CARBON 85 (2015) 212–220

Available at www.sciencedirect.com

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journal homepage: www.elsevier.com/locate/carbon

Effect of ultrasonication energy on engineering properties of carbon nanotube reinforced cement pastes

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ARTICLE INFO

Article history:
Received 28 October 2014
Accepted 21 December 2014
Available online 2 January 2015

ABSTRACT

Carbon nanotubes (CNTs) are attractive candidates as nanofillers in reinforcing ordinary Portland cement (OPC) due to their superior mechanical properties. In this study, the engineering properties of CNT–OPC pastes were investigated with varied ultrasonication energy (UE) and CNT concentration. It was found that UE could effectively improve the aqueous dispersion of surface functionalized CNTs with the aid of a polycarboxylate-based cement admixture (PC). A PC to CNTs mass ratio of 8 is recommended for ensuring effective dispersion of CNTs and maintaining workability of CNT–OPC pastes under sufficient ultrasonication. Furthermore, the mechanical property results of the hardened pastes obtained from pre-notched beam tests revealed the existence of an optimal UE for achieving mechanically superior CNT–OPC pastes, which was found to be 50 J/mL per unit CNTs to suspensions weight ratio. The Young's modulus E, flexural strength σ_f, and fracture energy G_F of CNT–OPC pastes were significantly improved compared to plain OPC pastes. These results clearly demonstrate the reinforcing effect of CNTs on cement pastes because they decrease the porosity and increase crack bridging capacity of cement pastes at nanoscale level, which will be complementary to conventional microfibers in reinforcing OPC pastes.

1. Introduction

The last decade has seen much investigation of the potential of carbon nanotubes (CNT) as nanofillers for reinforcing metal [1,2], polymer [3,4], ceramic [5,6], ordinary Portland cement (OPC) [7–9], and bio-materials [10,11]. Among all these matrices, OPC is the most widely used engineering material, its consumption being only less than water [12,13]. OPC is characterized as a quasi-brittle material with low tensile strength and fracture toughness due to the heterogeneous and complex pore structure [14]. These OPC characteristics create a real need for the incorporation of CNTs to form CNT–OPC composites with superior mechanical performances and durability.

Early studies focused on experimental characterization of the reinforcing effect of CNTs on cement composites. Li et al. [7,15] dispersed surface treated CNTs (0.5 wt% of cement) in cement mortar by means of a 30-min ultrasonic bath. The compressive and flexural strengths of the CNT–OPC composites were increased by 18.9% and 25.1%, respectively. In a

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http://dx.doi.org/10.1016/j.carbon.2014.12.094

series of studies by Konsta-Gdoutos et al. [16,17], the mechanical properties of cement pastes reinforced by pristine multi-walled CNTs with different lengths were tested. Effective dispersion of the CNTs was achieved by applying ultrasonic energy and the use of a surfactant. The flexural strength and Young's modulus of cement pastes improved by 25–40% and 35–45%, respectively, with the incorporation of only small amounts of multi-walled CNTs (from 0.02 wt% to 0.1 wt% of cement). Tyson et al. [18] and Abu Al-Rub et al. [19] added both CNTs and carbon nanofibers (CNFs) to cement in concentrations of 0.1 wt% and 0.2 wt% of cement. The CNTs and CNFs were dispersed using an ultrasonic mixer with a probe for 20–30 min. Improvements in strength, ductility, modulus of elasticity, and modulus of toughness suggested that the ultimate strength and ductility of cement could be effectively enhanced. In addition to mechanical properties, transport properties of CNT–cement composites have also been studied, and the results showed the incorporation of CNTs may effectively enhance the durability of cement-based composites [15,20]. These experimental investigations on CNT–OPC pastes demonstrated the feasibility of CNTs for reinforcing plain OPC pastes; however, the effect of ultrasonication on the mechanical reinforcing efficiency of CNTs in cement pastes and the workability of CNT–OPC pastes are poorly understood and further studies are sorely needed.

As can be seen, ultrasonication is one of the most commonly used technique to aqueous disperse CNTs by providing a high local shear to fray the CNT bundle [21]. It has been recognized that ultrasonication contributes on both the exfoliation of CNTs from large agglomerates [22] and the shortening of tubes [23,24]. A proper UE may bring more pronounced reinforcing effect than either at low or excessive ultrasonication [25,26]. Therefore, it is of vital importance of determining an optimal UE that balances the dispersion and shortening effects in the fabrication of CNT–OPC pastes to achieve superior mechanical properties.

Recently, the authors developed a theoretical framework [27] by incorporating the log-normal length distribution of CNTs into Li's micromechanics based crack bridging stress-crack separation model [28]. The theoretical model predicted that there is an optimum ultrasonication energy (UE) that produces the best reinforcing effect of CNTs in CNT composites. Different levels of UE can alter the log-normal nanotube length distribution and the concentration of dispersed CNTs; thereby affecting their reinforcing efficiency. Moreover, studies have shown that UE changes the degree of dispersion of CNTs [27], consequently altering the contact surface area between CNTs and cement matrix [29], which can lead to change in the amount of surfactant absorbed by CNTs and hence affect the workability of OPC.

The aim of this study is to quantify the effect of UE on the engineering properties of CNT–OPC pastes that include CNT dispersion, workability, Young's modulus E, flexural strength σ_f, and fracture energy G_F. The influence of UE on the dispersion of CNTs was analyzed via UV–vis and optical microscope observations. The workability and mechanical properties of CNT–OPC pastes were assessed by the mini-slump and notched beam tests, respectively. Moreover, a CNT dosage-independent optimum UE is determined for practical applications. The results may also serve as evidence to underpin the previously proposed theoretical framework for predicting the optimum UE [27], and the principles discovered in the model may also be applicable to other CNT reinforced materials.

2. Experimental program

2.1. *Materials*

Type GP ordinary Portland cement, conforming to the requirements of Australian Standard AS 3972 [30], was used as the binder material. The multi-walled CNTs functionalized with COOH groups were purchased from Nanocyl S.A. in Belgium. The physical properties of the nanotubes are shown in Table 1. A commercially available polycarboxylate-based cement superplasticizer (PC), named as ADVA 210 (supplied by Grace Australia Pty. Ltd.), was used. The PC contains both active non-polar groups for adsorption on the surface of CNTs and polar groups to attach on cement particles/water in aqueous solution; thereby assisting in the dispersion of both cement and CNTs [29,31–33].

2.2. *Mix design for CNT suspensions and CNT–OPC pastes*

A total of 12 cement mixes containing four components, namely distilled water (w), PC (p), CNTs (C), and dry cement powder (c), were prepared. The amounts of CNTs and PC in CNT suspensions are defined as CNTs to suspensions weight percentage C/s and PC to suspensions weight percentage p/s, respectively. The amounts of CNTs and PC in CNT–OPC pastes are defined as CNTs to cement weight percentage C/c and PC to cement weight percentage p/c, respectively. 800 grams of cement power was adopted for all the mixes. The suspensions (s, including w and p) were fixed at 320 g, giving the fixed suspensions to cement weight ratio (s/c or water to cement ratio) of 0.4. As shown in Table 2, two mixes of reference plain OPC pastes with p/c of 0.55 wt% and 0.70 wt% were designed, denoted R1 and R2, respectively. Two series of CNT–OPC mixes with two different C/c and five various UEs were designed and denoted CNT-1 series and CNT-2 series.

2.3. *Preparation and characterization of CNT suspensions*

CNT suspensions were prepared by mixing CNT powder with PC in aqueous solutions under ultrasonication using a horn

Table 1 – Properties of functionalized CNTs.

Aspect ratio	Average diameter (nm)	Average length (μm)	Carbon purity (%)	–COOH functionalization (%)	Specific surface area (m^2/g)
150	9.5	1.5	>95	<4	250–300