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Flexible artificial stone developed with waste tire and waste glass agglomerated by a biopolymeric resin

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ABSTRACT

Artificial stones are building materials developed with stony waste aggregates and a polymeric resin as an agglomerate. Its mechanical properties, in general, overcome natural stone's properties, since the use of resin makes it possible to manufacture a less porous, that is, a denser material, more impermeable, and with greater mechanical resistance. However, its development is costly because it requires the use of high-quality aggregates. Waste can replace these aggregates, developing an economically and environmentally advantageous novel, sustainable artificial stone. This work's main goal is to develop a flexible sustainable artificial stone based on waste glass and waste tire agglomerated with a biopolymeric resin, polyurethane from castor oil, and evaluate its properties. Plates were manufactured with 22% of polyurethane resin and 78% of different proportions of the two wastes (glass and tire) mixed up. The molding was carried out under a 600 mmHg vacuum, a 6Hz vibration, and an 80° hot pressing for 20 min. The stones developed, named AS50GT and AS66GT, were lighter than other developed artificial stones, but less resistant to bending efforts since rubber tire is a polymeric material. However, they displayed a high Izod impact strength, evidencing that the development of artificial stones with glass and tire wastes and biopolymeric polyurethane resin is viable, not only from an economic and environmental point of view but also technically viable once both developed stones can be marked in the building construction industry.

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1. Introduction

The development of industrial and agricultural activities has resulted in an extraordinary rise in waste generation, which generates several environmental problems. For this reason, the search for more environmentally friendly alternatives for the management of solid waste stands out. Therefore, the use of waste in the development of novel civil construction materials has been an area of intense research recently [1].

The development of the automotive sector, for example, represented an increase in the demand for tires, reaching 2.5 billion pieces in 2020 worldwide, generating large amounts of waste tires (WT), causing severe pollution due to improper disposal, which has become an environmental issue [2], since tires cannot return to the natural environment by biodegradation, hydrolysis or decomposition like plants or animals owing to their cross-linked structure composed of rubber (60–65% by weight), filler (25–35% by weight) and the presence of stabilizers and other additives [3]. Not to mention that abandoned tires also represent a threat to public health, as their configuration favors the retention of rainwater, fertile ground for the proliferation of mosquitoes and rats, and vectors of diseases such as dengue, yellow fever, and leptospirosis [4].

The WT is made of approximately 67.9–89.5 wt % of carbon, 6.6–8.7 wt% of hydrogen, 0.3–1.9 wt% of nitrogen, 0.92–2.3 wt % of sulfur, 0.8–17.4 wt% of oxygen. It can also be characterized by 61.3–69.8 wt % of volatile compounds (e.g. plasticizers, processing aids, curing additives, etc.), 0–1.4% of moisture content and 23.5–33.5% of fixed carbon, 4.16–7.3% of ash [5]. Regarding its thermal behavior, at 150 °C the WT starts to decompose and lose moisture and its polymer organics start decomposing between 150 and 420 °C. Above that temperature, less degradation occurs, with a 10% mass loss [6].

Another material commonly found as waste is glass, due to its various applications such as containers, windows, screens, and bottles, among others. Waste glass (WG), after sorting and cleaning, can be remelted to manufacture new glass products but the recycling process is limited due to its variety of colors and contamination, either by organic materials, plastics, or other waste; diminishing the recycling rate of glass, which is more often landfilled or just stored somewhere, not only polluting the environment but also generating wastage of resources [7].

Hence, the alternative of the reintroduction of WG into the manufacturing of secondary products such as building materials has been widely studied and has proven to be a promising way to better manage WG, with advantages such as low energy consumption (since it does not require melting as normal recycling would) and the simplicity of waste treatment (since there is no need for cleaning and color segregation) [8]. Worldwide efforts have been made over many decades to develop various waste glass-based products such as foam glass [9,10] and concrete [11]. These products, however, have low market value/custom acceptance or cannot absorb a large amount of waste glass produced worldwide. Therefore, it is imperative to develop value-added products to completely consume accumulated glass waste [7].

Inserted in this context, artificial stones are innovative materials that are manufactured with a polymeric resin and a high percentage of natural aggregates, which can be replaced by waste to some extent. The mechanical properties of artificial stones surpass natural stones, since the use of resin in their production results in a less porous material, with a lower rate of water absorption and better mechanical resistance, making them suitable for more demanding applications, such as floors and walls [12]. Nevertheless, its manufacture is one of the most onerous among construction materials, as it requires high-quality and expensive aggregates. For this reason, several studies are focusing on the use of waste to replace conventional aggregates and reduce manufacturing costs [13].

Polymeric resins are among the biggest environmental villains for several reasons: their decomposition takes centuries, their improper disposal occupies a large part of landfills, and they are derived from petrochemicals, having in their compositions various toxic and carcinogenic substances, such as VOCs (volatile organic compounds). As a more sustainable option, biopolymers, polymers synthesized from renewable sources such as vegetables, meet the requirements of preserving nature during all stages of its life cycle [14]. Some works used castor oil polyurethane as a replacement of synthetic resins, such as epoxy and polyester, in the development of artificial stones. The PU resin was used as a binder, and the particles used were different stony wastes, to know: quartzite [15] and granite [16] wastes; both authors were able to manufacture artificial stone with properties suitable for use in the civil construction industry, but so far, no research has studied the effects of replacing part not only the synthetic resin by a biopolymer resin but also part of the stony aggregates by WT.

On the other hand, other civil construction materials had been successfully developed with WT by other researchers, like Revelo et al. [17], that manufactured a flexible tile with a polyurethane resin and waste tire, generating a flexible composite that could work for structural applications of low solicitations, such as wall covers, soft floors, and barriers. Hamzani et al. [18] and also developed a civil construction material, a semi-flexible pavement, by adding WT powder to an asphalt binding material and the developed composite had its properties improved its by increasing the resistance to permanent deformation, that is, decreasing its stiffness and reducing its potential for thermal cracking.

For this reason, this study proposes the development of a novel artificial stone, manufactured with a biopolymer resin, polyurethane (PU) resin from castor oil, and two wastes as aggregates: tire rubber waste and glass waste. These represent an extremely advantageous waste management path, not only from an environmental point of view but also from an economic one since the use of waste would decrease the costs of manufacturing the artificial stone.

This study's main goal is to manufacture a flexible artificial stone based on waste glass and tire rubber bonded by polyurethane resin, as well as study the mechanical properties of this newly developed material.

2. Materials and methods

The raw materials used in this work were: waste glass (WG) from glass beverage bottles collected by the authors in

Campos dos Goytacazes, Brazil; waste tire (WT) supplied from a tire retreading company and polyurethane (PU) resin (density: 1.08 g/cm^3) from castor oil, a by-component prepared by hot mixing of a prepolymer (component A) and a polyol (component B) in 1:1,18 ratio, supplied by Imperverg, Brazil. Some of the tests were also performed for an artificial stone called "Granito Itaúnas" for comparison purposes.

To determine the WT and WG compositions to be used in the manufacturing of artificial stone, a highest-packed mixture test was performed as per ABNT NBR MB-3388 [19], which postulates that 10 mixtures should be tested, based on an experimental Simplex numerical modeling grid (Simplex-Lattice Design).

The selection of the highest-packed mixture is imperative for the quality of the final product, the artificial stone, as it ensures that among all possible mixtures designs, the mixture chosen to manufacture the artificial stone will be the one with the lower void volume (VV), that is, the mixture that would produce the least number of voids, which is desired because the denser the stone the better its mechanical properties, as it is known that voids act as a stress concentrator.

In the 10 mixtures proposed, three granulometric sizes were considered, according to the standard: fine granulometry (less than 63 μm), medium (74–63 μm), and coarse (2380–707 μm). The WG was sieved to suit fine granulometry and the WT was sieved to suit the medium and coarse ones.

The mixtures were prepared and placed in a 1013.24 cm^3 steel vessel that was vibrated at 60 Hz while pressed down with a 10 kg weight apparatus for 10 min. The mixtures were then weighed to calculate the vibration density. Each of the 10 mixtures was tested three times to ensure the statistical reliability of the results, which was confirmed by a completely randomized design (CRD) analysis of variance (ANOVA) ($p \leq 0.05$) and a subsequent Tukey test ($p \leq 0.05$) to corroborate the results.

To calculate the amount of resin to be used on the manufacturing of the artificial stone (AS), the void volume was determined according to Equation (1) [20]:

$$VV\% = 1 - \left(\frac{vibrate\ density}{highest\ packed\ mixture\ real\ density}\right)*100 \qquad (1)$$

The true density of the highest-packed mixture was determined by the pycnometer method. Then, according to Equation (2), the minimum amount of resin was calculated [12]:

$$MAR\% = \frac{VV\%*\rho_{resin}}{VV\%*\rho_{resin} + (100 - VV\%)\rho_{\text{highest packed mixture}}} \qquad (2)$$

Determining the Minimum Amount of Resin (MAR) is crucial for producing artificial stones with the optimal amount of resin. This is particularly important for the civil construction industry as MAR represents the exact amount of resin needed to fill the void volume of the chosen mixture for manufacturing the stones. If more resin is used, the resulting artificial stone would be more expensive, while a lower amount of resin would compromise the mechanical properties of the stone since the void volume would not be completely filled, leaving in the final product a remaining number of pores, that would impair its mechanical strength.

First, the wastes were oven dried at 100 °C for 24h and then mixed in the proportions determined by the highest packaging test and later with the PU resin in the percentage determined by MAR. The mixture was placed in a 100 × 100 × 10mm steel mold connected to a 600 mmHg vacuum system and a vibrating table set at 6Hz and 2 min. Still under vacuum, the mold was placed in a hot hydraulic press at 80 °C for 20min and then cooled to room temperature. The plates were unmoulded, sanded, and cut with a disk in dimensions that met the requirements of subsequent tests.

The physical indices are three properties of artificial stones known as apparent dry density, water absorption, and apparent porosity, which define basic relationships between the mass and the volume of stone samples. The term "apparent", used for density and porosity, indicates that the volume measured for the determinations is relative to the total volume of the samples, that is, the volume of solids plus the volume of pores (empty spaces).

In summary, the apparent porosity shows a direct relationship with the physical-mechanical resistance of the stones; water absorption, with the possibility of liquid infiltration; and the apparent density, with aspects of physical-mechanical resistance, in addition to allowing the calculation of the individual weight of the plates specified in the architectural design of an edification.

For the determination of these properties, ten (10) slabs measuring 50x50 × 10mm were subjected to the physical indices' tests according to ABNT NBR 15845–2 [21]. The samples were put into a recipient and water was added up to 1/3 of their height. After 4h, more water was added up to 2/3 of the height and after another 4h, the samples were completely submersed, remaining saturated in deionized water for 40 h. Then, the samples were weighed three times: the submerged mass was determined with the samples weighted when submerged, the saturated (Msat) with the samples saturated in water, and the dry mass (Mdry) after the samples were oven-dried at 70 °C until they reached a constant mass. These measurements were used to determine the physical indices according to Equations (3)–(5) [21]:

Apparent density (g/cm^3):

$$ad = \frac{M_{dry}}{(M_{sat} - M_{sub})}x100 \qquad [3]$$

Apparent porosity (%):

$$ap = \frac{(M_{sat-}M_{dry})}{(M_{sat} - M_{sub})}x100 \qquad [4]$$

Water absorption (%):

$$w\alpha = \frac{(M_{sat} - M_{dry})}{(M_{dry})}x100 \qquad [5]$$

Six (6) slabs measuring 10x25 × 100mm were subjected to a three-point bending test according to ABNT NBR 15845–6 [22] at a speed of 0.25 mm/min, a load cell of 100 KN and two points distance of 80 mm. The ruptured surface, as well as the polished surface, were characterized by scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (SEM-EDS) brand JEOL model JSM 6700R in high vacuum mode.

Two (2) slabs measuring 70x70 × 30mm were evaluated for wear resistance in a MAQTEST Amsler machine to evaluate its thickness loss thickness following the guidelines of ABNT NBR 12.042 [23]. Ten (10) notched slabs of size 62x12 × 10mm were tested on a PANTEC XC-50 machine following the ASTM D256 standard [24] to determine the Izod-type impact strength.

3. Results and discussion

3.1. *Determination of the parameters for the development of the artificial stones*

Table 1 shows the compositions and vibrate density of the 10 mixtures proposed for the highest packing test.

As can be seen in Table 1, mixture 10 (16.66% coarse waste tire, 16.66% medium waste tire, and 66.66% fine particles waste glass particles) presented the highest vibrate density. The results of vibrate density were statistically treated with ANOVA considering a CRD and a 95% confidence level ($p \leq 0.05$), as shown in Table 2.

Table 2 shows there is a statistical difference, that is, more than one mixture is differentiated among the 10 proposals. Subsequently, the Tukey test was performed to assess the mean contrast ($p \leq 0.05$) between the vibratory densities, as shown in Table 3.

Tukey's test evidenced that not only mixture 10 but also mixture 5 (50% coarse WT and 50% fine WG) had statistically corresponding vibrate densities, therefore, are the highest packed mixtures. As explained above, the highest packing mixture was selected to determine the composition of WT and WG that would ensure the manufacturing of an artificial stone with the best mechanical properties possible for these aggregates since the highest vibrated density provides the information of the mixture that would produce a stone with less voids and, as a consequence, a better quality. For this reason, this study manufactured two different artificial stones with WG and WT with different mix compositions as determined by the highest packaging test.

A pycnometer determined the real density of the chosen mixtures as 1.48 g/cm^3 and 1.55 g/cm^3 for mixtures 5 and 10, respectively. The minimum amount of resin was calculated through equations (1) and (2) as 21.85% and 21.10%, respectively, representing the minimum amount of PU resin that would be sufficient to fill the void volume of the mixtures, aiming to infuse the empty spaces without leaving room for the formation of voids.

The two artificial stones were developed with 22% weight of PU resin and 78% by particles. The difference between them is the content of 78% of particles, which have the compositions of mixture 5 (AS50GT) and mixture 10 (AS66GT), as described in Table 1.

Table 1 – Vibrate density of the 10 mixtures proposed for ASRGs development.

Mixtures	Coarse WT (%)	Medium WT (%)	Fine WG (%)	Vibrate density (g/cm^3)
1	100%	0%	0%	0.453 ± 0.014
2	0%	100%	0%	0.508 ± 0.010
3	0%	0%	100%	0.973 ± 0.055
4	50%	50%	0%	0.518 ± 0.008
5	50%	0%	50%	1.070 ± 0.010
6	0%	50%	50%	1.013 ± 0.047
7	33.33%	33.33%	33.33%	0.992 ± 0.018
8	66.66%	16.66%	16.66%	0.710 ± 0.005
9	16.66%	66.66%	16.66%	0.745 ± 0.005
10	**16.66%**	**16.66%**	**66.66%**	**1.123 ± 0.029**

Table 2 – ANOVA test results on the CRD of vibrate density ($p \leq 0.05$).

FV	GL	SQ	QM	F
Treatment	9	1.7529	0.1948	281.9332
Waste	20	0.0138	0.0007	
Total	29	1.7667		

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

3.2. *Chemical characterization of the stones developed*

Energy Dispersion X-ray Spectroscopy (EDS) with elemental mapping was performed on the surface of ASGTs to study their chemical composition, as displayed in Fig. 1 (AS50GT) and 2 (AS66GT), where Figs. 1a and 2a represent the SEM image of the surface region where the analysis took place, Figs. 1b and 2b show the EDS spectrum and in Fig. 1c–h) and 2c-g) the elemental mapping is illustrated.

Tables 4 and 5 show the quantitation of the elements of AS50GT and AS66GT, respectively.

Observing Figs. 1 and 2, it is possible to notice the presence of a concentration of C (in red) in one region and an outstanding presence of Si (light blue) in another one. Therefore, it is possible to conclude that the WG is represented by the lighter rounded grains that are composed of silica, the material on which the glass is based, and without a high concentration of C since the glass is not an organic material. The other regions represent WT and PU resin, making it possible to state that the biopolymeric resin agglomerated the tire rubber more efficiently than glass, which will be further discussed below.

Table 3 – Tukey test for contrasting density averages ($p \leq 0.05$).

Treatment	Average	Tukey test[a]
10	1.12	A
5	1.07	AB
6	1.01	BC
7	0.99	CD
3	0.97	CD
9	0.74	E
8	0.71	EF
4	0.51	G
2	0.50	GH
1	0.45	GH

[a] The averages followed by the same letter, in the column, do not differ from each other at 5% probability using the Tukey Test.

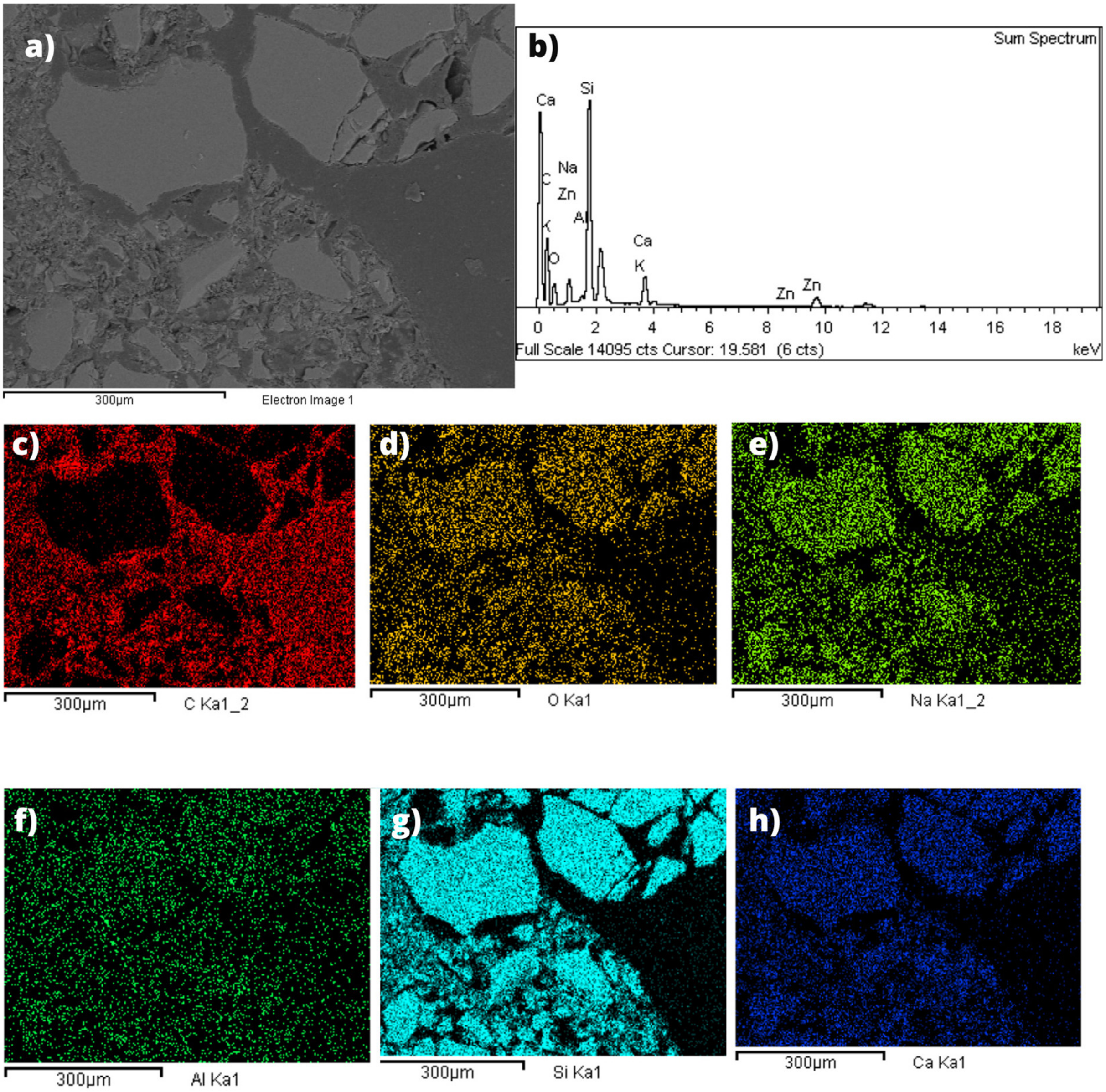

Fig. 1 – SEM-EDS micrographs of AS50GT (a), EDS spectrum (b) and corresponding elements maps of C (c), O (d), Na (e), Al (f), Si (g), Ca (h).

Tables 4 and 5 reveal that the ASGTs have a high amount of C, O, and Si, which was expected due to their raw materials, WT and WG, as well as a little presence of Ca and Na, which was expected due to the WG chemical composition of approximately (wt. %) 60.21 of SiO_2, 7.40% of CaO, 2.93 of Al_2O_3, 2.61% of Na_2O, 1.65% of MgO, 0.29% of Fe_2O_3, and 0.23% of K_2O [25]. Therefore, the elements found in less quantity in the elemental mapping are the primary chemical elements of the oxides (SiO_2, NaO_2 and CaO) from which glass is made and the high amount of carbon can be attributed to the WT chemical composition [5].

3.3. *Physical indices*

The determined physical indices are shown in Table 6.

The densities of AS50GT and AS66GT are 1.48 (±0.05) g/cm^3 and 1.65 (±0.01) g/cm^3. It can be seen in Table 6 that AS50GT had a lower density value than AS66GT and both developed stones also have a lower density than Granito Itaúnas, which was expected because AS50GT contains less glass and more rubber. Thus, it can be seen that density values decrease with increasing WT content.

These values are below the range of similar materials, such as Barreto et al. [26] who developed an engineered stone of 2.26 ± 0.01 g/cm^3 with WG, but mixed with quartz waste and epoxy resin; Gomes et al. [16] and Agrizzi et al. [15] who developed artificial stones with the same PU resin from castor oil, but with granite waste (2.24 ± 0.01 g/cm^3) and quartzite waste (2.22 ± 0.04 g/cm^3), respectively; and Lee et al. [12] who manufactured stones with waste glass mixed with granite varying pressure, temperature and vacuum conditions, which presented density values ranging from 2.03 to 2.45 g/cm^3.

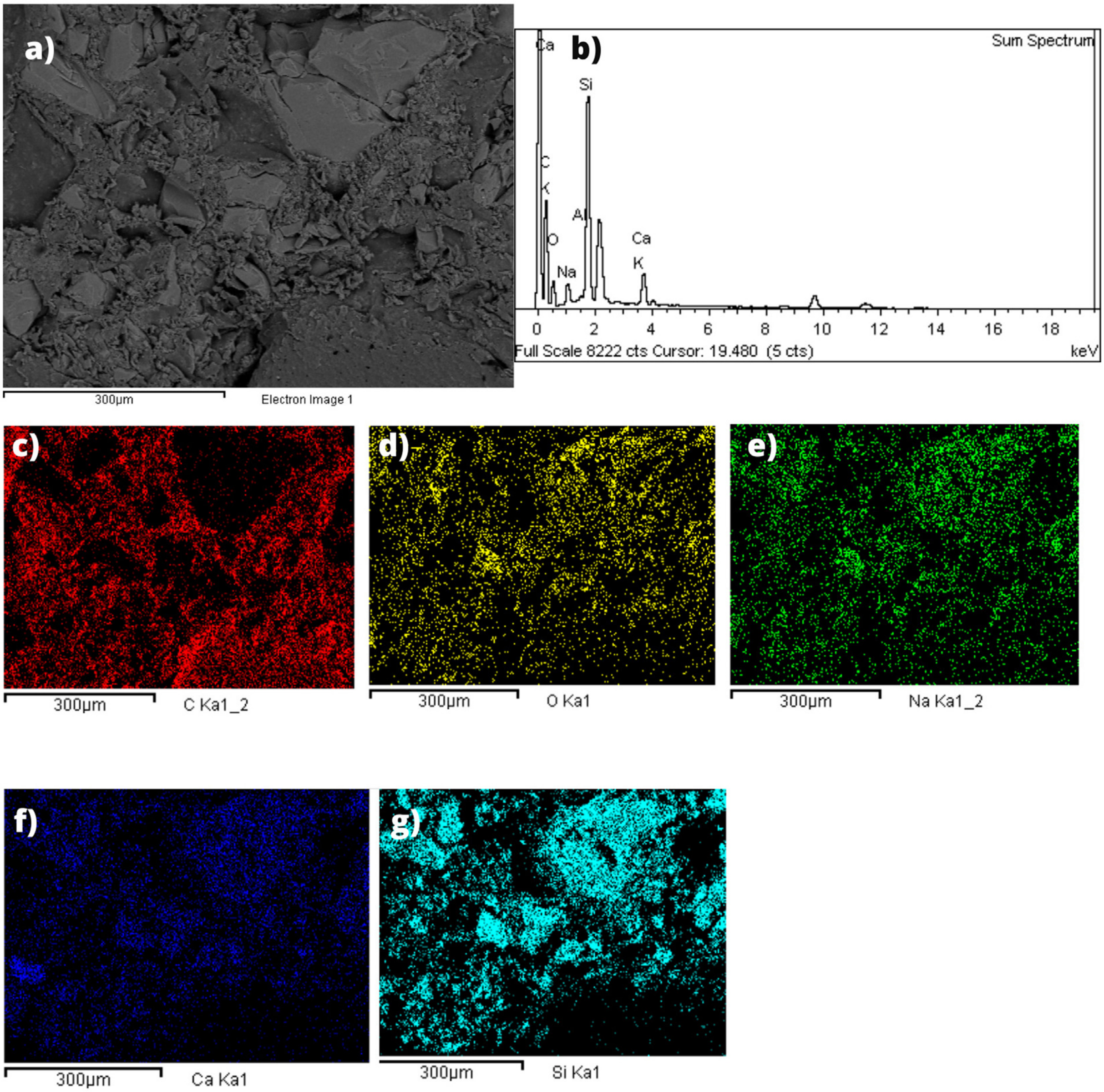

Fig. 2 – SEM-EDS micrographs of AS66GT (a), EDS spectrum (b) and corresponding elements maps of C (c), O (d), Na (e), Al (f), Si (g), Ca (h).

Therefore, it is noticeable that the density values found for ASGTs are lower than those found in the literature for artificial stones, which was already expected due to the use of tire rubber as a replacement for part of the aggregate content since the rubber has a lower density compared to commonly used wastes, stony aggregate materials. A lighter artificial stone could be advantageous if the reduction in transport costs is considered.

The water absorption of the AS50GT and the AS66GT were 0.36 ± 0.08% and 0.64 ± 0.08%, respectively. The ASGTs values were higher than those found by Gomes et al. [16] and Agrizzi et al. [15] who developed artificial stones with PU and stony aggregates. Chiodi and Rodrigues [27] classify, in their Guide for Applications of Stones, that the quality of stones to be applied as coating and cladding, according to their water absorption range, is: high-quality stones are between 0.1 and

Table 4 – EDS element quantification (% weight) of AS50GT.

C	O	Si	Ca	Na	Al	K	Mg
51.19	20.59	19.42	4.73	3.31	0.37	0.21	0.17

Table 5 – EDS element quantification (% weight) of AS66GT.

C	O	Si	Ca	Na	Al	K
65.01	16.56	12.74	3.33	2.01	0.21	0.16

Table 6 – Physical indices of the ASRG developed.

Artificial Stone	Density (g/cm^3)	Water absorption (%)	Apparent porosity (%)
AS50GT	1.48 ± 0.05	0.36 ± 0.08	0.52 ± 0.14
AS66GT	1.65 ± 0.01	0.64 ± 0.08	1.06 ± 0.14
Granito Itaúnas	2.64 ± 0.02	0.27 ± 0.08	0.72 ± 0.22

0.4% and medium-quality stones are between 0.4 and 1%. According to its classification, AS50GT could be classified as high quality and AS66GT could be classified as medium quality. Therefore, the artificial stone is suitable for application as a cladding in surfaces with regular wetting (AS66GT) and frequent wetting (AS50GT).

Chiodi and Rodrigues [27] also present a classification for stones to be applied for coating and cladding that considers porosity values: low porosity stones are between 0.5 - 1.0% and medium porosity stones are between 1.0 - 3.0%. Therefore, AS50GT and AS66GT can be classified as low and medium-porosity stones, respectively, when it comes to their use as a coating in civil construction.

3.4. *3-point bending strength*

Fig. 3 displays the stress x strain curves of the 3-point flexural strength tests of AS50GT, AS66GT, "Granito Itaúnas" and PU resin.

In Fig. 3, it is possible to observe that the AS66GT has a higher flexural strength than the AS50GT. This can be attributed to the higher WG content of AS66GT, which is 1.3 times that of AS50GT, and materials are known to become harder as the percentage of hard particles enhances, causing flexural modulus to rise [12]. On the contrary, the addition of rubber (flexible particles) made the material more flexible, that is, decreased the stiffness, making the material more capable of being deformed when subjected to bending efforts, as can be seen in the graph. Granito Itaunas displayed very high stiffness and a rupture with almost no deformation, with was expected, as Granito Itaunas is a common commercial artificial stone, and artificial stones are usually manufactured with stony aggregates, which are fragile materials. The lower stiffness observed in the developed stones, AS66GT and AS50GT, can be attributed to the WT in its composition, a flexible material, and it can be seen that the stiffness decreases with the increase of WT content since AS50GT (with 50%WT) presented higher deformation than AS66GT (34% WT). The PU resin presented the highest deformation, which was also expected, as it is a flexible material [17] and was tested pure, that is, with zero adition of rigid particles, such as waste glass. Fig. 4 displays the specimens ruptured after the 3-point bend test.

Table 7 shows the maximum bending strength for AS50GT, AS66GT, PU resin, and Granito Itaúnas.

Regarding the 3-point bending strength of stones, ABNT NBR 15845–6 [22] postulates that stones must have more than 10 MPa to be applied as a coating. Therefore, AS50GT did not meet the flexural strength requirements to be used as a building coating material, but AS66GT is suitable for use as coating since its flexural strength was above 10 MPa.

Comparing the results of the ASGTs with other studies that developed artificial stones with the same biopolymeric resin and obtained 17.31 ± 0.82 MPa [16] and 10.67 ± 0.64 MPa [15], it is possible to observe that the 3-point bend resistance the AS50GT was inferior to similar materials and of the AS66GT was greater than that developed by Agrizzi et al. [15] with quartzite waste but lower than that developed by Gomes et al. [16] with granite waste. Regarding Granito Itaúnas, the commercial stone studied in this work, it can be observed that its resistance is higher than AS50GT but lower than AS66GT. Since Granito Itaúnas is a commercialized product, it is possible to say that AS66GT has the potential to be commercialized replacing the stones currently marketed.

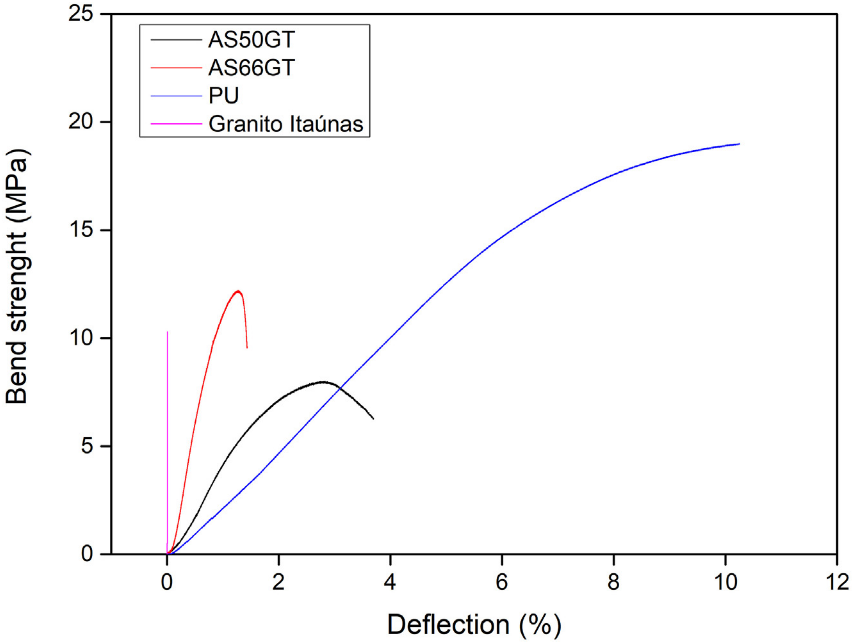

Fig. 3 – Stress x strain curves of AS50GT, AS66GT, Granito Itaúnas stone and PU resin.

Fig. 4 – Specimens after bending test.

It was expected that the addition of WT would jeopardize the material's mechanical strength, as pointed out by authors who previously added tires to other construction materials, such as polymeric mortars [28] and concrete [29]. Figure 4 shows the specimens ruptured after the 3-point bending strength test.

3.5. SEM micrographs

Figures 5 (AS50GT) and 6 (AS66GT) show the SEM fracuted region micrographs. In Figs. 5a and 6a, it is possible to notice the presence of empty holes, representing regions of grain detachment (white circles), which is common to occur in materials ruptured by bending, since the path of rupture by flexion efforts is transverse to the grains. Likewise, it is possible to note that the presence of voids is reduced, characteristic of products manufactured in a vacuum, since the negative pressure gradient sucks the resin filling the voids [26] and in this work, vibration and compaction were also used to ease this process and promote better filler/matrix adhesion, improving the mechanical properties of the composite [30].

Table 7 – Bending strength resistance of AS50GT, AS66GT, PU resin and Granito Itaúnas stone.

	AS50GT	AS66GT	PU	Granito Itaúnas
Three-point bending strength (MPa)	8.49 ± 1.55	12.22 ± 0.52	23 ± 5.3	10.19 ± 0.97

In a comparison between the two ASGTs, it is possible to observe that the AS50GT had a better particle/matrix adhesion due to its higher WT content, as indicated by SEM-EDS results, explained by the optimal WT/PU adhesion, as evidenced by the green circles in Figs. 5b and 6b. In turn, the yellow circles in Figs. 5b and 6b denote the WG particles, with a lighter color and more visible particle/matrix interface, as discussed above in the elemental mapping demonstrated in Figs. 1 and 2.

Despite AS66GT having a lower content of WT and a higher content of glass (66% vs 50%), it still exhibited better mechanical resistance, likely due to the presence of rigid glass particles, which are more resistant to bending than flexible rubber tire particles.

3.6. Wear resistance

Table 8 shows the wear resistance of the ASGTs after Amsler wear tests in average thickness loss after an abrasion course of 500 and 1000 m.

When it comes to the Amsler wear resistance of artificial stones, no standard specifies a maximum thickness loss or classifies their quality according to it. However, the technological parameters of Chiodi Filho and Rodrigues [27] classify the quality of artificial stones for floors and pavements. The maximum thickness losses are 6, 3, and 1.5 mm for low, medium, and high-traffic stones, respectively. Therefore, based on the parameters described above, AS50GT and Granito Itaúnas can be applied to high-traffic pavements, while AS66GT can be applied to medium-traffic pavements.

In previous work, Barreto et al. [26] manufactured an artificial stone agglomerated with epoxy resin and, as aggregates, a mixture of the glass waste with quartz dust. The material presented a thickness loss of 2.86 mm in a 1000 m track, which means that the thickness loss of the AS66RT was similar to previous works, even though was greater than the AS50T and the Granito Itaúnas.

Concerning the same biopolymeric matrices, the PU-granite stone developed by Gomes et al. [16] had a thickness loss of 1.75 mm while the PU-quartzite stone developed by Agrizzi et al. [15] had a thickness loss of thickness of 1.21 ± 0.60 mm. Therefore, when compared with other PU-based stones, the stone with less WG, AS50GT, performed better in wear resistance, while the stone with more WG, AS66GT, performed worse. This can be attributed to the already explained fact that the PU resin agglomerated rubber more efficiently than glass, which, for wear resistance could mean the glass was looser, showing greater detachment, causing the stone with the highest glass content, AS66GT, to have lower wear resistance.

3.7. Izod impact strength

The impact resistance was determined by an Izod impact test as shown in Table 9.

As illustrated in Table 9, the impact strenght of the AS50GT, which has 50% tire in its aggregate composition, was 71.18 ± 11.12 J/m, more than twice greater than AS66GT, of

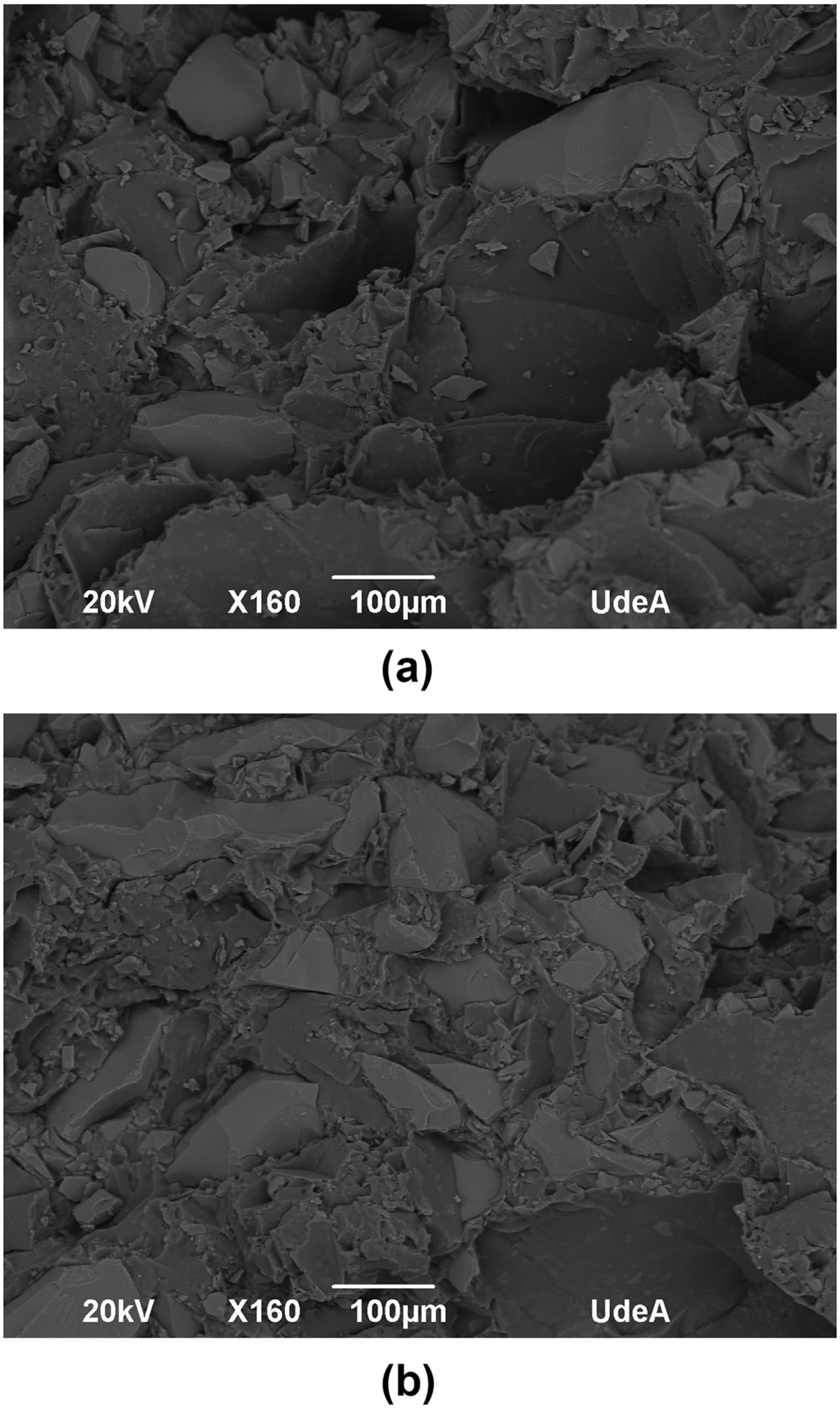

Fig. 5 – AS50GT SEM micrographs of fractured surface micrographs 160x.

29.05 ± 8.65 J/m. This may be related to the nature of the waste used as aggregates, as AS50GT has a higher WT content and as explained above in the bending-strength tests, the addition of rubber made the material more flexible, which can be seen in Fig. 3.

There is currently no standardized limit that defines the quality of artificial stones based on the Impact Izod test. Nevertheless, the test is crucial as it has been demonstrated through the 3-point bend test that the inclusion of WT can improve the material's resistance to permanent deformation.

Carvalho et al. [31] conducted a study to evaluate the effect of *Arapaima gigas* fish scales as a reinforcement for artificial stones made from epoxy resin and quartz dust. The researchers found that the impact strenght of the stone without scales was 24.1 ± 4.9 J/m, while the stones reinforced with fish scales had an impact strength of 28.3 ± 4.6 J/m. When

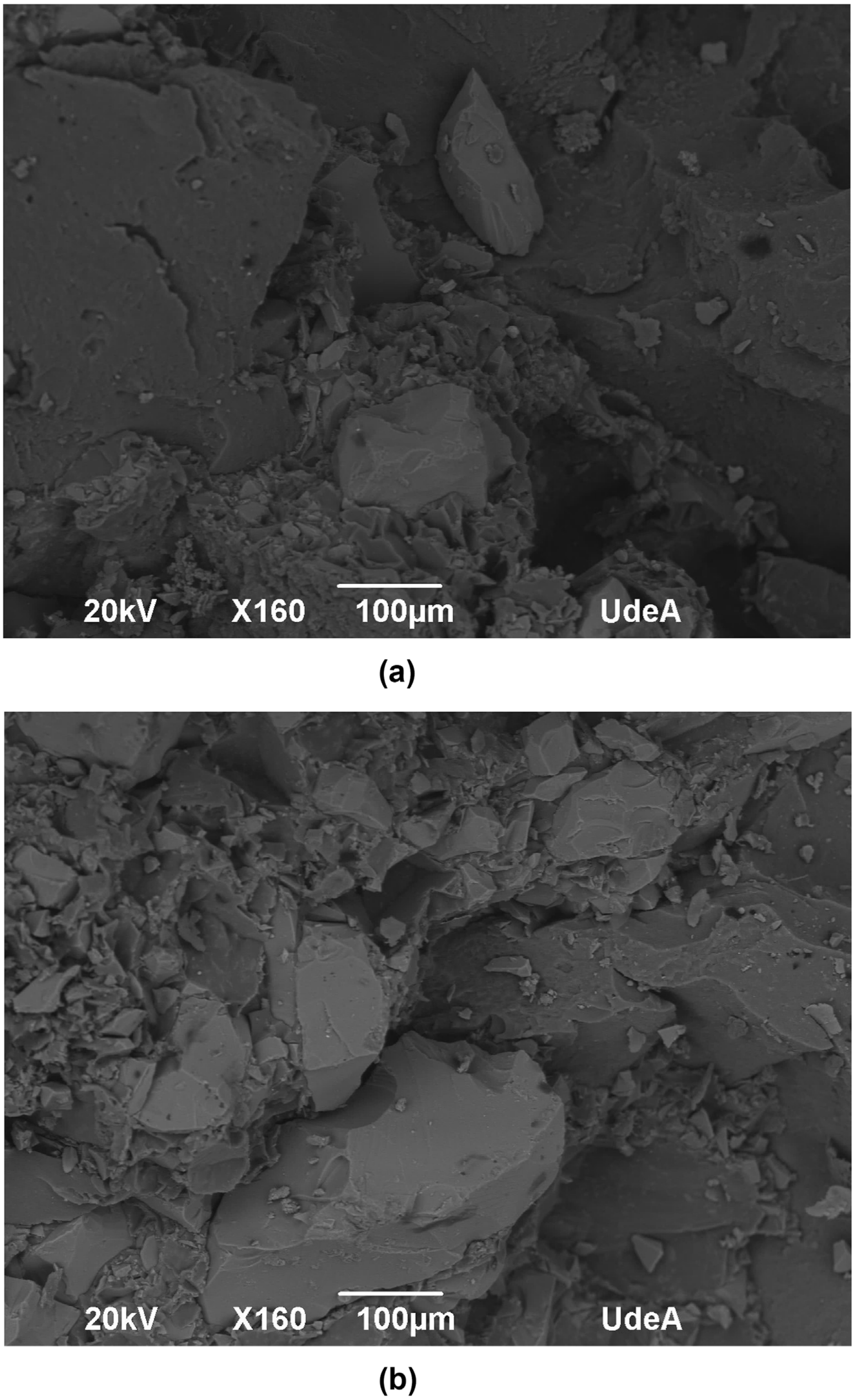

Fig. 6 – AS66GT SEM micrographs of fractured surface micrographs with 160x.

Table 8 – Amsler abrasive wear through thickness reduction of AS50GT, AS66GT and Granito Itaúnas.

Material	Thickness reduction (mm)	
	500 m	1000 m
AS50GT	0.28 ± 0.22	0.46 ± 0.19
AS66GT	1.04 ± 0.03	2.23 ± 0.21
Granito Itaúnas	0.42 ± 0.01	0.90 ± 0.01

Table 9 – Impact strength of ASGTs determined by Izod impact test.

Material	Impact strength (J/m)
AS50GT	71.18 ± 11.12
AS66GT	29.05 ± 8.65

Fig. 7 – Specimens after impact test.

compared to the stones developed with WT and WG, it is clear that even the stone with the lowest amount of WT (AS66GT) had a higher impact strenght than those developed by Carvalho et al. [31], highlighting its superior impact strenght compared to similar materials.

Regarding macroscopic fractures, all specimens were split into two parts and ruptured at the notch, in accordance with the standard, after being subjected to the Izod hammer impact, as depicted in Fig. 7.

As a consequence, although the addition of WT to artificial stones may impair the material's flexural strength, it has the potential to greatly enhance its impact strength, which can be advantageous for many applications. The addition of WT must be done in controlled amounts to compensate for these effects and to manufacture a material with the required properties.

4. Conclusions

This work aimed to manufacture a flexible artificial stone based on biopolymer resin, polyurethane from castor oil, and two mixed residues: glass and tire, and to study their mechanical properties.

For this, two artificial stones were developed with 22% weight of PU resin and 78% by waste. The stone called AS50GT has 50% WG and 50% WT in its composition and the one called AS66GT is composed of 66% WG and 34% WT.

SEM-EDs of the surface of the material showed that the PU resin agglomerated the tire rubber better than the glass.

The water absorption, apparent porosity, and density of AS50GT were 0.36 ± 0.08%, 0.52 ± 0.14%, and 1.48 ± 0.05 g/cm^3, respectively. AS66GT showed 0.64 ± 0.08% water absorption, 1.06 ± 0.14% apparent porosity, and 1.65 ± 0.01 g/cm^3 density. Density values decrease with increasing WT content, which means that both AS50GT and AS66GT are below the values of similar materials, being an advantage for these stones, as transport costs would be reduced.

As for water absorption, according to the Guide of Aplications for Stones [27], AS50GT can be classified as high quality and AS66GT were classified as low medium-porosity stones. quality to be applied as coatings in building construction, and it is suitable to be used in wet environments. Regarding porosity, folloing the same guidelines, AS50GT and AS66GT were classified as low and medium-porosity stones, respectively, for application in civil construction coatings.

The three-point bending strength results were 8.49 (±1.55) MPa for AS50GT and 12.22 (±0.52) MPa for AS66GT. The increase in rubber content made the material have a more ductile behavior, increasing flexibility and impairing flexural strength. If a stones will be used as a coating, it must have a 3-point flexural strength above 10 MPa. Therefore, AS66GT meets this requirements and can be applied as a coating, but AS50GT cannot be used for this specific application.

The Amsler wear thickness loss was 0.46 ± 0.19 mm and 2.23 ± 0.21 mm on a 1000 mat for AS50GT and AS66GT, respectively. Thus, the AS50GT can be applied on high-traffic floors and the AS66GT can be applied on medium-traffic floors. The Izod impact strength was 71.18 ± 11.12 *J*/m for AS50GT and 29.05 ± 8.65 for AS66GT. The addition of tire rubber significantly increases the material's impact strength while impairing the 3-point flexural strength, which means that the incorporation of WT into artificial stones must be done in controlled amounts to achieve the expected effect on the final properties of the materials depending on your future application.

On that account, two novel sustainable artificial stones were developed and were proven to be technically and economically viable, having the potential to replace commonly marketed artificial stones and representing an alternative path for the management of WT and WG.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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