Advanced Thermoplastic Carbon Fibre Reinforced Pultruded Composites

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ABSTRACT: The aim of this work is to optimize the production of new continuous carbon fibers reinforced thermoplastic matrix pre-impregnated materials (towpregs) continuously processed by dry deposition of polymer powders in a new equipment developed by the Institute for Polymers and Composites (IPC). The processing of the produced towpregs by pultrusion, in a developed prototype equipment existing in the Engineering School of the Polytechnic Institute of Porto (ISEP), was also optimized.

Two different thermoplastic matrices were studied: one for commercial applications (polypropylene) and another for advanced markets (Primospire®).
The optimization was made by studying the influence of the most relevant processing parameters in the final properties of the produced towpregs and composites. The final pultruded composite profiles were submitted to mechanical tests in order to obtain 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 fibre/matrix contact prior to final composite fabrication. Alternatively, intimate contact processes allow the production of cheap and promising pre-impregnated materials, such as, commingled fibres, co-woven fabrics and powder coated towpregs.
Sometimes, thermoplastic compatibilizers were added to the matrices to improve their adhesion and facilitate impregnation to reinforcements [10].
In this work two different raw-materials were used in the production of the thermoplastic matrix towpregs, 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 fibre and polypropylene.

2 EXPERIMENTAL

2.1 *Raw-Materials*

The following raw materials were used to produce CF/PP pre-impregnated materials for this work, for commercial markets: 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 (Fig. 1), ii) Some batches of CF/PP towpregs were also produced using PP powder (ICORENE 9184B P®) with 1% in mass content of maleic anhydride additive, S 47 29608 707® from Merck Schuchardt OHG, in order to assess the possible enhancement of fibre/matrix adhesion [10-14].

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 TORAYCA. Table 1 presents the most relevant properties determined for these raw materials.

Table 1. Properties of towpregs raw-materials

Property	PP powder (ICORENE 9184B P®)		Primospire®		Carbon fiber (TORAY M30 SC®)	
	Manufacturer datasheet	Experimental	Manufacturer datasheet	Experimental	Manufacturer datasheet	Experimental
Linear density (Tex)	-	-	-	-	760	-
Specific gravity (Mg/m^3)	0.91	0.91	1.21	-	1.73	-
Tensile strength (MPa)	Yield Strength 30	Yield Strength 19	207	104.0	5490	2731
Young Modulus (GPa)	1.3	0.98	8.3	8.0	294	194,5
Poisson´s ratio	-	0.21	-	-	-	-
Average powder particle size (μm)	440	163	-	139	-	-
Glass transition temperature (T_g)	-	-	158	156	-	-
Melting temperature (T_m)	Typical value 170	166	-	-	-	-
Average fiber diameter	-	-	-	-	-	7,37

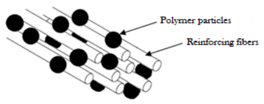

Figure 1. CF/PP and CF/Primospire pre-impregnated products

2.2 *Production of towpregs*

Towpregs were produced in a dry powder coating equipment schematically shown in Fig. 2 [14,15]. It consists of six main parts: wind-off system, fiber spreader unit, heating section, coating section, consolidation unit and a wind-up section. Initially, the reinforcing fibers are wound-off and pulled through a pneumatic spreader and then coated with polymer by heating in a convection oven and made to pass into a polymer powder vibrating bath. A gravity system allows maintaining the amount of polymer powder constant. The consolidation unit oven allows softening the polymer powder, promoting its adhesion to the fiber surface. Finally, the thermoplastic matrix towpreg is cooled down and wound-up on a spool.

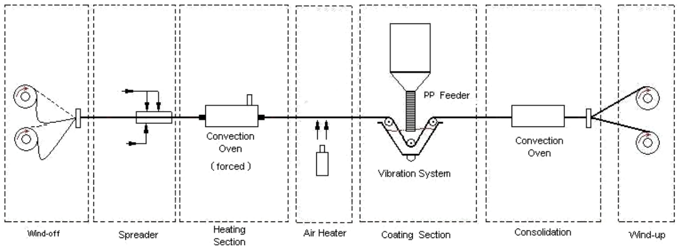

Figure 2. Powder coating line setup

2.3 *Towpreg CF/PP production optimization*

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 ºC);
- consolidation oven temperature (350, 400 and 450 ºC);
- linear pull speed (4, 6 and 8 m/min).

The Taguchi approach was applied to the towpregs production process in order to obtain the condition that maximizes polymer powder content.

The polymer mass fraction in the towpregs, was determined by weighting towpreg strips produced in those different conditions.

Table 2 shows the used processing conditions and obtained results, according to the established design of experiments. The average polymer mass content in towpregs, established by the design of experiences was 34.5%.

Table 2. Taguchi approach applied to towpregs manufacturing process

Experiments	Processing variables			Results:
	Heating oven temperature (ºC)	Consolidation furnace temperature (ºC)	Linear pulling speed (m/min)	Polymer mass fraction (%)
1	600	350	4	32.2
2	600	400	6	31.4
3	600	420	8	20.6
4	650	350	8	27.9
5	650	400	4	39.9
6	650	420	6	40.7
7	700	350	6	35.6
8	700	400	8	40.6
9	700	420	4	40.4
			Average	34.5

The mains effects of the processing variables on the results can be seen from Fig. 3.

The optimal condition obtained from Taguchi method application led to the following operating parameters selection: heating oven temperature and consolidation oven temperatures of 700 ºC and 400ºC respectively, and a linear pulling speed of 4 m/min. Using this optimal operative condition, the amount of polymer should increase up to 45.6%. However, the operative condition that has 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 content (40%, enough for the of use of towpregs in the pultrusion process). Also, the addition of 1% of maleic anhydride to the PP polymer had no influence on the towpreg polymer mass fraction.

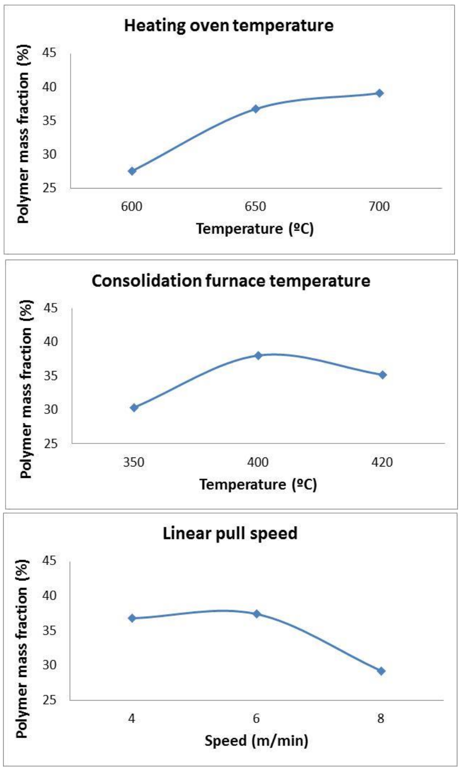

Figure 3. Variation of towpreg polymer content with processing parameters

2.4 *Towpreg CF/ Primospire® production*

In order to produce CF/Primospire towpregs, the powder coating equipment was operated at different woven temperatures and fibre linear pull speeds (see Table 3). 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 ºC;
- consolidation oven temperature - 525 ºC;
- linear pull speed - 6 m/min.
Using those conditions towpregs with a polymer mass content of aprox. 40% were produced.

Table 3. Best conditions to produce towpregs used in composites for advanced markets.

Variable	Units	Values
		CF/Primospire® towpregs
Convective oven temperature	ºC	700
Consolidation furnace temperature	ºC	500-550
Coating line pulling speed	m/min	4-6

2.5 *Pre-impregnated materials processing*

Towpregs were processed into composite bar profiles using a 10 kN prototype pultrusion line equipment [16, 17], schematic depicted in Fig.4. The equipment consists in five main parts: i) an initial towpreg bobbins holding cabinet; ii) guiding system; iii) pultrusion head, that includes a pre-heating furnace and the pressurization/consolidation and cooling dies; iv) pulling system and, v) the final profile cutting system.

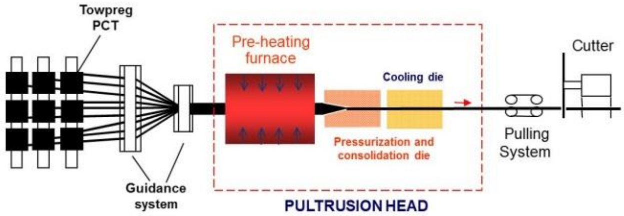

Fig. 4. Schematic diagram of the pultrusion line

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 die to be heated up and consolidated to the required size in its first zone and, after cooled down in order to solidify. The pultruded material is then cut into specified lengths.
A die with a cavity of 20 ×2 (mm) was used to produce a composite rectangular shaped bar.

2.5.1 *Towpreg CF/PP processing and optimization*

Bar profiles were manufactured by pultrusion from different towpregs, using operating conditions in order to optimize the processing. The studied processing variables were:
-Furnace temperature (160 and 180 ºC);
-Heating die temperature (240 and 260 ºC);
-Linear pull-speed (0.2 and 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 ºC, respectively.
By using higher values in 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, respectively.
Table 4 summarizes the flexural test results obtained with the studied processing conditions.

Table 4. Flexural testing results from CF/PP towpregs

Exper.	Processing variables			Flexural properties	
	Furnace temperature (ºC)	Heating die temperature (ºC)	Linear pulling speed (m/min)	Flexural modulus (GPa)	Flexural strength (MPa)
1	160	240	0.2	86.7 ± 1.3	229.0 ± 7.3
2	180	240	0.2	79.5 ± 2.0	212.4 ± 12.6
3	160	260	0.2	91.0 ± 0.4	241.2 ± 1.6
4	180	260	0.2	85.1 ± 1.7	218.2 ± 9.1
5	160	240	0.3	82.1 ± 2.8	241.7 ± 13.1
6	180	240	0.3	87.5 ± 1.9	239.6 ± 13.3
7	160	260	0.3	85.0 ± 4.4	234.5 ± 11.5
8	180	260	0.3	83.7 ± 2.8	221.3 ± 7.1

The variation of the flexural modulus and strength with the selected processing parameters can be seen in Figures 5 and 6.
The optimal condition concerning flexural stiffness maximization obtained led to the following operating parameters selection: furnace and heated die oven temperatures of 160 ºC and 260ºC respectively, and a linear pulling speed of 0.2 m/min. For optimizing the

flexural strength the obtained parameters combination was: furnace and heated die oven temperatures of 160 ºC and 240ºC respectively, and a linear pulling speed of 0.3 m/min.

It is possible observe that the furnace temperature of 160ºC lead to the better results. That could be explained by the lower polymer reflux on the entrance of the heated die. The optimal operating conditions to maximize both flexural proprieties (modulus and strength) were: furnace and heated die oven temperatures of 160 ºC and 260ºC respectively, and a linear pulling speed of 0.2 m/min.

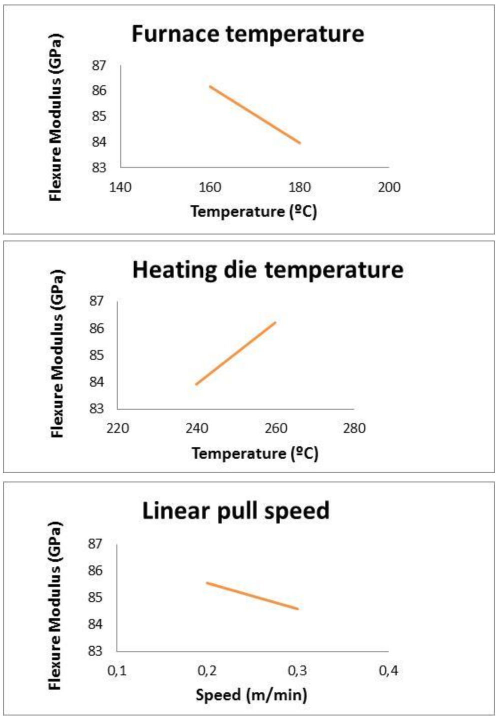

Figure 5. Variation of the flexural modulus with the selected processing parameters

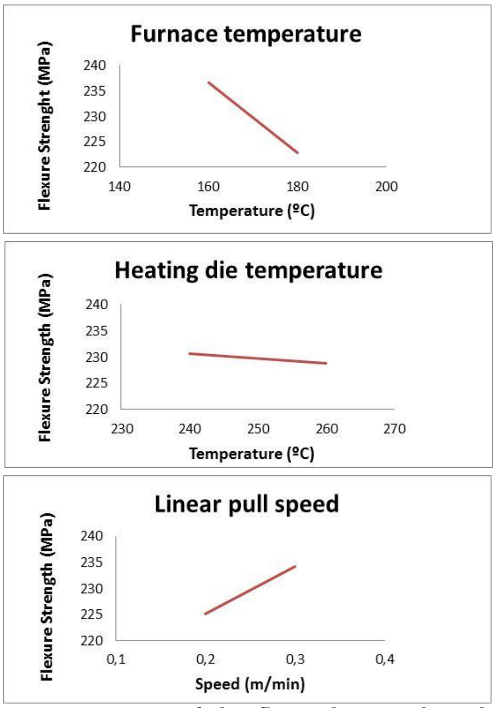

Figure 6. Variation of the flexural strength with the selected processing parameters

Finally, towpregs with additive were also pultruded into bars using the condition that optimizes both flexural properties and two more conditions (see Table 5).

Table 5. Flexural properties of towpregs with additive processed by pultrusion

Exper.	Processing variables			Flexural properties	
	Furnace temperature (ºC)	Heating die temperature (ºC)	Linear pulling speed (m/min)	Flexural modulus (GPa)	Flexural strength (GPa)
1	160	260	0,2	229.0 ± 7.3	87.6± 1,3
2	160	240	0,2	191.7 ± 7.8	70.4 ± 2.8
3	160	240	0,3	237.4 ± 11.8	80.5 ± 2.6

Table 6 shows the obtained results from flexural tests using towpreg pultruded bars with and without additive of maleic anhydride. It is possible to conclude that use of additive had no significant influence on the flexural properties.

Table 6. Flexural test results on towpreg bars with and without additive

Processing parameters		Flexural modulus (GPa)		Flexural strenght (GPa)	
		Without additive	With additive	Without additive	With additive
Furnace temperature (ºC)	160	90.1 ± 0.4	87.6 ± 1.3	241.2 ±1.6	229.0 ± 7.3
Heating die temperature (ºC)	260				
Linear pulling speed (m/min)	0,2				

2.5.2 *Towpreg CF/ Primospire® processing*

The CF/Primospire pultruded bars were produced in this work with the operational conditions presented in Table 7.

Table 7. Conditions used to process the pultruded composite bars from the CF/Primospire towpregs

Variable	Units	Values
		CF/Primospire® towpregs
Pultrusion pull speed	m/min	0.2
Pre-heating furnace temperature	ºC	380-400
Pressurisation/consolidation die temperature	ºC	420-475
Cooling die temperature	ºC	20

As it may be seen and as 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 to be used in the pultrusion of the CF/Primospire® towpregs.

2.6 *Composite testing*

Samples of pultruded bars were submitted to flexural, tensile, interlaminar and calcination tests according to the ISO standards 14125, 527, 14130 and 1172, respectively.

Table 8 summarizes all experimentally obtained test results with CF/PP composites.

Table 8. Composite CF/PP mechanical test results

Test Type	Property	Pultrusion	
		Towpreg	*Towpreg with additive*
Flexural	Flexure Modulus (GPa)	90.1±0.4	87.6±1.3
	Flexure Modulus / Fibre volume fraction (GPa)	178.1±0.8	173.5±2.6
	Flexure Strength (MPa)	241.2±1.6	229.0±7.3
	Flexure Strength / Fibre volume fraction (MPa)	476.7±3.2	453.5±14.5
Tensile	Tensile Modulus (GPa)	110.6±5.9	106.1±6.3
	Tensile Modulus / Fibre volume fraction (GPa)	218.6±11.7	210.1±12.5
	Tensile Strength (MPa)	1069±43	-
	Tensile Strength / Fibre volume fraction (GPa)	2112.3±85	-
Inter-laminar Shear	Interlaminar Shear Strength (MPa)	12.3±0.3	13.0±0.4
Fibre volume fraction (%)		50.6	50.5

Table 9 summarizes all experimentally obtained test results with CF/Primospire composites.

Table 9. Composite CF/Primospire mechanical test results

Test Type	Property	Pultrusion
		CF/Primospire® towpreg
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)	> 600
Inter-laminar Shear	Interlaminar Shear Strength (MPa)	25.4±2.1

3 CONCLUSIONS

Obtained results allow the conclusion that all the pre-impregnated products studied in this work presented enough good properties to be employed in the major commercial engineering structural applications.

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. The tests made using a proprietary pultrusion equipment already allow the conclusion to be possible to produce in good conditions profiles from almost all commercial available thermoplastic matrix pre-impregnated raw-materials using pull speeds of about 0.3 m/min. It was possible to optimize the production of CF/PP pultruded profiles and towpregs, through the use of Taguchi method, achieving optimal conditions. The addition of the compatibilizing agent (1% maleic anhydride) did not improve the polymer mass content in towpregs and the mechanical properties on the final composites.

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