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Mechanical properties of mortar containing recycled *Acanthocardia tuberculata* seashells as aggregate partial replacement

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ABSTRACT

Waste management is a most current topic, and as such, numerous articles in literature discuss over the recycling and re-use of waste materials from various fields. A common solution is the to use these materials as partial substituent of the inert fraction in concretes and mortars. This work focuses on the possibility of using *Acanthocardia tuberculata* seashells, which constitute a food waste destined to landfilling, as partial substituents of inert in mortars. The results obtained evidenced that the reduction in mechanical properties (in terms of toughness and flexural stress) is mainly due to the water absorption properties of seashells aggregates, which affect the hydration of the cement. However, as experimentally demonstrated, such decrease in mechanical properties in any case does not compromise the performance of the material when used for civil applications.

Propiedades mecánicas del mortero que contiene conchas marinas *Acanthocardia tuberculata* recicladas como reemplazo parcial del agregado mineral

Palabras clave:
Mortero
Propiedades mecánicas
Desechos alimentarios
Sostenibilidad
Reciclaje de conchas marinas

RESUMEN

La gestión de residuos es un tema actual, y como tal, numerosos artículos en la literatura discuten sobre el reciclaje y la reutilización de materiales de desecho de diversos campos. Una solución común es utilizar estos materiales como sustituyentes parciales de la fracción inerte en hormigones y morteros. Este trabajo se enfoca en el posible uso de conchas marinas *Acanthocardia tuberculata*, que constituyen un desperdicio de alimentos destinados al relleno sanitario, como sustituyente parcial del inerte del mortero. Los resultados obtenidos evidenciaron que la reducción de las propiedades mecánicas (en términos de tenacidad y

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resistencia a flexión) se debe principalmente a las propiedades de absorción de agua de las conchas marinas, que afectan la hidratación del cemento. Sin embargo, como se demostró experimentalmente, dicha disminución de las propiedades mecánicas en cualquier caso no compromete el rendimiento del material cuando viene empleado en aplicaciones civiles.

Introduction

The aquaculture industry provides food and employment for humans and plays an important role in the economy of nations [1]. Seashells are the protective exoskeleton of shellfishes and constitute by-products of the aquaculture industry. Furthermore, a variety of shellfishes is consumed everyday as food while the inedible shells are discarded. China is currently the largest producer of shellfish (oyster, clam, scallop, and mussel shells, etc.) in the world, with about 10 million tons of waste seashells disposed annually [2]. The European Union is estimated to produce 600,000 tons of shellfish waste [3]. These seashells have little or no commercial value and are often dumped in open fields or landfills, thereby creating unsightly appearance and unpleasant smell. Additionally, untreated seashell wastes left for a long time can lead to microbial decomposition of salts into (undesired) gases such as hydrogen sulfide, ammonia and amines [4]. Therefore, when large quantities of seashell wastes are produced, they could cause serious environmental concerns. A promising solution to the challenge of seashell waste management is to use them as aggregate in concrete [5]. Natural aggregate such as sand, gravel or crushed rock is the major constituent of concrete in terms of both volume and mass. Since huge quantity of concrete is produced annually, it reasonably follows that a large amount of natural aggregate is mined to produce concrete. A conservative estimate of the world's consumption of aggregate exceeds 40 billion tons a year, and between 64% and 75% of the mined aggregate is used for concrete [6]. In the literature, several waste materials have been used into concrete and mortar mixtures, for example plastics, glasses, or construction demolition waste [7–10]. However, all these waste materials present a second problem in the demolition process. Plastics, in particular, has very long degradation times which exceed the life time of a building [11]. Because of their properties, previous attempts have been made to use seashells as a partial or total substitute for natural aggregate in mortar and concrete mixtures [12–14]. The use of seashells is advantageous because they have physical properties that are very close to those of the natural aggregates normally used. Lastly, using seashells in construction contributes to the protection of the environment in addition to preservation of natural resources with a cost save form materials [15].

Therefore, the final aim of this paper is to evaluate the possible use of seashells as replacement of the aggregate fraction in mortar. Materials were prepared by adding *Acanthocardia tuberculata* seashells, which constitute a food waste destined to landfilling, as partial substituents of inert in mortars and composites were characterized from both a chemical and mechanical point of view.

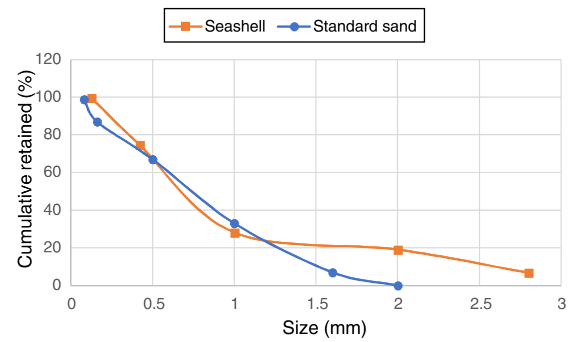

Fig. 1 – Particle size distribution of crushed seashell (orange line) and CEN standard sand (blue line).

Materials and methods

Oil-well cement Class G (Lafarge North America), CEN Standard sand (a natural siliceous sand consisting of rounded particles having a silica content of at least 98%, whose particle size distribution lies within specific limits according to UNI EN 196-1) was purchased from Societé Nouvelle Du Littoral, deionized water and seashell *Acanthocardia tuberculata* (SH in the text) (recovered from open air fish market of Turin) were materials used for this experimental study. The SH was previously washed and crushed using a ball milling machine to obtain approximately the same particle size distribution of the sand as shown by the particle size distribution (Fig. 1).

Four types of mortar specimens were made, with different substitution percentage in weigh of aggregate with seashells (0%, 5%, 10%, and 15%). All mixtures were prepared with a water-to-cement ratio (w/c) equal to 0.50 and a cement-to-aggregate ratio of 1:3. All the materials were weighted according to the amounts required in the mix design (Table 1) and mixed according to the UNI EN 196-1:2005. First deionized water and cement were mixed for 30 s, then either the sand or the SH and sand powder (previously weighed and mixed together inside a beaker) were gradually poured into the solution within the first 30 s of the mixture. In the next 30 s, all the materials were mixed at high speed, after that, the mixer was stopped for 90 s: in the first 30 s, the material residues remaining on the bowl walls were removed, then the mixture was let stand. After the break, the mixer was reactivated at high speed for another 60 s. At the end of the mixing phase, the cement mixture was slowly transferred into the steel mold, made up of four $20 \times 20 \times 80$ mm prismatic specimens, carefully avoiding air entrainment, and then put inside an oven at 85 °C for 24 h at 100% humidity.

Table 1 – Mix design of samples prepared.

Mortar mix	Description	Cement [g]	w/c	Water [g]	Sand [g]	Seashell [g]
Mortar	Ordinary mortar mix	100	0.50	50	300	–
SH 5%	Mix with 5% of SH as substituent	100	0.50	50	285	15
SH 10%	Mix with 10% of SH as substituent	100	0.50	50	270	30
SH 15%	Mix with 15% of SH as substituent	100	0.50	50	255	45

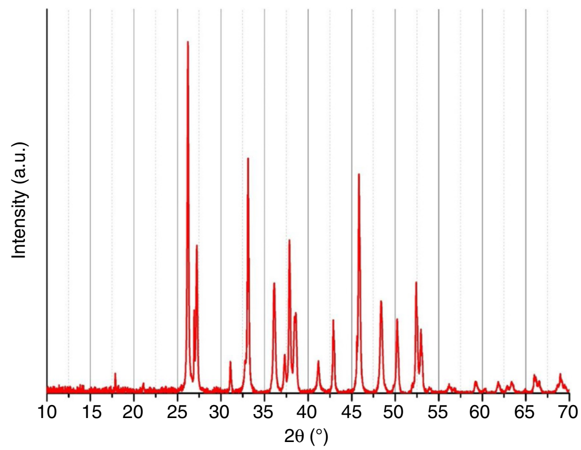

Fig. 2 – XRD diffraction of *Acanthocardia tuberculata* shells used as substitution of aggregate.

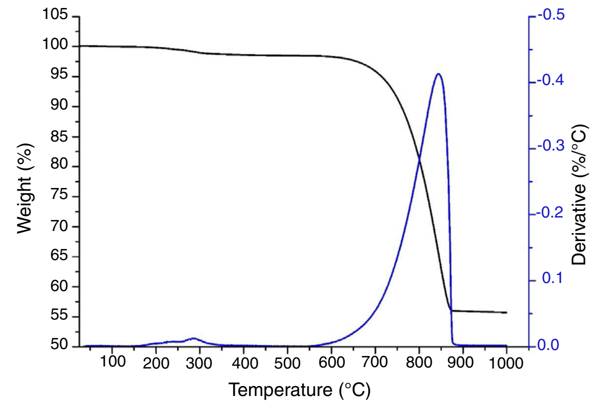

Fig. 3 – Thermo-gravimetric analysis of *Acanthocardia tuberculata* shells (black) and derivative (blue) under air atmosphere.

Once the maturation of the samples was finished, a U-shaped cut, 6 mm deep, was made in the middle of the face orthogonal to the pouring surface of all the specimens, following the geometry and dimensions recommendations described in the JCI-S-001 standard. The samples underwent three points bending tests in Crack Mouth Opening Displacement (CMOD) by using a clip-on gauge, to evaluate both flexural strength and toughness, as explained in the literature [16]. Subsequently the two halves of the broken prism have been subjected to compression tests. All tests were performed using a Zwick Z050 universal test machine. X-ray diffraction (XRD) patterns were obtained using the X-ray diffractometer PW3040/60 X'Pert PRO MPD from PANalytical in a Bragg–Brentano geometry, with Cu Kα anode source at 40 kV and 40 mA. Thermo-gravimetric analysis was conducted in a TGA instrument Mettler Toledo 1600, in air. Samples were heated from 25 °C to 1000 °C with a constant heating ramp of 10 °C min^{-1}. The air was supplied with a constant flow rate (50 mL min^{-1}). Stereomicroscope Leica EZ4 W was used to investigate the structure of crushed seashell and standard sand. The tap density was evaluate following the standard normative ASTM B527-15.

Results and discussion

The XRD pattern of the powdered seashells is reported in Fig. 2. As suggested in the literature [17,18], the structure of *Acanthocardia tuberculata* shells is pure aragonite (which is a particular polymorph of $CaCO_3$, according to the JCPDS card number 05-453). The cell parameters, calculated through a structure refinement by using the software *Maud*, are $a = 4.9669$ Å, $b = 7.9690$ Å, $c = 5.7511$ Å, respectively. These parameters demonstrate a slight deflection from the values of the geological aragonite, in particular along *c* direction, due to the biogenic origin of the shell [18,19].

In order to understand the organic ratio of seashells, the thermo-gravimetric analysis of seashell is shown in Fig. 3. The curves profile revealed two main thermal phenomena: (i) a weight loss around 150 °C due to oxidation and removal of organic material from the seashell [20], followed by (ii) a more relevant weight loss that begins at ca. 550 °C and continues until ca. 850 °C which is attributable to the $CaCO_3$ chemical decomposition into calcium oxide with release of volatile carbon dioxide, according to literature [21], leaving a final residue at 1000 °C being ca. 55 wt.%.

Mechanical test results are presented in Fig. 4: it is clear from the figure that both flexural stress and toughness decrease slightly. For the former, the use of 5%, 10% and 15% of SH showed a reduction of 7%, 22%, 10%, respectively, with respect to the mortar mix. In terms of toughness, there was a reduction of about 16.5% in the case of SH 5% and 30% for both SH 10% and SH 15% with respect to the mix without SH (i.e., Mortar). Such reductions, if compared to the mortar mix, are not present in the case of compression tests: for the mixes with 5% and 15% SH substitution, there was a light reduction in compressive strength of less than 1% and 6%, respectively. However, in the case of the SH 10% samples, there was a resistance loss of about 12%. These reduction in mechanical properties is in line with other results present in literature with other types of shells. The average reduction of mechanical properties is about 13% for 5% of substitution and 6.5% for 10%, and, particularly, our results on compression strength are higher with respect to 5% of substitution and slighter lower with respect of 10% [12,13].

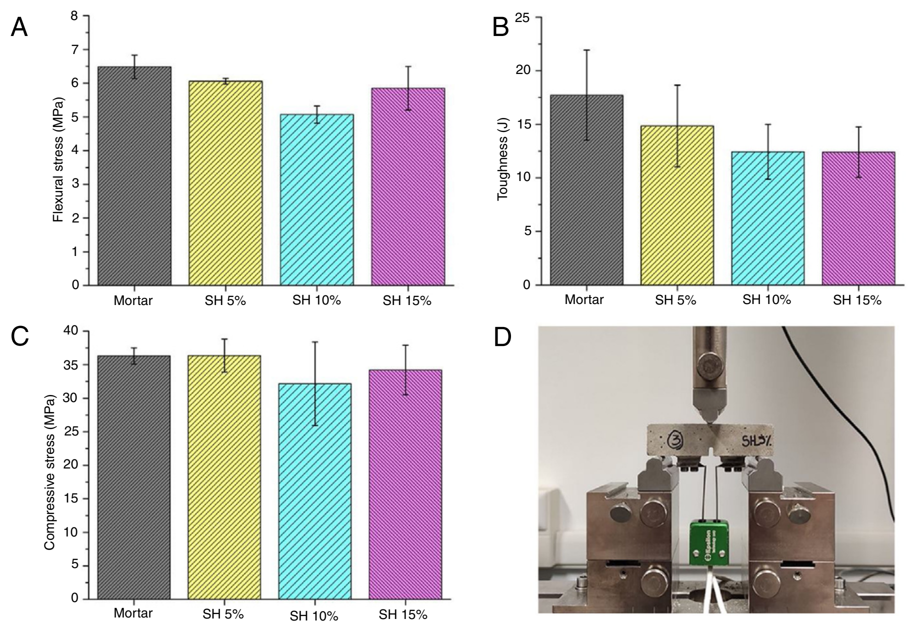

Fig. 4 – Flexural stress (A), toughness (B), compressive stress (C) and prismatic sample of cement composite undergoing flexural testing in CMOD control mode (D).

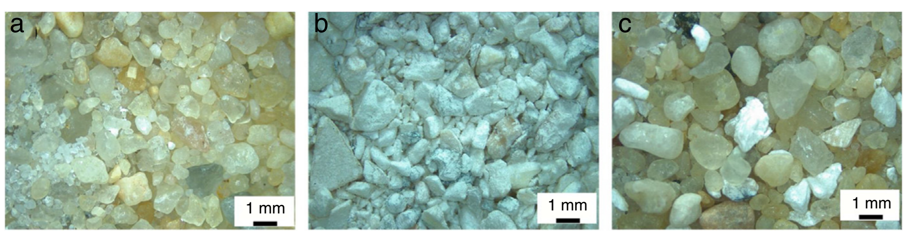

Fig. 5 – Macrographs taken by stereomicroscope of standard sand (a), Crushed seashell (b) and mix SH 15% (c) used for the preparation of the samples.

Table 2 – Properties of the bare aggregates (i.e., standard sand and seashell SH) as well as the aggregates containing 15% of seashell (SH 15%/sand 85%).

Materials	Bulk density[g/cm^3]	Tap density[g/cm^3]	Specific gravity[g/cm^3]	Packing degree[%]
Sand	1.64	1.84	2.67	69
SH	1.54	1.84	2.93	63
SH 15%/sand 85%	1.66	1.89	2.71	70

This phenomenon (i.e., the flexural stress and toughness reduction in mortar) is largely attributed to the higher water absorption of seashell aggregates. Experimental tests performed in samples, demonstrated that the SH absorbs about 10.5% of water with respect to its weight, leading to a decrease in the water-to-cement ratio and consequently a non-optimal hydration of the cement. The presence of organic matter, as confirmed by thermogravimetric analysis can influence also the reduction in mechanical properties. Eziefula et al. [12] find a possible explanation to the higher surface-to-volume ratio of the seashells results in less surface coated by cement paste, thereby causing reduction in bond strength. In contrast with the literature explanation of low compactness [20], the crushed shells used in this work mixed with standard sand have a good arrangement shape, and similar morphology (Fig. 5). Although, the compaction level measured is better than that of normalized sand and seashells (Table 2), as it is known, the seashell structure is more brittle than the natural aggregate (the open porosity calculated from water absorption is around 30.6%). As reported in the literature, seashells have a lower resistance to fragmentation regarding natural aggregate, which would explain the obtained mechanical results [21].

Nguyen et al. [21] evidence that the mechanical properties for similar composites are strongly influenced from the granular arrangement between seashell and aggregate. In particular, the mechanical results reported in the literature [12,14] for similar substrates show a general decrease in terms of mechanical properties at different percentages of replacement of the aggregate. However, it should be taken into account that both these studies are relative to the use of seashells with different density and porosity respect to the one investigated in this study (namely, *Acanthocardia tuberculata*). Interestingly, the compression strength measured in this work shows a lesser decrease in mechanical properties in comparison to the literature analyzed, whereas the flexural strength has results in line with the data collected for composites containing other types of shells. The comparison with the state-of-the-art revealed that the results obtained using *Acanthocardia tuberculata* are promising, even if these systems are intrinsic variable and subjected to the type of shell used.

Conclusions

In this study, grounded seashells of *Acanthocardia tuberculata* were used as partial replacement of the aggregate inert fraction in mortars. The analysis of the mechanical properties of mortars containing different amount of seashells revealed a depletion of the mechanical properties of composites. However, even if flexural strength and toughness are partially lowered by using seashells as aggregate replacement in mortar, the inclusion of seashells still guarantees acceptable strengths for various structural and plastering applications. For what concerns compressive strength, no notable differences were found with respect to mortars used in civil applications. Lastly, using waste seashells in concrete and mortars is an interesting solution since beneficial in terms of costs, waste reduction and environmental sustainability.

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