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Type of materials, pyrolysis conditions, carbon content and size dimensions: the parameters that influence the mechanical properties of biochar cement-based composites

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ABSTRACT: The interest regarding the biochar, the sub-product of biomass pyrolysis process, has increased enormously in the last few years, finding several applications in different fields (agricultural, construction, thermal insulation, etc...). The experimental activities previously conducted at Politecnico di Torino has shown how some biochar processes' parameters (production process, temperature, heating rate, pressure) as well as some biochar features (carbon content, particle size distribution, porosity…) influence dramatically the efficiency to enhance the mechanical properties of the cement composites. In this research, a standardized biochar provided by the UK Biochar Centre has been used: its principle characteristic lies in the standardization of its production, that makes it suitable to been used as filler in cement-based composites, ensuring the reproducibility of the cement mixtures. However, it has been noticed that the pyrolysis production parameters and the content of carbon in the standardized biochar have negatively influenced the mechanical results that, in terms of flexural strength and fracture energy, have been worse than those obtained in previous studies. Despite this, a general enhancement of mechanical properties has been recorded also with standardized biochar with respect the traditional pure cement pastes. This result is extremely important, because it means that, even the parameters are not optimal, biochar can be used to create new green building materials because of its effectiveness in cementitious composites.

***Key words*:** pyrolysis; biochar; cement-based composites; carbon nanoparticles; mechanical properties; ductility.

1. Introduction

The cement industry is currently facing multiple challenges such as: depletion of fossil fuel reserves, scarcity of raw materials, increasing demand for construction materials, as well as increasing environmental concerns such as air pollution and climate change. The production of Ordinary Portland Cement (OPC) yearly releases into the atmosphere roughly 6% of all man-made carbon dioxide emissions [1]. This makes cement the most studied material and the use of green concrete is spreading through partial substitution of raw materials and partial replacement of clinker with alternative constituents such as fly ashes, blast-furnace slag, silica fume (Supplementary Cementitious Materials, SCMs) or leading to the development of alternative binders such as calcium sulfoaluminate cement, magnesium oxide based cement, geopolymers, CO_2-cured cement (Alternative Cementitious Materials, ACMs).

Another material - emerging, called biochar - is receiving more and more attention, given its extraordinary chemical and physical properties and above all because it is a waste product, difficult to dispose of. In fact, it derives from the pyrolysis process, which is the thermal decomposition of biomass in a limited or zero oxygen environment [2]. Biochar is a fine, porous and light material, with a great absorption capacity and a large surface area. Furthermore, it has a basic pH and is rich in carbon. The biochar is chemically stable for long periods of time (hundreds or thousands of years) and, consequently, it is believed that it could be effective for long-term CO_2 sequestration [3-4]. Biochar is used mainly in agriculture as soil improver, increasing soil fertility and allowing the capture of carbon in soils, contributing to climate change mitigation [5]. It is used as a food supplement in cattle breeding, as reducing agent for metal production in industrial processing and to clean grey water. Another field is textile one: here it is introduced as a component of some fabrics for sportswear and can perform the functions of an absorber. It is also experimented inside batteries, always because of its propensity to be a chemical reducing agent. It also found application as a component in asphalts. Moreover, biochar has excellent insulating properties and it is also able to act as a filter for the air because of its porous structure, improving air quality. It can therefore easily absorb moisture and work as electromagnetic shielding [8]. Furthermore, it can be used as an insulating material in buildings [9].

From several years, at Politecnico di Torino, biochar has been investigated as nano/micro particles in cement-based composites, in order to obtain an enhancement of the mechanical properties and ductility of cementitious materials [10]. It has been proved that biochar can be easily inserted into the cement mixture as a filler, since it does not react with the cement matrix, and at the nano/micro scale it reduces the porosity and consequently improves the porosity and consequently improving the durability of concrete. In particular, Politecnico di Torino's researchers focused their attention on agro-food industry waste: coffee powder, cocoa husks, pellets of parchment coffee, rice husk and hazelnut shells and many others more has been pyrolyzed via a lab-scale reactor system, by evaluating their contribution into the cementitious composites. The results of those experiences are hereafter summarized.

1. Micro-carbonized particles obtained from hemp hurd (HH) by controlled pyrolysis were used as additive in self-consolidating cement composites. In [7], an investigation on four different additions (i.e. 0.08, 0.20, 1.00 and 3.00 by wt% of biochar in cement) is reported. The analysis of flexural strength values showed a mixed trend of increase and decrease in proportion by varying the content of carbonized particles addition. A slight increase of 7% in the modulus of rupture MOR was achieved by adding 0.08 wt% HH while a noticeable decrease on further addition up to 3% was found. Evaluated toughness indices (I5 & I10, determined according to the standard ASTM C1018 [11]) of the cement composites clearly demonstrate that the addition of HH significantly increases the fracture toughness. It is believed that the presence of a high number of irregular shaped carbonized particles influences the crack paths by increasing their tortuosity [7].
2. Pyrolyzed polyethylene beads (CNBs) and coconuts shells (Cocos nucifera, CCNs) were produced to investigate the potential beneficial effects of carbon micro/nanoparticles addition to cement pastes for improving the mechanical properties of the resulting composites. When added to cement paste, up to 0.08 wt%, both pyrolyzed CNBs and CCNs proved to be effective in increasing the cement matrix compressive strength and toughness. The dependence of the aggregate shape on toughening is critical and angular grains are needed to produce effective aggregate-bridging. Carbon nano/micro-particles were prepared by chemical vapor deposition (CVD) using low-density polyethylene (LDPE) as a precursor. These particles proved to be spherical and interconnected for the CNBs, while the CCNs were irregular in shape, as the result of the grinding step. A pressure of 3 bars was fixed inside the

reacting chamber while the temperature was maintained in the range 750 to 850°C and an inert carrier gas was used in the experiment [10].

3. Nano/micro carbonized particles produced from waste bagasse fibers have been explored to modify the mechanical properties and fracture patterns of the resulting cementitious composites. When added with cement paste up to 1 wt% (six different amounts were investigated), the carbonized bagasse particles were found effective in significant enhancement of mechanical strength as well as fracture toughness. The increment of mechanical strength is observed up to an addition of 0.2 wt%. Also in this case, an inverse trend was observed beyond this content. The results demonstrated that an addition of these carbonized particles by 0.2wt% improved the flexural resistance measured in terms of MOR by 69.9% while an increment of 46.4% and 61.2% was achieved in first crack and ultimate fracture toughness, respectively. The dependence of the particle shape on toughening is critical and angular grains are needed to produce effective crack-bridging [11].
4. Nano/micro-sized carbonized particles were synthesized from hazelnut and peanut shells for producing high-performance cement composites. Carbon nano/microparticles obtained by controlled pyrolysis of peanut (PS) and hazelnut (HS) shells were investigated. When added to cement paste, up to 1 wt%, these materials led to an increase of the cement matrix flexural strength and of toughness. Moreover, with respect to plain cement, the total increase in electromagnetic radiation shielding effect when adding 0.5 wt% of PS or HS in cement composites is much higher in comparison to the ones reported in the literature for CNTs used in the same content. In the case of PS addition, the percentage of particles which ensures a maximum shielding effectiveness gives rise also coincides with a maximum value of the fracture energy, making possible to prepare cementitious materials optimized both from a mechanical and an electromagnetic shielding point of view [8].
5. Cement composites are quasi-brittle in nature and possess extremely low tensile strength as compared to their compressive strength. The experimental results indicate that the incorporation of micro sized inert particles acted as the obstacles in the growth of the cracks thus improving the ductility and the energy absorption capacity of the self-consolidating cementitious composites [12].

6. Nano/micro-sized pyrolyzed hazelnut shells and pyrolyzed coffee powder particles were used as "zero cost" aggregates in cement pastes, in order to improve strength and toughness. Results showed an increase of the mechanical properties of tested specimens, specifically an improvement in strength, toughness and ductility. Furthermore, mechanical properties strongly improved for certain specific content of carbonized nano-micro materials (0.8 wt% with respect to cement). Pyrolyzed nano/micro particles can interact with the fracture evolution by means of the "overlapping effect". Moreover, they are strong enough to force a change of the path and the growth of microcracks, thus increasing the fracture surface and consequently the fracture energy [13].
7. Two types of pyrolyzed agro-food waste, coffee powder and hazelnut shells, were investigated as carbon nano-aggregates, in different percentages of addition with respect to the weight of the cement. The results relative to 7 days curing showed that nanoparticles have substantially improved all evaluated mechanical parameters with respect to the original cement-based composites. It can be noted how the two biochars ‘‘worked better" at different contents. By evaluating the MOR results, the most effective addition for pyrolyzed hazelnut shells is equal to 0.8 wt%, while for coffee powder it is 0.5 wt%. Regarding the fracture energy results, the trend follows the results by three-point bending TPB tests. Also in the case of 28 days curing, there is an improvement of the mechanical properties due to the presence of the pyrolyzed nanoparticles. The better percentages of addition are the same as those of the 7 days mechanical tests [14].
8. Coarse particles of pyrolyzed hazelnut shells, already investigated at the nanoscale, were used to evaluate the mechanical properties of cement-based composites. The particle size distribution used was in the range from some micron up to 140 µm. The experimental results demonstrated that it was possible to use pyrolyzed materials with coarser particle size, guaranteeing the improvement of the mechanical properties in terms of flexural and compressive strength, but not in terms of ductility, observed when using smaller particles. In this case the lowest percentage of addition (0.5 wt%) was optimal, showing an increment of 48% and of 62% at 7 days and of 23% and 61% at 28 days for flexural and compressive strength, respectively. Presumably, the carbonaceous particles, being coarser, a small percentage of them is enough for filling only the larger pores in the matrix, conferring

to the cementitious composites enhanced mechanical properties. The results showed an increase of fracture energy at 7 days with the maximum measured value for 0.8 wt% of biochar content (84% greater fracture energy respect to the plain specimens). On the other hands, at 28 days, this increment vanishes, and a decrease of GF was observed for all mixtures (with decrements between 17% for 0.5 wt% of particles addition and of 4% for the addition of 1 wt%) [15].

Although these results were satisfactory in terms of mechanical properties, it cannot be omitted that the self-produced biochar cannot be considered at zero cost: in fact, the annealing and functional procedures and energy consumption for grinding procedures both impact on the sustainability of the material.

For this reason the effectiveness of standardized biochar – named Softwood Biochar SWC and provided by the UK Biochar Centre, has been investigated with the main goal to guarantee the reproducibility of the cementitious mixtures. The used material in this research is a biochar produced from pyrolyzed feedstock with nominal peak temperature of 700°C, with a carbon content of 90.21 wt% and with a stability of 97.27 % C-basis [16].

2. Materials and methods

2.1 Manufacturing of materials and specimens

Ordinary Portland Cement, deionized water, superplasticizer, and biochar were used for the preparation of cement mixes. Ordinary Portland Cement (CEM I 52.5 R) was produced by Ciments Vigier SA. It is characterized by the rapid development of the initial resistance, in accordance to the harmonized European standard UNI EN 197/1 and is labeled with CE marking according to European Regulation 305/2011 (CPR). Its composition, physical, mechanical, and chemical requirements are reported in Tables 1-3.

Table 1. Cement – Composition.

Type	Designation	Notation	Clinker Portland	Secondary Constituents
CEM I	Cement Portland	CEM I	95-100%	0-5%

Table 2. Cement – Physical and Mechanical Requirements.

Class of Strength	Setting time (min)	Stability (mm)
52.5 R	⩾ 45	⩽ 10

Table 3. Cement - Chemical Requirements.

Properties	Requirements	Indicative Values Vigier
Sulphate Content	⩽ 4.0 %	<3%
Chloride Content	⩽ 0.10 %	<0.06%

A Superplasticizer (Isoflow6600), produced by Cemex, was used to achieve a good workability of the mix and in the meanwhile to reduce the w/c ratio to 0.35; its additional percentage with respect to the weight of cement was 1 wt%. Its characteristics are shown in Table 4.

Table 4. Characteristics of Superplasticizer "Isoflow6600" of Cemex.

Characteristics	Value	Regulation
Form	liquid	
Color	light brown	
pH (at 20 °C)	6.1 ± 1	ISO 4316
Boiling Temperature	100 °C	
Density (at 20 °C)	1.08 ± 0.02 g/cm3	ISO 758
Solubility	soluble in water	

Softwood Biochar SWC was added as nano/microparticles in the cementitious composites. of the investigated additions were 0.8 wt% and 1 wt% with respect to cement on the basis of previous studies [15]. Its basic utility properties, the production parameters and the toxicant reporting are shown in the Tables 5-7.

Table 5. SWC Basic Utility Properties.

Properties	Unit of measure	Value
Moisture	wt %	1.00
C_{tot}	wt %	90.21
H	wt %	1.83
O	wt %	6.02
C_{org}	wt %	tbd*
$H:C_{org}$	Molar ratio	tbd*
$H:C_{tot}$	Molar ratio	0.24
$O:C_{tot}$	Molar ratio	0.05
Total ash	wt %	1.89

Total N	wt %	< 0.01
pH	-	8.44
Electric conductivity	dS/m	0.16
Biochar C stability	% C-basis	97.27

*tbd = to be defined in next version,

Table 6. SWC Toxicant Reporting - Total Content

Toxicity	Unit of measure	Value
Dioxin/ Furan (PCDD/ Fs)	mg/kg dry wet	3.30
Polycyclic Aromatic Hydrocarbons (EPA16)	mg/kg dry wet	0.18
Polychlorinated Biphenyls (PCBs)	mg/kg dry wet	0.17
As	mg/kg dry wet	0.61
Cd	mg/kg dry wet	8.16
Cr	mg/kg dry wet	123.35
Co	mg/kg dry wet	4.37
Cu	mg/kg dry wet	9.66
Pb	mg/kg dry wet	bdl*
Hg	mg/kg dry wet	bdl*
Mo	% C-basis	38.54
Ni	mg/kg dry wet	74.07
Se	mg/kg dry wet	bdl*
Zn	mg/kg dry wet	99.60

* bdl = below detection limit

Table 7. SWC Production Parameters

Parameters	Unit of measure	Value
Nominal HTT*	°C	700
Max. char HTT*	°C	680
Reactor wall temp.	°C	700
Heating rate	°C	680
Kiln residence time	min	12
Mean time at HTT*	min	5
Biochar yield	wt %	87
Pyrolysis liquid yield	wt %	27.64
Pyrolysis gas yield	wt %	54.05
Pyrolysis liquid HHV*	MJ/kg	1.06
Pyrolysis gas HHV*	MJ/kg	12.6

*HTT=highest treatment temperature, HHV = higher heating value

The standardized biochar SWCwas first manually ground in agate mortar with an agate pestle and then sieved with a 125 µm sieve. Subsequently, it was milled in ethanol in agate jars with agate balls (5 mm in diameter) in a planetary mill (Pulverisette 5) (Figure 1).

Fig. 1: SWC Biochar - Grinding operation with planetary multi-station mill

At the end of each grinding cycle the particle sizes were measured by means of laser granulometry "Analysette 22 Compact" of Fritsch. (Figure 2) The average particle size reached was in the range between 2-6 µm. (Figure 3). The biochar solution in ethanol was finally placed into the oven for few days in order to dry the material and then pulverized it to make it ready for cement mixes preparation.

Fig. 2: SWC Biochar - Granulometric Analysis.

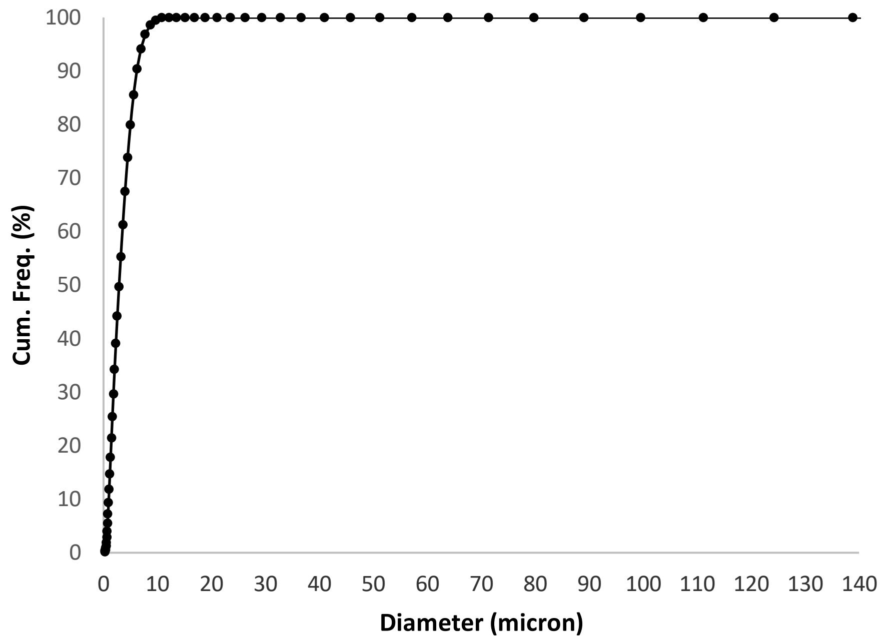

Fig. 3: SWC Biochar - Granulometric Curve

Through the Scanning Electron Microscope with Field Emission source (FE-SEM) it was possible to characterize the morphology of the particles with a resolution around the nanometer. The images of FE-SEM measurements are reported in Figure 4.

a b

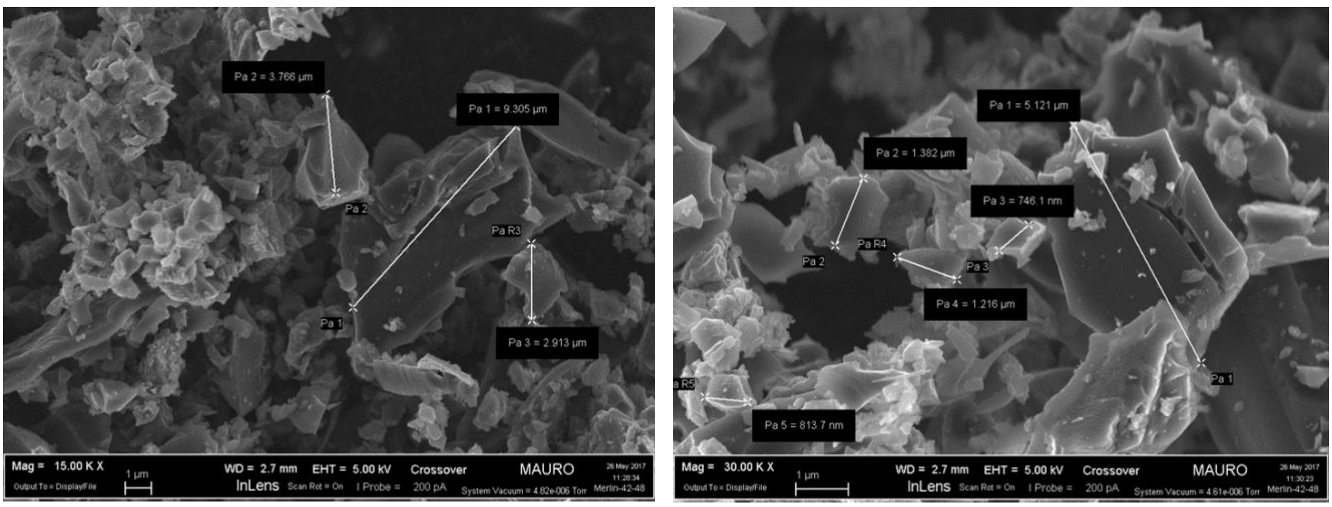

Fig. 4: (a) FE-SEM scale 10 µm with measurement; (b) FE-SEM scale 1 µm with measurement

For each experimental set (OPC - Sp 1%; SWC 0.8% - Sp 1%; SWC 1% - Sp 1%), 8 specimens were prepared, (two steel formworks, made up of four 20 x 20 x 80 mm^3 prismatic moulds) 4 of whom were tested after 7 days of curing and the remaining 4 were tested after 28 days of curing (Table 8).

Table 8. Set of Experimental Specimens

Mixture ID	Number specimens (7 days of curing)	Number specimens (28 days of curing)
OPC - Sp 1%	4	4
SWC 0.8% - Sp 1%	4	4
SWC 1% - Sp 1%	4	4

Table 9 shows the mix-design used to prepare the three sets of the experimental specimens. The water/cement ratio was fixed to 0.35 and the additional percentages of the superplasticizer with respect to the weight of cement was 1%, while the pyrolyzed nanoparticles were added in different percentages (0.8 wt% and 1 wt%) with respect to the weight of cement.

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Table 9. Cement mix-design

Materials		Mix-design N° 1 0%* SWC	Mix-design N° 2 0.8%* SWC	Mix-design N° 3 1%* SWC
Cement	[g]	230	230	230
Water	[g]	80.5	80.5	80.5
w/c ratio	[-]	0.35	0.35	0.35
Superplasticizer	[g]	2.3	2.3	2.3
Biochar SWC	[g]	0	1.84	2.3

*with respect to the weight of cement

All the materials were first weighed according to the amounts reported in table 9. Deionized water, superplasticizer and the standardized biochar were weighed and mixed together inside a plastic beaker, subsequently immersed in an ultrasonic bath for 10 minutes in order to allow a good mixing and homogenization suspension. Then, the cement was gradually added into the suspension within the first minute and the mixture was then subjected to mechanical mixing by means of a vertical rod agitator with a four wings steel propeller with a direct motor with variation of speed, by taking care that the mixture remained fluid and homogeneous. Specifically, in the first and in the second minute, the mixing was performed with the same speed, while in the third and fourth mixing minutes the mixing speed was slightly increased. At the end of the mixing phase, the cement mixture was slowly transferred into the steel formworks, made up of four 20 x 20 x 80 mm^3 prismatic moulds, avoiding air entrainment. Then, the experimental specimens were stored inside these moulds in a humid atmosphere for at least 24 hours and, once they were demolded, they were immersed in water for 7 and 28 days curing.

2.2 Experimental tests

Through the Scanning Electron Microscope with Field Emission source (FE-SEM, Zeiss Merlin) it was possible to characterize the morphology of the particles with a resolution around the nanometer. Each experimental specimen was submitted to three points bending test. Before performing the TPB tests, a 6 mm in depth and 2 mm in width notch was realized on each specimen by means of a metallographic truncator "TR 100 S Remet" in the centre line of the specimen on the face orthogonal to the casting surface, according to JCI-S-001 recommendation [17]. The TPB tests were performed using a Zwick Line-Z050, a single column displacement-controlled testing machine with load cell of 1 kN. All the specimens were tested in Crack Mouth Opening Displacement mode (CMOD) through a clip-on gauge (Figure 5). A span of 65 mm and a test speed of 0.005 mm/min were adopted.

Flexural strength, σ_f, was determined as it follows [17]:

$$\sigma_{f,max} = F_{max} \cdot \frac{3L}{2bh^2} \quad [MPa] \tag{1}$$

in which *L* is the span equal to 65 mm, *b* is the specimen depth equal to 20 mm and *h* is the net ligament height equal to 14 mm.

The TPB tests let to evaluate the Fracture Energy, G_F, by using the equation proposed in the JCI-S-001 standard [17]:

$$G_F = \frac{0.75W_0 + W_1}{A_{lig}} = G_{F0} + G_{Fcorr} \quad \left[\frac{N}{mm}\right] \tag{2}$$

in which A_{lig} [mm^2] is the area of the nominal ligament, W_0 [N·mm] is the area below CMOD curve up to rupture of specimen and W_1 [N·mm] is the work done by deadweight of specimen and loading and defined as follow:

$$W_1 = 0.75\left(\frac{S}{L}m_1 + 2m_2\right) g \cdot CMOD_c \ \ [N \cdot mm] \tag{3}$$

in which S is the loading span, L is the total length of specimen, m_1 is the mass of the notched specimen, m_2 is the mass of the loading arrangement part not attached to testing machine but placed on beam until rupture, g is the gravity acceleration and $CMODc$ is the crack mouth opening displacement at the rupture.

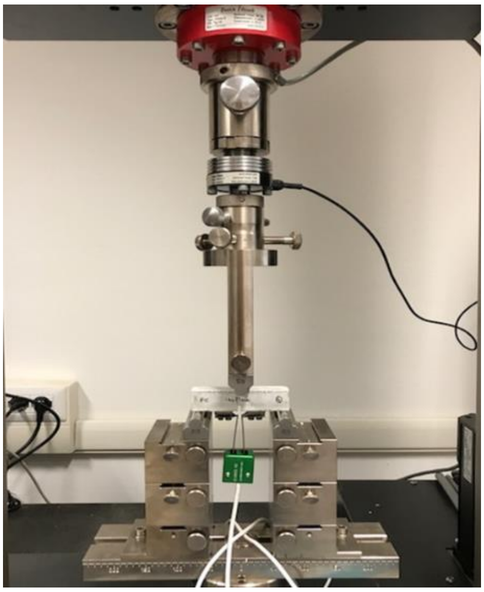

Figure 5: Three Points Bending Test in CMOD control mode

3. Results and discussion

3.1 Composites mechanical testing

The experimental results obtained by TPB tests showed very interesting indications. In general, it is possible to notice that the standardized biochar improves the mechanical properties of cement-based composites in comparison to the standard ones. The results reported in Table 10 (7 days tested specimens) and Table 11 (28 days tested specimens) were processed with statistical tools, specifically the mean value and the standard deviation of the Maximum Force F_{max}, the Flexural Strength σ_f and the Fracture Energy G_F respectively:

Table 10. Experimental Results – TPB tests 7 days

Specimen ID	N°	F_{max} [N]	F_{max} mean	F_{max} st. dev.	σ_f [MPa]	σ_f mean	σ_f st. dev	G_F [N/mm]	G_F mean	G_F st. dev
OPC - Sp 1%	1	68.10	73.20	6.66	1.69	1.82	0.17	0.008	0.013	0.004
OPC - Sp 1%	2	73.80			1.84			0.011		
OPC - Sp 1%	3	82.40			2.05			0.018		
OPC - Sp 1%	4	68.50			1.70			0.014		
SWC 0.8 % - Sp 1%	1	75.20	83.88	8.72	1.87	2.16	0.23	0.010	0.014	0.004
SWC 0.8 % - Sp 1%	2	78.40			1.95			0.010		
SWC 0.8 % - Sp 1%	3	95.80			2.38			0.019		
SWC 0.8 % - Sp 1%	4	86.10			2.14			0.014		
SWC 1 % - Sp 1%	1	111.00	89.88	15.87	2.76	2.24	0.39	0.024	0.022	0.004
SWC 1 % - Sp 1%	2	88.60			2.20			0.026		
SWC 1 % - Sp 1%	3	87.40			2.17			0.017		
SWC 1 % - Sp 1%	4	72.50			1.80			0.022		

Table 11. Experimental Results – TPB tests 28 days

Specimen ID	N°	F_{max} [N]	F_{max} mean	F_{max} st. dev.	σ_f [MPa]	σ_f mean	σ_f st. dev	G_F [N/mm]	G_F mean	G_F st. dev
OPC - Sp 1%	1	89.00	82.85	6.30	2.21	2.06	0.17	0.008	0.014	0.007
OPC - Sp 1%	2	78.30			1.95			0.007		
OPC - Sp 1%	3	76.60			1.91			0.020		
OPC - Sp 1%	4	87.50			2.18			0.020		
SWC 0.8 % - Sp 1%	1	101.00	99.71	15.82	2.51	2.48	0.48	0.009	0.016	0.007
SWC 0.8 % - Sp 1%	2	78.60			1.95			0.012		
SWC 0.8 % - Sp 1%	3	116.94			2.91			0.024		
SWC 0.8 % - Sp 1%	4	102.30			2.54			0.020		
SWC 1 % - Sp 1%	1	113.00	100.23	10.70	2.81	2.49	0.27	0.018	0.023	0.007
SWC 1 % - Sp 1%	2	87.10			2.17			0.026		
SWC 1 % - Sp 1%	3	98.44			2.45			0.030		
SWC 1 % - Sp 1%	4	102.37			2.55			0.016		

The specimens containing the biochar showed a certain dispersion of the MOR values (Table 11). This is probably due to the problems encountered during the preparation phase of the composites, that is the non-uniform dispersion of the nanoparticles into the cement paste [18].

However, samples characterized by the addition of biochar have a greater flexural strength than the plain cement, either at 7 days or at 28 days; this increase amounts to around 20%. Furthermore, there was no substantial difference between the two studied biochar contents (Figure 6). Starting from TPB tests, it was possible to study the Fracture Energy of the experimental specimens and it was observed that its mean value slightly increased with the introduction of biochar in the cement, both at 7 and 28 days (Figure 7).

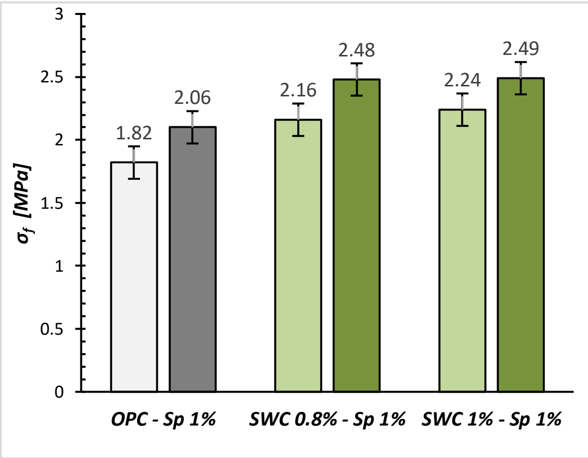

Fig. 6: TPB Test: Flexural strength – 7 and 28 days

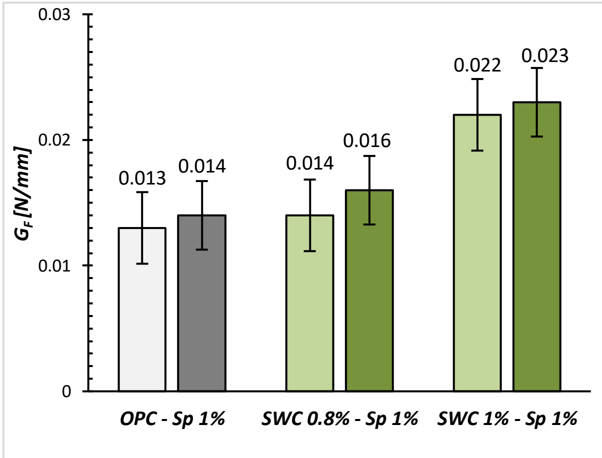

Fig. 7: Fracture Energy – 7 and 28 days - JCI-S-001 standard

a b

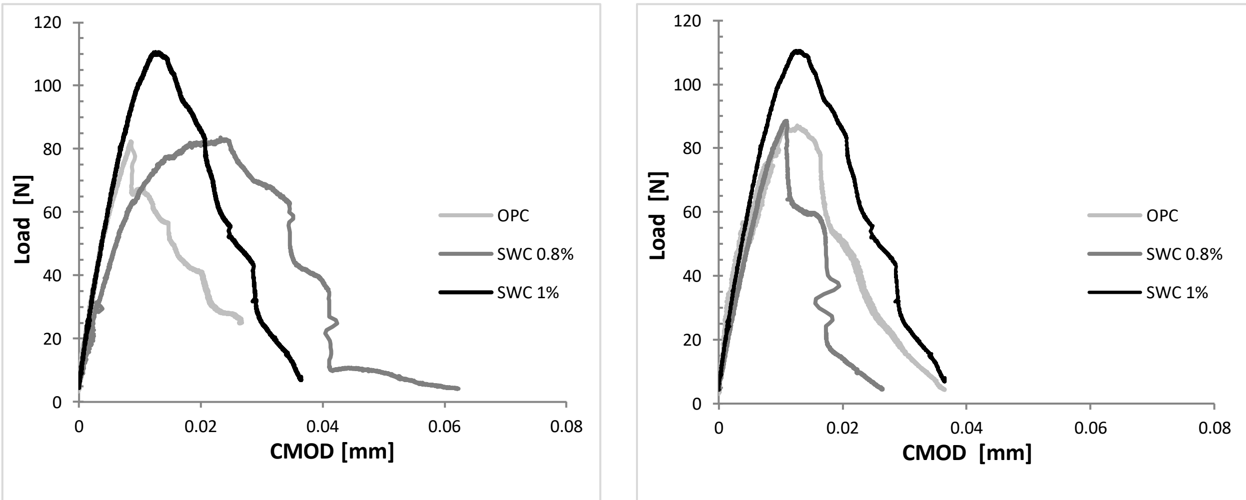

Fig. 8: (a) Load vs CMOD Curve, 7 days and (b) Load vs CMOD Curve, 28 days for the most significative tests

From the Load-CMOD curves graph (Figure 8) it was possible to notice that the pyrolyzed nanoparticles within the cement-based composites led to a better mechanical behavior in terms of peak-load and post-peak response, directly linked to the flexural strength and toughness results.

From the FE-SEM observations, the biochar particles showed sharp edges and irregular shapes but also appeared very porous; the carbon nanoparticles have a high surface-area to volume ratio (SA/V), that means an increment of the contact area between the particles and the surrounding cementitious matrix, hence allowing a higher interaction with the matrix and more efficient behavior. This aspect could lead to a good adhesion of the particles to the cement matrix. Moreover, the FESEM observations conducted in previous studies [19] showed that specimens with pyrolyzed material have a more articulated and tortuous fracture path and therefore less linear than the typical brittle fracture observed in cements. This explains the variation in the post-peak behavior of the material and the increase in the ability to absorb energy before breaking [18].

3.2 Comparison between past investigations and current research

The previous studies on the effectiveness of biochar into cement-based materials demonstrated that it was possible to use pyrolyzed materials with coarser particle size, guaranteeing the improvement of the mechanical properties in terms of flexural and compressive strength, but not in terms of ductility, as obtained by using smaller particles [15]. Restuccia and Ferro [15] used two different biomasses of agro-food wastes: coffee powder and hazelnut shells. For both biochars, the addition with respect to weight of cement were 0.5, 0.8 and 1 %. These materials were subjected to the pyrolysis process with a heating ramp of 6 °C/min and a final temperature set point of 800 °C. By evaluating the Flexural Strength and Fracture Energy results, the most effective additional percentage for pyrolyzed hazelnut shells was equal to 0.8 wt%,, while for coffee powder was 0.5 wt%,. In comparison with the present research, it is possible to notice that σ_f and G_F tend to increase with the increasing content of biochar. The average values of F_{max}, σ_f and G_F of the present work are generally lower than those reported in [18] although using pyrolyzed materials with comparable sizes (Figures 9-10).

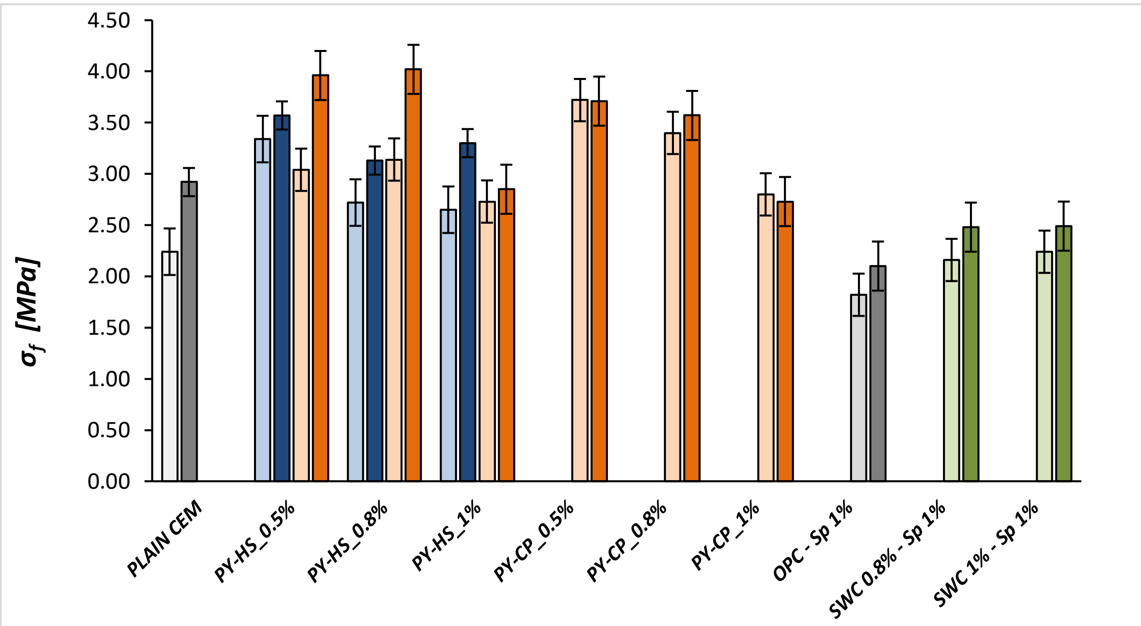

Fig. 9: Flexural Strength - Comparison between PY-HS, PY-CP and standardized SWC specimens, 7 and 28 days. (PY-HS=pyrolyzed hazelnut shell, PY-CP=pyrolyzed coffee powder)

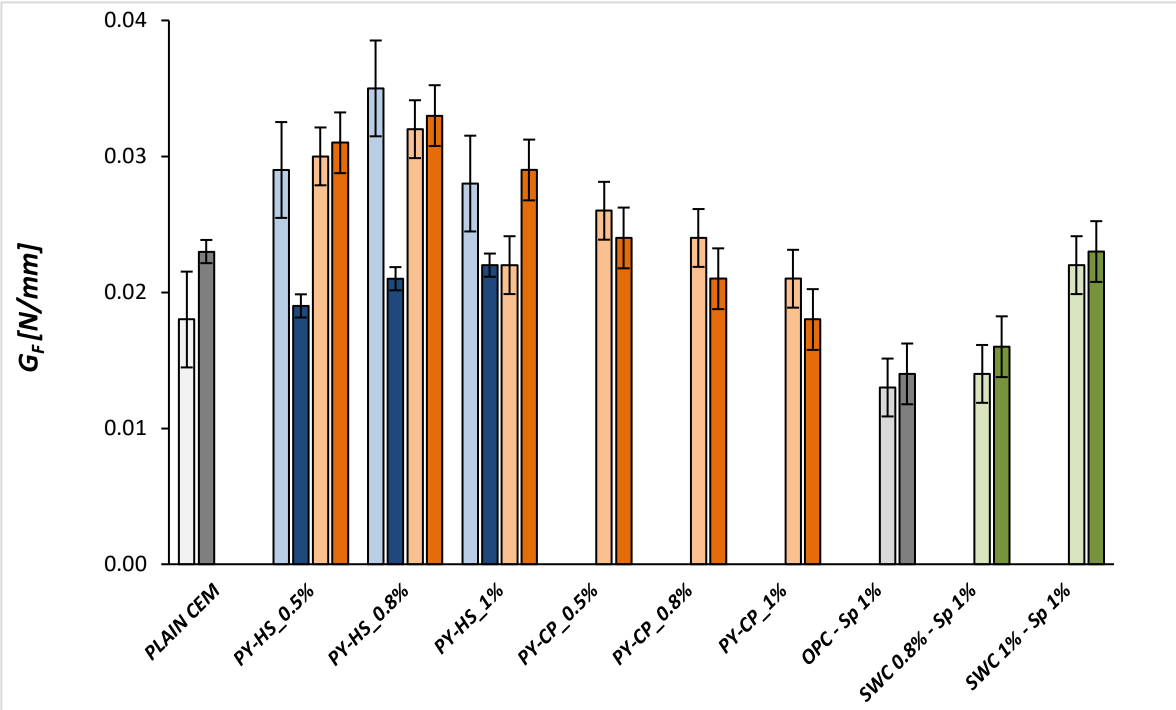

Fig.10: Fracture Energy - Comparison between PY-HS, PY-CP and standardized SWC specimens, 7 and 28 days.

The percentage of carbon present inside the standardized biochar used in this work (90.21%) is lower than the one of the self-produced biochar used in the previous study [17] (97.8%) as well as the pyrolysis temperature (700 ° C compared to 800 ° C). These two features have a great influence on the yield and efficiency of the biochar production, as also highlighted by other literature studies [19-20]. Gupta and Kua [19] underlined the biochar key production factors (specifically, pyrolysis temperature, heating rate, and pressure) that determine the potential of biochar as a carbon capturing and sequestering construction material.

Other results were analyzed to understand the effectiveness of the biochar and the influence of the pyrolysis conditions on the mechanical properties of cementitious composites. Montenegro et al [21] found that strength and ductility are increased by adding a percentage equal to 0.08 wt% of pyrolyzed coffee particles into the cementitious matrix. In fact, the F_{MAX} growed from 130 N to about 180 N and, at the same time, the fracture energy increased by 40%. The pyrolysis of coffee powder, cocoa husk and parchment coffee, rice husk and hazelnut shell pellets had been carried out. The influence of two different conditions on the distribution of the mass and energy of the obtained products had been investigated. The hazelnut shell biomass substrate had generated the highest energetic chemical energy yield (86%). These inert carbonized particles can generate high performance cement composites, by increasing the compressive strength, the peak load under bending, and their fracture energy and can improve the post peak response. These inert carbonized particles also modify the fracture path, thus resulting in a larger fracture zone.

These results are in agreement with [22], where air-dried spruce wood was pyrolyzed up to 2400°C. These Authors determined by means of the nanoindentation technique that the mechanical properties of heat treated materials can roughly be divided into three temperature regions: (i) $T< 400$°C, (ii) $400<T<1000$°C and (iii) $T>1000$°C. Specifically, in the temperature range from 600° to 1000°C, the elastic modulus linearly increases from about 20 to 40 GPa. So, does also the hardness. At around 800°C, the elastic modulus and the hardness reach their maximum values. This raise of the Young’s modulus and of the hardness can be correlated to the increase in the density of the material observed between 600° and 900°C as well as to the increasing covalent carbon bonds formation.

4. Conclusions

The new building materials must always be more performing and innovative, at the same time the traditional manufacturing process will have to become increasingly efficient and sustainable to cope with the environmental and climate change emergencies, with the aim of producing traditional building materials with better performance and with a lower energy consumption.

The present research focused on the use of the standardized biochar in cement-based composites in different percentages of addition with respect to the weight of cement, in line with previous experimental studies [15-18]. In these previous studies, the biochar used was self-produced through the pyrolysis of agro-food waste unlike that used in the present experimental activity which was standardized in view of a possible industrial production of biochar cement-based composites..

The results of the mechanical tests showed a promising improvement in strength, toughness, and ductility.

In fact, higher flexural strength and fracture energy values were recorded for specimens with the addition of biochar compared to those of the plain cement specimens.

However, the flexural strength and fracture energy results are lower than those of previous studies [15-18]. This fact could be linked to the different pyrolysis parameters used in the production of biochar (temperature, heating rate, and pressure). The results could therefore be influenced by the type of carbonaceous material and by the production parameters (which influence the strong covalent carbon bonds formation) rather than by the carbon particles size. Selection of suitable conditions to produce a biochar with desired properties therefore requires knowledge of dependencies and influencing factors. From an economic point of view, these carbon particles have are low-cost, as they are the waste of the biomass pyrolysis process. For this reason, they represent a good material for new green construction materials.

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