

OPTIMIZING THE PRODUCTION AND PROCESSING OF FIBRE REINFORCED THERMOPLASTIC PRE-IMPREGNATED MATERIALS

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Abstract

The aim of this work is to optimize the production of new continuous carbon fibres reinforced polypropylene matrix pre-impregnated materials (towpregs) continuously processed by dry deposition of polypropylene (PP) powder. The processing of the produced towpregs by pultrusion using a prototype equipment was also optimized.

The method of Taguchi/DOE (Design of Experiments) was used to achieve this goal allowing improved choices of processing windows.

Towpregs were characterized by scanning electron microscopy (SEM), visual analysis and their polymer mass contents were also determined. The final pultruded composite profiles were also submitted to tensile, interlaminar, flexural, calcination and optical microscopy tests.

1. Introduction

During the last decades, composites have successfully replaced traditional materials in many engineering applications due to its excellent properties, mainly their excellent mechanical properties combined with low density [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. 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, 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].

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 (Fig. 1a), ii) PP powder Moplen RP348U[®] from Basell and the carbon fibre roving already mentioned were used to manufacture the CF/PP tapes (Fig. 1b). Table 1 present the properties of these raw-materials.

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].

Property	PP powder (ICORENE 9184B P [®])		PP granules (MOPLEN RP348U [®])	Carbon fibre (TORAY M30 SC [®])	
	Manufacturer datasheet	Experimental	Manufacturer datasheet	Manufacturer datasheet	Typical values
Linear density (Tex)	-	-	-	760	-
Specific gravity (Mg/m ³)	0.91	0.91	900	1.73	1.75
Tensile strength (MPa)	30 ¹	19 ¹	301	5490	2600
Young Modulus (GPa)	1.3	0.98	1.1	294	170
Poisson's ratio	-	0.21	-	-	-
Average powder size (µm)	440	163	-	-	-

¹ Yield Strength

Table 1. Properties of carbon fibre and polypropylene raw-materials

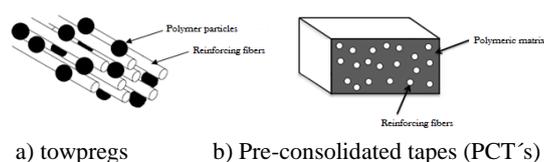


Fig. 1. CF/PP pre-impregnated products under study

2.2. Production of Thermoplastic Matrix Pre-Impregnated Products

2.2.1 Production of towpregs

The CF/PP 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, fibre spreader unit, heating section, coating section, consolidation unit and a wind-up section. Initially, the reinforcing fibres 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 fibre surface. Finally, the thermoplastic matrix towpreg is cooled down and wound-up on a spool.

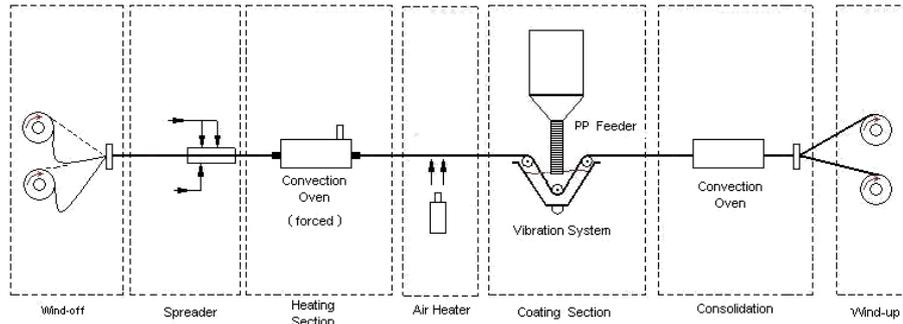


Fig. 2. Powder coating line setup

2.2.2 Towpreg 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 °C);
- consolidation oven temperature (350, 400 and 450 °C);
- 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.

Experiments	Processing variables			Results:
	Heating oven temperature (°C)	Consolidation furnace temperature (°C)	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

Table 2. Taguchi approach applied to towpregs manufacturing process

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 °C and 400°C 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.

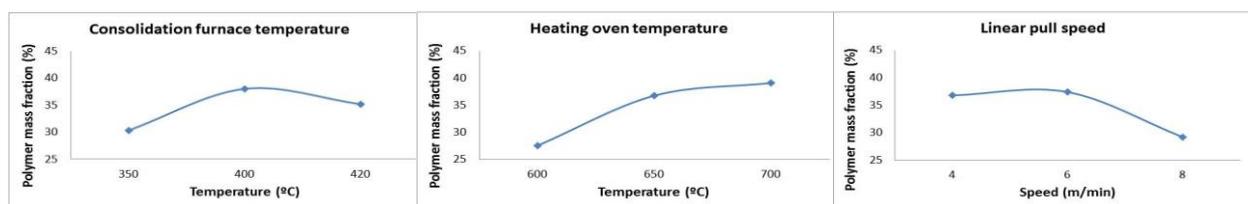


Fig. 3. Variation of towpreg polymer content with processing parameters

2.2.3 Production of pre-consolidate tapes (PCT)

The CF/PP PCT used in this work was produced in a cross-head extrusion equipment existing in our laboratories (see Fig. 4). The core of this technology is an impregnation unit where the carbon fibres are introduced, spread and impregnated by the polymer melt. Impregnation is achieved by pressurizing the molten polymer trapped between the unit's spreading elements and the fibre rovings.

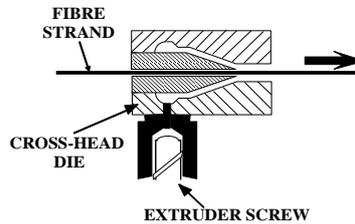


Fig. 4. Cross-head extrusion die

The apparatus consists of a creel holding system for fibre rovings, a guidance unit allowing an adequate transport of fibre 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 [17]. Main properties of the PCTs produced by this way are given in Table 3.

Property	Description
Fiber type	Carbon, 760 Tex
Filament diameter	5 μm
Fiber content	45 wt. %
Matrix type	Polypropylene (PP)
Tape width	25 mm
Tape linear density	14000 Tex

Table 3. Overview of the main properties of the produced pre-consolidated tapes (PCT's)

2.3 Processing of the pre-impregnated materials

The CF/PP pre-impregnated materials (towpregs and PCT's) were processed into composite bar profiles using a prototype pultrusion line [17, 18]. Our developed 10 kN pultrusion equipment, schematic depicted in Fig. 5, 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.

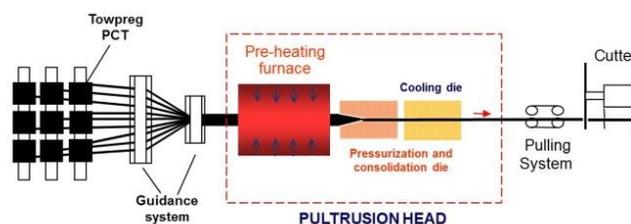


Fig. 5. Schematic diagram of the pultrusion line

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 x 2 (mm) was used to produce a composite rectangular shaped bar.

2.3.1 Towpreg 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 °C);
- Heating die temperature (240 and 260 °C);
- 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 °C, 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.

Exper.	Processing variables			Flexural properties	
	Furnace temperature (°C)	Heating die temperature (°C)	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

Table 4. Flexural testing results from towpregs

The variation of the flexural modulus and strength with the selected processing parameters can be seen in Figures 6 and 7. The optimal condition concerning flexural stiffness maximization obtained led to the following operating parameters selection: furnace and heated die oven temperatures of 160 °C and 260°C 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 °C and 240°C respectively, and a linear pulling speed of 0.3 m/min. It is possible observe that the furnace temperature of 160°C 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 °C and 260°C respectively, and a linear pulling speed of 0.2 m/min.

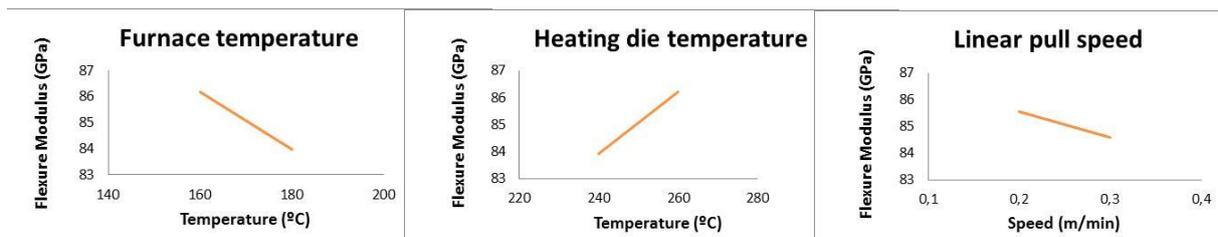


Fig. 6. Variation of the flexural modulus with the selected processing parameters

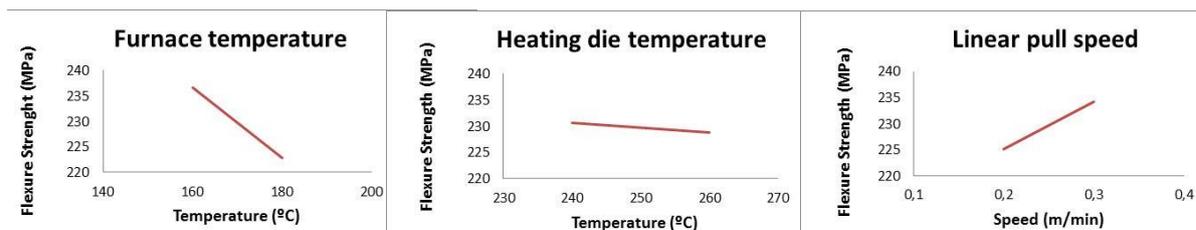


Fig. 7. Variation of the flexural strength with the selected processing parameters

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

Exper.	Processing variables			Flexural properties	
	Furnace temperature (°C)	Heating die temperature (°C)	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 5. Flexural properties of towpregs with additive processed by pultrusion

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.

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

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

2.3.2 Pre-consolidate tapes processing

CF/PP PCT were processed into composite bar profiles using the already mentioned pultrusion equipment die and the following typical operating conditions:

- Furnace temperature (160 °C);
- Heating die temperature (260 °C);
- Linear pull-speed (0.2 m/min).

2.4 Testing

2.4.1 Towpreg testing

Towpregs were characterized by scanning electron microscopy (SEM) and visual analysis. Several CF/PP produced towpreg samples were analysed under a Nova NanoSEM 200 Scanning Electron Microscope to evaluate the adhesion of the polymer powder to the fibres and its distribution. Figure 8 show SEM micrographs of towpreg samples. As may be seen, a reasonable degree of adhesion between the carbon fibres and the polymer powder particles was obtained. Also, the polymer particles distribution on the fibres can be considered sufficient and eventually improved.

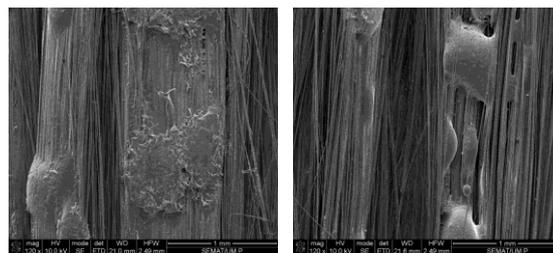


Fig. 8. Typical towpreg SEM micrographs (magnification of 120×)

2.4.2 Composites 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, and had their cross-sections studied under optical Microscopy (see Fig. 9). PCT's were also submitted to the same tests.

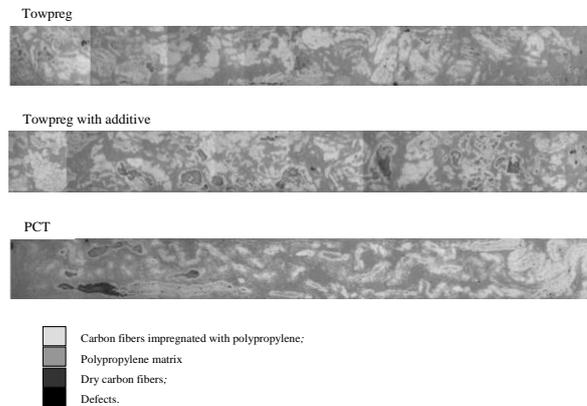


Fig. 9. Optical micrographs of the pultruded profiles cross-section (magnification of 8.75×)

2.4.3 Test results

Table 7 summarizes all experimentally obtained test results.

Test Type	Property		Pultrusion		
			Towpreg	Towpreg with additive	PCT
Flexural	Flexure Modulus (GPa)	Experimental	90.1±0.4	87.6±1.3	37.7±2.2
		Theoretical	85.7	85.5	54.0
	Flexure Modulus / Fibre volume fraction (GPa)		178.1±0.8	173.5±2.6	118.2±6.9
	Flexure Strength (MPa)	Experimental	241.2±1.6	229.0±7.3	158.7±4.2
Theoretical		1311.0	1308.4	825.8	
Flexure Strength / Fibre volume fraction (MPa)		476.7±3.2	453.5±14.5	497.5±13.2	
Tensile	Tensile Modulus (GPa)	Experimental	110.6±5.9	106.1±6.3	63.5±4.3
		Theoretical	85.7	85.5	54.0
	Tensile Modulus / Fibre volume fraction (GPa)		218.6±11.7	210.1±12.5	199.1±13.5
	Tensile Strength (MPa)	Experimental	1068.8	-	-
Theoretical		1311.0	-	-	
Tensile Strength / Fibre volume fraction (GPa)		2112.3	-	-	
Inter-laminar Shear	Interlaminar Shear Strength (MPa)		12.3±0.3	13.0±0.4	14.0±0.2
Fibre volume fraction (%)			50.6	50.5	31.9

Table 7. Composite mechanical test results

The tensile strength and modulus of the CF/PP plates were predicted from the fibre and polymer properties using the well-known law of mixtures.

As can be seen from Table 7, experimental strength results are lower than those theoretically predicted. The experimental moduli obtained are in good agreement with the theoretical ones. In table 8, different common engineering materials are compared concerning flexural mechanical properties.

Material	Density	Flexural Properties			
	(kg/m ³)	Strength (MPa)	Specific strength (kN*m ³ /Kg)	Modulus (GPa)	Specific modulus (MN*m ³ /Kg)
CF/PP [35%] (without additive)	1320	241.2	182.7	90.9	68.9
CF/PP [35%] (with additive)	1320	228.9	173.4	86.6	65.6
CF/Epoxy [40%]	1410	1800	1276.6	120	85.1
Stainless steel	7850	980	124.8	185	25.4
Aluminium	2700	90	33.3	70	25.9
Aluminium alloy	2810	500	177.9	71	25.2
Nylon 66 (PA)	1060	85	80.6	2.8	2.6
Polyester	1200	90	75.0	2.3	1.9
Polypropylene	905	40	44.2	1.5	1.6
PEEK	1380	-	-	3.8	2.7

Table 8. Comparison of flexural properties of different engineering materials

3. Conclusions

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. Composites processed from the PCTs demonstrated to have better mechanical strength than those produced from towpregs. As can be seen from the Fig. 9, all profiles have a reasonable distribution of the reinforcing fibres over the cross-sections. However, large differences in impregnation quality occur between the different samples that are likely to be related, directly, to the impregnation state of the semi-finished used on pultrusion. The samples of towpreg with additive show a higher quantity of dry zones than the ones without additive. It also 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 7 correspond to maximum force applied in the test. The tests made using a proprietary pultrusion equipment already allow concluding being possible to produce in good conditions profiles from almost all commercial available thermoplastic matrix pre-impregnated raw-materials using pull speeds of 0.3 m/min. It was possible to optimize the production of 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.

References

- [1] Sanjay Mazumdar, *High Performance Composites*, (May 2012).
- [2] Bechtold G., Wiedmer S., Friedrich K., *J. Thermoplast. Compos. Mater.*, **15**, 443-465 (2002).
- [3] Nguyen-Chung, T., Friedrich, K. and Mennig, G., *Reserch Letter in Materials Science*, **2007**.
- [3] J. F. Silva, J. P. Nunes, F. W. Van-Hattum, C. A. Bernardo and A. T. Marques "Improving Low-Cost Continuous Fibre Thermoplastic Composites by Tailoring Fibre-Matrix Adhesion". International Workshop on Thermoplastic Matrix Composites, 11-12 September, Gallipoli, Italy, 2003.
- [4] Åström T., Carlsson A., *Compos. Part A: Appl. Sci. Manuf.*, **29A**, 585-593 (1998).
- [5] Miller, A. H., Dodds, N., Hale, J.M., Gibson, A. G., *Compos. Part A: Appl. Sci. Manuf.*, **29A**, 773-782 (1998).
- [6] Nunes, J. P., Silva, J. F., van Hattum, F.W. J., Bernardo, C. A., Marques, A. T., Brito, A. M. e Pouzada, A. S., Production of Thermoplastic Towpregs and Towpreg-based Composites in "Polymer Composites – From Nano- to Macro-Scale", Eds K. Friedrich, S. Fakirov and Z. Zhang, Eds Kluwer Academic Publishers, 2005.
- [7] Ramani, K., Borgaonkar, H., Hoyle, C., *Composites Manufacturing*, **6**, 35-43 (1995).
- [8] Sala, G., Cutolo, D., *Compos. Part A: Appl. Sci. Manuf.*, **28A**, 637-646 (1997).
- [9] Purnima, D., Maiti, S. N., Gupta A. K., *J. Appl. Polym. Sci.*, **102** (6), 5528–5532 (2006).
- [10] Oever, M. and Peijjs, T., *Compos. Part A: Appl. Sci. Manuf.*, **29** (3), 227-239 (1998).
- [11] Kim, H.-S., Lee, B.-H., Choi, S.-W., Kim, S., Kim, H.-J., *Compos. Part A: Appl. Sci. Manuf.*, **38**, 1473-1482 (2007).
- [12] Janevski, A., Bogoeva-Gaceva, G. and Mader, *J. Adhes. Sci. Technol.*, **14** (3), 363-380 (2000).
- [13] Nunes, J. P., Silva, J. F. and Marques, A.T., "Using additives to improve the properties of composites made from towpregs", Proceedings of ANTEC'05, Boston, USA, May 1-5 (2005).
- [14] R. F. Silva, J. F. Silva, J. P. Nunes, C. A. Bernardo and A. T. Marques, *Mater. Science Forum*, **587-588**, 246-250 (2008).
- [15] Fazenda, R., Silva, J. F., Nunes, J. P., Bernardo, C. A., New Coating Equipment To Produce Long Fibre Thermoplastic Matrix Towpregs at Industrial Scale, Proceedings of ANTEC'07, Cincinnati, Ohio/USA, May 6-10 (2007).
- [16] P. J. Novo, J. F. Silva, J. P. Nunes, F. W. J. van Hattum, A. T. Marques, "Development of a new pultrusion equipment to manufacture thermoplastic matrix composite profiles", ECCM 15, June 24-28, Venice, Italy, 2012.
- [17] J. P. Nunes, J. F. Silva, P. J. Novo, *Adv. Polym. Technol.*, **32** (S2), E302-E312 (2013).