

# Properties of Carbon Nanotube (CNT) Reinforced Cement

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**Abstract :** Carbon nanotubes (CNTs) have great potential to improve the strength and toughness of traditional cement-based building materials. After effective dispersion in water with a surfactant, followed by separation using a centrifuge, multi-walled carbon nanotubes (MWCNTs) can be stored stably for over three months. Our study focused on the microstructure and compressive strength of Portland cement reinforced with MWCNTs. As the proportion of added MWCNTs was increased from 0% to 0.2% by weight of cement, the mechanical properties of the cement paste correspondingly improved. With the addition of 0.1 wt% MWCNT, the 7-day and 28-day compressive strengths increased by 22% and 15%, respectively. The cement paste flexural strength was also improved by addition of MWCNTs. Scanning electron microscopy (SEM) analysis showed that the carbon nanotubes were well dispersed in the cement hydration products. Debonding, bridging, and mesh filling were also observed by SEM. Pressured-mercury testing was used to measure pore distribution in the MWCNT-reinforced cement pastes, and it was found that the pore size distribution tilted in favor of gel pores, pores that have a positive influence on mechanical strength.

**Keywords:** Carbon nanotubes, Mechanical properties, Nanocomposites

## 1. Introduction

The brittleness of cementitious materials is the main reason for concrete cracking. Traditional fibers (e.g. steel fiber or PVA fiber) show good crack resistance and can improve the crack-resistance of concrete and restrain crack propagation when crack width reaches the macro scale, but have little effect on delaying microcrack initiation. The discovery of carbon nanotubes (CNTs) brings with it the opportunity to improve the microstructure of cementitious materials. The strength, toughness, and specific surface area of CNTs are far superior to those of ordinary fibers. The tensile strength of CNTs is between 11 and 63 GPa, which is 100 times higher than that of steel. The Young's modulus of CNTs is around 1 TPa and the fracture strain is as high as 280% [i ,ii]. CNTs possess excellent mechanical and chemical properties, which make them the ideal reinforcing material.

However, little research has been carried out on CNT-reinforced cementitious composites because of the low yield and high price of CNTs. Large-scale production of carbon nanotubes now guarantees the application of CNTs as a structural material. Makar et al. [iii] reported that when commercially available single-walled carbon nanotubes

(SWCNTs), dispersed by sonication in isopropanol, were added to 2 wt% of cement, the resulting hydration products were found to be connected by SWCNTs, and bundles and crack bridging were observed with SEM imaging. Collins et al. [iv] attempted to disperse MWCNTs with several kinds of surfactants. Their liquid suspensions remained stable for nine days following ultrasonic dispersion, but the compressive strength and consistency of the resulting cement pastes were significantly diminished by the addition of MWCNTs. Some researchers have also studied CNT-enhanced high-performance concrete [v ,vi]. However, divergent and conflicting conclusions have been obtained regarding the reinforcement with MWCNTs of cementitious composites. The first question addressed in the present study is the dispersion of CNTs. CNTs have an extremely high specific surface area greater than  $200 \text{ m}^2 \text{ g}^{-1}$  and are prone to aggregate and form bundle structures because of their high surface energy. Proper dispersion and mixing methods are known to be key factors affecting the performance of nanocomposites, as poor dispersion of MWCNTs leads to several defects in the nanocomposites and decreases the reinforcing effect of the MWCNTs [vii ,viii]. Additionally, unreasonable dispersion too leads to the damage of MWCNTs [ix]. Currently, there are two methods that are commonly used for CNT dispersion. The first is chemical modification, which introduces functional groups on the surface of CNTs using chemical reagents, highenergy discharge, ultraviolet radiation or other processes [x,xi]. The second is physical modification, which employs mechanical stress through processes such as crushing and ultrasonic dispersion to activate the surface of the CNTs [xii].

The second question we address here concerns the important factor that is the interfacial bonding strength between the hydration products and CNTs. With a high bonding strength, CNTs can in theory provide a bigger and stronger interface for stress transfer and delay micro-crack propagation [xiii]. A study by Musso et al. [xiv] indicated that the chemical and physical properties of CNTs could affect the mechanical behavior of composites. The compressive strength of composites was increased by 10-20% with asgrown and annealed MWCNTs, while compressive and flexural tests results showed 80% diminution with functionalized MWCNTs. Li et al. [xv] reported that the addition of MWCNTs modified by a  $\text{H}_2\text{SO}_4/\text{HNO}_3$  mixture to mortar optimized the pore size distribution and enhanced both the compressive and flexural strengths. Moreover, the treated CNTs were found to be tightly coated with a calcium-silicate-hydrate (C-S-H) gel. In another report [xvi], polyacrylic acid was used to modify the surface of MWCNTs. The resulting carboxyl functional groups reacted with the C-S-H gel,

improving the bonding strength between MWCNTs and the matrix.

Finally, we address the issue of the optimal values of length and proportion of CNTs in their composites with cement. Previous findings indicate that CNT volume fraction, length, and diameter all influence the mechanical properties of cement pastes. KonstaGdoutos et al. [xvii] compared the effect of different lengths (10– 30  $\mu\text{m}$ , 10–100  $\mu\text{m}$ ) of MWCNTs on the mechanical properties of CNT–cement pastes. Compared to short MWCNTs, longer MWCNTs achieved the same level of mechanical performance at lower concentrations. However, it was found that longer the MWCNTs were, more difficult it was to disperse them.

In the present work, an effective surfactant was used to achieve optimum MWCNT dispersion, and then a stable liquid suspension of MWCNTs was obtained by a sonication and centrifugation process. Several different concentrations of MWCNT were mixed into cement paste. The mechanical properties of the resulting composites were tested at 7 and 28 days of aging. The microstructures of MWCNT and cement hydration products were studied using scanning electron microscopy (SEM). Mercury intrusion porosimetry (MIP) was used to measure the pore distribution of cement pastes.

## 2.Experimental

### 2.1. Materials

Ordinary Portland cement P O 42.5 was used. MWCNTs were provided by Shenzhen Nanotech Port Co. Ltd in China, and its properties are shown in Table 1. An agent for dispersing CNTs in water (TNWDIS), provided by Chengdu Organic of added MWCNTs were considered (relative to the cement quantity), in addition to a control: 0 wt% (control), 0.025 wt%, 0.05 wt%, 0.1 wt%, and 0.2 wt%. The ratio of water to cement was 0.33 for all preparations. After the ultrasonication and centrifugation, the concentration of liquid suspended MWCNTs was 2 wt%. Before its addition to the cement paste, the MWCNT suspension was diluted with water to achieve the target levels of concentrations for the experiments. The water content in the MWCNT suspension is included in the overall target water: cement ratio of 0.33.

**Table 1 Properties of MWCNTs.**

Diameter (nm)	Length ( $\mu\text{m}$ )	w (ash) (%)	Purity (%)	Specific surface area ( $\text{m}^2/\text{g}$ )	Electric conductivity ( $\text{s}/\text{cm}^2$ )
40–80	5–15	<3	>95	40–300	(15–30) $10^3$

### 2.2. Dispersion of MWCNTs

Because there are strong van der Waals forces between CNTs, if the initial aggregated bundles are not separated, then these aggregates may emerge later as matrix defects in cement composites. Researchers have tried dispersing CNTs in several ways [ii,xv,xvi]. The duration that a CNT solution is stable is a measure of the effectiveness of the dispersion process. Surfactants and functionalization of CNTs yield dispersion stability times of only several days or even a few hours. Beyond these durations though, CNTs increasingly aggregated and precipitated out of the suspension.

In the present study, an effective surfactant was carefully selected. The amount of surfactant added was approximately 20% of the weight of the MWCNTs; this amount was so small that it could be ignored during the hydration of the cement samples. The TNWDIS used has both an aromatic ring and a hydrophilic group, and the two are connected by long carbon chains. During the dispersion process, the aromatic ring attaches to the surfaces of the MWCNTs, while the hydrophilic group increases the dispersibility of the MWCNTs in water. The entire dispersion procedure can be divided into the following four steps:

- (1) 1.0 g of the TNWDIS was dissolved in 200 g water and stirred evenly. Then, 5.0 g of the MWCNT powder was placed in this solution and stirred until the MWCNTs had been completely wetted.
- (2) A Scientz-IID ultrasonic disrupter (20 KHz, 600 W) was employed to disperse the MWCNTs in the solution. The sonication process was performed six times, with the duration of each stage being 5 min. It was found that sonication caused both the heating and the foaming of the dispersion fluid. Therefore, we placed the dispersion fluid in ice water to defoam it after each sonication stage.
- (3) The MWCNT dispersion was subjected to centrifugation; the centrifugal speed was 2000 rpm and the centrifugation time was 30 min. During centrifugation, owing to the strong force generated, the settling of the MWCNTs at the bottom of the container was accelerated.
- (4) The sediment in the bottom was filtered from the solution and weighed. The MWCNT aggregates were dispersed by repeated dilution, sonication, and centrifugation until the bundles of CNTs had been separated into individual strands.

The final dispersion concentration was 2 wt% CNTs and remained homogeneous with storage for over 3 months. Bundles and large agglomerates of MWCNTs were observed by SEM (Quanta 650, by FEI) before the dispersion process (Fig. 1(a)). After the MWCNTs were dispersed into solution, individual MWCNTs were observed with SEM as shown in Fig. 1(b). The typical CNT length in the experiment was 5–15  $\mu\text{m}$ , with the lengths of most being less than 10  $\mu\text{m}$ . The short CNT length may be due to damage that probably occurred during the dispersion process.

### 2.3. Preparation of the specimens

The JJ-5 mixer (which complies with Chinese national standard GB/1764-1999) was used in this experiment. The CNT dispersion and water were placed in the mixing pot and stirred for 60 s. Then, cement particles were added and stirred for 300 s. When this mixing process was finished, the cement paste appeared to be homogeneous. The resulting paste was then poured into molds (of dimensions 50 mm 50 mm 50 mm or 40 mm 40 mm 160 mm) and vibrated for compaction. Specimens were removed from the mold after 24 h and cured in water at 20 C until the testing age. They were then dried for 3 h at room temperature before testing.

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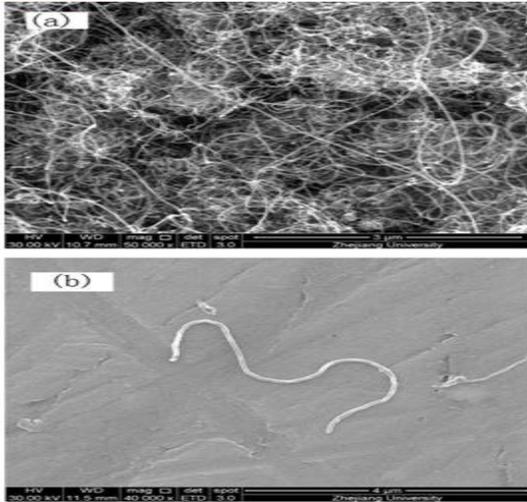


Fig. 1. SEM image of MWCNTs: (a) before dispersion (b) after dispersion.

### 2.5. Testing procedures

The compressive strength at ages 7 days and 28 days was tested at a loading rate of 0.5 MPa/s. Three-point bending tests were carried out to quantify the influence of the MWCNTs on nanocomposites' flexural strength, and the distance between the two supports was 120 mm. The specimens were tested using an Instron Model 8802 universal material testing machine (with 0.1 mm/min loading speed) at 7 and 28 days. The Quanta 650 instrument was used to study the microstructure of the cement composites. After testing, some fragments of diameter 3 mm to 5 mm were picked up by forceps and stored in ethanol to prevent hydration. Before SEM scanning, the samples were removed from ethanol and dried under vacuum at 60 C. Pore structure and pore size distribution were investigated by MIP (AutoPore IV 9510).

## 3. Results

### 3.1. Mechanical properties

The mixture proportions and compressive strength testing results are shown in Table 2. With the consistent water-cement ratio of 0.33, the compressive strength increased with increasing MWCNT content. At 0.025 wt%, 0.05 wt%, and 0.1 wt% MWCNT content, the compressive strength was enhanced (relative to the control) by 9%, 18%, and 22% at 7 days; and by 6%, 13%, and 15% at 28 days, respectively. Clearly, the early age strength of cement paste was greatly improved by MWCNT addition. MWCNTs enhanced the flexural and compressive strengths simultaneously. The results of the three-point bending tests showed that the peak value of flexural stress

was significantly influenced by the amount of MWCNT added.

Table 2 Mix proportions and mechanical properties

Sample	Mixproportion (kg)			Compressive strength (MPa)		Flexural strength (MPa)
	Cement	CNTs	Water	7 day	28 day	28 days
C0	100	0	33	40.4	84.8	4.0
C1	100	0.025	33	44.2	90.1	4.3
C2	100	0.050	33	47.8	95.6	4.6
C3	100	0.100	33	49.2	97.2	5.2
C4	100	0.200	33	-	-	5.6

It was found that flexural strength increased with increasing MWCNT content. Relative to the control, flexural strength increased by 30% and 40% with 0.1 wt% and 0.2 wt% MWCNT content, respectively. In previous literatures, KonstaGdoutos et al [xvii] found that the flexural strength of cement paste (w/c = 0.3) without MWCNTs was about 5 MPa at the age of 28 days. In another report [ix], the compressive strength of the cement paste specimens was about 80 MPa when the water-to-cement ratio was 0.3, but the flexural strength was only 3.0 MPa. The water-cement ratio has great influence on the flexural strength of cement paste, and a water/cement ratio of 0.33 was used to improve the fluidity and dispersion of the composites in this study. However, a few defects, such as pores, caves and microcracks, were still observed within the specimens. Microcracks form readily under tensile stress when a specimen is bent. Thus, the cement paste samples were more sensitive to defects in the state of tension. So, the three-point bending test results of cement paste were reasonable and reliable in this study. The addition of CNTs reduced the porosity and improved the microstructure of the paste samples. Therefore, the flexural strength increased with the increase of MWCNT amount.

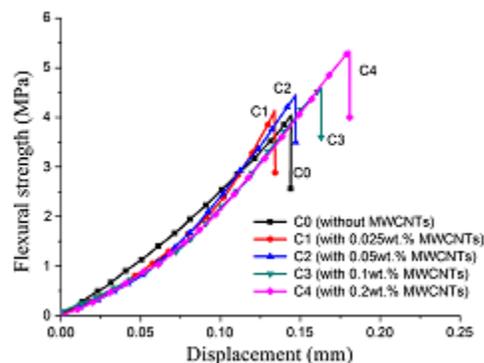


Fig. 2: Typical flexural stress-strain curves of MWCNT cement

Fig. 2 shows the flexural stress-strain curves of the composites. Even with the increase in the MWCNT content, the deformation ability of the composites did not improve significantly. This might be because while the MWCNTs did improve the first-crack strength of the matrix, the microfibrers (CNTs) were probably not of much help in delaying the propagation of macrocracks. In addition, the

amount of MWCNTs added might have been too small to ensure that the MWCNTs were distributed uniformly in the composite matrix.

### 3.2. Micrograph

MWCNTs are easier to observe with SEM in the samples at an early age. The large surface energy of MWCNTs is expected to attract cement hydration products, which will then coat the MWCNTs, obscuring them from view. Fig. 3 shows the microstructure of the control group, in which the main constituents of the cement paste are  $\text{Ca}(\text{OH})_2$ , C-S-H gel, pores, cracks, and unhydrated cement particles. Ettringite (AFt) and  $\text{Ca}(\text{OH})_2$  sheets can also be seen in the hydration product. Comparing Fig. 3(b) and (c), it can be observed that the degree of hydration is higher while the porosity level is lower for the cement paste at 28 days of aging compared to cements aged for lesser durations. In this study, no effects of MWCNT addition were found on the flowability of the cement pastes, and few visible holes were found to be present on the fractured surfaces. However, there were many nanoscale pores and cracks in the C-S-H gel that affected the strength and durability of the specimens, as shown in Fig. 3(b).

As shown in Fig. 4, the microstructures of mixtures C1, C2, and C3 were uniform and compact. When MWCNTs are uniformly dispersed in the paste, owing to their high surface energy, they provide nucleation sites for the growth of hydration products. Fig. 4(a) shows the microstructure of cement hydration products in a cross-section magnified 2500 times; a crack and CNTs surrounding it can be seen. Several cracks appeared in the weaker areas of the matrix that could not be reinforced by MWCNTs in the C1 samples given their low content of only 0.025 wt%. When the amount of MWCNTs mixed reached 0.1 wt%, they exhibited a network-like distribution, as shown in the Fig. 4(c). As the MWCNT content in C2 was twice that in C1, the distribution of MWCNTs in C2 was more intensive. Fig. 4 illustrates that MWCNTs were well dispersed in the cement matrix in all the samples. Also, there is no evidence of fiber crimping or agglomeration, and each MWCNT seems to act as a single root. The randomly oriented MWCNTs and the cement hydration products combine to form a multiphase material, which helps improve the mechanical properties of the composites.

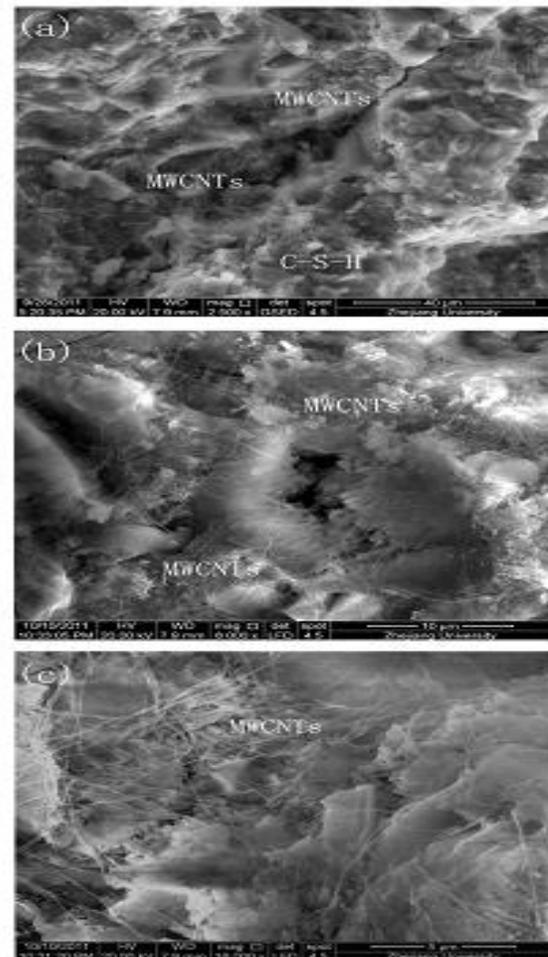
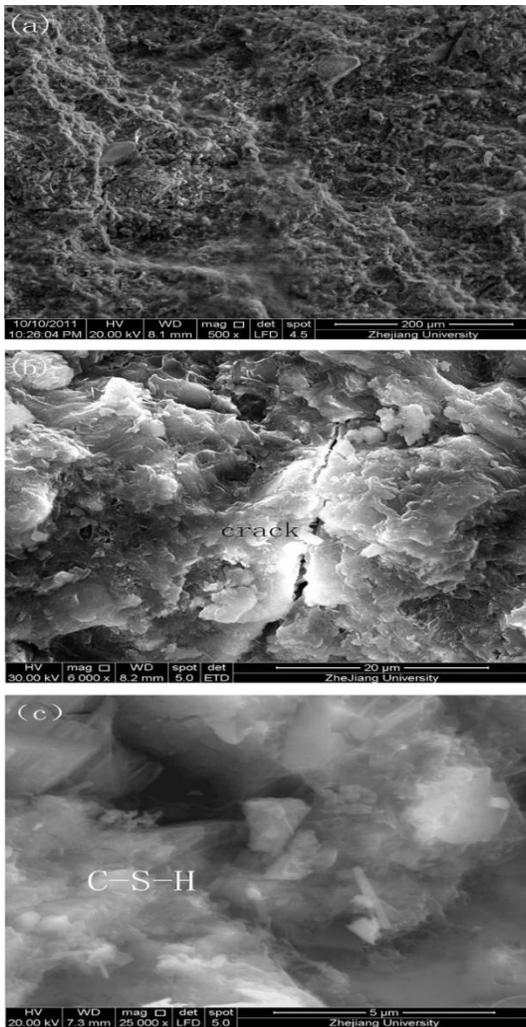
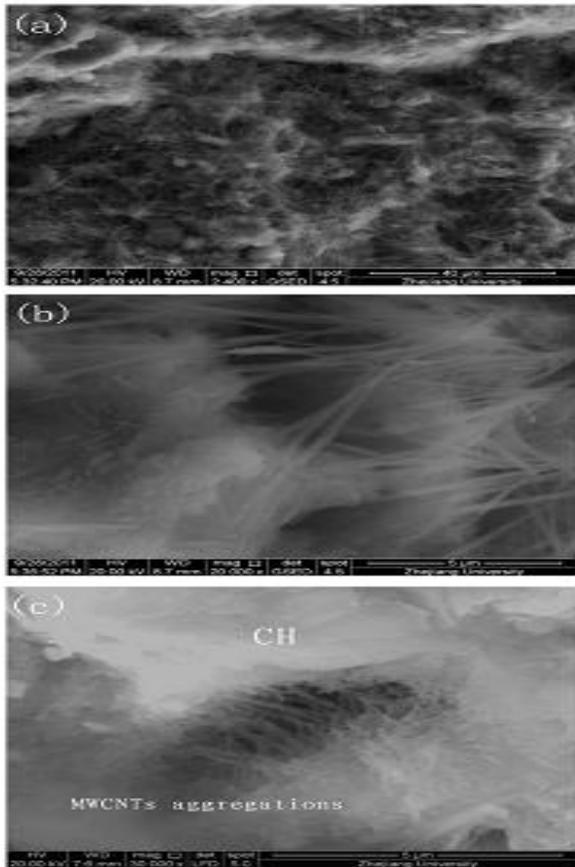


Fig. 4. SEM image of (a) C1, (b) C2 and (c) C3 at 28 days

Fig. 3. SEM image of C0 at (a and b) 7 days and (c) 28 days.

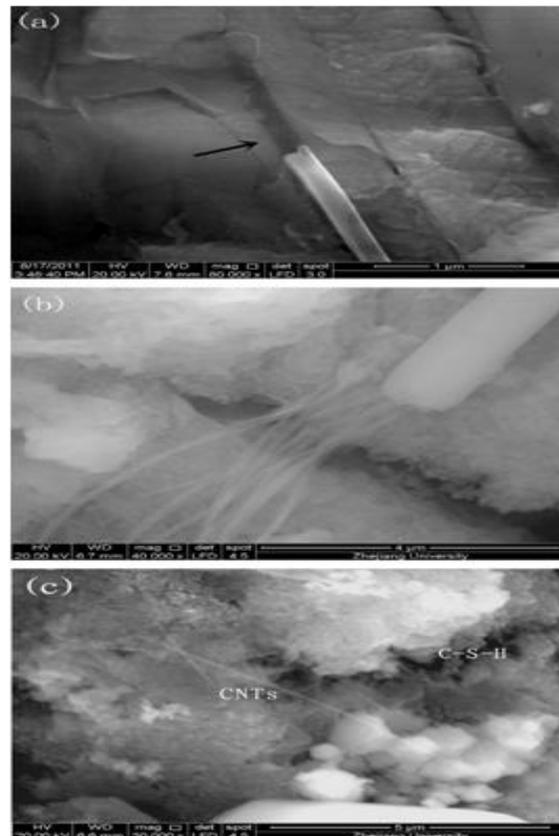


**Fig. 5. SEM image of C4 composites.**

Fig. 5 is a microscopic image of the paste with the highest CNT content. The MWCNTs can be seen to have formed an intertwined mesh, and the hydration products are connected as a whole. Although the pre-dispersion and mixing processes improved the homogeneity of the MWCNTs effectively, some agglomerated CNTs can be seen in Fig. 5(c). The agglomeration is concentrated in the middle region, while other regions have little CNTs. This agglomeration is attributed to the localization of a high content of CNTs and van der Waals forces. Such agglomerated CNTs create weak zones in the form of pores. Previous studies have shown that excessive CNT content does not improve strength, and sometimes even deteriorates material properties dramatically. However, 0.2 wt% of MWCNT was the maximum level added in this experiment. Although the enhancement of the composite's mechanical properties was less marked as the CNT content grew, it did however continue with increasing CNT. Thus, even the highest content of CNTs, 0.2 wt%, had no negative effects on the nanocomposites. This may be explained as follows. The diameter of Portland cement particles was more than ten micrometers, much larger than the size of MWCNTs and still large relative to the size of the aggregated or reunited MWCNTs, which could fill the voids between the larger cement particles. Also, the hydration products grow around the MWCNTs, which act as nucleation sites. On the whole, reunited MWCNTs have

limited influence on mechanical properties when their concentration is not very high.

When the cement matrix reached its ultimate tensile strength, cracks appeared and MWCNT was pulled out because of their low bonding strength. Debonding and crack bridging were observed in cement-CNT composites as indicated by the arrow in Fig. 6. The slip of a CNT in the cement matrix and the corresponding groove can be seen clearly in Fig. 6(a). Although the diameters of most of the MWCNTs were 40–80 nm, a few of the MWCNTs had diameters greater than 80 nm. The morphology of the hydration products in the corresponding area indicated that this fiber was an individual MWCNT rather than cement hydration crystals. In addition, the groove noticed in Fig. 6(a) and the corresponding MWCNT was oriented along the same axis and had the same diameter. Therefore, it is most likely a slip of a MWCNT, which suggests that the bonding strength between the CNTs and the matrix was not strong enough. It can be seen in Fig. 6(b) that MWCNTs acted as bridges across a crack; however, one end of the MWCNTs extended into cement paste while the other was pulled out. Debonding and pullout of the MWCNTs play an important role in toughening of nanocomposite. The tensile strength of CNTs is more than 10 GPa, which far higher than that of the cement matrix, and fibers will be pulled out inevitably when a crack develops to a certain degree. Fracture toughness thus will increase as the result of debonding at the interface between the MWCNTs and the matrix.



**Fig. 6 -Image of (a) Debonding, (b) crack bridging, and (c) a single CNT in hydration**

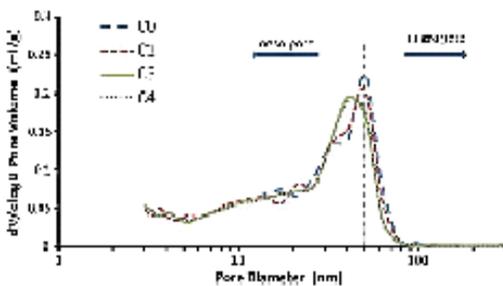
### 3.3. Porosity and pore size distribution

Porosity parameters are very important to determine the quality and functionality of the concrete material, given that high porosity reduces the mechanical strength and durability of concrete materials. There exists a direct correlation between deterioration of concrete performance and porosity, as evidenced by the deleterious effects of pores after pore formation. Mercury injection method is considered an effective method for testing the total porosity and pore size distribution of cementitious materials. In this study, the pore structure of the cement pastes with different added amounts of MWCNTs was characterized using MIP.

The results of MIP of C0, C1, C3, and C4 samples are shown in Table 3. The addition of MWCNTs reduced the porosity and total pore volume of the cement paste. Compared to the other groups, the one with 0.2 wt% MWCNT was found to exhibit the lowest total intruded volume (0.1167 ml/g). The total intruded volume reduced with increasing MWCNT percentage in cement pastes. For cement pastes with 0.1 wt% and 0.2 wt% MWCNT, the total porosities were 21.1034% and 20.9686%, respectively. Both total porosity and total surface area decreased with increasing MWCNT content up to 0.2 wt%. MWCNTs fill the large pores of the hydration products causing the compaction of the cement paste.

**Table 3** MIP analysis of Portland cement–MWCNTs pastes.

Sample	Total intruded volume (ml/g)	Average pore diameter (nm)	Total porosity (%)	Total surface area (m <sup>2</sup> /g)
C0	0.1241	16.5	21.9575	30
C1	0.1212	16.3	21.6202	29.756
C3	0.1181	16.0	21.1034	29.499
C4	0.1167	15.9	20.9686	29.348



**Fig. 7.** Pore size distribution of C0, C1, C3 and C4 samples at 28 days.

mercury porosimetry graphs showing the distribution of pore diameters of the cement pastes with different added amounts of MWCNTs are shown in Fig. 7. The  $dV/d(\log D)$  value decreases with the increase in MWCNT content. For the C0 group, the value of  $dV/d(\log D)$  is about 0.25 ml/g, while it is only 0.20 ml/g for the C4 group. Pores can be classified into two groups depending on size distribution: macropores ( $d > 50$  nm) and mesopores ( $d < 50$  nm). It can be seen from Fig. 7 that the pore size tends

to reduce with increasing MWCNT content, with the number of pores larger than 50 nm reducing significantly.

### 4. Discussion

Though several researchers have studied the effects of the addition of CNTs on the strength of cement-based materials (shown in Table 4), no consensus yet has been reached on the effects. It was seen that for a CNT content of 0.5–1.0 wt% the compressive strength of the matrix increased by about 10%. Compared with ordinary CNTs, the compressive strength of the matrix was reduced significantly with the use of functionalized CNTs in Musso’s research [xiv]; Li et al., however, found that the compressive strength increased by up to 19% [xv]. The reasons for this difference in the effects of functionalized CNTs may be one or a combination of the functionalization process, the surfactant used, and the dispersion method. Consequently, the carboxylic acid groups on the surface of MWCNTs chemically react with C–S–H or Ca(OH)<sub>2</sub>. In this study, the compressive strength increased by 22% using only 0.1 wt% of MWCNT, an MWCNT content that is only a fifth of that used by Li et al. [xv]. One reason for the increase in strength and improvement in mechanical properties is the fiber bridging effect, which involves the combining of the various components of hydration products in cement. The other reason is the packing effect resulting from the small CNTs, acting as fillers, filling the interstitial spaces in the hydration products thereby increasing cement density. In order to obtain the abovementioned effects, the follow methods to ensure maximum time of dispersion stability without aggregation; (2) uniformly dispersing MWCNTs in the matrix with the appropriate mixing method.

**Table 4** Comparison of compressive strengths of cement-based composites reinforced with CNTs.

Researcher	Matrix	Amount of CNTs (wt.% of cement)	Strength increase (%)	
			Compressive	Flexural
Collins et al. [iv]	Paste	0.5	8	-
Cwirzen et al. [ix]	Paste	0.042	-	10
Musso et al. [xiv]	Paste	0.5	11	-
Li et al. [xv]	Mortar	0.5	19	25
Nochaiva et al. [xxi]	Paste	1	17	-
Xun and Eil [xxii]	Paste	0.1	7	-
Torkattikul and Chaipamich [xxiii]	Paste	1	10	-
Chaipamich et al. [xxiv]	Mortar	1	10	-
Xu et al. [xxv]	Mortar	0.02	15.9	20.7

The interfacial shear strength is another important factor for fiber-reinforced composites for only an optimum value can improve the performance of composite materials [xviii]. Debonding and fiber-bridging were observed in the cement matrix, which indicated the existence of bonding between CNTs and the C–S–H gel. CNTs delay the initiation of microcracks, thus improving macro-mechanical properties. The size of Portland cement particles is usually between 7 and 200 micrometers, and 70% of the products from the hydration of calcium silicate hydrate gel particles are nanomaterials. Hydration products include amorphous crystals and crystal water from nanometer to micrometer scale, and the mechanical properties of these products on the macroscale are affected by

micro and nano scale properties [xix,xx]. In this study, it was observed that the compatibility between CNTs and the cement hydration products was very good, and that the microstructure of the hydration products improved at the nanoscale.

### 5. Conclusions

In this study, the mechanical properties and microstructure of cement pastes reinforced with MWCNTs were investigated through experiments, and the following conclusions were drawn:

- (1) The proposed method for dispersing MWCNTs in water is effective. The dispersion itself was stable even after 3 months, and it was observed that MWCNTs were well dispersed using SEM analysis.
- (2) The mechanical properties of different MWCNTs–cement paste composite samples with different amounts of MWCNTs (0.025 wt%, 0.05 wt%, 0.1 wt% and 0.2 wt%, respectively) were evaluated. The compressive strength and flexural strength were improved with increasing MWCNT content. Also, MWCNT addition was found to improve the compressive strength significantly at 7 days of aging.
- (3) The micro-morphology of the composites was characterized by SEM in order to understand the mechanism of improvement by MWCNTs. It was found that the MWCNTs were covered with hydration products, and that debonding and crack bridging are the major failure modes of MWCNTs in cement paste. Furthermore, it was observed that the hydration products were connected with the MWCNTs as a whole.
- (4) MIP was used for measuring the porosity distribution of MWCNT–cement paste samples. The total porosity of the cement paste was found to decrease with the incorporation of MWCNTs, resulting in a high-density material. MWCNT addition also improved pore diameter distribution: the number of harmful pores (pore diameter > 50 nm) was reduced, while that of the gel pores (pore diameter < 50 nm) was increased.

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