Experimental and mechanical analysis of cement–nanotube nanocomposites

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Abstract. Composites of multi-walled carbon nanotubes (MWCNTs) and cement layers were manufactured by grinding carbon nanotubes and cement powder in a planetary ball mill. Tiny cement nanoparticles were fabricated using an ethylene-glycol-assisted synthesis procedure with successive hydrolysis and condensation reactions. Cement–nanotube nanocomposites were then produced by adding functionalized nanotube powder to the colloidal cement nanoparticles suspended in ethylene glycol (weight ratio of nanotubes to cement = 1:1). Modal analysis of five-walled carbon nanotube nanocomposites with 1–5 cement layers was performed via the finite-element method. The five-walled carbon nanotube nanocomposites with different shapes were modelled using three-dimensional elastic beams of carbon bonds, nodal carbon point masses and cement layer shell elements. The natural frequency, von Mises stress and strain energy of the elements were calculated by considering the Van der Waals forces between the carbon atoms in the hexagonal lattice. In the modal analysis, the greatest variation in displacement was observed along the *x*-axis, and the maximum values of the total displacement appeared to be larger at the cement layers than at the MWCNTs. The cement–nanotube nanocomposites exhibited a gradual decrease in deformation and vibration as the number of cement layers was increased.

Keywords. Carbon nanotubes; cement; nanocomposites; finite-element method; modal analysis.

1. Introduction

Researchers have attempted to estimate the mechanical properties of multi- and single-walled nanotubes (MWNTs and SWNTs, respectively) in many ways, including experimental, molecular dynamics (MD) and elastic continuum modelling methods. The discovery of carbon nanotubes (CNTs) brings with it the opportunity to improve the microstructure of cement materials. The strength, toughness and specific surface area of CNTs are far superior to those of ordinary fibres. In particular, CNTs exhibit a tensile strength between 11 and 63 GPa (100 times higher than that of steel), a Young's modulus of around 1 TPa and a fracture strain as high as 280% [1].

Ansari and Rouhi [2] developed an atomistic finite-element model to study the buckling behaviour of single-walled carbon nanotubes (SWCNTs) with different boundary conditions. The nanotubes were modelled using three-dimensional elastic beam elements for the bonds and point mass elements for the atoms. The elastic moduli of the beam elements were determined via a linkage between molecular and structural mechanics. Based on the devised model, the critical compressive forces of SWCNTs with different boundary conditions, geometries and chiralities were obtained and subsequently compared. Fan *et al* [3] developed a finite-element simulation technique for estimating the mechanical properties of multi-walled carbon nanotubes (MWCNTs). An individual CNT

was simulated as a frame-like structure, while primary bonds between nearest neighbour atoms were treated as beam elements. The beam element properties were determined through the concept of energy equivalence between MD and structural mechanics. A simulation of the interlayer Van der Waals (VDW) force, which has intrinsic nonlinearity and a complicated region of applicability, was ultimately performed.

Collins *et al* [4] attempted to disperse MWCNTs with several types of surfactants. The synthesized liquid suspensions remained stable for 9 days following ultrasonic dispersion, but the compressive strength and consistency of the resulting cement pastes were significantly diminished by the addition of MWCNTs.

Giannopoulos *et al* [5] developed a finite-element formulation that is appropriate for calculating the Young's and shear moduli of SWCNTs. To develop an equivalent continuum model for a single-layered graphene sheet, Hemmasizadeh *et al* [6] applied MD for an exact numerical solution, while shell theory was employed as an analytical method. As a result, the effective Young's modulus and mechanical thickness of the sheet wall were independently obtained.

Korpa *et al* [7] also studied CNT-enhanced high-performance concrete. The authors used highly reactive colloidal silica produced by a pyrogenic route (pyrogenic oxides) as a representative nanoscale pozzolanic additive. Colloidal silica shortens the induction period to an extent that it can

be qualitatively correlated to both the size of primary silica particles and the specific surface area.

The first issue 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 aggregation. Consequently, CNTs tend to form bundle-like structures due to their high surface energy. Proper dispersion and mixing methods are known to be key factors affecting the performance of nanocomposites. In particular, poor MWCNT dispersion leads to the formation of defects in the nanocomposites and decreases the reinforcing effect of the MWCNTs [8].

Li and Chou [9] reported on the elastic behaviour of MWCNTs. Interlayer VDW forces were represented by the Lennard-Jones potential and simulated using a nonlinear truss rod model. The Young's and shear moduli calculated for the MWCNTs were in the ranges of 1.05–0.05 and 0.40–0.05 TPa, respectively.

Currently, there are two methods that are commonly employed for CNT dispersion. The first is chemical modification, whereby functional groups are introduced on the surface of CNTs through the use of chemical reagents, high-energy discharge, ultraviolet radiation or other processes [10,11]. The second approach is physical modification, which involves the application of mechanical stress through various processes (e.g., crushing and ultrasonic dispersion) in order to activate the surface of the CNTs [12]. Liu *et al* [13] found that electron-beam irradiation can increase interaction forces. The Hamaker constant for both the CNTs and the gold surface was obtained from theoretical calculations and experimental results.

Mir *et al* [14] studied the vibrational response of two well-known types of SWCNTs, zigzag and armchair, which are also investigated in this work. The natural frequencies and corresponding modes of deformation *vs.* the change in geometry were determined for the structures. It was found that an increase in the nanotube diameter gave rise to an increase in frequency. However, the frequency increase was not uniform for the armchair nanotubes.

In the present work, both an effective surfactant and ball milling with dry ice were utilized to achieve optimum MWCNT dispersion. A stable liquid suspension of MWCNTs was then obtained by a sonication and centrifugation procedure. Several functionalized concentrations of MWCNTs were mixed into the cement paste, and the mechanical properties of the resulting composites were tested after approximately 28 days of aging. The microstructures of the cement–nanotube nanocomposites were studied using scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM) and finite-element method (FEM) modelling.

The natural frequencies and mode shapes of CNTs with cement layers were calculated under cantilever boundary conditions by applying a mass finite-element model. A FEM modelling approach using ANSYS was implemented to achieve this result and describe the cement layers; FEM modelling for modal analysis was carried out using ICEM CFD.

Here, MWCNTs with one–five cement layers were modelled by beam, mass and shell elements.

2. Experimental

2.1 Preparation of functionalized nanotube nanoparticles

CNT power was purchased from the Kumho Petrochemical Co., Ltd (KKPC), while dry ice was procured from the Fine Dry Ice Co., Ltd (Korea). All other solvents were supplied by the Taemyong Scientific Co., Ltd (Korea) and used without further purification. CNT nanoparticles were prepared by ball milling the CNT power in a planetary ball mill in the presence of dry ice. In a typical experiment, 5 g of the CNT power and 50 g of dry ice were placed into a stainless-steel capsule containing stainless-steel balls (300–320 g) with a diameter of 5 mm. The capsule was then sealed, fixed in the planetary ball mill and agitated at 400 rpm for 24 h [24].

The resultant mixture was placed in 1 mol of HCl for 48 h to completely acidify the carboxylates and remove metallic impurities. This was followed by successive washing of the mixture with 300 ml of Milli-Q water, 200 ml of HCl (30%, Taemyong) and 200 ml of ethanol (30%, Taemyong).

The washed mixture was divided into five portions, and each portion was filtered through a vacuum filter. During the filtering step, distilled water was continually introduced into the divided mixtures until a neutral pH was established.

After filtering, the mixture was cooled in a freezer for approximately 1 day. The resulting functionalized nanotube powder was then collected by filtration and vacuum dried.

2.2 Preparation of cement nanoparticles

Functionalized cement powder was collected using the same purification method mentioned earlier. Cement nanoparticles were produced via an ethylene-glycol-assisted synthesis method involving successive hydrolysis and condensation reactions [25]. Briefly, 50 ml of ethylene glycol (99.8%, Sigma-Aldrich) was heated at 150°C for 10 min to remove water, and then cooled to 80°C . Next, 0.50 g of polyvinylpyrrolidone (MW 40000, K30, Daejung) as a stabilizer and 5 g of cement power were sequentially added to the ethylene glycol with stirring at 300 rpm. After 30 min, the resulting dark suspension of cement nanoparticles was cooled to room temperature (25°C).

2.3 Fabrication of cement–nanotube nanocomposites

Cement–nanotube nanocomposites were produced by adding functionalized nanotube powder to colloidal cement nanoparticles suspended in ethylene glycol at a 1:1 weight ratio of nanotubes to cement. The mixture was subsequently placed in agate mortars and stirred by hand with a pestle at approximately 50 rpm for 30 min. The contact pressure exerted by the pestle head was around 20 psi at room temperature.

Figure 1. SEM image and chemical analysis results obtained for the cement–nanotube nanocomposites: (a) surface morphology of Sample 1 and (b) elemental analysis graph.

Table 1. Elemental analysis of the cement–nanotube nanocomposites.

Element (wt%)	C	O	Ge	Al	Si	Ca
Sample 1	73.49	12.06	5.23	0.80	1.59	6.83
Sample 2	64.78	12.51	12.82	0.75	2.15	7.98

For the purification step, the mixture was filtered through polyester fibre (Carpenter Co., USA). The final product was freeze-dried with a freeze dryer at -40°C under reduced pressure for 24 h to yield 7 g of dark black powder (figure 1a). The cement–nanotube powder was collected using the same purification method mentioned earlier.

Table 1 shows the elemental analysis results acquired for the cement–nanotube nanocomposite samples (Samples 1 and 2) at random positions. The detailed mechanism of carboxylation via a mechano-chemical ball milling process has been confirmed by various spectroscopic measurements and is presented elsewhere [16].

Portland cement is composed of CaO (64%), SiO_2 (22%) and Al_2O_3 (5.8%); the principal mineral components are $3\text{CaO} \cdot \text{SiO}_2$ (45.7%), $2\text{CaO} \cdot \text{SiO}_2$ (25.7%) and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ (9.7%).

Elemental analyses showed that the oxygen content in the samples varied after ball milling for 24 h. As displayed in table 1, the oxygen concentration increased from 12.06 to 12.51%, while the carbon content decreased from 73.49 to 64.78%. Furthermore, it was revealed that the oxygen concentration increased at longer ball milling times. A continuous decrease in the sample grain size was also observed up to a milling time of 24 h, at which point a steady state was reached. This is evident in figure 2a–d, which shows typical HRTEM (JEOL JEM-2010) images of cement–nanotube nanocomposites made from pristine CNT flakes. The specimens were initially composed of irregular nanoparticles with nanotube layers having smooth surfaces. As revealed in

figure 2b–d, more homogenous but much smaller cement–nanotube nanocomposites were formed after ball milling for 24 h.

A worm-like structure consisting of nanotubes coated with several black particles is observed in figure 2a; the scale bar is 50 nm. Such a configuration is typical for thin sheets of cement pastes. The diameters of the MWCNTs were generally between 10 and 40 nm with 4–12 nanotube layers. The number of layers selected for the current study was approximately 5, as indicated by the arrows in figure 2. The HRTEM images in figure 2c and d clearly show the presence of nanotube layers. The nanotubes exfoliated into nanocomposites in the dispersion used for the HRTEM sample preparation. Consequently, the structures exhibited wrinkles typical of flexible layers.

Under higher magnification, the thin cement pastes assembled on the nanotubes appeared as black in the TEM images (arrows in figure 2). These cement pastes were mostly located at the centre of the nanotube columns. Furthermore, more than five nanotube layers were typically observed in the HRTEM images.

The obtained results clearly indicate that the pristine nanotube flakes could have been directly exfoliated into fewer layers via a combination of ball milling in the presence of dry ice and dispersion in polar solvents. Therefore, the ball milling method, which requires neither hazardous chemicals nor tedious procedures, outperforms current methods for fabricating high-quality cement–nanotube nanocomposites at minimal cost.

The experiment is unexpectedly simple in the fabrication procedure of the composite of cement and nanotubes, and is easily checked using TEM or SEM. One downside is the limitation in consistent mass fabrications of the composites. However, we chose this fabrication method to avoid the techniques that are complex and costly, and confirmed that some composites can be easily made this way. The time and economic factors have also been taken into account.

Figure 2. HRTEM images obtained from randomly selected cement–nanotube nanocomposites at different magnifications. The scale bars are (a) 50 nm, (b) 5 nm, (c) 5 nm and (d) 2 nm. The number of nanotube layers indicated by arrows is approximately 5.

3. Simulation of molecular bonds by VDW force

The MWCNTs were treated as a frame structure in which their bonds were beam members and carbon atoms were joints. To establish a linkage between the force constants in molecular mechanics and the beam element stiffness in structural mechanics, the energy equivalence concept proposed by Li and Chou [17] was employed.

In general, the total steric potential energy of the force field in MD can be expressed as the sum of the bonded and non-bonded interaction energies, i.e., [18]

$$U_{\text{total}} = \Sigma U_r + \Sigma U_\theta + \Sigma U_\varphi + \Sigma U_\omega + \Sigma U_{\text{vdw}}, \quad (1)$$

where U_r , U_θ , U_φ , U_ω and U_{vdw} are the energies associated with bond stretching, bond angle bending, dihedral angle torsion, out-of-plane torsion and non-bonded VDW interactions, respectively.

VDW force is an intermolecular force arising from a fluctuating electromagnetic field that induces instantaneous electrical and magnetic polarizations between atoms and molecules. Extensive research into VDW forces has been conducted, and many reports can be found in the literature [19,21]. Yang and Qian [15] developed a non-uniform rational B-spline (NURBS) surface approach for VDW force computation. In a system of two carbon atoms modelled as spherical

particles with radii r_1 and r_2 [22,23] and a separation of d , the non-retarded VDW force between the two spheres was expressed by Chen and Anandarajah [20] as follows:

$$F = [-A(d + r_1 + r_2)/3] \left[-1/2d(r_1 + r_2) + 1/4r_1r_2 + 1/4d^2(r_1 + r_2)^2 + r_1r_2/8r_1r_2 + r_1r_2/8r_1r_2 \right]. \quad (2)$$

From equation (2), three geometric parameters, the separation distance d and the two sphere radii r_1 and r_2 , are required to calculate the VDW forces for sphere–sphere interactions. In this case, we adopt the same separation distance, $d = 2.442$ nm, and fix the sphere radii ($r_1 = r_2$) and Hamaker constant (A) as 0.07 nm and 0.284×10^{-19} J, respectively [15].

4. Implementation of the finite-element model

The actual shape of the composite manufactured from the experiment was checked by SEM and TEM. The computer modelling was done in ICEM CFD of ANSYS using the shape measured by TEM. With the model as the standard, a Mechanical APDL source code file has been made and interpreted.

We endeavoured to make the model as close to the actual shape as possible. Based on the size, shape, VDW force and modelling concept described earlier, the finite-element model was implemented for the cement–nanotube nanocomposites using the ANSYS commercial code. The C–C bonds, carbon atoms and cement nanocomposites were simulated as beam, mass and shell elements, respectively.

The interpretation procedure was (1) static analysis → modal analysis, (2) transient analysis (convergence analysis) → modal analysis, and was checked using ANSYS and VisualFEA (www.visualFEA.com). As shown in figure 3, in modelling of the nanotubes and the composite, the number of beam elements used to model each bond between the carbon atoms is 7730, and the number of nodes is 4950. The number of shell elements in the first layer of each cement is 1333.

The total length of the MWCNT FEM model was 60.3185 nm along the z -axis, 19.18434 nm along the x -axis and 19.21164 nm along the y -axis. Cement elements in contact with the MWCNT were modelled as shell elements such that the outermost first layer of the nanotube to the innermost fifth layer were sequentially formed. The shape of the model was configured so as to closely match that observed in the TEM images. The nanotube had five layers, thereby yielding a quintuple-layered cement nanocomposite with a thickness in the range of 0.67476–0.67848 nm. A 0.67848 nm spacing existed between the walls of the MWCNT along the x – y direction.

The cement plates were modelled by matching the nodes of beams in the nanotube hexagonal bonds with the nodes of the triangular shells in cement plates. If the matching does not occur, we can use link elements or spring elements.

The devised MWCNT finite-element models are shown in figure 3a and b, while cement elements in contact with the MWCNT are displayed in figure 3c.

Concentrated masses were used to model carbon atoms as point elements with up to six degrees of freedom: translations in the nodal x , y and z directions and rotations about the nodal x , y and z axes. A different mass and rotary inertia could be assigned to each coordinate direction [22,23]. The mass element was defined as a single node with concentrated mass components in the element coordinate directions.

The VDW forces modelled in the FEM analysis is described in detail in authors' previous papers [22–24]. In this paper, through direct calculation, it was loaded with the SFBEAM, ALL and PRES commands in ANSYS.

Studying the change in the elastic properties of the nanotubes is another open research area. There are researchers who have already done it. The data on the initial elastic properties are already tabulated in Ref. [23].

Before inputting the data for the beam, mass and shell element properties, the dimensions of the parameters were further adjusted to avoid possible matrix flow errors during the numerical computation. This modification step was performed in accordance with research outlined in previous

Figure 3. Finite-element model of cement–nanotube nanocomposites at different magnifications and view directions: (a) y – z axes, right view, (b) x – y axes, front view and (c) isometric view with shell elements.

work [23]. The numerical analysis methods employed here are described in Ref. [22]. After the analysis, the node and element with the maximum absolute values of natural frequency, strain energy and von Mises stress at the tenth mode were determined for five types of cement–nanotube nanocomposites.

5. Results and discussion

The natural frequency of a structure is related to its geometry, mass and boundary conditions. For the nanotubes considered here, the mass was assumed to be that of each carbon atom, 2.0×10^{-26} kg; rotational degrees of freedom of the atom were neglected due to its extremely small diameter. Cantilever-type boundary conditions were implemented, i.e., one end of the nanotubes was fixed while the other end was free.

The nanotubes with 1–5 layers of cement and cantilever-type boundary conditions were modelled using 3-D beam, mass and shell elements. Variations in the frequency vs. the mode of vibration for the cement–nanotube nanocomposites are compared in figures 4 and 5.

As shown in figure 4, the frequency of the nanotube with no cement layer increased gradually from mode 1 to 10. This was followed by a rapid rise in frequency between modes 10 and 11, and then another gradual increase after mode 11. Given these trends, the behaviour at mode 10 was analysed. Since the frequencies of the nanotubes with 1–5 cement layers were clustered towards the bottom of the plot in figure 4, this region was enlarged so as to better resolve the data. The resulting graph for the nanotubes with 1–5 layers is displayed in figure 5. As evident in the figure, the frequencies of

the nanotubes with 1–5 layers began to increase at modes 2, 1, 5, 5 and 7, in order.

The frequency of the nanotubes was found to decrease as the number of cement layers was increased. Furthermore, a significant difference was observed between the frequencies of the nanotubes with single and multiple (2–5) layers, while only small discrepancies in frequency appeared for the structures with 3–5 layers at mode 20. Such findings indicate that the frequency approaches a certain value as the number of layers increases. This trend could be attributed to the structural shape of the MWCNTs.

The animation in figure 6 displays the displacements of the nanotube with no cement layer at modes 1–20. Here, ‘SUB’ indicates the mode, ‘FREQ’ denotes the frequency and ‘USUM’ represents the average value of the combined displacements at the x , y and z axes. For modes 1–10, the point of maximum displacement (MX) is found at the right end of the nanotube. In contrast, the MX point is located on the side of the nanotube for modes 11–20. Such a finding explains the rapid increase in frequency between modes 10 and 11. Frequency increases when the position of the maximum point of displacement changes from the end of the nanotube to the side. This indicates that a cement-layered nanocomposite can be formed well beyond mode 10. The gaps on the side of the structure widen and, due to larger area exposed, the nanotube can be more easily coated with cement. On supplementary video ‘figure 6.mp4’, we can observe the position change of MX in modal analysis. For modes 1–9 (SUB = 1–9 in the supplementary video), the maximum value of displacement happens on the end of the tube, whereas for mode 10, it happens on the side of the nanotube. Considering this phenomenon, we inferred that combining of cement and nanotube begins at mode 10. If we look at the procedure of fabrication,

Figure 4. Variation in the natural frequency of the cement–nanotube structures with 0–5 layers of cement.

Figure 5. Variation in the natural frequency of the cement–nanotube structures with 1–5 layers of cement.

Figure 6. Animation showing the displacements of a MWCNT without cement layers.

formation of composite never happens on the end of the nanotube. This indicates that structural formation of composite never occurs below mode 10. The purpose of this paper is to find the point at which composite has been formed. One of the methods we adopted is vibration analysis to find the optimized state of the nanotube for fabrication. Since we confirmed that composite can be formed by considering ready-completed composite, although the change in displacement is random, we attempted to find the most probably optimized state by looking at MX.

Situational differences could exist based on the boundary conditions. For modes 1–10, the formation of a cement coating is more difficult due to the lower level of vibration on the wide side of the tapered nanotube when compared with that at the narrow end.

Table 2 shows the displacements along the x -axis for 1–5 cement layers at the tenth mode; red and blue colours represent the largest and smallest displacements, while MX and MN denote the maximum and minimum displacement values, respectively. Among the three axial directions, the largest displacements were observed along x -axis. In particular, the maximum displacements were found to be 0.016063 and 0.002079 nm with one and five layers, respectively. The animations in the table clearly display the displacement, position and shape at different modes. The maximum displacement occurs at the end of the cement layers.

The displacements along the x -axis at the tenth mode are shown in each figure of table 2. In the analysis results, displacements along the x -axis exhibited somewhat large variations, while the difference in displacements along the

Table 2. Structural displacements along x -axis and displacement vector sum for cement layers at the tenth mode.

y and z axes was relatively small. A similar phenomenon also appeared for all of the cement layers, where an especially large variation in displacement was noted along the x -axis. Overall, the maximum displacement values were smaller with 4–5 layers than with 1–3 layers.

The increase along the x -axis was uniform at lower modes of frequency but irregular at higher modes. Furthermore, the increases in the pattern of displacement variation for 3–5 cement layers were more regular at lower modes when compared with those for 1–2 layers.

This is closely related to the asymmetric shape and unit weight of the cement layers. The deformation shape according to each node was confirmed from the displacement results of table 2.

Table 3 displays the von Mises stress and strain energy at the tenth mode. The von Mises stress value for 1 cement layer was $10,189.3 \text{ N nm}^{-2}$ (as shown in the colour scale), and a minimum von Mises stress of 210.01 N nm^{-2} was obtained

with 5 cement layers. The arrows in table 3 denote the position of maximum von Mises stress on each layer in the diagram. The von Mises stress starts to decrease significantly with 2 cement layers. Ultimately, the value of the von Mises stress with 1 layer was 50 times greater than that obtained with 5 layers. While the position of the MX point is not perfectly stationary, it does seem to occur on the side of the nanotube. As the number of layers was increased, the nanotube became more stable. The other modes of deformation can be explained in a similar manner. Therefore, the numerical results indicate that the nanotubes underwent a gradual decrease in deformation and vibration as the number of cement layers increased. The value of the strain energy varied from 2.80356 J (1 layer) to 0.001084 J (5 layers) depending on the number of cement layers.

The variations in the strain energy with respect to the number of layers were similar to those observed for the von Mises stress.

Table 3. The von Mises stress and strain energy of cement layers at the tenth mode.

Cement layers	von Mises stress	Strain energy
1 Layer
2 Layers
3 Layers
4 Layers
5 Layers

The M_x , M_y and M_z structural moments at mode 10 for MWCNTs with cement layers and cantilever boundary conditions are shown in table 4. For the structure with one cement layer, maximum absolute values of the negative M_x , M_y and M_z moments (denoted with blue bars) were observed in elements 6603, 7345 and 6656, respectively. With 5 cement layers, the maximum values of the positive M_x , M_y and M_z moments (represented with red bars) were found in elements 5404, 4835 and 5266, respectively.

It is important to note that the moments along x , y and z axes decrease as the number of cement layers on the CNT increases. In addition, the maximum absolute value of the moment shifted from negative (–) to positive (+) with an increase in the number of cement layers. This is apparent upon examining the results obtained for the 5-layer structure, where the absolute value of the negative moment (blue bar) along each axis is greater than that of the positive moment (red bar).

The mechanical properties of the MWCNT with 5 cement layers were found to be significantly different from those of the other structures. These discrepancies can be attributed to

the geometric position and weight of the 5 layers. Furthermore, the strain energies with 1 and 3 cement layers (shown in table 3) were higher than those observed with 2 and 4 layers, respectively. Meanwhile, the strain energies with 3 cement layers were higher than those observed with 2 layers. Also, the von Mises stresses (also displayed in table 3) with 1 and 4 cement layers were higher than those obtained with 2 and 5 layers, respectively. Meanwhile, the von Mises stresses with 3 cement layers were higher than those obtained with 2 layers.

6. Conclusions

Several functionalized concentrations of MWCNTs were mixed into a cement paste. The resulting mixture consisted of five-walled CNTs coated with one cement layer. The microstructures of the cement–nanotube nanocomposites were examined via SEM, HRTEM and FEM modelling.

The vibrational behaviours of the MWCNT composites with 1–5 cement layers were studied using a FEM with beam,

Table 4. Structural moments of cement layer elements at the tenth mode.

Cement layers	Element moments		
	M_x	M_y	M_z
1 Layer
2 Layers
3 Layers
4 Layers
5 Layers

mass and shell elements in a three-dimensional coordinate system. In order to explore the vibrational behaviour, the influence of the cement layers on the natural frequencies of the cantilever boundary conditions was considered. The dynamic behaviour at the tenth mode in the modal analysis was also interpreted and analysed by constructing animations based on the structural displacement, von Mises stress, strain energy and element moment results.

An increase in the number of cement layers resulted in a frequency decrease of the modes. However, this decrease was not severe for modes 1–10 of the MWCNTs. The results also show that 1–2 cement layers undergo more extensive deformation with a decreased number of elements when compared with 3–5 cement layers at the same mode. Therefore, an increase in the number of cement layers can serve to enhance structural equilibrium.

The von Mises stress and strain energy data imply that the stable frequency of the nanotube composites is dependent on the boundary conditions and the number of cement layers at all modes of vibration.

In the modal analysis, the displacement results obtained along all primary axes showed the greatest variation in the x direction, and the maximum values of the displacement appeared larger at the cement layers than at the MWCNT. This is thought to be related to the geometrical position and unit weight of the cement layers.

Although the optimal expansion of the carbon bonds in mode 10 has been identified in the mode analysis, its application to the fabrication procedure of the actual composite is a difficult problem. We intend to further continue the research and experiments on the order or method of the injection of cement and nanotubes while keeping constant the frequency at mode 10 in the vibration machine, or on addition of more effective dispersion fluid. Optimum expansion of the carbon bonds was achieved when the mode was greater than 10. As such, this mode condition should be utilized in the manufacturing of high-quality cement–nanotube nanocomposites.

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Electronic supplementary material

Supplementary material pertaining to this article is available on the *Bulletin of Materials Science* website (www.ias.ac.in/matricsci).

References

- [1] Yu M F, Lourie O and Dyer M J 2000 *Science* **287** 637
- [2] Ansari R and Rouhi S 2010 *Physica E* **43** 58
- [3] Fan C W, Liu Y Y and Chyanbin H 2009 *Appl. Phys. A* **95** 819
- [4] Collins F, John L and Duan W 2012 *Cement Concr. Compos.* **34** 201
- [5] Giannopoulos G I, Kakavas P A and Anifantis N K 2008 *Comput. Mater. Sci.* **41** 561
- [6] Hemmasizadeh A, Mahzoon M, Hadi E and Khandan R 2008 *Thin Solid Films* **516** 7636
- [7] Korpa A, Kowald T and Trettin R 2008 *Cement Concr. Res.* **38** 955
- [8] Xie X L, Mai Y W and Zhou X P 2005 *Mater. Sci. Eng. R* **49** 89
- [9] Li C and Chou T W 2003 *Compos. Sci. Technol.* **63** 1517
- [10] Liu J, Casavant M J and Cox M 1999 *Chem. Phys. Lett.* **303** 125
- [11] Huang W, Lin Y, Taylor S, Gaillard J, Rao A M and Sun Y P 2002 *Nano Lett.* **2** 231
- [12] Sandler J, Shaffer M S P and Prasse T 1999 *Polymer* **40** 5967
- [13] Liu P, Nakajima M, Yang Z, Fukuda T and Arai F 2007 *Proceedings of the 7th IEEE international conference on nanotechnology*, August 2–5, Hong Kong
- [14] Mir M, Hosseini A and Majzoubi G H 2008 *Comput. Mater. Sci.* **43** 540
- [15] Yang P and Qian X 2009 *J. Colloid Interface Sci.* **337** 594
- [16] Jeon I Y, Shin Y R, Sohn G J, Choi H J, Bae S Y, Mahmood J et al 2012 *Proc. Natl. Acad. Sci. USA* **109** 5588
- [17] Li C and Chou T W 2003 *Int. J. Solids Struct.* **40** 2487
- [18] Meo M and Rossi M 2006 *Compos. Sci. Technol.* **66** 1597
- [19] Montgomery S W, Franchek M A and Goldschmidt V W 2000 *J. Colloid Interface Sci.* **227** 567
- [20] Chen J and Anandarajah A 1996 *J. Colloid Interface Sci.* **180** 519
- [21] Israelachvili J N 1974 *Contemp. Phys.* **15** 159
- [22] Lee J H, Lee B S, Au F T K, Zhang J and Zeng Y 2012 *Comput. Mater. Sci.* **56** 131
- [23] Lee J H and Lee B S 2012 *Comput. Mater. Sci.* **51** 30
- [24] Lee J H, Shim C M and Lee B S 2013 *Int. J. Mater. Sci. Appl.* **2** 209
- [25] Dreyer D R, Park S, Bielawski C W and Ruoff R S 2010 *Chem. Soc. Rev.* **39** 228