1 Introduction

The aim of the present work was to study and compare the processing conditions and final mechanical properties of continuous glass-fiber reinforced polypropylene composites (GF/PP) manufactured by using available thermoplastic pre-impregnated materials produced by different methods.

In the last years, thermoplastic matrices have been replacing with success thermosetting matrices in long/continuous fiber reinforced composites in almost markets due to the numerous advantages they present. However, it remains a challenge developing cost-effective technologies to allow wetting and impregnating fibers with thermoplastic matrices, characterized for being much more viscous than thermosets [1-3].

Today, two major technologies are being used to allow wet reinforcing fibers with thermoplastic polymers [2, 3]: i) the direct melting of the polymer and, ii) the intimate fiber/matrix contact prior to final composite fabrication. Continuous fiber reinforced thermoplastic matrix pre-impregnated tapes are, for example, produced by direct melting processes. Alternatively, intimate contact processes allow producing cheap and promising pre-impregnated materials, such as, commingled fibers, co-woven fabrics and towpregs.

This work studies and compares the processability of final composite parts by using three different pre-impregnated materials produced by each one of both above mentioned wetting techniques. All studied pre-impregnated materials were based on a continuous glass fibers reinforced polypropylene matrix (GF/PP) system. One is a pre-consolidate tape (Fig. 1 b)) that was produced by the melting process (cross-head extrusion) in a previous work [4] and, from the other two produced by fiber/matrix intimate contact methods, one is a commercial available commingled fibers product (Fig. 1 c) and the other a towpreg (Fig. 1 a)) produced by our own developed dry coating prototype line [5]. Pultrusion and compression molding were the selected manufacturing methods for processing all these pre-impregnated materials into composite parts.

To assess the quality of the three different GF/PP pre-impregnated materials, the final manufactured composite parts were finally submitted to mechanical testing and microscopy analysis. The obtained properties were compared between each other and to those theoretical ones that can be predicted by using the Classical Lamination Theory (CLT).

2 Experimental

2.1 Raw Materials

The following raw materials were used to produce GF/PP pre-impregnated materials in the course of
this work: i) a PP powder ICORENE 9184B P® and Type E glass fiber direct rovings 305E-TYPE 30® from the ICO Polymers and Owens Corning, respectively, were used to produce the GF/PP towpregs (Fig. 1 a)), ii) the PP Moplen RP348U® and the type E glass fiber roving TufRov 4599® from the Basell and PPG Industries, respectively, were used to manufacture the GF/PP tapes (Fig. 1 b)). Tables 1 and 2 present the properties of these raw-materials.

The commercial available Twintex® R PP 60 B 1870 FU from Owens Corning was the commingled fibers product used (see Fig. 1 c)). Table 3 shows properties of this product mentioned in the manufacturer datasheets.

Being well-known that maleic anhydride usually enhances the fiber/matrix adhesion [6-10], some batches of GF/PP towpregs were also produced using the PP powder (ICORENE 9184B P®) additivated with 1% mass content of maleic anhydride, S 47 29608 707® from Merck Schuchardt OHG, to confirm that effect.

2.2 Production of Thermoplastic Matrix
Pre-Impregnated Products

The GF/PP towpregs were produced in a developed dry powder coating equipment schematically shown in Fig. 2 and illustrated in the photo of Fig. 3 [5, 11]. 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.

To try maximizing the polymer powder content in the 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.

The polymer mass fraction in the towpregs, \( \omega_p \), was determined by weighting towpreg strips produced in those different conditions and using the following equation:

\[
\omega_p = \frac{W_t - W_f}{W_t} \tag{1}
\]

where \( W_t \) and \( W_f \) are the measured unit length weights of the towpreg strip and fiber roving, respectively.

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 30.0 % ± 7.2 %.

Unexpectedly, very low polymer mass fractions (~10% - 16%) were obtained when the PP powder add with 1% of maleic anhydride was used in the production of the GF/PP towpregs. Thus, the idea of using this additive to improve adhesion of the PP matrix to the glass fibers was abandoned.

The GF/PP pre-consolidated tapes (PCT) used in this work were, on other hand, produced in a cross-head extrusion equipment (see Fig. 4) from our own laboratories [4]. The core of this technology is an impregnation unit where the glass fibers are introduced, spread and impregnated by the polymer melt. Impregnation is achieved by building-up the pressure acting on the molten polymer trapped between the unit’s spreading elements and the fiber rovings.

The apparatus consists of a creel holding system for fiber rovings, a guidance unit allowing an adequate transport of fiber into the impregnation section, an extruder to melt and feed the molten polymer into the impregnation unit, the impregnation unit itself and, subsequently, a cooling unit, a puller, and a take-up device where the composite tape is collected. An overview of main properties of the PCTs produced by this means is given in Table 4.

Today, some pre-consolidated thermoplastic matrix tapes (PCTs) produced in similar way are commercially available through the company Comp Tape Lda. [12].

2.3 Composites Processing

All three GF/PP pre-impregnated materials were then process into composite bar profiles and plates
by pultrusion and heated compression molding, respectively. A prototype pultrusion line (Fig. 5) [13] and a 400 kN Moore hot platen press were used to all these fiber reinforced thermoplastic matrix pre-impregnated products.

2.3.1 Pultrusion

Our own developed 10 kN pultrusion equipment, schematic depicted in Fig. 6, 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.

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. The pre-heating furnace may reach a temperature of 1000 °C and was designed to allow processing almost every type of fiber/thermoplastic-based pre-impregnated materials. A rectangular 20 × 2 (mm) die was used in the present work to produce a tape-shaped thermoplastic matrix composite profile.

Twenty pre-impregnated towpreg rovings were used to process the rectangular 20 × 2 (mm) composite pultruded profiles from the towpregs. To determine the best processing window, the main processing conditions were varied following ranges by maintaining the cooling die at 25 ºC:
- pre-heating temperature (ºC): 170 - 180
- press./consolidation die temperature (ºC): 240 - 300
- linear pultrusion speed (m/min): 0.2 - 0.4

Results have shown that was not possible to produce in steady conditions pultruded profiles from towpregs at pultrusion speeds and pressurization/consolidation die temperatures higher than 0.3 m/min and 280 ºC, respectively. By using higher values in these two parameters the process became unsteady mainly due to high level of fiber breakage between dies and reflux and accumulation of the thermoplastic polymer at entrances of the pressurization/consolidation and cooling dies, respectively (see Fig. 7). The same processing problems occurred when temperatures below 270º C were used in the pressurization/consolidation die and, because of that, it was decided maintaining constant the temperature of 280 ºC in this die.

By maintaining constant the temperatures in the cooling and pressurization/consolidation dies at 25 ºC and 280 ºC, respectively, composite profiles pultruded in different processing conditions were submitted to the flexural tests, as described in next paragraph 2.4, for optimizing the above mentioned processing variables in order to obtain the profiles presenting best mechanical performance. As may be seen from the obtained results summarized in Table 5, very similar values of flexural moduli and strengths were found by using pre-heating furnace temperatures and linear pultrusion pulling speeds in the ranges of 170 - 180 (ºC) and 0.2 - 0.3 m/min, respectively. While the slower pultrusion pulling speed of 0.2 m/min seemed to generate profiles with higher absolute values, this was not confirmed by the flexural properties divided by the determined fiber volume fraction depicted in two last the columns of Table 5. On the other hand, higher flexural strength values, both in absolute and relative terms, were obtained at the higher temperature of 180 ºC in pre-heating furnace.

Thus, it was concluded to use as optimal pultrusion operating window the following one:
- pre-heating temperature (ºC): 170 - 180
- press./consolidation die temperature (ºC): 280
- cooling die temperature (ºC): 25
- linear pultrusion speed (m/min): 0.2 - 0.3

The same above mentioned processing window was used to process, without major difficulties, rectangular 20 × 2 (mm) composite pultruded profiles from the both other thermoplastic matrix pre-impregnated materials studied in this work: the GF/PP tapes and Twintex® commingled fibers.

2.3.1 Heated Compression Molding

In the present work, all the three different GF/PP thermoplastic fiber reinforced pre-impregnated products studied were also processed into rectangular 180 × 180 × 2 (mm) composite plates. After having been cut and weighted all pre-impregnated were introduced in a 180 × 180 (mm) cavity placed between the heated platen of a 400 kN
Moore press. After a 10 min delay at press platen temperature, the press was closed until reaching the maximum compression force of 200 kN. One minute after reaching the maximum force, the press platen were cooled down maintaining constant the press closing force. When the temperature of 30 ºC was reached, the press platen were opened and the final composite plate finally removed from the mold. Thus, the unidirectional fiber reinforced composite plates were produce by using the following processing conditions:
- press platen temperature (ºC): 250
- pre-heating time (min): 10
- press closing force (kN): 200
- delay at maximum closing force (min): 1.0
- opening platen temperature (ºC): 30

2.4 Composites Testing

The final manufactured composites were tested to determine their glass fiber mass content and flexural, tensile and interlaminar mechanical properties. Their cross-sections were also analyzed under optical microscopy to evaluate the fiber distribution and fiber/matrix adhesion.

2.4.1 Testing Procedures

Glass fiber mass content in the composites was determined by using calcination tests according to the EN ISO 1172 standard. After calcining the composite sample inside a crucible in a furnace at 600 ºC, the glass fiber mass fraction, \( \omega_f \), was obtained by:

\[
\omega_f = \frac{m_3 - m_1}{m_2 - m_{1t}}
\]

where \( m_1, m_2 \) and \( m_3 \) are the measured crucible and composite sample plus crucible initial weights and the final measure weight of crucible plus residue. Furthermore, by knowing the fiber and polymer densities, \( \rho_f \) and \( \rho_p \), respectively, the fiber mass fraction (\( \omega_f \)) may be converted in fiber volume fraction (\( \nu_f \)) by:

\[
\nu_f = \frac{\omega_f / \rho_f}{\omega_f / \rho_f - (1 - \omega_f) / \rho_f}
\]

Tensile tests were conducted according to the ISO 527 standard in a 100 kN Shimadzu universal testing machine at the crosshead speed of 2 mm/min using a 50 mm Shimadzu strain gauge. Well-known Eq. 4 was used to determine composite stress, \( \sigma \), as:

\[
\sigma = \frac{F}{S}
\]

where \( F \) and \( S \) are the measured force and sample cross section area, respectively.

The tensile modulus, \( E_t \), was determined from the slope of the initial linear portion of the experimental stress/strain curve acquired from the tensile test. Three-point flexural tests were also conducted on five \( 110 \times 15 \times 2 \) (mm) composite specimens, using 100 kN Shimadzu universal testing machine and a distance between supports of 80 mm, according to ISO 14125 standard at the crosshead speed of 1 mm/min. The flexure stress, \( \sigma_f \), was determined from Eq. 5:

\[
\sigma_f = \frac{3 \cdot F \cdot L}{2 \cdot l \cdot h^2}
\]

where \( F, L, l \) and \( h \) are the applied force, distance between supports and sample width and thickness, respectively. The flexure modulus, \( E_f \), was also determined by:

\[
E_f = \frac{l^3 \cdot m_d}{4 \cdot l \cdot h^3}
\]

where \( m_d \) is the initial linear slope of the force versus displacement acquired from the flexural test. Samples with dimensions of \( 20 \times 15 \times 2 \) (mm) cut from the compression molded composites plates were submitted to interlaminar shear tests according to ASTM D2344 standard. The tests were conducted in a 50 kN Shimadzu universal testing machine by using an initial pre-charge of 1 N at the crosshead speed of 1 mm/min and a 10 mm span between supports. The interlaminar shear strength, \( F_{SBS} \), has been determined as:

\[
F_{SBS} = 0.75 \cdot \frac{P_m}{b \cdot h}
\]

where \( P_m, b \) and \( h \) are the maximum failure force and the sample width and thickness, respectively.
2.4.2 Discussion of Results

Table 6 summarizes all results obtained from the unidirectional composites processed by pultrusion and compression molding from the pre-impregnated products under study. The high strength of unidirectional composite specimens didn’t permit break them in the tensile tests made in fiber direction due to grip slippage and, due to that, their respective tensile strengths are not shown in the table.

To better evaluate and compare the mechanical properties obtained on the composites processed from the different pre-impregnated products studied, Table 6 also presents theoretical expected values and relative values of those properties divided by the obtained fiber volume fraction, from which they are supposed to be linearly dependents.

The theoretical values of moduli, $E$, and strengths, $\sigma_{ult}$ were directly obtained from the rule of mixtures by using the raw-materials properties presented in Table 1 as can be seen in the following Eqs. 8 and 9:

$$E = E_f \cdot v_f + E_p \cdot (1 - v_f) \tag{8}$$

$$\sigma_{ult} = \sigma_{fult} \cdot v_f + \sigma_{pult} \cdot (1 - v_f) \tag{9}$$

where, $E_f$, $E_p$, $\sigma_{ult}$, $\sigma_{ult}$ are the fiber modulus, polymer modulus and fiber and polymer matrix tensile strengths, respectively.

As the raw-materials presented in Table 1 were not used to manufacture the commingle fibers Twintex® and PCTs, the theoretical predictions for properties of the composites made from these materials may present more important deviations from the real values obtained.

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

From results in Table 6 it is possible concluding that commingled fibers Twintex® presented, in general, better properties and had also shown to be more adjusted to commercial application demands and adapted for being easily processed into final composites by the currently used manufacturing methods, probably because they have already been available for longer time in the market.

Nevertheless, the GF/PP pre-impregnated products produced in our laboratories (towpregs and PCTs) have already demonstrated to have very good mechanical behavior, namely, in terms of stiffness. In fact, the composites manufactured from these products presented experimental moduli values very nearby 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 plus 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.

As Fig. 8 shows, under optical microcopy still was possible distinguish important discontinuities on the cross section of composites pultruded from towpregs, where it may be seen zones very rich in polymer contrasting with others with much greater quantity of fibers.

Finally, it may be noted that any of composites made from the towpregs and PCTs 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 Table 6 correspond to maximum force applied in the test. It must be also referred that values of interlaminar shear strength for composites processed from the commingled fibers Twintex® don’t appear on Table 6 because such composites were not submitted to interlaminar shear tests.

3 Conclusions

Three different commercial promising glass fiber reinforced thermoplastic matrix pre-impregnated materials were easily processed by pultrusion and compression molding in the present work: a commercial available GF/PP commingled fibers product and also GF/PP towpregs and tapes manufactured in our own laboratories.

The production of and processing of GF/PP towpregs and tapes were optimized.

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 fibers Twintex® presented slight better mechanical properties and have shown
to be more adjusted for composite processing than the other pre-impregnated products due to being already for longer time in the market.

More research must be done to try increasing the processing speeds of GF/PP towpregs and tapes and improve the uniformity and dispersion of raw-materials in the composites made from the towpregs.

Acknowledgments

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References


Tables

Table 1. Properties of GF/PP Towpregs raw-materials

<table>
<thead>
<tr>
<th>Property</th>
<th>PP powder (ICORENE 9184B P®)</th>
<th>Glass fiber (305E-TYPE 30®)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manufacturer datasheet</td>
<td>Experimental</td>
<td>Experimental</td>
</tr>
<tr>
<td>Linear density (Tex)</td>
<td>-</td>
<td>2400</td>
</tr>
<tr>
<td>Specific gravity (Mg/m³)</td>
<td>910</td>
<td>2650</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>30¹</td>
<td>3500</td>
</tr>
<tr>
<td>Young Modulus (GPa)</td>
<td>1.3</td>
<td>76</td>
</tr>
<tr>
<td>Poisson’s ratio</td>
<td>-</td>
<td>0.26</td>
</tr>
<tr>
<td>Average powder particle size (µm)</td>
<td>440</td>
<td>-</td>
</tr>
<tr>
<td>Average fiber diameter (µm)</td>
<td>-</td>
<td>17</td>
</tr>
</tbody>
</table>

¹ Yield Strength

Table 2. Properties of the raw-materials used to produce GF/PP tapes accordingly to manufacturers datasheets

<table>
<thead>
<tr>
<th>Property</th>
<th>PP granules (Moplen RP348U® from Basell)</th>
<th>Type E Glass fiber roving (TufRov 4599® from PPG)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manufacturer datasheet</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Linear density (Tex)</td>
<td>-</td>
<td>2400</td>
</tr>
<tr>
<td>Specific gravity (Mg/m³)</td>
<td>900</td>
<td>2540-2600²</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>30²</td>
<td>1900-2400²</td>
</tr>
<tr>
<td>Young Modulus (GPa)</td>
<td>1.1</td>
<td>69-76b</td>
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<tr>
<td>Average fiber diameter (µm)</td>
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<td>17</td>
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</table>

² Yield Strength

Table 3. Twintex® R PP 60 B 1870 FU from Owens Corning

<table>
<thead>
<tr>
<th>Property</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear density (Tex)</td>
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<td>Tensile strength (MPa)</td>
<td>760</td>
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<td>Young Modulus (GPa)</td>
<td>29.5</td>
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<td>Fiber mass content (%)</td>
<td>60</td>
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</table>
Table 4. Overview of the main properties of the produced pre-consolidated tapes (PCTs)

<table>
<thead>
<tr>
<th>Property</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>Fiber type</td>
<td>E-Glass, 2400 Tex</td>
</tr>
<tr>
<td>Filament diameter</td>
<td>17 µm</td>
</tr>
<tr>
<td>Fiber content</td>
<td>60 wt.%</td>
</tr>
<tr>
<td>Matrix type</td>
<td>Polypropylene (PP)</td>
</tr>
<tr>
<td>Tape width</td>
<td>25 mm</td>
</tr>
<tr>
<td>Tape linear density</td>
<td>16000 Tex</td>
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Table 5. Influence of pultrusion conditions on the flexural properties of profiles made from towpregs

<table>
<thead>
<tr>
<th>Pultrusion conditions</th>
<th>Flexural properties</th>
<th>Fiber content</th>
<th>Flexural properties / fiber volume fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Modulus (GPa)</td>
<td>Strength (MPa)</td>
<td>Mass (%)</td>
</tr>
<tr>
<td>Pre-heating temperature (°C)</td>
<td>Pultrusion speed (m/min)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>170</td>
<td>0.2</td>
<td>29.1±0.6</td>
<td>149.2±14.4</td>
</tr>
<tr>
<td>170</td>
<td>0.3</td>
<td>28.6±1.2</td>
<td>142.3±16.2</td>
</tr>
<tr>
<td>180</td>
<td>0.2</td>
<td>29.5±0.1</td>
<td>156.1±5.1</td>
</tr>
<tr>
<td>180</td>
<td>0.3</td>
<td>28.6±0.9</td>
<td>157.7±12.3</td>
</tr>
</tbody>
</table>

Table 6. Results of the tests on the processed GF/PP composites

<table>
<thead>
<tr>
<th>Test Type</th>
<th>Property</th>
<th>Pultrusion</th>
<th>Compression Molding</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Commingled fibers</td>
<td>Towpregs</td>
</tr>
<tr>
<td>Bending</td>
<td>Flexure Modulus (GPa)</td>
<td>Experimental</td>
<td>26.2±2.0</td>
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<td></td>
<td></td>
<td>Theoretical</td>
<td>23.8</td>
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<tr>
<td></td>
<td>Flexure Modulus / Fiber volume fraction (GPa)</td>
<td>Experimental</td>
<td>70.6±5.4</td>
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<td></td>
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<td>Theoretical</td>
<td>595.0±24</td>
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<td></td>
<td>Flexure Strength (MPa)</td>
<td>Experimental</td>
<td>626.7</td>
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<td>Theoretical</td>
<td>1603.8±64.7</td>
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<tr>
<td>Tensile</td>
<td>Tensile Modulus (GPa)</td>
<td>Experimental</td>
<td>24.9±1.1</td>
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<td></td>
<td></td>
<td>Theoretical</td>
<td>23.8</td>
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<td></td>
<td>Tensile Modulus / Fiber volume fraction (GPa)</td>
<td>Experimental</td>
<td>67.1±3.0</td>
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<td></td>
<td></td>
<td>Theoretical</td>
<td>216.3±12.4</td>
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<tr>
<td>Interlaminar Shear</td>
<td>Interlaminar Shear Strength (MPa)</td>
<td>Experimental</td>
<td>&gt;416a</td>
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<tr>
<td></td>
<td></td>
<td>Theoretical</td>
<td>12.3±0.3</td>
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<tr>
<td></td>
<td>Fiber volume fraction (%)</td>
<td></td>
<td>37.1</td>
</tr>
</tbody>
</table>

a: higher value achieved in the test. It was not possible breaking specimens
b: Property not determined
Figures

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

Figure 1. GF/PP pre-impregnated products under studied

Figure 2. Powder coating line setup.

Figure 3. Prototype coating line equipment used to produce towpregs
Figure 4. Cross-head extrusion die

Figure 5. Developed prototype pultrusion line

Figure 6. Schematic diagram of the pultrusion line.
Figure 7. Major pultrusion problems

Figure 8. Cross-section of profile pultruded from towpregs observe under optical microscope