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Procedia Structural Integrity 39 (2022) 71–80

Structural Integrity
Procedia

www.elsevier.com/locate/procedia

7th International Conference on Crack Paths

Fracture energy of sustainable geopolymer composites with and without the addition of slaughterhouse by-products as fibre-reinforcement: an experimental investigation

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Abstract

This work focuses on the development and on the mechanical characterization of geopolymer composites to be used as sustainable plasters or mortars. The starting point of the work is the synthesis of a geopolymer binder, which is subsequently used for the production of two different mortars: the first one is obtained by simply adding fine aggregates (control mortar), while in the second case, also slaughterhouse wastes (SHW) are included in the admixture. Nowadays, slaughtering industry produces a large amount of biological wastes, that are usually discarded via incineration or landfills. Among SHW, horns and hooves, which are rich in keratin, can be potentially used as additives in the manufacturing process of mortars, both in the form of fibre-reinforcement, as well as fine aggregates and fillers. In the second mortar considered in this work, 2% of SHW fibres and 2% of SHW filler are added in the admixture. The mechanical properties of the three products are experimentally investigated and compared to each other. Apart for compressive strength, close attention is paid to the flexural behaviour and to the determination of fracture energy. To evaluate the effect of SHW addition on crack propagation and width, digital image correlation technique is also adopted.

Peer-review under responsibility of CP 2021 – Guest Editors

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2452-3216
Peer-review under responsibility of CP 2021 – Guest Editors
10.1016/j.prostr.2022.03.074

Keywords: fracture energy; geopolymer; slaughterhouse by-products; sustainable mortars; recycling

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1. Introduction

Nowadays, there is a growing awareness that the construction sector is largely responsible for environmental pollution and climate changes. As documented by the IEA (International Energy Agency), about 7% of global CO_2 emissions is attributable solely to the production of Ordinary Portland Cement (OPC), which is commonly used as binder for concretes and mortars. For this reason, the reaching of the carbon reduction targets planned by 2050 to limit global warming obviously requires a large application of carbon mitigation strategies in cement manufacturing, that go from the use of alternative fuels in the production process, to the adoption of innovative techniques like carbon capture, to the reduction of clinker content. In the last years, an increasing attention has been also paid to the possible use of more sustainable binding materials as alternative to OPC, like for example alkali activated binders, also known as geopolymers (Huseien et al., 2017, Okoye, 2017, Bergamonti et al., 2018, Zhang et al., 2018, Carreño-Gallardo et al., 2018, Singh and Middendorf, 2020, Shapakidze et al., 2021). Geopolymers are formed by the dissolution of a variety of natural or industrial waste aluminosilicate precursors (metakaolin, ground granulated blast furnace slag, fly ash, etc.) in an alkaline environment, followed by a polycondensation reaction (Davidovits, 1989, Gordon et al., 2011, Davidovits, 2013). As highlighted in several research works from the literature, geopolymer binders offer a twofold advantage: from one hand, they may generate 70-80% less carbon dioxide than OPC, so largely contributing to the reduction greenhouse gas emissions; on the other hand, their technology easily allows the inclusion of secondary raw materials in the production process, as well as of higher amounts of industrial by-products and wastes than OPC (Heath et al., 2013, Part et al., 2015, Mehta and Siddique, 2016, Azad and Samarakoon, 2021).

In this work, the effect of slaughterhouse by-products on the mechanical and fracture properties of geopolymer mortars is investigated. The expansion of slaughtering industries worldwide is having serious adverse environmental impacts, due to the large increase in biological wastes, that are usually discarded via incineration or landfills. For this reason, there is great deal to encourage the re-processing of several types of by-products coming from meat processing, for both agricultural and industrial uses. Hooves and horns, which are rich in keratin, are usually reused in cosmetic and pharmaceutical industry, or in sustainable agriculture, as organic fertilizer. On the contrary, their application in the building industry is still scanty, although different application of keratin fibers from chicken feather, or human hair for the development of sustainable concretes can be found in recent literature (Alao et al., 2017, Mendoza et al., 2019, Bheel et al., 2020).

The experimental work discussed in the paper is basically structured into two subsequent stages. The starting point of the research is the synthesis of a geopolymer binder, and the study of the influence of the curing treatment on its hardened-state mechanical properties. The geopolymer binder is subsequently used for the development of a control mortar (by only adding silica sand to the admixture, as fine aggregate), and of an innovative sustainable mortar through a further addition of 2% fibers and 2% filler obtained from milled and dried bovine hooves and horns. As is well known, the addition of fibers as reinforcement for mortars allows an improvement of the tensile strength and fracture toughness, which are generally much lower than the compressive strength. On the contrary, the addition of SHW powder as filler enhances the formation of small air pores in the admixture, so giving greater lightness and improved thermal properties to the mortar. These two aspects may become particularly relevant in the case of a possible application of this product as plaster.

2. Experimental program

2.1. Synthesis of the geopolymer binder and analysis of the effects of the curing treatment on its mechanical properties

For the synthesis of the geopolymer binder, it was chosen to use metakaolin (MK) - an aluminosilicate clay mineral as precursor, because it is generally recognized that MK improves the mechanical strength while reducing the transport of water and salts in the final product. Metakaolin powder and alkaline activator solution with a mass ratio of 3:1 were put together in a mortar mixer for 5 minutes to reach good homogenization. The alkaline activator consisted in low molar sodium hydroxide solution (4M) and sodium silicate solution (3M) in a ratio of 4:1. Water was added to the binder in a ratio approximately equal to 0.8. The slag was then poured into steel moulds (40 mm x40 mm x160 mm) and vibrated for 2 minutes to remove the entrapped air.

It is well known from the literature that in case of alkali-activated materials the curing treatment strongly affects the mechanical properties and their evolution with time (Nath and Sarker, 2012, Patil et. Al, 2014, Nurruddin et al., 2018, Khalil et al., 2020). It is generally recognized that oven curing is preferable for geopolymers, since it results in a significant strength improvement; however, the need of an initial thermal treatment limits the possible applications of this material only to precast structures, and it is clearly not feasible when casting should be done on the construction site (as it normally happens for standard concrete). For this reason, in this work the specimens were cured at ambient conditions, by analyzing the influence of the different methods suggested in the literature on the compressive and flexural strengths. More in detail, the following four curing method were applied: ambient air curing (T = 20±2° C, RH ≅ 65%), water curing, curing of the specimens within closed plastic bags, and curing within a standard cabinet, under controlled temperature and moisture conditions (T = 20±2° C, RH ≅ 95%). To this end, a total of 12 prismatic specimens were prepared, so to have 3 specimens for each curing treatment.

Mechanical properties of the binder were determined at an age of 28 days according to UNI EN 1015-11. Flexural strength was determined from prismatic samples subjected to three-point bending, by using a MTS Universal testing machine (Fig. 1a). Tests were carried out at a constant speed, so to reach the failure between 30 s and 90 s. Subsequently, the two remaining halves of each specimen were tested in compression, by using an Instron 5882 Universal machine working under loading control (Fig. 1b). A loading rate of 200 N/s was chosen, as suggested by the standard for mortars with an expected strength of about 5 MPa. The compression load was applied through 40 mm x 40 mm steel platens.

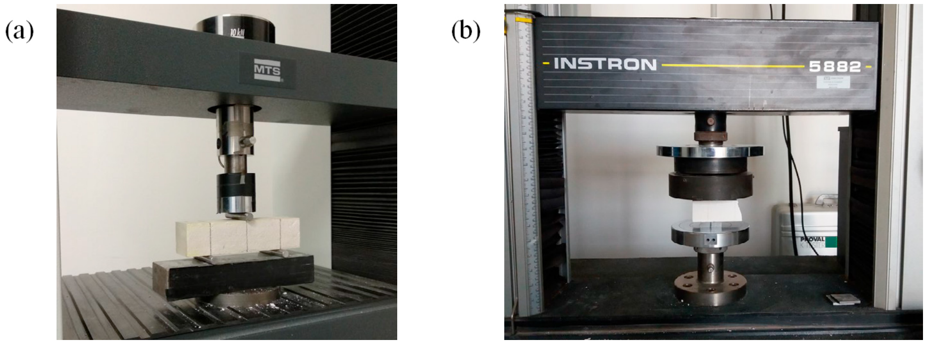

Fig. 1. Experimental setup for: (a) flexural tests; (b) compression tests, according to UNI EN 1015-11.

2.2. Mortars with and without the addition of slaughterhouse wastes: specimen preparation and testing procedure

To explore the possibility of including industrial by-products in the admixture, and to evaluate their influence on the main mechanical properties at the hardened state, a control mortar was initially developed by simply adding silica sand as fine aggregate (SiO_2 content 75%, granulometry 0.5 mm ÷ 1.4 mm), with a binder to aggregate ratio equal to 1/3.

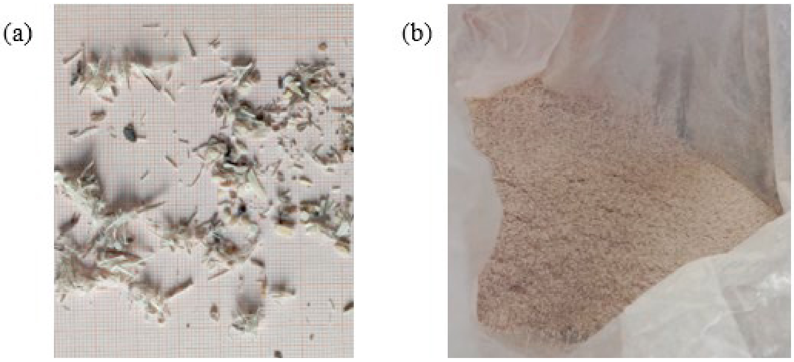

Fig. 2. (a) SHW fibers; (b) SHW filler.

At this stage, no additives – which enhance mortar workability and its adhesion to the support - were added in the admixture, since they usually alter also the mechanical properties of the final product. Mortar samples were prepared according to the procedure already described for the binder, by keeping the same water/binder ratio (approximately equal to 0.8).

The "green mortar" with SHW wastes had the same composition of the control one, except for the addition of milled and dried horns and hooves coming from slaughtering and beef processing, with the following dosages: 2% of SHW fibers, with a length up to 6 mm, and 2% of SHW filler with a diameter ranging between 0.1 ÷ 0.5 mm (Fig. 2). The chemical features of the samples were preliminary investigated by FTIR measurements, on Thermo-Nicolet Nexus spectrometer equipped with a Thermo Smart Orbit ATR diamond accessory (Singaravelu et al., 2015). For each spectrum 64 scans, at intervals of 1 cm^{-1} in the 4000 cm^{-1} and 400 cm^{-1} range, were averaged. X-ray diffraction pattern on the geopolymer powder with SHW wastes was carried out with a Thermo ARL X'TRA X-ray diffractometer with Si-Li detector, using Cu-Kα radiation at 40 kV and 40 mA at 0.2°/sec scan rate (in 2θ) in the range 0–80°. For 2θ calibration were used the powdered silicon reflections.

Both the control mortar and the green one, were cured for 28 days within a standard cabinet, under controlled temperature and moisture conditions.

In order to investigate the fracture behavior of geopolymer mortars, the test setup was slightly modified with respect to that followed for flexural and compression tests on the binder, as discussed in Section 2.1. According to the Japanese Standard JCI-S-001-2003, the specimens were then notched at their mid-length (with a notch depth equal to 0.3 times the beam depth, see Fig. 3a) and the tests were performed under Crack Mouth Opening Displacement (CMOD) control, by using an Instron 8862 Universal testing machine. In this way, it was possible to determine the flexural tensile strength and the fracture energy. Subsequently, the two remaining halves of each specimen were tested in compression, according to the same procedure already discussed in Section 2.1.

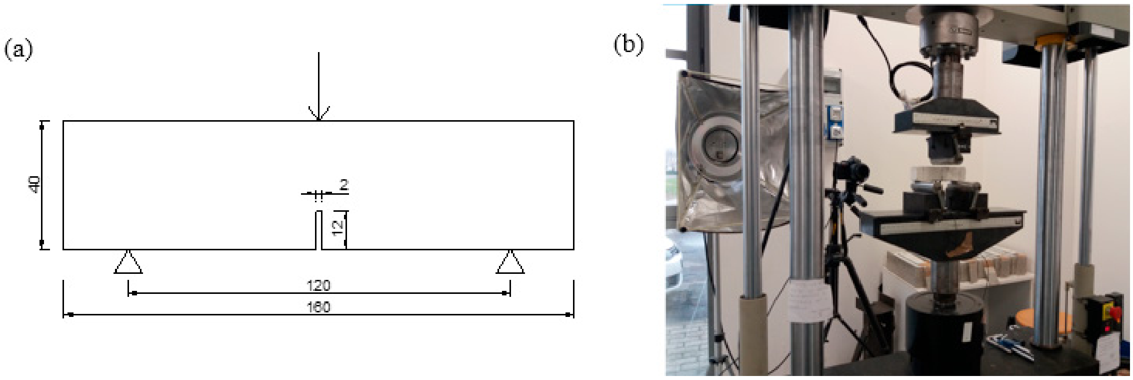

Fig. 3. (a) Sketch of three-point bending tests on notched mortar specimens (dimensions in mm); (b) general view of fracture energy tests and of DIC equipment.

During the execution of fracture energy tests, Digital Image Correlation (DIC) technique was adopted to complete the measurement acquisition in terms of displacements, strains and crack pattern. As known, in recent years DIC has become a powerful tool for material characterization, above all when the behavior is affected by cracking occurrence, as in cement-based matrices. The specimen surface was smoothed and a speckle pattern, consisting of randomly distributed black dots over a white background, was realized by means of spray-painting. A high-resolution camera (Nikon D5100) was used and placed on a stiff frame, and stable lighting conditions were guaranteed. Digital images were taken at a constant time interval of 5s. The sequence of digital images was processed by means of the software program Ncorr, developed in MATLAB environment.

These fracture energy tests were repeated on 2 specimens for each geopolymer product: the binder (GEOPL), the control mortar (MGEOPL), and the mortar with SHW wastes (MGOPLHH). The tests were carried out also on the geopolymer binder, so to evaluate the reduction in mechanical properties produced by the addition of fine aggregates into the admixture.

In the fresh state the three geopolymer products were characterized by a similar consistence, ranging from 175 mm for the binder, to 170 mm and 176 mm for the two MGEOPL and MGEOPLHH mortars, respectively. The consistency of the fresh mortar was determined according UNI EN 1015-3.

3. Results and discussions

3.1. Effects of the curing treatment on the mechanical properties of geopolymer binder

The experimental results are reported in form of histograms in Figure 4, while the mean values of flexural and compressive strengths for each curing treatment are summarized in Table 1. From the reported results, it can be seen that similar strengths were obtained for the specimens cured at ambient air condition, and for those cured within closed plastic bags. The first ones, however, were characterized by the presence of several thin surface cracks due to shrinkage. Lower strength values were instead obtained in case of water curing; in this case, flexural tests were performed only on two specimens, since the third one broke during demoulding. Flexural and compressive strength for the specimens cured in the standard cabinet were slightly lower than those referred to curing within plastic bags, but the results appear to be less dispersed.

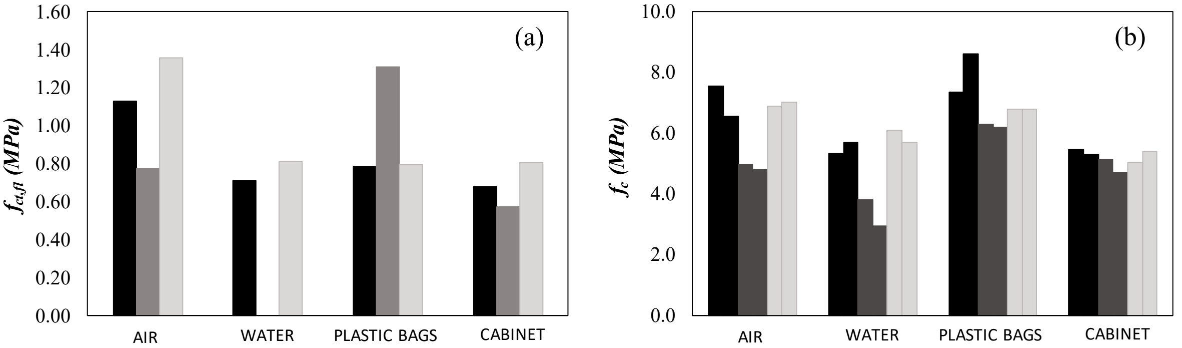

Fig. 4. Influence of curing treatment on mechanical properties of geopolymer binder: (a) flexural strength; (b) compressive strength.

Table 1. Mean values of the mechanical properties of geopolymer binder.

	Air	Water	Plastic bags	Cabinet
$f_{ct,fl\ mean}$ (MPa)	1.09	0.76*	0.96	0.69
$f_{c\ mean}$ (MPa)	6.30	4.93	7.00	5.17

* mean on two specimens

3.2. Chemical and microstructural characterization of SHW wastes

Figure 5 shows the results of the FTIR and XRD analyses carried out on SHW by-products. The FTIR spectrum of horns and hooves from slaughtering wastes shows the typical features of keratin. The broad peak in the region of 3300 cm^{-1}, corresponds to hydrogen-bonded -N-H and -O-H stretching vibration of amide functional group and absorbed water. The stretching vibration of amide carbonyl (-C=O) functional group is observed peak at 1630 cm^{-1} and the bending vibration of -C-N-H group occur at 1525 cm^{-1}. The peak at 1230 cm^{-1} corresponds to -CNH group comprising -C-N- and -C-C- groups stretching vibrations and -N-H group bending vibration.

The diffraction peaks at $2\theta = 9.4°$ and at $2\theta = 20.50$ ° in the XRD pattern of horns and hooves from slaughtering wastes correspond to the keratin α-helix and β-sheet structure, respectively.

As clearly visible in the image acquired under optical microscope shown in Figure 6a, horns and hooves from slaughtering wastes fibers are formed by bundles of microfibers with a diameter of about 500 μm and length ranging from 0.5 mm to 6 mm. The length of fibers can be also deduced from Figure 6b, which shows some fibers lying over graph paper and enlarged through a magnifying lens.

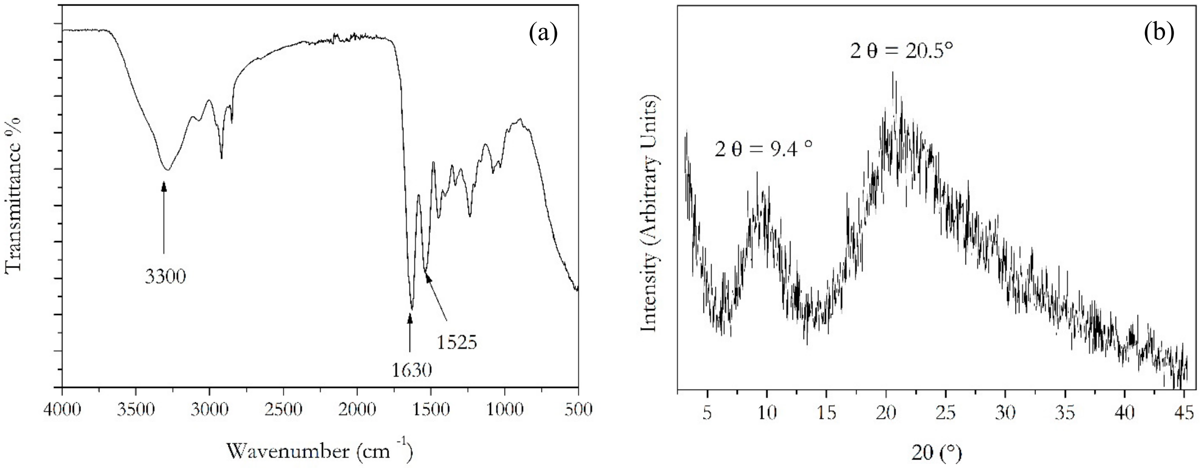

Fig. 5. (a) FTIR spectrum of horns and hooves from slaughtering wastes; (b) XRD pattern of horns and hooves from slaughtering wastes.

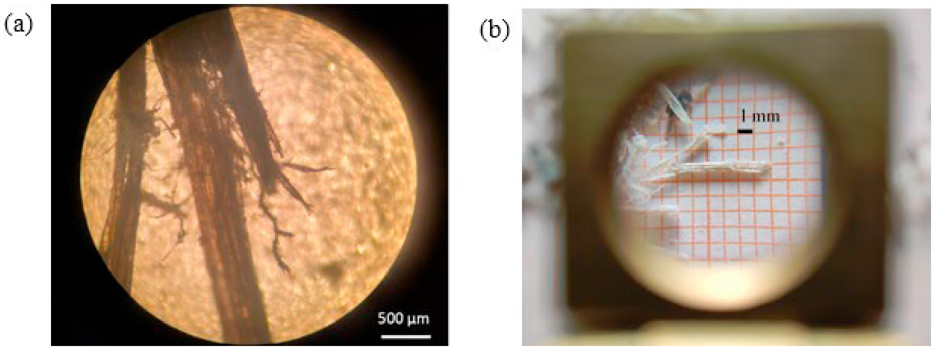

Fig. 6. (a) Optical micrographs of horns and hooves from slaughtering wastes (50x), (b) fibers under a magnifying lens.

3.3. Fracture properties of geopolymer mortars with and without the addition of SHW wastes

Figure 7 shows the load-CMOD curves obtained for the 6 tested specimens, while the experimental values of flexural strength and fracture energy for the three geopolymer products are summarized through the histograms reported in Figure 8. As can be expected, the addition of fine aggregates in the admixture determined an abrupt reduction of both the peak load (about 61% less) and of the fracture energy with respect to the reference condition represented by pure binder. If we instead compare the results obtained for the 2 mortars, it can be seen that the peak load slightly reduced with the addition of slaughterhouse by-products, while fracture energy increased of about 57%, since the post peak part of the curve was less steep thanks to the bridging contribution of keratin fibres.

The values of fracture energy $G_{f,CMOD}$ reported in Figure 8b were derived from the load-CMOD curve according to the relation suggested in the Japanese Standard Code JCI-S-001-2003:

$$G_{f,CMOD} = \frac{0.75\,W_0 + W_1}{A_{lig}} \tag{1}$$

where W_0 is the area below load-CMOD curve up to specimen failure, W_1 the work done by the specimen deadweight and by that of the loading jig, and A_{lig} the area of the broken ligament. The applicability of this relation (which was originally developed for standard concrete) to geopolymer mortars was preliminary checked by comparing the so obtained fracture energy with that calculated as the total work of fracture given by the area under the complete load-midspan deflection curve obtained through the post-processing of DIC images, divided by the ligament area.

Crack pattern evolution was analysed through DIC image elaboration in terms of horizontal strains around the specimen notch, as depicted in Fig. 7c. Images reveal a clear localization at crack tip. It can be seen that the binder was characterized by lower strain values at each loading stage, while the horizontal strains obtained for the two mortars had comparable values. The crack pattern of the specimens with slaughterhouse wastes was however characterized by a more pronounced tortuosity of the crack pattern, which might be due to fibre distribution within the admixture, as well as to the non-uniform distribution of air pores within the specimen.

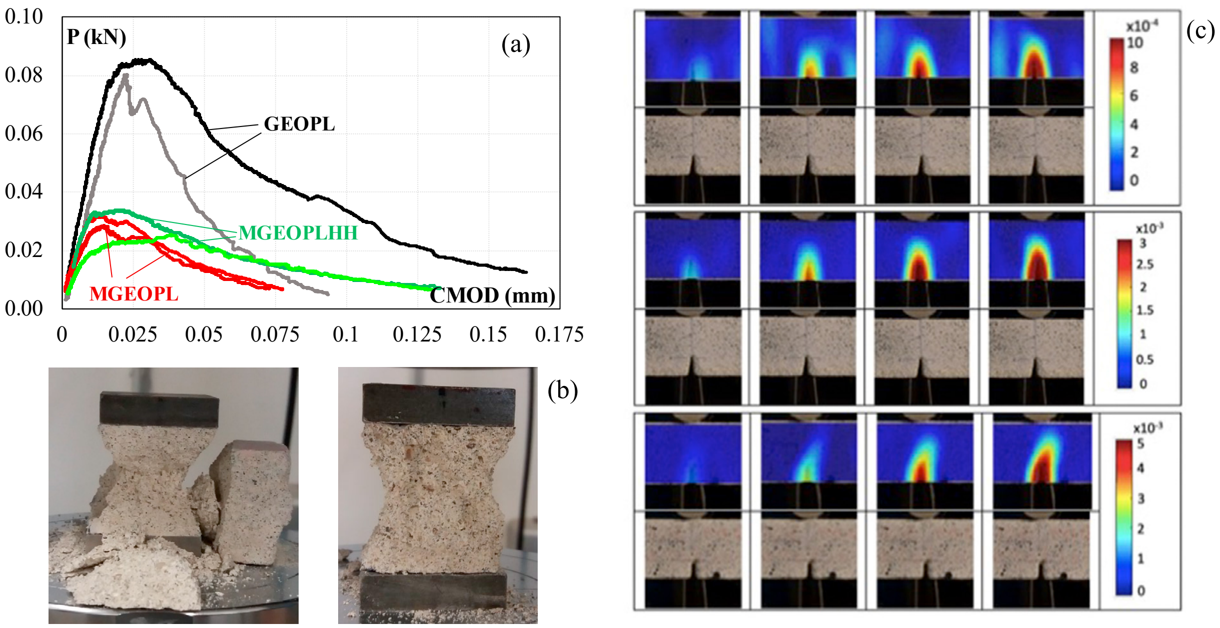

Fig. 7. (a) Load-CMOD curves for the three investigated geopolymer products; (b) crack pattern at the end of the compression tests for MGEOP (on the left) and MGEOPHH (on the right) mortar specimens; (c) crack pattern evolution during TPB tests, analyzed through DIC image elaboration (from top to bottom: GEOP, MGEOPL, MGEOPLHH specimens).

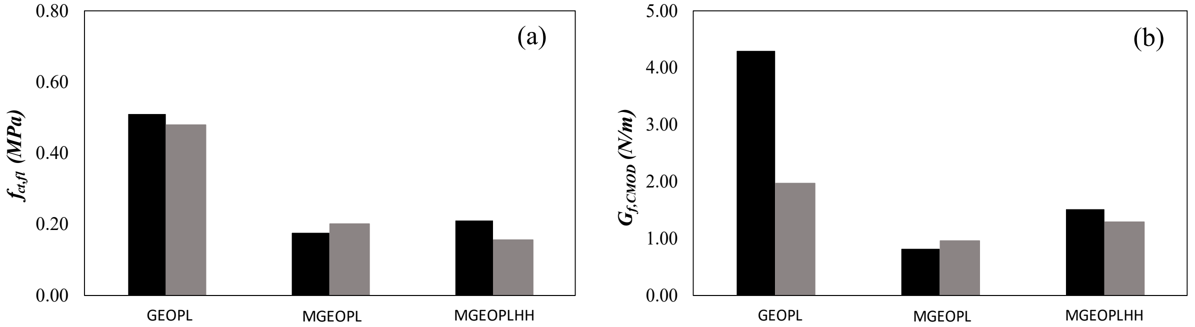

Fig. 8. (a) Flexural strength and (b) fracture energy obtained from TPB tests on notched specimens.

After the execution of three-point bending tests, compression tests were also performed on each of the 2 halves of the specimens, according to UNI EN 1015-11. Also in this case, it was evident an abrupt reduction of the strength when passing from the pure binder to mortar products, and a further slight reduction (of about 20%) when passing from control mortar to that with slaughterhouse wastes (Fig. 9, Tab. 2). From the final crack pattern in compression (Fig. 7b), it can be seen that the consistence of these latter specimens appeared more friable, due to the presence of pores, caused by the presence of the SHW filler.

Table 2. Mechanical properties of geopolymer binder and mortars.

	GEOPL	MGEOPL	MGEOPLHH
$f_{ct,fl\ mean}$ (MPa)	0.49	0.19	0.18
$G_{f,CMOD,\ mean}$ (N/m)	3.14	0.90	1.41
$f_{c\ mean}$ (MPa)	4.40	1.33	1.09

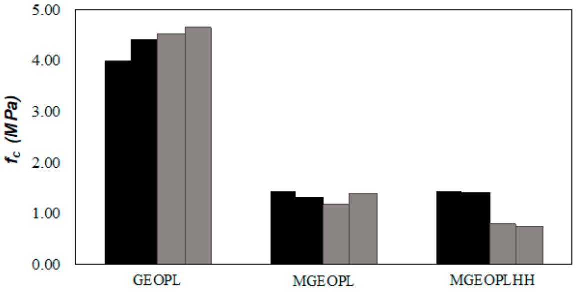

Fig. 9. Compressive strength values.

4. Conclusions

This work represents the first step of a research devoted to the development of a new greener product to be used as mortar or plaster in building construction. The environmental sustainability of the final product is pursued in a twofold way: from one hand by developing a cement free geopolymer binder, and from the other hand, through the addition of slaughterhouse wastes rich in keratin in the admixture, in the form of fibers and filler.

The main results from these preliminary tests highlight that:

1) The curing condition chosen for the geopolymer binder affects its mechanical properties at the hardened state. The worst results are obtained in case of water curing, while the use of a standard cabinet with controlled temperature and moisture conditions seems preferable, since strength values appear less scattered.
2) When considering mortars, it can be seen that the addition of bovine hooves and horns exerts a negligible

influence on the flexural strength, while producing a slight reduction of the compressive strength and an increase of the fracture energy. Since mechanical properties are not too negatively affected by slaughterhouse wastes addition, their use for the development of new sustainable admixture, characterized by a higher recycling rate, seems feasible.

However further tests are necessary, not only to confirm these preliminary results, but also to better investigate from a chemical point of view the interaction between these industrial by-products and the mixing water, as well as with the alkali-activator solution.

Acknowledgements

Authors would gratefully acknowledge MICROCHIMICA S.r.l., 7/C, Via Giuseppina – 26048 Sospiro (CR) – Italia, for supplying SHW wastes used in the admixtures.

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