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Replacement of quartz in cementitious composites using PET particles: a statistical analysis of the physical and mechanical properties

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Abstract: This work investigates the mechanical behaviour of cementitious composites (mortar) when quartz inclusions are totally or partially replaced with polyethylene terephthalate (PET) particles. A full factorial design is performed to identify the effect of the water/cement ratio and the range of quartz particles size used in the replacement on the different mechanical and physical parameters (bulk density, apparent porosity, water absorption, oxygen permeability, compressive strength and modulus
of elasticity). The results show a general reduction of the mechanical properties when the replacement with quartz particles is put in place. The composites made by replacing the coarse quartz particles showed acceptable mechanical properties for non-structural civil engineering applications, with a significant amount of PET recycling to be used as aggregates for some specific end-user cases.

**Keywords:** PET wastes, Cementitious composites, Mechanical properties, Microstructural analysis

**Introduction**

The use of synthetic fibres in different classes of materials, such as ceramics and polymers, has provided a sustainable alternative for the re-use of waste in the manufacturing of new lightweight materials (Wang and Tsai, 2006; Chandra and Berntsson, 2003; Choi et al., 2005). The increasing consumption of manufactured products has resulted in an uncontrolled increase of solid waste. In Brazil, the production of solid waste has grown more than six times the population rate (ABRELPE, 2010). Nearly two hundred thousands of tonnes of solid waste are discarded daily in the country, 42.4% of the total ending up in landfills (ABRELPE, 2010; Williams, 1998). In Europe, approximately 1.8 billion tonnes of waste are generated per year, with plastics representing 46.4 million of tonnes, and waste from polyethylene terephthalate (PET) bottles being near to 2.784 million of tonnes (PLASTICS-THE FACTS, 2011). The European Commission has set in 2006 the objective to reduce the amount of packaging waste by 70% (Coelho et al., 2011). On a global basis the consumption of PET for packaging is forecast to reach €24 billion by 2011. Statistics show that the United States is the largest user of PET packaging, followed by China and Mexico. Asia Pacific central and Eastern Europe, and parts of Latin America have shown the strongest growth of PET usage between 2001 and 2006 (Butschili, 2006).

Plastic materials have been investigated as potential aggregate into concrete and mortar (Batayneh et al., 2007; Kim et al., 2010). A well-known lightweight plastic material with a low density
and porosity is Polyethylene terephthalate (PET) (Hannawi et al., 2010). PET is a thermoplastic polymer that has been used in a variety of products due to its lightweight characteristics, ease of handling and storing. Although it is mostly known for its use in plastic bottles, it was introduced first for applications in the textile industry. PET wastes have been recently considered as lightweight aggregates for cementitious composites (Satapathy and Nando, 2008) in civil engineering. The PET residues can also be used as matrix in laminates (Onal and Adanur, 2005) and particulate composites (Hannawi et al., 2010). Modro et al. have investigated the effect on the mechanical strength of Portland cement concrete when adding PET waste, observing a reduction in strength for increasing volume fraction of PET aggregates (Modro et al. 2009). Albano et al. have investigated the effect of adding PET bottle waste (10 and 20%), its particle size (0.26 to 1.14 cm) and water/cement ratio (0.50 and 0.60) on the mechanical properties of concrete (Albano et al., 2009). The results from that work clearly show that when PET aggregates are used in increasing volume and sizes, the compressive strength and modulus of the concrete decreases and - at the same time - the water absorption increases significantly.

Foti (2011) has proposed the use of PET bottles to produce fibres for reinforcement and improve the ductility of the concrete. Tests have shown that PET fibres could provide an increase in toughness of the concrete matrix.

Although the use of recycled materials in cement products has substantially increased, most applications have to focus on the use of precast products, due to their intrinsic structural safety and the difficulty of controlling the homogeneity of recycled raw materials. The use of a robust statistical methodology based on full factorial design can reveal the effective contributions of individual constituents and material parameters on the overall physical and mechanical properties of these complex composite materials. This work describes a novel mortar material based on the use PET waste and quartz particles, and Portland cement. A full factorial design ($2^4$) was conducted to evaluate the effect of quartz/PET particle replacement on the physical and mechanical properties of cementitious composites in masonry cement mortar.
Materials and Methods

Composite Material

The composite was made of a matrix phase (Portland cement), inclusions consisting of particles of quartz and/or PET. The Portland cement (ASTM type III) was supplied by Cauê Industry (Brazil). PET flakes (washed and dried) were supplied by the MinasPet Packaging Company (Brazil). The PET flakes were milled using a lab knife mill to obtain particles. The quartz particles were supplied by the Moinhos Gerais Company (Brazil). Both quartz and PET particles were classified by sieving to achieve the particle size ranges as recommended by the ASTM C144 (2011) standard:

- Coarse particles (C): 30wt% of particle size range from 4.75 mm to 850 μm (4-20 US-Tyler);
- Medium particles (M): 50wt% of particle size ranging between 850 μm and 300 μm (20-50 US-Tyler);
- Fine particles (F): 20wt% of particle size from 300 μm to 75 μm (50-200 US-Tyler).

Four reference conditions (i.e., samples) were produced as benchmark for the Design of Experiment (DoE). The four reference conditions are shown in Table 1, and were manufactured based on the combination of the factors (levels) such as the type of particle used for the dispersion (quartz and PET), and the water to cement ratio (0.45 and 0.55). All references conditions have followed the particle size distribution recommended by ASTM C144 (2011).

Full factorial design (DoE)

The Design of experiments (DoE) and the Analysis of Variance (ANOVA) are used to evaluate not only the direct effect of individual factors, but also their mutual interaction when affecting the responses at a confidence interval of 95%. A full factorial design \( n^k \) is made from all possible combinations of the experimental factors \( k \) and its respective levels \( n \). The DoE approach was based on a randomized design to eliminate redundant observations and to reduce the number of tests, in order
then to obtain statistically robust information about the interactions existing among variables (Montgomery, 2005).

A full factorial design of $2^{4\times1}$ (Table 2) was identified to perform the DoE process. The levels considered were the water/cement ratio (0.45 and 0.55) and particle size ranges of quartz replacement (coarse particles (C), medium particles (M), fine particles (F), coarse and medium particles (CM) and medium and fine particles (MF)). The responses of the DoE analysis were the density, porosity, water absorption, permeability, compressive strength and the modulus of elasticity of the composites. A microstructural analysis was performed to observe the particles distribution and the presence of internal pores.

**Fabrication and testing**

The composite samples were manually manufactured by mixing Portland cement, quartz particles, PET particles and water for 5 minutes at room temperature (22°C). The water/cement ratio levels used in this work were similar to the ones existing in commercial cement precast products. The paste was poured into cylindrical moulds of 50mm in diameter and 100mm in height. The presence of entrapped air was limited by the use of a vibrating table (5 min) to compact the samples. The specimens were kept inside sealed plastic bags to avoid the evaporation of water. The samples were taken out from the moulds after 28 days of curing time at room temperature (22°C). Eight specimens were fabricated for each experimental condition, leading to a total of 224 different samples. Replicate specimens allow to estimate the variability associated with the tested phenomenon (Wu and Hamada, 2000). The magnitude of this error is important for the identification of significant effects attributed to the factor selection. A randomization procedure was also adopted during the manufacturing of the samples and the experimental tests, making the whole numerical process more robust against variables that are unknown to the experiment, but which may impact on the response (Montgomery, 2005; Wu and Hamada, 2000).
Following the recommendations of the BS1881-121 (1993) standard, the two end cross sections of the cylindrical specimens were coated with sulphur paste to ensure the parallelism required during the compressive loading. The mechanical testing was performed using an Instron test machine with 100kN load cell capacity. Four samples were tested for each experimental condition and replicate.

The modulus of elasticity was determined according to the BS1881-121 (1993) standard. The bulk density was calculated by dividing the dry weight by the bulk volume of the samples. The apparent porosity $Po$ represents the percentage of the volume of open pores in the bulk volume of the sample. The apparent porosity was determined using the vacuum saturation method (BS10545-3, 1997) using the equation:

$$Po = \frac{W_2 - W_1}{W_2 - W_3} \times 100$$

(1)

Where $W_1$ is the dry mass of the specimen, $W_2$ is the mass of specimen saturated with water and $W_3$ is the mass of the specimen fully submerged in water. The water absorption $A_b$ was determined from the percentage of the water absorbed by a specimen after immersion in water on constant negative pressure:

$$A_b = \frac{W_2 - W_1}{W_1} \times 100$$

(2)

The permeability coefficient was determined using the oxygen permeameter system developed by Cabrera and Lynsdale (1988). The system allows the measurement of the permeability coefficient by differential gas pressure. The repeatability and reproducibility of results, as well as the description of the operation of the system are reported in Cabrera and Lynsdale (1988).

**Results**

The statistical software Minitab 16 was used to perform the Design of Experiment (DOE) and the Analysis of Variance (ANOVA). The P-values from ANOVA (Table 3) indicate which effects are statistically significant based on the examination of the experimental data from replicates #1 and #2.
If the P-value is less than or equal to 0.05, the effect is considered to be significant. A $\alpha$-level of 0.05 is the level of significance that implies a 95% probability of the effect being significant (Wu and Hamada, 2000). The results are presented via ‘main effect’ and ‘interaction’ plots. The main effect of a factor can be only interpreted individually if there is no evidence that it does not interact with other factors. When one or more interaction effects with superior order are significant, the factors that interact might be considered together (Montgomery, 2005).

The value of ‘R² adjusted’ exhibited in the ANOVA provided how well the model predicts responses for new observations. The closer the coefficient is to 1 (or 100%), suggests models of greater predictive ability. The R² values for the responses varied from 74.40% to 99.21%, which indicates satisfactory accuracy of the models. The P-values underlined in Table 3 corresponds to the significant factors affecting the responses and those in bold text indicate the factors and/or interactions of superior order which will be illustrated in the effect plots.

**Reference conditions**

Table 4 shows the physical and mechanical properties for the reference conditions. The reference condition RC3 made of quartz particles (Q) has a higher strength and stiffness compared to RC1, which was fabricated using a smaller amount of water (see Table 1). The water is responsible not only for the hydration of the cement grains, but also provides improved manufacturability. However, a large amount of water can also cause a decrease of the mechanical performance of the composite, because water excess evaporates and forms internal pores. Table 4 however shows an opposite behaviour, since the apparent porosity and water absorption responses have been reduced for RC3 and RC4 when 0.55 of water/cement ratio was considered. This behaviour possibly indicates that the water/cement ratio of 0.45 (RC1 and RC2) was not sufficient to provide the complete hydration of the cement grains.

**Bulk density**

The bulk density varied from 1.63 g/cm³ to 2.18 g/cm³. The P-value of 0.002, lower than 0.05, reveals a significant interaction presented in the bulk density response (Table 3). Fig. 1 shows the
interaction effect plot of water/cement ratio and the replacement of the quartz particle for the bulk density. A lower amount of water (w/c 0.45) provides an increase in the bulk density, except when coarse quartz particles (4-20US-Tyler) are replaced by PET particulates. In general, the replacement of the quartz particles by PET leads to a decrease of the bulk density of the composites, which is attributed to the significant physical difference between the aggregates. Moreover, the replacement of the quartz aggregate with a lighter material provides a larger volume of PET aggregates. A lower bulk density was achieved when coarse - medium (CM) and medium - fine (MF) quartz particles were replaced. Higher bulk densities were obtained by using coarse (C), medium (M) and fine (F) particles, with the highest value of the density corresponding to the case when fine (F) quartz particles were replaced by PET dispersions, which also represents the lower amount of particle replacement (20wt%).

Table 4 shows that a total replacement of quartz by PET particles provides a reduction of 37.60% and 36.75% in bulk density when the composites are fabricated with water/cement ratios of 0.45 (RC1 and RC2) and 0.55 (RC4 and RC3), respectively.

**Apparent porosity**

The apparent porosity varied from 10.57% to 33.33%. Fig. 2 shows the plot of the main effect provided by the water/cement ratio for the apparent porosity. A higher water/cement contribution (0.55) gives a 63.96% reduction of the average value of the apparent porosity. Since the rheology of the two systems was quite similar, this result indicates the likehood that the low level of w/c ratio (0.45) was not sufficient to fully hydrate the cement grains. This effect was intensified when the composites were manufactured with 100wt% of quartz particles, revealing an increase of 144% on porosity while w/c ratio of 0.45 was considered (see Table 4), likely to be caused by the internal pores of the mineral particles that absorb some water. The replacement with 100wt% of quartz particles has minimized this effect, showing a 19% increase of porosity when the w/c ratio of 0.45 was used (see Table 4). The particle volume fraction is also increased when the PET aggregates are used, leading to a reduction in the cement volume fraction that is also responsible for the porosity of the composite
material.

Fig. 3 shows the main effect plot related to the apparent porosity when the quartz particle replacement is considered. The use of monomodal PET particles rather than quartz leads to lower porosity in comparison to the use of bimodal PET inclusions (CM and MF). This result seems to indicate that the increase of PET inclusions damages the packing of the particles, with an increase of porosity of the composites. The irregular shape of the PET particles due to the milling process might have also provided a significant contribution (Albano et al., 2009). Table 4 shows that the total replacement of quartz by using PET particles is able to increase the porosity in a significant manner, by 97% and 302% when using 0.45 and 0.55 of w/c ratio respectively. This result indicates that the pore formation is due not only to cement hydration products, but also to the presence of the interfacial transition zone (ITZ).

**Water absorption**

The water absorption varied between 5.6% to 27.6%. Only the main factors were responsible for this response, since the P-values were lower than 0.05 (see Table 3). When observing Fig. 4 (main effect plot of the water/cement ratio related to the water absorption) it is possible to notice that the higher level of the w/c ratio has not only reduced the porosity but also the level of the water absorption response in the composites. Moreover, a w/c ratio of 0.45 may have compromised the level of hydration of the cement products. Table 4 indicates that the largest amount of water (0.55) has reduced the water absorption of both 100wt% quartz and 100wt% PET particles composites.

Fig. 5 shows the plot related to the main effect on the water absorption when considering the quartz particle replacement factor. Similarly to the results related to the apparent porosity (Fig. 3), high water absorption is achieved when large amounts of quartz particles (CM and MF) have been replaced by PET. The replacement of the coarse quartz particles has shown to provide the lowest water absorption for all the composites considered. The total replacement of quartz by PET particles (Table
4) does increase substantially the water absorption, up to 186% for w/c values of 0.45 and 302% when w/c = 0.55.

**Permeability**

The permeability is the most important factor to quantify the durability of cement-based composites when particles from waste sources are incorporated (Wang and Meyer, 2012; Zhou, 2014). Only a limited number of open literature papers have described the durability of concrete containing plastic aggregates. However, existing data indicate that the inclusion of plastic aggregate can reduce the permeability of the concrete, making it more durable against aggressive chemical attacks (Saikia and Brito, 2012). In the current study the permeability varied between $0.02 \times 10^{-16}$ m$^2$ to $0.18 \times 10^{-16}$ m$^2$. Fig. 6 shows the main effect over the permeability against the water/cement ratio. The composites made from the highest water/cement ratio levels (0.55) presented lower permeability, apparent porosity (see Fig. 2) and water absorption (Fig. 5). The low level of w/c ratio (0.45) appears not to be able to hydrate entirely the cement paste.

Fig. 7 shows the main effect provided by the size of the quartz particle replacement over the permeability. The permeability is significantly affected by the quantity of the PET particles added to the system. Increase of the permeability is observed with the replacement of the coarse-medium (CM), medium-fine (MF) and fine (F) quartz particles. This behaviour can be attributed to the increased amount of PET particles in the system, which raises the number of pores around the particle/matrix interface. The porosity around the ITZ is also observed when fine PET particles are incorporated, which cause the presence of larger surface area.

**Compressive strength**

Compressive strength values varied from 1.43 MPa to 14.88 MPa. Fig. 8 shows the plot related to the interaction effect between factors like water/cement ratio and quartz particle replacement. It is evident the influence that these factors have over the compressive strength (see Table 3). Low levels of w/c ratio lead to higher mechanical strength, mainly due to the reduction of pores existing in the
composites microstructure (Choi et al., 2005; Neville, 1981). In this work, the w/c ratio of 0.45 results in a lower strength compared to the value of 0.55. The lowest level of water/cement ratio (0.45) corresponded to an increase in the bulk density, besides increasing at the same time the porosity, water absorption and permeability of the composites. This behaviour implies that the low amount of water might not be sufficient to hydrate totally the cement grains, therefore affecting the interfacial transition zone (ITZ). As previously observed, the increase of the quartz particle replacement on a weight basis also leads to higher PET volume fractions, which can also be responsible to the degradation of the physical and mechanical properties of the composites.

Cota et al. (2012), Ollitrault-Fichet et al. (1998) and Sakai and Sugita (1995) have observed that ITZ affects the mechanical strength of modified cement composites and helps to enhance the particle-matrix bond. The replacement of coarse quartz particles has provided the highest mechanical strength, followed by the replacement of fine quartz particles, in a similar way to what observed for the other physical parameters investigated. The replacement of medium quartz particles (M and CM) has significantly reduced the compressive strength of the composites, a behaviour that can be explained by the packing factor effect. Table 4 shows that the total replacement of quartz with PET particles has led to a very significant reduction of the compressive strength (1436%). The coarse quartz replacement (C) provides however a compressive strength close to 14.9 MPa, which is an interesting value for non-structural applications (Chandra and Berntsson, 2003). The addition of recycled PET does not contribute however to the strength of the cementitious composite, similarly to what observed by other authors (Nacif et al. 2013; Rossignolo and Agnesini, 2002; Akçaözoğlu and Ulu, 2014).

Young’s modulus

The modulus of elasticity of the composites varied from 0.28 GPa to 2.85 GPa. From the variation of the Young’s modulus according to water/cement ratio and quartz particle replacement (Fig. 9) it can be observed the lowest level of w/c ratio (0.45) has provided the lowest modulus of elasticity. Higher Young’s moduli were obtained using coarse (C) and fine (F) quartz particle
replacements, in accordance with what has been observed for the compressive strength (Fig. 8). The medium size quartz particle (M, CM and MF) replacements have however substantially reduced the modulus of elasticity of the composites. Based on the properties of the reference condition fabricated with 100wt% of quartz particles and w/c ratio of 0.55 (Table 4), the moduli of elasticity found in the C6 and C8 composites (~2.85GPa) can be however considered valid for use in some engineering applications.

**Microstructural analysis**

The microstructure of the composites was inspected using a TM-3000 Hitachi Microscope with a backscatter detector and accelerating voltage of 15kV. It must be noticed that chemical components with high electron density, i.e. quartz particles, have high backscatter coefficients, and appear bright in the backscattered images. Pores are however represented by the darker and/or black images (Diamond, 2004).

Fig. 10 shows the backscatter electron image of C1 (a) and C6 (b) composites at 100× of magnification. The C1 and C6 composites were made by replacing the coarse quartz particle sizes (4-20 US-Tyler) using water/cement ratios of 0.45 and 0.55, respectively. It is possible to observe the existence of internal macro pores when low levels of w/c ratio are presented (Fig. 10a), which can be considered as being the main cause for the reduction in strength and the increase of porosity and permeability. Fig. 11 presents the SEM images associated to samples belong to the RC3 and RC4 references, made of quartz particles (w/c = 0.55) and PET particles (w/c =0.55). Quartz particles (Fig. 11a) appear to exhibit better packing within the cement-based matrix in comparison with composites having PET particles only (Fig. 11c). The Portland cement matrix in the RC3 composites (Fig. 11b) looked also brighter than the RC4 case for the same w/c ratio of 0.55 (Fig. 11d), implying a larger water consumption.

**Conclusions**
A cementitious composite material consisted of quartz/PET particles for non-structural applications of civil engineering has been evaluated using a DoE methodology. The interaction between water/cement ratio and quantity of quartz particle replacement significantly affected the bulk density, compressive strength and the Young’s modulus of these composite. Main DoE factors associated to w/c ratio and again quartz particle replacement significantly affected also the apparent porosity, water absorption and permeability. The replacement of coarse quartz particles by PET particles with 0.55 of w/c ratio has shown a significant decrease of the apparent porosity, the water absorption and permeability, and a maximisation of the compressive strength and modulus of the cementitious composites. It was not possible to achieve acceptable mechanical properties at low levels of water/cement ratio (0.45), possibly because of the lower cement hydration and the formation of internal pores. Quartz particles were instrumental on creating a more homogeneous microstructure texture in the cement-based matrix than the PET inclusions. Between the various types of composites produced, the samples with PET particles replacing coarse quartz inclusions and with a 0.55 w/c ratio have shown interesting mechanical properties, like a compressive strength and modulus at nearly 15MPa and 3GPa respectively. These properties suggest the use of these particular types of sustainable composites to be used in precast non-structural applications, enabling at the same time the recycling of PET waste. In practice, the replacement of coarse quartz by PET particles not only represents a reasonable recycling amount (30wt%) to be used in a mortar aggregate, but also provides a cheaper alternative to non-structural casts at large scales, because that specific particle size is easier to obtain via grinding process.

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