Carbon Nano Beads (CNBs): a new ingredient in reinforcing materials

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ABSTRACT. The on-going research on carbon nano beads (CNBs) are focusing on applications ranging from high strength composites, catalyst carriers, lubricants, electronic devices, weather resistant materials, molecular ball bearings, drug delivery vehicles (Bio-medical), semiconductors/transistors, high-capacity batteries and Hydrogen reservoir for the automotive industry. The commercial applications of CNBs are novel and yet immature for market. Experimental activity concerning a Research Program on Polymer-carbon nano tubes (CNTs) composite included also a limited number of test specimens prepared with CNBs. These specimens highlighted an increase in tensile strength visibly over the average results of the Polymer-CNTs composite tested in the same program. This result was considered indicative of a prospective CNBs adoption in new composites. Carbon group in Politecnico di Torino initiated an in-house small-scale research aimed to define and test a cost effective synthesis process of CNBs. The next step is the use of these CNBs in obtaining different kind of concretes and mortars, trying to enhance mechanical properties. The experimental tests on these materials are going to start during the redaction of the present paper.

KEYWORDS. CNBs; Nano-Fiber reinforced materials; Nanomechanics of concrete.

INTRODUCTION

While carrying out experimental activity concerning a Research Program on Polymer-carbon nano tubes (CNTs) composite, a limited number of test specimens were prepared using CNBs instead of CNTs. Results of mechanical characterization of these specimens highlighted an increase in tensile strength around 1.6 times over the average results of the Polymer-CNTs composite tested previously. Following this observations, which cast a new light on the possible use of CNBs for a new generation of composites, Carbon group at Politecnico di Torino initiated an in-house small scale research aimed to define and test a cost effective synthesis process of CNBs.

The researches presently on going on CNBs are focusing in fields of application ranging from high strength composites, catalyst carriers, lubricants, electronic devices, wear resistant materials, molecular ball bearings, to drug delivery vehicles (Bio-medical), semiconductors/transistors, high-capacity batteries and Hydrogen reservoir for the automotive industry. The commercial applications of Nano beads are novel and yet immature in their applications. Carbon Nano-beads literature is not very prolific, insights can be found, for instance, in [1-5].

The discovery of fullerenes [6] has led to an upsurge interest in the structures and shapes of carbon containing materials, in particular when the carbon are in the "nano" regime [7, 8]. In the past two decades many differently shaped carbon nanostructures have been synthesized and characterized, and their properties in a range of different environments were studied.

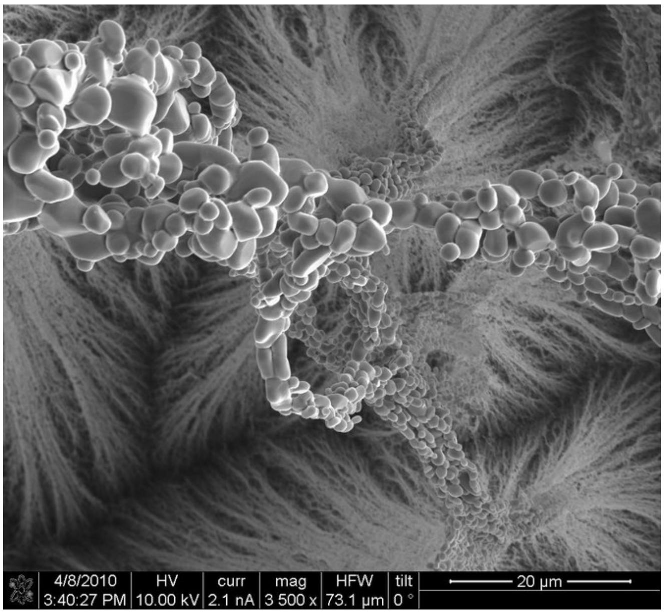

Figure 1: CNT coated with Nano-beats. In many instances CNBs have been synthesized accidentally as a byproduct in the synthesis of CNTs by chemical vapor deposition (CVD).

Most of these differently shaped nanostructures cannot be classified as diamond or graphite; therefore, a classification of carbon on the basis of ratio of sp^2 to sp^3 carbon atoms present in the material may be more appropriate than the conventional classification [1]. Following these considerations it is possible to classify carbon into three forms: diamond (100% sp^3), intermediate carbon (with different ratios of sp^2 to sp^3 carbon atoms), and graphite (100% sp^2), all forms of carbon fall into one of these three categories. *Carbon Nano beads fall into the intermediate group of carbon because they contain different ratios of* sp^3 *to* sp^2. Although carbon spheres have been known for decades, studies on the synthesis of spherically shaped carbon has become topical in the last few years. These spherically shaped materials have been referred to as *nano-sized carbon spheres* [9-12], carbon nano beads [13], carbon spherules [14], nano balls [15], carbon pearls, or simply as hollow nano spheres [16]. In many instances CNBs have been synthesized accidentally as a by-product in the synthesis of CNTs by chemical vapour deposition (CVD) (Fig. 1). The interest in products made of graphitic carbon relates to their high strength, high thermal resistance, lightweight and conductivity. Further, carbon spheres have also been used in high strength composites, catalyst carriers, lubricants, electronic devices and as wear resistant materials [17].

CNBs DOCUMENTED SYNTHESIS METHODS

Puri et al. [3] prepared by CVD process a thick films of carbon nano beads out of Brassica nigra oil[1] at 850 C. Micro-Raman spectroscopy, scanning electron microscopy, transmission electron microscopy and Fourier transform infrared spectroscopy were used to characterize the product. The as synthesized carbon nano beads displays a spherical morphology with diameters of 0,6÷2,5 mm and have the wall thickness of ≈ 100 nm. An absorption properties study of as-prepared film in Ku-band shows the maximum absorption bandwidth of 0,8 and 0,6 GHz, with absorption efficiency of ≈ 75÷90%. Rajesh Kumar et al. [5], used Castor[2] oil (combination of fatty acids) precursor, containing hydrocarbon with less amount of oxygen first time for synthesis of different carbon nanostructures. The agglomerated carbon nanoparticles, carbon Nano beads and carbon tubular structure were synthesized by applying CVD method at different temperature using castor oil as new carbon precursor without any catalyst. The synthesis of carbon nanostructures is free from additional catalyst as this hydrocarbon, castor oil, is cheap with abundant sources of carbon.

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[1] *Brassica nigra oil, also called Mustard oil, is extracted from the black mustard seeds, which have been macerated in warm water by steam or water distillation. The main chemical component of mustard oil is no less than 92% allyl isothiocyanate.*

[2] *Castor oil is a vegetable oil obtained from the castor bean (technically castor seed as the castor plant, Ricinus communis (Euphorbiaceae). Castor oil is a colorless to very pale yellow liquid with mild or no odor or taste. Its boiling point is 313 °C (595 °F) and its density is 961* kg/m^3*. It is a triglyceride in which approximately 90 % of fatty acid chains are ricinoleic acid, Oleic and Linoleic acids are the other significant components.*

The effect of pyrolysis temperatures on the size, quality and quantity of the synthesized carbon shape were also investigated. Interestingly, the morphology of the carbon nanostructures can be controlled in shape from agglomerated carbon nanoparticles to Nano beads to carbon tubular structure just by increasing the temperature from 750 °C to 800 °C to 850 °C, respectively. These Nano beads are chains of uniform size of graphitized carbon spheres. These chains comprised individual carbon particles size of around 450 nm. The products were characterized by X-ray powder diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR). Maheshwar Sharon and Madhuri Sharon [19], synthesized for the first time, by pyrolysing camphor vapour at 1000 C in an argon atmosphere, using ferrocene, as catalyst, spherical carbon Nano beads (solid and hollow) of two sizes of around 500÷850 nm (large) and 250 nm (small). The EEL spectrum suggests the carbon beads to be non-graphitic and these are covered by a graphitic shell of 80÷100 nm, revealed by transmission electron microscopy (TEM) micrograph. The outer shell interconnects the larger beads, more than 10. After covering the train of carbon, the beads take the shape of fibrous graphitic carbon, which perhaps gives the spongy elastic character to the material. The average surface area of the Nano beads determined by BET studies was estimated to be 16 m^2/g. It is suggested that this material may be a useful anode for secondary lithium ion batteries. Spherical shape is the shape adopted by materials during synthesis (growth, nucleation) [18] and is determined by considerations of energy minimization [19]. The circumference of bead is made of broken graphene sheet of about 80 nm thickness. The inner portion of the bead is made of amorphous carbon [1].

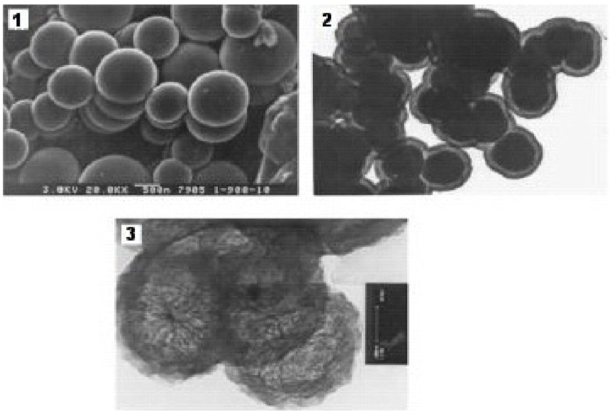

Figure 2: CNB images. Carbon Nano beads synthesized from camphor with the CVD process. (1) Solid carbon Nano beads. (2) The inner portion is amorphous, and the circumference is made of graphitic carbon and is interconnected. (3) Carbon Nano beads with a graphitic surface and an inner mesh-type structure [20].

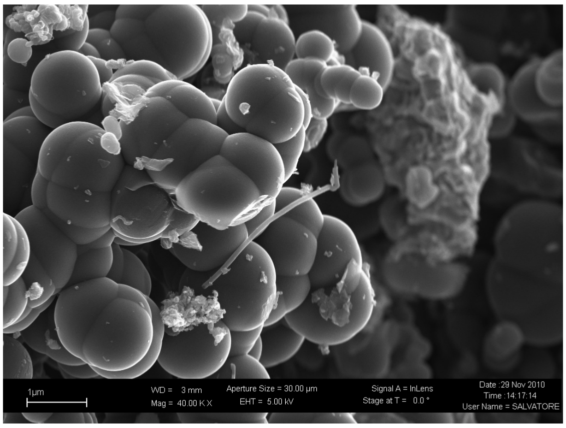

Figure 3: FE-SEM of Carbon Nano beads, utilized previously at the Polytechnic of Turin in the context of mentioned Program on Polymer-carbon nano tubes (CNTs) composite.

S. Maheshwar and colleagues [20] have been able to synthesize various types of carbon Nano beads, Fig. 2 refers, through pyrolysis of camphor. Solid beads staggered together like a collection of soccer balls (Fig. 2-1), could be obtained by using cobalt nano-size powder as a catalyst during the pyrolysis of camphor (Fig. 2). The circumference of nanobeads is made of broken graphene sheet about 80 nm in thickness. The inner portions of the beads (Fig. 2-2) are made of amorphous carbon and these beads are interconnected. Nano-beads shaped like wheels (Fig. 2-3) were obtained by using nano-size powder of Ni/Co alloy. Fig. 3 shows CNBs used for early testing at Polytechnic of Turin in the context of mentioned Program on Polymer-carbon nano tubes (CNTs) composite.

In the present overview of literature reported here, agglomerated carbon nanoparticles, carbon Nano beads and carbon tubular structure have been produced by CVD method using horizontal furnace. The method provides a means for the continuous production of high purity carbon Nano beads with uniform diameter in the absence of catalyst. Previously in other methods, such as hydrothermal method, pyrolysis of carbon sources and catalysts [21], arc plasma techniques [22], mixed-valence oxide catalytic carbonation [23] and reduction of carbides with metal catalysts have been reported for the synthesis of carbon spheres [24, 25].

The products of these processes were characterized by X-ray powder diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR).

CNBS SYNTHESIS METHOD

While CNTs have been widely used as reinforcement material for cement, there no evidence that the same has been researched using CNBs. It is expected that also CNBs would give to concrete and mortars an higher mechanical strength and improve durability in areas subject to corrosion and degradation from chemicals. Moreover, CNB-SCC or mortars may adapt well to any shape allowing flexibility in design of concrete structure and / or injectability when used for masonry wall consolidation. Their use should reduce production costs in comparison with presently used building / consolidation techniques. CNBs were synthetized with a CVD method. A general layout of the the laboratory CVD reactor used for CNBs production is schematically represented in the Fig. 4.

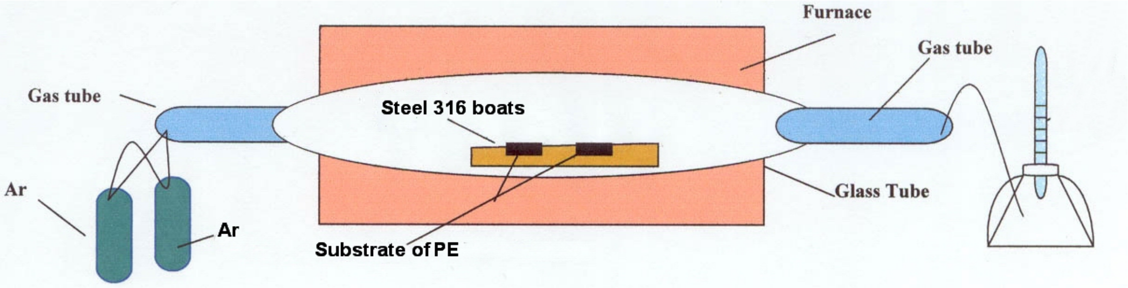

Figure 4: Basic scheme of the CVD apparatus utilized for CNBs synthesis.

It consists of a precursor delivery system, a reaction zone, a particle collector and a pumping system. The energy for the conversion of the reactants into nanoparticles is supplied an external furnace. A major difficulty associated with a CVS process is the identification / availability of appropriate precursor materials. Generally precursors used are metal-organics, in our case in order to synthetize CNBs industrial grade PE,[3] in form of fine dimensions particles, was used successfully. The precursor PE was hosted in small boats, of size compatible with the furnace, were made out of Steel 316, which thanks to his own composition[4], acted as catalyst of the CVD synthesis as well. The nanoparticles synthetized in the CVD process were extracted from the boats by means scrubbing. The most important process parameters determining the quality and usability of the nano-particles are the total pressure, typical range from 100 to 100000 Pa (0.00011 bar). The precursor material (decomposition kinetics and ligands determining the impurity level), the partial pressure of the precursor (determining the production rate and particle size), the temperature or power of the energy source, the carrier gas (mass flow determining the residence time) and the reactor geometry. In the present study CNBs are produced by Chemical vapor deposition (CVD) using linear density Polyethylene (LDPE) as a precursor.

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[3] *Polyethylene (PE) is a thermoplastic made from petroleum. It was the first grade of polyethylene, produced in 1933 by Imperial Chemical Industries (ICI) using a high pressure process via free radical polymerization.*

[4] *Grade 316 steel is the standard molybdenum-bearing grade, second in importance to 304 amongst the austenitic stainless steels. Thanks to its chemical composition, Fe, <0.03% C, 16-18.5% Cr, 10-14% Ni, 2-3% Mo, <2% Mn, <1% Si, <0.045% P, <0.03% S, it is able to act as catalyst in CNBs synthesis.*

The precursor holder is made out of Steel 316. As iron is a catalyst for the growth of carbon nanostructures this will favor CNB formation [26]. A pressure of 3 bars is maintained inside the reacting chamber while the temperature is maintained in the range 700÷850 °C. Inert carrier gases are used in the experiment.
The CNBs batches this paper is referring to were synthesized January 2012.
The batch, identified as FCPS-2, was synthesized January 11, 2012 (Fig. 5).

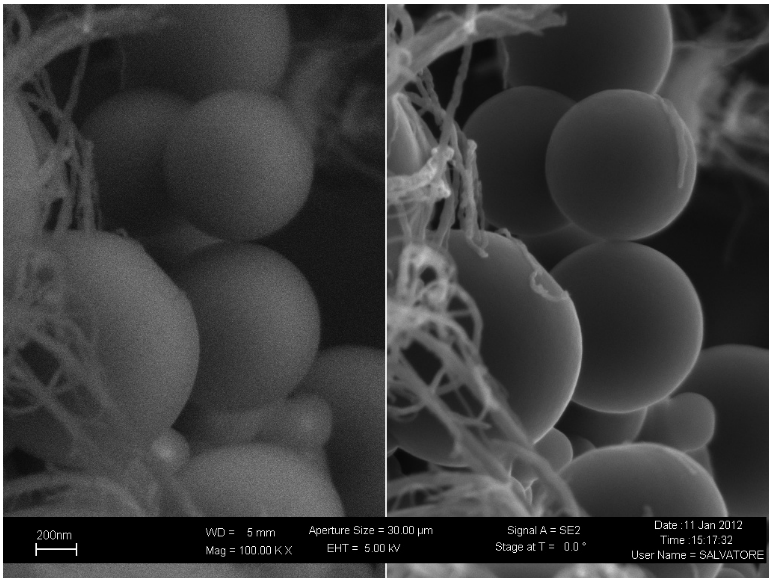

Figure 5: FE-SEM of CNBs Batch 2. Carbon nanobeads and limited quantity of Carbon nanotubes by-product of the CVD process.

The CNTs synthetized in this batch appear to be the by-product of the CVD synthesis carried out with the aim to produce CNB. FE-SEM characterization allow to identify CNBs, of the size between 600÷800 nm, and a limited quantity of CNTs with the apparent diameter of 80÷90 nm.
The obtained CNBs are analyzed with the help of FE-SEM, Micro Raman and Thermo-Gravimetric analysis (TGA).

DISCUSSION

The obtained CNBs were analyzed with the help of FE-SEM, Micro Raman and Thermo-Gravimetric analysis (TGA). Results of the analysis show that CNB are spherical and not hollow. They have diameters ranging from in 100nm to 1000 nm and are interconnected, *Fig. 6 refers.*

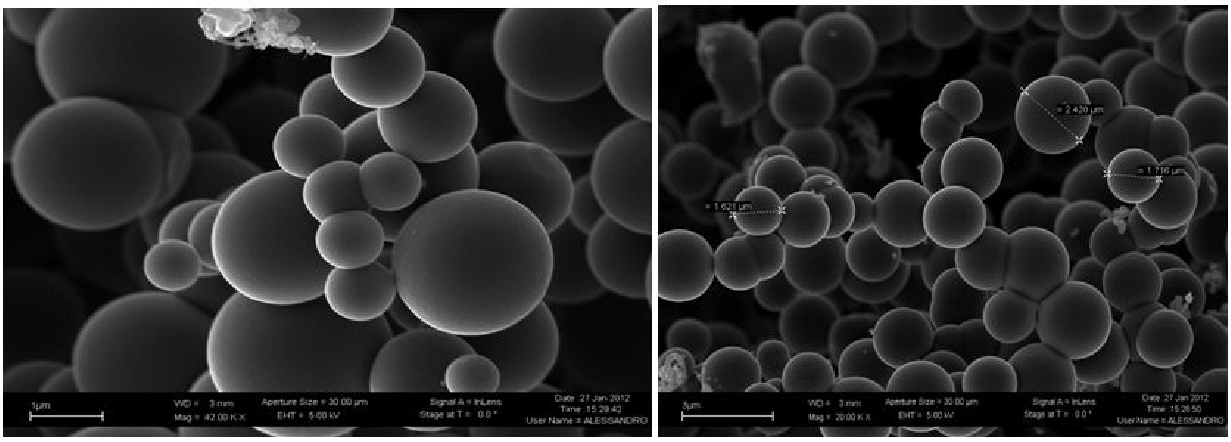

Figure 6: FE-SEM of Carbon nano beads (CNBs).

Raman analysis shows that the material is more graphitized with fewer defects in it (ID/IG=0.74), Fig. 7 refers. Thermo-Gravimetric analysis performed in air with a temperature ramp of 10 °C/min. CNBs degrade thermally after 550 °C and a 6÷7 % of impurities (amorphous carbon and metal residue) are found, Fig. 8 refers.

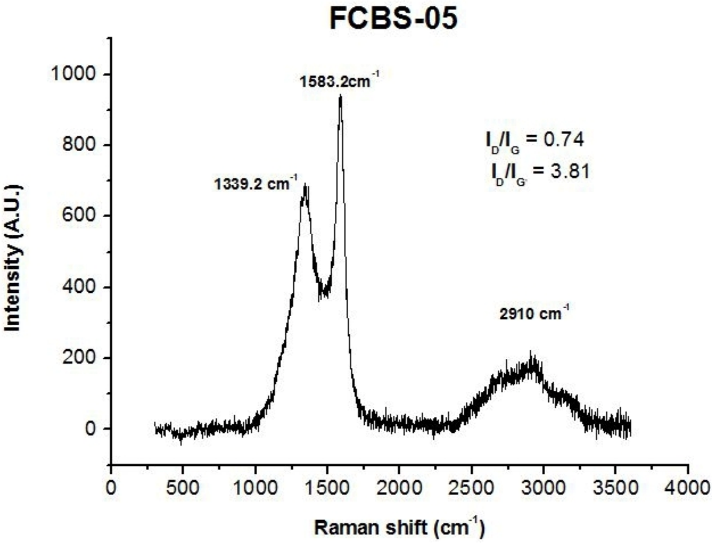

Figure 7: Raman analysis of CNBs.

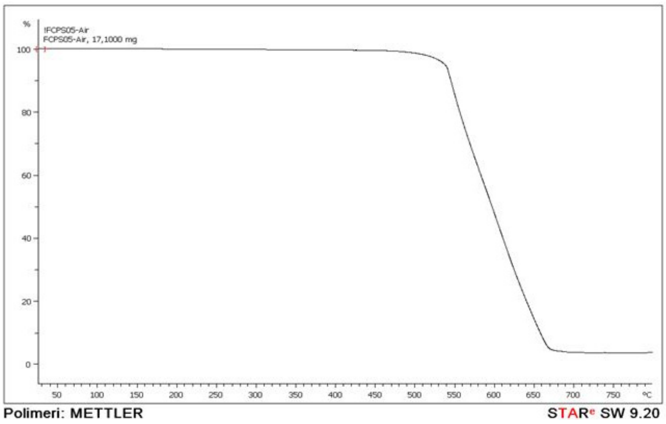

Figure 8: Thermo-Gravimetric analysis of CNBs.

CONCLUSIONS

The CNBs production set at laboratory scale at Politecnico di Torino, Dept. of Applied Science and Technology (DISAT), have demonstrated the effectiveness of the CVD- LDPE process. It is now considered worth to continue with a limited experimentation on CNBs and Concretes. While CNTs have been widely used in researches concerning reinforcement material for cement/concretes, there no evidence that the same kind of researches have been carried out using CNBs. It is expected that also CNBs would give to concretes and mortars an higher mechanical strength and improve durability in areas subject to corrosion and degradation from chemicals. In the next few months a small scale test program is going to be carried out at the Politecnico di Torino, Dept. of Structural Engineering, Construction and Soil Mechanics (DISEG), with the aim to define whether CNBs are suitable to act as reinforcers in concrete and if their contribution is comparable or better the one provided by the CNTs. Moreover, CNB-SCC or mortars may adapt well to any shape allowing flexibility in design of concrete structure and/or injectability when used for masonry wall consolidation. Their use should reduce production costs in comparison with presently used building / consolidation techniques.

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