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Mechanical and damping properties of CNT-reinforced cementitious composites

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ABSTRACT

The mechanical and damping properties of CNT-reinforced cementitious composite structures were experimentally examined. In the experiments, an aromatic modified polyethylene glycol ether named TNWDIS and polyvinylpyrrolidone (PVP) were used to disperse CNTs, which were ultra-effective and compatible with cement hydrates. The growth of cement hydrates on the CNT surface was observed by Scanning Electron Microscopy (SEM) and identified by Energy Dispersive Spectrometry (EDS). X-ray Powder Diffraction (XRD) analysis suggested that the mechanism by which the CNTs and cement hydrates were combined was a physical process. The compressive and flexural strengths of CNT/cement composites were improved by 17.3 and 16.3%, respectively, through the addition of 0.1 wt.% CNTs dispersed by PVP, while the addition of CNTs dispersed by TNWDIS led to a very limited improvement in strength. In addition, the loss factor of CNT/cement matrix was measured, and 0.1 wt.% CNTs dispersed by TNWDIS improved the loss factor by 25.9%, which is nearly twice greater than the improvement caused by 0.1 wt.% CNTs dispersed by PVP.

1. Introduction

Cementitious composites are the most commonly used building material in the world, but it is difficult for them to meet many aspects of the engineering demands due to their brittleness, low strength against tension, and cracking problem. Nowadays, the introduction of a variety of materials into the composites has been tried and with the development of nanotechnology, the introduction of nanomaterials such as nano-silica, carbon nanotubes (CNTs), and so on has become a hot spot for researchers [1,2]. CNTs, a tube-shaped allotrope of carbon like rolled graphene, are potentially very advantageous for nano-strengthening of the cement matrix because of their ultra-high aspect ratio (length-to-diameter ratio), ultra-large surface area, and outstanding mechanical properties [3–6]. CNTs are categorized as single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). CNTs can have diameters ranging from 1 to 100 nm and lengths in the range of 0.1–100 μm [7]. Typical properties of CNTs include a tensile strength 100 times greater than that of steel,

an ultimate strain of more than 10%, and a Young's modulus approaching 1 TPa [8,9]. Unlike microfiber reinforcements in cement matrix that help to delay the development of microcracks, CNTs which are distributed at a much finer scale than common fibers, stop crack growth at the nanoscale and hinder the creation of micro-cracks [10].

The main difficulties in the application of CNTs in cement matrix relate to the dispersion of the CNTs and the efficient bonding of the CNTs with cement hydration products [11]. There is a strong tendency for individual CNTs to agglomerate due to Van der Waals attraction, which originates from their polarizable extended π-electron systems [10,12,13]. Commonly, the mixing process using a Hobart mixer cannot ensure proper dispersion of CNTs within the matrix [6], so CNTs are dispersed in aqueous solutions before mixing [14]. The most common ways to make CNT solutions are through the use of ultrasonication and surfactant. Ultrasonication is a physical method of dispersing CNTs by exposing them to cavitation, which exfoliates them [15]. However, Van der Waals forces exist permanently, so the solutions are temporarily dispersed by sonication [16]. Surfactant, which contains hydrophobic groups and hydrophilic groups, is a chemical method to attach hydrophobic groups on the CNT surface while hydrophilic groups generate electrostatic repulsion that separates the individ-

ual CNTs from bundles and change the wettability of the CNT surface [16–18]. Combined with ultrasonication, surfactant can keep CNT solutions stable. In addition, the functional groups, such as carboxyl (–COOH) and hydroxyl (–OH) groups, which are attached to the CNT structure with H_2SO_4 and HNO_3 mixture, can also ameliorate the CNT dispersion in aqueous solutions [19]. So far, the dispersion of CNTs has been widely researched and solved well by many surfactants combined with sonication, such as superplasticizer (SP) and sodium dodecylbenzene (SDBS) [3,20]. However, there is very limited knowledge about the actual strength of the bonding occurring between the CNTs and the hydrates [21]. The bonding between CNTs and cement hydrates is often weak due to the very low surface friction between them [22]. Szleifer and Yerushalmi-Rozen [16] researched the interactions of polymers and CNTs, and their work indicated that different forms of modifications existed on the CNT surface structure due to the decoration of polymers on it. Trettin and Kowald [23] employed different types of polycarboxylate-based SPs as surfactants and found that the CNTs produced different levels of improvement in the compressive and bending strengths, showing the interfacial bonding between the tubes and matrix is affected by the types of SPs. In addition, the incorporation of CNT in cement paste created multiform interfaces between CNTs and the matrix, which may change the damping properties of cement paste, especially considering the ultra-large surface area [24–26]. Therefore, it can create excellent value for the application of CNTs in aseismic engineering. Cinquin et al. [27] reported the effect of interface bonding of glass-fiber-reinforced composites with dynamic mechanical analysis (DMA), which gives an accurate measurement of interfacial damping. So it is feasible to investigate the damping performance of CNT-reinforced composites and the interface reaction between the CNT surface and the adjacent cement hydrates through the use of the DMA technique.

The present work first focused on the dispersion ability of the surfactants and the morphology of CNTs in cement hydrates and then compared the results obtained with the compressive and flexural measurements performed on a referenced plain cement and CNT/cement composites containing different amounts of CNTs. Furthermore, another aim of this study is to research the damping performance of CNT/cement composites with varying CNT contents using DMA. The effects of different surfactants on the modification of the CNT surface and the bonding strength between the CNTs and cement hydrates are discussed. The combining mechanism (physical or chemical interaction) between the CNTs and cement paste was investigated and analyzed.

2. Experimental program

2.1. Raw material

Ordinary Portland Cement type 42.5R was used as the binder material, conforming to the requirements of the Chinese Standard GB175-2007. Hydroxylated MWCNTs (CNT-OH) produced by the chemical vapor deposition (CVD) method were purchased from Chengdu Organic Chemicals Co. (China). The physical properties of MWCNTs are presented in Table 1. Two types of nonionic surfactants were employed to disperse CNT-OH: a non-ionic liquid surfactant named TNWDIS and polyvinylpyrrolidone (PVP), supplied

by Chengdu Organic Chemicals Co. (China) and Shenzhen Benno Industrial Co., respectively. The molecular structural formulas of TNWDIS and PVP are shown in Fig. 1. TNWDIS is actually an aromatic modified polyethylene glycol ether. Aromatic rings of TNWDIS are hydrophobic and bond with hydrophilic groups through carbon chains. PVP is a powdery material that contains pyrrolidone groups and carbon chains that are hydrophilic and hydrophobic, respectively.

2.2. Preparation of suspensions

To prepare CNT suspensions, one of two surfactants (10% of the CNT weight for PVP; 20% of the CNT weight for TNWDIS) was added to a beaker, followed by the addition of CNTs (0.375 or 0.750 g) and 100 g of water. Two identical suspensions with the same CNT concentration and same surfactant were made for the accurate identification of dispersion with ultraviolet–visible (UV–vis) spectroscopy. All suspensions were treated with the same physical methods: magnetic stirring for 15 min and ultrasonication for 30 min. Finally, the two suspensions were poured into 400 g of water and then mixed with 1500 g cement. The ultrasonication was produced by an ultrasonic cell crusher (JY92-IIN, 650 W) with a cylindrical tip. The sonicator was set up with a cycle of 2 s working and 2 s intervals in order to deliver ultrasonic energy while avoiding overheating of the suspension. The input power of the sonicator was fixed at 30% of the maximum amplitude (650 W), corresponding to an energy delivery of 195 W.

In order to research the compatibility of surfactants with cement hydrates, suspensions containing only surfactants were made. Then, 0.15 g of PVP and 0.15 g of TNWDIS were added to 100 g water in a beaker, respectively. Two identical suspensions were made with the same amount and type of surfactant. The solutions were treated with 15 min of magnetic stirring and 30 min of ultrasonication. Finally, the two suspensions were poured into 400 g of water and then mixed with 1500 g cement.

2.3. Preparation of cementitious composites

Specimens had a size of 40 × 40 × 160 mm for the compressive and flexural strength test and 5 × 12 × 100 mm for the DMA test. All specimens were cast with a water-to-cement ratio of 0.4. The compositions of all mixtures are presented in Table 2. Two different batches of CNTs dispersed by the two types of surfactant, respectively, were made at two different concentrations: 0.05 and 0.1 wt.% by weight of the cement. For each batch, six replicates were made in order to get representative measurements for the mechanical and damping properties. Plain cement specimens were cast as a reference. The P-C0 and T-C0 mixtures were cast in order to research the effects of TNWDIS and PVP on the cement pastes.

Cement was mixed together with the prepared solutions for 7 min using a cement paste mixer to get the fresh cementitious composites. The mixture was then poured into 40 × 40 × 160 mm molds and 5 × 12 × 100 mm molds smeared with oil. To remove air bubbles that generated during the pouring process, the molds were placed on an electrical vibrator table and vibrated 30 times. The specimens were demolded after 24 h and placed in a curing chamber with a temperature of 20 °C and relatively humidity of

Table 1
Property of MWCNTs.

Type	Aspect ratio	OD	Length	FGC	Purity	Ash	SSA
MWCNT-OH	>400	>50 nm	20 μm	0.76 wt.%	>90 wt.%	<6 wt.%	>40 m^2/g

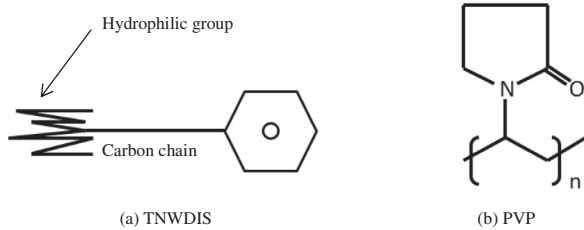Note: OD-Outer diameter; FGC-Functional group content; SSA-Specific surface area.

Fig. 1. Molecular structural formula of PVP and TNWDIS.

95% until testing. All specimens were cured for 27 days, leading to a total curing time of 28 days.

2.4. Material characterization tests

2.4.1. Microstructure and constituents

To view the surface morphologies of the hydrated CNT-reinforced cementitious composites, Scanning Electron Microscopy (SEM) (Hitachi, SU-70, Japan) was performed. The SEM sample was prepared in pellet form. Energy Dispersive Spectrometry (EDS) was used to identify the chemical constituents on the surface of the CNT structure. The constituent analysis of all the specimens was carried out by X-ray Powder Diffraction (XRD) (Bruker, AXS D8, German) using CuKa radiation (k = 1.540598 Å) in the scattering range (2θ) of 10–70° with a scan rate of 0.1°/sec and a slit width of 0.02°. The powder for XRD analysis was obtained by grinding fragments of broken specimens and then sieving with a 40 μm sieve. The samples for these tests were taken from the central zone of the 40 × 40 × 160 mm specimens after the compressive test.

2.4.2. Mechanical properties

The tests of flexural strength and compressive strength were conducted according to ASTM C 348 and ASTM C 349, respectively. The loads were measured and recorded by the software connected with the machine and then converted to the flexural and compressive strengths according to Eqs. (1) and (2). Six replicates of each test were conducted and average values are reported.

$$P_f = \frac{3FL}{2bh^2} \tag{1}$$

$$P_c = \frac{F}{h^2} \tag{2}$$

where F is the maximum force in a bent beam at the instant of failure, L is the span between two supports (100 mm), b is the beam width (40 mm), and h is the height (40 mm).

2.4.3. Damping property

In this study, the loss factor of CNT/cement composites (5 × 12 × 100 mm) was determined on a DMA machine (Metravib, DMA + 1000, France) to investigate the damping property of the composites. Fig. 2(a) shows the DMA instrument. The working mechanism of DMA is as follows: a sinusoidal force or deformation is applied to a sample of known geometry and the phase shift of the sinusoidal force and sinusoidal displacement are measured to obtain the loss factor (the tan delta of the phase shift), as shown in Fig. 2(b). The span of two supports is 80 mm and the specimens were subjected to a periodic deformation of 0.007 mm with frequencies varying from 0.5 to 2.5 Hz. All tests were conducted at room temperature.

3. Results and discussion

3.1. Characterization of CNT suspensions

The effectiveness for the dispersion of CNTs was characterized by UV–vis spectroscopy with a wavelength range of 200–1200 nm (Fig. 3). Individual CNTs are active in the wavelength region between 200 and 1200 nm, while CNT agglomerates are not active in this range [28]. The value of absorbance (ABS) at a certain wavelength is proportional to the concentration of individual CNTs in the diluted suspension according to Beer-Lambert's law. All the suspensions mentioned below for UV–vis measurement were diluted by a factor of 1000 in advance.

According to the ABS curves, the hydroxyl groups on the CNT structure showed a very limited improvement in the dispersion of CNT in aqueous solution. But when surfactants were employed, all the ABS curves had a peak at 260 nm, which was determined by the chirality and diameter of the CNT structure [28,29]. The ABS value at 600 nm (representing the degree of dispersion of CNTs [20]) for CNTs dispersed by one surfactant was proportional to the concentration of CNTs in water. In addition, more ultrasonication energy or more surfactants can't further improve the dispersion degree, which indicated that the CNTs were dispersed to the greatest extent. Compared with the dosage of other surfactants for dispersing CNTs like SP (eight times the weight of CNTs [20]) and SDBS (four times the weight of CNTs [3]), TNWDIS and PVP are ultra-effective in the dispersion of CNT bundles. In addition, the suspensions possessed good stability according to the ABS measurement of suspensions after three days, as proved by [30] and [31], who reported that TNWDIS and PVP, respectively, can keep CNT suspensions stable.

### 3.2. The microstructure and components of CNT/cement material

The morphologies of hydrated CNT-reinforced cementitious composites with a CNT concentration of 0.10 wt.% (by weight of cement) dispersed by TNWDIS or PVP after 28 days of curing are shown in Fig. 4. From the pictures, it can be seen that the CNTs were well mixed in the cement matrix no matter what kind of surfactant was employed. Fig. 4(a) and (c) both show CNTs bridging the gap of cement hydrates, which provided the essential condition for bonding with the cement matrix. Some other CNTs in the pictures can be observed to be embedded in the cement hydrates with the opposite ends free. The incorporation of nanosize CNTs into

Table 2
Mix design of CNT reinforced cementitious composites.

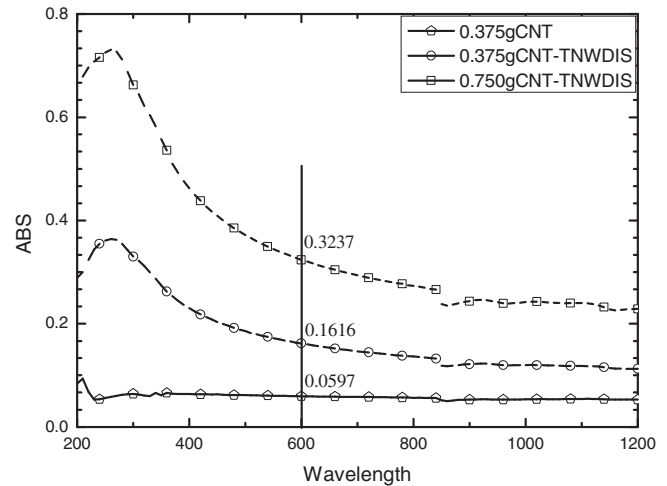| Mix	Cement (g)	Water (g)	CNT (g)	PVP (g)	TNWDIS (g)	CNT/cement
C0	1500	600	–	–	–	0
T-C0	1500	600	–	–	0.300	0
P-C0	1500	600	–	0.300	–	0
C1	1500	600	0.75	–	0.150	0.05 wt.%
C2	1500	600	0.75	0.075	–	0.05 wt.%
C3	1500	600	1.50	–	0.300	0.10 wt.%
C4	1500	600	1.50	0.150	–	0.10 wt.%
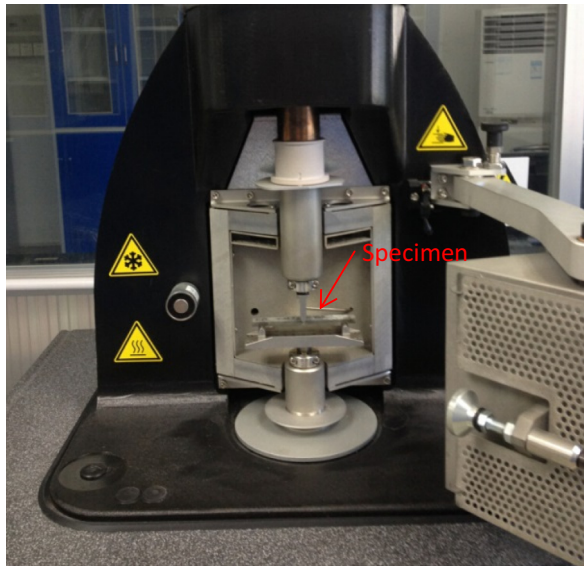
(a) The DMA instrument
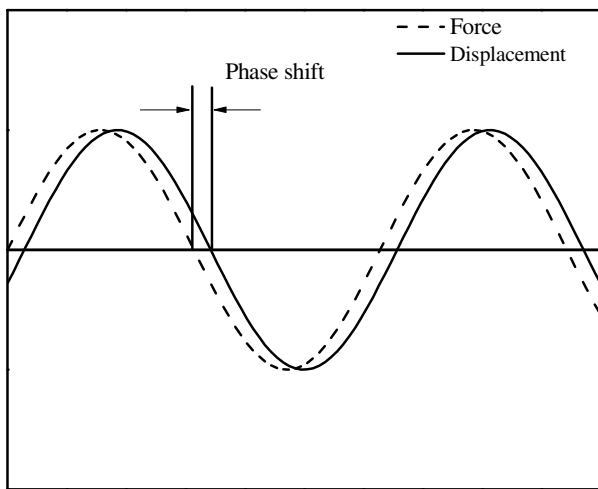
(b) The relationship of the applied sinusoidal force to displacement with the resultant phase shift.
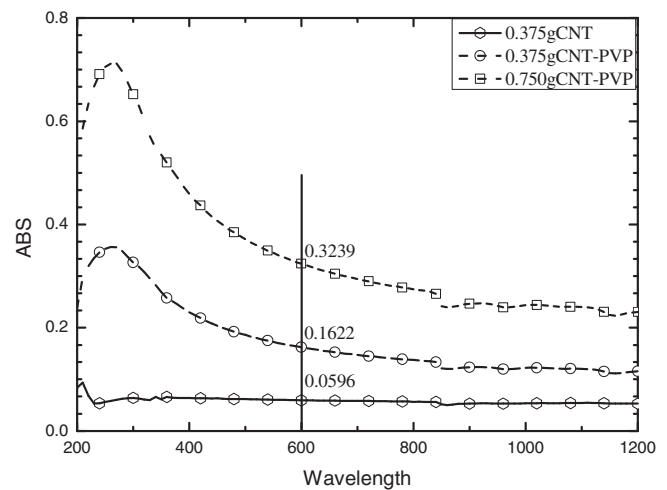
Fig. 2. The DMA instrument and the relationship of the applied sinusoidal force to displacement with the resultant phase shift. (a) The DMA instrument. (b) The relationship of the applied sinusoidal force to displacement with the resultant phase shift.

(a) CNT-OH dispersed by TNWDIS by the 20% weight of CNT-OH

(b) CNT-OH dispersed by PVP by the 10% weight of CNT-OH

Fig. 3. The absorbance of CNT suspensions containing different concentration of CNT-OH (diluted by 1000 for UV–vis measurement). (a) CNT-OH dispersed by TNWDIS by the 20% weight of CNT-OH; (b) CNT-OH dispersed by PVP by the 10% weight of CNT-OH; (a) CNT-OH dispersed by TNWDIS by the 20% weight of CNT-OH. (b) CNT-OH dispersed by PVP by the 10% weight of CNT-OH.

coarse microsize cement hydrates creates multi-phase boundaries and multiform interfaces, as described in [32]. Products can be observed on the CNTs in Fig. 4(a) and (d), and EDS analysis proved that they were the hydration products of cement (Fig. 5). Besides the elements Ca, Si and O, the existence of other elements like Al indicated that the components of the products on the CNT surfaces were not only C-S-H gel consisting of Ca, Si, O and H, and Ca(OH)$_2$ consisting of Ca, O and H, unlike carboxylated CNTs, which combine with C-S-H gel and Ca(OH)$_2$ through chemical reaction [33].

The XRD patterns of CNT/cement matrix with the addition of 0.1 wt.% CNT content (by weight of cement) after 28 days of curing are shown in Fig. 6. It can be seen that all specimens have almost the same curve, implying that no new products were produced. The incorporation of CNTs into cement paste didn't cause visible change of the peak values of Ca(OH)$_2$ by comparing Fig. 6

(b) and (c) with (a). This indicates that CNTs do not cause any change in the hydration process, unlike the carboxylated CNTs, which hamper the proper hydration of the cement paste due to their strong hydrophilicity [34]. Singh et al. [35] found that a strong covalent force existed between pristine MWCNTs and cement matrix due to several new and strong peaks arising in the range of 15–25° in the XRD pattern, which implied that in our study the hydroxylated CNTs combined with hydrates by physical interaction. In addition, the two surfactants had no effect on the XRD pattern (not shown), which indicated that TNWDIS and PVP produced no harmful or beneficial effects on cement hydration.

3.3. Mechanical properties

The flexural and compressive strengths of CNT/cement specimens (40 mm × 40 mm × 160 mm) with the addition of 0, 0.05, and 0.10 wt.% CNTs (by weight of cement) at the curing age of 28 days are shown in Figs. 7 and 8, respectively. Compared with
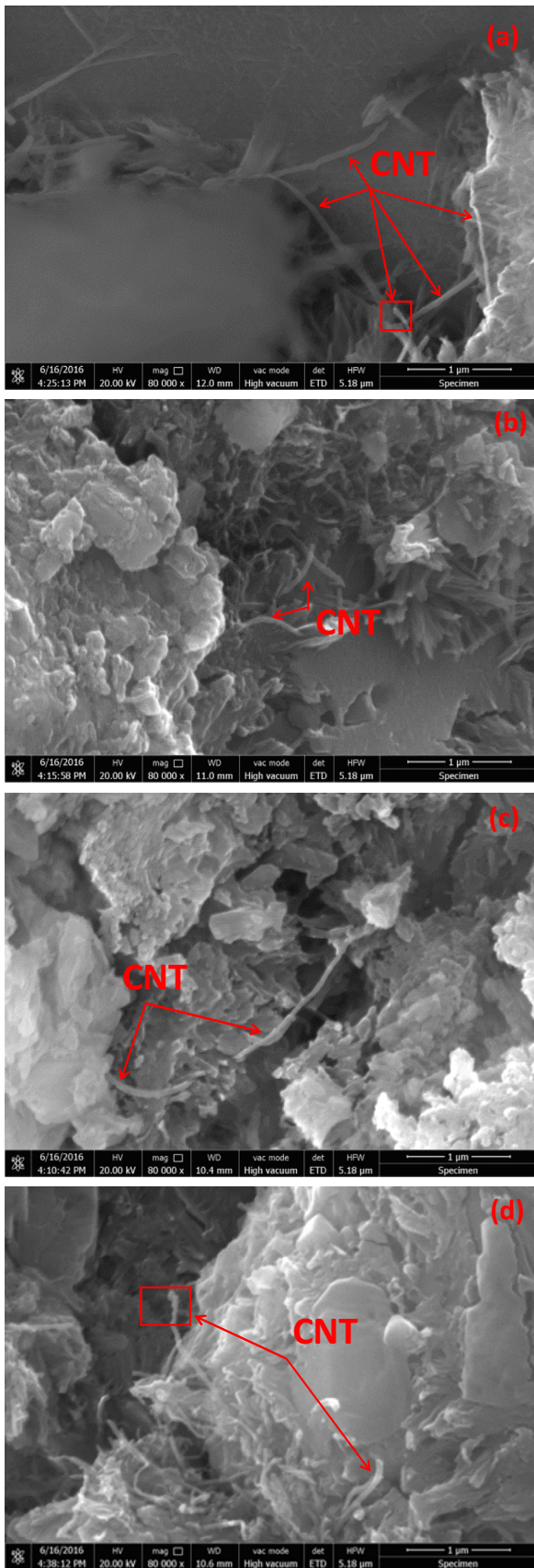
Fig. 4. The morphologies of 0.1 wt.% CNT/cement composites that dispersed by TNWDIS ((a) and (b)), and PVP ((c) and (d)) after 28 days curing.
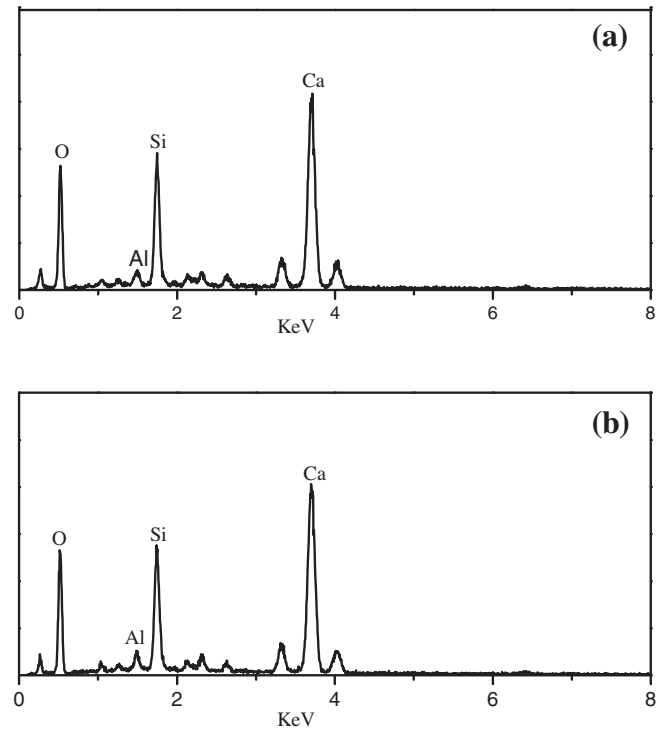

Fig. 5. EDS analysis of the products on carbon nanotubes of 0.1 wt.% CNT/cement pastes from: (a) Fig. 4(a) and (b) Fig. 4(c).

the plain cement paste (reference C0), the 0.05 wt.% CNTs dispersed by TNWDIS enhanced the compressive strength by 2.5% but decreased the flexural strength by 3.9%, indicating 0.05 wt.% CNT content has a limited effect on the mechanical properties of cement paste. The 0.10 wt.% CNTs dispersed by TNWDIS enhanced the compressive strength by 6.5% and the flexural strength by 2.8%, so it can be concluded that this CNT content led to a slight increase in the compressive strength but had a limited effect on the flexural strength. Considering that TNWDIS was ultra-effective in dispersing CNTs and had no potential reaction with the cement hydrates, it can be inferred that the bonding strength was not high enough to provide an efficient load transfer when the CNTs were decorated by TNWDIS. The same conclusion was drawn by Cwirzen et al. [6], who dispersed CNTs with polyacrylic acid polymer (an efficient dispersant) and found that no effective bonding formed to enhance the compressive and flexural strengths. The weak bonding results from the very limited surface friction of the CNTs with the cement matrix material [22], and the modification of the CNT surface by TNWDIS does not improve the situation.

In contrast, the 0.05 wt.% CNTs dispersed by PVP enhanced the flexural and compressive strengths by 7.4 and 9.3%, respectively. The 0.10 wt.% CNTs dispersed by PVP enhanced the flexural and compressive strengths by 17.3 and 16.3%, respectively. So it can be seen that the CNT content of 0.05 wt.% led to a slight increase in the mechanical properties and the 0.10 wt.% CNT content led to an obvious increase in the mechanical properties. It can be concluded that efficient load transfer was provided by the CNTs that were dispersed by PVP. It was also found by other researchers [36] that CNTs dispersed by PVP can provide an efficient bonding strength to enhance the mechanical properties of cement paste.

In addition, the effect of TNWDIS and PVP on the mechanical properties was measured as well. TNWDIS decreased the flexural strength by 2.5% while enhancing the compressive strength by
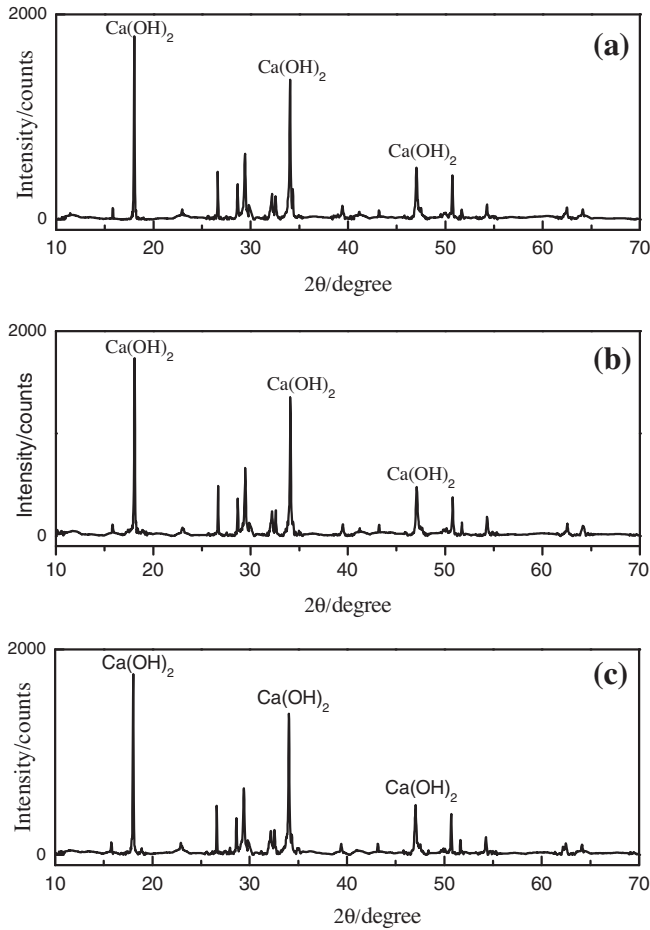
Fig. 6. The XRD patterns of CNT/cement matrix with the addition of 0.1 wt.% CNT content (by the weight of cement) after 28 days curing. (a) C0; (b) 0.1 wt.% CNT (dispersed by TNWDIS)/cement composites; and (c) 0.1 wt.% CNT (dispersed by PVP)/cement composites.
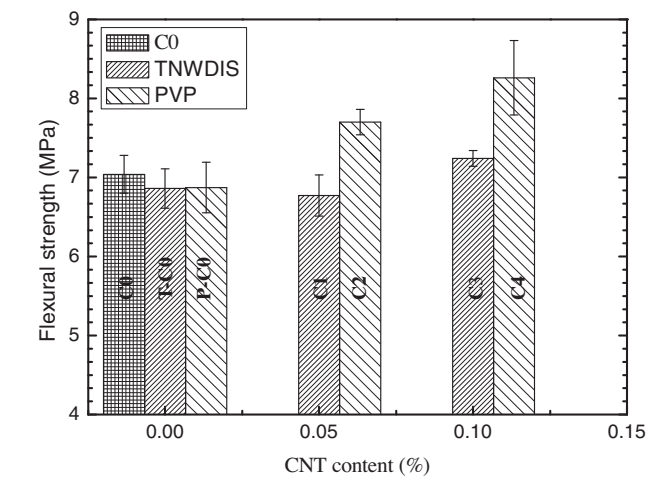

Fig. 7. Flexural strength of specimens at 28 days.

1.9%. PVP decreased the flexural and compressive strengths slightly, by 2.4 and 1.4%, respectively. So it can be concluded that TNWDIS and PVP had no effect on the cement hydrates, considering the existence of experimental error.
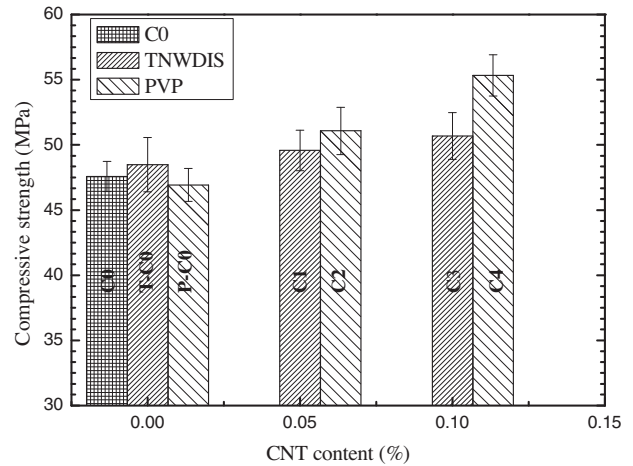

Fig. 8. Compressive strength of specimens at 28 days.

3.4. Damping property

The loss factor (or damping factor) is an important parameter that represents the damping performance of a material. The damping capacity means the ability of a material subjected to an external load to convert mechanical energy to heat energy [37,38]. The loss factor of CNT-reinforced cementitious composites ($5 \times 12 \times 100$ mm) incorporating 0, 0.05, or 0.1 wt.% CNTs dispersed by TNWDIS or PVP is shown in Fig. 9. All the specimens showed the lowest loss factor at 0.5 Hz and the highest at 1 Hz. The loss factor of CNT/cement composites decreased after 1 Hz with increasing vibration frequency. It was found that 0.05 and 0.10 wt.% CNTs dispersed by PVP improved the loss factor by 8.8 and 13.4% at 1 Hz, respectively, whereas 0.05 and 0.10 wt.% CNTs dispersed by TNWDIS improved the loss factor by 18.3 and 25.9% at 1 Hz, respectively. The rate of increase of the loss factor decreased with increasing CNT content, and CNTs dispersed by TNWDIS had almost twice the rate of increase compared to the same content of CNTs dispersed by PVP in enhancing the loss factor of the cement matrix. It can be observed from the figure that 0.05 wt.% CNTs dispersed by TNWDIS had an even greater loss factor than 0.1 wt.% CNTs dispersed by PVP. The loss factors were improved to a similar degree at other frequencies compared with
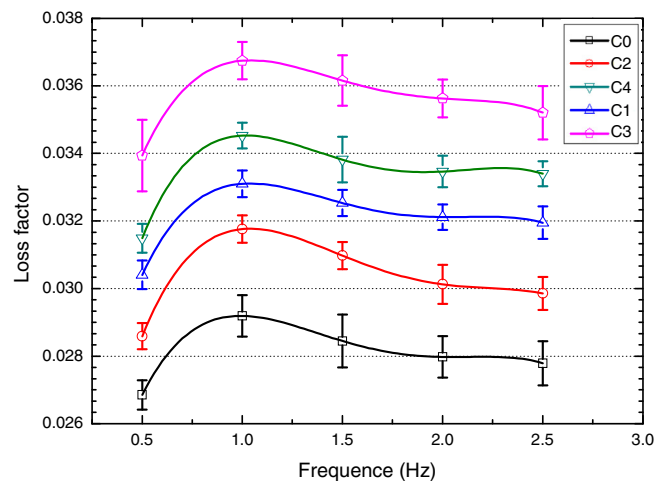

Fig. 9. The loss factor of CNT/cement composites incorporating 0.05 wt.% and 0.10 wt.% CNT that dispersed by TNWDIS and PVP, respectively.

1 Hz, indicating that the degree of reinforcement provided by the loss factor is not associated with the vibration frequency.

3.5. Discussion

According to the SEM, EDS, and XRD research results, it can be concluded that the CNTs with surfactants were well mixed in the cement paste and combined with cement hydrates through a physical reaction, because a new peak appears in the XRD pattern if a chemical reaction takes place between the CNTs and the cement [35] and the peak value of Ca(OH)$_2$ changes if the hydration process is accelerated or hampered by a chemical reaction [39]. The main factor affecting the enhancement of the mechanical properties of the cement composites provided by the CNTs is the bonding strength between the CNT structure and the adjacent hydrates [11]. Comparing the reinforcing effect of CNTs with absorbed TNWDIS and CNTs with absorbed PVP, PVP obviously improves the surface friction of the CNT structure with the hydrates more effectively. It is common sense that the chemical structure of surfactants affects the interaction force between surfactants and CNTs [40], the form of decoration of the surfactants on the CNT structure [41], and the position of the decoration on the tube [42]. A possible reason for the better enhancement phenomenon produced by PVP is that part of the chains of the PVP molecule has a stronger reaction with the CNT structure, while the rest of the chains are anchored well in the cement hydrates. Qiu et al. [31] applied Raman spectrum analysis to confirm that a chemical graft reaction occurred between the MWCNTs and PVP. This differs from the working mechanism of PVP on SWCNTs, as the PVP wrapped around the tubes evenly through a physical reaction [43]. A possible reason for the limited reinforcing effect of CNTs with TNWDIS is that the sorption of TNWDIS (a kind of aromatic compound) onto CNTs was a process of physical interaction that is easy to break. Lin et al. [40] systematically investigated the sorption mechanism of aromatic compounds and reported a process of physical interaction of the aromatic compounds with the CNTs. This was confirmed by several articles [44–46]. The benzene derivatives (acting as π-acceptors) and CNTs (acting as π-donors) form π–π bonding (a kind of weak interaction) [40]. When many benzene rings of a TNWDIS molecule are absorbed on the CNT surface, the rest of the chains are short and are insufficient to provide efficient bonding with the hydrates [23], which is another explanation for the limited reinforcing effect of CNTs dispersed with TNWDIS.

The incorporation of CNTs increased the loss factor of cement paste. The reasons for the enhancement of the damping property can be explained by the following:

(1) The energy dissipation of CNTs due to their viscoelasticity [25]. The viscous and elastic behavior dominates and leads to different degrees of dissipation of energy as heat at varying frequencies [47]. In addition, CNTs have a remarkable Young's modulus and deformability, indicating high damping capability [48,49]. A single MWCNT contains several concentric tubes and the interface slip and friction between tubes results in energy dissipation [50].

(2) The energy dissipation due to the matrix–tube interface [37,51]. Xu et al. [52] observed a sliding trace of CNTs in cement matrix using SEM analysis, which indicated the existence of unbound regions between the CNTs and the matrix interface. The slip of CNTs produces non-negligible frictional damping [25]. Some very weak bonding might be debonded due to periodic vibration and could enhance the interfacial friction [51]. Multi-phase boundaries and multiform interfaces are generated due to the incorporation of CNTs and then produce great interfacial friction and slippage while vibrating [32]. As shown in Fig. 4(c), the long CNTs can easily induce friction at the middle with the two ends anchored in the cement hydrates.

(3) Damping due to the interphase [25]. The interphase [53] is the region adjacent to the CNT surface all along the tube. The interphase property is affected by the working mechanisms of the CNT surface with adjacent hydrates, like interfacial chemical bonds, van der Waals forces, and mechanical interlocking [51]. Chandra et al. [25] proposed that the nature of the interphase (weak, ideal, and strong) accordingly affects the mechanical behavior and in turn the damping properties of the composites.

Although PVP is better at modifying the CNT surface to enhance its bonding strength with cement hydrates, the loss factor shows that CNTs dispersed with TNWDIS are better at enhancing the damping property of the CNT/cement composites. The results indicate that better enhancement of the mechanical properties of CNT-reinforced composites is related to relatively weak improvement of the damping properties. An explanation for this is that there is more interface friction due to the weaker bonding strength between the matrix and the dispersed CNTs. The main difference between CNT-reinforced composites dispersed by TNWDIS and those dispersed by PVP is the interface, due to the differences in how they decorate the CNT surface. Cinquin et al. [27] proved that an increase in damping is associated with a decrease in interfacial bonding. Zhou et al. [51] also proposed that high damping can be achieved by taking advantage of relatively weak bonding.

4. Conclusions

The article presents the results of the mechanical and damping properties of CNT-reinforced cementitious composites at different concentrations of CNTs (0, 0.05, and 0.10 wt.%) using two dispersing surfactants. The conclusions of these investigations are summarized as follows:

(1) The two proposed methods (TNWDIS and PVP) of dispersing CNTs in aqueous solution are both effective and have the same dispersion ability. Neither surfactant causes a change in the hydration process. CNTs were well distributed in the cementitious composites according to the SEM analysis.

(2) The mechanical properties of CNT-reinforced cementitious composites increased with increasing CNT content. CNTs dispersed by PVP are more beneficial for enhancing the mechanical properties of cement paste than those dispersed by TNWDIS, indicating the better bonding strength between the CNTs and the matrix.

(3) The results of EDS and XRD analysis suggest that hydroxylated CNTs combine with hydrates via a physical interaction, which provides the potential for increasing the damping behavior of CNT-reinforced composites.

(4) The DMA tests proved the ameliorating effects of CNTs on the damping performance of the composites. The loss factor of the composites exhibited an obvious increase with CNT content. The enhancement of the damping behavior is mainly due to the generation of multi-phase boundaries and multiform interfaces.

(5) The increase in the loss factor was more pronounced in CNT-reinforced cementitious composites dispersed by TNWDIS than in those dispersed by PVP, indicating the greater interface friction and slippage due to weaker bonding in the former.

Acknowledgements

References

[1] Laurenzi S, Pastore R, Giannini G, Marchetti M. Experimental study of impact resistance in multi-walled carbon nanotube reinforced epoxy. Compos Struct 2013;99(5):62–8.

[2] Fakhru'l-Razi A, Atieh MA, Girun N, Chuah TG, El-Sadig M, Biak DRA. Effect of multi-wall carbon nanotubes on the mechanical properties of natural rubber. Compos Struct 2006;75(1–4):496–500.

[3] Konsta-Gdoutos MS, Metaxa ZS, Shah SP. Highly dispersed carbon nanotube reinforced cement based materials. Cem Concr Res 2010;40(7):1052–9.

[4] Khalili SMR, Haghbin A. Investigation on design parameters of single-walled carbon nanotube reinforced nanocomposites under impact loads. Compos Struct 2013;98:253–60.

[5] Kim HK, Park IS, Lee HK. Improved piezoresistive sensitivity and stability of CNT/cement mortar composites with low water–binder ratio. Compos Struct 2014;116(1):713–9.

[6] Kim H, Nam I, Lee H. Enhanced effect of carbon nanotube on mechanical and electrical properties of cement composites by incorporation of silica fume. Compos Struct 2014;107:60–9.

[7] Han B, Sun S, Ding S, Zhang L, Yu X, Ou J. Review of nanocarbon-engineered multifunctional cementitious composites. Compos A Appl Sci Manuf 2015;70:69–81.

[8] Abu Al-Rub RK, Ashour AI, Tyson BM. On the aspect ratio effect of multi-walled carbon nanotube reinforcements on the mechanical properties of cementitious nanocomposites. Constr Build Mater 2012;35:647–55.

[9] Konsta-Gdoutos MS, Aza CA. Self sensing carbon nanotube (CNT) and nanofiber (CNF) cementitious composites for real time damage assessment in smart structures. Cement Concr Compos 2014;53:162–9.

[10] Parveen S, Rana S, Fangueiro R. A review on nanomaterial dispersion, microstructure, and mechanical properties of carbon nanotube and nanofiber reinforced cementitious composites. J Nanomater 2013;710175:1–19.

[11] Cwirzen A, Habermehl-Cwirzen K, Nasibulin AG, Kaupinen EI, Mudimela PR, Penttala V. SEM/AFM studies of cementitious binder modified by MWCNT and nano-sized Fe needles. Mater Charact 2009;60(7):735–40.

[12] Girifalco L, Hodak M, Lee RS. Carbon nanotubes, buckyballs, ropes, and a universal graphitic potential. Phys Rev B 2000;62(19):13104.

[13] Islam M, Rojas E, Bergey D, Johnson A, Yodh A. High weight fraction surfactant solubilization of single-wall carbon nanotubes in water. Nano Lett 2003;3(2):269–73.

[14] Cota FdP, Panzera TH, Schiavon MA, Christoforo AL, Borges PHR, Bowen C, et al. Full factorial design analysis of carbon nanotube polymer-cement composites. Mater Res 2012;15(4):573–80.

[15] Yu J, Grossiord N, Koning CE, Loos J. Controlling the dispersion of multi-wall carbon nanotubes in aqueous surfactant solution. Carbon 2007;45(3):618–23.

[16] Szleifer I, Yerushalmi-Rozen R. Polymers and carbon nanotubes—dimensionality, interactions and nanotechnology. Polymer 2005;46(19):7803–18.

[17] Kim GM, Naeem F, Kim HK, Lee HK. Heating and heat-dependent mechanical characteristics of CNT-embedded cementitious composites. Compos Struct 2016;136:162–70.

[18] Collins F, Lambert J, Duan WH. The influences of admixtures on the dispersion, workability, and strength of carbon nanotube–OPC paste mixtures. Cement Concr Compos 2012;34(2):201–7.

[19] Datsyuk V, Kalyva M, Papagelis K, Parthenios J, Tasis D, Siokou A, et al. Chemical oxidation of multiwalled carbon nanotubes. Carbon 2008;46(6):833–40.

[20] Zou B, Chen SJ, Korayem AH, Collins F, Wang CM, Duan WH. Effect of ultrasonication energy on engineering properties of carbon nanotube reinforced cement pastes. Carbon 2015;85:212–20.

[21] T. Kowald, R. Trettin, Influence of surface-modified carbon nanotubes on ultrahigh performance concrete, in: Proceedings of International Symposium on Ultra High Performance Concrete (2004) 195–203.

[22] Tamimi A, Hassan NM, Fattah K, Talachi A. Performance of cementitious materials produced by incorporating surface treated multiwall carbon nanotubes and silica fume. Constr Build Mater 2016;114:934–45.

[23] Trettin R, Kowald T. Nanotubes für Hochleistungsbetone. Betonwerk und Fertigteil-Technik. 2005;71(2):20–1.

[24] Jeon E-B, Ahn S, Lee I-G, Koh H-I, Park J, Kim H-S. Investigation of mechanical/dynamic properties of carbon fiber reinforced polymer concrete for low noise railway slab. Compos Struct 2015;134:27–35.

[25] Chandra R, Singh S, Gupta K. Damping studies in fiber-reinforced composites–a review. Compos Struct 1999;46(1):41–51.

[26] Ahn S, Jeon E-B, Koh H-I, Kim H-S, Park J. Identification of stiffness distribution of fatigue loaded polymer concrete through vibration measurements. Compos Struct 2016;136:11–5.

[27] Cinquin J, Chabert B, Chauchard J, Morel E, Trotignon J. Characterization of a thermoplastic (polyamide 66) reinforced with unidirectional glass fibres. Matrix additives and fibres surface treatment influence on the mechanical and viscoelastic properties. Composites 1990;21(2):141–7.

[28] Grossiord N, Regev O, Loos J, Meuldijk J, Koning CE. Time-dependent study of the exfoliation process of carbon nanotubes in aqueous dispersions by using UV-visible spectroscopy. Anal Chem 2005;77(16):5135–9.

[29] Kataura H, Kumazawa Y, Maniwa Y, Umezu I, Suzuki S, Ohtsuka Y, et al. Optical properties of single-wall carbon nanotubes. Synth Met 1999;103(1):2555–8.

[30] Cheng J, Zheng P, Zhao F, Ma X. The composites based on plasticized starch and carbon nanotubes. Int J Biol Macromol 2013;59:13–9.

[31] Qiu J, Wang G, Shang J. Multi-walled carbon nanotubes modified by poly (vinyl pyrrolidone). Acta Polymerica Sinica 2007;4:327.

[32] Luo J, Duan Z, Xian G, Li Q, Zhao T. Damping performances of carbon nanotube reinforced cement composite. Mech Adv Mater Struct 2015;22(3):224–32.

[33] Li GY, Wang PM, Zhao X. Mechanical behavior and microstructure of cement composites incorporating surface-treated multi-walled carbon nanotubes. Carbon 2005;43(6):1239–45.

[34] Musso S, Tulliani J-M, Ferro G, Tagliaferro A. Influence of carbon nanotubes structure on the mechanical behavior of cement composites. Compos Sci Technol 2009;69(11):1985–90.

[35] Singh AP, Gupta BK, Mishra M, Chandra A, Mathur R, Dhawan S. Multiwalled carbon nanotube/cement composites with exceptional electromagnetic interference shielding properties. Carbon 2013;56:86–96.

[36] Chan LY, Andrawes B. Finite element analysis of carbon nanotube/cement composite with degraded bond strength. Comput Mater Sci 2010;47(4):994–1004.

[37] Mukherjee A, Joshi M. FRPC reinforced concrete beam-column joints under cyclic excitation. Compos Struct 2005;70(2):185–99.

[38] Khan SU, Li CY, Siddiqui NA, Kim J-K. Vibration damping characteristics of carbon fiber-reinforced composites containing multi-walled carbon nanotubes. Compos Sci Technol 2011;71(12):1486–94.

[39] Qing Y, Zenan Z, Deyu K, Rongshen C. Influence of nano-SiO$_2$ addition on properties of hardened cement paste as compared with silica fume. Constr Build Mater 2007;21(3):539–45.

[40] Lin D, Xing B. Adsorption of phenolic compounds by carbon nanotubes: role of aromaticity and substitution of hydroxyl groups. Environ Sci Technol 2008;42(19):7254–9.

[41] Yurekli K, Mitchell CA, Krishnamoorti R. Small-angle neutron scattering from surfactant-assisted aqueous dispersions of carbon nanotubes. J Am Chem Soc 2004;126(32):9902–3.

[42] Bandyopadhyaya R, Nativ-Roth E, Regev O, Yerushalmi-Rozen R. Stabilization of individual carbon nanotubes in aqueous solutions. Nano Lett 2002;2(1):25–8.

[43] O'Connell MJ, Boul P, Ericson LM, Huffman C, Wang Y, Haroz E, et al. Reversible water-solubilization of single-walled carbon nanotubes by polymer wrapping. Chem Phys Lett 2001;342(3):265–71.

[44] Gotovac S, Honda H, Hattori Y, Takahashi K, Kanoh H, Kaneko K. Effect of nanoscale curvature of single-walled carbon nanotubes on adsorption of polycyclic aromatic hydrocarbons. Nano Lett 2007;7(3):583–7.

[45] Wang Z, Liu C, Liu Z, Xiang H, Li Z, Gong Q. Π–π Interaction enhancement on the ultrafast third-order optical nonlinearity of carbon nanotubes/polymer composites. Chem Phys Lett 2005;407(1):35–9.

[46] Zhang Y, Yuan S, Zhou W, Xu J, Li Y. Spectroscopic evidence and molecular simulation investigation of the interaction between pyrene molecules and carbon nanotubes. J Nanosci Nanotechnol 2007;7(2):2366–75.

[47] Xu M, Futaba DN, Yamada T, Yumura M, Hata K. Carbon nanotubes with temperature-invariant viscoelasticity from −196 to 1000 °C. Science 2010;330(6009):1364–8.

[48] Wong EW, Sheehan PE, Lieber CM. Nanobeam mechanics: elasticity, strength, and toughness of nanorods and nanotubes. Science 1997;277(5334):1971–5.

[49] Yu M-F, Lourie O, Dyer MJ, Moloni K, Kelly TF, Ruoff RS. Strength and breaking mechanism of multiwalled carbon nanotubes under tensile load. Science 2000;287(5453):637–40.

[50] Z. Duan, J. Luo, Effect of multi-walled carbon nanotubes on the vibration-reduction behavior of cement, in: International Conference on Smart Materials and Nanotechnology in Engineering: International Society for Optics and Photonics (2007) p. 64230R/1-6.

[51] Zhou X, Shin E, Wang K, Bakis C. Interfacial damping characteristics of carbon nanotube-based composites. Compos Sci Technol 2004;64(15):2425–37.

[52] Xu S, Liu J, Li Q. Mechanical properties and microstructure of multi-walled carbon nanotube-reinforced cement paste. Constr Build Mater 2015;76:16–23.

[53] R. Gibson, S. Hwang, H. Kwak, Micromechanical modeling of damping in composites including interphase effects, in: 36th Intern SAMPE Symposium, Soc for the Adv of Mat and Process Eng, Covina. (1991) 592–606.