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Ultra high performance cement-based composites incorporating low dosage of plasma synthesized carbon nanotubes

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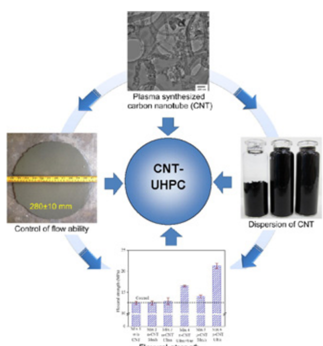
HIGHLIGHTS

- Use of plasma synthesized carbon nanotubes (p-CNTs) results in much improved dispersion and stability in cement system.
- p-CNTs dispersed uniformly through ultrasonication without the need of surfactant or surface chemical modification.
- This leads to significant enhancement in the flexural strength of UHPC reinforced with p-CNTs at low dosage.

GRAPHICAL ABSTRACT



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ABSTRACT

Ultra high performance cement-based composites (UHPCs) have gathered more attention and interest due to their excellent properties. In this study, a new type of carbon nanotubes (p-CNTs) synthesized by plasma process was used to modify the mechanical properties of UHPC at low dosage. The dispersion and sedimentation of p-CNTs were investigated and the mechanical properties of the resulting CNT modified UHPCs (CNT-UHPCs) were studied. The results showed that p-CNTs can be dispersed uniformly in water through ultrasonication without the need of surfactant or chemical modification on surface. In addition, the p-CNTs showed a much improved dispersion and stability as compared to the normal CVD synthesized CNTs. Well-dispersed p-CNTs greatly enhanced the flexural strength of UHPC from 12.5 to 21.2 MPa at a dosage of only 0.067% by the weight of cement. This highlighted the importance of dispersion of CNTs which not only improved the bridging efficiency but also reduced the CNT dosage and cost. All of these make the applications of nano-material feasible and more economical attractive.

1. Introduction

Recently, ultra high performance cement-based composites (UHPCs) have gathered more attention and interest due to their potential to enhance structural load capacity, to reduce member size, and to improve durability. UHPCs are characterized by ultra high compressive strength exceeding 150 MPa and extremely low transport properties [1,2]. The development of UHPCs is typically achieved by reducing the water-to-cement ratio, by adopting higher cement content, by improving the packing density through proper control of workability, and by using special processing and curing methods [3–5]. Another proposed method is to incorporate ultra fine functional particles into cement mortar to further improve the matrix packing and to reduce the porosity

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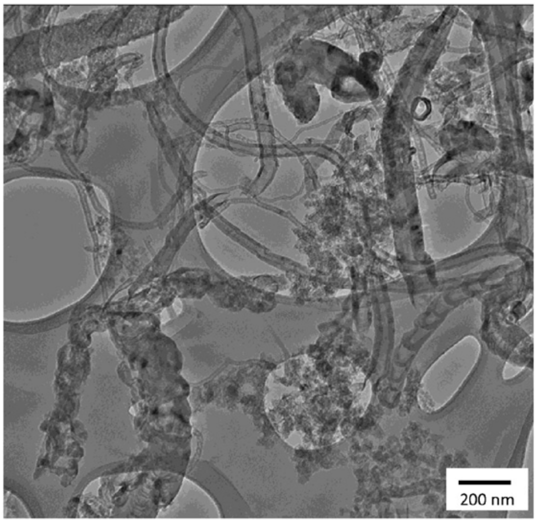

Fig. 1. TEM image of p-CNTs.

and shrinkage [6–10]. For example, researchers have reported that the incorporation of nano-SiO_2 improves workability and compressive strength of concrete and increases resistance to water penetration.

The main drawback of all cement-based structural materials is their brittle nature and tendency to cracking. It is generally understood that concrete brittleness, i.e. fracture without appreciable prior plastic deformation, increases with the increase of strength. Therefore, one critical disadvantage of ultra high strength is ultra brittleness and very low cracking resistance. To overcome this bottleneck, fibers are commonly used to impart toughness and cracking resistance of high strength concrete. Various fibers such as steel fibers [11], carbon fiber [12], glass fiber [13], and polymer fibers [14], have been considered and used. To enhance the fiber bridging capacity, high dosage of micro-/macro-fibers is often used to achieve required performance. High volume fraction of fiber, however, results in high cost and considerable processing problems. Fiber dispersion becomes difficult because of high viscosity of the mix due to high surface area of the fibers and the mechanical interaction between the fibers, along with the difficulties in handling and placing.

Carbon nanotubes (CNTs), being the strongest known fiber, are first discovered by Iijima in 1991 [15]. The remarkable mechanical properties, ultra high aspect ratio, and excellent electrical conductivity make CNTs an ideal reinforcing fiber to develop new nanocomposites [16, 17] and to impart piezoresistivity into cement-based material for strain and damage sensing [18–21]. However, studies have shown inconsistent and sometimes contradictory results of the effects of CNTs on concrete properties, the compressive and the tensile strengths in particular [22]. The most significant issue for all nanomaterials applied to composites is that of effective dispersion. CNTs appear as black powder with the diameter of 10 to 200 nm with strong tendency to agglomerate due to the nano size and strong van der Waal forces. Dispersion of CNTs is a critical issue which strongly influences the mechanical properties of the resulting CNTs reinforced cementitious composites. The mixer used for the preparation of cement mortar and paste is not able to disperse CNT powder in the fresh cementitious mixture. Therefore, CNTs need to be dispersed before mixing into cement material. Unfortunately, dispersion of CNTs in water is less likely due to its hydrophobic nature [23]. This is identified as the major challenge associated with the incorporation of CNTs in cement-based material. Poor dispersion not only reduces the reinforcing efficiency of CNTs and therefore high dosage is required and associated cost but also leads to the formation of many CNT agglomerates which are virtual defect sites in the cement matrix resulting in the reduction of the strength of the concrete. The hydrophobic surface of CNT also leads to a weak CNT/matrix interfacial bond which limits the efficiency of CNT bridging.

Many previous studies have focused on the dispersion of CNTs in water or various polymers by using physical and/or chemical methods [24–26]. The basic physical technique used for CNTs dispersion is ultrasonication, which is often used in combination with the chemical methods such as the addition of solvent [27–29]. However, the degree of dispersion depends on the properties of CNTs such as length, entanglement density and attractive force. Addition of surfactant can also effectively disperse and stabilize CNTs in aqueous solutions. However, the type and structure of surfactant also have a significant influence on dispersion of CNTs in water. Improved dispersion may be achieved at high ultrasonic energy level when a proprietary surfactant is used [30,31]. Many research have indicated that the addition of dispersed functionalized CNTs have obvious influence on mechanical properties of CNT reinforced cementitious composites. Konsta-Gdoutos et al. [30] investigated the effect of highly dispersed CNTs obtained by applying ultrasonic energy and in combination with surfactant on properties of cement based materials. The results indicated that the tensile strength and Young's modulus of cement matrix increased through proper dispersion of small amounts of multi-walled CNTs (MWCNTs, 0.048 wt.% and 0.08 wt.%). Parveen et al. [32] also reported that the flexural and compressive strengths of single-walled CNTs (SWCNTs, 0.1 wt.%) reinforced cement mortar increased by 7% and 19% when compared to the plain mortar. A novel dispersion technique was developed by incorporating special dispersion agent of Pluronic, which can further improve the mechanical properties of CNT reinforced cementitious composites [32].

To further improve CNTs dispersion, many studies proposed surface treatment of the CNTs via chemical modification [33,34]. For example, the surface modification with acid mixture to create a carboxyl surface enabled the dispersion of MWCNTs in water [35]. Combined acid and subsequent other chemical modification can further improve the dispersion stability and obtain the best dispersion [27]. Surface treatment by means of plasma can also modify the surface characteristics of CNTs by incorporation of hydrophilic functional groups and thus improve the dispersion capability of CNTs in water [36]. The influence of surface modification on the properties of the resulting CNT reinforced concrete; however, are controversial. Li et al. [35] reported a 25% increase in the flexural strength from 6.7 MPa to 8.4 MPa and a 19% increase in the compressive strength from 52 MPa to 62 MPa of a

Table 1
Properties of multiwall carbon nanotubes (MWCNTs).

Type of CNTs	Purity (%)	Outer diameter (nm)	Length (μm)	Surface area (m^2/g)	Zeta potential (mV)
n-CNTs	>90	10–30	10–30	>140	−10.8
p-CNTs	>95	10–30	~10	>180	+33.2

Table 2
Dispersion regime of two types of CNTs.

No.	CNT (g)	Water (g)	SP (g)	CNT type	Dispersion method
1	0.3	100	–	n-CNT	Ultrasonic
2	0.3	100	4.5	n-CNT	Ultrasonic + surfactant
3	0.3	100	–	p-CNT	Ultrasonic

Table 3
Mix design of CNT modified UHPCs (unit: relative portion in weight).

Mix	Cement	M4 sand	Water	SP	CNT	CNT type	Dispersion method
1	1.00	0.40	0.22	0.010	0	–	–
2	1.00	0.40	0.22	0.011	0.00067	n-CNT	Mechanical
3	1.00	0.40	0.22	0.012	0.00067	n-CNT	Ultrasonic
4	1.00	0.40	0.22	0.017	0.00067	n-CNT	Ultrasonic + surfactant
5	1.00	0.40	0.22	0.011	0.00067	p-CNT	Mechanical
6	1.00	0.40	0.22	0.011	0.00067	p-CNT	Ultrasonic