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Master's degree in civil engineering

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Rheological and mechanical properties of cementitious materials with the addition of Biochar: A strategy to obtain 3D printability.

Tutor
Prof. Luciana Restuccia
Prof. Jean Marc Christian Tulliani

Co-Tutor
Devid Falliano
Daniel Suarez

Candidate
Juan Felipe Carvajal Pardey

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Companies Involved
Nera Biochar s.r.l

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BIOCHAR

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ABSTRACT

CO_2 emissions in recent years have reached the highest levels historically, with peaks in 2018 and stabilization in 2020 due to the pandemic. Construction and materials production is among the most contributing industries to the greenhouse gas emission *(GHG)* effect. Architectural design has become an essential tool to face this environmental problem, just like civil engineering with creating, manipulating, and implementing less toxic and harmful building materials, and the energy consumption control in the structure's life cycle, becoming strategies for the significant reduction of anthropogenic emissions. Charcoal manages to store 50% of its carbon content for centuries, while Biochar, due to its pyrolysis production process and natural decomposition, releases up to 90% of carbon in the first ten years.

Biochar, the solid subproduct of the pyrolysis process, is widely considered an effective water retention composite thanks to its morphology and high surface area. The opportunity of using it to improve the mechanical properties and achieve rheological requirements in cement pastes and cement mortar on a micro-scale is explored in this study. The results have demonstrated that with small percentages (1 - 5% and 7%) of Biochar used as a filler and substitution by cement weight in the sample preparation process, not only the compressive and flexural strength are increasing, but also the fracture energy, with a more tortuous crack path that increases the final fracture surface at an early age of maturation. However, this same behavior is not reflected at a late maturation age since there is an enhancement compared to the plain cement samples, but not as significant as that which occurs at an early maturation.

In cement paste samples, Biochar used as 2% filler by cement weight can increase by 63% and 23% the flexural and compressive strength after 7-days of curing, respectively, while 29% and 13% the flexural and compressive strength after 28-days of curing, respectively. When taking about fracture energy and ductility factor, the behavior still being positive, with an improvement of 124% and 18% respectively after 7-days of curing, while 150% and 14% respectively after 28-days of curing. In cement mortar samples, Biochar was used as a filler and as substitution by cement weight. In this case, the samples do not seem to follow the same trend or behavior as the cement paste, especially at a late maturity; the mechanical properties seem to remain the same as the plain mortar, close to about 6 MPa and 70 MPa at flexural and compressive strength, respectively. The rheological tests' experimental results suggest that the addition of Biochar can increase the consistency of cementitious paste at the fresh state (e.g., increase in plastic viscosity, shear stress, and yield stress) compared to the reference mixture, also offering a way to waste recycling. This main rheological parameter evaluated appears to increment as the addition of Biochar increments,

making the sample more viscous. Biochar's effect in the cement matrix in main rheological properties depends on the sample's preparation and the agglomeration of the particles and their content in each preparation.

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INTRODUCTION

New technologies and modern construction materials are currently being used in the construction field that little by little has been implemented and finding a place among the most conservative, ancient, and reliable materials. However, cement and concrete as a construction material, for many decades and even centuries *(1st century B.C.)* [1], has been the construction material most used for performance, economy, and excellence, as this compound of elements and materials has excellent resistance and is economical in the industrial field, concrete being the most widely used construction material around the world.

Thanks to its low cost and good performance, concrete is established as the construction material most desired by engineers, architects, and builders. However, this material over the years has undergone several changes, modifications, additions [2], evolutions that depend on the specific type of the mentioned modification, has managed to improve or maintain its mechanical properties, its application properties, and so on. However, its base design does not change in essence but proportions. The following are the essential components of a concrete mix [3]

- Cement (usually Portland cement)
- Water
- Aggregates (fine and coarse)

After these three essential components, hundreds of additional components can be used to modify some of the properties of concrete or modify some of the behavior of concrete, such as accelerating or retarding admixtures, plasticizer or viscosity admixtures, admixtures that improve the capacity resistance to flexural bending in horizontal or vertical elements and many more types of additives that are offered in the market.

Additionally, there is a great variety of aggregates, both fine and coarse, which depend on their proportion and their implementation, have their construction objective. These aggregates usually come from quarries that generally classify and modify said aggregates to find the most suitable proportion and dimension based on the mix design requirements and, like all components, it is sought to dose very precisely to preserve the mix design and guarantee its properties strictly. This is usually a standardization process, which, apart from maintaining the standards, helps to simplify the processes.

Having said that, the additives that are used to modify and change some of the properties and behaviors of concrete tend to have a high cost in the market, as their production is implied by changes in chemical and physical composition that involve the participation of machinery that must reach high temperatures and/or pressures to be able to make the required changes. In the same way, these additives are prescribed, made, prepared, and distributed for the construction industry, being mainly used in concrete mixtures that have a special requirement, and thanks to these additives, this requirement may or may not be satisfied.

Thus, different companies and researchers have taken on the task of studying concrete in its different stages to find different products that replace or reduce the use of additives due to their high cost. For this, they have mainly sought products that are waste from another chemical process, and that is usually a waste of a very low-cost product [4], which is why one of the materials that have been used for the modification and improvement of concrete properties has been the Biochar, which is generally biomass obtained from pyrolysis chemical process [43].

Therefore, this research's primary work is to obtain an optimal concrete rheological behavior for the 3D printing of this complex composite. In this way, it seeks to study the rheological properties of concrete and find its optimal design mixture that facilitates workability, but at the same time has an adequate viscosity to be able to model as required with the mechanical arm of the printer through the application of Biocarbon nanoparticles in their cement matrix in order to reduce or to eliminate the use of plasticizer or superplasticizer additives, lowering production costs.

SECTION 1: STATE OF THE ART

1. BIOCHAR

1.1 What is Biochar?

Biochar is defined as a solid rich in carbon obtained through thermal decomposition and molecular cracking of organic matter, called biomass, which undergoes a thermal combustion process at temperatures between 300 and 1000 ºC. It is, essentially, fine-grained charred charcoal [34]. The transformation is an anaerobic process, which means that it is carried out under limited oxygen conditions, almost nil. The International Biochar Initiative or IBI *(2012)*, in its "Standardized Product Definition and Product Testing Guidelines for Biochar that is Used in Soil," defines Biochar as "a solid material obtained from a thermochemical conversion of biomass in an oxygen-limited environment" [43].

The organic feedstock that is commonly used for Biochar production is quite diverse, among which are wood, wood waste, biomass crops, agricultural by-products such as cereal straw, crop residues, rice husks, quinoa and lupine residues, tobacco seeds, algae biomass, paper mill sludge, yucca rhizome, olive mill sludge, among others [31,34,43].

As mentioned above, agricultural waste and many agricultural by-products are an important source of raw materials for biochar production after heat treatment, but a valuable source is urban solid waste. An example of the latter one can be sludge, a feedstock for the creation of Biochar that promises thanks to its high content of carbon and nutrients such as ammonia. This sludge is a waste created from the wastewater treatment process, which, thanks to its treatment, will be used as biomass to produce a biological compound for improvement purposes, instead of being waste that little by little release leachate and toxic substances that have a harmful impact on the environment and people.

When talking about biomass crops, it should be taken into account that these crops continue to be investigated and criticized for being lands that can be used for food production and not for being used to produce biomass to make Biochar.

Biochar has had a good reception and a great deal of attention in recent years due to its own advantages and properties, such as adsorption, which is its primary mechanism for removing heavy metals and organic pollutants. Biochar's adsorption capacity is directly related to its physicochemical properties, such as its high carbon content and cation exchange capacity, a large specific surface area, the pore size distribution, and a stable structure (Rizwan et al., 2016) [49,53].

Biochar incentivized this and many more investigations. It also encouraged its application in different fields, not only soil and agriculture. An example is the application of Biochar in construction materials, such as cement paste, mortars, and concretes, which until now have shown positive behavior, improving their rheological and mechanical properties.

1.1.1 Physicochemical characteristics

Regarding its physical properties, Biochar is a black compound because it is a carbonaceous solid with an amorphous structure and a disordered surface, according to studies carried out by Qiu et al. (2008) [37], whose structural properties and construction characteristics vary depending on the feedstock, and the time it takes to carry out the chemical decomposition process for its production. The size of the biochar particles varies according to the pyrolysis time, especially the size of the biomass used for its production. (Lehmann, 2007) [42]. One of the main physical characteristics of Biochar is that it is a highly porous compound, where macro, meso, and micropores can be found. Micropores are usually <2 nm in diameter and are generated in the pyrolysis process, with a linear relationship between temperature and micro-porosity. From a constructive point of view, micropores are associated with the adsorption of liquid and gas compounds; therefore, retaining water in a cement mix helps internal curing by realizing the retained water in the hardening process of the cementitious composites, improving mechanical properties. On the other hand, macropores are inherent in the raw material. They are considered macropores when their main diameter is >50 nm, which allows the transport of sorbates allowing the transport of potent molecules. Finally, the mesoporous ones go from 2-50 nm [31,34,49].

Other characteristics that Biochar has is its low apparent density and its high surface area. Regarding its apparent density, there are values between 0.3 to 0.43 g/cm3; however, this value will depend on the raw material used. For example, higher values are found when the biomass comes from wood, such as white oak. (Pastor et al., 1993) [54]. Regarding the specific area, there are values between 200 and 400 m2/g; however, values of up to 14 m2/g can be found for Biochar produced from safflower seed or even values close to 1000 m2/g when biomass comes from denser materials [31]. It is crucial to bear in mind that Biochar undergoes chemical changes over time, and some of its main characteristics may even undergo structural changes. From the point of view of adding Biochar to cement mixtures, characteristics such as high porosity, specific area, and low density make Biochar a fairly good supplementary cementing material. The low density makes the cement mixture lighter. The high porosity, despite not being its best feature, helps the particles interlock better with each other. Finally, concerning the specific area, the larger this, the greater the adsorption of liquids and the better internal curing of cement or concrete paste [34].

Previously, it was explained that Biochar is a carbonaceous compound, and that is why its dark color, because despite being composed of several elements, its main structure is carbon, exceeding 60% in most Biochar. However, this percentage varies depending on the raw material or biomass, its origin, and the time set in the pyrolysis or chemical decomposition process. For example, white and red oak as feedstock for the production of Biochar from pyrolysis, the composition is 90.8% carbon, 7.2% oxygen, 1.7% hydrogen, and 0.3% ash (Cheng et al. 2008) [35,36] composed of small, light and porous particles. Now, if the feedstock is wheat and rice, the composition is 80.4 and 80.7% of carbon, 9.03 and 9.11% of oxygen, and 2.75 and 2.79% of hydrogen, respectively, but as in the scoop, it is important to preserve a structure mainly of carbon (Qiu et al., 2008) [37].

1.1.2 History and origin of Biochar

The different biomasses from which Biochar is derived are not recently discovered materials. At the end of the 19th century, the scientists' Smith and Hartt (1879 and 1885 respectively) rediscovered the black lands of the Amazonian Indians, called initially "Terra preta do índio" which translates black lands [32,33], which, unlike the surrounding soils, the latter were rich in kaolinite with a low cation exchange capacity and were also considered acidic soils (low pH), considerably reducing soil fertility [31,34].

Smith and Hartt noted the existence of dark and fertile soils in the Brazilian Amazon, but it was not until 2012 that Falcao [38], through his research, consider that these soils developed over time due to deposits of organic matter derived from the burning of biomass and remains of skeletons of marine amphibians left by the indigenous populations of the time, which is why these soils were considered rich in nutrients, being once again fertile soils. On the other hand, the scientist Sombroek [55], in the middle of the 20th century in his book "Amazon Soils - A reconnaissance of the soils of the Brazilian Amazon region," said that these soils were established 3000 and 5000 years ago, and that they were highly fertile and with high carbon content. This theory is supported by Glaser et al. [33] in 2001, saying that the large concentrations of carbon in the black lands of the Indians come mainly from cooking coal, fire debris, and non-combustible products. Theories about the anthropogenic origin of this type of carbonaceous soils include, as mentioned just before, the burning of forests for cultivation, settlements, and weed removal, which left the ashes at the mercy of the soil. All researchers agree that these lands are constituted by a high content of essential nutrients such as phosphorus *(P)*, Calcium *(Ca)*, and Potassium *(K)*, which makes these black lands of Indians highly fertile lands, with an alkaline pH and rich in nutrients [31]. This fertility and its color are due to its high content of carbonaceous material that has up to 70 times more Biochar than the closest soils surrounding these black lands, with a content of around 150g C/kg compared to 20-30g C/kg of land lacking nutrients and carbon.

The black lands of the Indians go back to the last times of the pre-Columbian period in the Amazonian part of South America (neves et al., 2003) [39]. However, recently this type of soils have been found in Central America and North America, in Mexico and the United States (Orlando 2012) [40], as well as evidence of black lands in Africa and Borneo (Sheil et al., 2012) [41] for more than 10 thousand years ago. These lands' origin is believed to have been caused by fires, both natural and intentional, in wooded areas and grasslands.

About the characteristics of these soils with high carbon content, it can be noted that they present a range of beneficial properties, such as the high content of organic material, a great variety of nutrients, and a good moisture content, allowing greater microbiological activity and cation exchange. (Lehmann and Joseph, 2009) [42]. Several studies published by different authors [35-38] describe a practice in China for the addition of Biochar in different soils as carbon stores for intensive crops that the Dutch scientist Sombroek called new black land. From here comes the practice of burning plant waste, and other types of biomasses, to be stored in the soils as a way to partially capture (carbon sequestration) excess atmospheric carbon to combat climate change.

During the early 20th century, Biochar began to gain more notoriety in different fields, especially in farmland, for its fatty composition in nutrients, promoting fertility. Japan has used a pyrolyzed biochar based on rice husks as biomass, which they called *Kuntan*, used as a moisture and gas absorbing material, as well as water purification. Thanks to its absorption property, activated biocarbon is used in gas masks to prevent the breathing of polluted air. However, biocarbon has many more characteristics and applications that motivate this and future research.

1.1.3 Chemical composition

The chemical composition of Biochar can be highly variable. Biochar is mainly composed of an amorphous and rigid carbon structure, which is complemented by ash, oxygen, and hydrogen; this is the main reason it is a dark material. However, there are two very important variables that influence the structure and composition of Biochar, which are the raw material or biomass and the chemical decomposition process for the production of this.

Biochar owes its black and dark color to its high carbon content in its composition (>60%) [31], which is made up of small particles that can be little, medium, or highly porous. It is also composed of ash and other additional compounds, which depend properly on the biomass used as feedstock for its production. Biochar currently plays a significant role in soil improvement thanks to fertilization, the sequestration of heavy metals and pesticide gases, water and nutrient retention, cation exchange capacity (CEC), and microbiological activity.

In the section on Biochar's physicochemical characteristics *(Sec. 1.1.1)*, it can be noted some of each element's percentages that make up the biochar compound. As can be seen, it is influenced by and depends on two main factors, which are biomass and the chemical decomposition process to obtain Biochar. These two processes are emphasized because they are essential to obtain a compound that works according to its purposes because they do not all serve the same aims.

1.1.4 Feedstocks

The raw materials that can be used as biomass or base for Biochar production are highly varied. Basically, there are numerous residues and wastes that are used to produce Biochar, providing a benefit to the environment by eliminating said residues for the production of a compound that serves to restructure the environment itself. One of the limitations for selecting biomass is that this raw material is not used to generate products of greater economic value, which are used for the production of food or public or environmental services.

Biomass can also be a wide variety of residual material, such as crop residues, animal manure, or firewood from tree felling, which under the process of pyrolysis can be converted into carbon or Biochar; therefore, energy is produced as a by-product. [44]. The "Globally available annual feedstock" presented by Woolf et al. (2010) [56] establishes an approximate 2.27 Pg C/year (1) of matter that is transformed into Biochar, distributed among crops, waste, and forestry as follows:

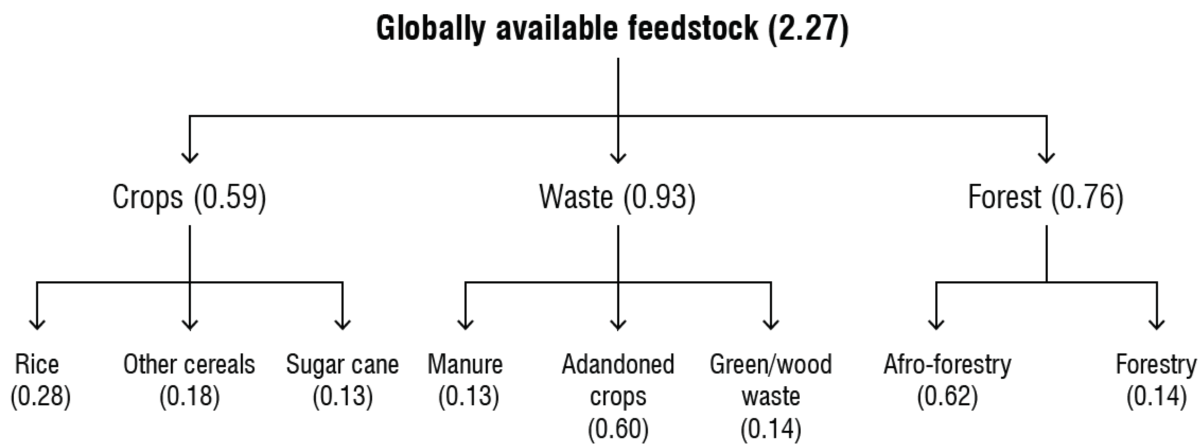


Figure 1. Globally available annual feedstock (in Pg C/year) and their distribution in different biomass [36].

These results presented in Figure 1 are an estimated and approximate value of the origin of a feedstock. However, they are not precise or accurate due to the yield of the biochar changes in accordance with the biomass and the pyrolysis conditions used in the thermochemical transformation process.

Lehmann and Joseph (2009) [42] state in their research that the feedstock can be wood, crop residues, manure, and leaves, but these are only one part of the many sources of biomass, such as biomass residues crops, the biomass of trees, dry plants, olive residues, rice or paper waste and the most important organic waste, such as sludge generated from human waste. There are other feedstocks that Brick (2010) [46] includes, which are orange peels, walnuts, bird beds, and algae that, when they go through their transformation into Biochar, ensure the exclusion of germs that could be harmful to human or animal consumption crops allowing the implementation of this type of Biochar for agriculture.

In this document, it has already been mentioned a couple of times that both the biomass used as feedstock and the characteristics that are set for the thermochemical transformation process in pyrolysis define the specific structural and chemical characteristics of Biochar, giving rise to materials that are considered heterogeneous according to Antal and Grønli, 2003; Brick, 2010 [45,46]. The resulting Biochar comprises a series of physical and chemical properties that define the beneficial effects that Biochar has and its residence time in the soil that depends almost exclusively on the organic components that make up the biomass [31,43]. The following table shows in more detail what type of biomass is used and how much its yield is with respect to Biochar.

Table 1. List of biochar yield from different feedstock [34].

Biomass	Process	Biochar Yield (% wt.)	References
Oak wood	Fast pyrolysis at 500°C	31.2	Novak et al. 2009
Corn husks	Fast pyrolysis at 500°C	26.0	Purevsuren et al. 2003
Olives stones	Slow pyrolysis at 600°C	39.7	Mullen et al. 2010
Pine wood	Fast pyrolysis at 800°C	32.1	Mullen et al. 2010
Olive bagasse	Slow pyrolysis at 500°C	39.7	Spokas et al. 2010
Palm shell	Slow pyrolysis at 400°C	24.8	Spokas et al. 2010
Pine saw dust	Slow pyrolysis at 800°C	24.3	Spokas et al. 2010
Spruce wood	Fast pyrolysis at 600°C	37.5	Spokas et al. 2010; Sukartono et al. 2011
Euclyptus wood	Slow pyrolysis at 400°C	42.2	Spokas et al. 2010
Olive husk	Fast pyrolysis at 800°C	39.7	Spokas et al. 2010
Beech wood	Slow pyrolysis at 500°C	26.2	Spokas et al. 2010
Corn cob	Slow pyrolysis at 800°C	23.2	Tsai et al. 2012; Zhao et al. 2013
Rapeseed stalks	Slow pyrolysis at 400°C	32.1	Zhao et al. 2013
Pitch pine	Fast pyrolysis at 500°C	39.7	Zhao et al. 2013
Straw pellets	Slow pyrolysis at 400°C	24.8	Zhao et al. 2013
Willow pellets	Fast pyrolysis at 700°C	24.3	Kim et al. 2012
Conocarpus waste	Fast pyrolysis at 500°C	37.5	Al.Wabel et al. 2013; Masek et al. 2013
Walnut-shell	Slow pyrolysis at 500°C	21.8	Masek et al. 2013

Vassilev et al. (2013) pointed out that biomass can be classified according to its source into groups such as woody, aquatic, agricultural, animal, and human waste (urban sludge) and industrial waste biomass. The primary source of biomass from firewood residues is forest areas, consisting of stems, branches, bark, chips, and leaves of different types of trees.

Agricultural crops and their residues constitute the second leading source, which considers stalks, straw, corn, sawdust, and shells of their respective crops.

In addition to the considerations of Vassilev et al. (2013), the classification based on lignin and cellulose is useful when it is expected to obtain a certain product after treatment and chemical transformation through pyrolysis. Classifying biomass estimates its own content of lignin and cellulose, being woody or agricultural biomass containing less sulfur than biomass from industrial or animal waste [47].

1.2 Production process

Production of Biochar, thermochemical technologies are considered to transform the different biomass types into renewable energy sources. Laird et al. (2009) [48] divide these technologies into slow pyrolysis, fast pyrolysis, and ultra-fast pyrolysis (Flash pyrolysis).

Pyrolysis, also called bioenergetic conversion [50], is a thermochemical process that is carried out in oxygen-free conditions at a temperature that varies between 300 and 900 ºC that aims to transform biomass and other low energy density organic materials to high energy density solids such as Biochar, as well as liquids and gases, which can be bio-oils or syngas respectively (Cf. Figure 2).

When temperatures higher than 300 or 500 ºC are reached, the organic materials that make up the biomass thermally decompose, generating a vapor phase that produces a residual solid part called Biochar. When this vapor goes through a rapid cooling process, it condenses and creates the liquid phase that is the bio-oil. Finally, those particles of the most volatile part of the compound are the syngas [31-34,47]. The pyrolysis process is essential to obtain high-performance Biochar, with a large percentage of carbon, usually above 90% of the final product.

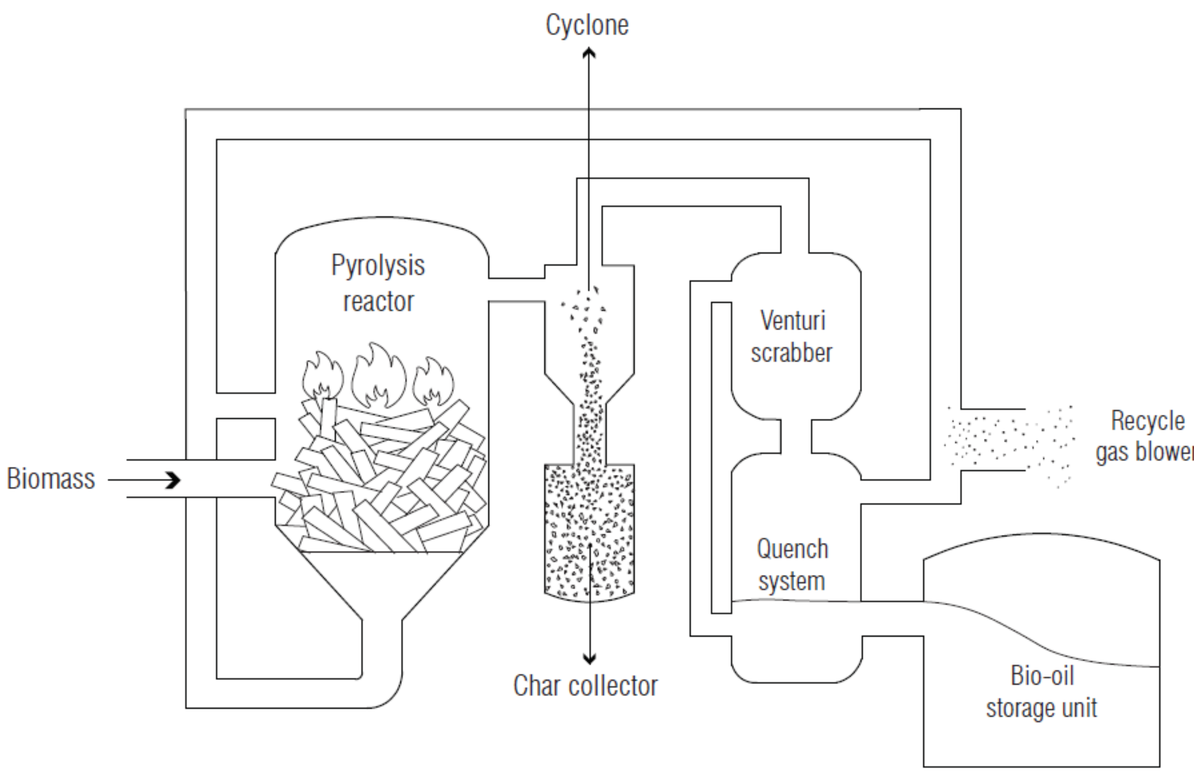


Figure 2. The general model of Pyrolysis process [34].

1.2.1 Slow pyrolysis

It is considered the process with the highest yield of Biochar according to the scientist Gheorghe et al., (2009) [57] because this process is characterized by slow and paused periods of heating of the biomass, low average temperatures and long periods of residence, where residence times for biomass can be found between minutes to days, and shorter times for gases, which usually take more than 5 seconds [31]. Heating grows at a slow rate between 0.1 to 2.5 ºC/s and temperatures reach 500 ºC. In the slow pyrolysis process, the raw material is placed in a reactor at the beginning of the pyrolysis, while, in the fast pyrolysis, the raw material is placed in the reactor when the desired temperature has already been reached [49].

1.2.2 Fast pyrolysis

In this process, unlike the previous process, the biochar production is much lower according to Farag et al., 2002 investigations [58] due to the temperature and the rate of increase. Heating grows at a rapid rate, between 10-200 ºC/s and temperatures quickly exceed 550 ºC, reaching 900-1200 ºC. The raw material must be added to the reactor when the desired temperature is reached, but it cannot be at the end nor at the very beginning. The thermochemical process causes the breakdown of the raw material's polymers into condensable vapors that form liquids.

The residence time of the steam is short, between 5 and 10 seconds, producing high-quality products; Regarding liquids, bio-oils are produced in around 60 to 70% of the final product; Regarding gases, ethylene-rich syngas is produced that is used mainly to produce alcohols and even gasoline. According to Mullen et al. (2010) [59], Fast pyrolysis can become a safe method to eliminate toxins in contaminated raw materials.

1.2.3 Ultra-Fast pyrolysis

In the present thermochemical process, the temperatures are more moderate than the slow and fast pyrolysis process, around 400-600 °C, with a heating rate increase between 2-4 ° C/s. Residence times are even shorter than fast pyrolysis, usually less than 2 s. Sadaka et al. (2007) [60] point out for liquid and oily products, such as the production of bio-oils, reach their highest yield, around 75-85% using ultra-fast pyrolysis. There are particular and alternative cases in which the temperatures are very high, between 800-1200 °C with heating rates >500 ° C/s, achieving a better liquid product performance.

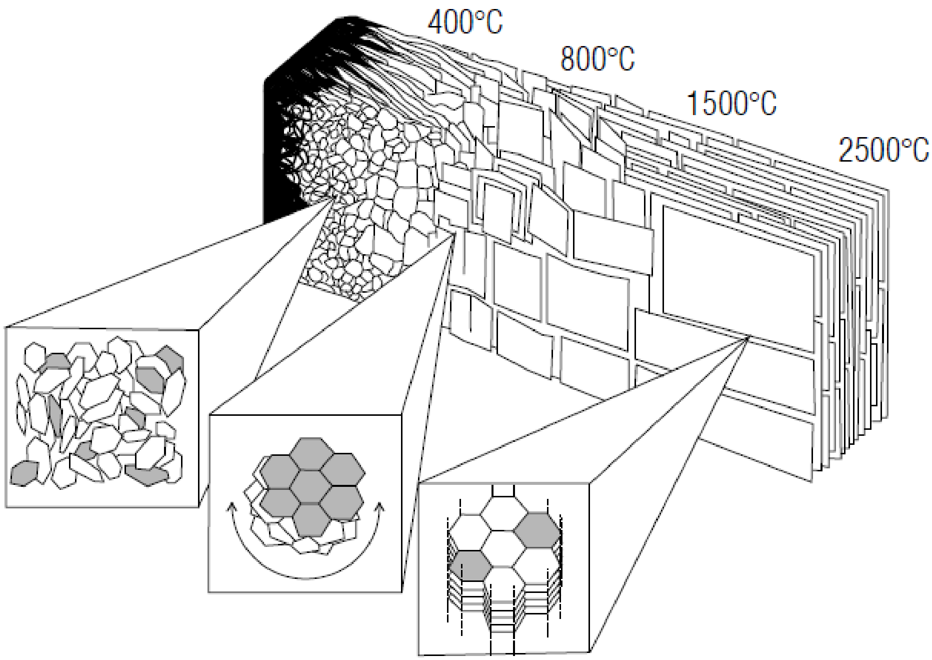


Figure 3. Stabilization of the carbon at different pyrolysis temperatures [34].

Figure 3 shows the final product's stability when the temperature at which the system is found is higher in the pyrolysis process. When the system exceeds 380 °C, the amorphous matrix C begins to reduce; consequently, the polyaromatic graphene sheets begin to expand. When the temperature exceeds 600 °C, carbonization begins, and the graphene sheets begin to align [31-34].

The yielding of the Biochar and any by-product of the pyrolysis process depends on the temperature of the pyrolysis type and, consequently, the feedstock. Both characteristics are intertwined because the same feedstock has not the same yielding or performance passing through different pyrolysis types. In the end, it is cooperative work.

Table 2. Comparison of temperature effect on biochar yield for different biomass [34].

Authors	Biomass	Temperature range (ºC)	Biochar yield (%)
Shabangu et al.	Pine	300-450	26-58
Sanchez et al.	Sewage slug	350-950	39-52
Ayhan Demirbas	Olive husk	450-1250	19,4-44,5
Aysu and Kusuk	Ferula orientalis L	350-600	26,29-40,26
Zhang et al.	Corncob	400-700	20,2-34,2
William and Nugranad	Rice husk	400-600	25,5-33
Ayhan Demirbas	Corncob	450-1250	5,7-30,6

1.3 Properties and applications

Biochar is a thin, fragile, porous, and light compound, with a large surface area and absorption capacity, useful for liquid retention. Like its origins, it has a basic pH and high carbon content like the black lands of Indians. Its properties vary depending on the biomass from which the feedstock is extracted and the thermochemical transformation process, as well as the input parameters. The carbon content of the Biochar is linked to the biomass, for example, the Biochar produced by the Nera Biochar company that uses oak and other wood derivatives as biomass contains a carbon percentage greater than 90-95%, the carbon content makes it stable for long periods. One of Biochar's properties is its capacity and effectiveness of carbon sequestration, benefiting and improving the properties of soils and the environment [51].

Researchers and scientists have received Biochar well for its characteristics and benefits in soil improvement and its carbon sequestration ability to heal the environment. Biochar is usually used in cases where the soil is not very fertile, promoting the growth of plants and vegetation, directly affecting the soil's physical properties, mainly due to the liquid and nutrients retain capacity that are later released for hydration and feeding the vegetation, increasing the pH and reducing the emissions of carbon dioxide *(CO_2)*, nitrous oxide *(N_2O)* and other compounds that, when released, pollute the environment.

Current research points to using Biochar as an agent to remove organic and inorganic impurities. One of the applications pointed out in subsequent work is eliminating irradiated or contaminated soils and waters with a high content of bacteria and low pH. Activated carbon is a widely used compound for the removal of pollutants, such as antibiotics, polycyclic aromatic hydrocarbons *(PAHs)*, polychlorinated biphenyls *(PCBs)*, volatile organic compounds *(VOCs)*, agrochemicals, and in special a series of inorganic contaminants. It is intended that Biochar may also be an economical solution to these problems in the future, replacing and complementing the use of activated carbon and biocarbon, and similar agents. [51,61-68]

Beyond Biochar's benefits for the environment, the inclusion of Biochar in the construction field has expanded, motivating this research. Bio-products derived from wood has been included as a feedstock for the improvement of cement paste, mortar, concrete, among other construction materials included in different forms, such as Biochar Nanotubes *(Biochar NTBs)*, micro and nanoparticles that can alter the cement matrix without reacting in the absence of water, to improve its rheological and mechanical properties.

Different investigations focus on the use of Biochar in the construction industry have included this compound in the different mixtures as a filler on a micro or nanoscale because it does not react with the cement matrix. One of the characteristics of Biochar is its ability to retain liquids thanks to its high porosity; this is of vital importance because the water is gradually released as the cement goes through its hardening state, helping the hydration and curing of the cement in the first days, providing a good polymerization condition for the cement or concrete which allows the development of the microstructure, shrinking pores that weaken the structure and the fines washing by the flow of water through these pores. Thanks to these characteristics and properties, it is expected that cement mixtures improve their rheological and mechanical properties. Additionally, its inclusion in construction materials is expected to reduce polluting gases such as carbon dioxide.

The different investigations, including the investigation of this document, look for an optimal recipe for cement and concrete with the inclusion of Biochar, where the best performance of the mixture can be obtained, reaching the most efficient mechanical and rheological requirements, taking into account the reduction of the environmental impact of materials. [69-74]

The advantage of Biochar is that it is a component that is obtained from a waste, which the application of this can always bring significant environmental benefits, and as evidenced in the literature, also for construction materials and impurities removal treatments, making it a potentially used and researched material for many scientific fields.

1.4 Production biomass in Italy and Nera Company

In Italy, the production of Biochar is still being implemented by some companies that seek to transform biomass into bio-oils, Biochar, and syngas that can be used as products to improve and treat other processes that may require it. In total, 42 [34] pyrolysis units are currently in Italian territory, with various input materials, pyrolysis processes, and final product.

There is a company called Ecco soluzioni located in Vimercate *(M.B.)*, producing Biochar with a limited number of pyrolysis units. This company works directly with the biomass and waste from which its Biochar is produced. The European Regional Development Fund (ERDF) finances a project directed by The Laimburg Experimentation Center and Unibz in the University of Bolzano facilities called "*Wood-up,"* aiming to implement and improve production Biochar to obtain a better performance based on wood as biomass. Alto Adige Sud Tylor has gasifiers and pyrolizators (around 36 units) to produce syngas and charcoal. His focus is on charcoal used as a biomass improvement for Biochar production with a higher yield, reinforcing the cycle.

In Rome, the Romana Maceri company focuses on recycling and storing paper, plastic, glass, and wood [34]. They have two pyrolysis machines and produce syngas and Biochar. They also focus on Biochar's performance that is used to remove impurities from the water, while syngas is used as an enhancer of the Biochar production process, improving the production cycle.

1.4.1 Nera Biochar Company s.r.l

This company is located in Italy, in the Piedmont region, city of Ivrea. The company has been characterized by using products without synthetic substances, focused on the environment. The company defines itself as "Unlike other biochar (vegetable carbon) derived from gasification residues, ours is 100% guaranteed because we only produce Biochar (vegetable carbon)", found in the original language as "*A differenza degli altri biochar (carbone vegetale) che derivano dagli scarti della gassificazione, il nostro è garantito al 100%, perché noi produciamo solo Biochar (carbone vegetale)*" [52].

The Biochar produced by the Nera company uses wood from a controlled supply chain such as biomass to produce its bioproduct. One of the Biochar with the highest yielding is that from wood or wood residues as feedstock. This research uses a high-quality controlled Biochar with guaranteed origin and significant-good performance.

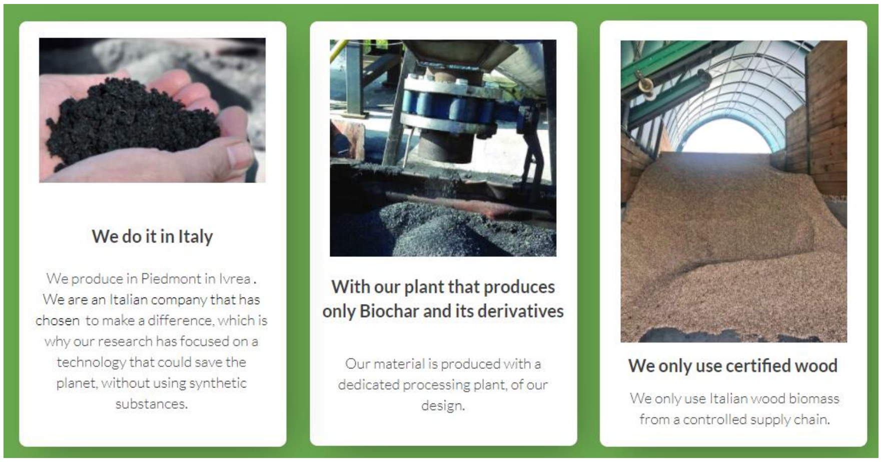


Figure 4. Nera Biochar Company s.r.l. "Who we are" [52].

2. RHEOLOGY

After military engineering, civil engineering is the first engineering, addressed and specialized in construction, design, and maintenance of the environment's infrastructures, including roads, buildings, bridges, tunnels, and other related constructions [5]. Research dates *"The earliest civil engineering practices could have started between 4.000 and 2.000 B.C. in Ancient Egypt and Mesopotamia when humans began to abandon the nomadic existence, creating the need for shelter. During this time, transport began to increase its importance, which led to the development of the wheel and navigation"* [5], thus being one of the oldest practices developed by man, due to its indispensable need for development and everyday life.

This is how, since that time, both the manner of building and the different construction materials have undergone some drastic and important changes allowed the development of new, modern and more massive constructions to date. It can be credited that the evolution in studies and the growing population are the main detonators of these changes in construction.

At present, the construction material most used in architecture and engineering works worldwide is concrete, followed by steel. The combination of these two materials, which is called reinforced concrete, which comprises a majority part of the concrete and a minor part of reinforcing steel, increases the mechanical properties of concrete such as shear strength, bending moment and bearing moment capacity. Hence, concrete, adding the value of its low cost, has been and will continue to be the construction material par excellence.

To continue using concrete or cement composite, it is important and required to study its properties and understand how cement works to improve said properties and find an optimal mixture that allows the cement to improve its mechanical behavior. Nonetheless, first, the concrete must be studied in a fresh-state and obtain all its characterization and attributes, to then study its properties in a hard or solid-state and obtain a compound with a genuinely exemplary performance while maintaining its low cost. Here is where the science of rheology comes in, a new science of flow and deformation of a material, thus characterizing the stress-strain relationship of a material that has the ability, such as cement and concrete, to flow. [6]

It is recalled that this ability to flow occurs in the cement's fresh state, a state that lasts very little, a few minutes, and allows the mixture to adapt to the mold or adapt to the shape previously indicated.

2.1 Rheology of concrete

Eugene Bingham introduces the definition of rheology as

"*Rheology is the part of physics that studies the relationship between stress and strain in materials that are capable of flowing. One of the most important goals in rheology is to find constitutive equations to model the behavior of materials. These equations are generally tensorial in nature…*" [7]

The mechanical properties studied by rheology can be measured using rheometers, devices that allow the material to be subjected to different types of controlled deformations, and to measure the stresses. Some of the most important rheological properties are:

- Apparent viscosity (is the shear stress applied to a fluid divided by the shear rate. For a Newtonian fluid, the apparent viscosity is constant and equal to the Newtonian viscosity of the fluid)
- Coefficients of normal efforts
- Complex viscosity (response to oscillatory shear stress)
- Storage modulus and loss modulus (linear viscoelastic behavior): relates to the material's ability to store energy elastically. Similarly, the loss modulus (G" or E") of a material is the ratio of the viscous (out of phase) component to the stress and is related to the material's ability to dissipate stress through heat.
- Complex nonlinear viscoelasticity functions

Eugene Bingham looks at the etymological sense of the word "rheology" it could define it as "*the science of flow. Rheology describes the deformation of a body under the influence of stress…*" [7] it can be applied to all types of material, solid, liquid, or gas.

An ideal solid is elastically deformed, and the energy required for deformation is fully recovered when the applied stress is removed. While ideal fluids are irreversibly deformed, they flow, and the energy required for deformation is dissipated within the fluid as heat and cannot be recovered by removing the applied stress. However, only a few liquids behave as ideal liquids; The huge majority of liquids show a rheological behavior classified in an intermediate region between liquids and solids: they are both elastic and viscous why they are called "*viscoelastic.*" On the other hand, real solids can be irreversibly deformed under the influence of forces with sufficient magnitude; in short, they can flow.

In this classification of the rheological behaviors of materials in relation to their response to applied stresses, a new parameter has to be introduced: the time scale in which the deformation is applied. To do this, a new magnitude is defined that considers the observation time; it is the Deborah number: $De = \lambda/t$, where λ is the relaxation time, and t is the observation time. Hence, a large Deborah number defines a solid type of behavior, and a small Deborah number defines a liquid type behavior.

2.2 Cement paste

The construction field employs cement for every work that is performed, because it has a huge amount of uses in this field and because it's the base for the concrete. Some researchers and engineers employ cement paste and cement grout as the same composite, which is cement and water in a mix. It is a semantic confusion produced by the definition that each cement and aggregate producer gives it.

While some companies define cement paste as a paste that is added on top of cement and water, other companies sell the meaning of cement paste as the mixture between cement and water only.

The *cement company Sisco* in its article *cement paste* exposes

"Cement paste is a paste, to be prepared on-site, which results from mixing a paste prepared at the factory (base paste) to which cement and water are added. The resulting final mixture is a highly plastic paste, easy to apply, which constitutes a highly hard coating, with significant resistance to extreme weather conditions." [8]

Instead of, in the case of the ongoing investigation, it will be understood that the cement grout is the mixture between cement and water (as defined by 360EnConcreto) [2] and will be treated with the term "Bianco," which will later be added the biochar component and the superplasticizer additive, to be studied and to know what the main effect of Biochar on the rheological properties of cement is.

2.3 Mortar

Huaman Bautista Yuval and Eng. Jorge Julian Castro [6], in their article "Rheological behavior of fresh concrete" with the original language in Spanish, define rheology as

"As mentioned above, rheology is the science of the flow and deformation of the material. It is the relationship between stress and strain in materials with the ability to flow. Is science that is currently considered new…" and they add, "In the construction industry, concrete is probably the most important composite material, emplaced mainly in a fluid state, which is why studying its rheological properties, despite its complex composition, is not usually an easy job." [6]

The ACI (American Concrete Institute) [9] refers to some properties of the concrete that are critical when it comes to the application: workability, compaction, stability, and consistency. On the other hand, the following definitions are subjective but link commonly used words with physical factors that can be measured:

- Stability: exudation and segregation
- Compaction: density
- Mobility: friction angle, adherence and viscosity.

Of which, those that are measured in the fresh state (fluid state) intrinsically measure their rheological properties.

2.4 Rheological properties

The rheological properties of the cement paste and mortar worked on in this study are directly linked to knowing the properties in the fresh state that allows these cement-based materials to flow and, in turn, support their own weight and the weight of the overlayers. The main objective of the admixtures implementation, in this case, Nera Biochar, is to achieve certain fresh state properties that allow workability, flow, and viscosity for the use of this mixture in the digital manufacturing of cement and mortar paste. The construction with the absence of formworks brings economic advantages, saving time and materials produced by the assembly and disassembly of formworks. At the same time, it brings a challenge in materials engineering since the properties and the deposit of the material must satisfy the requirements that were previously provided by the forms. According to those mentioned above, it is crucial to control rheological properties and hydration to guarantee exudation [102,103].

From a rheological perspective, a balance must be found between flowability before and during the digital fabrication process and the structuring rate just after deposition. In the same way, cement is very sensitive to hydration, and the addition of Biochar can influence this behavior, which is why it is important to predict the flow rate to manage the deposition speed adequately. Therefore, the purpose of this study is to seek a strategy through the addition of Biochar on the cement and mortar paste to obtain the mechanical and rheological properties necessary for digital manufacturing, from workability, viscosity, and flowability, to its early and late maturing characteristics.

The rheological properties related to flowability and workability are important because, from those, the efficiency and success of the layering are determined, especially in the case of automated construction of cement-based compounds. From a practical perspective, viscosity and workability can be defined from rheological parameters such as plastic viscosity, shear stress, and yield stress. According to Wallevik et al. [104], plastic viscosity describes the resistance to flow, which decreases as the shear rate increases up to a certain point of minimum plastic viscosity (η_{min}) and then begins to increase slightly with increasing shear rate. Besides, the stress above which the flow begins is called yield stress (τ_y), and below this, the flow tends to finish [103], but more importantly, it determines the stability of the suspension [105].

The mix design influences and directly affects the rheological properties of cement, especially when Nera Biochar and any other supplementary cementitious material or additives are added. Additionally, cement-based mixtures are sensitive to aggregates, and their size since the interaction between particles and shape plays an important role, altering the sample's rheological and mechanical behavior. The current study seeks to add Biochar as an admixture to model a cement and mortar mix that acquires the properties of digital manufacturing. For the automated construction of cement-based mixtures, it is sought to implement Nera Biochar with the appropriate proportion, plus applying a plasticizer additive in a balanced combination to achieve the required rheological properties without affecting the compound mechanical properties.

2.4.1 Modified Slump Test:

Due to the high costs of rheometer tests, it was proposed to use the modified Slump test, considering that its original test is one of the most widely used worldwide. The normal slump test or concrete slump test measures the consistency of fresh concrete before it sets. It is carried out to check the workability of the freshly made concrete and the facility with which the concrete flows. In addition, the slump test is used to ensure uniformity for different concrete loads under field conditions.

Developed at the National Institute of Standards and Technologies NIST in the united states, the slump-time curve depends on both the static stress and the plastic viscosity; this slump-time relationship led to the conclusion that time is the appropriate parameter to complete the slump test. Measurements made of the slump as a function of time showed curves that could be computer-simulated assuming the concrete in the fresh state as a Bingham material (Cf. Figure 5)

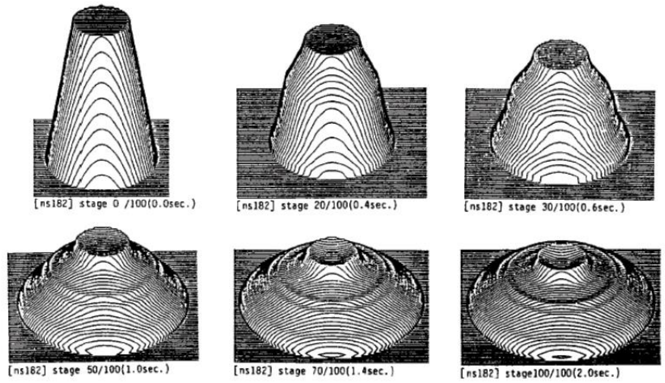


Figure 5. Slump test simulation[10].

Here is the modified slump test equipment and procedure.

- Horizontal base with the addition of a 35 cm high steel bar.
- Standard slump cone (ASTM C 143-90). [10]
- Sliding plate.
- Rod for tamping.
- Graduated ruler.
- Stopwatch with an approximation of 0.01s.

The concrete is placed in the same way as in the standard slump test (ASTM C 143/ITINTEC 339.035). Then the following steps are performed.

1. Using a wet cloth, wipe the part of the center rod that is above the concrete sample.
2. Slide the plate along the rod until it is in contact with the concrete surface.
3. Carefully lift the cone vertically while operating the timer.
4. While the concrete is flowing, continually watch the plate and stop the timer as soon as the plate stops moving.
5. Once the slump is stabilized or after one minute after starting the test, remove the plate and measure the slump with the graduated ruler (Cf. Figure 6).

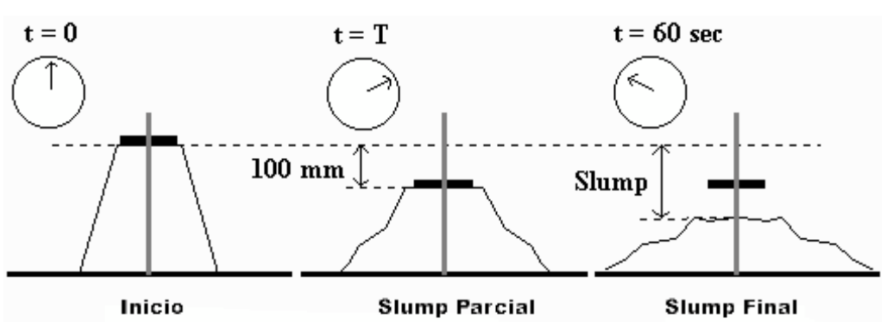


Figure 6. Modified Slump test schem [10].

Model for evaluating static stress

To find the static stress, the following formula was proposed considering the analysis of the Bingham model for the slump test and the static stress measurements using the rheometer.

$$\tau_0 = \frac{\rho(300 - s)}{347} + 212$$

Where:

ρ: concrete density [kg/m^2]
s: slum measured [mm]
τ_0: static stress [Pa]

The static stress prediction given by this model is quite acceptable, having an average error of 162 Pa, compared to other models with high error values.

2.4.2 Semi-empirical model to evaluate plastic viscosity.

To evaluate the plastic viscosity of the modified slump test results, the following hypothesis was used: for the same final slump and the same concrete density, a difference in slump time can be attributed to a different plastic viscosity. Performing the dimensional analysis of the test parameters and the measurements made in a rheometer, the following formulas are proposed:

$$\mu = 1.08 \cdot 10^{-3}(s - 175)\rho T \quad 200 < s < 260\ mm$$
$$\mu = 25 \cdot 10^{-3}\rho T \quad s < 200\ mm$$

Where

ρ: concrete density [kg/m^2]
s: slum measured [mm]
T: time of slump [s]
μ: viscosity [Pa]

In this way, the characteristic viscosity of the mixture is known, one of the main properties to characterize a specific composite based on the rheological properties of concrete. It is highlight that studying the properties in the fresh state of concrete, despite being difficult to characterize, is one of the main steps to characterize rheology of a sample of cement paste or concrete.

3. SPECIAL CONCRETE

Special concretes are those cement-based compounds that are both slightly and strongly modified to obtain better cement paste characteristics or concrete characteristics. Special concrete is not only sought to improve the characteristics of cement-based material, such as rheological or mechanical properties but also to obtain more sustainable and economical product by looking for alternative materials, especially waste material that can be reused in a new process to reduce the contamination produced by itself and in this way use them in the production of cement paste and concrete.

Cement is the main binder for concrete, thus making it an essential component in civil infrastructure production. However, despite its outstanding performance, cement has a very harmful production process for the environment, especially in clinker production, which requires temperatures above 1400ºC for its production, using large amounts of energy and significant damage to the atmosphere. Additionally, cement has a performance that can be improved thanks to different materials added at different scales, such as in the cement matrix at the microscale and at different stages of making the cement or concrete paste.

In order to create a compound that favors the rheological and mechanical properties of concrete and likewise be able to complement cement as the main binder with the addition of alternative binder materials, the following special concretes and compounds are presented, which follow the objectives of this research, like alternative cementitious materials *(ACM's)*, supplementary cementing materials *(SCM's)* and nanomodified of cementing materials *(NMCM's)*.

3.1 ACM's

Sustainability goals and the associated demand for taking care of the collective environmental impacts of cement or concrete production are the major impetus for change in cement technology. Considering impact effects that should be reduced in order to care the environment involves greenhouse gas emissions of carbon dioxide CO_2e, extractions of virgin materials, energy consumption, water extraction, and water use [23], which can be compounded due to the low durability that require a replacement in early age. That is why they are introduced in the study the alternative cementitious material ACM's because they have the potential to provide a major reduction in these impacts [17]. An important issue of these ACM's is that they can be produced with significantly lower greenhouse gas emissions and required lower energy consumption than the portland cement composites. Forward quantity results of saved CO_2e can be observed and see that the mixtures' durability and mechanical properties based on alternative binders are improved to the Portland cement. The water consumption is expected to be lower than the non-Portland cement base, as equal to the increase of the freezing and thawing resistance. Then increasing the service life [17,18].

3.1.1 Specifying alternative binders

The construction materials used today have technical specifications for implementation that regulate their use around the world. These specifications are generally classified as prescriptive or performance-based. [17,18] Those performance-based specifications are flexible enough to allow the use of a non-Portland cement-based binder, while those specifications that are prescriptive for Portland cement exclude the use of an alternative binder material. The ASTM (American Society for Testing and Materials) in the United States has provided in parallel the standard ASTM C150 [19] for prescriptive and the standard ASTM C1157/C1157M [20] for performance-based; However, the latter one has not yet been widely accepted by the state regulatory authorities, limiting it is widespread and use of the same standard method. One of the most recent standards that have been adopted and cover the broader category of rapid hardening hydraulic cement in a performance-based approach is the ASTM C1600 [24] Standard.[18] On the other hand, and also conservative, the European Union (EN) is a predominantly prescriptive cement standard EN 197-1 [21], which is referenced by the EN 206-1 [22] concrete standard, thus disfavoring the implementation of non-Portland cement in its territory, unless product-specific Technical Approvals can be obtained. However, being partially independent nations and with their research bases and appendices, which are below those established by the EN, they seem to be more flexible with the implementation of alternative materials, under specifications, such as concrete binders.

The ACM's testing methods' main standards focus on hydraulic cement are listed in Table 3.

Table 3. Main standards for some ACM's.[17]

Standard	Hydraulic fly ash cem.	Activated slag cem.	Calcium Aluminate Cem.	Calcium Sulfualuminate Cem.	Magnesia Cem.
ASTM C1157/C1157M	Meets	Meets	Meets	Meets	No
ASTM C1600/C1600M	Meets	No	Meets	Meets	No
ACI 318-14	Meets	Meets	Questionable	Meets	No

Moving a bit away from the two most conservative and widely used state regulatory authorities globally, nations like Canada and Australia have a great scope for accepting alternative materials based on previously researched and regulated performance. In the same way, there is also in Ukraine a highly developed framework of prescriptive standards governing classes and specific formulations of non-Portland cement, which have been generated throughout 50 years of development of alkaline activation technology.

3.1.2 RILEM technical committee 224-AAM

This committee is driving and supervising the development of non-Portland cement standards, using ACM's binders instead of ordinary Portland cement, at an international level. Despite its focus on alkali-activated binders, which is currently not specifically limited to this alternative, the availability of performance-based standards is motivated by using performance rather than chemistry as the primary criterion for acceptance of a binder type since composition-based criteria are necessarily binder-specific.

3.1.3 Challenges in standards

"how a testing regime may be designed which is sufficiently inclusive to enable its users to test and validate a wide range of binder systems, but which is also restrictive enough to ensure good performance of materials when they are mixed and placed under less-controlled real-world conditions." [18]. This is a daunting challenge for researchers who are facing the development of performance-based standards. One of the delicate procedures is selecting the curing conditions; as observed in the forward section, curing time and curing temperature con modify and give large range variability in mechanical conditions, even the durability. Another is the critical test composite if it should be done in precursors, pastes, mortars, or concretes, and how to transfer the knowledge of this new binder system from new Portland cement and concrete technologies. In essential is required the contribution of the industry and the researchers.

3.1.4 Alternative binders

The alternative cementitious materials and binders have been developed to be implemented instead of Portland cement to reduce carbon dioxide emission *(CO_2e)*. Those alternatives cementitious materials and binders *(ACM's)* include calcium sulfoaluminate cement *(CSA)*, calcium sulfoaluminate belite cement *(CSAB)*, calcium aluminate cement *(CAC)*, magnesium phosphate cement *(MPC)*, carbonate binders, and alkali-activated binders *(A.A.)*, super sulfated cements *(S.S.)* [17,18], but are not limited to those, there another's that are usually less used but the same positive impact.

The ACM's mentioned above are mainly used for two main reasons. First, they require less energy and production temperature than ordinary Portland cement *(OPC)*, thus reducing the amount of CO_2 released from the burning of fuels used to generate adequate kiln temperatures. The second, because they have less calcium dioxide C_aO content. In this way, greenhouse gas emissions into the environment are much lower than those produced by ordinary Portland cement.

To support the information and have some quantity values, Gartner [15] computes rough estimates of the quantity of CO_2e that could be not released if the ACM's replace with an equal quantity, by mass, the ordinary Portland cement OPC.

Table 4. CO_2 emitted in the manufacture of "pure" cement compounds. Emissions are produced by the production of raw materials associated with each type of cement. [17]

CO2e (g/g)	Grams CO2e /g of cement	%CO2e V using OPC
OPC	0.55	100%
CSA	0.28	51%
CSAB	0.46	84%
CAC	0.29	53%
AA	Emissions result from manufacture of alkali solutions and transportation.	44% - 64%

As just mentioned, the calculation is made considering a 1:1 mass between the OPC and ACM's. Emissions data was only available for a fraction of the phases making up each material. For simplistic analysis, the quantity of CO_2e associated with other phases was assumed to be negligible, and the percentage of phases normalized the quantity of CO2e for each material accounted for by the emissions-phase data.

Analyzing Table 4, the greenhouse emissions that are being saved, thanks to the employ ACM's materials concerning the OPC, are noticeable and significant. For example, calcium sulfoaluminate cement *(CSA)* contributes to 49% savings in CO2 gases emitted into the environment. Furthermore, calcium aluminate cement *(CAC)* follows a saving of 47%, being a smaller saving, but that in construction quantities means a substantial positive impact. The other alternative materials are not far behind, as they have a lower impact but still generate a much lower gas emission than OPC.

The benefits of using these alternative materials, among others, are not limited to the environmental impact and sustainability due to the reduction of greenhouse gases emitted, especially CO_2e, but the mechanical benefits, contributing to the mechanical resistance and durability of concrete. The main advantage of using ACM's of higher resistance lies in the use of smaller quantities of cement per volume of concrete, maintaining a resistance equal to or greater than that of conventional concrete, with greater sustainability. In the same way, it can be expected that if the mechanical properties increase significantly, sections with smaller dimensions can be made, reducing the volume of concrete necessary for the same section of the structure, and this affects the reduction of the dead load of the structure [16]. Therefore, by globalizing ideas, ACM's reduce the dimensions of the sections, reduce dead load, increase durability and mechanical properties, require less cement per volume of concrete, and reduce gas emissions, being much more sustainable.

Nevertheless, despite its virtues as a sustainable cement and improvements in strength and durability, the use of these new and sophisticated materials is not yet standardized and is not used very frequently in the construction world, currently concentrating on the niche of repairs. One of the most important factors is that the industrialization of cementitious compounds leads to a variation in the mineralogical components that results in a significant variation in early age and long-term properties, challenging to predict. For example, in some cases, in alkali-activated systems, the material's variability is derived from the variation of the precursor materials, which are common industrial by-products. Furthermore, in particular cases, relatively small changes in the composition or procedure or a small variation in the materials' sources lead to huge variations in the short and long-term performance. Here is an example with the alkali-activated binder compound:

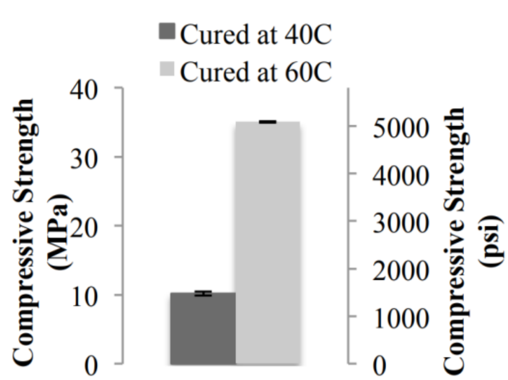


Figure 7. The influence of curing temperature on alkali activated binder concrete strength. [17]

As mentioned above, a small variation in a procedure (i.e., curing temperature) can mean a significant change in the concrete's behavior and a definite change in its properties. In Figure 7, It can be noted that 20ºC in the curing temperature means a change in compressive strength of more than 30%, where curing carried out at 60ºC reaches a compressive strength of 35 MPa approximately, while a cure at 40ºC reaches a maximum compression of 10 MPa. Furthermore, it can be noted that the variation in compressive strength with respect to temperature is not linear, so an error in curing conditions can lead to a significant loss of compressive strength.

Unfortunately, many challenges have been encountered along the way to upscale the use of alternative materials ACM's as an indeed used material in construction and large infrastructures, out of the repair niche. These challenges are mainly:

- lack of knowledge concerning mixture design parameters and conditions required for proper curing
- Challenges obtaining workable mixtures with adequate working time and finish ability
- Availability of test methods that can quickly evaluate and correlate quality and workmanship to the long-term durability of placed materials
- Standardization of the results obtained by the standardization of the test method to be truly compared with the intrinsic characterization of the OPC

Despite everything and its significant positive impact, many challenges stand in the way of successfully using ACM's for broad infrastructure performance. However, nowadays, thanks to technology and researchers, this ACM's materials are finding a light to be upscale in the construction field.

3.1.5 Conclusions

In recent years, those ACM's has demonstrated to be a good material that can replace the use of OPC as a binder for the concrete. They have shown a dramatic improvement in the performance, not to mention its sustainability, reducing greenhouse gas CO_2e emissions, and energy consumption. The chemistries reaction mechanism and properties development have been extensively studied and show an improvement in its functioning. However, having investigated and testing their improvement, they are still alternative materials with niche applications that have not seen their widespread use.

From an economic point of view, it seems to be a barrier because it higher cost compared to the Portland cement, considering the prescriptive nature of specifications for binders in concrete. Nevertheless, everything is not bad news, as performed-based specifications become prevalent, it seems the use of alternative binders will increase, carriying out with itself more and more investigation in this field, not even say that the investigation on Portland cement is still active to lead this material to a high-performance level.

Finally, it is important to highlight that standardization both in industry and application methods or techniques could allow a fast widespread use of the alternative cementing material worldwide, increasing the properties, reducing the amounts of material, and more importantly, the sustainability ACM's could envisage.

3.1.6 Correlation with Biochar application

Biochar application here in this type of cementing materials is not involved intrinsically, because Biochar intends to be a supplementary material that is added in cement matrix at nano and microscale to enhance the properties, but moreover, to reach a fluidity and viscosity point to allow a mix cement design to be printed. In future investigations, Biochar could be added in ACM's to enhance the concrete properties as envisaged in this document

3.2 SCM's

Supplementary cementing materials [11] are those materials that provide properties to concrete mixtures, which are distinguished by a decrease in permeability, an increase in stress, and viscosity, among others. Besides, it has an added value, and is that thanks to its origin, it is more economical to modify the properties of concrete with the addition of these supplements.

Supplementary cementing materials *(SCM's)* contribute to hardened concrete properties through hydraulic or pozzolanic activity. Based on Thomas [12], *"The pozzolanic activity of the material is the ability to react with calcium hydroxide,"* complementing the idea, Massazza [13] adds that the rate of reaction of pozzolanic material with calcium hydroxide depends on the specific surface area of the pozzolan, water/solid ratio, and alkaline content in Portland cement and temperature.

These SCM's could be fly ashes, slag cement (ground, granulated blast-furnace slag), and silica fume. These can be used individually with Portland or blended cement or in different combinations.

Therefore, considering fly ashes as SCM's material, it can give the concrete mixtures splendid enhancement of the main properties and reduce costs. Based on Siddique and Iqbal Khan in his book Supplementary cement material [14], the objective of using fly ash in concrete is to achieve one or more of the following improvements:

- Reducing the cement content to reduce costs

- Improving workability
- Obtaining reduced heat of hydration, especially in mass concreting
- Attaining required levels of strength in concrete at ages beyond 56 days

So, looking forward, Siddique and Iqbal Khan establish that the inclusion of fly ashes in cement paste or concrete mixtures has several benefits depends on the type of fly ashes; for example, in a mixed point of view, consider the proportion used, other mix ingredients and mixing procedure. On the other hand, consider the field conditions and placements. Hence some benefits of add fly ashes in concrete are:

- Reduce bleeding and segregation: improve the pumpability due to the increase of soil/water ratio, making the concrete less prone to segregation increasing concrete pumpability
- Improve workability: for equal w/c ratio is allowed greater workability due to the spherical shape and glassy surface of the fly ash particles.
- Reduce permeability: due to the increase in cementitious material and decrease in water content, the mixture decreases in the number of pores, decreasing the permeability. The reduction in permeability improves long-term durability and resistance to deterioration.
- Resistance to corrosion improves the long-term corrosion resistance of concrete

Here just beforementioned some of the benefits of adding fly ashes to concrete, not to mention that it can come between four to six additional high impact benefits

3.2.1 Biochar as SCM's

As mentioned by Siddique et al. (2011) [14] in their book supplementary cementitious material with the inclusion of fly ash, silica fume, among others, this document seeks to improve the properties of concrete and cement paste from the inclusion and addition of NERA biochar in the mix as SCM's material.

However, not only does this research seeks to improve the properties of the cement paste or concrete by adding NERA Biochar, but it also wants to achieve a reduction in the use of expensive additives to achieve a desired viscosity and workability, using the appropriate dosage of Biochar reaching these properties and maintaining the low production cost of the concrete or cement paste.

3.2.2 Conclusion

SCM's have recently been investigated and used to improve and modify the properties of cement-based compounds. For this research, it is sought to include NERA Biochar in the cement matrix to improve the cement paste and mortar's mechanical properties. It also seeks to modify the rheological properties, such as yield stress, viscosity, and a shear rate of the cement paste and mortar to obtain an appropriate mixture for 3D printing.

Previous research has shown that with the addition of carbon nanotubes *(CNTB's)*, as in the research by Restuccia and Ferro (2016) [4], or the addition of Biochar from different sources and raw materials, as in the research by Gupta et al. (2017) [71], the mechanical properties of cement-based compounds can be improved, such as flexural stress, compressive stress, and fracture energy.

These investigations just mentioned motivating to carry out the present investigation, which seeks to use NERA Biochar as SCM's to achieve the desired rheological and mechanical properties.

3.3 NMCM's

In recent years, nanotechnology in the field of construction, applied to processes and materials, has attracted great attention from researchers, architects, and engineers who seek to innovate, improve, be more sustainable, be more economical, and have less greenhouse gas emission in the construction field. Studies and results have shown that the nanomodification of cementitious materials (NMCM's) can significantly improve the mechanical properties, compactness, and durability [27] as long as good distribution and application of the different micro and nanomaterials are made.[26] The distribution and dispersion of nanocomposites are very influential in the results obtained from the mechanical properties and how it altered the probability of Young's modulus corresponding to the porous phase, low stiffness C-S-H, high stiffness C-S-H and calcium hydroxide [25,28]. Shah et al. [27] proposed a nanoparticle dispersion method that will be described in the next section.

Research in the field of NMCM's says that the most recently implemented nanomaterials are nano-SiO_2, nano-clay, nano-Al_2O_3, and carbon nanomaterials [27] (carbon nanotubes *CNTs, MWCNTs* [26] and nanofibers), and from them can be obtained a stronger, greener, and more durable cementitious material through the help of nanomodification.

3.3.1 Chemical composition of Portland cement

To understand the changes that are made at the micro or nanoscale in different compounds, first, the chemical composition of a grain of Portland cement will be seen. The Portland cement grain is mainly made up of four chief minerals present; each of these minerals can be decomposed into basic oxides of calcium, silicon, aluminum, and iron. Additionally, cement chemists use an abbreviated nomenclature based on oxides of various elements to indicate relevant chemical formulas: $C = CaO$, $S = SiO_2$, $A = Al_2O_3$, $F = Fe_2O_3$. [24,25] The four elements are described below in Table 5, along with their oxide composition and abbreviation.

Table 5. Chemical Composition of Portland Cement. [24]

Mineral	Chemical formula	Oxide composition	Abbreviation
Tricalcium silicate (alite)	Ca_3SiO_5	$3CaO.SiO_2$	C3S
Dicalcium silicate (belite)	Ca_2SiO_4	$2CaO.SiO_2$	C2S
Tricalcium aluminate	$Ca_3Al_2O_4$	$3CaO.Al_2O_3$	C3A
Tetracalcium aluminoferrite	$Ca_4Al_nFe_{2-n}O_7$	$4CaO.Al_nFe_{2-n}O_3$	C4AF

A typical variation of the mineral content in a Portland cement grain can be: [24,25]

- C3S: 50 – 70%
- C2S: 15 – 30%
- C3A: 5 – 10%
- C4AF: 5 – 15%
- Other mineral or additive: 3 – 8% e.g. calcium and magnesium oxide.

The continuous phase around the other mineral crystallites is formed by calcium aluminoferrite *(C_4AF)*, as the iron-containing species act as a fluxing agent in the rotary kiln during cement production and are the last to solidify, forming a capsule on the others as exemplified below

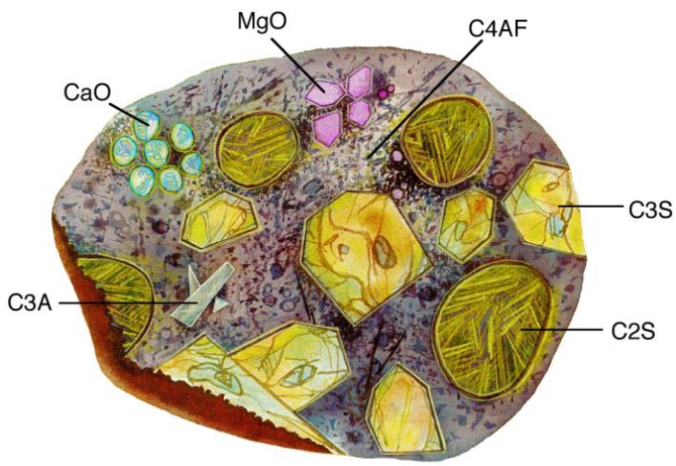


Figure 8. Chemical Composition of Portland Cement grain. [24]

The mineral content in each cement grain can be slightly variable, even in the adjacent grain. Heterogeneity comes not only within a particle but also from one grain to another or one batch to another. A homogeneous behavior can be guaranteed, but the slight variation just mentioned may exist at the particle level.

3.3.2 Nano-sized feature

The cement-based materials' characteristics can be changed by applying some external element or composite that is usually an additive. However, these characteristics can be well modified in micro and nanoscale, given novel functionalities due to nanomaterial applications thanks to their small size. The used nanomaterials in cement-based materials have a smaller size than 100 nm and are those of 0D, 1D, and 2D, being nanoparticles, nanofibers, and nano foil, respectively. Usually, nanomaterials greater than 100nm can alter the normal positive performance of the composite.

The concrete's performance with the addition of nano and micro materials will be affected in all ages, also both the fluid and the hardened state. The NMCM's plays significant effects on the hydration and hardening process when added to cement-base materials.

3.3.3 Main effects of nanomaterials in cement-based composites

One of the most important and in some way influencing effects, thanks to nanomaterials' addition to cement-based compounds, is the acceleration of cement hydration, known as the *hydration seeding effect* [27]. This is produced by the absorption of water from the nanomaterials, causing the water to be consumed faster than the standard way, speeding up the hydration process, and somehow retaining a percentage of the water content.

The *filling effect* [27] seeks to densify the cement paste with a smaller amount of binder, hoping to reduce the voids that exist or that can be generated in a cement paste or concrete in its preparation; in this way, pollutants or chemical agents cannot spread to through these voids in the most polluted or hostile environments. Fine powders such as finely ground pozzolana are used as micro and nanomaterials to obtain a more compact and dense structure to reduce the voids. With the help of these fine powders, the useful life and service life of cement-based structures being increased, this technique has been the foundation of high-strength/high-performance concrete.

In order to achieve a dense and homogeneous skeleton for an ultra-high performance concrete *UHPC*, a high binder content is not necessary; it can be replaced by nanomaterials of different composition and different sizes to achieve the desired density, little binder, and better mechanical characteristics, as resistance to sulfates and aggressive agents. [16-18-29] This effect and the hydration seeding effect make the concrete compact at the nanoscale, therefore, compact as a composite at full scale.

3.3.4 Correlation with Biochar application

What is sought with the inclusion of nanomaterials in cement-based composites is to improve and increase the mechanical properties of cement and concrete at nano and micro-scales, reflecting better behavior at a real scale. Biochar is a compound that will be added to the cement matrix at a microscale to improve the hydration of the cement during internal curing after being treated to obtain the appropriate dimensions. Additionally, the use of Biochar in the cement matrix densifies the compound, generating a filling effect (reduction of voids), which, as seen in the NMCM's, is important when there are contaminated or hostile environments, regarding that having voids can reduce the flexural strength and the compression stress of cement-based materials drastically.

Some of the main characteristics of Biochar and how it directly affects the behavior of cement paste and concrete will be discussed forward. Additionally, microscopic images will be seen that will help to understand why the mechanical properties and rheological properties are improved from the combination of NERA biochar as a compound and its reaction after the hydration and curing process.

4. 3D PRINTING

Three-dimensional printing has marked a milestone in technological, industrial, medical, educational advances, and countless other areas still under study today. This technology's valuable contribution has facilitated creating many objects that have specific purposes in a more profitable, faster, more precise, and more sustainable way, the latter in the industry particularly. Nowadays, three-dimensional printing is used to recreate objects with outstanding precision that allow and involve the construction of highly complex and geometric 3D models, which create difficulties for any other technology, even modern.

4.1 3D Technology

3D printing, also known as additive manufacturing [29] or digitization manufacturing [30], constitutes a group of additive manufacturing technologies capable of forming a three-dimensional object by applying thin layers superimposed (overlapping) one after another, capable of withstanding the buckling and creep forces of a specific material that varies according to the function and purpose of the object. It is a process by which layering materials create physical objects according to a digital model. In the processes related to the implementation of materials used in construction, they call it "automatic construction," thanks to the fact that this technology constitutes a degree of automation. That also eliminates some tasks required force to produce concrete elements.

Since 1976 the first prototypes for 3D printing had already been developed, which, a couple of years later, in 1981, were invented two manufacturing methods *AM* of a three-dimensional plastic model based on a photo-hardenable polymer by scientist Hideo Kodema [29,31]. In 1984 the 3D printing method that uses ultraviolet *(U.V.)* light to cause the hardened, layer by layer, of a photopolymer or resin called stereolithography *(SLA)*, had featured a couple of successful prototypes, with the creation of its first commercial machine in 1992. Unlike Kodema's approach, this gave rise to the STL (STereoLithography) file format widely used today proposed by the scientist Chuck Hull, who defined the process as *"a system to generate three-dimensional objects by creating a cross-sectional pattern of the object to be formed"* [31]. The Wake Forest Institute of Regenerative Medicine, a year before the 21st century, achieved the first organ raised in the laboratory through a project that sought to create organs and tissues through 3D printing technology.

Science has advanced a lot with 3D printing technology, especially to make different objects that can guarantee a clean, precise, complex process and especially more profitable than traditional manufacturing, even with the different advances in its specialty. Since the beginning of the 2000s, additive manufacturing technology, accommodating three-dimensional printing, has expanded and significantly evolved in the sectors of medical industries, education, geographic information systems, and industrial design. Additionally, it is found in fields such as jewelry, footwear, furniture, among others. Finally, one of the fields in which it has been involved the most is in architecture, civil engineering, construction, automotive and the aerospace sector, and many more.

These advances have been such that for the year 2011, an uncrewed aircraft was designed based on manufacturing by addition or manufacturing by digitization by the corps of engineers at the University of Southampton [30]. In the main medical or medicinal advances, implementation has been seen in the dental field, bone prostheses, and organs based on stem cells' interaction. It is applied in paleontology to reconstruct fossils and their parts or as the replica of antiquities in archeology in science.

Within this framework, one of the aims of this document is to discuss in terms of the properties of fresh concrete the rheological requirements of mortar with the addition of Biochar that are needed to obtain a printable and buildable mixture with the absence of rigid mold or any framework, where the high rigidity of the mold, compared to the forces induced by gravity, are not those that balance the stresses at the interface between the material and the stresses induced by gravity when depositing the mixed material; It is intended that the mortar is capable of supporting its own weight at the layer level and that it can support its own weight and support buckling and cracking at the structure level [30].

4.2 Advances in concrete printing technology

There are currently various three-dimensional printing techniques that are classified by the way they have the modeling process and the materials used to form the object. In the case of concrete or mortar, the main differences lie in the way in which the layers are deposited [30], taking into account the relationship between the nozzle and the rheological properties of the deposited material.

The most common technology used for 3D printing concrete or mortar is a technology similar to fused deposition modeling *(FDM)* called additive extrusion manufacturing. What this FDM method does is deposit thermoplastic materials such as eutectic metals or thermoplastic polyurethane *(TPU)* that have been previously melted to obtain a semi-liquid and viscous shape that allows the manageability and formation of a complex geometric pattern layer by layer on a horizontal surface. Generally, this process occurs in thin layers, one after another, until the digital model is completed. The deposited material can be a sheared bulk material, a non-laminar flow that passes through a conical nozzle, or an unsheared bulk material, a laminar flow deposited through a rectangular nozzle and is covered, followed by passing through the nozzle, with a thin layer of lubricant [30] (Cf. Figure 9).

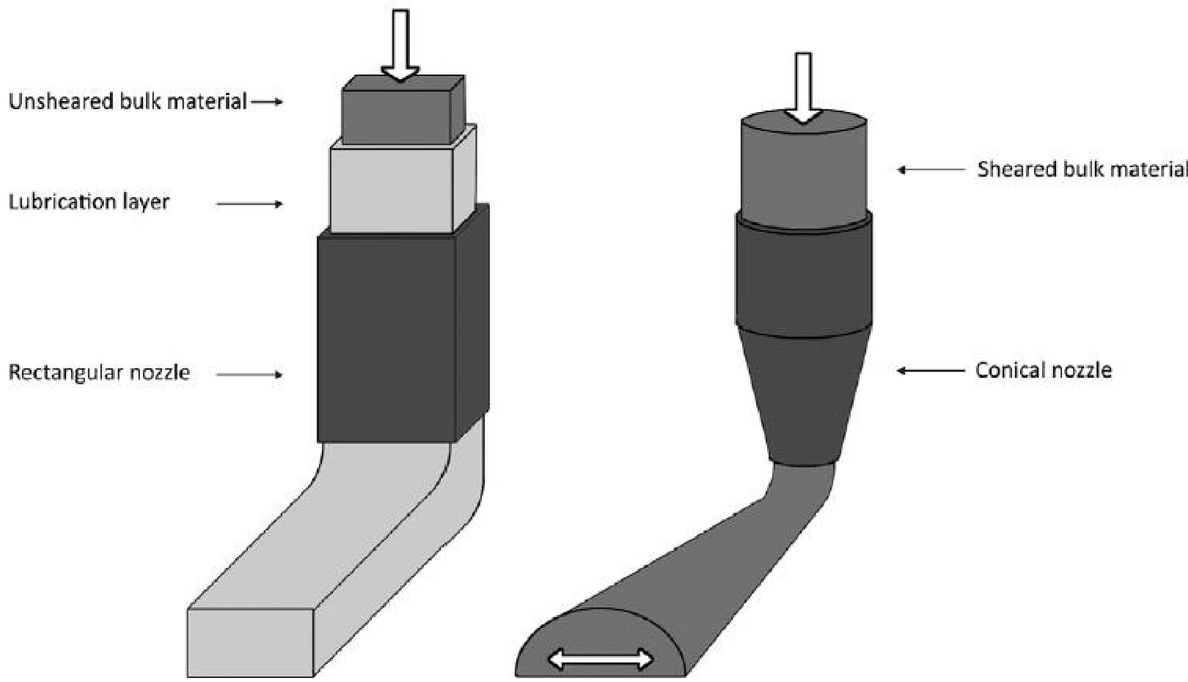


Figure 9. Left: Laminar flow deposited through a rectangular nozzle. Lubrication layer and unsheared zone at the center of the extrusion head. Right: non-laminar flow through a conical nozzle [30].

When concrete or mortar must be printed, the process is carried out through additive manufacturing by extrusion and deposition of the mixture in layers of height h_0 on a horizontal and flat surface (Cf. Figure 10a). Finally, after the additive manufacturing process by extrusion of concrete or mortar, the final model is presented, composed of several layers of height h_0 superimposed, with a final height H. (Cf. Figure 10b).

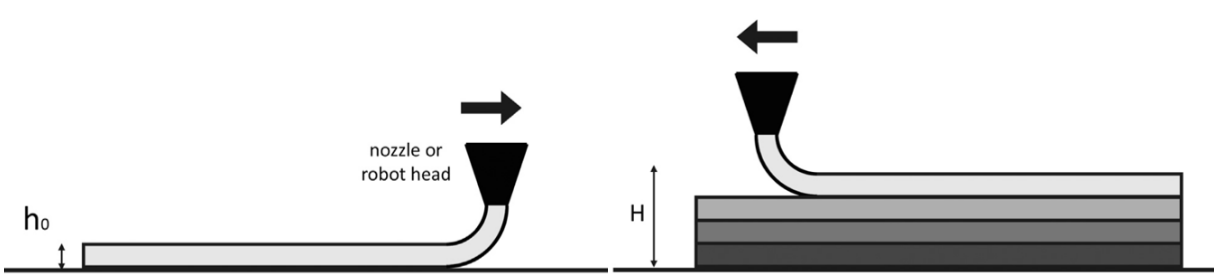


Figure 10. Left a). Extrusion and deposition of a layer on a flat support with thickness h_0. Right b). Extrusion-based additive manufacturing of a wall. shades of grey indicate maturation of the material. Final high H [30].

SECTION 2: PROBLEM STATEMENT AND MATERIALS

5. PARADIGM OF THE RESEARCH

One of the biggest steps to achieve a good investigation is to know the goal and the objectives to be achieved. Knowing the different objectives on which the research is based allows the researcher to know the path and position in which he is and to find an adequate route to reach the goal, going through the possible scenarios that may pose difficulties and problems and later learn the different outputs that allow the solution of the problems. Thus, the first step for formulating an investigation is to know the paradigm that will guide the solution to the problem raised.

Getting ourselves in the paradigm situation will allow us to find a research path that leads us to achieve this thesis's objectives. This paradigm will serve as a reference and model for this and future research. According to the physicist and philosopher Thomas Kuhn [76], *"Scientific achievements that generate models that, over a more or less long period, and in a more or less explicit way, guide the subsequent development of research exclusively in the search for solutions for the problems posed by these,"* are the paradigms correctly posed for a particular research model or project.

Investigations certainly change and are different in each of the scientific areas, and in each of the branches that compose it, that means, is possible to find very similar investigations. However, different objectives are raised, and they follow different routes, as well as each researcher has his own point of view, reality, purpose, and even beliefs; consequently, the paradigms are different.

In the scientific field, there are interpretive paradigms, which have a qualitative approach, and positivistic paradigms, which have a quantitative, rational, and technologically scientific approach [51,77]. Positivistic paradigms test their hypotheses by statistical means or numerical expressions that support the research focus.

This document proposes a positivistic paradigm investigation because it seeks to prove through numerical expressions that the inclusion of NERA Biochar as supplementary cementitious material *(SCM's)* to the cement matrix on a micro-scale, improves the performance of mechanical properties, such as flexural and compressive capacity and fracture energy of the cement paste and mortar. Furthermore, altering the rheological properties to design a cementitious mixture that meets the flow and viscosity characteristics and the bond and shared forces to be printed in 3D through an extrusion process for the digital manufacturing of cement-based compounds.

5.1 Naturality of research

The thesis's objective developed in this document seeks to evaluate the mechanical and rheological properties obtained in some samples of cement paste and mortar when their cement matrix is modified with the addition of Biochar at a microscale, produced by NERA Biochar company. It is a company that is responsible for producing charcoal and bio-charcoal from a type of wood from a high-quality controlled chain such as biomass. This company, located in Italy, has been characterized by using products without synthetic substances, focused on the environment.

Biochar is used in different proportions with respect to the weight of cement as an environmentally friendly supplementary cementitious material that seeks to improve the properties of the mixture subjected to flexural, compression, viscosity, and yield stress tests.

A group of specimens must be prepared with different percentages of this additive's content to carry out an evaluation process and predict a trend that allows us to understand the behavior of the material at different scales. The research has real data taken from the laboratory under controlled conditions, collecting all relevant information to simulate the conditions in any field in which anyone wants to verify the approach or continue with the paradigm that supports this document.

6. MATERIALS

The main materials used for preparing the specimens are cement, water, superplasticizer, fine aggregate, and Biochar.

6.1 Cement

The binder used in this research is Portland Cement type I 52.5 R (provided by Buzzi Unicem S.p.A.), a type of cement with very high normalized strength and high initial strength. (Cf. Table 7). This cement contains at least 95% Clinker, while the rest is made up of secondary components following the composition prescribed by the UNI EN 197-1 standard. The chemical, physical and mechanical requirements are presented in Table 6 and Table 7.

Table 6. Chemical requirements [78].

Parameter	Test method	Indicative values	Characteristic limits of norm
Sulphates (SO_3)	UNI EN 196/2	< 3,7%	≤ 4,0%
Chlorides (Cl -)	UNI EN 196/2	< 0,08%	≤ 0,10%
Loss to fire	UNI EN 196/2	< 5,0%	≤ 5,0%
Insoluble residue	UNI EN 196/2	< 1,0%	≤ 5,0%
Chromium VI soluble in water	UNI EN 196/10	≤ 2 ppm	≤ 2 ppm

Table 7. Physical-Mechanical requirements [78].

Parameter	Test method	Indicative values	Characteristic limits of norm
Blaine specific surface	EN 196/6	4000-5500 cm2/g	
Setting start time	EN 196/3	> 90 min	≥ 45 min
Volume stability	EN 196/3	≤ 10 mm	≤ 10 mm
Texture on mortar	UNI 7044	> 70%	
Compressive strengths after curing of	EN 196/1		
2 days		> 35.0 MPa	≥ 30.0 MPa
28 days		> 56.0 MPa	≥ 52.5 MPa

6.2 superplasticizer

MasterEase 7000 (ME7) [79] is a superplasticizer additive based on dispersant polymers. It has been designed to impart exceptional rheological properties to fresh concrete by making mixes less viscous. Its use facilitates the pumping of concrete, optimizing packaging ready-mixed concrete with a low water-cement ratio and good maintenance of workability, excellent mechanical resistance to short and long curing, and long-lasting according to EN 206-1 and UNI 11104.

ME7 is chloride-free, compatible with all cement meeting the EN 197 [79]. It is based on innovative polymer chemistry, and BASF patents it. This superplasticizer delvers many advantages both in fresh concrete on hardened concrete like

- A decrease in viscosity of concretes at constant W/C.
- Reduction possible to the W/C ratio without affecting the viscosity of concretes.
- In the cured state, improvement of sustainability.

Its characteristics are shown in Table 8 in accordance with the standard EN 934-2: 2012.

Table 8. Declared performance for MasterEase 7000 [79].

Essential characteristics	Performance
Chloride ion content	≤ 0,1% by mass
Alkali content (Na2O equivalent)	≤ 3,0%
Corrosion behavior	Contains nitrates (component from EN 934-1: 2008 Annex A.2)
Compressive strength	Equal consistence: 24h ≥ 140% 28 days >= 115% Equal w/c ratio: 28 days ≥ 90%
Air content	Equal consistence: ≤ 2,0 % Equal w/c ratio: ≤ 2,0 %
Water reduction	≥ 12,0 %
Consistency	Increase: ≥ 120 mm Retention: comply 3.2 (2)

6.3 Biochar

Provided by NERA Company [52], Biochar, also called vegetable charcoal, is a concrete solution to the climate crisis because it removes CO_2 from the atmosphere and fights desertification. Charcoal is a product that derives from wood chips, coming from the cleaning of green areas and woods and wood processing waste. This company's wood chips biomass comes from a controlled supply chain and is obtained by a fast pyrolysis process.

Biochar structure is made up of more than 75% carbon. Thanks to its enormous porosity (> 475 m^2/g), it retains water and nutrients by slowly releasing them into the cement mix design and marketing them available to curing only when necessary in the first age of the sample [52].

The precise Biochar used from NERA Biochar company is shown in Figure 11.

Figure 11. NERA Biochar employed in this research. a) front of the Biochar bag. b) back of Biochar bag [52].

Nera Biochar was ground using the ball milling method. This method seeks to mash hard, medium-hard, soft, and brittle materials. This procedure is done considering that previous studies suggest that the smaller the average size of the Biochar particle, the better the performance of the cement mix will be obtained: when the surface area of the particle increases, the interaction between the particles and the cement matrix that surrounds it increases [4,71,85].

6.4.1 Ground procedure

The ground procedure used to achieve the expected particle size was the *ball milling procedure*. This method seeks to mash hard, medium-hard, soft, and brittle materials. The procedure consists of putting the Biochar and medium ceramic spheres into a jar or container and then making it spin; thus, spheres crush the Biochar against the wall of the container making it into smaller particles. This procedure is usually done in dry conditions.

Procedure

1. Put the desired amount of Biochar into a container. The capacity lies in the container.
2. Put the medium size spheres just after the material.
3. Close the container and put it into the spin jar machine and set the experimental time.

4. Imposed velocity: 1 rps = 60 rpm (standard velocity for the machine)

After these steps, it should probably have more than 50 grams of available Biochar to use in the cement paste, mortar, and rheological samples.

There were two configurations of this ball milling method described below.

Table 9. Settings of the ball milling method.

	ID	Container	Grind time	Biochar
NERA Biochar	BC'	Plastic jar	6 Hours	50 grams
	BC"	Ceramic jar	7 Hours	100 grams

Additionally, the biochar that was made in the ceramic jar *(BC")* for 7 hours has a little percentage *(<5%)* of particles greater than 200 microns, therefore it is sieved for 30 minutes, using an ASTM mesh 80 *(180 Micron)* sieve, utilizing a short-period oscillatory movement produced by the compact vibration sieve, to remove any particles larger than 180 microns (Cf. Figure 12).

Figure 12. shaker for sieve and sieve 180 micron.

6.4.2 Chemical and physical characteristics of NERA Biochar.

After the milling process that the Biochar undergone to reach a desirable particle size of a few nanometers, the final composite was studied to know its main chemical and physical properties: the granulometry analysis to know the average particle size, the analysis of X-ray fluorescence (XRF) to study the elemental composition, the Brunauer-Emmett-Teller (BET) analysis to know the specific surface area and the pore volume, the field emission scanning electron microscopy (FE-SEM) to evaluate the morphology of the nanoparticles, and finally the water retention capacity. Those laboratory procedures were carried out in the Department of Applied Science and Technology *(DISAT)* at Politecnico di Torino.

It is important to highlight that the Biochar characterization and study was performed to the 7 hours ground Biochar (BC'') because its particle size was considered more effective and get close values to the ones suggested in literature [4,71,85].

6.4.1.1 Granulometry analysis

The granulometry of the biochar samples was carried out using the "Malvern Mastersizer 3000 Aeros S" machine (provided by Malvern Panalytical Ltd.), which uses laser diffraction as a measurement method. The laser beam passes through a sample of particles, and the angular change in light intensity is measured. Scattering from smaller particles occurs at wider angles while scattering from larger particles occurs at smaller angles [80]. (Cf. Figure 13)

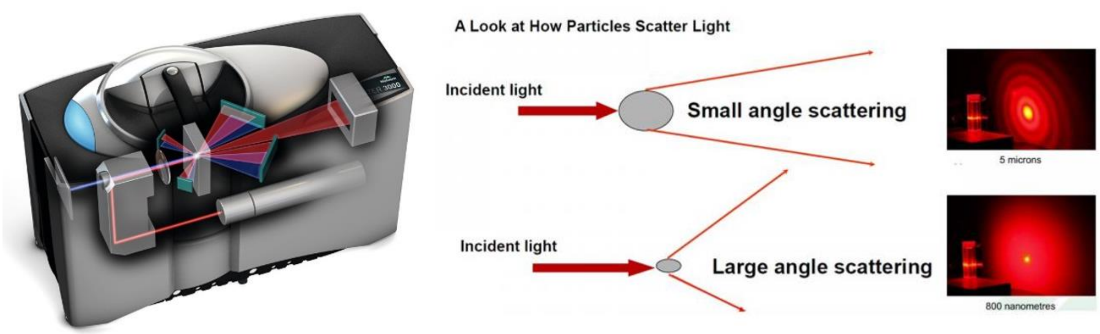


Figure 13. a) Granulometry machine. b) Light scattering according to particle size [80].

For this purpose, sample batches of 1-2 g of Biochar were prepared and introduced into a conical steel cell in the machine's upper part, protected by a mesh that prevented large particles' passage (Cf. Figure 14). The sample was then passed through a vibrating belt to separate the particles randomly. Finally, they were deposited in a tube that began to suck the small sample so that it began to pass through laser diffraction. This procedure was carried out with each of the batches until having a minimum standard deviation value.

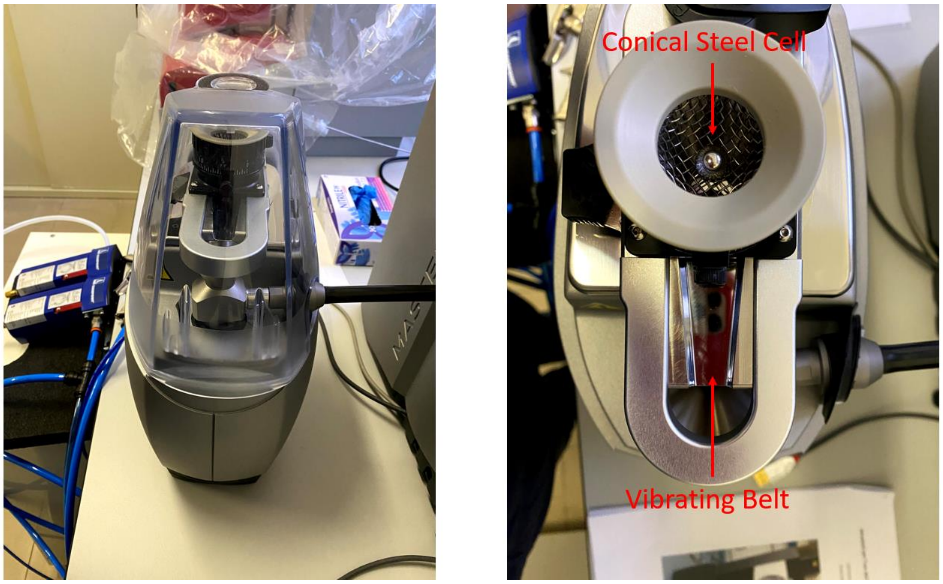


Figure 14. a) Granulometry test device. b) Conical steel cell and vibrating belt.

6.4.1.2 X-ray fluorescence *(XRF)*

The qualitative chemical analysis performed by using a XRF analysis of pyrolyzed microparticles has been very useful to analyze the main qualitative composition of Nera Biochar, in this way it will possible to evaluate the potential properties conferred when added to the mix cement based compounds.

6.4.1.3 BET analysis.

The specific surface area and pore volume were determined by means of the Brunauer-Emmett-Teller *(BET)* analysis method [86] using a TriStar II Krypton 3020 V1.03 through an adsorption isotherm and desorption of nitrogen *(N_2)* physisorption analysis at -195.8 ºC, on a Nera Biochar sample previously degasified for a period of 2 h at 200 ºC to remove moisture/water adsorption and pollution from the atmosphere [87].

6.4.1.4 FE-SEM

The shape and morphology of the ground and sieved Biochar was observed throught the SEM-EDS microscope by zeiss, whit and increase up to x5K at 20 kV.

6.4.1.5 Water retention capacity

Biochar is used mainly as a fertilizer for plants, which promotes their growth thanks to the fact that it consumes the nutrients that are around it to distribute it in the plants. Additionally, the Biochar retains liquids to release later as the plants or the environment need it.

In this context, Biochar is used in the materials area because it stores the water used as an activation medium in cement mixtures and then releases it little by little in the mixtures' curing process. Biochar stores good amounts of water thanks to its morphology and surface area *(Cf. section 6.4.1.4)*, making it a material with great potential for retaining liquids in cement paste and mortar mixtures, being a key point in the internal curing of the mixture.

The process for calculating the water retention capacity of biochar is based on the method proposed by Gupta et al., [71] and Daniel [51]. First, two Biochar samples are taken, each of 10 g, and placed in a beaker that is then put in a ventilated oven at 90ºC for 24 hours (Cf. Figure 15a); in this way, the Biochar natural and acquired humidity is eliminated before testing. Each of the 10 g biochar samples is filled with 100 g of distilled water (Cf. Figure 15. b-c) left to stand and sealed for 48 hours in each container (Cf. Figure 16). A vacuum filtration test is prepared, in which a funnel with a cellulose filter (Whatman 150 mm Ø) is used to extract all the surface liquid mass (Cf. Figure 17). Taking the weight of the wet and filtered biochar, then subtracting the dry biochar's weight, the compound's fluid retention capacity is obtained.

Figure 15. a) Specimen 1 right and 2 left on the oven. b) Dry Biochar. c) Adding 100g of water to specimen.

Figure 16. a) Specimen 1 & 2 sealed after adding water. b) Specimen 1 & 2 after 48h in wet conditions.

Figure 17. Vacuum filtering process.

6.4.3 Results of chemical and physical characteristics of NERA Biochar.

The following chapter aims to show the results obtained in the physical and chemical characterization tests of the Nera Biochar studied in the current document. The characterization of Biochar is important to know its structure and to be able to understand the behavior and performance it has on the mechanical and rheological properties of the cement paste and mortar.

6.4.3.1 Granulometry analysis

After having carried out the granulometry test five times, until the value of the standard deviation considering each of the evaluations was the minimum, an average particle size of a few micrometers, 7.9 µm, was obtained. This particle size is considered adequate when applying biochar to the cement matrix to improve its mechanical and rheological properties. Table 10 shows the granulometry obtained for the five samples, and their respective granulometric curve is shown in Figure 18.

Table 10. Results for granulometry analysis of Nera Biochar (BC").

Record No.	Sample Name	Dx (10)	Dx (50)	Dx (90)	Dx (100)	Average [µm]
1	Ball Milling Ceramic (7 Hours) + Sieving 180 Micron	1,80	7,92	24,10	85,7	Dx (10) 1,78 Dx (50) 7,88 Dx (90) 23,96 D[4,3] 11,00
2		1,75	7,85	24,30	75,9	
3		1,79	7,87	24,40	75,9	
4		1,76	7,90	23,70	86,2	
5		1,81	7,87	23,30	111	

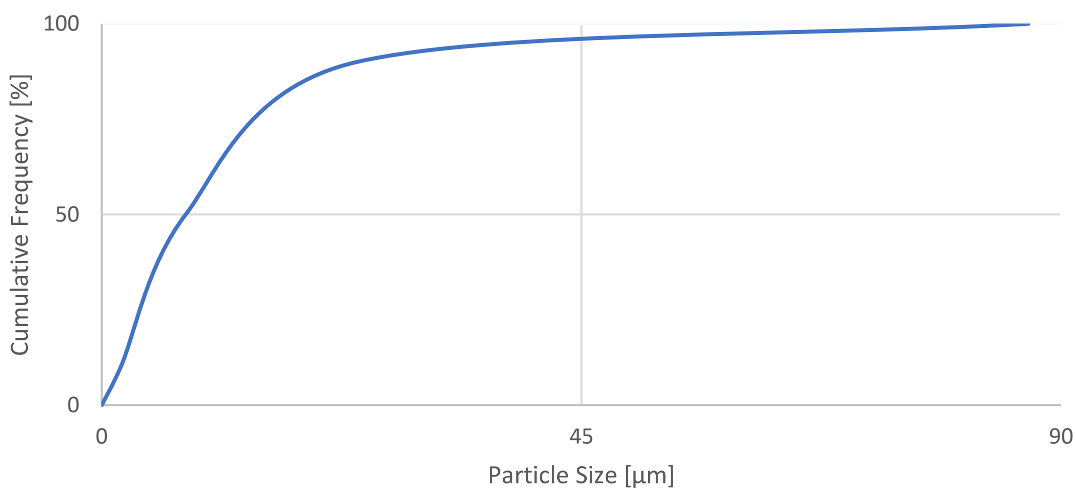


Figure 18. Granulometry curve for Nera Biochar

6.4.3.2 X-ray fluorescence *(XRF)*

The qualitative chemical characteristics of Nera Biochar *(BC)* is reported in Figure 19. After passing the heat treatment, the griding and the sieved filtered process shows that the material is mostly amorphous (seen from the very large peak centered at about 24° in 2theta relative to the amorphous carbon), some peaks of calcium carbonate (indicated in blue) and of quartz (indicated in black) are visible. However, both quartz and calcium carbonate are present in traces. This characterization predominated of amorphous carbon especially make this pyrolyzed biomass great as aggregate, null difficult dispersion in the water and superplasticizer solution and the particles shows high resistance in comparison to the cement matrix.

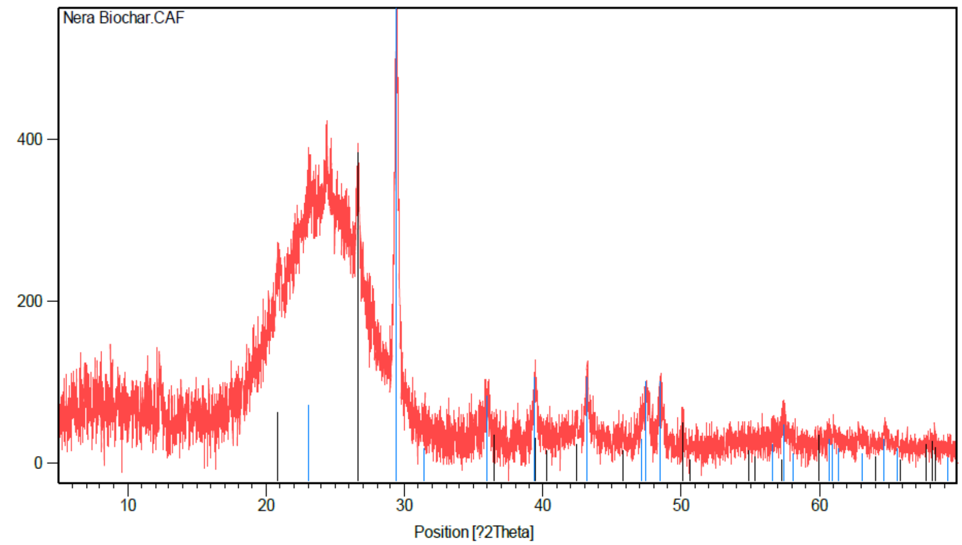


Figure 19. Results of XRF analysis.

6.4.3.3 BET analysis.

The analysis shows that the specific area calculated through the BET method is 35,60 m^2/g, the t-plot microstructure volume and the micropore area is 0.015 cm3/g and 25,27 m2/g, respectively, and the adsorption and desorption average pore width according to the BJH method is 122,82 Å, or 1,22 nm and 207,44 Å, or 2,10 nm. Respectively. According to Brewer [87] it allows an efficient CO2 adsorption, because the gas adsorption occurs when there are micropores, it translates in pores less than 2nm.

6.4.1.4 FE-SEM

FE-SEM images allow observing the structural configuration of Nera Biochar particles at different microscopic scales. The morphology and pore surface of the Nera Biochar particles are illustrated in Figure 20a and Figure 20b, respectively. Figure 20a shows that the biochar particles have a wood chip structure, sharper and more prolonged, consistent with the feedstock and pyrolysis process used; additionally, some surrounding particles have a honeycomb pore structure. These Nera Biochar particles do not appear to have excess pores, which does not allow absorption and great saturation (Cf. Sec. 6.4.1.5), making them less effective than other Biochar concerning the retention of liquids and gases [99]. The pores came from the pyrolysis process thanks to the volatility or the organics belonging to the feedstock. On the other hand, in Figure 20(b), a surface of the pore can be observed in a size range of 10 - 20 microns, where a series of smaller particles are evidenced within these cavities in a range between 2 - 4 microns or smaller. In this same image, the structure of its smallest pores can be observed, and it can be noted that its structure is that of firewood or wood; this is strictly linked to the feedstock used as biomass.

Figure 20c and Figure 20d show an even smaller scale, the limit reached when performing FE-SEM images, where it can be observed that the pores have an approximate diameter of 1 - 3 microns or smaller. However, they are very scarce, or very few per Biochar particle, decreasing the liquids and gases retention capacity. Lehmann [100] suggests in his studies that pores smaller than 30 μm are more efficient at retaining water in place. Likewise, Shafie et al. [101] supports this theory but suggests that the highest efficiency is found with a pore diameter between 5 - 6 μm, tending to greater fluid retention. In conclusion, pore sizes between 10 - 30 μm tend to absorb the water better in the mix, thus reducing the free water content in a cement mix [71].

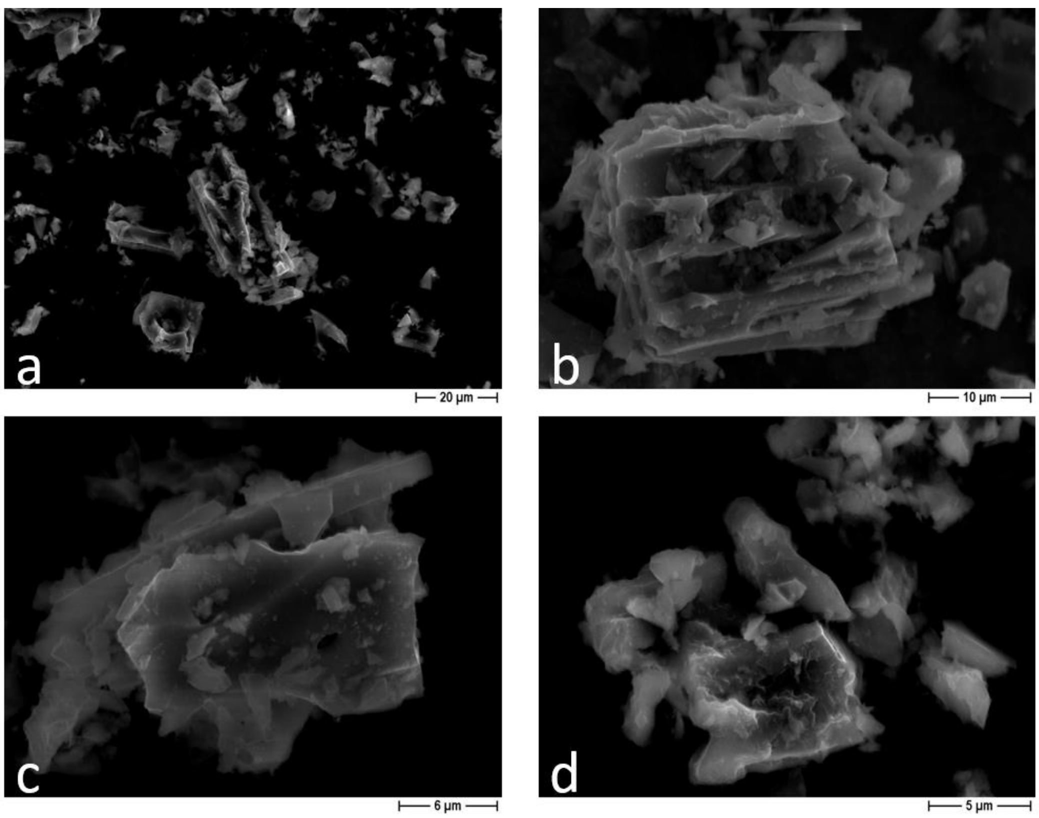


Figure 20. FE-SEM image analysis: grinded Nera Biochar 7 hours and sieved. (a) x1000; (b) x2500; (c) x4000; (d) x5000.

6.4.1.5 Water retention capacity

The compound's fluid retention capacity is obtained by taking the weight of the wet and filtered Biochar and subtracting the dry Biochar's weight. The water retention capacity expressed as the mass of absorber water per gram of dry Biochar was calculated as 0,94 ± 0.02 g of H_2O/g of dry Biochar. Table 11 shows the experimental variables followed to evaluate the water retention capacity.

Table 11. Water retention capacity of Nera Biochar

Specimen 1		Specimen 2	
Biochar [g]	10,03	Biochar [g]	10,04
Beaker [g]	104,82	Beaker [g]	102,22
Dry Biochar [g]	9,470	Dry Biochar [g]	9,462
Funnel + wet filter [g]	371,87	Funnel [g]	377,30
Wet Biochar [g]	18,43	Wet Biochar [g]	18,30
Water retention [g]	8,96	Water retention [g]	8,84
g absorber water / g dry biochar	0,95	g absorber water / g dry biochar	0,93

The water retention capacity was expected to be a higher value, close to other types of Biochar already studied, such as Biochar from the pyrolysis of mixed wood sawdust used by Gupta et al. [71] where the liquid retention capacity was 2.5 + 0.2 g/g. On the other hand, Suarez [51] used the same method to evaluate the water retention capacity proposed in this article, obtaining 2.17 g/g of water retention for the Borgotaro Biochar. In this vein, it is found that biochar has a much lower water retention capacity than other types of Biochar. This could happen due to the low porosity, and its wood chip shape does not allow the same absorption capacity.

7. RECIPIES, PROCEDURE AND PREPARATION OF THE SPECIMENS

7.1 Procedure to prepare samples subjected to rheological tests.

This section of the chapter explains the recipes and procedures followed to prepare the cement paste and mortar samples subjected to rheological tests, where the yield stress, shear stress, shear viscosity, and shear rate, fresh state characterization of cement-based composites are evaluated. Moreover, going to be explained the instruments employed and the procedures to obtain the respective samples.

7.1.1 cement paste

The cement paste samples subjected to rheological tests were prepared in the SISCON_Infraestructure laboratory, DISAT, of the Politecnico di Torino. Six types of cement paste specimens were prepared (Cf. Table 12) at least twice to make the comparison a to corroborate the experimental results, except for Rec. 6. BC'' 7%, that was made to confirm and understand the trend behavior. The mixtures were prepared with a w/c ratio of 0.35, with 1% of superplasticizer MasterEase 7000 (ME7) concerning cement weight, just strictly they were prepared to make the samples subjected to the mechanical test, but this time in different amount. The relation between each composite and the amount of cement in the mix (Cf. Table 13) is presented to control all the quantities and make an adjustment if needed.

Table 12. Recipes of the cement paste samples to rheological test.

Recipe	ID	Description	Cem*	Water*	ME7*	Biochar*
No. 1	OPC	Plain Cement Paste	50	17,5	0,5	0
No. 2	BC" 1%	Paste with 1% of biochar in mix	50	17,5	0,5	0,5
No. 3	BC" 2%	Paste with 2% of biochar in mix	50	17,5	0,5	1
No. 4	BC" 3%	Paste with 3% of biochar in mix	50	17,5	0,5	1,5
No. 5	BC" 5%	Paste with 5% of biochar in mix	50	17,5	0,5	2,5
No. 6	BC" 7%	Paste with 7% of biochar in mix	50	17,5	0,5	3,5

** The unit of the material in grams.*

Table 13. Grams of a compound relative to the amount of cement in the mix in cement paste.

		[g] of material / [g] of cement			
Recipe	**ID**	**cement**	**water**	**ME7**	**Biochar**
No. 1	OPC	1	0,35	0,01	0
No. 2	BC" 1%	1	0,35	0,01	0,01
No. 3	BC" 2%	1	0,35	0,01	0,02
No. 4	BC" 3%	1	0,35	0,01	0,03
No. 5	BC" 5%	1	0,35	0,01	0,05
No. 6	BC" 7%	1	0,35	0,01	0,07

Using a Kern KB 240-3N laboratory technology balance, the materials were weighed and put in a suitable baker. Then the next procedure was applied to obtain the fresh state cement paste subjected to a rheological test.

1. Pour the water and the superplasticizer into a beaker; Mix them for 15 s.
2. Add the NERA Biochar (if the recipe indicates it) into the water and superplasticizer beaker. Mix the Biochar and the liquid part until they are a homogeneous liquid, avoiding lumps in the mix. (Cf. Figure 21)
3. Using an Overhead stirrer WB2000-A from Wiggens, the following configuration of the speed was set.

- 3 minutes at 480 rpm. Room temperature is 25ºC ± 2ºC.
- 3 minutes at 840 rpm. Room temperature is 25ºC ± 2ºC.

In the first 2 minutes, gradually pour the cement.

4. Prepare the Kinexus DSR Series rheological machine, provided by Malvern, to perform the rheological requirements.
5. Pour the fresh state cement mix in the cylindrical stainless-steel container in the Kinexus platform (Cf. Figure 21)
6. Set and adjust the Kinexus DSR Series machine parameters.

Figure 21. Specimen manufacturing for rheological test. b) Specimen poured in the cylindrical stain-less container.

the particular study of the rheology of the mortar, as well as the study carried out for the cement paste, will be addressed in a later study that will be published in a scientific journal of the sector.

7.2 Procedure to prepare samples subjected to mechanical tests.

This section of the chapter explains the recipes and procedures followed to prepare the cement paste and mortar samples that were subjected to mechanical tests, such as flexural strength, compression strength, and fracture energy, as well as all the instruments used and their procedures to obtain each of the samples, are exposed.

7.2.1 Cement paste

The cement paste samples subjected to mechanical tests were prepared in the MASTR-LAB of the Department of Structural, Building and Geotechnical Engineering, DISEG, of the Politecnico di Torino. Eight types of cement paste specimens were prepared (Cf. Tab. 10). The mixtures were prepared with a w/c ratio of 0.35, all of them with 1% of superplasticizer MasterEase 7000 *(ME7)* concerning cement weight; this is due to the Biochar absorb a significant and quick amount of water in the mixing procedures thanks to its high porosity, then it is required this little percentage of superplasticizer additive. It is always important to know the relationship of the different components of the composite with respect to the cement matrix, in this way, it is possible to find an error or discontinuity in the process, but more important to comprehend the composite and change proportion if it is necessary in order to obtain the desire solution (Cf. Tab. 11).

Table 14. Recipes of the cement paste samples to mechanical test.

Recipe	ID	Description	Cem*	Water*	ME7*	Biochar*
No. 1	OPC	Plain Cement Paste	460	161	4,6	0
No. 2	BC' 1%	Paste with 1% of biochar in mix	460	161	4,6	4,6
No. 3	BC' 2%	Paste with 2% of biochar in mix	460	161	4,6	9,2
No. 4	BC' 3%	Paste with 3% of biochar in mix	460	161	4,6	13,8
No. 5	BC'' 1%	Paste with 1% of biochar in mix	460	161	4,6	4,6
No. 6	BC'' 2%	Paste with 2% of biochar in mix	460	161	4,6	9,2
No. 7	BC'' 3%	Paste with 3% of biochar in mix	460	161	4,6	13,8
No. 8	BC'' 5%	Paste with 5% of biochar in mix	460	161	4,6	23

** The unit of the material is grams.*

Table 15. Grams of a compound relative to the amount of cement in the mix in cement paste.

		[g] of material / [g] of cement			
Recipe	**ID**	**cement**	**water**	**ME7**	**Biochar**
No. 1	OPC	1	0,35	0,01	0
No. 2	BC' 1%	1	0,35	0,01	0,01
No. 3	BC' 2%	1	0,35	0,01	0,02
No. 4	BC' 3%	1	0,35	0,01	0,03
No. 5	BC'' 1%	1	0,35	0,01	0,01
No. 6	BC'' 2%	1	0,35	0,01	0,02
No. 7	BC'' 3%	1	0,35	0,01	0,03
No. 8	BC'' 5%	1	0,35	0,01	0,05

These materials were weighed using a Kern KB 240-3N laboratory technology balance (Cf. Figure 22b) following the weight indicated in the Table 14. Once all the materials are weighed and put into a suitable beaker (Cf. Figure 23), follow the next procedure to obtain the mixed design.

1. Pour the water into a beaker.
2. Add the superplasticizer.
3. Add the NERA Biochar (if the recipe indicates it) into the water and superplasticizer beaker.
4. Mix very well with the help of a spatula until obtaining a homogeneous liquid mass. (Cf. Figure 23)
5. Using an Overhead stirrer WB2000-M from Wiggens, the next configuration of the speed was set

   - 3 minutes at the 4-speed motor. Room temperature is 25ºC ± 1ºC
   - 3 minutes at the 6-speed motor. Room temperature is 25ºC ± 1ºC

   In the first 2 minutes, gradually pour the cement.

6. Impregnate the steel framework with a release agent.
7. Pour the sample slowly to avoid air confinement into the steel formwork made up of four 20x20x80 mm^3. For each recipe, 8 joists were made, 4 will be tested in compression and flexion at 7 days of curing, and the remaining 4 at 28 days of curing.
8. Cover the samples with a polyethylene sheet and preserve them in a maturation room, approximately 90% of humidity.
9. After passing 24 hours, the samples were stripped, named (Cf. Tab. 12.), and put into a water tank for curing, with the environment temperature controlled.
10. One day before the test, make a u-notch of 6 mm depth and 2 mm width in each sample to control the displacement, using in the test the crack mouth opening displacement (CMOD) technic.

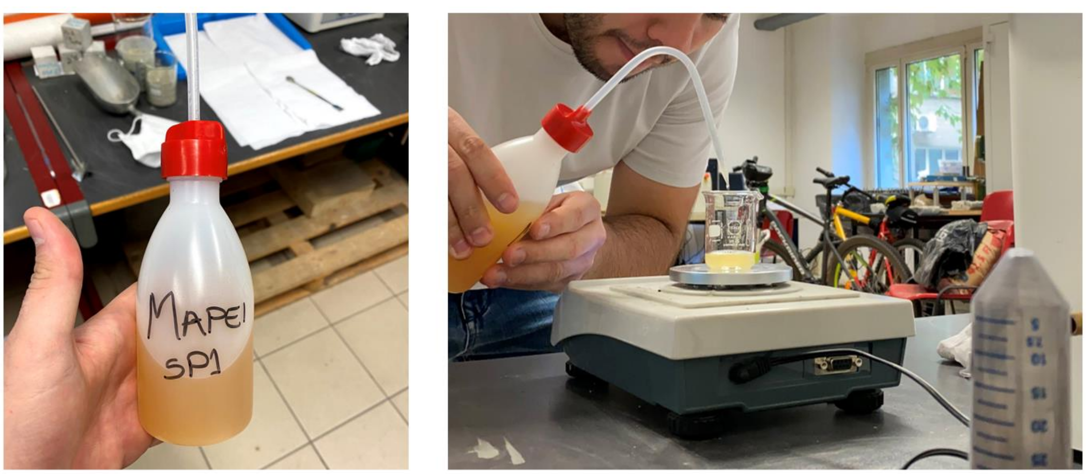


Figure 22. a) Superplasticizer Master Ease 7000 (ME7). b) Weighing the precise amount of the recipe.

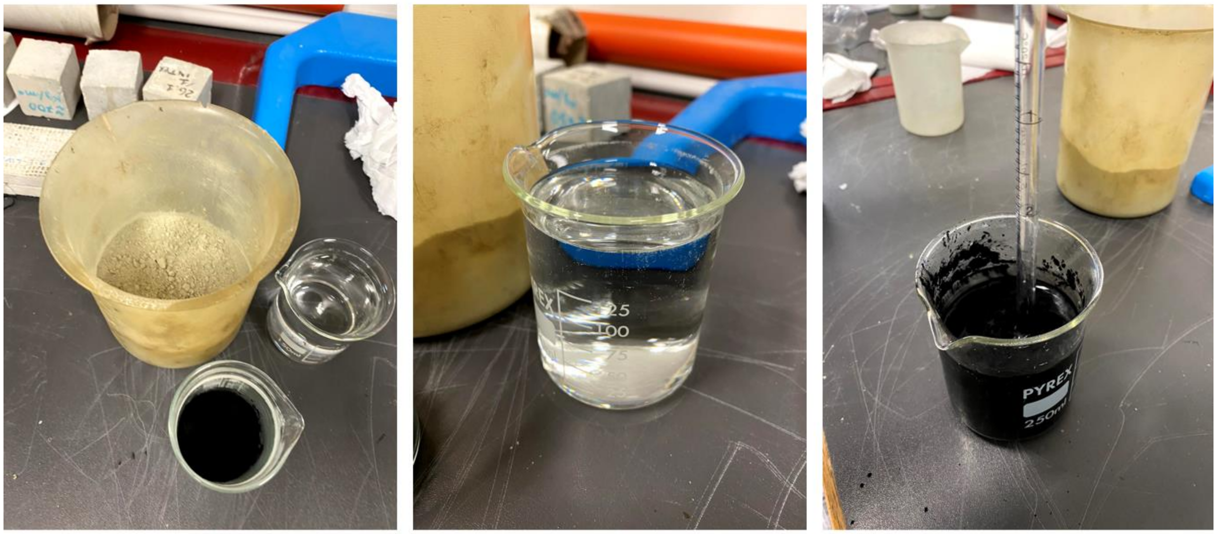


Figure 23. a) and b) Weighed material into in appropriate bakers. c) Biochar mixed with water and ME7.

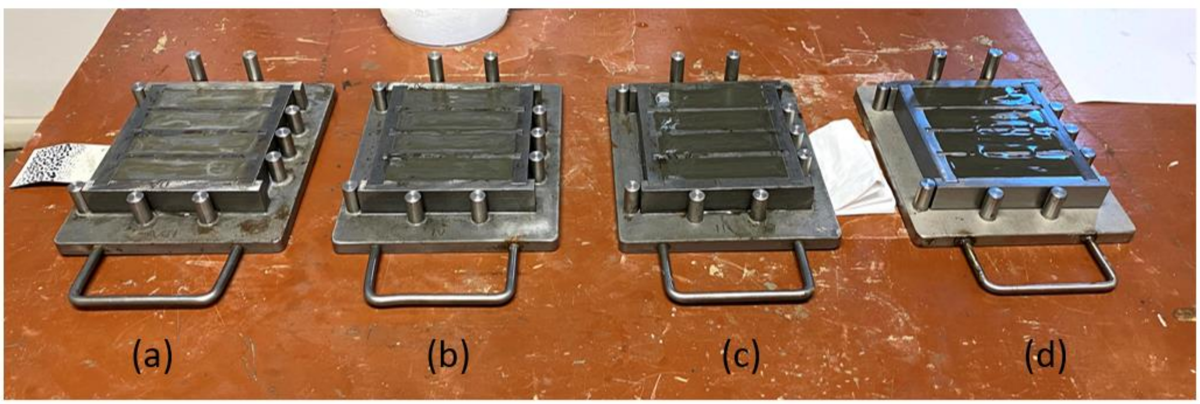


Figure 24. Casting time (24H).

Figure 25. a) Demolding the samples. b) samples in the curing tank.

Table 16. specifies the number of samples made for each recipe and the name assigned in the sample.

To make the U-notch of 2x60 mm, a Miter saw BRILLANT 220 (Cf. Figure 26a) provided by QTAM Quality assured made in German. The BRILLANT 220 is a compact, easy-to-use precision wet miter saw. It can be equipped with automatic movement along the three axes (X, Y, Z) and with different cutting systems to offer maximum flexibility and ideal use of the cutting space [82]. Its dimensions are specified in Fig. 17.b

Table 16. Number of samples per recipe for cement paste

Recipe	ID	ID on sample	No. samples at 7-days	No. samples at 28-days
No. 1	OPC	OPC – ME7 – (1/4) – (7-28)	4	4
No. 2	BC' 1%	BC' 1% – ME7 – (1/4) – (7-28)	4	4
No. 3	BC' 2%	BC' 2% – ME7 – (1/4) – (7-28)	4	4
No. 4	BC' 3%	BC' 3% – ME7 – (1/4) – (7-28)	4	4
No. 5	BC'' 1%	BC'' 1% – ME7 – (1/4) – (7-28)	4	4
No. 6	BC'' 2%	BC'' 2% – ME7 – (1/4) – (7-28)	4	4
No. 7	BC'' 3%	BC'' 3% – ME7 – (1/4) – (7-28)	4	4
No. 8	BC'' 5%	BC'' 5% – ME7 – (1/4) – (7-28)	4	4

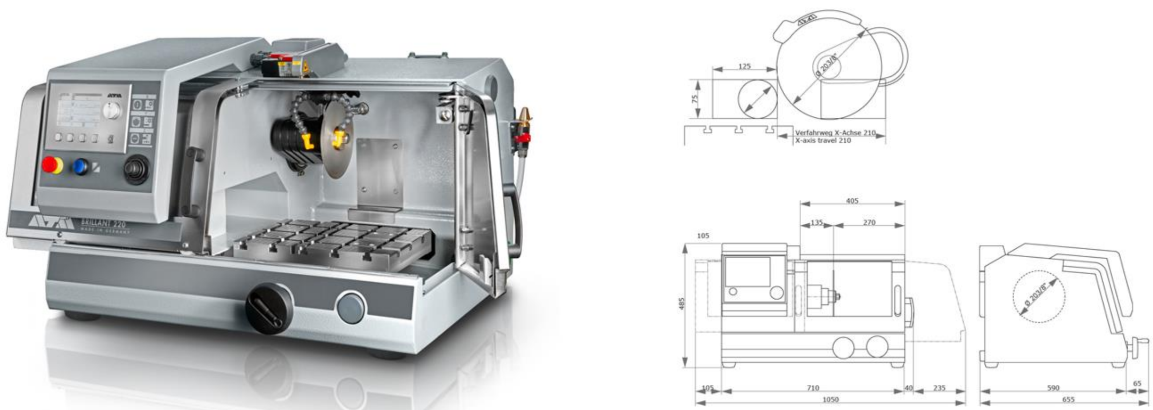


Figure 26. a) Miter saw BRILLIANT 200 cut machine. b) Dimensions of the BRILLIANT 220 machine [87].

Figure 27. a) Shaft and cutting disc of the machine. B) U-notch sample cut.

7.2.2 Mortar

The procedure to prepare the mortar lies in Code EN 196-1 [75]. The mortar samples subjected to mechanical tests were made in the MASTR-LAB of the Department of Structural, Building and Geotechnical Engineering, DISEG, of the Politecnico di Torino. Seven types of mortar specimens were prepared (Cf. Tab. 13). The mixtures were prepared with a w/c ratio of 0.5, and it reminds constant even when the biochar is used as a substitution of cement composite. The fine aggregate is Cen standard sand certified in EN 196-1 in agreement with ISO 679:2009 (See particle size distribution in annex A). The sand cement sd/c ratio is 3 and all the relationship between each component with respect the cement matrix is presented in Table 18.

Table 17. Recipes of the mortar samples to mechanical test.

Recipe	ID	Description	Cem*	Water*	Sand*	Biochar*
No. 1	OPC	Plain Cement Paste	450	225	1350	0
No. 2	BC" 1% - FI	1% BC in mix as filler	450	225	1350	4,5
No. 2-2	BC" 1% - SO	1% BC in mix as substitution	445,5	225	1350	4,5
No. 3	BC" 3% - FI	3% BC in mix as filler	450	225	1350	13,5
No. 3-2	BC" 3% - SO	3% BC in mix as substitution	436,5	225	1350	13,5
No. 4	BC" 5% - FI	5% BC in mix as filler	450	225	1350	22,5
No. 4-2	BC" 5% - SO	5% BC in mix as substitution	423,5	225	1350	22,5

Table 18. Grams of a compound relative to the amount of cement in the mix in mortar.

		[g] of material / [g] of cement			
Recipe	**ID**	**cement**	**water**	**Sand**	**Biochar**
No. 1	OPC	1	0,5	3	0
No. 2	BC" 1% - FI	1	0,5	3	0,01
No. 2-2	BC" 1% - SO	1	0,5	3	0,01
No. 3	BC" 3% - FI	1	0,5	3	0,03
No. 3-2	BC" 3% - SO	1	0,5	3	0,03
No. 4	BC" 5% - FI	1	0,5	3	0,05
No. 4-2	BC" 5% - SO	1	0,5	3	0,05

These materials were weighed using a Kern KB 240-3N laboratory technology balance (Cf. Figure 22b) following the weight indicated in Table 17. After having all the materials weighted, mix each batch of mortar mechanically using the 5qt Benchtop Laboratory Mixer (230V / 50Hz) (Cf. Figure 28a) [83] specified in the code EN 196-1 [75].

1. Pour the water into the bowl and add the cement. If the mix specifies biochar's content, it should be poured into the water and mixed previously to be added to the machine exactly as was made in the cement paste procedure *(section 7.2.1)*

2. Start the mixer immediately at low speed (Cf. Tab. 15), and after 30 s add the sand steadily during the next 30s.
3. Switch the mixer to the higher speed and continue for an additional 30s.

Table 19. Speeds of mixer blade. From EN 196-1 [75].

	Rotation $[min^{-1}]$	Planetary movement $[min^{-1}]$
Low Speed	140 ± 5	62 ± 5
High speed	285 ± 10	25± 10

4. Stop the mixer for 1 min 30 s. During the first 15 s remove employing a rubber scraper all the mortar adhering the wall and bottom part of the bowl and place in the middle of the bowl.
5. Continue the mixing at high speed for 60 s.

The timing of the various mixing stages shall be adhered to within ± 1 s.

6. Impregnate the steel framework made up of 40x40x160 mm^3 with a release agent. Mold the specimens immediately after the preparation of the mortar. With the mold and hopper firmly clamped to the jolting table. Introduce the first layer of mortar (about 300 g) into each of the mold compartments. Spread the layer uniformly and compact the first layer using 60 jolts. Then Introduce the second layer of mortar, level it, and compact with a further 60 jolts.
7. Strike off the excess mortar and smooth the surface with the straight metal edge.
8. Cover the samples with a polyethylene sheet and preserve them in a maturation room, approximately 90% of humidity.
9. After passing 24 hours, the samples were stripped, named, and put into a water tank for curing, with the environment temperature controlled *(24±1ºC)*.
10. One day before the test, make a u-notch of 12 mm depth and 2 mm width in each sample to control the displacement, using in the test the crack mouth opening displacement (CMOD) technic.

Figure 28. a) Preparation of the mortar mix. b) Mortar mix ready to mold.

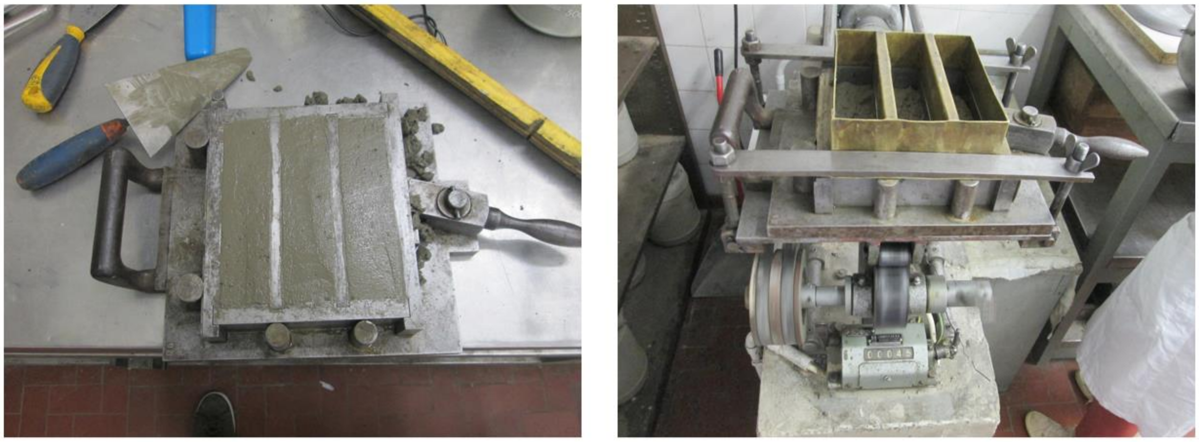


Figure 29. a) Mortar specimens. b) Mold and hopper firmly clamped to the jolting table.

Figure 30. Demolding and named the mortar specimens.

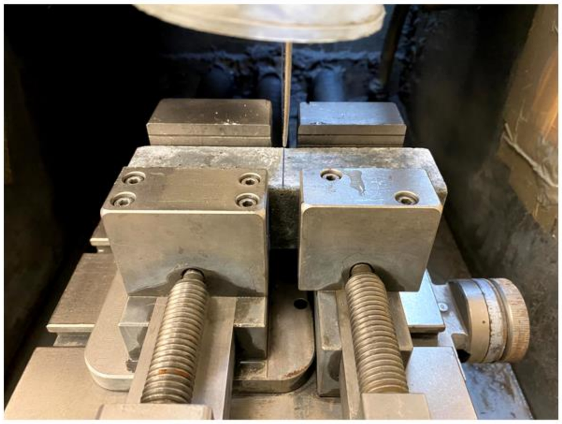
Table 20. specifies the number of samples made for each recipe and the name assigned in the sample.

The U-notch of 2x120 mm was made using the Miter saw BRILLANT 220 (Cf. Figure 31a) provided by QTAM Quality assured, the same cutter machine utilized for U-notch cut of the cement paste specimens. Specifications in *section 7.2.1.*

Table 20. Number of samples per recipe for mortar.

Recipe	ID	ID on sample	No. samples at 7-days	No. samples at 28-days
No. 1	OPC	OPC – ME7 – (1/4) – (7-28)	3	3
No. 2	BC" 1% - FI	BC" 1% – FI – (1/4) – (7-28)	3	3
No. 2-2	BC" 1% - SO	BC" 1% – SO – (1/4) – (7-28)	3	3
No. 3	BC" 3% - FI	BC" 3% – FI – (1/4) – (7-28)	3	3
No. 3-2	BC" 3% - SO	BC" 3% – SO – (1/4) – (7-28)	3	3

No. 4	BC'' 5% - FI	BC'' 5% – FI – (1/4) – (7-28)	3	3
No. 4-2	BC'' 5% - SO	BC'' 5% – SO – (1/4) – (7-28)	3	3



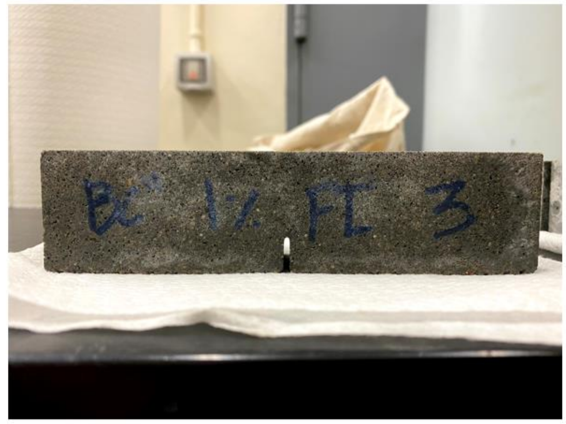


Figure 31. a) Shaft and cutting disc of the machine. B) U-notch sample cut.

SECTION 3: LABORATORY AND EXPERIMENTAL PROCEDURE

8. RHEOLOGICAL TEST ACTIVITY

This chapter will expose the tests that were made to determine cement paste and mortar rheological properties. For both cement-based compounds, shear viscosity (η), shear rate (γ), shear stress (τ), yield stress (τ), rheological index (n) and plastic viscosity (η_{plas}) were evaluated from the flow curve test. The tests were conducted by a co-axial cylinder rotary viscosimeter provided by Malvern Panalytical Company with a KINEXUS DSR SERIES, configured with a Peltier Cylinder Cartridge geometer (Cf. Figure 32) in the Burner Rig laboratory, DISAT, Politecnico di Torino.

Rheological behaviors are the essential workability characteristics of fresh concrete. Carbonaceous additives and natural derivatives from pyrolysis are important for modern concrete, significantly influencing concrete rheology. In this document, an experiment was designed to investigate the shear thickening and yield stress behaviors of cement paste and cement mortar, filled and substituted by Nera Biochar *(BC' & BC")*.

The results show that the cement paste plastic viscosity discussed in the current study decreases prominently first and then remains constant, with a slight increase as the shear rate increases. Therefore, there is a minimum plastic viscosity (η_{min}), critical shear rate (γ_{crit}) and critical shear stress (τ_{crit}) in the flow curves at the beginning of the shear thickening taking place. The addition of Nera Biochar *(BC")* in the cement paste not only increases the η_{min}, γ_{crit} and τ_{crit} but does not easily exhibit shear thickening, moreover, it increases the rheological index *(n)*, leading to an increase in the intensity of the shear thickening.

8.1 Cement paste

Flow curve tests were conducted by a co-axial cylinder rotary viscosimeter provided by Malvern Panalytical Company with a KINEXUS DSR SERIES, configured with a Peltier Cylinder Cartridge geometer (Cf. Figure 32). The gap between the inner and outer cylinder was 1.15 mm, while the gap between the base of the cylindrical container and the co-axial cylinder is 5 mm [93]. The temperature of the system was maintained at 23 ± 1.0 ºC with a Peltier setting. The specimens were tested 1 min after the mixing procedure. Then, the flow curve test was performed by increasing the shear rate using a step-up approach from $0{,}1\ s^{-1}$ to $200\ s^{-1}$ in a time span of 6 min. Bingham model parameters (Cf. Eq. (*1*)) were determined using an ordinary least squared regression that best fit the linear equation to find the slope and the intercept with the ordinate axis.

$$\tau = \tau_y + \eta\gamma \tag{1}$$

Where τ is the shear stress (Pa), τ_y is the yield stress (Pa), η is the plastic viscosity coefficient $(Pa \cdot s)$, and γ is the shear rate (s^{-1}). In this case, the cement paste is considered a non-newton fluid, then the plastic viscosity η is variable and decrease as a shear rate increase. The term rheological material functions are used to indicate that rheological parameters such as viscosity, storage modulus, among others, are not constant over time, depending on other characteristics and parameters such as shear rate, shear stress, or yield stress. According to Morrison [96], when working with the Bingham material, the plastic viscosity approaches infinity when the shear stress is less than the yield stress, but when the stress is greater than the yield stress, the viscosity will be a function of the shear rate and their respective shear stresses. In this scenario, the behavior begins to be linear.

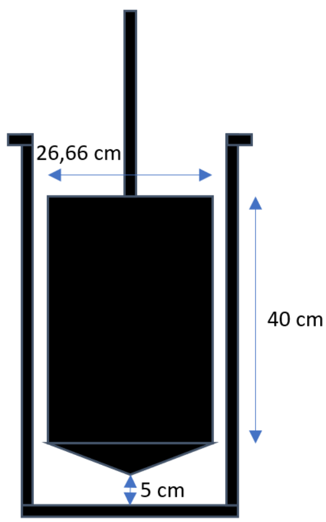


Figure 32. Co-axial cylinder.

Once the mixture is prepared, based on the method followed in section 7.2, pour the mixture little by little into the cylindrical Peltier Cylinder Cartridge geometer container, without exceeding the limits of the container so as not to alter the correct operation and therefore the results (Cf. Figure 33a). Then adjust the mean test temperature and start the 6-minute total duration experiment comprising a shear rate change from $0{,}1\ s^{-1}$ to $200\ s^{-1}$. After carrying out the rheological test, it is important to deposit the remains of the cement paste used before it begins to set or carry out the thixotropic process since the splinters generated by the hardening process can scratch, damage, and decalibrate the measuring machine, especially the Peltier Cylinder Cartridge (Cf. Figure 33b).

Figure 33. a) Content of the cement sample poured into the cylindrical test container. b) Peltier Cylinder Cartridge geometer

After the experimental phases, the flow curves are obtained individually, where the information must be refined and reorganized the flow curves to be able to make comparisons between the different samples tested. From the shear rate vs. plastic viscosity curve, it is possible to find the minimum viscosity (η_{min}) and then the critical shear rate (γ_{crit}). On the other hand, from the shear rate vs. shear stress curve, the critical shear stress (τ_{crit}) is determined, previously knowing the critical shear rate.

9. RHEOLOGICAL TEST RESULTS

This chapter will expose results obtained from the rheological test activity for the cement paste and the mortar to show the fresh state characteristics and properties. The rheological test activity was performed for plain cement samples *(OPC)* and samples with Biochar content in different percentages as it was explained in the recipe detail for rheological activity. Results for plain cement-based compounds will be exposed separate and all together to comprehend the effect of the addition of Biochar and what is the main effect of biochar in cement paste and mortar.

9.1 Cement Paste

The following analysis will deal with the test results obtained from the rheological test in cement paste to show the fresh state characteristics and properties. The rheological test activity was performed for plain cement *(OPC)* and samples with Biochar addition at least twice to corroborate the expected results. Results for plain cement-based compounds and samples with Biochar addition will be exposed in Figure 38 and Figure 39, to comprehend the effect of Biochar addition in cement paste.

9.1.1 Effect of Biochar on rheological curves

Studies of the rheological behavior of the cement paste with the addition of Biochar *(BC'')* provide essential information to understand the response control mechanism of the shear thinning and shear thickening to which the mixture is subjected with different addition percentages of the carbonaceous compound. The experimental procedure was performed twice to comprehend and compare the experimental data (Cf. Table 21). Figure 34 and Figure 36 show the shear rate vs. plastic viscosity flow curves, Figure 35 and Figure 37 show the shear rate vs. shear stress flow curves for Rec. 4. BC'' 3% and Rec. 5. BC'' 5%, respectively. From these curves, the behavior and similarity of the results between the first experimental phase and the second experimental phase can be evaluated, from which it is possible to conclude that the rheological properties evaluation procedure was standardized and successfully carried out. In accordance with the statement just mentioned, the critical rheological parameters such as shear stress (τ_{crit}), shear rate (γ_{crit}), and minimum plastic viscosity (η_{min}), are those values that are representative of the batch of samples for each of the recipes and experimental phases (Cf. Table 21). Then, due to the similarities in the flow curves, the analytical plot will be just one of the experimental phases that better represent the flow behavior.

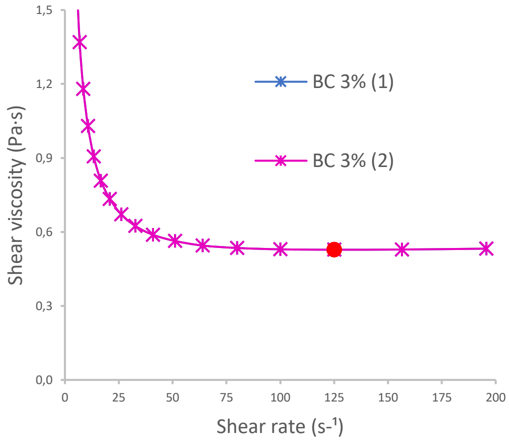


Figure 34. Shear rate vs. plastic viscosity for Rec. 4. BC" 3%.

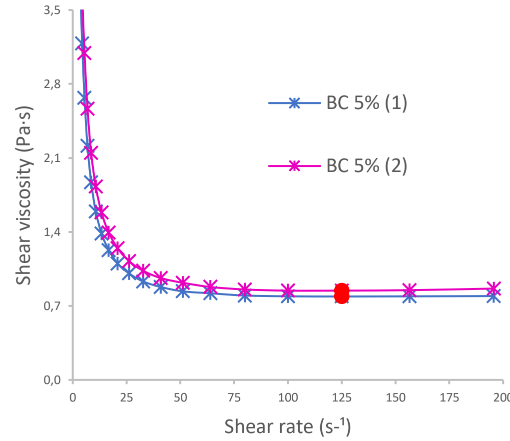


Figure 36. Shear rate vs. plastic viscosity for Rec. 5. BC" 5%.

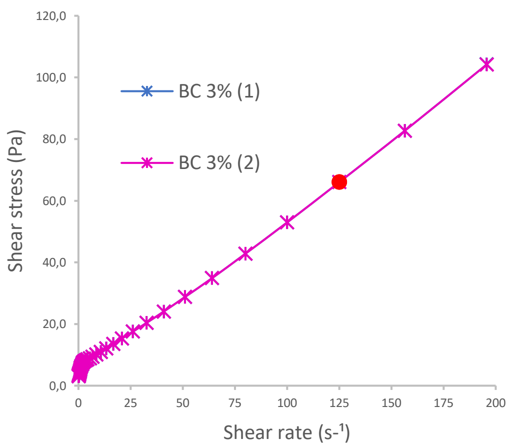


Figure 35. Shear rate vs. shear stress for Rec. 4. BC" 3%.

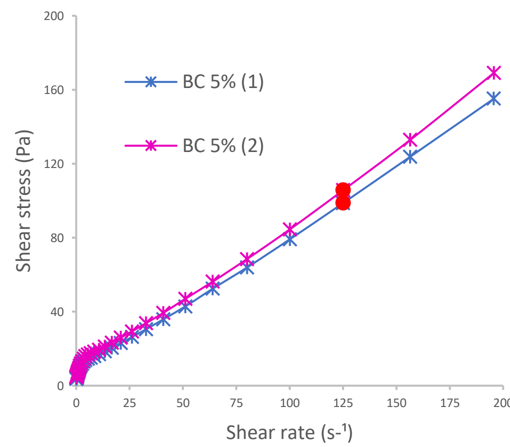


Figure 37. Shear rate vs. shear stress for Rec. 5. BC" 5%.

Figure 38 illustrates the shear rate vs. plastic viscosity flow curves for both the plain cement sample and the mixtures with a certain percentage of Biochar. Figure 39 illustrates the shear rate vs. shear stress curves of the reference sample and the mixtures influenced by Biochar. In Figure 38, it can be seen that any percentage of Biochar addition on the cement paste, with the increase in the shear rate, the plastic viscosity always decreases until reaching the critical point (red points) and then remains constant, with a shear thickening practically negligible. Put differently, shear-thinning occurs initially and then remains almost constant after the lowest plastic viscosity is reached. When shear thinning is ending and a process of transformation to shear thickening should begin, points A, B, C, D, E, and F are found (Cf. Figure 38), representing the lowest plastic viscosity (η_{min}), indicating that the critical shear rate (γ_{crit}) is at that point. When the critical shear rate threshold is exceeded, the plastic viscosity will begin to develop as the shear rate increases; however, for the tests performed to OPC, BC'' 1, 2, 3, and 5 wt% show a slight shear thickening, which is not considered significant, assuming constant behavior. On the other hand, for the BC'' 7% wt specimen test, the γ_{crit} Is the maximum value of shear rate that the test reached, but at this point, it cannot be considered critical other than by default. In Figure 38, it is observed that as higher the biochar content, η_{min} increases and γ_{crit} is quietly constant around $125\ s^{-1}$. It is likely that when testing with a shear rate exceeding the threshold of $200\ s^{-1}$ Mixtures with the influence of Biochar may have greater difficulty in presenting shear thickening. In other words, tends to be constant.

Once the critical points in the shear rate vs. plastic viscosity curve are found, referring to γ_{Crit} and η_{min} respectively, represented graphically in Figure 38, the critical shear stress (τ_{Crit}) can be determined, interpolating the value corresponding to the critical shear rate from the shear rate vs. shear stress flow curve (Cf. Figure 39). The critical points A', B', C', D', E' and F' that correspond to the curves OPC, BC'' 1, 2, 3, 5, and 7 wt% respectively are found graphically in Figure 39 shear rate vs. shear stress curve. From the same figure, the change in the Rheological index *(n)* can be seen, representing the change in slope of the final part of the straight curve. Rheological index *(n)* illustrates the intensity of the shear thickening; then, the increase in n means the increase in the intensity of the shear thickening of the cement paste (Cf. Table 21), which evidently increases with the increase in the percentage of Nera Biochar in the sample. From Figure 38 and Figure 39, it can be inferred that the addition of Biochar in different amounts to the cement paste influences the rheological parameters of the cement to a great extent, as it increases and decreases the critical parameters such as γ_{Crit}, τ_{Crit} and η_{min} (Cf. Table 21). Therefore, γ_{Crit}, τ_{Crit} and η_{min} can be considered as parameters that describe and compare the rheological behavior, shear thinning and shear thickening of cement paste.

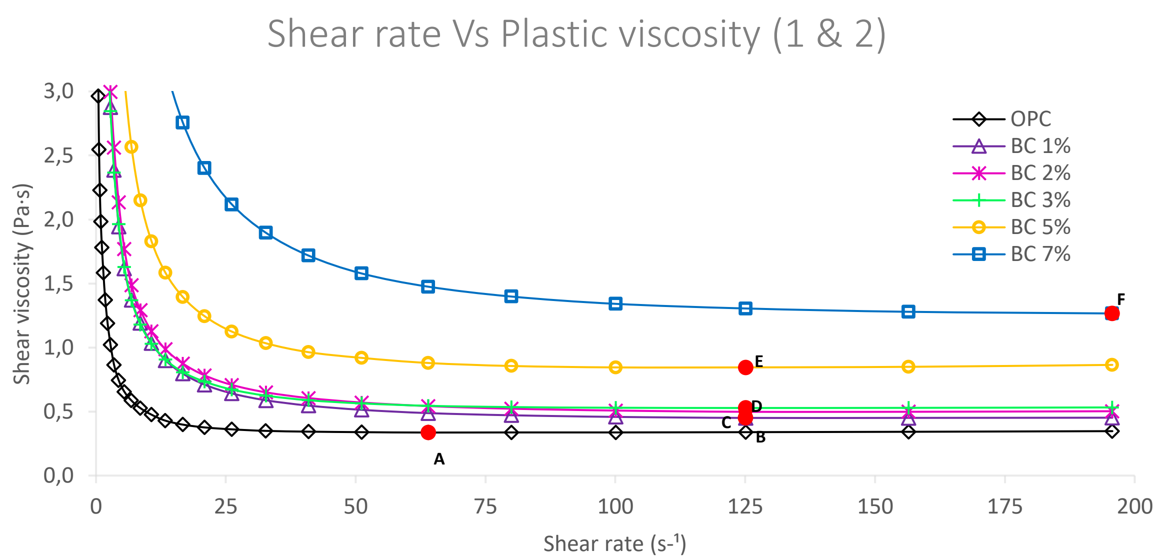


Figure 38. Shear rate vs. plastic viscosity for plain cement and samples with Nera Biochar.

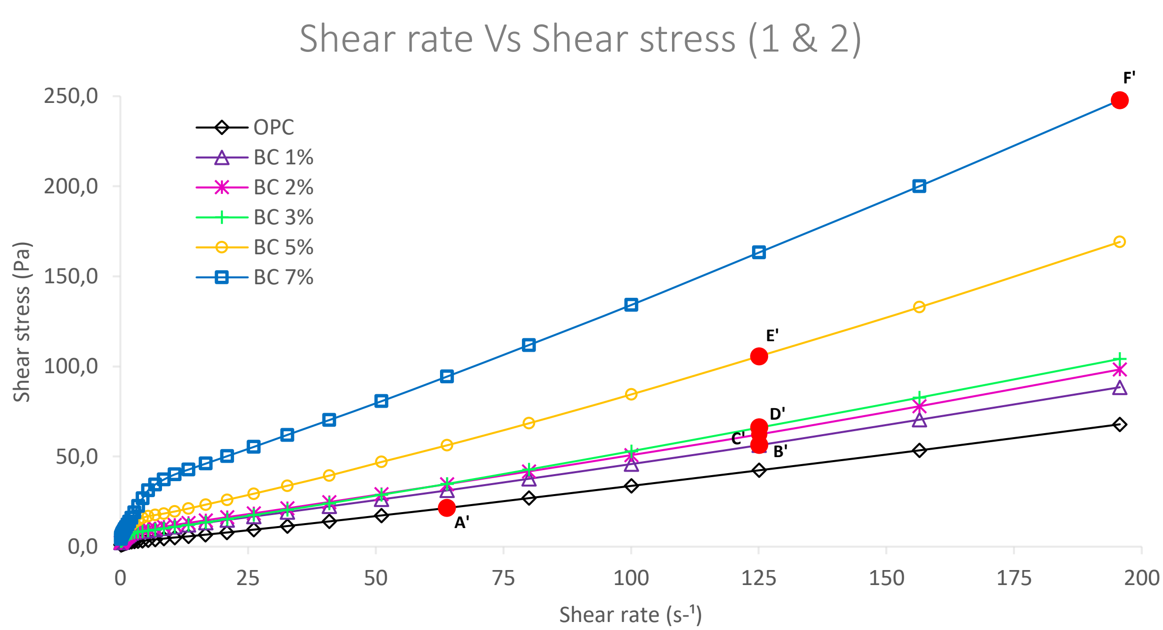


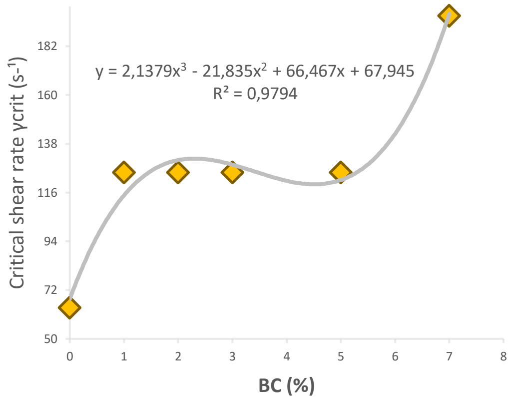
Figure 39. Shear rate vs. shear stress for plain cement and samples with Nera Biochar.

9.1.2 Effect of Biochar on rheological parameters: γ_{Crit}, τ_{Crit} and η_{min}

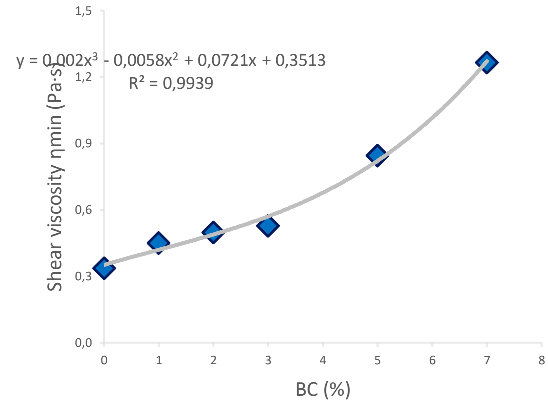
Table 21 shows the rheological parameters fitted from the Bingham model (Cf. Equ. (*1*)) of cement paste with different Biochar contents. Results in Table 21 illustrate that the γ_{Crit} of plain cement paste is $63.99\ s^{-1}$, indicating plain cement paste is a shear thinning paste until the shear rate increases to a high rate. However, with the increase of Biochar percentage, γ_{Crit} fist increase, then reminds constant until BC'' 5% and finally increase reaching $196\ s^{-1}$ (Cf. Figure 40a), illustrating that cement paste are hardly to take on shear thickening after the addition of Biochar.

Each percentage of Biochar contributes different viscosity and stress to the cement sample. From the studied results of rheological behavior of cement paste with the addition of Biochar, it is not hard to find the same effects of the Biochar on cement paste are that they increase η_{min}, γ_{Crit} and τ_{Crit} to a certain point and increases again with high Biochar content (Cf. Table 21). However, there is a great difference for percentage addition to influencing the rheological parameters of cement paste. Figure 40 *(a)* to *(c)* show the influence of Biochar on shear thinning and shear thickening parameters, including η_{min}, γ_{Crit} and τ_{Crit}. A third-order quadratic regression is performed to find the relationship between the rheological parameters and the influence of Nera Biochar on the cement paste. Figure 40 *(a)* to *(c)* show η_{min}, γ_{Crit} and τ_{Crit} increase along with Biochar content increasing. Rec. 2. BC'' 1% to Rec. 5. BC'' 5% the critical shear rate reminds constant and increases concerning plain cement paste. Besides, η_{min} and τ_{Crit} increases gradually until BC'' 5%, with an exponential growth mainly seen when BC 7 wt% is added concerning BC 3 and 5 wt% (Cf. Figure 40*b* and Figure 40*c)*, making it more viscous. As can be seen from Figure 40 *(a)*, when Biochar content is 1 to 5 wt% γ_{Crit} take a constant value $125\ s^{-1}$ after being in $63.99\ s^{-1}$ for plain cement, which means hardly shear-thickening take place. As shown in Figure 40 *(b)* to *(c)*, Biochar content 1 to 3 wt% η_{min} and τ_{Crit} , has a constant behavior with a slight increase when the percentage of biochar increases, but in any case are larger than the plain cement, making the shear-thickening hard to exhibit. Further, the plain cement and any other mixture with biochar addition do not exhibit shear thickening, especially when the Biochar content increases. For example, Rec. 6. BC'' 7%, does not exhibit any shear thickening or constant behavior because γ_{Crit} is the shear rate reached by the experiment.

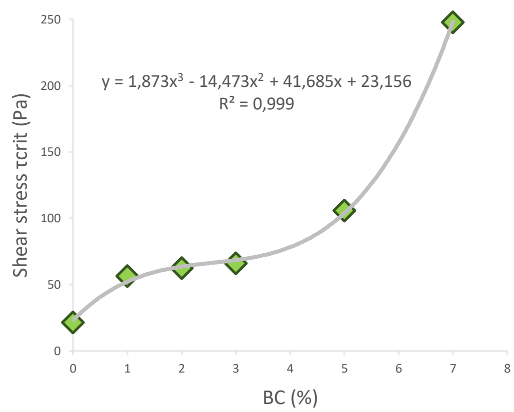
Unlike other compounds or additives added to the cement paste, where its behavior can be highly varied [97], the Nera biochar in the cement paste seems to have more consistent behavior, where the different rheological parameters evaluated seem to increase to as the percentage of Biochar in the sample increases. It is important to emphasize this behavior because a similar trend is expected as the percentage of Biochar increases or decreases without affecting the cement composite performance



(a)



(b)



(c)

Figure 40. Influence of Nera Biochar on rheological parameters.

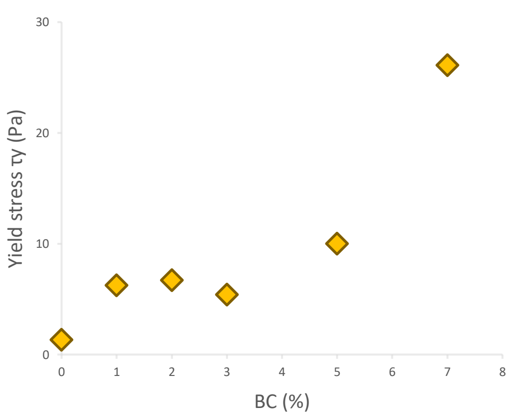
9.1.3 Effect of Biochar on yield stress: τ_y

The yield stress (τ_y) was calculated according to the Bingham model (Cf. Equ. (*1*)), where the straight line of the shear rate vs. Shear stress curve was extrapolated (Cf. Figure 39) to find the intersection of this curve with the ordinate axis *(Y-axis)*, this point being the yield stress and the slope being the rheological index *(n)* corresponding to a particular sample [97]. The Bingham model is valid for linear behavior in the flow curve, being valid for all flow curves Shear rate vs. Shear stress of the plain cement and Biochar influenced mixtures in this study (Cf. Table 40), taking into account the coefficient of determination *(R^2)* was kept above 0.99 for all samples. Figure 41 illustrates the effect of the addition of Biochar on the rheological property yield stress (τ_y) of each of the samples. The plain cement reference sample reaches $1.4\ pa$ of τ_y. Samples with Biochar content BC'' 1, 2 and 3 wt% show an increase of 400%, with a yield stress around $6\,pa$ almost constant among this recipe, while samples BC'' 5% shows an increase of τ_y, reaching almost the double concerning BC'' 1 to 3 wt%, with $\tau_y = 10\,pa$. Biochar's effect in the cement matrix in main rheological properties depends on the sample's preparation and the agglomeration of the particles and their content in each preparation. The process of preparing samples matters and greatly influences the sample's behavior both in the fresh state and in the hardened state [93,94].

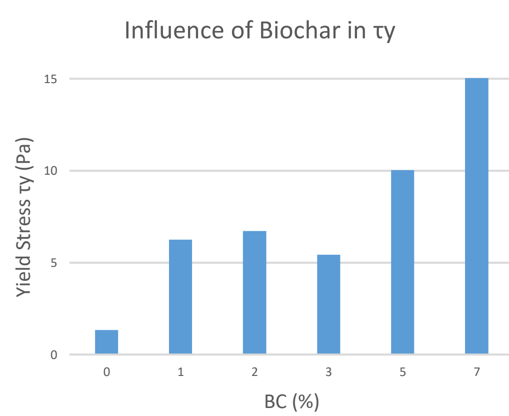
Table 21. Rheological parameters of cement paste with different percentages of Biochar.

ID	BC (%)	$\gamma_{Crit}\ (s^{-1})$	$\eta_{min}\ (Pa \cdot s)$	$\tau_{Crit}\ (Pa)$	$\tau_y\ (Pa)$	n
OPC	0	125,100	0,407	50,880	5,13	0,375
BC 1%	1	125,100	0,450	56,340	6,25	0,409
BC 2%	2	125,100	0,498	62,310	6,71	0,455
BC 3%	3	125,100	0,528	66,070	5,44	0,490
BC 5%	5	100,100	0,845	105,700	10,03	0,780
BC 7%	7	195,700	1,266	247,800	26,12	1,109

All samples containing Nera Biochar show increased and higher yield stresses than the plain cement reference sample. In the case of the Rec. 6. BC'' 7% sample, the yield stress reaches $26.12\,pa$, an increase of 1847% with respect plain cement and 160% with respect to the BC 5% sample (Cf. Figure 41). It seems that the addition of Biochar increases the viscosity and the yield stress because the agglomeration and absorption of water by the mostly carbonaceous particles reduce the free water for the cement particles, making the samples less humid, less fluid, and higher τ_y, reducing the pressure that the mixture makes on the formworks, in turn, seeking to de-implement the use of these for civil construction. Thus, a cement-based compound is created with better short-term mechanical properties, maintaining its long-term characteristics, allowing a newer and faster construction system, and sequestering the CO_2 from the air, making it a pseudo-eco-friendly material.



(a)



(b)

Figure 41. Influence of Nera Biochar on yield stress τ_y.

Evaluating the main rheological parameters of the cement paste, such as η_{min}, γ_{Crit}, τ_{Crit} and τ_y It can be seen that Biochar in any percentage of addition influences the characteristics in the fresh state. In the case of Nera Biochar, the critical parameters increase with the minimum addition of BC'' 1 wt% of cement, and it tends to have a constant behavior, in general, up to an addition of Biochar BC'' 3 wt%, subsequently, it tends to have exponential growth, such as the case of shear stress *(τ_{Crit})* or yield stress *(τ_y)*. The increase in the critical rheological parameters and the constant behavior after crossing the critical shear rate *(γ_{Crit})* observable in the flow curve shear rate vs. plastic viscosity, indicate that the cement paste with the Biochar content presents a difficult scenario to shear thickening takes place. The behavior expected in the cement paste with Nera Biochar content was a cement paste that could easily take place shear thickening.

Some parameters affect the behavior of the shear thickening. According to Maranzano et al. [98], the particle size, particle distribution, particle shape, volume fraction, and the interaction between the particles of the two compounds are these parameters. For example, mixtures containing particles that are in the nano and micro scale range often exhibit shear thickening; particles with amorphous structure and having an irregular shape easily show shear thickening; the high dispersion of the particles, more and more polydispersed, the intensity *(n)* of the shear thickening begins to decrease. In the current study, the percentage of Biochar in the cement mix was relatively low, reaching BC'' 5 to 7 wt% in the cement paste, and the dispersion was fairly regular, not wholly well dispersed, making it difficult to present shear thickening, because the severity of the shear thickening depends on the concentration of the particles in proportion to the maximum packing fraction. From a practical point of view, shear thickening occurs when the suspension is deflocculated, which was not the case in the current study, where it was observed that the Biochar particles were not all dispersed among themselves and that there were lumps of scattered particles that acted as crack path attractors. From this point of view, it is implied that not only the structure of the particle, the shape, or its ability to water retention is essential, but also that the dispersion process of the particles and the sample preparation influence the ability to provide shear-thinning behavior that then results in shear thickening taking place.

This document is worked with Nera Biochar ground for 7 hours and sieved through a 180-micron sieve, regulated by ASTM, obtaining a particle of a few micrometers 7.9 µm, and surface area obtained through the BET method 35.60 m^2/g. Regarding the shape and constitution of the particle, Nera Biochar is an irregular particle, shaped like a wood chip with small and medium pores (due to its biomass), predominantly made of amorphous carbon *C*, with calcium carbonate content $CaCO_3$ and small amounts of quartz SiO_2.

Based on the statements above and the recent characterization of Biochar, it would be expected for the cement paste containing Biochar to present shear-thickening easily, based on the conditions proposed by Maranzano et al. [98]. However, the agglomeration of the particles, presenting a flocculated suspension state, hinders its development. Means, plain cement, and the pastes with Biochar content present Shear-thinning until reaching the minimum plastic viscosity (η_{min}) and then present a constant viscosity as the shear rate increases.

From a 3D printing point of view of the cement paste, there is a more viscous paste with little Biochar content. Around BC'' 5 and 7 wt% of cement, a more suitable flow and texture paste for implementing 3D technology will be obtained. However, up to now, the cement paste extrusion has not been experimented. It is intended to carry out this procedure for the mortar. Referring to the critical rheological parameters evaluated in this document, η_{min}, γ_{Crit}, τ_{Crit} and τ_y, similar behavior is obtained when Fly Ash, Slag, and limestone powder are added to the cement paste in the document proposed by Ma et al. [97]; that is, when the mineral admixture percentage is increased, γ_{Crit} and τ_{Crit} increases; same behavior with the cement paste containing Biochar *(BC'')*. Regarding shear thickening, the results show opposite behavior. As larger the amount of mineral admixture, lower plastic viscosity, larger rheological index, easily shear-thickening taking place. For the current study, shear thickening is not present in any of the Biochar addition proportions.

10. MECHANICAL TEST ACTIVITY

This chapter will expose the tests that were made to determine cement paste and mortar mechanical properties. For both cement-based compounds, flexural and compressive strength and fracture energy were evaluated, applying the three-point bending tests and the compression test. Both tests were carried out in the laboratory of construction risk and durability center, DISEG, Politecnico di Torino.

10.1 Three-point bending test.

10.1.1 Cement paste

A single column Zwick Line-Z010 testing machine, with a 1 kN load cell device and the clip-on strain gauge equipped to measure the crack Mouth Opening Displacement *(CMOD)*, was used to test each notched specimen subjected to the three-point bending test *(TPB test)*. The span adopted was 65 mm, and the test speed of 0.005 mm/min has been set (Cf. Figure 43a). The evaluation of the flexural strength, the modulus of rupture MOR model, was employed:

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

Where Fmax is the force on the prism at the failure time, L is the span (distance among the supports) equal to 65 mm, b the specimen depth, and h the net ligament height equal to 20 mm and 14 mm, respectively.

The Fracture energy evaluation is important because many of the structures and buildings fail not always due to overloads and overcoming the elastic limit of the different elements throughout the structures, but also failures and collapses due to internal and external cracks that finally lead to the final creep and loss of the elements resistance; therefore the damage of the structure. To identify the mechanical capacity, it is necessary to study the nucleation and propagation of cracks through the fracture mechanism.

The fracture mechanism is the science that studies the mechanism and the process of crack propagation in solids subjected to an external tensile load. Griffith [89] suggested this science with his work on the crack propagation criteria in solids, based on the concept of the transformation of elastic energy into surface energy, known as the energetic formulation of the fracture mechanism. This postulation means that the energetic formulation of the fracture mechanism consists of comparing the energy available for the propagation of a crack in the structure with the energy necessary to produce said crack. The energy required for cracking is called the fracture energy *(GF),* and the energy available is called the energy release rate *(G)*.

In quasi-brittle materials, the Japan Concrete Institute Standard JCI-S-001 [88] describes the process to find the fracture energy from the TPB test, measuring the amount of energy absorbed until the samples break into two prisms. The size specifications of the prismatic specimens and procedure are:

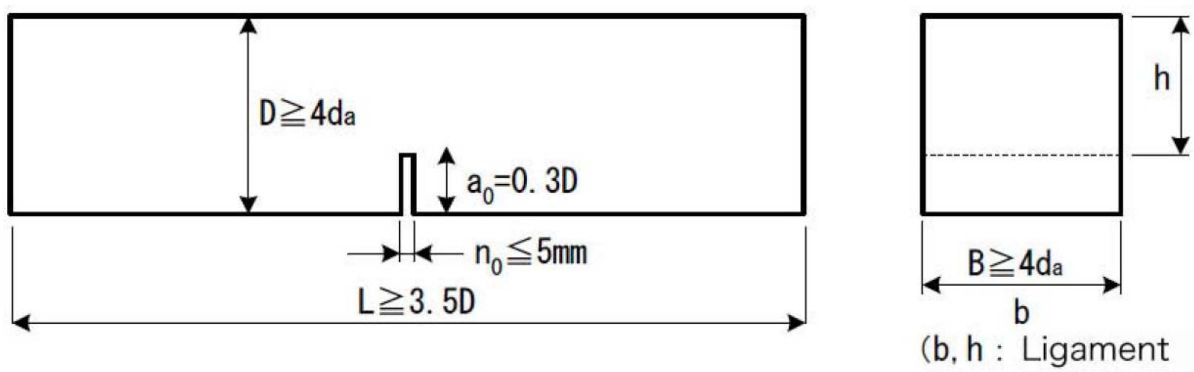


Figure 42. Specimen Dimensions

After the TPB test, the following procedure is computed

$$G_F = \frac{0.75W_0 + W_1}{A_{lig}} = G_{F0} + G_{Fcorr} \quad [N/mm] \tag{3}$$

Where A_{lig} is the area of the nominal ligament equal to 280 mm^2, W_0 $[N \cdot mm]$ is the area below CMOD curve up to rupture of specimen and W_1 $[N \cdot mm]$ is the work done by deadweight of specimen and loading, evaluated as

$$W_1 = 0.75\left(\frac{l}{L}m_1 + 2m_2\right)g \cdot CMOD_c \quad [N \cdot mm] \tag{4}$$

Where l is the loading span (distance among the supports) equal to 65 mm, L is the total length of specimen equal to 80 mm, m_1 $[kg]$ is the mass of the notched specimen, m_2 $[kg]$ is the mass composed by the arrangement for the evaluation of the displacement placed on the beam until it breaks, without being attached to the testing machine, g is the gravity acceleration and $CMOD_c$ is the crack mouth opening displacement at the rupture.

Before starting each TPB test, samples should be prepared to adapt the clip-on gauge to control the crack mouth opening displacements permitting to set the test speed as 0,005 mm/min. First, measure 2 cm from the face of the U-notch forwards to the prism. Then glue the knives and let them be dry; those devices allow the strain gauge connection (Cf. Figure 43).

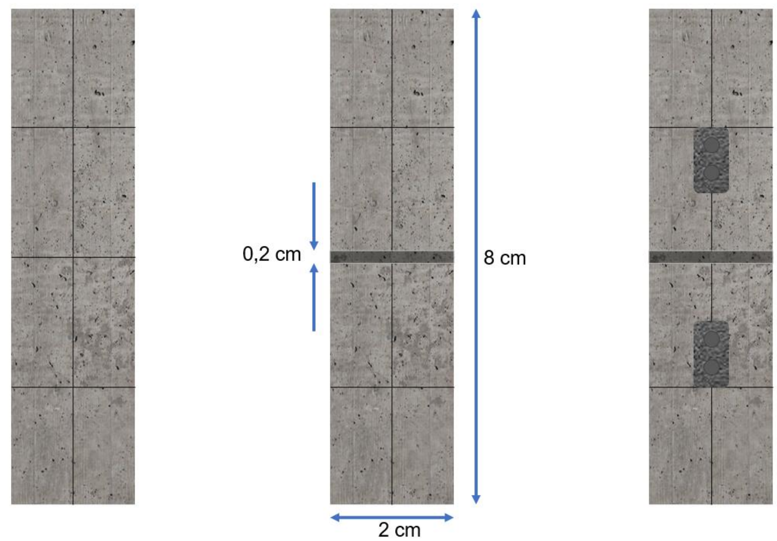


Figure 43. a) cement paste specimen. b) specimen with the u-notch. c) specimen with the u-notch and the arrangement to set the strain gauge.

Once the specimens were prepared, the Zwick Line-Z010 testing machine was prepared, setting the parameter to run the mechanical prove and finally put the sample, with the clip-on gauge device in the supports (Cf. Figure 45a).

10.1.2 Mortar

The TPB test was performed using the same testing machine used for the TPB test in cement paste, with a 50 kN load cell device used to test each mortar notched specimen. The span adopted was 120 mm, and the test speed of 0.03 mm/min has been set (Cf. Figure 44). Once more, the modulus of rupture MOR model was employed to evaluate the TPB test (Cf. eq(*2*)).

Follow Eq (*3*) & (*4*) to obtain the fracture energy evaluation, applying the same procedure explained in *section 8.1.1* Cement paste.

Before starting each TPB test, it should be prepared to adapt the clip-on gauge that allows the control of the crack mouth opening displacements permitting to set the test speed as 0,03 mm/min. First, measure 2 cm from the face of the U-notch forwards to the prism. Then glue the knives and let them be dry; those devices allow the strain gauge connection (Cf. Figure 44).

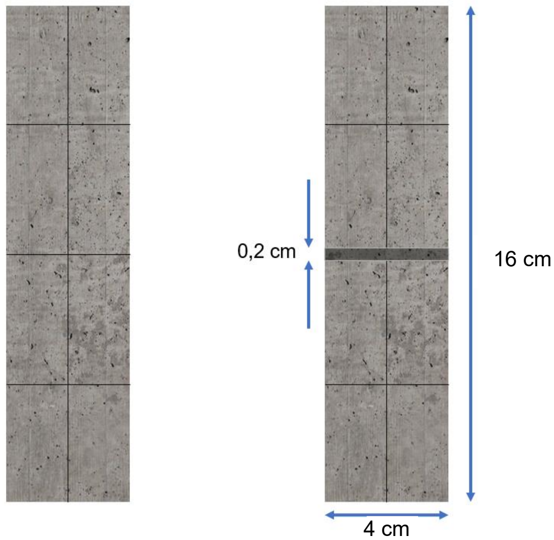


Figure 44. a) Mortar specimen. b) specimen with the u-notch. c) specimen with the u-notch and the arrangement to set the strain gauge.

Once the mortar specimens were prepared, the Zwick Line-Z010 testing machine was prepared, setting the parameter to run the mechanical proof and finally putting the sample with the support's clip-on gauge device (Cf. Figure 45b).

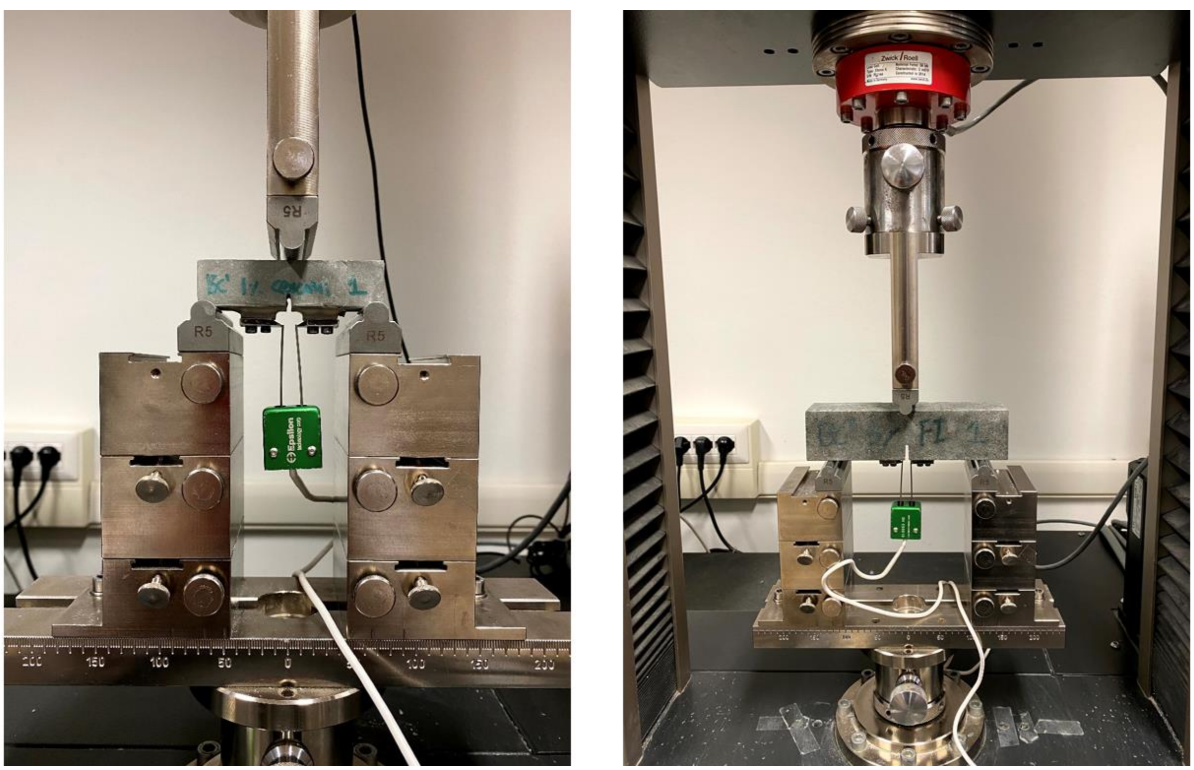


Figure 45. Zwick Line-Z010 testing machine with the CMODc arrangement. a) Cement paste spacimen. b) Mortar specimen.

10.2 Compression test

10.2.1 Cement paste

The compression test was made employing the same single column Zwick Line-Z010 testing machine by changing the load cell capacity to 50 kN and a test rate velocity equal to 60 N/s, using the two broken prisms coming from the TPB test. To evaluate compressive strength, the most common performance measure used by engineers in designing buildings and structures, it should be found the maximum force by testing and then applying:

$$\sigma_{c,max} = \frac{F_{max}}{bh} \quad [MPa] \tag{5}$$

Where F_{max} is the maximum force supported by the specimen before rupture, b and h is the specimen thickness in both directions equal to 20 mm (Cf. Figure 46).

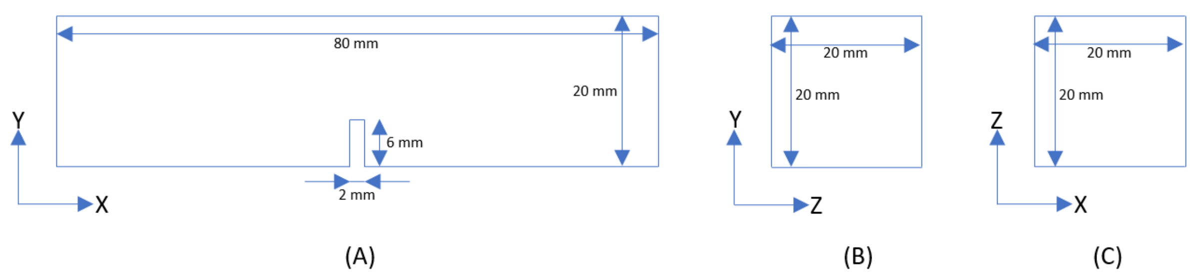


Figure 46. Measurement's specifications of the cement paste specimen.

After the TPB test, two prisms' specimens remain (Cf. Figure 47) placed one by one in the test device (Cf. Figure 49) that is fitted to the compression machine. Then, the process carried out to obtain each specimen's compression strength capacity is exemplified.

In Figure 47, the specimens that remain after the flexural test are shown, where the image in the upper part shows the failure path and the lower part the failure surface. In the left part, there are blank test tubes *(Rec. 1. OPC)*, which do not have Biochar addition; in the central and right part, there are test tubes Rec. 3. BC' 2% and Rec. 4. BC'' 5% addition of biochar, respectively. All the specimen's failure path and failure surface can be found in annex A.

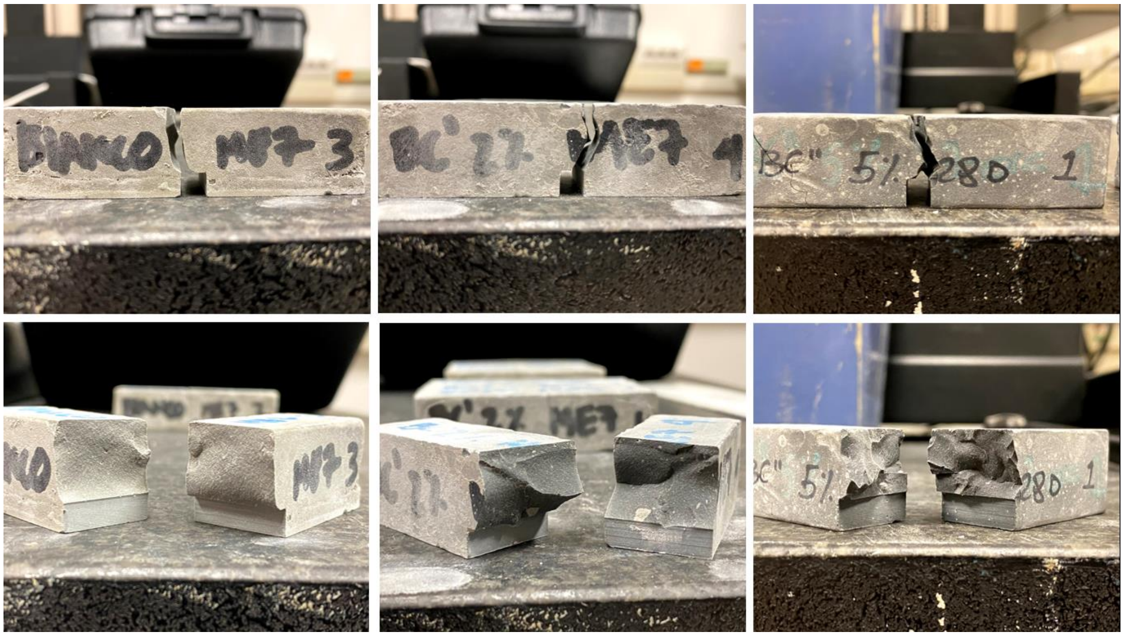


Figure 47. Samples after TPB test. a) Rec. 1. OPC. b) Rec. 3. BC' 2%. c) Rec. 8. BC'' 5%.

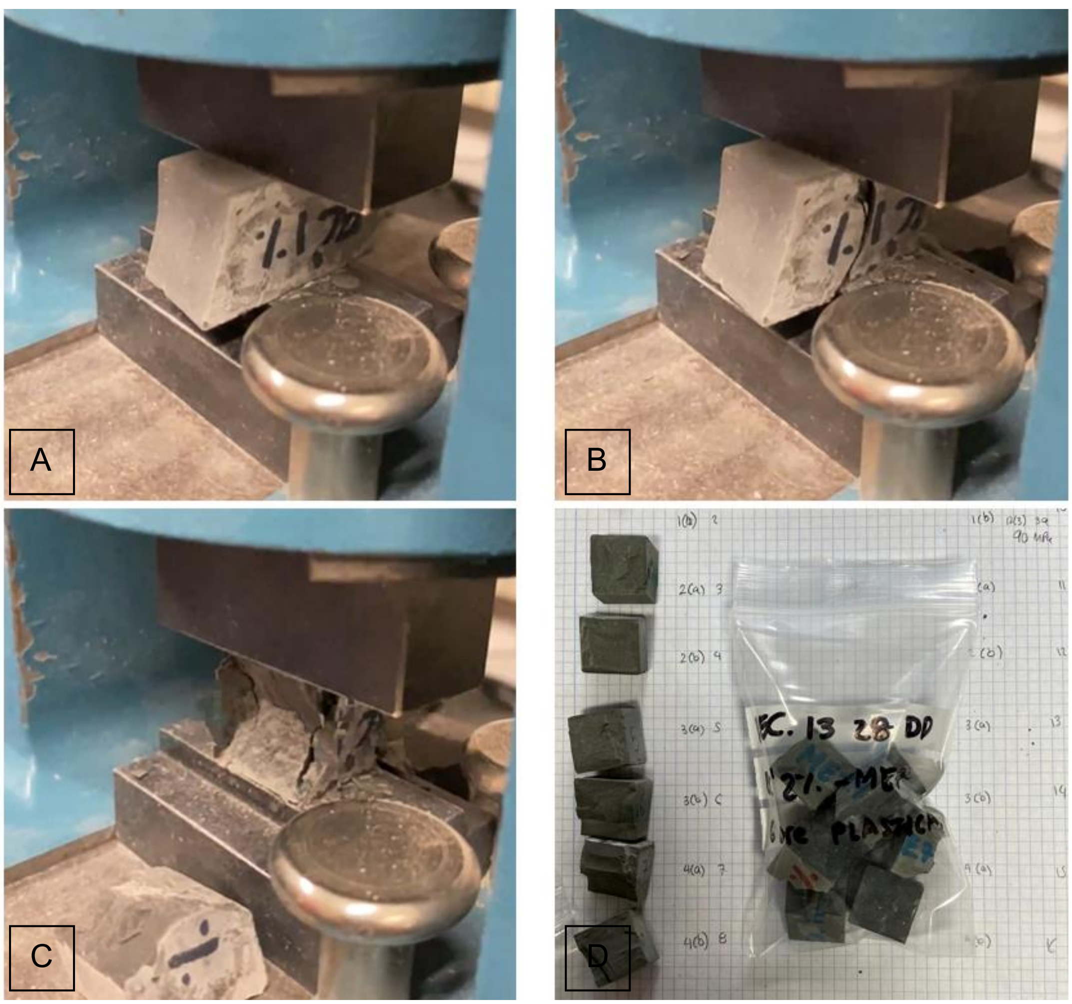


Figure 48. Compressive test performance for cement paste specimens.

Figure 48 shows the samples' failure process in order to evaluate the compressive strength. a) shows the accommodation of the sample at the beginning of the test, b) shows the sample failure moment, c) shows the collapsed specimen, and d) shows how samples are stored for analysis.

Figure 49. Test device fitted to the compression machine.

10.2.1 Mortar

The compression test was made employing the same single column Zwick Line-Z010 testing machine by changing the load cell capacity to 50 kN and a test rate velocity equal to 2400 N/s, using the two broken prisms coming from the TPB test. To evaluate compressive strength, Eq (*5*) was employed, changing the specimen thickness equal to 40 mm (Cf. Figure 50)

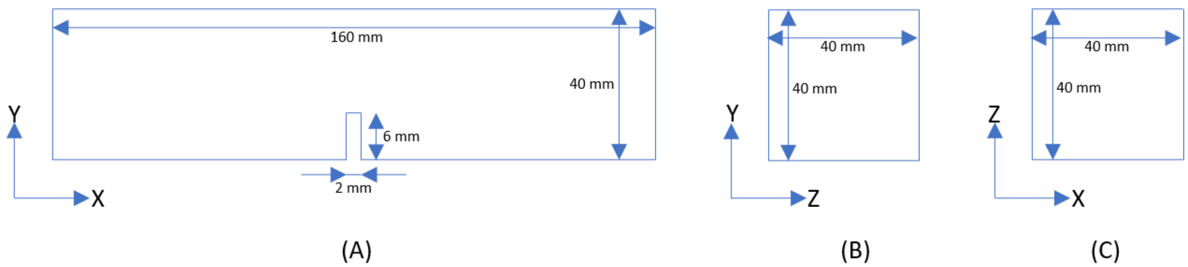


Figure 50. Measurement's specifications of the mortar specimen.

After the TPB test, two prisms' specimens remain (Cf. Figure 51) placed one by one in the test device (Cf. Figure 52) that is fitted to the compression machine. Then, the process carried out to obtain each specimen's compression strength capacity is exemplified.

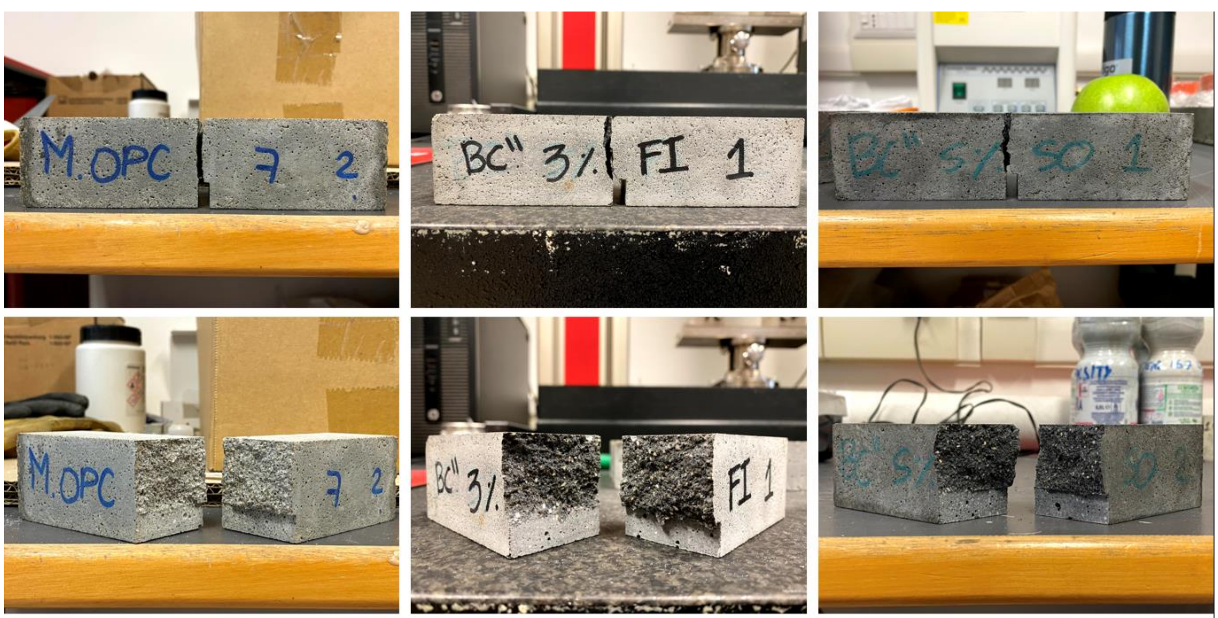


Figure 51.Samples after TPB test. a) Rec. 1. OPC. b) Rec. 3. BC" 3% - FI. c) Rec. 4-2. BC'' 5% - SO.

In Figure 51, the specimens that remain after the flexural test are shown, where the image in the upper part shows the failure path and the lower part the failure surface. In the left part, there are blank test tubes *(Rec. 1. OPC)*, which do not have Biochar addition; in the central and right part, there are test tubes Rec. 3. BC'' 3% - FI and Rec.

4-2. BC'' 5% - SO addition of biochar, respectively. All the specimen's failure path and failure surface can be found in annex A.

Figure 52. Test device fitted to the compression machine.

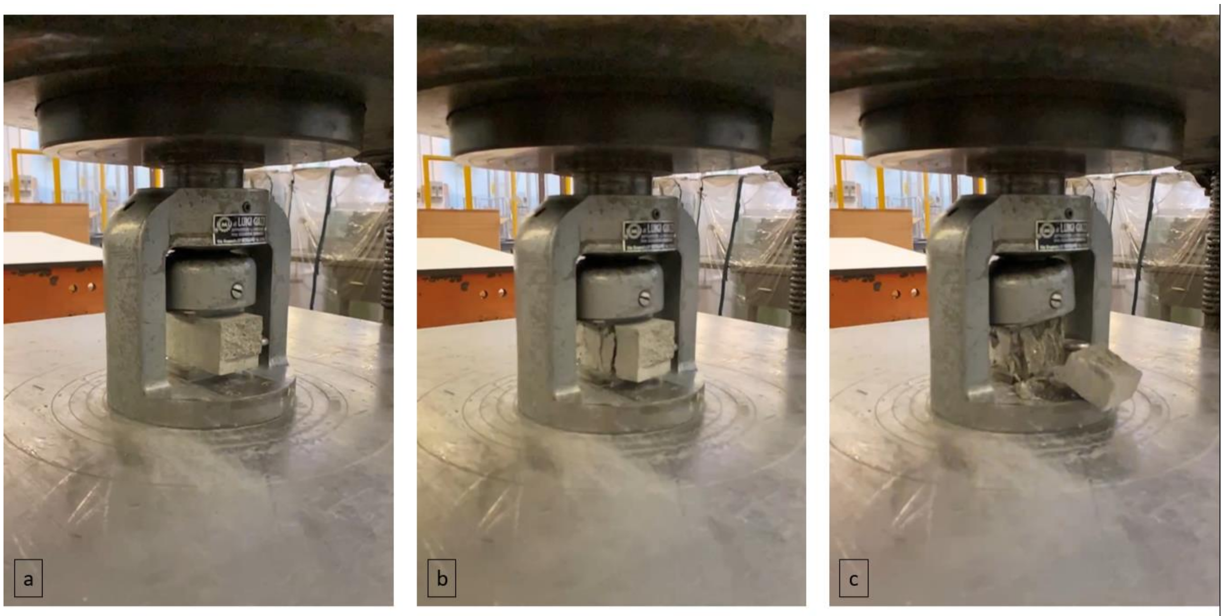


Figure 53. Compressive test performance for mortar specimens.

Figure 53 shows the samples' failure process to evaluate the compressive strength. a) shows the accommodation of the sample at the beginning of the test, b) shows the sample failure moment, and c) shows the collapsed specimen.

11. MECHANICAL TEST RESULTS

This chapter will expose results obtained from the mechanical test activity for the cement paste and the mortar to show the mechanical properties. The mechanical test activity was performed for OPC (plain samples) and samples with Biochar addition in different percentages as it was explained in the chapter before. Results for plain cement-based compounds will be exposed separate and all together to comprehend the effect of the addition of biochar and what is the main effect of biochar in cement paste and mortar.

11.1 Three-point bending test.

The three-point bending test allows obtaining the results of the flexural strength (σ_f), the fracture energy *(GF)* and the elastic modulus or Young's modulus *(E)*. The specimens used in the TPB test correspond to those described in section 8.1, maintaining the distance between supports used in the Japan Concrete Institute Standard JCI-S-001 [88] for both the cement paste and the mortar specimens, following also the specimen's measures specified in said standard.

Assuming the stress distribution similar to that shown in Figure 54, the flexural strength (σ_f) and fracture energy *(GF)* values were determined, and later with the load-deformation curves, the elastic modulus or Young's modulus *(E)* and ductility factor could also be obtained.

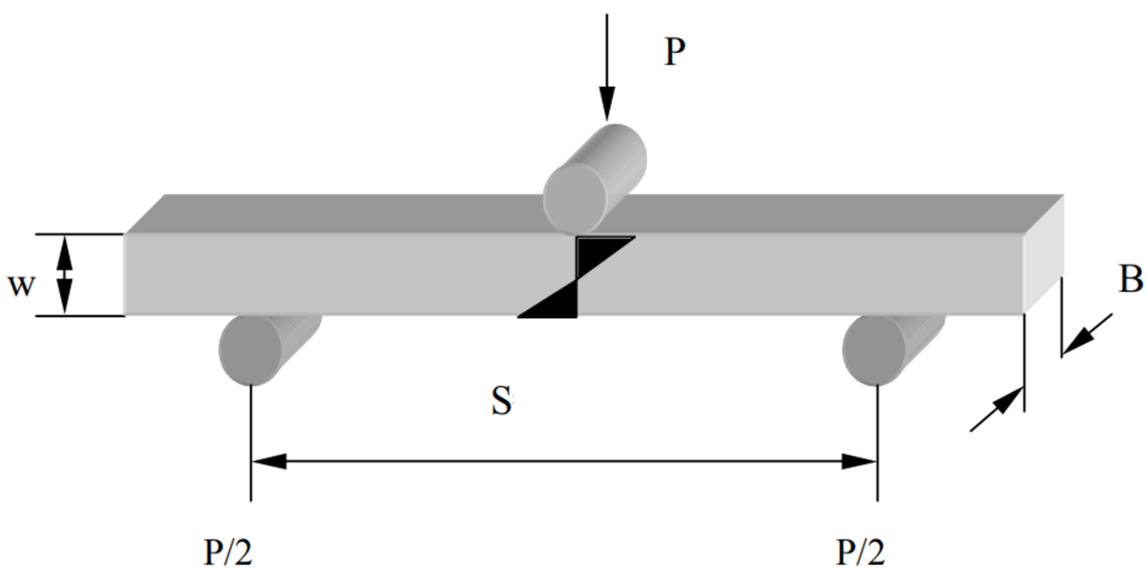


Figure 54. experimental arrangement of the bending test and stress distribution in the central section of the specimens [90].

11.1.1 Cement paste

Once the fracture force is reached in cement-based specimens, it undergoes its first microfracture, leading to brittle collapse and likewise flows until the sample collapses. When a test is performed without an extensometer, it is expected that the collapse will be practically imminent when the microfracture occurs. However, in this case, the clip-on gauge was used to control the opening of the sample by the crack mouth opening displacement method *(CMOD)* the load is expected to decrease as the opening (displacement) increases and then identify the fracture energy *(GF)* and the ductility factor *(μ)* (Cf. Figure 59). When referring to the specimens made with cement paste, the results are partially challenging to interpret since the results have a high standard deviation when it comes to samples with the same percentage of Nera Biochar (BC' and BC'') addition.

When talking about the standard deviation, the lower, it is understood that it has a more congruent behavior. It is expected that the samples prepared in the same batch present the same or at least very similar mechanical properties; however, in some cases and especially in the tests made on the cement paste samples, the values were variable, particularly for the tests made with BC'' 1% as regards the flexural strength (Cf. Table 25). Nevertheless, there were low standard deviation values for the rest of the tests, which provides credibility in the results.

The following tables and graphs show the results obtained for the samples made with cement paste observed by implementing a reference sample with ordinary portland cement, Nera Biochar ground for 6 hours *(BC'),* and Nera Biochar ground for 7 hours and sieved *(BC'')*.

Table 22 shows the settings and parameters input in each type of test. Then Table 23 and Table 24 shows the TPB test results for 7 and 28 days, respectively, the flexural strength (σ_f) and the fracture energy *(GF)*, while Table 25 and Table 26 show the standard deviation of the same results.

Table 22. Settings and parameters input in each type of test for CP.

Flexural Test		**Fracture Energy**	
Loading Span [mm]	65	Total length specimen L [mm]	80
Test Velocity [mm/min]	0,005	a0 [mm]	6
		Ligament height [mm]	14
Compression test		Alig [mm2]	280
Specimen Thickness [mm]	20	Loading Span l [mm]	65
Specimen Length [mm]	20	m1 [kg]	0,064
Test Velocity [N/s]	600	m2 [kg]	3,35

Table 23. Flexural strength and fracture energy experimental test results. CMOD, 7 days.

				Flexural strength			Fracture energy	
Specimen				F_{max}	σ_f	$\sigma_f\ (mean)$	G_f	$G_f\ (mean)$
Recipe		ID	Nº	[N]	[MPa]	[MPa]	[N/mm]	[N/mm]
OPC	Rec. N° 1	OPC - ME7	1	72,5	1,76	1,49	0,01	0,011
		OPC - ME7	2	57,1	1,42		0,01	
		OPC - ME7	3	54,5	1,30		0,01	
		OPC - ME7	4	23,2	0,56*			
Ground 6	Rec. N° 2	BC' 1% - ME7	1			2,18		0,022
		BC' 1% - ME7	2	81,2	2,10		0,03	
		BC' 1% - ME7	3	88,5	2,23		0,03	
		BC' 1% - ME7	4	86,2	2,19		0,01	
Ground 6	Rec. N° 3	BC' 2% - ME7	1	72,8	1,81	1,81	0,01	0,021
		BC' 2% - ME7	2	64	1,62		0,01	
		BC' 2% - ME7	3	70,6	1,80		0,02	
		BC' 2% - ME7	4	80,4	2,00		0,03	
Ground 6	Rec. N° 4	BC' 3% - ME7	1	108	2,71	2,60	0,02	0,029
		BC' 3% - ME7	2	74,4	1,88*		0,04	
		BC' 3% - ME7	3	99	2,49		0,04	
		BC' 3% - ME7	4					
Ground 7	Rec. N° 5	BC'' 1% - ME7	1	126	3,07	2,85	0,02	0,025
		BC'' 1% - ME7	2	94,5	2,35		0,02	
		BC'' 1% - ME7	3	102	2,56		0,03*	
		BC'' 1% - ME7	4	135	3,41			
Ground 7	Rec. N° 6	BC'' 2% - ME7	1	102	2,60	2,43	0,03	0,024
		BC'' 2% - ME7	2	127	3,08*		0,07*	
		BC'' 2% - ME7	3	94,5	2,44		0,02	
		BC'' 2% - ME7	4	92,1	2,26		0,02	
Ground 7	Rec. N° 7	BC'' 3% - ME7	1	98	2,43	2,43	0,04	0,031
		BC'' 3% - ME7	2	65	1,62*		0,02	
		BC'' 3% - ME7	3	33	0,81*		0,02	
		BC'' 3% - ME7	4	98	2,48		0,05	
Ground 7	Rec. N° 8	BC'' 5% - ME7	1	110	2,78	2,86	0,03	0,027
		BC'' 5% - ME7	2	107	2,76		0,02	
		BC'' 5% - ME7	3	121	3,02		0,03	
		BC'' 5% - ME7	4	69	1,71*		0,02	

** Values measured that were not considered due to its high difference to other in the same batch.*

Table 24. Flexural strength and fracture energy experimental test results. CMOD, 28 days.

				Flexural strength			Fracture energy	
Specimen				F_{max}	σ_f	$\sigma_f\ (mean)$	G_f	$G_f\ (mean)$
Recipe		ID	Nº	[N]	[MPa]	[MPa]	[N/mm]	[N/mm]
OPC	Rec. N° 1	OPC - ME7	1	216	5,37*	2,54	0,01	0,012
		OPC - ME7	2	140	3,48		0,01	
		OPC - ME7	3	95,1	2,37		0,01	
		OPC - ME7	4	69,3	1,76		0,01*	
Ground 6	Rec. N° 2	BC' 1% - ME7	1	94,8	2,27	2,13	0,021	0,023
		BC' 1% - ME7	2	109	2,71		0,025	
		BC' 1% - ME7	3	69,8	1,74		0,026	
		BC' 1% - ME7	4	71,9	1,79		0,021	

Ground 6	Rec. N° 3	BC' 2% - ME7	1	82,4	2,08	1,93	0,040	0,045
		BC' 2% - ME7	2	78,7	1,96		0,051	
		BC' 2% - ME7	3	70,1	1,76		0,073*	
		BC' 2% - ME7	4	154	3,70*		0,059*	
Ground 6	Rec. N° 4	BC' 3% - ME7	1	91,7	2,35	1,84	0,052	0,036
		BC' 3% - ME7	2	63,5	1,60		0,025	
		BC' 3% - ME7	3	65	1,63		0,028	
		BC' 3% - ME7	4	72,2	1,80		0,040	
Ground 7	Rec. N° 5	BC'' 1% - ME7	1	84,4	2,08	2,24	0,03	0,030
		BC'' 1% - ME7	2	77,6	1,96		0,02*	
		BC'' 1% - ME7	3	106,8	2,74		0,03	
		BC'' 1% - ME7	4	87,3	2,19		0,06*	
Ground 7	Rec. N° 6	BC'' 2% - ME7	1	74,3	1,86*	3,28	0,03	0,031
		BC'' 2% - ME7	2	95,5	2,39		0,03*	
		BC'' 2% - ME7	3	119,3	3,02		0,06*	
		BC'' 2% - ME7	4	176,8	4,43		0,03	
Ground 7	Rec. N° 7	BC'' 3% - ME7	1	118,3	3,02	2,28	0,05*	0,032
		BC'' 3% - ME7	2	71,0	1,78		0,03*	
		BC'' 3% - ME7	3	79,7	2,02		0,03	
		BC'' 3% - ME7	4	89,2	2,29		0,03	
Ground 7	Rec. N° 8	BC'' 5% - ME7	1	85,8	2,21	2,33	0,03	0,041
		BC'' 5% - ME7	2	107,5	2,70		0,04	
		BC'' 5% - ME7	3	72,7	1,81		0,04	
		BC'' 5% - ME7	4	105,9	2,61		0,05	

** Values measured that were not considered due to its high difference to other in the same batch.*

Table 25. Flexural strength and fracture energy - standard deviation value for sets of experimental specimens for CP. CMOD, 7 days.

Notation	N° specimens	Stand. Dev $\boldsymbol{\sigma_f}$	N° specimens	Stand. Dev $\boldsymbol{G_f}$
	(7 day)	(7 day)	(7 day)	(7 day)
Rec. N° 1 - OPC	3	0,24	3	0,002
Rec. N° 2 – BC' 1%	3	0,07	3	0,008
Rec. N° 3 – BC' 2%	4	0,16	4	0,009
Rec. N° 4 – BC' 3%	2	0,16	2	0,014
Rec. N° 5 – BC'' 1%	4	0,48	3	0,007
Rec. N° 6 – BC'' 2%	3	0,17	3	0,002
Rec. N° 7 – BC'' 3%	2	0,04	4	0,020
Rec. N° 8 – BC'' 5%	3	0,15	3	0,002

Table 26. Flexural strength and fracture energy - standard deviation value for sets of experimental specimens for CP. CMOD, 28 days.

Notation	N° specimens	Stand. Dev $\boldsymbol{\sigma_f}$	N° specimens	Stand. Dev $\boldsymbol{G_f}$
	(7 day)	(7 day)	(7 day)	(7 day)
Rec. N° 1 - OPC	3	0,87	3	0,002
Rec. N° 2 – BC' 1%	4	0,46	3	0,003
Rec. N° 3 – BC' 2%	3	0,16	4	0,008
Rec. N° 4 – BC' 3%	4	0,35	2	0,012
Rec. N° 5 – BC'' 1%	4	0,34	3	0,007
Rec. N° 6 – BC'' 2%	3	1,05	3	0,000
Rec. N° 7 – BC'' 3%	4	0,54	4	0,003
Rec. N° 8 – BC'' 5%	4	0,41	3	0,006

In Table 25 and Table 26, the number of specimens varies depending on the mechanical test-results, because some of the values, due to its high dispersion, were not considered in the mean value, then the standard deviation just considers the same values consider finding the mean flexural strength.

From the load-CMOD curves graph (Cf. Figure 59) it is possible to evaluate the ductility factor μ (Cf. Figure 61 and Figure 62), that is defined as the ratio between the ultimate displacements δ_U and the displacements corresponding to the peak load δ_P

$$\mu = \delta_U / \delta_P \tag{6}$$

Literature suggests that a proper dispersion of the nanoparticles in the final mix is essential to achieve homogeneous materials. This is strictly related to the particles size: as lower the particle size, close to the nanoscale, the higher surface area per unit volume is reached, becoming in more molecules and atoms in the surface, stand for string Van der Waals forces among atoms and electrostatic force between the nanoparticles, which greatly their re-agglomeration [91,92].

Based on the results obtained in Figure 55 and Figure 56 and in the previous suggestions, the analysis of the ductility factor µ and for further preparations, like the rheological analysis of cement paste and mechanical and rheological analysis for the mortar samples, just Nera Biochar grounded for 7 hours and sieved, called BC'' will be the one who is going to be added and implemented in the cementitious based material.

Figures from Figure 55 to Figure 58 graphically represented the results for 7 and 28-days of curing of mechanical experimental test results with extensometer CMOD. Figure 59 and Figure 60 show Load-CMOD curves for all the specimens regarding just the use of BC'' addition in the samples for 7 and 28-days of curing, respectively.

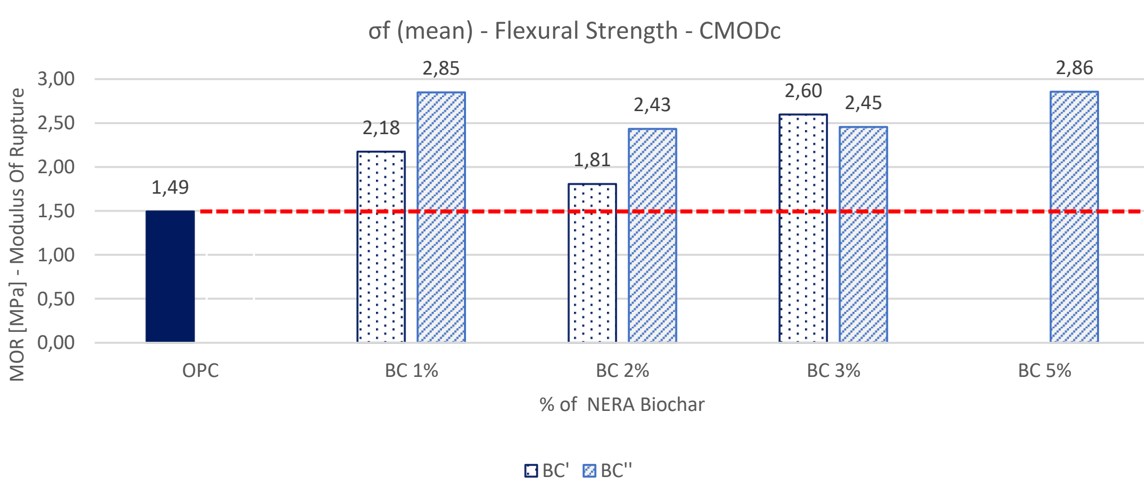


Figure 55. MOR - comparison between different type and % of CP Nera BC specimens with CMOD, 7 days.

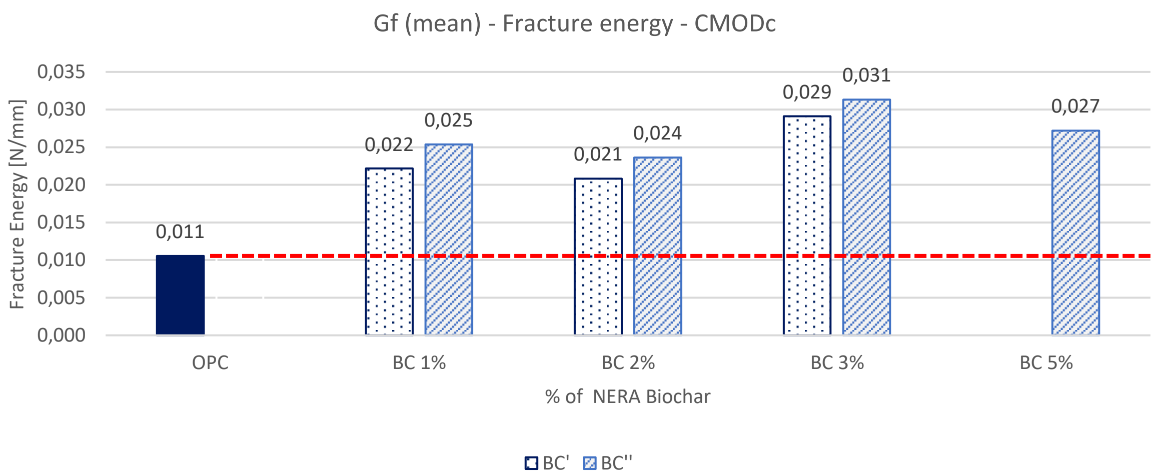


Figure 56. Fracture energy - comparison between different type and % CP Nera BC specimens with CMOD, 7 days.

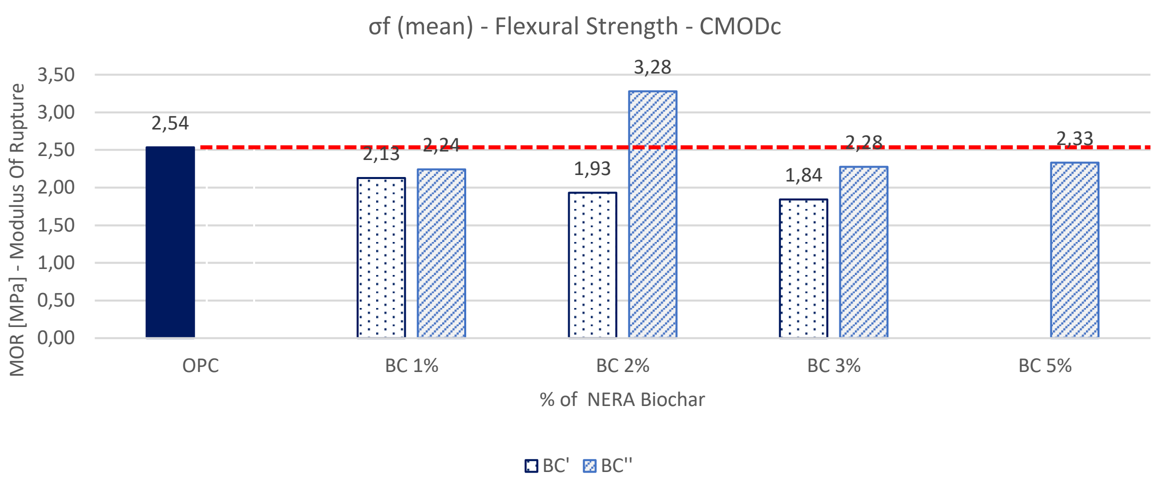


Figure 57. MOR - comparison between different type and % of CP Nera BC specimens with CMOD, 28 days.

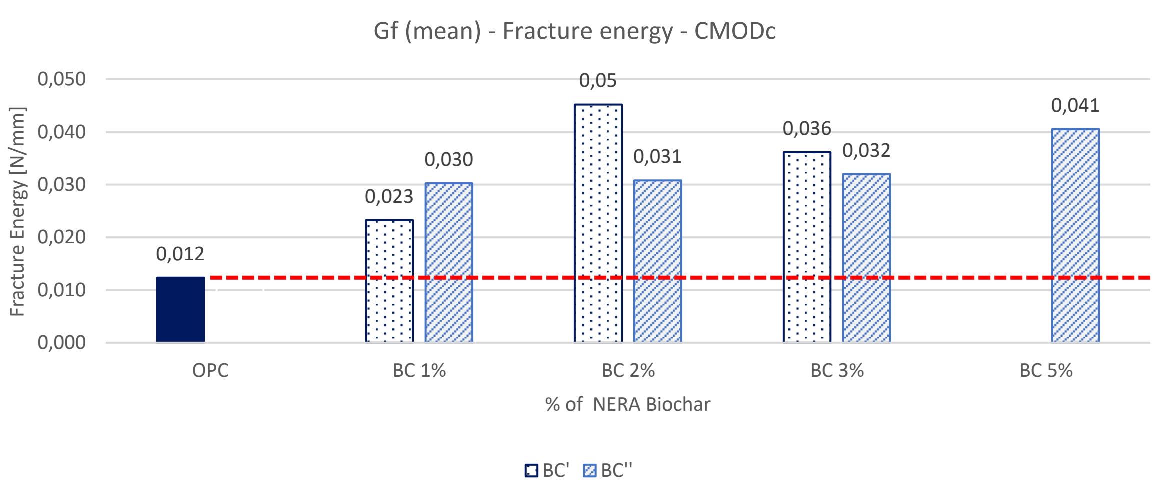


Figure 58. Fracture energy - comparison between different type and % CP Nera BC specimens with CMOD, 28 days.

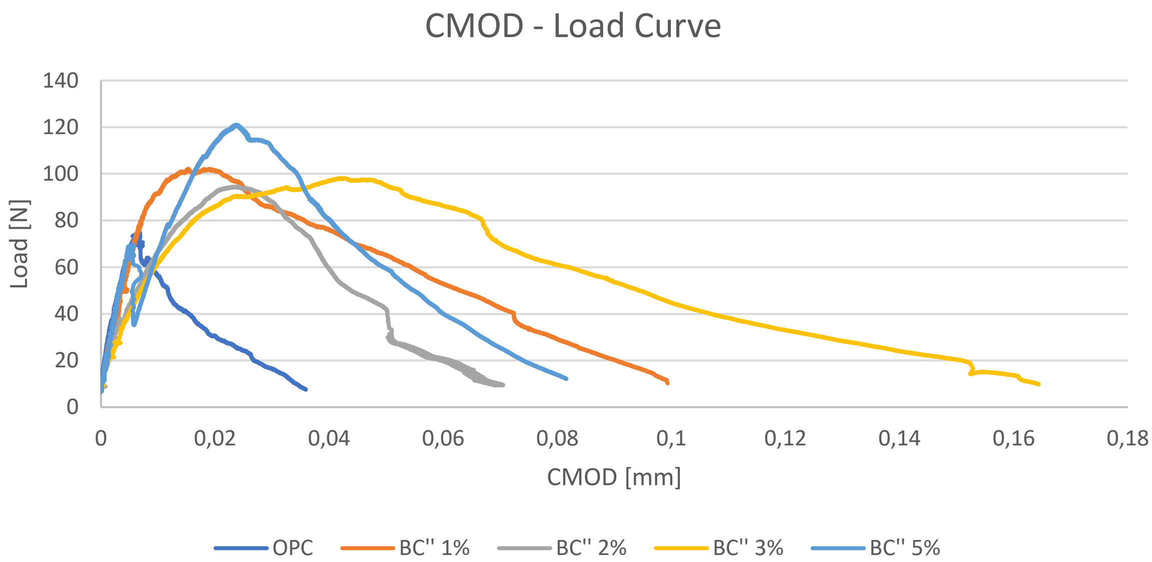


Figure 59. Comparison between best percentage just considering BC'' specimens with CMOD, 7 days.

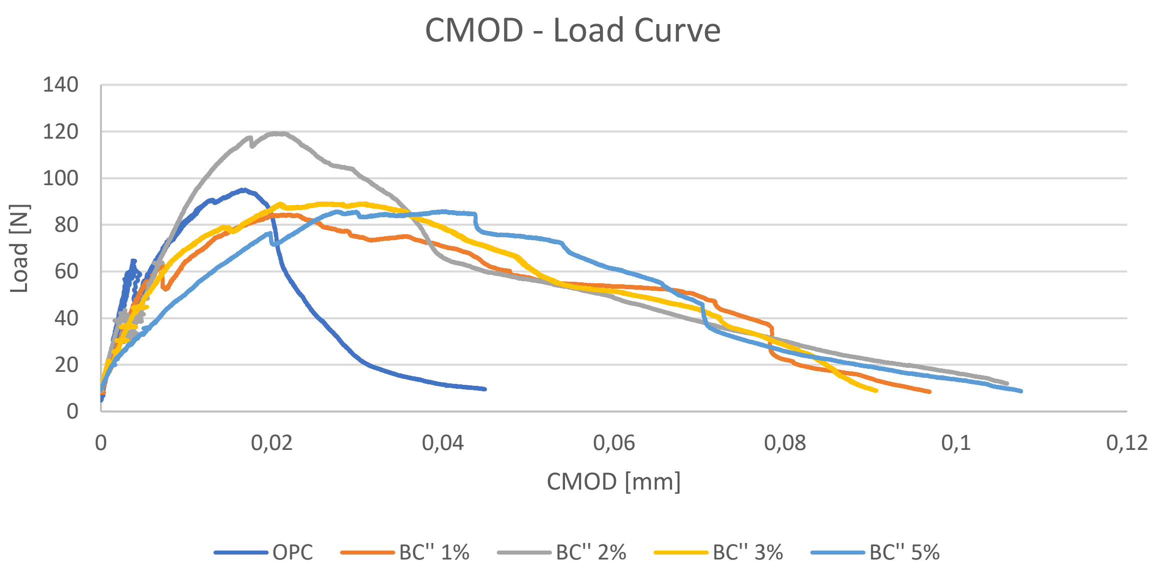


Figure 60. Comparison between best percentage just considering BC'' specimens with CMOD, 28 days.

For the analysis of the ductility factor μ, the parameters of ultimate displacement δ_U and the displacements corresponding to the peak load δ_P (Cf. Equ. (*6*) are obtained from figures Figure 59 and Figure 60, corresponding to 7 and 28 days, respectively. For the results, the use of a bar graph is implemented, instead of using a data table, as has been used for the other mechanical properties, since with these, it is possible to analyze the data more easily, allowing comparison and feedback of the results immediately. The bar graph allows to identify the difference between the data visually, quickly, and reliably. Additionally, it identifies the mean of the data, which is the reference value, and which values obtain a better or worse performance based on the value of reference, which in this document is Rec. 1. OPC.

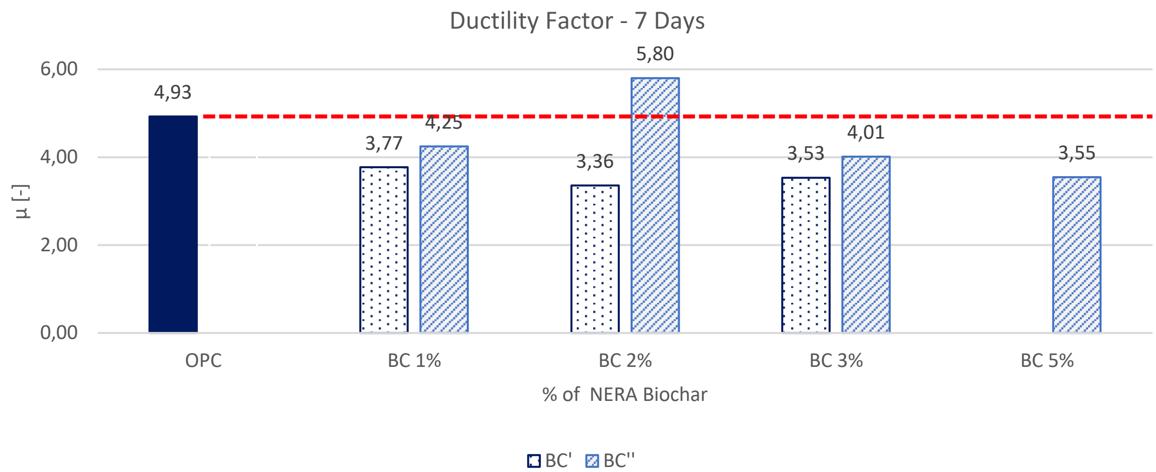


Figure 61. Ductility factor m. 7 days for cement paste.

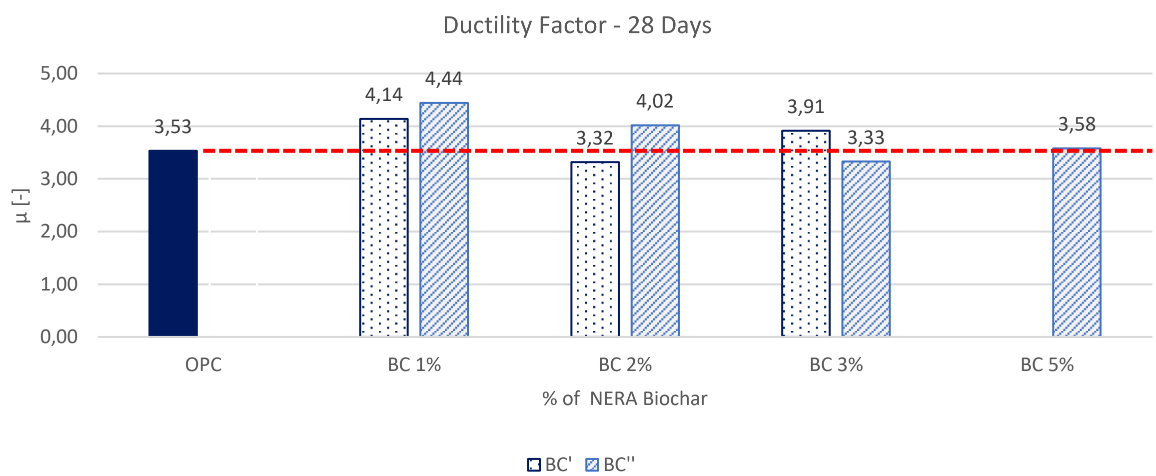


Figure 62. Ductility factor m. 28 days for cement paste.

When talking about flexural resistance or flexural strength (σ_f), the results show interesting indications. This low-cost material composed chiefly of carbon can increase flexural strength in small percentages of addition of Biochar, as would carbon nanoparticles *(i.e., CNTs or MWCNTs)*. It can also be compared with materials from other pyrolysis processes, such as coffee powder *(CP)* and hazelnut shells *(HS)* studied by Restuccia and Ferro [4] in their article.

It is important to emphasize that a high data dispersion was obtained in the cement paste samples, which can be attributed to a complex situation to be addressed in the treatment/inclusion of nano and microparticles: an adequate dispersion. In the existing literature, dispersion has a fundamental role when it comes to improving compounds with nanoparticles, making dispersion a frequent topic to study [4,91,93,94].

The standard deviation values are usually higher in the mixtures containing Nera biochar (Cf. Table 25 and Table 26) because high standard deviation values are directly related to the incomplete dispersion of the nanoparticles within the cement matrix. Therefore, the superplasticizer greatly helped the Nera biochar nanoparticles added to the cement matrix to have a more homogeneous dispersion within the prepared mix and avoid possible agglomerations, which can significantly benefit the rupture path, making it more tortuous crack path, consuming more energy, thus explaining its increased fracture energy (G_F).

The flexural test results related to the 7-days of curing (Cf. Table 24, Figure 55 & Figure 56) show that the addition of nanoparticles to the cement mix has significantly improved the mechanical properties concerning plain cement. It can be seen that both the biochar ground for 6 hours *(BC')* and the Biochar ground for 7 hours and sieved *(BC")* have had a better performance; they have worked very well, for any percentage of Biochar.

After evaluating the MOR results, the most effective mixture occurs when adding BC’ 3% and BC’’ 1% & 5% with an increase of 75% for BC' 3% and 91% for both BC" 1% & 5%; However, by any percentage of Biochar, its performance was better than the plain cement paste. This trend occurs in very similar proportions in the study proposed by Restuccia et al. [4], where the addition of CP and HS in small percentages always improved the mechanical behavior of the samples: the most effective addition occurs when adding 0.5% of CP and 0.8% of HS with an increase of 75% and 45% concerning plain cement, respectively.

Evaluating the fracture energy results, the most effective addition is 3% for both types of biochar, with an increase of 64% and 81% for BC' and BC" respectively. Following the comparison, the parallel study currently evaluated, the fracture energy works best when its lowest percentage is added, which is 0.5%, increasing up to 75% for CP and 71% for HS.

The flexural test results related to the 28-days of curing (Cf. Table 25, Figure 57 & Figure 58) show that the addition of the nanoparticles to the cement mix presents results very similar to the reference sample, which generally decreases in minimal percentages, between 5% and 15%, for samples with BC' 3%. Whereas, for samples with BC", they reach a decrease of only 5%. On the other hand, for Rec. 6. BC’’ 2%, There is a 30% increase in flexural strength, making BC’’ 2 wt% a suitable percentage for implementing and improving flexural strength. Furthermore, evaluated the TPB test results, for the samples suggested by Restuccia et al. [4], in the case of 28-days, there is an improvement in σ_f and G_F very similar to the results after 7-days of curing, in the lowest percentage *(0.5%)* of nanoparticles proposed by the same study, for which there is coherence, being different for the current study.

Evaluating the fracture energy results, the most effective addition is presented at 2% for BC' and 5% for BC", with an increase of 315% and 250%, respectively, concerning 28-days of curing.

In a general point of view, analyzing the behavior of the cement paste subjected to the TPB test, the most effective percentage at the time of evaluating 7 and 28-days of curing is Rec. 6. BC" 2%, with an increase of 64% and 20% of σ_f and G_F respectively for 7-days of curing; 64% and 20% of σ_f and G_F respectively for 28-days of curing (Cf. Table 35). This phenomenon can occur thanks to the interaction of the particles in its hydration stage, which can be interpreted as accelerating additives, especially considering the results presented in 7-days of curing. This effect may be due to the potassium and calcium salt reaction, which, acting as alkali activating, can help accelerate the hydration or internal curing process, improving the hardness development and mechanical properties at a young age of cement-based compounds.

One of the benefits of hydration and short-term high resistance is particularly given to large-scale construction systems, where the cement-based structure is required to support itself in the shortest possible time, avoiding the use of formwork when using a more sophisticated system such as 3D printing of structural elements.

Returning to the ductility factor, this being one of the most important parameters in this study. Figure 59 and Figure 60 show the Load-CMOD representative curves for each recipe, from which the Equ (*6*) parameters are obtained to know μ. Figure 61 and Figure 62 show in a bar graph the ductility factor versus the % of Biochar added. Regarding 7-days of curing, BC'' 2% has an increase of μ of 18%, being the only percentage BC addition that improves the performance of the ductility factor for this curing time. On the contrary, at 28 days of curing, the most effective percentage is achieved with BC" 1% followed by BC" 2% with an increase of 25% and 15% respectively, taking into account that any % of Biochar addition increases μ yield after 28-days of curing.

This behavior is quite peculiar because the flexural strength (σ_f) at 28-days of curing is usually lower, while the ductility factor is higher and better performance at 28-days, showing that, despite maintaining the same flexural strength concerning plain cement, it has a greater capacity to deform until collapse, which promotes the use of this type of low-cost materials, produced from natural biomass for cement implementation.

11.1.2 Mortar

The clip-on gauge was used to control the opening of the sample by the crack mouth opening displacement method *(CMOD)*, the same one as the cement paste samples. The load is expected to increase with certain young modulus until the first fracture occurs, then the load begins to decrease as the opening (displacement) increases, identifying the fracture energy (G_F) and the ductility factor (μ) of each sample tested (Cf. Figure 67). When referring to mortar *(MT)* specimens, the results are partially easy to analyze compared to the cement paste TPB test results because the behavior of the Load-CMOD curve is homogeneous, and the standard deviation, despite being higher, are values expected for mortar.

Rec. 2 and Rec. 3 are the cases where there is higher dispersion, being 0.51 and 0.45 respectively, regarding flexural strength when passing 7-days of curing (Cf. Table 30), and Rec 1. Palin cement with 0.64 when passing 28-days of curing (Cf. Table 31). Nevertheless, there were low standard deviation values for the rest of the tests, providing credibility in the results.

The following tables and graphs show the results obtained for the mortar samples observed by implementing a reference sample with ordinary Portland cement and Nera Biochar ground for 7 hours and sieved *(BC")*. In this case, the analysis will not be performed with Biochar ground for 6 hours *(BC')* due to its regular performance in cement paste samples.

Table 27 shows the settings and parameters input in each type of mechanical test. Then Table 28 and Table 29 shows the TPB test results for 7 and 28 days, respectively, for flexural strength (σ_f) and the fracture energy *(G_F)*, while Table 30 and Table 31 show the standard deviation of the same results.

Table 27. Settings and parameters input in each type of test for MT.

Flexural Test		**Fracture Energy**	
Loading Span [mm]	120	Total length specimen L [mm]	160
Test Velocity [mm/min]	0,03	a0 [mm]	12
		Ligament height [mm]	28
Compression test		Alig [mm2]	1120
Specimen Thickness [mm]	40	Loading Span l [mm]	120
Specimen Length [mm]	40	m1 [kg]	0,577
Test Velocity [N/s]	2400	m2 [kg]	3,35

Table 28. Flexural strength and fracture energy experimental test results. CMOD, 7 days.

Specimen			Flexural strength			Fracture energy	
			F_{max}	σ_f	$\sigma_f\ (mean)$	G_f	$G_f\ (mean)$
Recipe	ID	Nº	[N]	[MPa]	[MPa]	[N/mm]	[N/mm]
OPC Rec. N° 1	OPC	1	873	5,01		0,06	
	OPC	2	870	4,99		0,07	
	OPC	3	901	5,17	5,37	0,08	0,071
	OPC	4	957	5,49		0,08	
	OPC	5	1000	5,74		0,06	
	OPC	6	1010	5,80		0,08	
Ground 7 Rec. N° 2	BC'' 1% - FI	1	857	4,92		0,07	
	BC'' 1% - FI	2	1011	5,80	5,21	0,08	0,076
	BC'' 1% - FI	3	857	4,92		0,08	
Ground 7 Rec. N° 2-2	BC'' 1% - SO	1	984	5,65		0,09	
	BC'' 1% - SO	2	989	5,68	5,71	0,07	0,085
	BC'' 1% - SO	3	1013	5,82		0,10	
Ground 7 Rec. N° 3	BC'' 3% - FI	1	983	5,64		0,06	
	BC'' 3% - FI	2	898	5,15	5,18	0,05	0,057
	BC'' 3% - FI	3	826	4,74		0,05	
Ground 7 Rec. N° 3-2	BC'' 3% - SO	1	865	4,96		0,05	
	BC'' 3% - SO	2	892	5,12	5,07	0,06	0,056
	BC'' 3% - SO	3	894	5,13		0,06	
Ground 7 Rec. N° 4	BC'' 5% - FI	1	832	4,78		0,05	
	BC'' 5% - FI	2	803	4,61	4,75	0,05	0,056
	BC'' 5% - FI	3	847	4,86		0,06	
Ground 7 Rec. N° 4-2	BC'' 5% - SO	1	877	5,03		0,06	
	BC'' 5% - SO	2	851	4,88	4,80	0,06	0,056
	BC'' 5% - SO	3	782	4,49		0,05	

Table 29. Flexural strength and fracture energy experimental test results. CMOD, 28 days.

Specimen			Flexural strength			Fracture energy	
			F_{max}	σ_f	$\sigma_f\ (mean)$	G_f	$G_f\ (mean)$
Recipe	ID	Nº	[N]	[MPa]	[MPa]	[N/mm]	[N/mm]
OPC Rec. N° 1	OPC	1	877,13	5,03		0,08	
	OPC	2	1192,20	6,84		0,07	
	OPC	3	1123,77	6,45	6,09	0,08	0,080
	OPC	4	1022,30	5,87		0,08	
	OPC	5	1127,51	6,47		0,08	
	OPC	6	1024,73	5,88		0,10	
Ground 7 Rec. N° 2	BC'' 1% - FI	1	996,91	5,72		0,07	
	BC'' 1% - FI	2	1040,55	5,97	5,76	0,07	0,066
	BC'' 1% - FI	3	972,65	5,58		0,06	
Ground 7 Rec. N° 2-2	BC'' 1% - SO	1	889,22	5,10		0,11	
	BC'' 1% - SO	2	1010,59	5,80	5,38	0,07	0,087
	BC'' 1% - SO	3	913,73	5,24		0,08	
Ground 7 Rec. N° 3	BC'' 3% - FI	1	1031,42	5,92		0,09	
	BC'' 3% - FI	2	1121,15	6,44	5,87	0,11	0,094
	BC'' 3% - FI	3	914,89	5,25		0,09	

Ground 7	Rec. N° 3-2	BC'' 3% - SO	1	1086,76	6,24		0,12	
		BC'' 3% - SO	2	1023,89	5,88	5,97	0,11	0,105
		BC'' 3% - SO	3	1012,04	5,81		0,09	
Ground 7	Rec. N° 4	BC'' 5% - FI	1	1021,72	5,86		0,11	
		BC'' 5% - FI	2	993,20	5,70	5,74	0,11	0,101
		BC'' 5% - FI	3	987,53	5,67		0,09	
Ground 7	Rec. N° 4-2	BC'' 5% - SO	1	999,40	5,74		0,08	
		BC'' 5% - SO	2	1022,97	5,87	5,91	0,07	0,080
		BC'' 5% - SO	3	1065,22	6,11		0,09	

Table 30. Flexural strength and fracture energy - standard deviation value for sets of experimental specimens for MT. CMOD, 7 days.

Notation	N° specimens	Stand. Dev σ_f	N° specimens	Stand. Dev G_f
	(7 day)	(7 day)	(7 day)	(7 day)
Rec. N° 1 - OPC	6	0,36	6	0,008
Rec. N° 2 – BC'' 1% - FI	3	0,51	3	0,004
Rec. N° 2-2 – BC'' 1% - SO	3	0,09	3	0,014
Rec. N° 3 – BC'' 3% - FI	3	0,45	3	0,005
Rec. N° 3-2 – BC'' 3% - SO	3	0,09	3	0,002
Rec. N° 4 – BC'' 5% -FI	3	0,13	3	0,008
Rec. N° 4-2 – BC'' 5% - SO	3	0,28	3	0,004

Table 31. Flexural strength and fracture energy - standard deviation value for sets of experimental specimens for MT. CMOD, 28 days.

Notation	N° specimens	Stand. Dev σ_f	N° specimens	Stand. Dev G_f
	(7 day)	(7 day)	(7 day)	(7 day)
Rec. N° 1 - OPC	6	0,64	6	0,009
Rec. N° 2 – BC'' 1% - FI	3	0,20	3	0,004
Rec. N° 2-2 – BC'' 1% - SO	3	0,37	3	0,019
Rec. N° 3 – BC'' 3% - FI	3	0,59	3	0,01
Rec. N° 3-2 – BC'' 3% - SO	3	0,23	3	0,015
Rec. N° 4 – BC'' 5% -FI	3	0,11	3	0,013
Rec. N° 4-2 – BC'' 5% - SO	3	0,19	3	0,014

From the load-CMOD curves graph (Cf. Figure 67) and Equation (*6*), it is going to be determined the ductility factor μ (Cf. Figure 69) for the mortar specimens.

Figure 63 to Figure 66 graphically represented the results for 7 and 28-days curing mechanical experimental test results with extensometer CMOD. Figure 67 and Figure 68 show Load-CMOD curves for all the mortar specimens regarding just the use of BC'' addition in the samples for 7 and 28-days of curing, respectively.

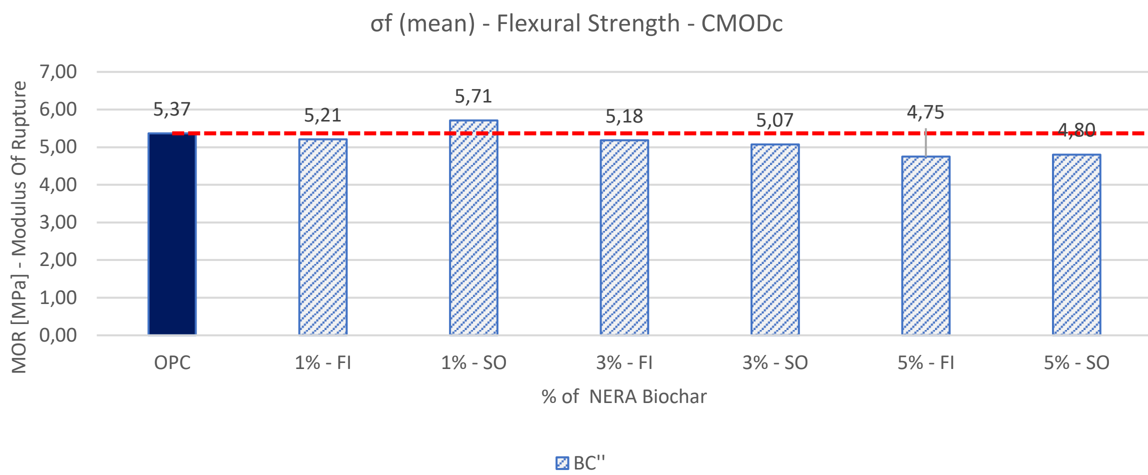


Figure 63. MOR - comparison between different type and % of MT Nera BC specimens with CMOD, 7 days.

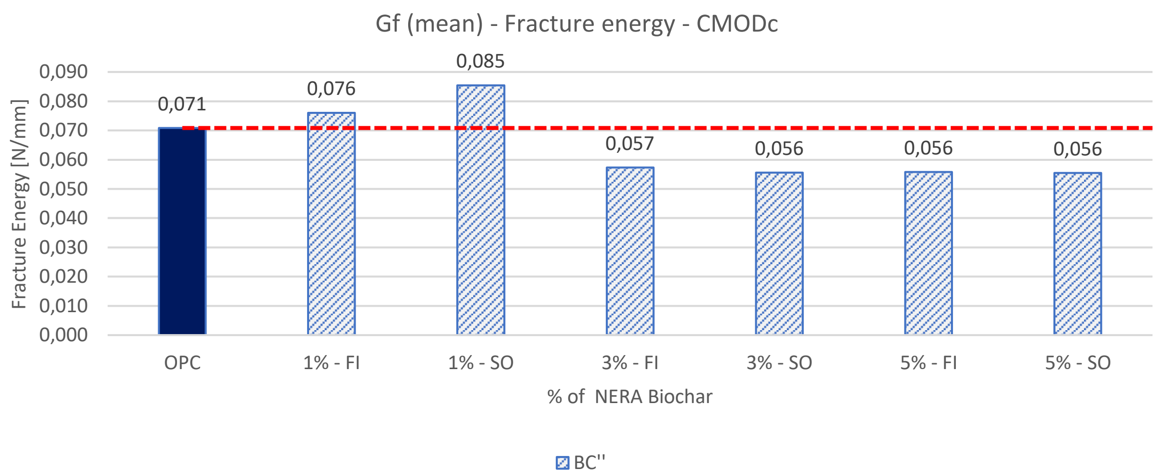


Figure 64. Fracture energy - comparison between different type and % MT Nera BC specimens with CMOD, 7 days.

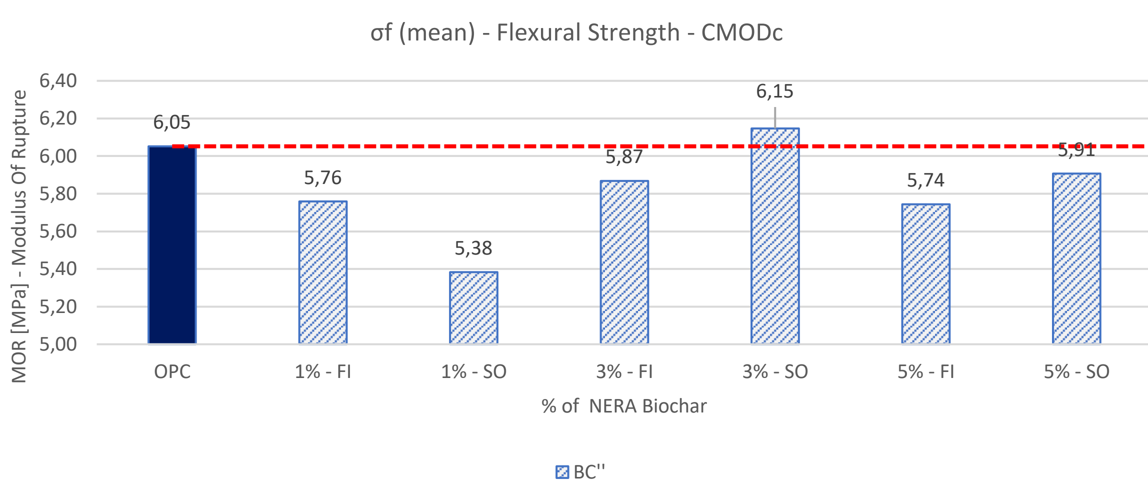


Figure 65. MOR - comparison between different type and % of MT Nera BC specimens with CMOD, 28 days.

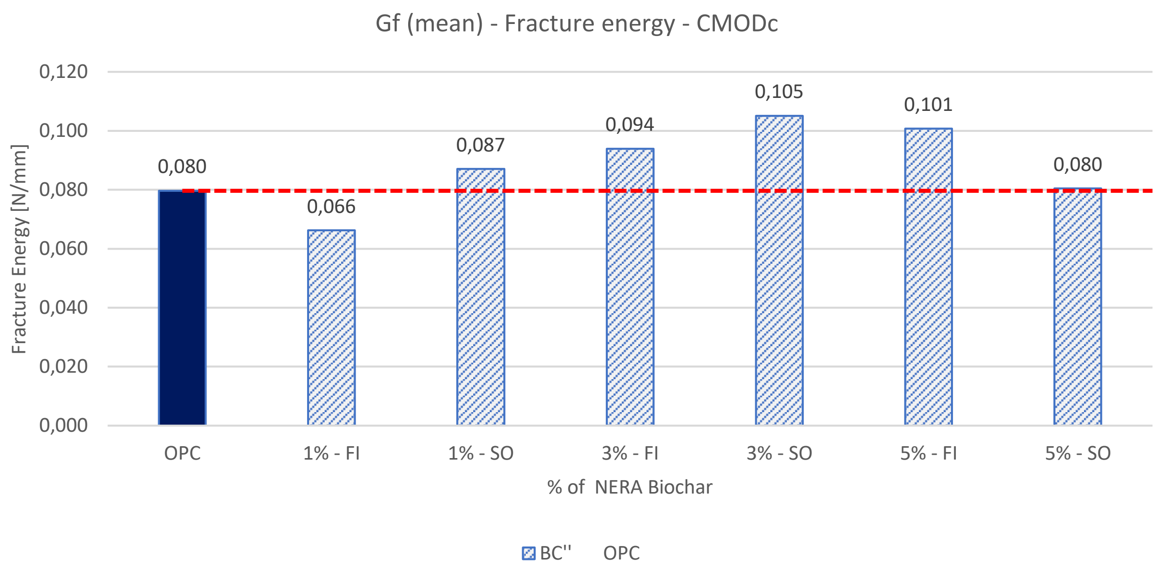


Figure 66. Fracture energy - comparison between different type and % MT Nera BC specimens with CMOD, 28 days.

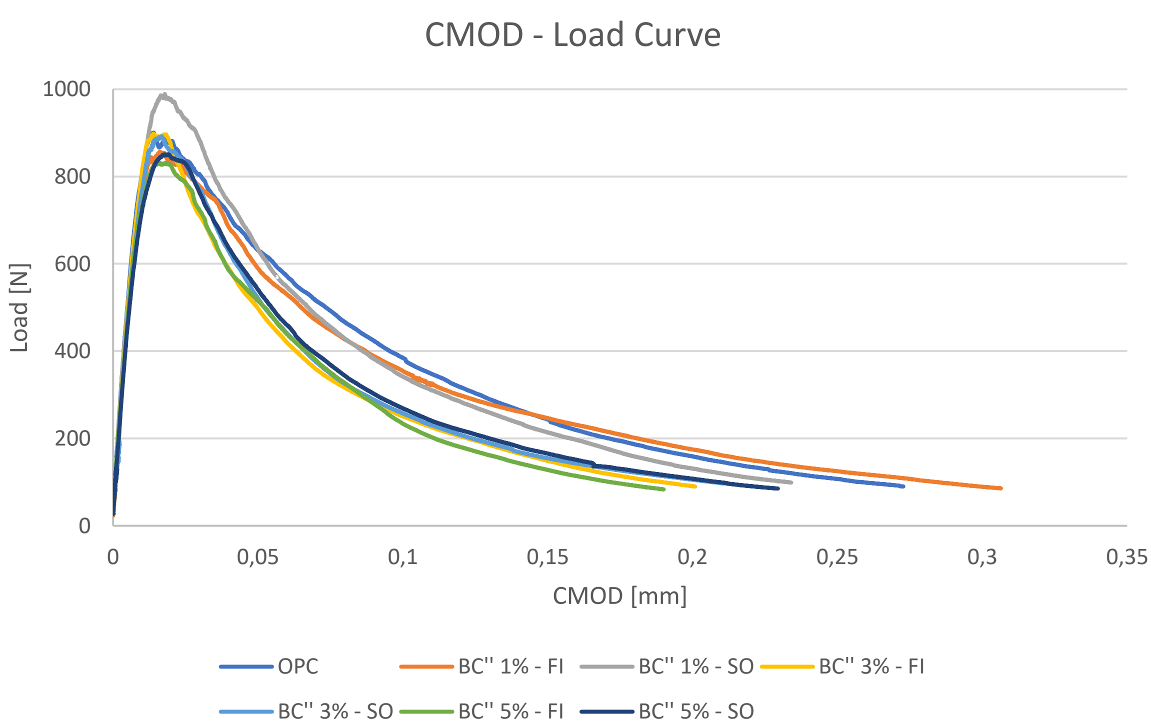


Figure 67. Comparison between best percentage of BC'' specimens with CMOD, 7 days.

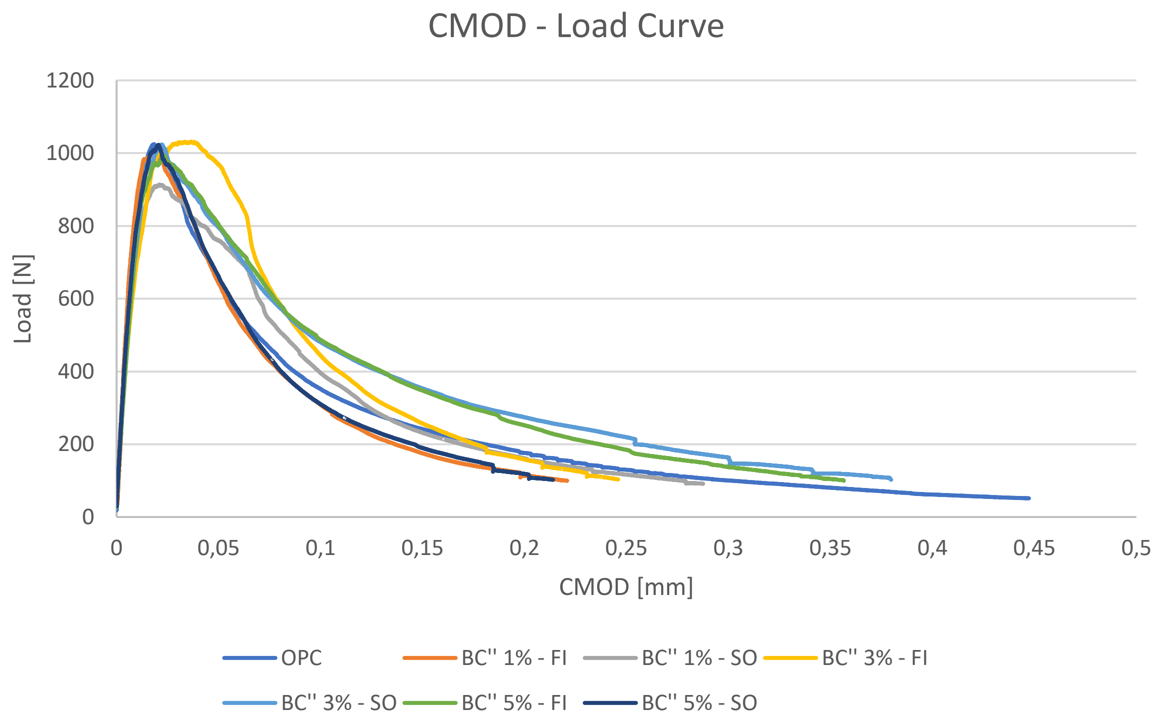


Figure 68. Comparison between best percentage of BC'' specimens with CMOD, 28 days.

For the analysis of the ductility factor μ, the parameters of ultimate displacement δ_U and the displacements corresponding to the peak load δ_P (Cf. Equ. (6)) are obtained from figures Figure 67 and Figure 68, corresponding to 7 and 28 days, respectively. Results are easily analyzed when results are presented in a bar graph with the same nomenclature as cement paste results.

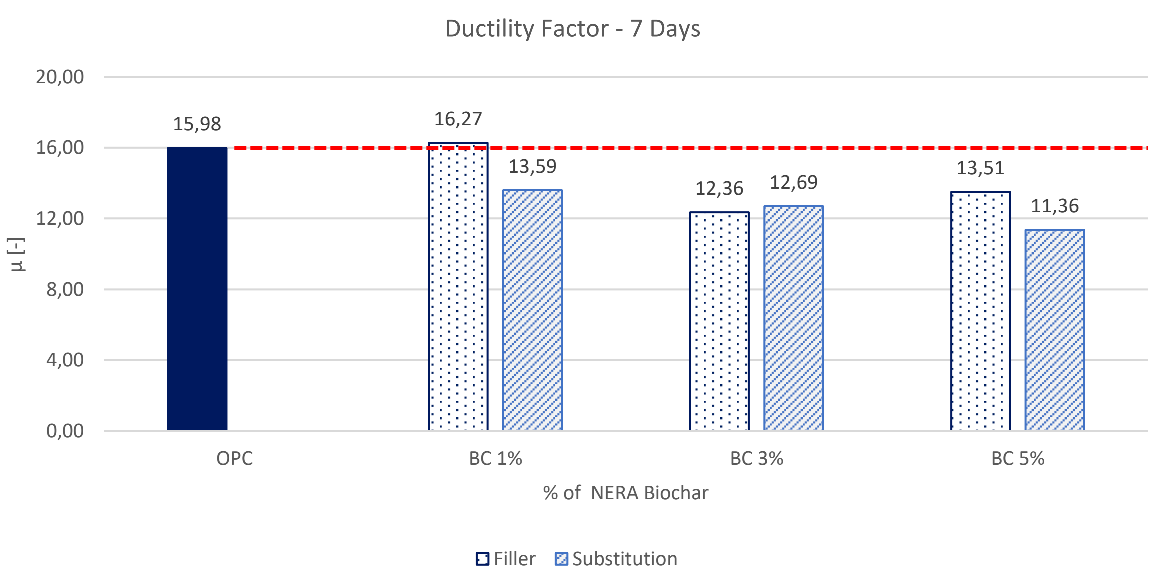


Figure 69. Ductility factor m. 7 days for mortar.

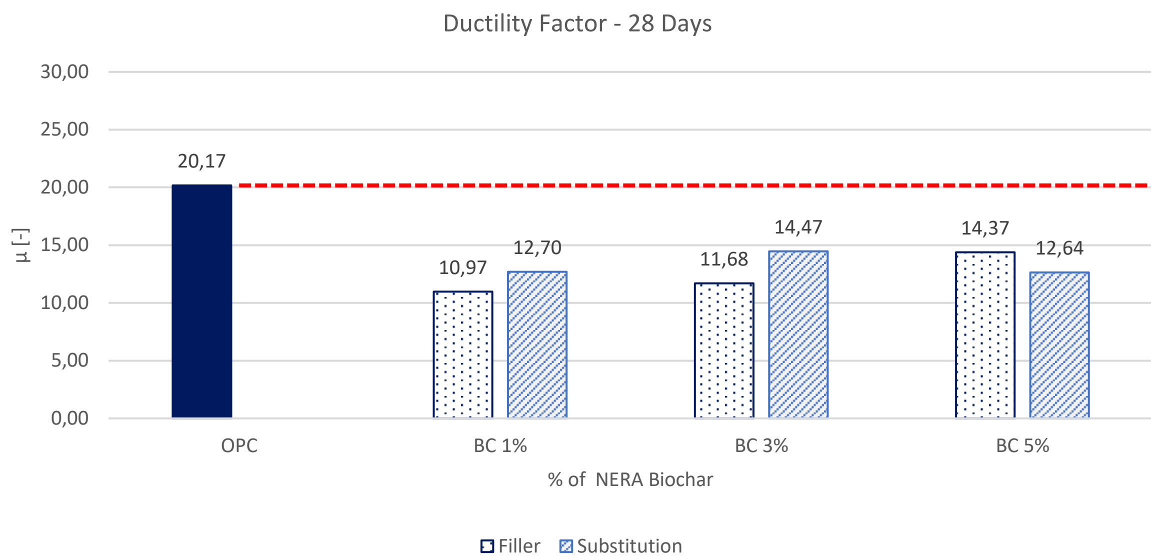


Figure 70. Ductility factor m. 28 days for mortar.

When we talk about flexural resistance or flexural strength (σ_f), the results do not seem to have the same effect or at least a similar effect regarding cement paste specimens. In this case, with the mortar specimens, the flexural strength at 7-days with any percentage of biochar addition is very similar, almost the same as the plain cement sample, showing that adding or not adding the biochar does not generate a particular benefit to the mortar mixture subject to σ_f except in the case of Rec 2-2. BC'' 1% - SO, where is found an increase in σ_f of 8%. In the case of σ_f at 28-days, we find two cases that stand out above the others, the case of Rec. 2-2. BC'' 1% - SO where there is a negative yield close to 88% compared to plain cement, and the case of Rec. 3-2. BC" 3% - SO, where the only performance that exceeds the plain cement threshold is found, with an increase in σ_f of 2%, which is not considered to conclude Biochar addition generated a significant change; therefore will not worth the use.

The results show interesting indications for the case of a Rec. 2-2. BC'' 1% - SO, particular case, since the flexural strength results diverge in their entirety at 7 and 28 days after curing. For 7-days of curing, this recipe presents the best performance, while for the 28-days of curing, it presents the worst performance, this may occur because the biochar retains its weight in water 1:1, and it is possible that in the first days of maturation, this water has been released quickly and therefore its performance could be better thanks to the internal curing in the 7-day tests, after this stage, the internal curing was precarious, decreasing the performance and causing a decrease in the σ_f.

Evaluating the fracture energy results, the most effective addition is presented at 1% - SO and 3% - SO, with an increase of 22% and 32% respectively for 7 and 28 days of curing. Different studies such as the one proposed by Gupta et al. [71] suggest that the relationship between flexural strength and fracture energy in most cases are directly proportional so that in the current study, the trend is maintained. Additionally, following the trend of the flexural strength, the fracture energy does not show a significant increase or decrease for a 7-days of curing, but for the case of 28-days of curing, the fracture energy shows a positive performance, it means that the mortar specimen needs more energy along the surface to cause the crack. Therefore, Biochar will not have good advantages in the flexural strength; however, it demonstrated its performance to withstand more energy, causing that the crack has a more tortuous path and therefore makes it difficult for the element to collapse.

From a general point of view, analyzing the behavior of the mortar subjected to TPB test, the most effective percentage regarding 7-days of curing is Rec. 2-2. BC'' 1% - SO, with a σ_f higher by 8% and G_F by 22%. Whereas evaluating 28-days of curing, Rec. 3-2. BC'' 3% - SO, is the most effective percentage, with a σ_f higher by 2% and a G_F by 32%. It is presumed that in the case of mortar, the results are not as positive as in cement paste due to the sand used as aggregate. One of the main characteristics and aptitudes of the cement paste is that the biochar acted as an attractor of the crack, increasing the tortuosity of the crack path, requiring more energy and, therefore, greater flexural strength. In the case of mortar, the biochar microparticles were too small and few to modify and alter the crack path, being the sand as fine aggregate that dominated this characteristic of energy attractor, resulting in values of flexural strength and fracture energy very similar between the plain cement and the specimens with the addition of supplementary cementitious material Biochar.

The positive thing about using this component in mortar mixes is its ability to flow reduce, avoiding using a viscous additive that can significantly increase the cost of the mix. When it is intended to implement 3D printing technology for the manufacture of the structure, the mortar mixture must reach a particular viscosity that allows it to support its own weight, its own layer and the layers that are superimposed on it. To achieve this objective, producers conventionally use viscous or plasticizers additives. On the other hand, the mortar mix must be shear just before being deposited to reduce the shear force produced by the internal forces of the final element. It is urgently sought to implement this type of 3D printing technologies for structural elements to reduce the use of formworks, which considerably increase the cost and production time of structural elements or the building itself by default.

Figure 69 and Figure 70 show the results of the ductility factor μ, where it can be seen that this property decreases considerably when biochar is added to the mortar. It means that the collapse of the element, where its ultimate deformation occurs, is significantly earlier once it reaches its plastic deformation. This collapse event occurs later in both cases of maturation, for 7 and 28-days of curing. Except in the case of Rec. 2. BC'' 1% - FI, where the ductility factor had a minimum increase of 2%, partially the same as the reference sample.

To conclude, it is pertinent to say that the addition of Biochar to the mortar mixture is not feasible from the point of view of mechanical properties since the flexural strength, the fracture energy, and the ductility factor present substantial decreases depending on the percentage of biochar in the mix, just a few recipes improve in small quantities the mechanical performance. However, it should be noted that the 1% addition of Biochar in the mixture wt% is the percentage that in general presents the best characteristics, which is positive because it shows that it should not be a large percentage of addition to maintain its performance and that this percentage helps, on the other hand, to increase the viscosity of the mixture without high-cost additives.

11.2 Compression test.

The compression test was made employing the same tested machine of the TPB test by changing the load cell capacity to 50 kN, the compression device, and a displacement rate equal to 0.5 mm/min, using the two broken prisms from the TPB test.

The compression test allows, as the name implies, obtaining the results of the compressive strength (σ_c) of each prism. To obtain the σ_c of each recipe, the average of all the samples with the same Biochar addition is estimated, same procedure performed for the TPB test results. The specimens used in the compression test correspond to those described in section 8.2, maintaining the standard and the force/area (Cf. Equ. (5)) relationship. Assuming the scheme similar to that shown in Figure 71, the compression test (σ_c) values were determined.

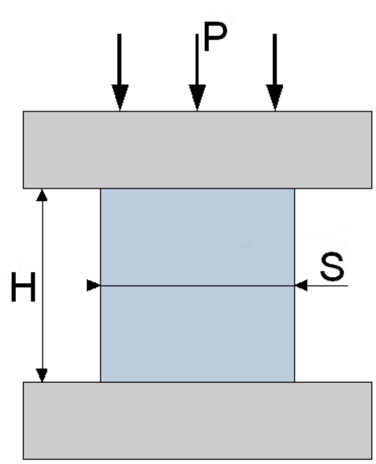


Figure 71. experimental arrangement of the compressive test and force distribution in the central section of the specimens [95].

11.2.1 Cement paste

One of the most important characteristics of cement is that its compression performance is optimal. However, it is well known that its flexural strength is significantly lower than its compressive strength. Therefore, one of the main characteristics of this study is to try to use biochar in the cement matrix to help improve the most precarious property, the flexural strength, without neglecting the compression results; that is why very similar compression results or with slightly better performance than plain cement are expected.

Table 32 and Table 33 refer to the values obtained from compressive stress at 7 and 28 days, respectively. Table 34 shows the standard deviation results that were obtained for each batch of samples with different addition of biochar for 7 and 28-days.

Table 32. Compressive strength experimental test results. 7 days.

				Compressive strength		
Specimen				F_{max}	σ_c	$\sigma_c\ (mean)$
Recipe		ID	Nº	[N]	[MPa]	[MPa]
OPC	Rec. N° 1	OPC - ME7	1			64,56
		OPC - ME7	2	24000	60,00	
		OPC - ME7	3	27650	69,13	
		OPC - ME7	4			
Ground 6	Rec. N° 2	BC' 1% - ME7	1	35746	89,36	84,70
		BC' 1% - ME7	2	33049	82,62	
		BC' 1% - ME7	3	35874	89,69	
		BC' 1% - ME7	4	30851	77,13	
Ground 6	Rec. N° 3	BC' 2% - ME7	1			72,69
		BC' 2% - ME7	2	29050	72,63	
		BC' 2% - ME7	3	29100	72,75	
		BC' 2% - ME7	4			
Ground 6	Rec. N° 4	BC' 3% - ME7	1	32365	80,91	82,39
		BC' 3% - ME7	2	33500	83,75	
		BC' 3% - ME7	3	32143	80,36	
		BC' 3% - ME7	4	33822	84,56	
Ground 7	Rec. N° 5	BC'' 1% - ME7	1	30549	76,37	85,93
		BC'' 1% - ME7	2	37990	94,97	
		BC'' 1% - ME7	3	34576	86,44	
		BC'' 1% - ME7	4	23943	59,86*	
Ground 7	Rec. N° 6	BC'' 2% - ME7	1	32038	80,10	79,38
		BC'' 2% - ME7	2	24808	62,02*	
		BC'' 2% - ME7	3	30405	76,01	
		BC'' 2% - ME7	4	32808	82,02	
Ground 7	Rec. N° 7	BC'' 3% - ME7	1	29550	73,875	71,63
		BC'' 3% - ME7	2	28600	71,5	
		BC'' 3% - ME7	3	28650	71,625	
		BC'' 3% - ME7	4	27800	69,5	

Ground 7	Rec. N° 8	BC'' 5% - ME7	1	25300	63,25	70,66
		BC'' 5% - ME7	2	27600	69	
		BC'' 5% - ME7	3	32600	81,5	
		BC'' 5% - ME7	4	27550	68,875	

** Values measured that were not considered due to its high difference to other in the same batch.*

Table 33. Compressive strength experimental test results. 28 days.

				Compressive strength		
		Specimen		F_{max}	σ_c	$\sigma_c\ (mean)$
Recipe		ID	Nº	[N]	[MPa]	[MPa]
OPC	Rec. N° 1	OPC - ME7	1	35550	88,88	88,38
		OPC - ME7	2	27350	68,38	
		OPC - ME7	3	34850	87,13	
		OPC - ME7	4	35650	89,13	
Ground 6	Rec. N° 2	BC' 1% - ME7	1	32600	81,50	84,79
		BC' 1% - ME7	2	35650	89,13	
		BC' 1% - ME7	3	22750	56,88*	
		BC' 1% - ME7	4	33500	83,75	
Ground 6	Rec. N° 3	BC' 2% - ME7	1	35910	89,77	88,40
		BC' 2% - ME7	2	34811	87,03	
		BC' 2% - ME7	3	29803	74,51*	
		BC' 2% - ME7	4	39530	98,83*	
Ground 6	Rec. N° 4	BC' 3% - ME7	1	29200	73,00	80,84
		BC' 3% - ME7	2	36200	90,50	
		BC' 3% - ME7	3	33450	83,63	
		BC' 3% - ME7	4	30500	76,25	
Ground 7	Rec. N° 5	BC'' 1% - ME7	1	34800	87,00	83,28
		BC'' 1% - ME7	2	36900	92,25	
		BC'' 1% - ME7	3	29900	74,75	
		BC'' 1% - ME7	4	31650	79,13	
Ground 7	Rec. N° 6	BC'' 2% - ME7	1	37900	94,75	99,67
		BC'' 2% - ME7	2	31700	79,25	
		BC'' 2% - ME7	3	40700	101,75	
		BC'' 2% - ME7	4	41000	102,50	
Ground 7	Rec. N° 7	BC'' 3% - ME7	1	31300	78,25*	95,33
		BC'' 3% - ME7	2	37500	93,75	
		BC'' 3% - ME7	3	39100	97,75	
		BC'' 3% - ME7	4	37800	94,50	
Ground 7	Rec. N° 8	BC'' 5% - ME7	1	33000	82,50	86,31
		BC'' 5% - ME7	2	34050	85,13	
		BC'' 5% - ME7	3	33400	83,50	
		BC'' 5% - ME7	4	37650	94,13	

** Values measured that were not considered due to its high difference to other in the same batch.*

Table 34. Compressive strength - standard deviation value for sets of experimental specimens for CP. 7 & 28 days.

Notation	N° specimens (7 day)	Stand. Dev $\boldsymbol{\sigma_c}$ (7 day)	N° specimens (28 day)	Stand. Dev $\boldsymbol{\sigma_c}$ (28 day)
Rec. N° 1 - OPC	2	6,45	4	1,09
Rec. N° 2 – BC' 1%	4	6,01	3	3,92
Rec. N° 3 – BC' 2%	2	0,09	2	1,94
Rec. N° 4 – BC' 3%	4	2,07	4	7,82
Rec. N° 5 – BC'' 1%	3	9,31	4	7,84

Rec. N° 6 – BC'' 2%	3	3,07	4	4,27
Rec. N° 7 – BC'' 3%	4	1,79	3	2,13
Rec. N° 8 – BC'' 5%	4	7,71	4	5,32

In Table 34, the number of specimens varies depending on the mechanical test results because some of the values, due to its high dispersion, were not considered in the mean value, then the standard deviation considers the same values consider finding the mean compressive strength.

Chapter 9.1 references the importance of making an appropriate dispersion of the biochar nanoparticles in the mixture, both for cement paste, and mortar, to obtain a homogeneous mixture.

Figures From Figure 55 to Figure 58 graphically represented the mechanical experimental test results for 7 and 28-days of curing.

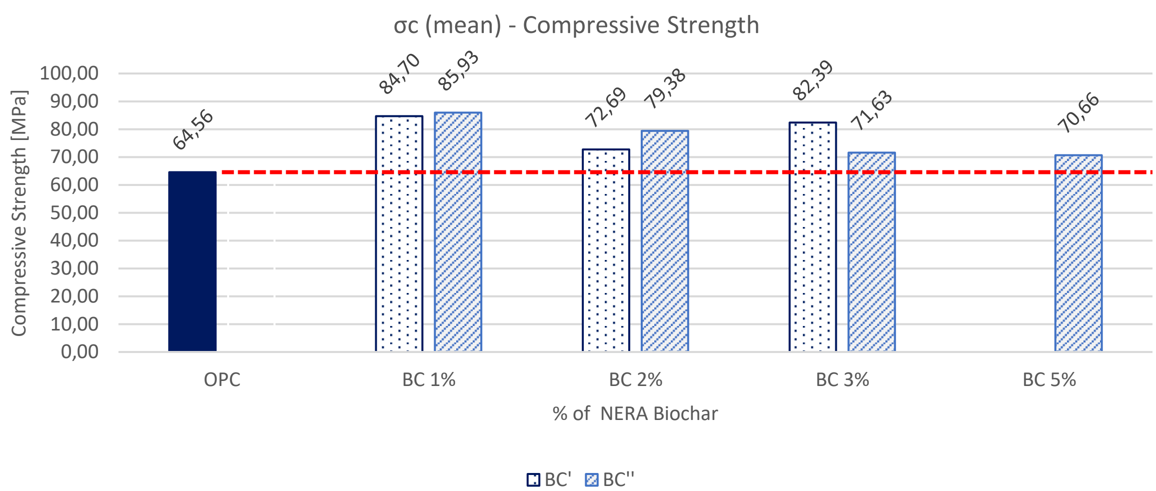


Figure 72. Compressive strength - comparison between different types and % of CP Nera BC specimens, 7 days.

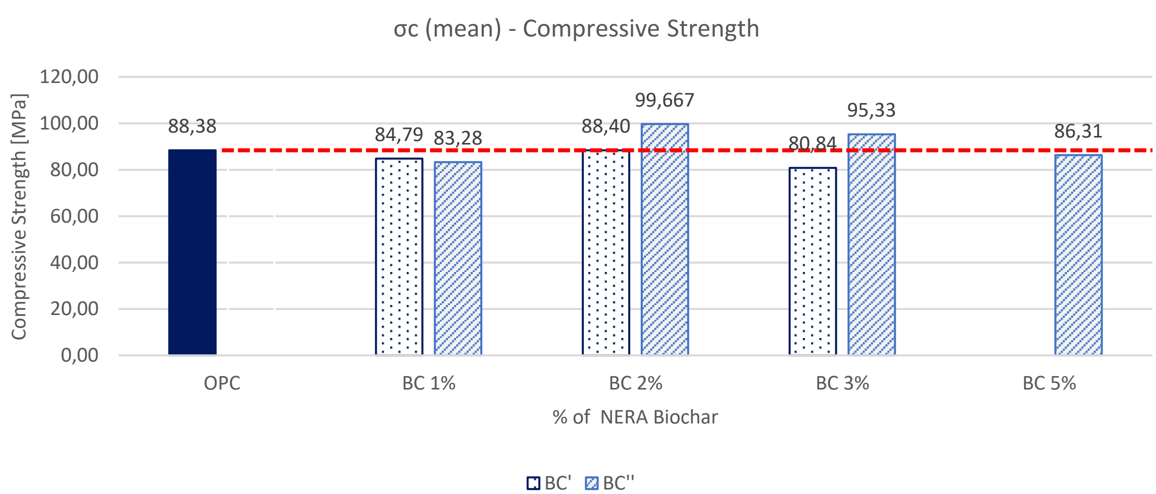


Figure 73. Compressive strength - comparison between different types and % of CP Nera BC specimens, 28 days.

When talking about the resistance to compression or compressive strength *(σ_c)*, the results show interesting behavior. As beforementioned, Biochar is a low cost material composed mostly of carbon coming even from waste from other chemical processes. It can increase the compressive strength even with small percentages of Biochar, as would high-cost materials, such as carbon nanotubes *(CNTs or MWCNTs)*. As in the analysis of flexural strength and fracture energy, a comparison can be made between other natural materials from pyrolysis like coffee powder *(CP)* and the hazelnut shells *(HS)* of the article proposed by Restuccia and Ferro [4] and the Borgotaro Biochar that includes the studies carried out by Daniel Suarez [51].

As in the flexural strength analysis, it has been seen that the results have a high data dispersion for the cement paste; this occurs because, when dealing with such tiny particles, it becomes more difficult to control its dispersion, creating possible voids and/or agglomerations in different parts of the specimens that can directly influence the mechanical and rheological behavior [93,94]. The superplasticizer greatly helped the Nera Biochar nanoparticles added to the cement matrix to have a more homogeneous dispersion within the prepared mixture and avoid possible agglomerations.

The compression test results related to 7-days of curing (Cf. Table 32 and Figure 72) show that the addition of nanoparticles to the cement mix has significantly improved the mechanical properties compared to plain cement. It is evident that both the biochar ground for 6 hours *(BC')* and the Biochar ground for 7 hours and sieved *(BC")* have shown better performance; they have worked efficiently for all the addition percentages.

Now, analyzing the compressive strength results *(σ_c)*, the most effective addition after 7-days of preparation occurs when 1% for BC' and BC" are added with an increase of 31% for BC' and 33% for BC", to reach a compressive strength of 84.7 MPa and 85.9 MPa, respectively. However, at any percentage of Biochar, its performance was better than the reference plain cement paste. This trend occurs in very similar proportions in the study proposed by Restuccia et al. [4], where the addition of CP and HS in small percentages always improved the mechanical behavior of the samples: the most effective addition occurs when adding 0.5% for CP and HS with an increase of 71% and 75% with respect to plain cement after 7-days of curing, respectively. Daniel [51] finds that with an addition percentage of 2.5% of gray Borgotaro Biochar, he obtains 15% better compressive strength than reference mixture, reaching σ_c of 60 MPa.

The compression test results related to the 28-days of curing (Cf. Table 33 and Figure 73) show behavior that follows the same trend as flexural strength results at 28-days in the cement paste. These show that the addition of nanoparticles to the cement mix presents very similar compressive strengths, with a slight increase or decrease concerning plain cement sample, presenting decreases of σ_c in percentages between

0.5% and 1 % for samples of BC' 1% and BC' 3%, respectively. While for BC'' samples, its compressive strength increases between 1% and 2% in the case of Rec. 6. BC'' 2%, making it an optimal percentage for the implementation and improvement of the mechanical properties of cement paste, taking into account its performance in flexural strength (σ_f), fracture energy (G_F) and compressive strength (σ_c). The reduction of the σ_c can be attributed to poor dispersion of the Biochar particles in the mixture; this fact can generate localized weak zones affecting the strength of the cementitious paste.

Evaluated the compression test results, for the samples suggested by Restuccia et al. [4], for a minimum percentage of addition (0.5 wt%) of CP and HS to the mixture, their compressive strength increases 72% and 64%, respectively, making these samples very likely to be used in the cement paste as an economical option for the mechanical properties improvement. The gray Borgotario Biochar from Daniel's study [51] presents compressive strength qualities very similar to those obtained with the Nera biochar from the current study since it is not improved taking into account any addition of Borgotaro Biochar from Daniel’s study, justifying that the poor dispersion of the supplementary cementitious material generates weakness areas, causing inefficient performance.

Analyzing the cement paste behavior subjected to mechanical tests such as three-point bending test and compression test, the most effective percentage, showing a significant increase in some tests, and a non-negative performance in other tests, considering the results at 7 and 28-days of curing is Rec. 6. BC'' 2% (Biochar ground for 7 hours and sieved 120 microns), with the following general results

Table 35. Summary of mechanical properties of cement paste at 7 & 28-days.

	7-Days			28-Days		
	Plain Cement	Rec. 6 BC'' 2%	Efficiency	Plain Cement	Rec. 6 BC'' 2%	Efficiency
σ_f	1,49 Mpa	2,43 Mpa	↑ 63 %	2,54 Mpa	3,28 Mpa	↑ 29 %
σ_C	64,56 Mpa	79,38 Mpa	↑ 23 %	88,38 Mpa	99,67 Mpa	↑ 13 %
GF	0,011 N/mm	0,024 N/mm	↑ 124 %	0,012 N/mm	0,031 N/mm	↑ 150 %
μ	4,93	5,80	↑ 18 %	3,53	4,02	↑ 14 %

As observed in Table 35, the efficiency in the mechanical tests has a positive performance after the BC’’ 2% addition, both at 7 & 28-days of curing. The efficiency at 7-days is presented especially because the Biochar compound has the ability to retain water and release it as its environment requires (Cf. Section 1.3), promoting the internal curing of the cement paste, allowing it to obtain a more “healthy” compound in its hydration stage, being reflected in its mechanical properties. This effect may be due to the potassium salt and calcium reaction, which, acting as alkali activating, can help accelerate the hydration or internal curing process, improving the development of hardness and mechanical properties at a young age for cement-based compounds.

One of the benefits is given particularly to large-scale construction systems, where the cement-based structure is required to support itself in a shorter period than the conventional setting time, avoiding formworks when using a more sophisticated system such as 3D printing of structural elements.

11.2.2 Mortar

Like cement paste, materials such as mortar are designed to be used as an optimal construction material mainly focused on compression performance elements, without neglecting the bending that those different elements can suffer, which are usually reinforced with a quantity of steel greater than that used in compression zones. This is why this study's main characteristics are to try to use Biochar in the cement matrix to help improve flexural strength without neglecting and optimizing compressive strength, which is why results are expected from compression very similar or with a little better performance than plain cement.

Table 36 refers to the values obtained from compressive strength at 7 and 28-days. Table 37 shows the standard deviation results obtained for each batch of samples with different addition of biochar for 7 and 28-days.

Table 36. Compressive strength experimental test results. 7 & 28 days.

				Compressive strength (7 days)			Compressive strength (28 days)		
Specimen				F_{max}	σ_c	$\sigma_c\ (mean)$	F_{max}	σ_c	$\sigma_c\ (mean)$
Recipe		ID	Nº	[N]	[MPa]	[MPa]	[N]	[MPa]	[MPa]
OPC	Rec. N° 1	OPC	1	91450	57,16		115750	72,34	
		OPC	2	87050	54,41		117863	73,66	
		OPC	3	89500	55,94	56,14	117639	73,52	73,18
		OPC	4	100350	62,72				
		OPC	5	90050	56,28				
		OPC	6	80500	50,31				
Ground 7	Rec. N° 2	BC" 1% - FI	1	92000	57,50		114000	71,25	
		BC" 1% - FI	2	93850	58,66	54,89	116000	72,50	72,50
		BC" 1% - FI	3	77600	48,50		118000	73,75	
Ground 7	Rec. N° 2 2	BC" 1% - SO	1	81950	51,22		118000	73,75	
		BC" 1% - SO	2	85300	53,31	51,36	119500	74,69	74,79
		BC" 1% - SO	3	79300	49,56		121500	75,94	
Ground 7	Rec. N° 2	BC" 3% - FI	1	88000	55,00		115000	71,88	
		BC" 3% - FI	2	85050	53,16	54,02	115000	71,88	70,52
		BC" 3% - FI	3	86250	53,91		108500	67,81	
Ground 7	Rec. N° 2 2	BC" 3% - SO	1	78700	49,19		103350	64,59	
		BC" 3% - SO	2	85000	53,13	50,59	99000	61,88	65,07
		BC" 3% - SO	3	79150	49,47		110000	68,75	
Ground 7	Rec. N° 4	BC" 5% - FI	1	78650	49,16		96850	60,53	
		BC" 5% - FI	2	78050	48,78	49,74	111000	69,38	64,23
		BC" 5% - FI	3	82050	51,28		100450	62,78	

Ground 7	Rec. N°	BC" 5% - SO	1	82750	51,72		104250	65,16	
		BC" 5% - SO	2	83350	52,09	50,03	103500	64,69	65,78
		BC" 5% - SO	3	74050	46,28		108000	67,50	

Table 37. Compressive strength - standard deviation value for sets of experimental specimens for MT. 7 & 28 days.

Notation	N° specimens (7 day)	Stand. Dev σ_c (7 day)	N° specimens (28 day)	Stand. Dev σ_c (28 day)
Rec. N° 1 - OPC	6	4.03	3	0,73
Rec. N° 2 – BC'' 1% - FI	3	5.56	3	1,25
Rec. N° 2-2 – BC'' 1% - SO	3	1.88	3	1,10
Rec. N° 3 – BC'' 3% - FI	3	0,93	3	2,35
Rec. N° 3-2 – BC'' 3% - SO	3	2,20	3	3,46
Rec. N° 4 – BC'' 5% -FI	3	1,35	3	4,60
Rec. N° 4-2 – BC'' 5% - SO	3	3,25	3	1,51

Figure 74 and Figure 75 are graphically represented the 7 and 28-days compressive strength results, respectively.

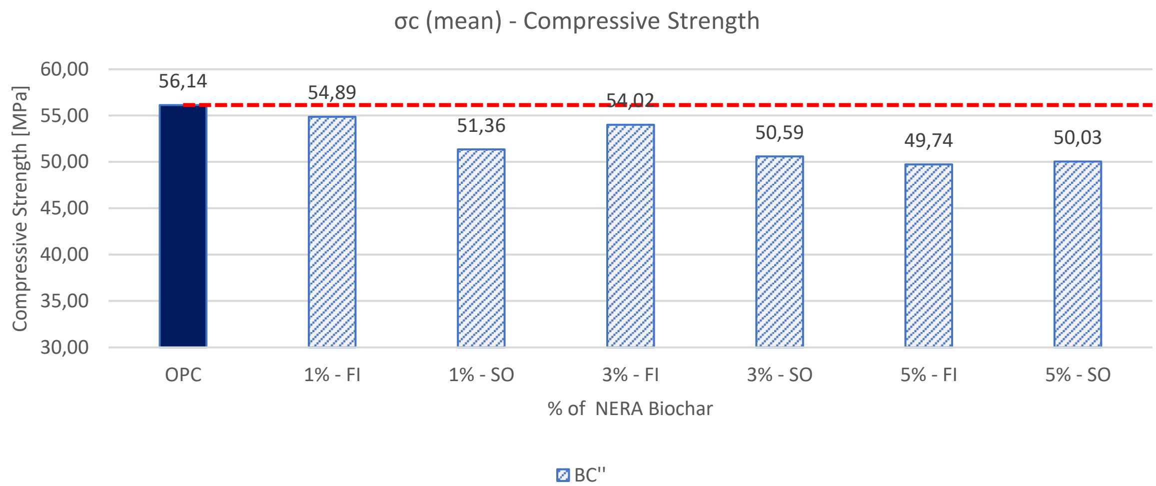


Figure 74. Compressive strength - comparison between different % of MT Nera BC specimens, 7 days

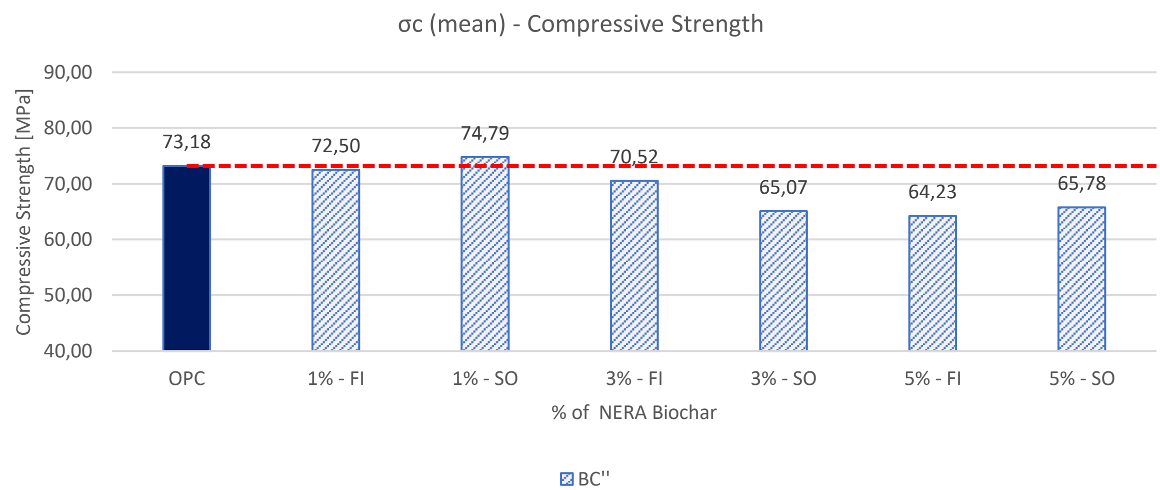


Figure 75. Compressive strength - comparison between different % of MT Nera BC specimens, 28 days

When talking about compression resistance or compressive strength *(σ_c)*, the results show a non-positive behavior, going against the trend or the expected results. In the case of the tests at 7-days of curing, not only there is not better performance, but in the case of BC'' 5% as substitution or filling, the compressive strength decreases by 10%, reaching a σ_c of 50 MPa, which, from a technical point of view, is a good resistance. However, seeing the reference values that were obtained with plain cement, they are negative indicators. In the case at 28-days of curing, the BC'' 5% reiterates its behavior and is again a sample with negative yields. However, the resistance achieved by this batch of samples is well accepted by the American standards and European standards that regulate the strengths and capacities of a batch of mortar samples. For this last-mentioned case, Rec. 2-2. BC'' 1% - SO increases σ_c by 2.5% with a σ_c of 75 MPa, reaching relatively high compressive strength values, given its reference standard in the European framework [95].

Given the results obtained in the mechanical tests such as flexural and compressive strength performed on the mortar, it is not feasible to recommend an optimal and favorable percentage that improves the performance of the aforementioned mechanical properties, as it would be a mistake to ensure that the behavior will be better or at least the same when adding a certain percentage of biochar to the mixture. Then, Table 38 shows the most effective recipe according to the specific mechanical property, the Nera Biochar percentage, and the efficiency.

Table 38. Summary of mechanical properties of mortar at 7 & 28-days.

	7-Days				**28-Days**			
	Plain Cement	Recipe		Efficiency	Plain Cement	Recipe		Efficiency
σ_f	5,37 Mpa	1% - SO	5,71 Mpa	↑ 6 %	6,05 Mpa	BC 3% - SO	6,15 Mpa	↑ 2 %
σ_C	56,14 Mpa	1% - FI	54,89 Mpa	↓ -2 %	73,18 Mpa	BC 1% - SO	74,79 Mpa	↑ 2 %
GF	0,071 N/mm	1% - SO	0,085 N/mm	↑ 21 %	0,08 N/mm	BC 3% - SO	0,105 N/mm	↑ 32 %
μ	15,98	1% - FI	16,27	↑ 2 %	20,17	BC 3% - SO	14,47	↓ -28 %

In Table 38, it can be seen that mortar mixtures where 1% of Biochar was implemented in the cement matrix have a better performance in the tests carried out 7-days after preparation, while those mixtures where a 3% of Biochar in its cement matrix has better behavior and better mechanical properties when evaluated 28-days after its preparation. The case of Rec. 2-2. BC'' 3% - SO gives a great benefit to the project's budget since biochar is a low-cost compound that can be used as a substitute (by 3%) for cement, reducing mortar production costs on a large scale construction and civil projects.

CONCLUSIONS

As mentioned in the introduction section, cement is par excellence the most used construction material by professionals in architecture and engineering. It is considered a resistant material, with easy handling both in the manufacture and in preparation. However, it is also responsible for the majority of CO_2 emissions in the world. Additionally, cement-based materials are inexpensive and easily modified to obtain desired conditions, such as accelerating or delaying the setting time, such as changing their viscosity, flowability, and workability with the help of additives, usually high-cost, altering the behavior of materials. However, currently, modern constructions require construction materials with greater resistance, better mechanical behavior, and that meet the rheological requirements for optimal deposition, but mainly that reduce the environmental impact, using alternative and supplementary materials that do not increase the cost of production or generate a significant negative impact, as would the reinforcements and conventional additives do.

Due to the previous statement, the current document sought the implementation of supplementary cementitious materials that are a by-product of another industrial process that is considered an expense, and a waste product, to recycle and use it in the production of a better performance cement. This is why Nera Biochar was used in microparticles in the cement matrix to improve the mechanical behavior, acquire certain strategy rheological requirements for digital manufacturing, and reduce CO_2 emission in the air, as long as the production of this was less polluting than the green footprint it can produce.

The recipes and proportions used in this study are based on previous studies that have already proposed different types of Biochar as an admixture improving mechanical resistance, such as the Suarez study [51], Marchon et al. [103], Roussel [30], Restuccia and Ferro [4] among others [69-74,106-108]. Then, the most noteworthy characteristics of the study, related to the rheological and mechanical tests are presented below:

Cement Paste

- The plain cement paste exhibits a plastic viscosity close to $0{,}34\ Pa \cdot s$, lower than any mix design containing Biochar, indicating less resistance to flow compared to mixes containing Biochar, meaning that it is a more fluid mixture, less viscous.

- The plastic viscosity of the cement paste containing Biochar BC'' 1, 2 and 3 wt% cement is $0{,}49\ Pa \cdot s$ on average for the three recipes, increasing the viscosity by 57% with respect to plain cement, showing an increase in flow resistance and with a double shear rate. However, the addition of BC'' 1 and 3 wt% of cement presents approximately the same minimum viscosity and an equal shear rate, so it is better to use 2% Biochar to avoid wasting the material since the behavior is very similar.

- The plastic viscosity increases as the percentage of Biochar in the sample increases, indicating that the mixture begins to be more viscous with the Biochar content, obtaining a flow and texture more suitable for 3D printing of cement paste.

- Like the plastic viscosity, the yield stress also increases as the content of biochar in the sample increases, meaning higher suspension stability, more stress is needed for the flowing of the mixture, which is good because when depositing the mixture through the nozzle in the 3D printing method, the mixture will require more stress to start flowing. Hence, the requirement is to stay in equilibrium at the moment prior to setting on the deposition surface.

- The sample of the BC'' 5 wt% cement seems to be a good mixture of cement paste from the point of view of rheological properties since it contemplates a plastic viscosity 159% and yield stress 647% higher than plain cement. Strategically speaking, this mixture seems to have an advantage over the others for digital manufacturing since it is fluid enough to pass through the nozzle. Furthermore, the shear rate is medium, proposing a suitable shear thinning and shear thickening so that the mixture is kept in a fresh state before and during the deposition and a pseudo-solid state after the deposition due to the high yield stress, avoiding the use of formworks that involves high costs and time.

- Regardin the mechanical properties, the most significant contribution in this field is that apart from the improvement in flexural and compressive strength, there was a better behavior in the fracture energy and the ductility factor, counterintuitive with what usually happens with conventional materials, where it is expected that an increase in strength leads to an increase in brittleness, and the most common trend is that with increasing strength in cement-based composites, the ductility is significantly lower.

- The overall best performance was obtained when the Biochar content was BC'' 2 wt% of cement, where flexural strength increased by 63% and 29%, the compressive strength increased by 23% and 13%, and the fracture energy increase by 124% and 150% for 7 and 28 days of curing, respectively. The fracture energy G_F was one of the properties that had the highest increment; this is because the agglomerated of Nera Biochar particles function as an attractor of the crack path surface, deriving a more tortuous path, requiring more energy to collapse the sample. Evaluating the ductility factor μ, the results are consistent with the other mechanical properties, with an increment of 18% and 14% for early and late maturation, respectively, concerning the plain cement sample. From the physical properties, it is known that Biochar microparticles intensify the hydration process, causing a more efficient development of mechanical properties.

- In general, for the cement paste, it seems that any Biochar content is beneficial for the mechanical properties, considering that the best performance occurs at an early maturing time and with a Biochar percentage of 2 wt% of cement. The improvement of short-term mechanical performance is an advantage that can be used especially in cases where rapid maturation is required to speed up construction times, or when there are special loads that are exerted in the first phase.

Mortar

- When 1% of Nera Biochar is added to the mortar mix, the mechanical properties are similar, with slightly better performance. It is important that the properties, in this case, can be comparable because Biochar can be used as a replacement material for cement, maintaining good mechanical performance but saving cement costs and more ecofriendly material, saving CO_2 emission, which will be significant at large building scales. This short-term better performance is beneficial when faster and rapid large scale construction is required, in turn, when special loads that are exerted in the primary phase.

- When replacing 1% of cement with Biochar content, the fracture energy increases by 21% and 8% for the 7 and 28 days of curing, respectively, increasing the tortuosity of the failure path of the sample due to small agglomerations of Biochar that attract the trajectory of the crack path.

- Doing a hypothetical cost analysis, based on the study proposed by Suarez [51], it is possible to conclude that the use of Biochar in the cement paste can lead to a minimal budget increase compared to the plain cement mix. The production of 1 m^3 of cement paste using Rec. 6. BC'' 2% has an additional value close to 1 euro, and saving this minimum percentage in cement when using Biochar as a substitute, the budget can decrease by 1-2% of the value of cement. It is highlighted that Biochar in many cases is considered a potential waste, then its cheap implementation brings benefits to mortar and especially to the environment due to the carbon sequestration.

- When dealing with waste and its environmental impact, it is common to hear criticism about the amount of waste produced by industry, generating negative impacts on the environment. In this case, Biochar is produced through pyrolysis, a process that, although it requires energy, considerably reduces the environmental impact compared to current incineration. The use of this process improves the management of waste products from other processes such as the felling of trees and sanitary sludge, reducing municipal waste, reducing the greenhouse gas emissions thanks to the CO_2 sequestration from polluted air.

After analyzing the properties provided by the Biochar content in cement-based mixtures, it is possible to conclude that the aim of this thesis document, linked to the proposed objectives, gives a positive and satisfactory results. This research was motivated by previous studies where it was used different supplementary cementitious materials and other types of Biochar to increase the mechanical capacity and achieve specific rheological properties, expectations that were met with the application of Nera biochar, 100% Italian and certified product. It is expected that the current and past research will continue to motivate the scientific field and future research on building materials, meeting quality standards and improving the mechanical and rheological properties of cement-based composites. Additionally, the creation of a more environmentally friendly type of cement paste and paste was achieved, reducing the emission of CO_2 gases thanks to Nera Biochar's ability to sequester carbon dioxide in polluted air. Always emphasizing that this type of waste already generates a negative impact on the environment, and that, thanks to the implementation in the engineering of the materials, it can contribute to the reduction of this waste, generating a clearly positive impact.

ANNEXS

Particle size distribution of the sand. Section 7.1.2

Table 39. Particle size distribution of CEN reference sand [21].

Square mesh size [mm]	Cumulative sieve residue [%]
2	0
1,6	7 ± 5
1	33 ± 5
0,5	67 ± 5
0,2	87 ± 5
0,008	99 ± 5

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Tipo I 52,5 R

Questo cemento contiene almeno il 95% di clinker e fino ad un massimo del 5% di costituenti minori. Le percentuali indicate non tengono conto delle aggiunte di solfato di calcio e di additivi.

Il cemento, caratterizzato dal rapido sviluppo delle resistenze iniziali, è conforme alla norma europea armonizzata EN 197/1 ed è dotato di marchio come previsto dal regolamento europeo 305/2011 (CPR).

Caratteristiche chimiche

Parametro	Metodo di prova	Valori indicativi (1)	Limiti caratteristici di norma
Solfati (SO_3)	UNI EN 196/2	<3,7%	<=4,0%
Cloruri (Cl -)	UNI EN 196/2	<0,08%	<=0,10%
Perdita al fuoco	UNI EN 196/2	<5,0%	<=5,0%
Residuo insolubile	UNI EN 196/2	<1,0%	<=5,0%
Cromo VI solubile in acqua	UNI EN 196/10	<=2 ppm	<=2 ppm

Caratteristiche fisico-meccaniche

Parametro	Metodo di prova	Valori indicativi [1]	Limiti caratteristici di norma
Superficie specifica Blaine	EN 196/6	4000-5500 cm2/g	
Tempo di inizio presa	EN 196/3	>90 min	>=45 min
Stabilità di volume	EN 196/3	<=10 mm	<=10 mm
Consistenza su malta	UNI 7044	>70%	
Resistenze a compressione dopo stagionatura di	EN 196/1		
2 giorni		>35,0 MPa	>=30,0 MPa
28 giorni		>56,0 MPa	>=52,5 MPa

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[1] I valori rappresentano il livello al di sopra (o al di sotto) del quale è lecito attendersi il posizionamento dei valori medi, per i parametri indicati, dei cementi BUZZI UNICEM appartenenti al tipo ed alla classe indicati in testata, calcolati su base annua e considerando i dati dell'autocontrollo interno.

Impieghi correnti

- Calcestruzzo armato, normale e non, per opere con elevate resistenze iniziali e finali
- Calcestruzzo per strutture prefabbricate e/o precompresse anche con cavi pre-tesi
- Calcestruzzo per opere che richiedono il disarmo in tempi ravvicinati al getto
- Calcestruzzo per manufatti prefabbricati con o senza maturazione accelerata

CONSIGLIO NAZIONALE DELLE RICERCHE
Istituto per le Tecnologie della Costruzione
ITC

ITC

CPR NB n. 0970
ITC – CNR
Via Lombardia, 49
20098 San Giuliano Milanese (MI) - Italia

CERTIFICATO DI COSTANZA DELLA PRESTAZIONE

0970-CPR-0126/CE/0202

In conformità al Regolamento 305/2011/UE del Parlamento Europeo e del Consiglio del 9 marzo 2011 (Regolamento Prodotti da Costruzione o CPR) questo certificato si applica al prodotto da costruzione

CEM I 52,5 R

immesso sul mercato da

Buzzi Unicem SpA
Via Luigi Buzzi, 6 - 15033 Casale Monferrato (AL) - Italia

e prodotto nella Fabbrica di

Via di Testi, 10 - Passo dei Pecorai - 50020
Testi di Greve in Chianti (FI) – Italia

Questo certificato attesta che tutte le disposizioni riguardanti la valutazione e la verifica della costanza della prestazione descritta nell'allegato ZA della norma

EN 197-1:2011

nell'ambito del Sistema 1+ per la prestazione indicata in questo certificato sono applicate e che il controllo di produzione in fabbrica condotto dal fabbricante è valutato per assicurare la costanza della prestazione del prodotto da costruzione.

Questo certificato è stato rilasciato la prima volta il 18-03-2002 ed ha validità sino a che la norma armonizzata, il prodotto da costruzione, i metodi di AVCP o le condizioni di produzione in fabbrica non siano modificate significativamente, a meno che non sia sospeso o ritirato dall'Organismo di certificazione di prodotto notificato.

San Giuliano Milanese, 01 luglio 2019
Revisione n. 07

Il Direttore Tecnico
ing. Antonio Bonati

BONATI
ANTONIO
01.07.2019
06:10:11 UTC

Testi Cementi

DICHIARAZIONE DI PRESTAZIONE
N° 0970-CPR-0126/CE/0202
Ai sensi del REGOLAMENTO DELEGATO (UE) n° 574/2014 del 21 febbraio 2014

1. Codice di identificazione unico del prodotto-tipo:

Cemento Portland EN 197-1 – CEM I 52,5 R

2. Usi previsti:

Preparazione di calcestruzzo, malta, malta per iniezione o altre miscele per costruzione e fabbricazione di prodotti da costruzione, etc.

3. Fabbricante:

Testi Cementi s.r.l. c/o BUZZI UNICEM S.p.A. – Via L. Buzzi 6 – 15033 Casale Monferrato (AL) – ITALIA

4. Mandatario:

Non applicabile

5. Sistema di VVCP: (Valutazione e Verifica della Costanza della Prestazione)

Sistema 1+

6.a Norma armonizzata:

UNI EN 197-1:2011

Organismi notificati:

ITC-CNR, notificato con il numero 0970, ha effettuato la determinazione di prodotto-tipo sulla base delle prove (compreso il campionamento), l'ispezione iniziale dello stabilimento e del controllo di produzione della fabbrica, la sorveglianza, la valutazione e la verifica continue del controllo di produzione di fabbrica, e le prove di verifica di tipo dei campioni prelevati prima della immissione sul mercato del prodotto sotto il sistema 1+ e ha rilasciato il relativo certificato.

7. Prestazioni dichiarate

Caratteristiche essenziali	Prestazione
Costituenti e composizione del cemento comune	CEM I
Resistenza a compressione (normalizzata e iniziale)	52,5 R
Tempo di presa Residuo insolubile	*Passa* *Passa*
Perdita al fuoco	*Passa*
Stabilità - Espansione - Contenuto di SO_3	 *Passa* *Passa*
Contenuto di cloruro	*Passa*

8. Documentazione tecnica appropriata e/o documentazione tecnica specifica:

Non applicabile

La prestazione del prodotto sopra identificato è conforme all'insieme delle prestazioni dichiarate. La presente dichiarazione di prestazione viene emessa, in conformità al regolamento (UE) n. 305/2011, sotto la sola responsabilità del fabbricante sopra identificato.

Firmato a nome e per conto del fabbricante da:

Michele Buzzi – Amministratore Delegato

Casale Monferrato, 01.07.2019

Rev. 0

DECLARATION OF PERFORMANCE

n° IT0332/01

MasterEase 7000

1) Unique identification code of the product-type

EN 934-2 Table 3.1 – 3.2

2) Intended use or uses

High range water reducing/superplasticizing admixtures

3) Manufacturer

Master Builders Solutions Italia SpA via Vicinale delle Corti 21, 31100 Treviso

4) System or systems of assessment and verification of constancy of performance (AVCP)

System 2+

5) Harmonized standard:

EN 934-2: 2012

Notified body/ies

ICMQ SpA, identification number 1305

7) Declared performances

Essential characteristics	Performance	Harmonized technical specification
Chloride ion content	<= 0,1% by mass	EN 934-2: 2012
Alkali content (Na_2O equivalent)	<= 3,0%	
Corrosion behaviour	Contains nitrates (component from EN 934-1: 2008 Annex A.2)	
Compressive strength	Equal consistence: 24h >= 140% 28 days >= 115% Equal w/c ratio: 28 days >= 90%	
Air content	Equal consistence: <= 2,0 % Equal w/c ratio: <= 2,0 %	
Air content (entrained air)	NPD	
Air void characteristic	NPD	
Water reduction	>= 12,0 %	
Bleeding	NPD	
Setting Time	NPD	
Hardening time/ strength development	NPD	
Capillary absorption	NPD	
Consistency	Increase: >= 120 mm Retention: comply 3.2 (2)	
Dangerous substances	See MSDS	
Segregated portion (SR)	NPD	

The performance of the product identified above is in conformity with the set of declared performances. This declaration of performance is issued in accordance with Regulation (EU) No. 305/2011, under the sole responsibility of the manufacturer identified above.

Signed for and on behalf of the manufacturer by:
Dario Micheletto
Resp. Quality Control   Treviso, 01 January 2021

MasterEase 7000

New superplasticizer technology imparts advanced rheological properties delivering a significant decrease in the viscosity of concretes and extended rheology maintenance.

MATERIAL DESCRIPTION

MasterEase 7000 is a superplasticizer, high range water reducer from recent research work of R & D laboratories of Master Builders Solutions.

MasterEase 7000 is especially engineered for ready-mix Rheoplastic concrete having fluid consistence and self-compacting concrete, **to impart exceptional rheological properties and having a very high workability retention, in all weather conditions. It improves considerably the placing and finishing of concretes and enhances the ease of concrete pumping for all construction activities.**

MasterEase 7000 is chloride free, meets UNI EN 934-2 and it is compatible with all cements meeting the EN 197-1 standard.

INNOVATION

MasterEase 7000 is based on an innovative polymer chemistry and it is patented by Master Builder Solutions. Its action differs from traditional superplasticizers, to the extent that the adsorption of polymers of MasterEase 7000 on binder particles is provided by a flexible chemical bond which does not impede the flow of concretes.

This innovation significantly improves rheological behaviour of concretes treated by MasterEase 7000, they have a low yield stress, low viscosity with additional feature of long workability retention.

LOW VISCOSITY CONCRETE

Low Viscosity Concrete is an innovative concept dedicated to the viscosity (rheology) of concretes. It is based on the use of MasterEase polymer with dedicated technical services of Master Builders Solutions.

This concept not only allows the achievement of a significant reduction in concrete viscosity but also optimizing the performance of concrete.

BENEFITS FOR READY-MIX PRODUCER

MasterEase 7000 is recommended for the production of standard and self-compacting concrete requiring low viscosity, long workability retention and high compressive strength. MasterEase 7000 is specially formulated for the concrete industry. It is also suitable for applications in the general Civil and building sites.

It can be used for the realization and achievement of the following:

- concrete complying to EN 206-1;
- ready-mix and Site Mix concretes;
- superior Concrete pumping;
- reduction of Concrete waste;
- ease of compacting and finishing concrete;
- high performance and ultra-high strength concrete;
- concrete for low environmental impact and high in mineral additions;
- architectural concrete.

FEATURES AND BENEFITS

The MasterEase 7000 delivers many advantages both in the fresh concrete on hardened concrete.

At fresh state, optimizing the rheology:

Decrease in the viscosity of concretes at constant W/C

- Improved pumping (lower pressure and longer distance).
- Better response to vibration.
- Greater Ease of Pumping.
- Superior finishing, floating and smoothing operations.
- Excellent flexibility, mobility and flow of self-compacting concrete.

Reduction possible to the W/C ratio without affecting the viscosity of concretes.

- New windows for technical and economic optimization of concrete mix designs (addition and types of binder, choice of aggregates).
- High strength and resistance to segregation.
- Workability retention over 60-90 minutes without retardation.
- Good compatibility with all types of cement and mineral additions.

In the cured state, improvement of sustainability

i. excellent early and late compressive strength
ii. Improvement of quality of surface finishes
iii. As part of a reduction of W/C
   - Increased mechanical resistances
   - Decreased porosity and permeability
   - Decreased shrinkage and cracking
   - Enhanced durability

A brand of MBCC GROUP

MASTER®
BUILDERS
SOLUTIONS

MasterEase 7000

New superplasticizer technology imparts advanced rheological properties delivering a significant decrease in the viscosity of concretes and extended rheology maintenance.

In compliance with the European Regulation (EU No 305/2011 and EU No. 574/2014) the product is provided with the CE marking according to UNI EN 934-2 and the relative DoP (Declaration of Performance).

CE 1305
EN 934-2 **Table 3.1 – 3.2** High range water reducing/superplasticizing admixtures

DOSAGE

The recommended dosage rate range is 0.6 to 1.2 liters per 100 kg of binder. Other dosages may be recommended in special cases according to specific job site conditions. In such cases please consult our Technical Service Department for advice.

PACKAGING

MasterEase 7000 is available in 10L cans, 1.000L tanks or in bulk.

STORAGE

MasterEase 7000 must be stored in a place where the temperature does not drop below 5 °C.
In case of freezing, warm up and homogenise the admixture solution before using.

Technical Information	
Form	Liquid
Relative density (g/cc at 20°C)	1.030 – 1.060
Essential characteristic in accordance to EN 934-2	**Performance**
Chloride ion content	≤ 0,1% by mass
Alkali content (Na2O equivalent)	≤ 3,0%
Corrosion behaviour	Contains only components from EN 934-1 2008 Annex 1
Compressive strength	Equal consistence: 24h ≥ 140% 28 days ≥ 115% Equal w/c ratio: 28 days ≥90%
Air content	Equal consistence: ≤ 2,0 % Equal w/c ratio: ≤ 2,0 %
Water reduction	≥ 12%
Consistency	Increase: ≥ 120 mm Retention: comply 3.2 (2)

DIRECTIONS FOR USE

MasterEase 7000 is a liquid admixture to be added to the concrete during the mixing process:

- mix cement and secondary binders, sand, coarse aggregates and the mix water until a stiff, yet homogeneous, mixture is obtained;
- optimal mixing water reduction is obtained if MasterEase 7000 is mixed into the concrete right after the addition of the initial 80-90% of the total water;
- avoid adding the admixture to the dry aggregates;
- add MasterEase 7000 admixture and mix again for to 60 seconds in order to disperse it homogeneously;
- continue mixing until required workability is obtained, with addition of the remaining water.

MasterEase 7000

New superplasticizer technology imparts advanced rheological properties delivering a significant decrease in the viscosity of concretes and extended rheology maintenance.

COMPATIBILITY

In order to optimise some special properties of the concrete, use of the following complementary admixtures is suggested:

- demoulding agent from MasterFinish line for good surface appearance. curing agent
- curing agent MasterKure for sealing the surface of freshly finished concrete against rapid evaporation of water which may cause plastic shrinkage cracking.

MasterEase 7000 is not compatible with all admixtures of MasterRheobuild series.

OTHER SERVICES

For price analysis, specifications, supplementary brochures, references, reports and technical assistance, visit the website www.master-builders-solutions.com/it-it or contact infomac@mbcc-group.com.

Scan the QR code to visit the product page and download the latest version of this datasheet.

Since 16/12/1992, Master Builders Solutions Italia Spa has been operating under a Certified Quality System compliant with the UNI EN ISO 9001 Standard. Furthermore, the Environmental Management System is certified according to the UNI EN ISO 14001 Standard and the Safety Management System is certified according to the UNI ISO 45001 Standard.

Master Builders Solutions Italia Spa
Via Vicinale delle Corti, 21 – 31100 Treviso – Italia
T +39 0422 429200 F +39 0422 421802
www.master-builders-solutions.com/it-it
e-mail: infomac@mbcc-group.com

For further information, please consult the local Technician of Master Builders Solutions. The technical advice on how to use our products, either written or verbally given, are based on the current state of our scientific and practical expertise, and does not imply the assumption of any guarantee and/or responsibility for the final results of works executed using our products.
Therefore, the customer is not exempted from the exclusive task and responsibility of verifying the suitability of our products for the intended use and purposes.
This version supersedes all the previous ones.

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N°1 in Italia nel Biochar

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Biochar 15 Lt

Sii il primo a recensire questo prodotto

45,00 €

Tasse escl.: 43,27 €

DISPONIBILE

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Avvisami quando il prezzo scende

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AGGIUNGI ALLA LISTA DESIDERI
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Cosa è:

E' un fertilizzante indicato per le colture intensive, l'orticoltura e le piante d'appartamento.

Benefici:

1. Combatte la desertificazione,
2. Sottrae anidride carbonica al pianeta,
3. Trattiene l'acqua dai terreni e la rilascia lentamente e ne aumenta l'aerazione rendendo le piante più forti e più sane
4. Ha una durata pluriennale.
5. Aggiungendo il biochar al terreno dal 10 al 20%, si raddoppia la crescita delle piante.

Dettagli | Recensioni

Cosa è il biochar:

Il biochar, anche detto carbone vegetale, è una soluzione concreta alla crisi climatica perché sottrae CO2 dall'atmosfera e combatte la desertificazione. Il biochar è un prodotto che deriva dal cippato, proveniente dalla pulizia delle aree verdi e dei boschi e dagli gli scarti di lavorazione della legna. Durante la sua produzione, imprigiona letteralmente la CO2 nella sua struttura, composta infatti da carbonio per oltre il 75% e la immagazzina nel terreno sottoforma di fertilizzante, creando un circolo virtuoso. Grazie alla sua enorme porosità (>475 m2/g) trattiene acqua e nutrienti rilasciandoli lentamente nel terreno e rendendoli disponibili alle piante solo quando necessario.

Come lo facciamo:

A differenza degli altri biochar che derivano dagli scarti della gassificazione, il nostro è garantito al 100%, perché noi produciamo solo Biochar:

LO FACCIAMO IN ITALIA

Produciamo in Piemonte. Siamo un'azienda italiana che ha scelto di fare la differenza, per questo la nostra ricerca si è concentrata su una tecnologia che potesse salvare il pianeta, senza usare sostanze sintetiche.

CON UN NOSTRO IMPIANTO CHE PRODUCE SOLO BIOCHAR

Il nostro materiale viene prodotto con un impianto di trasformazione dedicato, di nostra progettazione.

USIAMO SOLO LEGNA CERTIFICATA

Utilizziamo solo biomassa legnosa italiana derivante da filiera controllata.

Come si usa:

Applicare dal 10% al 20% di biochar a compost o terriccio mescolando bene.

Da utilizzare esclusivamente per scopi agricoli.

PARAMETRO	VALORE
Granulometria	
Frazione passante	
<0,5 mm	6,5%
<2 mm	74,6%
<5 mm	100%
Azoto (N) Totale	0,3%
Potassio (K_2O) Totale	848 mg/kg
Fosforo (P_2O_5) Totale	294mg/kg
Calcio (CaO) Totale	3685 mg/Kg
Magnesio (MgO) Totale	1007 mg/Kg
Sodio (Na_2O) Totale	49,4 mg/Kg
% C da carbonato	<0,5%
Test Fitotossicità e Accrescimento	Idoneo
Max ritenzione idrica	62%
Umidità Totale	>10%
Carbonio (C) Totale di Origine Biologica	>75 %
Contenuto Ceneri	3,39 %
Salinità	514 meq/100g
pH	9,8
Rapporto H/C Molare	0,07
Classe di Qualità	1 (premium)

CEMENT PASTE RECIPIES

CEMENT PASTE RECIPIES			
Recipe No. 1 - OPC			
Name	Felipe / Daniel / Devid	**ID**	OPC - ME7 - 7 & 28 Days
Materials	**Unit**	**Quantity**	**wt%**
Cement (type I 52,5 R Buzzi Unicem)	g	460	
Normal Water	g	161	35%
Superplasticizer (MasterEase 7000)	g	4,6	1%
Nera Biochar	g	0	0%
Dates		**Mixing Procedure**	
Preparation	21/12/2020	3 minutes at 480 rpm	
Formwork Removal	22/12/2020	3 minutes at 4840 rpm	
Test 7-Days	28/12/2020	Gradually pour the cement (2 min)	
Test 28-Days	18/01/2021	Total mixing time 6 minutes	

CEMENT PASTE RECIPIES			
Recipe No. 2 – BC' 1%			
Name	Felipe / Daniel / Devid	**ID**	BC' 1% - ME7 - 7 & 28 Days
Materials	**Unit**	**Quantity**	**wt%**
Cement (type I 52,5 R Buzzi Unicem)	g	460	
Normal Water	g	161	35%
Superplasticizer (MasterEase 7000)	g	4,6	1%
Nera Biochar	g	4,6	1%
Dates		**Mixing Procedure**	
Preparation	21/12/2020	3 minutes at 480 rpm	
Formwork Removal	22/12/2020	3 minutes at 4840 rpm	
Test 7-Days	28/12/2020	Gradually pour the cement (2 min)	
Test 28-Days	18/01/2021	Total mixing time 6 minutes	

CEMENT PASTE RECIPIES			
Recipe No. 3 – BC' 2%			
Name	Felipe / Daniel / Devid	**ID**	BC' 2% - ME7 - 7 & 28 Days

Materials	Unit	Quantity	wt%
Cement (type I 52,5 R Buzzi Unicem)	g	460	
Normal Water	g	161	35%
Superplasticizer (MasterEase 7000)	g	4,6	1%
Nera Biochar	g	9,2	2%

Dates		Mixing Procedure
Preparation	13/01/2021	3 minutes at 480 rpm
Formwork Removal	14/01/2021	3 minutes at 4840 rpm
Test 7-Days	20/01/2021	Gradually pour the cement (2 min)
Test 28-Days	27/01/2021	Total mixing time 6 minutes

CEMENT PASTE RECIPIES			
Recipe No. 4 – BC' 3%			
Name	Felipe / Daniel / Devid	**ID**	BC' 3% - ME7 - 7 & 28 Days

Materials	Unit	Quantity	wt%
Cement (type I 52,5 R Buzzi Unicem)	g	460	
Normal Water	g	161	35%
Superplasticizer (MasterEase 7000)	g	4,6	1%
Nera Biochar	g	13,8	3%

Dates		Mixing Procedure
Preparation	13/01/2021	3 minutes at 480 rpm
Formwork Removal	14/01/2021	3 minutes at 4840 rpm
Test 7-Days	20/01/2021	Gradually pour the cement (2 min)
Test 28-Days	27/01/2021	Total mixing time 6 minutes

CEMENT PASTE RECIPIES			
Recipe No. 5 – BC’’ 1%			

Name	Felipe / Daniel / Devid	**ID**	BC’’ 1% - ME7 - 7 & 28 Days

Materials	Unit	Quantity	wt%
Cement (type I 52,5 R Buzzi Unicem)	g	460	
Normal Water	g	161	35%
Superplasticizer (MasterEase 7000)	g	4,6	1%
Nera Biochar	g	4,6	1%

Dates		Mixing Procedure
Preparation	15/01/2021	3 minutes at 480 rpm
Formwork Removal	16/01/2021	3 minutes at 4840 rpm
Test 7-Days	22/01/2021	Gradually pour the cement (2 min)
Test 28-Days	29/01/2021	Total mixing time 6 minutes

CEMENT PASTE RECIPIES			
Recipe No. 6 – BC’’ 2%			

Name	Felipe / Daniel / Devid	**ID**	BC’’ 2% - ME7 - 7 & 28 Days

Materials	Unit	Quantity	wt%
Cement (type I 52,5 R Buzzi Unicem)	g	460	
Normal Water	g	161	35%
Superplasticizer (MasterEase 7000)	g	4,6	1%
Nera Biochar	g	9,2	2%

Dates		Mixing Procedure
Preparation	10/02/2021	3 minutes at 480 rpm
Formwork Removal	11/02/2021	3 minutes at 4840 rpm
Test 7-Days	17/02/2021	Gradually pour the cement (2 min)
Test 28-Days	24/02/2021	Total mixing time 6 minutes

CEMENT PASTE RECIPIES			
Recipe No. 7 – BC'' 3%			
Name	Felipe / Daniel / Devid	**ID**	BC'' 3% - ME7 - 7 & 28 Days

Materials	**Unit**	**Quantity**	**wt%**
Cement (type I 52,5 R Buzzi Unicem)	g	460	
Normal Water	g	161	35%
Superplasticizer (MasterEase 7000)	g	4,6	1%
Nera Biochar	g	13,8	3%

Dates		**Mixing Procedure**
Preparation	10/02/2021	3 minutes at 480 rpm
Formwork Removal	11/02/2021	3 minutes at 4840 rpm
Test 7-Days	17/02/2021	Gradually pour the cement (2 min)
Test 28-Days	24/02/2021	Total mixing time 6 minutes

MORTAR RECIPES

MORTAR RECIPIES			
Recipe No. 1 – OPC			
Name	Felipe / Daniel	**ID**	OPC - 7 & 28 Days

Materials	**Unit**	**Quantity**	**wt% of cement**
Cement (type I 52,5 R Buzzi Unicem)	g	450	
Normal Water	g	225	50%
Sand	g	1350	3
Nera Biochar	g	0	0%

Dates		**Mixing Procedure**
Preparation	26/02/2021	30 sec at low speed
Formwork Removal	27/02/2021	30 sec at high speed
Test 7-Days	05/03/2021	Stop 1,5 min (remove scraper)
Test 28-Days	12/03/2021	60 sec at high speed

MORTAR RECIPIES			
Recipe No. 2 – BC’’ 1% - Biochar as Filler			
Name	Felipe / Daniel	**ID**	BC’’ 1% - FI - 7 & 28 Days

Materials	**Unit**	**Quantity**	**wt% of cement**
Cement (type I 52,5 R Buzzi Unicem)	g	450	
Normal Water	g	225	50%
Sand	g	1350	3
Nera Biochar	g	4,5	1%

Dates		**Mixing Procedure**
Preparation	27/02/2021	30 sec at low speed
Formwork Removal	28/02/2021	30 sec at high speed
Test 7-Days	06/03/2021	Stop 1,5 min (remove scraper)
Test 28-Days	13/03/2021	60 sec at high speed

MORTAR RECIPIES			
Recipe No. 2-2 – BC’’ 1% - Biochar as Substitution			
Name	Felipe / Daniel	**ID**	BC’’ 1% - SO - 7 & 28 Days

Materials	**Unit**	**Quantity**	**wt% of cement**
Cement (type I 52,5 R Buzzi Unicem)	g	445,5	
Normal Water	g	222,75	50%
Sand	g	1350	3
Nera Biochar	g	4,5	1%

Dates		**Mixing Procedure**
Preparation	27/02/2021	30 sec at low speed
Formwork Removal	28/02/2021	30 sec at high speed
Test 7-Days	06/03/2021	Stop 1,5 min (remove scraper)
Test 28-Days	13/03/2021	60 sec at high speed

MORTAR RECIPIES			
Recipe No. 3 – BC’’ 3% - Biochar as Filler			
Name	Felipe / Daniel	**ID**	BC’’ 3% - FI - 7 & 28 Days

Materials	**Unit**	**Quantity**	**wt% of cement**
Cement (type I 52,5 R Buzzi Unicem)	g	450	
Normal Water	g	225	50%
Sand	g	1350	3
Nera Biochar	g	13,5	3%

Dates		**Mixing Procedure**
Preparation	27/02/2021	30 sec at low speed
Formwork Removal	28/02/2021	30 sec at high speed
Test 7-Days	06/03/2021	Stop 1,5 min (remove scraper)
Test 28-Days	13/03/2021	60 sec at high speed

MORTAR RECIPIES			
Recipe No. 3-2 – BC’’ 3% - Biochar as Substitution			
Name	Felipe / Daniel	**ID**	BC’’ 3% - SO - 7 & 28 Days

Materials	**Unit**	**Quantity**	**wt% of cement**
Cement (type I 52,5 R Buzzi Unicem)	g	436,5	
Normal Water	g	218,25	50%
Sand	g	1350	3
Nera Biochar	g	13,5	3%

Dates		**Mixing Procedure**
Preparation	27/02/2021	30 sec at low speed
Formwork Removal	28/02/2021	30 sec at high speed
Test 7-Days	06/03/2021	Stop 1,5 min (remove scraper)
Test 28-Days	13/03/2021	60 sec at high speed

MORTAR RECIPIES			
Recipe No. 4 – BC'' 5% - Biochar as Filler			
Name	Felipe / Daniel	**ID**	BC'' 5% - FI - 7 & 28 Days

Materials	Unit	Quantity	wt% of cement
Cement (type I 52,5 R Buzzi Unicem)	g	450	
Normal Water	g	225	50%
Sand	g	1350	3
Nera Biochar	g	22,5	5%

Dates		Mixing Procedure
Preparation	04/03/2021	30 sec at low speed
Formwork Removal	05/03/2021	30 sec at high speed
Test 7-Days	11/03/2021	Stop 1,5 min (remove scraper)
Test 28-Days	28/03/2021	60 sec at high speed

MORTAR RECIPIES			
Recipe No. 4-2 – BC'' 5% - Biochar as Substitution			
Name	Felipe / Daniel	**ID**	BC'' 5% - SO - 7 & 28 Days

Materials	Unit	Quantity	wt% of cement
Cement (type I 52,5 R Buzzi Unicem)	g	427,5	
Normal Water	g	213,75	50%
Sand	g	1350	3
Nera Biochar	g	22,5	5%

Dates		Mixing Procedure
Preparation	04/03/2021	30 sec at low speed
Formwork Removal	05/03/2021	30 sec at high speed
Test 7-Days	11/03/2021	Stop 1,5 min (remove scraper)
Test 28-Days	28/03/2021	60 sec at high speed

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