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Carbon Nanotube/Cement Composites – Early Results and Potential Applications

Jon Makar, Jim Margeson and Jeanne Luh*
National Research Council Canada, Canada

*Now at:
University of Illinois at Urbana-Champaign, USA

Abstract

Carbon nanotubes (CNT) have unique mechanical properties that make them close to ideal reinforcing materials. Single walled CNT have a modulus of elasticity of approximately 1 TPa, yield strengths measured at between 20 and 60 GPa, and measured elastic strains at yield that are greater than 10%. In addition, CNT typically have aspect ratios of 1000 or more.

These attractive properties have led to considerable research on CNT composites. While particular attention has been paid to polymer based materials, metal and ceramic matrix materials have also been described in the literature. A new area of research involves CNT/cement systems. Early results investigating the microstructure of these systems show promise for the eventual development of carbon nanotube/cement composites. Scanning electron microscopy at the National Research Council has observed crack bridging and fiber pull-out in CNT/cement composites. Evidence for bonding between CNT and the cement matrix has also been observed. These reinforcing mechanisms have been shown to produce higher microhardness measurements at early stages of sample hydration as compared to cement control samples without CNT. This paper describes current developments in the production of CNT-cement composites. Possible applications for a successful composite material and areas of potential structural research activity are also discussed.

Keywords: cement, carbon nanotubes, nanotechnology, concrete, composites, Vickers hardness

Jon Makar
Institute for Research in Construction
National Research Council Canada
1200 Montreal Road, Ottawa, Ontario K1A 0R6
Canada

Email: jon.makar@nrc-cnrc.gc.ca
Tel: 613-993-3797

1.0 Introduction

The concept of nanotechnology comprises a range of techniques that allow researchers to probe the behaviour of matter at length scales between 1 and 100 nm, at the boundary between the quantum mechanical behaviour of individual atoms and the classical behaviour of bulk matter. Nanoscale materials can exhibit unique properties, as well as behaviours that can differ by orders of magnitude from those seen in larger scale materials. Nanotechnology developments are already essential features in products as diverse as computer hard drives, cosmetics, and oil refining technology, where they provide greatly enhanced performance compared to the materials they replaced.

Work has begun on the application of the techniques and concepts of nanoscale science to construction materials¹. While many different construction materials are under investigation using these methods, there is particular interest in developing nanotechnology for cement and concrete. Both the chemistry that forms cement hydration products and the physical behaviour of those products are amenable to manipulation through nanotechnology. One goal of the development of cement related nanotechnology is the production of stronger and tougher concrete products. There are a number of different routes that may lead to that goal, such as the addition of nanoscale cementitious particles to reduce porosity or the development of new methods of delivering cement admixtures to control the rate of hydration product growth. However, these approaches will still produce a brittle material that is much weaker in flexure than in compression. Here, we describe a different approach, where the cement paste is combined with carbon nanotubes to produce improved binder properties, including flexural strength and fracture toughness.

1.1 Carbon Nanotubes

Discovered in 1991, carbon nanotubes (CNT) are a unique form of carbon that has desirable mechanical, thermal and electronic properties. They can be easily visualized by considering a single graphene sheet, a lattice of carbon atoms distributed in a hexagonal (honeycomb) pattern. A piece of graphite is composed of many such sheets layered on top of each other. A single walled CNT looks like a single sheet rolled up into a tube, while multiwalled CNT look like multiple sheets rolled into a series of tubes, one inside the other. A single walled CNT is typically 1-3 nm in diameter and a micrometer or more long. Multiwalled CNT typically range in diameter from 10 to 40 nm, but have the same lengths as the single walled variety. CNT are not produced, however, by rolling up graphite sheets, but rather by a growth process from one end. Details of the structure and production of CNT can be found in the literature.^{2,3}

Mechanically, CNT show elastic behaviour, with a Young's Modulus of approximately 1 TPa.⁴ Single walled CNT have measured yield stresses of between 20 and 60 GPa⁵, with measured yield strains of up to 10%⁶. Difficulties in making measurements on single tubes mean that there is not exact correspondence between the reported stress and strain values. Theoretical considerations suggest that the yield stress for single walled CNT may be as high as 100 GPa⁵.

Depending on their precise structure, CNT may be metallic or semiconductors³. Changes in structure along the length of tube through defects or diameter changes can produce changes in conductivity. CNT are also believed to be the best thermal conductors known⁷. For both electrical and thermal conductivity a major constraint is high contact resistance, which reduces the transfer of heat or electrons from between CNT or between a CNT and another material. However, the conductivity of CNT is high enough that multiwalled nanotubes are currently being added to polymers to produce conductive commercial products.

1.2 Carbon Nanotubes as Reinforcing Materials in Composites

The mechanical properties of CNT have drawn intense interest in their potential for use as reinforcements in composite materials. In addition to their high strength and elastic constant, CNT have extremely high aspect ratios, with values typically higher than 1000:1 and reaching as high as 2,500,000:1.⁸ The size and aspect ratios of CNT mean that they can be distributed on a much finer scale than commonly used reinforcing fibers. As a result, cracks are interrupted much more quickly during propagation in a CNT reinforced matrix, producing much lower crack widths at the point of first contact between the moving crack front and the reinforcement. As a result of these properties, CNT reinforcements are expected to produce significantly stronger and tougher composites than traditional reinforcing materials.

Unlike other important matrix materials, little work has been done on the use of cements to produce CNT composites, with only very preliminary work being reported.^{9,10} The majority of research on CNT composites has instead focused on polymer matrices, with ceramics and metals also being considered for this role. While initial results were generally disappointing, often showing little or no improvement in composite properties over traditional reinforcing materials,¹¹ more recent results have been much more promising, with individual researchers showing significant improvements in fracture toughness, hardness and strength in both ceramic^{12,13} and polymer^{14,15} matrices. Key factors that have contributed to these improvements include the process of distributing the CNT in the matrix material and the degree of bonding between the reinforcement and the matrix. Traditional reinforcing mechanisms such as crack bridging, fiber pull out and crack deflection have been identified in ceramic matrices, with additional, nanoscale reinforcement mechanisms also being seen.¹³

2.0 Experimental Approach

The work reported here used a modification of a technique developed for use on alumina.¹² Commercial single walled carbon nanotubes (Carbon Nanotechnologies, USA) were dispersed by sonication (vibration by ultrasound) in isopropanol. Sufficient Type 10 ordinary Portland cement to produce a 0.02 by weight CNT/cement ratio was then added to the beaker containing the CNT while maintaining continuous sonication. After four hours, the sonication was stopped and the isopropanol was allowed to desiccate, with additional hand stirring taking place part way through the desiccation process. The resulting cement/carbon nanotube cake was then broken apart and ground using a hand mortar. This treatment produced cement particles coated with bundles of carbon nanotubes (Figure 1). Thermal analysis was used to confirm that the process did not result in hydration of the cement.

Samples were then prepared at a variety of water/cement ratios. Mixes with water/cement (w/c) ratios of 0.8 and 0.5 were prepared without superplasticizer. However, the CNT composite material was quite viscous during mixing even when prepared with a 0.8 w/c ratio. As a result, samples with 0.4 w/c ratios were prepared with the addition of varying amounts of superplasticizer, rather than with the use of water alone. Table 1 shows the mix designs discussed in this paper. After each batch of composite powder had been mixed with water and possibly superplasticizer, the mixture was placed in acrylic plastic moulds, with the top and bottom of each mould sealed with Parawax film and capped with glass microscope slides. The mould assemblies were then placed in sealed containers that were maintained at 100% relative humidity and room temperature for the required time of hydration. Table 1 also shows the times at which hydration was stopped for individual samples to allow testing.

Table 1: Sample Details

Mix #	Water/cement ratio	Superplasticizer Content	Time of Hydration for Measurements (days)
1	0.8	None	1, 2, 3, 4, 8, 16, 22
2	0.5	None	1, 2, 3, 4, 7, 14, 21
3	0.4	10 g/L	1, 2, 3, 7, 14, 21, 28

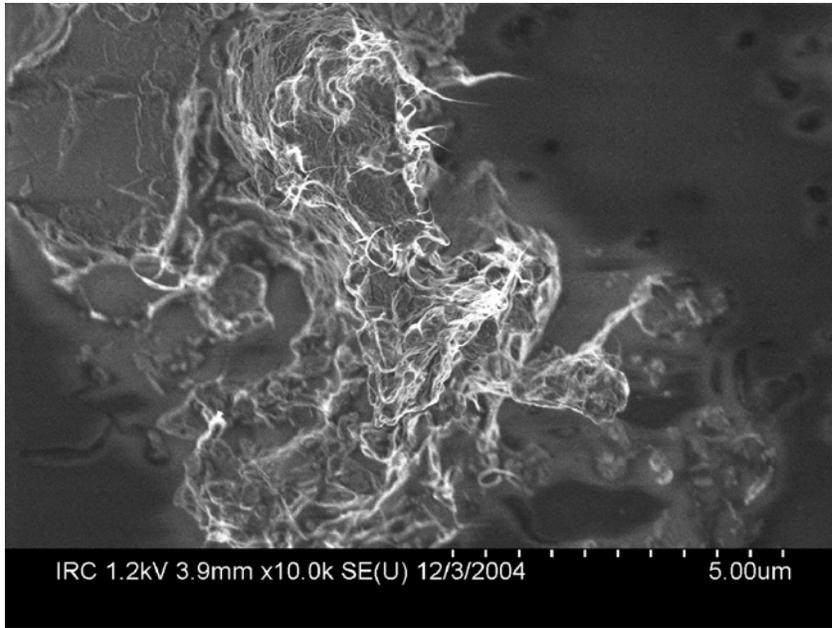


Figure 1. Carbon nanotube bundles distributed on unhydrated cement powder

A variety of tests were conducted on the hydrated samples, including scanning electron microscope (SEM) examination of fracture surfaces and ground powder, Vickers hardness testing, thermal analysis, and X-ray diffraction measurements. Details of the thermal analysis, x-ray diffraction results and further mix designs will be presented in a forth coming paper. Vickers hardness was measured using a Leitz Wetzlar hardness tester. The hardness tests of the cement paste are of interest because previous work¹⁶ has shown that Vickers hardness measurements on cement paste can be directly correlated to the elastic modulus and the compressive strength of the material. Vickers hardness testing can therefore provide a route to obtaining information on the mechanical behaviour of the CNT/cement paste composite without the need for large samples. It should be noted, however, that hardness measurements will at best provide an indirect route to investigate the impact of CNT on properties such as fracture toughness and bending strength.

Once the Vickers hardness tests were completed the same cement samples were used for the other experimental methods. In particular, the samples were broken up to induce cracks and expose fracture surfaces for examination. Pieces of the sample with intact fracture surfaces were mounted for SEM imaging and the remaining material hand ground to produce further damage. Both the

pieces and the ground powder from each sample were imaged using a Hitachi Instruments S4800 field emission gun SEM with an attached Oxford Instruments electron dispersion x-ray analysis system. The low accelerating voltages possible with this instrument meant that it was not necessary to coat the samples in order to produce acceptable images.

3.0 Results

3.1 Evidence for Reinforcement Mechanisms

Figures 2 to 4 show field emission gun SEM images of fracture surfaces of the three day hydration sample from mix design 3. Similar images were obtained from mixes 1 and 2, although both of those samples showed more extensive porosity. Figure 2 is a typical image of a fracture surface. It shows a crack crossing the centre of the fracture surface, regions of dense hydration products and, in the upper right corner of the image, a region of higher porosity. The spacing between the white bars in the image is one tenth that of the full scale (in this case the full scale is 5 μm), while the width of the white bars themselves is 1/100 the full scale (here 50 nm). Some of the regions where carbon nanotubes bridge the large crack are indicated by the black arrows, while the white areas on the image are regions where carbon nanotubes are exposed on the fracture surface after fiber pull out. Only bundles of carbon nanotubes can be imaged, not individual tubes. These images therefore underestimate the extent of CNT presence and dispersion.

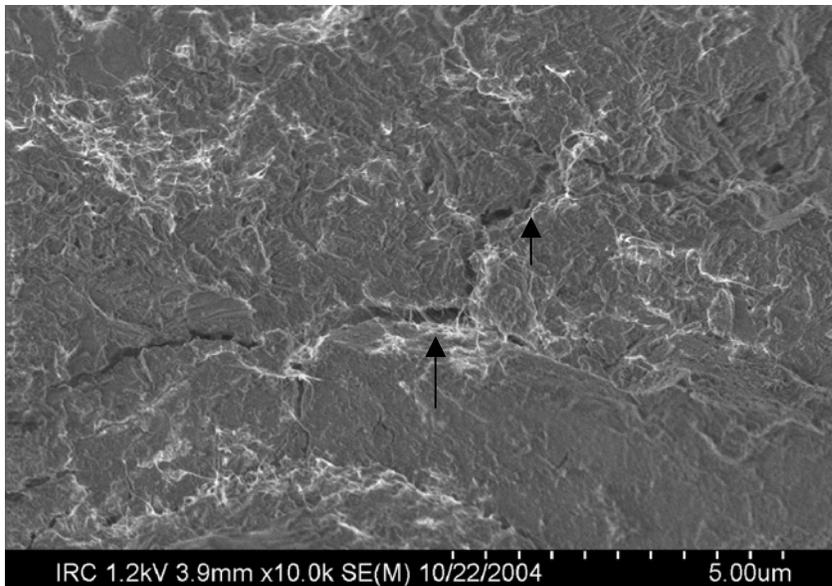


Figure 2. Image of fracture surface of group 3 sample (3 days hydration)

Figure 3 shows an image from the powdered material. Here bundles of pulled out CNT can be clearly seen. In this case the small hydrated cement particles indicated by the black arrows are being held to the larger background particle by the CNT bundles. Figure 4 shows a second example of crack bridging, with a narrow crack being crossed by a number of nanotubes. Crack bridging is readily identified in all of the composite samples produced to date, independent of water and superplasticizer content. The close up image in Figure 4 shows typical behaviour of the CNT across a crack, with the majority of the bundles being pulled in approximately the same

direction as the crack parts. The bundles that appear to lie in a different direction were found upon imaging to be partially above the fracture surface, suggesting that they represent bundles that have experienced fiber pull-out, rather than remaining attached to both sides of the crack. An important point here is that the crack is approximately 500 nm wide, which is about half the actual length of the individual CNT. They would therefore be expected to be anchored well inside the hydration products. The smallest bundles imaged here have diameters that are less than 5 nm, suggesting that they are composed of only a few 1.4 nm diameter single walled CNT. Careful imaging of this region also shows that there are additional CNT bridging the crack in the same area that are out of the focal plane of these particular images. It is worth noting that the distribution of the CNT in the hydrated samples (Figures 2 to 4) is not the same as seen on the unhydrated cement powder (Figure 1), with the CNT bundles in Figures 2 to 4 being smaller in apparent diameter and more widely distributed.

3.2 Hardness Measurements

Figure 5 shows average Vickers hardness measurements for the three mix designs discussed here. Between 28 and 46 measurements were made for each time at each mix design, with 42 measurements being the desired target value for control samples and 54 measurements for the nanotube composite samples. Measurements found upon examination to be taken directly above pores were discarded. The error bars show the standard deviation for each set of measurements. The graph shows consistent differences between the control and nanotube composite samples before 14 days hydration in all cases and throughout the measurement period in the case of the 0.8 w/c ratio sample.

Statistical analysis was performed on the hardness tests in order to confirm these apparent differences. The analysis assumed that the hardness measurements would have a normal distribution and used a null hypothesis that the two sets of measurements represented the same population (i.e. that the carbon nanotubes were *not* affecting the behaviour of the cement paste). Table 2 shows the results of this analysis. All tests show that the results before day 14 and throughout the 0.8 w/c ratio measurements rejected the null hypothesis with better than 98% probability and almost all reject it with better than 99.8% probability. These results strongly indicate that the results shown in Figure 5 represent a real difference in behaviour. In contrast, the result for the 0.4 and 0.5 w/c ratio samples beyond 14 days appear to be from the same population.

4.0 Discussion

As noted earlier, CNT should not be expected to have a direct effect on the hardness measurements. Hardness correlates well with compressive strength and the primary effects of the reinforcement would be expected to affect properties such as fracture toughness, tensile strength or bending strength. The results presented here may not, therefore, represent the effects of simple reinforcing behaviour.

SEM and optical microscopy of the 0.8 w/c ratio samples shows that the CNT composite sample was highly porous. The additional water in the mixture as compared to the 0.5 w/c samples did not improve the rheology of the composite samples during mixing, but instead appears to have acted as a barrier between hydrating cement grains, reducing the likelihood of the hydration products forming a strong, consistent bond across the sample. This effect resulted in the reduced hardness values seen in Figure 5 for the composite material.

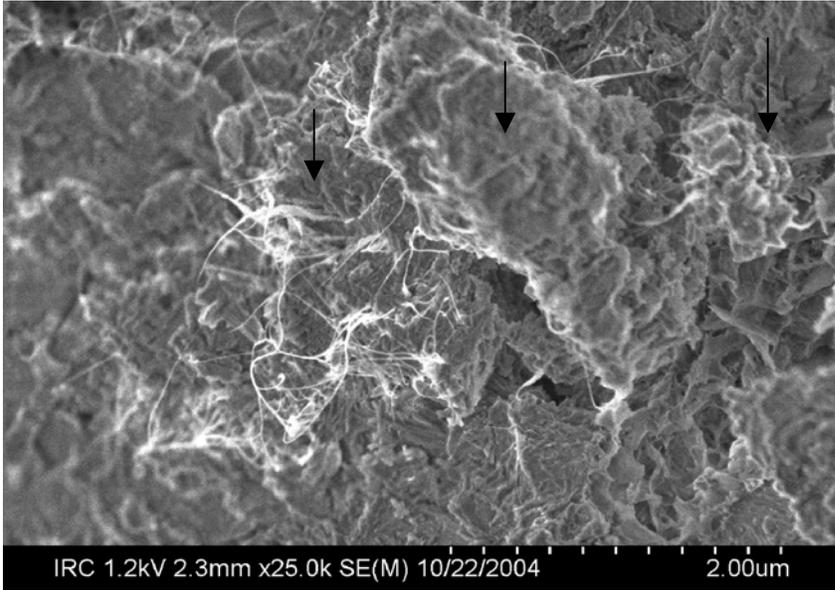


Figure 3. Fiber pullout along fracture surface of group 3 sample (3 days hydration)

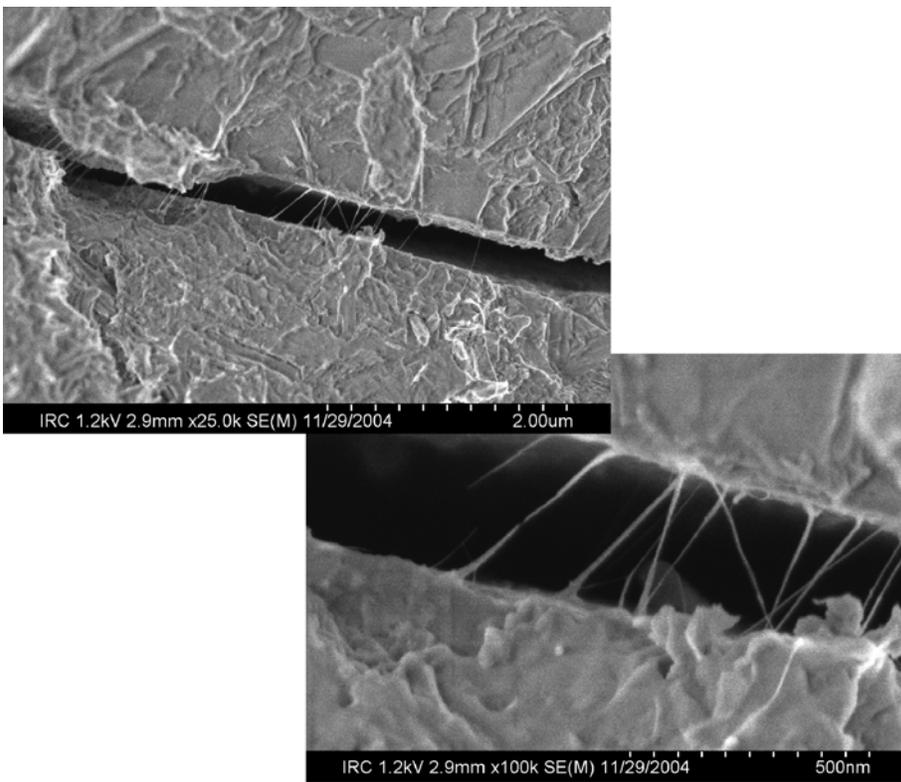


Figure 4. Crack bridging across group 3 sample (3 days hydration)

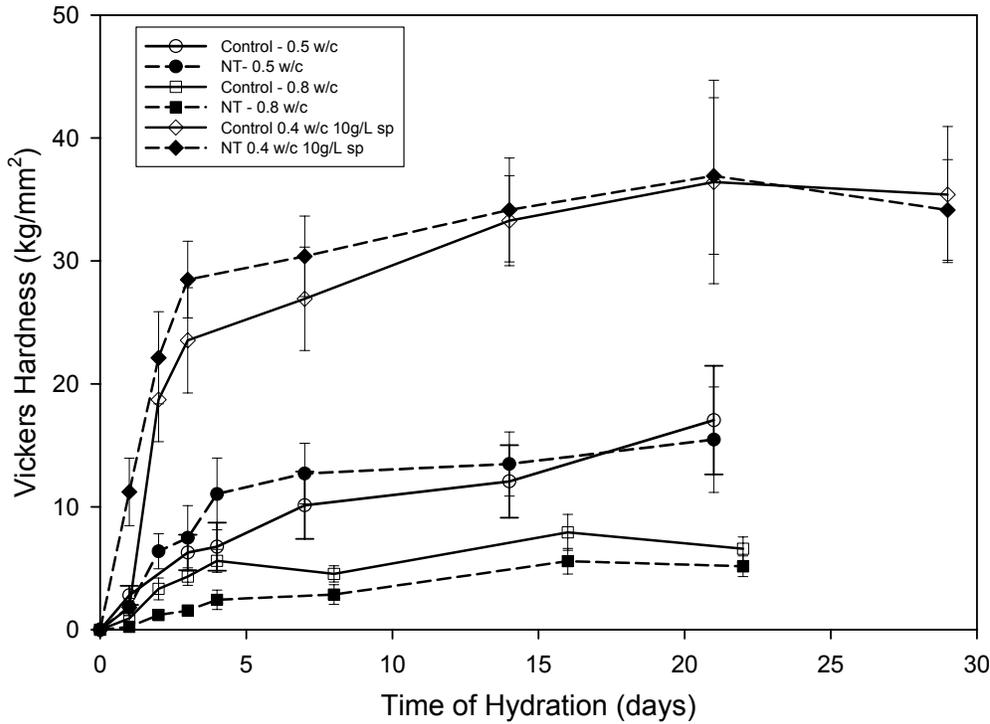


Figure 5 – Vickers Hardness Comparisons between control and composite samples.

Table 2: Statistical analysis of hardness measurements

0.8 w/c ratio		0.5 w/c ratio		0.4 w/c ratio, 10 g/L superplasticizer	
Hydration time (days)	Z for Vickers Hardness measurements	Hydration time (days)	Z for Vickers Hardness measurements	Hydration time (days)	Z for Vickers Hardness measurements
1	15.34	1	5.69	1	-21.60
2	13.96	3	-2.56	2	-4.23
3	22.52	4	-7.91	3	-5.77
4	16.62	7	-4.51	7	-4.15
8	10.51	14	-2.31	14	-1.03
16	8.48	21	1.62	21	-0.29
22	7.16			29	1.17

The early improvements in the hardness of the 0.4 and 0.5 w/c ratio composite samples, followed by minimal differences at later ages, suggest that the presence of the CNT accelerates the growth of one or more hydration products. Once the hydration process slows in the composite sample, the hardness of the control samples gradually reaches the same level as the CNT composites. This

result, combined with the evidence for reinforcing behaviour seen in Figures 2 to 4, indicates the presence of a direct interaction that produces bonding between the CNT and the cement paste. Recent work in polymer-CNT composites has shown that such interactions are necessary to establish strong reinforcing behaviour^{16,17}. The results presented here therefore show a potential for developing successful cement-CNT composites. However, further work will be necessary to explore the manner in which CNT affect the cement hydration process and to fully develop the potential of the composite material.

The potential applications for carbon nanotube-cement composites will be controlled by three factors: its environmental impact, the composite material's performance and its price. Environmental impact studies of CNT are currently underway¹⁹. While CNT are chemically inert, their fibrous nature means that caution must be used in their handling until these studies are completed. Some additional work will likely be necessary to explore the environmental behaviour of the cement-carbon nanotube composite behaviour.

The results in this paper are from a preliminary stage of research and the ultimate performance of the cement-CNT composites under development remain unknown. However, the current indications of bonding between cement paste and CNT are sufficient to allow comparison with recent work on ceramic and polymer composites. A five fold improvement or greater improvement in fracture toughness would therefore appear to be a reasonable estimate of expected performance, along with corresponding improvements in flexural strength.

Price is inevitably a factor in determining the extent of use of construction materials. CNT are currently very expensive. While it is expected that their price will fall by several orders of magnitude over the next few years, they are unlikely to reach the price where they will be routinely added to cement for use in all concrete. The additional cost of processing the cement into a composite material and any extra costs associated with demolition beyond those of normal cements must also be considered. The most probable applications for carbon nanotube composite materials are therefore in high value projects such as bridges and other structures where strength is at a premium. Other applications will be found where the electrical, electronic and/or thermal properties of the material will provide additional benefits.

5.0 Conclusions

Carbon nanotube-cement composite materials show classical reinforcing behaviour, with examples of crack bridging and fiber pullout being easily identified. Particles of powdered hydrated cement being held together by CNT bundles can also be seen during SEM imaging. Evidence from hardness tests suggest that the CNT directly affect the early hydration process, producing higher hydration rates than those experienced by control samples with 0.4 and 0.5 w/c ratios. This acceleration is seen in samples both with and without the addition of superplasticizer. The combination of the SEM and hardness test results suggest that a strong bond can be produced possible between the cement paste and the CNT.

While considerable work remains to be done to prove the utility of cement/carbon nanotube composite materials, the nature of the cement hydration process means that multiple, nanotechnology based routes to stronger and tougher concretes are likely to be found. These new materials will allow existing structural designs to be produced with reduced material volumes, but they may also allow for entirely new structural designs and concepts. Research is needed to explore these possibilities. Nanotechnology has developed quickly as a discipline because of

strong synergies between theoreticians and experimentalists. A similar synergy is needed between material researchers and structural engineers to apply nanotechnology to the construction industry.

6.0 References

1. Zhu, W., Gibbs, J.C. and Bartos, P.J.M, "Application of nanotechnology in construction – current status and future potential", *Nanotechnology in Construction, Proceeding of the 1st International Symposium on Nanotechnology in Construction, Paisley, Scotland, June 2003*, Royal Society of Chemistry, London, 2004, pp. 31-46.
2. Dai, H, 2002. Carbon nanotubes: opportunities and challenges, *Surface Science* **500**: 218-241.
3. Sinnott, S.B. and Andrews, R., 2001. Carbon Nanotubes: Synthesis, Properties and Applications, *Critical Reviews in Solid State and Materials Science*, **26**(3): 145-249.
4. Salvetat, J.-P., et. al. 1999. , Mechanical Properties of Carbon Nanotubes, *Applied. Physics A*, **69**: 255-260.
5. Yu, M.-F. , et al., 2000, Strength and Breaking Mechanism of Multiwalled Carbon Nanotubes Under Tensile Load, *Science*, **287**: 637-640.
6. Walters, D.A., et al., Elastic strain of freely suspended single-wall carbon nanotube ropes, *Applied Physics Letters*, 1999, **74**: 3803-3805.
7. Berber, S., Kwon, Y.-K., and Tomanek, D., Unusually High Thermal Conductivity of Carbon Nanotubes, *Physical Review Letters*, 2000, **84**: 4613-4616.
8. Zheng, X.L., et al., 2004. Ultralong single-wall carbon nanotubes, *Nature Materials*, **3**(10): 673-676
9. Makar, J.M. and Beaudoin, J.J., Carbon nanotubes and their application in the construction industry, *Nanotechnology in Construction, Proceeding of the 1st International Symposium on Nanotechnology in Construction, Paisley, Scotland, June 2003*, Royal Society of Chemistry, London, 2004, pp.
10. Campillo, I., Dolado, J.S., and Porro, A., High-performance nanostructured materials for construction, *Nanotechnology in Construction, Proceeding of the 1st International Symposium on Nanotechnology in Construction, Paisley, Scotland, June 2003*, Royal Society of Chemistry, London, 2004, pp.
- 11 Ajayan, P.M. and Zhou, O.Z., 2001. Applications of Carbon Nanotubes, *Topics in Applied Physics* **80**:391-425.
- 12 G.-D. Zhan, J. D. Kuntz, J. Wan and A. K. Mukherjee, 2003. Single-wall carbon nanotubes as attractive toughening agents in alumina-based nanocomposites *Nature Materials*, **2** (1): 38-42.
- 13 Xia, Z., et al., Direct observation of toughening mechanisms in carbon nanotube ceramic matrix composites, *Acta Materialia* **52**(4): 931-944.
- 14 Sandler, J.K.W., et. al., 2004. A comparative study of melt spun polyamide-12 fibres reinforced with carbon nanotubes and nanofibres, *Polymer* **45**: 2001-2015.
- 15 Thostenson, E.T. and Chou, T.-W., 2002. Aligned multi-walled carbon nanotube-reinforced composites: processing and mechanical characterization, *Journal of Physics D: Applied Physics*, **35**: L77-L80.
- 16 Beaudoin, J.J. and Feldman, R.F., 1975. A study of mechanical properties of autoclaved calcium silicate systems, *Cement and Concrete Research*, **5**(2): 103-118.