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CHARACTERISATION OF THE PORE STRUCTURE OF PORTLAND CEMENT-CARBON NANOTUBE COMPOSITES COMPARED WITH CEMENT PASTES

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ABSTRACT

Portland cement is one of the most widely-used construction materials in the world, but it has a poor tensile strength and strain capacity, limiting its utility for a broad range of structural applications. In order to meet the demand for increasingly efficient construction materials that are stronger, more durable, economic and environmentally sustainable, there has been a great deal of recent research interest in promising composites that incorporate nanomaterials, including carbon nanotubes (CNTs), into the cementitious matrix.

The majority of research into Portland cement-carbon nanotube composites (OPC-CNT) to date has focussed upon the mechanical reinforcing effect of the CNTs within the cementitious matrix. In some cases, experimental results have exhibited improvements in excess of 50%, but they are highly variable, most likely due to the difficulty in obtaining adequate dispersion of CNTs within the cement matrix. Other important properties of OPC-CNT composites, such as the porosity and pore size distribution, have received little attention in the literature. Our results show that the addition of CNTs to cement can have a significant influence upon the pore size distribution and total pore volume of the composite, particularly in the medium capillary porosity range. However, questions remain, including: by how much does varying the percentage of CNTs alter the porosity; do well-dispersed CNTs alter the pore structure in a different way to poorly-dispersed CNTs within the OPC-CNT; and how does the pore structure of OPC-CNT develop with the cement hydration?

This paper presents results from a comparative study of the meso-scale pore size distributions in pure OPC and OPC-CNT, using nitrogen adsorption porosimetry. This research investigates the influences that CNTs have upon the pore size distribution of OPC-CNT composites. The results of this study are being used to support understanding of the mechanical properties and transport/durability properties of OPC-CNT composites.

Keywords: Portland cement, carbon nanotubes, composites, porosity, pore size distribution.

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1. INTRODUCTION

Portland cement, as the principal binder in concrete, forms a significant and important portion of built infrastructure throughout the world. A material with low tensile strength and strain capacity, reinforcement is typically added to cementitious materials in the form of reinforcing bars, or, more recently, macro- or micro-scale fibres, which can result in a significant improvement in the mechanical properties of the resulting composite (Akkaya et al. 2001) . However, the availability of advanced nanoscale materials, particularly carbon nanotubes (CNTs), has opened up new avenues for modifying the properties of cement at the nanoscale (Makar and Beaudoin 2003).

Individual or concentric cylinders of graphene with diameters 1-100nm and aspect ratios generally in excess of 10^3, CNTs exhibit exceptional mechanical, electrical and chemical properties (Yu et al. 2000) that can make them potentially ideally suited to act as nanoscale tensile reinforcement for a host of materials, including cements.

The majority of research into the emerging field of CNT nanomodification of Portland cement has focussed upon the mechanical or electrical properties of the resulting Portland cement-carbon nanotube composite (OPC-CNT), with some impressive improvements, but a great deal of variability between studies (Chen et al 2011). The principal reason for this is the difficulty in overcoming the very strong van der Waals attractions between CNTs (Girifalco et al. 2000) that cause them to become highly-bundled within the cement matrix, and much research has explored finding methods suitable for OPC-CNT.

However, other important properties of the material, including its pore structure, have been relatively unexplored, even though early studies have suggested that CNTs may act as nucleation sites for cement hydration products (Makar and Chan 2009) and could potentially result in significant changes to microstructure and pore structure of the composite. Previous experiments have characterized the pore size distribution (PSD) of OPC-CNT over a wide pore diameter range using mercury intrusion porosimetry, with varying results. Nochaiya & Chaipanich (Nochaiya and Chaipanich 2011) found that the addition of CNTs lowered the porosity and total surface area, but did not alter the mean pore diameter. Conversely, Li et al. (Li et al. 2005) compared pure cement, OPC-CNT and a cement-carbon fibre composite, and found that, in addition to a reduction in total porosity, the addition of CNTs to the cement resulted in a significant reduction in the mean pore diameter. However, in contrast, Kowald & Trettin (Kowald and Trettin 2009) found a significant increase in the proportion of pores smaller than 30nm radius and a decrease in pores larger than 30nm in radius, when compared to a pure cement sample.

Consequently, given the conflicting results presented in the literature, this study investigates the influence that CNTs have upon the pore structure and particularly the pore size distribution of OPC using a different experimental technique that can characterise the fine pore structure: nitrogen adsorption porosimetry. In addition, as adequate CNT dispersion is a critical criterion for OPC-CNT materials, the effectiveness of the CNT dispersion method used in this study is assessed using

scanning electron microscopy, to ensure that the specimens tested are representative of a well-dispersed OPC-CNT material.

2. EXPERIMENTAL PROGRAMME

2.1. Materials used in this study

The multi-walled carbon nanotubes used in this research were provided by Hythane Company LLC (USA), with a reported typical diameter range of 20-30nm, lengths ranging from sub-micron to several microns and a carbon purity of >95%.

Table 1: Chemical composition and loss on ignition of Australian Type GP cement.

Constituent	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	TiO_2	K_2O	MnO	P_2O_5	SO_3	LOI
OPC (%)	19.90	4.70	3.38	1.30	63.93	0.17	0.245	0.446	0.079	0.063	2.54	2.97

Australian Type GP (general purpose) cement, the chemical composition of which is presented in Table 1, was used as the binder in this study, while a readily-available polycarboxylate-based superplasticisier was used as the surfactant, acting both as CNT dispersant and cement plasticizer.

2.2. Sample preparation

The dispersed CNTs used in this study were prepared according to a method developed in a prior study (MacLeod et al. 2012). The water used in the mix design of the paste samples was first mixed with the required surfactant quantity using a 2Mag MIX 1 magnetic stirrer, operating at 400rpm for 2 minutes so as to ensure homogenous surfactant distribution within the mix water. The dry mass of CNTs required for the mix design (1% by weight of cement) was then added to the surfactant solution and ultrasonicated in order to adequately disperse the CNTs within the solution. The ultrasonicator employed in this study was a Sonics and Materials Vibra-Cell VCX 500 ultrasonic processor with temperature control (500W), equipped with a 19mm solid cylindrical probe, operating at 35% amplitude for a total input energy of 20,000J. The mix water for the reference specimen was not ultrasonicated.

The cement paste mixes, with a water-to-cement ratio of 0.35, were prepared with the pre-dispersed CNT solutions (or water and surfactant solution for the reference specimen) according to ASTM Standard C1738 (ASTM 2011), using a Cement Test Equipment Model 7000 Constant Speed Mixer high-shear mixer. The freshly mixed paste mixtures were poured into 100mm x 50mm diameter cylindrical moulds. At the same time, the slump diameters of the cement pastes were tested using a mini-slump test after (Collins et al. 2012). Cylinder demoulding took place after 24 hours, with cylinders subsequently cured in lime saturated water for a further 6 days.

7 days after mixing, the cured cylinders were broken apart and 15 to 30 cubes, each approximately 1.5-3mm in size, were cut from interior sections of the cylinder samples. The cubes were immersed in ethanol for 3 days to arrest cement hydration, after (Zhang and Scherer 2011), followed by drying

in a vacuum desiccator for 48 hours. Specimen quantities for the porosimetry tests, each approximately 0.1g, were selected from the dried cube specimens and additionally vacuum dried for 2 hours during the pretreatment stage of the porosimetry testing.

Table 2 summarises the CNT and surfactant proportions of the cylinder samples prepared for porosimetry testing and SEM examination, along with the slump test results for the fresh pastes.

Table 2: CNT dose and slump results for prepared paste mixes.

Sample	*CNT dose (% wt. of cement)*	*Surfactant dose (% wt. of cement)*	*Mini slump diameter (mm)*
OPC	-	0.25	114.5
OPC-CNT	1.0	5.0	115.7

Earlier studies exploring suitable methods for surfactant-assisted CNT dispersion (Konsta-Gdoutos et al 2010) have found that a high surfactant-to-CNT ratio is necessary to adequately disperse CNTs within water, as well as to provide a sufficiently workable paste. For this study, a surfactant:CNT ratio of 5:1 was selected for the pastes mixed with 1% (by weight of cement) CNTs. No adverse effects on the setting times for the OPC-CNT composite samples were observed, but the use of such a high percentage of surfactant in the pure cement specimens was not possible, as superplasticisers are known to cause hydration retardation in paste specimens (Cheung et al. 2011), and a dose as large as 5% (wt. of cement) can cause cement particle segregation in the paste prior to setting. Consequently, a surfactant percentage of 0.25% was used for the pure cement samples, as this surfactant percentage resulted in slump properties comparable to the OPC-CNT composite, as measured using the mini slump test.

2.3. Nitrogen adsorption porosimetry

Nitrogen adsorption isotherms were measured at 77.35K using a BEL Japan BELsorp-mini II instrument. Both adsorption and desorption isotherms were measured for each specimen, and a dead volume reference cell was used to improve measurement accuracy at each pressure step.

The surface area of the samples tested was calculated using the Brunauer, Emmett and Teller (BET) method (Brunauer et al. 1938) over a relative pressure range of 0.05 to 0.35 on the adsorption isotherm, while the pore size distribution for each sample was calculated from the desorption isotherm according to the Barrett, Joyner and Halenda (BJH) method (Barrett et al. 1951). Calculations were performed using the BELMaster analysis software (Version 6.1.0.4) from BEL Japan.

2.4. SEM examination of CNT distribution in cement specimens

Qualitative electron microscopic analysis of the distribution of CNTs within the cementitious matrix of the OPC-CNT composite was undertaken using a JEOL JSM-7001F FEGSEM (2008), operating in secondary electron imaging mode at an accelerating voltage of 30kV. Microscopy specimens

were selected from the vacuum dried samples prepared for porosimetry, and were sputter coated in a thin layer of platinum prior to examination.

3. RESULTS AND DISCUSSION

3.1. Surface area and total pore volume

The results of the BET surface area analysis and the total pore volume results obtained from the BJH pore size distribution analysis are summarised in Table 3, below.

Table 3: BET surface area and BJH total pore volume results.

Specimen	a_s (m^2/g) *BET*	$d_{p,avg}$ (nm) *BET*	V_p (cm^3/g) *BJH*	V_p (cm^3/g) *averaged*
OPC – 1	19.839	23.617	0.1225	0.1231
OPC – 2	19.655	23.737	0.1237	
OPC-CNT – 1	22.492	20.868	0.1235	0.1170
OPC-CNT – 2	20.004	20.981	0.1105	

A comparison of the specific surface area, a_s, and total pore volume, V_p, for each specimen tested shows that, although the results for the OPC-CNT composite specimens show a greater variability than those for pure cement, the composite specimens exhibit a higher specific surface area, but a smaller average total pore volume. This indicates that the pore structure of the material becomes finer with the addition of CNTs, and is reflected in the reduced average pore diameter, $d_{p,avg}$, of the OPC-CNT composite compared with the pure cement specimens.

Although the causes of the observed changes will require further research, it is proposed that the changes to the specific surface area and pore volume may be a result of a combination of physical and chemical effects; the physical blocking of pores by CNTs, and a possible calcium silicate hydrate (C-S-H) nucleation effect, as first reported by Makar & Chan (Makar and Chan 2009).

3.2. Pore size distribution analysis

Figure 1 presents plots of the calculated differential pore size distributions (PSDs) for the pure cement and composite specimens over the measured pore diameter range of 2.5nm to 185nm. If the classification of pore sizes according to Mindess et al. (Mindess et al. 2002) is used, this analysis encompasses small (or gel) capillary pores (2.5-10nm), medium capillaries (10-50nm) and large capillary pores (50nm-185nm).

The gel capillary pores measured using nitrogen adsorption may be interpreted as representing the inter-globule spacing between low density C-S-H globules, while gel pores between high density C-S-H globules are thought to be inaccessible to nitrogen, according to the model of the structure of C-S-H proposed by Jennings and Tennis (Jennings and Tennis 1994). This implies that a greater measured peak in the 2-5nm range means that there is a greater proportion of low density C-S-H gel present in the material, while high density C-S-H material is not measurable by this technique. The

medium capillary pores, meanwhile, are known to be important for paste properties, particularly strength and permeability (Mindess et al. 2002).

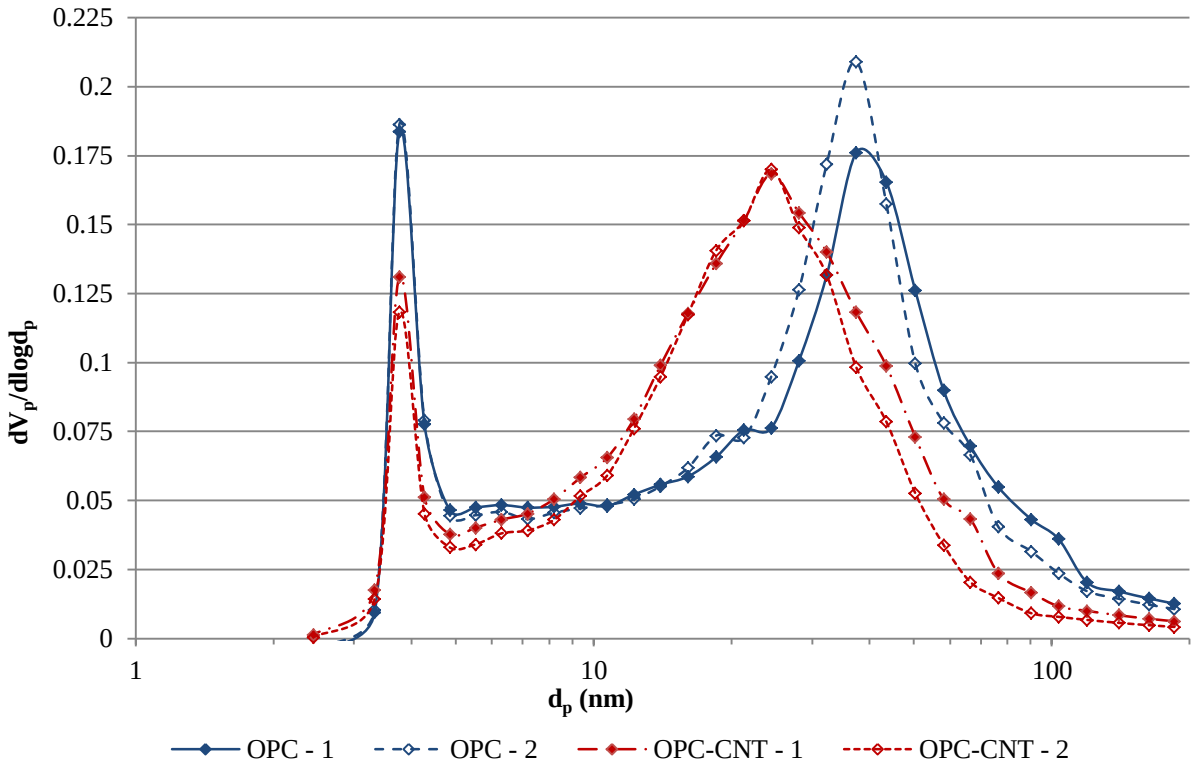


Figure 1: Pore size distributions of OPC and OPC-CNT.

Accordingly, the distributions for the pure cement specimens exhibit some clear features: a peak at 3.77nm, corresponding to the gel capillaries, and a broader peak at 37.4nm, which corresponds to the medium capillary pores, and makes up a significant proportion of the measured porosity of the cement material.

Conversely, the OPC-CNT composite specimens show significant deviations from the pure cement pore size distributions: a significant decrease at the 3.77nm peak, and a dramatic shift in the peak in capillary porosity, from 37.4nm to 24.4nm. Most notably, the capillary pore size distribution exhibits 'smearing' or a spreading of the distribution, with an overall fining of the pores. At pore diameters above 30nm, the PSDs for the OPC-CNT specimens have a smaller contributing proportion of their porosity from these medium and larger capillary pores.

On their own, the results presented can only suggest as to possible causes for such significant changes to the pore size distribution with the addition of CNTs, and further research is required to investigate possible mechanisms. However, a tentative C-S-H nucleation effect may explain the significant reduction in gel capillary porosity with the addition of CNTs; the nucleation of high density C-S-H on the surface of CNTs could result in a reduction in the production of low density C-S-H in the composite matrix, as well as the observed shift in medium capillary porosity, through a combination of physical pore-blocking and pore diameter reduction through C-S-H nucleation.

3.3. Qualitative SEM examination

Micrographs showing representative CNTs observed on the surface of fracture specimens taken from the OPC-CNT composite material are presented in Figure 2. Solid highlighted regions denote materials attached to the CNT surface, indicating a strong interaction between the CNT and cement gel material, while dashed circles highlight CNT embedment locations.

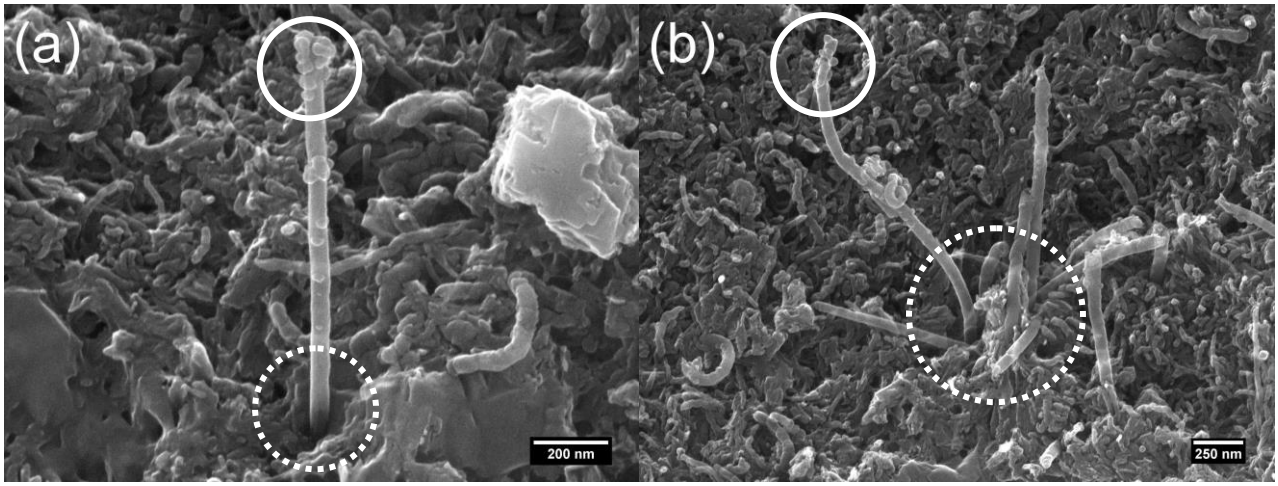


Figure 2: Micrographs of CNT distribution observed in the OPC-CNT specimen examined.

Figure 2 (a) shows an example of a well-dispersed CNT with good embedment within the cement matrix. Only minor CNT agglomerations, as shown in Figure 2 (b), were observed in the fracture specimens examined. As a result of this qualitative SEM examination, the method employed to disperse CNTs in water and subsequently in cement paste in this study was deemed adequate.

4. CONCLUSIONS

This paper presents results from a comparative study conducted upon the pore size distributions of Portland cement and OPC-CNT composite materials with adequately-dispersed CNTs. The results support the hypothesis that, unlike larger fibres added to cement, CNTs may act as nucleation sites for the formation of high-density calcium silicate hydrate gel. Although further research is required to verify the mechanisms involved, these findings contribute to the understanding of the pore structure of OPC-CNT materials, which is important for improving understanding of the microstructure and strength characteristics as well as the durability and transport properties of these composite materials.

5. ACKNOWLEDGMENTS

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