conversion (b) and viscosity (c) evolution within the pultrusion die heated at 110°C and with pulling speed of 40 mm/min"

Fig. 4a shows the profiles of temperature in the centre and the composite/die interface when the die is heated at 110°C and the pulling speed is of 40 mm/min. The composite layer to contact with the wall of the die reaches the setting temperature in a short period of time; differing the centre composite region where the phenomenon is more gradual, as evidenced by the lower slope of the initial temperature curve. These considerations are confirmed in Fig. 4b

and c, that shown the conversion and viscosity evolution during the pultrusion process in the center of the composite and at the composite/die interface.

Initially the heat transmission direction is from the walls towards the centre of the material. Consequently greater values of conversion are noticed in the border than in the centre of the composite. Due to coupled effects of exothermic heat of the resin, generated during the curing reaction, and the conductive heat transfer between composite and die, at about 0.2 m, an inversion point is had. The heat, now, is transmitted from the centre towards the walls. The cure within the die is accelerated by the reaction heat of resin. Therefore the conversion and the viscosity increase rapidly in the centre of the composite.
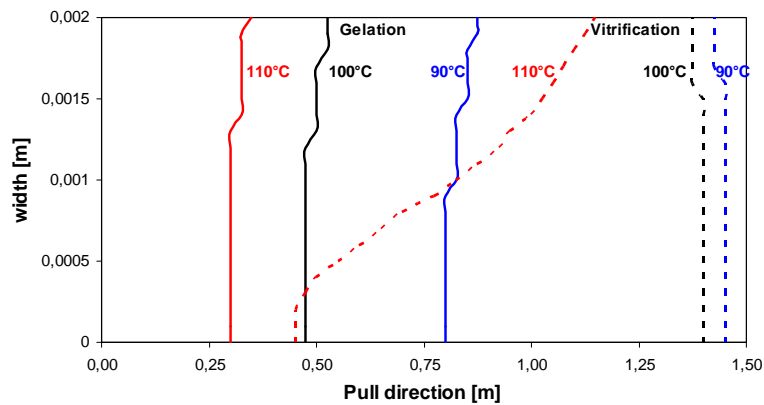

"**Fig. 5.** Schematization Phase transformation zone of the resin within the pultrusion die heated at 110°C and with pulling speed of 40 mm/min"

The temperature, conversion and viscosity profiles, forecasted by the implicit finite difference numerical model, have been used with the purpose to study the phase transformations of the thermoset resin that take place during the curing within the pultrusion die. A simplified scheme of the phase transitions liquid-rubbery-solid of resin for a heating temperature of the die of 110°C and a pulling speed of 40 mm/min is reported in Fig. 5. The central region of the composite profile reaches the solidification earlier than the border. This consideration is less evident for the gelation; in fact the liquid gel interface line is quite linear and orthogonal with the pulling direction.

4.3.1 Effect of the temperature
Fig. 6 shows that the position of the gelation and vitrification transition in the pulling direction during the pultrusion process across the width is moved in the entrance as the temperature profile of the mould increases (the simulations are performed at the same pulling speed of 50 cm/min). This is due at the cure reaction of the resin that is thermally activated; consequently the material begins to react earlier in the die.
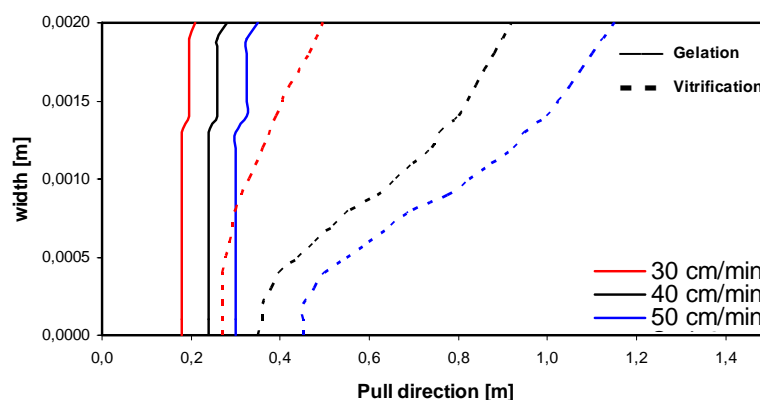
For each simulation, the liquid-gel transition take place in a same position in the pulling direction. This phenomenon is not influenced by the curing temperature. The transition occurs at first in the centreline and then in contact with the die wall. The gel-solid transition in the width direction is, instead, heavy influenced by the curing temperature. In particular at low temperature the material reaches the vitrification earlier in the edge profile than the centreline. But this transition appears out of the die, during the cooling phase. This is unsafe for the finite product quality. At high temperature profile of the mould, the solidification of the thermoset resin happens more before in the centreline than in the composite/die interface. Therefore the setting temperature of 110°C for the mould is preferred to obtain a good solidification within the die.

"**Fig. 6**. Effect of the temperature on the gelation and vitrification zone"

4.3.1 Effect of the pulling speed

Fig. 7 shows the gelation and vitrification transition line for three pull speeds but with the same die wall temperature (110°C). It can be seen that, with the increase of the pull speed, the gelation and vitrification transitions take place in a short distance from the die tapered region, in the pulling direction. This is caused by the fact that, as the pulling speed is increased the time available for heat transfer to the composite became shorter. Therefore the curing time of the composite part is reduced. More differences are evidenced for the vitrification lines than the gelation ones. In fact on the vitrification profile, it is possible to see that the composite material near the die wall reaches the vitrification later than the centre region. The discrepancy between the centreline and the composite edge vitrification position is more evident as the pulling speed is increased. This could cause internal stresses induced by different resin shrinkage in the width. On the other hand a low pulling speed induces a premature gelation and vitrification within the initial zone of the die. This phenomenon provokes elevated pulling force and increases the risk of pultrusion process stop consequent to complete resin solidification within the die.

"**Fig. 7.** Effect of the pulling speed on the gelation and vitrification zone "

At a pulling speed of 50 cm/min, the vitrification transition of the composite/die interface takes place too much near the mould exit (1.2 m). To obtain a suitably cured composite material with high production times, either the die wall temperature or the die length has to be increased.

5. CONCLUSIONS

Calorimetric and rheological analysis of a polyester thermoset resin, used for pultrusion process, was realised; the experimental data compared with theoretical models shows good predictive properties of the proposed models.

Then to investigate the die temperature, curing degree and viscosity profile of fibreglass composite during the pultrusion process, a mathematical model, based on implicit finite differences, was developed.

The numerical results evidence as the vitrification, differencing by the gelation, of the resin is heavy influenced by process conditions (as temperature and pulling velocity). The optimal conditions are obtained for 110°C, a worth pulling velocity could compromise good solidification within the die and consequently the final product quality.

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