

ADVANCES IN THERMOPLASTIC PULTRUDED COMPOSITES

P. J. Novo¹, J. F. Silva², J. P. Nunes³ and A. T. Marques⁴

¹Dep. of Mechanical Engineering, ESTG, Polytechnic Institute of Leiria
Campus 2, Morro do Lena – Alto Vieiro, Apartado 4163, 2411-901 Leiria, Portugal
Email: paulo.novo@ipleiria.pt, web page: <http://www.ipleiria.pt>

²Department of Mechanical Engineering, ISEP
R. Dr. Antonio Bernardino de Almeida 431, 4200-072 Porto, Portugal
Email: jfs@isep.ipp.pt, web page: <http://www.isep.ipp.pt>

³Institute of Polymers and Composites/I3N, Minho University
Campus de Azurem, 4800-058 Guimaraes, Portugal
Email: jpn@dep.uminho.pt, web page: <http://www.uminho.pt>

⁴DEMEGI, INEGI, FEUP
R. Dr. Roberto Frias, s/n, 4200-465 Porto, Portugal
Email: marques@fe.up.pt, web page: <http://www.fe.up.pt>

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ABSTRACT

Pultrusion is a versatile continuous high speed production technology allowing the production of fibre reinforced complex profiles. Thermosetting resins are normally used as matrices in the production of structural constant cross section profiles.

Although only recently thermoplastic matrices have been used in long and continuous fibre reinforced composites replacing with success thermosetting matrices, the number of their applications is increasing due to their better ecological and mechanical performance. Composites with thermoplastic matrices offers increased fracture toughness, higher impact tolerance, short processing cycle time 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]

In this work continuous fibres reinforced thermoplastic matrix towpregs were produced using equipment developed by the Institute for Polymers and Composites (IPC). The processing of the towpregs was made by pultrusion, in a developed prototype equipment existing in the Engineering School of the Polytechnic Institute of Porto (ISEP).

Different thermoplastic matrices and fibres raw-materials were used in this study to manufacture pultruded composites for commercial applications (glass and carbon fibre/ polypropylene) and for advanced markets (carbon fibre/Primospire®).

To improve the temperature distribution profile in heating die, different modifications were performed. In order to optimize both processes, towpregs production and pultruded composites profiles were analysed to determine the influence of the most relevant processing parameters in the final properties. The final pultruded composite profiles were submitted to mechanical tests to obtain the relevant properties.

1 INTRODUCTION

During the last decades, composites have successfully replaced traditional materials in many engineering applications due to its excellent properties, mainly their excellent specific mechanical properties [1, 2].

Pultrusion is a continuous manufacturing process used to shape polymeric composite materials into parts with constant cross section. The reinforcement fibres in the form of continuous strands or mats are pulled through a guide plate and impregnated passing by a thermosetting resin bath.

So far, almost all applications of pultrusion manufacturing technologies use thermosetting resins due to inherent difficulties associated with the use of thermoplastic matrices in this process. However, with recent developments, the use of preforms to facilitate impregnation, such as pre-consolidated tapes, commingled yarns and towpregs, allowed the thermoplastic pultrusion to gain a great interest [3].

Composites with thermoplastic matrices offers increased fracture toughness, higher impact tolerance, short processing cycle time 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 [2,4-9].

Today, two major technologies are being used to allow wet reinforcing fibres with thermoplastic polymers [6-9]: i) the direct melting of the polymer and, ii) the intimate fiber/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 (Figure 1).

Sometimes, thermoplastic compatibilizers were added to the matrices to improve their adhesion and facilitate impregnation to reinforcements [10].

Different raw-materials were used in the production of thermoplastic matrix pre-impregnated materials: those to be used in parts for highly demanding markets were based on carbon fibres and Primospire[®] and those for more commercial composites on carbon or glass fibres and polypropylene.

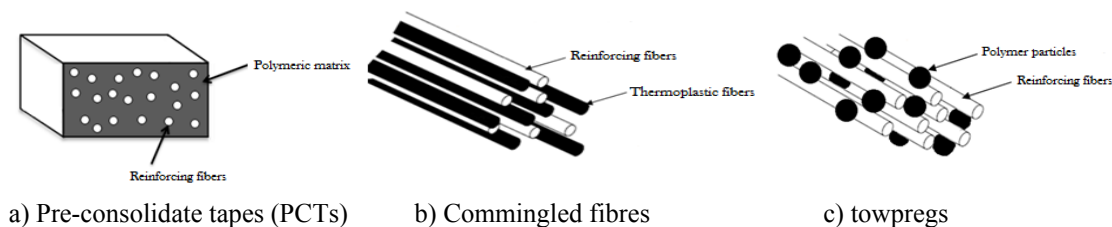


Figure 1. Pre-impregnated products under study

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[®] and carbon fibre roving M30 SC[®] from the ICO Polymers and TORAY, respectively, were used to produce the CF/PP towpregs, ii) PP powder Moplen RP348U[®] 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[®] PR 120 from Solvay Advanced Polymers, and 760 Tex M30SC carbon fibre tows TORAY.

For the GF/PP towpregs, a 2400 Tex type E fibre rovings from Owens Corning and Icorene[®] 9184B P polypropylene from ICO Polymers France were used. Also, the GF/PP PCT tapes were manufactured

with glass fibres (TufRov 4599) from PPG Industries and a polypropylene matrix (Moplen RP348U[®]) from Basell.

Commercial commingled GF/PP fibres TWINTEX[®] R PP 60 B 1870 FU from Owens Corning were also used in the production of pultrusion thermoplastic composite profiles, as reference of a current commercially available pre-impregnated product.

Some batches of CF/PP and GF/PP towpregs were also produced using PP powder (ICORENE 9184B P[®]) blended with 1% in mass content of maleic anhydride S 47 29608 707[®] from Merck Schuchardt OHG, in order to assess the possible enhancement of fibre/matrix adhesion [9-12].

Tables 1 and 2 summarise relevant properties of the polypropylene, glass and carbon fibres used in present work to produce pre-impregnated raw materials (towpregs and PCT's). Table 3 shows the manufacturer datasheets properties of TWINTEX[®].

Table 1. Properties of Towpregs and PCT PP raw-materials

Property	PP powder (ICORENE 9184B P [®])		Primospire [®]		PP granules (Moplen RP348U [®])
	Manufacturer datasheet	Experimental	Manufacturer datasheet	Experimental	Manufacturer datasheet
Specific gravity (Mg/m ³)	0.91	0.91	1.21	-	0.90
Tensile strength (MPa)	Yield Strength 30	Yield Strength 19	207	104	Yield Strength 30
Young Modulus (GPa)	1.3	0.98	8.3	8.0	1.1
Poisson's ratio	-	0.21	-	-	-
Average powder particle size (µm)	440	163	-	139	-
Glass transition temperature (T _g)	Typical value 0-20	-	158	156	Typical value 0-20
Melting temperature (T _m)	Typical value 170	166	-	-	Typical value 170

Table 2. Properties of Towpregs and PCT fibres raw-materials

Property	Glass fibre (305E-TYPE 30 [®])		(TufRov 4599 [®])	Carbon fibre (TORAY M30 SC [®])	
	Manufacturer datasheet	Experimental	Manufacturer datasheet	Manufacturer datasheet	Experimental
Linear density (Tex)	2400	-	2400	760	-
Specific gravity (Mg/m ³)	2.65	-	2.54-2.6	1.73	-
Tensile strength (MPa)	3500	1657	1900-2400	5490	2731
Young Modulus (GPa)	76	62.5	69-76	294	194.5
Average fibre diameter	17	13.7	17	5	7.37

Table 3. TWINTEX[®] R PP 60 B 1870 FU from Owens Corning

Property	Values
Linear density (Tex)	1870
Tensile strength (MPa)	760
Young Modulus (GPa)	29.5
Fibre mass content (%)	60

2.2 Production of Thermoplastic Matrix Pre-Impregnated Products

The dry powder coating equipment used to produce fibre reinforced towpregs is schematically depicted in Figure 2 [13-15].

The pre-consolidated tapes (PCT's) used in this work were produced in a cross-head extrusion equipment (see Figure 3) from our own laboratories [14].

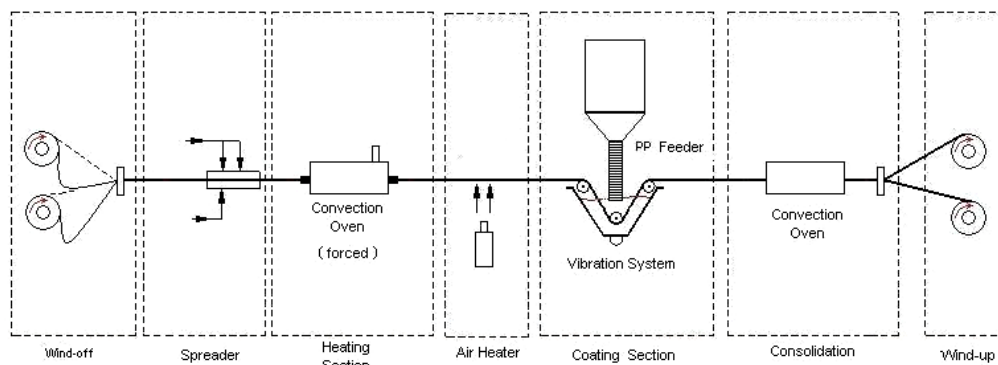


Figure 2. Powder coating line setup.

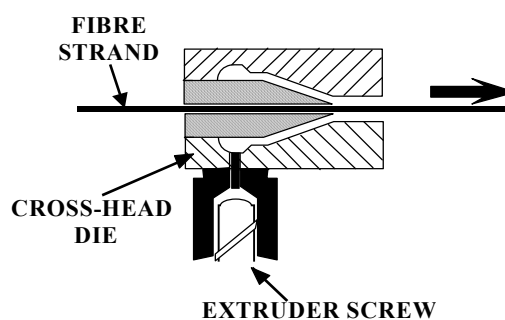


Figure 3. Cross-head extrusion die

2.2.1. CF/PP, CF/Primospire[®] and GF/PP towpregs production

In order to optimize the production of CF/PP powder coated towpregs, different processing variables combinations were experimented and the number of trials optimized using the Taguchi approach. The studied operational parameters were:

- heating oven temperature (600, 650 and 700 °C); consolidation oven temperature (350, 400 and 450 °C); linear pull speed (4, 6 and 8 m/min).

The optimal condition obtained led to the following operating parameters selection: heating oven temperature and consolidation oven temperatures of 700 °C and 400°C respectively, and a linear pulling speed of 4 m/min. However, the operative condition that was chosen as optimal had a line pull speed of 6 m/min allowing a high rate of production, lower processing problems and sufficiently levels of polymer mass content (40%, enough for the use of towpregs in the pultrusion process).

To try maximizing the polymer powder content in the GF/PP towpregs the following processing conditions were varied within the next ranges: i) convective oven temperature (°C): 650 - 700; ii) Consolidation furnace temperature (°C): 350 – 450; iii) Coating line pulling speed (m/min): 4 – 6.

From the polymer mass fractions obtained in produced towpreg strips it was possible to establish as optimal the following operating parameters: convective and consolidation oven temperatures of 700 °C and 400°C respectively, and a linear pulling speed of 6 m/min. In such operational conditions the GF/PP towpregs were continuously produced with polymer mass content of 30.7 %.

In order to produce CF/Primospire towpregs, the powder coating equipment was operated at different following woven temperatures and fibre linear pull speeds:

- heating oven temperature (700 °C); consolidation oven temperature (500 - 550 °C); linear pull speed (4 and 6 m/min). From such work the best values of the operational variables, which allow simultaneously producing towpregs in good and stable circumstances and having the maximum polymer powder content were:

- heating oven temperature - 700 °C; consolidation oven temperature - 525 °C and linear pull speed - 6 m/min. Using those conditions towpregs with a polymer mass content of approx. 40% were produced.

2.3 Pultrusion of pre-impregnated materials

The towpregs, PCT's and commingled fibres were processed into composite bar profiles using the laboratorial pultrusion line, Figure 4 [15, 16].

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 mm² bar-shaped profile.

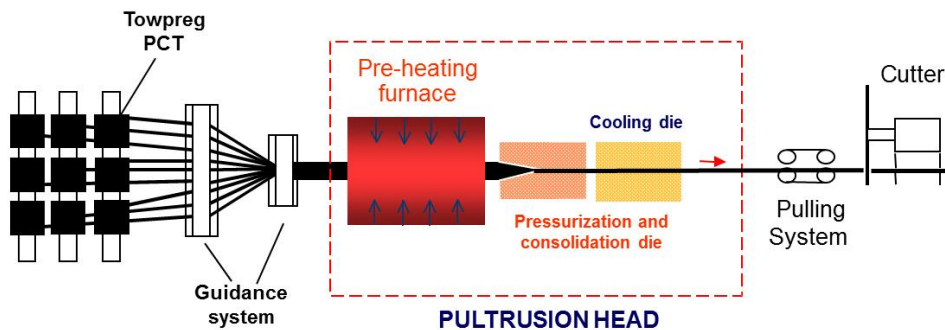


Figure 4. Schematic diagram of the pultrusion line

Those profiles were manufactured from different pre-impregnated materials, using operating conditions in order to optimize the processing. The heating elements were conveniently placed in the die improving the temperature distribution profile, as can be seen in Figure 5.

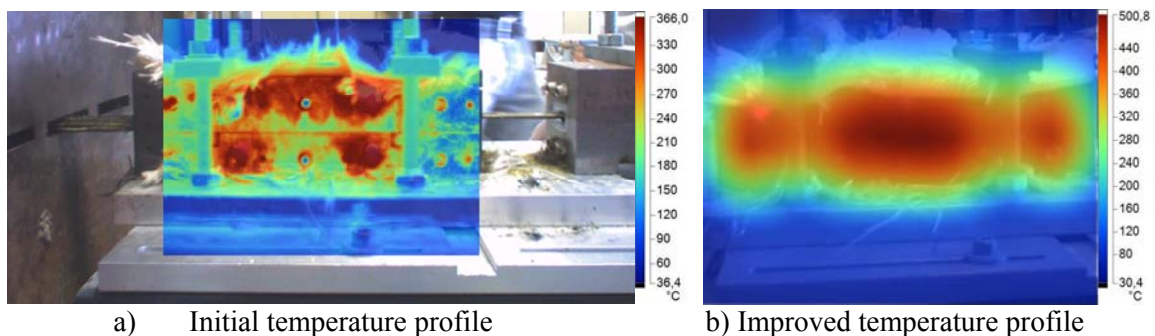


Figure 5. Heated die temperatures distribution profiles

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, maintaining the cooling die at 25 °C, in order to optimize the processing parameters:

i) furnace temperature (160 or 180 °C); ii) heating die temperature (240 or 260 °C); iii) linear pull-speed (0.2 or 0.3 m/min).

Results have shown that was not possible to produce, in steady, conditions pultruded profiles from towpregs at pultrusion speeds and consolidation die temperatures higher than 0.4 m/min and 260 °C,

respectively. By using higher values of these two parameters, the process became unsteady, mainly due to reflux and accumulation of the thermoplastic polymer at the entrances of the consolidation and cooling dies.

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 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.

To determine the best processing window for GF/PP towpregs, the main processing conditions were varied, maintaining the cooling die at 25 °C: i) furnace temperature (°C): 170 – 180; ii) heated die temperature (°C): 240 – 300; iii) linear pulling speed (m/min): 0.2 - 0.4.

Results have shown that was not possible to produce, in steady conditions, profiles from towpregs at pultrusion speeds and heated die temperatures higher than 0.3 m/min and 280 °C, respectively. By using higher values the process became unsteady as it was already found for CF/PP towpregs processing. Problems also occurred for temperatures below 270° C in the heated die.

It was concluded to use as optimal pultrusion operating window for GF/PP towpregs the following one: i) furnace temperature (°C): 170 – 180; ii) heated die temperature (°C): 280; iii) cooling die temperature (°C): 25; iv) linear pulling speed (m/min): 0.2 - 0.3.

2.3.2 Pre-consolidate tapes(PCT's) and Twintex[®] processing

PCT's and Twintex[®] were processed into rectangular 20×2 (mm²) bar using the already mentioned pultrusion equipment being operating conditions shown in Table 4.

Table 4. Pultrusion processing parameters for PCT's and Twintex[®]

Raw-material	Heated die temperature (°C)	Cooled die temperature (°C)	Furnace temperature (°C)	Pulling speed (m/min)
CF/PP PCT	230		160	
GF/PP PCT	230	50	170	0.2
Twintex [®]	300		170	

2.4 Testing

Bar samples were submitted to flexural, tensile and interlaminar testing according to the ISO standards 14125, 527 and 14130, respectively.

The mechanical properties were compared to the theoretical ones predicted by using the Rule of Mixtures (ROM).

Tensile tests were conducted, according to ISO 527, in a 100 kN universal testing machine at the crosshead speed of 2 mm/min using 180×20×2 mm³ rectangular samples.

The tensile modulus was determined from the slope of the initial linear portion of the experimental stress/strain curve. A SG Shimadzu[®] 50 mm length strain-gauge was used up to 0.3% strain, for accurate determination of the tensile modulus.

Regarding the determination of tensile strength, it was not possible to proceed with the test until specimen failure due to grip slippage. Hence, new specimen geometry was designed and tested with good results (Figure 6).

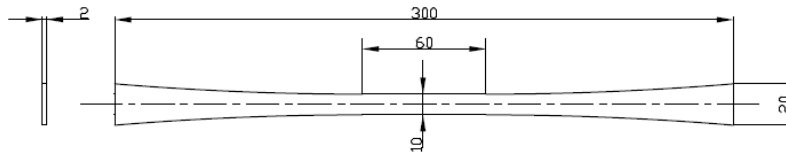


Figure 6. Geometry of the tensile test specimens

Three-point flexural tests were also conducted on five $100 \times 20 \times 2$ (mm³) composite specimens, 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 $20 \times 20 \times 2$ (mm³), cut from composites processed from each pre-impregnated raw material, were submitted to interlaminar shear tests according to ISO 14130. 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.

Carbon and glass fibre composites 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.

3 Results and Discussion

Tables 5, 6 and 7 summarize all experimentally results obtained from the CF/PP, CF/Primospire® and GF/PP composites processed by pultrusion 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, tables also present theoretical expected values and relative values of specific properties.

As can be seen from Tables 5 and 6, the experimental moduli obtained from the CF/PP and GF/PP composites are in good agreement with the predicted theoretical ones. Some experimental values are even higher than the theoretical expected ones. This can be explained considering that the volume fraction content of some samples can be higher than the determined by the calcination tests.

Using the proposed new geometry (Figure 6) for the tensile test specimens, it was possible to reach breaking loads and therefore determine their tensile strengths.

Analysing Table 5, 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, the CF/Primospire composites shown a much higher value than CF/PP probably due to the better mechanical properties that the Primospire matrix exhibits. As it may be seen and expected, the CF/Primospire® 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.

From Table 6, it is possible to conclude that commingled fibres (TWINTEX®) presented, in general, better properties and had also shown to be more adjusted to commercial application demands and to be easily processed into final composites by the currently used manufacturing methods, probably because their easy consolidation.

In any case, worse flexural strength and modulus results were found in GF/PP towpreg and PCT pultruded composites, respectively. These lower results obtained in the flexural tests are probably consequence of the inferior degree of impregnation observed in the towpreg based composites and, in the case of PCT tape based composites, result from the higher rich polymer regions exhibited by this material in its outside layers.

Table 5. CF/PP composite mechanical test results

Test Type	Property		Pultrusion		
			Towpreg	Towpreg with additive	PCT
Flexural	Flexure Modulus (GPa)	Experimental	90.1±0.4	87.6±1.3	37.7±2.2
		Theoretical	98.9	98.7	62.7
	Flexure Modulus / Fibre volume fraction (GPa)		178.1±0.8	173.5±2.6	118.2±6.9
	Flexure Strength (MPa)	Experimental	241.2±1.6	229.0±7.3	158.7±4.2
		Flexure Strength / Fibre volume fraction (MPa)		476.7±3.2	453.5±14.5
Tensile	Tensile Modulus (GPa)	Experimental	110.6±5.9	106.1±6.3	63.5±4.3
		Theoretical	98.9	98.7	62.7
	Tensile Modulus / Fibre volume fraction (GPa)		218.6±11.7	210.1±12.5	199.1±13.5
	Tensile Strength (MPa)	Experimental	1060.8±43.1	1129.3±34.6	636.9±38.4
		Tensile Strength / Fibre volume fraction (MPa)		2096.4±85.2	2236.2±68.5
Inter-laminar Shear	Interlaminar Shear Strength (MPa)		12.3±0.3	13.0±0.4	14.0±0.2
Fibre volume fraction (%)			50.6	50.5	31.9

Table 6. Test results on the processed GF/PP composites

Test Type	Property		Pultrusion		
			Commingled fibres	Towpregs	PCT
Flexural	Flexure Modulus (GPa)	Experimental	26.2±2.0	28.6±0.9	16.8±1.5
		Theoretical	23.8	33.1	19.1
	Flexure Modulus / Fibre volume fraction (GPa)		70.6±5.4	54.9±1.7	56.0±5.0
	Flexure Strength (MPa)	Experimental	595.0±24	158.0±12.3	329.0±30
Flexure Strength / Fibre volume fraction (MPa)		1603.8±64.7	303.3±23.6	1096.7±100	
Tensile	Tensile Modulus (GPa)	Experimental	24.9±1.1	33.9±1.5	21.4±1.5
		Theoretical	23.8	33.1	19.1
	Tensile Modulus / Fibre volume fraction (GPa)		67.1±3.0	63.5±2.9	71.3±5.0
	Tensile Strength (MPa)	Experimental	545.9±31.7	>336.3±22.3	355.8±53.2
Tensile Strength / Fibre volume fraction (MPa)		1471.4±85.4	>645.5±42.8	1186.0±177.3	
Inter-laminar Shear	Interlaminar Shear Strength (MPa)		26.8±1.7	7.5±0.1	27.8±0.6
Fibre volume fraction (%)			37.1	52.1	30.0

Table 7. Test results on the processed CF/Primospire[®] composites

<i>Test Type</i>	<i>Property</i>	<i>Pultrusion</i>
		<i>Towpreg FC/Primospire</i>
Flexural	Flexure Modulus (GPa)	56.1±2.9
	Flexure Strength (MPa)	253.6±16.1
Tensile	Tensile Modulus (GPa)	92.2±5.6
	Tensile Strength (MPa)	839.2±28.7
Inter-laminar Shear	Interlaminar Shear Strength (MPa)	25.4±2.1
Fibre volume fraction (%)		~ 45%

Nevertheless, the GF/PP pre-impregnated products produced in our laboratories (towpregs and PCTs) have already demonstrated very good mechanical behaviour, namely, in terms of stiffness. In fact, the composites manufactured from these products presented experimental moduli values very closed to the theoretical expected ones. While composites processed from the PCTs demonstrated to have better mechanical strength, those produced from towpregs presented higher moduli. As mechanical strength values are more affected by small defects than those from moduli, the composites manufactured from PCTs seem to profit from the pre-consolidate state already presented by this product before final processing. 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 5 and 6 correspond to maximum force applied in the test.

4 Conclusions

The tests made using a proprietary pultrusion equipment already allow to conclude that 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.

Existing powder-coating equipment was shown to be suitable to produce CF/PP, CF/Primospire[®] and GF/PP towpregs that could be adequately processed into pultruded profiles. From the tests made, the towpregs can be easily and continuously produced at industrial production speeds between 2 a 8 m/min.

It was possible to optimize the production of CF/PP pultruded profiles and CF/PP towpregs, through the use of Taguchi/DOE method, achieving optimal conditions.

A process window was established for the production of PCT's and towpregs and for the pultrusion of towpregs, PCT's and commingled fibres.

The mechanical properties of the composites processed from all those three GF/PP pre-impregnated were determined and evaluated. All of them demonstrated to have mechanical properties compatible with the requirements of the major current structural engineering applications. In general, commingled fibres TWINTEX[®] presented slight better mechanical properties and have shown to be more adjusted for composite processing than the other pre-impregnated products.

In particular, very good agreement was found between the experimental moduli values of all composites produced and the theoretical ones.

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

CF/Primospire[®] composites showed a higher value for the interlaminar strength than all other ones. Due to higher processing temperatures, further tests should be done to optimise the operational conditions and further improve the obtained composite mechanical properties.

The mechanical properties obtained in all pultruded composites allow predicting their adequate use either in general or structural engineering applications.

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