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The Effect of SWCNT and Other Nanomaterials on Cement Hydration and Reinforcement

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Abstract Additions of nanomaterials to cement pastes and concretes may have a significant effect on the performance of ordinary Portland cement (OPC), OPC blends and concrete. Due to the scale of these particles, they may not only modify the bulk behavior of the matrix in a manner similar to micro- and macroscopic additions, but also influence the formation and structure of the C-S-H and other products formed during hydration. Nanoscale additives also have the potential to add new capabilities to concrete. There is therefore growing interest in producing composite materials that include nanomaterials.

Single walled carbon nanotubes (SWCNT) are of particular interest due to their desirable properties as reinforcing materials. They have recently been shown to nucleate the formation of C-S-H during the hydration of ordinary Portland cement (OPC). A series of complementary studies are presented here. The effects of nano-titania, nano-calcium carbonate and nano-alumina dispersed by sonication with OPC on hydration are discussed and compared to the effect of SWCNT dispersed by the same method. The impact of dispersing the SWCNT in blends of admixture and mix water on the hydration of both tricalcium silicate and OPC are investigated. Fracture surfaces of OPC samples blended with all four nanomaterials and hydrated for 7 days are analyzed. Classical reinforcing behaviour was identified in the SWCNT/OPC composite alone. A new, nanoscale reinforcing mechanism based on SWCNT bundle pull out is described. The experimental results are used to draw conclusions about the nucleation mechanism in SWCNT composites and on the impact of SWCNT dispersion method on the performance of those composites.

1. Introduction

The addition of nanomaterials, such as nanotubes, nanoparticles and ultrahigh surface area particles to cement and concrete is one of the most promising areas of research for the application of nanotechnology to construction materials. In addi-

tion to being a bulk material formed by chemical reactions [Taylor 1997], C-S-H, the main component in hydrated ordinary Portland cement (OPC) and other cements is known to have a fine structure on the order of a few nanometers [Taylor 1997]. As a result, the addition of nanomaterials to hydrating OPC and other cements has the potential to affect both the physical structure of the C-S-H and the hydration reactions themselves.

While studies of nanomaterials mixed with hydrating OPC may provide fundamental insight into the behaviour of cement and concrete, interest in these blends has been driven by the possibility of producing novel and/or superior properties in concrete that may be directly applicable to the construction industry. As a result, considerable attention has been paid both to adding carbon nanotubes and to adding a variety of nanoparticulates to OPC.

Carbon nanotubes (CNTs) are particularly attractive for use in cementitious systems because they appear to be close to ideal reinforcing materials. Ultrahigh aspect ratios [Zheng et al. 2004], extremely high yield strengths [Yu et al. 2000] and moduli of elasticity [Salvetat et al. 1999], and elastic behaviour [Walters et al. 1999] all point to the potential of CNTs in reinforcing applications. In addition, the nanometric diameters of CNT means that if they are well dispersed in a matrix, cracks will encounter one or more reinforcements soon after formation, inhibiting growth at the earliest stage possible. Most work to date has been done on multi-walled carbon nanotubes (MWCNT), which are less expensive and more readily available than single walled carbon nanotubes (SWCNT). There are a number of reports describing both mechanical [Campillo et al. 2004, Ibarra et al. 2006, Li, et al. 2005, Xiang et al. 2005, Cwirzen et al. 2008, Konsta-Gdoutos et al. 2010] and electrical [Li et al. 2007, Wansom et al. 2006] properties of these composites. A recent summary of carbon nanotube/cement composite research [Makar 2009] and an overview of the topic [Raki et al. 2010] can both be found elsewhere.

Less work has been done on OPC/SWCNT composites. SWCNT, however, have higher aspect ratios than MWCNT and individual tube diameters that are close to estimates of the structural spacing of C-S-H layers in hydrated OPC [Taylor 1997b]. They are therefore potentially more desirable as reinforcing materials than are MWCNT. The work presented here is part of a longer term study on the behaviour of cementitious materials when hydrated in the presence of SWCNT.

Early studies [Makar et al. 2005] used Vicker's microhardness testing to show that the mechanical performance of SWCNT/OPC could be as high as 600% of OPC alone. The improvement in performance was seen to be highest during the first few days of hydration, which suggested that the effect may have been as much due to the SWCNT accelerating the hydration process as due to reinforcing behaviour. A subsequent detailed study [Makar and Chan 2009] that used SWCNT distributed on OPC grains by sonication showed that SWCNT do indeed act to nucleate cement hydration reactions. The work presented here expands on that study. The results of an alternative approach to dispersing SWCNT in cementitious systems using sonication in admixture and mix water are presented. The

results of the previous hydration study are also compared to the hydration behaviour of OPC sonicated with 3 different nano-materials (nanoparticulate calcium carbonate and ultra-high surface area alumina and titania). Microscopic evidence for classical reinforcing behaviour is described and the implications of reinforcing by bundles of SWCNT, as opposed to individual nanotubes, are discussed. The results are used to provide further insight into the nucleation mechanisms behind the observed effects of SWCNT on OPC hydration. Finally, the implications of the two different methods of dispersing SWCNT on the ability of the SWCNT to reinforce hydrated cement matrices is discussed.

1.1 Effects of SWCNT on the hydration of sonicated OPC

An extensive study of the hydration of OPC sonicated with SWCNT in isopropanol has been published elsewhere [Makar and Chan 2009]. In summary, sonication of OPC alone reduced the maximum heat flow and retarded its timing compared to the as-delivered OPC control. Secondary C_3A and C_4AF reactions [Pratt and Ghose 1983, Makar and Chan 2008] were suppressed or spread out in time compared to the control. The SWCNT bundles accelerated the hydration reaction compared to both the control as-delivered OPC and OPC sonicated alone. They also produced a higher maximum heat flow. The heat generated by the secondary C_3A and C_4AF reactions was similar to that in the as-delivered OPC, not the OPC sonicated alone.

This behaviour was attributed to the SWCNT appearing to act as nucleating sites for the C_3S hydration reactions, with the C-S-H forming directly on the SWCNT. As a result, the C-S-H formed a network on the surface of the OPC grains before growing away from the surface. Evidence of fiber pullout was observed in the sample material by 24 hours of hydration. No evidence was observed for C_3A hydration products forming on the SWCNT bundles, but the ettringite formed in the initial hydration processes did have a reduced aspect ratio compared to the control samples, suggesting that the presence of the SWCNT inhibited their growth.

Two different mechanisms were proposed to explain the nucleating effect of the SWCNT. First, it is possible that electrostatic behaviour drove the nucleation process. Both the attractive force of image charges due to the local presence of ions and trapping of water molecules by polarization effects may have occurred. Secondly, it is also possible that metallic ions (i.e. Ca^{2+}) may have been adsorbed on the SWCNT. In either case, the trapping of some of the constituents necessary for C-S-H formation against the SWCNT resulted in the observed nucleation effects.

2. Experiment

2.1 Materials

Samples were prepared from GU type (US type 10) ordinary Portland cement (OPC) produced by Lafarge Canada or from monoclinic tricalcium silicate ($3\text{CaO}\cdot\text{SiO}_2$ or C_3S) supplied by CTL Inc (Skokie, Ill). Details of the OPC composition have been given elsewhere [Makar and Chan 2008]. Single walled carbon nanotubes from two sources were used. Work on evidence for classical reinforcing behaviour was primarily conducted using SWCNT produced by Carbon Nanotechnologies (USA, now Unidym), with a diameter of ~ 1.0 nm and typical lengths of 0.1 to 1 μm . These SWCNT were produced using the HiPCo method and acid purified [Chiang et al. 2001]. Samples used to investigate reinforcing behaviour had at 2% by mass SWCNT content added to the OPC. Work on hydration behaviour and confirmation work on classical reinforcing behaviour was conducted using SWCNT produced by the National Research Council Canada using laser ablation [Kingston et al. 2004] and purified using a solvent based method [Kingston, et al. In preparation]. Alumina and titania nanomaterials were supplied by Nanoscale Materials Inc (Manhattan, KS). The alumina was amorphous and had a surface area of $550\text{ m}^2/\text{g}$, while the titania had a surface area of greater than $400\text{ m}^2/\text{g}$ and a crystallite size of less than 20 nm. Reagent grade CaCO_3 nanoparticles were supplied by READE (Riverside, RI). They had typical diameters on the order of 50-100 nm and a surface area of $20.5\text{ m}^2/\text{g}$. The nanomaterial content was 2% of the mass of the OPC in each blend investigated.

2.2 Dispersion of SWCNT for use in cementitious composites

Dispersion of nanomaterials is one of the key issues facing the development of all nanocomposites. Nanomaterials need to be evenly dispersed in the matrix material in order to produce repeatable and consistent effects. Well dispersed nanomaterials may also be expected to produce desirable properties with a lower mass content. Successful dispersion may, however, also be difficult to obtain as the very high surface areas of nanomaterials can cause them to adhere together due to electrostatic effects and van der Waals forces. The latter effect is particularly important in SWCNT due to their highly ordered structure. The van der Waals forces between SWCNT have been estimated to be as high as 11 GPa [Vodenitcharova et al. 2007].

There are additional complications in the dispersion of SWCNT for use in a cementitious matrix. SWCNT are hydrophobic and will not readily disperse in mix water. At the same time, the organic solvents where SWCNT are known to disperse [Ausman et al 2000] may be undesirable in cementitious systems.

Despite these difficulties, at least two methods have been used to disperse SWCNT in cementitious systems. The first, dispersion by sonication, has been discussed in detail elsewhere [Makar and Chan 2009]. The second method, dispersion in cement admixtures, will be addressed below. The results presented later in this chapter are, however, drawn from samples prepared with both methods. The first method is more useful for investigating interactions between the cementitious material and the SWCNT, while the second is likely more practicable for producing larger samples and production materials.

Cement admixtures are particularly desirable as dispersing agents since their behaviour in cementitious systems is already well understood. In addition, once the SWCNT are dispersed in the admixture, the mixture can, in principle, be added to the mix water and cement as would be the case for the admixture alone. The literature reports that polycarboxylate superplasticizers have been used successfully to disperse multiwalled carbon nanotubes (MWCNT) [Campillo et al. 2004, Ibarra et al. 2006, Li, et al. 2005, Xiang et al. 2005] in cementitious systems. Tests were therefore conducted on dispersing SWCNT using a variety of different cement admixtures (Tab. 1). In all cases sonication was employed to break up bundles of the purified SWCNT and the maximum allowable concentration of the admixture was used.

Admixture	Manufacturer	Composition	Application
Air Extra	Euclid Chemicals, Cleveland, OH	Sulfonated fatty acids	Air Entrainment
Eucon 37	Euclid Chemicals, Cleveland, OH	Naphthalene sulfonate	Superplasticizer
Eucoplast 911	Euclid Chemicals, Cleveland, OH	Melamine	Superplasticizer
Glennium 3400	BASF, Cleveland, OH	Polycarboxylate	High-Range Water-Reducing Admixture
Disal	Handy Chemicals, Candiatic, QC	Poly-naphthalene sulfonate sodium salt	Superplasticizer

Tab. 1 Admixtures investigated as means of dispersing SWCNT

Despite the success of the polycarboxylate superplasticizer in dispersing MWCNT, it was not found to be effective in preventing the SWCNT from clumping together again in bundles once sonication had ceased. The air entraining agent and the two Euclid supplied superplasticizers were also unsuccessful. The SWCNT were, however, found to be readily dispersible [Makar and Chan 2009, Makar et al 2005] in Disal at a concentration of 8 g/L. SWCNT sonicated in Disal and water at that concentration were found to be evenly and stably dispersed, forming a black liquid that showed increasing viscosity with increasing SWCNT content. A maximum SWCNT content of 3% of the mass of the mix water was

found to be possible before the dispersion was too stiff to be readily mixed with cement. The dispersion was found to be quite stable, remaining fluid and well dispersed for over a year from the date of production.

2.2 Procedure

Two methods of dispersing nanomaterials were used. In the first, single walled carbon nanotubes and nanomaterials were dispersed on the OPC by following a procedure originally developed for use in dispersing carbon nanotubes in alumina composites [Zhan et al 2002]. Mixtures of unhydrated OPC and each of the various nanoscale materials were placed in small glass jars. Each sample was then sonicated using an high intensity ultrasonic processor (model VCX600, Sonics and Materials, Newtown Connecticut) in isopropanol for 4 hours to evenly disperse the nanoscale material. Sonication took place in an ice bath to avoid overheating the sample. The jars were sealed around the sonicator probe during the sonication process to avoid release of the nanomaterials. All work was done in a fume hood to provide additional environmental protection. Past work has shown that the sonication in isopropanol procedure used here disperses the SWCNT in bundles of a few SWCNT [Makar and Chan 2009].

Sonicated samples were vacuum dried in a specially designed glassware system in order to prevent carbonation of the samples and nanoparticulate release. Samples were then checked by scanning electron microscopy to ensure that the nanomaterials had been adequately dispersed on the surface of the OPC grains. Between 2 and 5 grams of the resulting materials were then hydrated for 7 days at 0.5 w/c ratio for seven days using ultrahigh purity (>1 ppm contaminant) water (Anachemia, Inc.). Hydration characteristics were measured using isothermal conduction calorimetry (TA Instruments, New Castle, Delaware).

Hydration of the samples was stopped by washing in isopropanol. Samples were then vacuum dried and stored under vacuum until needed. They were broken up in a mortar and pestle by hand and the fracture surfaces imaged using high resolution scanning electron microscopy (Hitachi S-4800). Typical imaging conditions were a 1.2 keV accelerating voltage, a 2.5-3 mm working distance and 7 μ A emission current. Imaging was done under high vacuum conditions in order to obtain the maximum possible resolution. A discussion of the advantages and disadvantages of using this approach to imaging hydrated OPC samples is given elsewhere [Makar and Chan 2008]. Samples were typically imaged at 40-50,000x magnification, but magnifications as high as 180,000x were used as appropriate. Although the theoretical limit of the resolution of the instrument is ~ 1 nm, experience has shown that the practical resolution of the instrument in cement samples is on the order of ~ 3 nm. Individual SWCNT were therefore unlikely to be seen, but it was possible to image bundles of SWCNT with widths of 3 or more

SWCNT. The higher diameter nanoparticles used in the research were easily resolved.

In the second method, SWCNT were sonicated in a solution of 8 g/L Disal in ultrahigh purity water, a commercial poly-naphthalene sulfonate sodium salt superplasticizer. Concentrations of SWCNT ranged from 0.5% by mass of water to 3%. The resulting dispersion was then mixed with both OPC and commercially produced tricalcium silicate (C_3S) at 0.5 w/c, resulting in SWCNT/cementitious material ratios of 0.25% to 1.5% by mass. Samples were again hydrated for 7 days in an isothermal conduction calorimeter.

3. Effects of SWCNT and other nanomaterials on the hydration of C_3S and OPC

3.1 Comparisons between the hydration effects of SWCNT and other nanomaterials in sonicated systems

One route to improved understanding of the nucleating effects of SWCNT is by comparison to the effects produced by other nanomaterials. Isothermal conduction calorimetry measurements on OPC sonicated with three different nanomaterials are shown in Fig. 1. The OPC was from the same source as the previous work with SWCNT [Makar and Chan 2009]. The three nanomaterials were chosen both for high surface areas and because they were not expected to form reaction products with the hydrating OPC. There were, however, several significant differences between the nanoparticles and SWCNT. All of the comparison nanomaterials were non-conducting, had lower surface areas than the SWCNT and had much lower aspect ratios. The nano-alumina and nano-titania were also in the form of agglomerated particles with total sizes on the order of 5 μm .

A detailed discussion of the mechanisms behind the results in Fig. 1 will be presented elsewhere [Makar and Chan, in preparation]. In comparison to Figure 1 in Makar and Chan, however, examination of Fig. 1 above shows that the extent of the differences between effect of the SWCNT on the hydration process and that observed for other nano-materials. As would be expected from previous work [Sato and Beaudoin 2006, Sato and Beaudoin, in submission], the nano-calcium carbonate additions produce an acceleration of the hydration process. The development of the heat flow was otherwise similar to that produced by the hydration of the OPC sonicated alone. The nano-alumina produced more complex behaviour, with a higher maximum heat flow than any of the other sonicated samples. In addition, the early heat generated by the hydration of the OPC sonicated with the nano-alumina suggests that the addition of that nanoparticle nucleates C_3A hydration reactions. Finally, the sonication of nano-titania with the OPC both retards the

hydration reactions and reduces the maximum heat flow generated during hydration.

Fig. 1 Heat flow generated by OPC sonicated for 2 hours with and without 2% nanoparticle additions

The effects on OPC hydration produced by the presence of the nanomaterials differed from those reported previously for SWCNT [Makar and Chan 2009] both in terms of magnitude and quality. None of the nanomaterials accelerated the hydration reactions compared to the as-delivered control OPC, nor did they produce higher heat flows. Both characteristics were observed for the OPC sonicated with SWCNT [Makar and Chan 2009]. In addition, the pattern of the heat flow generation by the samples sonicated with nanomaterials was, in general, similar to that of the OPC sonicated alone, with the exception being the early heat flow of the OPC sonicated with nano-alumina. The OPC sonicated with SWCNT had the same general behaviour as the control, unsonicated OPC.

3.2 SWCNT nucleation mechanisms

The heat flow measurements in Fig. 1 tend to argue against adsorption as the dominant mechanism behind the observed nucleation effects produced by

SWCNT during OPC hydration processes. All of the nanomaterials in Fig. 1 were non-conductive, eliminating electrostatic effects as a possible nucleation mechanism in their case. Adsorption, however, would remain a possible factor in the hydration of the OPC in the presence of the nanomaterials. In fact, it is possible that the retarding effect of the nano-titania was due to adsorption of the ions in the solution on to the surface of the titania, preventing them from taking part in the hydration reactions. While one would expect different degrees of effect from the different nanomaterials if adsorption is the predominant nucleating mechanism, one would still expect to see the same general hydration behaviour in each case. The differences between the hydration behaviour of the samples sonicated with SWCNT and those sonicated with the nanomaterials instead suggests that nucleation effects in the former be attributed to the electrostatic mechanisms that rely on the metallic properties of the SWCNT.

A second line of evidence against the adsorption of metallic ions as a nucleation mechanism is the relative disparity between the nucleation of C-S-H and Ca(OH)_2 on the SWCNT bundles. Only one example of Ca(OH)_2 nucleating on SWCNT was observed (Fig. 2), with all other episodes of crack bridging occurring in C-S-H. In addition, examination of SWCNT bundles on OPC surfaces during the early stages of hydration did not show evidence of Ca(OH)_2 forming around the SWCNT. Although Ca(OH)_2 appeared to be less common on the surfaces of OPC during the early stages of hydration than is C-S-H [Makar and Chan 2008, Makar et al. 2007], it was readily identified when it did form. Investigation of the effect of SWCNT on the formation of Ca(OH)_2 , however, has shown that the same amount of Ca(OH)_2 was present in samples with and without SWCNT when the same amount of hydration had occurred [Makar and Chan 2008]. The three observations together suggest the SWCNT may be preferentially nucleating C-S-H, with the Ca(OH)_2 forming elsewhere in the system.

It is this relative imbalance between formation of C-S-H around SWCNT bundles and Ca(OH)_2 that supports the prevalence of electrostatic effects as a nucleation mechanism. Electrostatic effects would be expected to cause both Ca^{2+} and Si^{4+} ions to nucleate on the SWCNT surfaces. On the other hand, adsorption of metallic ions would be expected to primarily nucleate Ca^{2+} . In that case, a preferential formation of Ca(OH)_2 would be the most likely outcome, not of C-S-H.

Fig. 2 Crack bridging in $\text{Ca}(\text{OH})_2$ crystal (2% SWCNT, 7 days hydration)

3.3 Effect of distribution of SWCNT in Disal on the hydration of C_3S

While the effect of SWCNT on the hydration of sonicated OPC was found to be due to electrostatic nucleation effects, other factors came into play when the hydration behaviour of SWCNT/Disal/cement systems were considered. Fig. 3 shows isothermal calorimetry data for C_3S hydrated with and without the presence of Disal and SWCNT. SWCNT content is shown as a percentage of the mass of the C_3S in the mix (i.e. half the percentage of SWCNT by mass of mix water).

As would be expected in a pure C_3S system, the concentration of Disal used in mix water greatly delayed the hydration process. Adding increasing amounts of SWCNT to the mix appears to counteract the retarding effect of the Disal. At 1.5% SWCNT content the hydration process has been accelerated to the point where it is only marginally delayed compared to the control sample without Disal. The apparent acceleration compared to sonicated Disal alone that was produced by the presence of the SWCNT in Fig. 4 was far larger than that seen for samples where the SWCNT were dispersed by sonication [Makar and Chan 2009].

Fig. 3 Effect of SWCNT dispersed in sonicated Disal on C_3S hydration reactions

The concentration of SWCNT in the mix to the time of the maximum heat flow of the sample is compared in Fig. 4. The individual data points can be readily fitted to a decaying exponential curve with the empirical equation:

$$t_{\max} = 7.73 + 29.7e^{-1.55C} \quad (1)$$

where $t_{\max}$ is the time of the maxima in heat flow in hours and C is the concentration of SWCNT as a percentage of the mass of C_3S . The fitted curve has an $r^2 = 0.994$.

It is interesting to note that the asymptotic value of the fitted curve is below the time of maximum of the heat flow of the sample without Disal. As shown in Fig. 4, a concentration of $\sim 2.25\%$ by mass SWCNT should be sufficient to eliminate the delay induced by the presence of the Disal. This estimate could not be confirmed experimentally due to the inability to mix C_3S with mix water containing higher concentrations of SWCNT. Fig. 4 also suggests that further additions of SWCNT beyond 2.25% by weight would produce a slight accelerating effect, with a maximum acceleration of ~ 1 hour at the asymptotic value compared to the C_3S alone. This result compares to the ~ 2 hour acceleration due to enhanced nucleation effects seen for OPC sonicated with 1% SWCNT [Makar and Chan 2009].

Fig. 4 Change in timing of maxima in heat flow due to the presence of SWCNT dispersed by sonication in 8 g/L Disal.

Comparison between the previously published results on OPC sonicated with SWCNT [Makar and Chan 2009] and those here suggests that the major effect on the hydration of the C₃S/sonicated Disal system was not due to SWCNT acting as nucleating sites for the hydration reactions. Instead, the acceleration would appear to have been due to the interaction of the Disal with the SWCNT inhibiting the Disal/C₃S interaction. A separate experiment (not shown) indicates that increasing Disal content in a pure C₃S system results in an exponential growth of the timing of the heat flow maximum. An exponential decay in the timing of the heat flow maximum would therefore be expected if the SWCNT were inhibiting the interaction of the C₃S and Disal.

The loss of interaction with the C₃S in turn suggests that the Disal may be dispersing the SWCNT by wrapping individual nanotubes or bundles. If the Disal molecules were taken up in this form, they would no longer be able to interact with the C₃S. Examples of other molecules wrapping SWCNT can be found in the literature [Narimatsu et al. 2006, Stranos 2006].

3.4 Effect of distribution of SWCNT in Disal on the hydration of OPC

Although the effect of SWCNT/Disal combination was pronounced in C_3S systems, Fig. 5 shows that it was significantly reduced in OPC mixes. In addition, the monotonic progression in effect seen in Fig. 4 was not apparent. Instead, SWCNTs between 0.25 and 1.5% by mass all had approximately the same effect on the time of the OPC's major C_3S hydration reaction. The presence of the SWCNT also appeared to accelerate and possibly enhance the secondary C_3A and C_4AF reactions [Makar and Chan 2008, Pratt and Ghose 1983]. These reactions are marked by arrows in Fig. 5 for the control samples without SWCNT and by stars for the samples with SWCNT. The heat flow reached a maximum value for both the main C_3S reaction and the secondary reactions at 0.5% by mass SWCNT concentration and fell off with increasing concentration.

Fig. 5 Effect of SWCNT dispersed in Disal on OPC hydration reactions

The acceleration of the secondary reactions in the OPC/SWCNT/Disal system was in direct contrast to the results of the previous work using isopropanol dispersion. There, evidence was provided that the presence of the SWCNT altered the aspect ratio of ettringite formed by very early hydration reactions. No evidence for nucleation of ettringite or other aluminate hydration products was seen and the

secondary reaction peak did not appear to be significantly altered from that of the control sample without sonication.

The results of Fig. 5 in comparison to Fig. 3 and the earlier work [Makar and Chan 2009] suggest that although the Disal was taken up by the SWCNT, with a resulting reduction on the effect of the Disal on C_3S hydration, the superplasticizer was still adsorbed on the C_3A surfaces despite the presence of the nanotubes. As a result, the aluminate reactions were enhanced.

The results in Fig. 3 to 5 have a number of implications for the mechanical performance of SWCNT/cement composite materials. As will be discussed in more detail below, the nucleation of C-S-H on SWCNT in sonicated samples appears to produce a high degree of mechanical bonding between the two materials. This bonding would be expected to contribute to the development of classical reinforcing behaviour in the composite materials. If the Disal was wrapping the SWCNT, as suggested by Fig. 3 and 4, nucleation of C-S-H on the SWCNT would be inhibited, potentially reducing the extent of bonding between the two materials. Moreover, if the Disal/SWCNT mixture was preferentially adsorbed on the calcium aluminate surfaces, the results may have been an uneven distribution of SWCNT throughout the matrix. This effect would be expected to be detrimental to the performance of the SWCNT as reinforcement. Not only would areas of minimal reinforcement exist in the matrix, but a sufficiently high concentration of SWCNT in a small number of locations might even act as a crack former in the matrix.

4. Reinforcing Behavior in SWCNT Composites

4.1 Evidence for classical reinforcing behavior

4.1.1 Classical reinforcing behaviour

Non-continuous fibers reinforce matrices by absorbing some of the energy associated with crack formation and propagation. Classical microscope evidence for reinforcing behavior by fibers is generally considered to include three different types of behaviour:

- crack bridging (Fig. 6a), where cracks that would otherwise propagate through a matrix are shown to be crossed by fibers;
- fiber pull-out (Fig. 6b) where larger cracks have caused fibers to leave the matrix; and
- crack deflection (Fig. 6c), where a crack that does not cross the fibers is still deflected around them, rather than propagating in an essentially straight line.

Fig. 6. Schematic Representation of Fiber Reinforcement Mechanisms

Crack bridging and fiber pull out absorb energy as the bond between the fiber and the matrix is broken and the two materials pull away. Crack deflection absorbs energy due to the increased path length of the crack as it goes around the

reinforcements. It is also possible for cracks to be deflected to an extent that they no longer propagate perpendicularly to the direction of loading on the composite material, requiring additional energy to continue the failure process.

4.1.2 Reinforcing Behaviour in SWCNT/OPC composites

All three classical reinforcing mechanisms were observed in SWCNT/OPC composites. Crack bridging was particularly common, being observed in almost all samples hydrated for a day or more. A small section of a particularly striking example of crack bridging can be seen in Fig. 7. Here a crack had propagated in a zig-zag pattern across a 1 mm wide particle of cement paste. Typical widths of the crack were less than 1 μm and additional cracks branched away from it where it changed direction. SWCNT bridged the crack throughout its length and had clearly held the two pieces of the grain together, preventing a complete fracture.

Fig. 7. Crack bridging and fiber pull out (white arrow) in SWCNT/OPC composite (2% SWCNT, 7 days hydration)

An individual example of fiber pull out is also indicated by the arrow in Fig. 7. Fiber pull out was relatively easy to detect during the early stages of hydration [Makar and Chan 2009], but was much less readily observed in sample hydrated for longer periods such as are shown here. It is possible that the lack of observed SWCNT pull outs was due to the adhesion of the pulled out fibers to the matrix along the fracture surface, making observation by SEM difficult. However, other

explanations lie in the distribution of the SWCNT on the surface of the OPC grains and the behaviour of the SWCNT bundles. These points will be discussed further below.

As noted earlier, while almost all incidents of crack bridging were seen in C-S-H, cracking bridging was also seen in a fractured calcium hydroxide crystal (Fig. 2), which was large enough for positive identification by X-ray dispersive spectroscopy in the SEM. This image was particularly significant as it demonstrates that the ability of SWCNT to nucleate hydration reactions was not limited to the formation of C-S-H alone.

The two different examples of crack bridging also show differences in the condition of the SWCNT. In Fig. 7 the nanotube bundles were clearly under tension, with a very linear appearance. In Fig. 2 some of the bundles are also linear, but more appear relaxed, suggesting that the two parts of the Ca(OH)_2 crystal had moved together somewhat after the fracture had taken place.

One feature both images have in common is that the ends of many of the bundles branched apart where they were attached to the fracture surfaces. This effect may be due to the way in which the SWCNT bundles were distributed over the surface of the OPC grains. SWCNT bundles distributed by sonication often intersect or overlay each other (Fig. 8). The appearance of the SWCNT in Fig. 7 and Fig. 2 suggests that these contacts are not affected by the hydration process.

Crack deflection (Fig. 9, solid arrows) was also seen in the samples, although again less commonly than crack bridging. It was more obvious in those samples with lower quality of dispersion, where the bundles were thicker and more closely located together. The adhesion of the bundles to the surface of the C-S-H is indicative of a deflection process. As mentioned earlier, SWCNT have elastic moduli of around 1 TPa and, as a result, tend to stand away from the C-S-H once pulled out of the matrix. The dashed arrow in Fig. 9 indicates an example of such a pulled out bundle.

4.1.3 Comparisons to fracture surfaces in control and other samples

Comparisons between the OPC-SWCNT composite fracture surfaces shown in section 4.1.2 and those created when other hydrated nanomaterial/OPC blends were fractured help to highlight the importance of the SWCNT in modifying the structure of the C-S-H and in creating reinforcing behaviour. A typical fracture surface for a control sample of OPC sonicated alone and then hydrated for 7 days is shown in Fig. 10, while Fig. 11 to 14 show the effects of addition of the nano-alumina, nano-calcium carbonate and nano-titania.

Fig. 8 SWCNT distributed by sonication on OPC surface (1% SWCNT by mass), showing overlaps and intersections of nanotube bundles

Fig. 9. Crack deflection (solid arrows) and fiber pullout (dashed arrow) in SWCNT/OPC composite

Details about the fracture samples and their analysis will be given elsewhere [Makar and Chan, in preparation]. In general, however, the fracture surfaces at 7 days of hydration of OPC sonicated alone showed a mixture of $\text{Ca}(\text{OH})_2$ and C-S-H, with C-S-H predominating. In the case of Fig. 10, a small amount of calcium hydroxide was seen (arrow, identified by morphology), with most of the image taken up by the C-S-H. Other images showed more massive $\text{Ca}(\text{OH})_2$ structures. Some images showed ettringite crystals with aspect ratios of 10 or more, which appear to have formed in pores in the structure. The overall structure appeared to be dense at the scale examined.

Fig. 10 Typical fracture surface for OPC sonicated in isopropanol (7 days hydration), showing $\text{Ca}(\text{OH})_2$ crystal (arrow)

In contrast, the structure of the fracture surfaces of the OPC sonicated with 2% nano-alumina (Fig. 11) after 7 days of hydration appeared to be less dense, with larger pores visible on the surface. The fracture surfaces themselves were rougher, with a number of images having multiple features similar to that indicated by the arrow in Fig. 11. Both ettringite and $\text{Ca}(\text{OH})_2$ were less visible along the fracture surfaces.

The images of the fracture surfaces of the OPC sonicated with 2% nanocalcium carbonate (Fig. 12) had a similar density to that for the OPC sonicated alone. However, the overall surfaces were rougher than the OPC sonicated alone and there was a much higher prevalence of ettringite on the fracture surfaces (82% and 21% of the images of samples with and without nanocalcium carbonate, respec-

tively). None of the images from the nanocalcium carbonate samples show fractures exposing Ca(OH)_2 .

Finally, the images of the fracture surfaces from the 7 day hydration samples of OPC sonicated with 2% nano-titania showed either large quantities of Ca(OH)_2 (Fig. 13) or relatively dense C-S-H (Fig. 14). The latter surfaces were not dissimilar to those seen for hydrated OPC that was sonicated alone. The prevalence of massive Ca(OH)_2 was, however, higher than in any of the other samples.

The observed prevalence of the hydration products discussed above should not be taken to represent the actual distribution of C-S-H, Ca(OH)_2 or ettringite in the samples. Instead, it indicated only what is present along the line of fracture of the

Fig. 11 Typical fracture surface for OPC – 2% nano-alumina composite (7 days hydration), showing typical surface texture (arrow)

Fig. 12 Typical fracture surface for OPC – 2% nano calcium carbonate composite (7 days hydration) showing ettringite (rods) and C-S-H

Fig. 13 OPC – 2% nano-titania composite fracture surface with massive Ca(OH)₂ (7 days hydration)

Fig. 14 OPC – 2% nano-titania composite fracture surface with C-S-H (7 days hydration)

samples. With that condition in mind, an analysis of the images suggests that the individual grains of cement in the samples hydrated in the presence of the nano calcium carbonate and the nano-alumina were less well bonded together than the control sample of OPC hydrated alone and the sample hydrated in the presence of nano-titania. In addition to the differences in structure and surface texture described above, fracture of the latter two samples produced larger particles, indicating the presence of a tougher matrix.

Despite the differences between the different fracture surfaces described above, all of the four samples had greater similarities to each other than they had to the surfaces of the OPC sonicated with 2% SWCNT samples. As shown in Fig. 7 and 9, the presence of the SWCNT creates a dense matrix with a smoother fracture surface than the other samples. The broken pieces of the matrix were typically much larger than those of the other samples, being in some cases millimeters, rather than micrometers across. Most significantly, no evidence was seen in the other samples of significant cracking such as shown in Fig. 2 and 7. Once cracks had formed in those samples they appear to have propagated through the matrix, causing complete fracture. It was only in the samples containing SWCNT that the crack growth was arrested.

4.2 Evidence for strength of bond

Two types of qualitative evidence were observed in SEM images of SWCNT/OPC composite fracture surfaces. In some cases two pieces of the composite material had fractured entirely and remained connected by bridging SWCNT. Subsequently the distance between the pieces of matrix decreased, causing the SWCNT to relax. As a result of the two pieces of the sample moving together, the SWCNT bundles develop curves or bends. SWCNT have elastic moduli of 1 TPa [Salvetat et al. 1999] and a tight bend is therefore indicative of considerable stored energy in the bundle. An equivalent amount of energy would need to be available in the bond between the SWCNT bundle and the matrix in order to prevent the bundle from detaching.

Examples of this process can be seen in Fig. 15, where a pair of SWCNT bundles are shown in the center of image. Both bundles were highly curved and it was not obvious which sections of the bundles are continuous with each other. Closer examination suggested the connections shown by the arrows. The two ends of the bundle marked by the solid arrows and the lower end of the bundle marked by the dashed arrows were attached to C-S-H structures that are in the same approximate focal plane as the bundles themselves, suggesting that the tight curvature seen in the former bundle was real and not an artifact of the angle of

Fig. 15. Adhesion of SWCNT ropes to OPC surface (arrows of same type indicate continuous SWCNT bundles)

imaging. The bundle marked by the dashed arrows, however, appeared to become narrower as it moves towards its upper contact with the C-S-H, suggesting that its curvature may have been less than would be estimated by direct measurement on the image.

Two other types of bending experienced by SWCNT bundles in cement matrices are shown in Fig. 16. Here the bundles were again bridging a gap between two pieces of C-S-H. These bundles were thicker and had not been as well distributed as those discussed in Makar and Chan [2009] and it was possible that they were present in sufficient concentration to act as a crack former, rather than a reinforcement. They do, however, clearly illustrate several important points about the interaction between the C-S-H and the SWCNTs.

The appearance of the gap and the SWCNT between the pieces of C-S-H suggests that they may have rotated slightly as well as being pulled apart. Bundle 1 in Fig. 16 appeared to be curved or buckled in the middle, while the remaining bundles were either straight or pulled completely apart. In addition to the curvature in the bundle 1, all of the bundles showed curvature towards the point of contact with the C-S-H. This effect appeared to be due to each bundle being anchored at a number of places on or in the C-S-H, but held together by van der Waals forces in the centre of the bundle. The bending of the SWCNT bundles also suggests a considerable amount of energy was stored in the bundles, again indicating a strong bonding situation.

Fig. 16 SWCNT bundles in the process of being pulled apart

The bundles in Fig. 16 also provide another indication of the strength of bond between the SWCNT and the C-S-H. While bundle 1 was curved and bundle 4 was straight and appears to be under some degree of tension, bundles 2, 3 and 5 appear to have been pulled apart at the time of the separation of the C-S-H. In each case corresponding bundle ends, appearing to thin to a lower number of SWCNT, can be seen at the top and bottom of the image. The ends of the separated bundles did not precisely align with each other, likely due to the bundles deflecting to minimize their energy once the two parts of the bundle had separated. Fig. 17 shows a schematic of the separation process.

Individual SWCNT are held in bundles by van der Waal's forces, which have been estimated as being as high as 11 GPa. While it is impossible to determine from the images the degree to which the individual SWCNT contacted each other, the adhesion of the bundles to the C-S-H when fracture occurs, rather than to other SWCNT, again suggests that the two materials were strongly bonded together.

The apparent degree of bundle to matrix adhesion, as opposed to SWCNT to SWCNT adhesion, was particularly significant when the effect of the size of the bundles was taken into consideration. The strength of bond between the matrix and a SWCNT bundle, as opposed to a single SWCNT, is dependent on the amount of surface contact between the bundles and the matrix. A thicker bundle, with more SWCNT, will have proportionately less contact than a thinner bundle. Bundles of more than 6 SWCNT would be likely to have more SWCNT to SWCNT contact by surface area than SWCNT to matrix. The fact that the SWCNT remained attached to the matrix even when in the form of the relatively thick bundles seen in Fig. 16 also helps to emphasize the strength of the SWCNT/matrix bond.

Fig. 17 Separation of a SWCNT bundle into two due to fracture of C-S-H matrix. SWCNT bonded to each side of the fracture (A) slide apart as the crack grows (B), eventually separating entirely (C).

It is worth noting that the branched bundles seen in Fig. 16 may be advantageous with respect to bonding and reinforcement. A branched system would be expected to have greater contact with the matrix than a single linear bundle with the same total number of SWCNT. Secondly, the branches mean that the applied forces producing the crack may not necessarily be aligned perpendicularly to the SWCNT in the matrix even if they are aligned perpendicularly to the crack, reducing the effective load applied to the SWCNT and their bond with the matrix.

While examination of the SEM images provides qualitative information on the strength of the C-S-H/SWCNT bond, direct measurement of the strength of bond between a matrix material and SWCNT is a difficult undertaking. Examples in the literature have relied on attaching one end of an individual nanotube to an AFM probe or other structure and immersing it in unhardened matrix material [ref]. This method can work well when bonds are expected to be weak, but in the case of a well bonded material the results may be affected by changes in the attachment between the sample support structure and the SWCNT as well as the matrix.

Another approach would be to calculate the apparent strength of the bond based on SWCNT or SWCNT bundle deflections. This method uses the known 1 TPa value of the elastic modulus of the SWCNT [Salvetat et al. 1999] and the estimated curvature of bent SWCNT to estimate the energy associated with the interaction between the matrix and the nanotubes. In principle, this calculation could produce quantitative results for bond energy, but there several issues limit its utility. First, determination of degree of curvature is limited by the quality and nature of the images involved. This issue has been discussed above with respect to Fig. 15. Secondly, precise estimates of the number of SWCNT in a bundle can not be obtained from this form of SEM imaging. Finally, it is impossible to determine the extent to which the SWCNT bundles penetrate the surface of the C-S-H. As a result, there is no way to determine the precise length of SWCNT bonded to the C-S-H. In the case of the sliding behaviour shown in Fig. 16, the second and third limitations also apply. In particular, it is certainly possible that there are more SWCNT attached to C-S-H than were present in the center of the bundle.

Given these limitations the best estimate that can be made of the bond strength is that it is likely within an order of magnitude of the van der Waals forces holding the SWCNT bundles together. This estimate arises directly from the behaviour shown in Fig. 16 and 17, where the ends of the bundle remain attached to the matrix, rather than one end completely detaching from the matrix. This estimate in turn suggests that the bonding between the matrix and the SWCNT bundles may itself arise from van der Waals forces. If this is indeed the case, the C-S-H immediately around the SWCNT may be significantly more ordered than the bulk material. Further work, particularly using high resolution transmission electron microscopy, is needed to investigate this possibility.

4.3 Implications of methods of dispersion for composite performance

The apparent high degree of bonding between the SWCNT bundles and the matrix suggests a corresponding degree of reinforcing capability. Fully taking advantage of that capability requires dispersing the SWCNT as evenly as possible throughout the C-S-H matrix. The cement hydration process, where outer product grows outward from the surface of the grain and inner product forms underneath it limits the locations where reinforcement can take place. Reinforcement is likely to be limited to the outer product unless the reinforcing material can remain in solution and is sufficiently small that it can be carried into the inner product zone before diffusion of ions through the existing hydration products becomes the predominant hydration mechanism [Taylor, 1997].

Neither of the two methods of dispersing SWCNT discussed here is likely to provide a means of reinforcing the inner product. Depositing the SWCNT on the grain surface accelerates the onset of the hydration reactions and provides localized reinforcing behaviour, but once the hydration products have covered them, any remaining product that forms between the cement grains will not be directly reinforced. Similarly, dispersing SWCNT or nanoparticles in superplasticizer appears to be likely to cause concentrations of the nanomaterial on or near C_3A in the unhydrated OPC. The remainder of the OPC is likely to experience a reduced degree of reinforcement, with bonding potentially hampered by the superplasticizer itself.

It is certainly possible that other methods of dispersion of carbon nanotubes and/or other nanomaterials could be developed to position them so that they would stand perpendicularly away from the surface (in the case of nanotubes or nanorods) or remain suspended in the hydration water. Such processes would still leave the inner product region unreinforced, but would improve the extent of outer product reinforcement.

5. Conclusions

At the microscopic level, SWCNT/OPC composites showed evidence of classical reinforcing behaviour in the form crack bridging, fiber pullout and crack deflection. This reinforcing behaviour occurred even when the SWCNT were present in the form of bundles, rather than individual nanotubes. The high degree of adhesion between SWCNT in a bundle means that separation of a bundle during crack formation acts as a fourth form of reinforcing mechanism, with energy being absorbed as the van der Waal's forces holding the bundle together are overcome.

The ability of the hydrated OPC matrix to remain attached to the ends of the SWCNT bundles during crack growth suggested that a high degree of bonding existed between the two materials. A qualitative estimate of the strength of bond is

that it was within an order of magnitude of the van der Waals forces in the bundle, but no numerical estimate was possible with the data examined here. The high strength of bond appeared to be due to the nucleation of the C-S-H by the SWCNTs and its formation along the SWCNT bundles. Comparisons between the performance of the SWCNT as a nucleating agent and that of other nano-materials, as well as the preferential nucleation of C-S-H instead of Ca(OH)_2 on the SWCNT, suggested that the predominant nucleation mechanism was electrostatic in nature, rather than adsorption of metallic ions.

Dispersion remains a challenge in the use of SWCNT in cement systems. While SWCNT can be successfully dispersed in Disal, the hydration behaviour of those systems suggests that the SWCNT were being wrapped by the admixture, which appeared to inhibit the nucleation behaviour produced by SWCNT dispersed by sonication. In addition, the presence of the admixture appeared to cause the SWCNT to nucleate C_3A and C_4AF reaction products, in addition to C-S-H. Further work is needed on dispersion issues to reach the full potential of SWCNT as a reinforcing material.

Despite the need for improved dispersion techniques, SWCNT remain extremely promising as nanometric reinforcing materials. As with other nanomaterials, the real challenges to use in the field are not the development of the material. Instead, they involve the safe and appropriate use of the material in construction. Scaling laboratory procedures to industrial production, producing the material in a manner safe for construction construction workers (i.e. without release of nanomaterials in the cement or ready mix plant), and following appropriate environmental and health guidelines through the product's life cycle from placement to demolition all present significant, long term challenges that need to be overcome.

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