Controlling Properties of Concrete through Nanotechnology

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ABSTRACT: This article is a summation of recent work at the Centre for Advanced Cement-Based Materials (ACBM) at Northwestern University. ACBM's areas of focus currently include self-consolidating concrete (SCC) and nano-modification of paste matrices with carbon nanotubes. Concerning SCC, three projects discussed here include reducing formwork pressure through use of nanoclays, quality control of fibre-reinforced SCC using an AC-IS method, and development of an improved slipform paving concrete. All of these topics share innovative processing techniques to ensure superior concretes that can further today's growing need for reliable high performance concretes.

1 INTRODUCTION

The future of today's high strength and high performance concrete relies on both new processing techniques as well as new types of admixtures specifically geared towards the nanostructure of cement paste. This article is a summation of recent work at the Centre for Advanced Cement-Based Materials (ACBM) at Northwestern University.

ACBM's areas of focus currently include self-consolidating concrete (SCC) and nano-modification of paste matrices with carbon nanotubes. SCC has seen a growing share in the concrete industry, and at ACBM, research has focused on formwork pressure, fibre reinforcement and modification for slipform applications. Both of these topics share innovative processing techniques to ensure superior concretes that can meet today's growing need for reliable high performance concretes.

2 REDUCED FORMWORK PRESSURE OF SCC

A key advantage of SCC is accelerated casting and placing since vibration is not required for consolidation. However, faster casting rates may lead to higher lateral pressure on formwork; this is a major concern for cast-in-place applications, especially when casting tall elements, and has raised questions about the adequacy of using current formwork design practices for SCC. Since the development of formwork pressure is not fully understood in SCC, construction codes in the USA require design of formwork withstand full hydrostatic pressure due to the fluidity of the concrete. However, it has been demonstrated that the formwork pressure of SCC can be less than hydrostatic (Fedroff & Frosch 2004) due to the rebuilding of a three-dimensional structure when the concrete is left at rest (Sun et al. 2007). The mechanisms behind this stiffening phenomenon are of particular interest to users of SCC. Ideally, SCC should be flowable enough to self-consolidate, then immediately stiffen to gain green strength (or strength right after casting) once at rest. This will prevent formwork pressures from reaching hydrostatic pressures during the casting process and allow a more efficient design of formwork. Underestimating the pressure may cause deformed structural elements or even formwork collapse, while overestimating the pressure leads to unnecessary costs due to over-built formwork.

Formwork pressure and structural rebuilding of SCC is highly influenced by the mixture proportioning of the paste matrix. With proper design, it may be possible to achieve significant reductions in lateral pressure development. In order to test formwork pressure for different mixes, a pressure device was developed that subjects a sample of plastic concrete to a vertical load using a universal testing machine. Lateral pressure and pore water-pressure transducers are used to determine the total lateral pressure and pore-water pressure, respectively, generated by the vertical loading. This pressurised cylinder setup, referred to as the piston method, consists of a cylinder 300 mm in height that enables it to measure lateral pressure variations over time in the laboratory for concrete subjected to various vertical loads that correspond to different casting heights, and is shown in Figure 1.

Figure 1. Formwork pressure device.

Using this device, two SCC mixtures were tested; both were proportioned using a fine-to-coarse aggregate ratio of

0.47, w/b ratio of 0.35, and paste volume of 36%. A constant VMA dosage of 400 ml/100 kg of binder was used in all of the mixtures, and the superplasticiser content was adjusted to an initial slump flow of 670 ± 12.5 mm. The formwork pressure results are shown in Figure 2 (Ferron et al. 2007).

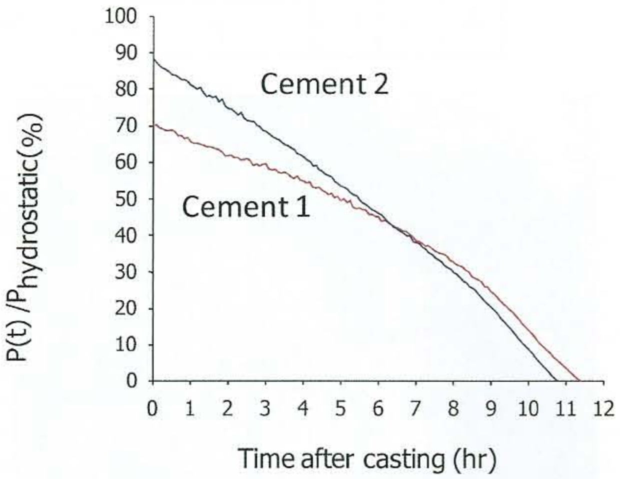

Figure 2. Evolution of pressure decay, where P(t) is the formwork pressure of the concrete at a specific time; $P_{hydrostatic}$ is constant and corresponds to the total vertical pressure applied at the end of casting (approximately 240 kPa). The casting height was 10 m (33 ft), and the casting rate was 7 m/hr (23ft/hr).

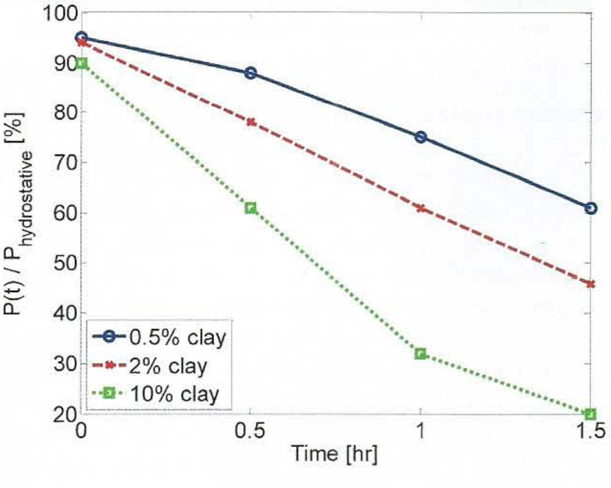

Figure 3. Influence of a metakaolin clay on formwork pressure.

The main difference between the mixtures was the composition of the paste matrix, specifically the type of cement used in the concrete. Although both cements were ASTM Type 1 cements, the alkali and C3A content of the mixtures was significantly different

(Cement 1 had a lower alkali/C3A content). As seen in Figure 2, a 30% reduction in formwork pressure (with respect to the hydrostatic pressure) was produced by altering the paste matrix. In this case, Cement 1, with a lower alkali/C3A content, required less superplasticiser in order to maintain the same slump flow diameter as Cement 2 (Ferron 2008).

ACBM is currently investigating how the addition of small amounts of processed clays can increase the reduction of formwork pressure. Previously, clay particles have been shown to enhance green strength and allow a stiffer structure in concrete to develop (Curcio & DeAngelis 1998). Figure 3 shows the fraction of vertical pressure of SCC transferred as lateral pressure for 0.5, 2.0, and 10.0% replacement of cement with a metakaolin clay.

3 FRESH STATE MICROSTRUCTURE OF SCC

To understand why changes in alkali/C3A or clay amounts affect the structural rebuilding, research has focused on the microstructure, and more recently, the nanostructure, of fresh state concrete. Characterising the structure of cement suspensions is difficult due to the polydisperse, high solids concentration and hydration characteristics. Thus, there is a lack of knowledge about the fresh state structure of cementitious materials, which is especially important during the processing of concrete. Furthermore, the initial fresh state microstructure affects the final microstructure, thereby influencing mechanical properties of hydrated paste or concrete (Struble 1991). Rheology of concrete is related to the degree of flocculation/ coagulation of the paste matrix, which in turn is a function of the interparticle forces. Thus, perhaps the most representative parameter for studying the flocculation process (and indirectly the interparticle forces) is to monitor the change in size of the particle flocs.

A novel experimental method using a focused beam reflectance measurement (FBRM) probe was recently used by researchers at ACBM to examine the floc size evolution of concentrated cement paste suspensions subjected to shear (Ferron 2008). This is one of the first experiments for in-situ investigations of the microstructural response of concentrated cement paste suspensions subjected to shear-induced stresses. Results of compositions shown in Table 1 are presented in Figure 4.

Table 1. Mix compositions for FBRM pastes.

Mix	w/b	SP/b [%]	VMA dosage
P1	0.4	–	–
P1-SP	0.4	0.8	–
P1-VMA_H	0.4	–	high
P1-SP-VMA_H	0.4	0.8	high
P1-SP-VMA_M	0.4	–	medium

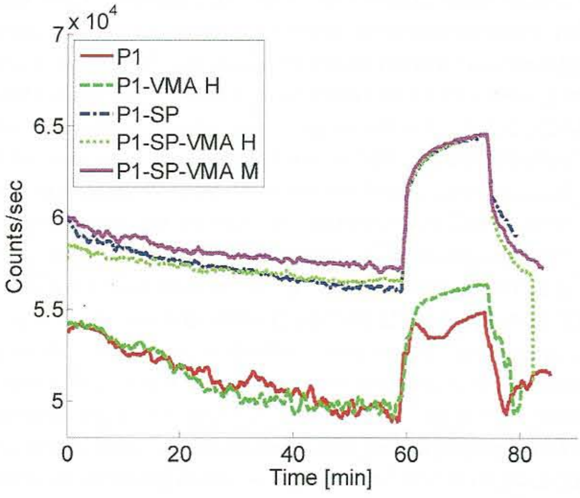

Figure 4. Influence of chemical admixtures on floc evolution

The FBRM floc size measurements were conducted while subjecting the sample to a 40 rpm mixing intensity followed by a 400 rpm mixing intensity. Generally, higher count numbers indicate mixtures with fresh state microstructures that are less agglomerated.

As seen in Figure 4, no substantial changes in the number of chords counted were seen when VMA was added (compare P1 and P1-VMA_H), which is an indication that additional flocculation of the cement particles was not due to the incorporation of this VMA. Rather, the superplasticiser was shown to be the dominating factor affecting the chord length measurements – a significant increase in the number of counts occurred when superplasticiser was used (compare P1 with P1-SP). This shows that the superplasticiser molecules directly interact with the cement particles such that the cement particles are deflocculated, which increases the number of particles in the system. When both VMA and superplasticiser are used in a paste, the flocculation behaviour is more similar to that of a paste with just superplasticiser. This behaviour is seen regardless of the VMA dosage (compare P1-SP, P1- SP-VMA_M, and P1- SP-VMA_H). It can be concluded that the VMA did not interact with the cement particles, or if it did, it did not have any influence on the flocculation properties.

Thus, it is likely that the increase in cohesiveness when this particular VMA is used is garnered from the polymers binding to the water phase.

Developing a quantitative relationship between paste, mortar, and concrete rheology is perhaps the most fundamental issue concerning concrete rheology. The relationship among paste, mortar, and concrete rheology is complex, but the ability to link these three behaviours is beneficial because this would allow for the prediction of concrete rheology solely from the characterisation of the paste or mortar phase.

4 FIBRE-REINFORCED SCC

Currently, the concrete industry is interested in the possible use of steel fibres as a partial or even total replacement of secondary reinforcement in concrete. The negative effects of fibres on concrete workability as well as improper placement and compaction may cause poor fibre distribution (Ferrara & Meda 2006). Regions with reduced amounts of fibres act as flaws, triggering early failure and activating unforeseen mechanisms. This leads to compromised structural performance, e.g. in terms of deflection stiffness, crack opening toughness, and load-bearing capacity. The advantage of adding steel fibres to SCC lies in the self compactability of SCC as well as the rheological stability of SCC in the fresh state (Ferrara et al. 2008a). It has been shown that with an adequate mix design (Ferrara et al. 2007) fibres can be oriented along the flow direction. By suitably tailoring the casting process to the foreseen application, fibre orientation can be designed to match the anticipated stress pattern (direction of the principal tensile stresses) within the structural element during service(Ferrara et al. 2008b, Stahili et al. 2008). The possibility of modelling the casting of fresh concrete, e.g. through Computational Fluid Dynamics (CFD) (Roussel et al. 2007), can help predict the direction of flow lines along which fibres may orient and optimise the whole process. Monitoring fibre dispersion related issues through suitable non destructive methods, such as the Alternating Current Impedance Spectroscopy (Ozyurt et al. 2006) would also be crucial for reliable quality control.

Thorough investigation on these subjects has been performed jointly by Politecnico di Milano and ACBM. Four 1m×0.5m×0.1m slabs were cast with a self-consolidating steel fibre reinforced concrete (SCSFRC) containing 50 kg/m^3 of steel fibres. The fibres were 60 mm long with a 0.8 mm diameter. The slump flow diameter of each slab was 600 mm. Each slab was cut into beams and the fibres were counted on the beam side faces to determine fibre orientation factor, $\alpha = n_{fibers} V_{fiber} / A_{fiber}$, where nfibre is the specific number of fibres on the examined surface, Vf$_{iber}$ is fibre volume fraction (0.67% in this case), and Afibre area of the fibre cross section.

The casting flow process, as shown in the upper part of Figure 5, was simulated by a CFD code (Polyflow 3D), shown

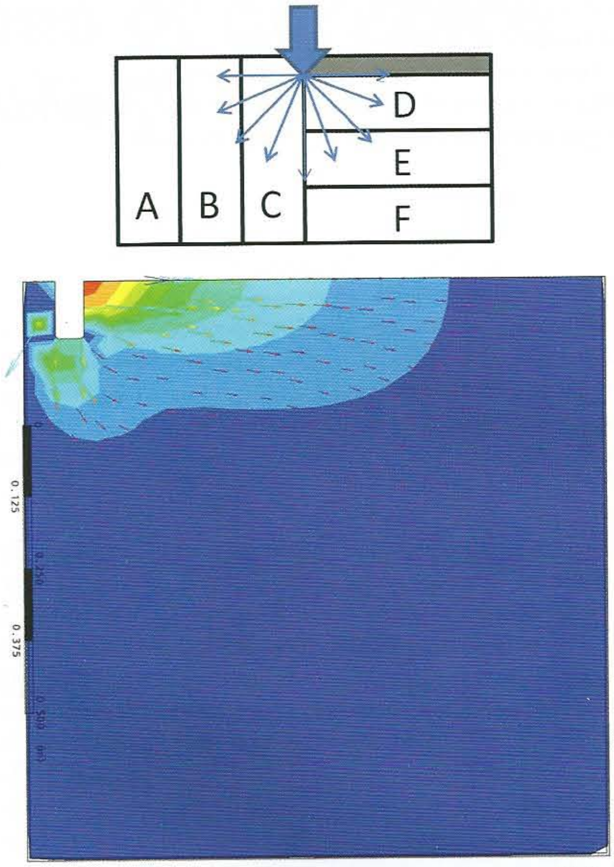

Figure 5. Schematic of the casting of the test-slab and results of CFD modelling (shear rate vectors highlighted).

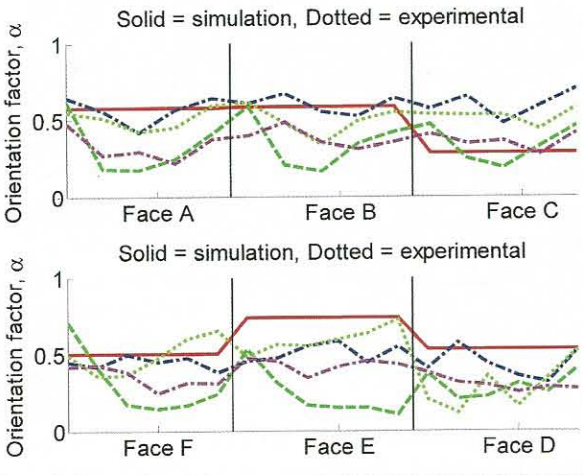

Figure 6. Comparison between experimental orientation factors in the 4 test slabs (A-F 1 to 4) and numerical ones, computed from shear rate vectors from CFD modelling.

in the lower part of Figure 5. For the sake of simplicity, a 2-D homogeneous single fluid simulation was performed by suitably calibrating the input parameters (Bingham fluid $\tau0 = 100$ Pa, $\mu = 100$ Pas) for the fresh state behaviour of the SCSFRC composite. The orientation of the fluid concrete flow lines (shear rate vectors) as computed with respect to relevant surfaces within the slab, has been compared with the fibre orientation factor. Considering the 2D features of the simulation, numerically computed orientation factors always provide an upper bound estimate of the experimental ones.

The results (Figure 6) are encouraging and stand as an interesting step in paving the way towards a more widespread use of simulation of fresh concrete flow, including at the industrial scale.

5 IMPROVED SLIPFORM PAVING WITH SCC

The slip-form paving process is used extensively to create highways and other pavements worldwide. This process combines concrete placing, casting, consolidation, and finishing into one efficient process. The stiff concrete used in slip-form paving machines requires extensive internal vibration, a process that can lead to durability issues. It has been shown that over-consolidation caused by the internal vibrators contribute to the formation of premature cracks. Typically, pavements are designed to last 25-30 years, however in several instances in the United States, slip-cast pavements have shown significant cracks at three years. ACBM, in conjunction with the Centre for Portland Cement Concrete Pavement at Iowa State University, has developed several promising mixture proportions of a low compaction energy concrete which is tentatively called slip-form self-consolidating concrete, SF-SCC (Pekmezci et al. 2007).

Fundamental research on particle packing and flocculation mechanisms provided insight on how to eliminate internal vibration and durability issues associated with longitudinal cracking along the vibration trail. The development of SF-SCC required changing the microstructure by combining concepts from particle packing, admixture technology, and rheology. Specifically, the addition of different materials such as nanoclays and fly ash to the composition made it possible to maintain a balance between flowability during compaction and stability after compaction (Tregger et al. 2009). For this research, a model minipaver that simulates the slipform paving process without the application of internal or external vibration was developed. Concrete slabs of mixes modified with fly ash or fly ash and clay showed much better shape stability and surface smoothness than the slab with a standard slipform concrete mix as shown in Figure 7.

It was also demonstrated that very small amounts of clays (0.3% by volume of concrete) resulted in large increases in green strength (as high as 30%) while maintaining fluidity (Tregger et al. 2009). This was also shown to be the case for mixes used in formwork pressure tests containing clays. Future work at ACBM is focused on understanding the reasons for the change in green strength due to clays using rheology as well as FBRM methods.

Figure 7. (a) Minipaver slab with typical slipform concrete. Rough surfaces indicate poor consolidation. (b) Minipaver slab with SF-SCC mix. Smooth surface indicates proper consolidation while straight edges indicate adequate green strength.

6 NANO-MODIFICATION WITH CARBON NANOTUBES

Cement-based materials are typically characterised as quasi-brittle materials that exhibit low tensile strength. Typical reinforcement of cementitious materials exists at the millimeter scale and/or at the micro scale using macrofibres and microfibres, respectively.

However, cement matrices still exhibit flaws at the nanoscale. The development of new nanosized fibres, such as carbon nanotubes (CNTs), has opened a new field for nanosized reinforcement within concrete. The remarkable mechanical properties of CNTs suggest that they are ideal candidates for high performance cementitious composites. The major drawback however, associated with the incorporation of CNTs in cement based materials is poor dispersion (Groert 2007). To achieve good reinforcement in a composite, it is critical to have uniform dispersion of CNTs within the matrix (Xie et al. 2005). Few attempts have been made to add CNTs in cementitious matrices at an amount ranging from 0.5 to 2.0% by weight of cement. Previous studies have focused on the dispersion of CNTs in liquids by pretreatment of the nanotube's surface via chemical modification (e.g. Cwirzen et al. 2008). Preliminary research has shown that small amounts of CNTs can be effectively dispersed in a cementitious matrix (Konsta-Gdoutos et al. 2008).

At ACBM, the effectiveness of the dispersing method was investigated through nanoimaging of the fracture surfaces of samples reinforced with 0.08% CNTS by weight of cement. Results from SEM images of cement paste samples reinforced with CNTs that were added to cement as received (without dispersion) and CNTs that were dispersed following the method described elsewhere (Konsta-Gdoutos 2008) are presented in

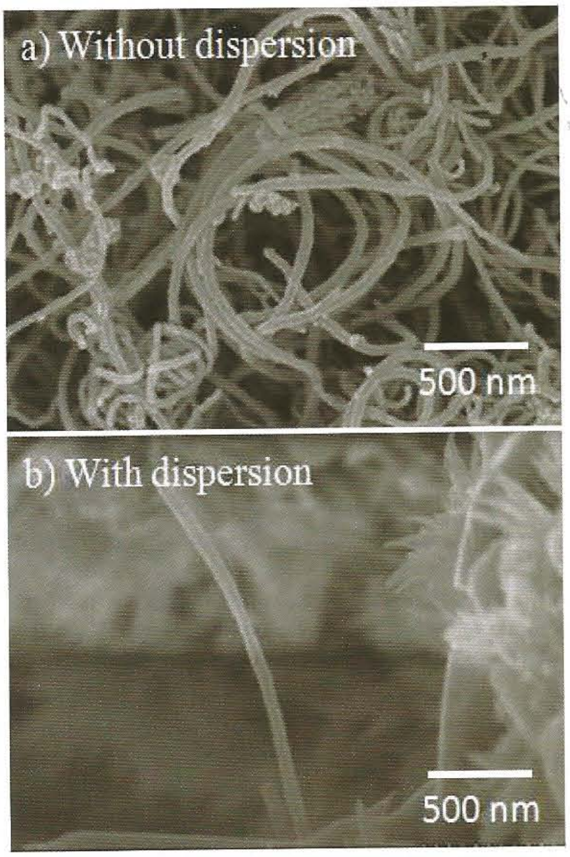

Figure 8. SEM images of cement paste reinforced with CNTs dispersed with (b) and without (a) the application of ultrasonic energy and the use of surfactant.

Fig. 8. As expected, in the samples where no dispersing technique was used [Figure 8 (a)] CNTs appear poorly dispersed, forming large agglomerates and bundles. On the other hand, in the samples where dispersion was achieved by applying ultrasonic energy and using a surfactant [Figure 8 (b)] only individual CNTs were identified on the fracture surface. The results indicate that the application of ultrasonic energy and the use of surfactant can be employed to effectively disperse CNTs in a cementitious matrix.

To evaluate the reinforcing effect of CNTs, fracture mechanics tests were performed using MWCNTs with aspect ratios of 700 and 1600 for short and long CNTs, respectively. Additionally, to investigate the effect of CNTs concentration, cement paste samples reinforced with lower and higher amounts of CNTs (0.048wt% and 0.08wt%, respectively) were tested. The Young's modulus results from the fracture mechanics tests are shown in Figure 9. In all cases, the samples reinforced with CNTs exhibit much higher Young's modulus than plain cement paste. More specifically, it is observed that the specimens reinforced with either short CNTs at an amount of 0.08wt% or long CNTs at an amount of 0.048wt% provide the same level of mechanical performance. Generally, it can be concluded that the optimum amount of CNTs depends on the aspect ratio of CNTs. When CNTs with low aspect ratio are used a higher amount of close to 0.08wt% by weight of cement is needed to achieve effective reinforcement. However, when CNTs with high aspect ratio are used, a smaller amount of CNTs of close to 0.048 wt% is required to achieve the same level of mechanical performance.

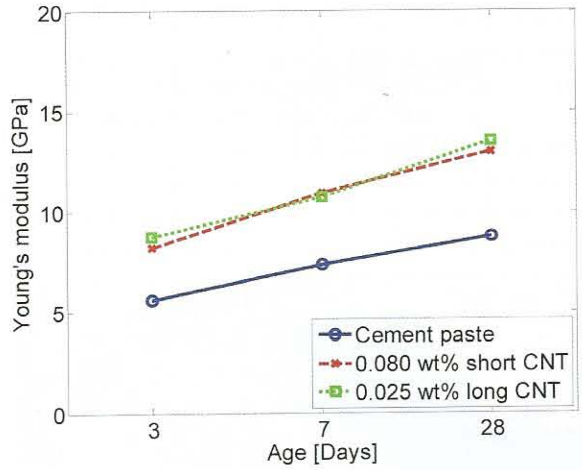

Figure 9. Young's modulus results from fracture mechanics tests of CNTs nanocomposites which exhibit the best mechanical performance among the different mixes tested.

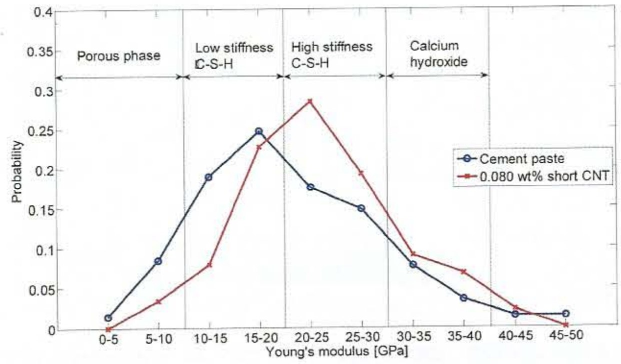

Figure 10. Probability plots of the Young's modulus of 28 day cement pastes with and without 0.08 wt% short CNTs for a w/c of 0.5.

Comparing the 28 days Young's modulus of the nanocomposites with that of the plain cement paste, a 50% increase is observed. Based on the parallel model [16] the predicted Young's modulus of cement paste nanocomposites reinforced with either 0.048wt% or 0.08 wt% CNTs at the age of 28 days (~9.1 GPa) is much lower than the experimental values obtained (~13 GPa). In addition, nanoindentation was performed on samples with and without CNTs. Figure 10 shows the probability plot of the 28 days Young's modulus of plain cement paste and cement paste reinforced with 0.08wt% short CNTs.

The probability plots are in good agreement with results from the literature (Constantindes & Ulm 2008, Mondal et al. 2008). Young's modulus values less than 50 GPa represent four different phases of cement paste corresponding to the porous phase, low stiffness C-S-H, high stiffness C-S-H and calcium hydroxide phase, while values greater than 50 GPa are attributed to unhydrated particles (Constantindes & Ulm 2008, Mondal et al. 2008). The different phases have been found to exhibit properties that are considered as inherent material properties and are independent of the mix proportions. As expected, the peak of the probability plots of plain cement paste with w/c=0.5 falls in the area of the low stiffness C-S-H, which is the dominant phase of cement nanostructure. On the other hand, the peaks of the probability plots of the nanocomposites are in the area of 20 to 25 GPa which corresponds to the high stiffness C-S-H, suggesting that the addition of CNTs results in a stronger material with increased amount of high stiffness C-S-H. Moreover, it is observed that the probability of Young's modulus below 10 GPa

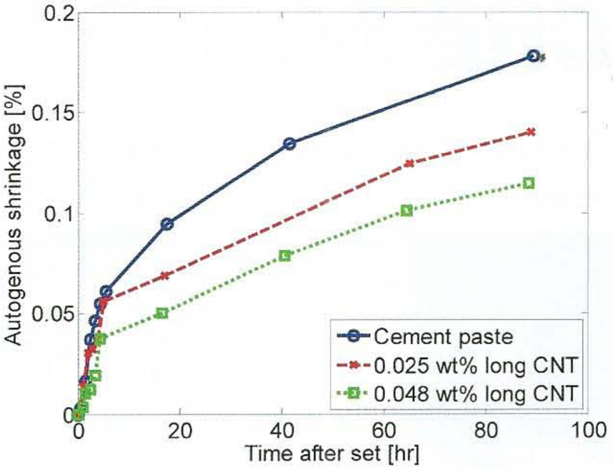

Figure 11. Improvement of autogenous shrinkage for cement pastes containing 0.025 and 0.048 wt% of CNTs for w/c of 0.3.

is significantly reduced for the samples with CNTs for both water-to-cement ratios. The nanoindentation results provide an indirect method of estimating the volume fraction of the capillary pores, indicating that the CNTs reduce the amount of fine pores by filling the area between the C-S-H gel (Shah et al. 2009), which may be one reason why current research has shown other improved properties with CNTs including autogenous shrinkage. Autogenous shrinkage measurements are shown in Figure 10, comparing plain cement paste with paste containing long CNTs at 0.025% and 0.048% by weight, all with a w/c of 0.3.

7 CONCLUSIONS

To meet the increasing need for high-performance, durable construction materials, ACBM has taken a back-to-basics approach to improve understanding of the properties of cement-based materials at a small scale and to develop new materials. Innovative ways to improve SCC in terms of formwork pressure, fibre dispersion and green strength have been developed through concepts of particle packing and flocculation, admixture technology, and rheology.

Incorporation of carbon nanotubes has seen very promising results, while the nanoscale characterisation of cement paste samples showed that the mechanical properties of the C-S-H gel—the glue in concrete—vary in a wide range, requiring complex modelling. Yet understanding cement-based materials at this scale can provide new ways to improve the high-strength and high performance concretes of today.

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