PROCESSING OF CARBON REINFORCED THERMOPLASTIC PRE-IMPREGNATED MATERIALS

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Abstract

The aim of this work is to produce and optimize the processing of carbon fibres thermoplastic matrix pre-impregnated materials (towpregs and PCT´s). Pultrusion and heated compression moulding were the selected manufacturing methods for processing all carbon fibres thermoplastic matrix pre-impregnated materials into composite parts.

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 method of Taguchi / DOE (Design of Experiments) was used to achieve this aim as it allowed making more rational choices of processing windows.

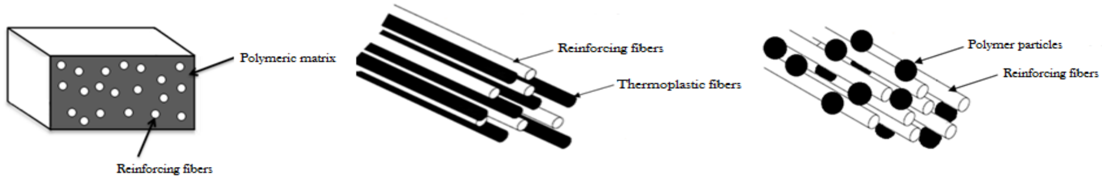
The composite relevant mechanical properties were determined and studied. The final composites were also submitted to SEM microscopy analysis.

1. Introduction

Historically, thermoset resins have dominated the composite industry but thermosets start to be replaced by thermoplastics. 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 [1-6].

Today, two major technologies are being used to allow wet reinforcing fibres with thermoplastic polymers: 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 (Figure 1).

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 fibres and polypropylene.
Heated compression moulding and pultrusion were the processing methods used to obtain final composite parts. Thus, the efficient processing windows allowing producing continuously the thermoplastic matrix towpregs and PCT´s and also transform them into composites were established.



a) Pre-consolidate tapes (PCTs) b) Commingled fibres c) towpregs

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.
Tables 1 and 2 summarise relevant properties of the polypropylene, Primospire® and carbon fibres used in present work to produce pre-impregnated raw materials (towpregs and PCT´s).

Table 1. Properties of Towpregs and PCT powders 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 fibre raw-materials.

Property	Carbon fibre (TORAY M30 SC®)	
	Manufacturer datasheet	Experimental
Linear density (Tex)	760	-
Specific gravity (Mg/m^3)	1.73	-
Tensile strength (MPa)	5490	2731
Young Modulus (GPa)	294	194.5
Average fibre diameter	5	7.37

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 [7-10].
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 [10].

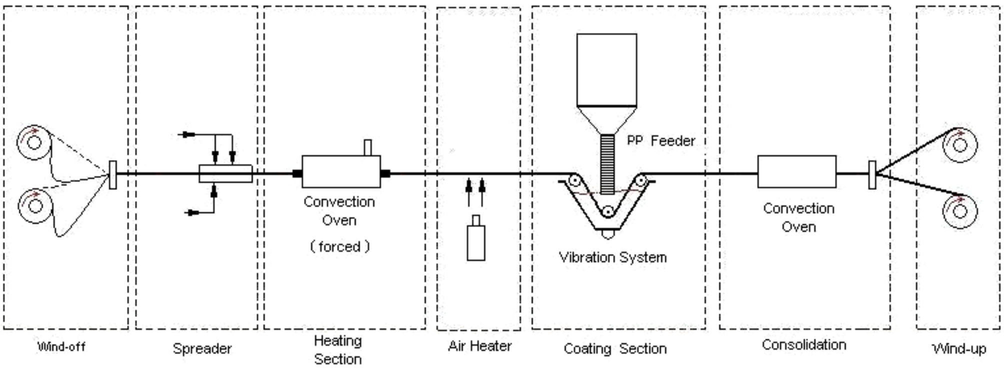


Figure 2. Powder coating line setup.

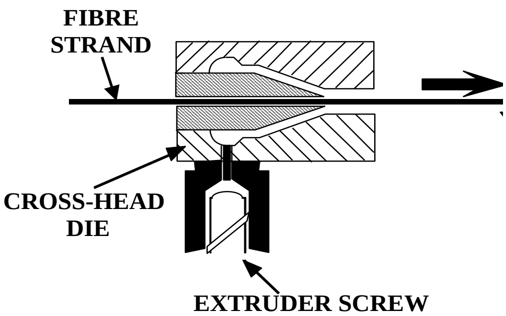


Figure 3. Cross-head extrusion die.

2.2.1. CF/PP and CF/Primospire® 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 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.
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 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 towpregs, the powder coating equipment was operated at different following woven temperatures and fibre linear pull speeds:
- heating oven temperature (700 ºC); consolidation oven temperature (500 - 550 ºC); 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 ºC; consolidation oven temperature - 525 ºC 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 and PCT's were processed into composite bar profiles using the laboratorial pultrusion line, Figure 4 [7-10].
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.

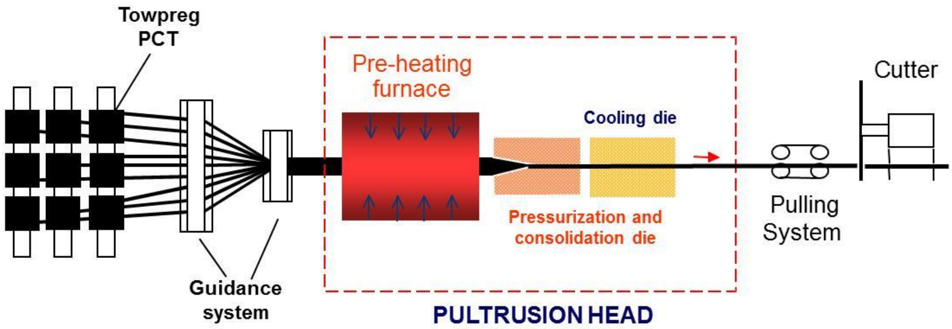


Figure 4. Schematic diagram of the pultrusion line

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

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 ºC, in order to optimize the processing parameters:
i) furnace temperature (160 or180 ºC); ii) heating die temperature (240 or 260 ºC); 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 ºC, 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 ºC and 260ºC 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 ºC); ii) heating die temperature (420 - 475 ºC); 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 (mm2) bar using the already mentioned pultrusion equipment being operating conditions shown in Table 3.

Table 3. Pultrusion processing parameters for PCT´s.

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

2.4. Compression moulding of CF/Primospire® towpregs

A technique described elsewhere [11] was used to produce unidirectional fibre reinforced laminate plates with 100×100×4 mm directly from the towpregs. First, the towpreg were wound over a plate with appropriate dimensions and the resultant pre-form then conveniently placed in the cavity of a heated mould. A 400 kN SATIM hot platen press was used to obtain the desired consolidation pressure. After heating the cavity, pressure was applied and, finally, the mould was cooled down to room temperature and the final composite laminate plate removed.
Table 4 shows the compression moulding conditions used to process composites from CF/Primospire® towpregs.

Table 4. Conditions used to process composites by compression moulding by using the towpregs.

Variable	Units	Values
		CF/Primospire® towpregs
Platen temperature	ºC	320
Compression pressure	MPa	20
Compression time	min	20
Final cooling temperature (at press opening)	ºC	30

2.4 Testing

2.4.1 Microscopy analysis

CF/PP and CF/Primospire® towpregs samples were characterized by scanning electron microscopy (SEM) to evaluate the adhesion of the polymer powder to the fibres and its distribution.

2.4.2 Mechanical 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 mm^3 rectangular samples obtained from pultrusion.
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.
Three-point flexural tests were also conducted on five 100 × 20 × 2 mm^3 pultruded profiles specimens and 100 × 15 × 4 mm^3 for the compression moulded samples, 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 × 20 × 2 (mm3), cut from composites processed from each pre-impregnated raw material, were submitted to interlaminar shear tests according to ISO 14130. The

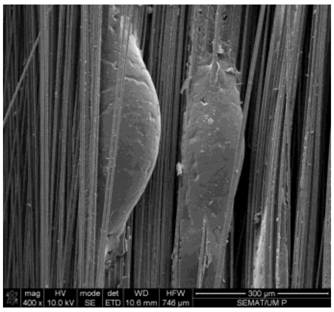
tests were conducted in a 50 kN universal testing machine by using an initial pre-load of 1 N at the crosshead speed of 1 mm/min and a 10 mm span between supports.

2.4.3 Calcination testing

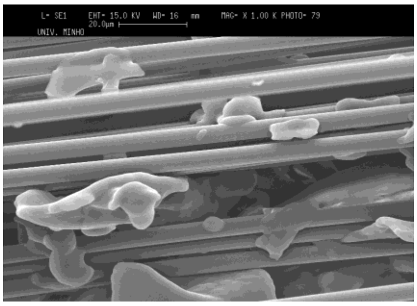
CF/PP composites fibre mass content was determined by using calcination tests according to the EN ISO 1172. Composite samples, weighting approximately 2 g, were submitted to calcination inside a crucible in a muffle furnace during 10 min at 625º C.

3. Results and Discussion

Figure 5 show representative SEM micrographs of the studied CF/PP and CF/Primospire® towpregs.



CF/PP towpreg (magnification 400×).



CF/Primospire® towpreg (magnification 1000×).

Figure 5 - Micrographs of Carbon/Primospire® towpreg under SEM.

As may be seen, most of the polymer particles exhibit bigger size than the fibre diameter and, even after heating, the polymer particles present an irregular shape. It is also possible to observe that some degree of adhesion between fibres and polymer powder was achieved, especially in the case of CF/PP towpregs.

Tables 5 and 6 summarize all experimentally results obtained from the CF/PP and CF/Primospire® 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 the tables also present theoretical expected values and relative values of specific properties.

As can be seen from Tables 5 the experimental moduli obtained from de CF/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.

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.

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.

As may be seen from Table 7, flexural properties compatible with the applications envisaged for the composites processed by compression moulding from the produced towpregs were obtained in this work.

Table 5. CF/PP composite mechanical test results.

Test Type	**Property**		***Pultrusion***	
			Towpreg	***PCT***
Flexural	Flexure Modulus (GPa)	Experimental	90.1±0.4	37.7±2.2
		Theoretical	98.9	62.7
	Flexure Modulus / Fibre volume fraction (GPa)		178.1±0.8	118.2±6.9
	Flexure Strength (MPa)	Experimental	241.2±1.6	158.7±4.2
	Flexure Strength / Fibre volume fraction (MPa)		476.7±3.2	497.5±13.2
Tensile	Tensile Modulus (GPa)	Experimental	110.6±5.9	63.5±4.3
		Theoretical	98.9	62.7
	Tensile Modulus / Fibre volume fraction (GPa)		218.6±11.7	199.1±13.5
	Tensile Strength (MPa)	Experimental	1060.8±43.1	636.9±38.4
	Tensile Strength / Fibre volume fraction (MPa)		2096.4±85.2	1996.6±120.4
Inter-laminar Shear	Interlaminar Shear Strength (MPa)		12.3±0.3	14.0±0.2
Fibre volume fraction (%)			50.6	31.9

Table 6. Test results on the processed CF/Primospire® composites.

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)	839.2±28.7
Inter-laminar Shear	Interlaminar Shear Strength (MPa)	25.4±2.1
Fibre volume fraction (%)		~ 45%

Table 7. Properties of composite plates made by compression moulding from the CF/Primospire® towpregs.

Property	**Units**	**Compression moulding CF/Primospire®**
Flexural strength	MPa	124.3±15.0
Flexural modulus	GPa	30.0±5.0
Fibre mass fraction	%	59.7±0.3

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 and CF/Primospire® 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.

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.

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

CF/Primospire® composites obtained by pultrusion 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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