Development of New Thermoset Polymeric Composites Using Recycled CFRP Powder Mixture and Recovered CF

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The growing utilisation of carbon materials increases the waste generation. Therefore, the development of new composites using recycled carbon fiber reinforced polymer (rCFRP) within the present study was driven by environmental and economic factors. Six configurations of new polymeric matrix composites were developed and evaluated by mechanical tests (flexural, compression and interlaminar stress), microscopic and thermal analysis. Four configurations of composites were obtained by filling the matrix with rCFRP powder and fibrous elements mixture, the reinforcement phase being produced by grinding carbon fiber reinforced polymer (CFRP) waste. The new composite configurations showed an increase in mechanical properties with rising the reinforcement fraction. The samples analyzed by stereomicroscopy reveled a fairly homogeneous distribution of the reinforcement in the matrix for 5%wt. up to 30%wt., whereas thermal analysis showed no significant changes in the glass transition temperatures of developed materials. Two configurations of composites were obtained by chemical etching of the matrix and recovering carbon fiber woven, used subsequently as reinforcement phase for new composite configurations. The same method was used for determining the volume fraction of CFRP composite constituents. Initial results demonstrate that recycled carbon remains a highly satisfactory engineering material. These results showed that recycled FRP composites can be used to develop new less demanding composite materials or improve some properties of FRP composites.

Keywords: composite, recycled carbon fiber reinforced polymer (rCFRP), mechanical tests, epoxy resin

The increasing use of carbon fibre reinforced polymers (CFRP) has raised an environmental and economic awareness for the need to recycle the CFRP waste [1]. Today sustainable development becomes a necessity for design and manufacturing, less material-energy consumption for a controlled and reduced pollution are the key objectives [2]. The increasing volumes of all types of waste are leading to concern over methods of disposal and ways in which waste can be prevented. Waste management legislation places a focus on dealing with waste through the waste hierarchy of preventing (reducing), re-using, recycling, and recovering energy from waste before disposing of it in landfill as a last resort. Such waste legislation will put more pressure on solving waste management of composite material through recycling and re-use. Pressures from European directives are likely to increase further in the future [3]. The global demand for CFRP is rising and until 2020 is estimated to be around 208.000 tonnes. Around 54% of the carbon fibre produced world-wide is used for manufacturing prepregs, of which 42% are based on unidirectional fabrics and 12% on woven fabrics. 5% of carbon fibre is used to make semi-finished products such as fabrics, braids etc., which are in turn used to make CRP (carbon reinforced polymer) parts via an infiltration process (e.g. RTM). The winding (approx. 15%) and pultrusion (approx. 8%) processes are also important techniques in CRP production. Here the fibres are used in the form of yarns [4]. Despite all advantages associated with CFRPs, the increasing use generates an also increasing amount of CFRP waste [1]. It is clear that turning CFRP waste into a valuable resource and closing the loop in the CFRP life cycle is vital for the continued use of the material in some applications, e.g. the automotive industry [5]. Recycling composite waste has been the subject of much investigation over the past 15 years. Carbon-fiber-reinforced thermoset composites continue to be difficult to recycle, as they are a complex mixture of different materials such as thermosetting polymers, carbon fibers, and fillers; they may also contain foam cores, metal inserts, wire meshing, paints, and other contaminants. Furthermore, the cross-linked nature of thermosetting polymers prevents remolding. Recycling a composite means: i) having a recycling technology available, ii) getting a dismantle solution and an access for the product, and iii) disposing identification plus selection possibilities to the materials. Thus, carbon fibres recovery would both help design engineers to balance energy efficiency and cost, and open new opportunities for developing second life composites, dedicated to the manufacture of medium or low loaded parts (non-structural in many cases) [2]. Several techniques exist in order to recycle CFRCs [6]. The mechanical recycling consists in grinding fibre and matrix. It's cheap but very aggressive and destructive for the carbon fibres [7-9]. The thermal recycling can be led by oxidation in fluidized bed, by pyrolysis, or by treatment in molten salt bath [1]. The chemical recycling includes all methods of cold recycling (temperature lower than 450°C, and pressure around 250 bar, depending on the matrix polymerization degree), with the use of chemicals [1].

Experimental part

Mechanical recycling

The matrix was an epoxy system that comprise an epoxy resin (Resoltech 1050) and a hardener (Resoltech 1058). The CFRP waste consist of carbon fiber reinforced M49 epoxy laminates (prepreg HexPyM49/42%/ 200T2X2/CHS-3K). The CFRP laminates were cut into pieces (dimensions 10x5x2 mm) and then grinded, resulting a powder and

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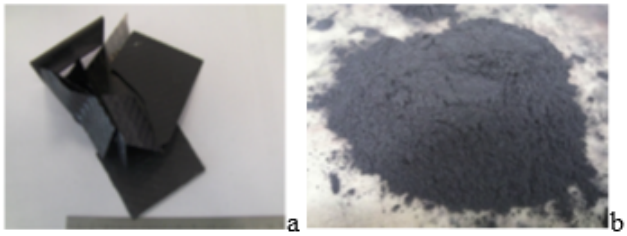

Fig.1 a) CFRP laminate waste; b) rCFRP recycled powder

Config.	Matrix (% wt.)	Filler/reinforcement (% wt.)	Specimen code
0	100	0 (Reference sample)	1-2, 2-1, 2-2, 3-1, 3-2, 10-1
1	95	5	4-1, 4-2, 4-3, 4-4, 4-6, 5-1, 10-2
2	95	5 + carbon fiber 50K strand	5-3
3	90	10	6-1, 6-2, 6-3, 6-4, 6-8
4	70	30	7-1, 7-2, 7-3, 7-4, 7-7, 10-3, 10-4

Table 1
COMPOSITE MATERIALS CONFIGURATIONS

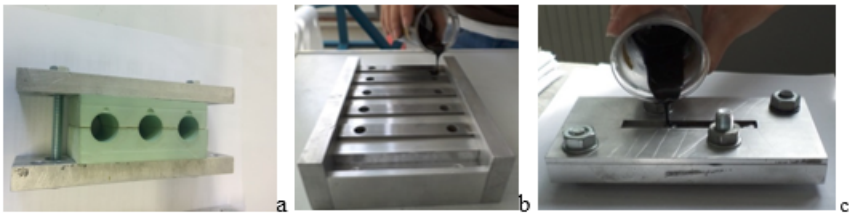

Fig. 2 a) Necuron cast resin mould for ASTM D 695-8:2008 [13] compression samples; b,c) Metallic mould for flexure and compression casted specimens

chopped strand mat (short fibres) elements mixture (rCFRP). The rCFRP mixture (fig. 1b) material was then screened with a fine-mesh sieve of 315μm diameter.

The configuration of the new composite materials samples is presented in table 1.

The materials were weighed, mixed in a berzelius beaker at room temperature, casted (fig. 2) in a metallic (flexure and compression samples) and Necuron cast resin (compression samples) molds and then cured in the oven at 60°C/10 h.

The effect of rCFRp powder reinforcement of the matrix in a CFRP laminate on the interlaminar strength, was assessed by conducting uniaxial tension tests and determining interlaminar normal stress. Four samples were manufactures using for each sample 350 plies of 25 x 25 x 0.24 mm and two OLC45 T profiles (for samples attachment in the testing machine grips). The active surfaces of the T profiles 25 x 25 mm were polished using 80 SiC paper previously to plies lay-down in order to enhance adhesion. Two samples (specimen code 11-1) used as reference were developed using carbon fiber reinforced epoxy prepreg plies (dimensions were: 85 x 25 x 25 mm), whereas the two other specimens (code 11-2) were developed using carbon fiber reinforced epoxy prepreg plies reinforced in addition after each 10 plies (of the 350 plies) with 0.2 g of recycled rCFRP powder and fibrouse elements mixture (<314μm) obtaining 87 x 25 x 25 mm samples. The four samples were baged sealed, vacuumed at -0.9bar and cured in the autoclave at 140°C (heating rate 3°C/min.), 2 h at 7 bars (cooling rate up to 40°C using 4°C/min.). The mechanical tests were performed in uniaxial tension regime (at room temperature, using 2 mm/min.), determining the initiation of delamination loads, final failure stresses and total displacements (fig. 3).

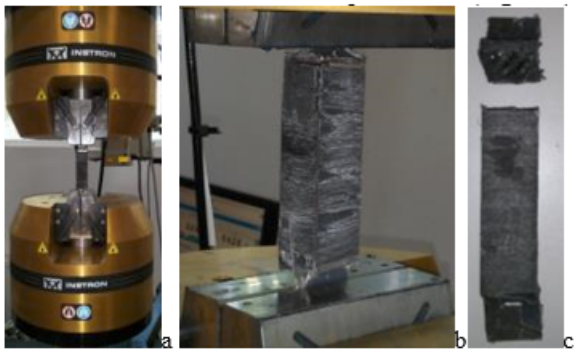

Fig. 3 Samples tested in uniaxial tension regime for interlaminar strength assessment

Chemical recycling

The chemical method was performed according to ASTM D 3171-99 method 2, for determining the PMC composite materials mass, volume fractions of constituents. The chemical etching (fig. 4) consisted in immersing the waste material (i.e. CFRP laminate discarded, out of expiry date prepregs, out of service FRP structures, etc.) in a reactive medium solution 40 mL of 95-97% sulphuric acid H_2SO_4, heating up to 60°C and adding when exotermic reaction was activated 70 mL of 30% perhidrol H_2O_2. The polymeric resin was decomposed into relatively large oligomers, while the carbon fibers remain inert, reached the surface of the solution that became incolor and were subsequently collected. Following the

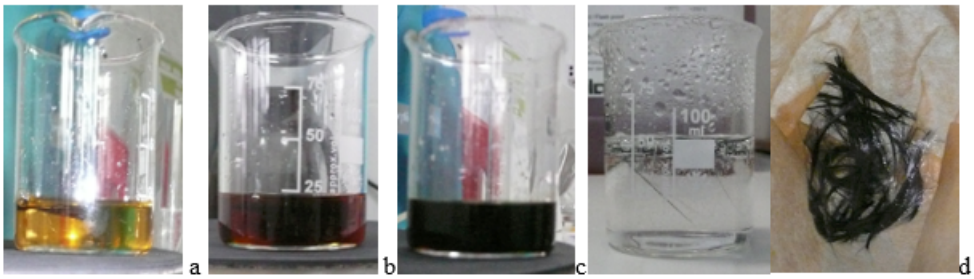

Fig.4. Stages of the chemical etching of the plymeric matrix a) imerssion; b,c) initiation and exotermic reaction; d) following perhidrol H_2O_2 addition and carbon fiber recovering

chemical etching of the matrix, the carbon fibers were recovered, washed and dyed in an oven at 60°C.

The recovered carbon fibers were used as reinforcement phase for new composite configurations.Two configurations of composites were obtained. One configuration consisted in reinforcing the epoxy resin matrix (Resoltech 1050: hardener Resoltech 1058/100:35) with vergin carbon fibers and the second one with recovered carbon fibers. Both configurations were evaluated using tensile mecahnical tests.

Mechanical characterization

Flexural tests were carried out in accordance to SR EN ISO 14125:2000 (3 point loading). Tests were performed at room temperature using a cross-speed of 1-2 mm/min (I class specimens: 80x10x4 mm) and 4 mm/min (IV class specimens: 100x15x2 mm), in a universal testing machine Tinius Olsen (Hounsfield) H 25 KT using an appropiate device.

Compression tests were performed according to SR EN ISO 14126:2003 [11] using 100x15x2 mm specimens, on a universal testing machine Tinius Olsen (Hounsfield) H 25 KT at temperature of 25°C, humidity 65% and speed of 1 mm/min. The second series of compression tests was performed according to ASTM D 695-8:2008 [12] using cylindrical specimens with the length twice its diameter (30x15 mm), using a universal testing machine Instron 8802, at room temperature with the speed of 1.3±0.3 mm/min.

Tensile tests were carried out in accordance to SR EN ISO:527-4 using a universal testing machine Instron 8802, at room temperature using 2 mm/min.

Structural analysis

The composites specimens were investigated post process. DSC analysis was performed on a Linseis DSC PT10, using two heating/cooling cycles for each samples in the rage of [-80 +200°C] using 10°C/min, in order to determinate the glass transition temperatures on the new composite configurations. Micrographs of the surfaces were observed by optical microscopy to evaluate how homogenous was the distribution of the powder used as reinforcement in the matrix. High Resolution Scanning Electron Microscope analysis were performed on a FEI Inspect F50 (Field Emission Gun) equipment with a 1.2 nm resolution, in order to observe the recovered carbon fibers reinforcement following chemical etching of the matrix.

Results and discussions

Both series of 3 point flexure tests showed an increase in both strength and modulus with increasing the reinforcement ratio when compared with the reference specimens. The flexural strength values ranged between 95÷181 MPa (for Ist class specimens) and 53÷88 MPa (for IVth class specimens). The highest values (for Ist class specimens) was achieved on the specimen 5-3 reinforced with 5% wt. rCFRP powder and chopped strand mat fibres mixture (315 μm diameter) and carbon fiber 50K strand (maximum strength 181.16 MPa, E modulus 5.58 GPa) and respectively (for IVth class specimens) on specimen 7-3, reinforced with 30% wt. rCFRP powder (88.69 MPa). In figure 5 are the resulted curves of the flexure and in plane compression tests.

The maximum value of the flexure modulus were observed as expected for specimen 7-1 reinforced with 30% wt. rCFRP powder (5.73 GPa), value is double compared with the flexure modulus of the reference (2.69 GPa). Analysing the in-plane compression results (performed according to SR EN ISO 14126:2003) it was observed a similar behaviour of the mechanical characteristics witch increase with rising of reinforcement proportion, values of the strength ranging between 72 MPa and 87 MPa.

Figure 6, shows the obtained rersults of the tested specimens during compression tests performed according to ASTM D 695-8:2008

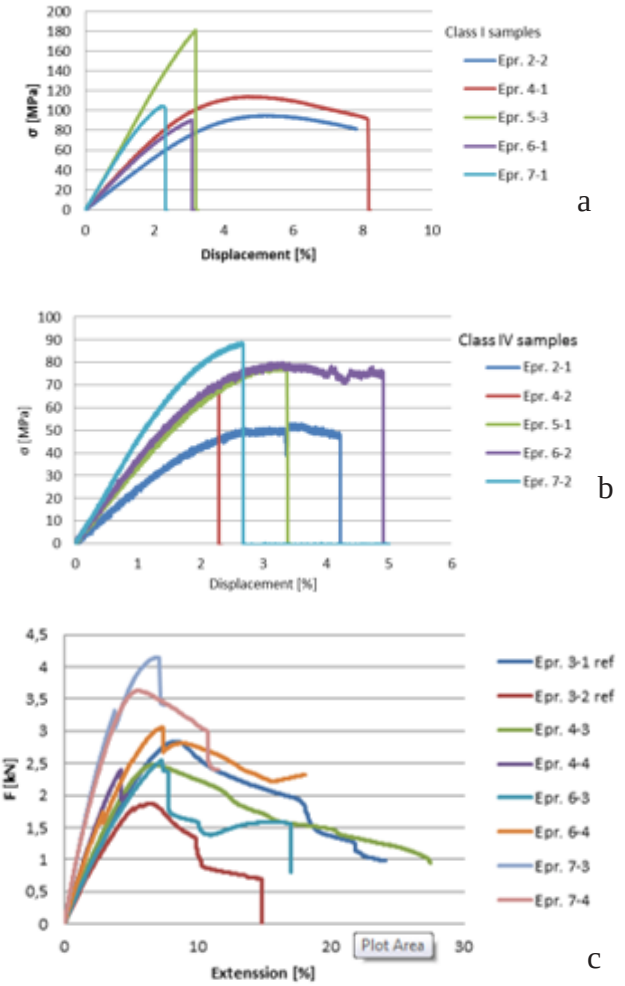

Fig.5. Flexure curve of the tested specimens a) Class I; b) Class IV; c) In plane compression curve for the tested specimens

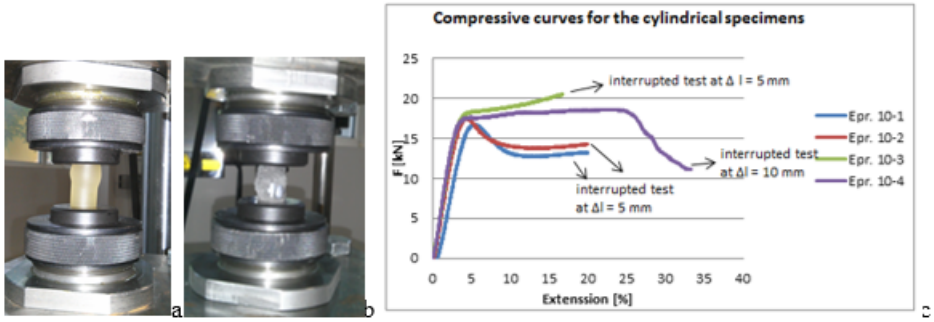

Fig.6 The specimens during compression tests; a) the reference specimen; b) the specimen reinforced with 30% wt. rCFRP powder; c) Compression curves for the cylindrical specimens

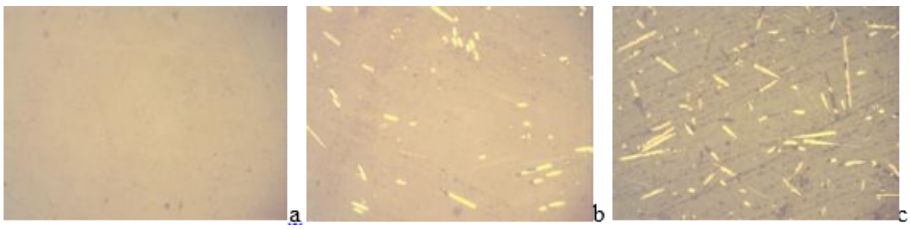

Fig. 7 Microscopic analysis images (magnification 200x) of the a) 1-2 – reference (resin 1050, hardener 1058); rCFRP reinforcement b) 6-8 (10% wt.); c) 7-7 (30% wt.)

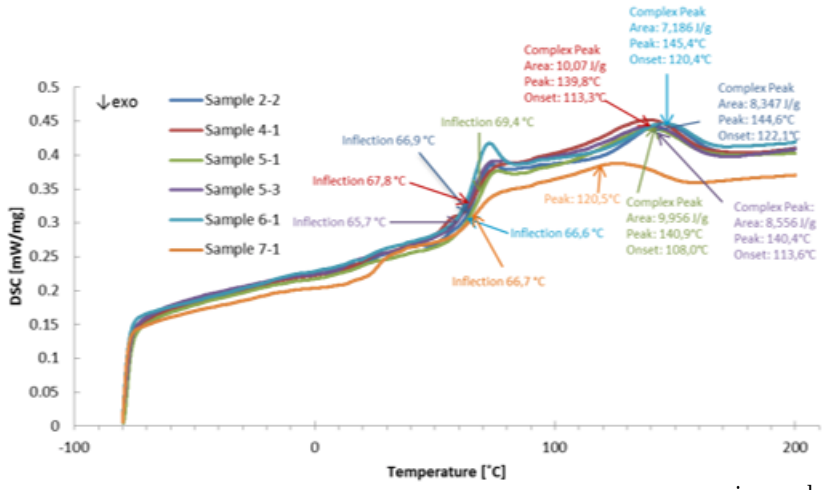

Fig.8 The DSC curve for the composite samples under study (table 1)

The compression test results showed an increase in maximum strength with rising the recycled rCFRP reinforcement phase, from 95 up to 116 MPa. Both recycled reinforcement increased proportion and fairly homogenous distribution lead to a 23% higher compression strength. In addition, as expected the material ductility was increased. Figure 7 presents the microscopic images on the composite materials configurations obtained by reinforcing a Resoltech 1050 epoxy matrix with different fraction recycled rCFRP mixture of powder and chopped strand mat short fibres (315 μm diameters).

The reference cast samples (resin 1050: hardener 1058/ 100:35) presented some voids following the curing process, whereas the reinforced specimens (5% wt., 10% wt., 30% wt.) showed no voids and a fairly homogenous distribution of the reinforcement phase.

Figure 8 shows the differential scanning calorimetry (DSC) analysis up to 200ÚC of composite samples under study (table 1). From the thermal analysis it can be observed that reinforcing the epoxy matrix with recycled reinforcement phase rCFRP in various proportions do not induce significant changes in its glass transition temperature (Tg). Nevertheless, for both specimens (4-1 and respectively 5-1) a slightly increase in Tg was observed.

The results of the uniaxial tensile tests (presented in fig. 9) performed in order to investigate the effect of rCFRp powder reinforcement of the matrix in a thick CFRP laminate on the interlaminar strength, showed that the maximum load of the specimens reinforced with recycled rCFRP mixture is 37% higher than those without the reinforcing interlayers, nevertheless, the final failure displacement decreased significantly.

Within the chemical recycling study, two approaches were followed. The chemical etching was performed according to ASTM D 3171-99 (method II), first for determining the carbon fiber reinforced epoxy matrix composite materials mass, volumetric fractions of constituents and secondly to recover carbon fibres and use it as reinforcement phase for new composite materials development. Previously to chemical etching the CFRP laminate sample 40 mm^2 and 2 mm thickness was weighted (1.1983g). The CFRP composite laminate density was of 1.47g/cm^3, whereas the epoxy resin was 1.18g/ cm^3 and the carbon fibers density was 1.78g/m^3. The recovered carbon fibers yarns were weighted (0.9203g). The volume fraction of fibers was determined to be 68.70% when compared to the technical data sheet of the HexPyM49/42%/200T2X2/CHS-3K used to manufacture the laminate (indicating a 65% vol. fraction of CF). Figure 10 presents the electronic microscopic analyses performed were on the recovered carbon fibers. From morphological point of view the secondary electron images showed that the fibers were not affected and do not present any damage being inert to the chemical etching. The backscattered electron images showed clearly the chemical contrast between the fibers and the resin still present locally, in some areas all along the carbon fibers. SEM observations explained this difference for volume fraction determinate experimentally when compared to the material technical data sheet value.

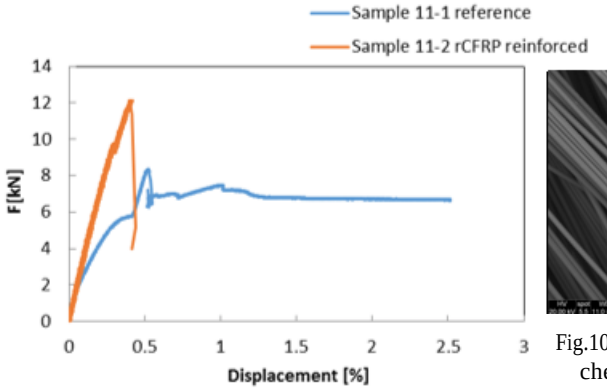

Fig.9. Uniaxial tensile tests results

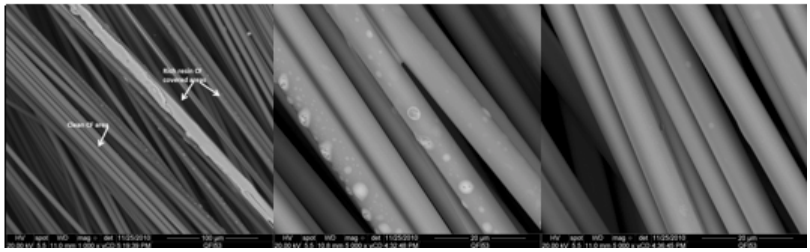

Fig.10. SEM images (backscattered electrons) of the recovered carbon fibers using chemical etching of the matrix showing rich resin areas covering some fibers

The recovered carbon fibers were used as reinforcement phase for new composite configurations. Two configurations of composites were obtained. One configuration consisted in reinforcing the epoxy resin matrix (Resoltech 1050: hardener Resoltech 1058/100:35) with virgin carbon fibers and the second one with recovered carbon fibers. Both configurations were evaluated using tensile mecahnical tests. The composite materials based on epoxy matrix reinforced with recovered carbon fibers showed only 5% lower tensile strength when compared with the same matrix reinforced with virgin carbon fibers, sustaining the morphological analysis that showed no damage, the recovered fibers being inert to the chemical etching. Thus, initial results demonstrate that recycled carbon fibers remains a highly satisfactory engineering material.

Conclusions

In the context of intensive development of composite materials industry that continually led to large waste storages, finding ways of wastes capitalization is critical. This study results showed clearly that (C)FRP composite can be recycled by mechanical, chemical methods and used subsequently as filler, reinforcement phase for new less demanding composite materials structures, to feature physical, mechanical characteristics or into a mix with a reinforcement phase up to 35%wt. of formerly unused material (i.e resin). In the present study epoxy matrix reinforcement with recycled rCFRP powder and chopped strand mat short fibres mixture provides a loss of fluid viscosity, the present study showing that additions shall not exceed 35 wt.%. However, this flow loss can be compensated using resins or hardeners with more fluidity. Likewise, a slight increase in the density of the composites was observed but there is no significant effect on the glass transition temperatures of developed materials. All the mechanical test performed showed that the recycled rCFRP powder mixture used as reinforcement for an epoxy matrix or a CFRP laminate structures, improved the characteristics of the composite, especially the elastic modulus and compression strength, flexural strength and interlaminar strength (in uniaxial tensile regime), which proportionally increased with the reinforcement phase fraction. As final conclusion, both mechanical and chemical methods can be successfully applied for recycling FRP composite structures, components and use it to develop new less demanding composite materials or improve some properties of new FRP composites.

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Manuscript received: 7.10.2015