The composite reinforcement production in digital manufacturing: experimental validation of the heat transfer and cure modeling results

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Abstract. The experimental validation of the heat transfer and cure modeling results for 8-mm fiber-reinforced thermosetting composite reinforcement is reported in this article. The temperature and degree of cure of composite reinforcement are predicted using a two-dimensional heat transfer and curing model. The model uses the infrared radiant heating theory and takes into account the heat transfer between the composite rod and the surrounding air. The implicit finite difference method was used to solve the system of governing equations. The results obtained using mathematical model was compared to experimental data: the temperature field inside the composite reinforcement was measured by means of naked thermocouple; Differential Scanning Calorimetry (DSC) was used to measure the degree of cure of the final product. Calculated and measured temperature and degree of cure fields were in good agreement.

1. Introduction

The Fiber reinforced plastic (FRP) composite rods, presenting a high strength to weight ratio, resistant to repeated loading and not subjected to corrosion. Thanks to these features they are becoming more and more widespread in the construction industry as reinforcement for concrete structures [1], electrical insulators [2] and pump rods, pit-prop anchors in the mining industry, and area of their application is constantly expanding. The composite reinforcement is usually made of glass or basalt fibers and has special outer relief providing a good adhesion to concrete. The carbon fiber has higher characteristics but rarely used because of its high cost.

Among the several available techniques to produce composite reinforcement, nidltrusion process is becoming the most widespread and cost-effective continuous processing technique in Russia. One of the main attractions of this manufacturing method is the simplicity of tooling and low labor requirements. In this process, dry reinforcement fibers in the form of continuous strands (roving) are pulled through a resin bath for impregnation. After the wetting process, the reinforcement pack is collimated in the forming taper into a performed shape before entering the heating chamber where it cured. The forming taper is typically characterized by a conical convergent shape, in order to promote compaction of the material, the removal of the air and excess resin. The circle shape of the rod cross section is fixed by spiral protrusions formed by a helical winding device. The forming taper and helical winding devices are practically always combined in one. Due to the spiral protrusions the rod
acquires some anisotropic characteristics [3], but their impact on the mechanical characteristics of the rod is usually neglected. The composite reinforcement is cured in the heating chamber without touching its walls in contrast to conventional pultrusion process. The heat provided by means of infrared (IR) heaters activates the exothermic cure reaction of the thermoset resin. Finally, outside the chamber, the composite reinforcement already polymerized and is pulled by a pulling system. Then a cut-off saw cuts the part into a desired length.

2. Theoretical modeling and numerical implementation
There have been several mathematical models [2, 4, 5] presented in the literature describing the cure process during pultrusion. However, these models are based on the assumption that the outer surface of the composite rod is in direct contact with the walls of a heated die. Therefore, in relation to the pultrusion process such models are not appropriate.

Assuming the thermal conductivity along the radius is a constant, and is absent along the die due to the dimensions of composite rod in longitudinal direction is much greater than the dimensions in the transverse direction. Then, for the steady-state pultrusion process heat transfer equation [4] can be rewritten as

\[
\rho_c U \frac{\partial T}{\partial x} = \rho_f \cdot (1 - v_f) \cdot H_{tot} \cdot \frac{d\alpha}{dt} + \frac{\lambda_1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right),
\]

where \( \rho \) - density of composite, \( c_v \) - specific heat, \( U \) is the pull speed, \( \rho_r \) - density of resin, \( H_{tot} \) - the total heat generated by the exothermic reaction of resin, \( \lambda_1 \) - heat-transfer coefficient, \( r \) - radial direction, \( v_f \) - fiber volume fraction.

The density of composite, \( \rho \) and resin density, \( \rho_r \), can be expressed as follows:

\[
\rho = (1 - v_f) \cdot \rho_f + v_f \cdot \rho_r,
\]

where \( \rho_f \) is the fiber density, \( \rho_r^u \), \( \rho_r^c \) are uncured and cured resin densities correspondingly.

The specific heat capacities of composite material and resin are calculated in a similar manner:

\[
c = (1 - v_f) \cdot c_v + v_f \cdot c_r,
\]

where \( c_f \) is the specific heat of the fiber, \( c_r^u \), \( c_r^c \) are uncured and cured resin specific heat correspondingly.

In the present investigation the well-established Kamal model has been adopted to describe the evolution of the cure reaction [6]:

\[
\frac{d\alpha}{dt} = (k_i + k_{\alpha^n} \cdot (1 - \alpha)^n) \cdot (1 - \alpha)_i, \quad k_i = A_i \cdot \exp \left( - \frac{E_{act}}{RT} \right),
\]

where \( k_i \) is the reaction rate, \( A_i \) is the pre-exponential factor, \( E_{act} \) is the activation energy, \( R \) is the gas constant, \( n, m \) are the equation superscripts.

Usually the heating chamber is equipped with IR heaters and the boundary conditions for the governing equation are:

\[
T_{i=0} = T_0, \quad \frac{\partial T}{\partial r} \bigg|_{r=R} = \gamma_1 + \gamma_2, \quad \frac{\partial T}{\partial r} \bigg|_{r=0} = 0,
\]

where \( T_0 \) is initial composite temperature at the computational domain inlet.

The net heat transfer through radiation is calculated using the Stefan-Boltzmann law [7]:

\[
\gamma_1 = \varepsilon_r \cdot C_0 \left( T^4 \bigg|_{r=R} - T_{wall}^4 \right), \quad \gamma_2 = \varepsilon_r \cdot C_0 \left( T^4 \bigg|_{r=R} - T_{wall}^4 \right),
\]
where $\varepsilon_r$ is the emissivity of the surface, $C_0$ is the Stefan-Boltzmann constant ($5.67 \times 10^{-8}$ W/(m$^2$·K$^4$)), $T_{sat}$ – the steady temperature of the air in the heating chamber sections, $T_H$ – the IR heater temperature.

The implicit finite difference method was used to solve the system of governing equations (1-6). This method is based on discretizing the space and time domain through transformation into a finite difference form and solving the subsequent system of algebraic equations for the temperature and cure fields. For each time step, starting from the second ($t$), the unknown temperature is determined by using eq. (1, 4) taking into account the boundary conditions, temperature and the degree of cure at the previous time step ($t-1$). Then, the degree of cure is determined from the equation (4) for the current time step ($t$). Thus, the solution is determined in all nodes of finite-difference grid.

3. Experimental work and discussion of the results

This study is focused on the experimental validation of the heat transfer and cure modeling results for 8-mm fiber-reinforced thermosetting composite reinforcement.

The E-glass fibers were used as filler. The fiber volume fraction is $v_f = 0.6$.

An epoxy resin CYD-128 (bisphenol-A) was blended with Vestamin IPD (cycloaliphatic diamine) as hardener with the weight ratio 388:100. According with a mixture usually used for nidltrusion manufacturing process, several additives were added to reduce the product costs and improve the quality of the product. The DSC measurements were made in dynamic mode at METTLER TOLEDO using “STAR” software. The next cure kinetic parameters were obtained:

$$\frac{d\alpha}{dt} = (18 \cdot \exp(-23820/R \cdot T) + 2850 \cdot \exp(-38400/R \cdot T) \cdot \alpha^{0.85} \cdot (1-\alpha)^{1.9}) \cdot H_{sat} = 456.44 \text{ J/g.}$$

The properties of components for nidltrusion simulation program are listed in Table 1.

| Property                           | Value |
|------------------------------------|-------|
| Fiber density, g/cm$^3$            | 2.56  |
| Uncured resin density, g/cm$^3$    | 1.06  |
| Completely cured resin density, g/cm$^3$ | 1.27  |
| Heat-transfer coefficient, $\lambda$, W/(m·K) | 0.25  |
| Specific heat capacity of the fibers, J/(g·K) | 0.84  |
| Specific heat capacity of uncured resin, J/(g·K) | 1.69  |
| Specific heat capacity of cured resin, J/(g·K) | 1.36  |
| The emissivity of the surface, $\varepsilon_r$ | 0.7   |
| Inlet temperature, °C              | 24    |
| The IR heater temperature, $T_H$, °C | 300   |

The experiment to determine the temperature field of the composite reinforcement was performed using the heating chamber equipped with IR heaters (FSR 250 W, max operating temperature 400°C). The heating chamber has 6 m length and consists of 8 sections. It was experimentally determined that the surface temperature of the heater is approximately 70°C higher than the temperature setting for the corresponding section. Six IR heaters are usually placed in each section of the heating chamber and total 48 IR ceramic heaters are engaged in manufacturing process. During the experiment the naked thermocouple was placed inside the rod. All sections of the heating chamber were heated up to 230°C (the temperature setting).
The simulated and experimental results are presented on Figure 1 (the points denote the experimental data). The simulation reproduce well the experiment up to 250°C. Probably, at the temperature above 250°C cured resin degradation occurs with the release of additional heat. Since the experiments to determine the exact value of the degradation temperature for the resin were not carried out, it was decided to accept this value as the temperature limit at which the developed mathematical model can be used with sufficient reliability.

![Figure 1. Temperature profiles within the rod along the heating chamber](image)

The obtained degree-of-cure (DOC) curves are presented on Figure 2 and indicate the changes inside the composite reinforcement during the production. Estimated values of the DOC at the heating chamber output are 0.969 (for the nidltrusion speed of 2.5 m/min) and 0.942 (for the speed of 3 m/min).

![Figure 2. Degree-of-cure distributions within the rod](image)

Several composite reinforcement rods were produced at the mentioned above temperature setting and pull speeds. After what, the samples 4x4 mm in size and weight of the composite material up to 15 mg were made by means of guillotine shears. The residual thermal effects of post-curing were determined using DSC to obtain the degree of cure of the composite reinforcement samples at the pulling speeds of 2.5 m/min and 3 m/min.

The DOC of the resin $\alpha$ was defined as the ratio of the difference between the thermal effects of curing the resin without filler ($\Delta H_r$) and after curing ($\Delta H_c$) of the sample to the original value of the thermal effect of the curing reaction of the resin $\Delta H_r$:
\[ \alpha = \left(1 - \frac{\Delta H_c}{\Delta H_c \cdot C_r}\right), \]  

(7)

where \( C_r \) – the resin mass fraction in composite rod.

The table below shows the calculated and experimental values of the degree of cure.

**Table 2.** Calculated and experimental values of DOC

| Pulling speed, m/min | \( \Delta H_c, J/g \) | DOC (computed) | DOC (experimental) |
|----------------------|----------------------|----------------|-------------------|
| 2.5                  | 2.715                | 0.969          | 0.973±0.03        |
| 3                    | 6.25                 | 0.942          | 0.939±0.03        |

4. Conclusion

The theoretical and practical work was presented regarding the mathematical modeling based on the mutual interactions between heat transfer, cure reaction and variation in the material properties for the nidltrusion process. Two-dimensional heat transfer and curing model is used to predict the temperature and degree of cure of composite reinforcement. Complex boundary conditions are considered, including prescribed temperature and heat radiation. The model uses the IR radiant heating theory and takes into account the heat transfer between the composite rod and the surrounding air.

The results obtained using mathematical model was compared to experimental data: the temperature field inside the composite reinforcement was measured by means of naked thermocouple; Differential Scanning Calorimetry (DSC) was used to measure the degree of cure of the final product. It was shown the calculated and measured temperature and degree of cure fields are in good agreement.

This thermal response model will be used in further studies of nidltrusion process. If the necessary material parameters are determined, this model can be further applied in different kinds of composite materials.

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