REUSABILITY ASSESSMENT OF THERMOSET POLYMERIC COMPOSITE WASTES AS REINFORCEMENT AND FILLER REPLACEMENT FOR POLYMER CONCRETE MATERIALS

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1 Introduction

The development and applications of thermoset polymeric composites, namely fiber reinforced polymers (FRP), have shifted in the last decades more and more into the mass market [1]. Production and consume have increased tremendously mainly for the construction, transportation and automobile sectors [2, 3].

Although the many successful uses of thermoset composite materials, recycling process of by-products and end of lifecycle products constitutes a more difficult issue. The perceived lack of recyclability of composite materials is now increasingly important and seen as a key barrier to the development or even continued used of these materials in some markets [4, 5].

This increase awareness of environmental matters and seeking sustainable materials, stressed by the more restrictive directives of European Commission, have driven that several recycling techniques have been analyzed and proposed, mainly for GFRP and CFRP waste materials [6]. Thermal and/or chemical recycling, with fiber recovering, have been proposed mostly for CFRP due to inherent economic value of carbon fiber reinforcement; whereas for GFRP materials, mechanical recycling by shredding and milling processes, with reduction to fibrous and/or powdered products, has been considered as a more viable recycling method [4, 7, 8]. Ensuring that feasible markets outlets exist, mechanical recycling is so far considered the favored recovering technique, at least for relative low cost and clean FRP waste materials. Although considered as green and friendly materials, recyclates from mechanically recycled GFRP waste remain however, somehow as *'little beautiful girls, well dressed, but no place to go'*, hindered by the scarceness of feasible end-use applications.

The pressure on the development of new and economically viable markets for the recyclates, towards materials sustainability, have led over the last 20 years a relative great amount of research work on potential added value applications [9-12]. Several promising end-use applications have been investigated. The most extensive research work has been carried out on Portland cement concrete, in which grinded GFRP waste scrap has been incorporated either as reinforcement, aggregate or filler replacement [13-15]. Reported added values, besides environmental assets, as function of specific mix design, comprise slight increase on mechanical properties, lower permeability leading to improved durability, a less drying shrinkage and a global cost reduction of raw materials. Potential applications of GFRP waste in concrete include pre-cast paving slabs, roof tiles, wall panels, paving blocks and architectural cladding materials [13-15].

These end-use applications bring however, depending upon glass fiber nature, some incompatibility problems arisen from alkalis silica reaction (ASR) [16]. This drawback, brought by cementious binder matrix, could be avoid using as host material a cementless concrete like polymer based concrete (PC) materials.

PC materials are high performance resin based concretes, in which a polymer acts as binder matrix for the mineral aggregates. High strength to weight ratio, improved resistance to chemical and frost attack, very fast curing and excellent bond to several substrates, are the main advantages of these materials over cement based concretes [17. 18].

Moreover, due to hermetic nature of resin matrix, polymer concrete and mortar composites present a great ability for incorporating recycled waste materials. Recycling and waste encapsulation constitute nowadays the new and emerging branch market for PCs. Most of the successful applications reported involve either industrial wastes and by-products, or end-of-life products [18-21]. Regardless of the relative large amount of research work undertaken recycled wastes in polymer based concretes, until now, few studies have focused on the incorporation of FRP recyclates into PCs.

2 Research Significance

Seeking filling this gap, the aim of the present work is to explore a potential waste management solution for GFRP waste (scrap, by-products and end-of-life products) as reinforcement, aggregate or filler replacement for polymer based mortars. Besides the evident environmental benefits, a viable and feasible solution for GFRP wastes would also conduct to significant economic advantages. For this purpose, different contents of recycled GFRP waste powder and fibers, with distinct size gradings, were incorporated into polyester based mortars as sand aggregates and filler replacements. Added value of recycling solution was evaluated by means of flexural and compressive loading capacity of GFRP admixed mortars with regard to waste-free polymer mortar materials. Obtained results allowed setting the best combination of material factors that drive to an optimal response of final product.

3 Experimental Program

3.2 Raw Materials

Unsaturated polyester resin, commercially available under the trade name of AROPOL FS3002 (Ashland®), with a styrene content of 42%, was used as binder matrix. This resin system is generally prescribed for pultrusion processes, though it can also be used in bulk and sheet moulding compounds. Polymerization process was induced by cobalt octoate (0,5 phr) as promoter, and 50% methyl ethyl ketone peroxide solution (2 phr), as initiator.

A siliceous foundry sand, with rather uniform particle size and an average diameter of 245 µm, was used as fine aggregate. Foundry sand is a generic term to denote sand with a high grade of silica (> 99%). This silica sand is extracted and processed by *Sibelco, Lda*, and supplied by *Fundipor*, under the commercial name of SP55. Particle size distribution is represented ahead in this paper, in Fig. 2, jointly with particle size distributions of milled GFRP waste materials.

Applied GFRP waste was supplied by a local pultrusion manufacturing company, *ALTO-Perfis Pultrudidos*, and it was proceeding from the shredding of the leftlovers (edges and small pieces) resultant from the cutting and assembly processes of pultrusion profiles. Presently, these leftlovers, jointly with unfinished products and scrap resulting from pultrusion manufacturing process, are landfilled, with an estimated cost of 80€ per ton, which results on an average cost of 3500€ per year for this company.

Shredded GFRP waste was further processed by milling in an heavy-duty cutting mill laboratory unit (SM2000, Retsch). Two different size gradings of GFRP recyclates were obtained using bottom sieves with different perforation sizes inside grinding chamber. Obtained recycled products, shown in Fig. 1, consist in a mix of powdered and fibrous material, with different quantities of varying length of glass fibres, hereinafter designated by coarse (CW) and fine (FW) pultrusion waste. GFRP recyclates were characterized with report to organic and inorganic fraction contents and particle size distributions.

Burning test carried out on five random samples of GFRP waste revealed an average inorganic material content of 71% (w/w), corresponding to glass fibre and calcium carbonate fractions, and an average resin content of 29% (w/w).

Fig. 1. GFRP recyclates: Samples of CW -coarse pultrusion waste (at left) and FW -fine pultrusion waste (at right).

Particle size distributions obtained by means of sieving processes of both types of recycled wastes, in accordance with EN 933-1:1997, are presented in Fig. 2. Particle size distributions of filler fractions (<74 µm) were further evaluated by laser diffraction technique using a Particle Size laboratory unit (Malvern Mastersizer 2000G).

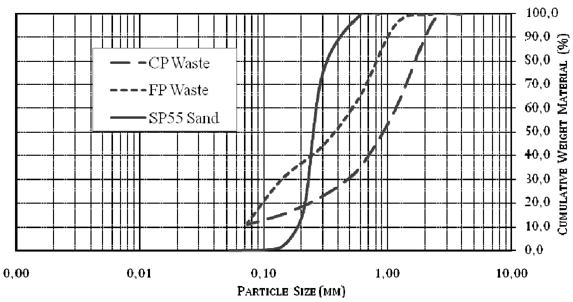

Fig. 2. Particle size distributions of GFRP waste recyclates and sand aggregates.

3.2 Mix Design and Casting Process

Six different GFRP waste admixed mortar formulations were analyzed, varying the type and content of GFRP powder and fibre mix waste. The following notation was adopted: CW and FW accounts for the type of GFRP recyclate, and the sequent number for the weight content of waste admixture. Control or free-waste polyester PMs (W-0) were also investigated for comparative analysis purposes. The composition of control formulation was designed in previous works on statistical significance of synergetic effects between material components [18]. Trials formulations analyzed in this study are described in Table I.

Table I. Mix proportions (w/w) of PM formulations.

Exp. Trials	Resin (%)	Sand (%)	GFRP Recyclates	
			FW (%)	CW (%)
W-0	20	80	-	-
FW-4	20	76	4	-
FW-8	20	72	8	-
FW-12	20	68	12	-
CW-4	20	76	-	4
CW-8	20	72	-	8
CW-12	20	68	-	12

Before manufacturing process, sand aggregates and GFRP recyclates were previously dried in an oven until constant weight, in order to prevent eventual inhibition of polymerization process due to moisture presence. PMs with binder formulations and mix design specified in Table 1 were mixed and casted into standard prismatic moulds (40x40x160 mm^3), according to RILEM recommendation CPT PC-2:1995. For each formulation six prismatic specimens were casted. All test specimens were allowed to cure 24 hours at 30ºC-50% RH and then, post-cured at 80ºC for 3 hours before being tested in bending and compression at room temperature. In Fig. 3, one broken specimen of each formulation, after being tested in bending, is illustrated.

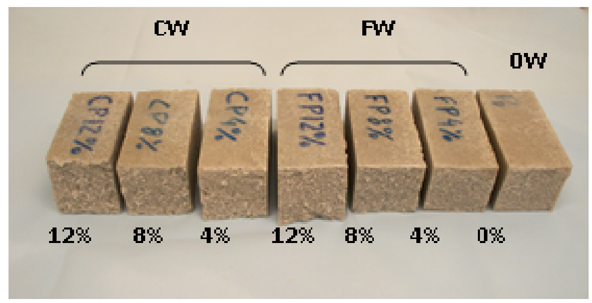

Fig. 3. PM specimens, after being tested in bending. –One specimen of each formulation in study-.

3.3 Testing Procedures

PM specimens were tested in three-point bending up to failure at the loading rate of 1 mm.min $^{-1}$, with a span length of 100 mm, according to RILEM CPT PCM-8 standard test method. The specifications of this standard, in terms of specimen geometry and span length, are similar to those specified in ASTM C348-08 standard test method for flexural strength of hydraulic cement mortars. Despite of the very low value of span to specimen thickness ratio, shear effect is disregarded and it is not considered. Mortar is assumed as an isotropic material and the theory of plane cross-section is used.

One of the two leftover parts, of each broken specimen in bending, were tested afterwards in compression at the loading rate of 1.25 mm.min^{-1}, following the procedure described in UNE 83821:1992 test standard. Both flexural and compressive testing set-ups are presented in Fig. 4.

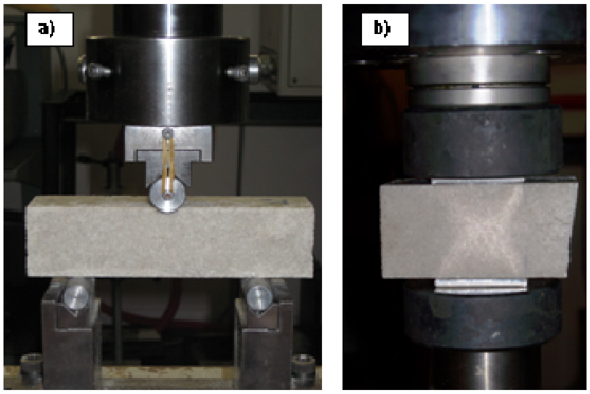

Fig.4. a) Flexural and b) compressive testing set-ups.

4 Results and Discussion

Mechanical test results are presented in Table II. Presented values represent the average flexural and compressive strengths of six specimens and correspondent standard deviations.

Relative increase of mechanical properties of GFRP waste admixed mortars over unmodified mortars can be observed in graphs of Fig. 5, for each type of waste admixture (CW and FW), and accounting for the average global effect of GFRP waste addition (CW/FW).

Table II. Mechanical test results.

Trial Formulation		Flex. Strength [MPa]	Comp. Strength [MPa]
W-0% (Ref.)		25.2 ± 1.3	76.3 ± 3.3
FW	4%	26.2 ± 1.5	78.0 ± 2.7
	8%	27.8 ± 1.6	84.7 ± 1.9
	12%	27.1 ± 1.5	81.0 ± 1.2
CW	4%	27.5 ± 0.6	83.4 ± 2.6
	8%	26.8 ± 1.4	86.2 ± 2.7
	12%	26.2 ± 1.1	82.0 ± 4.3

4.1 Effect of GFRP waste content

Obtained test results revealed that the incorporation of milled GFRP waste recyclates in polyester based mortars has an incremental effect on both flexural and compressive strengths of modified mortars, regardless of the GFRP waste type. However, two distinct trends were observed for the effect of waste admixture on mechanical strength of modified PMs according to the amount of waste addition: up to 8% content, the turning point, and above that value.

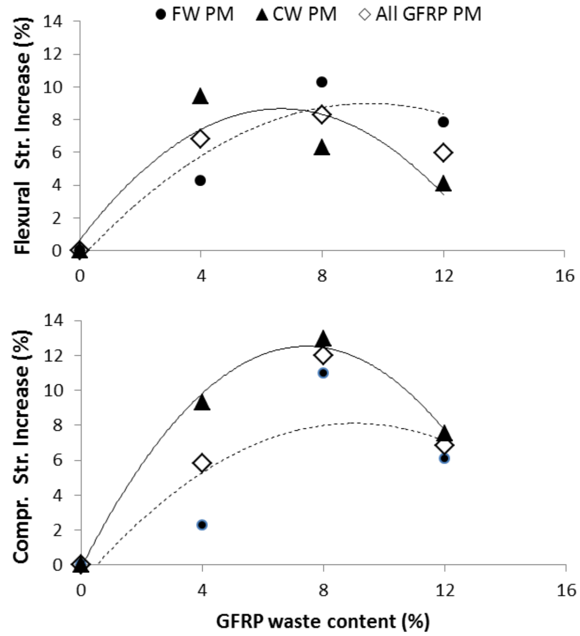

Fig.5. Relative flexural and compressive strength increases of GFRP waste admixed mortars over plain mortars –Trend curves-.

Up to 8% content in waste addition, apart from flexural load capacity of CW test series, in general, loading capacities of PMs increase with increasing addition of GFRP waste. This effect is clearer with regard to compressive behavior. Average compressive strength increases of 5.8% and 12.0% corresponding to the addition, respectively, of 4% and 8% in weight of GFRP waste, were observed with regard to unmodified PMs. The almost linear increase of compressive strength with GFRP waste content might be attributed to a more continuous particle size distribution of the mix sand/waste particles. The contribution of GFRP waste powder to filler fraction of sand aggregates, leading to an inferior void volume for dry-packed aggregate, has a relevant role in this feature. Generally, aggregate mixtures with the maximum bulk density lead to higher strength materials, due to improved aggregate agglomeration.

In flexural, this trend, the linear increase of loading capacity with increasing addition of GFRP waste, is not so clear. Average increases on bending capacity of 6.8% and 8.3% were found, respectively, for 4% and 8% in weight of GFRP waste additions. It was expected that fibrous fraction of GFRP waste would have a significant reinforcing effect, leading to a higher improvement on flexural behavior. Although this expected flexural improvement did actually occur for FW test series, in which progressive increases of 4.2% and 10.3% on bending strength were noticed for respectively FW-4 and FW-8 test formulations; slight decrease on flexural strength was observed for CW test series, when CW waste content was increased from 4% to 8%, and this tendency was kept for further addition amounts of coarser waste (CW-12). In the mixing and casting process of CW modified mortar specimens, some tendency for the agglomeration of waste fibres was observed, hindering somehow a perfect homogenization of the mixture. This feature, more notorious as higher the CW content, led to a non-homogeneous distribution of GFRP waste, and might be a possible explanation for obtained results. Another contributing factor might be the presence of larger particles on CW recyclate, which tend to be stress raisers, acting as failure initiation sites. This subject should be clarified in posterior study that will focus on microstructure analysis of fracture surface of mortar specimens

Above 8% content in waste addition, slight decreases on both flexural and compressive strengths occur with regard to PM formulations with lower contents of GFRP waste. Nevertheless, mechanical strengths remain higher than those of plain mortars: for 12% content in waste addition, average increases of 6.0% and 6.8% were observed on, respectively, flexural and compressive strengths of modified mortars. As larger amounts of sand were replaced by GFRP waste throughout CW and FW test series, from 0% to 12%, overall specific surface area of aggregates was progressively increased, while resin content was kept constant to 20% in weight in all formulations. Thus, higher specific surface area of GFRP waste particles as regards to sand particles, requiring higher contents of binder matrix for a proper wettability and cohesive bonding, is for certain the main reason for observed turning point on materials' behavior trend.

Although not stressed in this brief paper and not presented in test results, a less brittle failure of GFRP admixed mortars was observed, either in flexural or in compression. Improved ductility with increase GFRP waste content was more pronounced in compression than in flexural, with higher retention of load capacity after peak load.

4.2 Effect of GFRP waste size grading

Apart from flexural test results obtained with CW-8 and CW-12 mortar formulations, polymer mortars modified with CW present improved mechanical behavior over FW admixed mortars, for the same waste content. For 4% addition of CW recyclate, higher increases in mechanical strength were observed, either in flexural or compression, (9.4% and 9.3% increases, respectively, in flexural and compression strengths, against 4.2% and 2.3% obtained for the less coarse waste). 8% and 12 % additions of CW also lead to higher compressive strengths than the same contents of FW. CW recyclate presents a wide range of fibre lengths, varying between 25 mm and few micrometres (laser diffraction analysis of particle size distribution of CW filler fraction detected length fibres between at least 74 µm and 2000 µm). Maximum fibre length of FW is around 5 mm, thus, CW has a higher reinforcing effect than FW. This generally leads to improved mechanical behavior of host material, providing that a good interface bonding is ensured. In general terms, taking into account the distinct geometric characteristics of FW and CW recyclates, it can be stated that whereas FW acts more like a filler extension for sand aggregates of modified mortar, leading to a less void-volume of resultant material; CW acts mainly as reinforcing material, conducting to improved mechanical strength and less brittle behavior of modified mortar.

5 Conclusions

The main conclusions of the use of GFRP waste recyclates in PMs testing program are as follows:

- For the trial formulations analyzed in this study, the partial replacement of sand aggregates by GFRP waste materials has an incremental effect on both flexural and compressive strengths of resultant PMs, regardless of the GFRP waste type and content;
- 8% in GFRP waste content constitutes the turning point value on materials' behavior trend;
- For the same waste content, CW admixed PMs present in general improved mechanical behavior over PMs modified with FW, showing a superior reinforcing effect;
- Both types of GFRP waste improve ductility and lead to a less brittle failure of resultant mortars.

The findings of this study showed a viable technological option for improving the quality of GFRP filled polymer mortars, thus opening a door to selective recycling of GFRP waste and its use in the production of concrete-polymer based products. However, further studies will be necessary and are foreseen, in order to define efficient methods to prevent fibres agglomeration during mixing and casting processes, and to improve interface adhesion between fibre waste and resin matrix. It is expected that the futures studies will confirm the technical and economic viability for commercial exploitation of GFRP waste incorporation into PC composites.

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