IN-SITU POLYMERIZED CONTINUOUS FIBER THERMOPLASTIC COMPOSITE MANUFACTURED THROUGH LIQUID MOLDING PROCESSES

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Abstract

Composites with APA6 thermoplastic matrix were manufactured, reinforced with glass and carbon fabrics and, at different weights and percentages. For this purpose semi-industrial equipment specifically designed for this process was used. When the values of fiber weights and percentages where optimized, a complete mechanical characterization was carried out. For example, for PA6+GF was obtained, with modulus 30% higher than those obtained by traditional injection processes, with the same fiber volume, as well as PA6+CF composites.

1. Introduction

The automotive industry is challenged to reduce CO_2 emissions and is highly interested in lightweight materials as an alternative to metallic materials. Thermoplastic matrix composites (TPCs) and, especially, glass and carbon reinforced ones, exhibit the adequate stiffness for structural applications. The choice of the polyamide matrix also provides a good temperature resistance at moderate prices. Therefore, this combination is a cost efficient solution which combines the sufficient rigidity for many automotive components that are subjected to mechanical loads, and a wide variety of forms supplied up to now by injection molding [1, 2]. It’s a fact that composite materials have been introduced for many years in the car because of its low weight. However, the components and processes currently used in automotive, are usually based on short fiber materials, which doesn´t permit to achieve the requirements demanded. The use of continuous fiber composites, with high mechanical properties, involves the application of aeronautics technologies. These TPCs reinforced with textile fibers are increasingly being used for the manufacture of high performance lightweight structures, especially in aerospace and automotive industries. The challenge is to obtain the excellent properties of the thermoplastic matrix in combination with continuous fibers, to obtain a composite.

Continuous fiber reinforced TPCs have been developed as an alternative to thermoset composites. A wide variety of polymers are available, ranging from the cheapest ones, also known as commodity plastics, to the most expensive ones, called high performance polymers. The fact of combining a thermoplastic matrix with continuous fiber reinforcement has proved to be feasible in numerous applications [3]. Traditionally, fiber reinforced TPCs are melt processed by stacking the alternating layers of textile fibers and polymer sheets in a hot press

[4]. An alternative to this process comprise the reactive processing of the thermoplastic composites containing matrixes like PA, PBT or CBT. After impregnation of the fibers with a low density precursor, is carried out the in situ polymerization of the thermoplastic matrix is carried out [5]. This polymerization can be initiated by temperature and requires a catalytic system, prior to the impregnation. Polyamide 6 (PA 6) is an engineering thermoplastic polymer with excellent mechanical and heat resistance properties and, therefore, has many applications [6] , as that described in this article, a matrix for composites reinforced with textile fibers. The low melt point of its monomer (ε-Caprolactam) and its low viscosity in the melt state make it easy to process and, generally, achieve a good fiber impregnation [7]. Due to the low viscosity of the monomer, this impregnation can be achieved without the need of high processing pressures. Moreover, fabric reinforced TPCs can be manufactured with low pressure processes. A preform (previously dried) is placed inside a closed mold and the precursor is infused, with the assistance of pressure or vacuum [8, 9, 10]. Figure 1 shows an example of a part manufactured with continuous fiber and thermoplastic matrix.

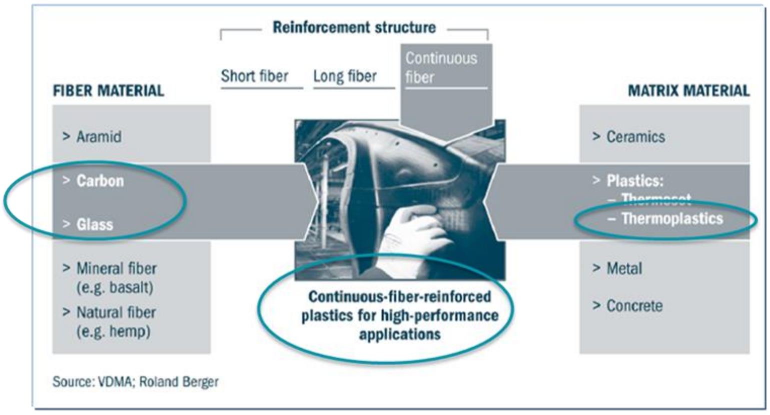


Figure 1. Example of a continuous fiber reinforced high performance TPC.

The first part of this study focuses on thermoplastic composites with different percentages of glass fiber (GF) with silane sizing, which are commercially available. These fabrics can form chemical bonds with the anionic matrix of PA 6 and, therefore, were specifically selected [11, 12]. In this first part, a wide search of both adequate carbon fibers (CF) was carried out, and specific thermal treatment necessary to make it compatible with the matrix and the process was developed. The second part of this study, which is described in this article consists of a complete mechanical study of the TPCs reinforced with the previously selected fibers.

2. Experimental

2.1. Materials

2.1.1. Anionic polyamide-6 matrix material

Anionic polymerization ε-Caprolactam (ε-CL) supplied by BASF was used in this study, since it has a low moisture content (<0.04%). The monomer was stored at 25ºC under dry atmospheric conditions to keep it dry without causing the monomer flakes to fuse together due to sublimation and recrystallization. Sodium lactamate and isocyanate were added as activator and initiator.

2.1.2. Glass and Carbon fabrics

Glass and carbon fabrics were used as reinforcements, glass fabric being supplied by Johns Manville with a weight of 600gr/m^{2}and silane sizing, and carbon fabric being supplied by Hexcel with a weight of 200gr/m^2 and desized. Both fabrics have a maximum moisture content of 15%. Both fabrics are 0/90º, being the carbon fabric balanced 50/50 and the glass fabric 80/20.

2.2. Processing methods

The samples were prepared using liquid molding processes, as can be observed in Figure 2. With this purpose, desired fabric layers were placed inside the mold. Then, the reaction mixture was introduced on it, which polymerize in the mold itself, obtaining the TPC.

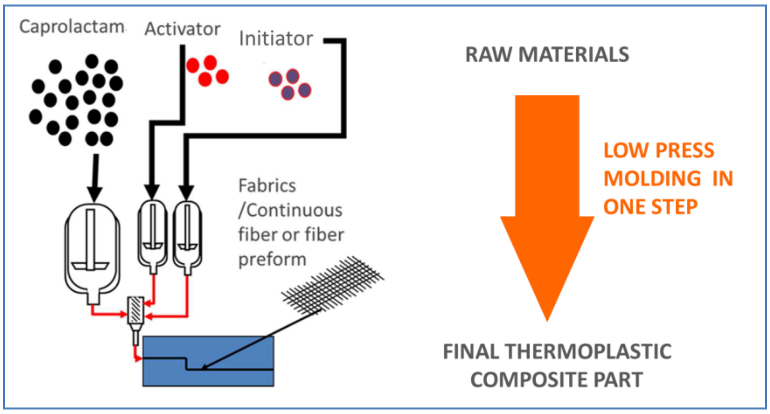


Figure 2. Liquid molding processes for thermoplastic composites.

Table 1 shows the weights and volume percentages of carbon and glass fibers used for the manufacturing of the plates.

Fiber	% Weight	% Volume
Glass fiber	68	48
Carbon fiber	60	48

Table 1. Percentages of fiber used for manufacture the TPCs.

3. Results and Discussion

3.1. Results

Tests were made in a room at 21ºC and 50% relative humidity and their results are presented next. Before testing, the samples were conditioned at 1wt% of moisture. For the mechanical characterization at least five specimens were tested per material and test. In Figure 3 a collection of test specimens can be seen.

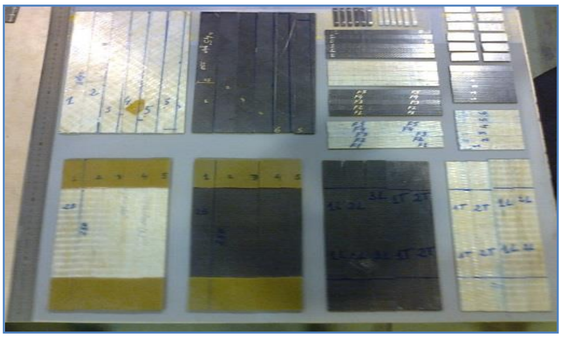


Figure 3. Test specimens.

3.1.1. Tensile tests

Tensile tests, according to ASTM D3039 standard using an Instron machine, model 5500, were done on specimens of (PA+GF) and (PA+CF), at a speed of 2mm/min. An extensometer was used to measure the elongation of the specimen in a measure range of 50mm. Both samples were tested with and without TABS. Specimens without TABS, were tested in longitudinal (L) and transversal (T) directions, while specimens with TABS were tested only longitudinally. The specimen sizes were: 250*25*3mm. Table 2 and Figure 4 show the results of the tests.

Sample	**Tensile**		
	Modulus (GPa)	**Strength (MPa)**	**Elongation (%)**
GF.TABS.L	30.6	633	1.98
GF.L	31.4	670	2.24
GF.T	11.6	190	2.40
CF.TABS.L	48.4	618	1.44
CF.L	48.2	629	1.55
CF.T	48.2	561	1.28

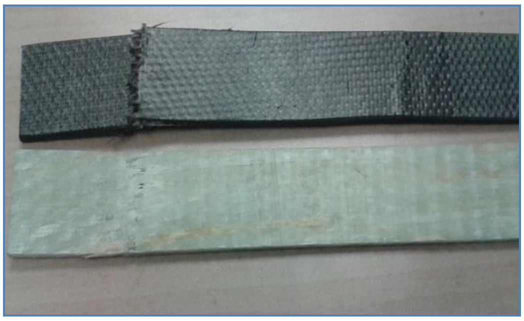


Table 2. Results of tensile tests. **Figure 4.** Samples tested.

3.1.2. Flexural tests

Flexural tests were conducted according to ISO 14125 for both composites. This test consists of supporting the specimens in two points with a gap between supports of 30 times the thickness, and a central load. The test was performed with two different specimen sizes: 120*15*3mm (wide) and 140*10*3mm (tight). The test was conducted on the same machine as that of the tensile test s and the test speed was of 5mm/min. Table 3 and Figure 5 show the results of the tests.

Sample	**Flexural**	
	Modulus (GPa)	**Strength (MPa)**
GF.WIDE	27.9	531
GF.TIGHT	25.5	415
CF.WIDE	42.3	274
CF.TIGHT	40.1	215

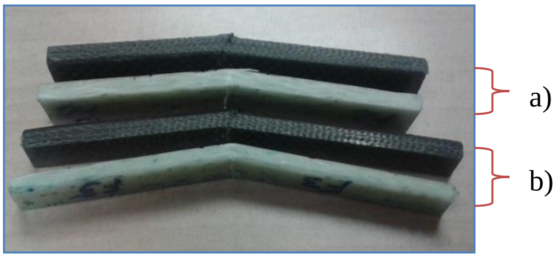


Table 3. Results of the flexural tests. **Figure 5.** Samples tested: a) Wide and b) Tight.

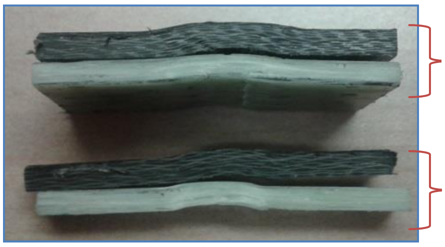
3.1.3. Interlaminar shear tests

Specimens were tested according to two different standards, with a test speed of 1mm/min.

- ASTM D 2344. The specimen size was 40*6*3.2mm, with a gap between supports of 4 times the thickness.
- ISO 14130. The specimen size was 35*17*3mm, with a gap between supports of 5 times the thickness.

Table 4 and Figure 6 show the results of the tests.

Sample	Apparent interlaminar strength (MPa)
GF.ASTM	43.8
GF.ISO	42.0
CF.ASTM	17.5
CF.ISO	17.2



a)

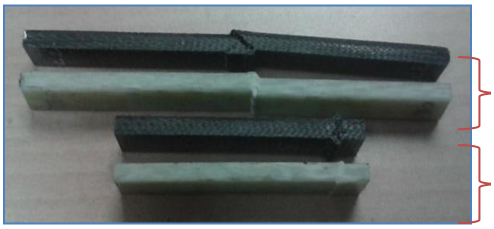
b)

Table 4. Results of the interlaminar shear tests. **Figure 6.** Samples tested: a) ASTM and b) ISO.

3.1.4. Compression modulus and strength tests

It should be noted that compression modulus and strength test are two different kind of tests. Compression modulus tests were conducted according to ASTM D 695 (modified) and ISO 14126 standards, for both composites. The specimen size was 80*12.5*3mm and test speed was 1mm/min. An extensometer was used to measure the elongation of the specimen in a measure range of 25mm, placed in the thickness. Compression strength tests were conducted according to ASTM D 3410 and ISO 14126, for both composites. The specimens size was 140*10*3mm with 63.5*10mm friction TABS made from emery cloth. The tests speed was 1.5mm/min. Table 5 and Figure 7 show the results of the tests.

Sample	Compression	
	Modulus (GPa)	Strength (MPa)
GF	33.6	312
CF	53.9	140



a)

b)

Table 5. Results of the compression modulus and strength tests. **Figure 7.** Samples tested: a) Strength and b) Modulus.

3.1.5. Impact tests

Specimens were first tested according to DIN 53453 (6J) with a Charpy pendulum, without notch, but specimens did not break. Therefore, specimens were tested according to ISO 179-1 (15J), also with a Charpy pendulum and without notch. The specimens size was 120*15*3mm, with a gap between supports of 70mm. The test orientations were longitudinal and transversal, for both materials. Table 6 and Figure 8 show the results of the tests

Sample	Charpy Impact strength (KJ/m^2)
GF.L	225
GF.T	124
CF.L	125
CF.T	137

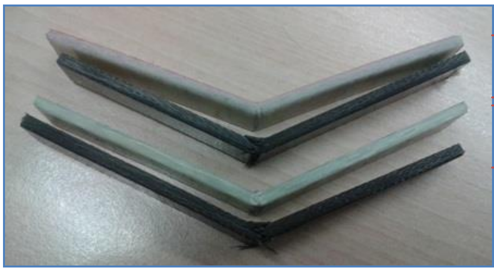


Table 6. Results of the impact tests. **Figure 8.** Samples tested: a) Transversal and b) Longitudinal.

3.1.6. In-plane shear tests

Specimens were tested according to ISO 14129 and ASTM D 3518 with a specimen size of 250*25*3mm. This is a tensile test at ±45º. Two gauges were used (one in the longitudinal direction, at 0º, and the other one in the transversal direction, at 90º) to measure the modulus of the specimens. The speed of the test was 2mm/min. Table 7 and Figure 9 show the results of the tests.

Sample	In-plane shear	
	Modulus (GPa)	Strength at 5% deformation (MPa)
GF	2.00	31.7
CF	1.63	27.7

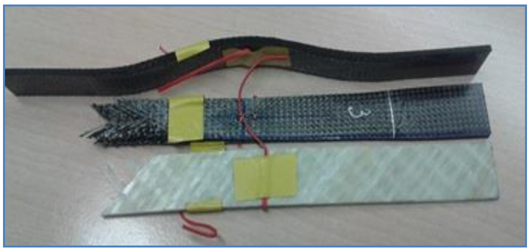


Table 7. Results of the in-plane shear tests. **Figure 9.** Samples tested.

3.2. Discussion

The highest value of Young modulus and strength of the samples of PA6+GF were found for the cases without TABS and in the longitudinal direction. However, the use of TABS is not necessary because the difference between both modules is not significant. In the transversal direction, the values are not so high because the fabric is 80/20. The fiber content in the transversal direction is a 75% lower and the results are 63% lower. Therefore, the results make sense. In the case of PA6+CF samples for tensile test, the maximum value of strength was achieved without TABS in the longitudinal direction, as happened in the case of PA6+GF. Modulus values, however, were the same in the three types of specimens manufactured. In this case, there is not difference between longitudinal and transversal directions because the fabric is balanced. The highest value of flexural strength was obtained with the samples manufactured with PA6+GF, while the highest flexural modulus was obtained with the samples manufactured with PA6+CF. The size of the samples did not affect the results in the properties of the specimens. In all cases the failure of the material happened. Regarding interlaminar shear tests, the expected mode of failure (delamination of the specimens) didn’t occur. This test was the most suitable for a unidirectional tape. In this case, it consisted of a 0/90 fabric and a thermoplastic matrix, more ductile than a thermoset one, so the values were lower than expected because delamination did not happen. In view of the values, it can also be concluded that the specimens size did not affect the value of strength.
Compression modulus and compression strength were tested independently, instead doing a unique test for both parameters. The reason for doing this was that the standard which allows measuring modulus and strength in a unique test, defines a specimen where measuring both

parameters is not easy because of geometrical aspects, leaving to little space between TABS. Modulus values were similar to the ones obtained in the tensile tests. However, regarding strength, GF has an aminosilane sizing, which is particularly compatible with the PA 6, and forms chemical bonds with it. These chemical these chemical bonds allow the composite structure work correctly under pressure loads. CF, however, had a thermal treatment that desizes the fiber, and which makes it possible that anionic polymerization process be compatible, but it does not provide a suitable chemical bond between the carbon fiber and the matrix. Therefore CF samples didn't show good behavior to compression. Impact tests represent the energy absorbed by specimens until failure. The higher the impact strength, the more energy the material will be able to before breaking. The samples manufactured with GF or CF, in both directions, failed with a "hinge" break type. Furthermore, longitudinal GF specimens showed higher impact strength than the transversal ones. The specimens manufactured with CF had similar values in both orientations. These results are the expected ones, because samples of CF are 0/90º balanced but GF ones are 80/20. In-plane shear test consist of a ±45 tensile specimens being subjected to a tensile test. The samples manufactured with GF had lower shear modulus than the samples manufactured with CF because of the orientation of the GF fiber is 80/20 and CF 50/50.

4. Conclusions

In Table 8, there is a comparison between the materials obtained experimentally in this work and the commercially existing ones, called organosheet and manufactured in a high pressure and temperature process.

Material		*Warp-Weft*	*% Fiber in volume*	*Modulus (GPa)*	*Strength (MPa)*
PA 6 Fabric (this work)	GF.L	80/20	48	31.4	670
	GF.T			11.6	190
	CF.L	50/50		48.2	629
	CF.T			48.2	561
PA 6 Organosheet [13]	GF.L.	80/20	47	30.1	605
	GF.T			12	125
PA 66 Organosheet [13]	CF.L	50/50	47	53	785
	CF.T			51	725

Table 8. Comparison of experimental and commercial materials.

In view of the table above, it can be concluded that the materials obtained in this study are comparable in properties to commercially existing ones, with the advantages of being obtained by means of a low pressure process and lower temperatures that do not need a second process to obtain the final part, as is the case of organosheet materials. In this work the behavior of the anionic PA6 reinforced with different types of fibers was studied. All specimens were tested after conditioning at 1wt% moisture, as the part in service will always be subjected to environmental conditions. The results of the tests show that:

- The continuous fibers are the responsible for the good structural properties of the TPCs. They allow the composite to have has high specific properties in several tests in the longitudinal direction. Glass fabric is 80/20 and because of this, the properties in the transversal direction, are lower. Carbon fabric, however, is balanced, so the properties in both directions are similar
- The specimen size or the use of TABS do not improve the properties

- The ductile behavior of the thermoplastic matrix avoids the delamination of the material
- The sizing applied to the fiber has a big importance in some properties, such as compression, impact or in-plane shear, so it will be necessary to apply a sizing to the CF

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