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On the friability of mussel shells as abrasive

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ABSTRACT

The spread of raft-farming of mussels in river estuaries around the world produces about 1.4 million tons of shell waste which mainly ends up in landfills. In addition, the United Nations and the European Union promote the sustainable development goals (SDG) for sustainable food production, which requires adequate waste management to analyse the life cycle and reuse of goods and materials. This work proposes to use mussels shells by-products created by the canning industry as abrasive in the sandblasting process. One of the main characteristic of abrasive grains is the friability, which determines the behaviour of the abrasive in the sandblasting process. Shells need to be prepared before using in sandblasting, a conditioning that involves cleaning, grinding and sieving of shells. The purpose of this work is to examine the friability of mussel shells from two points of view, the effect of the cleaning process and a comparison with a common abrasive material, the garnet. The characterisation of the friability of mussel shells allows to foresee the behaviour as abrasive and to define the most suitable applications. The obtained results reveal that garnet is four times more friable than shells thanks to shells biocomposite nature. This interesting feature enlarges the life of sand in close cycles and foresees a promising future to the new abrasive.

1. Introduction

Mussel aquaculture accounts for the 13% of the global bivalve production, which has grown up steadily to 2 Mt in 2019 (FAO, 2020; Avdelas et al., 2021). But in production regions, that delicious food hides a dark side: the amount of shell generated is obviously proportional. Shell weight is approximately 2/3 of the mussel according to the species and environment conditions. 1.4 Mt of mussel shells had to be managed in 2019. Only in Galicia (NW Spain), the 35% of mussel production destined to the canning industry produced 59 kt of mussel shell by-product in the same year (Xunta, 2020). The importance of this waste, due to the large volume and the difficulty to manage, has led some countries to quantify the amount and carry out tailored management plans. At the same time, several research groups are studying new valorisation opportunities for mussel shells. Mussel shells, unlike white shells, form sharp edges when grinding which are inadequate to use as bird food supplement. Regarding the environmental impact of uncontrolled dumping of shells, solutions to extend the life of shells have been proposed promoting their use as raw material for other purposes and, thus, revaluing the shell waste (Medina Uzcategui et al., 2022). It has been proposed to use as gravel for concrete and roads (Martínez-García et al., 2017; El Biriane and Barbachi, 2021). In these applications large quantities can be managed, but because of the necessary cleaning treatment and transport costs, they cannot compete with the usual cheap gravel. There is a loophole use of shells as acidic soils neutraliser on agricultural floors (Álvarez et al., 2012), as the European administrations have not determined the risk of this animal's origin waste yet. Contaminated soils amendment (Santás-Miguel et al., 2022) and valorisation as biofilters in water treatment for removing metals (Papadimitriou et al., 2017; Salim et al., 2021; Odeh et al., 2022) are two promising applications for shells. Although high purity carbonate derived from shells with special treatments can be used, as filler (plastics, paper) (Owuamanam and Cree, 2020), catalyst in biodiesel production (Rezaei et al., 2013), whitening and reactive (chemical, pharmaceutical, and cosmetic) (Matthews and Asadov, 2020; Mititelu et al., 2021), its use is not widespread. Meanwhile, several research groups are trying to find new applications for this waste.

The use of waste, from aquaculture, industry and other sectors, as abrasives means a reduction in the consumption of raw materials, usually from non-renewable sources (Aydin et al., 2017). In the literature, no proposal has been found for the use of shells as abrasive. This work proposes a new application: the use of ground shells as abrasive, mainly in sandblasting processes. In sandblasting, abrasive

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Table 1
Sterilisation treatments found in literature for shells.

	Treatment conditions	Authors
Heat treatment	105 °C 24 h	Othman et al. (2013), Yang et al. (2005, 2010) and Agbede and Manasseh (2009)
	135 °C 32 min (EC) 1069/2009	Martínez-García et al. (2017)
	250–300 °C	Sahari and Mijan (2011)
Chemical treatment	NaClO solution	Kelley (2009)
	White vinegar + 48 h in sodium bicarbonate solution	Kelley (2009)

grits are propelled at high speeds using compressed air against the surface that is intended to smooth or clean (Momber, 2007). The energy exchange in the interaction surface determines the intensity of the operation: removal of paint/rust traces without damaging the surface, or the formation of compressive stresses by plastic deformation of the surface. For a specific application, the appropriate abrasive is chosen according to its properties (Linke, 2015). The density of the abrasive determines the collision energy. The grit morphology (pointed, rounded, cubic or elongated) determines the interaction with the target surface. Hardness is important if the objective is to deform or scratch the surface; besides, harder grits maintain sharp edges for a longer time. Finally, the friability of the abrasive, besides absorbing the impact energy, governs the reusability of the grains. The usual abrasive materials include mineral (silicon, garnet), synthetic (furnace slag, alumina, silicon carbide, glass beds, ceramics) or metallic (steel) origin. "Soft" abrasives are used to do as little damage as possible to the surface such as those of agricultural origin (walnut shells, fruit bones, starch) or synthetic (sodium bicarbonate, recycled plastic, dry ice). Furthermore, mussel shell abrasive could be used in other abrasive processes too, such as waterjet (Aydin et al., 2017).

When the hard, fragile mussel shells of calcium carbonate are ground, the sharp edges needed by the abrasives are naturally created. Besides calcium carbonate, 5% of the shells are composed of organic matter (Agbaje et al., 2018). The European Parliament and the Council (EC) 1069/2009 directive (Regulation, 2009) establishes the health rules as regards animal by-products and derived products not intended for human consumption. It states that animal origin by-products must guarantee not to pose unacceptable risks to public and animal health. It explicitly specifies that mollusc shells whose soft tissue or flesh has been removed are outside the scope of the regulation. The management of such remains is entrusted to the good practice guides decreed by each member country. However, the Spanish government has not yet developed a guide to the proper uses of shells, and requires full compliance of 1069/2009 (EC) regulation. Thus, the dumping in landfills or the second use of shells requires a previous sterilisation treatment, i.e., a treatment that eliminates, deactivates or kills all forms of life (especially microorganisms) (Rutala and Weber, 2008). Sterilisation can be achieved in various ways, such as thermal, chemical, irradiation, high pressure, and filtration. Table 1 compiles the treatments (thermal and chemical) that have been proposed for the sterilisation of shells in literature. Regulation 1069/2009 cites explicitly the thermal sterilisation treatment (135 °C, 20 min, 3 bar); if a different treatment type is used its efficacy must be verified (Regulation, 2009).

The conditioning of shells as abrasive involves cleaning, sterilisation, drying, grinding, and sieving operations (Fig. 1). The conditioning has influence on sand characteristics. The cleaning aims to remove traces of organic matter (byssus, serpulids, barnacles and algae) that are stuck to shells. Shells are washed rubbing each other in a rotating drum filled of water. Sterilisation removes bacterial life to avoid unpleasant smells and ensure health safety. But the sterilisation process may affect the friability of the abrasive due to the induced damage on the organic matter, which plays the bonding material role between calcium carbonate crystals. The mill used in grinding affects the morphology and size distribution of the grits. Finally, ground shells are transferred to the sieve shaker where are sorted according to grain size.

The objective of this work is to evaluate the characteristics of shells to use them as abrasive in sandblasting. Besides the chemical structure, density and hardness, the attention is focused on the characterisation of the friability of shells. Knowledge of this property enables to determine the adequate application areas of shells as abrasive. Friability denotes the tendency of a solid material to break into smaller pieces under contact (Momber, 2007). Friable materials tend to break up without significant plastic deformation, unable to absorb deformation energy. Friability is measured by dynamic tests. In the industrial environment, the friability index (FI) and the toughness index (TI) are used. There is no international norm to measure or evaluate the friability, only the American ANSI B74.8 has been proposed for the abrasive industry (Ansi, 2007). An amount of abrasive of a known grit size is ground for ten minutes in the planetary mill, to analyse the proportion in weight of grains that do not break (FI) or do break (TI). Using similar procedures, different sectors have developed *ad hoc* tests and equipment (mining, pharmaceutics, abrasives, diamonds…) (Shepler and Whitney, 1978; Jackson and Davim, 2011; Vollstädt, 2016).

In sandblasting, friable abrasives are used in single-use applications (shipbuilding, building and monument restoration, …). In turn, high toughness is required by the industry in order to reuse the abrasive several times. Very friable abrasives are also appropriate for fine operations, which minimise damage on the part surface at the expense of the grit integrity; similar effect is achieved with tough and low density abrasives, which reduces the impact energy (e.g. plastic abrasives in aeronautics). Friability and hardness are not directly related, but hard abrasives are usually fragile. Grit size and friability are related: since smaller solids and crystals have smaller surfaces, they show fewer defects (Field and Freeman, 1981).

In this work, the friability of shells has been studied from two points of view. The first one evaluates the effect of the sterilisation treatment on the cohesion of calcium carbonate crystals due to the induced damage in organic matter. The influence of four sterilisation treatments of shells on friability is compared; the study comprises one thermal treatment and two chemical treatments (hydrogen peroxide and sodium hypochlorite). No comparison has been presented up-to-date in the literature, nor the analysis of the variation of physical and mechanical properties of shells after sterilisation. The second point of view compares the friability of mussel shells and garnet (a common abrasive material) according to ANSI B74.8 (Ansi, 2007). Few works on friability have been presented in literature, as (Yashima et al., 1987). The study of friability will offer the true profile of shells as abrasive as a whole.

This work has the following structure. The second section presents the methodology and structure of experimental work followed. The third section describes the calcium carbonate crystal layer structure of mussel shells. The section also looks deeply into physical and chemical properties of mussels. The fourth section examines the effects of sterilisation processes on the organic matter and friability of shells by means of a tailor-made test. In turn, the fifth section compares the friability of mussels and garnet. The last two sections correspond to discussion and conclusions, which the evaluates the results and propose feasible applications of mussel shells to be used as abrasive.

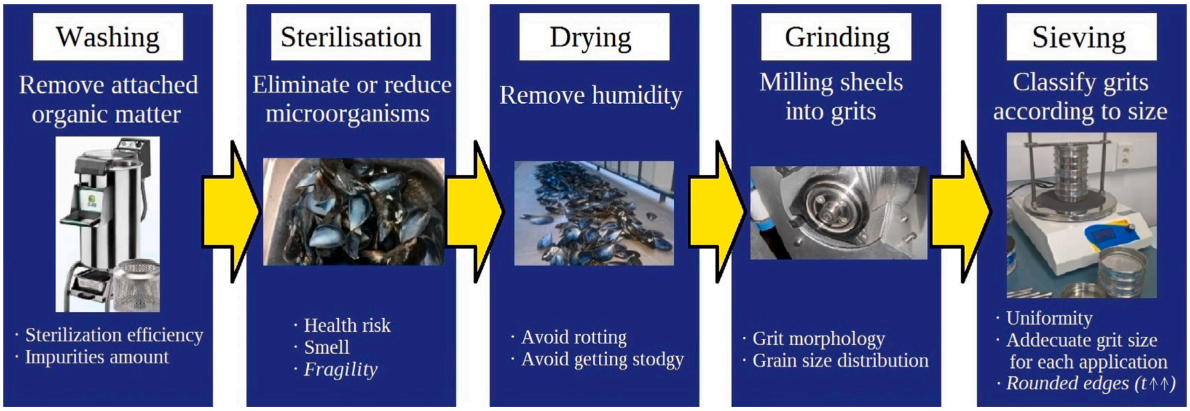


Fig. 1. Flow-chart of the steps to turn shells into abrasive sand. The effects and damage of the operation on the abrasive characteristics are listed below.

2. Materials and methodology

Different mussel species are farmed all over the world; the blue mussel (*Mytilus edulis*), the Mediterranean mussel (*Mytilus galloprovincialis*), the green mussel (*Perna viridis*), the Chilean blue mussel (*Mytilus chilensis*), the green-lipped mussel (*Perna canaliculus*), and the thick shell mussel (*Mytilus coruscus*) are the main ones. Shells used in this work have been provided by a restaurant specialised in mussels (La Mejillonera, San Sebastian). They come from O Grove, Galicia (NW Spain), where Mediterranean mussels (*Mytilus Galloprovincialis*) are grown. They belong to E-2 and N-1 commercial calibres (28–32 units/kg). Once mussels have been cooked for 5 min at 55 °C, they are served with one of the shells removed, the one used in our research. In that way, those shells have been almost untouched, without suffering heat damage and free of oil. These conditions are similar to the ones used in the canning industries.

Garnet origin is United Arab Emirates (Blasbrite Gulf). The mixture consists mainly of garnet (98%), almandine and pyrope minerals. The free crystalline silica fraction is less than 0.03%, far from the 1% threshold set by international labour safety regulations (Baron et al., 2002). It is known that the inhalation of free crystalline silica causes the silicosis labour disease.

The experimental work is divided into three parts (Fig. 2). The first part comprises the characterisation of the materials, mainly mussels shells, but also garnet. Among others, chemical composition and physical properties of shells have been studied. The second and third parts study the friability of mussel shells: the second studies the effects of the sterilisation treatment, whereas the third one compares the friability of shells and garnet.

2.1. Structure and physical–chemical properties of mussel shells

Table 2 compiles the description of the tests performed to characterise the physical and chemical properties of mussel shells and the equipment used. Among others, density, hardness, biometry, and mass of shells have been measured. The chemical composition and layer structure of shells has been studied too. Special effort has been put into the definition of the organic matter content by thermogravimetric analysis (TGA) and under isothermic conditions at 525 °C in the muffle.

The chemical composition and structure of shells determine their physical properties, such as density, hardness, and friability. The organic matter of shells leads the need for a sterilisation treatment to reduce microbial life. Physical properties have a direct effect on the potential energy and efficiency of the grain in the drilling process. The biometric dimensions of shells, besides defining the initial conditions of the grinding process, have a direct effect on the maximum grain size, especially thickness. Samples for hardness tests have been prepared embedding shells in polyurethane blocks (Cronodur PU-90, Plastiform). The effect of the topography has been minimised by finely polishing the sample surface with alumina grits (0.3–0.5 μm).

Grain morphology depends on the grinding technique. In this work, the planetary ball mill has been used, where friability tests have been conducted. The grinding efficiency has been evaluated examining the grain size distribution by sieving. Each test has been repeated twice. A biometric study has been carried out to determine the size of shells used in this work. In addition, grain morphology has been studied by means of optical microscope.

2.2. The effect of sterilisation of shells

The organic bonding material of shells, as an organic-mineral composite, may be damaged by the sterilisation process. It would be desirable that the sterilisation of shells would create as little damage as possible in organic matter. The influence of the sterilisation process has been studied from two points of view: the fraction of organic matter by isotherm degradation in the muffle and the friability. The isotherm testing conditions agree the ones described in Table 2. In turn, the friability test in the planetary mill has been adapted to allow the use of large pieces of shell.

Four cleaning conditions have been considered. All samples are washed previously for 25 min in the drum washer with bare water to remove the organic matter attached to the shells (flesh remains, byssus, algae, …). Table 3 introduces the conditions of the four sterilisation processes studied. The sterilisation treatments have been applied on entire (no ground) shells in batches of 0.5 kg. Heat treatment has been applied on an oven (JC Selecta Vaciotem-TV) placed uniformly on two trays. Chemically treated shells have been immediately washed again to rinse the chemical products and, afterwards, they have been dried up in ambient conditions for two days. The liquid-to-solid ratio (L/S) considers dry mass of shells. Their features are compared with non-treated shells, which are the reference.

Although sterilisation is intended to destroy microorganisms, the probability of survival of a microorganism is never zero. The thermal treatment conditions comply the (EC) 1069/2009 regulation. Hydrogen peroxide (H_2O_2), although not found as treatment for shells in literature, has been added to this study because it is common in sterilisation treatments (Rutala and Weber, 2008; Mendoza et al., 2021). The sodium hypochlorite (NaClO) has been tested under two conditions: stirring for 10 min, and soaking for 12 h. The vinegar treatment has been disregarded because one of its components, the acetic acid, dissolves the calcium carbonate. Further tests are needed to optimise the concentrations and duration of chemical treatments according to the number of surviving microorganisms (Regulation, 2009). Higher concentrations do not ensure greater efficiencies and speeds.

The friability test aims to examine the consequences of possible harm produced by sterilisation. The standard friability test (Ansi, 2007)

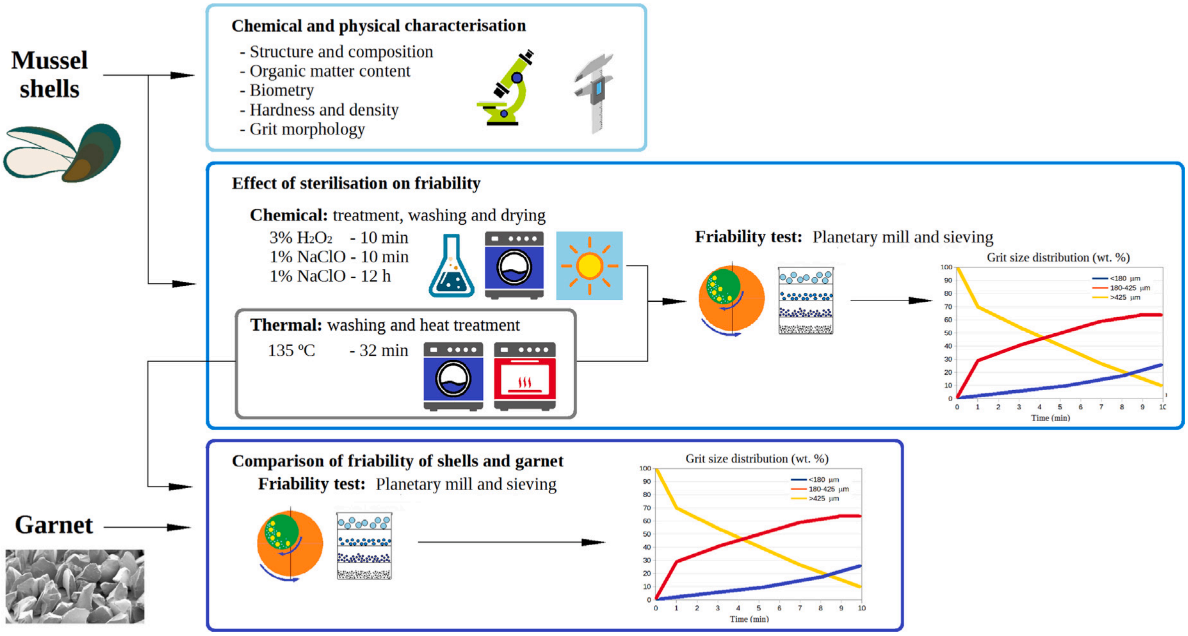


Fig. 2. Flow-chart of this work divided in three steps: the analysis of the chemical–physical properties of mussel shells, the effect of the sterilisation on friability, and the comparison of the friability of shells and garnet.

Table 2
Measurements of chemical and physical properties of mussel shells and the equipment used.

Chemical composition	Description and conditions	Equipment
Organic fraction	TGA thermogravimetry, a sample of 4 mg is heated from 25 °C to 800 °C in inert nitrogen atmosphere at 10 °C/min. Isotherm conditions in muffle, three samples of 1.2–1.9 g of shells have been kept for two hours at 525 °C for each treatment.	Mettler Toledo TGA/SDTA 851 Carbolite - Gero ELF
Physical properties	Description and conditions	Equipment
Density (g/ml)	Shells: shell fragments (solid material) using the Archimedes principle in water environment, the density of 8 samples between 0.38–0.77 g have been measured with a densimeter. Garnet: garnet sand (granular material) using the Archimedes principle in water environment, the density of 8 samples between 4.1–5.5 g have been measured with a pycnometer.	Mettler Toledo AJ50 Pycnometer
Hardness (HV)	Vickers surface hardness (HV), average value of >40 measurements of hardness of each layer (calcite and nacre). Load $P = 0.3$ kg, dwell time $t = 12$ s	HVS-1000
Biometry (mm)	Measurement of the dimensions of shells (length, width, height, and thickness); sample size: 100 shells.	Caliper
Mass (g)	Measurement of the mass of shells; sample size: 100 shells.	Nahita KBC001
Grinding	Planetary ball mill: shells together with steel balls are ground in a closed container with planetary motion (two rotations: the container itself and an orbit).	Retsch PM100
Sieving	Grits are sorted according to size by passing from large to small mesh with aid of vibration.	Cisa BA200N
Microscopy	Optical microscope	Nikon Eclipse 80i

Table 3
Sterilisation conditions.

No treatment	Thermal	Chemical		
(reference)		Hydrogen peroxide H_2O_2	Sodium hypochlorite NaClO	Sodium hypochlorite NaClO
Washing 25 min ↓ Drying	Washing 25 min ↓ 135 °C 32 min	$[H_2O_2] = 3\%$ L/S = 3.6 ml/g 10 min stirring up ↓ Washing 25 min ↓ Drying	[NaClO] = 1% L/S = 3.6 ml/g 10 min stirring up ↓ Washing 25 min ↓ Drying	[NaClO] = 1% L/S = 3.6 ml/g 12 h soaking ↓ Washing 25 min ↓ Drying

has been adapted to study the breaking trend of shells. In the planetary mill (Retsch PM100), after grinding pieces of shells (almost entire) for a certain time, the size distribution in weight has been measured: the more fragmented material, the more fragile it is. Each case has been tested twice.

Preliminary tests have been conducted to determine the testing conditions. Maximum rotational speed has been set, 650 rpm, because shells do not break at low and moderate speeds. 30 steel balls (diameter 10 mm, 127 g in total) and shells cleaned with water (size > 1120 μm, 100 g) have been ground in a 250 ml jar in the planetary mill. The grit size distribution has been measure every minute, 10 min in total. The sieve sizes used are 1120 μm, 425 μm, and 180 μm.

2.3. Comparison of the friability of shells and garnet

The friability of mussel shells and garnet (a conventional abrasive) have been compared according to ANSI B74.8 standard friability test. After the heat treatment, the shell sample has been prepared with a Retsch SM100 cutting mill. Samples of known size (425–600 μm) have been ground for 10 min in the planetary mill and the grit size distribution has been measured sieving them. This particular size has been deliberately chosen, because the average thickness of mussels shells lies in this interval. To analyse the development of the grinding process, the grit size has been measured every minute. The same volume of the two materials has been ground (100 ml); but, as they differ in density, the mass of shells and garnet samples are different (135 g and 210 g respectively). Sieves of 425 μm and 180 μm mesh size have been used and, as in the previous test, 30 steel balls of 10 mm of diameter and 250 ml volume jar. The test has been repeated twice for both materials.

3. Physical–chemical properties of mussel shells

This section has three parts. First the layer structure of mussels shells is described. Then the focus is on the organic mater content of shells. Finally, the physical and mechanical properties of the shells, derived from the structure and chemical composition of the layers, have been studied.

3.1. Structure of mussels shells

Mussels are marine lamelibranchian bivalves. They live in the shallow waters of the estuaries and marine intertidal coasts. The shell has a sharp shape at one end, and rounded at the other. The shell surface is flat, only the growth lines are noticeable. The shell is black and bluish, blue tinted inside. The shell has three layers (Kennedy et al., 1969): the periostracum and two calcium carbonate layers (Fig. 3). The periostracum is the outer organic layer that, not only supports the growth of calcium carbonate crystals, it also seals the inner space to achieve supersaturation conditions. The two mineral layers are polymorphous calcium carbonate; the order of the molecules within the crystalline networks is the only difference between them (Zhang et al., 2012). The aragonite forms the nacreous inner iridescent layer; arranged in parallel, it consists of 0.5 μm thick and 10-20 μm wide platelets. The tilted prismatic structure of calcite fibres between nacre and periostracum form the middle layer.

Even though the organic matter fraction is lower than 5% of the shell, it plays an important role in mineral nucleation and growth (Agbaje et al., 2018). A significant part of the organic phase consists of insoluble biomacromolecules rich in acid branches, including chitin. The surface periostracum consists of organic matter, where calcium carbonate crystals are deposited inside by precipitation. These form the scaffold of the inorganic phase (Song et al., 2003). Nacre is considered to be a ceramic composite with its microarchitecture of brick and mortar (BM), where bricks are flat polygonal crystals and mortar is the bonding material composed of polysaccharide and protein fibres. Several studies have shown that the improved resistance and toughness of nacre arises from this especial microarchitecture. For example, the toughness of abalone nacre is 3000 times larger than a single crystal of pure mineral. Although no mention has been found, the intermediate calcite layer forms a similar BM structure, where the platelet aragonite is replaced by needle like prismatic calcite. It must be added that the sandwich-like layer arrangement of shells, periostracum–calcite–nacre, and the curved dome geometry, improves significantly the mechanical behaviour of the shells on the macro-scale. Therefore, they are more tough and resistant than expected for a high mineral content biomaterial (Chakraborty et al., 2020).

3.2. Organic matter content

After collecting the structural information of layers of mussel shells in literature, the organic material content of the *Mytilus Galloprovincialis* shell used in our work have been studied through the degradation of shells at high temperature. Shell specimens have not undergone sterilisation treatment. The thermograms of Fig. 4 show the development of thermal degradation in shells. The first zone (I), between 25 °C and 150 °C, is related to the humidity of mussels shells, with a loss of 0.53% regarding the initial mass. In the second zone (II), the observed mass loss between 150 °C and 500 °C corresponds to the organic fraction of mussel shells (polysaccharides, proteins and glycoproteins) (Martínez-García et al., 2017). This mass loss reaches the 3.5% regarding the initial mass. Finally, in the third zone, between 500 °C and 800 °C, notices the decomposition of $CaCO_3$ in the CaO and CO_2 compounds (Martínez-García et al., 2017).

Thermal degradation analysis has also been conducted under isotherm conditions in the muffle (2 h at 525 °C). The weight loss of the sample has been attributed to the organic matter fraction. The results have determined 5.07 ± 0.12% content of organic matter, which agrees the results found in the literature (Agbaje et al., 2018). The differences between TGA and isotherm degradation can be attributed to the different boundary conditions: nitrogen atmosphere and dynamic heating in TGA, while muffle contains oxygen and the temperature is constant.

3.3. Physical properties of mussel shells

As mentioned in the introduction, density, hardness and friability of the abrasive have influence on the sandblasting process. In this section, the first two properties are examined, whereas the following sections are focused on the friability. This section includes the biometry of shells and grit morphology analyses.

Regarding the density, shells show a density of 2.60 ± 0.04 g/ml, about a quarter smaller than garnet (3.52 g/ml). This has a direct impact on the potential energy of grains during sandblasting: with the same projection speed, shell grits will have 26% less energy than garnet.

The average Vickers hardness of the inner nacre layer is 2.934 ± 0.76 GPa, whereas the middle calcite layer shows an average hardness of 1.949 ± 0.26 GPa. The standard deviation of aragonite is higher because it depends on the orientation of the cutting plane of the measuring block surface: the hardness values observed on the oblique plane are higher (3.24 GPa) than on the perpendicular (2.69 GPa) and the parallel (2.61 GPa) planes regarding the platelet layer. In turn, the calcite does not show dependence on the measurement orientation. The periostracum, as organic layer, has the smallest hardness values (0.33 GPa). However, the cleaning of shells removes significantly this layer due to the friction mechanism between them. Once shells are ground, hardness lies between these three values; the same grit may also have several hardness values depending on the layers that form the grit (see Fig. 3). Some studies have observed that the hardness of shells is load independent. This is probably due to BM structures of nacre and calcite layers (Chakraborty et al., 2020; Mohammadi et al., 2019). On the other hand, the garnet has shown a hardness of 12.59 ± 1.78 GPa, four

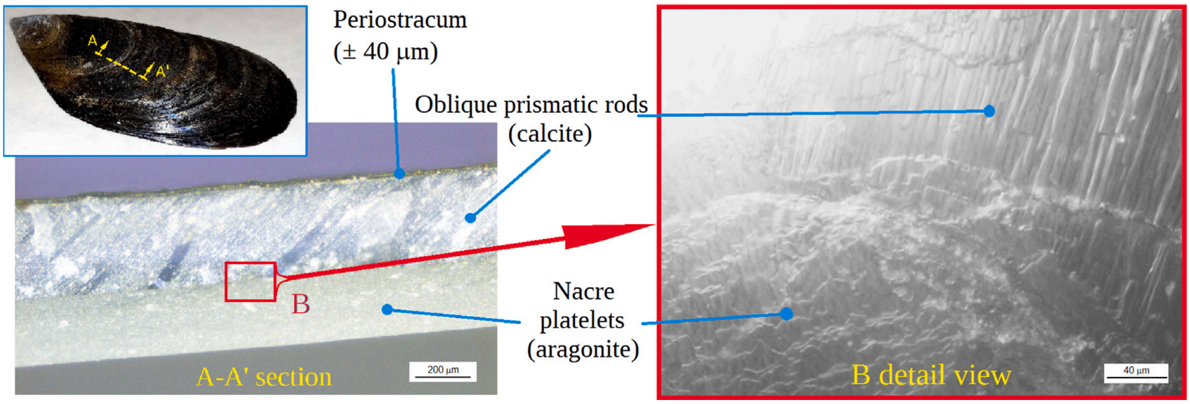


Fig. 3. *Mytilus Galloprovincialis* mussel shell section observed by optical microscope. The organic outer layer (periostracum), besides protection, plays a key role in the precipitation of calcium carbonate throughout the growth of the shell (Klünder et al., 2008). The crystalline part of the shell consists of two layers: calcite and aragonite nacre (Kennedy et al., 1969).

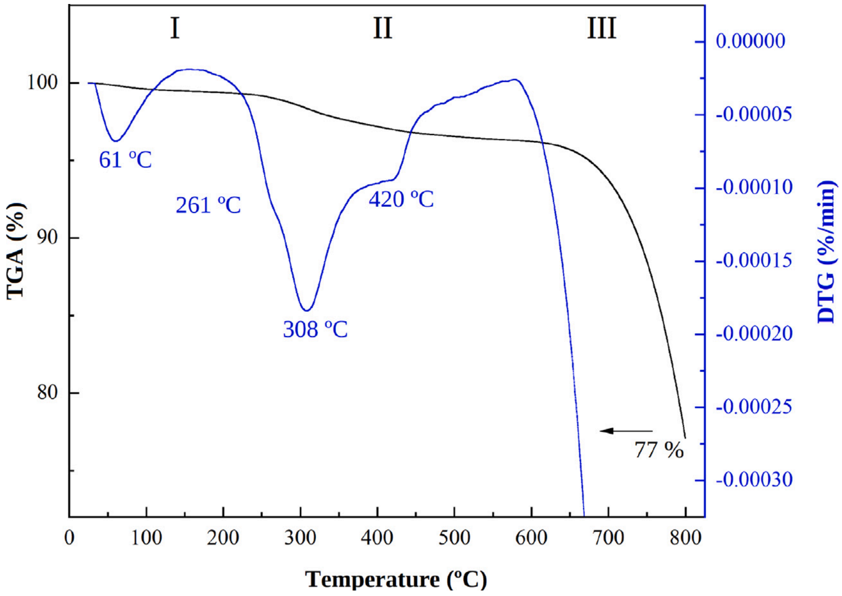


Fig. 4. TG/DTG thermograms of mussel shell powder.

times higher than nacre's. In sandblasting, hardness is an important characteristic, but not the most: during the impact between the grit and target surface, there is an energy exchange. If the grit is softer, it may absorb more energy in form of plastic deformation and the impact is less aggressive for the surface. So according to the application, soft abrasives may be more suitable than hard ones, e.g. aluminium parts in aeronautics.

Biometric measurements have been made to determine the dimensions (length, width, height, and thickness) of *Mytilus Galloprovincialis* shells. 100 shells have been chosen randomly after washing and drying (Zorita et al., 2019). Shell thickness has been measured in three areas (T1, T2 and T3). Since the thickness is variable at the measurement point, the shell thickness index (STI) has been used (Babarro et al., 2020):

$$\mathrm{STI} = \frac{1000m}{\pi L\sqrt{H^2 + W^2}}$$

where m is the dried shell weight, L is the length, H is the height and W is the width. A higher shell thickness index indicates a thicker shell. Table 4, besides the dimensions and position of thickness measurement points, also provides the results of the biometric measurements. Results make evident the dispersion of dimensions, because the growth degree of mussels amongst them differs, even though they belong to the same commercial calibre.

Shell thickness determines the maximum size of grains. Shell thickness depends on the point of measurement within the shell: younger sites (0.38 – 0.80 mm) are thinner than the older ones (0.60 – 1.12 mm). Thus, the maximum average grain size that can be obtained is 0.60 mm, enough for most sandblasting applications. Grits can be composed of one, two or, if they get the whole thickness, three layers. Therefore, physical properties of grains (hardness, friability, resistance, etc.) are directional, as well as edge morphology. The mixture of grains homogenises properties, which is precisely observed in experiments.

The morphology of ground grains also affects the performance in sandblasting. Taking into account the random nature of grain morphology, grain may be cubic or elongated according to the aspect ratio (the relation between the largest and the smallest dimension of a grit). They may also have sharp or rounded edges. These properties have direct influence on the interaction of the abrasive with the workpiece surface, on the way of energy transmission and on the grit dynamics in the bounce. Although it may seem otherwise, sharp-edged grains are not always more suitable than rounded ones, especially when the objective is to clean surfaces (Momber, 2007). Grain morphology also affects the apparent density: small grains and those with a high aspect ratio tend

Table 4
Average values (x) and standard deviation (s) of the measured parameters; on the right, figure that points out the measured dimensions and thickness measurement points on shells.

	Feature	$x \pm s$	Max.	Min.
Dimensions	**L (mm)**	76.70 ± 8.50	101.8	61.5
	W (mm)	38.20 ± 4.00	49.7	31.4
	H (mm)	12.40 ± 1.60	17.6	9.0
	L/W	2.01 ± 0.10	2.23	1.79
Thickness	**T1 (mm)**	0.87 ± 0.15	1.12	0.60
	T2 (mm)	0.69 ± 0.14	0.90	0.45
	T3 (mm)	0.58 ± 0.11	0.80	0.38
	STI (mm)	0.72 ± 0.14	0.97	0.42
Mass	**m (g)**	5.40 ± 1.70	12.0	2.6

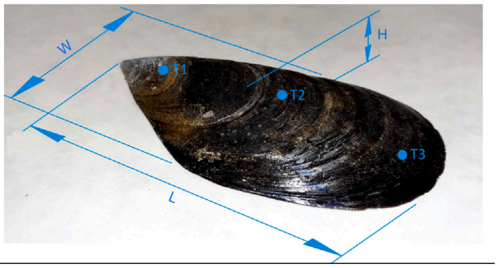
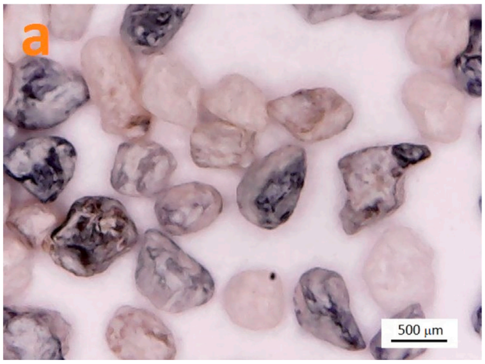
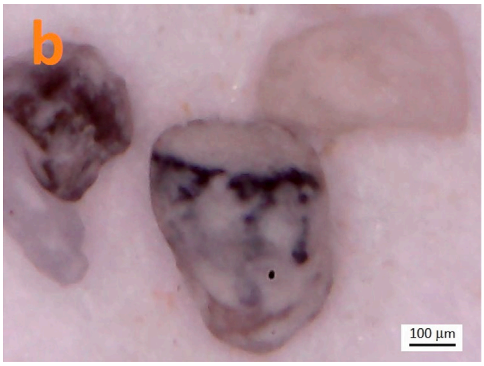
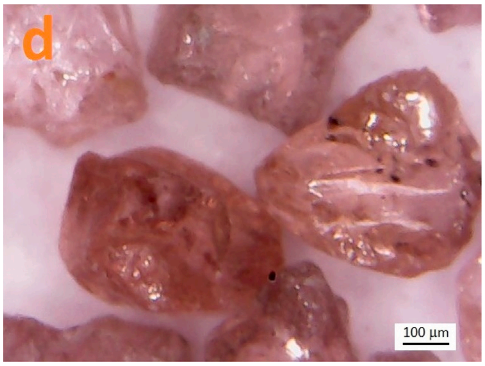


Table 5
Morphology analysis of grits by optical microscopy: (a, b) rounded shell grains ground in a planetary mill, layers can be distinguished within the grains; (c, d) garnet has natural origin, impurities can be noticed.

 	
 	
Shells (a, b) · Round edges. · Geometry: cubic and oval. · Aspect ratio: 1.2–1.5. · Colour: white, dark blue and black. · Structure: layers, crystalline with organic bond.	**Garnet (c, d)** · Sharp edges. · Geometry: angular (tetrahedric) and cubic. · Aspect ratio: 1.1–1.6. · Colour: burgundy. · Structure: crystalline (bright faces), amorphous.

to have a lower apparent density. Grit morphology has been studied with optical microscopy for ground shells and garnet (Table 5).

Grain morphology depends on the grinding process. In this work the planetary ball mill has been mainly used to grind shells on a laboratory scale. When grinding, shell grains interact with the steel balls and other grains. The friction between them leads rounded edges. In turn, if a cutting mill were used, shells would break in a fragile way obtaining sharp edges. At the same time, the grinding conditions in a given mill affect the grain size distribution obtained: the aperture of the bottom sieve in the cutting mill and the grinding time in the planetary ball mill.

4. The effect of the sterilisation treatment on shells

The effect of shell sterilisation treatment on the organic matter content and friability is analysed in this section. Five cleaning conditions have been studied (see Table 3). Shells washed with water are the reference.

4.1. Organic matter

The organic matter content has been measured by means of isotherm degradation in muffle (2 h at 525 °C). The specimens have been selected regarding surface cleanness (without byssus, serpulids and barnacles), regular growth (without injuries and deformations) and similar dimensions (80 mm length and 40 mm width). Shells are cut in three zones in order to identify differences in content between older and newer shell regions (Fig. 5). Entire parts have been tested in the muffle. The graph shown in Fig. 6 compiles the results.

Results show that region I has the highest organic matter content, around 1.2% higher than regions II and III. Regarding the sterilisation treatment, the heat treatment has lost the most the organic matter (1%), the hydrogen peroxide the least (0.1%), and the sodium hypochlorite lays in between, regarding treatment conditions (0.6% and 0.8%).

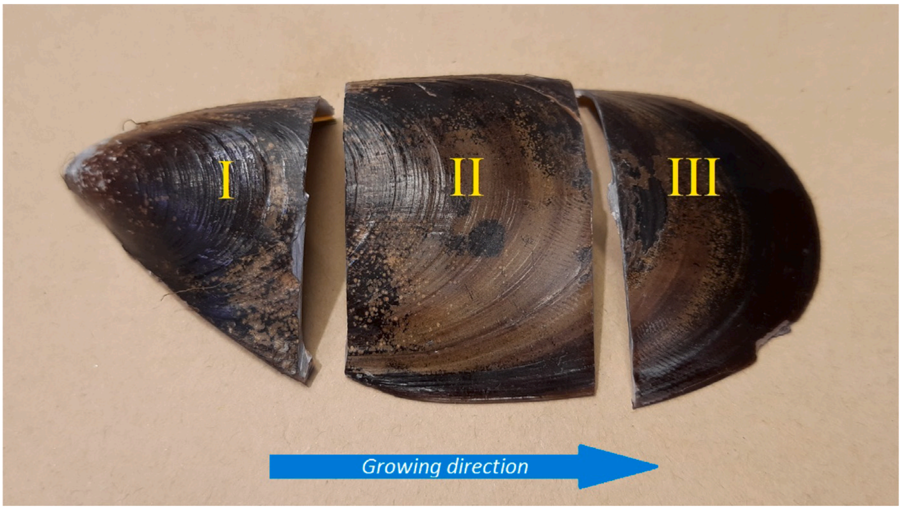


Fig. 5. Shell regions studied in the muffle: (I) region corresponds to the oldest and thickest region, whereas (III) is the newest and thinnest one.

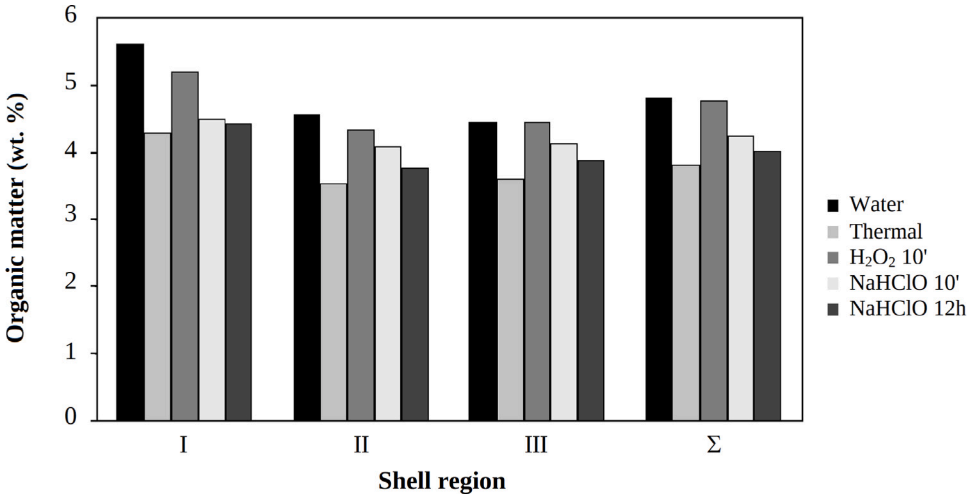


Fig. 6. Percentage of organic matter content on each shell region (I, II, III) and sum of them (Σ).

4.2. Friability

Preliminary tests were made with untreated shells to know the development of the grinding process and to set the test parameters. The grit size distribution has been measured every minute, 10 min in total. Fig. 7 presents the development of the grit size distribution in the grinding process.

The graph of Fig. 7 shows that half the shells broke in the first two minutes. The fraction of small grains (<180 μm) increases linearly over time. The intermediate size (425–1120 μm) at first increases rapidly, but then it gets the maximum and tends downward. This behaviour is the result of two effects: on the one hand, the proportion of them is increased as large pieces break into large grains, on the other hand, they are also ground by the steel balls.

Based on these results, it has been decided to test the friability regarding the sterilisation treatments measuring the grain size distribution of 100 g shells after grinding for two minutes at 650 rpm and 30 steel balls of ø10 mm. Each test has been repeated twice; the results in Fig. 8 are average values.

In the graph of Fig. 8, it is remarkable that for all sterilisation conditions in two minutes test, more than half in weight reduces the size to <1120 μm. However, there are differences between them: from 48% of untreated shells to 36% of NaClO 12 h. The three other treatments have shown similar friability, being the H_2O_2 samples slightly tougher (up to 2%–3%). Looking at the smallest size fraction (<180 μm), NaClO 12 h samples are the most friable (19%), showing the other four cases similar results (between 14% and 15%).

The isotherm degradation analyses show that the heat treatment damages the most the organic matter. The highest toughness is achieved by washing the shells with water (the reference); however, H_2O_2 treatment has shown the best behaviour among the sterilisation treatments. It has been decided to continue the work with the heat treatment, since the waste water of H_2O_2 treatment requires purification before being released into the environment. In addition, the heat treatment already meets European health regulations; it does not require further validation tests and certification of microbial life and sterilisation performance.

5. Comparison of the friability of shells and garnet

Once the sterilisation process has been defined, the hardness and friability of heat treated mussel shells face a conventional abrasive, the garnet.

The Vickers hardness of garnet has been measured under the conditions described in Table 2. Garnet hardness, 12.6 ± 1.8 GPa, stands out regarding nacre (2.9 GPa) and calcite (1.95 GPa) because of its crystalline silica structure.

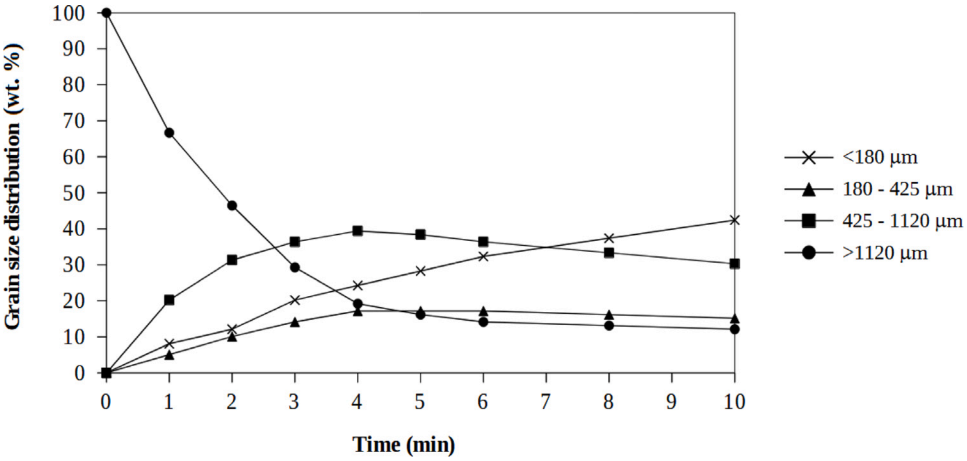


Fig. 7. Preliminary friability test with untreated shells, evolution of the grain size distribution.

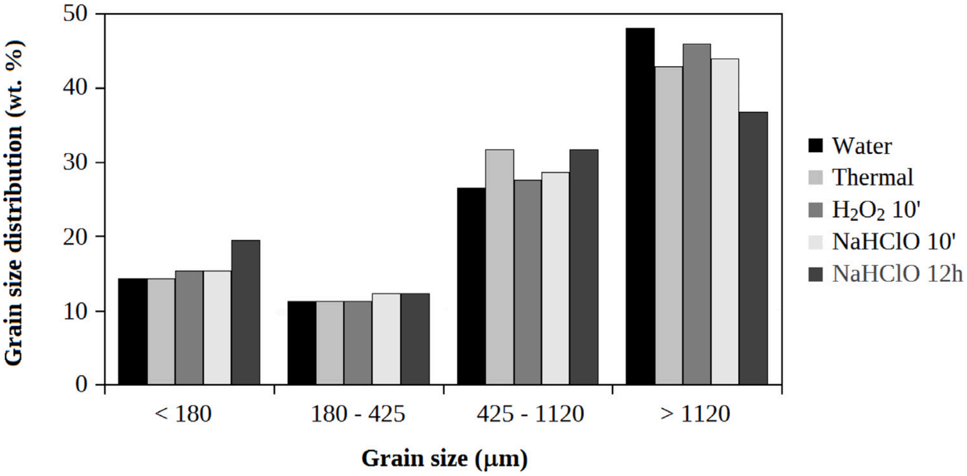


Fig. 8. Grit size distribution after two minutes of friability tests in the planetary mill regarding the sterilisation treatment.

The friability of shells and garnet has been compared according to the standard ANSI B74.8 (see Section 2.3). Figs. 9 and 10 show the grain size distribution of each material per minute. In turn, Fig. 11 combines the results of the two materials focusing on the unbroken fraction every minute (> 425 μm).

Analysing Figs. 9–11, it is evident that garnet is more friable. In the first minute, 30% of the garnet breaks, when only 10% does in the shells. High fracture rates are observed at the beginning, because grains with faults (cracks, pores, inclusions) break almost without effort. Shells must be ground for almost four minutes to reach 30% level. After the first minute, the >425 μm fraction maintains a linear breaking rate on both cases: 8%/min for the garnet and 6%/min for the shells. After 10 min, the difference is noticeable: 90% of the garnet reduces the initial size, compared to the 57% of the shells. In the garnet, 250–425 μm fraction reaches the maximum in the 7th minute, while shells achieve the maximum in the 10th minute.

6. Discussion

In this work, the characteristics of mussel shells have been studied to be used as abrasive in sandblasting. Special attention has been paid to friability, an essential property in the industry but scarcely cited in literature.

Shells are layered structure biocomposite materials which combine mineral nature calcium carbonate crystals and organic matter. The grinding of mussel shells form heterogeneous grits composed of one, two or three layers with different structure and orientation. This hinders to foresee fracture behaviour of a single grit, but the analysis of several grits altogether homogenises the overall behaviour. The sharpness or roundness of the grits depend on the grinding process. The planetary ball mill produces rounded edges due to friction between grains, but sharp edges can be obtained using a different type of grinding mill. In this way, the sharpness of grains can be adjusted to the sandblasting process.

It has been analysed the effect of four sterilisation treatments on shells, in particular on the organic matter content and friability. H_2O_2 treatment maintains the organic matter fraction, whereas NaClO losses 0.6–0.8%. The heat treatment losses the most organic matter in the isotherm degradation, due to those shells already have lost the inherent humidity. Regarding friability, treated shells reduce between 2% and 3% comparing with untreated shells. However, the enlarged NaClO treatment increases friability up to 12%; this occurs because its BM structure has been more exposed to NaClO and, thus, organic matter has been degraded more. The heat treatment has been chosen instead of chemical treatments to avoid the waste water management and certification procedures. There has not been studied the influence of mass and exposure of shells on the heat treatment. Heat treatment conditions could be used to adapt the friability for a given sandblasting application and, thus, it would become a versatile abrasive.

Then, the friabilities of heat treated shells and garnet (a common abrasive) have been compared. Results agree other researches assessment regarding the improvement of mechanical properties due to the

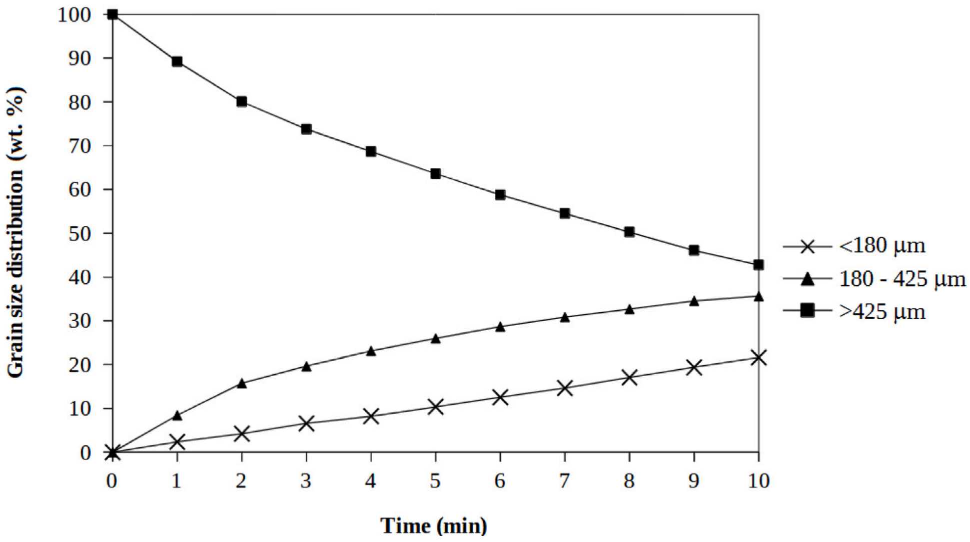


Fig. 9. Shell friability test: grain size distribution in weight.

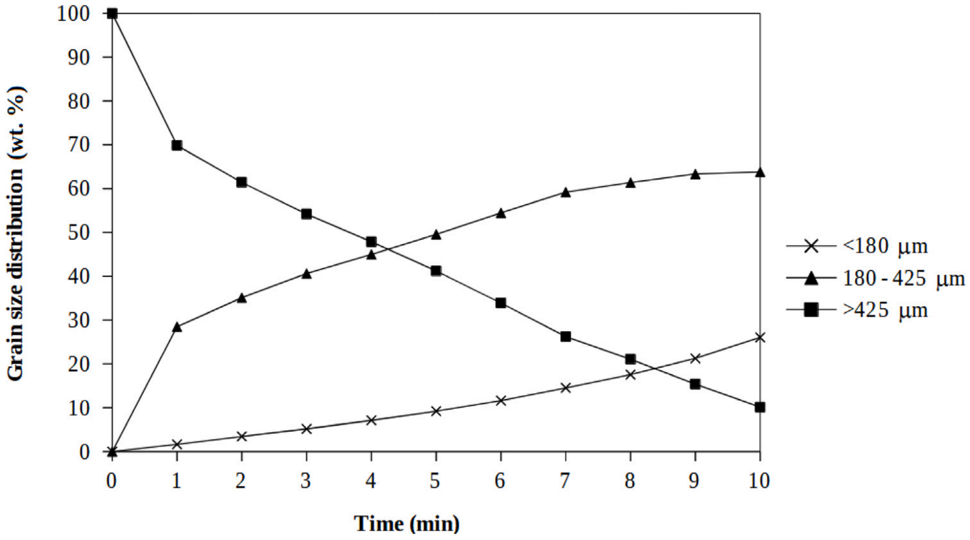


Fig. 10. Garnet friability test: grain size distribution in weight.

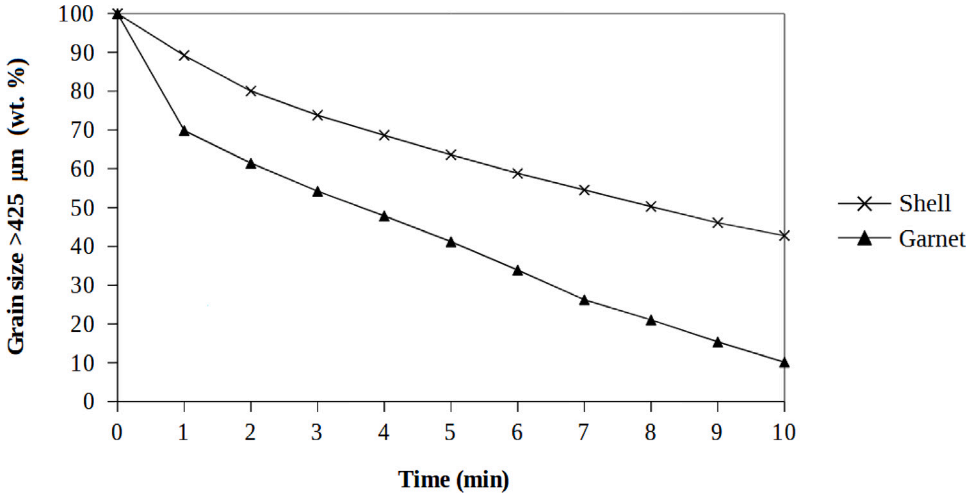


Fig. 11. Comparison of shells and garnet friability: evolution of the unbroken fraction (> 425 µm).

BM structure of shells, specially toughness is greatly increased. Taking into account the fragile nature of the calcium carbonate, the organic matter not only distributes the forces between calcium carbonate crystals, it also allows a little relative movement between them, which absorbs the impact energy as deformation. Garnet is four times more friable than shells. This means that shell grains endure more impacts maintaining their integrity and, thus, they can be reused in several cycles in the sandblasting process, thus reducing sand consumption.

However, the density of shells is one-third smaller than garnet's. Knowing that the main mechanism of sandblasting is the energy exchange in the impact of the grit on the workpiece surface, the kinetic energy of the grit is proportional to its mass. Then a softer impact is expected from shells, less aggressive than the garnet. This makes it interesting for delicate applications that have high added value, such as aerospace industry or art restoration. As a biomaterial, it is environmental friendly and it is also suitable for outdoor interventions, such as building and structure restoration, or in shipbuilding. In these applications, if there is a loss of abrasive or just one use, calcium carbonate will not cause any environmental damage.

Regarding the sustainability issues of the new abrasive, it is difficult to quantify the degree of sustainability achieved. From the environmental point of view, a life cycle assessment (LCA) for a given application would be required. On the one hand, waste is used as raw material. On the other hand, energy is consumed in the transportation and in the transformation into sand of shells (mainly in the heat treatment). Chemical sterilisation treatments would require to purify waste waters. To reduce the transportation energy consume, it would be advisable to locate the abrasive processing plant and the end consumer as close as possible from mussel farms. The abrasive processing could be done within mussel canning plants. As mussel culture is spread all over the world, the supplier and consumer could be close each other. However, mussel culture, besides the obvious role of generator of nutritive proteins, mitigates the huge environmental and social impacts of terrestrial food production systems (Suplicy, 2020). The small impact of bivalve aquaculture on the environment has been assessed, where the difficulties for collecting shell of fresh consumed mussels hinders the management of this $CaCO_3$ source (Iribarren et al., 2010; Alonso et al., 2021).

In the same way, it is difficult to estimate the quantity of shells that could absorb the new abrasive: an intensive single use abrasive in shipyards, cleaning in a closed loop in metalwork or to fade denim in textile industry.

7. Conclusions

Shells entail the dark side of the mussel production regions, where traditionally shells have been treated as waste and have been deposited either on land or under the waters near the coast. Both options generate a strong environmental impact. The situation is turning over, the global community devotes an enormous effort to look for solutions to use the shell waste as $CaCO_3$ raw material. This work tackles the issue on the physical and mechanical characteristics of mussel shells: they are hard and brittle, so, once ground, the resulted sand can be used as abrasive in sandblasting.

The study concludes that shell abrasive can be classified as soft abrasive: medium density and hardness, edges can be sharp or round regarding the mill used and it shows low friability. In particular, the focus is put on the last feature, the friability, a property that deserves visibility in the literature. The results conclude that the BM structure of $CaCO_3$ crystals and organic matter provides an enhanced toughness, which is hardly expected from a mineral. A 5% of organic matter has been measured, which can bring salubrity problems. The heat treatment has been chosen to sterilise the shells, which does not damage excessively the inner structure and, thus, it maintains the friability.

The project will continue evaluating the efficiency of mussel shell abrasive in sandblasting for various materials and the impact on the environment (LCA). The variation of friability with the intensity of the heat treatment is also a promising line of research.

Lastly, this work has proposed the revaluation of a waste material, hard to reuse and manage, into a technical material of high added value. The goal is to promote circular economy and to ensure responsible management of residues giving them a second life.

CRediT authorship contribution statement

J.L. Osa: Conceptualization, Methodology, Investigation, Formal analysis, Writing – original draft. **G. Mondragon:** Investigation. **N. Ortega:** Validation, Writing – review & editing. **F.F. Marzo:** Validation, Writing – review & editing. **C. Peña-Rodriguez:** Conceptualization, Methodology, Writing – review & editing, Funding acquisition, Supervision.

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.

Data availability

Data will be made available on request.

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