NEW THERMOPLASTIC MATRIX COMPOSITES FOR DEMANDING APPLICATIONS

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ABSTRACT

The PRIMOSPIRE® PR 120 thermoplastic polymer from Solvay Advanced Polymers, a new polymeric material for highly demanding applications, was studied in this work. The relevant properties of the polymer were determined and a new prototype powder coating equipment was designed and manufactured in order to use the primospire polymer as a powder matrix in the production of carbon fibre based towpregs [1]. The obtained results lead us to conclude that this new polymer has very interesting mechanical properties for highly demanding markets. It was also possible to produce continuously good primospire/carbon fibre towpregs for being subsequently processed by compression moulding into final composite plates. Finally, relevant mechanical properties were determined on the manufactured composite plates.

1. INTRODUCTION

Higher performing composites are currently needed to face the new requirements that advanced markets demand. Good examples of these are the manufacture of composite overwrapped pressure vessels for space applications such as pressurised tanks for rocket trust vector control systems, propellant pressurisation, nitrogen inertly, cold gas propulsion and liquid propellant storage systems and structural components for the new generation of Reusable Launching Vehicles (RLV).

In recent years, composites based on high performance thermoplastic matrices (PEEK, PPS, PES, PI, PAI, PEI) have successfully replaced the thermosetting based ones, due to their lower weight, easier reparability and reusability associated with an higher durability and, above all, better toughness, damping and fatigue behaviour, even under severe temperatures.

In this paper a preliminary work on the production of a new continuous fibre reinforced thermoplastic raw material (towpreg) using a recently developed powder coating equipment will be reported. An amorphous highly aromatic thermoplastic polymer in powder form, the PRIMOSPIRE® PR 120 from Solvay Advanced Polymers, was conveniently deposited in continuous carbon fibres to produce the above mentioned towpregs.

The produced towpregs were subsequently processed into composites by compression moulding and their relevant flexural mechanical properties were obtained.

2. EXPERIMENTAL

2.1 Raw materials

The towpregs studied in this work were produced using a new polymer from Solvay Advanced Polymers as matrix, the PRIMOSPIRE® PR 120, and a 760 Tex M30SC carbon fibre roving from TORAYCA as reinforcement. The fibres and polymer have densities of 1.73 Mg/m^3 and 1.21 Mg/m^3, respectively. Furthermore, the PRIMOSPIRE supplier recommends the use of processing temperatures in the range of 310–350 ºC for this material.

2.2 Developed equipment and towpreg production

A new prototype powder coating equipment was designed and manufactured for producing Primospire/carbon and Primospire/glass towpregs [2]. It consists of six main parts (see Figure 1): a wind-off system, a fibres spreader unit, a heating section, a coating section, a consolidation unit and a wind-up section. In order to produce the desired amounts of pre-impregnated material, the process starts by winding-off fibres from their tows. In the next stage, the fibres pass trough a pneumatic spreader and are heated in a convection oven. Immediately after, the heated fibres pass into a vibrating bath of polymer powder and therefore being coated. A gravity system allows maintaining constant the amount of polymer powder. The oven of the consolidation unit allows softening the polymer powder, promoting its adhesion to the fibre surface. Finally, the thermoplastic matrix towpreg is cooled down and wound-up on the final spool.

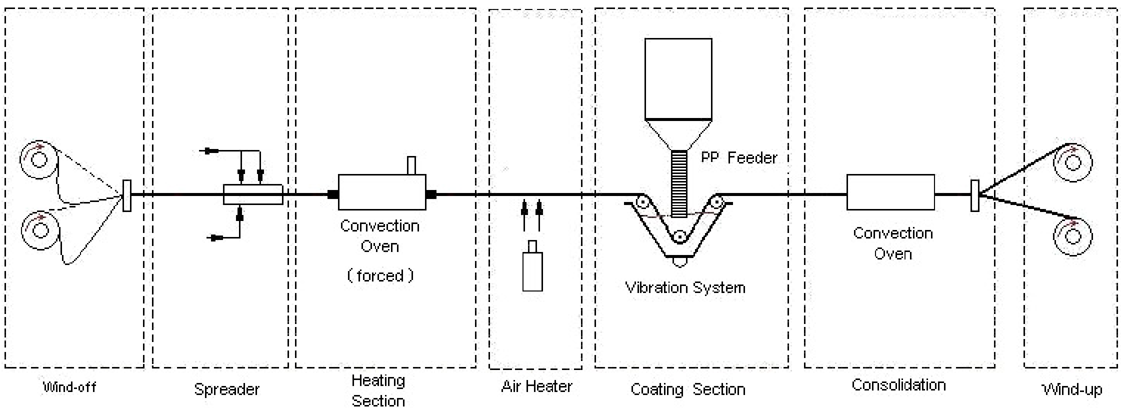


Figure 1. Schematic diagram of the powder-coating line set-up.

Using this equipment with the operational conditions summarized in table 1 it was possible to produce in continuous primospire/carbon towpregs with about 40% polymer mass fraction and a fair homogeneous distribution of the polymer powder on the fibres.

Table 1: Typical coating line operational conditions.

Variable	Units	Value
Fibre linear pull speed	m/min	4.6
Heating unit temperature	ºC	575-750
Spreader pressure	kPa	500
Consolidation unit temperature	ºC	520-650

The photography in Figure 2 shows a general overview of the developed powder coating equipment.

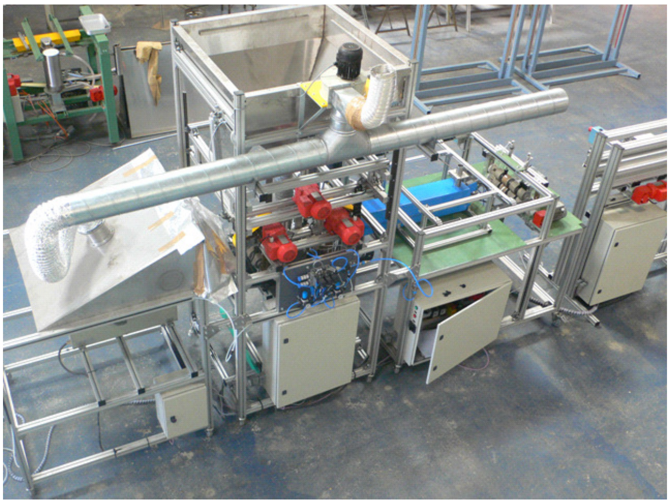


Figure 2. General overview of the developed powder coating equipment.

2.3 Consolidation by compression moulding

A technique described elsewhere [3] was used to produce unidirectional fibre reinforced laminate plates with 100×100×4 mm directly from the towpregs. First, the towpreg was wound over a plate with appropriate dimensions and the resultant pre-form was then conveniently placed in the cavity of a heated mould. A 400 kN SATIM hot platen press was used to obtain the desired consolidation pressure. After heating the cavity up to 320 ºC a pressure of 20 MPa was applied during 10 min using the press. Finally, the mould was cooled down to room temperature and the final laminate plate removed.

It were also produced plain woven fabrics from the towpreg tows by using a manual weaving loom. Four staked plies were used in the 200×200 mm composite plates manufactured from the produced woven fabrics using the same hot platen press and the above mentioned composite processing cycle. A typical woven fabric produced may be seen in Figure 3.

Figure 3. Produced primospire/carbon woven fabric.

3. RESULTS AND DISCUSSION

3.1 Carbon fibre characterization

The ASTM D 3379 standard was used to determine carbon fibre tensile mechanical properties. Following this standard procedure, single filaments were subjected to tensile forces in their axial direction until rupture. The carbon fibre tensile strength and modulus were then calculated from test data using the procedure described in the above mentioned standard. Table 2 summarizes the obtained values for the fibre mechanical properties as function of a reference fibre length.

Table 2: Determined carbon fibre mechanical properties

Reference length (mm)	**Number of tested fibres**	**Tensile strength (GPa)**		**Tensile modulus (GPa)**	
		Average	*Stand. Dev.*	*Average*	*Stand. Dev.*
15	33	3.190	0.594	196.447	29.131
30	36	2.833	0.577	199.986	20.603
40	40	2.575	0.706	193.982	19.899

As it may be observed in Table 2, while the carbon fibre tensile strength has shown to be highly dependent on fibre length, the modulus, by the contrary, may be considered roughly constant. The determined carbon fibre Young modulus average value (197 GPa) is much lower than the one found on the carbon fibre manufacturer datasheet (294 GPa).

3.2 PRIMOSPIRE® PR 120 characterisation

3.2.1 Sieving tests

The sieving technique was employed to determine the polymer powder particle size. Six sieves were used in the tests. These sieves had ASTM E11-EL 79 numbers of 18, 20, 30, 35, 50, 70, 100, 170, 200 and 230 that correspond, respectively, to aperture sizes of 1000, 850, 600, 500, 300, 212, 150, 90, 75 and 63 μm. The mass of particles accumulated in each sieve was then determined in a balance with an accuracy of 0.5 mg. The powder passing through all the sieves and received in the last retainer plate was considered as the mass of particles with diameters smaller than 63 μm.

Figure 4 summarizes the final experimental results obtained from 250 g of polymer powder in terms of accumulative frequencies. As can be seen, different plots are obtained when sieving data is plotted in terms of mass and in terms of number of particles.

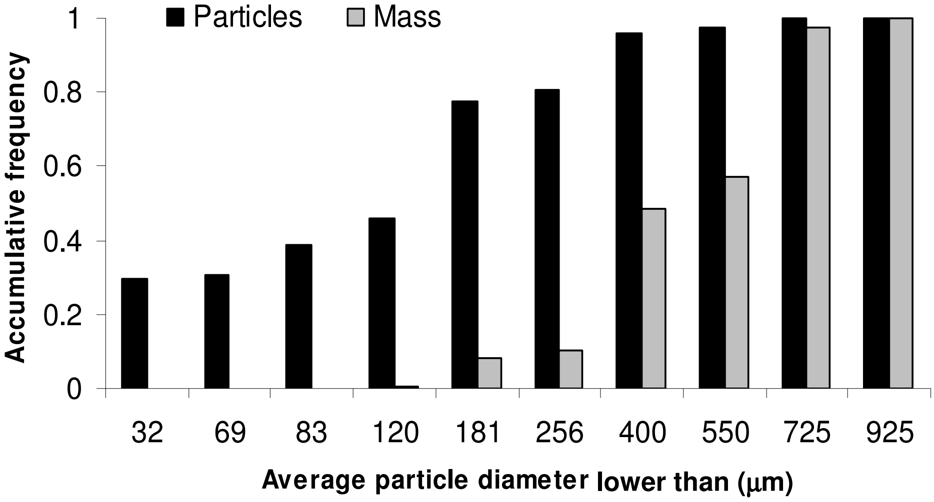


Figure 4. Sieving results in terms of accumulative frequencies

The polymer powder particle size was determined from the experimental data by means of the Weibull distribution using a procedure described elsewhere [4]. From the Weibull distribution functions it was possible to determine the main size properties of the PRIMOSPIRE® PR 120 powder particles. These results are summarised in Table 3 in terms of mass and number of particles.

Table 3: Primospire particles size determined in terms of mass and number of particles

Method used in the calculation	Average (µm)	Median (µm)	Variance (µm)²
mass of particles	457.6	455.6	24768.0
number of particles	139.4	98.1	18700.1

The average particle sizes determined are perfectly compatible with the dimensions of other thermoplastic particles used in previous works [1, 5] on the production of thermoplastic based towpregs.

3.2.2 Tensile tests

To obtain the PRIMOSPIRE® PR 120 tensile specimens according to EN ISO 527-2, plate samples were processed from the powder polymer by compression moulding using a 49 tonnes Moore hydraulic press. Two-minute cycles using the temperature of 320 ºC and the required compression pressure were employed to process the five tested samples. The obtained results are summarized in Table 4.

Table 4: Primospire tensile test results.

Sample	Maximum load (kN)	Maximum stress (MPa)	Maximum strain (%)	Young Modulus (GPa)
1	5.51	135.55	1.85	8.5
2	4.25	101.96	1.39	7.8
3	4.49	109.89	1.51	7.6
4	3.47	86.43	1.04	8.3
5	3.80	87.86	1.19	7.6
Average results	**4.30 ± 0.78**	**104.34 ± 20.02**	**1.40 ± 0.31**	**8.0 ± 0.4**

Very good agreement was been found between the experimental obtained modulus (8.0 ± 0.4 (GPa)) and the one supplied in the manufacturer datasheet (8.3 GPa).

However, lower values than those referred by the manufacturer (207 MPa) were obtained for the tensile strength (104.34 ± 20.02 (MPa)). Such discrepancy could be, at least, partially explained from the possible presence of defects that could derive from the use of non-optimised processing conditions.

3.2.3 DSC test

A Diamond Pyris Perkin Elmer DSC was used to determine the PRIMOSPIRE® PR120 thermal characteristics. Using this technique the glass transition temperature (Tg) of the polymer could be determined as 157.97 ºC, in perfect accordance with data supplied by it's manufacturer (158.0 ºC).

3.2.4 Rheological tests

The rheological characteristics of the PRIMOSPIRE® PR 120 were determined in oscillatory regimen using a parallel plate rheometer TA Instruments Weissenberg. The dependence of the elastic and dissipative modulli with the oscillatory frequency was obtained at 3 different temperatures: 320 ºC, 330 ºC and 340 ºC. Polymer discs with 25 mm of diameter produced by compression moulding were used in these tests. The Cox-Merz rule was used to establish the relation between the dynamic viscosity (function of the angular frequency) and the shear viscosity (function of the shear rate).

Figures 5 and 6 show the results obtained for the dependence of the viscosity on shear rate values at different temperatures using linear and logarithm scales, respectively.

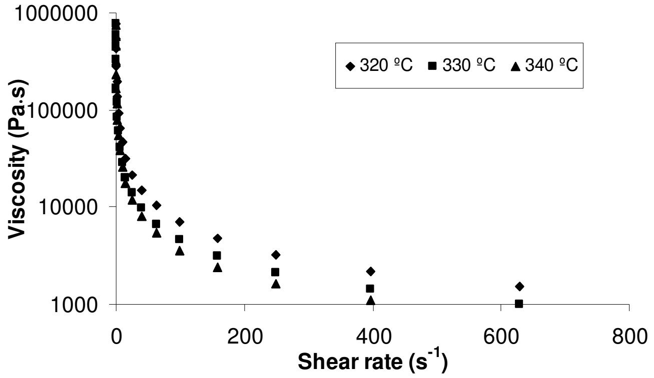


Figure 5. Viscosity dependence on shear rate at different temperatures.

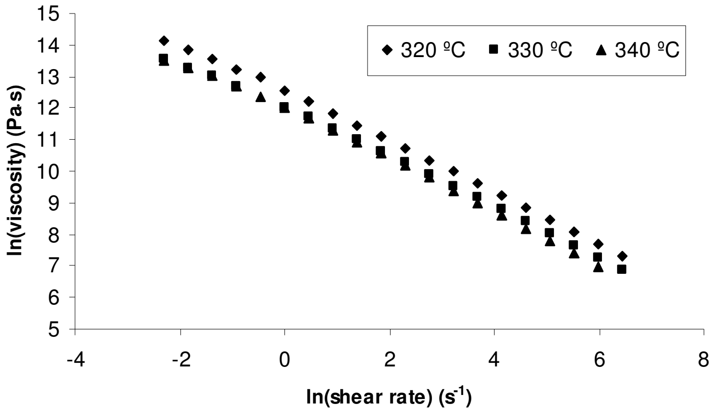
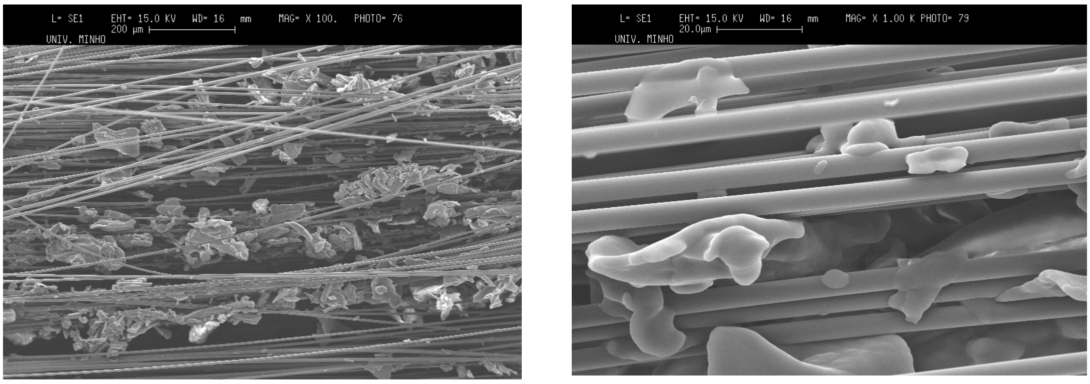


Figure 6. Viscosity dependence on shear rate at different temperatures in a ln-ln scale.

Using the typical value of 10 s^{-1} for the shear rate in compression moulding and the theory presented elsewhere [6], it was possible to estimate that the primospire/carbon towpregs has a total impregnation time of, approximately, 10 minutes.

3.3 Towpreg characterization by SEM

Several samples of the primospire/carbon towpregs were analysed under a Leica S360 scanning electron microscope for evaluating the polymer powder distribution and its adhesion to the fibres. Figure 7 shows two representative SEM micrographs.



a) Magnification: 100× *b) Magnification: 1000×*

Figure 7. Micrographs of Primospire/carbon towpreg under SEM

As can be seen, most of the polymer particles exhibit a bigger size than the fibre diameter and, even after heating, polymer particles present an irregular shape. It is possible to observe some degree of adhesion between fibres and polymer powder.

3.4 Composite mechanical testing results

Flexural properties were determined in four specimens of unidirectional and woven fabric fibre reinforced composite plates accordingly to ISO 178 Standard. Three point bending tests were performed at room temperature in the fibre directions of the 100×20 mm specimens using an Instron 4505 universal testing machine. The tests were conducted at the crosshead speed of 2 mm/min using a 80 mm span-distance between supports. Table 5 summarises the final results obtained.

Table 5: Flexural properties of composites made from towpregs.

Property		Units	Determined Values Average	Stand. Dev.
Flexural modulus (Unidirectional composite)	Experimental	GPa	30.0	5.0
	Theoretical		103.8	
Flexural modulus (woven fabrics)	Experimental		26.8	2.2
	Theoretical		53.8	
Flexural strength (Unidirectional composite)	Experimental	MPa	124.3	15.0
	Theoretical		867.0	
Flexural strength (woven fabrics)	Experimental		160	56
	Theoretical		459.0	
Fibre mass fraction	Experimental	%	59.7	0.3
Fibre volume fraction	Calculated		0.51	

The theoretical values presented in the above table were calculated from determined raw materials properties by using the rule of mixtures law (ROM).

As can be seen from Table 5, the composites manufactured from the woven fabrics presented mechanical properties in the better agreement with the theoretical expected ones than those reinforced with unidirectional fibres. The major causes for the differences found in these preliminary mechanical tests between the experimental and theoretical flexural stiffness and strength values are being attributed to a low fibre/matrix adhesion and also to fibre misalignments observed in the composite plates. Thus, in order to improve the produced composites mechanical properties a major effort is been currently carried out in order to better control the fibre misalignment and optimise the compression moulding cycle.

4. CONCLUSIONS

The tests made on the Primospire® PR 120 polymer showed that the material exhibits mechanical properties compatible with its use as matrix in highly-demanding composite markets. A new prototype powder-coating equipment suitable to produce in good conditions Primospire/Carbon towpregs has been developed in this work. From the initial tests made, it was found that those towpregs can be easily and continuously produced at speeds considered adequate for industrial production scale (~5 m/min).

Already enough good mechanical properties were obtained from the preliminary tests made on the unidirectional and woven fabric fibre reinforced composites easily processed by compression moulding from the produced towpregs. However, further work is currently been carried to improve these properties and optimise the composite processing cycles.

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