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Physical and Mechanical Characterization of Artificial Stone with Marble Calcite Waste and Epoxy Resin

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The incorporation of calcite marble waste in epoxy resin for the production of artificial stone can represent a technical-economical method and environmentally viable, reducing the amount of discarded residue in the environment, and adding economic value to marble waste and enabling the generation of jobs. The production of natural stone in Brazil recorded an exorbitant amount of waste generated in marble processing. Only 75% of marble taken from the deposits it becomes the finished product the rest is discarded. This study aimed to evaluate the mechanical and physical properties of produced artificial marble based in calcite marble waste and epoxy resin. The vacuum vibro compression was used for production as artificial marble and the specimens were cut according to standart NBR 15845. The results indicated that the artificial stones exhibit physical and mechanical results within the expected range for these kinds of materials. Artificial marble with a maximum flexural strength of 31,8 MPa, maximum compressive strength of 85,2 MPa, water absorption below 0.05% and a satisfactory adhesion between load and resin were obtained for the materials produced with 80% wt marble particles and 20% wt epoxy resin, enabling the development of an alternative material for civil construction applications.

Keywords: *Artificial marble, properties mechanical, calcite.*

1. Introduction

In recent years, the extraction of natural stone such as marble and granite presented a significant increase. This increase was mainly due to the use of these materials in works in construction and also for export. The Brazilian production of these materials during the year 2013, according to Abirochas, achieved a new record of 10.5 million tons[1]. In marble extraction and sawing of blocks, a significant volume of waste is generated, requiring larger spaces to deposit every day[2]. Today, Brazil is the fourth largest producer of ornamental stones in the world with a total production of 9.3 million tons in 2016[3].

The data from the production of natural stone in Brazil recorded an exorbitant amount of waste generated in marble processing. Only 75% of marble taken from the deposits it becomes the finished product the rest is discarded as waste[2]. According to the information Abirochas 01/2015[4], the Brazilian mining production during the year 2014 was estimated at 10.13 million tonnes, of which 64% allocated to the Southeast. There is an approximate 25% loss of the marble removed as waste. The advantage of this study, on the other hand, is that by-products of marble powder have priceless because waste is recycled[5].

In this context, to meet the requirements imposed for environmental laws, emerged new developments in materials, generating products known as artificial stones, produced with stone wastes and polymeric resin[4,6]. Epoxy resins are a good example of advancement in the development of composite materials and are one of the most important classes of thermosetting polymers because they offer an excellent combination of unattainable properties in other thermosetting resins[7].

Artificial stones has demonstrated a high market value and also an increasing demand in recent times[4]. Typically named as stone industrialized consists of 95% natural aggregates, that is, substantially a natural material. The aggregates that form 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]. Several studies have shown that size of the particles influence the mechanical properties. Usually attributed to the fine particle size distribution of the waste marble-by-product[9].

Renowned companies claim that the artificial marble has considerable qualities, which justifies the good acceptance in the consumer market. Among the advantages artificial stones are solid, impermeable, good mechanic resistant and had liquid penetration resistant, remaining only on the

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surface. This is caused by resin used in the manufacturing process, that provide adhesion between the stone particles and also penetrate between the interstices, eliminating the porosity of natural stones[6,10].

Several producers said about advantages of artificial stones. As comparative technical characteristics of the natural stones with artificial stones, Caesarstone[6] exhibits properties of artificial stones, such as flexural strength results having a superiority to natural calcite marbles of approximately 600%; yet for the compressive strength values, a superior 400% of the raw material (marble calcite); and only 0.02% as the percentage of water absorption.

Brazil, despite being one of the world's largest producers of natural ornamental rocks, still does not stand out when it comes to artificial rocks. A reflection of this is the large volume of artificial rocks imported annually[11]. Related to economic values, according with Abirochas[4] 12/2014, imports of artificial stones remained near to those of natural materials and, unlike them, had a significant increase in physical volume (+31.42%). Artificial stones showed imports of USD 43.9 million and 48.1 thousand tons in September of 2014. Its average price (USD 890.8/t) also remains higher than that of natural materials also imported (USD 705 8/t).

Thus, recycling and reuse of ornamental stone wastes for the development of artificial stones, can be technical-economic and environmentally viable, minimizing the amount of wastes disposed in environment, while incorporating economic value to residue and be able to create new jobs[12]. The marble particles obtained from can be reused instead of being deposited in the environment[13].

2. Material and Methods

The waste of calcite marble was used in this study, from Polita company, in Cachoeiro de Itapemirim, ES, Brazil, and as resin, it was used an epoxy resin diglycidyl ether of bisphenol A (DGEBA), supplied by Dow Chemical A/S; trade name: DER 331; density: 1,16 g/ml and molar mass: 340,41 g/mol. In addition, as hardener was used Tetraethylenepentamine amine (TEPA), supplied by Sigma Aldrich; density: 0.99 g/ml and molecular weight: 189.31.

The marble waste were classified among the sieves 10 and 200 mesh and divided into three different particle sizes. The larger particles (coarse) was classified in the range of 2 mm to 0,42 mm, the medium particles were comprised between 0,42 mm up to 0.075 mm, and fine particles were less than 0.075 mm. The ratio of each particle size was based on the study by Ribeiro[12], that investigated higher packings for calcite marble particles, seeking to increase properties of produced materials, because this composition was based on a study seeking better density and greater homogeneity, through in study of Ribeiro[12] that used a model mathematical -"simplex" to provide the most composition with better packing of waste marble.

2.1 Production of artificial marble slabs

The artificial marble slabs were produced in dimensions 200 x 200 x 10 mm through a vaccum vibro compression equipment developed for this line of research.

2.2 Characterization of artificial marble slabs

For the slabs of artificial stones were evaluated the physical and mechanical properties by standard tests such as density, water absorption, porosity, compressive strength, flexural strength, impact, abrasive wear, dynamic mechanical analysis, thermogravimetric analysis and scanning electron microscopy.

The determination of density, water absorption and apparent porosity was based in Annex B from ABNT NBR 15845, using 11 cubic samples, with dimensions (30 x 30 x 30) mm.

The compressive strength test was conducted in EMIC universal machine tests, model DL10000, based in appendix E from ABNT NBR 15845, using 10 dried cubic samples with dimensions 30 x 30 x 30 mm.

The flexural strength test at three points was conducted in EMIC universal machine tests, model DL10000, based in appendix F from ABNT NBR 15845, using 6 samples with dimensions 10 x 25 x 100 mm.

The abrasion test was conducted in AMSLER abrasive test equipment, based from NBR 12042, using two samples with dimensions 70 x 70 x 30 mm.

The impact test the hard body was based in appendix H from ABNT NBR 15845, using three samples with dimensions 10 x 200 x 200 mm.

For the thermal test was conducted the thermogravimetry with equipament TGA-Q5000 TA Instruments. Thermogravimetric analysis was performed in a temperature range from 30 ºC to 1000 ºC at a heating rate of 10 ºC/min using an air flow of 60 ml/min during testing.

The dynamic mechanical analysis was conducted on the thermal characterization unit DMA Q800 TA Instruments in a frequency of 1Hz, amplitude 20 µm, static force of 0.1 N and a heating rate of 3 ºC/min.

Scanning electron microscopy (SEM) analysis of gold sputtered fractured specimens, was conducted in a model Super Scan SSX-550 da SHIMADZU.

3. Results

3.1 Properties of Artificial Stone

3.1.1 Physical properties

The results are presented as average ± standard error.

The average apparent density obtained of the produced artificial marble was 2.23 ± 0.02 g/cm^3 that is 8% lower than those reported for the compound marble manufacturers that inform density values between 2.4 and 2.5 g/cm^3. Lee et al.[16] in his research of artificial stone has diversified compression level, pressure levels, vacuum level and vibration frequency in the production process and so found values ranging from 2.03 to 2.45 g/cm^3. Ribeiro et al.[14] using the same load of calcitic marble and polyester resin, obtained the value of from 2.27 g/cm^3. The density value found in this research is in agreement with the literature, with no significant changes in results.

With respect to water absorption value of artificial marble produced was found of 0.05 ± 0.01%. This value is 45% below the minimum expected for the industrialized artificial marble. This is because the values reported by artificial marble manufacturers are in the range from 0.09 to 0.40%[9]. According to Chiodi and Rodriguez[16], a value below 0.1% has a very high quality. This low absorption found in the production of artificial marbles occurred due to the efficient wetting of the load by the resin, providing a good interface in the material produced.

The value found for water absorption is also lower than recommended for calcite marble (material regulated by ASTM C503) should have the least absorption of from to 0.20%[17]. Lee et al.[17] changing the production variables has found values from 0.01 to 0.20%. Borsellino et al.[18] using residues marble and epoxy resin in open mold, obtained the value of 0.25%. Since compared with Ribeiro et al.[14], it reported an average of 0.19 ± 0.02%. Whereas that this used the same calcitic marble load and only varied the resin since it used the polyester resin it is inferred that low water absorption and porosity level found in this study indicate a good compacting and distribution of calcite residue in epoxy resin matrix used. For the apparent porosity was found a mean value of 0.11 ± 0.03% showing excellent physical properties of the formulated artificial marble. Chiodi and Rodriguez[16] said that high quality materials must have porosity below 0.5%. The low porosity was due to the good adhesion of the resin to the marble load and also because the resin occupied the voids, providing homogeneity to the system.

3.1.2 Mechanical properties

In the bending flexural strength test at three points it was obtained the value of 31.87 ± 2,58 MPa greater than the minimum expected for calcite marble regulated by ASTM C503 that should be greater than 7 MPa. The result indicates a low dispersion results and a considerable mechanical stability of the artificial material produced. Note that identified a considerable increase in the mechanical properties when compared to natural marbles, due to the inference that the degree of molecular interconnections efficiently occurred between the matrix and the load. Table 1 exhibited the Flexural strength values for the artificial marble produced.

Ribeiro et al.[14] obtained value of 21.5 ± 1,9 MPa for artificial stone produced with marble residues, polyester resin and a solvent, probably because Ribeiro et al.[14] used the solvent that decreased the strength of the chemical bonds of the final product. Other manufacturers of stone industrialized marble base reported values contained within the range of 13.6 to 17,2MPa. Borsellino et al.[18] was used marble residues and epoxy resin and obtained results as flexural strength values of 10.6 and 22,2 MPa, that is, the result obtained in this study is 43.5% above the expected results according to the manufacturers commercials. Borsellino et al.[18] however did not use the vacuum method for the production of artificial plates which justifies lower flexural values. It was that the faults of the vacuum provides a more porous material that act as stress concentrators.

Table 1. Flexural strength values for the artificial marble produced.

Material	Flexural strenght (MPa)
CP 01	30,50
CP 02	37,42
CP 03	33,49
CP 04	30,68
CP 05	31,49
CP 06	32,25

In compressive strength test it was found 85.20 ± 7,8 MPa and as elastic modulus was obtained value of 2.05 ± 0,28 GPa. The lowest values obtained to calcite marble to compressive strength demonstrated that such material was more easier have mobility of crystal planes at the time of efforts of compressive strength, feature occurring from the imperfections of its particles a fact that has been reduced in the production of artificial stone.

Although there are no a specific standard for compressive strenght rating for artificial stone, Chiodi and Rodriguez[16] reported that for ornamental flooring the amounts classified between 70 and 130 MPa have satisfactory compressive strenght classification. Table 2 shows the Compressive strength values for the artificial stone produced.

There is no standard to present limits to abrasive wear. Chiodi Filho and Rodriguez[16] had published paper presenting technological parameters for the use of ornamental stones in the flooring. These authors say that for high traffic floors, the wear must be less than 1.5 mm for average traffic should be less than 3 mm and to down traffic wear should be smaller than 6 mm. Thus, following the described technological parameters, the produced artificial stone can be used for high traffic floors due to low wear presented, below 1.5 mm on the track 1000 m.

In the result of resistance to hard body impact, it was noted that the artificial stone produced showed cracks happen from a height of 0.43 m. This amount was obtained by averaging the results of the test samples. It is considered that value as positive, since according to the study Frazão and Farjallat[19], the optimal values for granite must be greater than or equal to 0.4 m. Note that the granite characterized by these authors has superior strength the calcite marble used in this work.

Table 2. Compressive strength values for the artificial stone produced.

Material	Compressive strenght (MPa)
CP 01	95,89
CP 02	91,29
CP 03	89,36
CP 04	69,39
CP 05	88,77
CP 06	90,40
CP 07	78,90
CP 08	84,16
CP 09	76,68
CP 10	81,96
CP 11	90,39

Figure 1 shows the results of Mechanical test dynamic for the resin, artificial stone and natural marble.

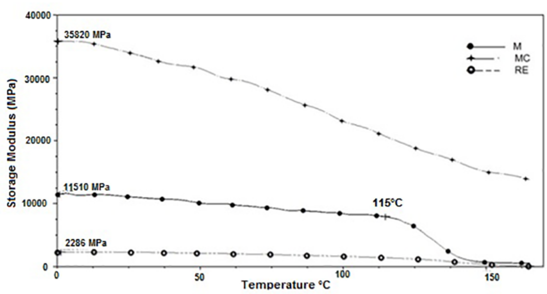

Figure 1. Mechanical test dynamic.

Ribeiro and Rodriguez[20] also made mechanical dynamic tests on artificial stones produced the base of calcite marble and polyester resin. For calcite marble the behavior was the same that was identified in this study. That is a fragile behavior is known for these naturals materials. As for the artificial material it identified a material with elastic-plastic behavior and the moment elastic at the beginning of the test and after reaching the yield point the plastic behavior predominated in this moment.

Identified that the artificial stone produced shows storage modulus greater than the epoxy system across the temperature range used in the mechanical test dinamic. Note also that the module found for the artificial stone is located between its constituents, as expected for a mixture. In the artificial stone produced, the movement of the molecular network is reduced by the presence of load. The Tg was value recorded near 140 ºC, indicating that the artificial material is in the glassy state ambient temperature.

Through dynamic mechanical testing was conducted a comparative study of the natural marble and artificial stone. Is observed for the artificial stone an elastic behavior at temperatures below 120 ºC with a storage modulus near 12000 MPa practically constant until the glass transition temperature of the aggregating agent of calcite particles, the resin DEGBA-TEPA.

The natural marble calcite (MC) has a much bigger storage module 36000 MPa showing a progressive decrease with increasing temperature probably associated with the porous structure of this material and keeping your elastic properties throughout the temperature range of the object of study.

3.1.3 Thermogravimetric and Microscopic Properties

The graph of the test of thermogravimetry is showed in Figure 2.

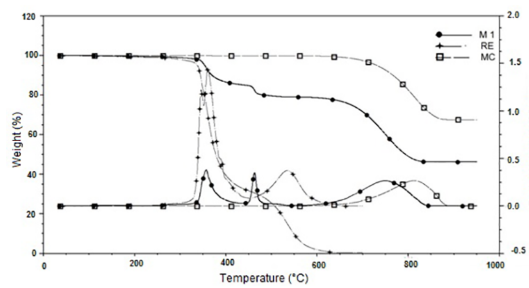

Figure 2. Thermogravimetry.

The curve of calcite marble has a mass loss around 45% of the total weight at approximate temperature of 830ºC due to the decomposition of the carbonate to oxide. The behavior observed for calcite marble in this study follows the same behavior observed by Souza and Bragança[15] that observed to calcite was observed a loss of approximately 43% by weight around 850 ºC. Barcina et al.[16] also observed similar profile to calcareous, observing a loss of about 44% by weight in the approximate temperature of 800 ºC. Ribeiro and Rodriguez[20] also conducted a survey of natural calcite marble and obtained 44% of weight loss in about 850 ºC.

The curve representing the epoxy resin registering a first mass loss of about 70% by weight at temperature of about 380 ºC due to decomposition of the resin. Already at about 550 ºC, the resin showed a decrease in mass around 90% of the mass due to combustion of the remaining breeze of the epoxy resin under high temperature.

The first stage of thermogravimetric curve of the artificial stone produced shows a weight loss of approximately 20% at the temperature of about 480 ºC concerning the decomposition of the resin. The second phase, between about 680 and 800 ºC, shows a loss of mass around 45% of the total weight due to decomposition of the carbonate to oxide.

There were no found evident pores showing that the fracture may have occurred through pores or fault of adesion among the resin and the load that may have acted as stress concentrators. The fracture surfaces showed surfaces intragranular fractures with mechanical disruption due to mechanical stress, as well as particles adhered to resin, demonstrating the effective interfacial adhesion in the materials, this fact was showed in Figure 3.

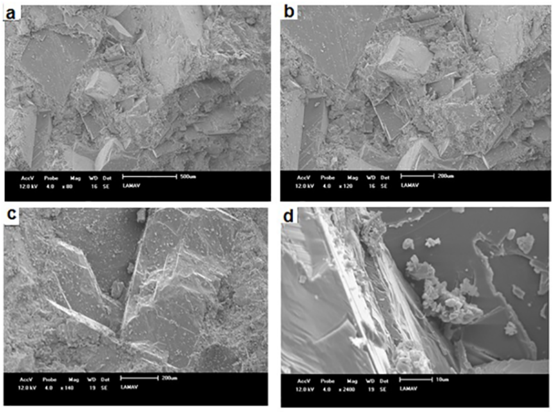

Figure 3. (a, b, c, d) Scanning electron micrographs of fracture surfaces of the artificial marble produced increases with 80x (a), 120x (b), 140x (c) and 2400x (d).

Increasing the resin phase improves the load on the resin adhesion and can reduce the loss factor in the formulations due to the reduced friction between the polymer and the calcitic particles in the interface[23].

It was also produced a stone artificial in proportion of 80% wt/tw of residues without the action of vacuum and compaction, that lower values of flexural strength of 28.8 MPa were obtained. In the same proportion of 80% calcitic residue under vacuum and compression (vibro compression methodology), a mean flexural strength of 31.8 MPa was obtained, showing the influence of these process variables on the mechanical properties, generating results with growth rates of 10% in the flexural strength only by varying these parameters due to the porosity which act as tensions concentrators.

Figure 4 (a, b, c, d) represent SEM (scanning electron microscopy) micrographs of the fracture surface of the artificial marble produced in the proportion of 60% wt/wt residue without vacuum action and compression in the formulation process.

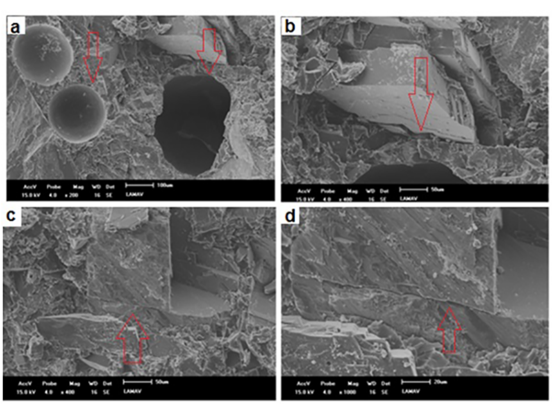

Figure 4. Scanning electron micrograph of the fracture region of the artificial marble with 60% wt/wt of residue without vacuum action and compaction with increases of 200x (a), 400x (b), 400x (c), 1000x (d) and 2000x (e).

Cavity and heterogeneity (according to blank-red-arrow in the micrographs showed in the Figure 4) are more pronounced than in the formulation of higher residue content. The presence of cavities / pores due to fault of vacuum action and inefficient wetting resulted in unsatisfactory adhesion of the resin and load. Particles in contact without the presence of the interface with the resin are observed as well as the presence of voids which may have acted as stress concentrators, resulting in lower mechanical properties as recorded in the three-point flexural tests.

4. Conclusions

The use of this epoxy resin together with the load of calcite generates a high-performance product with excellent properties, providing both environmental solutions for waste as benefits economics.The artificial marble produced can have a wide range of use, either in residential or commercial spaces. The use of this type of material provides style, elegance and constant innovation. In addition, artificial marble presents advantages over natural rocks, such as low porosity, low water absorption and considerable mechanical properties.

It was observed the flexural strength value for the artificial marble produced was 31.87 MPa, and has for compression was 85.20 MPa, such mechanical values are satisfactory. The physical results are also excellent porosity of only 0.11% and 0.05% of absorption, demonstrating the high impermeability and quality of the artificial material produced.

In the hard body test, the artificial stone had fails from a height of 0.43 m, good value for this type of artificial material. For abrasive wear of Amsler type testing, interesting results were also obtained inferred that the produced artificial marble can be used for high traffic floors due to low wear presented, below 1.5 mm in track 1000 m.

The results indicated thermogravimetric mass loss behavior as expected for artificial stones, epoxy system DGEBA / TEPA and natural calcitic stone. For the artificial marble was a decomposition of $CaCO_3$ into oxides.

The use of vibro vacuum compression allowed a better interface and adhesion of the load in the epoxy matrix, with lower porosity, providing better mechanical properties for the produced artificial marble. The Scanning electron micrographs of fracture indicated that calcite load had excellent adhesion to epoxy matrix DGEBA / TEPA, not being visible pores that may have acted as stress concentrators.

5. Acknowledgements

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