

# COMPRESSION MOLDING OF PULTRUDED CARBON REINFORCED THERMOPLASTIC COMPOSITES

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**Keywords:** carbon fiber; thermoplastic towpreg; pultrusion; compression molding; composite

## ABSTRACT

Historically, thermoset resins have dominated the composite industry but they start to be replaced by thermoplastics. In this study two different thermoplastic matrix carbon reinforced pre-impregnated materials were used, one produced in our laboratories (towpreg) and another obtained from co-extrusion process (PCT). Carbon fibre and two different thermoplastic matrices (polypropylene and PRIMOSPIRE<sup>®</sup>) were selected for the production of the pre-impregnated materials.

Heated compression moulding and pultrusion were the two manufacturing technologies used to obtain composite plates and profiles for study. The optimization of those processes was made by studying the influence of the most relevant processing parameters in the final properties of the produced carbon fibres thermoplastic matrix pre-impregnated materials and composites.

The composite relevant mechanical properties were determined and the final composites were submitted to Dynamic Mechanical Analysis (DMA), Scanning Electron Microscope (SEM), optical microscopy and calcination tests.

The determination of the fiber volume fraction of all studied composite was obtained comparing the results of thermogravimetric analysis (TGA), SEM and calcination tests.

## 1. Introduction

Composites with thermoplastic matrices offer increased fracture toughness, higher damage tolerance, short processing cycle times and excellent environmental stability. They are recyclable, post-formable and can be joined by welding. The use of long/continuous fibre reinforced thermoplastic matrix composites involves, however, great technological and scientific challenges since thermoplastics present much higher viscosity than thermosettings, which makes much difficult and complex the impregnation of reinforcements and consolidation tasks [1-4].

Today, two major technologies are being used to allow wet reinforcing fibres with thermoplastic polymers [5]: i) the direct melting of the polymer and, ii) the intimate fibre/matrix contact prior to final composite fabrication. Continuous fibre reinforced thermoplastic matrix pre-impregnated tapes (PCT's) are, for example, produced by direct melting processes. Alternatively, intimate contact processes allow producing cheap and promising pre-impregnated materials, such as, commingled fibres and powder coated towpregs.

Pultrusion was the selected manufacturing method for processing all these pre-impregnated materials into composite parts. It is a versatile continuous high speed production technology, allowing the production of fibre reinforced complex profiles. The optimization of the pultrusion process was

made by studying the influence of the most relevant processing parameters in the final properties of the produced pre-impregnated materials and composites [5-8].

The produced profiles were then processed by heated compression moulding into composite plates that can be used for manufacturing complex shapes.

The final composite parts were also submitted to interlaminar and flexural tests, as well as calcination, optical microscopy and SEM. The experimental results were compared with theoretical ones that can be predicted by using the ROM (Rule Of Mixtures).

The determination of the fibre volume fraction of a composite with a high melting temperature thermoplastic polymer used as matrix was obtained comparing the results of thermogravimetric analysis (TGA) with the calcination tests.

## **2. Experimental**

### **2.1. Raw Materials**

The following raw materials were used to produce CF/PP pre-impregnated materials for this work: i) a PP powder ICORENE 9184B P<sup>®</sup> and carbon fibre roving M30 SC<sup>®</sup> from the ICO Polymers and TORAY, respectively, were used to produce the CF/PP towpregs, ii) PP powder Moplen RP348U<sup>®</sup> from Basell and the carbon fibre roving already mentioned were used to manufacture the CF/PP PCT tapes. On other hand, composite parts for highly demanding advanced markets were processed from towpregs manufactured by using a highly aromatic amorphous thermoplastic polymer in powder form, the PRIMOSPIRE<sup>®</sup> PR 120 from Solvay Advanced Polymers, and 760 Tex M30SC carbon fibre tows TORAY.

### **2.2 Production of Thermoplastic Matrix Pre-Impregnated Products**

A dry powder coating equipment was used to produce fibre reinforced towpregs [7-8].

The optimal condition obtained from Taguchi method application led to the following operating parameters selection for the production of CF/PP towpregs: heating oven temperature and consolidation oven temperatures of 700 °C and 400°C respectively, and a linear pulling speed of 6 m/min. Using this optimal operative condition, the amount of polymer should increase up to 45.6%. However, it was found that the average polymer content in continuous towpreg production was only 40.0%.

In order to produce CF/PRIMOSPIRE<sup>®</sup> towpregs, the powder coating equipment was operated at the following processing conditions: 700 °C for the heating oven temperature, 525 °C for the consolidation oven temperature and a linear pull speed of 6 m/min. Using those conditions towpregs with a polymer mass content of approx. 40% were produced.

The pre-consolidated tapes (PCT's) used in this work were produced in a cross-head extrusion equipment from our own laboratories [7-8].

### **2.3 Pultrusion of pre-impregnated materials**

The towpregs and PCT's were processed into composite bar profiles using the laboratorial pultrusion line [7-8].

To produce composite profiles, the pre-impregnated materials are guided into the pre-heating furnace to be heated up to the required temperature. Then, they enter in the pultrusion heated die to be heated and consolidated to the required size and, after cooled down in the cooling die to solidify. In this work, it was designed and manufactured a die to allow producing a 20×2 mm<sup>2</sup> bar-shaped profile.

Those profiles were manufactured from different pre-impregnated materials, using operating conditions in order to optimize the processing.

#### **2.3.1 Towpreg processing**

CF/PP towpregs were manufactured by pultrusion into composite bar profiles using the most relevant operating conditions. The Taguchi's/DOE method was applied in order to optimize the

processing parameters. The found optimal operating conditions that maximize mechanical properties were: furnace and heated die oven temperatures of 160 °C and 260°C respectively, and a linear pulling speed of 0.2 m/min.

The CF/PRIMOSPIRE<sup>®</sup> pultruded bars were produced in this work with the following operational conditions: i) furnace temperature (380 - 400 °C); ii) heating die temperature (420 - 475 °C); iii) linear pull-speed of 0.2 m/min.

### 2.3.2 Pre-consolidate tapes (PCT's) processing

PCT's were processed into rectangular 20×2 (mm<sup>2</sup>) bar using the already mentioned pultrusion equipment being operating conditions shown in Table 1.

Raw-material	Heated die temperature (°C)	Cooled die temperature (°C)	Furnace temperature (°C)	Pulling speed (m/min)
CF/PP PCT	230	50	160	0.2

Table 1. Pultrusion processing parameters for PCT's

### 2.4 Heated compression moulding of pultrusion profiles

The different CF/PP and CF/PRIMOSPIRE thermoplastic fiber reinforced pre-impregnated profiles produced by pultrusion were also processed into rectangular 200×200×2 mm<sup>3</sup> composite plates.

The pultruded bars were introduced in a 200 × 200 (mm) cavity placed between the heated platen of a 200 kN GISLÓTICA S. A. heated plate press. For the production of CF/PP plates, after a 10 min delay at press platen temperature, the press was closed until reaching the maximum compression force of 200 kN. One minute after reaching the maximum force, the press platens were cooled down maintaining constant the press closing force. When the temperature of 30°C was reached, the press platen was opened and the final composite plate finally removed from the mold. In the case of CF/PRIMOSPIRE plates, the mould was closed and heated until 315 °C. Then pressure was applied during 10 minutes and after the cooling cycle was initiated. The mould was opened at 30 °C. Heated compression moulding cycle variables are summarized in table 2.

Variable	Units	Values	
		CF/PP Towpregs and PCT	CF/PRIMOSPIRE <sup>®</sup> towpregs
Platen temperature	°C	250	315
Compression force	kN	200	10
Compression time	min	1	10
Final cooling temperature (at press opening)	°C	30	30

Table 2. Conditions used to process composites by compression moulding.

## 2.4 Testing

### 2.4.1 Microscopy analysis

To determine the impregnation quality and to evaluate the fibre distribution and fibre/matrix adhesion of the thermoplastic composites, their cross-sections were studied under optical microscopy (CF/PP) and under by SEM-scanning electron microscopy (CF/PRIMOSPIRE<sup>®</sup>).

### 2.4.2 Mechanical testing

Bar samples were submitted to flexural and interlaminar testing according to the ISO standards 14125 and 14130, respectively. The mechanical properties were compared to the theoretical ones predicted by using the Rule of Mixtures (ROM).

Three-point flexural tests were also conducted on  $100 \times 20 \times 2 \text{ mm}^3$  using 100 kN universal testing machine and a distance between supports of 80 mm, according to ISO 14125, at a crosshead speed of 1 mm/min.

Samples with dimensions of  $20 \times 20 \times 2 \text{ mm}^3$ , cut from composites processed from each pre-impregnated raw material, were submitted to interlaminar shear tests. The tests were conducted in a 50 kN universal testing machine by using an initial pre-load of 1 N at the crosshead speed of 1 mm/min and a 10 mm span between supports.

### 2.4.3 TGA tests

The determination of mass fractions of composites made from carbon fibre and polymer with high temperature resistance like PRIMOSPIRE<sup>®</sup> is difficult and usually assessed by image processing techniques. Standard calcination tests are the mostly used with glass-reinforced plastics composites.

In this work, we used calcination tests for the evaluation of fibre mass fraction on carbon fibre and PRIMOSPIRE<sup>®</sup> composites, but since there's only a partial degradation of reinforcement and matrix, this method couldn't be applied directly as in the case of glass-reinforced plastics composites.

In order to obtain carbon fibre and PRIMOSPIRE<sup>®</sup> temperature degradation behaviour TGA test were carried out using a thermo-gravimetric balance TA Q500 under different atmospheres (inert, oxidative and air).

In tests made under inert ( $\text{N}_2$ ), oxidative ( $\text{O}_2$ ) and air atmospheres, carbon fibres and polymer samples were heated from 30/40/60°C until 900°C using a 10°C/min constant heating rate.

Being air the atmosphere in the muffle furnace for calcination, TGA tests were also carried out under the same condition.

Polypropylene polymer matrix was also submitted to TGA tests with air as atmosphere to evaluate its degradation behaviour which is a relevant parameter to the determination of the processing conditions of composites that uses this polymer.

To avoid weight loss due to air flow, this was not used in all TGA tests performed with air atmosphere.

### 2.4.4 Calcination testing

Calcination tests were carried on the CF/PRIMOSPIRE<sup>®</sup> composites using results obtained from the TGA tests since this polymer matrix exhibits high temperature resistance and so is not fully eliminated on conventional calcination tests.

Initially, matrix (PRIMOSPIRE<sup>®</sup>) and reinforcement (CF) mass loss curves as a function of time resulting from the TGA tests were evaluated. This analysis concluded that the temperature 700 °C was a good compromise between the end of PRIMOSPIRE<sup>®</sup> high degradation rate and the beginning of significant carbon fibre mass loss.

In order to simulate TGA behaviour calcination tests were performed on the constituents of the studied composite using the same thermal cycle (10° C/min) until the temperature of 700 °C was reached. The initial mass of the samples, placed in a ceramic crucible, was approximately 2 g in accordance with the conventional standard.

CF/PP composites fibre mass content was determined by using calcination tests according to the EN ISO 1172. Composite samples, weighting approximately 2 g, were submitted to calcination inside a crucible in a muffle furnace during 10 min at 625°C.

### 2.4.5 DMA tests

A Dynamic Mechanical Analysis Triton TRITEC 2000 was used to obtain the elasticity modulus dependence on temperature of the CF/PP PCT. The specimen, with  $40 \times 5 \times 1 \text{ mm}^3$ , was used in the three point bending configuration having a span of 30 mm. Temperature was increased at a rate of 5 °C per minute, from ambient until 155 °C.

### 3. Results and Discussion

The cross-sections of the pultruded composites were studied under optical Microscopy and SEM. As can be seen from Figures 1 and 2, all CF/PP and CF/PRIMOSPIRE<sup>®</sup> composite profiles from towpregs and PCT's have a reasonable distribution of the reinforcing fibres over the cross-sections. However, large differences in impregnation quality occur between the different samples that are likely to be related, directly, to the impregnation state of pre-impregnated materials used in pultrusion. It may be seen that the impregnation quality of the PCT composite samples is good, presenting almost all fibres completely surrounded ('wet-out') by the polymer. Only a few large dry spots were observed. This is most likely due to the good degree of impregnation already achieved in the PCT raw-material tape prior to the pultrusion step. In the case of PCT tape based composites, its outside layers exhibited richer polymer regions.

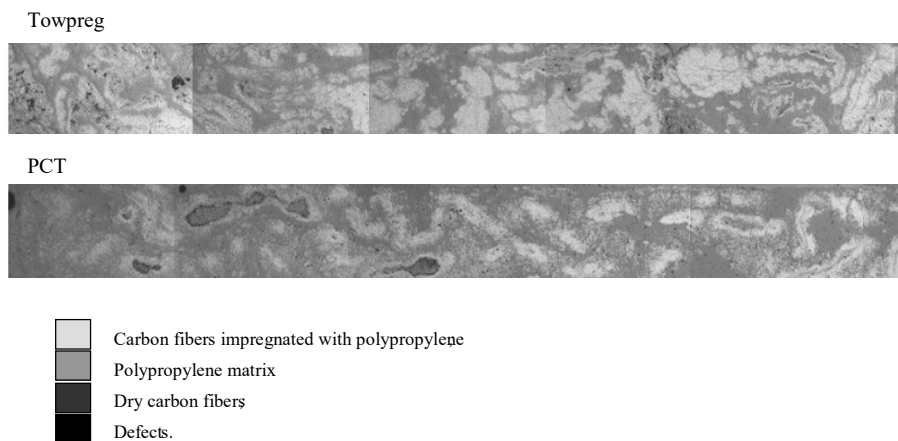


Figure 1. Optical micrographs of pultruded profiles cross-section (magnification of 8.75×)

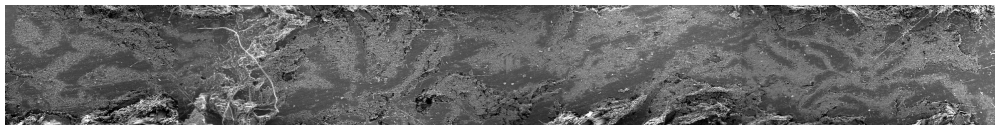


Figure 2. SEM image of CF/PRIMOSPIRE<sup>®</sup> pultruded profile cross-section sample (magnification of 40×)

The results obtained for carbon fibre and PRIMOSPIRE<sup>®</sup> TGA tests under air atmosphere (Figure 3) show that the degradation behaviour is between the one found for inert and oxidative atmospheres.

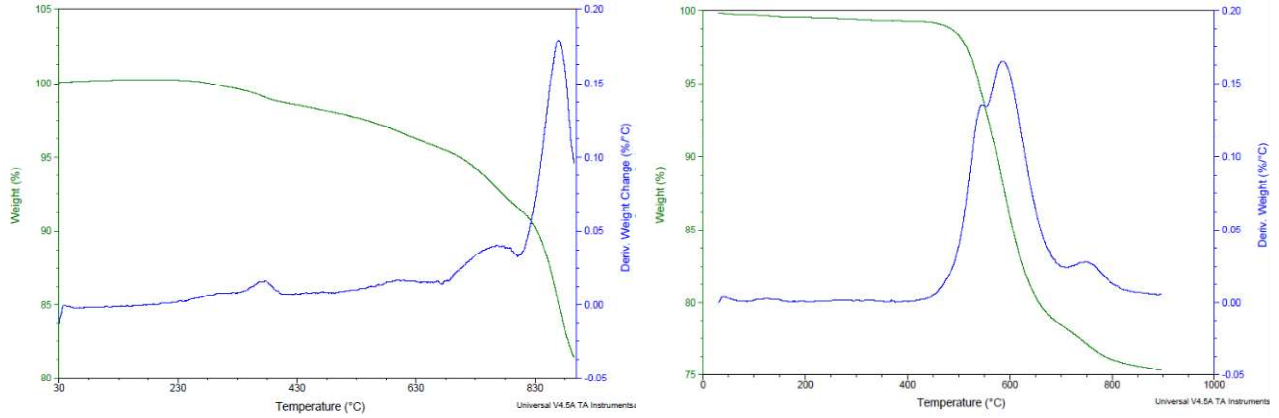


Figure 3. TGA results carried out on carbon fibres (left) and PRIMOSPIRE® (right) under air atmosphere

The results obtained in the calcination were similar to those of the TGA tests. The calcinations of PRIMOSPIRE® and carbon fibres at 700 °C allowed establishing 25.9% and 7.2% as average mass losses, respectively, and as a consequence, the proportion of the remaining mass was 74.1% (*wf*) and 92.8% (*wp*) In TGA tests, the average mass loss of carbon fibre and PRIMOSPIRE® was 21.55% and 5.97%, respectively. Then, it was applied to the composite the same calcination parameters that were used for the testing of their constitutive materials.

After calcining the composite sample, the carbon fibre mass fraction, *wfc*, was obtained by:

$$wfc = 1 - \frac{mc_f - wf \cdot mc_i}{mc_i \cdot (wp - wf)} \quad (1)$$

where *mc<sub>i</sub>* and *mc<sub>f</sub>* are the measured composite sample initial and final weights, respectively. Also, *wf* and *wp* are the carbon fibre and PRIMOSPIRE® remaining mass fractions, respectively.

Furthermore, by knowing the fibre and polymer densities,  $\rho_f$  and  $\rho_p$ , respectively, the fibre mass fraction (*wfc*) may be converted in fibre volume fraction (*vf*) by:

$$vf = \frac{\frac{wfc}{\rho_f}}{\frac{wfc}{\rho_f} + \frac{(1 - wfc)}{\rho_p}} \quad (2)$$

The composite calcination test obtained results allow determining the fibre mass fraction as 54.1% corresponding to a fibre volume fraction of 45.2%.

Those results were confirmed using the image processing software ImageJ. Using this software, the obtained fibre volume fraction was 44.7%.

Concerning polypropylene TGA tests, it was found that the degradation temperature was about 400 °C.

Tables 3 and 4 summarize all experimentally results obtained from the CF/PP and CF/PRIMOSPIRE® composites processed by pultrusion and heated compression moulding from the pre-impregnated products under study. To better evaluate and compare the mechanical properties obtained on the composites processed from the different pre-impregnated products studied. The tables also present theoretical expected values and relative values of specific properties.

As can be seen from Table 3 the experimental moduli obtained from de CF/PP towpreg composites are in good agreement with the predicted theoretical ones.

The heated compression moulding results show an increasing of the mechanical strength properties when compared to the ones obtained by pultrusion, possibly due to a better consolidation. Also, the elastic modulus exhibits no significant variations.

Still analysing Table 3, one can conclude that composites processed from the CF/PP PCT's demonstrated to have better flexural and interlaminar shear strengths than those produced from CF/PP towpregs.

Concerning the interlaminar shear tests in the pultrusion bars, the CF/PRIMOSPIRE<sup>®</sup> composites have shown a much higher value than CF/PP probably due to the better mechanical properties that the PRIMOSPIRE<sup>®</sup> matrix exhibits. As it may be seen and expected, the CF/PRIMOSPIRE<sup>®</sup> towpregs required the use of much higher temperatures than the CF/PP ones in pre-heating furnace and pressurization/consolidation die. Due to such higher temperatures, tests still continue being done to optimise the operational conditions and, consequently, the obtained mechanical properties.

Finally, it may be noted that any of composites made from pre-impregnated materials under study reached failure in the interlaminar shear tests. This fact reveals the high degree of ductility exhibited by these materials which may be relevant for many applications. Thus, the interlaminar shear strength results shown in Tables 3 and 4 correspond to maximum force applied in the test.

Test Type	Property		Pultrusion		Compression	
			CF/PP Towpreg	CF/PP PCT	CF/PP Towpreg	CF/PP PCT
Flexural	Flexure Modulus (GPa)	Experimental	90.1±0.4	37.7±2.2	93.3±5.5	42.9±3.2
		Theoretical	98.9	62.7	99.3	79.0
	Flexure Modulus / Fibre volume fraction (GPa)		178.1±0.8	118.2±6.9	183.7±10.8	106.2±7.9
	Flexure Strength (MPa)	Experimental	241.2±1.6	158.7±4.2	267.4±21.4	226.4±20.0
		Flexure Strength / Fibre volume fraction (MPa)		476.7±3.2	497.5±13.2	526.4±42.1
Inter-laminar Shear	Interlaminar Shear Strength (MPa)		12.3±0.3	14.0±0.2	13.3±0.2	15.9±0.4
Fibre volume fraction (%)			50.6	31.9	50.8	40.4

Table 3. CF/PP composite mechanical test results

Test Type	Property	CF/PRIMOSPIRE <sup>®</sup> towpreg	
		Pultrusion	Compression
Flexural	Flexure Modulus (GPa)	56.1±2.9	39.8±3.3
	Flexure Strength (MPa)	253.6±16.1	142.0±9.4
Inter-laminar Shear	Interlaminar Shear Strength (MPa)	25.4±2.1	-
Calcination	Fibre volume fraction (%)	45.2±5.3	43.8±0.1

Table 4. Test results on the processed CF/PRIMOSPIRE<sup>®</sup> composites

As can be seen in table 4, the flexural properties of the compression moulding plates are considerable lower than those obtained in the pultruded profiles. This is probably explained by the use of a mixture of different manufacturing conditions profiles and to a non-optimized heated compression moulding processing cycle variables.

The theoretical values of moduli, E, using the pultrusion results, were directly obtained from the rule of mixtures. In the case of CF/PRIMOSPIRE<sup>®</sup> composites, it was possible to estimate the fibre volume fraction as approximately 45%. This result is in good agreement whit the one obtained from calcination test (45.2).

As can be seen in figure 4, the elastic modulus at room temperature is in accordance with the one obtained from flexural tests. Also, as it would be expected, the elastic modulus decreases gradually with temperature.

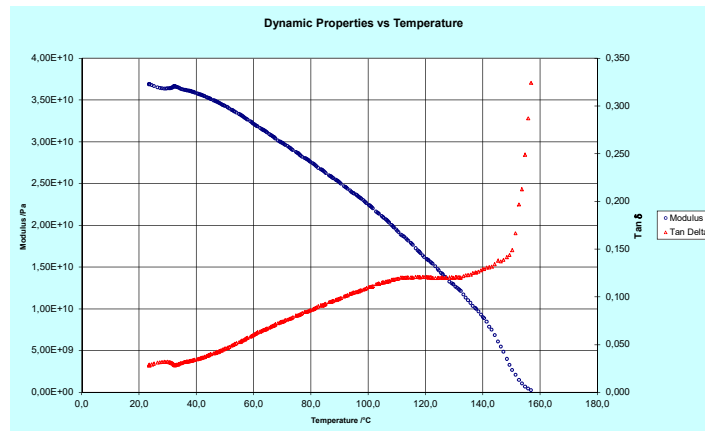


Figure 4. DMA test results for CF/PP PCT.

#### 4. Conclusions

The tests made using proprietary pultrusion equipment already allow to conclude that it is possible to produce, in good conditions, profiles from almost all available thermoplastic matrix pre-impregnated raw-materials using pull speeds of 0.3 m/min.

In particular, for CF/PP pultruded profiles, very good agreement was found between the experimental moduli values of all composites produced and the theoretical ones.

The compression moulding results obtained in CF/PRIMOSPIRE composites need to be further studied in order to achieve better mechanical properties. In the case of CF/PP composites produced by heated compression moulding, they reveal good mechanical properties and can be applied for the manufacture of complex shapes.

More research must be done in order to increase the processing speeds of CF/PP and CF/PRIMOSPIRE<sup>®</sup> towpregs as well as PCT's and to improve the impregnation, uniformity and dispersion of raw-materials in the composites.

CF/PRIMOSPIRE<sup>®</sup> composites obtained by pultrusion showed a higher value for the interlaminar strength than all other ones. Further tests should be done to optimise the operational conditions and to improve the obtained composite mechanical properties.

The calcination tests based on the results obtained from TGA tests reveal to be a very interesting method to experimentally determine composite mass fractions in the case of temperature resistant materials used as matrix and reinforcement.

#### References

- [1] Bechtold G., Wiedmer S., Friedrich K. "Pultrusion of Thermoplastic Composites – New Developments and Modelling Studies", *Journal of Thermoplastic Composite Materials*, Vol. 15, pp. 443-465, 2002.
- [2] Wiedmer. S, Manolesos. M., An Experimental Study of the Pultrusion of Carbon Fiber-Plyamide 12 Yarn, *Journal of the Thermoplastic Composite Materials*, **19**, pp. 97-112, 2006.
- [3] Sana Koubaa, Steven Le Corre and Christian Burtin, Thermoplastic pultrusion process: Modeling and optimal conditions for fibers impregnation, *Journal of Reinforced Plastics and Composites*; SEP, **32** (17), pp. 1285-1294, 2013.
- [4] Gibson, A. G., Manson, J. A. "Impregnation technology for thermoplastic matrix composites", *Comp. Manufacturing*, Vol 3 (4), pp. 223-233, 1992.
- [5] Ramani, K., Borgaonkar, H., Hoyle, C. "Experiments on compression moulding and pultrusion of thermoplastic powder impregnated towpregs", *Composites Manufacturing*, 6, Elsevier, pp. 35-43, 1995.
- [6] Sala, G., Cutolo, D. "The pultrusion of powder-impregnated thermoplastic composites", *Composites Part A*, 28A, Elsevier, pp. 637-646, 1997.
- [7] P. J. Novo, J. P. Nunes, J F. Silva and A. T. Marques., Processing of carbon reinforced thermoplastic composites, *Proceedings of 21<sup>th</sup> International Conference on Composite Materials, ICCM21*, Xi'an, China, 20-25th August 2017.
- [8] P. J. Novo, J F. Silva, J. P. Nunes and A. T. Marques. "Pultrusion of fibre reinforced thermoplastic pre-impregnated materials". *Composites Part B: Engineering*, 89:328-339, 2016.