EFFECT OF ALUMINA TRI-HYDRATE FILLER ON THE MECHANICAL AND OPTICAL PROPERTIES OF FLAME-RETARDANT ULTRAVIOLET CURED VINYL ESTER COMPOSITES

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Abstract

This research study is focused on the effect of alumina tri-hydrate (ATH) filler on the mechanical and optical properties of flame-retardant ultraviolet cured vinyl ester composites. In particular, vinyl ester formulations for out of die ultraviolet (UV) cured pultrusion has been analysed. Different matrix formulations varying the percentage of ATH (0 phr, 10 phr, 20 phr, 30 phr and 40 phr) have been compared. The through-thickness light transmission is critical in the studied process, in order to avoid the expansion at the exit of the die. Thus, the optical properties of the composite have been measured by a spectroradiometer during the curing process of the composites. The results show that the light transmission during the curing process is moderately affected (20%) by the presence of ATH up to 30 phr. In the case of 40 phr of ATH, the decrease of light transmission is more accused (35%). However, as the temperature of the composite increases as the ATH content increases, the curing degree is not negatively affected in these conditions. Regarding the mechanical properties, no significant differences of the interlaminar properties have been reported in the composites filled with ATH compared to the basic formulation (0 phr ATH).

1. Introduction

Pultrusion is a highly automated continuous process for manufacturing structural composite profiles. This manufacturing process has gained importance and popularity in civil infrastructure applications, including FRP bridge decks, internal FRP reinforcement for concrete structures, etc. [1]. However, pultrusion is restricted to constant radii, low productivity rates and high pulling force since the profile continues being cured inside the die [2]. Nevertheless, if the profile is cured out of the die, the main limitations of the use of the traditional pultrusion would be overcome [2-4].

However, the curing of the composite out from the die is not possible using the traditional thermal curing approach. Therefore, an alternative fast-curing method is needed. One of those alternative routes is the ultraviolet (UV) curing [2-4]. The UV curing industry using the energy of UV light in the formation of polymeric materials has approached a high degree of maturity in the last years. 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 [5]. Resins such as unsaturated vinyl esters, epoxy acrylates or unsaturated polyesters, when formulated with a proper photoinitiator can be cured quickly under exposure to UV light [5]. 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.

This new pultrusion process allows new design concepts to create complex 3D frames that could be interesting, for instance, for civil applications. However, the strict requirements of buildings on flame spread, smoke and toxicity, and fire ratings [6] have to be taken into account. Some research studies have proved that the fire performance of composites can be increased by adding mineral fillers (e.g., alumina tri-hydrate (ATH)) [1,6]. 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 through the material and the different types of reinforcements or fillers have direct influence into the curing process. Three main aspects should be controlled in a photocurable system [5]:

- The application. The curing process will be conditioned by aspects like the thickness, the absorption through the material or the presence of the fibre or fillers.
- 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.

The main problem of adding mineral fillers, as ATH, to the photo-curable matrix could be the possible decrease of light transmission through the composite thickness. A decrease in light transmission could affect negatively to the through thickness cure of the profiles during the out of die UV pultrusion process, reducing the maximum achievable depth.

Thus, this study is focused on the effect of alumina tri-hydrate (ATH) filler on the mechanical and optical properties of flame-retardant ultraviolet cured vinyl ester composites. In particular, vinyl ester formulation for out of die ultraviolet (UV) cured pultrusion has been analysed. Different vinyl ester matrix formulations varying the percentage of ATH have been analysed. Indeed, the effect of the ATH content on the optical properties, curing process and mechanical properties have been evaluated.

2. Experimental

2.1. Materials

The composite used in this study is a glass/UV cured vinyl ester composite. The reinforcement consists of 300 g/m^2 and 75 mm width quasi-unidirectional E-glass tape. The reinforcement is described as quasi-unidirectional due to the small proportion of fibres at 90º (8% in volume) which maintain the cohesion of the unidirectional fibres. Regarding the resin, a UV curable vinyl ester supplied by Irurena Group (IRUVIOL GFR-17 LED) has been used.

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). The first one is a depth curing photoinitiator, whereas the second is a superficial curing photoinitiator. It must be remarked that these photoinitiators have been demonstrated to be suitable for UV curing of similar composites by radical photoinitiation process [3, 4, 7].

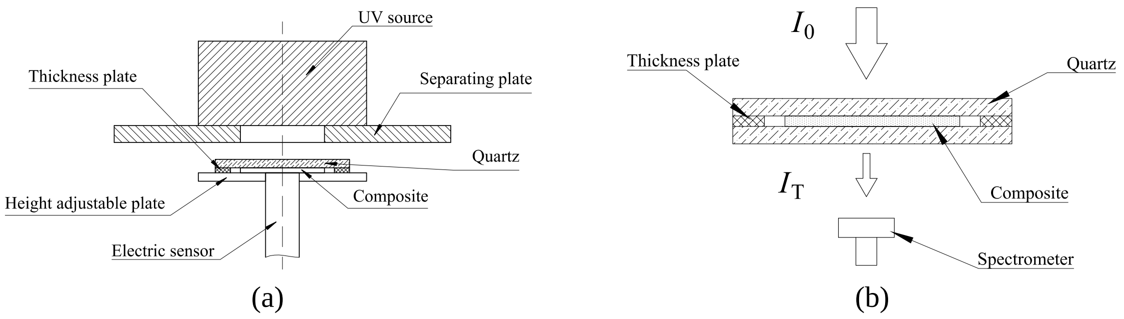
In order to increase the flame retardant efficiency of the formulation, the MoldX® P12 ATH filler has been selected. This product is recommended for pultrusion where fibreglass content is greater than 65% by weight, resin infusion moulding, vacuum bag moulding and filament winding. The most remarkable attributes of this filler are the halogen replacement, smoke suppression and reduced flame spread. For this study, different ATH content by weight has been analysed: 0 phr, 10 phr, 20 phr, 30 phr and 40 phr.

2.2 Manufacturing of specimens

In this research study, all the specimens were manufactured by hand layup process. The thickness of the specimens was 2 mm (ensured by calibrated plates in all the cases). The UV source used was a Phoseon FireFlex UV LED source, with an emitting window of 75×50 mm^2. The maximum intensity is 8 W/cm^2 and the emission peak of this UV source is found at 395 nm. It is necessary to mention that the specimens were only irradiated from one side as it is shown in Figure 1 with an intensity of 585 mW/cm^2.

2.3 Curing and optical characterisation

Related to the curing and optical analysis, two different setups have been used. The first one analyses the curing process (Figure 1a) and is based on measuring the electric resistance (following the procedure described by Tena *et al.* [4]) at the non-exposed surface (which is the last area to cure) of the composite through a sensor [4, 7]. In addition, the temperature of different parts of the composite has been analysed using thermocouples. The second tooling is used to analyse the transmittance of the light trough thickness during the curing process, the transmitted intensity (I_T) through the composite has been measured during the UV curing process. To that end, StellarNet Black-Comet spectrometer with a wavelength range of 190–850 nm has been used. The scheme of the optical analysis setup is shown in Figure 1b. The uncured composites manufactured by hand-layup were placed between two quartz plates, which were previously optically characterised. The distance between the UV source and the specimen for this test was 124 mm for all the specimens. The incident intensity (I_0) in the upper part of the composite was 585 mW/cm^2, which was previously measured with the spectrometer.



(a) (b)

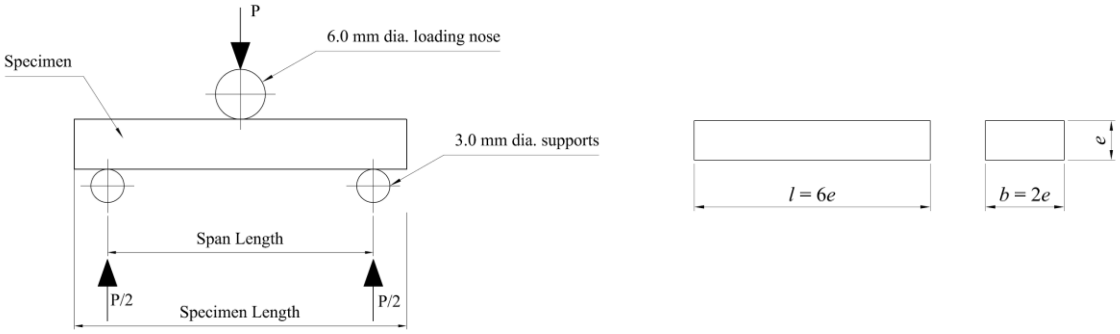
Figure 1. (a) Curing analysis setup diagram; (b) optical analysis setup diagram.

2.4 Mechanical characterisation

As the fibre-dominated tensile properties would present similar properties for all the specimens, in order to determine the effect of the ATH content in the curing process the interlaminar shear strength (*ILSS*) was selected since the failure mode is matrix dependent (Figure 2a). So as to determine the *ILSS* properties, the standard test method for short-beam strength has been used [8]. According to this method, the following specimen geometries were chosen (Figure 2b): 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*. 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:

$$F^{\mathrm{sbs}} = 0.75\frac{P_{\mathrm{m}}}{b \cdot e} \tag{1}$$

where, F^{sbs} is the short-beam strength (MPa) and P_{m} is the maximum load observed during the test (N).



(a) (b)

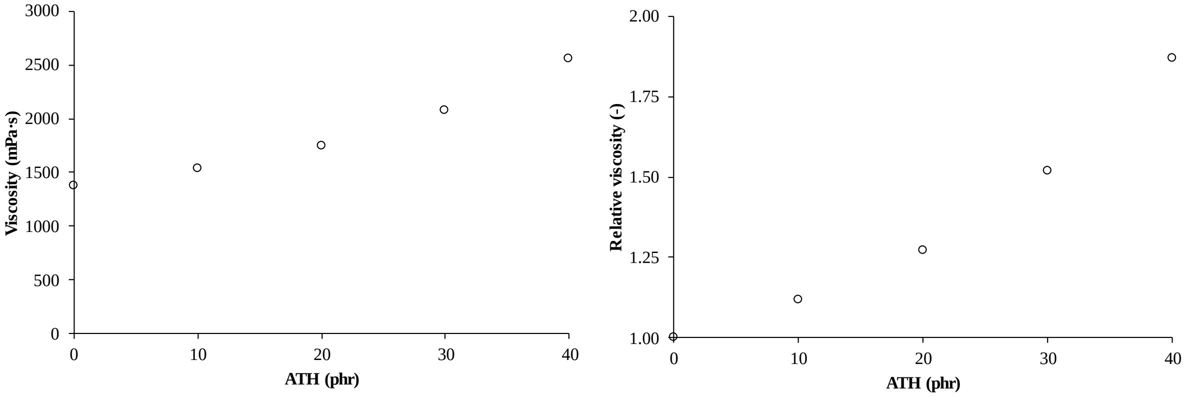
Figure 2. (a) Horizontal shear load diagram; (b) *ILSS* specimen configuration.

2.5 Physical characterisation

The viscosity of the different formulations was determined according to ISO 2555, using MYR VR 3000 rotational viscometer. Transversal polished sections of the manufactured specimens were examined by Scanning Electron Microscopy (SEM) using a FEI Nova Nano SEM 450 in order to analyse qualitatively the fibre and void distribution, the dispersion of the ATH and to corroborate the interlaminar failure (after *ILSS* tests).

3. Results and discussion

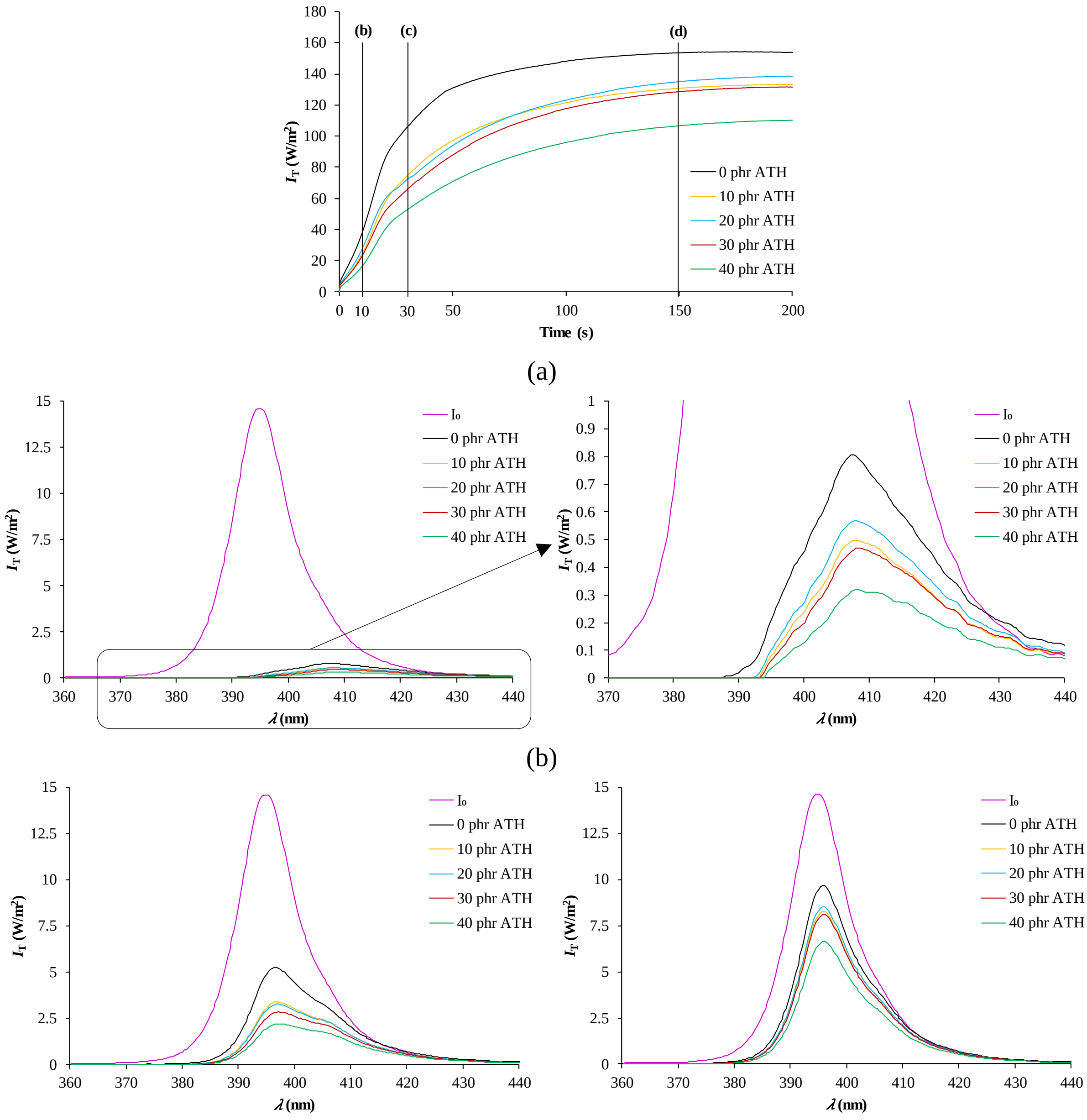
Even if the specimens of this study were manufactured by hand-layup, it is important to evaluate the increase of viscosity depending on ATH content. In this way, it would be possible to determine the suitability of each formulation to be implemented in the UV cured pultrusion. Figure 3 presents the evolution of the viscosity depending on the ATH content (Figure 3a) and referred to 0 phr ATH basic formulation (Figure 3b). It has been measured an increase of viscosity from 1500 mPa·s (0 phr ATH) to 2500 mPa·s (0 phr ATH) at room temperature. Based on the work carried out by Meyer [9], it can be determined that all the formulations are in the range of being suitable for their use in pultrusion (it is recommended a maximum of 3000 mPa·s depending on the reinforcement type).



(a) (b)

Figure 3. Evolution of the viscosity depending on ATH content: (a) viscosity in mPa·s and (b) relative viscosity increase referred to basic formulation.

With respect to the optical properties during the curing process, Figure 4a shows the evolution of the transmitted intensity in function of time for all the specimens. It can be noticed that the specimens filled with ATH between 10-30 phr present a reduction of approximately 20% of I_T; whereas in case of the specimen filled with 40 phr of ATH, the reduction is increased up to 35%. Figure 4b, Figure 4c and Figure 4d present the spectrum of I_T of all the specimens at 10 s, 30 s and 150 s of light exposure compared to I_0. In this figures the evolution of the absorption of the photoinitiator can be observed, being higher at the initial curing stages (Figure 4b and 4c). On the other hand, after those initial stages (Figure 4d), the shape of the curve of the transmitted intensity is less influenced by the absorption of the photoinitiator and is only decreased by the presence of ATH compared to the basic formulation.



(a)

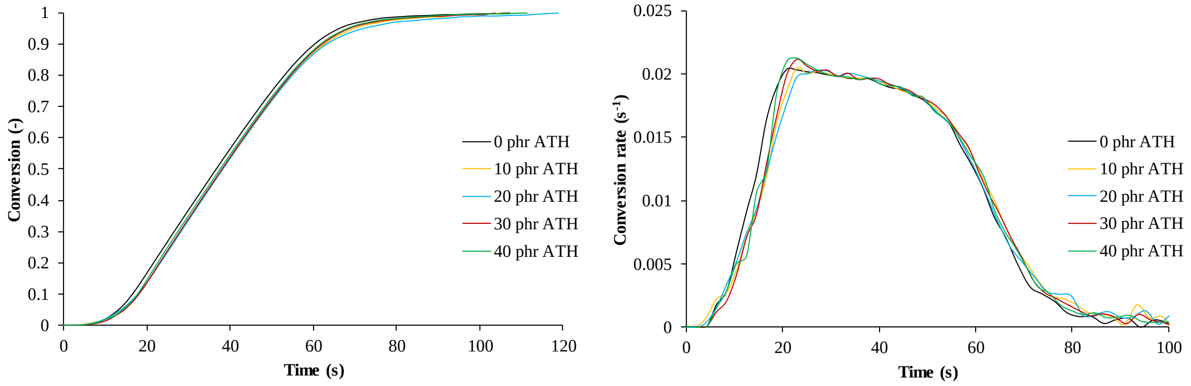
(b)

(c)

(d)

Figure 4. (a) Evolution of I_T in function of time for all the specimens during the curing process; the spectrum of I_T of all the specimens at (b) 10 s, (c) 30 s and (d)150 s of light exposure compared to I_0.

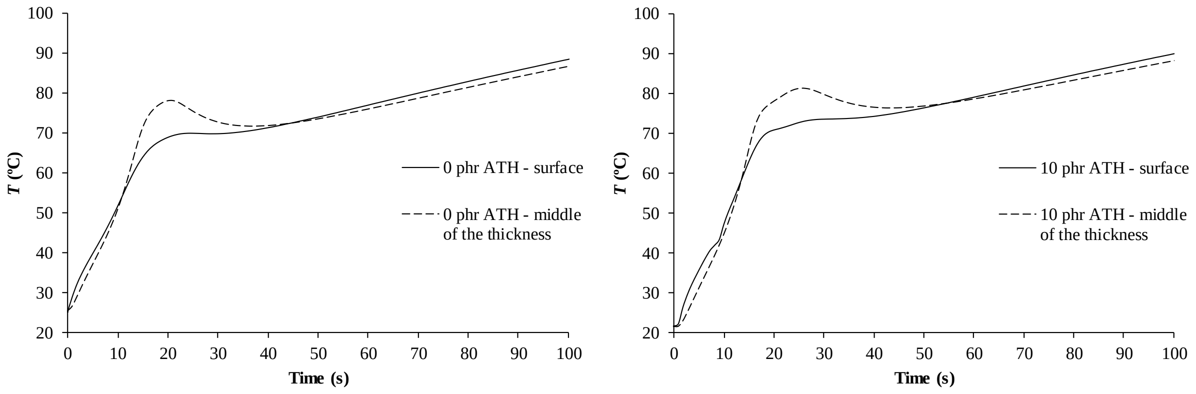
The analysis of the degree of cure based on the electric resistance of the composite is presented in Figure 5a. Analysing these curves, it can be stated, that even if the light transmittance is reduced due to the presence of ATH, the degree of cure of the composite is not negatively affected. Furthermore, all the specimens present almost the same evolution of the conversion and the conversion rate (Figure 5b) in function of time.



(a) (b)

Figure 5. Evolution of the (a) conversion and (b) conversion rate in function of time of all the specimens.

Figure 6 shows the temperatures on the surface and at the middle thickness of all the specimens during the curing process. All the curves follow the same pattern: first, a fast temperature increase occurs, and it reaches a maximum peak, which is more remarkable in the middle of the thickness; finally, it tends to a lower heating rate (heating of the UV source). A clear increase of this peak can be observed, being higher as the ATH content increases: from 75 ºC in the case of 0 phr ATH basic formulation to 95 ºC for 40 phr ATH in the middle thickness and from 70 ºC to 85 ºC on the surface, approximately (in the same curing conditions). Combining these results with the previous curing analysis, it can be noticed that the maximum temperature peak occurs at the same time than the maximum peak of the conversion rate (Figure 5b), which can be attributed to the exothermic peak of the curing reaction. Hence, it can be stated, that even if the transmitted light is reduced due to the presence of ATH filler, the curing degree is not affected due to the increase of temperature of the composite, which helps to increase the curing kinetics of the resin.



(a) (b)

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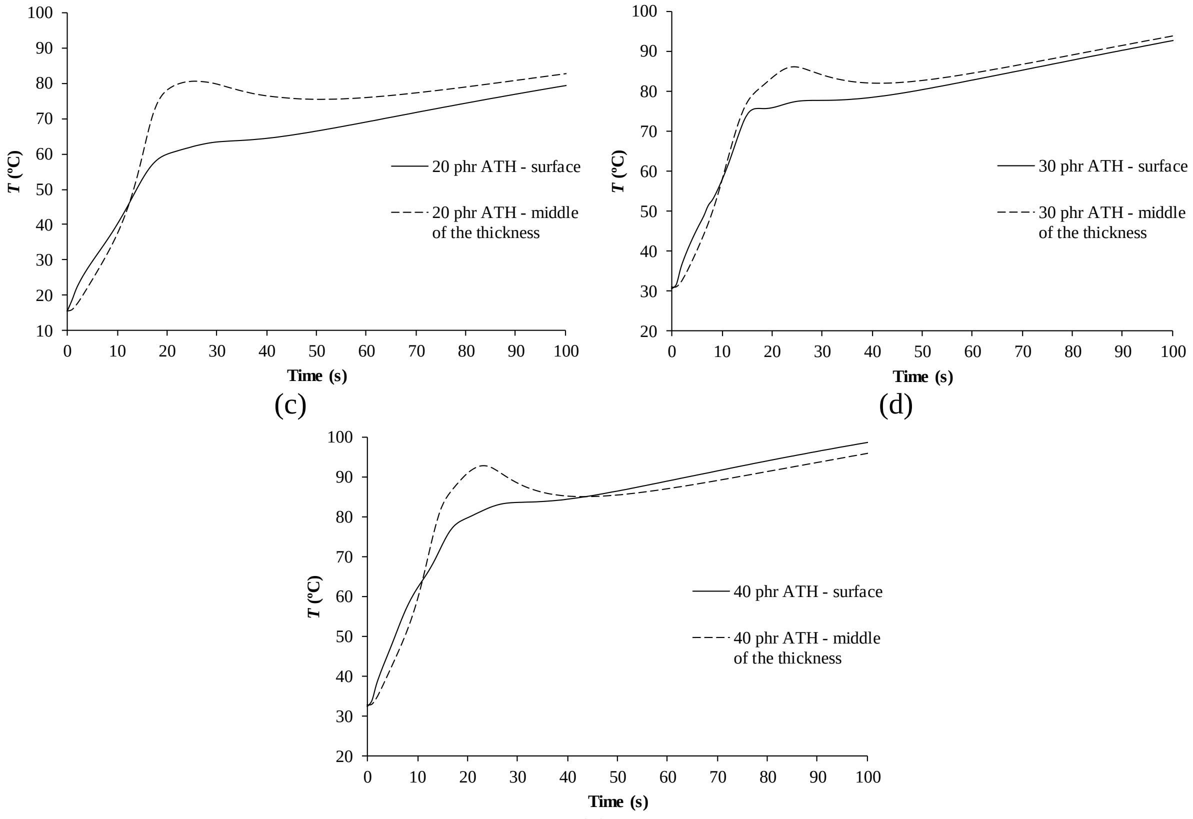
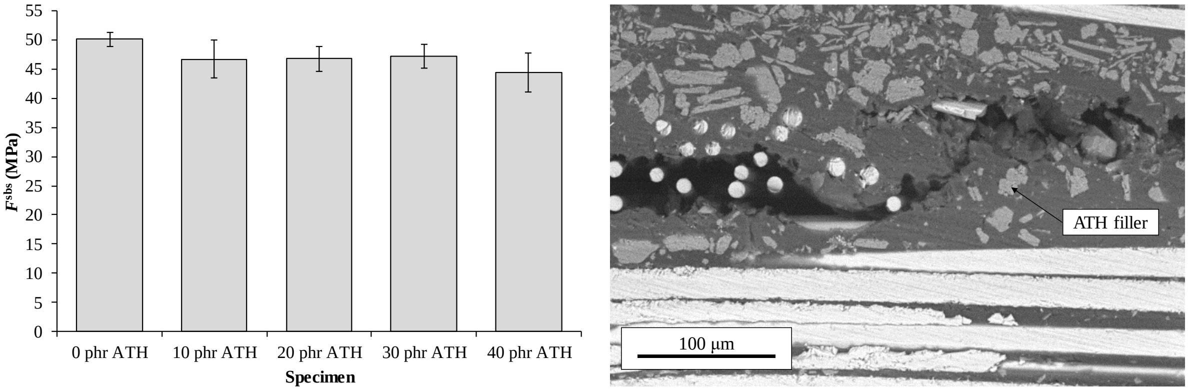


(c) (d)

(e)

Figure 6. Evolution of surface and middle thickness temperatures during the curing process: (a) 0 phr ATH, (b) 10 phr ATH, (c) 20 phr ATH, (d) 30 phr ATH and (e) 40 phr ATH.

Regarding mechanical characterisation, no significant differences of the interlaminar properties have been reported in the composites filled with ATH compared to the basic formulation (0 phr of ATH), as it is presented in Figure 7a. In order to determine if the failure of the tested specimens was interlaminar, all the specimens were analysed with a SEM after *ILSS* tests (Figure 7b). All the specimens present the same interlaminar failure mode after the short-beam test. Furthermore, the homogeneous dispersion of ATH fillers in the specimens can be corroborated analysing the Figure 7b.



(a) (b)

Figure 7. (a) Short-beam strength values for manufactured specimens; (b) detailed views of interlaminar failure of the specimens and ATH dispersion.

4. Conclusions

In this research study the effect of ATH filler on the mechanical and optical properties of flame-retardant ultraviolet cured vinyl ester composites has been studied. The following conclusions can be drawn from the carried work:

- The light transmission during the curing process is moderately affected by the presence of ATH up to 30 phr ATH: the transmitted intensity is reduced approximately 20% compared to 0 phr ATH basic formulation. In the case of 40 phr of ATH, the decrease of light transmission is more accused, reaching a reduction up to 35% of transmitted intensity.
- The temperature in the middle of the thickness of the specimens increases as the ATH content increases, from 75 ºC in the case of 0 phr ATH basic formulation to 95 ºC for 40 phr ATH in the same curing conditions.
- The evolution of the curing degree in function of time of all the specimens is almost the same in the studied range, even if the transmitted light is reduced due to the presence of ATH filler. This effect could be attributed to the measured temperature increase in the ATH filled specimens, which helps to increase the curing kinetics of the resin.
- Regarding the mechanical properties, no significant differences of the interlaminar properties have been reported in the composites filled with ATH compared to the basic formulation (0 phr of ATH).

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References

[1] M. Malik, V. Choudhary, I. K. Varma. Effect of non-halogen flame retardant additives on the properties of vinyl ester resins and their composites. *Journal of Fire Sciences*, 20(4), 329-342, 2002.
[2] D. Britnell, N. Tucker, G. Smith and S. Wong. Bent pultrusion - a method for the manufacture of pultrudate with controlled variation in curvature. *Journal of Materials Processing Technology*, 138: 311-315, 2003.
[3] I. Tena, A. Esnaola, M. Sarrionandia, I. Ulacia, J. Torre and J. Aurrekoetxea. Out of die ultraviolet cured pultrusion for automotive crash structures. *Composites Part B: Engineering*, 79: 209-216, 2015.
[4] I. Tena, M. Sarrionandia, J. Torre, J. Aurrekoetxea. The effect of process parameters on ultraviolet cured out of die bent pultrusion process. *Composites Part B: Engineering,* 89:9–17, 2016.
[5] A. Endruweit, M.S. Johnson and A.C. Long. Curing of composite components ultraviolet radiation: A review. *Polymer Composites*, 27 (2), 2006.
[6] M. R. Petersen, A. Chen, M. Roll, S. J. Jung, M. Yossef. Mechanical properties of fire-retardant glass fiber-reinforced polymer materials with alumina tri-hydrate filler. *Composites Part B: Engineering*, 78: 109-121, 2015.
[7] I. Saenz-Dominguez, I. Tena, M. Sarrionandia, J. Torre, J. Aurrekoetxea, Effect of ultraviolet curing kinetics on the mechanical properties of out of die pultruded vinyl ester composites. *Composites Part A: Applied Science and Manufacturing*, 109: 280-289, 2018.
[8] ASTM D2344. Standard Test Method for Short-Beam Strength of Polymer Matrix Composite Materials and Their Laminates, 2000.
[9] R. Meyer. Handbook of pultrusion technology. *Springer Science & Business Media*, 2012.