

Article

Eco-Efficient Artificial Stones Produced Using Quartzite Quarry Waste and Vegetable Resin

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Abstract: The ornamental stone industry plays a crucial role in the world economy, and thus the production process of ornamental stones generates a large volume of waste that is normally destined for landfills. Given the growing market import of artificial stones, there is a need for more sustainable practices to reduce waste and improve the use of natural resources. Thus, the present study aims to develop artificial stones with waste from the ornamental stone extraction process from the quarry, and vegetable polyurethane resin derived from castor oil, in order to analyze its viability in the production of artificial stone slabs. The wastes used in this work were three quartzites, fragmented and mixed with three grain sizes, called coarse, medium, and fine. These wastes were characterized using X-ray fluorescence (XRF), X-ray diffraction (XRD), Fourier transform infrared (FTIR), and thermal analysis (TGA/DTG/DSC). Artificial stone slabs were produced using 15 wt.% vegetable polyurethane resin derived from castor oil and 85 wt.% ornamental stone wastes (quartzite). These slabs underwent apparent density, water absorption, porosity, 3-point flexural strength, scanning electron microscopy (SEM), petrography, and X-ray diffraction (XRD) tests. According to the results obtained, it was possible to prove the technical viability of manufacturing artificial stones with ornamental stone wastes and with the use of vegetable polyurethane resin derived from castor oil. The use of these raw materials not only resulted in the manufacture of a new material but also in an environmentally conscious and sustainable approach, following precepts such as the circular economy. The creation of these eco-efficient products is a significant contribution to the search for solutions that value environmental preservation and the optimization of natural resources.

Keywords: artificial stone; ornamental stone waste; technological characterization



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1. Introduction

The ornamental stone industries are of paramount importance for the world market in the construction sector. The five countries that lead the production of these stones are, in order, China, India, Turkey, Brazil, and Iran. In 2020, total world production reached the mark of 155 million tons [1].

The main applications of these stones around the world are in the civil construction sector, where they are used as flooring and coverings. Brazil is recognized in this market for having stones and materials of great geodiversity, and exotic and striking beauty.

The ornamental stone industry plays a crucial role in Brazil's economy, with the country standing out as one of the world's main producers and exporters of these materials. Over the last 20 years, Brazilian performance in the international ornamental stone market has been comparable or even superior to that of other major competitors in the sector, with

the exception of China. In the first quarter of 2023, Brazilian ornamental stone exports totaled USD 223.8 million in revenue and 364.3 thousand tons in volume [2].

The Brazilian ornamental stone market stands out for the richness, geological diversity, and exuberance of its stones, with an emphasis on pegmatites and quartzites. Among these varieties, quartzite has gained a prominent position in the market due to its distinctive properties, mainly aesthetic, being highly valued and characterized by a high added value [3].

The production process of ornamental stones generates a large volume of waste that is normally sent to landfills. Production includes mining and processing. The mining stage involves the extraction of blocks, resulting in unused quarry waste. Processing, in turn, is divided into primary and secondary. The first transforms the blocks into slabs, generating fine and quarry wastes. Secondary processing consists of the final finishing of the slabs, which may involve polishing, honing, brushing, and resin treatments, among others, which also generate fine waste. These steps are crucial to ensure the quality of materials and meet market demands [4].

Waste generation is a significant issue in the ornamental stone production scenario. In 2020, 163 million tons of quarry waste and 63 million tons of waste from the processing of these stones were generated worldwide [1]. In Brazil, it is estimated that a considerable amount, around 22 million tons, of waste is produced, with approximately 20 million tons corresponding to quarry waste, while 2.5 million tons correspond to fine waste from industry. In the ornamental stone extraction and processing chain as a whole, approximately 80% of the raw material is transformed into waste that is deposited in specific landfills for this purpose [4].

To ensure sustainable development in the ornamental stone sector in Brazil, it is crucial to implement practices that promote a circular economy and align with ESG (environmental, social, and governance) principles. A sustainable approach involves reducing waste throughout the production chain and seeking innovative ways to reuse and recycle waste generated during the processing of ornamental stones. It is essential for the sector to encourage the adoption of responsible waste management practices, avoiding improper disposal in landfills and seeking more sustainable alternatives. Commitment to a circular economy and ESG principles not only helps reduce the sector's environmental impact but also strengthens Brazil's image and competitiveness in the international market, positioning it as a reference for responsible and sustainable production of ornamental stones.

The waste generated in the production of ornamental stones has a great capacity to be used as a by-product for the development of new materials, and thus several studies have been carried out with the aim of attesting to the technical feasibility of using this waste. There are studies that use the fine waste from processing to produce ceramics [5–7], cement, mortar and plaster [8], glass [9], coarse waste as an aggregate for civil construction [10], and artificial stones, among others.

Artificial stones are manufactured materials that combine natural mineral aggregates, synthetic binders (binding agents), and sometimes additives to create products with specific characteristics for construction and design purposes. These synthetic binders may include polymeric resins, hydraulic cement, or a combination of these materials, provided that the material consolidation process is irreversible in nature. According to the definition provided by Callister and Rethwisch [11], materials that are commercially available and that are manufactured with wastes of natural stones are called composite materials.

According to the report by the Associação Brasileira da Indústria de Rochas Ornamentais—ABIROCHAS [12], imports of artificial stone, also called agglomerated or artificial, reached a value of USD 23 million and 36.8 thousand tons from January to May 2022, while exports of these materials totaled USD 6.3 million and 4.5 thousand tons in the same period. In view of this discrepancy, analyzing imports of this material from Brazil, the opportunity to expand the artificial stone market is evident, since these materials offer numerous advantages in terms of the variety of colors, patterns, and applications, in

addition to representing a more sustainable alternative use of fine waste and quarry waste generated in the processing of natural stones.

With this, in order to seek more sustainable practices to reduce waste and improve the use of natural resources, the production of artificial stones is an option for the disposal of this waste. It can contribute to reducing the consumption of natural raw materials, reducing the amount of waste to be discarded in nature, and the production of an eco-efficient product that can contribute to increasing the economic cycle of products and creating jobs.

A wide range of studies has been devoted to the variables of artificial stone production, exploring a variety of wastes and materials, mostly from stones, and using different types of resins, such as polyurethane, epoxy, and polyester, among others [13–18].

Polyurethane resin based on castor oil is a vegetable resin that has been studied and used in several applications. Among the characteristics of this resin, one of the main ones is that this resin is solvent-free, non-toxic, and therefore not harmful to the environment and human beings. Its final polymerization takes around 24 h and it dries to the touch in 60 to 90 min, depending on the ambient temperature.

The present study aims to develop artificial stones with waste from the ornamental stone extraction process, from the quarry, and vegetable polyurethane resin derived from castor oil, in order to analyze its viability in the production of artificial stone slabs. In addition, the study aims to contribute to sustainable development with ecologically conscious alternatives in the use of industrial waste and the use of polyurethane resins of vegetable origin.

2. Materials and Methods

2.1. Materials

The materials used in this work for the manufacture of artificial stones were ornamental stone waste and vegetable polyurethane resin derived from castor oil. Three (3) quartzite wastes were used, from the extraction stage in an ornamental stone quarry in Brazil (Figure 1). These wastes are called coarse wastes.



Figure 1. Ornamental stone waste from the quarry: (a) quartzite 1, (b) quartzite 2, and (c) quartzite 3.

The three (3) wastes come from the same quarry but from a different geographic location. These three wastes were mixed and subsequently sieved into the desired particle sizes to manufacture artificial stones. The difference between them is minimal, as they all had similar chemical composition, with SiO_2 above 90%.

The chemical composition of the waste is shown in Table 1.

These wastes were fragmented using an Engesdrab roller mill, model MR-200 and series n° 1881, forming a mixture of granulometries called coarse, medium, and fine. Subsequently, granulometric selection was carried out with the aid of sieves according to the granulometric ranges, as shown in Table 2.

Table 1. Chemical composition (%) of quartzite wastes.

	Quartzite 1	Quartzite 2	Quartzite 3
SiO ₂	90.60	93.60	93.30
Al ₂ O ₃	5.10	4.50	5.10
MgO	1.30	0.43	0.17
K ₂ O	0.88	0.78	0.80
Fe ₂ O ₃	0.30	0.22	0.13
* LOI	1.40	0.51	0.50

* LOI—loss on ignition.

Table 2. Granulometric ranges used.

Granulometry	Mesh	Grain Size (mm)
Coarse	−8 Ø + 25	2.38 > Ø > 2.00
Medium	−25 Ø + 230	2.00 > Ø > 0.63
Fine	−230 Ø	0.63 > Ø

Mix design: a mix design based on the simplex lattice network was used. The procedure consisted of planning with 10 different mixtures where the proportion of granulometry of the quartzite wastes was varied, similar to the one performed by Agrizzi et al. [14]. The experiment was performed in duplicate and the evaluated response was the apparent density.

Based on the three particle size ranges, 10 different mixtures were proposed with different percentages of coarse, medium, and fine particles, as shown in Table 3. The planning was used to manufacture the artificial stones and to help determine the mix with the best apparent density.

Table 3. Experimental design with mixtures containing different granulometric proportions of ornamental stone waste.

Experiment	Coarse (%)	Medium (%)	Fine (%)
1	100.0	0.0	0.0
2	0.0	100.0	0.0
3	0.0	0.0	100.0
4	50.0	50.0	0.0
5	50.0	0.0	50.0
6	0.0	50.0	50.0
7	66.7	16.7	16.7
8	16.7	66.7	16.7
9	16.7	16.7	66.7
10	33.3	33.3	33.3

The vegetable polyurethane resin used was prepared by mixing a component A pre-polymer (resin) and a component B polyol (catalyst) in a ratio of 1 (A) to 1.5 (B), as indicated by the manufacturer, without releasing toxic vapors, with the characteristics of physical–chemical stability, elasticity, and impermeability. In addition, the resin had high durability properties, great resistance to ultraviolet rays, excellent penetration into the surface pores, ensuring good adhesion, and no volumetric shrinkage after curing. The resin and catalyst used were IMPERVEG AGT 1315.

2.2. Methods

X-ray fluorescence spectrometry (FRX): performed using a WDS spectrometer model Axios Max (Panalytical). The pellets were prepared using a VANEON automatic press and the chemical composition data were collected using an X-ray fluorescence instrument (WDS-2), model Axios Max (Panalytical).

X-ray diffraction (XRD): determined by the powder method, in a Bruker-D4 Endeavor instrument, under the following operating conditions: Co K α radiation (35 kV/40 mA); goniometer speed of 0.02° 2 θ per step with a count time of 1 s per step and collected from 5 to 80° 2 θ . Qualitative spectrum interpretations were performed by comparison with standards contained in the PDF02 database (ICDD, 2006) in Bruker AXS Diffrac.Plus software version 6.0.

Fourier transform infrared (FTIR): performed in a Bruker Tensor 27 instrument. The analysis was carried out in a spectrophotometer in the mid-infrared range (4000–600 cm^{−1}), with 32 sweeps performed. For the analysis of the samples, the technique called total attenuated reflectance (ATR) was used.

Thermal analysis (TGA/DTG/DSC): The thermal degradation behavior of the vegetable polyurethane resin was verified via thermogravimetric analysis (TGA), derived thermogravimetry (DTG), and differential scanning calorimetry (DSC) of the sample. The analysis was performed using a Setaran thermogravimetric analyzer, model LabSys Evo. The analysis was carried out in the temperature range of 30–500 °C, with a heating rate of 10 °C/min in a nitrogen atmosphere.

Artificial stone slabs were produced using 15 wt.% of vegetable resin derived from castor oil and 85 wt.% of ornamental stone wastes (quartzite) with dimensions of 200 × 200 × 10 mm (Figure 2).



Figure 2. Artificial stone produced.

First, the wastes were mixed in different particle sizes and proportions (shown in Tables 1 and 2) and dried in an oven for 24 h at 110 °C to remove humidity from the material until the moment of mixing. Subsequently, the resin (component A) and the catalyst (component B) were weighed according to the proportions indicated by the manufacturer, and with the granulometric mixtures of wastes, dry and still warm, the mixture was made. It was decided to prepare the mixtures while still warm, as this favors the fluidity and dispersion of the resin between the particles.

After the mixing step, the material was taken to a mold of size 200 × 200 × 10 mm and placed in a hydraulic press from the brand Bonevau under vibration, temperature, and vacuum, where the mass was compacted in a mold at a pressure of 33.29 MPa.

Subsequently, after 40 min in the hydraulic press at 60 °C, the artificial stone slab was removed from the mold and placed to cool at room temperature for 24 h. After that, the slabs went to the post-cure stage for a period of 3 days in an oven at 60 °C and 1 day at 80 °C.

After the post-curing stage, the surfaces of the slabs were honed with a Makita PK5001C manual polisher (Figure 3). To wear down the irregularities that existed on the surface of the slabs, two sandpapers were used, the 100 to leave the surface rough and the 200 as pre-finishing (beginning of the shine). Once this was done, the artificial

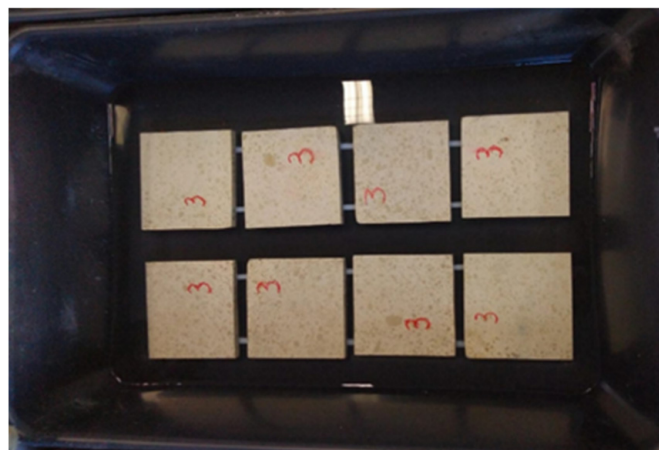
stone slabs that had been honed were cut using a conventional AR 350 cutter to make test specimens in the dimensions determined by the technical standards for each test carried out in the current study.



Figure 3. Artificial stone slab produced after honing.

To carry out the apparent density, water absorption, and porosity tests, the slabs produced with a size of 200×200 mm were cut into sizes of 100×100 mm. The tests were carried out in accordance with the recommendations of the EN 14617-1 standard [19].

First, the specimens were placed in an oven at a temperature of 70 ± 5 °C until reaching constant mass. The second part of the test consists of determining the saturated mass. To find the saturated mass, the specimens were placed in a container, in which they were immersed in deionized or distilled water under vacuum for 2 h (Figure 4a). The specimens were removed from the container, dried with a damp cloth, and weighed individually (Figure 4b), thus finding the “saturated mass” (m_{sat}).



(a)

Figure 4. Cont.

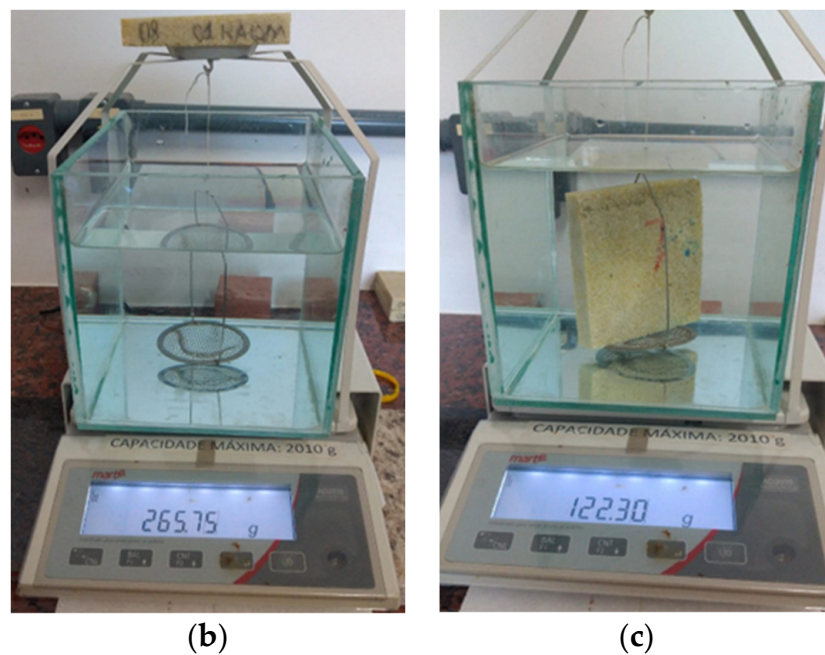


Figure 4. Procedure for determining the apparent density and water absorption: (a) slabs covered with 2 cm of distilled water, (b) determination of wet mass, and (c) determination of submerged mass.

The third and final step of the process consists of submerged weighing of the specimens in a container with water, using a wire attached under the scale (Figure 4c), or using an accessory for hydrostatic weighing. In this way, the “submerged mass” of each specimen (m_{sub}) was obtained.

Three-point flexural strength: determined in accordance with the EN 14617-2 standard [20]. The specimens were prepared in rectangular format with dimensions of 200×50 mm and the analysis was performed in dry conditions. For this, the specimens were kept at 70°C for 24 h in an oven and then allowed to cool at room temperature. The specimens were placed between the test machine rollers (Figure 5), on the two support rollers, and under the load roller.



Figure 5. Three-point flexural strength test.

The test was carried out in an EMIC universal testing machine, model DL 100 kN, with a loading rate of 0.0185 kN/s.

Scanning electron microscopy (SEM): FEI Quanta 400 equipment was used, in a high vacuum, electron acceleration voltage of 20 kV, with a backscattered electron detector. The samples were attached in nature to a support using double-sided adhesive tape, and covered with silver on a BalTech SCD 050 sputter (using an argon vacuum and applying a current of 30 mA for 300 s).

Petrography: petrographic analysis was performed in accordance with the ABNT NBR 15845 standard [21] and with the aid of a polarized light petrographic microscope (model: Axioskop 40 CARL ZEISS, brand: ZEISS).

X-ray diffraction (XRD): XRD of the slab produced was performed and determined using the powder method, in a Bruker-D4 Endeavor instrument, under the following operating conditions: Co K α radiation (35 kV/40 mA); goniometer speed of 0.02° 2 θ per step with a count time of 1 s per step and collected from 5 to 80° 2 θ . Qualitative spectrum interpretations were performed by comparison with standards contained in the PDF02 database (ICDD, 2006) in Bruker AXS Diffrac.Plus software.

3. Results and Discussion

3.1. Characterization

The quartzite wastes shown in Table 1 are predominantly made up of silicon oxide (SiO₂), which is a typical characteristic of silicate stone.

The variations found, between the concentrations of oxides in the quartzites studied in the present research and the quartzites from the works of other authors [22–25], are due to the fact that the quartzite stones are taken from different localities and the specific peculiarities of the geological formations that occurred in each location. Furthermore, for the same reason, based on the SiO₂ content observed in the wastes studied in this work, it can be stated that the quartzite samples collected in regions 1, 2, and 3 are purer and, therefore, richer in silicon oxide (SiO₂) and less rich in other oxides.

It is observed that the quartzite wastes showed low loss of calcination, and the low levels of aluminum oxide (Al₂O₃) and potassium oxide (K₂O) can be related to the presence of muscovite, which was observed in the petrographic analysis.

Figure 6 shows the X-ray diffractogram of the ornamental stone wastes (quartzite) from this research. It is observed that the wastes have crystal structures very similar to each other since all peaks occurred in the same positions and with comparable relative intensities. This fact was already expected due to the proximity of the places where their respective stones were removed from the ground.

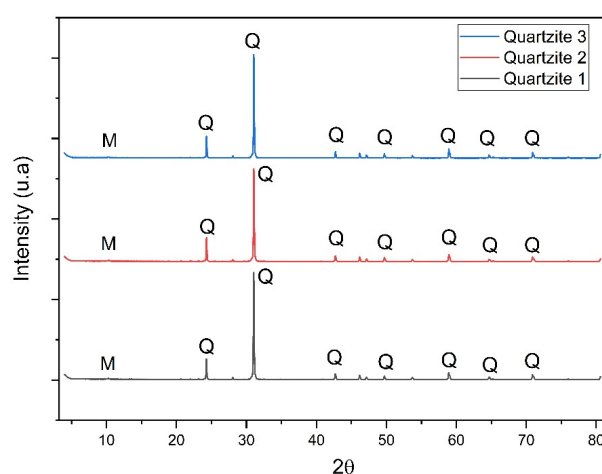


Figure 6. X-ray diffractogram of quartzite wastes 1, 2, and 3. Q: quartz (SiO₂), M: muscovite.

It was possible to identify the presence of characteristic peaks of the crystalline phases referring to quartz (SiO₂), which is the stable phase of silica at room temperature, and muscovite. These data confirm the information obtained based on X-ray fluorescence

(Table 3), which pointed to silicon and oxygen as the predominant elements in the samples under study.

Figure 7 shows the spectra obtained for samples of quartzite wastes 1, 2, and 3 and for a mixture containing an equal amount of these three wastes. When comparing the spectra obtained with the literature, one can observe corresponding bands for the vibrations of the Si–O–Si bonds at approximately 1060 cm^{-1} , 842 cm^{-1} , and 450 cm^{-1} , belonging to the stretching, bending, and rocking vibration modes [26–28]. Thus, it was possible to verify that the quartzite wastes have a spectrum similar to that of quartz, which contains a predominance of SiO_2 . Furthermore, it may be observed that all spectra have similar bands, which characterizes their similar composition. The spectra obtained from the quartzite wastes confirm the one obtained in X-ray fluorescence, with the majority presence of silicon and oxygen bonds.

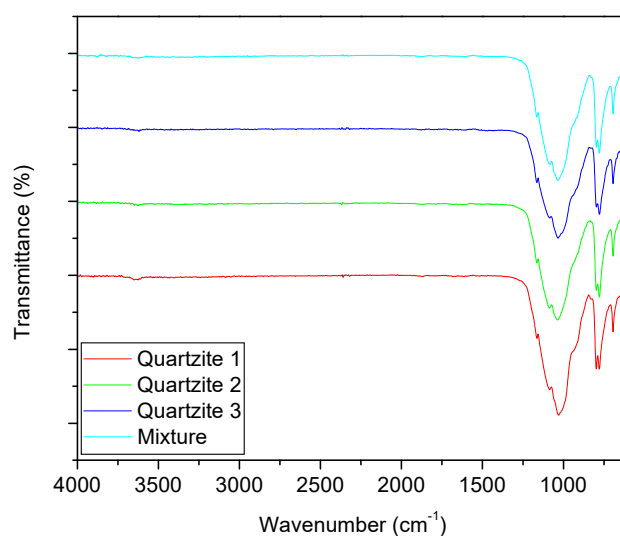


Figure 7. Spectra of ornamental stone wastes. Quartzite 1,2,3 and mixture.

Figure 8 shows the spectrum of the vegetable polyurethane resin. With this spectrum, it is possible to know qualitatively the functional groups present in the chemical structure of the resin under study.

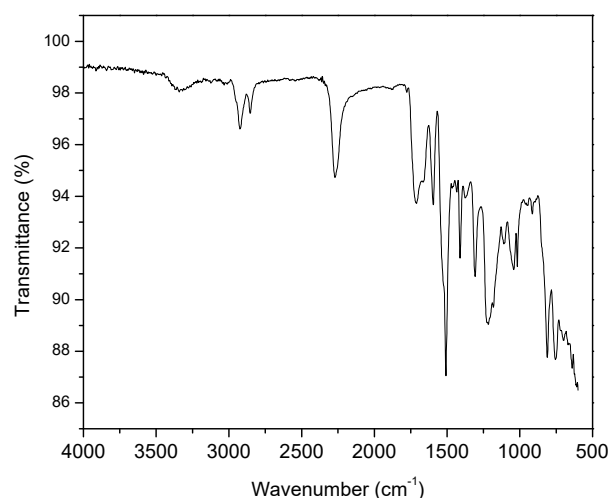


Figure 8. Spectrum of vegetable polyurethane resin.

Rodrigues [29] described the main absorption bands and vibrational modes of polyurethane in the infrared region. The vibrational modes for axial stretch include hydroxyl

(O–H), CH₂ and CH₃ (C–H), and ester (C=O) groups, with absorptions (cm^{−1}) at 3309, 2890, and 1720, respectively. The axial deformation groups are ester (C–O) and functional group (CH₂)_n (CH₂), with absorptions (cm^{−1}) at 1180 and 706, respectively.

In this spectrum, it is possible to observe that in the wave region 3421–3375 cm^{−1}, there is a bond between hydrogen and nitrogen that combine with the main group of OH. From 3000–2840 cm^{−1}, there is a C–H stretch, the class of this compound being an alkane, which is characteristic of molecules found in natural components [28]. It shows the carbonyl band (C=O) at 1720–1706 cm^{−1}. In addition to these analyses, it is possible to confirm the presence of the urethane group based on the presence of the bands from 1627 to 1545 cm^{−1}, due to the vibration of deformation by the N–H bond and C–N elongation. Also, the presence of a band at 1525 cm^{−1} is observed that is attributed to the NH folding of amide II, related to the formation of ureas; from 1187 to 1015 cm^{−1}, attributed to the elongation of C–N, C–C, and C–O; and in the region at 820–666 cm^{−1}, where we have N–H outside the plane [30,31].

The identification of the functional groups and chemical structure of the resin, obtained from the spectra, shows important information to confirm what is expected for this type of resin and its chemistry, as well as making it possible to understand the healing reaction of the resin and its interaction with quartzite in stone formation.

Carrying out the FTIR analysis of raw materials allows us to know the functional groups of each material. The possible interactions between the mixture of the three wastes and the resin would be shown through the displacement of the absorption bands of the artificial stone compared to those of the raw materials. The relevance of this for our study is knowing the chemical structure of the resin under study since not even the manufacturer indicates it, and also knowing the functional groups present in the waste. By knowing these functional groups, we can have an idea of the concepts of chemistry and the possibilities of these groups interacting with each other.

Figure 9 shows the thermogravimetric analysis (TG), derived thermogravimetry (DTG), and differential scanning calorimetry (DSC) curves of the vegetable polyurethane resin.

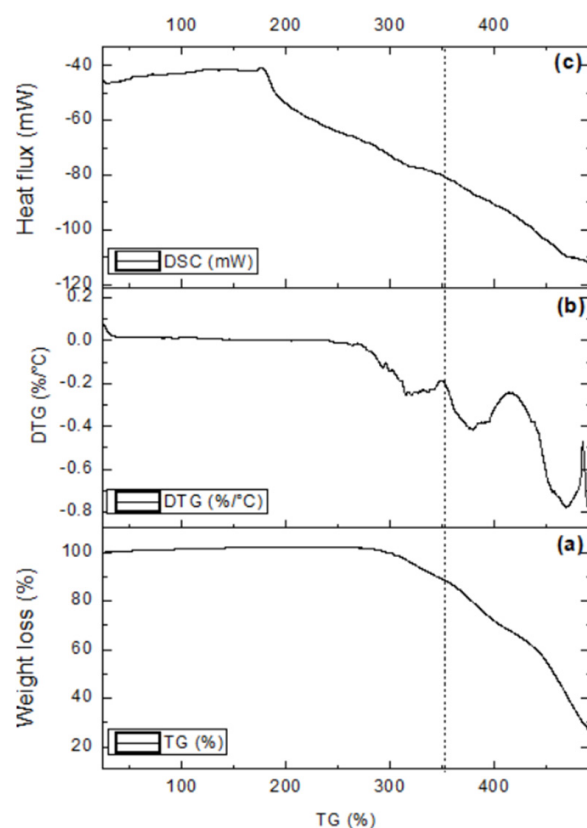


Figure 9. Thermogram of TGA (a), DTG (b), and DSC (c) for vegetable polyurethane resin.

Analyzing Figure 9a, it is possible to observe that up to approximately 286 °C the mass loss was insignificant. Resin decomposition starts at 297 °C with a mass loss of 11.5%. From this temperature, the first stage of the degradation process begins, which subsequently occurs in phases, specifically in three stages. The second occurred around 353 °C, referring to the decomposition of the rigid segments of the vegetable polyurethane resin, with a mass loss of 21.4%. The third stage occurred at 418 °C until the final decomposition with 40.7% mass loss associated with the degradation of the compounds produced in the second stage [32,33].

According to Gomes et al. [13], the thermal decomposition at 200 °C refers to urethane bond breakage, at 330 °C it is probably due to CO degradation, and in the third stage at 380 °C there is a mass loss of 57%.

Polyurethanes generally decompose in two or three events due to structural differences [34,35]. In the DTG curve (Figure 9b), one may note three stages of decomposition at 322, 377, and 471 °C. The DSC curve (Figure 9c) showed that the thermal decomposition process of the vegetal polyurethane resin occurs in an endothermic manner. The authors, Bortoletto-Santos, Ribeiro, and Polito [36] also investigated the vegetable polyurethane resin derived from castor oil and observed three main stages of mass loss. The first occurred between 250 and 300 °C, the second at 454 °C, and the third and last from 500 °C, representing the final loss of the process. Regarding the DSC analysis, the authors observed a weak peak characteristic of the melting process, which corresponded to a greater degree of polymerization of the sample of vegetable polyurethane resin derived from castor oil.

The authors Pinto et al. [37] also observed from the TG curve of the vegetable PU resin the occurrence of three main peaks of mass loss, with the onset of degradation from 200 °C due to the release of residual compounds from the synthesis process. The second stage occurred between 220 and 310 °C, attributed to the breakage of the PU resin chain into isocyanates, amines, alcohols, and carbon dioxide. The third stage, which occurred from 320 to 450 °C, pointed to the term decomposition of the castor oil structure used in the resin synthesis process. The authors also observed, via the DTA curve, endothermic peaks corresponding to the thermal degradation of the polymer.

In comparison with the results of other authors [32,33,38], it can be stated that the thermal decomposition of vegetable polyurethane resin presents three main stages of mass loss. These are verified through the three evident peaks in the DTG curve, with a totally endothermic process. It can be seen that polyurethane resin has good thermal stability, that is, it is resistant to a wide temperature range without suffering degradation, which makes its use in the production of artificial stones feasible.

3.2. Simplex Lattice Mix Design Analysis

A simplex lattice mixing design was used to aid in the execution of the experiment and in determining the mixture that contains the best apparent density. Table 4 shows the apparent density results for each combination performed in the planning.

At first, the composition that showed the highest apparent density was combination 7, with 66.7% of coarse particles and 16.7% of medium and fine particles. This combination was also the best found by Agrizzi et al. [14] for quartzite samples, resulting in a density of 1932 kg/m³.

Table 4. Apparent density and standard deviation values obtained for each experiment of the simplex lattice experimental design.

Experiment	Apparent Density (g/m ³)	Standard Deviation
1	1.75	0.04
2	1.83	0.03
3	1.60	0.02
4	1.89	0.15

Table 4. *Cont.*

Experiment	Apparent Density (g/cm ³)	Standard Deviation
5	2.08	0.05
6	1.82	0.10
7	2.16	0.09
8	1.97	0.03
9	1.80	0.02
10	2.08	0.05

The highlights shows that the experiment chosen for the manufacture of artificial stones was experiment 7.

3.3. Apparent Density, Water Absorption, and Apparent Porosity

Table 5 shows the average apparent density values (g/cm³), average water absorption (%), and average apparent porosity (%) with standard deviation values for experiment 7 of the artificial stone.

Table 5. Physical indices of the artificial stone produced.

	Density (g/cm ³)	Water Absorption (%)	Porosity (%)
Experiment 7	2.16 ± 0.09	0.15 ± 0.03	0.33 ± 0.06

Experiment 7 (2.16 ± 0.09 g/cm³) had the best density. The importance of density consists in the fact that the higher its value, the better the adhesion between the particles and the polymeric matrix, which reduces the occurrence of voids [39].

Agrizzi et al. [14] found a density for artificial stones produced with vegetable polyurethane resin of 2.22 ± 0.04 g/cm³, and when compared with a commercial material, the density was lower, probably due to the low density of the polyurethane polymer of 1.08 g/cm³. The density found for the commercial stone was 2.41 ± 0.01 g/cm³. Lee et al. [40] worked with different compression pressure levels, vacuum levels, and vibration frequencies in the production process and found density values in the range of 2.03 to 2.45 g/cm³.

Regarding water absorption, the value found was $0.15 \pm 0.03\%$ for experiment 7. The lower the water absorption, the lower the porosity, and, consequently, the better the quality of the artificial stone produced. The European standard for artificial stones UNE-EN 14617-1 [19] does not show the water absorption values of the stones. Thus, using only the test method to compare with the standard for natural stones NBR 15844 [41], where the absorption has to be less than 0.4%, is it noted that the artificial stone produced had a lower absorption than the stability for the natural stones.

Agrizzi et al. [14] also used the vacuum vibro-thermo-compression technique and found a value of $0.14 \pm 0.06\%$ for water absorption in their artificial stone manufactured with 15 wt.% vegetable polyurethane resin and 85 wt.% quartzite waste. Subsequently, the authors compared the artificial stone produced with the commercial one, which showed an absorption of $0.05 \pm 0.01\%$. However, commercial stone is manufactured with a different resin, usually polyester, and the mineral filler used is pure quartz with a much finer granulometry. Some commercial stones also use glass or mirrors in their composition.

The porosity found in experiment 7 was $0.33 \pm 0.06\%$. According to Chiodi Filho and Rodrigues [42], materials classified as high quality must have a porosity lower than 0.5%, and the porosity values found for the artificial stones produced in this work were lower than this value.

The low porosity of the artificial stone produced can be attributed to the homogeneity of the material, with the particles of ornamental stones (quartzite) well adhered to the vegetal polyurethane resin, guaranteeing the filling of the voids [13].

3.4. Three-Point Flexural Strength

Figure 10 shows the mechanical behavior of the artificial stone produced. The resistance test of experiment 7 was carried out to determine the artificial stone produced with the highest density. The average strength found was 20.46 MPa.

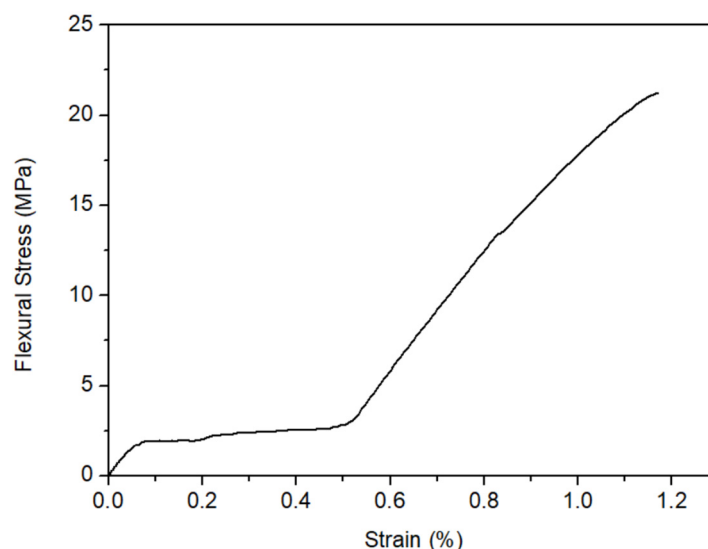


Figure 10. Mechanical behavior of the artificial stone produced.

When comparing the average value found with the Brazilian standard NBR 15844 [40] for natural stones for coatings, it can be seen that the value found is well above the minimum required by the standard, which is 10 MPa.

According to Chiodi Filho and Rodrigues [42], ornamental stones used as coatings in civil construction, with flexural strength above 20 MPa, are classified as highly resistant materials.

Agrizzi et al. [14] used quartzite waste (86 wt.%) and castor oil resin (14 wt.%), with the same methodology as this work, obtaining an average value of 27.86 MPa. Gadioli et al. [43] worked with artificial stone using quartzite waste as a natural aggregate and castor oil resin at levels of 6, 8, 10, 12, and 14 wt.%. The manufactured stone that showed the highest flexural strength was that of 10 wt.% of resin, reaching a maximum bending stress of approximately 21.4 MPa. Gomes et al. [44] produced artificial stone with ornamental stone wastes and vegetable polyurethane resin, 85 wt.% of granite, and 15 wt.% of vegetable polyurethane resin. The flexural strength value of its artificial stone was 18.10 MPa.

Note that, from the referred authors, the stress values for flexural strength are close to those obtained for the artificial stone in this work, made from the same polymeric matrix. The positive influence of the polymeric binder can be evidenced, influencing the final strength of the composite, in addition to the use of vacuum vibro-thermo-compression which provided better interfacial adhesion of the filler with the matrix, characterizing it as a material for applications in the construction sector.

3.5. Microstructural Analysis

Figure 11 shows the micrographs of the artificial stone slabs from experiment 7. According to the micrographs, there is little evidence of pores, proving the low water absorption and apparent porosity of the artificial stone produced using the methodology described in this work. It was found that the use of vegetable polyurethane resin associated with the vacuum vibro-thermo-compression technique contributed to better compaction of the material, thus generating less porosity. The pores are related to an unsatisfactory adhesion of the load in the resin grains.

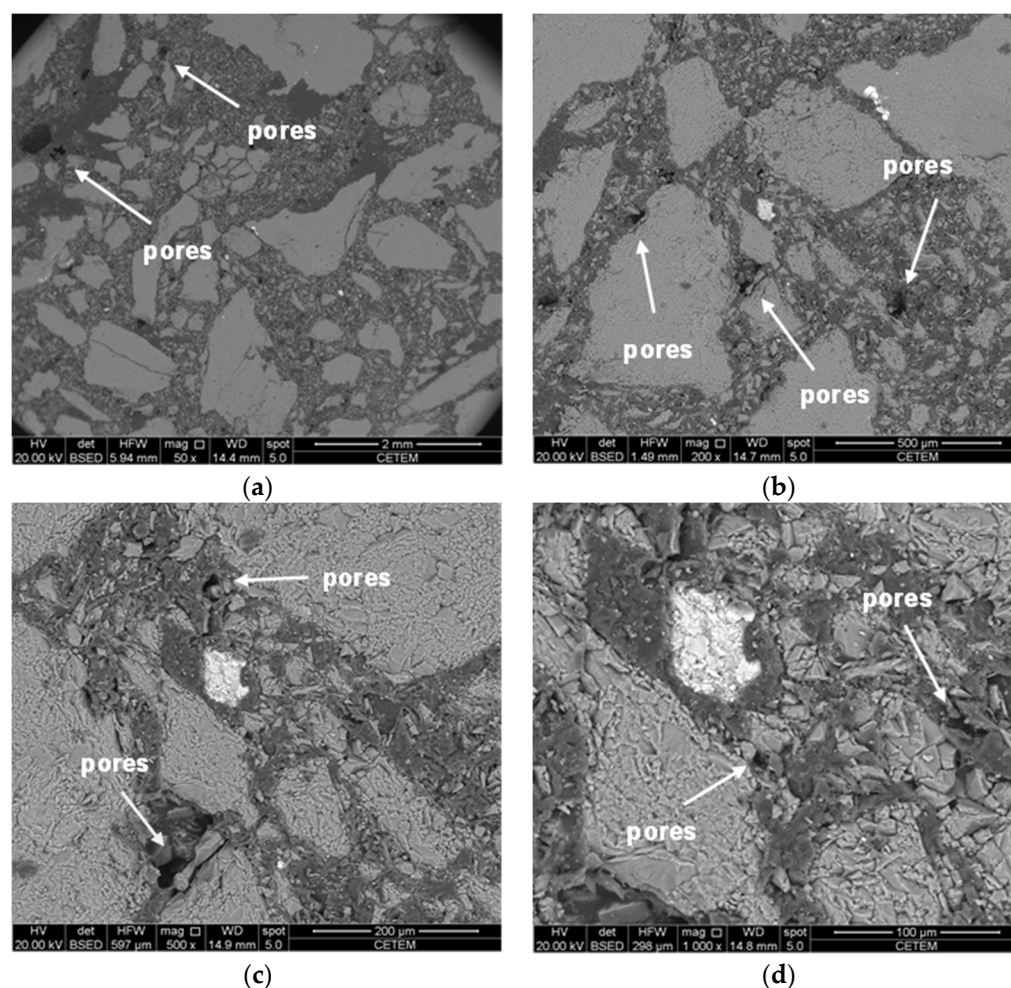


Figure 11. Scanning electron microscopy (SEM) for the artificial stone from experiment 7: (a) 50× magnification; (b) 200× magnification; (c) 500× magnification; (d) 1000× magnification.

There is also a high mechanical resistance due to the good adhesion of the waste particles with the resin. This was due to good interfacial wettability [45].

Gomes et al. [16], Agrizzi et al. [14], and Barreto et al. [15] found results similar to those of the present work, where the manufacture of artificial stones with waste from ornamental stones and resin showed low porosity and low water absorption.

3.6. Petrographic Analysis

Figure 12 shows the petrography obtained for the artificial stone from experiment 7. The petrography showed that the artificial stone has grains with hypidiform (some faces well defined) and xenomorphic (without a defined phase) appearance. The main mineral is quartz, and the other main constituent is resin. Quartz is colorless, having defined faceless grains with fine and coarse grains. The muscovite found is the accessory mineral. The matrix is formed by a very thin layer of resin (dark region) involving mineral particles (light regions).

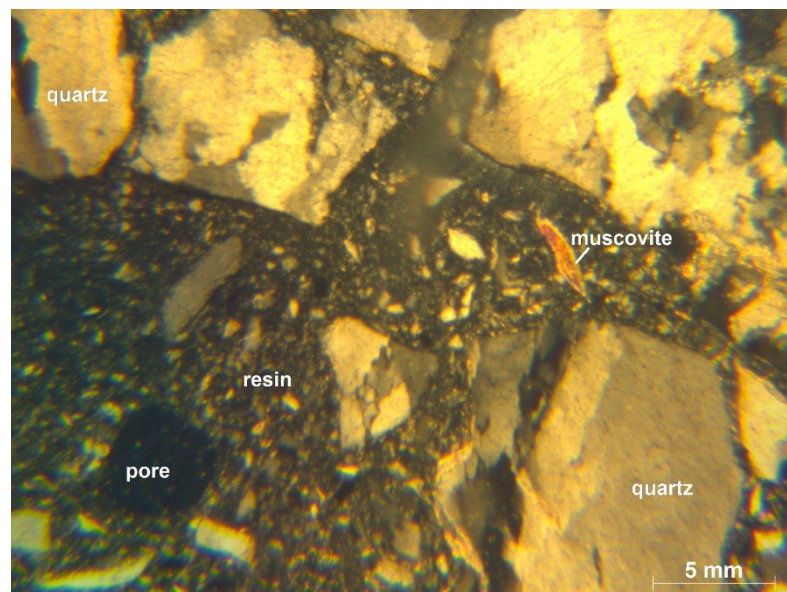


Figure 12. Thin petrographic section of artificial stone from experiment 7, cross-polarized, using a 5× magnification objective lens.

3.7. X-ray Diffractogram of the Slab Produced

Figure 13 shows the X-ray diffractogram of the artificial stone from experiment 7. It is possible to observe the presence of peaks indicative of the crystalline phase referring to quartz (SiO_2). This result confirms the information presented in Table 3, which showed SiO_2 as the predominant oxide.

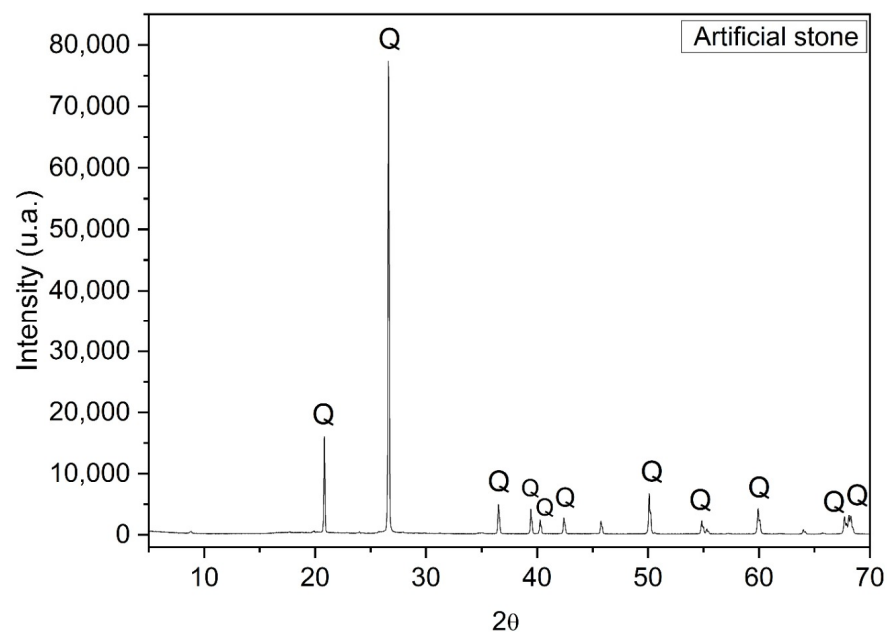


Figure 13. X-ray diffractogram of the artificial stone from experiment 7. Q: quartz (SiO_2).

An X-ray diffractogram of the natural stone was also obtained (Figure 6). It is noted that after manufacturing the stones there was no change in the crystalline phase and the stones remained with the same quartz peaks in their final composition.

4. Conclusions

The artificial stones manufactured with ornamental stone wastes and vegetable polyurethane resin derived from castor oil showed that:

- The characterization of the raw materials resulted in information that was fundamental for understanding the characteristics of the artificial stone. The quartzite wastes 1, 2, and 3 are formed by more than 90% of silicon oxide (SiO_2), and the results are consistent with those in the consulted literature. Regarding the chemical structure of the resin under study, it was possible to observe the presence of functional groups, such as hydroxyls, alkanes, and esters. In addition, through thermal analysis, it was verified that the polyurethane resin has good thermal stability, that is, it is a resin resistant to a wide temperature range without suffering degradation, which makes its use in the production of artificial stones feasible;
- A simplex lattice mix design was used to assist in the execution of the experiment and to help in determining which mixture has the best apparent density. The composition that showed the highest apparent density was combination 7, with 66.7% large particles, 16.7% medium particles, and 16.7% fine particles;
- The artificial stones produced had good physical properties, with porosity and water absorption values lower than the minimum required by the natural stone standard. The three-point flexural strength test showed that the resistance strain value obtained is higher than that indicated by standard NBR ABNT 15844 (2015). Therefore, they can be classified as high-quality materials;
- SEM micrographs and petrographic analysis showed little evidence of pores in addition to how the quartzite ornamental stone waste is distributed in relation to the castor oil vegetable polyurethane resin matrix. The pores are related to an unsatisfactory adhesion of the load in the resin grains. The technique of vacuum vibro-thermo-compression used in the manufacture of artificial stones contributed to better compaction of the material, generating a smaller porosity in the stone produced.

Therefore, according to the results obtained, it is possible to prove the technical feasibility of manufacturing artificial stones with ornamental stone wastes and with the use of vegetable polyurethane resin derived from castor oil. This, in turn, enables the production of modern, sustainable, and eco-efficient materials.

In addition, using ornamental stone waste to manufacture new products helps ensure sustainable development in the ornamental stone sector and promotes a circular economy and corporate sustainability. This contributes to reducing the extraction of raw materials from nature, preserving the environment, cutting costs, and strengthening the economy and responsibility within this sector.

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