Experimental validation of thermo-chemical algorithm for a simulation of pultrusion processes

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Abstract. To provide better understanding of the pultrusion processes without or with temperature control and to support the pultrusion tooling design, an algorithm based on the mixed time integration scheme and nodal control volumes method has been developed. At present study its experimental validation is carried out by the developed cure sensors measuring the electrical resistivity and temperature on the profile surface. By this verification process the set of initial data used for a simulation of the pultrusion process with rod profile has been successfully corrected and finally defined.

1. Introduction

Pultrusion is a continuous and cost-effective process for a production of composite structural components with a constant cross-sectional profile (figure 1). During pultrusion, the fibre reinforcements are saturated with the resin in a resin bath and then continuously pulled through a heated die by a puller. Inside the die, the resin gradually cures and solidifies to form a composite part with the same cross-section profile as in the die. At the final stage a travelling cut-off saw cuts the composite profile into desired lengths.

To provide better understanding of the pultrusion processes, to support the pultrusion tooling design and process control, a lot of numerical simulations have been done in the last thirty years [1–3]. Most of them are focusing on the analysis of the heat transfer and cure, on the pressure rise in the tapered zone of the die and on problems related to impregnation of reinforcing fibres to obtain a final product characterised by the desired mechanical properties. The effects of the processing parameters, like die temperature, pulling speed, post-cure temperature and time, filler and fibre type and content,

on the mechanical properties of composites produced with the pultrusion have been also intensively investigated [4–6]. It is necessary to note that numerical simulations of the pultrusion are carried out using non-commercial finite element codes and general-purpose finite element packages, and most of them are firmly connected with the final product and technology applied.

Also pultrusion processes have been investigated experimentally for various unidirectional composite profiles [7–9]. In these studies, experimental temperatures have been measured by using thermocouples inside the composite or die, but the degree of cure has been obtained from the differential scanning calorimetric (DSC) analysis of samples prepared from the pultruded
profiles. The experimental results have been used in most cases for a validation of the developed numerical algorithms.

At present study the algorithm based on the mixed time integration scheme and nodal control volumes method developed in [10] for a solution of the coupled temperature state and degree of cure by using an iteration technique is validated experimentally. For this purpose new cure sensors measuring the electrical resistivity and temperature on the profile surface have been produced and applied for a real-time monitoring of the degree of cure in pultrusion process with a complex temperature control. Since the set of initial data is not clearly defined, the parameters of technological process are precised comparing the temperatures on thermocouples and sensors with the numerically obtained.

2. Formulation of thermo-chemical problem in pultrusion

To investigate numerically the pultrusion process, the following thermo-chemical problem consisting of the energy equation for the tool, the energy equation for the composite moving in the pull direction and the species equation for the resin should be solved

\[
\begin{align*}
\rho c_p \frac{\partial T}{\partial t} - \rho \frac{\partial}{\partial x} \left( k_x \frac{\partial T}{\partial x} \right) - \rho \frac{\partial}{\partial y} \left( k_y \frac{\partial T}{\partial y} \right) - \rho \frac{\partial}{\partial z} \left( k_z \frac{\partial T}{\partial z} \right) - q_b &= 0, \\
\bar{\rho} \bar{c}_p \left( \frac{\partial T}{\partial t} + u \frac{\partial T}{\partial x} \right) - \bar{\rho} \frac{\partial}{\partial x} \left( \bar{k}_x \frac{\partial T}{\partial x} \right) - \bar{\rho} \frac{\partial}{\partial y} \left( \bar{k}_y \frac{\partial T}{\partial y} \right) - \bar{\rho} \frac{\partial}{\partial z} \left( \bar{k}_z \frac{\partial T}{\partial z} \right) - q &= 0, \\
\left( \frac{\partial \alpha}{\partial t} + u \frac{\partial \alpha}{\partial x} \right) &= R_r, \\
\end{align*}
\]

where \( T \) is the temperature, \( \rho \) and \( c_p \) are the density and specific heat of the tooling materials, \( k_x, k_y, k_z \) are the thermal conductivities of the tooling materials in \( x, y, z \) directions, \( q_b \) is the rate of energy exchange at the boundary, \( u \) is the pull speed, \( \bar{\rho} \) and \( \bar{c}_p \) are the lumped density and specific heat for the composite material, \( \bar{k}_x, \bar{k}_y, \bar{k}_z \) are the lumped thermal conductivities of the composite material in \( x, y, z \) directions, \( q \) is the generative term related to the internal heat generation due to the exothermic resin reaction, \( \alpha = H(t)/H_{tr} \) is the degree of cure and \( H(t) \) is the amount of heat evolved during the curing up to time \( t \).

Heat transfer in the composite occurs as a result of conduction and the generation of heat resulting from the exothermic chemical reaction initiated by the die temperature. The generative term related to the internal heat generation due to the exothermic resin reaction could be written as:

\[
q = V_r \rho_r H_{tr} R_r
\]

where \( V_r \) is the resin volume fraction, \( \rho_r \) is the resin density, \( H_{tr} \) is the total heat of reaction and \( R_r \) is the rate of resin reaction determined as:

\[
R_r(\alpha, T) = \frac{\partial \alpha}{\partial t} = \frac{1}{H_{tr}} \frac{dH(t)}{dt} = K(T) \cdot f(\alpha),
\]
where $f(\alpha)$ depends on the resin properties and varies with the applied resin reaction model, and $K(T)$ is defined by the Arrhenius relationship:

$$K(T) = K_0 \exp \left( -\frac{E}{RT} \right)$$  \hspace{1cm} (4)$$

where $R = 8.314 \text{ J/mol-K}$ is the universal gas constant. It is necessary to note that coefficients of the Arrhenius relationship: activation energy $E$ and frequency factor $K_0$ are physical values and are determined by the Kissinger method or ASTM E 698 standard methodology from DSC tests [11]. Coefficients of the selected function $f(\alpha)$ could be obtained in a simple way by a fitting of the experimental heat flow curves applying the least squares method [11].

The reinforcement is saturated with the resin before entering the heated die in pultrusion process. Therefore, it is reasonable to assume that the resin does not flow. In most cases the continuous model with lumped material properties is used for a simulation of the pultrusion processes. These properties are evaluated by the rule of mixture:

$$\bar{\rho} = (1 - V_r)\rho_f + V_r\rho_r,$$

$$\bar{c}_p = \frac{(1 - V_r)c_{pf} + V_r c_{pr}}{\bar{\rho}},$$

$$\bar{k} = \frac{k_f k_r \bar{\rho}}{(1 - V_r)\rho_f k_r + V_r \rho_r k_f},$$  \hspace{1cm} (5)$$

where indexes $f$ and $r$ relates to the fibres and resin, respectively.

The system of equations (1) could be solved by using the prescribed initial and boundary conditions. It is assumed that at time $t = 0$, for a curing composite the temperature is $T = T^0$ and the degree of cure is $\alpha = \alpha^0$, where index “0” denotes the initial values. The temperature of the composite at the die entrance and everywhere in the composite at the first step of numerical algorithm is prescribed as the pre-heat resin temperature. The value of the degree of cure at the die entrance and everywhere in the composite at the first step of numerical algorithm is taken as zero or very small value depending on the resin curing kinetic model. In some pultrusion processes this value could be much higher in relation to the ambient room temperature which is used also as the boundary condition for a die to describe the convection effect demonstrating the thermal energy transfer between a pultrusion die and an air surrounding it as a result of a temperature difference. It is important to note that the power flux at the entrance and exit of the composite in the die is specified as zero. The insulated boundary conditions could be applied also to reduce unnecessary heat losses and conserve energy in pultrusion processes.

3. Simulation of thermo-chemical problem
To solve the system of coupled energy and species equations (1), the numerical algorithm using ANSYS Mechanical environment and based on the mixed time integration scheme and nodal control volumes method has been developed in [10] and modified for a simulation of pultrusion processes with a temperature control (figure 2). It is seen in figure 2 that ANSYS software is applied only for a solution of the transient thermal problem.

4. An experimental set-up
An experimental set-up and simplified model of the pultrusion die developed for a validation of the numerical algorithm is presented in figure 3. The pultrusion process with a temperature control is investigated experimentally for a cylindrical rod with the diameter of 16 mm. Heating of the die is realised by 12 electrical heaters subdivided into 3 groups and controlled by the proportional-integral-derivative (PID) controller and thermocouples located inside each heaters.
Figure 2. Thermo-chemical algorithm for a simulation of pultrusion.

Table 1. Control temperatures.

| Thermocouple | Symbol (unit) | Initial | Corrected 1 | Corrected 2 |
|--------------|---------------|---------|--------------|-------------|
| 1            | $T_1$ ($^\circ$C) | 100     | 85           | 65          |
| 2            | $T_2$ ($^\circ$C) | 120     | 105          | 85          |
| 3            | $T_3$ ($^\circ$C) | 140     | 125          | 105         |

Table 2. Parameters of pultrusion process.

| Parameter                          | Symbol (unit) | Value |
|------------------------------------|---------------|-------|
| Room temperature                   | $T_{\text{room}}$ ($^\circ$C) | 17    |
| Resin temperature in the bath      | $T_{\text{resin}}$ ($^\circ$C) | 17    |
| Pull speed                         | $V_{\text{pull}}$ (m/min) | 0.18  |

group. The electrical power of each heater is 315 W. Initially it has been taken that the controller turns off the heaters groups when the temperature on the corresponding thermocouples reaches 100, 120, or 140$^\circ$C (table 1). Other parameters of the pultrusion process are given in table 2. For a real-time monitoring of the degree of cure and temperature in pultrusion processes, new cure sensors measuring the electrical resistivity and temperature on the profile surface have been developed and located on the die top. For a better contact with the rod profile, they have been produced with a curved contact surface (figure 4).
Figure 3. Pultrusion set-up.

Figure 4. Cure sensor for the rod profile.

Table 3. Thermal properties of die material.

| Property                | Symbol (unit) | Steel 40Cr | Initial | Corrected |
|-------------------------|---------------|------------|---------|-----------|
| Density                 | $\rho$ (kg/m$^3$) | 7850       | 7850    |           |
| Specific heat           | $C$ (J/(kg·K)) | 460        | 460     |           |
| Thermal conductivity $k_x$ (W/(m·K)) | 46 | 33 | |

Table 4. Thermal properties of pultruded material.

| Property                | Symbol (unit) | Unifilo 4800 tex | POLRES 305BV | Lumped |
|-------------------------|---------------|------------------|--------------|--------|
| Density                 | $\rho$ (kg/m$^3$) | 2500             | 1100         | 1870   |
| Specific heat           | $C$ (J/(kg·K)) | 1235             | 1360         | 1268   |
| Thermal conductivity $k_x$ (W/(m·K)) | 11 | 0.209 | 0.750 |
| Thermal conductivity $k_y$ (W/(m·K)) | 1 | 0.209 | 0.500 |
| Max allowable temperature | $T$ (°C)    | 1200             | 170          | —      |

The pultrusion die has been made of steel 40Cr with the thermal properties presented in table 3. Materials used for a production of the cylindrical rod are glass fibres Unifilo 4800 tex and polyester resin POLRES 305BV. The fibre volume content in the pultruded material is 55%. The thermal properties of constituent materials of the pultruded profile are given in table 4. The rate of resin reaction is described by using the Kamal-Sourour curing kinetic model:

$$\frac{\partial \alpha}{\partial t} = \left[ K_1 \exp\left(-\frac{E_1}{RT}\right) + K_2 \exp\left(-\frac{E_2}{RT}\right) \alpha^n \right] (1 - \alpha)^n$$

with the parameters presented in table 5 and determined by using dynamic DSC tests.

5. Experimental validation of thermo-chemical algorithm

The finite element model for a simulation of the thermo-chemical problem in pultrusion of cylindrical rod has been created in ANSYS Mechanical by using 3-D thermal solid finite elements SOLID 70. The finite element has eight nodes with a single degree of freedom, temperature,
at each node and the orthotropic material properties. Thermal insulation under the die is not taking into account in the finite element model. In this case symmetry of the simulated domain is used and only a quarter of the die is modelled. To analyse heat transfer and curing processes in the post-die region, the modelling of the profile is continued at the distance of 250 mm from the die exit. Fragment of the finite element model is presented in figure 5. The finite element mesh is regular in pull direction and has 240 elements along the profile. The total number of finite elements is 73040 and it consists of 7680 elements used for the composite modelling and 65360 elements used for the die including heaters and thermocouples. The time step of the solution is 1.67 s. During this time, composite travels in the pull direction on the distance equals to the dimension of one finite element (5 mm). Initial conditions are applied at time $t = 0$ when all nodal points of the composite have the room temperature and degree of cure equals $\alpha = 10^{-10}$.

Results of simulation, temperature and degree of cure obtained on sensors 1–3, together with the results of experimental measurements are presented in figure 6. This figure shows that close agreement between experimental and simulation results has not been obtained. If to suppose that experimental results are correct, a disagreement appeared should be identified. Smooth temperature curve at the end of measurement time on sensor 1 (figure 6 a) talks that this sensor is not screwed to the final position and for this reason the cavity appeared has been filled with uncured material. This is why sensor 1 not properly reacts on the heaters work. This phenomenon should be taken into account later analyzing the experimental and simulation results.

Figure 5. Fragment of the finite element model.

Table 5. Parameters of curing kinetic model.

| Parameter                     | Symbol (unit) | POLRES 305BV |
|-------------------------------|---------------|--------------|
| Heat reaction                 | $H_{tr}$ (J/kg) | 323074       |
| Frequency factor              | $K_1$ (s$^{-1}$) | 14289310986  |
| Frequency factor              | $K_2$ (s$^{-1}$) | 285.870      |
| Activation energy             | $E_1$ (J/mol)  | 85573        |
| Activation energy             | $E_2$ (J/mol)  | 33141        |
| Order of the reaction         | $n$            | 2.342        |
| Order of the reaction         | $m$            | 0.519        |
5.1. Correction of control temperatures

To identify disagreement between experimental and simulation results, the initial control temperatures (table 1) have been checked at first since the controller regulating these temperatures has been used by technologists as “the black box.” It is seen from figure 7 that sensor 1 is located very closely to thermocouple 2 with the distance of 20 mm between thermocouple and sensor axes. It is reasonable to assume that temperatures on sensor 1 and thermocouple 2 are very close or even the same. The results of the finite element simulation confirm this assumption (figure 8). Moreover, it is seen that the experimental temperature on sensor 1 is lower than the controlled temperature on thermocouple 2 (figure 8) and simulated temperatures on all sensors are larger anytime than the temperatures obtained experimentally (figure 6). For this reason it is assumed that the temperatures really controlled by thermocouples during an experiment are lower than taken initially. After that additional calculations have been performed with the corrected control temperatures. For thermocouples 2 and 3 they have been taken from the experimental results for sensors 1 and 3 respectively. The control temperature for thermocouple 1 has been taken proportionally to the temperatures on thermocouples 2 and 3. The corrected values of the control temperatures are given in table 1.

Experimental measurements together with the results of simulation, temperature and degree of cure obtained on sensors 1–3 with the corrected control temperatures, are presented in figure 9. It is seen that simulation temperatures have moved down and now more close agreement between experimental and simulation results has been obtained. The largest disagreement is visible for the temperatures after the first turn off of the heaters at time about 400 s from the process start. At this time the simulation temperature continues to rise according to the thermal inertia effect.
5.2. Correction of temperature control algorithm

To bring the temperature control algorithm used in simulations closer to the experimental conditions, reduction of the control temperatures for the first turn off of the heaters has been executed. The control temperatures have been reduced by 20°C (table 1). Experimental measurements together with the results of simulation, temperature and degree of cure obtained on sensors 1–3 with the corrected first and main control temperatures, are presented in figure 10. It is seen that the first simulation peak has been reduced considerably and more close agreement between experimental and simulation results has been obtained. However, some disagreement is visible now for the duration of temperature cycles. Obviously, that this effect is dependent on the thermal conductivity of die material.

5.3. Correction of die thermal properties

To avoid last disagreement, the thermal properties of die material have been verified and it has been found that they differ considerably in different material data sheets. The corrected properties are given in table 3. Experimental measurements together with the results of simulation, temperature and degree of cure obtained on sensors 1–3 with the corrected control temperatures and die material properties, are presented in figure 11. It is seen that the duration
Figure 9. Temperature and degree of cure with corrected control temperatures on sensors 1 (a), 2 (b), and 3 (c).

of temperature cycles has been increased considerably and very good agreement between experimental and simulation temperatures has been obtained now. Final distribution of the temperature and degree of cure along the composite profile at centreline and on the surface is given in figure 12.

Figure 11 demonstrates that the degrees of cure predicted by the developed algorithm in general could be examined as a proper averaging of the values measured in real time by the developed sensors. Some noise in the online measurements appears due to not ideal contact between moved profile and electrodes. Comparing both results it is seen that difference between them is larger for sensor 1 (Figure 11 a), where the resin is at the gelation stage, but it is significantly reduced on sensor 2 (Figure 11 b). The difference between experimentally measured and simulation results is practically eliminated after the transient period on sensor 3 (figure 11 c) where the resin is almost fully cured.

Conclusions
The thermo-chemical algorithm based on the mixed time integration scheme and nodal control volumes method and developed for a simulation of pultrusion processes has been successfully validated by the pultrusion trial of the rod profile. For a real-time monitoring of the temperature and degree of cure, new cure sensors measuring the electrical resistivity and temperature on the profile surface have been developed. Comparing experimental and simulation temperatures in the validation process, very good agreement between them has been found correcting an inaccurate initial data set.

Numerical and experimental characterisation of the pultrusion process has shown that the
Figure 10. Temperature and degree of cure with corrected temperature control algorithm on sensors 1 (a), 2 (b), and 3 (c).

Figure 11. Temperature and degree of cure with corrected thermal properties of die material on sensors 1 (a), 2 (b), and 3 (c).
developed cure sensors require some improvements in the degree of cure measurements in the areas where the resin is at the gelation stage. The noise in the online measurements of the degree of cure appearing due to the not ideal contact between moved profile and electrodes should be removed from experimental results. However, it is necessary to note that in the areas where the resin is almost fully cured, negligible difference between experimentally measured and simulated degrees of cure has been obtained after the transient period.

Acknowledgments

The authors gratefully acknowledge the support of European Commission under FRAMEWORK 7 program, contract no. NMP2-SL-2013-609149, project “Development of an Innovative Manufacturing Process for the In-Line Coating of Pultruded Composites (COALINE).”

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Figure 12. Distribution of temperature and degree of cure along the composite profile.