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PULTRUSION AND COMPRESSION MOULDING OF THERMOPLASTIC PRE-IMPREGNATED MATERIALS REINFORCED BY CONTINUOUS GLASS FIBRES

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ABSTRACT

Four different pre-impregnated materials were used in this study: towpregs and tapes (PCT´s), both produced in our manufacturing lines and commingled fibres (TWINTEX®) and tapes (CompTape®) supplied by external companies. The laboratory made pre-impregnated materials consisted of carbon and glass fibres and a polypropylene thermoplastic matrix.
Pultrusion and heated compression moulding processes were used to obtain composite profiles and plates and were described in this paper. The optimization of those processes was made by studying the influence of the most relevant processing parameters – preheating, heating and cooling inside the die and speed for the pultrusion, and heating temperature, pressure and time for compression moulding - in the final properties of the produced carbon and glass fibres thermoplastic matrix pre-impregnated materials and composites. One interesting target to be achieved was the increase of pultrusion speeds to meet the industrial needs. This was possible particularly with the thermoplastic composite Tape due to its consistency. The composite relevant mechanical properties were determined and the final composites had optical microscopy and calcination tests.

KEYWORDS
Thermoplastic composites; towpreg; pultrusion; compression molding; composite tape

1. INTRODUCTION

Two major technologies were used to allow wet reinforcing fibres with thermoplastic polymers [1, 2-4]: i) the direct melting of the polymer and, ii) the intimate fibre/matrix contact prior to final composite fabrication. Continuous fibre reinforced thermoplastic matrix Tapes and PCT´s are, for example, produced by direct melting processes using a cross-head extrusion technique [5]. Intimate contact processes allow producing commingled fibres and powder-coated towpregs. Sometimes, thermoplastic compatibilizers are added to the matrices to improve their adhesion and facilitate impregnation to reinforcements [6].

The processability of different pre-impregnated materials produced by each one of the above mentioned impregnation techniques into final composites was studied. Pultrusion and heated compression moulding were the selected manufacturing methods for processing. The pultrusion optimization was made by studying the influence of the most relevant processing parameters in the final properties of the produced pre-impregnated materials and composites, using the Taguchi method. A similar methodology was used to process pultruded rectangular profiles into composite plates by heated compression moulding [7-9].

2. EXPERIMENTAL

2.1. Raw Materials

Table 1 – TWINTEX® R PP 60 B 1870 FU from Owens Corning (W_f 60%)

Property	Values
Linear density (Tex)	1870
Tensile strength (MPa)	760
Young Modulus (GPa)	29.5

For GF/PP pre-impregnated materials, i) a PP powder ICORENE 9184B P®/E glass fiber rovings 305E-TYPE 30®, were used for the GF/PP towpregs, ii) PP Moplen RP348U® and E glass fiber roving TufRov 4599® were used for the GF/PP Tapes and PCT’s. Twintex® R PP 60 B 1870 FU was the commingled fibers used (Table 1).

Table 2 – Properties of polymer raw-materials

Property	PP powder (ICORENE 9184B P®)		PP powder (ICORENE 4014®)	PP granules (Moplen RP348U ®)
	Manufacturer	Experimental	Manufacturer	Manufacturer
Specific gravity (Mg/m^3)	0.91	0.91	0.9	0.90
Tensile strength (MPa)	Yield Strength 30	Yield Strength 19	Yield Strength 24	Yield Strength 30
Young Modulus (GPa)	1.3	0.98	1.15	1.1
Poisson´s ratio	-	0.21	0.21	-
Average powder particle size (μm)	440	163	400	-
Glass transition temperature (T_g)	Typical value 0-20	-	Typical value 0-20	Typical value 0-20

For CF/PP pre-impregnated materials, i) PP powder ICORENE 9184B P® and CF roving M30 SC® and PP powder ICORENE 4014® and CF roving SIGRAFIL® C30 T050 TP1 were used to produce the CF/PP towpregs, ii) PP powder Moplen RP348U® and the CF roving already mentioned were used for the CF/PP PCT tapes (Table 2). [10]

Table 3 – Properties of fibres raw-materials

Property	Glass fibre			Carbon fibre		
	305E-TYPE 30®		TufRov 4599®	TORAY M30 SC®		SIGRAFIL® C30 T050 TP1
	Manufacturer	Experimental	Manufacturer	Manufacturer	Experimental	Manufacturer
Linear density (Tex)	2400	-	2400	760	-	3280
Specific gravity (Mg/m^3)	2.65	-	2.54-2.6	1.73	-	1.8
Tensile strength (MPa)	3500	1657	1900-2400	5490	2731	4000
Young Modulus (GPa)	76	62.5	69-76	294	194.5	240
Average fibre diameter	17	13.7	17	5	7.37	7

2.2 Transformation of thermoplastic pre-impregnated materials by pultrusion and the pultruded profiles by heated compression moulding

2.2.1 Processing GF pre-impregnated materials

Tapes were processed by pultrusion and heated compression moulding. The set-up parameters in pultrusion were: i) pre-heating oven temperature: 160 °C; ii) heated die temperature: 200 °C; iii) Cooling die temperature: 25 °C; - Pulling Speed: 0.2 – 0.7 (m/min).

At the beginning of the processing, a range of temperatures was tested to determine what could be the maximum and minimum temperature of the consolidation and pressurization die. It was determined that the maximum set-point was 210°C and minimum of 190°C. When using temperatures higher than the maximum referred, reflux problems in the consolidation die occurred, and lower temperatures would create problems in the first die.

The processing by pultrusion of the other GF/PP pre-impregnated materials can be found in [10].

The GF/PP Tape and the pultruded profiles from this type of pre-impregnated material were also processed into rectangular 290 × 200 × 2 (mm^3) composite plates. To manufacture a plate from GF/PP Tape, a weaving technique was also performed. Each weaved prepreg tape consisted in a ply, and a lay-up was done with four layers. In this case because of the rigidity of the GF/PP Tape the same number of fibres was not possible to achieve, being the number of fibres in one direction higher than in the other direction. With that in mind, the plate was produced in a symmetrical lay-up, using a 200 kN Hot Plate Press. A temperature of 230°C for processing was selected to ensure the uniformity of the laminate, allowing the melting polymer to migrate to all areas inside the mould (Table 4).

Table 4 – Heated Compression Moulding steps for weaved prepreg

Step	Stage	Temperature (°C)	Pressure (MPa)	Time (min)
1	Heating	230	0	25
2	Consolidation	230	0	10
3	Compression	230	2.0	1
4	Cooling	50	2.0	25

GF/PP Tape pultruded profiles were also processed by heated compression moulding, using the same setup, only varying the heating, consolidation and compression temperatures from 230 to 250 ºC.

2.2.2 Processing CF pre-impregnated materials

Different processing variables and combinations were tested with a dry powder coating equipment for fibre reinforced towpregs [7-8] and the process was optimized by the Taguchi approach. The optimal parameters for CF/PP towpregs were: i) convection oven: 700°C for 760 Tex and 650ºC for 3280 Tex carbon fibre; ii) onsolidation oven: 400°C; iii) linear pull speed: 6 m/min. The best conditions for processing the towpregs by pultrusion are presented in Table 5 and were established from processing window defined in previous works. For hot press moulding, the temperatures chosen to process the pultruded profiles on the plates were selected taking into account the temperatures used in the heated die of the pultrusion process.

Table 5 – Pultrusion and heated compression moulding process parameters

Condition	Carbon Fibre	Polypropylene	Pultrusion				Heated Compression
	Tex	Reference	Pre-heating oven (°C)	Heated die temperature (°C)	Cooled die temperature (°C)	Pull Speed (m/min)	Temperature (°C)
1	3280	*ICORENE®* 4014	160	250	25	0,2	-
2							200
3							250
4	760		70	200			-
5							200
6							250
7						0,3	-
8							200
9		*ICORENE®* 9184B P [12]	160 [12]	240 [12]		0,2 [12]	-
10							250

Heated compression moulding was carried out in a 200 kN Gislotica heated plate press installed in ISEP to manufacture a composite laminate. The pultruded composites were placed in a frame and a PTFE based releasing film was used. Two processing temperatures were employed: 200 and 250°C. In Figure 3 the assembly for heated compression moulding can be seen. To manufacture the laminate, the pultruded material was heated up to 250°C and maintained that temperature for 10 minutes to ensure the uniformity of temperature in all areas inside the mould. Then, a compression force was done to consolidate the laminate. Finally, it was cooled down and the laminate was taken out of the mould. The main stages and processing conditions of the heated compression moulding process are described in Table 6.

Table 6 – Heated Compression Moulding process parameters

Process		Temperature (°C)	Force (ton)	Pressure (MPa)	Time (min)
1	Heating	200 / 250	0	0	20 / 25
2	Temperature maintenance	200 / 250	0	0	10
3	Compression	200 / 250	20	2,0	1
4	Cooling	50	20	2,0	25 / 30

The processing by pultrusion and heated compression moulding of the other CF/PP pre-impregnated materials can be found in [11, 13].

2.3 Testing and Results

2.3.1 Testing GF composites

The flexural properties of the pultruded profiles were determined by doing a series of three-point flexure tests according to ISO 14125. The dimensions of the specimens were 20 mm x 2 mm. The outer span was 80 millimetres and testing speed 2 mm/min. The flexural mechanical properties of the pultruded profiles were determined and presented in Table 7.

Table 7 - Mechanical properties of pultruded profiles

Condition	Pulling Speed (m/min)	Flexural Strength (MPa)[a]	Flexural Modulus (GPa)	Fibre Volume Fraction (%)	Specific Strength (MPa)	Specific Modulus (GPa)
1	0.2	416.6±13.0	20.9±0.9	36.28	1148.3	57.6
2	0.3	351.8±14.2	19.3±1.4	35.11	1001.9	54.9
3	0.4	324.1±24.0	18.2±1.1	35.51	912.6	51.1
4	0.5	320.0±11.4	18.5±0.8	34.99	914.6	53.0
5	0.6	300.8±31.4	17.5±0.3	35.08	857.4	50.0
6	0.7	271.0±16.6	17.4±0.8	34.51	785.2	50.4

[a] with the large-deflections correction

Analysing Table 6 it's possible to verify that the condition with the highest flexure strength and a relatively low standard deviation is condition 1. This condition was produced with a constant temperature of 200°C in the consolidation and pressurization die with the lowest pulling speed improving impregnation of the polymer in the fibres, enhancing the consolidation of the composite and reducing the amount of voids. It is also important to note that in condition 1, the deviation of the strength and modulus is relatively low, meaning the process is in control. Mechanical properties were expected to decrease with higher processing speeds. Higher pulling speeds make impregnation harder due to the reduced exposure time of the prepregs to temperature and pressure inside of heated die. Increasing the speed by 3.5 times lowers the flexural strength by 33.7% and the modulus by 16.7%.

Microscopy (Figures 1 to 4) of the transverse section of condition 1 and 6 was done to see how the fibres and the polymer are arranged after pultrusion at different processing speeds.

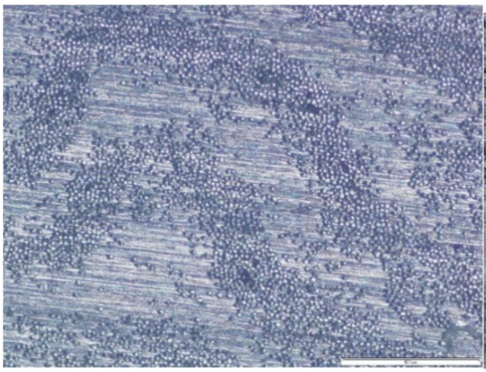

Figure 1 – Microscopy in pultrusion composites Condition 6 (0.7 m/min) (50x zoom)

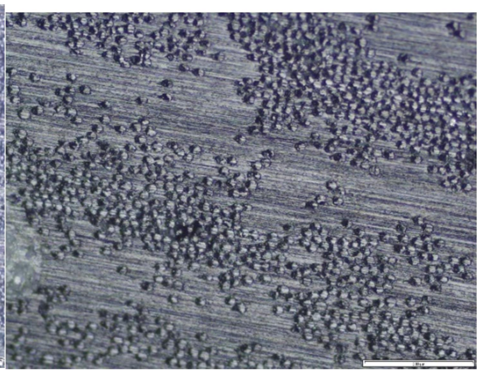

Figure 2 – Microscopy in pultrusion composites Condition 6 (0.7 m/min) (100x zoom)

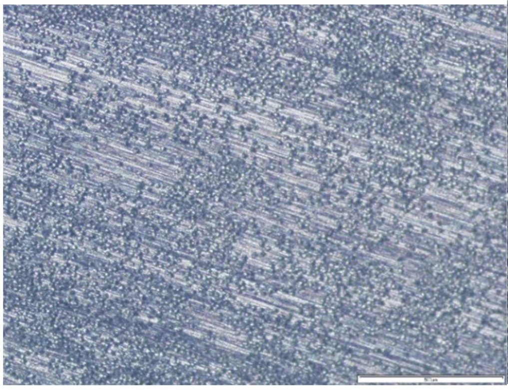

Figure 3 – Microscopy in pultrusion composites Condition 1 (0.2 m/min) (50x zoom)

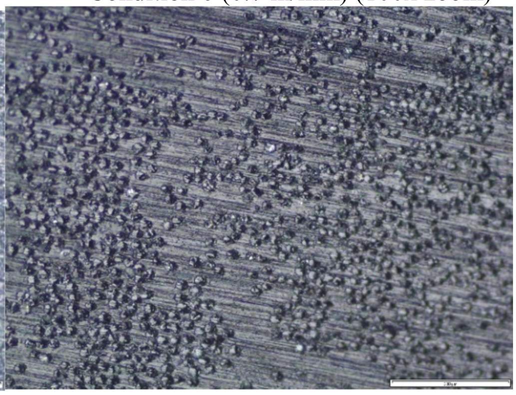

Figure 4 – Microscopy in pultrusion composites Condition 1 (0.2 m/min) (100x zoom)

Seeing condition 6 in Figure 1, a separation can be identified between fibres. The separation zone is filled with polymer and a very low quantity of fibres can be seen, meaning the impregnation during pultrusion was worst. If we zoom Figure 2, we can see separate areas in which there is a concentration of fibres with low polymer quantity around some of them. The distribution of the polymer and fibres through the area is very uneven. In the case of condition 1 (Figure 3), the dispersion of fibres and polymer is much equitable. The impregnation was more successful due to the parameters of processing. With lower speeds, it is expected that the polymer reaches a temperature high enough for processing and has time to migrate through the composite, improving impregnation and reducing the amount of voids. Observing Figure 4, we can see that even in the zones with fibre concentration, polymer is distributed around them. Table 8 summarizes the mechanical properties obtained.

Table 8 – Test results of pultrusion of processed GF/PP composites

Test Type	Property	Towpreg (V_f 52.1%)	Commingled Fibres (V_f 37.1%)	PCT (V_f 30.0%)	Tape (V_f 36.3%)
Bending	Flexure Modulus (GPa)	28.6±0.9	26.2±2.0	16.8±1.5	20.9±0.9
	Flexure Modulus/V_f (GPa)	54.9±1.7	70.6±5.4	56.0±5.0	57.6±2.4
	Flexure Strength (MPa)	158.0±12.3	595.0±24 [a]	329.0±30 [a]	416.6±13.0 [a]
	Flexure Strength/ V_f (GPa)	303.3±23.6	1603.8±64.7	1096.7±100	1148.3±35.8

[a] with the large-deflections correction

For the flexure modulus and strength, commingled fibres have best mechanical properties due to the quality of the impregnation. On the other hand, the flexure strengths per fibre volume fraction of the Tape and PCT are similar and much higher than Towpreg. These weaker results obtained can be due to the relatively high fibre volume fraction, making impregnation difficult and allowing the formation of voids in the composite. The flexure modulus per fibre volume fraction, Towpreg, PCT and Tape had relatively similar results.

Tensile properties of the produced thermoplastic cross-ply laminate by hot press moulding from GF/PP Tapes were determined - ISO 527-4 (Table 9).

Table 9 – Tensile test results of heated compression moulding processed GP/PP composites

Test Type	Property		Towpreg	Commingled Fibres	PCT	Tape (CPL)
Tensile	Tensile Modulus (GPa)	Experimental	37.0±1.3	27.7±0.4	21.2±4.0	15.6±0.3
		Theoretical	32.4	24.5	19.9	14.6
	Tensile Modulus / V_f (GPa)c		72.4±2.5	71.3±1.0	69.3±13.1	84.3±1.6
	Tensile Strength (MPa)		-[a]	-[a]	-[a]	296.3±1.4
Interlaminar Shear	Interlaminar Shear Strength (MPa)		12.0±0.7	28.6±0.3	27.2±0.9	16.4±0.8
	Interlaminar Shear Strength / V_f (MPa)d		23.5±1.4	74.7±0.8	88.9±2.9	88.7±4.3
Fibre Volume Fraction (%)			51.1	38.3	30.6	18.5[b]

[a] property not determined; [b] half value of fibre volume fraction

Table 10 shows the bending test results of heated compression moulding processed GP/PP from pultruded profiles processed in condition 1. GF/PP Tape composites presented, in general, better properties. Twintex® composites exhibits also very good mechanical behavior. GF/PP composites demonstrated similar relative flexure modulus. Towpreg composites present worse mechanical properties due to high fibre volume fraction and uneven distribution of the dry polymer powder.

Table 10 – Bending test results of heated compression moulding GP/PP composites

Test Type	Property	Towpreg (V_f 51.1)	Commingled Fibres (V_f 38.3)	PCT (V_f 30.6)	Tape (V_f 37.1)
Bending	Flexure Modulus (GPa)	34.4±3.4	25.5±1.0	20.1±1.0	23.4±0.7
	Flexure Modulus / V_f (GPa)[a]	67.3±6.5	66.6±2.6	65.7±3.3	63.1±1.9
	Flexure Strength (MPa)	184.0±19.1	666.5±53.9 [a]	456.0±32.1 [a]	733.4±78.7 [a]
	Flexure Strength / V_f (GPa)[b]	360.1±37.4	1740.2±140.7	1490.2±104.9	1976.8±212.1

[a] with the large-deflections correction

2.3.2 Testing CF composites

In Table 11, it is possible to see that increase in pultrusion speeds affects significantly the flexural strength of these composites. This is expected because a reduction in exposure time to temperature and pressure during processing, leads to a lower quality of impregnation. The percentage of voids is likely to be higher resulting in a less well-consolidated composite.

Table 11 – Mechanical properties of tested conditions

Condition	Flexural test				
	Flexure Strength (MPa)	Flexure Modulus (GPa)	Fibre volume fraction (%)	Specific Flexure Strength (MPa)	Specific Flexure Modulus (GPa)
1	89,4 (±7,4)	27,5 (±1,5)	58,1	153,8	47,3
2	133,8 (±28,8)	39,7 (±6,1)	60,0	223,0	66,2
3	207,6 (±16,5)	59,4 (±5,4)	58,2	356,8	102,0
4	211,2 (±18,8)	63,8 (±4,0)	46,4	455,2	137,6
5	242,6 (±16,7)	74,2 (±6,2)	46,8	518,4	158,5
6	265,7 (±11,9)	73,8 (±4,0)	47,2	562,9	156,3
7	134,9 (±14,7)	44,9 (±2,0)	47,1	286,4	95,3
8	209,4 (±8,8)	70,4 (±9,5)	47,0	445,6	149,9
9	229,0[2]	86,7[2]	49,9	458,9	173,7
10	267,4 (±21,4)	88,7 (±1,4)	50,8	526,4	174,7

The post processing by heated compression moulding improved the mechanical properties, especially for higher pultrusion speed. The improved impregnation due to the relatively higher exposure time to heat and pressure in the hot plate press allowed the polymer to migrate, filling the spaces between fibres and reducing voids. Fibre contents were similar due to polymer uniformization in the pultruded composites.

3. CONCLUSIONS

The main conclusions of the work carried out are the following:

- Existing powder-coating equipment is suitable to produce CF/PP and GF/PP towpregs that can be adequately processed into pultruded profiles.
- The tests made using a proprietary pultrusion equipment show that is possible to produce, in good conditions, profiles from almost all available thermoplastic matrix pre-impregnated raw materials using pull speeds from 0.2 to 0.7 m/min.
- A process window was established for the production of CF/PP towpregs with different Tex´s and pull speeds, for pultrusion of towpregs and Tapes and for heat compression moulding of GF/PP Tapes and pultruded profiles.
- More research must be done in order to increase the linear pull speed to processing by pultrusion of the towpregs as well as Tapes, and to improve the impregnation, uniformity and dispersion of raw-materials in the composites.
- The GF/PP composites processed by heated compression present better mechanical properties than those obtained by pultrusion.
- Mechanical properties of CF/PP pultruded profiles allowed to conclude that flexural strength and modulus are smaller with increasing pull speeds and carbon fibre Tex. The heated compression composites increased mechanical properties substantially in relation to the pultruded profiles, especially the ones pultruded at higher speeds and used carbon fibres with higher Tex.
- The mechanical properties obtained in all pultruded and compressed composites anticipate their adequate use either in general or in structural engineering applications.

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