CHARACTERISATION OF ULTRAVIOLET CURING RESINS FOR 3D PULTRUSION

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Abstract
The combination of pultrusion and ultraviolet (UV) curing allows to obtain bent profiles if the curing takes place out of die.Thus, photocurable resins with elevated curing kinetics have to be used in order to avoid the expansion of the profile at the exit of the die. On the other hand, another important aspect that is gaining importance in the industry is the reduction of volatile organic compounds (VOCs) during manufacturing process. In this way, the research of new resins that emit less quantity of VOCs has resulted, for instance, in styrene-free resins. Hence, the aim of this study is to compare two resins, unsatured polyester and styrene-free vinyl ester, in order to demonstrate the suitability of the new styrene-free resins. Curing kinetics , interlaminar shear strength (ILSS) and impact properties have been analysed. The results show that the styrene-free vinyl ester presents higher curing kinetics than the unsatured polyester with similar interlaminar and impact properties. Thus, based on the test performed on this study, the suitability of styrene-free vinyl ester has been demonstrated.

1. Introduction

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 (several kN). 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. However, these 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. Recently, Britnell *et al*. [1] and Tena *et al*. [2,3] have shown that those restrictions 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. 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.

Nevertheless, 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. One of those alternative routes is the ultraviolet (UV) curing. Resins such as vinyl ester [4], epoxy [5] and polyester [6], when

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formulated with a proper photoinitiator, can be cured quickly under exposure to UV light. In this way, photocurable resins with faster curing kinetics and elevated mechanical properties are needed in order to maintain the quality of the traditional pultrusion profiles.

On the other hand, the emission of volatile organic compounds (VOCs) is one of the concerning aspects in composite manufacturing processes. The emission of VOCs is significantly reduced in UV curing compared to thermal curing as Jung *et al*. [7] already demonstrated. However, the reduction of the emission of VOCS is still an important aspect to deal with. The use of photocurable resins that emit less quantity of VOCs is one of the alternatives to be taken into account, even when the UV pultrusion is more environmentally friendly than the traditional thermoset pultrusion. In this way, the research of new resins so as to reduce the emission of VOCs has resulted in styrene-free resins.

Hence, the aim of the present paper is to characterise two photocurable resins: the first one is based on an unsaturated polyester successfully used for pultrusion [2,3], whereas the second is a styrene-free vinyl ester resin. Thus, the comparison of both resins would demonstrate the suitability of the new styrene-free resins. Curing kinetics of both resins have been characterised through the analysis of the electric resistance of the material. In order to evaluate the mechanical properties, interlaminar shear strength and impact properties have been selected.

2. Experimental

2.1. Materials and light sources

The UV source used in this study 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 x 50 mm^2. The emission spectrum of the UV source is presented in Figure 1. It could be appreciated that the emission peak of this UV source is found in 395 nm. Thus, all the intensity is found at the UV range.

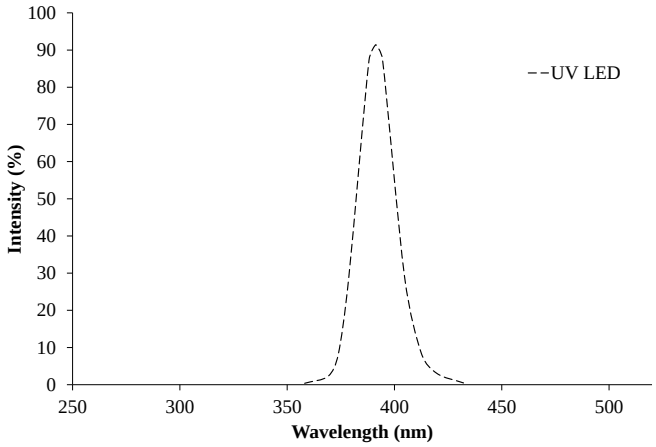

Figure 1. Emmiting spectrum of the UV LED.

On the other hand, the composite used in this study is a glass/UV cured composite with two different resins, polyester and vinyl ester. In the first case, the resin is UV curable unsaturated polyester supplied by Irurena S.A. whose commercial name is FPC-7621 NA. 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 aminoketone). This composite/UV source combination has been demonstrated to be suitable, as low porosity and high mechanical performance can be obtained [2]. While in the other case, the resin is a styrene–free vinyl ester resin supplied by DSM whose commercial name is Beyone 120TM-Q-01. The recommended

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emitting spectrum for this resin is between 365-420 nm. Therefore, the emitting spectrum of the UV LED source used in this study is adequate.

The reinforcement used in this study is a 300 g/m^2 and 75 mm width quasi unidirectional E-glass ribbon. The reinforcement is described as quasi unidirectional because of the small proportion of fibers (8%) at 90º which maintain the cohesion of the unidirectional fibers.

All the specimens were manufactured by hand layup process with an intensity of 1 W/cm^2. In order to maintain the repeatability of the thickness in all the specimens, a thickness plate has been used during the curing process as it is shown in the Figure 2. As it is said before, two different resins have been used in the fabrication of those specimens: unsatured polyester resin and styrene-free vinyl ester; and two different test have been done in order to achieve the interlaminar shear strength and impact properties of both materials. Thus, 4 different types of specimen were manufactured (Table 1): two of them related to the ILSS test; and another two for the impact behaviour test for both resins.

Specimen	Resin	Test	Thickness (mm)	Dimensions (mm^2)
P_ILSS	Polyester	ILSS	3.01 ± 0.04	18 × 6
V_ILSS	Vinyl ester	ILSS	2.97 ± 0.04	18 × 6
P_IMP	Polyester	IMPACT	3.10 ± 0.03	75 × 50
V_IMP	Vinyl ester	IMPACT	3.07 ± 0.03	75 × 50

Table 1. Manufactured specimens.

2.2. Test geometry and procedures

Related to the curing analysis, the electric resistance of the material was monitored during the UV curing by an electric sensor. As Tena *et al*. [3] demonstrated, this analysis technique is a suitable option for the analysis of the UV curing of composites. A specific tool has been developed to control the curing process. The specimens were manufactured by hand layup process. Thus, after the impregnation of the fibres, the uncured specimens were placed into the curing tool. Figure 2 shows a description of the curing analysis tool, which permits to change the next main curing parameters: the UV source, the distance between the source and the specimen, the thickness of the specimen. The curing analysis is made by the control of the electric resistance of the material in the non-exposed surface, which is the last area to cure.

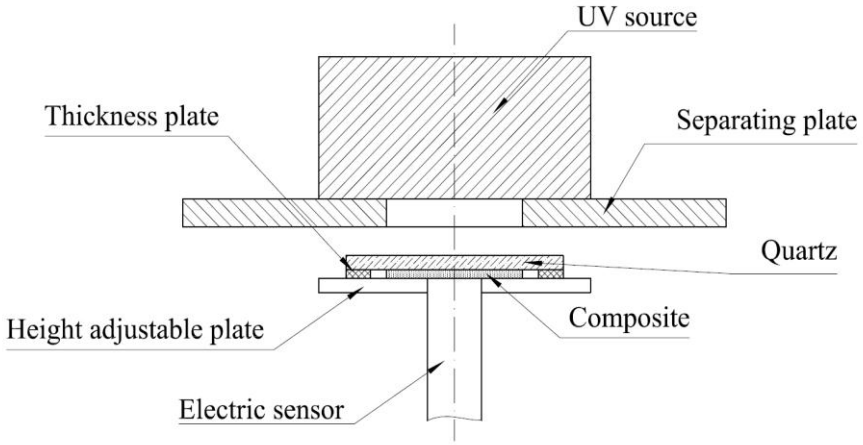

Figure 2. Description of the curing analysis system

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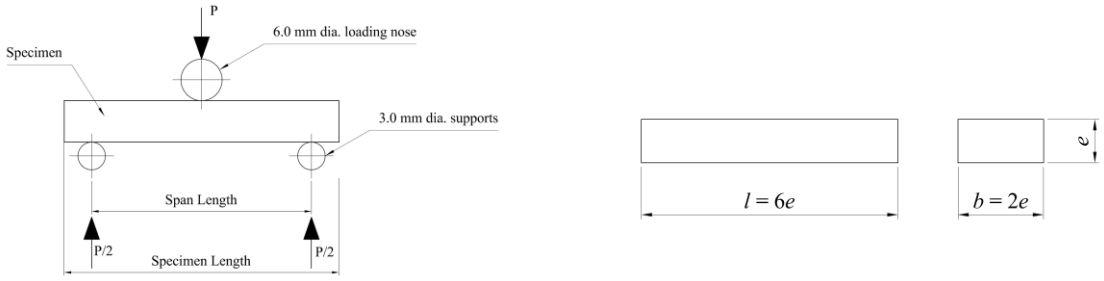
As it is shown in the figure above, the electric sensor is located in contact with the non-exposed surface, measuring the variation of the electric resistance of that area of the composite during all the curing process. So as to obtain a repeatable thickness for different specimens, some plates (thickness plates) were used between the quartz plate and height adjustable plate. The quartz (UV transmittance of 92 %) has been employed to compress the composite up to the thickness plate. The height adjustable plate permits different curing conditions by changing the distance between the UV source and the composite. In order to ensure that all the specimens are fully cured, the next statement should be satisfied [8]: the composite will be fully cured when there are not significant changes in the electric resistance and the hardness of the exposed and non-exposed surfaces are equal. The surface hardness was measured using a Barcol durometer, which is recommended for the use with composites. Additionally, the temperature of the composite will be measured at the non-exposed surface using the temperature sensor that is incorporated in the electric sensor.

As the fibre-dominated tensile properties would present similar properties for each pair of specimen type, in order to determine the effect of the UV source in the curing process the interlaminar shear strength (ILSS) was selected (Figure 3a), since the failure mode is matrix dependent. So as to determine the ILSS properties, the standard test method for short-beam strength has been used [9]. According to this method, the following specimen geometries were chosen (Figure 3b): on the one hand, the specimen length, *l*, should be six times the thickness, *e*; on the other hand, the specimen width, *b* should be two times *e*. Finally, the span length should be four times *e*.



(a) (b)

Figure 3. (a) Horizontal shear load diagram. (b) ILSS specimen configuration.

All tests were performed at displacement rate of 1 mm/min and using a 5 kN load cell. Five specimens of each type were tested. The short-beam strength is calculated following the next equation:

$$F^{sbs}=0.75\frac{P_m}{b\cdot e} \quad (1)$$

where, F^{sbs} is the short-beam strength (MPa), P_m is the maximum load observed during the test (N), *b* is the specimen width (mm) and *e* is the specimen thickness (mm).

Related to the impact properties, three specimens have been manufactured of each type of resin. The specimens have a rectangular geometry (75 mm × 50 mm), limited by the UV source emitting window.

Low velocity impact tests were carried out in a falling weight test equipment (Fractovis-Plus, Ceast). The impactor was equipped with a 20 kN load cell attached to the impactor which recorded the contact force history. The hemispherical head of the impactor had a diameter of 20 mm, multiple collisions were avoided by anti-rebound device. The impactor mass was kept constant and equal to 4.3 kg. In order to achieve higher damage levels, the impactor velocity was set to 4.44 m/s and the mass of the striker was increased up to 9.30 kg. In all cases, the tests were carried out at room temperature. The samples were clamped into an annular ring with inner and outer diameters of 40 mm and 60 mm respectively.

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3. Results and discussion

The evolution of the degree of cure obtained from the electric resistance monitoring of the different specimens manufactured is shown in Figure 4. As the curing conditions of both materials are identical, the temperature in both specimens is very similar. Thus, it is not necessary to decouple the effect of the temperature from the electric resistance [3]. On the other hand, this curing degree is obtained using the relation between the measured Barcol hardness and the maximum achieved hardness at the non exposure surface. Hence, as it can be seen in Figure 4, the slope of the styrene-free vinyl ester is higher than the slope of the unsatured polyester resin. Hence, it can be concluded the styrene-free vinyl ester resin achieve the same curing degree than the unsatured polyester resin in less time. Specifically, styrene-free vinyl ester resin needs about 46% less time than unsatured polyester resin.

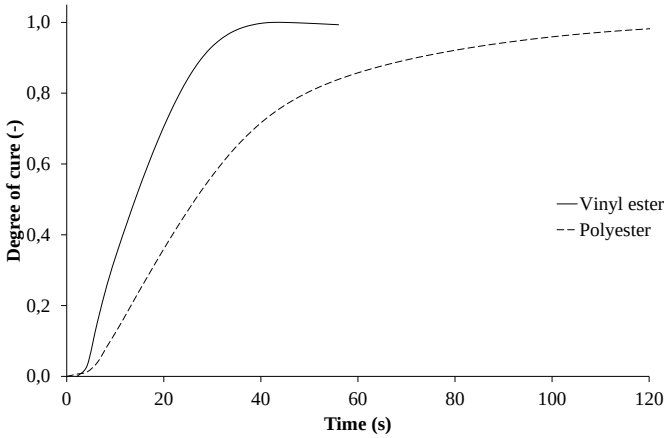

Figure 4. Curing time comparision

In order to determine if the failure of the tested specimens was interlaminar failure, all the specimens were analysed in a macroscope after ILSS tests. All the specimens present the same interlaminar failure mode after the short-beam test. After that it can be concluded that the values obtained for those specimens can be compared as the same failure pattern is found in all the specimens. Furthermore, in order to ensure the repetitivility 5 specimens of each type of resin has been analysed.

Figure 5 shows the results of the ILSS test, where it can be seen the interlaminar shear strength of the analysed specimens. These results show that there is not significant differences between the specimens manufactured with polyester resin and specimens manufactured with styrene-free Vinyl ester resin. Moreover, the same deviation was found in both type of specimens. Hence, it can be concluded that both type of photocurable resins have the same interlaminar shear strength.

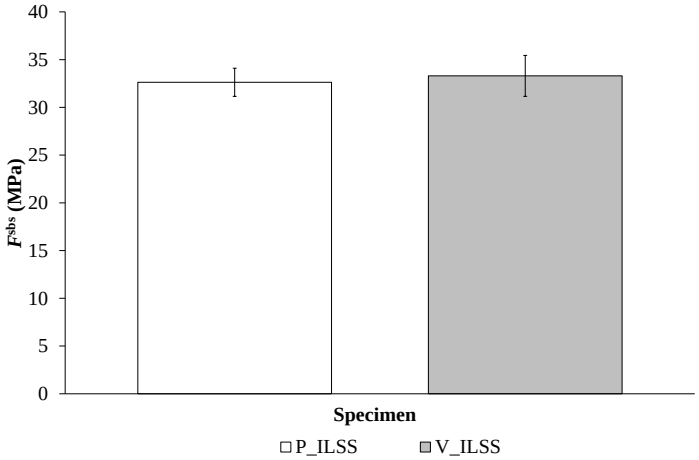

Figure 5. Short-beam strength for manufactured specimens.

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The most representative force *vs*. time curves of impact test are shown in Figure 6. In this figure can be seen how both resins describe similar curve patterns. In addition, the results of energy absortion of both resisn are realy similar, where the styrene-free vinyl ester has an average of 59.81 ± 3.98 J, whereas the unsatured polyester has an average of 59.28 ± 5.45 J. The differences in peak force are also irrelevant. Hence, it can be concluded that the difference between both resins is not appreciable, since the contribution of the glass fibre in perforation tests like these ones is higher than that of the matrix.

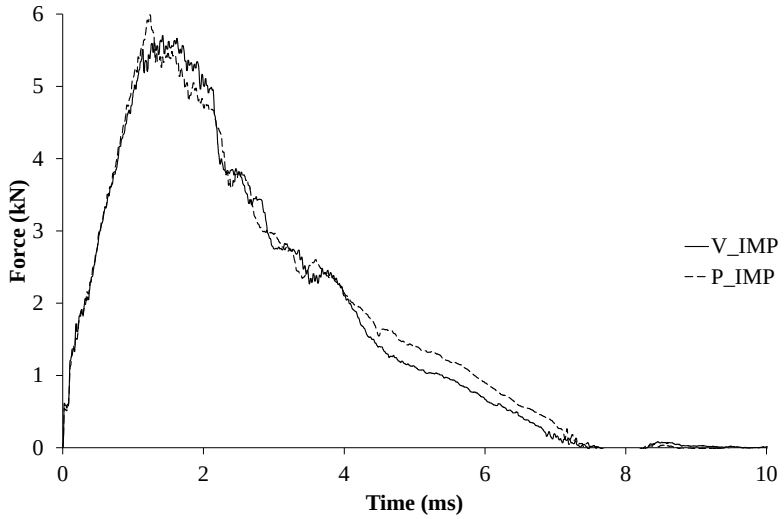

Figure 6. Representative force-time curves for both specimens.

3. Conclusions

In the present paper a comparison of two resins, unsatured polyester and styrene-free vinyl ester, has been developed in order to demonstrate the suitability of the new styrene-free resins for out of die ultraviolet cured 3D pultrusion process. For that propose, curing kinetics, interlaminar shear strength and impact properties have been analysed.

The following conclusions have been obtained:

- Styrene-free vinyl ester needs about 46% less time to be cured than unsatured polyester.
- No significant differences between both resins were found in the ILSS test.
- In the impact test, there is no appreciable difference between both resins.
- Based on the test performed on this study, the suitability of styrene-free vinyl ester has been demonstrated.

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