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New Concepts for Next Generation of High Performance Concretes

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Abstract

With the development of high-speed railway, long span bridges and high-rise buildings, new concretes need to increase strength and toughness. Adding fibers to concrete matrix has been long recognized as a way to enhance the energy absorption capacity and crack resistance of the plain concrete. In recent years, particular attention has been paid to the distribution of fibers: very small and well dispersed fibers may control the microcracks in the matrix from the very beginning of their opening and particularly high deformability of the composite may be obtained [3-5]. Carbon nanotubes (CNTs) used as reinforcing fibers has been also explored [6-8], the functional effect of their addition in a concrete equals to the one obtained with the addition of fibers. CNTs also provide a better ductility and an increase of the fracture energy. However, agglomeration and the relative high price seem to limit their application in cement based composite materials [14]. In this work, the potential beneficial effects of carbon micro/nanoparticles addition to cement pastes for improving the mechanical properties of the resulting composites has been investigated [15]. Pyrolyzed polyethylene beads (CNBs) and coconuts shells (Cocos nucifera, CCNs) were produced at Politecnico di Torino and characterized by Raman spectroscopy, thermogravimetry and scanning electron microscopy (SEM). When added to cement paste, up to 0.08 wt%, both materials were effective in increasing the cement matrix compressive strength and toughness. From SEM observations it is evident that the presence of these small particles disturb the propagation of microcracks, which has to deviate from its trajectory and has to follow the carbon nano/micro-particles contour. This mechanism increases strongly the fracture surface during the test performed by imposing the monotonic increment of crack opening. Crack and crack pinning are the mechanisms which can explain the increase of toughness in the composite samples.

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1. Introduction

Concrete is the most used man-made material in the world. According to statistical data, updated to the year 2006, about 7.5 billion cubic meters of concrete are made each year, that corresponds to more than one cubic meter for every person on Earth [1]. However, concrete is a brittle material with a cement paste binder having a pore structure that contains micro (<2 nm in diameter) and fine mesoporosity (2–50 nm). Depending on its constituents, it can be very strong in compression (>200 MPa ultimate strength), but it presents generally a low resistance in traction and a limited bending strength. It is characterized by a relatively low fracture toughness. However, with the development of high-speed railway, long span bridges and high-rise buildings, new concretes need to increase mechanical properties such as strength and toughness. Studies show that cement, aggregate and mineral admixture can improve the toughness of concrete, but the effect is not obvious.

Adding fibers to concrete matrix has been long recognized as a way to enhance the energy absorption capacity and crack resistance of the plane concrete. Therefore, fibers have been added to concrete for almost 50 years to increase its tensile and flexural strength, but for different types of fiber, the effect of toughness improvement is different, and some fibers reduce the workability of concrete. The influence of fibers on brittle matrix behavior may be reduced to two points: the control of crack propagation and the increase of the ultimate strain. The role of fibers depends on their volume, aspect ratio, strength and bond to the matrix [2]. In recent years, particular attention has been paid to the distribution of fibers: very small and well dispersed fibers may control the microcracks in the matrix form the very beginning of their opening and particularly high deformability of the composite may be obtained [2]. In particularly, microfibers can interact with the fracture evolution by arresting the growth of microcracks and can delay the propagation of microcracks, thus impeding their coalesce to form the first macrocrack.

In this research work, Pyrolyzed polyethylene beads (CNBs) and Coconuts shells (Cocos nucifera, CCNs) has been used as reinforcing fibers for improving the mechanical properties of the resulting composites and has been also explored the functional effect of their addition in the cement matrix.

2. Research significance

2.1 Crack and fracture energy in concrete

Cracks open or propagate under local stresses, which furnish the amount of energy necessary for rupture of material bonds and for the creation of new surfaces [3]. The replacement of a single crack by multiple cracks and microcracks is beneficial for the increase of strength and stiffness, the increase of fracture toughness, the improvement of durability through increased impermeability, etc…

In composite materials, crack propagation is blocked by various kinds of inclusions: aggregates grains, pores, voids and fibers [3]. On the crack path, the tensile strength of the matrix itself and its bond to inclusions must be overcome. The strength of the matrix against cracking is relatively low, and the abovementioned non-homogeneities help to control cracks by increasing their length. All these obstacles stop the cracks by arresting their propagating tips. These phenomena considerably increase the energy required for crack development and failure of the element, and are used in all methods of crack control. When a crack meets one of the abovementioned obstacles, it is stopped and a new input of energy by increase of load is required for its further propagation. Then, the crack may pass across the obstacle or may contour it to follow another path along a weaker region or layer [3]. A crack may then be divided into several finer cracks; that is, crack branching is induced at an obstacle. Additional energy is also used for breaking the grain or for destroying the bond strength in the interface around it. All kinds of inhomogeneities, which produce crack deviation, branching or multiplication increase the total area of fracture surface which becomes several times the area of the cross-section of the element [3].

Moreover, it is known in the literature that fine aggregates addition to cement paste matrix increases the fracture toughness [11] and this increase in fracture energy must be related to the occurrence of aggregate/ligament bridging in mortar [12]. In concrete, fracture energy increases with specimen size and maximum aggregate size. Thus, the key to toughening lies in understanding how cracks intercept aggregate zones and this in turn is influenced by the nature of the interfacial bond between the aggregate and the matrix [13]. If the particle is fully bonded to the matrix there is no guarantee that the toughness is increased. This may be due to the crack detaching from the aggregate

early and not allowing the formation of a bridge. There is also no basis for toughening when the aggregate is spherical, whether bonded or unbonded to the matrix, because there is no irregularity in shape and consequently no pinning points.

3. Experimental details

3.1 Preparation of specimens

CNBs are produced by chemical vapour deposition (CVD) using low-density Polyethylene (LDPE) as a precursor. The process has been described elsewhere [9]. The precursor PE was hosted in small boats, made of stainless steel AISI grade 316, which acted as a catalyst of the CVD synthesis as well [9]. A pressure of 3 bars was fixed inside the reacting chamber while the temperature was maintained in the range 750 to 850°C and an inert carrier gas was used in the experiment. The CNBs material produced by the CVD process were collected from the steel 316 boats by scrubbing, and then reduced manually to powder by means of an agate mortar and an agate pestle. Once ground, CNBs were collected in a laboratory plastic container. The process was repeated for each of the six CNBs Chemical Vapour Deposition production batches and for each of them preliminary FE-SEM observations (Zeiss Supra 40) were carried out. Before starting the specimens production, all CNBs produced were mixed together by means of a mortar and a pestle, and finally collected in the storage container.

CCNs are low-cost carbon materials obtained starting from coconuts shells broken in small pieces and then, soaked for 24h in a solution made of iron oxide and ammonium hydroxide. This soaking process allowed the coconut shell making the fibres free. These fibres were then dried in an oven at 80°C for one hour and pyrolysed in a furnace under an inert atmosphere in the temperature range 800-900°C at the ambient pressure. The process for producing CCNs is simpler and more efficient than the one employed for CNBs preparation.

3.2 Concrete specimens casting and curing

Carbon micro/nanoparticles were first added and mechanically dispersed in the water required for the cement pastes mixing and then, sonicated for three hours before mixing with cement. Surfactants were also used to this aim. In our case, Mapei Dynamon SP2 was added to the water in an amount of 1.5 wt% with respect to cement. After preliminary tests, the water to cement ratio (w/c) used was 0.30, as a good compromise between the workability of the fresh cement paste and the mechanical strength of the hardened samples. Type I ordinary Portland cement 52.5 R (according to EN197/1 standard; manufactured by Buzzi Unicem, Italy) was used as the binder. Beams of 20 x 20 x 75 mm^3 were then cast into plexiglass^{TM} molds. On the basis of Shah et al. results on MWCNTs added to cement pastes [15], the amount of used carbon micro/nanoparticles was kept below 0.08 wt% with respect to cement. Specifically, the prepared samples contained 0.025, 0.05 and 0.08 wt% of carbon micro/nanoparticles.

Curing of the specimens was done in accordance with the guidelines of Standard C192/C192M Practice for Making and Curing Concrete Test Specimens. Cement test samples were removed from the moulds, after 24 h, and then cured in a temperature and humidity controlled room for 27 days. At the end of the curing time and before cutting the notch required for the three-point flexural test, the cement specimens were weighed and their density was determined. The notches were made using a Remet Type TR100S saw, with a 2 mm thickness diamond cut-off wheel. Notches were cut on a single specimen at the time. Notch depth was equal to 6.8 mm.

3.3 Instrumentation

Raman analysis were carried out on carbon micro/nanoparticles using a micro-Raman spectrometer (Olympus BH-2 UMA, Japan) equipped with a CCD detector. Green laser (514 nm) line was used to excite the sample. Depth profile and mapping of a selected area was also obtained with Raman spectrometer. All the measurements were performed at room temperature. Thermo-Gravimetry analysis (TGA) under air in a static mode with a heating ramp of 10°C/min up to 800°C (Mettler-Toledo) was also used on carbonaceous materials. The results were evaluated by using Star 9.20 software TGA.

The test equipment used for mechanical characterization was manufactured by MTS Systems Corporation (Eden Prairie, Minnesota, USA). It is a servo-hydraulic test equipment with control of load, stroke and strain. For three-points bending tests, the beams were loaded in correspondence of the central section up to failure. The tests were performed in Crack Mouth Opening Displacement mode (CMOD). In other words, the load was function of the monotonic increase of the opening crack length. In our case, a clip-on gauge was used to control the displacement at

gap level during loading in order to determine the fracture energy. Specifically, the clip-on gauge MTS Model 632.03F-030 was employed. Installation of the clip-on gauge was done by means of two knives bolted on two intermediate bases glued on the specimen itself at the two sides of the notch. The gap between the knives was equal to 6 mm. Data sampling is adjustable and data were recorded at 10 Hz into a specific database by the MTS test machine PC. Complementary to the MTS machine data a back-up data base is recorded at 1 Hz by CatMan system which provides a real time graphics interface for the test operator.

3.4 Testing

The fracture energy is defined as the post-crack energy absorption ability of the material and it represents the energy that the structure will absorb during failure. The specific fracture energy, G_f (J/m^2), was calculated as the area under the force–displacement curve up to a defined displacement of 1.5 mm divided by the area of the fracture plain [10].

Compressive strength was also determined on 20 x 20 x 37.5 mm^3, by-products of the previous STM C 348 flexural test, in accordance to STM C 348 compressive strength standard. The testing machine was equipped with two steel bearing blocks with hardened faces. One bearing block was spherically seated and the other rigidly mounted. The testing machine was accurate with a tolerance of ± 1.0% of the compressive strength of the specimen. The load was applied with a speed of $5 \cdot 10^{-4}$ mm/s.

4. Results and discussion

4.1 Mechanical properties

The average density was 2.09 ± 0.01, 2.10 ± 0.03 and 2.10 ± 0.04 g/cm^3, respectively for plain cement, CNBs and CCNs-based prisms, demonstrating the rather good homogeneity of the prepared samples. The trend of the fracture energy (G_f) in function of CNBs content demonstrates that the higher the carbonaceous material added, the higher the fracture energy is: 9.64 ± 4.06, 11.21 ± 5.01, 11.92 ± 4.61 and 16.41 ± 6.28 J/m^2, respectively for plain cement, 0.025, 0.050 and 0.080% CNBs additions. The linear interpolation of the plot of the fracture energy vs CNBs amount indicates an increment over the investigated interval of around 72.90 J/m^2 per 0.01% addition of CNBs to the cement composite sample. Moreover, within the limits of the present work, the results support the idea that CNBs addition to cement increases the mechanical strength of the resulting composites too (Figure 1): 174.9 ± 35.8 N, 203.4 ± 43.4, 201.7 ± 5.6 and 207.6 ± 22.3 N, respectively for plain cement, 0.025, 0.050 and 0.080% CNBs additions.

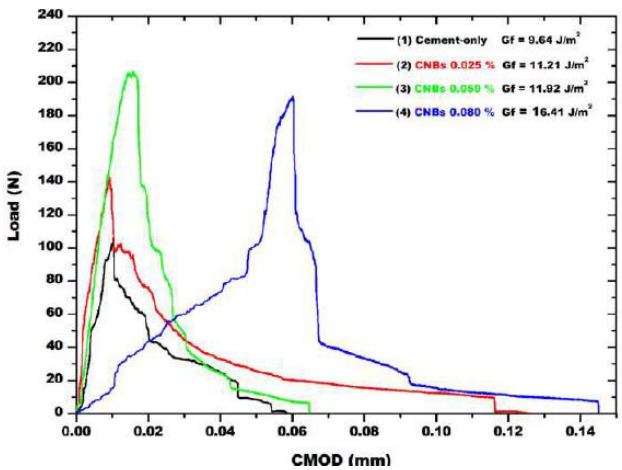

Fig. 1. Cement-CNBs composites: Fracture Energy (G_f) vs Load in function of the CMOD aperture.

The trend of the fracture energy (G_f) in function of CCNs content demonstrates that the higher the carbonaceous

material added, the higher the fracture energy is: 9.64 ± 4.06, 11.90 ± 2.01, 15.84 ± 2.25 and 17.29 ± 3. 20 J/m^2, respectively for plain cement, 0.025, 0.050 and 0.080% CCNs additions. The linear interpolation of the plot of the fracture energy vs CNBs amount indicates an increment over the investigated interval of around 104.80 J/m^2 per 0.01% addition of CCNs to the cement composite sample. Moreover, within the limits of the present work, the results support the idea that CNBs addition to cement increases the mechanical strength of the resulting composites too (Figure 2): 174.9 ± 35.8 N, 219.8 ± 26.7, 210.4 ± 21.9 and 145.3 ± 22.3 N, respectively for plain cement, 0.025, 0.050 and 0.080% CCNs additions.

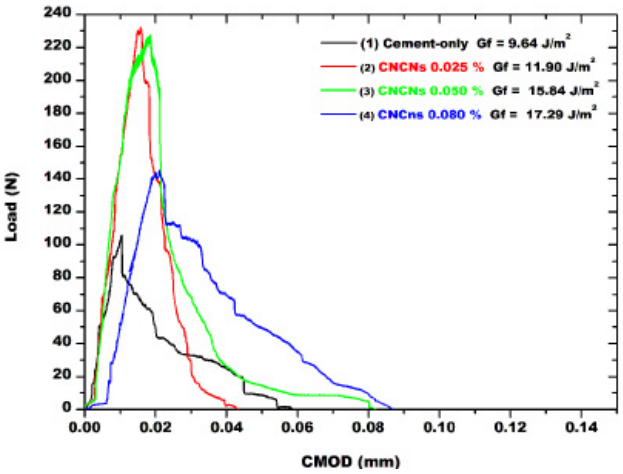

Fig. 2. Cement-CCNs composites: Fracture Energy (G_f) vs Load in function of the CMOD aperture.

To conclude, in the studied composition interval plain cement-cement up to 0.080% CNMs the fracture energy G_f has quite doubled after an addition of 0.08% of CNBs or of CCNs.

Mechanical characterization results demonstrated that addition of CNBs to cement paste increased notably the fracture energy. This result led us to believe that these CNBs would be found mainly in the vicinity or within the fracture surface cracks. However, FE-SEM observations did not support completely this hypothesis: CNBs are hosted sparsely in the matrix within the CSH (calcium silicate hydrates) crystals and the hydrated lime (portlandite, CH) and some particles were found sometimes in the vicinity, or within, the sample cracks. To conclude, some ambiguities still remain in order to support the theory that this kind of CNMs interacts within the CSH crystals of the matrix in order to prevent and eventually arrest microcracks. On the contrary, in the case of the cement CCNs-based samples FE-SEM observations (Figure 3) have evidenced that carbon nano/microparticles were structurally imbedded in the cementitious matrix and were present within the fracture path. Within the limit of the test program carried out, mechanical characterization results demonstrated that addition of CCNs to cement paste increased notably the fracture energy and the nominal strength. The rather limited presence of cement paste residue onto CNBs seems to indicate a weak interaction between the carbonaceous reinforcement particle and the cementitious matrix.

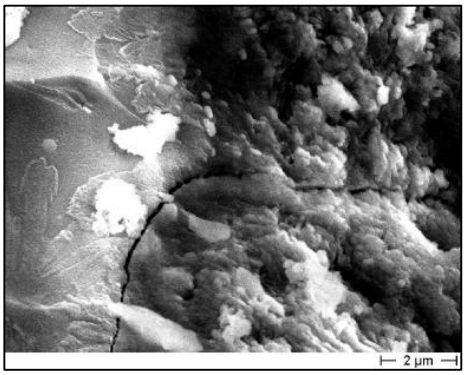

Fig. 3. FE-SEM micrograph of CCNs embedded in the cementitious matrix.

5. Conclusion

In this work, carbon nano/micro-particles were prepared from polyethylene beads and coconuts choir by CVD process and controlled pyrolysis, respectively. These particles proved to be spherical and interconnected for the CNBs, while the CCNs were irregular in shape, as the result of the grinding step. When added to cement paste, up to 0.08 wt%, both materials proved to be effective in increasing the cement matrix compressive strength and toughness. These particles proved to be spherical and interconnected for the CNBs, while the CCNs were irregular in shape, as the result of the grinding step. When added to cement paste, up to 0.08 wt%, both materials proved to be effective in increasing the cement matrix compressive strength and toughness.

The dependence of the aggregate shape on toughening is critical and angular grains are needed to produce effective aggregate-bridging. In our case, from what observed by means of FE-SEM, we believe that CCNs contouring by the crack and crack pinning are the mechanisms which can explain the increase of toughness in the composite samples.

Without an irregular shape, spherical aggregates are not able to prevent crack face separation [13]. However, in the case of CNBs, though these particles are smooth and almost perfectly spherical, there are also interconnected, therefore, they are effective in crack-bridging.

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