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NANOPARTICLES FROM FOOD WASTE: A "GREEN" FUTURE FOR TRADITIONAL BUILDING MATERIALS

L.RESTUCCIA AND G.A. FERRO

Politecnico di Torino
Torino, Italy
e-mail: luciana.restuccia@polito.it, ferro@polito.it

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Abstract: With the development of "mega-constructions" and especially of slender components in ever-higher buildings, new concretes need to be more performing. Therefore, compressive and flexural strength, toughness and durability are finding entry in concrete technology. In recent work, to meet the challenge of "green" high-performance concrete, Ferro et al. investigated pyrolyzed particles from food waste as inerts in the cement composites [1]. In fact, EU produces about 3 billion tons of organic waste per year, and 10% of these are agro-food industry wastes [2]. Pyrolysis is a promising approach that can be used to convert biomass wastes into energy, in the form of bio-oil, bio-char, and syngas [3]. In this work, pyrolyzed hazelnut shells have been used. They are capable of generating high performance cement composites, by increasing the compressive strength, the peak load under bending, the fracture energy and the durability. The increment of fracture energy is due to the tortuosity of the crack path for the presence of micro carbon aggregates in the cement matrix. Moreover, having a low cost, they can contribute to produce concrete in a more sustainable way, inducing a reduction of energy consumption and reduction of CO_2 emissions.

1 INTRODUCTION

The activities of the food chain are characterized by a high production of wastes and of by-products, thus creating serious problems for their management and disposal [4]. Despite the recommendation of the European Union, these wastes are constantly increasing and their disposal is an additional problem for food industries. In fact, most of the time, they are sent to disposal plants, without any kind of use/enhancement and with an extra-cost for the agro-food companies.

Pyrolysis is a promising approach that can be used to convert biomass wastes into chemical energy [5-6] and especially Bio-Char, the solid sub-product, has several prospective applications in the cement and concrete technology, such as micro-particles to add in the cement composites [7].

Generally, the production or manufacturing processes of nano/micro reinforcing particles are energy intensive and expensive, for i.e. silica fume or carbon nanotubes. In the last few years, researchers showed that the compressive and flexural strengths of cement mortars containing nanoparticles were higher than those of plain cement mortar and especially they demonstrated that Carbon Nanotubes and Carbon Nanofibers (CNT-CNF) can modify strength, modulus and ductility of concrete [9-22].

In this research work, we explored the utilization of Bio-char from pyrolysis of hazelnut shells as nano/micro inerts in the experimental cementitious-based composites.

Hazelnut shells were supplied by the agro-food industries in Piedmont [2], for example in the production of the famous Nutella, and, after pyrolysis process, they were used in different percentages of addition with respect to the weight of the cement. Mechanical parameters such as flexural and compressive strength were evaluated and, for each specimen, the fracture energy, which appears to be linked to the percentage of added waste in mix, has been analyzed [22-25].

The objective of this study is the "green" and cost-free use of Bio-Char into the cementitious-based composites, to obtain buildings materials with enhancement of mechanical properties such as strength, toughness and ductility and, at the same time, less energy consumption.

2 MATERIALS AND METHODS

In the present research, the materials used to manufacture cementitious-based composites and the manufacturing process are reported below.

2.1 Materials

The cement used is Portland, Type I, “CEM I 52,5R”, light grey color. It is characterized by the rapid development of the initial resistance and it conforms to the harmonized European standard UNI EN 197/1. Moreover, is equipped with CE marching as required by European Regulation 305/2011 (CPR).

For mixing procedure, deionized water was used, while tap water for cast and curing. Therefore, Superplasticizer Mapei Dynamon SP1 was used to efficiently disperse the cement grains and in the meanwhile for reducing the w/c ratio.

The Nano/Micro agro-food waste by pyrolysis of hazelnut shells were used as reinforcing inerts in cementitious-based composites. The additional percentages with respect to weight of cement are indicated in Table 1.

The values of these percentages reported in Table 1 derived from previously studies [22-25], in which different percentages were added to achieve an improvement of the mechanical properties of experimental cementitious composites.

Table 1. Added percentages of Nano/Micro Inert

Notation	**Weight (%)**	**Weight (g)**
PASTE CEM	0	0
CEM+0,5%	0,5	1,07
CEM+0,8%	0,8	1,71
CEM+1%	1	2,14

2.2 Methods

The pyrolysis process of hazelnut shells has occurred in a hermetically sealed reactor, in which it was guaranteed an inert environment thanks to the continuous flowing of nitrogen. In order to ensure the reproducibility and accuracy of the analysis, three replicates of the experimental runs were performed.

The heating ramp of the reactor was fixed at 6°C/min, with final temperature set points of 800°C. In each experiment, the total amount of Bio-waste used was equal to 3 g. and, after each test, the char was recovered from the bottom of the reactor and was weighed using by means of analytical scales.

After pyrolysis process, hazelnut shells were first milled in planetary mill for 10 minutes, in order to crush the bigger particles. At the end of this phase of grinding, to achieve smaller dimensions, pyrolyzed material was milled in attrition milling using alumina balls of 2 mm diameter and ethanol for grinding, for 1 hour. At the end of grinding cycle, the particle sizes were measured by means of laser granulometry: hazelnut shells reached some nanometers up to 10μm particle size range.

The agro-food waste by pyrolysis of hazelnut shells was analyzed using XRF analysis, which is very useful to assess if indeed this material can be used as inert material in a cementitious matrix. From Table 2, it can be seen that the char produced by pyrolysis of hazelnut shells has the characteristic of having high percentages of carbon and low quantities of impurities. This peculiarity make the pyrolyzed hazelnut shells perfect as inert, as it presents no difficulties dispersion in the solution of water and superplasticizer and because the particles are very strong compared to the cement matrix.

Table 2. Results of XRF analysis

Components	Weight (%)
C	97,90
Si	0,11
Mg	-
K	1,01
Ca	0,44
P	0,05
Zn	-
S	0,02
Cr	0,02
Cu	0,19
Fe	0,25

4 SPECIMENS MANUFACTURING

The mixing procedure of cementitious composites is very crucial for their performance in fresh as well in the hardened state. All the specimens were prepared with the same procedures, described below.

All elements were weighed according to the amounts required (Table 3) and the pyrolyzed hazelnut shells were joined with a solution of water and superplasticizer. The total solution (char/water/superplasticizer) was put in an ultrasonic bath for 15 minutes, and then the solution was transferred to the mixing bowl of homogenizer.

The homogenizer was operated at 440 rpm for 2 min and, during the first minute, the cement was gradually added into the solution. Exceeded 2 minutes, the mixing speed of homogenizer was increased to 630 rpm and continued mixing for further 2 min, thus making the total mixing time of 4 min.

The mixture was poured into acrylic molds, which had cavities of 20x20x75 mm^3 size and the molds were placed into the airtight plastic containers, having approximately 90% humidity level, at room temperature for 24 hours. After the completion of 24 hours, the samples were removed from the molds and immersed in tap water for curing. After maturation in water (7 or 28 days), 6 mm deep U shaped notches was realized in the specimens with Remet type TR100S abrasive cutter, having 2 mm thick diamond cut-off wheel.

Table 3. Amount required of elements

Notation	Water [g]	Cement [g]	Char [g]	Sp1 [g]
PASTE CEM	74,9	214	-	3,21
C.+0,5% PY-HS	74,9	214	1,07	3,21
C.+0,8% PY-HS	74,9	214	1,71	3,21
C.+1% PY-HS	74,9	214	2,14	3,21

For each notched sample, a three points bending test (TPB) was carried out, using a single column displacement controlled testing machine Zwick Line-Z010, with load cell of 1 kN. The test was performed by controlling the CMOD (Crack Mouth Opening Displacement) sample with a strain gauge and the test speed of 0,005 mm/min was adopted. The span adopted was 65 mm (Figure 1).

After the flexural testing, the portions of broken prisms were tested in compression with displacement controlled testing machine Zwick Line-Z010, with load cell capacity of 50 kN. The displacement rate was kept at 0,5 mm/min (Figure 2).

Figure 1: TPB test activity

Figure 2: Compressive test activity

5 RESULTS AND DISCUSSION

In this research, the addition of nano/micro particles of food waste pyrolyzed was analyzed to understand if these particles improve the behavior of the composites based on cement. In ordinary concrete, to the attainment of the load that causes the triggering of a crack, there is the collapse due to the rapid propagation of the lesion. Consequently, the deflection at the time of the first crack is a little lower (and almost coincident) to that corresponding to the complete break, as typically occurs in a brittle material. This remark is also valid for the paste cement flexural test (Figure 3, blue curve).

By evaluating the data related to TPB test of cementitious-based composites with pyrolyzed hazelnut shells, it is clear that the nano/micro particles significantly altered the post-cracking behavior (Figure 3, orange curve): the deformation that corresponds to the appearance of the first crack, is much lower than that recorded in complete rupture, as typically occurs in a ductile material.

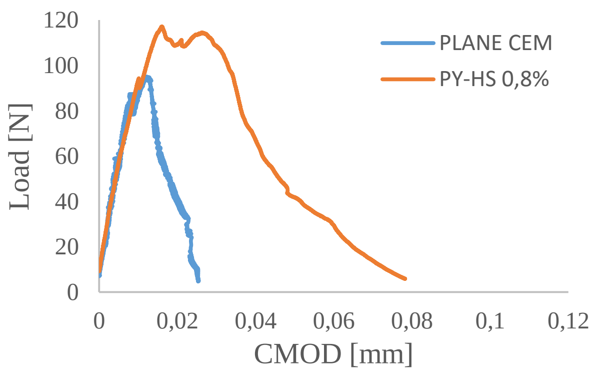

Figure 3: Load-CMOD curve, results for TPB tests.

From Figure 3, it quickly becomes clear that, besides the difference in terms of post-cracking behavior, the nano/micro particles are able to give to the cement a better mechanical behavior, especially as regards flexural strength that increases considerably.

This is probably due to the surface-area-to-volume (SA/V) ratio: in fact, if the size tends to nanoscale, the specific surface area tends to increase and a higher SA/V ratio means a larger contact area between the particles and the surrounding matrix, hence higher interaction with the matrix and more efficient reinforcing. Furthermore, the results indicate that the flexural strength improves with the maximum increment occurring at 0,8% inclusion, both in 7 days tests that in 28.

By bending tests, it was possible to study the fracture energy G_F of experimental specimens. In particular, in this research the JCI-S-001 standard was used to study the G_F, by analyzing the area below the load-CMOD curve. Results (Figure 4) for the micro-reinforced cements with char of hazelnut shells showed that the magnitude of the increase is substantial, even reaching an increase about 130% compared to plane cement (in the case of percentage of addition of 0,8%).

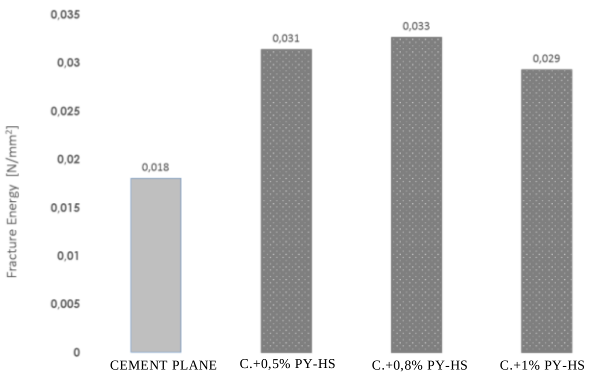

Figure 4: Fracture Energy GF

To obtain confirmation regarding the capacity of the bio-char to contribute in the process of stopping the fracture, were studied by FESEM the fracture surfaces of two sample, cement paste and micro-reinforced cement with 0,8% added of pyrolyzed hazelnut shells. As shown in Figure 5, the fracture is linear in plane cement, while in the case of the specimen with the addition of pyrolized char (Figure 6) the particles behave as attractors of fracture, since they can be seen as the inhomogeneity within the cement paste. These particles, being composed of carbon, have the property of deviating the trajectory of the fracture, forcing it in some way to generate a much more articulated and tortuous path and much less linear than the typical brittle fracture of the cement. From this, it derives the change of the post-peak material behavior, during the bending tests, and the increased ability to absorb energy before failure on the part of the material. Another factor to consider is the shape of the particles: in fact, prove to be very jagged and irregular in shape, providing a snug fit to the cement paste.

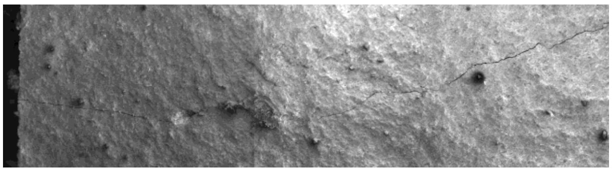

Figure 5. Crack path on cement paste surface

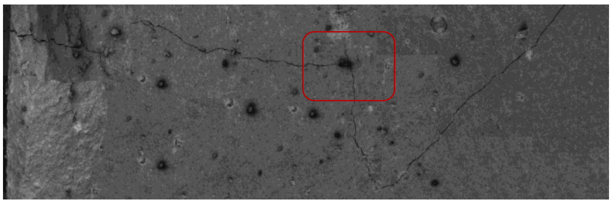

Figure 6. Crack path on PY_HS cement surface.

6 CONCLUSIONS

The main objectives of this research work was to investigate the use of food waste as "green" inert into the cementitious-based composites. Probably, the future challenge in construction will most likely be to get a traditional building material with better performance and less energy consumption.

In particular, pyrolysis is a promising approach that can be used to convert biomass wastes into energy, in the form of bio-oil, bio-char, and syngas. The Pyrolyzed micro-particles are very useful to enhance mechanical properties of cement composites and, having a low cost, they can contribute to produce building materials in a more sustainable way, inducing a reduction of energy consumption and a reduction of CO_2 emissions. Results showed an increase of the mechanical properties of experimental cements, especially a substantial improvement of strength, toughness and ductility. Furthermore, mechanical properties are very improved to certain specific content of carbonized nano-micro materials (0,8% with respect the weight of cement). Pyrolyzed nano/micro particles can interact with the fracture evolution by means the "overlapping effect". Moreover, they are strong enough to change the path and the growth of micro-cracks, thus increasing the fracture surface and consequently the fracture energy.

REFERENCES

[1] Ferro, G., Tulliani, J.M., Lopez, A., Jagdale, P. 2015. New cementitious composite building material with enhanced toughness. *Theoretical and applied fracture mechanics* 76:67–610.

[2] Regione Piemonte, Progetto di ricerca & innovazione per il miglioramento della sostenibilità della filiera agroalimentare piemontese: ECOFOOD (2010-2013).

[3] Yang, S.I., Wu, M.S., Wu, C.Y. 2014. Application of biomass fast pyrolysis part I: Pyrolysis characteristics and products. *Energy* 6: 1-10.

[4] Arancon, R., Lin, C.S.K., Chan, K.M., Kwan, H.T., Luque, R., 2013. Advances on waste valorization strategies: news horizons for a more sustainable society. *Energy Sci Eng 1*; pp. 53-71.

[5] Lin, C.S.K., Pfaltzgraff, L.A., Herrero-Davila, L., Luque, R. et al., 2013. Food waste as a valuable resource for the production of chemicals, materials and fuels. Current situation and perspective. *Energy Environ Sci 6*; pp. 426-464.

[6] Luque, R., Clark, J.H., 2013. Valorisation of food residues: waste to wealth using green chemical technologies. *Sustain Chem Process 1*; p. 10.

[7] Choi, W.C., Yun, H.D., Lee, J.Y., 2012.

Mechanical properties of mortar containing biochar from pyrolysis. *Journal of the Korea for structural maintenance inspection 3*; pp. 67-74.

[8] Constantinides, G., Ulm, F.-J., 2004. The Effect of Two Types of C-S-H on the Elasticity of Cement-Based Materials: Results from Nanoindentation and Micromechanical Modeling. *Cement and Concrete Research 34*; pp. 67-80.

[9] Dolado, J. S., Campillo, I., Erkizia, E., de Miguel, Y. R., de Ibarra, Y. S., Porro, A., Ayuela, A., 2005. Effects of Nanosilica Additions on Cement Pastes. *Concrete Design*; pp. 87-96.

[10] Fan, J.-J., Tang, J.-Y., Cong, L.-Q.,Mcolm, I. J., "Influence of Synthetic Nano-ZrO2 Powder on the Strength Property of Portland Cement", Jianzhu Cailiao Xuebao, 7, pp. 462-467, 2004.

[11] Hui, L., Hui-Gang, X., Jinping, O., 2004. A Study on Mechanical and Pressure-Sensitive Properties of Cement Mortar with Nanophase Materials", *Cement and Concrete Research 34*; pp. 435-438.

[12] Hui, L., Hui-Gang, X., Jie, Y., Jinping, O., 2004. Microstructure of Cement Mortar with Nano-Particles. Composites Part B. *Engineering 35*; pp. 185-189.

[13] Li, G., 2004. Properties of High-Volume Fly Ash Concrete Incorporating Nano-SiO2. *Cement and Concrete Research 34*; pp. 1043-1049.

[14] Li, G., Wang, Y.P.M., Zhao, X., 2005. Mechanical Behavior and Microstructure of Cement Composites Incorporating Surface-Treated Multi-Walled Carbon Nanotubes. *Carbon 43*; pp. 1239-124.

[15] Li, G., Wang, Y.P.M., Zhao, X., 2007. Pressure-Sensitive Properties and Microstructure of Carbon Nanotube Reinforced Cement Composites. *Cement and Concrete Composites 29*; pp. 377-382.

[16] Li, H., Zhang, M.H., Ou, J.P., 2006. Abrasion Resistance of Concrete Containing Nano-Particles for Pavement. *Wear 260*; pp. 1262-1266.

[17] Li, H., Xiao, H.G., Ou, J.P., 2004. A Study on Mechanical and Pressure-Sensitive Properties of Cement Mortar with Nanophase Materials. *Cement and Concrete Research 34*; pp. 435-438.

[18] Manzur, T., and N. Yazdani, 2010. Strength Enhancement of Cement Mortar with Carbon Nanotubes: Early Results and Potential. *Journal of the Transportation Research Board 2142*; pp. 102-108.

[19] Metaxa, Z. S., Konsta-Gdoutos, M. S., Shah., S.P., 2010. Carbon Nanofiber-Reinforced Cement-Based Materials. *Journal of the Transportation Research Board 2142*; pp. 114-118.

[20] Murray, S.J. Subramani, V.J., Selvam, R.P., Hall, K.D., 2010. Molecular Dynamics to Understand the Mechanical Behavior of Cement Paste. *Journal of the Transportation Research Board 2142*; pp. 75–82.

[21] Musso, S., Tulliani, J.M., Ferro, G.A., Tagliaferro, A., 2009. Influence of carbon nanotubes structure on the mechanical behavior of cement composites. *Composites Science and Technology 69*; pp. 1985-1990.

[22] Ferro, G.A., Ahmad, S., Khushnood, R.A., Restuccia, L., Tulliani, J.M., 2014. Improvements in self-consolidating cementitious composites by using micro carbonized aggregates. *Fracture and Structural Integrity 30*; pp.75-83.

[23] Ferro, G.A., Ahmad, S., Khushnood, R.A., Restuccia, L., Tulliani, J.M., Jagdale, P., 2015. Modified fracture properties of cement composites with nano/micro carbonized bagasse fibers. *Fracture and Structural Integrity 34*, pp.534-542.

[24] Ahmad, S., Khushnood, R.A., Jagdale, P., Tulliani, J.M., Ferro, G.A., 2015. High performance self-consolidating cementitious composites by using micro carbonized bamboo particles. *Materials and design 76*; pp.223-229.

[25] Ahmad, S., Ferro, G.A., Khushnood, R.A., Restuccia, L., Tulliani, J.M., Jagdale, P., 2015. Crack path and fracture surface modifications in cement composite. Fracture and Structural Integrity 34; pp.524-533.