

ANALYSIS OF AXIAL CRUSHING BEHAVIOUR OF UNSATURATED POLYESTER AND VINYL ESTER COMPOSITES MANUFACTURED BY OUT OF DIE ULTRAVIOLET CURED PULTRUSION

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Abstract

This paper analyses the axial crushing behaviour and flexural properties of novel unsaturated polyester (UP) and vinyl ester (VE) composites, manufactured by out of die ultraviolet (UV) cured pultrusion. The relation between axial crushing properties and microstructure have been analysed based on UV curing kinetics and physical characterisation. The results show that VE composites present higher specific energy absorption capability (SEA) than UP composites, about 18% higher, due to the higher fracture toughness of VE resin. However, the slow curing kinetics of VE resin implies an expansion of the profile at the exit of the die, and consequently a high presence of voids (7.4%). In contrast, UP resin presents faster curing kinetics and therefore, the presence of voids is lower (0.9%). This fact implies a reduction in flexural strength of VE composites, which is 17% lower than UP composites.

1. Introduction

The latest trends in the automotive industry show an increase in the demand for improving the safety of the passengers in a crash situation. The cost of road-accidents for society is huge since, despite success through previous European Union programs, 26,000 people died and 135,000 people resulted seriously injured in Europe in 2015. The road safety guidelines would aim to cut European road deaths by 50% by 2020 [1]. To do so, new materials and structures with higher impact energy absorption capabilities and damage tolerance are required. Many researchers have proved that fibre reinforced polymer (FRP) composites exhibit high specific energy absorption (SEA) capability [2,3]. It has also been found that materials, as well as the geometry of a composite impact structure, have a significant effect on the SEA values [4]. Even if the circular sectioned tubular impact structures exhibit higher SEA, the most used geometry in real applications is square sectioned tubular crash structure due to assembly and element integration feasibility.

The composite processes currently employed to manufacture profiles are not able to deal with the productivity required by automotive industry. For these reasons, huge efforts are being made to find and develop cost-effective routes for manufacturing composite materials. In this way, Bader [5] compared different composite manufacturing processes based on a defined composite part. The study concluded that one of the processes with less influence of the labour cost is pultrusion, which indicates a high automation level of the process. Thus, pultrusion is a promising technology for the

manufacturing of automotive energy absorbing tubular parts. In fact, several researchers have explored the feasibility of pultruded profiles as impact energy absorption structures [6,7]. 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). However, as the curing takes place inside the die, it has several drawbacks [8]; the high initial investment needed in machinery due to the high pulling forces, the high cost of the pultrusion dies, high process incidences, the production rate is not fast enough in some cases and it is geometrically limited to straight profiles of constant cross section.

Therefore, if the profile is cured out of the die, those limitations can be overcome, but an alternative fast-curing method is needed. Recent studies have shown the validity of curing the composites out of the pultrusion die by ultraviolet light (UV), achieving high SEA values (48.65 kJ/kg) for a polyester resin [8] and successfully applied to an automotive crash structure [3]. Additionally, this new pultrusion process approach allows manufacturing bent-profiles [9]. Nevertheless, other thermoset resins commonly used in conventional pultrusion, such as vinyl ester, could improve the mechanical properties currently obtained. In fact, Warrior *et al.* [10] have proved that composites manufactured with vinyl ester resin, present higher SEA values than the composites manufactured with polyester, by up to 20% higher. Although the composites manufactured in this study were cured thermally, other studies related to UV curing of vinyl ester composites have proved the feasibility to achieve the same mechanical properties than the composites cured thermally [11,12]. However, the properties obtained in these studies were achieved manufacturing the composites by hand lay-up, where fast curing kinetics are not needed.

Thus, the main objective of the present paper is to characterise the axial crushing properties of a new unsaturated polyester and a vinyl ester UV-cured pultruded composites. Additionally, the UV curing kinetics, physical and flexural properties of them are also characterised.

2. Experimental

2.1. Materials

UV curing requires highly transparent materials to UV light, so the reinforcement consists of 300 g/m² and 75 mm width quasi-unidirectional E-glass tape. The reinforcement is described as quasi-unidirectional because of the small proportion of fibres at 90° (8% in volume) which maintain the cohesion of the unidirectional fibres. Two photocurable resins were used in this study: unsaturated polyester (UP) and vinyl ester resin (VE), both supplied by Iurena Group, whose commercial names are IRUVIOL GFR-10 LED and IRUVIOL GFR-17 LED respectively. The selected photoinitiator system for both resins is the same; 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 photoinitiator system has been demonstrated to be suitable for UV curing of composites [8,9].

2.2. Manufacturing of specimens

The specimens used in this study were obtained from semi-hexagonal profiles of two millimetres of thickness (Figure 1a), manufactured by out of die UV cured pultrusion line (Figure 1b), which has been developed entirely by the research group at Mondragon University. The impregnation was done in an open resin bath system and the pull system is a Kuka KR 180 R2500 robot arm. The pulling speed to manufacture the profiles was 0.3 m/min. The UV source used was a Phoseon FireFlex UV LED source, with an emitting window of 75 × 50 mm². The maximum intensity is 8 W/cm² and the emission peak of this UV source is found at 395 nm. It is necessary to mention that the profile is only irradiated from one side.

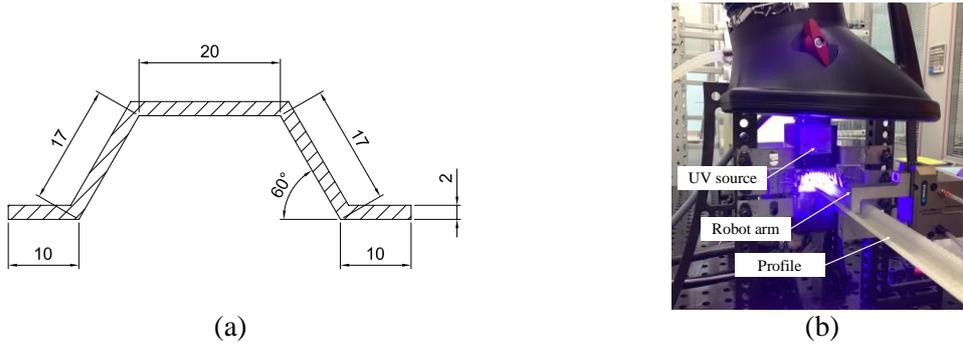


Figure 1. (a) Section of the pultruded profile; (b) manufacturing of the UV pultruded profile.

2.3. Energy absorption capabilities

In order to evaluate the crushing energy absorption capability of the material, quasi-static compression tests were carried out at 10 mm/min along 50 mm of collapse distance at room temperature. The specimens were the open sectioned semi-hexagonal profiles showed in Figure 1a, cut at 60 mm in length. In order to ensure a stable and progressive crushing a 45° chamfer trigger type was machined in all the specimens [13]. The equipment used is a universal testing machine equipped with a 100 kN load cell. In order to ensure the repeatability of the tests, 3 specimens have been tested. From force-displacement curves the following crushing characteristics were calculated: the maximum load at the first peak, P_{\max} (kN), the mean load of the collapse, P_{mean} (kN), the specific energy absorption of the material, SEA (kJ/kg) and the crushing efficiency η_c (%):

$$P_{\text{mean}} = \frac{\int_0^{l_{\max}} P(l)dl}{l_{\max}} \quad (1)$$

$$SEA = \frac{\int_0^{l_{\max}} P(l)dl}{m_t} \quad (2)$$

$$\eta_c = \frac{P_{\text{mean}}}{P_{\max}} \cdot 100 \quad (3)$$

where, l_{\max} (m) is the total collapsed length and m_t is the crushed specimen mass (kg).

2.4. Physical and curing kinetics characterisation

The physical characterisation was carried out determining the density of the resin and the composite according to ASTM D792-08; and the glass fibre volume fraction and void content following the procedure described in ASTM D3171-09 by burning off. Direct observation of the transversal polished sections of pultruded profiles 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 curing kinetics study has been carried out by a Differential Scanning Calorimetry (DSC), Mettler Toledo DSC 1, equipped with an accessory for the photo-calorimetry analysis (photo-DSC). All the measurements were made at 25 °C, with an intensity of 75 mW/cm². The emitting spectrum of DSC matches properly with the absorbance of the photoinitiator system and the representative peaks of photo-DSC are in the range of the emission peak of the UV LED source. The weight of the specimens was between 10 mg and 13 mg, in order to ensure the same radiation conditions for all the specimens.

2.5. Flexural properties

Three-point bending (3PB) analysis was carried out according to ASTM D790-10. All tests were performed at displacement rate of 1 mm/min and using a 5 kN load cell. Five specimens of each material were tested in the longitudinal direction (the main direction corresponding to the pulling direction) at room temperature. The dimensions of the samples, taken from the middle part of semi-hexagonal profiles (Figure 1a), were 2 mm × 12.7 mm × 45 mm. The flexural strength (σ_f) and the flexural modulus (E_f) are calculated by the next equations:

$$\sigma_f = \frac{3F_{\max}L}{2bd^2} \quad (4)$$

$$E_f = \frac{mL^3}{4bd^3} \quad (5)$$

where, L is the span (mm); b is the thickness of the specimen (mm); d is the width of the specimen (mm); F_{\max} is the maximum breaking force (N); and, m is the slope of the force deformation curve.

3. Results and discussion

3.1. Energy absorption capabilities

Figure 2a and Figure 2b show the load displacement curves of UP and VE specimens respectively, where it can be noticed that all the specimens had a stable and progressive crushing collapse. Moreover, the 3 deformation and fracture mechanisms have been observed: axial splitting, which is geometry dependent [14]; axial crack propagation along the centre of the laminate, so is matrix dependent; and fibre breakage and delamination, where delamination is dependent of interlaminar shear strength of the composite, fibre material and its orientation [15].

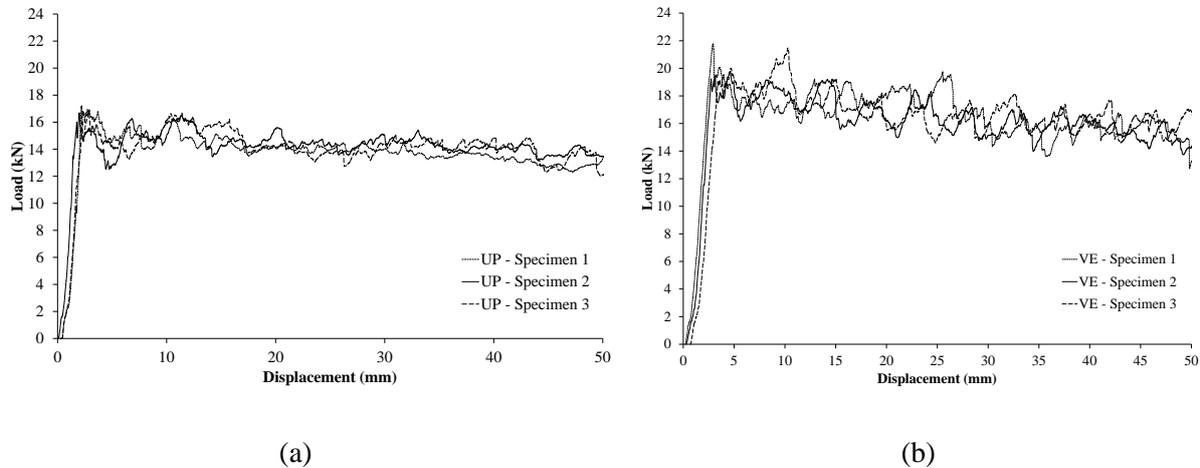


Figure 2. (a) Load vs. displacement curve of quasi-static compression test of UP; (b) load vs. displacement curve of VE.

Analysing the results showed in Table 1, it can be observed that both composites present higher *SEA* values than the found values in the literature of profiles with the same geometry and tested in the same

conditions [3,8,15]. VE composite presents higher *SEA* value than UP composite, about 18% higher, and a higher peak load, around 24%. However, in terms of efficiency levels, UP composite is about 6% higher than the values obtained with VE composite.

Table 1. Results of the quasi-static compression test.

Specimen	<i>SEA</i> (kJ/kg)	P_{max} (kN)	P_{mean} (kN)	η_c (%)
UP	51.2 ± 0.7	16.9 ± 0.3	13.9 ± 0.2	82 ± 2
VE	60.4 ± 3.0	21.0 ± 1.1	16.3 ± 0.8	77 ± 2

As the geometry of the specimens is the same, the difference between UP and VE composites are not due to the axial splitting mechanism. On the other hand, the fibre material and the orientation are equal in both composites. Hence, the differences in fibre breakage and delamination mechanism between both composites are due to the effect of the matrix. Consequently, as the axial crack propagation mechanism is also matrix dependent, it can be stated that the differences in the energy absorption properties are due to the properties of the resin and the possible defects in the composite, such as voids. Hence, the fact that VE composite presents higher *SEA* values than UP composite, could be explained due to the higher fracture toughness (K_{IC}) of VE [10]. According to the values observed from CES EduPack2016 of both resins, VE presents around three times higher K_{IC} (4.1 MPa m^{1/2} – 4.2 MPa m^{1/2}) than UP (1.1 MPa m^{1/2} – 1.7 MPa m^{1/2}).

3.2. Physical and curing kinetics characterisation

In order to understand the crush properties-microstructure-process relationships, the chemical and physical phenomenon at the die exit must be characterized. Regarding the measured density of the composites, UP presents a density of 1.97 ± 0.01 g/cm³, whereas the density of VE is 1.79 ± 0.01 g/cm³. Hence, UP composite presents about 10% higher density than VE composite. Comparing these results with measured densities of the resins, 1.22 ± 0.01 g/cm³ for UP and 1.16 ± 0.01 g/cm³ for VE, it can be observed that the difference decreases about 5%. As both composites have the same manufacturing conditions and reinforcement, the origin of the differences in density should be explained in terms of resin density and also of void content. Therefore, resin, fibre and void content characterisation of the pultruded parts are presented in Figure 4. Analysing the obtained values, high differences in void content are observed between the different pultruded parts, being higher in the case of the VE composite.

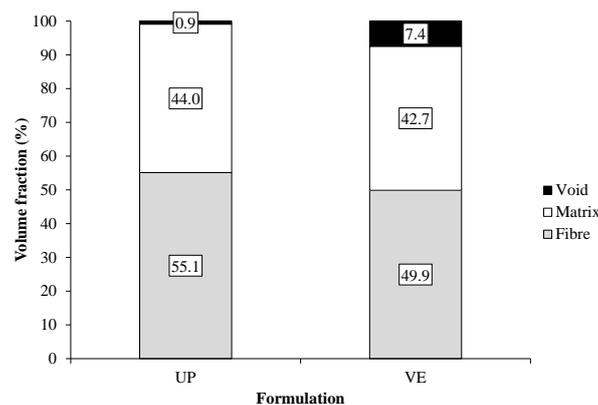


Figure 4. Physical characterisation results.

The results of the expansion justify the higher void content of VE composite, since UP composite parts present an expansion around 1% of the expected thickness (2 mm), whereas in the case of VE composite is about 10 %. However, although an expansion in the thickness of the profile is observed, the dimensional tolerances of the angles are maintained in all the specimens.

Finally, the origin of the voids is analysed based on the micrographs taken from the middle part of semi-hexagonal profiles by SEM. It can be observed in Figure 5 that the resin has impregnated all the spaces between the fibres into the yarns. Thus, it can be affirmed that both specimens have a proper impregnation. Therefore, it can be stated that the voids between the yarns are due to the expansion that occurs at the exit of the die, rather than to a wrong impregnation in the resin bath or into the die. In the same way, it can be noticed that in the resin rich areas, the UP composite (Figure 5a) has less distance between the yarns of fibres than VE composite (Figure 5b). This fact corroborates the expansion that occurs in the VE specimens. Moreover, the quantity of voids observed in the VE composites confirms the high void content measured in the physical test of VE composites.

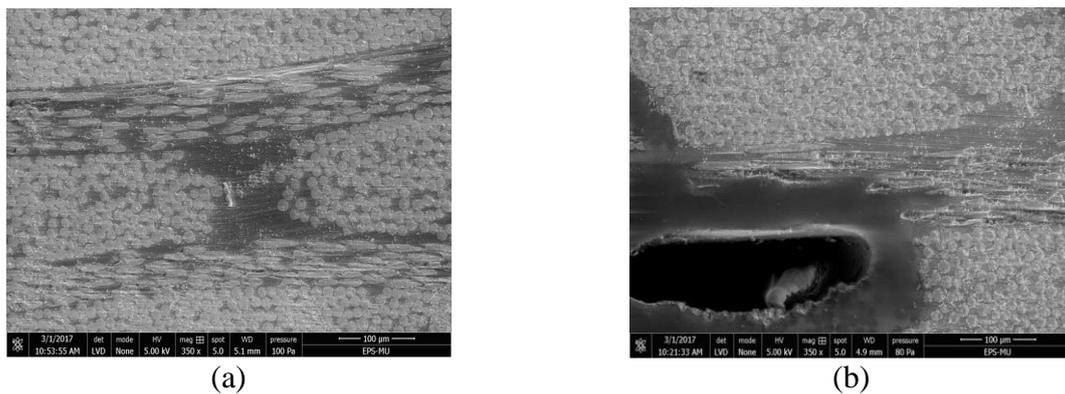


Figure 5. (a) SEM section view of UP composite; (b) SEM section view of VE composite.

In order to explain the expansion and the void generation, the UV curing kinetics must be studied. Figure 6a shows the most representative heat flow vs. time curves, obtained from the photo-DSC measurements. It can be noticed, that UP presents higher peak of heat flow (12 W/g) in less time (6 s) than VE (8 W/g in 19 s). Through these curves, the conversion rate vs. conversion curves have been obtained. Analysing the results (Figure 6b), it can be observed that the maximum conversion rate of UP (0.061 s⁻¹) is achieved at 22% of conversion, whereas VE achieves its maximum conversion rate (0.035 s⁻¹) at 42% of conversion.

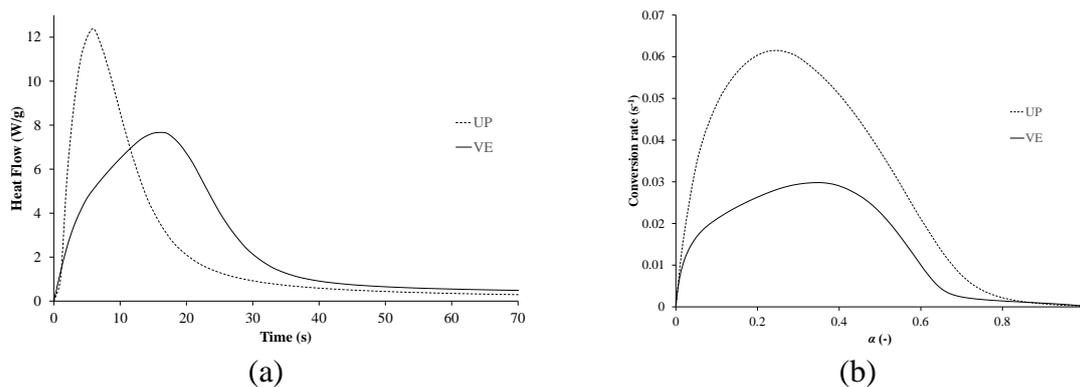


Figure 6. (a) Heat flow vs. time; (b) conversion rate vs. conversion.

Hence, the low conversion rate at the initial stage of the curing process of VE, can explain the expansion that suffered the VE composite at the exit of the die, and consequently, the high void content. In the same way, the energy absorption properties of VE composite may have been reduced due to its high void content [8].

3.3. Flexural properties

Flexural strength and modulus, determined from the 3PB test are shown in Figure 7a and Figure 7b respectively. Analysing the results, it can be observed that UP composites present higher values of flexural strength than the VE composites, about 20% higher. As the fibre type and configuration and manufacturing conditions are the same, it can be stated that the differences in the results are due to the resin and defects. Hence, in order to explain the differences between both composites, the flexural strength properties of both resins were obtained from CES EduPack2016. Comparing the results with the values of the flexural strength of VE (141-163 MPa) and UP (75-159 MPa), it can be said that the differences observed on the flexural strength between both composites are higher than expected. Thus, it can be concluded that the high content of voids due to the expansion at the exit of the die, reduces the flexural strength of VE composite. In the same way, the values of flexural modulus of UP composite are higher than VE composites, about 16% higher.

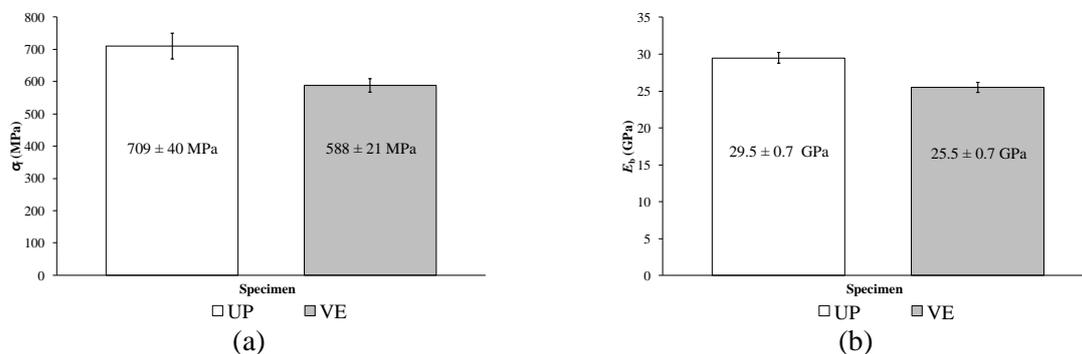


Figure 7. Flexural properties. (a) Flexural strength; (b) flexural modulus.

4. Conclusion

The present work has characterized the axial crushing behaviour and flexural properties of a new unsaturated polyester and vinyl ester UV pultruded composites. In addition, in order to identify the crushing properties-microstructure-process relationships, physical and chemical analysis have been done. The main conclusions are the followings:

- Both, UP and VE composites present higher *SEA* than other composites with the same geometry and test conditions observed in the literature, 51 kJ/kg and 60 kJ/kg respectively. On the other hand, VE composite presents higher *SEA* than UP composite (18% higher), but lower collapse efficiency (6% lower). The differences in *SEA* could be explained due to the differences in K_{IC} between both resins.
- The high void content of VE composite (7.4%) reduces its flexural properties, as it can be seen in the flexural strength that is among 20% lower than UP composite, which presents 0.9% of void content. In the same way, the *SEA* values of VE composite could have been affected by its high void content.
- The high void content of VE composite is due to the expansion that the profile suffers at the exit of the die. This fact is related to the curing kinetics of VE resin, which is not fast enough at the first stage of the curing process to avoid that expansion.

Thus, analysing the results of this study, it can be stated that if the UV curing kinetics of VE is improved in order to become faster, the content of voids would be reduced and consequently, both flexural properties and *SEA* values would be improved.

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