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Incorporation of Industrial Waste in the Development of Artificial Coating

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In these last decades, with the advance of industrialization, the enormous quantity of residue that is discarded by the industry has been generating discussions about eco-efficient solutions. This research has the objective of developing an artificial stone with residue of quartzite and fine quarry gravel (granite), utilizing the vibro-compression vacuum method. The residue was separated in three granulometric ranges with sieving: Large and medium (fine quarry gravel) and fine (quartzite). A statistical treatment was used in the acquired data, utilizing analysis of variance (ANOVA). The characterization was through a physical, mechanical, dilatometric and microstructural analysis. The obtained results classify the material as having high potential to be used for flooring in the civil construction industry, since it has low porosity <0.17% e water absorption < 0.3%, maximum flexural strength > 30 MPa, being able to be utilized in medium and low traffic environments.

Keywords: *Residue, artificial stone, resin, Coating.*

1. Introduction

The search for a delicate balance between economic growth and eco-efficiency has been a core issue for society. The underlying idea is that economies should be able to maintain a eco-efficient growth over time, but, at the same time, consume fewer natural resources and avoid the degradation of the environment[1]. The most challenging task is to use the waste from the industry in the right place. Waste comes out of the industry in many ways. Some waste causes air pollution and some waste is responsible for soil pollution[2].

Tons of ornamental stone residues are produced throughout the world every year. These residues are improperly discarded in the environment, causing serious public health problems, since they release powder into the atmosphere. When inhaled, these substances cause respiratory complications[3].

The Brazilian production of natural ornamental stones was estimated by ABIROCHAS at 9.0 Mt in 2020, maintaining the same production amounts of 2018 and 2019[4]. Although this sector is already consolidated, its production process is still rudimentary and inefficient, and the waste is primarily disposed of in a disorderly manner[5].

Brazilian exports of artificial stones, between January and May of 2022, totalled 4.5 thousand tonnes and US$ 6.3 millions, an increase of respectively 6.3% and 16.1% when compared with the same period of time in 2021. Now imports totalled 81 thousand tonnes and cost US$ 49.2 millions, pertaining to the year 2022[6,7]. This scenario shows the importance of research related to new artificial stone materials, as the Brazilian market has a lot to grow in the export area[5].

Artificial stones have demonstrated to be a high value market which also has an increasing demand in recent times. Typically named as engineered stone, they consist of 95% natural aggregates, that is, substantially a natural material. The aggregates that form an artificial stone may be composed of- pieces of marble, crushed granite, quartz sand, glass crystals, and other components - that are aggregated with bonds agents such as epoxy resin[8-10].

Among the advantages artificial stones are solid, impermeable, have good mechanical resistance and are resistant to liquid penetration, remaining only on the surface. This is caused by the resin used in the manufacturing process, that provides adhesion between the stone particles and also penetrate between the interstices, eliminating the porosity of natural stones[7].

The physical and mechanical properties of the artificial stone are the main influencing factors to its use in the construction industry. These properties are directly related to the resin content and the microstructure which can be seen in the production process[8].

The vacuum process represents a very important factor in the manufacture of plates made of artificial materials. This is because the vacuum facilitates the removal of air entrapped

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in the filler load and the matrix during the molding process, lowering the degree of porosity of the plate after molding. This fact helps in the search for good performance, since porosity can be a harmful factor[5,9].

Lee et al.[11] have recycled waste glass and stone fragments using vibratory compaction in a vacuum environment. Waste glass powder (40%) and fine granite aggregates (60%) were mixed with polymer resins (8%) as binder. Under a compaction pressure of 14.7 MPa, a vibration frequency of 33.3 Hz, and vacuum conditions at 50 mm Hg, artificial stone slabs with a high compressive strength of 148.8 MPa, a water absorption of less than 0.02%, a density of 2.445 g/cm^3, and a flexural strength of 51.1 MPa were obtained[11]. In the present water and environmental crises, the mineral sector envisions greater efficiency and the optimization of the use of resources because there is a constant need for recycling and minimizing the generation of waste. In addition to the environmental benefits, the reuse of waste materials allows for the improvement in products already commercialized, as well as a considerable reduction in cost[4]. During the explosion of quartzite in the mining operations, a large amount of residues is generated, up to 90% of the total extracted material. The reason for the high amounts of rejects is because the quartzite is used, fundamentally, to make tiles and, thus, it must be extracted as a plate, complying with thickness and length standards. The environmental problems include the deconfiguration of the natural terrain and landscape, siltation of nearby water streams and native vegetation and can destabilize slopes containing mining residues. On the other hand, if the rejected material complies with the standards used for the rocky materials on civil construction, it can arise as a feasible option to different applications[12].

Granite residue, considered waste from the process of obtaining gravel, are quarry fines with a granulometry of less than 4.8 mm, they are made in absurd numbers, are harmful to the environment because of the dust produced, the drainage siltation they cause and the space occupied in the quarry itself. These quarries create a significant amount of fine gravel, mainly in the crushing process. The quarry fines are accumulated in restricted sections around the crushing plants, because there's no appropriate use for them[13].

The main purpose of this research is the production of an artificial stone from the residues of quartzite and fine quarry gravel, with good physical and mechanical properties tied to an efficient bonding of the particles by the epoxy resin to a microstructural level, and to compare this artificial stone produced with other artificial stones manufactured by the industry.

When the recycling of the residues of quartzite and fine quarry gravel production is proved as a viable alternative from both, technical and ecological viewpoints, it will be possible to aggregate value to something that, while adequate to environmental laws present, would be otherwise discarded in nature.

2. Materials and Methods

The granite waste was collected as residue from the sieving process in the Itereré quarry located in the mountain region of Serra da Bela Vista, at 17 km from the city of Campos dos Goytacazes, north of the state of Rio de Janeiro, Brazil. And the quartzite residue was provided by the Center of Mineral Technology (CETEM), located at the city of Cachoeiro, state of Espirito Santo, Brazil. In which the quartzite's granulometry was encountered below 0.063 mm.

After collection, the fine quarry gravel waste was subjected to ball milling for further reduction in particle size. By means of dry sieving, the reduced waste was then separated into three granulometric classes: (i) large, from 2 to 0.71 mm (granite), (ii) medium, from 0.71 to 0.063 mm (granite), and (iii) fine particles, grains with a size of less than 0.063 mm (quartzite), based on the ABNT/NBR-7181 Brazilian standard[14].

The epoxy used as binding for the waste particles was the bisphenol A diglycidyl ether (DGEBA) resin mixed with the triethylenetetramine (TETA) supplied by Epoxyfber, Brazil. The supplier indicated the density of the epoxy as 1.15 g/cm^3.

2.1. Determination of the highest packaging granulometric composition

Based on three ranges of grains obtained, 10 different mixtures with different percentages of large, medium and fine particles were proposed. Figure 1 shows a complete ternary diagram developed in the Simplex-Lattice Design (SLD)[12] made to determinate greater packaging, each vertex of the triangle corresponds to 100%: large (L), medium (M) and fine (F) particles. The other points in the triangle display (in parenthesis) the fractions corresponding to the mixtures. To determine the proportion with the greatest packaging of the 10 mixtures, all were tested based on the ABNT/MB-3388 Brazilian standard (1991) – Determination of minimum index void ratio of cohesionless soils[15]. For each composition, the test was done three times to assure statistical validation. Each sample of waste compositional mixture was placed in a steel vessel and left vibrating for 2 minutes under a load of 10 kg. The mixture was weighted and the apparent density was calculated.

A statistical treatment was then realized of the results obtained in the previous experiment utilizing analysis of variance, or ANOVA, of the completely randomized design (CRD) ($p \leq 0.05$), with the objective of verifying the existence

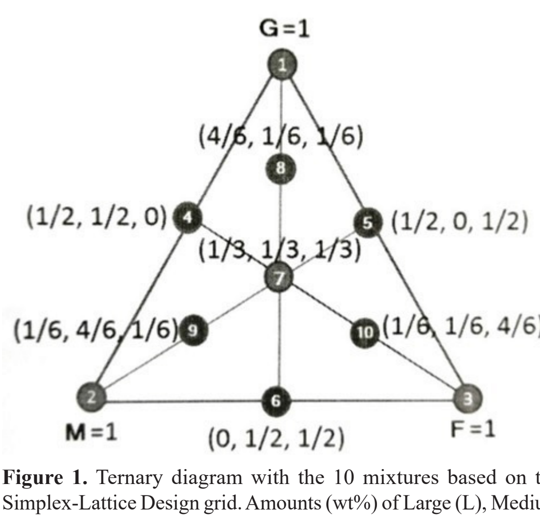

Figure 1. Ternary diagram with the 10 mixtures based on the Simplex-Lattice Design grid. Amounts (wt%) of Large (L), Medium (M) and Fine (F) particles.

of statistical significance of the experiment. Once proven that there was statistical difference, a mean comparison utilizing Tukey's test ($p \leq 0.05$), with the objective of verifying which mixture had the best results. The calculations were realized utilizing the Excel tool included in the Office package.

As described by Ribeiro[16] it was necessary to calculate the minimum amount of resin (MAR) for the best statistical results, necessary to the production of artificial stone, using Equations 1 and 2:

$$VV\% = \left(1 - \frac{\rho_{PA}}{\rho_Q}\right) * 100 \quad (1)$$

where:
VV% = Void volume present in the mixture of particles;
ρ_{PA} = Apparent density of particles, calculated by the packaging method; Ok
ρQ = Quartzite density, calculated by pycnometry;

By obtaining the void volume (VV%) value it was possible to calculate the minimum amount of resin (MAR), through Equation 2 below:

$$MAR\% = \frac{VV\% * \rho_{resin}}{VV\% * \rho_{resin} + (100 - VV\%) * \rho Q} \quad (2)$$

where:
MAR% = Minimum amount of resin to fill the void volume;
$VV\%$ = Void volume present in the mixture of particles;
ρ_{resin} = Epoxy resin and polyurethane resin density;
ρQ = Quartzite density, calculated by pycnometry;

2.2. Production of artificial stone plates

So, the production of the artificial stone of the mixtures 5 (½ large and fine), 7 (⅓ large, medium and fine) and 8 (⅔ large and ⅙ medium and fine), which were those that presented statistical difference, was made with 85%, in weight, of the residue and 15%, in weight, of the epoxy resin, amount that was determined with the MAR calculation. The artificial stones were produced with granite and quartzite residues (ASGQ 5, 7 and 8) with 100 mm in length, 100 mm in width and 25 mm in height as its dimensions utilizing the vibro-compression vacuum technology.

Initially, the residue was dried in an oven at 100 °C to remove moisture, then it was weighed and placed inside the mixer, and the resin was added to complete the entire mixture. After all the mass was mixed it was deposited in the mold and connected to a vacuum system. Already under vacuum, the mold was placed on a vibrating table, to promote the spreading of the mass in the mold cavity and facilitate the removal of air bubbles that might be in the mass. After the vibration time, the mold, still under vacuum, was taken and placed in the Marcone MA 098-A hydraulic press where specimens were produced with a compression pressure of 3 MPa at 90 °C[5,7,8].

Only after pressing was the mold disconnected from the vacuum system and cooled at room temperature (RT) to remove the ASGQ artificial stone plate, which was then sanded and cut according to the standard for each test.

2.3. Characterization of the artificial stone plates

The density, water absorption and porosity values were determined with standardized experiments in accordance with the norm ABNT NBR 15845-2:2015[17]. For each composition, 15 specimens were produced with 30×30×15 mm dimensions.

The 3-Point Bend Testing was made with a Instron model 5582 in accordance with the norm NBR 15.845-6:2015[18], 7 specimens were cut from each sample of ASGQ 5, 7 and 8 had.

The ASGQ fractured surface regions subjected to bending tests were observed through SHIMADZU's SuperScan SSX-550 scanning electron microscope (SEM) for microstructural analysis, at 20 kV with secondary electrons. The samples were prepared using an adhesive carbon tape coated with gold particles. The microstructural analysis is important to determine the quality of the adhesion between the particles and the epoxy resin, as well as the presence of voids.

Abrasive wear tests were performed in 2 prismatic specimens with 70×70×40 mm according to the Brazilian NBR 12.042:2012 standards[19] using a MAQTEST's Amsler equipment. For this purpose, the specimens had their initial thickness measured before the wear test and again after 500 and 1000 m of runway.

A test was realized for durability against wetting and drying cycles, adapted from norm NBR 13.554:2012[20]. Five specimens of each composition were utilized, with 100x25x10mm dimensions, and were subjected to 10 wetting and drying cycles. In each cycle, after drying, the specimens were subjected to brushing, with a steel brush, they received 4 brushings in each face. The mean mass loss of the specimens was analyzed, with their weight of before and after the experiment. The 3-Point Bend Testing was also made to evaluate their mechanical properties after 10 wetting and drying cycles. Even though, this test is not one of the ones used for the evaluation of stones, it does simulate the effect of wetting and drying cycles in the cohesion of the material. Also, this test simulates similar conditions as the ones stones have to endure when used in sinks and tanks.

The dilatometry test consists of identifying a variation in the material's volume when subjected to temperature variations, being able to dilate or contract. Even though this dilation/contraction happens in a tridimensional form, its measurement is linear and expressed as a coefficient. This test is important especially when it's about materials used for flooring exterior and interior areas**,** as displacement or deformation may occur in the material. The test was done using the equipment Netzsch DIL402PC with a heating range of 10ºC/min and temperature between 30 to 1000ºC.

3. Resultados

3.1. Statistical analysis

Table 1 presents the values obtained through the SLD method for the average density of vibrated mixtures of waste from granite and quartzite. Since they were a parameter of an average from the vibrated densities, a treatment of the data by analysis of variance considering the completely randomized design (CRD) realized with 95% of trust level ($p \leq 0.05$), with later contrasts of means by the Tukey's test. Table 2 presents the ANOVA for the vibrated densities parameter, while Table 3 presents Tukey's test for the same parameter, to the ANOVA, 3 repetitions were utilized for each of the 10 mixtures.

Analyzing the results obtained in Tables 2 and 3, it's possible to verify that the treatments analyzed presented statistical difference, which means that between the 10 mixtures, at least 3 are different. One thing that should be said is that the coefficient of variation for the experiment was 14.7%, which indicates that the results obtained are trustworthy.

To make the differentiation, Tukey's test was used, with the intention of verifying the existence of statistical significance between the treatments performed. Where it was possible to conclude that the treatments with the highest densities were 5, 7 and 8. The phenomenon of particle packing is problematic as it depends on the correct selection of the proportion and particle size of the materials used, in a way that the bigger void regions are filled with small particles, and the small void regions are filled with even smaller particles, and so on and on. Therefore, a material with the highest theoretical density possible would have no voids, and with that absence of voids the mechanical and physical properties of the artificial stone would improve. Theoretically, this condition is possible, but due to irregularities in particle morphology (particles aren't perfectly spherical) and the granulometric distribution, it's too difficult to accomplish maximum particle packaging.

It's too difficult to predict the behavior of the mixtures with non spherical particles because of the enormous quantity of possible forms, as well as the multiple combinations that can arise between them. The only prediction that can be made is that, as the particles become less and less spherical, so too will the packing density decrease, along with other correlated properties[21].

3.2. Physical properties

Table 4 presents the values for apparent density, water absorption, and apparent porosity, for ASGQ 5, 7 and 8. In accordance with brazilian technical norm NBR 15844, apparent density of artificial granite must be lower than 2.5 g/cm^3, maximum water absorption should be of 0.4% and apparent porosity at max can be 1%[22]. All 3 of the analyzed compositions of artificial stone produced were below those indicated values.

The ASGQ 5, 7 e 8, had apparent density values below the maximum recommended thanks to the utilization of a polymer with low density, making the material lighter, and consequently can decrease logistic costs, including transport, since for a fixed price per load, there will be a higher amount of cubic meters of material transported[8].

When there's a reduction to water absorption, the same does happen to the porosity, but not in a directly proportional way, because there can be variations in the pore interconnectivity and fissures. The water absorption will always be inferior to the porosity, because not all pores are interconnected and able to allow liquid percolation.

The use of this method was a positive factor in the improvement of physical properties, since the impregnation of resin in the particles of residue happens before the molding without solvent, which means there is more control on the void formation. The final microstructure depends on an efficient removal of air bubbles in the promoted formulation used by vacuum, vibration and compression[5].

By the classification of Chiodi and Rodriguez[23] and Costa et al.[24], the obtained values of water absorption were excellent, since they were inferior to 0.1%. Norm ASTM C615 days that, for granites and marbles, water absorption has to be below 0.4%[25].

The ASGQ-7 had the lowest values for water absorption, 0.6±0,02%, in comparison with ASGQ 5 e 8. The authors[7,8,21] used the same particle sizes in the three ranges, as a result of the packaging, the difference between the outcomes can be explained by the difference between the morphology of the particles. Particle packaging, which conditions the processing and multiple other properties of powder mixtures, is strongly correlated with the distribution of the particle sizes and morphology. Because of the enormous number

Table 1. Vibrated density of granite wastes (large and medium granulometry) and quartzite waste (fine granulometry).

	Density vibrated	
Mixtures	Compositions	Average (g/cm^3)
1	100% (L); 0% (M); 0% (F)	1.01 ±0.10
2	0% (L); 100% (M); 0% (F)	1.68 ±0.02
3	0% (L); 0% (M); 100% (F)	1.47 ±0.01
4	50% (L); 50% (M); 0% (F)	1.43 ±0.07
5	50% (L); 0% (M); 50% (F)	1.70 ±0.04
6	0% (L); 50% (M); 50% (F)	1.53 ±0.01
7	33% (L); 33% (M); 33% (F)	1.73 ±0.01
8	67% (L); 17% (M); 16% (F)	1.69 ±0.03
9	16% (L); 67% (M); 17% (F)	1.40 ±0.04
10	17% (L); 16% (M); 67% (F)	1.62 ±0.03

Table 2. ANOVA for DIC of vibrated density (p≤0,05).

FV	GL	SQ	QM	F
Tratamento	9.0000	1.3698	0.1522	109.7607
Resíduo	20.0000	0.0277	0.0014	
Total	29.0000	1.3975		

Conclusion: F calculated > F tabulated, there is static difference. F tabulated = 2.39

Table 3. Tukey's test for contrast of vibrated density means (p≤0.05).

Treatment	Average	Tukey Test
5	1.79 ±0.04	A
7	1.73 ±0.01	AB
8	1.70 ±0.04	AB
2	1.68 ±0.03	BC
10	1.62 ±0.03	CD
6	1.53 ±0.02	DE
3	1.47 ±0.01	EF
4	1.44 ±0.08	EF
9	1.41 ±0.05	F
1	1.02 ±0.02	G

Table 4. Physical properties of artificial stones produced from granite and quartzite with 15% of resin (ASGQ 5, 7, and 8).

Artificial Stone	Density (g/cm^3)	Absorption (%)	Porosity (%)
ASGQ-5	2.33 ±1.14	0.13 ±0.03	0.30 ±0.05
ASGQ -7	2.32 ±0.03	0.06 ±0.02	0.14 ±0.05
ASGQ -8	2.28 ±0.09	0.17 ±0.07	0.38 ±0.14

of particles and also of possible shapes, there is an infinity of possible combinations.

Costa et al.[24] analyzed the norms for stones and elaborated a general proposal of qualification for their use as flooring and they classified that with a porosity of below 0.5%, the stone is considered of low porosity or excellent quality. Agrizzi et al.[9] in their work characterized a natural stone of quartz, Cristallo as commercial name, and had their porosity determined as 0.13%, and the artificial stone, Branco Aldan as commercial name, had 0.68%, in which case ASGQ obtained better values compared to the artificial stone[6].

Without a specific norm that regulates the use of artificial stone (of granite and quartzite) in humid environments, using the established limits within other norms proves that the ASGQ is competent to be a substitute of natural stones in the same applications.

3.3 Three-points bend stress

Figure 2 shows bending stress versus strain curves of artificial stones using residue of fine gravel and quartzite in the given proportions determined by statistical methods (5, 7 and 8) and the epoxy resin.

It's possible to observe that the addition of particle load contributed to a more stiff material, in comparison with epoxy resin. That's the expected behavior, since the incorporation of stiffer materials (particles) in a polymeric matrix, most of the time, increases the flexural modulus[7]. Maximum performance can be reached if polymer adhesion to the reinforcement is perfect. The more powerful the reinforcement-matrix interface, better mechanical properties the artificial stone will develop[26].

The maximum bending stress for ASGQ-5 was 37.52±0.42 MPa, ASGQ-7 was 31±2.3 MPa and ASGQ-8 was 32±2.7 MPa. It can be observed that composition was the main factor, as the stone with the highest ultimate tensile stress didn't have particles with medium granulometry.

Zanelli et al.[27] made a research about reutilizing ornamental stone residues to develop polymer composites with thermoset polymer matrix and warranted the remarkable performance of the compressive and bending strengths obtained by the artificial stones with acrylic resin with white marble to how ease it was to get homogeneous granulometries which the white marble acquired in the grinding process, and that it was a factor for a favorable compression and cohesion of minerals enveloped by the resin. But the residue utilized to develop ASGQ is different (granite and quartzite), as well as, the resin used, the morphology and the densities.

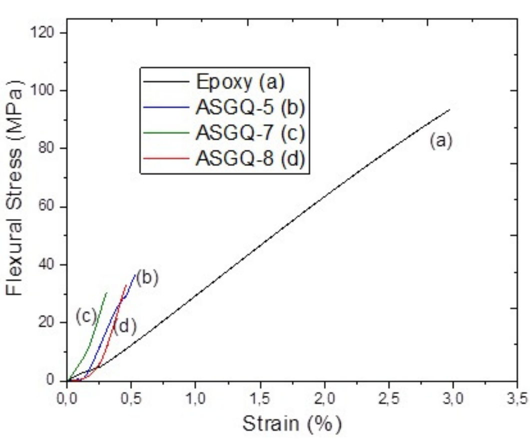

Figure 2. Mechanical behavior in 3-point bend test for Epoxy (a), and for artificial stone with granite and quartzite residue with epoxy resin, ASGQ-5 (b), ASGQ-7 (c) and ASGQ-8 (d).

Costa et al.[24], defined that stones for flooring are considered of very high resistance or excellent quality if their flexural strength is higher than 20/22 MPa, respectively[25]. Norm NBR 15844[22] stipulates that the minimum flexural strength in a 3-point bend test has to be 10 MPa, for stones used in flooring, while ASTM C503 says it's 7 MPa[28].

All three ASGQ compositions presented high values for flexural strength, being able to be used for panels fixed with metal inserts in building facades, since they will resist strong wind, or on suspended/raised floors without substrate.

3.4. Microstructural analysis

Figure 3 presents SEM micrographs of the fractured surface sections of ASGQ 5, 7 e 8, after the three-point flexural test. There are very few pores that are visible, as verified by the porosity values found in the previous test, for the three compositions. But these few are what could have contributed to the occurrence of the fracture, since it can be observed a good interfacial adhesion between resin and particles, in other words, adequate wetting of the particles by the resin occurred. According to Debnath et al.[26], the maximum system performance happens with great mineral load wetting by the epoxy resin. So, the better a reinforcement-matrix interface is, the better the mechanical properties of the material will be[26].

Figure 3a and 3c shows the fractured surface sections of ASGQ 5 and 8, illustrating the material filling all interstices between small and big particles. There is a discreet presence of microcavities (arrow), generated by the contact between particles. This created a weak adherence in the region, and so, with the stress applied, a shear formed between the planes, but since this didn't repeat throughout the sample, a satisfactory mechanical behavior was acquired.

Figure 3b shows an SEM micrograph of the fractured surface sections of the ASGQ-7, it can be seen that there are few air bubbles in the matrix, which were not eliminated during the vacuum process, which was previously confirmed by the results of porosity and water absorption (Table 4), it can be seen that the pores are not connected, as the water absorption was very small. These air bubbles may have been stress concentration points, which are related to the mechanical properties.

3.5. Abrasive wear

Since the use of an Amsler Wear Testing Machine is based on a norm used for ceramic materials, there are no established borderline values for comparison with the encountered values for the developed artificial stones. There is a paper published by Chiodi and Rodriguez[23] that defines parameters which serve to make comparisons for ornamental stones intended for flooring; those reference values can be found in Table 5.

Based on the above parameters, the results for the three compositions (ASGQ 5, 7 and 8) are pretty much satisfactory, being a good option to be used as flooring of low and medium traffic floors, since their wear was superior to 1.5 mm after 1000 m of running distance, as can be seen in Table 6.

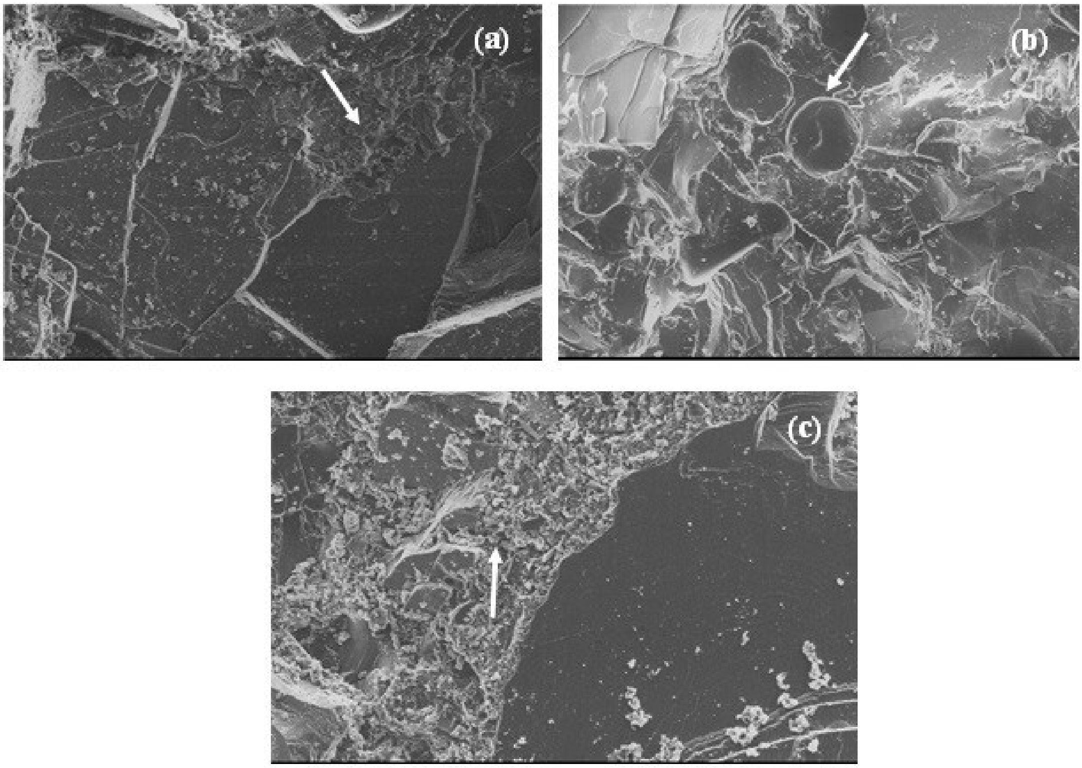

Figure 3. SEM of the fractured surface sections of artificial stone with granite and quartzite residue and epoxy resin as binder, ASGQ-5 (a), ASGQ-7 (b) and ASGQ-8 (c) at 100x magnification.

Table 5. Amsler abrasive wear parameters.

Traffic Intensity	Amsler Abrasive Wear (mm)
Low	> 3
Medium	> 1.5 - 3
High	< 1.5

Table 6. Wear thickness reduction of artificial stone with granite and quartzite residue ASGQ (5,7 and 8).

Wear thickness reduction (mm)		
Stone	Running distance	
	500 m	1000 m
ASGQ-5	0.75 ±0.16	1.64 ±0.36
ASGQ-7	0.86 ±0.16	1.56 ±0.01
ASGQ-8	0.73 ±0.24	1.50 ±0.57

3.6. Durability test in wetting and drying cycles

The test for durability against wetting and drying cycles is important to evaluate the quality of artificial stones, since they are produced with the intent to be used as coating in kitchen countertops and bathroom, being constantly exposed to water and to degradation caused by cleaning aid products. But the use of this test for rocky materials is still underutilized and there aren't many available papers for comparison.

Table 7 presents the loss of mass of ASGQ 5, 7 and 8 after wetting and drying cycles. With the presented results, it is observed that there wasn't much wear in all ASGQ compositions. This is related to the excellent interfacial bonds[29].

Table 7. Mass loss for the accelerated wear test in wetting and drying cycles of artificial stone with granite and quartzite residue of compositions 5, 7 and 8 (ASGQ-5, 7 and 8).

	weight loss (g)	**weight loss (%)**
ASGQ-5	0.21 ±6.70	0.30
ASGQ-7	0.04 ±0.62	0.05
ASGQ-8	0	0

Figure 4 shows the stress-strain curves for the three proposed compositions of ASGQ (5, 7 and 8) after the test for durability against wetting and drying cycles. It is observable that the test did not modify the mechanical properties of the three ASGQ compositions, the flexural strength reported was 37±0.4 MPa, 31±2 MPa and 32±2,5 MPa, for ASGQ-5, ASGQ-7 and ASGQ-8 respectively.

3.7. Dilatometry analysis

Numerous materials present dimensional variations after being exposed to a heating period, presenting dimensional variations under the effect of the contraction and expansion phenomena in their structures. These variations take place due to physical and chemical events that occur in the structures and chemical composition of the material. During the development of the artificial stones, in the curing stage that occurs through the polymerization reaction of the matrix with the residue, a thermal transformation happens[30,31]. The ASGQ, composed of quartzite and granite in an epoxy matrix, had excellent stability in the bending stress test, probably due to the acquired properties and characteristics of the aggregate in high temperature.

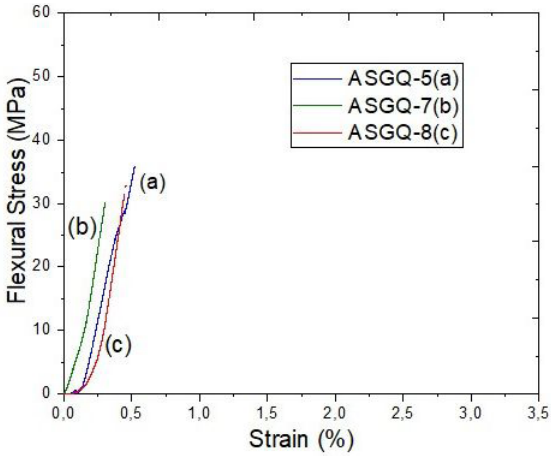

Figure 4. Mechanical behavior in the 3-point bending test, after the wetting and drying test: Artificial stone with granite and quartzite residue and epoxy resin as binder ASGQ-5 (a), ASGQ-7 (b) and ASGQ-8 (c).

In the Figure 5a, 5b and 5c, it can be observed the structural behavior of ASGQ-5, ASGQ-7 and ASGQ-8 in a heated environment in a temperature range from 0 to 1000 ºC, thus identifying the structural phenomena presented, like body temperature in an exact moment.

When analyzing the dilatometry results of quartzite, a loss of mass can be observed between 30 - 200 ºC, as can be observed in Figure 5a, 5b and 5c. Silva et al.[5] explained that this type of loss occurs because of the liberation of water adsorbed in the quartzite particles' surface, between 200 - 500 ºC there also is a loss of mass, now attributed to the combustion and oxidation of organic matter, and between 500 - 700 ºC the loss of mass occurs because of structural transition[4].

In the temperature range of 342-345°C an expansion of 1.65% (ASGQ-5); 0.94% (ASGQ-7) and 1.16% (ASGQ-8) little significant occurs, followed by a linear retraction around 385 ºC, the temperature in which the resin starts to decompose, with loss of mass[4].

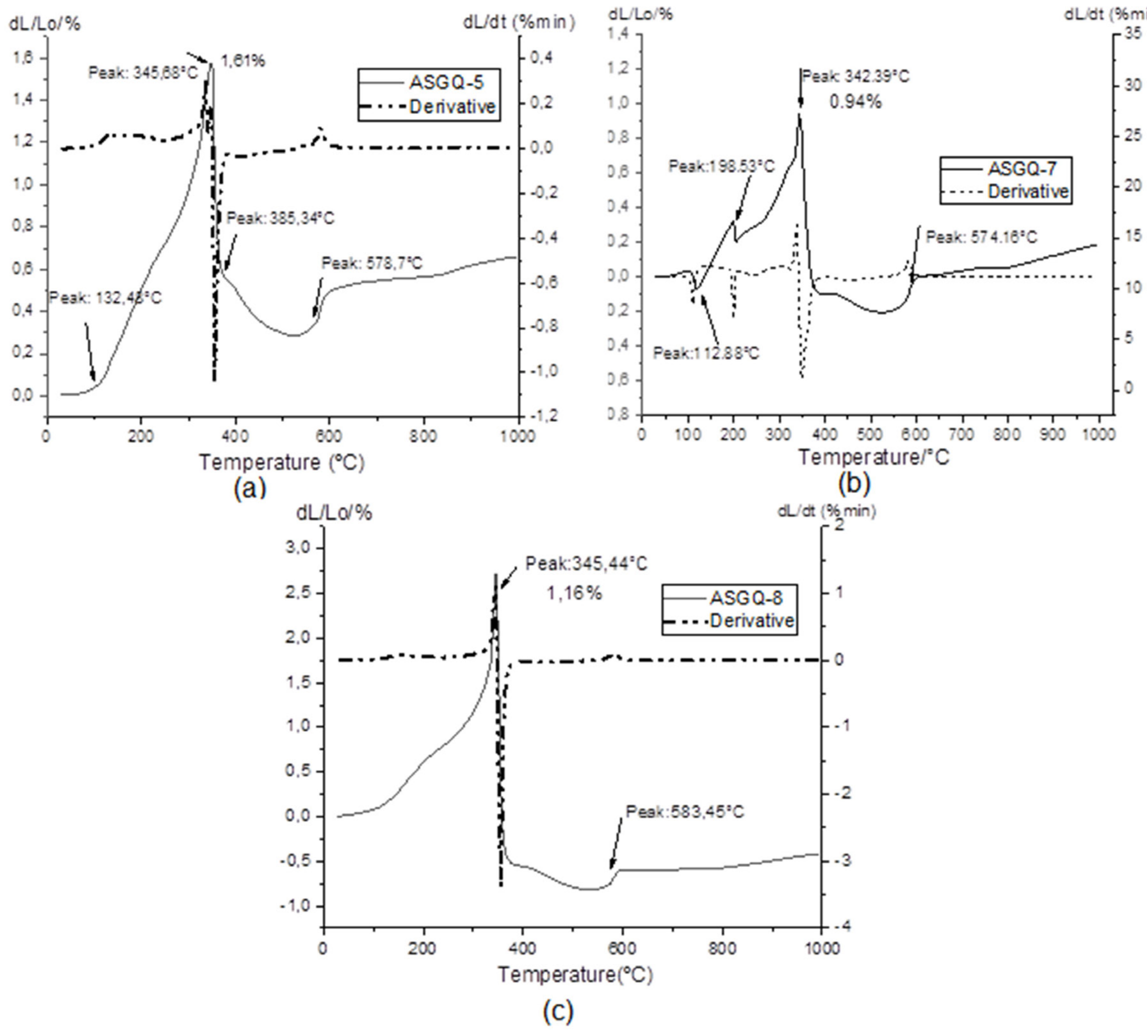

Figure 5. Dilatometer and curve derived from artificial stone with quartzite and quarry gravel residue (ASGQ), in compositions 5, 7 and 8. ASGQ-5 (a), ASGQ-7 (b) and ASGQ-8 (c).

As said by Silva et al.[5] the thermogravimetric curve of epoxy resin recorded the first mass loss of 70% around 380ºC because of resin decomposition[4]. And then, at 382.4ºC, occurs a continuous loss of mass until the end of the process, at 550ºC. After 600ºC, the structure suffers another contraction, and total weight loss because of resin decomposition. The granite powder had a discreet loss of mass[32].

The dilatometric curve of the material showed the existence of a sharp increase in linear thermal expansion around 550ºC, after which began the material densification process. According to what was analyzed, this experiment is important to define the spacing used for the floor laying process and vertical tiles used in facades exposed to insulation.

4. Conclusion

A new ornamental artificial stone (ASGQ) was developed with a mixture of granite and quartzite, which are abundant industrial waste, incorrectly discarded in the environment, in the northern region of Rio de Janeiro state, Brazil.

- Both granite and quartzite had the average density of vibrated mixtures determined utilizing the Simplex-Lattice Design method. The statistical treatment presented a statistical difference, which means that among the 10 mixtures, at least three distinguished themselves, those were compositions 5, 7 and 8.
- The better wettability with the DGEBA-TETA matrix and the residue was determined through the calculation of the minimum amount of resin (MAR), which was 15% of resin mass and 85% of residue mass (granite and quartzite).
- Physical characterization determined that the three compositions had excellent properties, with water absorption being ASGQ-5 (0.13%); ASGQ-7 (0.06%) e ASGQ-8 (0.17%), thus they can be used in wet environments.
- The flexural strength of ASGQ-5 was 37.52±0.42 MPa, ASGQ-7 was 31±2.3 MPa and ASGQ-8 was 32±2.7 MPa. Thus, they can be utilized for panels fixed with metal inserts in building facades, since they will resist strong wind, or on suspended/raised floors without substrate.
- There are little evidenced pores, since, as indicated by physical characterization, porosity values are very low for the three compositions. The results of the Amsler Wear Testing Machine are quite satisfactory, being a good option to be used as flooring of low and medium traffic floors, since their wear was superior to 1.5 mm after 1000 m of running distance.
- The test for durability against wetting and drying cycles, presented the following values of loss of mass for ASGQ 5, 7 e 8: 0.3%, 0.05% and 0% respectively, and it didn't affect the mechanical properties of the materials. In the dilatometry test, the three compositions got an expansion value of little significance of 1.65% (ASGQ-5), 0.94% (ASGQ-7) and 1.16% (ASGQ-8). According to what was analyzed, this experiment is important to define the spacing used for the floor laying process and vertical tiles used in facades exposed to insulation.

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6. References

1. Alcay A, Montañés A, Simón-Fernán M. Waste generation and the economic cycle in European countries. Has the Great Recession decoupled waste and economic development? Sci Total Environ. 2021;793:148585.
2. Kumar S, Dwivedi VK, Dwivedi SP. Waste material produced from industry and its utilization in development of green composite material: a review. Mater Today Proc. 2021;43:490-6.
3. Barros SVA, Marciano JEA, Ferreira HC, Menezes RR, Neves GA. Addition of quartzite residues on mortars: analysis of the alkali aggregate reaction and the mechanical behavior. Constr Build Mater. 2016;118:344-51.
4. Chiodi R Fo and Rodrigues EP. Stone coating application guide. Brasília: ABIROCHAS; 2021.
5. Silva MCA, Leão VA, Reis EL. Incorporation of quartzite fines in the production of red ceramics. J Clean Prod. 2021;288:125098.
6. Chiodi R Fo. Balance of Brazilian exports and imports of natural and artificial stone materials for ornamentation and coating in the period January-May 2022. Brasília: ABIROCHAS; 2022. [Portuguese].
7. Chiodi R Fo. Balance sheet of exports and imports Brazilian ornamental stones in the period January-November/2022. Brasília: ABIROCHAS; 2022. [Portuguese].
8. Peixoto J, Carvalho EAS, Gomes MLPM, Guimarães RS, Monteiro SN, Azevedo ARG et al. Incorporation of industrial glass waste into polymeric resin to develop artificial stones for civil construction. Arab J Sci Eng. 2021;47:4313-22.
9. Agrizzi CP, Carvalho EAS, Gadioli MCB, Barreto GNS, Azevedo ARG, Monteiro SN et al. Comparison between synthetic and biodegradable polymer matrices on the development of quartzite waste-based artificial stone. Sustainability. 2022;14(11):6388.
10. Silva FS, Ribeiro CEG, Rodriguez RJS. Physical and mechanical characterization of artificial stone with marble calcite waste and epoxy resin. Mater Res. 2018;21(1):e20160377.
11. Lee MY, Ko CH, Chang FC, Lo SL, Lin JD, Shan MY et al. Artificial stone slab production using waste glass, stone fragments and vacuum vibratory compaction. Cement Concr Compos. 2008;30:583-7.
12. Demartini TJC, Rodríguez RJS, Silva FS. Physical and mechanical evaluation of artificial marble produced with dolomitic marble residue processed by diamond-plated bladed gang-saws. J Mater Res Technol. 2018;7:308-13.
13. Barreto GNS, Carvalho EASC, Souza VSS, Gomes MLPM, Azevedo ARG, Monteiro SN et al. Engineered stone produced with glass packaging waste, quartz powder, and epoxy resin. Sustainability. 2022;14:7227.
14. ABNT: Associação Brasileira de Normas Técnicas. ABNT NBR 7181: soil—grain size analysis. Rio de Janeiro: ABNT; 2016. [Portuguese].
15. ABNT: Associação Brasileira de Normas Técnicas. MB 3388: soil—determination of the minimum void index of non-cohesive soils. Rio de Janeiro: ABNT; 1991. [Portuguese].
16. Ribeiro CEG. Development of an alternative artificial marble with residue from the marble and unsaturated polyester industry [thesis]. Rio de Janeiro: Universidade Estadual do Norte Fluminense Darcy Ribeiro; 2015. [Portuguese].
17. ABNT: Associação Brasileira de Normas Técnicas. ABNT NBR–15845-2: rocks of cladding— determination of apparent density, apparent porosity and water absorption. São Paulo: ABNT; 2015. [Portuguese].

18. ABNT: Associação Brasileira de Normas Técnicas. ABNT NBR–15845-6: rocks of cladding— determination of the modulus of rupture (bending by three-point loading). São Paulo: ABNT; 2015. [Portuguese].
19. ABNT: Associação Brasileira de Normas Técnicas. ABNT NBR 12042: inorganic material-determination of the resistance to abrasion. Rio de Janeiro: ABNT; 2012. [Portuguese].
20. ABNT: Associação Brasileira de Normas Técnicas. ABNT NBR 13.554: Soil-cement — wetting and drying durability test — test method. Rio de Janeiro: ABNT; 2012. [Portuguese].
21. Borselino C, Calabrese L, Di Bella G. Effects of powder concentration and type of resin on the performance of marble composite structures. Constr Build Mater. 2019;23:1915-21.
22. ABNT: Associação Brasileira de Normas Técnicas. ABNT NBR 15844: rocks for coating—requirements for granite. Rio de Janeiro: ABNT; 2015. [Portuguese].
23. Chiodi C Fo, Rodriguez EP. Application guide for stone in coating. São Paulo: ABIROCHAS; 2009. [Portuguese].
24. Costa FP, Fernandes JV, Melo LRL, Rodrigues AM, Menezes RR, Neves GN. The potential for natural stones from Northeastern Brazil to be used in civil construction. Minerals. 2021;11:440.
25. ASTM: American Society for Testing and Materials. ASTM C615: standard specification for granite dimension stone. West Conshohocken: ASTM; 2003.
26. Debnath S, Ranade R, Wunder SL, Mccool J, Boberick K, Baran G. Interface effects on mechanical properties of particle reinforced composites. Dent Mater. 2004;20:677-86.
27. Zanelli C, Conte S, Molinari C, Soldati R, Dondi M. Waste recycling in ceramic tiles: a technological outlook. Resour Conserv Recycling. 2021;168:105289.
28. ASTM: American Society for Testing and Materials. ASTM C503: standard specification for marble dimension stone. West Conshohocken: ASTM; 2008.
29. Ribeiro CEG. Influence of compaction pressure and particle content on thermal and mechanical behavior of artificial marbles with marble waste and unsaturated polyester [dissertation]. Rio de Janeiro: Universidade Estadual do Norte Fluminense Darcy Ribeiro; 2011.
30. Shena Y, Hec J, Xied Z, Zhoue X, Fange C, Zhang C. Synthesis and characterization of vegetable oil based polyurethanes with tunable thermomechanical performance. Ind Crops Prod. 2019;140:111711.
31. Monteiro SN, Vieira CMF. Solid state sintering of red ceramicsat lower temperatures. Ceram Int. 2004;30:381-7.
32. Gomes MLPM, Carvalho EAS, Barreto GNS, Rodriguez RJS, Monteiro SN, Vieira CMF. Development of sustainable artificial stone using granite waste and biodegradable polyurethane from castor oil. Sustainability. 2022;14(11):6380.