Original Article

Production and characterization of a novel artificial stone using brick residue and quarry dust in epoxy matrix

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A B S T R A C T

Nowadays there is an increasing tendency to reuse industrial residues in order to reduce their environmental impact. A typical alternative for a residue is to be incorporated into a productive process that could be economically viable. In this work, 80 wt% of residues, quarry dust and chamotte from brick industries, were incorporated into 20 wt% of epoxy resin for the production of a novel artificial ornamental stone to be used in civil construction. For preparation of test specimens the granulometric composition associated with the best packaging of residues was determined by the Simplex method. Artificial stone plates were produced using vibration and vacuum processes. Specimens were tested for mechanical, physical and thermal properties as well as chemical resistance. The developed artificial stone presented mechanical properties within the standard expected range, with rupture stress of 30 MPa. Density and thermal behavior were also found to comply with values of natural ornamental stones applied in civil construction. This artificial stone was resistant to chemical attack by HCl, one of the most aggressive acid, which caused a weight loss of only 0.08 g. According to wear test, the thickness reduction indicated that the artificial stone could be used for high traffic pavement.

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1. Introduction

Residues generated from practically all industrial sectors are more than ever of global concern owing not only to widespread environmental pollution but also unquestionable climate changes [1]. Air, river, lake, ocean and ground pollution cases are being accentuated by an increasing amount of industrial ashes and plastic wastes as well as particle residues. Incorporation of these wastes and residues in composite materials is currently considered a modern solution. Typical examples are composites in which fly ash is
incorporated into epoxy [2, 3], polyethylene terephthalate (PET) wastes into cement [4, 5], and steel dust into clay ceramics [6, 7]. An important case is that of civil construction residues. Indeed, the inappropriate disposal of these residues is today a worldwide problem, while their incorporation into a traditional material such as concrete can be a sustainable practice in India [8]. Two specific civil construction related residues deserve special attention due to their large scale generation. Quarry industrial practice generates dust particles in grinding, cutting, crushing and sieving operations during the production of civil construction stones. This dust, representing around 10% of processed stone blocks and gravel, is usually discarded in open air piles. Environmental problems have been reported in China due to disposal procedures done both on-site and off-site the quarry premises [9]. The conventional clay ceramic industry, responsible for the production of red bricks and structural blocks as well as floor and roofing tiles, also generates in Egypt million of tons a year of residues that are disposed in huge landfills [10]. The residual ceramic powders might eventually be used to pave roads, however, broken pieces of ceramic may not. These broken pieces of clay ceramics, known as chamotte or grog, cannot be directly recycled and constitute another residual problem to local environment.

In Brazil, both quarry dust and chamotte are also generated in large scale throughout the country. In particular, the northern region of the state of Rio de Janeiro, with many quarries and clay ceramic industries, is accumulating a considerable amount of these residues. Numerous research works have been dedicated to scientific and technical solutions for both types of residues: quarry dust [11–15] and chamotte [16–18]. The main idea is to remove them from the environment but at a low cost and, if possible, in a profitable way. A typical solution is the addition of these residues into polymeric matrix composites [11, 14, 15]. In particular, especially profitable composites are those simulating natural ornamental stones and commercialized as artificial stones [11]. Indeed, the practical possibility of using an artificial stone instead of natural one is based on technical advantages, such as the lower density of the polymeric matrix (~1 g/cm³) as compared to the natural stone (~2 g/cm³), which makes the artificial stone significantly lighter. Another relative advantage of artificial stones is the low amount of pores and flaws. By contrast, the high porosity and microstructural defects in natural ornamental stones facilitates its contamination from outside fluids and easy propagation of cracks causing brittle fracture [14, 15]. In the most recent work on the development of artificial stone with quarry waste in epoxy composites [11], wear parameters revealed that it could be used as pedestrian heavy traffic pavements.

In spite of all these works, it should be pointed out that so far no artificial stone has been fabricated with chamotte. The present work is another investigation of artificial stone fabrication by residue incorporation. However, as a novelty, for the first time, residues from both industrial sectors: dust from quarry and chamotte from red ceramic industry, are combined to fabricate epoxy matrix artificial stones. Furthermore, by using process techniques of vibration, vacuum and compression [19], it is expected to develop a new artificial stone with superior mechanical and physical properties as well as resistance to chemical attack. The main objective is to produce a novel product, which would not only contribute to reduce the amount of daily generated industrial residues but also combine technical and economical advantages for civil construction applications.

Fig. 1 – Ternary diagram with the 10 mixtures based on the complete cubic model of the Simplex. Amounts (wt%) of large (L), medium (M) and fine (F) particles.

2. Materials and methods

A brick residue, chamotte, supplied by the Cerâmica Indiana Ltda, Brazil, and a dust residue from Itérê quarry, Brazil, were used in this study. The polymer used as matrix was the diglycidyl ether of the bisphenol-A (DGEBA) epoxy resin mixed with stoichiometric phr = 13 triethylene tetramine (TETA) as hardener, both from Epoxypinar, Brazil. The residues were sieved according to ABNT NBR 7181 [20] and classified in three granulometric ranges: Large (from 2 mm up to 0.42 mm), Medium (from 0.42 mm up to 0.075 mm), and Fine particles (with grains with size inferior to 0.075 mm).

Based on these three granulometric classifications, 10 distinct mixtures were proposed for each type of residue for best-packed condition using the Simplex-Lattice Design (SLD) numerical modeling methodology. Fig. 1 shows schematically the mixture compositions investigated, which is similar to that applied elsewhere [11].

The determination of best-packed composition for the chamotte was associated with the highest dry apparent density. This density was obtained as per the Brazilian NBR 3388 standard [21] for 10 different compositions considered in the Simplex method, Fig. 1. For each composition, 3 samples were used to assure statistical validation. Each sample of chamotte compositional mixture was placed in a steel vessel and allowed to vibrate for 2 min under a load of 10 kg. The mixture was weighed and the apparent density calculated. A similar procedure was previously carried out for the quarry dust [11]. Compositions with highest apparent bulk density, associated with best-packed particles, were selected.
to be mixed in a final proportion of 60 wt% quarry dust and 40 wt% chamotte (60/40 for short) as addition to the artificial stone epoxy matrix. The selection of this final 60/40 proportion was due to the experimental finding of best wettability with epoxy resin among all other quarry dust/chamotte proportions. Before mixing with epoxy, this proportion had also its apparent dry density measured in triplicate.

Artificial ornamental stone (AOS) plates with the selected 60/40 residues proportion, corresponding to 48 wt% of quarry dust and 32 wt% of chamotte, were fabricated by mixing with 20 wt% of still fluid DGEBA/TETA epoxy inside a 100 × 100 × 10 mm³ steel mold. Initially, the residues were stoved at 100 ºC for 24 h to release moisture and then kept inside a desiccator jar until return to room temperature (RT), around 25 ºC. Each AOS fabrication was carried out under 600 mmHg vacuum, while the mold was vibrated for 2 min under a pressure of 10 MPa. The last stage of fabrication consisted of curing at 90 ºC for 20 min.

The density, water absorption and apparent porosity of the novel AOS were determined as per the Brazilian NBR 15845 standard [22]. Ten prismatic specimens, cut from the AOS plate with dimensions of 100 × 25 × 10 mm³, were three points bend tested in a model 5582 Instron machine following the recommendation for agglomerated stones as per the Spanish EN 14617 standard [23] as well as the Annex F of the Brazilian NBR 15845 standard [22]. Samples taken from the fracture surface of bend-ruptured specimens were gold sputtered and observed by scanning electron microscopy (SEM) in a model SSX-550 Shimadzu equipment operating with secondary electrons at 20 kV.

Abrasive wear tests were performed in 3 prismatic specimens with 70 × 70 × 40 mm³ according to the Brazilian NBR 1204 standard [24] using a model MAQTEST Amsler equipment. For this purpose, ten specimens had their initial thickness measured before the wear test and again after 500 and 1000 m of runway. The resistance to chemical attack was conducted in previously weighted 16 prismatic specimens with 50 × 50 × 10 mm³ according to the Annex H of the Brazilian NBR 13818 standard [25]. After being subjected to the chemical attack for 24 h of specific reagents, the specimens had corresponding weight loss determined.

Thermogravimetric analysis (TGA) and its derivative (DTG) were obtained as continuous curves in 5 mm diameter and 1 mm thick discs with ~10 mg samples inside a platinum pan under nitrogen (100 ml/min) from RT to 935 ºC with heating rate of 10 ºC/min. Not only the artificial stone but also the epoxy, chamotte and quarry dust were TGA/DTG analyzed in a model SDT 2860 TA Instruments thermal analyzer.

### 3. Results and discussion

Table 1 presents the values obtained by the SLD method for the average density of vibrated mixtures of chamotte according to Fig. 1. In this table, the highest density value was 1.018 ± 0.037 g/cm³, corresponding in Fig. 1 to the mixture of 50% large particles (L) and 50% fine particles (F) of chamotte. This is considered to be associated with the best-packed mixture and was used in the production of artificial stone. As for the highest density of quarry dust mixture, the value of 1.867 ± 0.033 g/cm³ was previously reported [11], corresponding in Fig. 1 to the mixture of 67% L, 16% M and 16% F particles. These two mixtures were then combined in different proportions and evaluated for that associated with best wettability with the DGEBA/TETA epoxy. As aforementioned, the proportion with best wettability was 60 wt% quarry dust (67L/17M/16F) and 40 wt% chamotte (50L/50F). The density of this 60/40 mixture was experimentally calculated as 1.334 ± 0.013 g/cm³, which is close to that of 1.527 g/cm³ obtained by the Rule of Mixtures. The difference may be attributed to particle size distribution and morphology [26].

Artificial ornamental stone (AOS) plates were then fabricated with four parts of this quarry dust/chamotte particles and one part of epoxy. In other words, this novel AOS composition was 48 wt% quarry dust, 32 wt% chamotte and 20 wt% epoxy.

Table 2 presents the experimental results found for: density, water absorption and porosity of the novel AOS. The apparent density value of 2.12 g/cm³ in Table 2 is within those reported by Lee et al. [27] in glass fiber/EPF composites. Using different compression, vacuum and vibration conditions, they found density varying from 2.03 to 2.45 g/cm³. In the present work, the novel AOS is found to have lower density than that of a commercial Stella artificial stone, indicated as 2.38 g/cm³ by Carvalho et al. [28].

As for the water absorption, the value of 0.38% in Table 2 for the novel AOS is significantly higher than 0.18% reported for the Stellar artificial stone [28]. A high water absorption of 0.25% was also obtained by Borsellino et al. [29] in their artificial marble using epoxy matrix. In principle, this might suggest that this novel AOS as well as Borsellino et al. [29] artificial marble would have higher open porosities than that of the Stellar [28], due to their relatively high water absorption. However, the novel AOS apparent porosity of 0.18% in Table 2 is much lower than that of 0.44% for the Stellar artificial stone [28]. A possible explanation is that the commercial Stellar could have been sealed with a coating intended for low water absorption.

Fig. 2 shows the flexural stress versus strain curves or the neat epoxy resin, reproduced with permission [11], together with that for the novel AOS. In this figure, one should notice

### Table 1 - Vacuum and vibrate density of chamotte.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Average density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.663 ± 0.051</td>
</tr>
<tr>
<td>2</td>
<td>0.938 ± 0.017</td>
</tr>
<tr>
<td>3</td>
<td>0.768 ± 0.089</td>
</tr>
<tr>
<td>4</td>
<td>0.832 ± 0.072</td>
</tr>
<tr>
<td>5</td>
<td>1.018 ± 0.037</td>
</tr>
<tr>
<td>6</td>
<td>0.939 ± 0.060</td>
</tr>
<tr>
<td>7</td>
<td>0.951 ± 0.097</td>
</tr>
<tr>
<td>8</td>
<td>0.943 ± 0.018</td>
</tr>
<tr>
<td>9</td>
<td>0.818 ± 0.023</td>
</tr>
<tr>
<td>10</td>
<td>0.938 ± 0.019</td>
</tr>
</tbody>
</table>

### Table 2 - Physical properties of novel artificial ornamental stone.

<table>
<thead>
<tr>
<th>Physical properties</th>
<th>AOS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>2.12 ± 0.01</td>
</tr>
<tr>
<td>Water absorption (%)</td>
<td>0.38 ± 0.06</td>
</tr>
<tr>
<td>Apparent porosity (%)</td>
<td>0.18 ± 0.03</td>
</tr>
</tbody>
</table>
that the ultimate stress of the neat epoxy, 94 ± 5 MPa is marked greater than that of the novel AOS, 30 ± 3 MPa. A similar value was found for an artificial ornamental stone with only quarry dust in 10 wt% epoxy [11]. In fact, a comparison with reported strength of other artificial stones, such as Stellar, 36 ± 2 MPa [28], artificial marble, 21 ± 2 MPa and different natural marbles, 16 to 27 MPa [29], indicate comparable values to AOS in Fig. 2. It is also important to mention that ornamental stones used in civil construction are considered high resistant materials when its rupture stress exceeds 20 MPa, which is the case of the novel AOS.

Fig. 3 presents SEM micrographs from AOS fracture surface. In these micrographs images, one should observe a good adhesion between the epoxy matrix and he residue particles. It is also worth noticing the presence, indicated by arrow, of pores and voids as well as small cavities and microcracks. In spite of the good particle/epoxy adhesion, these microstructural flaws contribute to impair the AOS strength, Fig. 2, as compared to the neat epoxy matrix. As aforementioned, however, the novel AOS strength corresponds to high resistant materials for civil construction.

Table 3 presents the results of wear test for the novel AOS and corresponding ones reported elsewhere [11]. In this table, it is important to note that the AOS displays the best wear

![Table 3 - Wear thickness reduction of artificial stones with quarry dust and chamotte in: AOS; quarry dust in epoxy matrix [11] and commercial Stellar [28].](image)

<table>
<thead>
<tr>
<th>Artificial stone</th>
<th>Running distance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>500 m</td>
</tr>
<tr>
<td>AOS</td>
<td>0.50 ± 0.02</td>
</tr>
<tr>
<td>90% quarry dust/epoxy [11]</td>
<td>0.66 ± 0.01</td>
</tr>
<tr>
<td>85% quarry dust/epoxy [11]</td>
<td>0.57 ± 0.03</td>
</tr>
<tr>
<td>Stellar [28]</td>
<td>0.70 ± 0.04</td>
</tr>
</tbody>
</table>

**Fig. 3** – Scanning electron micrograph of the fracture region of the AOS. (a) 100x; (b) 200x; (c) 400x.
resistance among other artificial stones. It should also be mentioned that after wear tests the AOS surface revealed changes in brightness and color. As for the application for civil construction, there are no requirements or limits imposed by Brazilian standards to wear reduction in abrasive tests. As general concerns, the Brazilian institution related to the use of stones, ABIROCHAS, recommends different wear reductions to be applied as parameters for pavement plates. According to Chiiodi Filho and Rodriguez [30], pavements associated with light traffic should have wear reduction less than 6 mm, while medium traffic less than 3 mm. For heavy traffic the recommended value is less than 1.5 mm. Based on these parameters, the novel AOS, Table 3, might be used for heavy traffic pavement.

Table 4 presents the weight loss suffered by samples of AOS subjected to chemical attack by different reagents. These reagents, required by the standard [25], are commonly contained in substances like cleaning products and atmospheric acids that may become in contact with an artificial stone applied in civil construction, like outdoor and indoor coverings. The results in Table 4 indicate that all normalized reagents cause a weight loss in the novel AOS. The most aggressive was hydrochloric acid (HCl), which is a strong acid with a high degree of ionization, resulting in a loss of 0.12 g in 24 h, or 0.06 cm³ per day. The corrosive action of HCl in ornamental stones is due to its reaction with carbonates. Bolonini and Godoy [31] evaluate the behavior of a granite cluster, typically existing in quarry residues with mineralogical and chemical composition similar to the quarry dust used in the novel AOS. The authors performed chemical attack with the same normalized reagents used in the present work as per the standard [25]. The chemical resistance was measured not by weight loss but by the loss in brightness caused by each reagent on the granite polished surface. The reagents that caused the most loss in brightness were HCl and potassium hydroxide (KOH). In Table 4 those same reagents caused the greatest weight losses and corroborated the conclusions of Bolonini and Godoy [31].

Fig. 4 depicts combined TGA/DTG curves for the composite precursors: epoxy, quarry dust and chamotte. It is also shown the corresponding curves for the novel AOS as well as relatively amplified DTG curves for the chamotte. The main point to be noticed in Fig. 4 is the comparatively higher weight loss for the neat epoxy, which is a consequence of its intense thermal degradation above 300 °C. However, the AOS with 20 wt% epoxy suffers only a relatively small, 20%, loss of weight in agreement with the composite matrix proportion. Both quarry dust and chamotte display a discrete weight loss, less than 3 wt%, up to 850 °C. In particular, the chamotte has two small DTG peaks. One around 60 °C assigned to the release of humidity still existing even after a previous drying of both residues. This might be attributed to a strong hygroscopic nature of clay ceramics. A second small peak around 500 °C can be ascribed to the transformation of kaolinite in metakaolinite. This is expected owing to the fact that the bricks, supplied by the Cerâmica Indiana, located in the northern region of the state of Rio de Janeiro, Brazil, are produced from kaolinite clays. Moreover, in that region bricks are commonly sintered at firing temperatures below 600 °C [32], which still allows metakaolinite transformation to occur in association with the chamotte small second peak shown in Fig. 4.

### Table 4 – Weight loss of after 24 h chemical attack of AOS samples.

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Initial weight (g)</th>
<th>Weight loss after 24 h (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄Cl</td>
<td>62.92</td>
<td>0.04 ± 0.01</td>
</tr>
<tr>
<td>C₆H₈O₄ (citric acid)</td>
<td>62.57</td>
<td>0.05 ± 0.01</td>
</tr>
<tr>
<td>KOH</td>
<td>59.21</td>
<td>0.08 ± 0.02</td>
</tr>
<tr>
<td>HCl</td>
<td>61.06</td>
<td>0.12 ± 0.02</td>
</tr>
<tr>
<td>NaClO</td>
<td>59.80</td>
<td>0.06 ± 0.01</td>
</tr>
</tbody>
</table>

4. Summary and conclusions

A novel artificial ornamental stone (AOS) was for the first time fabricated with a mixture of quarry dust and chamotte that are abundant industrial residues, incorrectly disposed to the environment, in the northern region of the state of Rio de Janeiro, Brazil.
Both the quarry dust and chamotte particle mixtures were determined based on the highest density, in terms of the best-packed characterization, found by means of the Simplex-Lattice Design method.

The best wettability with DEGEBAB®-TEA® matrix defined the proportion of 48 wt% quarry dust, 32 wt% chamotte and 20 wt% epoxy for vibratory compaction under vacuum fabrication of AOS.

The values of density, 2.12 g/cm³, water absorption, 0.18% and mechanical strength of 30 MPa for the AOS are within the Brazilian standards and considered adequate when compared to other ornamental stones used in civil construction.

Fractograph analysis disclosed a good adhesion between the residues particles and the epoxy matrix. However, microstructural flaws, such as pores, voids, cavities and micro-cracks contribute to decrease the AOS strength in comparison to that of pure epoxy.

Wear tests revealed relatively small thickness reduction, indicating that the novel AOS would have the best abrasion resistance among other artificial stones and might be used for heavy traffic pavement.

The novel AOS, as expected, was sensibly affected by HCl and KOH chemical attacks. Therefore, it is recommended protection against cleaning products and environmental conditions containing these reagents.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

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