Effects of biochar addition on long-term behavior of concrete

EFFECTS OF BIOCHAR ADDITION ON LONG-TERM BEHAVIOR OF CONCRETE

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ABSTRACT

In the context of circular economy, the production of innovative concretes that incorporate different kinds of waste material is gaining increasing interest among the researcher community, the regulatory agencies, and the policy makers. The rising awareness of the need of a sustainable development also in the building sector has indeed boosted the research towards the use, for concrete production, of waste material, which can be inserted as aggregate/cement replacement or as filler to improve specific properties of the mixtures. A waste material recently studied with this last aim is biochar, the solid by-product resulting from biomass pyro-gasification. This paper investigates the effects of biochar derived from forestry waste residues on the physical and mechanical performance of concrete, by adding it, during mixing, up to 5% by weight of cement. Density, workability, water absorption properties as well as compressive strength, flexural strength, and fracture energy were measured and compared to a reference concrete without biochar, focusing on long-term behavior. The results demonstrated a general improvement of mechanical properties and internal microstructure of concrete for an optimal biochar content of 2% by weight of cement.

KEYWORDS

Biochar; Concrete; Waste; Mechanical characterization; Durability; Sustainability.

1. INTRODUCTION

During recent decades, characterized by increased environmental impact awareness, there has been a growing interest in the utilization of different kinds of waste and by-products in construction materials. Special attention has been paid to concrete, which, with a production of over 30 billion tons each year [1], is the most widespread construction material worldwide. Due to its low production cost, excellent behavior under compression stresses, high durability, and excellent capacity to be cast in many different shapes, concrete – and more generally cement-based materials – is widely used in civil engineering practical applications. Moreover, the demand for concrete is ever-growing, especially for the needs of the developing countries. Hence, during the last decades, due to the high volumes produced and the negative environmental impacts related to its production, considerable efforts have been devoted to increasing the sustainability of the concrete industry. Thanks to the intrinsic characteristics of concrete, a broad range of waste has been studied to be inserted into the concrete mixture. The use of waste materials can indeed represent an answer to the increasing environmental and ecological problems associated with both waste management and concrete industry, by enhancing the recycling rate on one hand, and on the other, by lowering the carbon footprint and reducing the amount of energy and non-renewable resources needed for concrete production. Moreover, some waste can provide an increase in physical and mechanical performance of concretes, by boosting the hydration reactions or improving the microstructure. While some waste or by-products of industrial processes (such as fly ash, silica fume, ground-granulated blast-furnace slag as well as construction and demolition waste and post-consumer glass, [2–6]) are nowadays commonly used to produce cement-based materials, for others products the research is still in progress with the aim of investigating the potential applications. Among them, during the past few years a rising interest has been shown in the use of biochar, and it has been found that it can provide several advantages for the performance of cement-based materials.

Biochar is defined as the solid by-product coming from the thermal decomposition of biomasses during industrial processes of pyrolysis or gasification, aimed at heat and energy production. Biochar has been widely studied and applied in the agriculture sector as soil amendment; however, nowadays its range of uses is growing rapidly, including the building sector. It can be studied for non-structural applications, such as insulating buildings, regulating humidity, and adsorbing electromagnetic radiation and contaminants [7–11], as well as for developing green cement-based materials. Biochar is indeed a carbon-rich chemically stable material that can be successfully used as filler in cement pastes, mortars, and concretes to improve physical and mechanical properties, as outlined by recent works in the literature [12–14]. The beneficial influence of biochar on the performance of cement-based materials is mainly related to densification effects and water retention capacity. The fine grain size of biochar particles, acting as a micro-aggregate, enables filling the voids of the mixtures, while promoting additional hydration reaction, especially in the case of harsh curing, since biochar is able to absorb mixing water and release it at later stages. Extensive research has been done on the use of biochar as filler for the production of cement pastes and mortars, among others [15–24]. Once the optimal dosage is found, it can potentially increase compressive strength, flexural strength, toughness and ductility, whereas workability is generally reduced. However, the obtained results are scattered, since the beneficial effects provided by biochar strongly depend on the internal microstructure and chemical composition of biochar particles, which in turn derive from the working characteristics of the plant as well as the type of feedstock used for biochar production. Moreover, the use of biochar as filler for concrete is still scanty, and only a few works can be found in the literature on this topic [9,25,26]. Anyway, its introduction into concrete mix is surely interesting, since the massive use of concrete in the building industry and the higher percentages of biochar that can generally be adopted with respect to cement pastes and mortars, thus increasing the recycling rate. In addition, most of the studies in the literature on cement-based materials analyze biochars derived from laboratory or pilot-scale pyrolysis plants built on research purpose. On the contrary, few works analyze biochars derived from commercial plants intended for electrical-thermal energy production [27,28], with the consequence that the biochar produced from this kind of plants is commonly still disposed of in landfills. As well-known [29], the physical and chemical characteristics of biochar particles, such as the content of carbon, the surface area, the size and distribution of pores, are indeed influenced not only by biomass, but also by the characteristics of the process of production.

In this framework, this investigation wants to be a small step towards a more comprehensive and systematic understanding of the influence of biochar, which derives from a commercial plant, on concrete performance. Since the results are strongly influenced by the intrinsic characteristic of biochar particles, at first a morphological and chemical characterization of the carbonaceous material is provided. Then, an experimental program is carried out by including two percentages of biochar addition (2% and 5% by weight of cement) so to evaluate its effect on concrete in terms of both fresh and hardened properties. More in detail, workability, density, compressive and flexural strength, as well as post-cracking behavior and toughness were investigated and compared to that of a standard concrete without biochar. Even if structural concrete has an expected lifespan of at least 50 years for the most common in situ applications, there is a general lack in the literature on the analysis of long-term behavior and durability of biochar-added concrete. To this aim, this research analyzes also the performance of biochar-added concrete after 2 years of curing, also in terms of water absorption and sorptivity characteristics, so to give some insights also on durability behavior.

2. MATERIALS AND METHODS

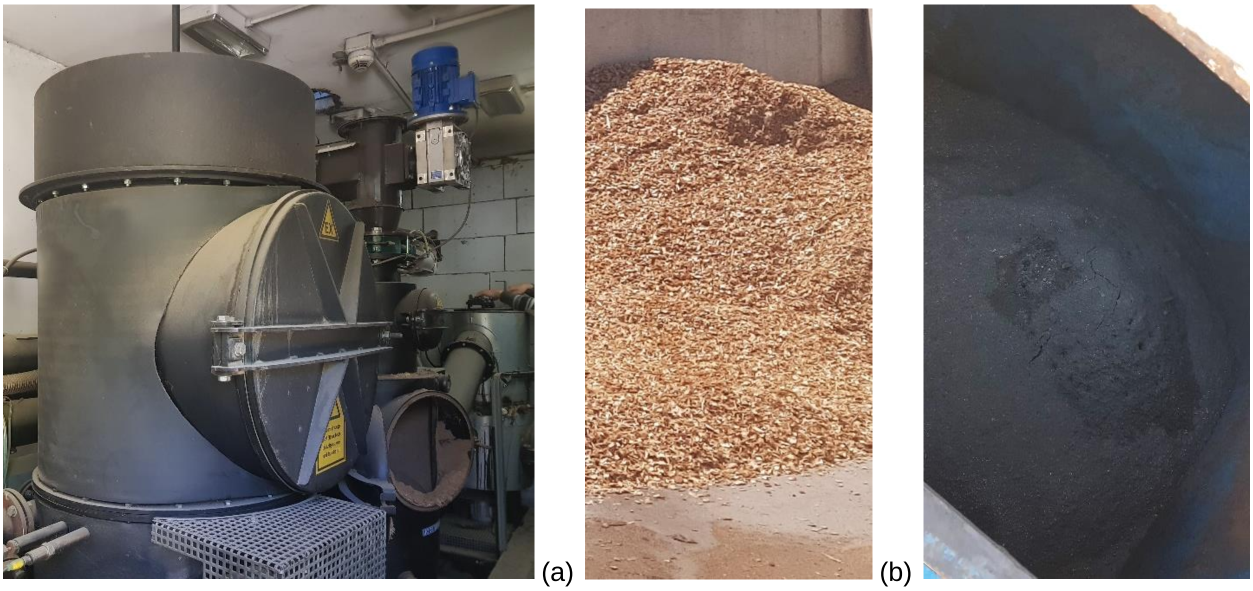
For the development of the experimental campaign, all the physical-chemical analyses concerning biochar were carried out at Mapei S.p.A. “R&D Laboratory”, while all the biochar-added concrete specimens were cast and tested at the “Materials and structures” Laboratory of the University of Parma.

2.1 Biochar

2.1.1 Production

The biochar used in this experimental program was produced in a power plant (Fig. 1a) located in the North of Italy, intended for energy and heat production. The feedstock is represented by woodchips (Fig. 1b), which are derived from wood waste of local forest, such as tree branches, tops of trunks, stumps, branches, and leaves. Different wood species constitute the biomass: deciduous trees (mainly beech and oak), and firs.

The power plant, which is a downdraft gasifier, produces almost tar-less wood gas from wood chips in a controlled process, in which many kinds of simultaneous or consecutive complex reactions [30,31] occur. At first, the woodchips are dried up, to assure that their moisture content does not exceed 15%. Subsequently, pyrolysis takes place in the absence of oxygen up to a temperature of 400 C, so producing carbon-rich solid, non-volatile particles. The volatiles are then vaporized to produce gases and tars. The waste solid fraction from the pyrolysis zone is represented by the carbon-rich non-volatile particles, i.e. biochar (Fig. 1c), which is cooled down and collected in a stainless-steel container.



(a) (b) (c)

Figure 1. (a) Biomass power plant for energy and heat production; (b) incoming biomass: woodchips; (c) solid waste from pyrolysis process (biochar).

2.1.2 Characterization

Particle size distribution was obtained by laser scattering analysis, by using Beckman Coulter LS 13320 laser light scattering instrument, with size range 0.04 µm to 2000 µm. This is based on laser diffraction and Mie Theory, and provides the distribution of different sizes within a sample. The differential and cumulative density values in % is reported in Figure 2 as a function of the particle size in µm.

As it appears from the particle size analysis, the biochar particles show very heterogeneous dimensions, ranging from few microns to millimeter size. The standard percentiles of grain size D10, D50, D90 values are respectively equal to 15.15, 177.0, 584.4 µm.

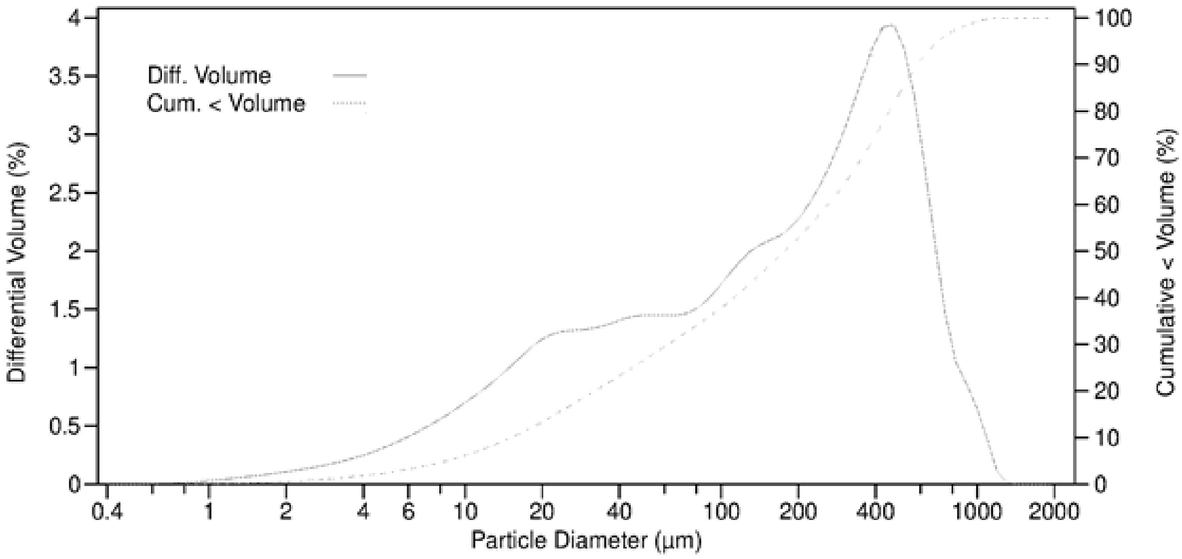


Figure 2. Volume distribution (differential and cumulative) of biochar particles.

The thermo-gravimetric and differential thermal analysis (TG-DTA) was carried out on biochar sample, opportunely weighted in an Alumina crucible. The sample was analyzed by TG 209F1 Iris Instrument (Netzsch) with a heating program from 30 to 980°C, and a heating rate of 30 K/min in air atmosphere.

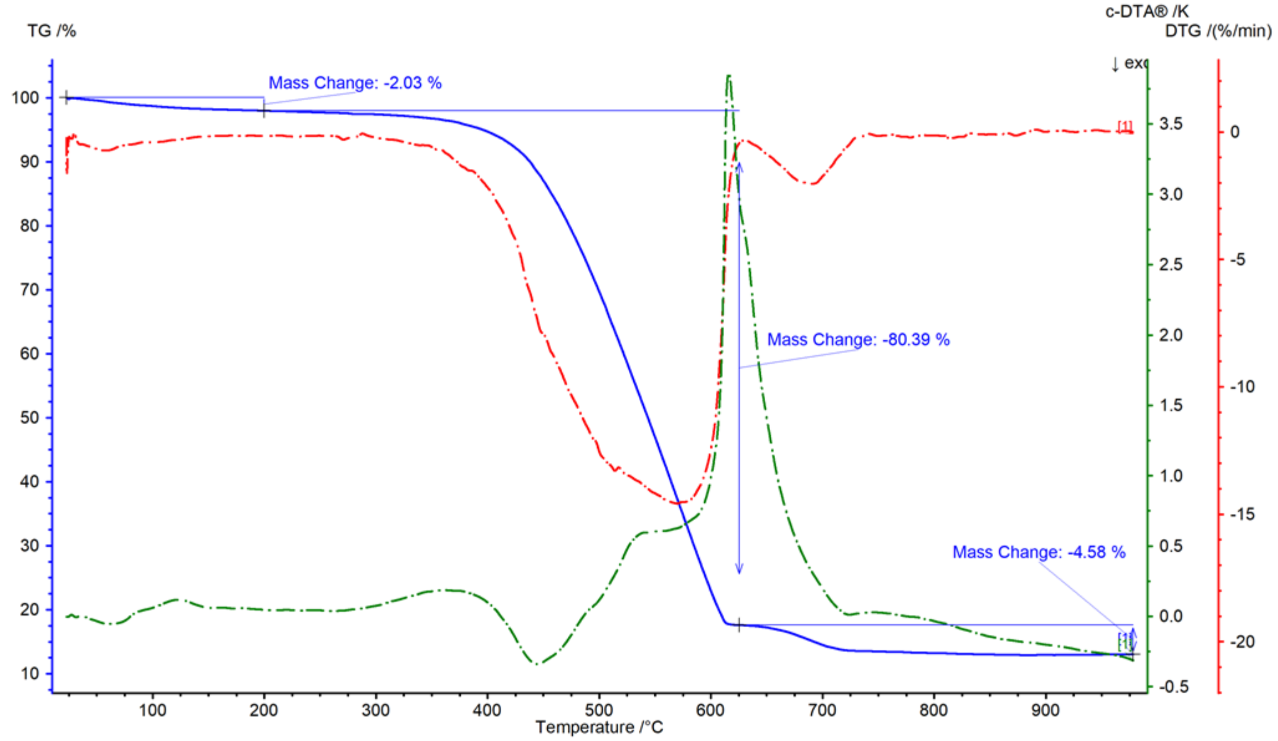


Figure 3. TG-DTA analysis of biochar sample.

The results, reported in Figure 3, show a good thermal stability up to 400°C, which is mainly related to the temperature of production. The biochar thermo-stability depends indeed on the temperature at which it was generated, since as the temperature of production increases, biochar consists of a more stable form of carbon with higher resistance to heat. The mass loss for temperature higher than 600°C, is more than 80%. Anyway, these results make biochar suitable to be used in concrete, especially considering the limited quantities of biochar addition considered in this study, i.e., up to maximum 5% by weight of cement.

By assuming the complete pyrolytic decomposition of the biochar carbonaceous portion, the inorganic component can be derived from the constant weight residue, which is equal to 10.63%.

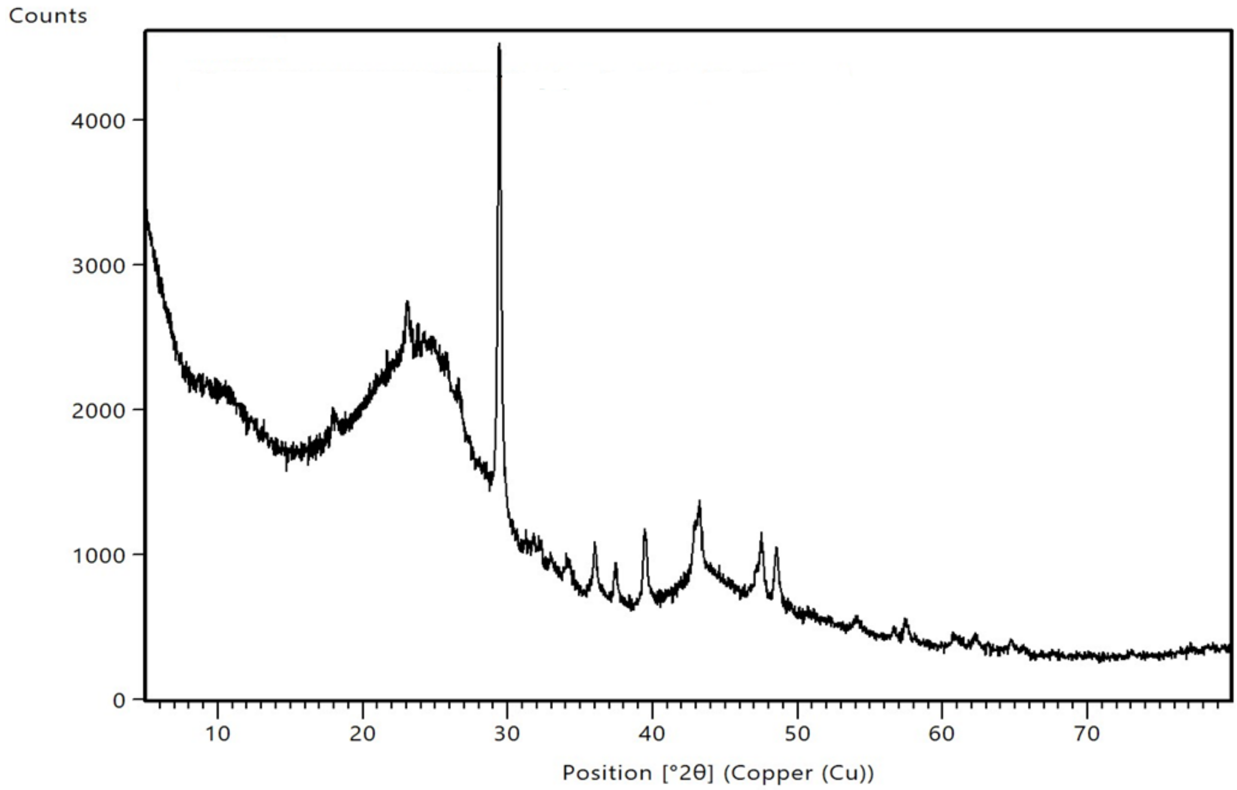


Figure 4. XRD pattern of biochar.

In order to have a first identification of the presence of amorphous and/or crystalline phases, X-Ray Powder Diffraction (XRPD) investigation was performed, by using a PANalytical X'pertPro MPD diffractometer with theta–theta geometry equipped with an X'Celerator detector working with the CuKα radiation (λ=0.154184 nm). Data collection was carried out in the 2theta angular range 5-80°, with a step size of 0.017° 2theta and a scan step time of 51.0 s. Then, the qualitative phase analyses were performed by means of the PANalytical X'Pert HighScore Plus (ver. 2.2) search/match software.

XRD pattern, reported in Figure 4, shows the presence of calcite ($CaCO_3$) as main crystalline phase, and this result is consistent with the production process of biochar. At about 350 C° depolymerisation of lignocellulose occurs resulting in the creation of an essentially amorphous C matrix, and there is evidence in literature [32–34] that carbonate in biochar samples is the main alkaline substance.

Samples morphology was observed by FEI ESEM-Quanta-FEG-250. The field emission gun allowed to obtain a much higher brilliance of the electronic source than the one of an ordinary SEM, as can be seen in Figure 5.

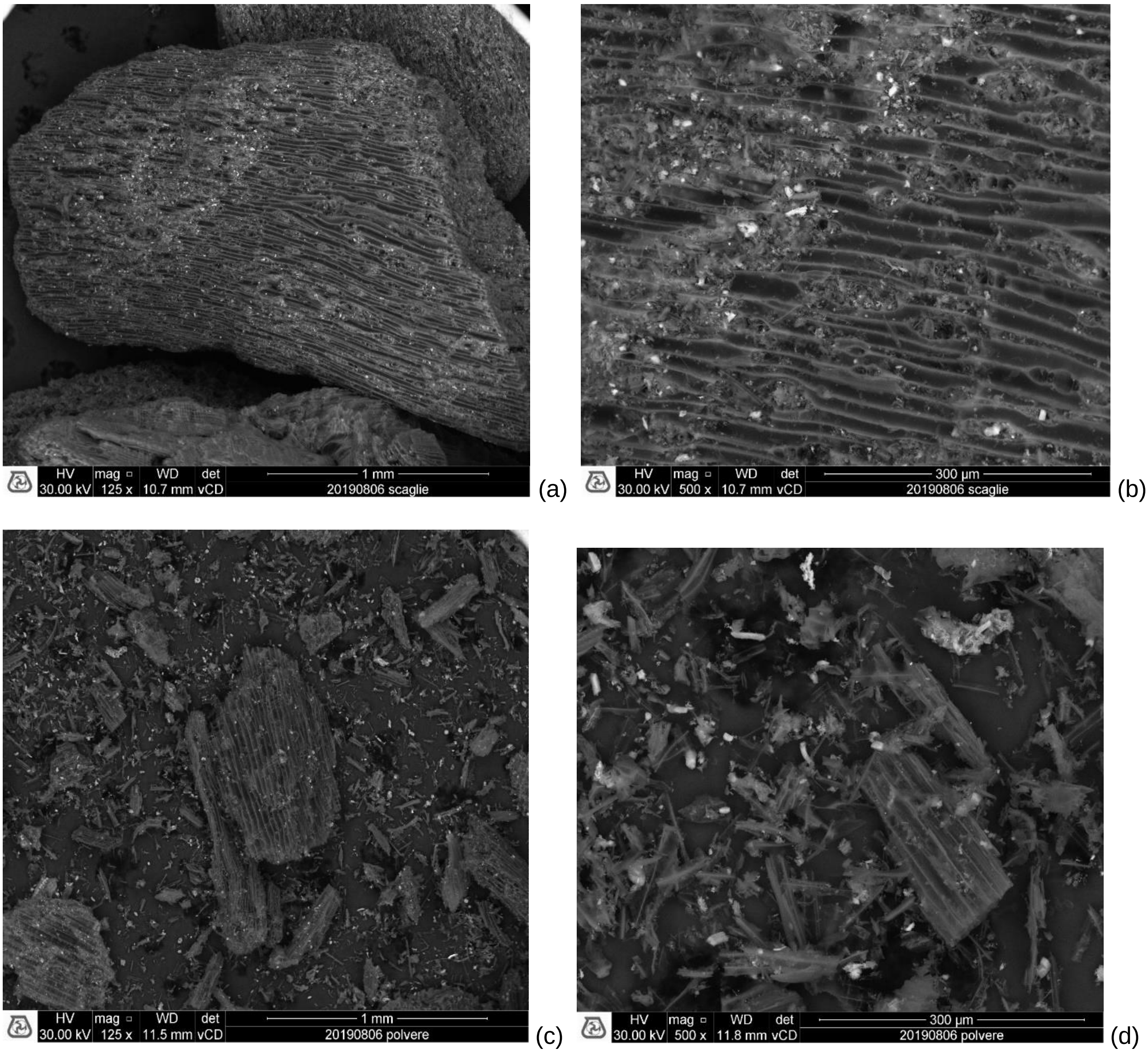


Figure 5. SEM images: different magnifications for (a), (b), biochar particles > 500µm and (c), (d), biochar particles < 500µm.

The relatively broad particle dimensions of the biochar highlighted by grain size analysis (Fig. 2), is confirmed also by the SEM images. Figure 5 reveals the porous tubular organization typical of wood, which represents the starting biomass for biochar production. Moreover, the SEM images highlight the presence of some inorganic compounds represented by the particles with higher image contrast that indicate a different composition compared to the biochar carbon-based compounds.

2.2 Preparation of concrete specimens

Three concrete mixes were investigated: two containing biochar as filler, and a conventional one, used as control.

The reference concrete (REF) was designed by considering the common mixture proportions that are used in the building industry, while biochar-added concretes (BIO2, BIO5), were obtained by adding biochar at 2% and 5% by weight of cement, respectively. 2% addition was chosen as it represents the optimum biochar content generally suggested in the literature for mortars [12,13], whereas 5% was investigated so increasing the recycling rate, since in concrete higher percentages can be generally adopted [25].

2.2.1 Cement, aggregates and additive

The materials used for the preparation of concrete specimens were cement, sand, gravel, water, and superplasticizer.

Portland-limestone cement II/ A-LL 42.5 R, which satisfies EN 197-1 [35] Standard, was used. This type of cement – which contains 80-94% Portland cement clinker and 6-20% limestone and it is characterized by a Blaine fineness of 390 m^2/kg – was selected as it is a commonly used cement.

Squared mesh size [mm]	**Cumulated sieve residue (%)**	
	Sand	**Gravel**
10	0.0	0.0
8.000	0.0	16.0
5.600	0.0	80.8
4.000	1.1	97.2
2.000	18.2	98.8
1.000	36.6	99.0
0.500	59.3	99.6
0.250	85.5	99.8
0.125	96.7	100.0
0.063	99.1	100.0
0.000	100.0	100.0

Table 1 – Sieve analysis of aggregates, in terms of squared mesh size [mm] vs. cumulated sieve residue percentage (%).

Calcareous sand and siliceous gravel were used as fine and coarse aggregate, respectively. These aggregates were selected as they are both locally available, resulting in lower concrete production costs and higher sustainability. The water absorption for both sand and gravel, i.e. the moisture contents for it at saturated surface dry (SSD) condition, was measured according to EN 1097-6 [36], so obtaining values equal to 1.75% and 2%, respectively. Sieve analysis was also completed on each aggregate: the grain size distributions of fine and coarse aggregates in terms of squared mesh size vs. cumulated sieve passing are reported in Table 1. The bulk and particle density of sand were equal to 1546 kg/m^3 and 2646 kg/m^3, respectively, whereas for gravel values of 1580 kg/m^3 and 2640 kg/m^3 were obtained. Moreover, sand and gravel showed a Mohs hardness of 5 and 6, respectively, whereas both the aggregates present a pH value equal to 7.

To obtain the desired workability, a wide used acrylic-based superplasticizer (Mapei Dynamon Xtend W202R) was also applied for the preparation of the specimens.

2.2.2 Mix proportions, casting and curing of specimens

Cement, sand, gravel and water were used in the proportion of 400:1126:526:204 by weight (kg), referring to 1 m^3 of concrete. The amount of superplasticizer was properly adjusted (see Table 2) so to obtain about the same slump values for all the mixes. The aim was to guarantee a consistence class S4, as defined in EN 206-1 [37], which is typical for several in-situ applications, such as foundations, pillars, beams, slabs, pumping and piling concretes.

The procedure of reference concrete preparation began with 5 minutes of mixing of dry aggregates with half of the required water in a standard concrete mixing machine. It is worth noticing that the aggregates were oven dried prior to mixing, and consequently the amount of water of the mix design was adjusted to make them reach the SSD condition. Then, the cement and a quarter of total water were added in the machine and the mix continued for about 3 minutes. Finally, the superplasticizer together with the remaining water were added for the last 4 minutes of mixing.

As regards biochar-added concretes, some adjustment was required in the mixing procedure. Biochar particles were pre-soaked for about 48h before mixing, by putting them in about 25% of the total required water, so to make biochar reach the saturation point, as suggested in [18,25]. The aim was to promote the ability of biochar of absorbing the mixing water and gradually releasing it with time, so enhancing the subsequent process of hydration of cement. Biochar was added in the first stage of mixing, together with the aggregates and 25% of the water required by the mix design, since another 25% of the total water is already contained in biochar particles. Then the following phases of mixing remained the same of reference concrete. It is worth noticing that all the mixtures were homogenous, without any tendency of segregation or bleeding, even in case of biochar addition.

The concrete mixes were cast, by using a vibrating table, into 40 mm x 40 mm x 160 mm prisms, devoted to three-point bending and compressive tests. Polythene sheets were put on the molds, until the scheduled demolding 24 hours after casting. Then, different curing times were scheduled: 7 days, 28 days, 1 year and 2 years, so to investigate the influence of biochar addition on strength development and on long-term behavior. For short-term tests (7 or 28 days) the specimens were wet cured until the day of testing, whereas for the tests at 1 and 2 years from casting, for the first 28 days the specimens were wet cured and then a dry curing at laboratory conditions was applied, in order to simulate common applications at construction sites. For each curing time and mix, three specimens were prepared. The specimens referring to 2 years curing of REF, BIO2 and BIO5 mixes, are reported in Figure 6a, b and c respectively; as can be seen, their color turned into darker shades for increasing amount of biochar addition.

For all the mixes, three 150 mm side cubes were prepared for density measurements. Moreover, for REF and BIO5 mixes, three additional 150 mm side cubes and two 100 mm diameter x 200 mm height cylinders were cast to perform water absorption tests.


(a)

(b)

(c)

Figure 6 – 40 mm x 40 mm x 160 mm prisms of: (a) REF, (b) BIO2, and (c) BIO5 mixes after 2 years curing.

3. EXPERIMENTAL TESTING

The fresh concrete properties of density and workability (in terms of slump value) were determined in compliance with EN 12350-6 [38] and EN 12350-2 [39], respectively. Moreover, the density of hardened concrete was evaluated 28 days after demolding, according to EN 12390-7 [40]: the specimens were dried in a ventilated oven at 105±2°C and the density was recorded when two successive measurements of the mass of the surface-dried samples at intervals of 24 hours indicated constant mass (which means a mass change less than 0.2%).

The water absorption behavior of concretes was evaluated in terms of sorptivity and total amount of absorbed water.

The first was evaluated on cylinders, in compliance with ASTM C1585-13 [41]. After 28 days of water curing, the 100 mm diameter and 200 mm height cylinders were cut, so to obtain cylinders of length equal to 50 mm. Then, they were dried at 50±2°C for 3 days. After these 3 days, the samples were stored in a sealed container at 23°C for 20 days. The aim was to make them reach an internal relative humidity of about 50%, while avoiding a moisture gradient inside the specimens. Then, they were sealed at sides with an epoxy resin coating, and the mass was determined. Subsequently, the samples were put over stainless steel rods in a pan with water, so that the level was assured to be maintained 2±1 mm above the top of the support devices for all test duration. Meanwhile, a plastic sheet was used to cover the top surface to prevent water evaporation. The mass was recorded at predefined intervals, as suggested by ASTM C1585-13 [41], and the test lasted for 8 days. The sorptivity *I* was then computed as:

$$I = \frac{M_c}{a_e d_w} \quad (1)$$

where M_c is the mass change during testing, a_e is the exposed area of the specimen, and d_w is the density of the water.

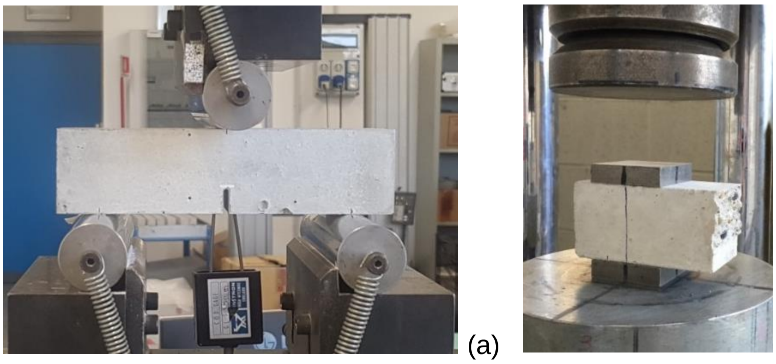
The total amount of absorbed water was obtained by saturation method on cubes of 150 mm side, according to ASTM C642-21 [42]. The samples were oven-dried at 105±2°C until constant mass was reached, so obtaining the oven-dry mass (M_d). Then, the specimens were immersed in water until the increase between two successive measurements at intervals of 24h was less than 0.5%, so obtaining saturated mass after immersion (M_a). The total amount of absorbed water *A* was computed as:

$$A = \frac{M_a - M_d}{M_d} \cdot 100\,. \quad (2)$$

The mechanical behavior was investigated in terms of compressive strength, flexural strength and fracture energy by means of prismatic samples 40 mm x 40 mm x 160 mm.

The specimens were subjected to three-point bending test (3PBT) to obtain both flexural strength and fracture energy. Prior to testing, a 12 mm deep notch *a* – which is 0.3 times the depth *d* of the sample – was made at midspan by following JCI-S-001 recommendations [43]. The tests were performed over a net span *S* of 120 mm under Crack Mouth Opening Displacement (CMOD) control, by using high precision testing machine (Instron 8862). The load was measured through the load cell, whereas CMOD was acquired with a clip-gauge mounted across the notch (Fig. 7a).

Compressive strength was obtained according to EN 196-1 [44], on the two halves of the broken prisms previously subjected to three-point bending test (Fig. 7b). A testing machine METROCOM UI 30 C was used for the scope, with a loading rate of 2400 N/s.



(a) (b)

Figure 7 – Testing arrangement for (a) three-point bending and (b) compressive tests.

4. RESULTS AND DISCUSSION

4.1 Workability

The workability of biochar-added concretes was evaluated in terms of superplasticizer required to obtain about the same slump values of control, as reported in Table 2. The addition of biochar strongly reduces the flowability of cementitious composites; hence, higher percentages of superplasticizer were adopted as biochar amount increased. It can be observed that the increase in superplasticizer dosage is not linear, since a higher increase was required to balance the loss in workability due to 5% biochar addition. This effect, which is in line to previous findings in technical literature [15,18,23,25,45], is related to the porous structure of biochar particles, which are able to absorb great amounts of water, so requiring higher dosages of superplasticizer.

Mix	Superplasticizer [%]	Slump value [mm]
C	1.0%	205
BIO2	1.2%	195
BIO5	1.6%	200

Table 2 – Superplasticizer amount (% by wt. of cement) and slump values.

4.2 Density

Biochar-added concretes present comparable density with respect to the reference mix. The values in terms of both fresh and hardened density values of concretes with different biochar additions are reported in Figure 8. As already observed in [23,25,46], the way that biochar addition affects density of cement-based materials, is related to two opposite effects. On one hand, the highly porous biochar particles are characterized by low density; but on the other hand, these particles, which are characterized by a wide size distribution, tend to fill the voids, so obtaining concretes with denser matrix and reduced porosity. As can be seen in Figure 8, as biochar content increases a slight variation in concrete density occurs, but the maximum increase in density, obtained for BIO5 in the hardened state, is less than 2% with respect to control samples, so completely negligible.

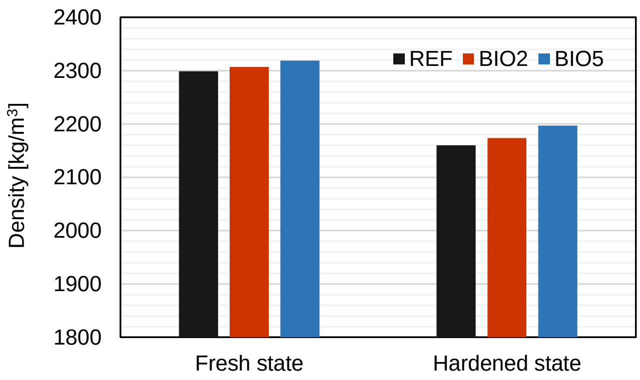


Figure 8 – Density at fresh and hardened state.

4.3 Water absorption and sorptivity

The attitude of concrete to absorb water was evaluated in terms of sorptivity and total amount of absorbed water. These properties help to obtain information concerning the microstructure of concrete as well as its durability, since water absorption and sorptivity can help to understand the attitude of concrete to resist against aggressive environments.

Figure 9 shows the sorptivity profile of concrete with 5% biochar with respect to control mix. The addition of biochar leads to a reduction of the absorption values, especially at the beginning of the test. This can be better appreciated by comparing the initial rate of water absorption of the two concretes. This quantity, which is obtained by using linear regression analysis for the data between 1 min and 6h, is defined as the slope of the line that best fits the sorptivity vs. √time in the first branch of the curve. 5% biochar addition results in an initial sorptivity rate equal to 0.0101 mm/√s, whereas the reference mix presents a value equal to 0.0124 mm/√s. It can be stated that the initial rate of water absorption is strongly reduced (by 18%) in case of biochar-added concrete with respect to the reference mix. This means that the addition of biochar is able to significantly reduce the presence of fine capillary pores, to which the initial sorptivity rate is related, since they are responsible for the initial rapid absorption of water when the concrete is immersed into water. This beneficial effect can be obtained thanks to the densification effect of biochar particles, which are able to reduce the porosity of the cement matrix by acting as filler as well as by retaining part of mixing water and releasing it during curing, so improving the hydration reactions.

The secondary rate of water absorption, which defines the second branch of the curve and is linked to macro-pores and air voids, cannot be evaluated, since it is not possible to find a linear relationship for the data between 1 and 7 days. However, as can be seen in Figure 9, the beneficial effect offered by biochar addition tends to be reduced for longer test periods. This corroborates the previous findings in the literature [18,19,47] on biochar-added cementitious materials that present enhanced initial sorptivity, whereas secondary sorptivity is comparable to, or higher than, reference specimens.

The results in terms of total amount of absorbed water confirm that biochar-added concrete is characterized by lower absorption, even if the beneficial effect is lower with respect to that offered to initial sorptivity rate. REF and BIO5 present water absorption values equal to 8.2% and 7.9%, respectively, which means a reduction of 3.64% when biochar is added to the mixture.

The results obtained suggest an overall improved microstructure of biochar-added concrete as well as improved durability, since the behavior of concrete in terms of water absorption and sorptivity is related to the resistance to sulfate attack and chloride ion diffusion [48].

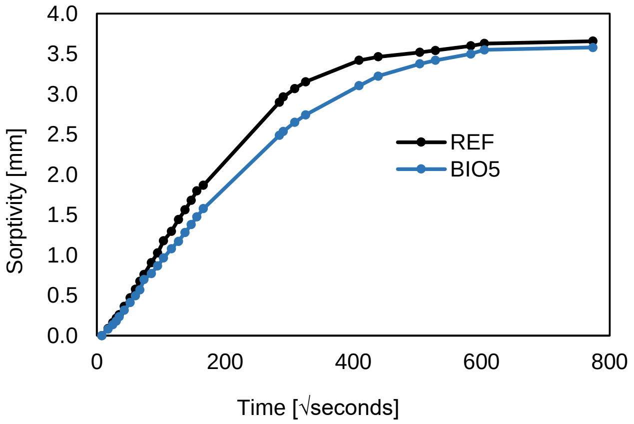


Figure 9 – Average absorption in terms of sorptivity profile vs. √time.

4.4 Compressive strength

Figure 10 shows the mean compressive strength after 7 days, 28 days, 1 year, and 2 years, for the different concrete mixes. 2% addition of biochar leads to a slight increase of compressive strength for all the curing times considered, and the improvement is more pronounced for longer curing. The addition of 2% biochar does not produce a significant effect at 7 days, whereas it improves the strength by 3%, 7% and 9% after 28 days, 1 year and 2 years, respectively. On the other hand, 5% addition tends to reduce compressive strength, especially for the first period after casting. Even if the comparison with reference concrete leads to different results for BIO2 and BIO5 series, a similar trend is observed as regards the improved development of compressive strength with time of biochar-added concretes.

The reference specimens show a compressive strength increase after 28 days, 1 year and 2 years with respect to the mean value at 7 days equal to 29%, 53% and 57%, respectively, whereas the development of strength is higher in case of biochar-added concretes. BIO2 samples present an improvement of 31%, 61% and 68% with respect to their mean value at 7 days, and these increases reach 39%, 68% and 72% when considering BIO5 mix.

The improved strength development is linked to the ability of biochar to act as filler as well as internal curing agent. Biochar particles, which are characterized by high water absorption capacity, retain part of mixing water, and release it with time to the concrete during hardening, as already highlighted in [15,18,25]. The promotion of the hydration reactions by biochar is more pronounced in case of dry conditions, applied in this experimental campaign after the first 28 days of water curing. After 1 year curing the strength development is almost concluded, even if after 2 years a slight compressive strength increase with respect to 1 year specimens can be still observed, above all for BIO2 specimens.

Moreover, the addition of biochar induces densification of concrete for two mechanisms. On one hand, it reduces the capillary porosity of concrete, since it lowers the amount of free water during concrete mixing. On the other hand, biochar fills the voids, so improving the packing pattern of the concrete matrix, as already observed in the analysis of density measurements. However, only low percentages of biochar addition improve the compressive strength of concrete, since biochar particles are weaker than the other constituents of concrete. Hence, the mechanical behavior of concrete worsens when considering too high additions of biochar, such as 5% in this study. This result is in line with previous research findings in the literature [12,17,19] that highlight a general reduction in compressive strength for biochar addition higher than 5%.

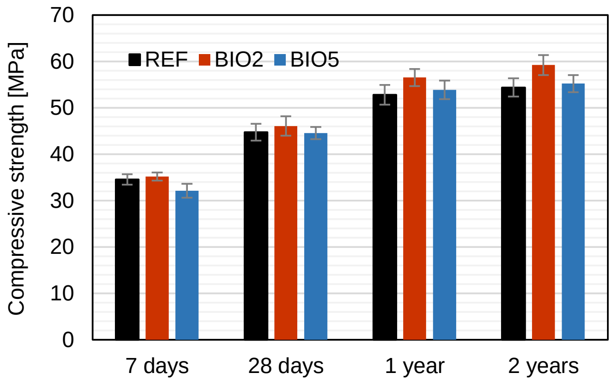


Figure 10 – Average compressive strength and corresponding standard deviation for different curing times.

4.5 Flexural strength and fracture energy

In order to give insights on long-term behavior, in the following the results from flexural tests are reported for 2 years curing specimens. Figure 11a shows the mean flexural strengths of biochar-added concretes with respect to reference mix. Flexural strength was computed on the basis of the peak load P_{max} of the load P – CMOD curves, as:

$$f_{ct,fl} = 1.5 \frac{P_{max} S}{b(d-a)^2} \qquad (3)$$

where *b* (equal to 40 mm) is the width of the cross-section of the specimens. The mean flexural curves obtained from 3PBT are shown in Figure 12a, for the three different concrete mixes.

As can be seen from Figure 11a, both biochar-added concretes show slightly higher flexural strength with respect to reference concrete. The experimental values of BIO2 and BIO5 present indeed an increase of 9% and 5% with respect to control mix. The results confirm the beneficial effects that biochar offers on long-term behavior of concrete, already observed for compressive strength. However, the flexural strengths of biochar-added specimens are higher than the values expected by applying the code formulas for traditional concrete starting from the corresponding compressive strengths. This effect can be better appreciated by analyzing Figure 11b, which relates compressive strength, as obtained from experimental results, to flexural strength, determined experimentally or by applying EC2 [49] relations. The same Figure reports the adopted relations, which enable to obtain the mean flexural strength $f_{ctm,fl}$ starting from the mean experimental cubic compressive strength $R_{cm,\ exp}$. While REF mix presents an experimental average flexural strength comparable to that evaluated according to EC2 formula, BIO2 and BIO5 are instead characterized by slightly higher values. These results are consistent with literature data for biochar-added concretes, which show a slight increase in flexural strength when biochar is added in the mixture [21,25,50].

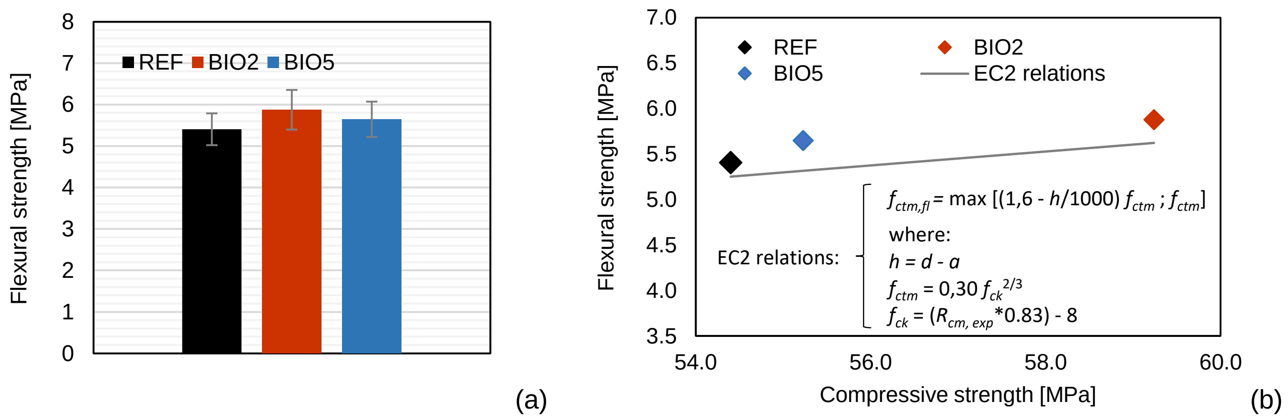


Figure 11 – (a) Average flexural strengths after 2 years curing and corresponding standard deviations, (b) correlation between flexural and compressive strengths.

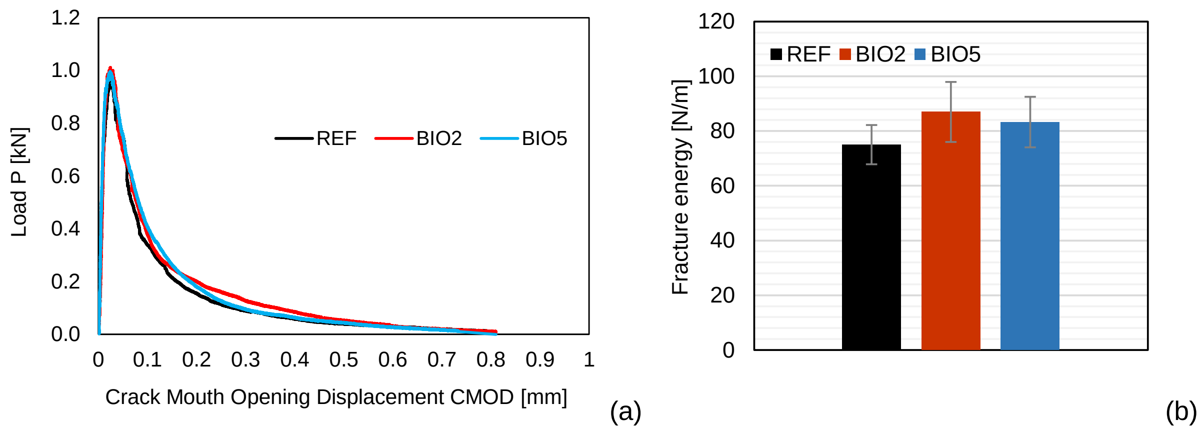


Figure 12 – (a) Average load P vs. CMOD, as obtained from 3PBT; (b) average fracture energy and corresponding standard deviation for the three tested concretes.

By performing three-point bending tests, it is also possible to evaluate the fracture energy G_f, since it is related to the ratio between the area W_0 under the P-CMOD curve (Fig. 12a) and the area of the nominal ligament A_{lig}, by also taking into account the work done by the deadweight of specimen and the loading equipment W_1. G_f was evaluated according to JCI-S-001 standard [43], as:

$$G_f = \frac{0.75W_0 + W_1}{A_{lig}} , \tag{4}$$

where $A_{lig} = b\,(d - a)$.

As can be seen in Figure 12a, the behavior after cracking slightly improves in case of biochar-addition, leading to higher residual loads in the post-peak branch of P-CMOD curve and higher energy absorbed during crack development. By comparing the experimental results reported in Figure 12b in terms of G_f, it can be stated that biochar tends indeed to increase the toughness of the material. 2% and 5% biochar additions produce an increase of G_f by 16% and 11% compared to that of control mix. As already observed for compressive and flexural strength, 2% biochar addition offers the best performance, also in terms of fracture energy. The use of biochar enhances also the ultimate displacements of concrete (in terms of maximum CMOD reached at failure, i.e. when the load is equal to 0.01 kN), which are about 5% higher than that of reference samples, so meaning a slightly increased ductility.

The ability of biochar to improve post-cracking behavior of cement-based materials is well known in the literature, however, its effect is strongly influenced by the characteristics of biochar particles, as well as the type of material considered (i.e. cement paste, mortar or concrete). This is the reason why the results in the literature are so scattered, even when considering an optimized percentage of biochar addition. Most of the studies (e.g. [16,19,20,22,24,47]) demonstrate that biochar addition leads to improvements in fracture energy values up to 100%, while others show that biochar does not significantly impact the post-cracking behavior, [25,26,46]. The influence on the fracture behavior depends on the grain sizes and the shape of biochar particles as well as the starting feedstock, which defines the quantity of stable carbon. An angular and elongated shape of particles, like that of the biochar used in this study and shown in SEM images (Fig. 5), enables to widen the surface of interaction with the surrounding cement matrix, so allowing the crack path to be more tortuous and delaying the typical brittle failure of cementitious materials. Also a wide grain size distribution is a key factor: the particles finer than the interfacial transition zone (ITZ) produce a densification effect, while others larger can extend over the ITZ, so proving stress redistribution during cracking. All these mechanisms enable to strongly enhance the post-cracking behavior of cement pastes and mortars, so proving a more ductile failure mode.

However, these effects are much reduced in case of concrete. The presence of aggregates of larger dimensions indeed strongly affects the crack development, by inducing deviations in the crack path, so providing the resistant contributions of bridging and interlocking across crack surfaces. Hence, as suggested also in [25], the presence of these mechanisms due to the coarse aggregates in concrete minimizes the beneficial effects that biochar particles can offer in case of cement pastes and mortars.

5. CONCLUSIONS

The results of this investigation suggest that biochar derived from commercial pyro-gasifiers that uses wood waste as incoming biomass can be successfully used as filler for concrete. Biochar improves the physical-mechanical performance of the concretes analyzed, especially when it is added by 2% by weight of cement, so confirming the optimal percentage already suggested in the literature for mortars. More in detail, the following conclusions can be drawn:

- Density is not significantly influenced by biochar addition, due to two opposite effects: biochar particles fill the voids, so leading to a densification of the matrix on one hand, but on the other hand, this doesn't affect concrete mass, due to the low particle density.
- Workability is reduced as biochar content increases. Nevertheless, a moderate increase in superplasticizer can counterbalance the adverse effect related to biochar addition.
- The reduced water absorption and sorptivity of biochar-added concrete confirm the improved microstructure due to the densification effect offered by biochar particles.
- 28 days compressive strength can be slightly increased by adding 2% biochar, whereas it is slightly reduced by 5% addition. Additional beneficial effects can be recognized for long dry curing, since the water trapped in biochar pores is gradually released so improving the hydration reactions and the strength development, resulting in an increase of compressive strength both for 1 and 2 years curing.
- Long-term tensile behavior in terms of both flexural strength and fracture energy is generally improved. By comparing the experimental results obtained for biochar-added concrete to previous research findings in technical literature on mortars and cement pastes, it can be stated that the same slight improvement in flexural strength is confirmed, while the enhancement in fracture energy is reduced. This reduction in concrete can be attributed to the activation of the prevailing resistant mechanisms of bridging and interlocking across crack surfaces offered by the coarse aggregates.
- On the basis of the water absorption results and mechanical performances after long curing, a good long-term behavior and durability of biochar-added concrete can be assumed, so confirming the potentiality of biochar to be used as filler for in situ applications of structural concretes.

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