OUT OF DIE ULTRAVIOLET PULTRUSION PROCESS SET-UP: LIMITATIONS OF PHOTO-DIFFERENTIAL SCANNING CALORIMETRY ANALYSIS

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Abstract
Pultrusion is a highly automated continuous process for manufacturing structural composite profiles. However, pultrusion is restricted to constant radii, low productivity rates and high pulling force since the profile continues being cured inside the die. If the profile is cured out of the die using ultraviolet (UV) curing, the main limitations of the use of the traditional pultrusion can be overcome. However, using UV curing instead of thermal curing, makes the process set-up completely different. Traditionally, one of the most extended curing characterisation technique for UV curing is the photo-DSC analysis. However, due to the limitations of this technique, the industry has developed some interesting technologies based on the electric properties of the composites. Hence, the aim of this study is to analyse the limitations of the traditional photo-differential scanning calorimetry (photo-DSC) analysis compared to electric monitoring (DC sensor) in the out of die ultraviolet (UV) pultrusion process set-up. The results demonstrates that the photo-DSC is not sensitive to curing aspects such as the photoinitiator type for UV curing of composites. On the other hand, the electric resistance monitoring is sensitive to those aspects, becoming in a feasible technique for UV cured pultrusion set-up.

1. Introduction

Ultraviolet (UV) curing of composite materials is an alternative curing method to the conventional thermal curing approaches. Resins such polyester, epoxy or vinylester, in combination with a photoinitiator system, can be cured in minutes under the UV exposure. Thereby, new curing conditions, parameters and strategies would be taken into account since the curing of thin systems is completely different to the curing of a composite material. One of the processes of composite manufacturing that can be combined with UV curing is pultrusion process. As the studies carried out by Britnell et al. [1] and Tena et al. [2,3] demonstrate, the out of die UV cured pultrusion can overcome the main limitations of the use of the traditional pultrusion (constant radii, low productivity rates and high pulling force since the profile continues being cured inside the die).

However, using UV curing instead of thermal curing, makes the process set-up completely different. UV curing process depends on the absorption of ultraviolet light by the photoinitiator, so that curing factors as the dispersion, the absorption or the reflexion of the light trough the material and the different types of reinforcements have direct influence into the curing process.

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Three main aspects should be controlled in a photocurable system [4]:

- The application. The curing process will be conditioned by aspects like the thickness, the absorption trough the material or the presence of the fibre.
- The formulation of the matrix. The proper formulation of the matrix and the photoinitiator system will allow reaching the desired mechanical properties, with an efficient use of the UV radiation and in the less time as possible.
- The UV source. The UV source (emitting spectrum, intensity, light stability, etc.) is crucial and it will condition the final mechanical properties, the formulation and the process itself.

Thus, the selection of a curing analysis technique sensitive to all this curing parameters is required. Traditionally, one of the most extended curing characterisation technique is the photo-differential scanning calorimetry (photo-DSC) analysis. This technique analyses the curing process of a small portion of resin (10-13 mg). This fact might be a problem when the curing process of composites is analysed, since the presence of the reinforcement, the absorption of the light, etc. are not taken into account. On the other hand, in the recent years, the industry has developed some interesting technologies based on the electric properties of the composites. This type of sensor has demonstrated to be a suitable option for analysing the curing process of composites [2, 5, 6]. DC sensors are based on correlations between electric resistance and state of cure of the resin and it can be used to analyse the curing process of composites, instead of analysing only the resin as in photo-DSC.

Thus, the aim of this study is to analyse the limitations of the traditional photo-DSC analysis compared to electric monitoring (DC sensor) in the out of die UV pultrusion process set-up. The photopolymerisation process of two different photo-curable resin formulation has been characterised through electric monitoring and photo-DSC techniques. Furthermore, rectangular cross-sectioned profiles have been manufactured with out of die UV cured pultrusion process using both resin formulations. Hence, the limitations of each curing analysis technique will be determined through the evaluation of the results from the curing process analysis and the physical and mechanical properties of the pultruded profiles.

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 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 fibres at 90º which maintain the cohesion of the unidirectional fibres. The resin is UV curable unsaturated polyester supplied by Irurena S.A. whose commercial name is FPC-7621 NA. In this study formulations with two different photoinitiator systems are analysed [7]: the first one (AHK-TPO) is a combination of α-Hydroxyketone (AHK) and Ethyl - 2,4,6 – Trimethylbenzoylphenylphosphinate (TPO); whereas the second (AHK-BAPO) is a mixture of α-Hydroxyketone (AHK) and Bis (2,4,6-trimethylbenzoyl)-phenyl – phosphine oxide (BAPO). Figure 1a presents the different absorption spectrums of the selected photoinitiators. Figure 1a presents the different absorption spectrums of the selected photoinitiators.

Two different lamps were used in this study: a flood type arc lamp with metal halide 400 W bulb provided by DYMAX (intensity of 1 W/cm^2), and Hamamatsu LC8 spot type lamp with a maximum intensity of 4.8 W/cm^2. The emission spectrums of the lamps are reported in the Figure 1b. As it can be seen, the main intensity peaks of both lamps are similar. The DYMAX lamp was placed in the pultrusion line, whereas the LC8 was used for the outline experimental work.

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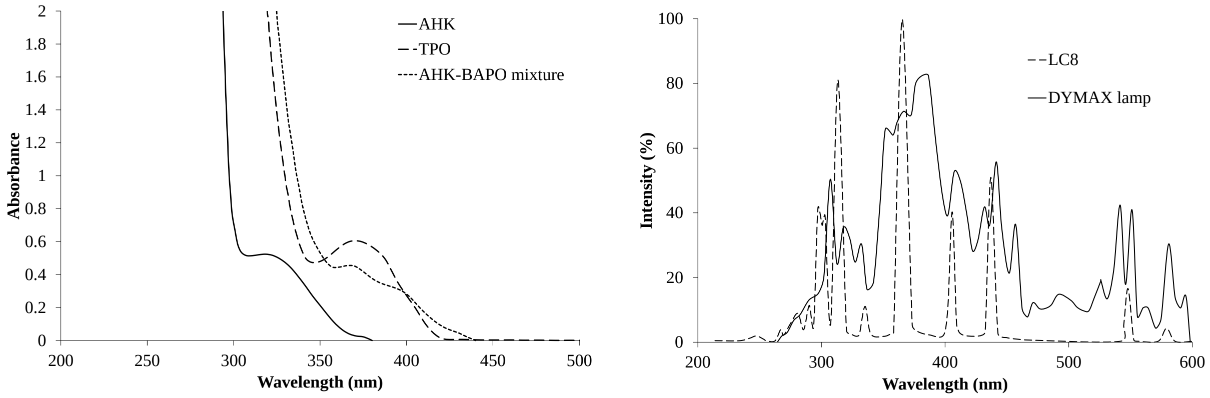

(a) (b)

Figure 1. (a) Absorption spectrums of the studied photoinitiators; (b) Emission spectrums of used UV sources.

2.3. Pultrusion processing

The pultrusion line has been developed entirely by the research group at Mondragon University. The selected pulling speed was 0.65 m/min. The impregnation was done by an open resin bath system and the pull system is a roller system developed specifically for the pultrusion line and the profile section. It has to be remarked that the profile is only irradiated with one UV source (Fig. 2). The die is designed to manufacture a rectangular cross-sectioned (75 mm × 3 mm) profile using 12 quasi-unidirectional glass fibre plies.

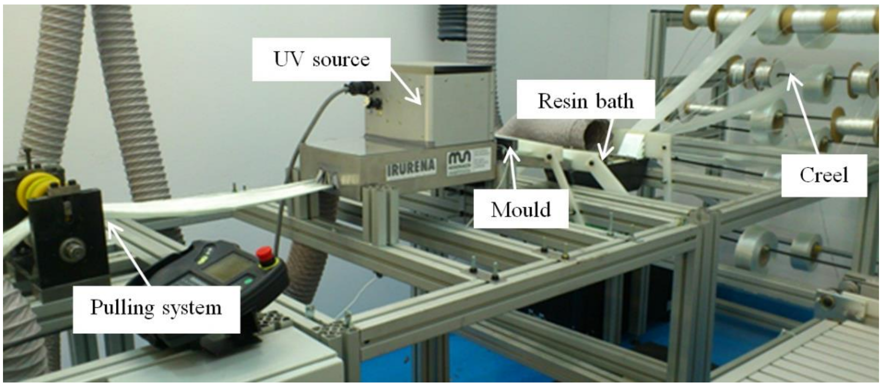

Figure 2. Out of die UV cured pultrusion line.

2.3. Photo-differential scanning calorimetry (photo-DSC)

The heat of the UV-curing reactions was measured by means of a Mettler Toledo DSC 1 differential scanning calorimeter (DSC) equipped with a photocalorimetry accessory. The UV-unit consist of the optical system including a mercury xenon lamp (Hamamtsu LC8), mirror, shutter and diaphragm, power source and control system to cause the lamp to turn on/off. The cell was sealed with a quartz window that let the UV light pass onto the open aluminium sample pans. The sample space was flushed with nitrogen. To ensure equal illumination conditions throughout the sample volume, the samples typically weighed between 10 and 13 mg. The measurements were carried out at intensity of 75 mW/cm^2 and at 25 ºC. The reaction was considered completed when the heat flux was constant. The variation of the enthalpy of the material is calculated integrating the area under the exothermic peak of the heat flux *vs.* time curve.

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2.4. Electric monitoring (DC sensor)

Related to the electric monitoring analysis, a specific tool has been developed to control the curing process. Analysed specimens were manufactured by hand layup process (3 mm thickness). Thus, after the impregnation of the fibres, uncured specimens where placed in the curing tool. Figure 3a shows a description of the curing analysis tool, which permits to change the 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. The relation between electric resistivity and the curing degree of the material is described in Figure 3b as it was presented in a previous research work [7].

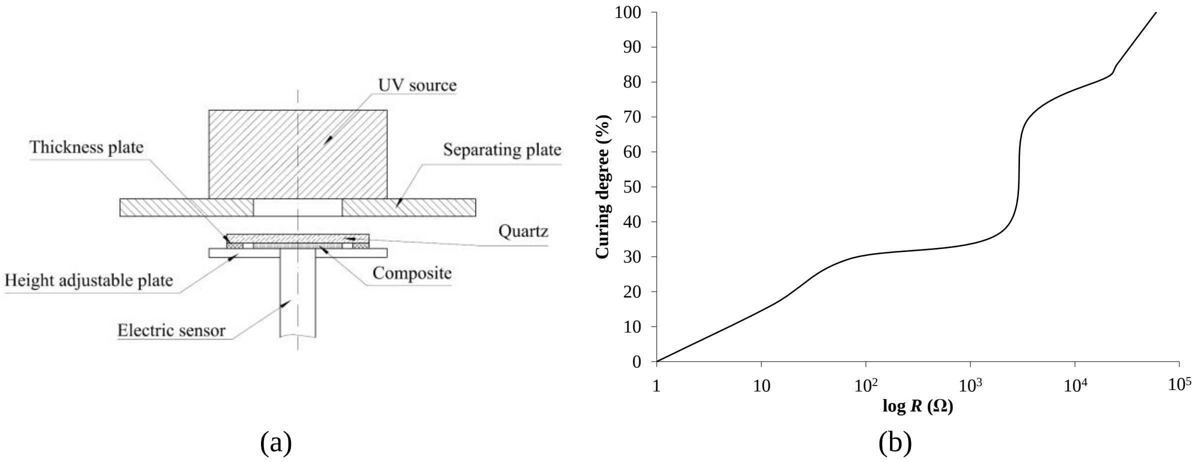

Figure 3. (a) Description of the electric monitoring system; (b) Relation between electric resistivity and the curing degree of the material.

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 [7]: 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.

2.5. Mechanical and physical properties – test geometry and procedures

The density of the composite was determined according to ASTM D792-08. Glass fibre volume fraction and void content were measured following the procedure described in ASTM D3171-09.

In order to evaluate the mechanical properties of the pultruded profiles 3 point bending test has been selected. Flexural properties obtained in longitudinal direction are fibre-dominated and would present similar properties for each pair of specimen type. Thus, in order to determine the effect of the UV source in the curing process, flexural properties obtained in transversal direction will be also evaluated, since the failure mode is matrix dependent. So as to determine the flexural properties, ASTM D790-03 standard test has been used [8].

All tests were performed at displacement rate of 1 mm/min and using a 5 kN load cell. Five specimens

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of each type were tested. The maximum flexural stress (σ_f) is calculated following the next equation.

$$\sigma_f = \frac{3F_{max}L}{2bd^2} \quad (1)$$

where, L is the support span; d is the thickness of the specimen; b is referred to the width of the specimen; and, F_{max} is the maximum breaking load.

The tangent modulus of elasticity (E_f) is determined drawing a tangent to the steepest initial straight-line portion of the load-deflection curve using the following equation.

$$E_f = \frac{mL^3}{4bd^3} \quad (2)$$

where, m is the slope of the tangent to the initial straight-line portion of the load-deflection curve.

3. Results and discussion

Regarding photo-DSC results, Figure 4 shows heat and conversion curves for both UV curable resin formulations. As it is reported in this figure, no significant differences between both formulations were found in the photo-DSC analysis. It can be concluded, that from the point of view of this characterisation technique no differences are reported between those formulations.

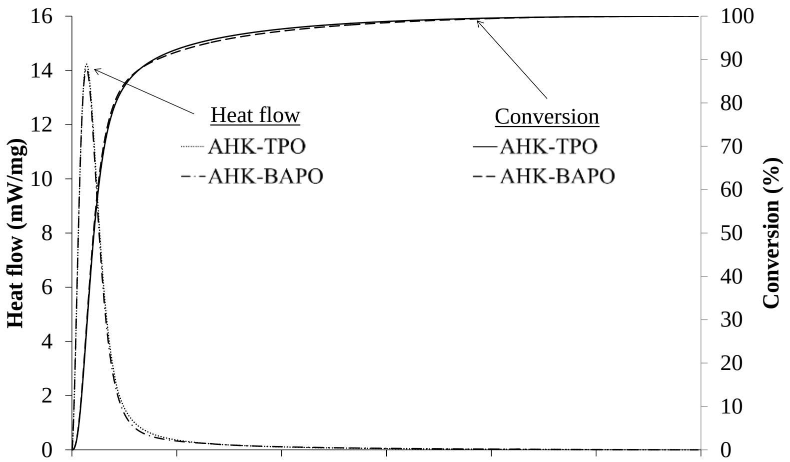

Figure 4. Photo-DSC results: heat flux and conversion curves.

On the other hand, the results of the electric resistance monitoring of the manufactured composites using both resin formulations are presented in Figure 5. Unlike the photo-DSC analysis, curing differences between the two analysed photoinitiator systems have been reported by the electric resistance monitoring. In fact, the AHK-BAPO formulation exhibits higher curing degree at the non-exposed surface, 80% and 40% respectively (this curing degree is obtained comparing the measured Barcol hardness in each specimen and the maximum achievable hardness). As the electric monitoring analyses the curing process of a composite instead of only a small portion of resin, parameters such as the presence of the reinforcement, the absorption and dispersion of the light trough thickness, etc. are taken into account. Hence, the electric monitoring seems to be more suitable for the pultrusion set-up process prior to the analysis of the physical and mechanical properties of the pultruded profiles.

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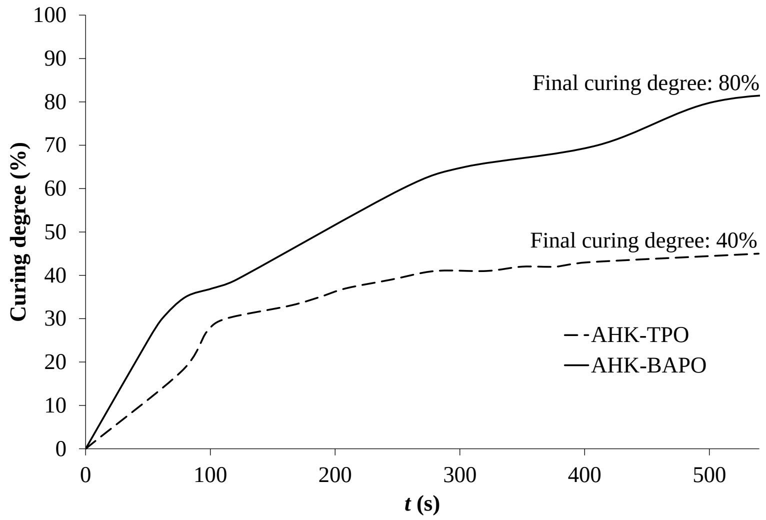

Figure 5. Electric resistance monitoring (curing degree) of the manufactured composites.

Table 1 presents the physical properties of the profiles manufactured using UV cured pultrusion. It has been observed that the impregnation of the fibres is adequate in all the specimens. Analysing physical parameters such as the density, fibre and void volume fractions, it has to be remarked that no significant differences has been found between both types of profiles.

Table 1. Physical properties of the pultruded profiles.

Specimen Type	Fibre volume fraction (%)	Void volume fraction (%)	Density (g/cm^3)
AHK-TPO	49.24±0.19	5.30±0.12	1.840±0.004
AHK-BAPO	48.62±0.11	7.37±0.08	1.806±0.002

Analysing the results from the flexural characterisation shown in Table 2, different conclusion can be drawn. The first one is that no differences are determined in the longitudinal direction. This result was expected since the fibre volume fraction is very similar in both cases, and this direction is fibre-dominated. However, in the transversal direction, where the flexural properties are matrix dependent, AHK-BAPO formulation exhibits higher flexural properties. Thus, it can be concluded that the higher curing degree at the non-exposed surface present in the profiles manufactured with AHK-BAPO formulation results in higher mechanical properties of the profile in the transversal direction.

Table 2. Mechanical properties of the pultruded profiles.

Specimen Type	Transversal		Longitudinal	
	Flexural stress (MPa)	Tangent modulus of elasticity (GPa)	Flexural stress (MPa)	Tangent modulus of elasticity (GPa)
AHK-TPO	81.5±8.5	2.37±0.33	428±26	22.7±0.5
AHK-BAPO	99.0±4.9	3.30±0.18		

4. Conclusions

In the present paper the limitations of the traditional photo-DSC analysis compared to electric monitoring (DC sensor) in the out of die UV pultrusion process set-up has been analysed.

The following conclusions have been obtained:

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- No significant differences between both formulations were found in the photo-DSC analysis.
- Unlike the photo-DSC analysis, curing differences between the two analysed photoinitiator systems have been reported by the electric resistance monitoring: the AHK-BAPO formulation exhibits higher curing degree at the non-exposed surface.
- Referring to the comparison of the characterization techniques, it has been demonstrated that the photo-DSC is not sensitive to curing aspects such as the laminate thickness, the reinforcement and the photoinitiator type for composites UV curing. On the other hand, the electric resistance monitoring is sensitive to those aspects. Thus, the electric resistance monitoring is a feasible technique for the monitoring of UV curing of composites in real time.
- The higher curing degree at the non-exposed surface present in the profiles manufactured with AHK-BAPO formulation results in higher mechanical properties of the profile in the transversal direction.
- The limitations found in the photo-DSC analysis makes the electric resistance monitoring with DC sensors a more feasible option for the out of die UV cured pultrusion process set-up.

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