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Influence of MWCNT/surfactant dispersions on the mechanical properties of Portland cement pastes

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Abstract. This work studies the reinforcing effect of Multi Walled Carbon Nanotubes (MWCNT) on cement pastes. A 0.35% solid concentration of MWCNT in powder was dispersed in deionized water with sodium dodecyl sulfate (cationic surfactant), cetylpyridinium chloride (anionic surfactant) and triton X-100 (amphoteric surfactant) using an ultrasonic tip processor. Three concentrations of each surfactant (1mM, 10mM and 100mM) were tested, and all samples were sonicated until an adequate dispersion degree was obtained. Cement pastes with additions of carbon nanotubes of 0.15% by mass of cement were produced in two steps; first the dispersions of MWCNT were combined with the mixing water using an ultrasonic tip processor to guarantee homogeneity, and then cement was added and mixed until a homogeneous paste was obtained. Direct tensile strength, apparent density and open porosity of the pastes were measured after 7 days of curing. It was found that the MWCNT/surfactants dispersions decrease the mechanical properties of the cement based matrix due to an increased porosity caused by the presence of surfactants.

1. Introduction

Multi Walled Carbon Nanotubes (MWCNT) reinforce cement based matrices submitted to flexural and tensile stresses by working as “bridges” across micro cracks and pores, forming a network capable of enhancing the load transmission capacity through the matrix [1], depending on the length of the nanotubes [2]. It has been proposed that MWCNT have potential to control crack propagation phenomena, giving additional strain capacity to the matrix by dissipating energy through multiple pull out of nanotubes from the matrix before reaching a critical state [3].

Surfactants, along with other dispersing agents, have been identified as an effective aid to disperse MWCNT in water [4]. A good dispersion degree of MWCNT throughout the matrix is necessary to obtain crack propagation control [5]. However, it is not clear what Another section of your paper the maximum reinforcing capacity of MWCNT is, and how it is affected by the use of surfactants. Small additions of MWCNT have been found to increase the flexural strength [6-9], modulus of rupture [10], fracture energy and fracture toughness [11] of cement pastes and mortars. This work aims to quantify the reinforcing efficiency of MWCNT/surfactant dispersions in cement pastes submitted to direct tensile stress.



2. Materials and methods

The materials class G cement, industrial grade NC7000 multi walled carbon nanotubes (MWCNT) produced by Nanocyl, sodium dodecyl sulfate (SDS) of 96% purity produced by J.T. Baker, cetylpyridinium chloride (CPC) 100% pure produced by Sigma Aldrich, triton X 100 (TX 100) of 98% purity produced by Sigma Aldrich, and Rheomac UW 410 viscosity modifying agent (VMA) produced by Basf Chemicals were used. Cement and VMA were characterized by X-ray Diffraction (XRD) in a Bruker D8 diffractometer equipped with a Cu radiation source ($K\alpha$, $\lambda=1.5418\text{\AA}$). Diffraction patterns were measured from 4 to 70° 2 θ with a step size of 0.05 and an accumulation time of 30 seconds.

Aqueous dispersions containing 0.35% MWCNT were prepared using the three types of surfactants in 1mM, 10mM and 100mM concentrations. Dispersions were sonicated using an ultrasonic tip, which applied a total energy of 390J/g to guarantee an adequate dispersion degree. Sonication was carried out in a 500W ultrasonic processor set to 40 % amplitude in 20 seconds on/off. These dispersions were used to produce cement pastes in a 600mL Chandler constant speed. All liquids were stirred first at 500rpm for 1 minute; then, cement was added and speed was increased to 2070rpm during 1 minute and maintained constant for 5 more minutes. The proportions of the pastes studied in this work are presented in Table 1.

Table 1. Proportions of the pastes studied.

Paste Name		w/c	VMA (% bwoc)
Surfactant and concentration	MWCNT solid addition (% bwoc)		
Ref	-		
SDS 1mM			
SDS 10mM			
SDS 100mM			
CPC 1mM			
CPC 10mM	0.15% MWCNT	0.55	1.00
CPC 100mM			
TX 100 1mM			
TX 100 10mM			
TX 100 100mM			

After mixing, pastes were poured in 11.5×11.5×2.5cm molds and cured in a high humidity environment for 7 days. At testing age, each sample was cut in four 115×25×12.5mm slabs with two 5mm notches at midspan in the 12.5mm faces. Two metal plates were glued at the edge of one the notches to couple a clip gauge used to measure crack mouth opening displacement (CMOD). Samples were held in place using pneumatic claws, leaving a gauge length of 50% of the total length of the sample. The load application rate was varied to maintain a constant deformation rate at the CMOD of 0.03%/min. Testing was carried out in a Shimadzu AGX 100 universal testing machine equipped with a 100kN load cell. Immediately after testing, apparent density and open porosity were measured for each sample by water absorption following equations (1) and (2).

$$P = \frac{m_s - m_d}{m_s - m_h} \times 100 \quad (1)$$

$$\rho = \frac{m_d}{m_s - m_h} \rho_w \quad (2)$$

Where: P: Open porosity (%); ρ : apparent density; m_s : saturated mass (g); m_d : dry mass (g); m_h : hydrostatic mass (g) and ρ_w : density of water (g/cm³).

3. Results and discussion

3.1. Raw materials characterization

XRD patterns obtained for cement (Left) and VMA (Right) are presented in Figure 1. Anhydrous calcium silicates, calcium carbonate and calcium sulphate were found for cement. It should be noticed that anhydrous calcium sulphate (anhydrite) was found to be predominant over hydrated calcium sulphate (gypsum), which indicates that clinker was grinded at a higher than expected temperature, causing gypsum dehydrate [12]. VMA was found to be composed mainly of cellulose mixed with sodium chloride and sodium sulphide.

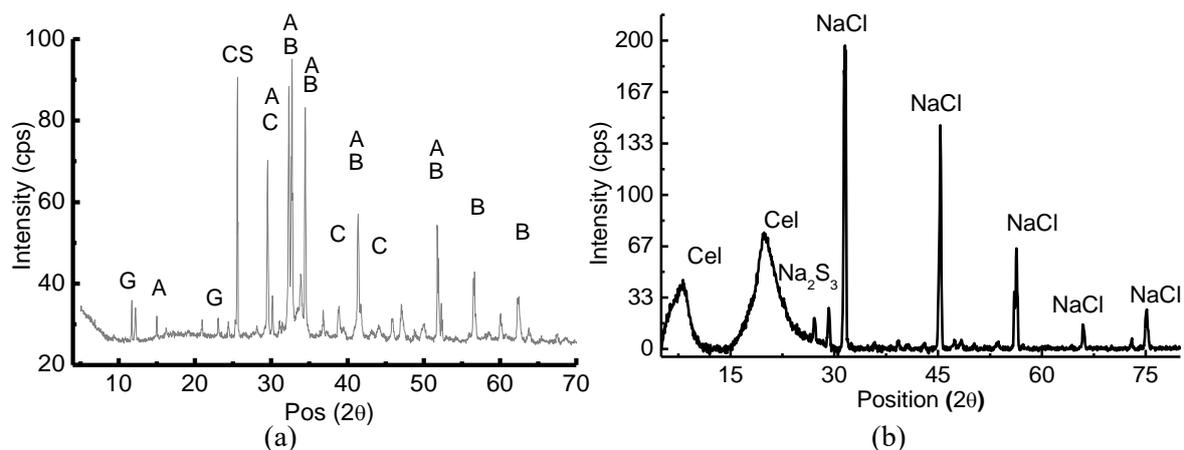


Figure 1. (a) X-Ray diffraction pattern of cement (G: Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), CS: Anhydrite (CaSO_4), A: Alite, B: Belite, C: Calcite, cps: counts per second) and (b) X-Ray diffraction pattern of VMA (Cel: Cellulose).

3.2. Density and porosity

Apparent density and open porosity results for all the pastes studied are presented in Figure 2. It was found that for a constant amount of MWCNT, both apparent density and open porosity of the pastes after 7 days of hydration decreased proportionally with the surfactant concentration. This can be related to a decrease in surface tension of water caused by surfactants. Air becomes entrapped in the paste in the mixing process, and this allows surfactant molecules to adsorb on the water-air boundaries, stabilizing the bubbles and maintaining them individual [12]. These individual bubbles will generate a non-connected porous structure, accounting for the fact that while apparent density decreases, open porosity also decreases rather than increasing.

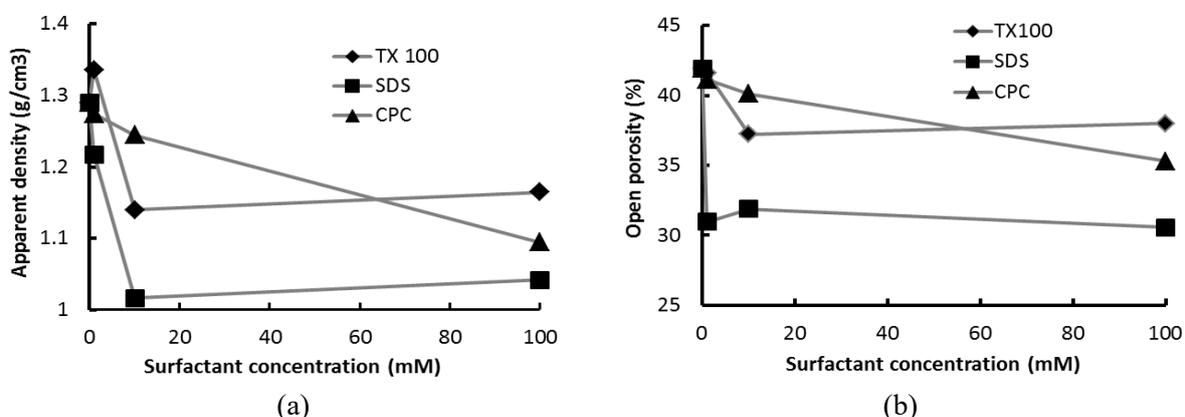


Figure 2. (a) Apparent density of the paste cured 7 days versus surfactant concentration and (b) open porosity of the paste cured 7 days versus surfactant concentration.

3.3. Tensile strength of pastes

Tensile strength results of all the pastes studied after 7 days of curing is presented in Figure 3. It was found that the MWCNT/surfactant dispersions considerably decreased the tensile strength of the cement matrix when comparing to the reference sample. Additionally, it can be seen that all three surfactants have similar effects, regardless of their concentration. This result is the opposite of the expected, since a reinforcing effect of MWCNT in the cement matrix would increase its tensile strength. Similar results have been reported in the literature before but for compressive strength [13] and have been related to agglomeration of the nanotubes which create stress concentration spots.

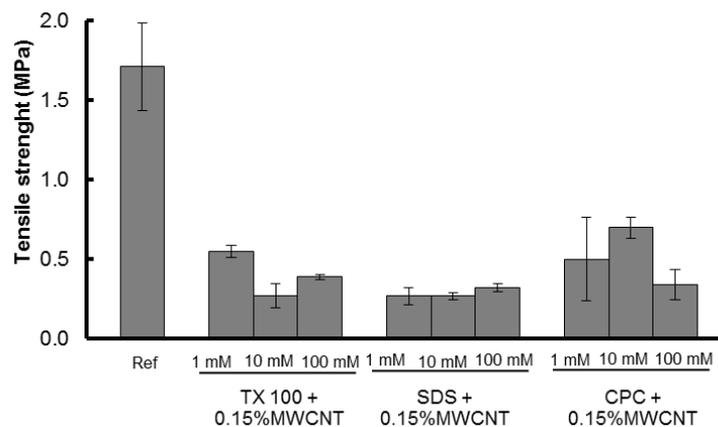


Figure 3. Tensile strength results of pastes after 7 days of curing.

4. Final discussion

A correlation between tensile strength and apparent density for all pastes studied is presented in Figure 4. It can be seen clearly that lower densities are associated with lower tensile strengths for all three types of surfactants studied. As it was previously shown, the decrease in density is directly related to the surfactant concentration used to produce the MWCNT/surfactant dispersion, rather than to the presence of MWCNT. This indicates that any reinforcing effect from MWCNT is much lower than the strength decrease induced by surfactants. This does not mean that the reinforcing effect of MWCNT does not exist, but rather that it is masked by the effect of surfactants. It has been reported that high amounts of surfactants are necessary to adequately disperse MWCNT in water [14], but these high amounts of surfactants seem to be incompatible with an application in the studied cement matrix.

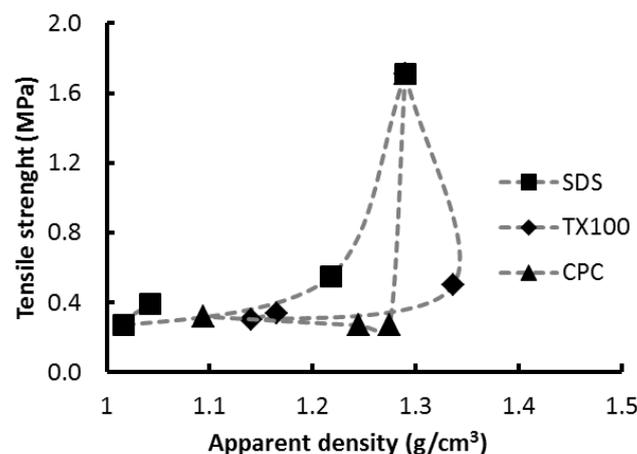


Figure 4. Tensile strength versus apparent density of the pastes studied.

5. Conclusions

The reinforcing effect of MWCNT/surfactants dispersions is masked by the effect of surfactants on the density and porosity of the cement matrix.

Decreases in density induced by surfactants are directly related to decreases in tensile strength of the cement matrix.

The amount of surfactant necessary to obtain an adequate dispersion of MWCNT in water is incompatible with a positive reinforcing effect of the MWCNT/surfactant dispersion in the studied cement matrix.

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