Production of Powder-Coated Towpregs and Composites

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ABSTRACT: An efficient and cost-effective dry coating process was developed to deposit polymer powders on continuous fibers and produce thermoplastic matrix towpregs to be processed into composites. The technological solutions used in the coating line construction and the influence of the processing parameters on manufactured glass fiber reinforced polypropylene (GF/PP) towpregs are detailed in this paper.

Composites were produced from characterized (GF/PP) towpregs using hot plate compression molding. The mechanical properties determined on the composites are compared with theoretical values predicted by the Classical Lamination Theory (CLT) using the experimentally determined raw material contents and tensile properties.

KEY WORDS: powder-coating process, towpregs, reinforced thermoplastics, long fiber composites, glass fiber, polypropylene, compression molding, mechanical properties.

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Journal of THERMOPLASTIC COMPOSITE MATERIALS, *Vol. 16—May 2003* 231

0892-7057/03/03 0231–18 $10.00/0 DOI: 10.1177/089270503025872

INTRODUCTION

IN RECENT YEARS, continuous fiber reinforced thermoplastic matrix composites have been successfully employed in the aircraft, military and aerospace industries due to their excellent properties [1]. In these and many other commercial engineering applications, they can replace other materials, such as thermoset composites. Their principal advantages are excellent toughness, durability and damping properties, easier storage, possibility of continuous processing, reshaping, reparability and more favorable recycling and processing routes that do not involve chemical reactions [1–3]. However, the high cost of the impregnation of continuous fiber thermoplastic composites, arising from the melting of the polymer or the use of solvents, still restricts their use in commercial applications. Hence, cost reduction largely depends on developing more efficient methods of impregnating fibers with high-viscosity thermoplastics and processing final composite parts.

In the present work, an industrial scale dry coating process was developed to produce low cost pre-impregnated GF/PP towpregs [4,5]. The article describes the built powder-coating equipment and discusses the influence of the processing parameters on the manufactured towpregs. Compression molding was the technique used to assess the processability of the GF/PP towpregs.

Raw materials and produced composites were submitted to mechanical testing and the obtained properties compared with typical ones and with those calculated from CLT. The obtained results have shown that the manufactured materials had enough good properties to be used in common engineering structures.

THEORETICAL BACKGROUND

Fiber Testing

FIBER TENSILE PROPERTIES

In the present work, the glass fiber tensile strength was estimated as described in [6,7], performing single filament tensile tests [8] at several fiber gauge lengths, and fitting a two-parameter Weibull distribution to the experimental data. The Weibull cumulative distribution function used was adapted to take into account fiber strength dependence on length. This was achieved adopting the "weakest link" approximation, assuming that the fiber is formed by L independent links of arbitrary unit length, each link failing or surviving at a given stress level, independently of its neighbors. Considering the strength distribution of each independent link described by

a simple Weibull distribution, characterized by identical parameters, the Weibull cumulative distribution function $F(\sigma;\sigma_0,m)$ and the corresponding mean strength ($\bar{\sigma}$), may be described by Equations (1) and (2), respectively:

$$F(\sigma;\sigma_0,m) = 1 - \exp\left[-L\left(\frac{\sigma}{\sigma_0}\right)^m\right] \tag{1}$$

$$\bar{\sigma} = \sigma_0 L^{-1/m}\Gamma\left(1+\frac{1}{m}\right) \tag{2}$$

where σ is the fiber tensile strength, σ_0 and m are the Weibull scale and shape parameters, respectively, and Γ is the gamma function.

The parameter estimation for the Weibull distribution was performed with the strength data obtained for all gauge lengths simultaneously, using the "maximum likelihood" method as developed by Stoner [9,10], and the procedure described elsewhere [11] to study the behavior of carbon fibers. In this way, a single set of parameters that fit all the gauge lengths tested simultaneously was obtained [12]. The estimation of tensile strength at any gauge length was finally obtained by replacing the calculated parameters in Equation (2), for the specific fiber length.

To determine the fiber tensile modulus, the force/displacement curves obtained from the single-filament testing were used to calculate the total compliance, C_t, for each fiber by:

$$C_t = \frac{\Delta L}{F} \tag{3}$$

where ΔL is the displacement, in mm, and F the force, in N.

Then, the fiber compliance data were plotted as a function of L_o/A_o, where L_o is the fiber gauge length and A_o the fiber cross section. A least-squares line was fitted to the plotted data and a system compliance C_s obtained from the intersection of the line with $L_o = 0$, and used to calculate the true fiber compliance C_f by the equation:

$$C_f = C_t - C_s \tag{4}$$

Finally, the tensile modulus of the fiber was calculated by:

$$E_f = \frac{L_o}{A_o C_f} \tag{5}$$

Mechanical Properties of Composites

The tensile strength and modulus in the fiber direction of the GF/PP plates, σ_l and E_l, respectively, were predicted from the properties determined on the fibers and polymer by the well-known law of mixtures:

$$\sigma_l = \sigma_f v_f + \sigma_m(1 - v_f) \tag{5}$$

and

$$E_l = E_f v_f + E_m(1 - v_f) \tag{6}$$

where σ_f, E_f and v_f are the glass fibers tensile strength, modulus and the volume fraction, respectively, and σ_m and E_m are the polymer matrix tensile strength for the fiber strain-to-break and modulus.

EXPERIMENTAL

Raw Materials

The towpregs were produced using a polypropylene (PP) powder ICORENE 9184B P (supplied by ICO Polymers France) as matrix and 2400 Tex 357D-AA glass fibers as reinforcement (supplied by Owens Corning). Fibers and polymer have densities of 2.56 Mg/m^3 and 0.905 Mg/m^3, respectively. Furthermore, the PP supplier recommends the use of processing temperatures in the range of 280–290°C for this material.

Equipment and Procedure

POWDER-COATING LINE

The powder-coating equipment developed to produce the *towpreg* is composed by five modules (see Figure 1): (i) fiber supplying system; (ii) pneumatic spreader; (iii) polymer powder feeder and coating chamber; (iv) furnace and (v) final towpreg wind-off system.

Using this equipment, the fibers pulled from the roving are spread using an acrylic pneumatic device. Then, the thermoplastic powder continuously supplied by an extruder coats the spread fibers in the deposition chamber. The three rolls mounted in the deposition chamber give the possibility of increasing the amount of deposited powder. The excess of powder is re-circulated using an air-fan located at the bottom of the deposition chamber to maintain a polymer cloud. A thermocouple associated to an air-heater allows control of the temperature inside the chamber. Next, to soften the polymer and promote its adhesion to the fiber surface, the material is passed through a furnace. Finally, the thermoplastic matrix towpreg is cooled down and wound up on the final spool.

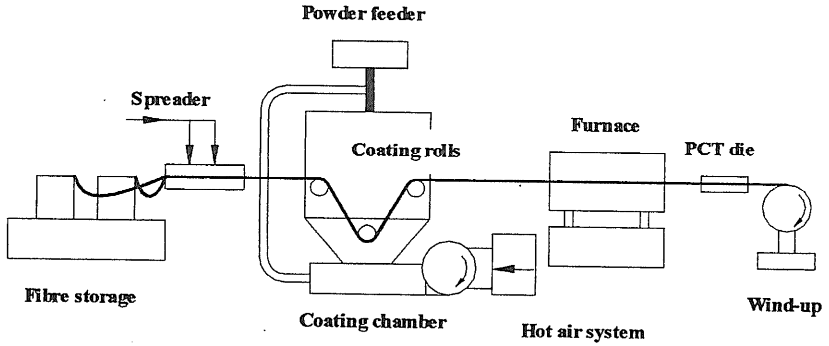


Figure 1. Schematic diagram of the powder-coating line.

Compared to other pre-existing equipments [2,13–15], the developed coating line presents the following advantages [4,5]:

1. a new fiber supplying system allowing the use of interior unwound common rovings
2. elimination of the system to control the pull-fiber tension
3. use of a new fiber spreading system allowing to improve the separation of filaments
4. a more favorable design of deposition chamber, which avoids the circulation of the polymer powder through the interior of the fan
5. possibility of controlling the temperature inside the coating chamber
6. use a more compact wind-off system that allows an easier positioning and removal of the final towpregs.

The fiber supplying system shown in Figure 2 consists of an aluminium structure manufactured in a 45 × 45 L Bosch standard profiles.

Figure 3 shows the acrylic pneumatic spreader used in the coating line. To separate the fibers in small filaments a 500 kPa air flux was forced to pass through a properly located system of injectors.

A variable speed (0–79 rpm) mini double-screw Brabender extruder is used to feed the polymer powder. As Figure 4 shows, the polymer powder that falls in the deposition chamber is re-circulated using the pre-heated air flux generated by a variable flow-rate centrifugal fan with 1000 m^{3}h^{-1} of maximum flow-rate from Sodeca (ref. CMP-514-LT). The air temperature can be varied between 20 and 60°C. Three rolls were conveniently placed inside the coating chamber to increase the path and consequently the time and amount of thermoplastic deposited on the fibers.

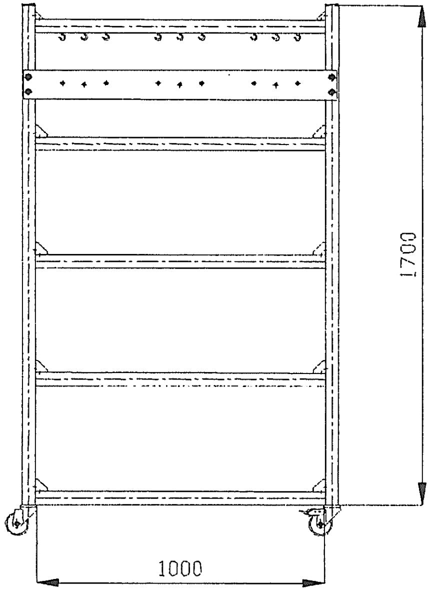


Figure 2. Fiber tow holder.

The manufactured 1000°C maximum temperature furnace used to soften the thermoplastic powder deposited on the towpreg surface can be seen in the equipment overview shown in Figure 5. Finally, the variable speed motor-reducer shown in Figure 6 enables the towpreg wind-up.

Table 1 shows the typical coating line operating conditions used to produce towpregs in this work.

Table 1. ***Typical coating line operational conditions.***

Variable	Units	Value
Linear fiber pull speed	m/min	0.7–1.2
PP Powder feeder	g/min	11.8
Fan speed	rpm	825
Furnace temperature	°C	240
Coating chamber temperature	°C	50
Spreader pressure	kPa	500

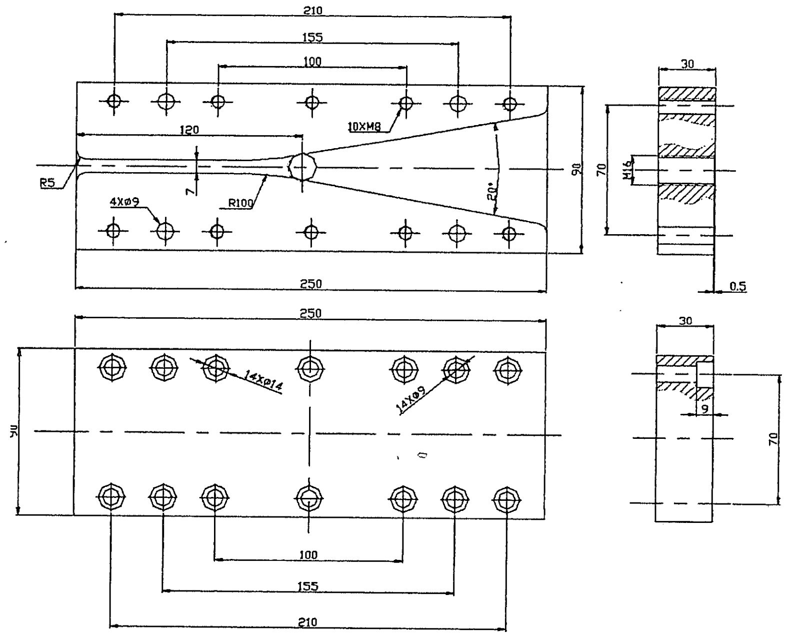


Figure 3. Pneumatic spreader.

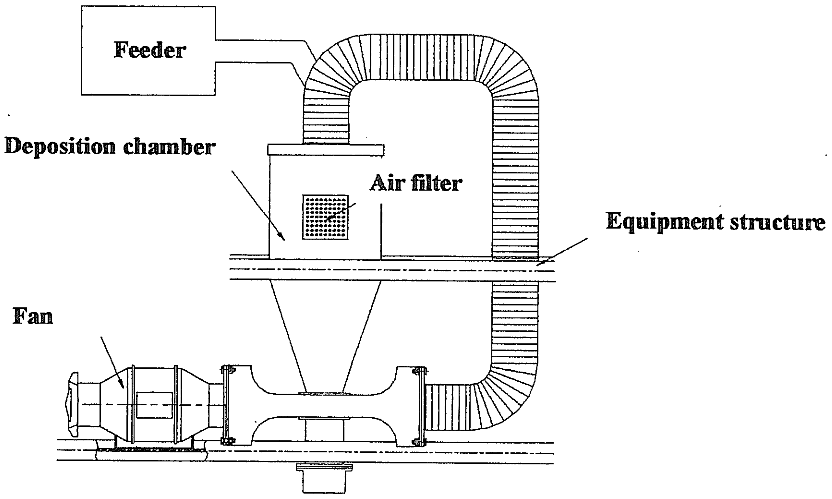


Figure 4. Polymer powder feeder and deposition chamber.

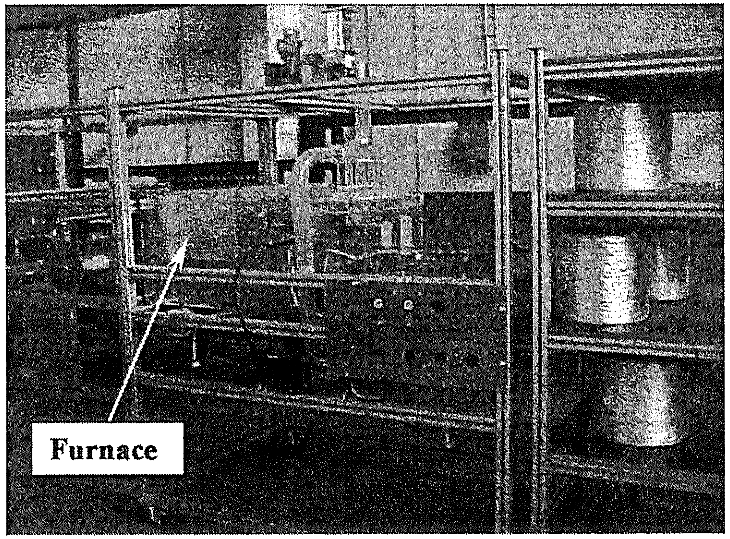


Figure 5. Furnace and general overview of the developed equipment.

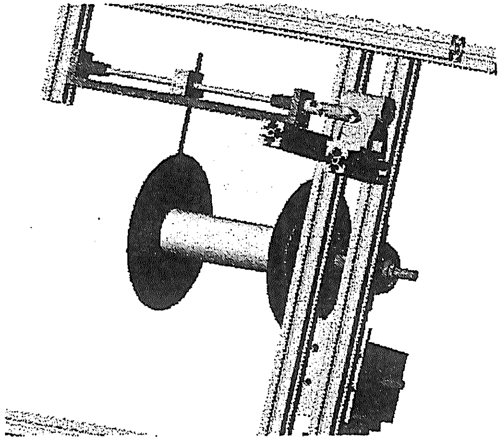


Figure 6. Final wind-up assembly.

Recently, to allow the increase of towpreg processability, a new final die was introduced in the powder-coating line [16,17] to produce Pre-impregnated Coated Tapes (PCT) (Figure 7). The main components introduced in the equipment were: (i) a coating chamber temperature

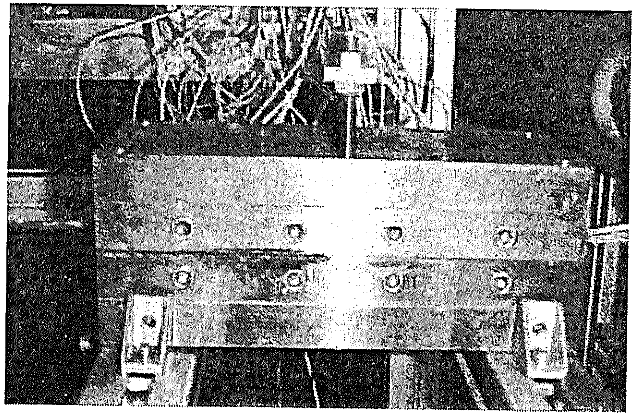


Figure 7. PCT die.

control and air heating system, (ii) three new rolls in the deposition chamber that allow the increase in the amount of deposited powder and (iii) a new final die to produce the PCT.

This final die allows pressurization and consolidation of the produced towpreg, at the desired temperature, just before the final wind-up, in order to obtain a pre-impregnated tape. The PCTs were produced in this work using temperatures of the die between 240 and 280 (°C) and typically mentioned in Table 1.

TOWPREG CONSOLIDATION

Towpreg laminate plates (100 mm × 100 mm × 2 mm), were produced using a technique described elsewhere [15]. Firstly, about 15 m of towpreg was wound up over an aluminium plate with the dimensions shown in Figure 8. Then, the towpreg was conveniently placed in the cavity of a heated and water cooled mold. A 400 kN SATIM hot plate press was used to obtain the desired consolidation pressure.

After heating the cavity up to 230°C a pressure of 15 MPa was applied for 10 min with the SATIM press. Finally, the mold was cooled down to room temperature and the final laminate plate removed. Plates with approximately 2 mm thickness were produced in these conditions (see Table 2). As the typical photo in Figure 9 clearly shows, fiber misalignments larger than the expected 3° can be easily observed with naked eye in the produced plates. In this figure, great irregularities can be also seen in fiber distribution along the produced plate surfaces (areas quite rich in fibers contrasting with polymer-rich areas).

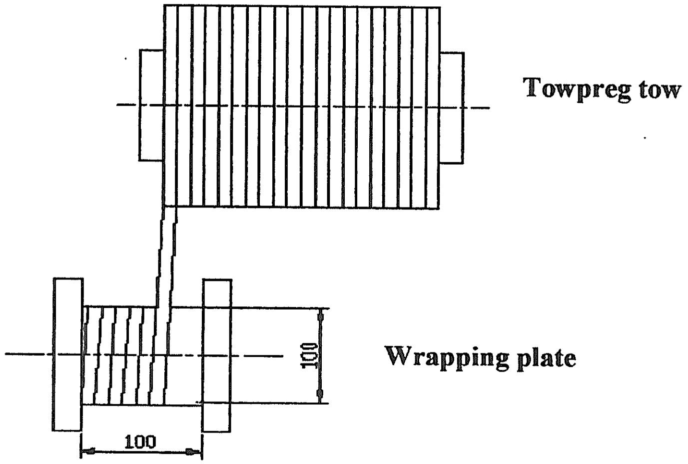


Figure 8. Wrapping technique used in the towpreg lay-up.

Table 2. ***Towpreg processing conditions.***

Variable	Units	Value
Mold temperature	°C	230
Pressure	MPa	15
Compression time	min	10

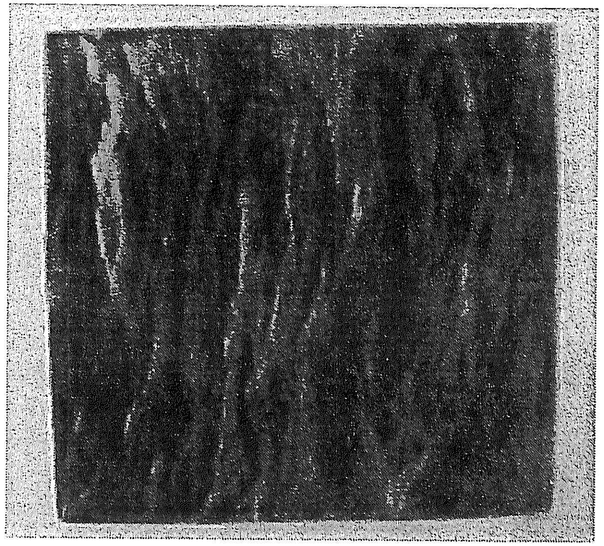


Figure 9. General aspect of a produced plate.

RESULTS AND DISCUSSION

Raw Materials Characterisation

MICROSCOPY AND SIEVING TECHNIQUE FOR THE CHARACTERIZATION OF THE PP POWDER

The PP powder size distribution was determined using sieving and microscopy techniques. Tests were made using eight 200 mm diameter sieves and aperture sizes progressively lower (numbers between 30 and 230 and a receiver) corresponding to 600, 425, 300, 250, 180, 125, 90, 63 and 0 μm. An initial weight of 100 g PP powder was passed through the sieves to determine the mass of particles retained in each one after 15 min vibration.

Figure 10 shows the obtained accumulative frequencies in terms of mass and particle number. Median particle diameters of 136 and 398 μm were obtained from these results taking into account the number of particles and their mass, respectively.

The shape of PP particles was observed under a Leica S360 scanning electron microscope (SEM). Figure 11 shows that PP particles with highly irregular shape and size were typically observed.

POLYPROPYLENE TENSILE TESTING

The tensile properties of the PP matrix were determined at room temperature using an Instron 4208 universal testing machine. Five type I test pieces with 150 mm × 8 mm × 2 mm (according to ISO 3268/78) were obtained from compression-molded plates of the powder material to be tested. The tests were conducted at a crosshead speed of 2 mm/min. A biaxial MTS 632.85 extensometer was used to determine the Poisson's ratio.

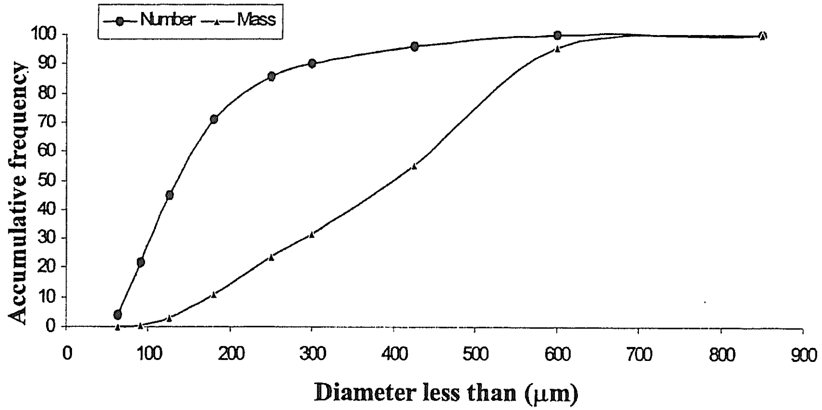


Figure 10. Sieving results in terms of mass and particle number accumulative frequencies.

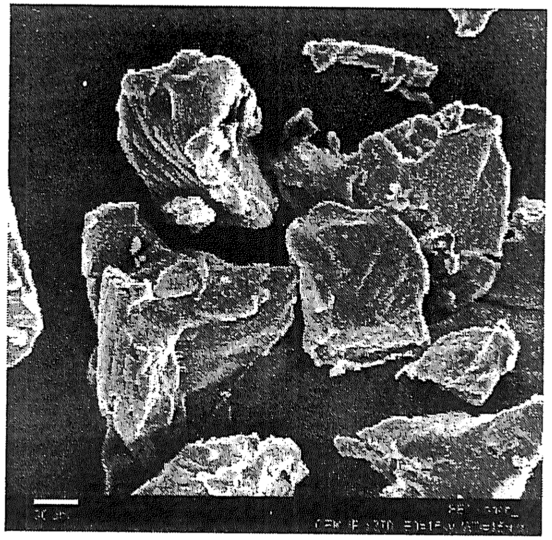


Figure 11. Micrograph of the PP powder under SEM (magnification of 270×).

Table 3. **Polypropylene tensile test results.**

Property	Units	Test Piece Reference					Average Result	Standard Deviation
		PP_1	PP_2	PP_3	PP_4	PP_5		
Tensile strength	MPa	19.2	17.8	19.8	19.0	19.4	19.0	0.75
Young's modulus (E)	GPa	1.12	1.00	1.00	0.930	0.839	0.978	0.10
Modulus at 1% strain	GPa	1.07	0.940	0.943	0.895	0.802	0.940	0.098
Poisson ratio (ν)	–	0.20	0.23	0.20	0.22	0.22	0.21	0.01

Table 3 shows the final tensile properties obtained. Those properties are in agreement with the typical ones for generic PP.

FIBER TENSILE TESTING

The properties of the fibers were assessed by tensile testing single filaments at three different gauge lengths. The test method used was adapted from the ASTM standard [8].

The diameter of the fibers was determined by a laser diffraction technique, with a 10 mW He–Ne laser beam [18].

The tensile tests were performed in an Instron 4505 testing machine equipped with a load cell of 2.5 N, at a crosshead speed of 0.5 mm/min. Fiber modulus and strain-to-break values were corrected to account for the compliance of the testing system [7,10].

The single filament tensile test data for the glass fibers are presented in Table 4. The tensile strength results show a slight decrease with increasing gauge length, as expected.

The estimated Weibull parameters that fit the experimental results of strength at all gauge lengths studied were 3.3 and 4.9 for the shape (m) and scale (σ_0) parameters, respectively. As Figure 12 shows, the fiber strength is largely dependent on the fiber length.

TOWPREG CHARACTERIZATION BY SEM

Several samples of the GF/PP towpreg were analyzed with a Leica S360 scanning electron microscope to evaluate the distribution of the PP powder and its adhesion to the fibers. Figure 13 shows two representative SEM micrographs.

As can be seen, the polymer is seen to wet and surround the glass fibers, suggesting good adhesion. The PP particles, with a much larger size than the

Table 4. **Single filament tensile test data.**

No. Fibers Tested	Diameter (μm) ± S.D.	Gauge Length (mm)	Tensile Strength (GPa) ± S.D.	Strain at Break (%) ± S.D.	Tensile Modulus (GPa) ± S.D.
43	13.7 ± 2.0	20	1.7 ± 0.5	1.5 ± 0.1	62.5 ± 13
48	13.7 ± 2.0	40	1.4 ± 0.5	1.7 ± 0.5	62.5 ± 13
42	13.7 ± 2.0	60	1.3 ± 0.5	1.6 ± 0.4	62.5 ± 13

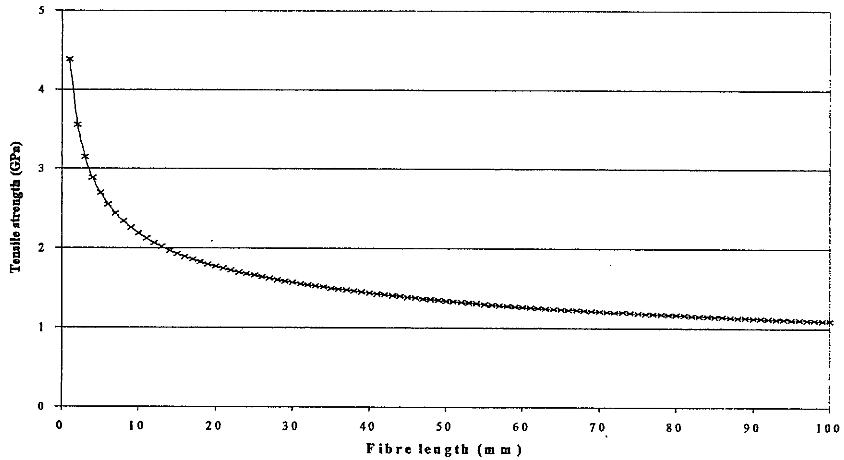
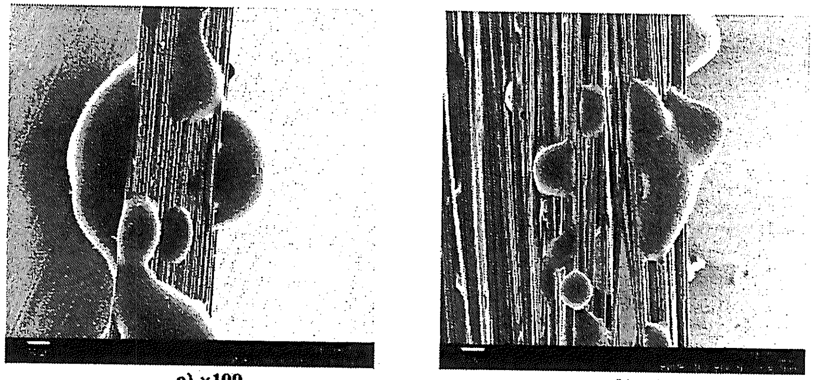


Figure 12. Dependence of the glass fiber strength on length.



a) ×100

b) ×100

Figure 13. *Micrographs of the GF/PP towpreg made with a polymer particle median size of 136 μm under SEM (magnification of 100×).*

fiber diameter, tend to become quasi-spherical as consequence of the surface tension of the softened PP.

Powder-Coating Line Processing Conditions

To study the influence of the amount of polymer deposited on the towpregs and to optimize the coating line processing conditions, the following parameters were varied: linear fiber pull speed, temperature and moisture in the coating chamber and PP powder particle. After varying each parameter, approximately 100 m of towpreg were weighted and the PP mass fraction determined using the density of the components.

The results are summarized in Figure 14. As can be seen, the polymer powder particle size and moisture have a great influence on the polymer mass fraction of the towpregs. The amount of deposited PP increases with the increment of moisture and particle size until values of the relative humidity and particle average diameter around 80% and 400 μm were reached, respectively.

Such results lead us to conclude that it is necessary to control moisture and temperature in the coating chamber. On other hand, it will also be desirable to control the particle size of the polymer to be used.

Composites Mechanical Testing

Five tensile specimens with dimensions of 100 mm × 20 mm × 2 mm were tensile tested in the fiber direction, at room temperature, using an Instron 4505 universal testing machine. The test was conducted at a crosshead speed of 1 mm/min. The elongation was determined by using a 10 mm Instron extensometer.

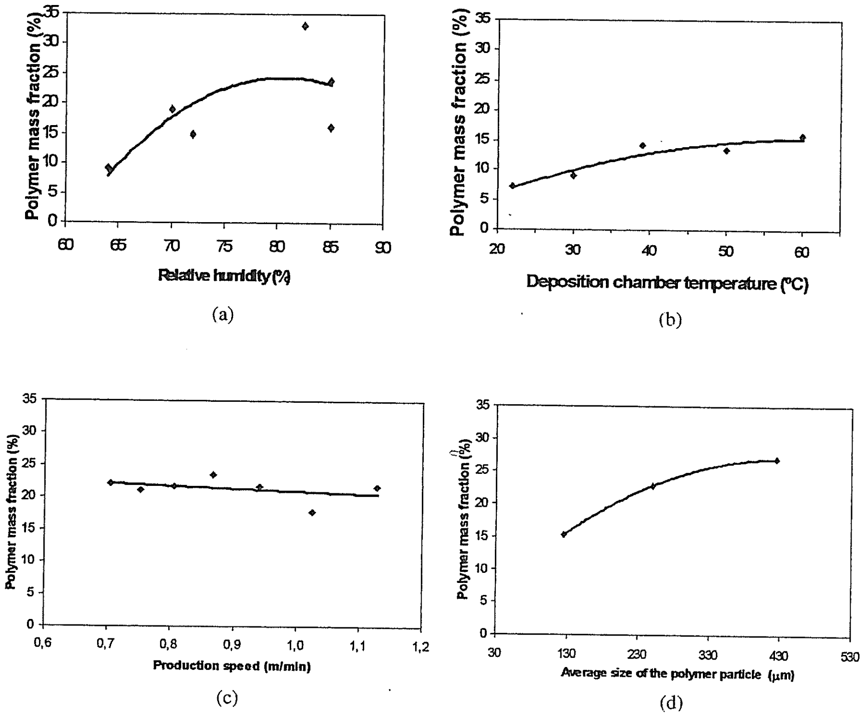


Figure 14. *Influence of the processing conditions on polymer mass fraction in towpreg. (a) Influence of moisture; (b) Influence of deposition chamber temperature; (c) Influence of the linear production speed; (d) Influence of the polymer particle size.*

Three-point bending tests were also conducted in the same testing equipment on five 120 mm × 15 mm × 2 mm specimens according to ISO 178 at 2 mm/min, using a distance between supports of 80 mm.

The mechanical properties were compared with those predicted by using Equations (5) and (6). In the prediction the following experimental properties were considered: $v_f = 0.673$, $E_f = 62.5\,\text{GPa}$, $\sigma_f = 1165\,\text{MPa}$, $E_m = 0.978\,\text{GPa}$ and $\sigma_m = 15.6\,\text{MPa}$. The value of σ_f at 80 mm gauge length was calculated by Equation (2) using the Weibull estimated parameters $m = 3.3$ and $\sigma_0 = 4.9\,\text{GPa}$. This corresponds to the length of the constant cross section part of the tensile specimens where a constant stress is applied to the fiber and to the distance between supports in the three-point bending tests.

Table 5. Consolidated laminate properties.

		Values			
		Experimental Results		Theoretical Expected Results	
Property	Units	Average	S.D.	Average	S.D.
Tensile strength	MPa	> 115	2.8	789	80
Tensile modulus	GPa	34.1	5.8	42.4	8.8
Flexure strength	MPa	66.3	9.4	790	80
Flexure modulus	GPa	24.7	2.6	42.4	8.8
Fiber mass fraction	(%)	85.6	1.6	85.6	–
Fiber volume fraction	(%)	67.3	2.9	67.3	–

Table 5 shows that the mechanical properties obtained experimentally are compatible with major commercial applications. The tensile strength results obtained may not be directly compared with the theoretical expected ones because specimens in general suffered grip breakage and due to the important fiber misalignments observed in the plates (see Figure 9). As the flexure breakage occurred by delamination in the section under the charging roll, the flexural strength results may not also be considered as valid ones.

However, the more representative values for laminate tensile modulus is fairly good if one takes into account the already referred to fiber misalignment. In fact, values slightly lower than the theoretical ones expected for a completely unidirectional laminate were obtained in the produced plates.

The lower value for the modulus obtained in bending seems to reflect an insufficient interlaminar adhesion. As this can be directly related with an incomplete consolidation, further research must be done on the optimization of consolidation conditions.

The values of fiber mass content shown in Table 5 were obtained from burn-off of the tensile and flexural tested samples according to EN 60. The correspondent fiber volume content was calculated using the fiber and polymer densities of 2.60 and 0.905 $\mathrm{Mg/m^3}$, respectively.

Equations (5) and (6) were used to derive the theoretical expected values for the axial strength and modulus, respectively.

CONCLUSIONS

The powder-coating line developed in the present work produces continuous cost-effective thermoplastic matrix towpregs and PCTs with desired fiber contents by varying the linear pull-speed. It has been shown that the coating chamber temperature and moisture are the major factors affecting the towpreg's final characteristics. In spite of its influence on the final product properties, the polymer power particle size has much slighter effect in the polymer deposition rate on the towpregs.

The first composites produced by compression molding from towpregs and PCTs seem to have an acceptable fiber–polymer adhesion. They presented also mechanical properties compatible with their use in the major commercial applications. Also, a fairly good laminate tensile modulus was obtained by taking into account the high fiber misalignment observed in the tested plates. However, as a lower value of modulus was obtained from the bending test, which seems to reflect insufficient interlaminar adhesion, making evident the need for further research in composite consolidation conditions.

ACKNOWLEDGMENTS

The authors are indebted to Pedro Vieira and Dirk Ronsijn for their technical support on experimental testing. This work was financially supported by the European Union/Portuguese Government funded Project Praxis XXI, *Development of New Technologies of Production and Characterization of Polymer Matrix Composites – An Integrated Project (PULTRU)*.

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