

Valorisation of Bivalve Shell Residues in Earthenware Pastes

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ABSTRACT

The valorisation of industrial waste/by-products has been gaining importance in recent years. Several alternatives have been studied aiming to reduce not only the amount of waste in landfills but also the natural raw materials consumption. In this context, the main objective of this work is the valorisation of bivalve shells residues, as calcite substitute, in earthenware pastes. The bivalve residues were characterized and compared with commercial calcite commonly used in these formulations. Through the mineralogical and chemical characterizations and the thermal analysis, it was concluded that these residues could be reused as a source of calcium carbonate, as biocalcite, not requiring any pre-treatment. Formulations were later developed with the gradual replacement of calcite (25, 50, 75 and 100%). Furthermore, formulations, exclusively with biocalcite, with different particle sizes were also developed. The shrinkage, water absorption, flexural strength, colour and linear thermal expansion coefficient of the fired products were evaluated and no significant differences were observed being all specimens within industrial limits. Therefore, this work proved that calcite can be totally substituted by bivalve shell residues in earthenware pastes reducing the virgin raw materials consumption and developing more sustainable products. Moreover, this new application will avoid the landfill deposition of the bivalve shell residues reducing the environmental impact of the food processing industry contributing also for the circular economy and industrial symbiosis.

Introduction

Globalization has increased economic and technological development, particularly in the services and industry. Nowadays, according to the linear economy model, industrial development is closely associated with productivity, leading to an increase in the consumption of natural resources and compromising their availability for future generations. For the same reason, there is also an increase in industrial by-products and waste generated, which requires an efficient waste management. In the model of linear economy practiced up until today, natural resources are extracted, used in the productive process and the final product is marketed¹. As it reaches the end of its life, it is considered waste, and most of the time it is disposed in landfills. In this model the energy and materials spent are not counted, nor is there an effort to reduce their consumption or to reuse the materials, which severely compromises future development. With the aim of ensuring sustainable development, the United Nations (UN) set 17 sustainable development goals (SDG) in 2015. To meet the proposed objectives, the European Union has created the European Climate Pact, in which commits itself to achieve climate neutrality by creating 50 measures aimed to reduce greenhouse gas emissions, and create opportunities for innovation, investment and employment by replacing the linear economy with circular economy². This new model of circular economy is based on sustainable and efficient economic development through the production of durable products and materials, which retain their value for longer periods¹. In this model, the reduction of the virgin raw materials consumed is promoted, and the repair, recovery and finally recycling of products and materials is strongly encouraged (by this order). This incentive leads to a product being made the most of until its end of life, reducing the impacts caused by the resources used in its production, being reintroduced into the productive cycle as resources or raw materials, closing the cycle of the circular economy. In the new concept, due to the policy of maximum efficiency, reuse and repair arises the need to increase the energy efficiency of current production processes and take advantage of waste and by-products from industry itself or as raw material for another sector. This requires the creation of a symbiosis environment for the efficient use of available resources and waste, as well as closed circuits (eco-parks) for the use of waste and by-products between various industries³.

In the production of ceramic pastes there is an intensive consumption of raw materials, water and energy, generating strong environmental impacts. These circumstances, coupled with circular economy, make the ceramics industry interesting for the incorporation of waste from other economic activities. The formulations of ceramic pastes vary widely in their composition, often showing fluctuations. Together with the fact that the final product is achieved by sintering at high temperatures, it is possible to introduce the most diverse types of waste into the ceramic matrices⁴. In Mota Ceramic Solutions, the company where the work was carried out, this practice is already recurrent. Non-compliant parts from other companies are collected and transported to the group's units and are labeled as glazed shards. In these units, the shards are milled and re-introduced into the formulations of pastes, generating less waste, and contributing to the sustainability of this sector. The incorporation of chromium and nickel sludge from galvanizing processes was also studied to colour stoneware pastes⁵ and red clay pastes⁶. In this type of pastes, studies were still found on the incorporation of fly ash from the burning of coal⁴.

In 2015 in Europe, 598,000 tons of bivalves⁷ were produced and in 2019, Portugal produced 6,683 tons, according to the PORDATA database, registering an increase of 300 % compared to 2014⁸. Therefore, the waste generated in these food industries, bivalve shells, also increased which corresponds to 75 % of the total weight of the mollusc⁹. The shell residue is generated daily, constituting a charge to the company, about 75 euros per ton of waste, according to the waste collection company VALORSUL¹⁰. In addition there is also the cost of transport between the source of the waste and the landfill. In the case of the catering sector, it is difficult to gain access to shellfish waste without restaurants specifically doing so, as in the shellfish products sold on commercial surfaces. That being said, the mollusc processing industry is in position to supply shells continuously to the ceramics industry, promoting a more sustainable development of both industries. Studies have shown that bivalve shells are composed by 95 to 99 % of calcium carbonate in the form of calcite or aragonite, and have a small organic matrix^{9,11}. After mollusc extraction, the shells contain organic residues and to be moist, not being ideal for direct introduction into the formulation of ceramic pastes. Ideally this waste should be dried and organic matter should be removed before delivery. According to the literature, these residues are currently reused as aggregates for construction⁹, as a biofilter for the treatment of waste water, as a calcium supplement in food or for soils¹² and also for applications in bioceramics¹³ or as a reinforcement for PLA biocomposites¹⁴.

In this context, the aim of this work is to use bivalve shells (oyster and mussels) as calcite replacement in the formulation of earthenware pastes and achieve similar chemical, physical, mechanical and thermal properties of the common earthenware pastes produced.

Materials and Methods

The natural raw materials necessary to formulate earthenware pastes (clays, kaolins, calcite, silica) were supplied by Mota Ceramic Solutions (MCS). The oyster residues were collected from a local restaurant and the mussel residues were supplied by Finisterra, a bivalve transformation unit located in Sagres, Algarve.

The oyster and mussel shells were dried in an oven at 100°C for 24h to remove the water content and to make them more brittle. Then two mixtures (biocalcites) of 8 % of kaolin and 92 % of each shell were submitted to milling in a planetary mill, with a porcelain jar (300g of capacity), alumina balls (400g) and water (251mL) until achieving the desired granulometry being then dried again. The particle size distribution was characterized using a laser diffraction analyser (MASTERSIZER 3000). Then the biocalcites were characterized along with the supplied calcite by: X-ray fluorescence (HITACHI X-SUPREME 8000); X-ray diffraction (PANalytical's X'Pert MRD); scanning electron microscope (HITACHI SU-70); colorimetry (Konica Minolta CR300); differential thermal analysis/ thermogravimetry (DTA/TG - NEXTA STA300); and colour deviation from the calcite according to equation 1.

The earthenware pastes studied were composed by 12 w.t % of calcite. Three pastes with different percentages of oyster biocalcite (0, 50 and 100 % in weight) were prepared, and for the mussel biocalcite two more substitution percentages were studied (0, 25, 50, 75 and 100 % in weight). The influence of the biocalcite particle size were also studied, being formulated three more pastes with total substitution of calcite and different D50 of the biocalcite (3, 5 and 6). In the table 1 the prepared formulations are presentend as well as the sources of calcium carbonate for each one.

Table 1. Formulations prepared.

Formulation	STD B	B25	B50	B75	B100	B100G3	B100G5	B100G6	STD O	OS50	OS100
Calcite	100	75	50	25					100	50	
Mussel Biocalcite		25	50	75	100	100	100	100			
Oyster Biocalcite										50	100

The pastes were later sintered at 1050°C for one hour, with a heating rate of 5°C/min. Cylindrical specimens (r=8 mm, l=100 mm) were prepared using a single piston extruder, and were used to characterize the thermal behaviour (NEXTA STA300) and the green, dry and fired properties, such as retraction (green-dry and dry-fired), flexural strength (ZICK ROWELL following ISO 10545-4), water absorption (following BS EN 1217: 1998), mineralogical composition (PANalytical's X'Pert MRD) and dilatometry (NETSCH DIL 402C). Rectangular specimens (l=98 mm, w=84 mm, t=7 mm) were pressed to evaluate the loss on ignition and colour (Konica MINOLTA CR300) after sintering. The colour deviation of the prepared pastes was also calculated (equation 1) using STD pastes as reference.

$$\Delta E = \sqrt{(L1 - L2)^2 + (a1 - a2)^2 + (b1 - b2)^2} \quad (1)$$

Where:

L1, a1 e b1 - Colorimetric coordinates of the reference;

L2, a2 e b2 - Colorimetric coordinates of the sample.

Results and Discussion

0.1 Characterization of calcite and residues

Figure 1 presents commercial calcite particle size distribution. The grinding of this material consists in multiple stages with different grinding systems until it reaches the desired particle distribution¹⁵. The calcite has a normal particle distribution, and the D50 is 4,36 µm. Since the main goal is to replace calcite for biocalcite directly, the particle size distribution of the biocalcites should be similar to the commercial calcite. The D50 (particle diameter of 50 % of the accumulated distribution) is used to compare the particle size distributions of the biocalcites (oyster and mussels) during milling and its value (4,36 µm) as reference for milling.

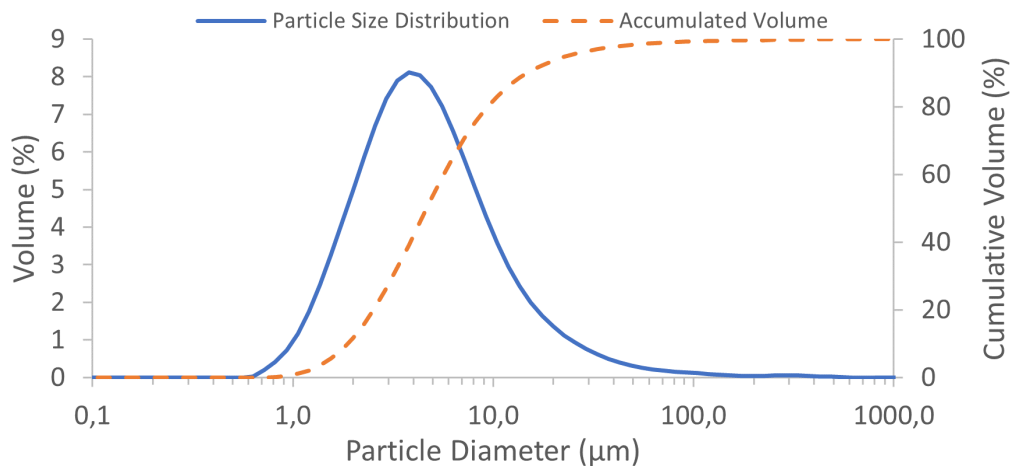


Figure 1. Particle distribution of the calcite.

The evolution of the D50 of the biocalcites (oyster and mussels) with the milling time is presented in figure 2 with the commercial calcite D50 value as goal. For mussel biocalcite to reach the desired D50 it took between 100 to 120 minutes and for oyster biocalcite it took between 300 to 330 minutes. The small variations in the total grinding time of each biocalcite are due to the interruption of the jar mill to collect samples for the evaluation of its particle size distribution, performing the laser diffraction tests.

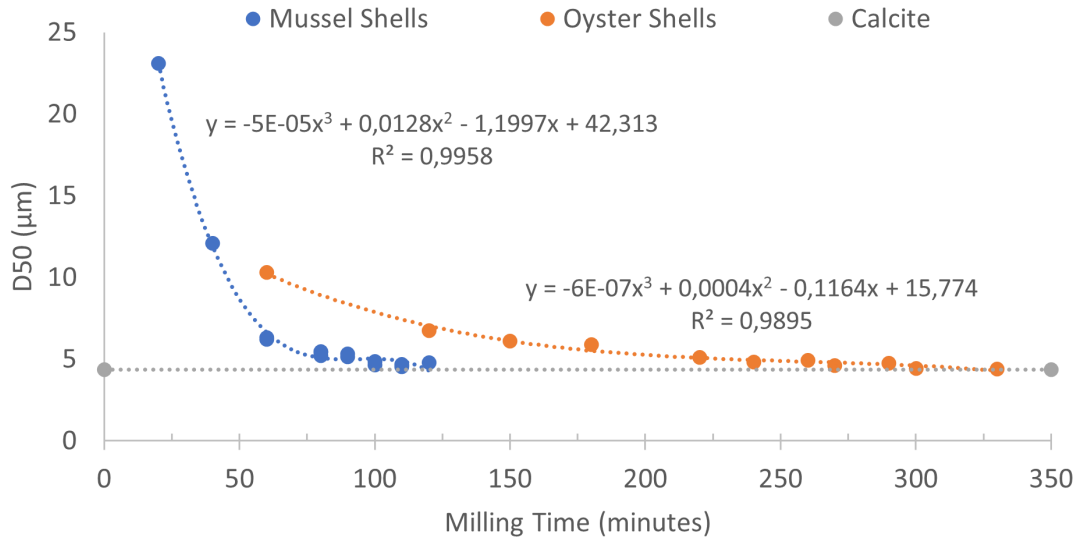


Figure 2. Influence of milling time on the biocalcites.

The chemical composition and loss on ignition (LOI) of the calcite and residues (mussel and oyster shells) is shown in 2. The main component present in all is CaO, and calcite is the one that has more of this oxide corresponding to 57.09 wt.%, and 35.8 wt. % of LOI. Both shell residues have lower content of calcium oxide (less 6 % and 3 % for mussel and oyster shells, respectively), more carbon content and higher LOI (more 9 % and 8 % for mussel and oyster shells, respectively), evidencing the presence of more organic content than calcite.

Table 2. Average chemical composition of the different calcium carbonate sources.

Component (wt.%)	Calcite	Mussel	Oyster
SiO ₂	1.43	1.62	1.08
Al ₂ O ₃	0.26	0.33	0.59
K ₂ O	0.02	0.06	0.06
MgO	0.33	0.45	0.56
CaO	57.09	51.27	54.72
Fe ₂ O ₃	0.04	0.06	0.02
S	0.03	0.03	0.03
C	8.95	10.16	9.14
Lost on Ignition (wt.%)	35.8	44.5	43.51

The XRD patterns of the commercial calcite and the two bivalve shells (mussel and oyster) as well as the crystalline phases detected are presented in 3. The commercial calcite and oyster shells are only composed by calcite being this phase the principal for mussel shells. This last bivalves shells also have aragonite, another calcium carbonate phase, as a secondary phase.

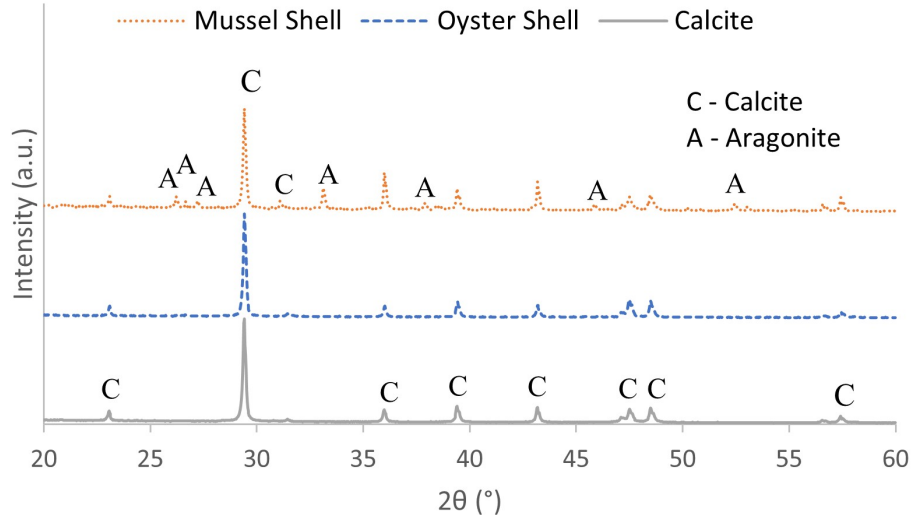


Figure 3. X-ray patterns of the different calcium carbonate sources.

The SEM micrographs of the calcite and both biocalcites powders are shown in figure 4. The commercial calcite is mainly composed by round particles while both biocalcites have also longer particles, being more abundant in oyster biocalcite.

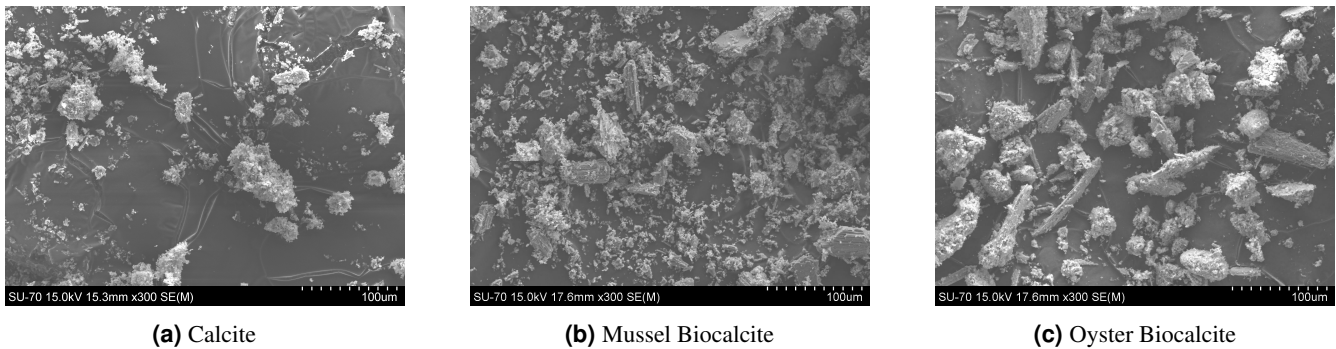


Figure 4. SEM micrographs of the different calcium carbonate powder sources.

In the figure 5 the thermal behaviour (DTA and TG) of the different calcium carbonate sources are presented. In the case of calcite it is possible to verify the typical ATD/TG of calcite¹⁶. Considering the thermogravimetric analysis, the only mass loss detected is between 750 and 800 °C, corresponding to a loss of 45 % of the initial mass, due to the decomposition of calcium carbonate into calcium oxide and carbon dioxide, which is an endothermic reaction. For the oyster shells, the same calcium carbonate decomposition reaction occurs for the same temperature, with a slightly higher mass loss, 46 % of the initial mass. In the mussel shells, a mass loss also occurs from 200 to 700°C due to the decomposition of organic matter, and there is also an exothermic reaction at 300°C associated with the transformation of aragonite to calcite^{13,17}. Finally, there is a more accentuated loss of mass (40 % of the initial mass) between 750 and 800°C, corresponding to the decomposition of calcite, described above.

The colour difference after sintering at 1000°C between the three calcium sources were calculated using the colorimetric coordinates of commercial calcite as reference ($L=93.06$, $a=0.23$ and $b=4.00$). The difference of colour between the calcite and the residues can be noticed by any observer ($\Delta E > 2$), being higher for the mussel shells ($L=89.96$, $a=-0.78$ and $b=6.89$; $\Delta E = 4.36$). The oyster shells ($L=94.91$, $a=-0.04$ and $b=2.80$) is the brightest one (higher L) and at the same time is the less yellowish (smaller b). Despite the colour differences observed, these calcium carbonate sources only count 12 % in weight of the total paste composition, so no influence in the final colour of the paste is expected.

0.2 Characterization of Pastes

In figure 6 the results obtained for the drying shrinkage and the dried flexural strength of the pastes prepared are represented. A slight decrease in the drying shrinkage is verified with the introduction of oyster shell biocalcite in the composition, from 4.7

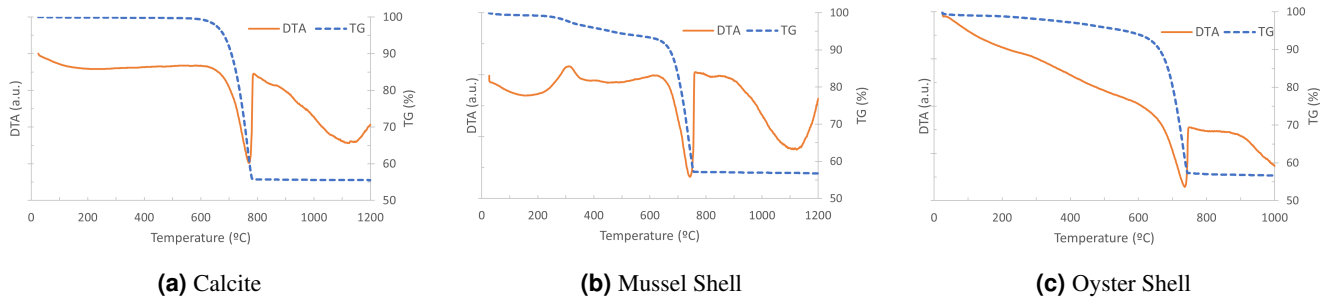


Figure 5. Thermal Analysis (DTA and TG) of the different calcium carbonate sources.

% (STD O) to 3.8 % (OS100) not being this difference significant. The dried flexural strength values are similar for the three calcium carbonate sources, being slightly lower for the OS100 paste (2 kgf/cm² less than the other pastes). This decrease in drying shrinkage and dried flexural strength can be justified by the greater irregularity in the particle morphology of the oyster shell biocalcite (figure 4, subfigure 5c), which leads to the lower compaction of this paste. A slight decrease in the drying shrinkage (from 4.94 % of the STD B paste to 4.38 % of the B100 paste) with the introduction of the mussel biocalcite can be noticed, and also a slight increase in the dried flexural strength for the same pastes, from 33.62 kgf/cm² of the STD B paste, to 35.18 kgf/cm² of the B100 paste. There was an increase of 19 % in the dry modulus of rupture for paste B100G3, compared to paste B100, due to the finer particle size of the biocalcite used, being the drying shrinkage of these pastes quite similar (0.40 % difference). For the B100G5 and B100G6 pastes there was a decrease in dried flexural strength, and a slight increase in drying shrinkage for the B100G5 paste (5.39 % of drying shrinkage).

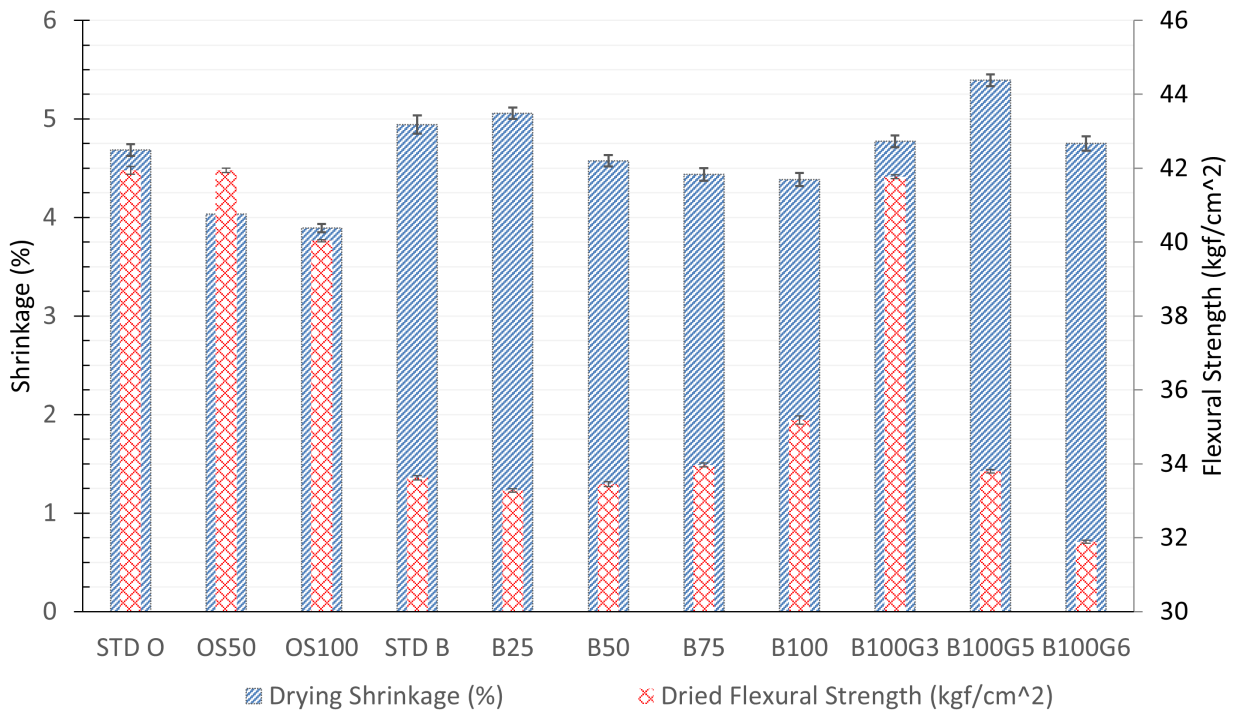


Figure 6. Drying Shrinkage and dried flexural strength of the pastes prepared.

The lost on ignition (w.t.%), water absorption (%), firing shrinkage (%) and flexural strength (kgf/cm²) of the prepared pastes are presented in the table 3. Starting by comparing the two control pastes (STD O and STD B), the only difference that can be found is in the flexural strength is less 18 kgf/cm² in flexural strength for STD B, while the remain properties don't have significant variations. The lost on ignition doesn't vary with the introduction of biocalcite (oyster or mussel) in the formulation since the calcium carbonate only counts 12 % in weight of the pastes. The water absorption decreases with the replacement of

calcite by oyster biocalcite (from 22.01 % for STD O to 19.57 % for OS100), and the firing shrinkage and flexural strength increase (from 0.62 % and 284.24 kgf/cm² for STD O to 2.11 % and 305.04 kgf/cm² for OS100). The total replacement of calcite by mussel biocalcite does not change the water absorption percentage being around 22.40 % for both formulations STD B and B100. These values are supported by the flexural strength achieved for the same formulations (266.91 kgf/cm² for STD B and 263.44 kgf/cm² for B100), being a slightly lower for B100. B50 that is composed 50 % of calcite and 50 % of mussel biocalcite has almost 1 % more of water absorption and less 7 kgf/cm² of flexural strength comparing to the control paste (STD B). There is an increase in firing shrinkage with the gradual replacement of calcite by mussel biocalcite, reaching almost the double of the STD B (0.48 %) with the total substitution of calcite (0.99 % for B100). The formulation with finer particles of mussel biocalcite (B100G3) present lower water absorption (21.25 %) and consequently higher flexural strength (279.04 kgf/cm²) and higher firing shrinkage (1.27 %) than STD B and B100, showing an improvement on the final properties of the fired paste. The two formulations, where a coarser mussel biocalcite was used (B100G5 and B100G6) have similar values for the presentend properties, having more water absorption (around 22.65 %), and consequently less flexural strength (around 224 kgf/cm²) than STD B and B100. The firing shrinkage values of both pastes are between the values obtained for STD B and B100 (0.74 and 0.53 for B100G5 and B100G6, respectively).

Table 3. Effect of the biocalcite on lost of ignition, water absorption, firing shrinkage and flexural strength.

Formulation	STD O	OS50	OS100	STD B	B25	B50
Lost on ignition (w.t.%)	11.50 ± 0.07	11.31 ± 0.01	11.31 ± 0.01	11.43 ± 0.04	11.69 ± 0.04	11.70 ± 0.02
Water absorption (%)	22.01 ± 0.001	21.12 ± 0.001	19.57 ± 0.001	22.40 ± 0.001	22.40 ± 0.001	23.18 ± 0.001
Firing shrinkage (%)	0.62±0.07	1.16±0.05	2.11 ± 0.04	0.48 ± 0.08	0.58 ± 0.06	0.88 ± 0.08
Flexural strength (kgf/cm ²)	284.24 ± 0.47	284.24 ± 0.17	305.04 ± 0.53	266.91 ±0.50	275.58 ±0.46	259.98±0.28
Formulation	B75	B100	B100G3	B100G5	B100G6	
Lost on ignition	11.74 ± 0.01	11.72 ± 0.02	11.57 ± 0.02	11.53 ± 0.05	11.64 ± 0.03	
Water absorption (%)	22.45 ± 0.001	22.43 ± 0.001	21.25 ± 0.001	22.64 ± 0.001	22.67 ± 0.001	
Firing shrinkage (%)	0.81 ± 0.06	0.99 ± 0.06	1.27 ± 0.08	0.74 ± 0.07	0.53 ± 0.06	
Flexural strength (kgf/cm ²)	266.91 ± 0.27	263.44 ± 0.42	279.04 ± 0.49	228.78 ± 0.04	220.11 ± 0.79	

The replacement of calcite by biocalcite leads to a decrease in the linear thermal expansion coefficient (α) of the pastes. The control paste STD has the higher linear thermal expansion coefficient (8,43E-06 °C⁻¹) between 100 and 500°C. The total replacement of calcite by oyster biocalcite (OS100) leads to a linear thermal expansion coefficient of 7,92E-06 °C⁻¹ as the replacement by mussel biocalcite doesn't affect so much that coefficient, being it's value of 8,08E-06 °C⁻¹. The introduction of mussel biocalcite with different particle size distribution vary the linear thermal expansion coefficient: the formulation with thinner biocalcite has the lowest coefficient of all pastes, 7,86E-06 °C⁻¹, as the formulations with coarser biocalcite have values more close to the STD paste, 8,23E-06 and 8,15E-06 °C⁻¹ for B100G5 and B100G3, respectively. Therefore, the introduction of biocalcite (oyster or mussel) leads to a insignificant decrease in the linear dilatation.

The tables 5 and 6 show the HunterLab color coordinates of all prepared pastes and the respective color variation (ΔE) from the standard paste. There are no significant changes for the partial replacement of calcite with oyster shell biocalcite (OS50), as the ΔE is 0.26. The OS100 paste shows a decrease in L value (less white) and an increase in b value (more yellow), compared to the standard. The value of ΔE is 2.67, so the difference in color between the pastes is visible.

Table 5. Colorimetric coordinates and colour difference (ΔE) of the pastes with oyster biocalcite.

HunterLab	STD O	OS50	OS100
L	91,14	91,11	90,03
a	3,44	3,67	3,77
b	9,73	9,85	12,14
ΔE	0	0,26	2,67

In pastes where calcite was replaced by mussel shell biocalcite, the total replacement of calcite by biocalcite with the same granulometry (B100) has no influence on the color of the prepared paste. The value of ΔE is 0.85, so no differences in the color are visible. For the pastes prepared with biocalcites of different granulometries the paste B100G3 is the one that exhibits a higher ΔE (1.40) due to the increase of b (more yellow), as verified in the pastes with oyster shell biocalcite. In the case of the pastes B100G5 and B100G6 the values of ΔE were 0.30 and 0.20 respectively, with no differences in color after sintering relative to the standard. In conclusion, the total replacement of calcite by oyster shells changes the color of the pastes, an effect that does not occur when the replacement is made by mussel shells.

Table 6. Colorimetric coordinates and colour difference (ΔE) of the pastes with mussel biocalcite.

HunterLab	STD B	B25	B50	B75	B100	B100G3	B100G5	B100G6
L	91,04	90,78	90,92	90,25	90,53	90,64	91,28	91,23
a	3,26	3,46	3,46	3,49	3,45	3,44	3,37	3,20
b	9,05	9,72	9,17	8,97	9,70	10,38	9,19	9,01
ΔE	0	0,75	0,26	0,83	0,85	1,40	0,30	0,20

Conclusions

The work developed and the results obtained demonstrate the feasibility of using bivalve waste as sources of calcium carbonate, more specifically oyster or mussel shells, for the formulation of earthenware pastes. These two types of shells can completely replace calcite, a virgin raw material, instead of being considered waste and being disposed of in landfills. The shells only have to be milled to be introduced in ceramic pastes, consuming energy during this process.

The laboratory developed earthenware pastes with different percentages of incorporation of bivalve shells exhibit properties (chemical and mineralogical composition, flexural modulus of rupture, thermal behavior and color) similar to earthenware pastes produced with calcite as a source of calcium carbonate. Decreasing the particle size of mussel shell biocalcite allowed improving the final properties of the paste, namely increasing 12 % the flexural modulus of rupture when baked and decreasing 1 % the water absorption. No relationship was found between the final properties obtained and the range of cooking temperatures tested, and it was not necessary to change the cooking cycles of the material when these biocalcites are used.

Finally, the replacement of calcite with oyster or mussel shells allows the consumption of natural resources to be reduced, leading to a reduction in the impact caused by the raw material extraction industry. Since oyster shells and mussel shells are waste products from the food industry, their reuse leads to a reduction in landfilling of these wastes, placing less of a burden on companies in this sector. For the ceramics industry, the introduction of this waste promotes the reduction of the environmental impact resulting from the production of earthenware products, promoting the development of more sustainable products and the circular economy between these two sectors.

Future Work

To meet the needs of the ceramic industry it is necessary to further study the replacement of calcite with shellfish waste. In this sense, as a future work it is suggested to analyze the economic feasibility and the environmental impact resulting from the use of bivalve shells in the formulation of ceramic pastes as a life cycle assessment.

It is also suggested the study of the replacement of calcite by biocalcite from other types of bivalve shells existing in the national territory, such as clams, limpets, cockles and longnose shells, being also suggested the development of a mixture of shells biocalcite, not restricting only to one type of bivalve shells.

Considering the different forming processes used in earthenware and the fact that calcite is also used in the pastes used for the production of tiles, it is also suggested to study the rheological characteristics of the slurries with biocalcite. The rheology of the suspensions will be fundamental for both the filling, in the case of faience, and for the atomization process, in the case of tile production.

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