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Preparation and characterization of glazes from combinations of different industrial wastes

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Abstract

The work reported here involves the preparation and characterization of ceramic glazes made from combinations of different industrial wastes. The wastes were float glass, granite and lime shale (a raw material waste from the oil shale industry in São Mateus do Sul, state of Paraná, Brazil), which were used to replace natural raw materials in a proportion of up to 50% in weight. The compositions were formulated using the Seger method and prepared by conventional ceramic processing. The stabilized suspensions were applied in commercial wall tile and porcelain stoneware tile, which were sintered at temperatures of 1080 °C and 1150 °C, respectively, using two different heating cycle. Three compositions were developed, two of which yielded opaque glazes and one a transparent glaze. Linear thermal expansion coefficients (α) of 80.10^{-7} $°C^{-1}$ to 100.10^{-7} $°C^{-1}$, and glaze softening temperatures of 600–700 °C were characterized by dilatometric analysis. The glaze compositions showed chemical resistance against acid and alkaline attack after 96 h, showing a mass loss of less than 0.1% in weight. The surface hardness of the glazes determined by the Mohs scale, Vickers microhardness and abrasion resistance (PEI indices) were between 6–7, 3–3.7 GPa and 3–4, respectively. These properties are compatible with those of commercial glazes for wall tiles and porcelain stoneware ceramics.

Keywords: A. Firing; B. Surfaces; C. Hardness; D. Traditional Ceramics; Glazes

1. Introduction

Improving the properties of materials, reducing costs and using all the potential of a raw material are becoming increasingly necessary for worldwide industry. Thus, research into the recycling and exploitation of industrial wastes for the manufacture of more value-added materials has become increasingly urgent. Industrialization processes generate a variety of wastes, which cause serious environmental impacts when they are discarded carelessly. In recent years, the recycling of these wastes has emerged as an alternative to reduce the consumption of natural raw material, minimize energy consumption and at the same time diminish environmental impacts.

Several studies have revealed the possibility of using a wide variety of wastes to produce different types of ceramic materials like as glass and glass–ceramics [1], floor tiles [2], bricks and roof tiles [3–5], red stoneware tiles [6], porcelain tile bodies [7–10].

Glazes serve to eliminate surface porosity, increase the mechanical strength of ceramic materials, and confer aesthetic qualities to decoration systems and can consist of a glassy or vitreous phase, heterogeneous phases, or glass–ceramic phases, with the glassy matrix corresponding to 80–90% of the layer and the remainder to one or more crystalline phases [11]. Thus, the production of glazes is an excellent alternative for recycling materials, since different types of wastes can be included in their compositions.

A great variety of colors can be obtained by varying the proportion of waste in the composition [12]. Borax sludge (1.5–5%) can be used in the production of frits for fast single-fired wall tile opaque glass–ceramic glazes in place of boric acid for B_2O_3 content in a frit with low zircon content, with properties similar to those of industrially produced standard glaze [13]. It is possible to recycle CRT glass in the production of ceramic glazes with aesthetic and mechanical properties similar to the standard ones [14]. Rice husk ash can be used as a substitute for

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quartz in the production of ceramic tile glazes [15]. Albite wastes can be used in zinc crystal glazes as an alternative to feldspar in soft porcelain crystalline glazes decreasing maturing temperature [16].

The aim of this work was to develop and characterize different types of glazes made from combinations of industrial wastes, frits and commercial natural raw materials. The industrial wastes which were used to replace frits and natural raw materials in a proportion of up to 50% in weight contained granite powder waste, float glass waste and lime-shale waste (a by-product of the process of shale oil production at the PETROBRAS plant in São Mateus do Sul, Paraná, Brazil). The properties of chemical resistance, abrasion resistance, hardness, color and coupling properties were characterized and compared with those of commercial glazes used on porcelain stoneware tiles and wall tiles.

2. Experimental

2.1. Selection and characterization of the raw materials

The raw materials were selected and characterized by chemical and X-ray diffraction analysis (SHIMADZU XRD 6000). The lime-shale waste was analyzed by differential thermal analysis (DTA) and thermogravimetric analysis (TG) using a NETZSCH model 409 EP instrument to verify the decomposition temperatures of the carbonates.

2.2. Glaze formulation, preparation and application method

Based on the results of the chemical and mineralogical characterizations, three glazes compositions (G1, G2 and G3) were formulated using the Seger method [17]. The quantitative chemical analyses were realized using the Philips PW 2400 Sequential WXRF Spectrometer operating with a Rh X-ray tube of 3 kW. The raw materials were first milled in a planetary mill until the resulting powder was 1–2 wt.% after passing through a 325 mesh sieve (Tyler). Slurries with densities of 1.50–1.55 g/cm^3 were prepared with deionized water. The deflocculation curves of the slurries were determined in an Ostwald viscosimeter using an optimized amount of sodium polyacrylate as dispersant agent, because it produces a better stabilization of the slurries instead of sodium silicate [18]. The rheological behavior of the slurries were determined at 20 °C in a Brookfield viscosimeter using a number 21 spindle and the pH values were determined with a Digimed model DM 20 pH meter. The glaze slurries were sprayed onto ceramic wall tiles and porcelain stoneware tiles using a compressed-air sprayer.

2.3. Firing

After the glaze slurries were applied on the ceramics, they were dried at 105 °C until they reached constant mass values. Two different heating cycle were applied, depending on the glaze formulation: (a) Cycle 1 – firing temperature/time of 1080 °C/2 h, heating rate of 3 °C/min, and (b) Cycle 2 – firing temperature/time of 1150 °C/2 h, heating rate of 10 °C/min. The glaze G3 was further heat-treated at 800 °C/12 h and characterized by X-ray diffraction analysis (SHIMADZU XRD 6000) to verify the growth of crystal inside the glass phase.

2.4. Characterization of the glazes

The glazes were characterized according to their thermal expansion, resistance to alkaline and acid attack, optical and hardness properties.

2.4.1. Thermal expansion

Thermal expansion curves of the glaze compositions and of the wall tiles and porcelain stoneware tiles were obtained by dilatometric analysis (NETZSCH model 402 EP dilatometer), applying a heating rate of 5 °C/min. The thermal expansion coefficients of the samples were determined, after which the differences in shrinkage (Δc) between the glaze and the ceramic (glaze/ceramic coupling) were calculated. The effective coupling temperature (T_a) of the glaze was also calculated, as follows:

$$T_a = \frac{(T_g + T_R)}{2} \tag{1}$$

where T_g is the glass transition temperature and T_R is the softening temperature of the glaze.

2.4.2. Chemical resistance

The chemical resistance tests were performed with a solution of 3% hydrochloric acid (HCl) and another of 3% potassium hydroxide (KOH). During the tests, the glazes were immersed for 96 h in the chemical reagents, and the solution was changed after 48 h. The glazes were then visually inspected to verify possible changes in color. The samples were weighed before and after the tests using an analytical balance.

2.4.3. Optical properties

The color of the glazes was determined in a Varian Cary 100 spectrophotometer operating with the following parameters: range 360–830 nm; break 1 nm; mode reflectance; slit 4 nm; lighting D65; observer 10°; CIELab color space.

2.4.4. Hardness

Hardness tests were first performed on commercial glazed stoneware tiles having PEI values of 3, 4 and 5, respectively, to compare them with the glazes developed in this work. The following tests were performed: Mohs hardness scale scratch test and Vickers microhardness test (Shimadzu), applying a load of 500 gf for 18 s.

2.4.5. Determination of the PEI index

Samples measuring 10 cm × 10 cm were prepared and subjected to abrasion resistance test by the PEI method, using a Servitech model CI 247 abrasiometer. The samples tested in this work were compared with commercial samples classified as PEI index 3, 4 and 5, subjected to the same test and above described condition.

3. Results and discussion

3.1. Characteristics of the raw materials and formulation of the glazes

Table 1 shows the chemical characteristics of the selected raw materials. Quartz, a natural raw material, is the main former of glass structures. In addition to quartz, other natural raw materials such as petalite, zircon and kaolin, also contribute to the formation of glass structures due to the presence of SiO_2 in their chemical compositions. In the present work, kaolin was also used in the compositions as source of Al_2O_3. The frit was mainly used as a source of B_2O_3 to act as a fusion agent and to decrease the viscosity and surface tension of the glaze. Li_2O, a glass network modifier, was added to the glaze composition containing petalite. ZnO was added in order to decrease the coefficient of thermal expansion of the glaze, while $ZrSiO_4$ was added to increase its abrasion resistance.

Lime-shale, float glass and granite powder are industrial wastes that have high SiO_2 contents (>30 wt.%) and are also sources of network modifiers such as Na_2O, K_2O and CaO. Network modifiers contribute to lower the fusion temperature of the glaze. Another important oxide in the composition of glazes is Al_2O_3, which is also one of the most expensive oxides. It appears in the chemical composition of all the wastes under study here, and its highest concentration was found in granite powder waste. This oxide can act as a glass network former or intermediate oxide in the glass. The presence of oxides such as Fe_2O_3 and TiO_2 in wastes is a negative factor because they are coloring agents in the glaze. However, their concentration was less than 1.0% in the float glass and lime-shale, while the granite powder waste contained 9.52% of Fe_2O_3 and 0.35% of TiO_2. To reduce the use of commercial natural raw materials to a minimum, the highest possible content of industrial wastes was used in the glaze compositions.

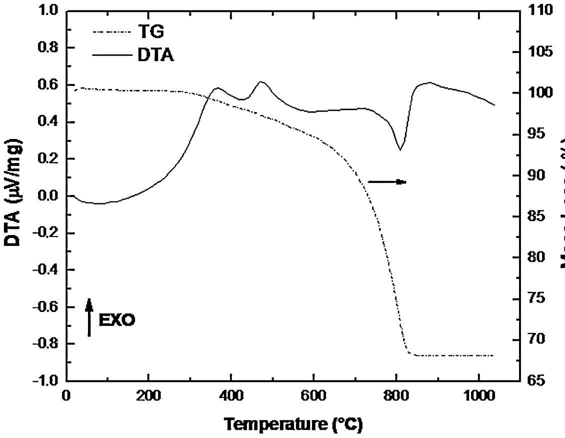

Fig. 1. DTA–TG analysis of the lime-shale waste.

The advantage of using float glass waste is that this material has undergone previous heat treatment, reducing the defects generated by the release of gases during sintering. Moreover, it introduces sodium and calcium oxides in the glaze composition, which are needed to lower its melting temperature.

Lime-shale waste contains large amounts of MgO and CaO. These oxides, as well as $ZrSiO_4$, are opacifying agents that are employed to produce opaque glazes. Fig. 1 shows the DTA–TG analysis of the lime-shale waste. A relative mass loss of 32% occurred between 300 °C and 840 °C. This mass loss can be attributed to two exothermic peaks at 360 °C and 470 °C and an endothermic peak at 810 °C in the DTA curves. In an earlier work [19], was detected the presence of sulfur and organic carbon in lime-shale. This mass loss may be caused by:

- The release of CO_2 from organic matter in the waste, which occurs at temperatures between 300 °C and 700 °C.
- The release of SO_2 starting at 450 °C.
- The decomposition of carbonates from dolomite and ankerite, starting at 700 °C [17].

Table 2 presents the molecular formula of the glazes (mols Seger) and Table 3 describes their chemical composition with the natural raw materials and wastes used in their formulations and the respective number of heating cycle. The chemical

Table 1
Chemical characteristics of the selected raw materials.

(%)	Lime-shale	Float glass	Granite waste	Frit	Petalite	Zinc oxide	Zircon	Abapã Kaolin	C. Alegre Kaolin	Pianaro quartz
Li_2O	–	–	–	–	4.00	–	–	–	–	–
Na_2O	–	14.69	5.58	5.57	0.53	–	–	2.28	0.04	0.01
K_2O	–	0.47	4.53	2.17	0.26	–	–	0.04	0.01	0.26
MgO	11.90	3.74	4.66	0.13	0.07	–	–	0.48	0.04	–
CaO	18.40	7.93	5.65	1.47	0.04	–	–	0.22	0.02	0.01
ZnO	–	–	0.01	1.53	–	99.95	–	–	–	–
B_2O_3	–	–	–	14.49	–	–	–	–	–	–
Al_2O_3	1.30	1.37	12.30	5.61	17.35	–	1.50	30.11	21.89	2.10
Fe_2O_3	0.90	0.08	9.52	0.09	0.08	–	0.15	0.11	0.47	0.05
SiO_2	30.60	71.68	54.60	66.49	76.80	–	34.00	54.74	67.89	96.43
TiO_2	–	–	0.35	0.02	–	–	0.20	0.90	0.43	0.08
ZrO_2	–	–	–	–	–	–	63.50	–	–	–
Others	0.72	0.04	0.45	2.43	0.07	–	0.50	2.25	0.56	0.26
P.F.	36.18	–	2.35	–	0.80	0.05	0.15	8.87	8.65	0.80

Table 2
Molecular formula of the ceramic glazes G1, G2 and G3.

Molecular formula (Seger)		
Basic oxides	Neutral oxides	Acid oxides
G1		
0.400 Li_2O	0.336 Al_2O_3	3.035 SiO_2
0.331 Na_2O	0.037 Fe_2O_3	0.009 TiO_2
0.045 K_2O	0.093 B_2O_3	
0.201 CaO		
0.181 MgO		
0.192 ZnO		
G2		
0.036 Li_2O	0.245 Al_2O_3	2.463 SiO_2
0.156 Na_2O	0.021 Fe_2O_3	0.006 TiO_2
0.028 K_2O	0.113 B_2O_3	
0.306 CaO		
0.286 MgO		
0.178 ZnO		
G3		
0.043 Li_2O	0.177 Al_2O_3	2.870 SiO_2
0.122 Na_2O	0.007 Fe_2O_3	0.003 TiO_2
0.014 K_2O	0.100 B_2O_3	0.247 ZrO_2
0.320 CaO		
0.288 MgO		
0.205 ZnO		

composition G1 was developed with the main purpose of obtaining a transparent and brilliant glaze chemically resistant to acid and alkaline corrosion. The chemical composition of this base composition was modified to produce an opaque glaze (G2) and a more abrasion-resistant glaze by introducing zircon (G3).

3.2. *Properties of the slurries*

The slurries with densities of 1.5 g/cm^3 were prepared with deionized water in a planetary ball mill. Fig. 2 shows their granulometric distribution curves. The higher contents of float glass and granite powder in composition G1 resulted in a larger mean grain size than that of compositions G2 and G3. These wastes are hard and therefore difficult to mill.

Table 3
Chemical compositions of the ceramic glazes and type of firing cycles.

Raw material	Composition (wt.%)		
	G1	G2	G3
Lime-shale[a]	–	25	25
Float glass[a]	30	10	10
Granite powder[a]	20	10	–
Frit[b]	15	20	15
Petalite[b]	10	10	10
Zinc Oxide[b]	5	5	5
Zirconite[b]	–	–	15
Abapã Kaolin[b]	20	15	–
C. Alegre Kaolin[b]	–	–	10
Pianaro quartz[b]	–	5	10
Type of firing cycles	1	1	2

[a] Wastes.

[b] Commercial raw materials.

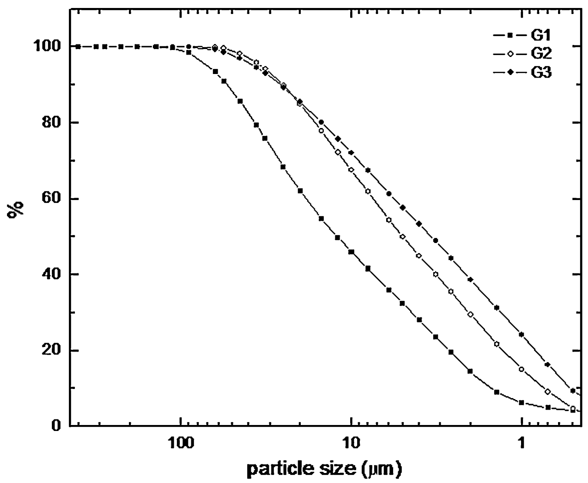

Fig. 2. Grain size distribution curves of the glaze slurries of compositions. G1, G2 and G3.

Table 4 lists the rheological properties of the slurries. All the slurries presented very similar values of viscosity and pseudoplastic behavior, although the viscosity of the G2 and G3 slurries changed over time, resulting in a pseudoplastic/thixotropic behavior.

3.3. *Melting test of the glazes*

Fig. 3 illustrates the melting and fluidity characteristics of the glazes in the two heating cycle studied. Note the higher fluidity of glaze G1 when compared with glaze G2 (1 firing cycle). This can be explained by the higher Na_2O and ZnO content and lower MgO content in composition G1. MgO is responsible for increasing the viscosity of melted glaze. Glaze G3 presented a high viscosity in the first firing cycle due to the presence of zircon. However, with the increase in sintering temperature in the second heating cycle, the viscosity decreased drastically and the fluidity of the glaze increased.

3.4. *XRD characterization of the glazes*

The XRD spectrum of glaze G3 (Fig. 4a) was characterized by the presence of zircon and diopside crystals as well as amorphous phase. Fig. 4b shows the XRD spectrum of glaze G3 heat-treated at 800 °C/12 h, showing an increase in the peak intensity of diopside, which suggests the growth of this crystal with columnar structure inside the glass phase, forming a glass–ceramic glaze [20,21].

Table 4
Rheological properties of the glaze slurries.

Composition	Viscosity 20 °C (cP)	Rheological behavior	pH	Sodium polyacrylate (wt.%)
G1	1520	Pseudoplastic	9.6	0.4
G2	1580	Pseudoplastic/thixotropic	9.1	0.6
G3	1510	Pseudoplastic/thixotropic	8.8	0.2

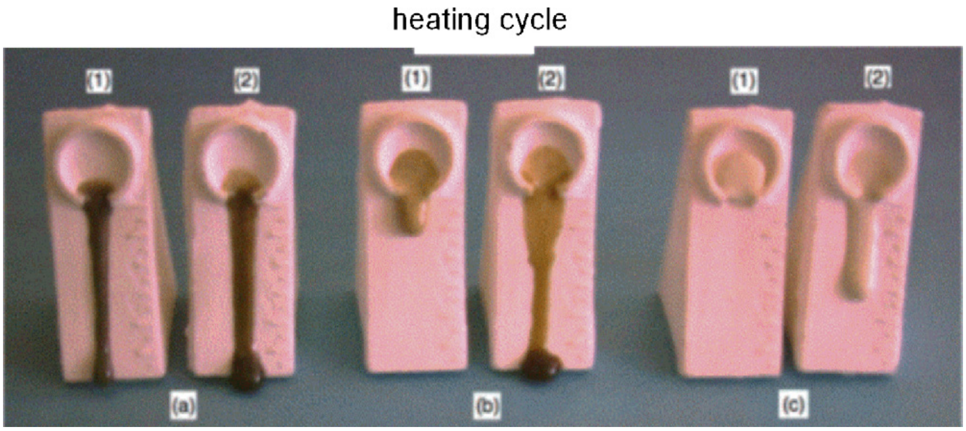

Fig. 3. Melting test of the glazes in different firing cycles: (a) G1, (b) G2 and (c) G3.

3.5. Color

Glazes G1 and G2 showed a brown color due to the presence of high Fe_2O_3 content from the granite waste. Decreasing the proportion of granite waste in the composition caused the color to change to yellow. The color of composition G3, which contained no granite waste, was white. Table 5 presents the optical parameters L^* [(−) black and white (+)], a^* [(−) green and red (+)] and b^* [(−) blue and yellow (+)], while Fig. 5 illustrates the reflectance curves.

Glaze G3 presented higher luminosity and whiteness due to the zircon in the composition. Zircon ($ZrSiO_4$) is a silicate widely used in commercial glaze compositions to produce opaque glazes [22]. The luminosity of G2 was higher than that of G1, showing a tendency to shift to yellow (coordinate + a^*) as a result of the crystallization of diopside in the glaze. The glaze G3 can be easily colored by commercial pigments considering that the color is white. On the other hand, the glazes G1 and G2 already present its natural coloration not being able to be colored later.

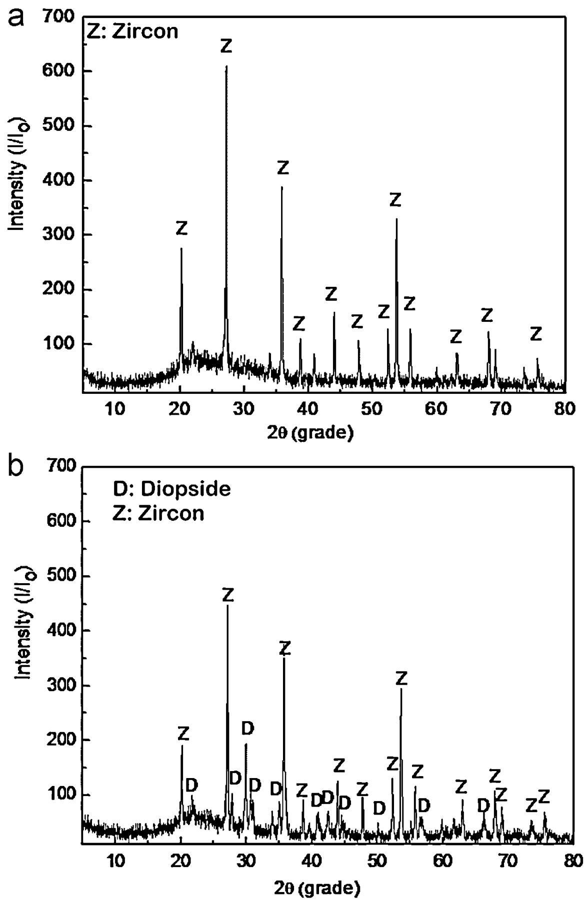

Fig. 4. XRD of G3: (a) as obtained, and (b) heat-treated at 800 °C/12 h.

3.6. Glaze–ceramic coupling

Fig. 6 depicts thermal expansion curves of glazes G1, G2 and G3, stoneware tile and wall tile, while Table 6 lists their

Table 5
Optical parameters L^*, a^* and b^*.

Glaze	L^*	a^*	b^*
G1	55.32	4.01	13.09
G2	70.19	1.78	20.87
G3	85.79	−0.13	12.98

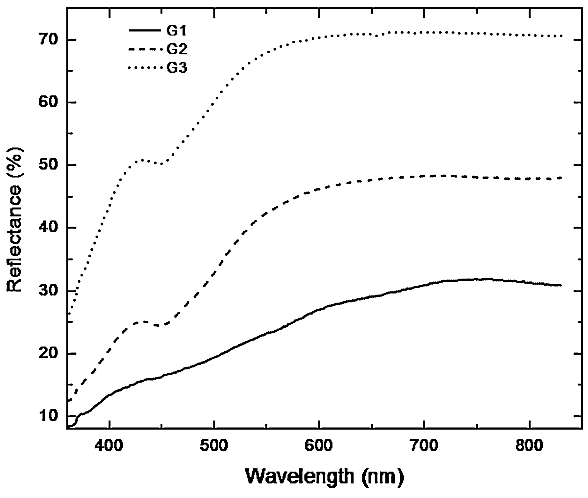

Fig. 5. Reflectance curves of the glazes.

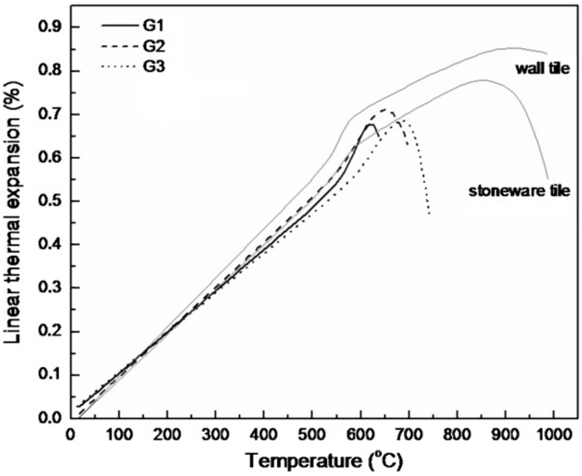

Fig. 6. Thermal expansion curves of glazes G1, G2 and G3, wall tile (cycle 1) and stoneware tile (cycle 2).

respective values of coefficient of thermal expansion (α), glass transition temperature (T_g), softening point temperature (T_R) and effective coupling temperature (T_a). This table also lists the α values of the ceramic stoneware tile and wall tile in the two heating cycle.

The lower α value of glaze G3 was due to the smaller amount of alkaline oxides and higher amount of zinc oxide in the composition. The high content of glass phase in glaze G1 contributed to reduce the α value when compared with composition G2. Glaze G3, whose composition contained refractory oxides such as $ZrSiO_4$ and MgO, was characterized by a high T_R value. On the other hand, in composition G1, which was rich in alkaline oxides, the T_R value was reached at lower temperatures. These curves indicate the good characteristics of glaze/ceramic coupling at ambient temperature.

The differences in shrinkage between the glazes and ceramic supports and the type of stress generated were calculated based on the curves, as indicated in Table 7.

Glazes G1/stoneware and G1/wall tile (cycle 1) were characterized by the compressive stress (the shrinkage of the glaze was lower than that of the ceramic support). On the other hand, glazes G2/stoneware and G3/wall tile (cycle2) were characterized by tensile stress (the shrinkage of the glaze was higher than that of the ceramic support). The glazes showed no cracking, indicating that the best condition was achieved when the glaze was subjected to a light compressive stress. This finding leads us to conclude that the glaze developed here presents good glaze/support coupling.

Table 6
Dilatometric data of the glazes and ceramic tiles.

Glaze/ceramic	$\alpha_{(40–350\ °C)}$ (°C^{-1})	T_g (°C)	T_R (°C)	T_a (°C)
G1	89.80×10^{-7}	570.0	620.0	595.0
G2	96.41×10^{-7}	565.0	650.0	607.5
G3	80.35×10^{-7}	600.0	680.0	640.0
Stoneware tile (cycle 2)	90.64×10^{-7}	–	–	–
Wall tile (cycle 1)	94.27×10^{-7}	–	–	–
Wall tile (cycle 2)	67.80×10^{-7}	–	–	–

Table 7
Differences in shrinkage (Δc%) between glazes and ceramic supports.

	Δc (%)	Stress
G1/stoneware	−0.020	Compression
G1/wall tile (cycle 1)	−0.091	Compression
G2/stoneware	0.017	Tension
G3/wall tile (cycle 2)	0.054	Tension

3.7. Hardness

Table 8 lists the results of the Moss and Vickers tests. These results were compared with the hardness of commercial glazed ceramics classified as PEI 3, 4 and 5, tested in the same conditions as our samples. Glaze G1 presented lower hardness than the commercial stoneware classified as PEI 3. This behavior can be explained by the glassy nature of the matrix. The hardness of glazes G2 and G3 was very similar and higher than that of glaze G1 due to the existence of diopside and zircon in the glass matrix. To compare the abrasion resistance of the different samples, they were subjected to the same testing conditions of 1500 cycles with metal and alumina powder, according to the PEI standard test, after which they were classified by the PEI index. Glaze G3 presented a visual aspect similar to that of the commercial samples after the abrasion test. The global properties of hardness and abrasion of the glazes were very similar to those of commercial glazes, suggesting the feasibility of using these wastes in place of commercial raw materials.

3.8. Chemical resistance

Glazes G1, G2 and G3 showed very good chemical resistance to acid and base corrosion, with no visual change on the surfaces of the samples after the tests. This good resistance can be attributed to the very well balanced composition of wastes and commercial raw materials. Table 9 shows the results of mass loss after 96 h corrosion tests involving the immersion of the samples in HCl and NaOH solutions. The mass loss was very low, detected only in the last decimal digit in some cases, showing that it is possible to develop glazes with excellent chemical resistance to strong acid and alkaline corrosion starting from different wastes associated with commercial raw materials. According to Levitskii et al. [23], the physical–chemical and aesthetic characteristics and

Table 8
Mohs and Vickers hardness of glazes G1, G2 and G3 and commercial stoneware tiles classified as PEI 3, 4 and 5.

Glaze	Mohs hardness	Vickers hardness (GPa)
G1	6	3.0
G2	7	3.6
G3	7	3.5
PEI 3[a]	6.5–7	3.4
PEI 4[a]	7	3.2
PEI 5[a]	7.5–8	3.9

[a] Commercial glazes classified as PEI 3, 4 and 5.

Table 9
Mass loss of the samples after chemical attack.

	Glaze	Mass before attack (g)	Mass after attack (g)	Mass loss (%)
Acid attack	G1	0.4545	0.4545	–
	G2	0.8054	0.8050	0.05
	G3	0.2146	0.2145	0.05
Alkaline attack	G1	0.3072	0.3070	0.07
	G2	0.8532	0.8531	0.01
	G3	0.3958	0.3958	–

the durability of the coatings are the result of a rational combination of crystalline opacifying phases and their distribution in the glassy matrix, forming a uniform glass crystal structure.

4. Conclusions

This work showed that glazes with properties very similar to those of commercial glazes can be obtained by combining different wastes and commercial raw materials with a balanced chemical composition. Transparent and opaque glazes were obtained with different hardnesses and excellent coupling properties with ceramic supports for wall tiles and stoneware tiles, all of them with excellent chemical resistance against alkaline and acid corrosion.

The float glass contributed by incorporating sodium and potassium oxides and also calcium and silicon oxides in the composition, partially substituting lime and feldspar, which are natural raw materials. The presence of oxides such as Fe_2O_3 and TiO_2 in granite waste is a negative factor because they are coloring agents in the glaze. Lime-shale waste was very important because it incorporated lime and magnesium oxide in the formulation, favoring increased hardness and yielding more opaque glazes. The G1 and G2 compositions showed higher Vickers hardness than that of commercials glazes classified as PEI 4, showing a result exceeding 3.6 GPa. The values of hardness on the Mohs scale were between 6 and 7. Glazes G2 and G3 presented excellent abrasion resistance classified as PEI 4, and their aspect was very similar to that of PEI 4 commercial stoneware tiles. The abrasion resistance of glaze G1 was lower than G2 and G3, and was characterized as PEI 3.

Acknowledgments

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