DEVELOPMENT OF RECYCLED PET COMPOSITES USING UNIDIRECTIONAL CONTINUOUS FIBER-REINFORCED THERMOPLASTIC TAPES

Guillermo Ulldemolins 1 , Begoña Galindo 1, Rocío Ruiz 1, Carolina Losada1 *, Samuel Requille2, Keo Murawka2

[1] Instituto Tecnológico del Plástico (AIMPLAS), 46980 Paterna (Valencia) Spain;

2 Coriolis Composites, F-56530 (Queven), France

ABSTRACT

Composites have added new dimensions to the design and manufacturing structural components on industrial areas such as aeronautical and automotive sectors. The most extended materials are metals and thermoset composite materials, but the emerging thermoplastic composite materials present a more attractive alternative. High productivity-rate, advanced mechanical properties, lightweight and the use of recycled materials are some of the benefits of thermoplastic composite materials. This study has developed thermoplastic unidirectional tapes reinforced with continue carbon fiber using both virgin and recycled polyethylene terephthalate matrix. Materials developed have been validated to be processed by automatic lay-up technologies using in-situ consolidation technique. Thermogravimetric, morphological and mechanical analysis have been evaluated and comparison results between both materials has been discussed. Recycled thermoplastic composite UD-tapes represent a good alternative for industrial sectors.

Keywords: continuous fiber reinforced, polyethylene terephthalate, thermoplastic composites; UD-tape

1. INTRODUCTION

Composite are defined as a material formed by of two or more components, in which the properties of the final product are superior to those of each separate component. These materials emerge from the continuous search for better performance in mechanical components. Depending on the polymeric matrix composition, it can be possible to work with thermoset or thermoplastic composites. Thermoplastic composites are those materials whose matrix is formed by a thermoplastic polymer and emerge as a real industrial alternative compared to traditional thermoset composites do to the following benefits [[1], [2],[3], [4]]:

- Reduce weight: a reduction of up to 20% compared to thermoset composites.
- High mechanical resistance with no loss of ductility.
- Adapted to different manufacturing processes: injection molding, compression molding and automatic deposition.
- Short manufacturing cycle times allow for high production volumes [5]
- Autoclave is not required
- Combination with other materials to create hybrid materials is possible
- Circular Economy:
  - Recyclable materials
  - UD-tapes materials do not generate as much industrial waste as organosheets, where up to 30% is waste after trimming to the desired shape.

The alternative is therefore to replace the thermosetting matrix with easily recyclable thermoplastic polymers, that can be re-melted in several processing cycles. Moreover, recycled and biodegradable polymers can also be used as matrices and even as reinforced fibers, thus resulting in a more sustainable solution [6], [7], [8] . PET present a promising raw material source and good matrix option for thermoplastic composites because of its lightweight and its recyclability. [8], [9], [10], [11]. This work proposes a solution for recycling PET post-consumer by re-introduction on thermoplastic composite sector as a recycled thermoplastic matrix.

Unidirectional tape (UD-tapes) materials offer some advantages for manufacturing structural components compared to traditional organosheets material format. With UD-tape materials, it is possible to achieve both reduction of time cycle production and the amount of scrap material [5]. UD-tapes can be used to orient the fibers in any load direction, enabling to manufacture load-specific components at a minimum scrap rate, so its use allows free orientation of the fiber and enhance the repeatability in complex geometries [12], [13]. Using long fiber allows the increasing of the stiffness without losing impact properties, furthermore, the final product reaches higher specific modulus, higher mechanical resistance and an improvement of recyclability [1]. Properties like stiffness, strength and toughness increase while the length of the fiber grow up. Property levels are low at short fiber length; as fiber length is increased the properties go through a region of rapid increase and then reach a plateau level for long fibers. [14]

Technological Institute of Plastic (AIMPLAS) has developed long fiber thermoplastic composites with continuous carbon fiber (LCF) as a reinforcement, and v-PET and r-PET as a matrix. In order to make it possible research activities, AIMPLAS has developed a thermoplastic pultrusion line by melting impregnation process. The aim of the process is to impregnate the reinforcement of long fiber by a melted thermoplastic matrix extruded on a co-rotative twin screw extruder [16]]. The processing of conventional thermoplastic materials in the field of composites is a great challenge due to its high viscosity and low flow index, making it difficult to impregnate the reinforcement. In the past, similar materials has been developed focusing on the obtainment of tow-preg composites based on continuous glass fibre with a recycled PET by pultrusion and successful result had been achieved. [9]

The interphase has an important role on the final mechanical properties, so it is needed that the adhesion or the interaction fiber-matrix will be as best as possible to obtain a final high quality product [17].

Automated manufacture encompasses any technology in which fibers are added to a part without manual handling by a human operator. Originally developed for the aerospace industry because of the need to improve the composites additive layup process, it gains more and more attraction from cost sensitive industries, such as the automotive one, as it allows an automated production of load optimized, near-net shape components [2]. The primary drivers for automated manufacturing are reduced labor costs, improvements to speed and efficiency, and tighter control of manufacturing processes and part tolerances [13]. Automated Tape Laying (ATL) is an additive process technology that allow the consolidation in situ (ISC) with no need for further manufacturing steps [5]. The layup process is a combination of different interdependent phenomena. Heat transfer by the heating device brings about a reduction in the tape viscosity, which helps fill voids by compression and makes it possible to achieve an intimate contact between the tape and the roller. As soon as intimate contact occurs, the healing (fusion) of the interfaces begins and provides the required bonding degree (Db) between the layers. [18]

The first laminate has a great importance and it is necessary to have enough material adhered to achieve the precise positioning of the adjacent tapes required for the complete build-up of the laminate [19]. The main problems that can be derive in lack of tack, an excess of tack, or a degradation of the material due to excess temperature and vacuum or air problems between layers due to bad pressure. These defects can lead to loss of mechanical properties of the parts obtained [[19], [20]].

There are many heating systems for the in-situ consolidation process of the material working with automated deposition technologies such as an infrared, hot gas, ultrasonic or laser heating systems [[21], [22]]. Experimental automatic deposition technologies had realized by Coriolis Composites, reference in Automated Fiber Placement (AFP) by using laser assisted heating systems for in-situ consolidation, and results are discussed in the following sections.

2. EXPERIMENTAL SECTION

2.1. Materials.

Post-consumer recycled PET (r-PET) flakes were supplied by PETALO which had an intrinsic viscosity of 0.7 dl/g and maximum contamination content of other polymers of 60 ppm. Multifilament virgin PET (v-PET) with an intrinsic viscosity of 0.64 dl/g was selected for comparison. Carbon fiber SGL SIGRAFIL 3070tex grade from SGL Carbon was used as a reinforcement.

2.2. Fabrication of reinforced thermoplastic UD- tapes

Carbon fiber was impregnated in a pilot plant thermoplastic pultrusion line developed by AIMPLAS to produce ½'' unidirectional tapes (Figure 1). The impregnation die was fed with melted polymer matrix by means of a twin screw extruder. A flat temperature profile of 280°C was used to process r-PET, while v-PET required 315°C to ensure good processability and fibers impregnation. Production rate was 1.1 m/min. Obtained tapes were reinforced with continuous carbon fiber (r-PET+CF and v-PET+CF). Developed tapes had an average thickness of 0.5 μm.

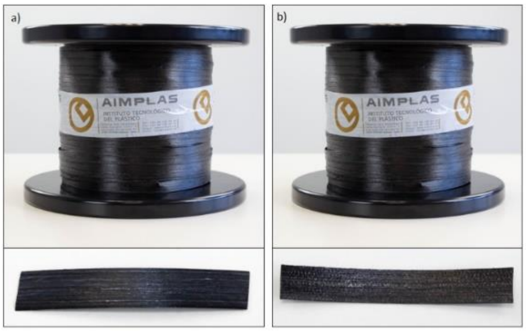

Figure 1. *v-PET/LCF (left) and r-PET/LCF (right) UD-tapes.*

2.3. Fabrication of thermoplastic panels by ATL

Both materials v-PET and r-PET thermoplastic ½" tape materials were processed by automated fiber placement (AFP). The machine used to manufacture the panels of this study is a state-of-the-art CORIOLIS COMPOSITES® Csolo, 1x1/2'' tows head mounted on a Comau robot. In order to heat the material to the required processing temperature, a 6kW laser source was used equipped with a homogenizer optics mounted on the fiber placement head creating a rectangular beam with adapted cross section dimensions. Panels were processed with a speed of 50 mm/s, corresponding to a speed in the range of in-situ consolidation layup speeds. A compaction force of 1000N and a power laser at 540W was used for first ply deposition. Panels were manufactured with dimensions 500 mm x 250 mm and with a stacking [0°;90°;0°;90°;0°] defined. Panels were manufactured by in-situ consolidation technique (**Figure 2**).

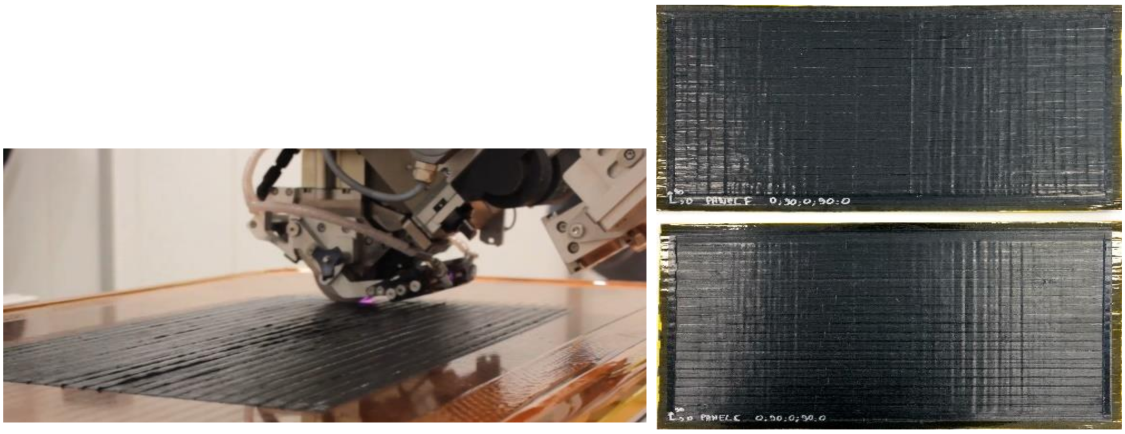

***Figure 2**. Manufactured panels by Csolo from Coriolis.*

2.5. Characterization.

Morphology

SEM of UD-tapes

Scanning electron microscopy (SEM) images were evaluated on a field emission scanning electron microscope (SEM model Electronic Phenom World Pro X) operating at 15 kV and detector used was electro dispersed electrons (topography). Samples were cut at the cross-section surface and were adhered to the microscope slide, which had previously been covered with a conductive self-adhesive base. Samples were coated with gold using the sputter coating technique to ensure electrical conductivity during electron bombardment.

Composition

Fiber content of UD-tapes

In order to evaluate the thermal stability and fiber content of the produced tapes, thermogravimetric analysis (TGA) was performed using TGA Q5000IR equipment (TA Instruments, USA). Samples (5-10 mg) were weighed in zirconia crucibles and heated under nitrogen atmosphere from 25 to 750 °C at a heating rate of 10 °C·min-1.

Mechanical

Tensile test of UD-tapes

Tensile tests of single UD-tapes were performed using a Universal Testing Machine (Allround Z250-Zwick/Roell). The mechanical parameters were determined from average of five specimens tested, according to UNE EN ISO 527-4. For all tests a tensile speed of 2 mm/min and a load cell of 250KN were used. Environmental condition during the test was (23±2) °C and (50±10) %HR. Young’s Modulus, tensile strength and elongation at break were characterized.

Tensile test of panels

Tensile tests were performed both specimens for each system. The support span was set to 50mm in accordance with ASTM D3039. The tests were conducted on a Universal Testing Machine (Allround Z250-Zwick/Roell). All the specimens were tested at a crosshead speed of 2 mm/min until the specimen break. Load and longitudinal deformation measurements were recorded electronically throughout the duration of the test. Environmental condition during the test was (23±2) °C and (50±10)%HR. Young’s Modulus, tensile strength and elongation at break were characterized.

Bending test of panels

For the structural strength evaluation of the developed panels, three-points bend tests were performed on five specimens for each system. The support span was set to 35mm with a center point load in accordance with ASTM D790. The tests were conducted on a Universal Testing Machine (Allround Z250-Zwick/Roell). All the specimens were tested at a crosshead speed of 1 mm/min until the specimen break. Load and deflection measurements were recorded electronically throughout the duration of the test.

3. RESULTS AND DISCUSSION

3.1. Morphology characterization UD-tapes

The microstructures of the v-PET and r-PET matrices reinforced with long carbon fibers (LCF) were characterized by scanning electron microscopy (SEM). Figure 3 shows the SEM micrographs of the fracture surface morphology of the v-PET/LCF and r-PET/CF tapes, respectively. The cryofracture cross-section of the tapes is shown in Figure 3. The homogeneous distribution of the carbon fiber could and the well adhesion of the matrix to LCF plays an important role in the mechanical properties of the resulting composites.

In both composites it is observed a good the interfacial adhesion between the matrix and the carbon fibers. However, close-up images show slight differences in interfacial adhesion between LCF and v-PET and r-PET matrices. For r-PET / LCF tapes, it could be clearly seen that interfacial adhesion (Figure 4) was better than for virgin PET / LCF one. The presence of a greater amount of bare carbon fibers in the v-PET / LCF tape contributes to a poorer adhesion, and therefore, a less effective load transfer across the interface between the v-PET and LCF was achieved in UD-tapes. In contrast, a greater amount of polymer can be seen on the surface of the carbon fibers in r-PET tape, indicating better wettability and interaction. According to other authors [23] the difference in the wettability of v-PET and r-PET to LCF can be associated to the difference in chemical affinity.

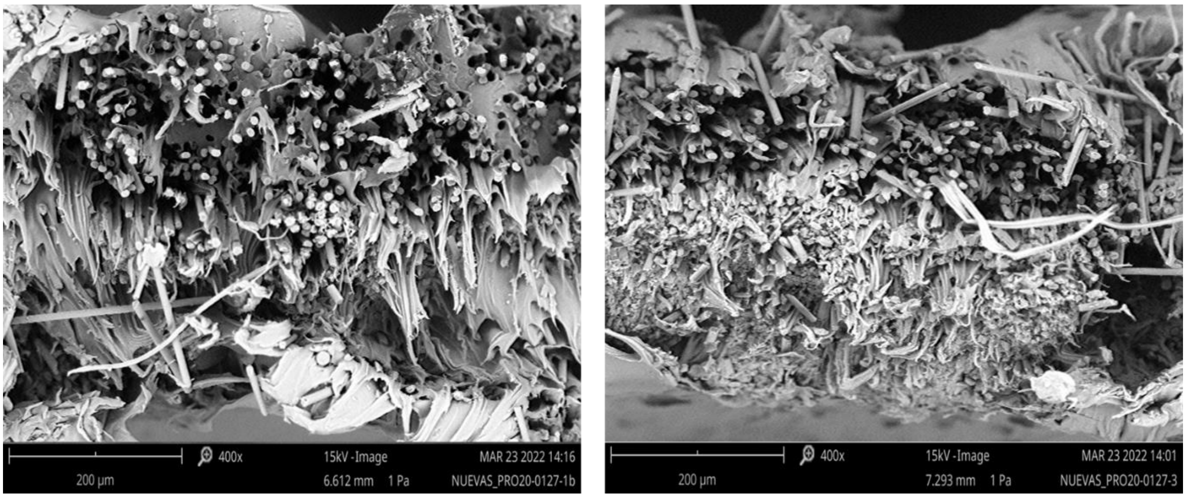

***Figure 3**. Cross-section r-PET/LCF (left) and cross-section v-PET/LCF.*

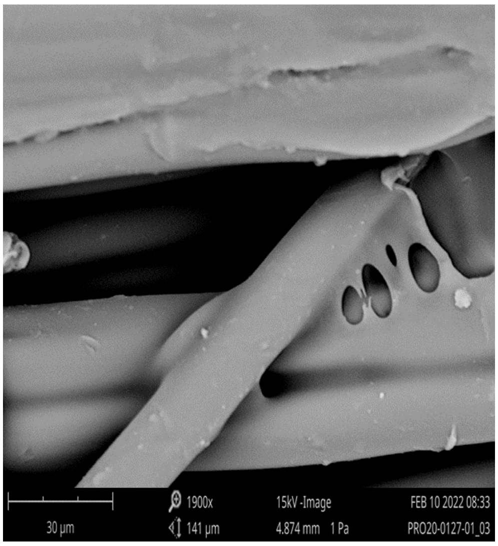

Figure 4. *r-PET matrix impregnation of carbon fiber filaments.*

3.2. Fiber Content of UD-tapes

Fiber content was evaluated by thermogravimetric curves, analyzing shifts in the onset temperature of mass loss. Figure 5 shows mass loss (TG) curves with the temperature of the studied PET pellets and composites. The thermograms of studied PET samples showed a only one degradation step of mass loss between 350 °C and 500 °C, which was attributed to the decomposition of the main polymer chain, resulting in the formation of different oligomers [24]. No significant changes in the thermal degradation behavior of r-PET, compared to virgin PET, were observed. The temperatures of maximum decomposition rate for v-PET and r-PET were 439 °C and 437 °C, respectively, and such values are in agreement with those reported by other authors [2].

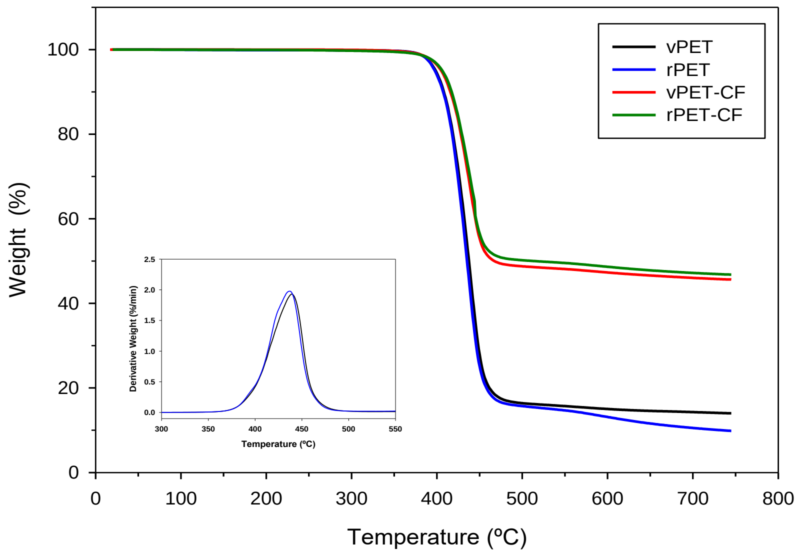

Figure 5*. TGA thermograms of studied pellets and composites. Inset: zoom of derivative weight vs temperature region for PET pellets.*

In the case of PET composites reinforced with long carbon fibers, both samples exhibit similar to TGA thermogram, showing a shift in the onset temperature of mass loss towards higher temperatures. After decomposition stage at 700 °C, the residual amount indicates the carbon fiber content in the v-PET-CF tape (49.9%) and r-PET-CF tape (46.1%) respectively (Figure 6).

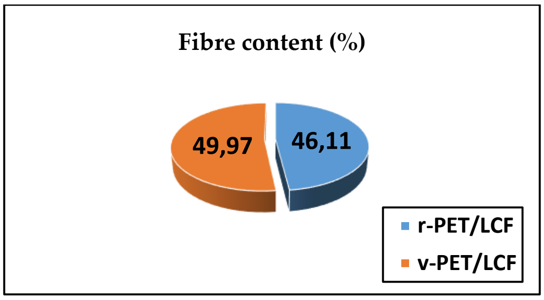

***Figure 6**. Fibre content of UD-tapes.*

3.3. Tensile test of UD-tapes.

In order to evaluate the tensile behavior of v-PET and r-PET reinforced with continuous carbon fiber (LCF). Five samples of each material have been evaluated by tensile test in order to characterize stiffness, mechanical resistance and strain properties. Table 1 presents an average of the results and a comparative of different materials is shown in Figure 7.

***Table 1**. Mechanical properties of r-PET/LCF and v-PET/LCF.*

Sample	E_t (MPa)	σ_m (MPa)	ε_m (%)	σ_b (MPa)	ε_b (%)
Matrix/reinforcement	**Modulus of elasticity**	**Tensile strength**	**Tensile strain**	**Tensile strength at break**	**Tensile strain at break**
r-PET/LCF	61400 ± 730	657 ± 37,1	0,99 ± 0,04	657 ± 37,1	0,991 ± 0,04
v-PET/LCF	50100 ± 2490	493 ± 72,5	0,95 ± 0,09	493 ± 72,5	0,954 ± 0,09

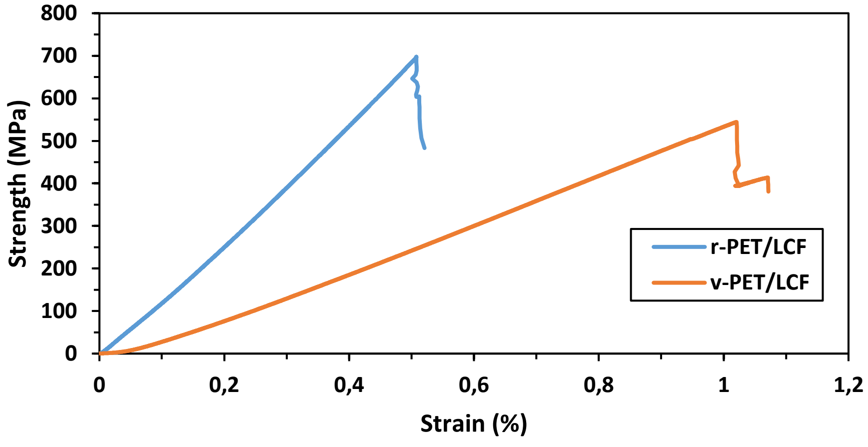

***Figure 7**. Behavior comparative of r-PET/LCF and v-PET/LCF r front at tensile test.*

It can be seen that the composites exhibit a brittle fracture and show linear deformation at lower stresses and nonlinear deformation at higher stresses. The Young's modulus and tensile strength for v-PET/LCF tape are lower than those for r-PET/LCF tape. UD-tapes of r-PET/LCF has presented better interphase adhesion, consequently, better interaction fibre-matrix has obtained and better mechanical properties has achieved.

3.5. *Tensile and bending test of panels*

Tensile and bending test has been evaluated and a comparative of its results has discussed. Figure 8 it is possible to make an evaluation between r-PET/LCF and v-PET/LCF, and the results show that mechanical behavior of v-PET/LCF is significantly higher than r-PET/LCF. Process parameters of automated tape deposition can affect to the final quality panels, so it possible than defects such us gaps between UD-Tapes induce to porosity between different layers. These gaps are the result of a non-uniform or non-constant width of the material developed. A lack of matrix impregnation in some zones of the UD-tape can induce to theses defects too.

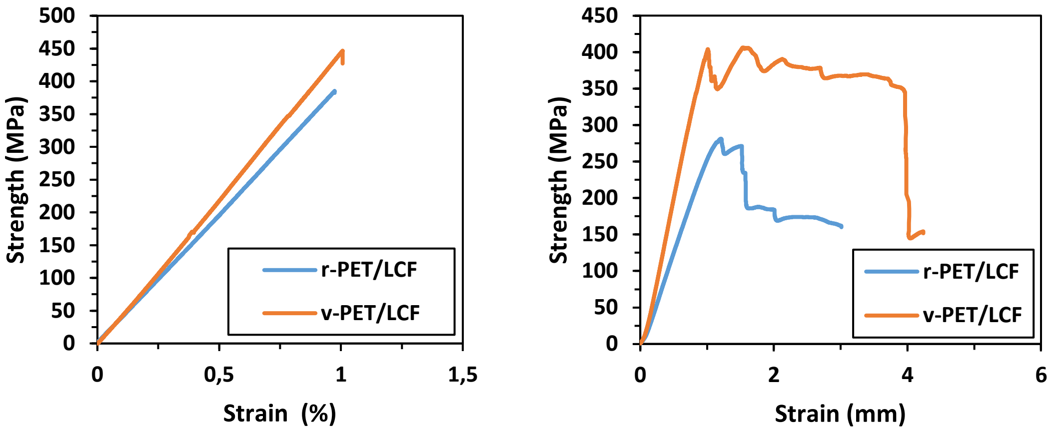

Figure 8. *Tensile test (left) and bending test (right) of the panels.*

Table 2 presents an average of the results obtained with five samples of each material. Flexural modulus in case of bending test and young modulus in case of tensile test are correlated with strength results, obtaining better stiffness with v-PET/LCF rather than with r-PET/LCF.

Table 2. *Mechanical properties of tensile and bending test of panels manufactured.*

Panel	Flexural Modulus (MPa)	Flexural strength (MPa)	Deflection (mm)	Young's Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
r-PET/LCF	20500 ± 1880	312± 30,4	1.26 ± 0.14	37000 ± 1750	397 ± 16,7	1.1 ± 0.1
v-PET/LCF	44300 ± 1250	410 ± 15,1	1.97 ± 0.73	42400 ± 1360	448 ± 17,1	1.0 ± 0.1

4. CONCLUSIONS

Carbon fiber are mainly used to reinforced composite materials for light and high mechanical properties. Thermoplastic composites are emerging in the transport sector. They make it possible to recycle the end-of-life products and thus, reducing the environmental impact. The study presented in this article shows the potential of new generation of continuous fiber thermoplastic composites and its capabilities to be used recycled materials. Virgin polyethylene terephthalate and recycled polyethylene terephthalate has been successfully reinforced with continuous fiber by melting impregnation process using AIMPLAS pultrusion line.

In order to characterize and make a comparative between each UD-tape, morphology, thermal and mechanical test have been realized. Results of UD-tapes developments show that better mechanical properties are achieved by using r-PET/LCF rather than with v-PET/LCF. This fact may be because of having better interaction fiber-matrix and stronger interphase. Even so, SEM study presents a good adhesion and impregnation between fiber and matrix in both cases because of adequate flow index in their processability. Thermogravimetric analysis has allowed to characterize fiber content of UD-tapes with results around content of 50%, a common value regarding thermoset commercial materials. Materials developed in this project are validated for processing by automatic deposition technologies using Csolo machine from Coriolis Composite entity. From r-PET/LCF and v-PET/LCF UD-tapes developed and technology from Coriolis has been possible to manufacture high quality panels. Again, mechanical analysis are characterized different panels but, in this case, v-PET/LCF panel shows better properties due to a less porosity found between layers than in r-PET/LCF panel.

These findings show a great advance for the recyclability that would reduce its accumulation in landfills and make possible to use a post-consumer material for high technical applications.

Conflicts of Interest: The authors declare no conflict of interest.

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