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The effect of process parameters on ultraviolet cured out of die bent pultrusion process

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ABSTRACT

In this paper the effect of emitting intensity and pulling speed on ultraviolet (UV) cured out of die bent pultrusion process has been analysed. The curing process of the composite at the exit of the die has been characterised (kinetic model) through the analysis of the evolution of the electrical resistivity (DC sensor) of the material. Combining the studied pulling speeds and emitting intensities, the developed curing model can predict accurately the curing degree at the exit of the die of the profiles. In addition, through the analysis of the final quality of all the manufactured bent profiles in the pultrusion line, the experimental optimum process window has been defined. Indeed, in this study, the optimum process window is limited approximately to the parameters resulting in a curing degree from 5% to 12% at the non-exposed surface (at the exit of the die).

1. Introduction

The pultrusion is a highly automated continuous process for manufacturing structural composite profiles. In conventional thermoset pultrusion process, continuous fibres are impregnated in a resin bath and pulled through a long heated die (traditionally 1 m long at least). Resin cures inside the die, causing high forces of friction along the die wall: 50–150 kN [1]. Traditional thermoset pultrusion process is geometrically limited to straight profiles of constant cross section. Recently, some variants of the traditional pultrusion have succeeded in obtaining curved profiles [2,3]. However, those processes are restricted to constant radii, low productivity rates and high pulling force since the profile continues being cured inside the die. Moreover, complex structures or frames and variable radii cannot be manufactured with those processes.

As Britnell and co-workers [1] demonstrated, the restrictions to achieve this aim can be overcome if the profile is cured out of the die. In this new approach the die is only required to define the geometry of the fibre/resin bundle and to remove excess of resin. Thus, the pulling force is much reduced [4]. It is therefore possible to pull the fibres through the die by using a robot arm. By careful control of the robot and the curing conditions, it is also possible to manipulate the fibres so that a structure complete with radii and corners can be produced, without the need of any kind of additional tool.

However, the curing of the composite out from the die is not possible using the traditional thermal curing method. Therefore, an alternative fast-curing method is needed [5]. One of those alternative routes is the ultraviolet (UV) curing [6–9]. The UV curing industry, using the energy of UV light in the formation of polymeric materials, has approached the last years, high degree of maturity. The development of monomers, oligomers, and photoinitiators during this time has allowed the technology to advance into very efficient formulations for a wide variety of applications [10]. Resins such as vinylester [7], epoxy [8] and polyester [9], when formulated with a proper photoinitiator, can be cured quickly under exposure to UV light. Hence, it can be stated that the combination of the pultrusion and UV curing can overcome the main limitations of the use of the traditional pultrusion.

Literature searches reveal that previous works have been developed in order to apply the benefits offered by ultraviolet curing to the pultrusion process [1,4,11]. The only research work around non-linear out of die pultrusion is the study carried out by Britnell and co-workers [1]. This work demonstrates the capacity of the process to produce non-linear profiles. Anyway, aspects related to the process as the effect of the UV source and resin formulation, die design, force estimation, pulling speed, path design, process

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simulation and monitoring techniques, final mechanical properties, and so on, are not studied yet.

The pulling speed and the UV exposure conditions are directly related to the final curing degree achieved during the out of die UV cured pultrusion process. Moreover, trough-thickness cure is critical at the exit of the die as Tena et al. [4] have demonstrated. In addition, one of the critical issues in pultrusion and in composite manufacturing processes is also directly related to the trough-thickness cure distribution: residual stresses and strains. As it has been analysed in some recent studies [12–14], the internal residual stresses and strains have a direct effect on the mechanical performance of the composite part. It has been probed that one of the main mechanisms that generate residual stresses/strains is the non-uniform through-thickness cure and temperature gradients. Hence, it can be stated that the trough-thickness cure is critical for the process. However, during bent pultrusion, the effect of the curing degree at the exit of the die has not been evaluated yet. The undercure or overcure of the composite at the exit of the die could be translated into defective bent profiles.

Thus, in this paper the effect of the degree of cure at the exit of the die for UV bent pultrusion process has been studied. The combination of different curing conditions (UV intensity and pulling speed) has been analysed. In addition, the curing process of the composite has been characterised (kinetic model) through the analysis of the evolution of the electrical resistivity [15–21] of the composite at the exit of the die.

2. Experimental

2.1. Materials and light sources

The composite used in this study is a glass/UV cured polyester composite. The reinforcement consists of 4800 TEX unidirectional E-glass roving. The resin is UV curable unsaturated polyester supplied by Irurena S.A., whose commercial name is FPC-7621 NA. The UV source used is a high intensity Phoseon FireFlex UV LED curing system with a maximum intensity of 8 W/cm^2 (variable) and an emitting window of 75 $\times$ 50 mm^2. The selected photoinitiator system is a combination of Bis (2,4,6-trimethylbenzoyl)-phenylphosphine oxide (BAPO) and 2-Dimethylamino-2-(4-methyl-benzyl)-1-(4-morpholin-4-yl-phenyl)-butan-1-one (α amino-ketone). This composite/UV source combination has been demonstrated to be suitable, as low porosity and high mechanical performance can be obtained [4].

2.2. Bent pultrusion processing

The bent pultrusion (Fig. 1a) line has been developed entirely by the research group. The impregnation was done by an open resin bath system and the non-linear pulling is made using a Staübli TX60 6 axis robot arm and a pneumatic gripper. A discontinuous pulling strategy is used: after bending the profile the gripper releases the cured part and the process is stopped. Afterwards, the robot grips again the profile and pulls a straight part. Finally, the profile is cut by a saw. A continuous pulling process would be achieved using a complementary robot arm. It must be remarked that the profile is only irradiated from one side. The die was designed to manufacture continuous rectangular sectioned profiles (10 mm width and 2 mm thickness). The die length is 100 mm. The manufactured bent specimen has a radius of 50 mm and the angle at the corner between the straight parts is 90° (Fig. 1b).

In this study, three different pulling speeds have been used: 2, 3 and 4°/s (1.75, 2.62 and 3.50 mm/s limited by the robot arm system); and five emitting intensities from 0.8 to 8 W/cm^2 have been analysed (0.8, 2.4, 4, 6 and 8 W/cm^2). 3 specimens for each intensity have been tested in order to ensure the repeatability of the tests. The samples quality was evaluated based on the geometrical defects as well as using a NOVA NANOSEM 450 scanning electron microscope.

2.3. DC sensor monitoring

In order to analyse the experimental evolution of the degree of cure at the exit of the die the monitoring of the electrical resistance and temperature using a direct current, DC sensor (an Optimold system provided by Synthesites Innovative Technologies Ltd.) has been employed. This type of sensor has demonstrated to be a suitable option for analysing the curing process of composites [4,18,19]. DC sensors are based on correlations between resistivity and state of cure of the resin. Resistivity of a polymer is determined by measurement of the potential drop across the sample and the electric current applied to the sample [18]. Hence, the changes in the measured resistance reflect the changes in the degree of cure and glass transition temperature (T_g) [20]. Furthermore, the electrical resistance (R) is a function of the degree of cure and temperature [20]. Based on literature [16,22] it can be assumed that the electrical resistivity (R) could be expressed separately by a degree of cure (α)function f_1 (α)and temperature (T) function f_2 (T) as follows:

$$R = f_1(\alpha) f_2(T) \tag{1}$$

To correlate the electrical resistivity to T_g and degree of cure, it is desirable to remove the temperature influence on the measured electrical resistivity. As the curing process is initiated by the UV radiation, temperature is not a controllable parameter. Temperature is the sum of the effects of the exothermic reaction and the heat from the UV lamp. Thus, is not possible to analyse isothermal curing cycles in order to remover the influence of the temperature on the measured electrical resistivity. Indeed, the correlation between resistance and temperature might change depending on the state of the material (liquid or cured resin). However, as the gel-time in UV curing is negligible [6], the effect of the temperature in the liquid state of the resin can be neglected. Hence, the effect of the temperature for glassy polymers may be well represented by an Arrhenius equation [16,17]:

$$f_2(T) = a \cdot exp\left(\frac{b}{T}\right) \tag{2}$$

where, a and b are experimentally obtained measuring the electrical resistivity during cooling process at room temperature after UV curing.

Combining 1 and 2 equations, the temperature decoupled signal ($R_{\text{decoupled}}$) can be obtained:

$$R = f_1(\alpha) \cdot \left(a \cdot exp\left(\frac{b}{T}\right)\right) \rightarrow f_1(\alpha) = \frac{R}{\left(a \cdot exp\left(\frac{b}{T}\right)\right)} = R_{\text{decoupled}} \tag{3}$$

Thus, the degree of cure (α) can be defined as the following equation [17,21]:

$$\alpha = \frac{\log\left(R_{\text{decoupled}}\right) - \log\left(\left(R_{\text{decoupled}}\right)_{\text{min}}\right)}{\log\left(\left(R_{\text{decoupled}}\right)_{max}\right) - \log\left(\left(R_{\text{decoupled}}\right)_{\text{min}}\right)} \cdot \alpha_{\text{final}} \tag{4}$$

where, $(R_{\text{decoupled}})_{\text{min}}$ and $(R_{\text{decoupled}})_{\text{max}}$ are the minimum and maximum values for $R_{\text{decoupled}}$ respectively; and, α_{final} is the maximum cure degree (obtained experimentally as it is described in Section 2.4).