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**NEW RECYCLING APPROACHES FOR THERMOSET POLYMERIC  
COMPOSITE WASTES  
– AN EXPERIMENTAL STUDY ON POLYESTER BASED CONCRETE  
MATERIALS FILLED WITH FIBRE REINFORCED PLASTIC RECYCLATES -**

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**ABSTRACT**

In this study, a new waste management solution for thermoset glass fibre reinforced polymer (GFRP) based products was assessed. Mechanical recycling approach, with reduction of GFRP waste to powdered and fibrous materials was applied, and the prospective added-value of obtained recyclates was experimentally investigated as raw material for polyester based mortars. Different GFRP waste admixed mortar formulations were analyzed varying the content, between 4% up to 12% in weight, of GFRP powder and fibre mix waste. The effect of incorporation of a silane coupling agent was also assessed. Design of experiments and data treatment was accomplished through implementation of full factorial design and analysis of variance ANOVA. Added value of potential recycling solution was assessed by means of flexural and compressive loading capacity of GFRP waste admixed mortars with regard to unmodified polymer mortars. The key findings of this study showed a viable technological option for improving the quality of polyester based mortars and highlight a potential cost-effective waste management solution for thermoset composite materials in the production of sustainable concrete-polymer based products.

**Keywords:** Thermoset Fibre Reinforced Polymer; Recycling; Concrete-polymer composites

**INTRODUCTION**

The development and applications of thermoset polymeric composites, namely fibre reinforced polymers (FRP), have shifted in the last decades more and more into the mass market. FRP materials are generally made of glass (GFRP), carbon (CFRP), aramide (AFRP) or basalt (BFRP) fibres dispersed in an organic matrix, usually polyester resin, widely used in several fields, from building to aeronautic and military applications [1-2]. The high strength to weight ratio, low maintenance, corrosion resistance, design flexibility and tailor made properties made up FRP based materials an interesting alternative to steel, metals and other similar materials [3]. Despite of all of these advantages, the increasing production and consume also lead to an increasing amount of FRP wastes, either end-of-life products or scrap generated by the manufacturing process itself. Whereas thermoplastic FRPs can be easily recycled, by remelting and remoulding, recyclability of thermosetting FRPs constitutes a more difficult task due to inherent cross-linked nature of resin matrix. To date, most of the thermoset based FRP waste is being incinerated or landfilled, leading to negative environmental impacts and supplementary added costs to FRP producers and suppliers. Further, in the near future, due to increasing severity and restrictions of waste management legislations, FRP suppliers risk losing their market share to metals and other industries if they cannot ensure that their FRP products and components can be reused or recycled

at the end of their life cycle [4]. This actual framework is putting increasing pressure on the industry to address the options available for FRP waste management, being an important driver for applied research undertaken cost efficient recycling methods. In spite of this, research on recycling solutions for thermoset composites is still at an elementary stage. Thermal and/or chemical recycling processes, with partial fibre and energy recovering, have been proposed mostly for CFRP composites due to inherent economic value of carbon fibre reinforcement; whereas for GFRP based products, mechanical recycling by means of milling and grinding processes, with reduction to fibrous and/or powdered products, has been considered a more viable recycling method [5]. The most extensive research work has been carried out either on bulk (BMC) and sheet moulding compounds (SMC), or on Portland cement concrete, in which mechanically-recycled GFRP wastes have been incorporated either as reinforcement, aggregate or filler replacement [6-7]. Though, at the moment, few solutions in the reuse of GFRP recyclates into added value products are being explored. Seeking filling this gap, in this study, a new waste management solution for thermoset GFRP based products was assessed. Mechanical recycling approach was applied and the potential added value of obtained recyclates was experimentally investigated as raw material for polyester based mortars. The use of a cementless mortar as host material for the recyclates, instead of conventional Portland cement based mortars, presents an important asset in avoiding the eventual incompatibility problems arisen from alkalis silica reaction between glass fibres and cementitious matrix binder. In addition, due to hermetic nature of resin binder, polymer based concrete materials present greater ability for incorporating recycled waste products [8]. Applied GFRP waste material was supplied by a local pultrusion manufacturing company (*Alto, Perfis Pultrudidos Lda.*), and it was proceeding from the shredding of the leftovers resultant from the cutting and assembly processes of GFRP pultrusion profiles. Currently, these leftovers, jointly with non-conform products and scrap resulting from the manufacturing process itself, are landfilled with an estimated cost of 80€ per ton which represents for this company on an average cost of 3500€ per year. Thus, besides the manifest environmental benefits, a viable and feasible solution for these wastes would also conduct to significant economic advantages.

## EXPERIMENTS AND PROCEDURES

Polymer mortar (PM) specimens were prepared by mixing an unsaturated polyester resin (20% w/w) with different sand aggregates/GFRP waste ratios. Processed GFRP wastes were used as partial substitute for sand aggregates at the proportion of 4%, 8% and 12% in weight of total mass. Plain mortar specimens were also casted and tested in order to compare mechanical and functional properties over those of GFRP waste admixed mortars. Mix design of plain formulation was in accordance with previous works carried out by Ribeiro and Ribeiro et al. [8-9]. In order to investigate the effect of an adhesion promoter, a second series of experiments was carried out in which 1% of active silane coupling agent by weight of resin was added to all formulations in analysis.

### Raw Materials and Characterization

Commercially available unsaturated polyester resin (Aropol® FS3992), with a styrene content of 42%, was applied as polymer binder. Polymerization process was induced by cobalt octoate (0.5 phr) and 50% methyl ethyl ketone peroxide solution (2.0 phr). An organofunctional silane chemical solution (Dow Corning® Z-6032), with 40% of active silane in methanol, was applied as adhesion promoter of resin binder to inorganic sand aggregates and GFRP recyclates. Z-6032, when applied, was previously mixed with polyester resin binder prior sand and GFRP recyclates addition. A siliceous foundry sand (slica content > 99.0%), with rather uniform particle size and an average diameter of 245 µm was used as fine aggregate. Detailed characterization of applied foundry sand can be found elsewhere (9).

GFRP wastes, supplied by the local pultrusion manufacturing company, were further processed in a heavy duty cutting mill laboratory unit (Type SM2000, Retsch). Obtained mechanically-recycled products, illustrated in Fig.1, consist in a mix of powdered and fibrous material with different quantities of varying length of glass fibres and bulk particulate material. Particle size distribution GFRP recyclates, obtained by sieving and laser diffraction techniques, revealed a range of particles size (or fibre diameter) between 1.5 µm up to 2500 µm, an average diameter of 950 µm, and a fineness modulus of 2.69.

### Experimental Plan and Testing

Eight different PM formulations were investigated varying the content of both GFRP waste admixture (0%, 4%, 8% and 12% of total mass) and silane coupling agent (0% and 1% by weight of resin content), hereinafter designated, respectively, by material factors W and S. Experimental trials are presented in Table 1 and correspond to a two-factor ( $4^1 \times 2^1$ ) full factorial design. PM formulations, with the specified mix proportions were casted into standard prismatic moulds ( $40 \times 40 \times 160 \text{ mm}^3$ ) according to RILEM recommendation CPT PC-2:1995 (1995). For each formulation, four prismatic specimens were casted. All test specimens were allowed to cure 24 hours at  $30^\circ\text{C} / 50\% \text{ RH}$ , and then post-cured at  $80^\circ\text{C}$  for 3 hours, before being tested in bending and compression at room temperature. PM specimens were tested in three-point bending up to failure at the loading rate of  $1 \text{ mm}\cdot\text{min}^{-1}$ , over a span length of 100 mm, according to RILEM CPT PCM-8 standard test method (1995). One of the two leftover parts of each broken specimen in bending, were tested afterwards in compression at the loading rate of  $1.25 \text{ mm}\cdot\text{min}^{-1}$ , following the procedure described in UNE 83821 standard (1992). Both testing set-ups are shown in Fig.1.

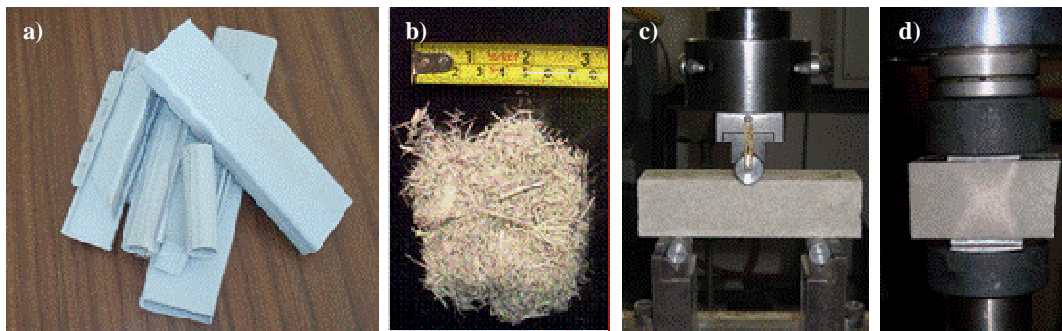


Fig. 1. a) GFRP wastes; b) Mechanically-recycled GFRP waste; c) and d) Mechanical test set-ups.

## RESULTS AND DISCUSSION

### Mechanical Test Results

For each PM formulation, obtained flexural and compressive strengths are detailed in Table 1. Presented values represent the average mechanical properties obtained for the four replicates and correspondent standard deviations. The main effects of each material factor, and the interaction effect between the two factors, are highlighted in response graphics displayed in Fig. 2. Response graphics allow the evaluation of the relative importance of each factor, or interaction, in a much easier way than the numeric values of effects. For principal effects, the interpretation of response graphics is straightforward: each point represents the average response for a certain level of the factor and the numeric value of the effect is the difference between the set of points; the higher the difference, the higher the influence of the factor. The interaction is graphically defined by the parallelism between the set of lines: the smaller the parallelism, the higher the interaction [10].

Table 1. Mechanical test results for mix design formulations of PMs.

Mix Trials	Resin Binder [%]	Foundry Sand [%]	GFRP Waste [%]	Silane Agent [%]	Flexural Strength [MPa]	Compressive Strength [MPa]
1. W 0-0	20	80	0	0	$25.17 \pm 0.74$	$76.89 \pm 0.89$
2. W 4-0	20	76	4	0	$27.74 \pm 0.31$	$83.27 \pm 2.02$
3. W 8-0	20	72	8	0	$26.29 \pm 0.99$	$86.22 \pm 2.12$
4. W 12-0	20	68	12	0	$26.18 \pm 0.51$	$82.81 \pm 2.91$
5. WS 0-1	20	80	0	1	$36.00 \pm 0.53$	$81.29 \pm 0.74$
6. WS 4-1	20	76	4	1	$40.35 \pm 0.93$	$97.52 \pm 1.00$
7. WS 8-1	20	72	8	1	$41.70 \pm 1.81$	$104.69 \pm 0.66$
8. WS 12-1	20	68	12	1	$39.28 \pm 1.44$	$82.42 \pm 2.42$

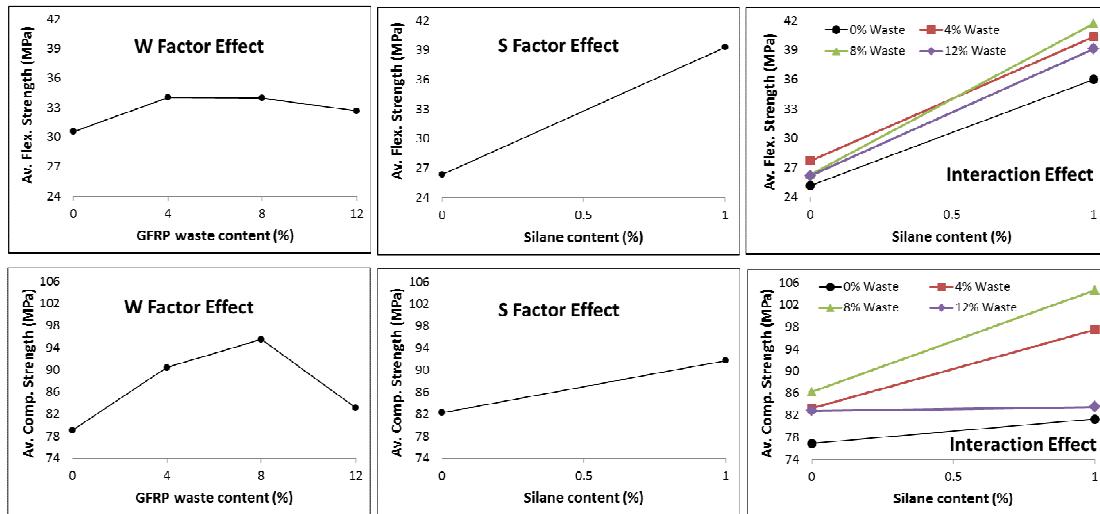


Fig. 2. Response graphs of main and interaction effects with respect to both mechanical strengths.

### Analysis of Variance ANOVA

Analyses of variance for the properties in study are given in Tables 2 and 3 in terms of sum of squares (SS), degrees of freedom (DF), mean squares values (MS) and F-test values for a significance level of 5%. Obtained calculated values allow assessing the relative significance of each factor and interaction on target responses of the experiment. The F-test statistic,  $F_0$ , is calculated as the ratio between the mean of squares of the group (factor or interaction) and the mean of squares of the random error. The percentage of contribution, in the last columns, indicates the relative influence of the factor and/or interaction on the global variation observed, and it is derived from the expected value of the variance due exclusively to that factor or interaction [9-10].

Table 2. Analysis of Variance for Flexural Strength Data.

Source of Variation	SS [MPa <sup>2</sup> ]	DF	MS [MPa <sup>2</sup> ]	F <sub>0</sub> Values	F <sub>crit</sub> Values	Cont. P [%]
Factor S –Silane content	1342.07	1	1342.07	629.74	4.75	92.29
Factor W –Waste content	62.99	3	21.00	9.85	3.49	3.90
Interaction SW	21.28	3	7.09	3.33	3.49	1.02
Error	25.57	12	2.13	-	-	-
Total	1451.92	31	-	-	-	-

Table 3. Analysis of Variance for Compressive Strength Data.

Source of Variation	SS [MPa <sup>2</sup> ]	DF	MS [MPa <sup>2</sup> ]	F <sub>0</sub> Values	F <sub>crit</sub> Values	Cont. P [%]
Factor S –Silane content	714.23	1	714.23	139.75	4.75	28.68
Factor W –Waste content	1283.13	3	427.71	83.69	3.49	51.28
Interaction SW	413.57	3	137.86	26.97	3.49	16.11
Error	61.33	12	5.11	-	-	-
Total	2472.26	31	-	-	-	-

### Effect of Material GFRP Waste Content

Experimental test results, presented in Table 1, show that the partial replacement of sand aggregates by milled GFRP waste recyclates in polyester based mortars has an incremental effect on both flexural and compressive strengths of modified mortars, regardless of GFRP waste content and silane coupling agent addition. Though, the effect of GFRP waste on mechanical strength is clearly more pronounced regarding compressive behavior than flexural performance, as displayed

in responses' graphics of the main effect of this factor (Factor W) and confirmed by analysis of variance: a) Slopes of lines of compressive strength response graphic are sharper, in opposition with the smooth slopes occurring for flexural strength response (see Fig. 2); b) The contribution of this factor to global variance of compressive strength of PMs is higher than 50%, whereas for flexural strength, the contribution does not reach 4% (see Tables 2 and 3).

Although the global improvement effect of GFRP recyclates incorporation on mechanical strength of resultant modified PMs, two distinct trends were observed for this effect according to the amount of waste addition (or sand replacement): up to 8% content and above that value.

Up to 8% content in waste addition, in general, loading capacities of PMs increase with increasing addition of GFRP waste. Once again, this feature is more pronounced with regard to compressive behaviour. Average compressive strength increases of 14% and 21% corresponding to the addition, respectively, of 4% and 8% in weight of GFRP waste, were observed with regard to waste-free 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, aggregates 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 increase addition of GFRP waste, is not so clear. Average increases on bending capacity of 11% and 10% 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 behaviour. Although this expected flexural improvement did actually occur for test series modified with silane coupling agent, in which progressive increases of 12% and 16% on bending strength were noticed for respectively WS4-1 and WS8-1 test formulations; slight decrease on flexural strength was observed for silane-free test series, when GFRP waste content was increased from 4% to 8%, and this tendency was kept for further addition amounts of waste (W12-0). In the mixing process of GFRP modified PMs, 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 waste content, led to a non-homogeneous distribution of GFRP waste fibres, and might be a possible explanation for obtained results. Another contributing factor might be the presence of larger particles on GFRP recyclates, which tend to be stress raisers, acting as failure initiation sites. Further, being true this assumption, this weakness would be more critical under tensile than under compressive stresses. This subject should be clarified in posterior study that will focus on microstructure analysis 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, but even so, mechanical strengths remain higher than those of plain mortars. It must be stressed that resin content was kept constant to 20% in weight in all formulations; and, as larger amounts of sand were replaced by GFRP waste throughout W and WS test series, from 0% to 12%, overall specific surface area of aggregates was progressively increased. Thus, the higher specific surface area of GFRP waste particles as regards to sand particles, requiring higher binder contents for a proper wettability and cohesive bonding, is for certain the main reason for observed turning point.

#### **Effect of Material Factor Silane Coupling Agent**

As already expected, the incorporation of silane coupling agent had a significant improvement effect on mechanical strength of PM formulations. S factor's effect is especially remarkable with regard to flexural strength response, contributing with more than 92% for the global variance. The numeric value of this effect on flexural strength is 12.9 MPa, which means that, in average, PMs with incorporation of 1% silane, regardless of GFRP waste content, present a flexural strength higher in 12.9 MPa over silane-free PMs. The inherent contribution of silane coupling agent as adhesion promoter at interface, between resin matrix and both sand aggregates and glass fibres waste, improving the organic-inorganic phase bridge, is for certain the main reason for the observed strong effect of this factor on flexural strength response of PMs. With regard to compressive strength response, a minor contribution for global variance was observed (29%), prevailing the GFRP waste content as the most influencing and significant factor. As only two levels of variation were considered for this factor, 0% and 1%, no considerations could be done regarding the linear or quadratic effect of silane content addition on mechanical properties of PMs.

### Effect of Interaction between Factors

According to F-test results of analysis of variance, for a significance level of 5%, there is no significant interaction between GFRP waste content and adhesion promoter with regard to flexural strength response. Calculated  $F_0$  value is less than  $F_{crit}$ , and thus the null hypothesis is accepted, which means that the groups are not significantly different, i.e., the interaction is not significant. The almost absence of interaction is graphically visualized by the similar slopes of the set of lines corresponding to 0%, 4%, 8% and 12% waste test series on interaction response graphic (Fig. 2).

A different scenario was found for the effect of this interaction on compressive strength response. Interaction between the analyzed main factors contributes with 16% for global variance of compressive strength which cannot be disregarded. The effect of this interaction is mainly due to dissimilar behaviours of W and WS test series when GFRP waste content is increased from 8% to 12%. Drop of compressive strength is very pronounced for PMs with incorporation of silane agent (21 MPa in average) and mostly smooth for those without adhesion promoter (3 MPa in average).

### CONCLUSIONS

With basis on obtained results, the following conclusions may be drawn:

- 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 content and silane coupling agent addition.
- Both material factors have a significant positive effect on mechanical behavior of modified PMs; though, whereas GFRP waste content is the more influencing factor on compressive strength response, contributing with 51% to global variance of this property; 92% of the global variance of flexural strength response is due to silane coupling agent addition.
- The interaction between the two factors has no significant effect on flexural strength of PM formulations; however, this interaction cannot be disregarded with respect to compressive response, especially for GFRP waste contents above 8% (w/w).
- 8% in weight of GFRP waste content constitutes the turning point value on materials' behavior trend for both analyzed properties.

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.

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