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Highly concentrated carbon nanotube admixture for nano-fiber reinforced cementitious materials

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ABSTRACT

The use of effectively dispersed multiwalled carbon nanotube (MWCNT)/aqueous/surfactant suspensions in cement based materials have been shown to substantially improve their mechanical properties. The produced MWCNT suspensions have a high aqueous content, which corresponds to the mixing water. In the present work, a method for preparing highly concentrated MWCNT suspensions is presented, thus reducing the volume of the resulting admixture that is required in cement based materials. A centrifugal process, that uses two different ultracentrifuge rotors, was employed to reduce the quantity of water in the suspensions. Optical absorbance spectroscopy shows that the ultracentrifugation process increases the concentration of the MWCNT suspensions by a factor of 5. Using the highly concentrated MWCNT suspensions following dilution results in nanocomposites with mechanical properties that are comparable to the performance of samples prepared using the non-concentrated suspensions. These results verify that the ultracentrifugation concentration method successfully preserves the solubility of the MWCNT suspensions without affecting the reinforcing properties of the admixture. In this manner, the ultracentrifugation concentration method may constitute an effective preparation step for large-scale implementation of MWCNT admixtures.

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1. Introduction

The utilization of highly dispersed multi-walled carbon nanotubes (MWCNTs) in cementitious materials has shown to substantially improve the mechanical and other properties of the cementitious matrix. It was found that by adding a very low amount of MWCNTs or carbon nanofibers (CNFs), at concentrations of 0.025–0.08 wt.% of cement, the strength and stiffness of cement beams increases up to 50% and 70%, respectively [1–6]. The application of low concentration of MWCNTs and CNFs enables the control of matrix cracks at the nanoscale level [7]. Also, at such low concentrations of CNTs, the cost of CNT reinforced concrete is comparable to or even lower than that of fiber reinforced concrete, suggesting that of the use of CNTs in concrete is economically feasible. In addition to the benefits of reinforcement, autogenous shrinkage tests have demonstrated that MWCNTs can also have beneficial effects on the early age strain capacity of cementitious materials, which leads to an improved durability of the cement matrix [1].

The current preparation method of MWCNT suspensions for use in cementitious materials includes a simple one step technique, which involves the application of ultrasonic energy and the use of a commercially available surfactant [2,8]. The MWCNT suspensions prepared by this method have a high aqueous content of 98.68%, which corresponds to the mixing water. By concentrating the MWCNT suspensions, this high aqueous content is reduced, which decreases the volume and cost of the transportation and delivery of these admixtures in large-scale cement applications. Therefore, the development of a technique that will effectively concentrate the MWCNT suspensions, without compromising their performance in cementitious materials following subsequent aqueous dilution, is essential.

A number of solution-phase processes exist, where carbon nanomaterials, such as CNTs and graphene flakes, are concentrated by the removal of their solvent. This can be achieved by precipitation via addition of organic solvent and vacuum filtration [9], solvent exchange utilizing polymer–organic solvent [10] and sedimentation and decantation by ultracentrifugation [11]. Among these processes, the ultracentrifugation method is ideal for applications where the presence of organic solvents will become a hindrance. Ultracentrifugation process has been proven as a facile method to increase the concentration of CNTs in aqueous solutions

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prior to being used in a technique called density gradient ultracentrifugation (DGU) [12–16]. In DGU, a preparative ultracentrifugation process called pelleting, generally used to sediment solidified organic compounds out of solutions, has been adapted from biology [17,18] to maximize the yield of process. During this technique, nanomaterials in aqueous suspensions are presented under a centrifugal force inside a tube and travel towards the bottom at certain sedimentation rate, forming a highly concentrated region which can be recovered after decantation (Fig. 1).

The objective of this research is to develop a method to effectively concentrate MWCNT suspensions for cementitious materials. To accomplish this, the aforementioned ultracentrifugation method was adapted and employed to reduce the amount of water in the MWCNT/water/surfactant suspension, thus increasing the MWCNT concentration. The effect of two ultracentrifuge rotors, the swing bucket and the fixed angle rotor, on developing highly concentrated MWCNT suspensions was investigated. Optical absorbance spectroscopy was used to evaluate the concentration of the suspensions after ultracentrifugation. Cementitious nanocomposite samples were prepared using the highly concentrated MWCNT suspensions, after they were diluted in the mixing water. Dilution was conducted by simply adding water to the suspensions prior to mixing with cement. The mechanical properties, i.e. flexural strength and modulus of elasticity, of the nanocomposites produced with the highly concentrated/diluted MWCNT suspensions were evaluated and compared with the properties exhibited by the nanocomposites produced with the original, non-concentrated MWCNT suspensions.

2. Experimental study

2.1. Method of MWCNT concentration

Purified multiwalled carbon nanotubes (MWCNTs), produced by the chemical vapor deposition method (CVD), with a diameter of ~20–40 nm, length of ~10–30 μm and purity >95% were used as received. The suspensions were prepared using MWCNTs at a concentration of 0.26 wt.%. To homogeneously disperse the MWCNTs in the mixing water, they were added in an aqueous solution containing a surfactant to MWCNTs weight ratio of 4.0. The mixture was then ultrasonicated using a 500 W cup-horn high intensity ultrasonic processor with a 13 mm diameter tip, operating at 50% of its maximum amplitude delivering 1900–2100 J/min. Energy was applied in cycles of 20 s to prevent the suspensions from overheating.

2.1.1. Laboratory scale concentration method for MWCNT suspension

Ultracentrifuges are typically available with a wide variety of rotors. The most widely used configurations of rotors are the swing bucket and the fixed angle. The swing bucket rotors allow the tubes to hang on hinges so that they reorient to the horizontal as the rotor initially accelerates [19]. During ultracentrifugation the material travels down the entire length of the centrifuge through the media within the tube [20]. Fixed angle rotors are made of a single block of metal and hold the tubes in cavities bored at a predetermined angle [19]. The materials are forced against the side of the centrifuge tube, and then slide down the wall of the tube [20].

In this study, following dispersion, the suspensions were concentrated by ultracentrifugation using both a swing bucket and a fixed angle rotor. Initially, sedimentation of the MWCNTs was explored using a swing bucket SW41 rotor (Beckman-Coulter) with ambient temperature at 22 °C and at 41,000 rpm using centrifuge tubes that can hold 12 ml of suspension. In the aforementioned DGU process, OptiPrep containing 60% (w/v) of iodixanol was used as the density medium for the concentration process to increase the viscosity of concentrated dispersion for the subsequent density gradient separations. However, since the MWCNTs used have a density of 2.1 g/ml which is higher than the density of OptiPrep (1.32 g/ml) and furthermore there is no need for their viscosity adjustment, the suspensions with uniform density were simply added to the centrifugation tubes. The sedimentation of the MWCNTs in the centrifugation tube was monitored at 30, 45 and 60 min. Fig. 2 shows a photograph of the centrifuged tubes for various durations of ultracentrifugation. At the durations of 30 and 45 min, it was observed that the nanotubes started to concentrate at the bottom of the tube. At 60 min, the suspension was fully sedimented at the bottom of the tube.

After centrifugation, the supernatant solution was decanted down to approximately 2 cm from the bottom of the tube, enabling retrieval of 2.5 ml of concentrated suspension, which corresponds to about 20% of the total volume of the suspension. MWCNT concentration in the solution before and after centrifugation was quantified using optical absorbance spectroscopy (OAS). It was observed that the absorption of the suspension after centrifugation was lower than the sample before centrifugation. A close observation of the samples revealed the formation of a solid pellet of MWCNTs at the bottom of the tube, which may be attributed to the agglomeration of the MWCNTs. Several researchers have reported that the presence of MWCNTs agglomerates causes a decrease in the absorption spectrum because the MWCNTs bundles do not optically absorb in the wavelength region between 200 and 1200 nm [21]. The formation of the pellet caused by the agglomeration of the MWCNs might therefore be a possible explanation for the observed reduction of the absorption.

In an optimized experiment, the MWCNT suspension was ultracentrifuged at 20,500 rpm and it was observed that the MWCNTs

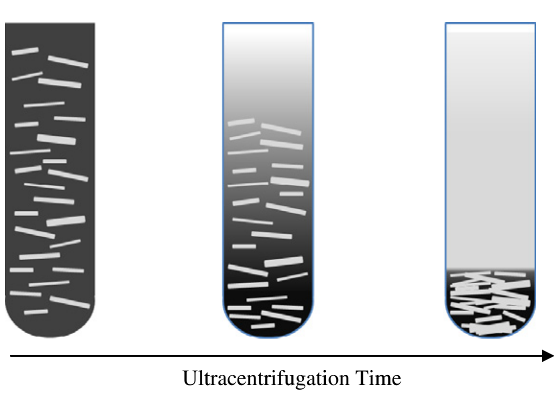

Fig. 1. Schematic figure showing the progression of sedimentation of nanomaterials inside a tube during ultracentrifugation.

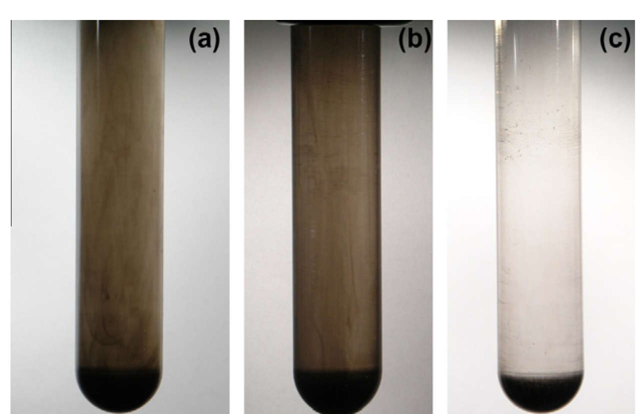

Fig. 2. MWCNTs suspensions ultracentrifuged for (a) 30 min, (b) 45 min and (c) 60 min.

had fully concentrated at the bottom of the tube after 4 h. After ultracentrifugation and decantation, the hardened pellet of concentrated MWCNTs and surfactant-encapsulated MWCNTs were re-suspended by ultrasonication inside the centrifuge tube submerged in an ice bath using the Sonic Dismembrator 500 from Fisher Scientific with a 1/8″ microtip attachment at 20% power for 5 min.

The aforementioned technique can load approximately 12 ml of MWCNT suspension per ultracentrifuge tube, which limits the yield of concentrated materials and precludes even the production of laboratory scale specimens. To be able to apply the method to cementitious samples, larger scale ultracentrifugation needs to be employed to increase the loading and yield.

2.1.2. Scale up of the MWCNT concentration method

Two rapid scale-up rotors were chosen for this study. Firstly, a swing bucket Ti 32 rotor, which can hold tubes of 38 ml capacity, was used. The samples were centrifuged for 11 h at 28,000 rpm to achieve complete sedimentation of the MWCNTs. After centrifugation, the supernatant solution was decanted down to approximately 8 mm from the bottom of the tube, leaving 7.6 ml of concentrated suspension which corresponds to 20% of the initial solution volume. The remaining material was re-suspended by ultrasonication at 25% power for 40 min, using the same technique described above.

The second rotor studied was the JLA-16.250 fixed-angle style rotor, which can hold approximately 200 ml per tube. The samples were centrifuged for 11 h applying 14,000 rpm, which is close to the maximum speed of the rotor. Generally, substances in a given rotational environment precipitate faster with fixed angle rotors [20]. The speed and the time of ultracentrifugation were estimated by calculating the cut-off threshold for sedimentation rate of MWCNTs, using the geometry of the rotors used and their average g force applied so as to simulate the laboratory scale procedure. After decantation, the remaining 50 ml of concentrated suspension was ultrasonicated at 40% power for 90 min to re-disperse any MWCNTs agglomerates created by the process.

After concentration, the MWCNT suspensions were diluted back to their initial concentration. The dilution was conducted by simply adding the same amount of water that was removed during decantation. The concentration of the suspensions after dilution was evaluated using optical absorbance spectroscopy. The results of the highly concentrated/diluted MWCNT suspensions were compared with the reference, non-concentrated MWCNT suspensions.

The diluted suspensions were then used to prepare cementitious samples with Type I ordinary Portland cement (OPC), at a water to cement ratio (w/c) of 0.3. The materials were mixed using a standard Hobart mixer following the procedure outlined in the ASTM C305. After mixing, the paste was placed in 20 × 20 × 80 mm molds. After demolding, the samples were cured in water saturated with lime until testing.

2.2. Characterization

Initial evaluation of the concentration of MWCNTs in the aqueous surfactant solution was performed by optical absorbance spectroscopy (OAS). The test was conducted at a wavelength range of 260–400 nm using a Cary 5000 UV–Vis–NIR spectrophotometer from Varian Instruments.

Three-point bending tests of beams with a 6 mm notch cut at the midspan were performed to evaluate the mechanical properties of cement based nanocomposites reinforced with the concentrated and the original MWCNTs suspensions. Following the testing procedure described in [2], the beams were tested at the age of 3, 7 and 28 days. Based on ASTM C348, three specimens were tested for each curing age. The tests were performed with a closed-loop MTS servo-hydraulic testing machine with a 20 kip (~89 kN) capacity. A crack mouth opening displacement (CMOD) extensometer was used to control the test with a constant opening velocity of 0.009 mm/min. Load versus CMOD graphs were plotted from the test results. Young's modulus was then calculated from these graphs using the two-parameter fracture model by Jenq and Shah [22]. Flexural strength was calculated using the net specimen depth.

3. Results and discussion

3.1. Absorbance spectra

The results of the absorbance spectra of the suspensions before and after centrifugation using the laboratory method (swing bucket SW41 rotor) are presented in Fig. 3. The UV/visible spectra display an increasing absorbance with a maximum around 261 nm, attributed from the graphitic π-plasmon resonance. For the concentrated suspension, the peak is not as well distinguished, indicating that the MWCNTs are relatively more concentrated. The concentration of MWCNTs in the suspensions has been quantified using Beer's law, which illustrates a linear relationship between the optical absorbance and concentration of substance. Generally, the intensity of the corresponding spectra depends on the concentration of CNTs – i.e., samples with higher concentration exhibit higher absorbance [21]. At the wavelength of 280 nm, it is observed that the absorbance of the concentrated suspensions is approximately five times higher than that of the samples before centrifugation, indicating that the concentration of MWCNTs increased concomitantly. This result suggests that this technique, which involves ultracentrifugation, decantation, and ultrasonication of the remaining suspensions, may be used to effectively concentrate the MWCNT suspensions creating a MWCNT admixture for cement based materials.

Fig. 4 depicts the results of the absorbance spectra of the samples concentrated using either the swing bucket Ti 32 or the fixed angle JLA-16.250 rotors. The results of the reference suspensions are shown for comparison. It is observed that for the samples concentrated using the swing configuration the absorption spectra is substantially higher, for example at a wavelength of 280 nm the absorbance increases approximately by a factor of five, from 0.54 to 2.70. This is in good agreement with the small scale tests, shown previously in Fig. 3. Nevertheless, the absorption in the samples concentrated using the fixed angle rotor was increased only by a factor of three. This can be attributed to the incomplete sedimentation of the suspensions, which led to a significant loss of MWCNTs during decantation.

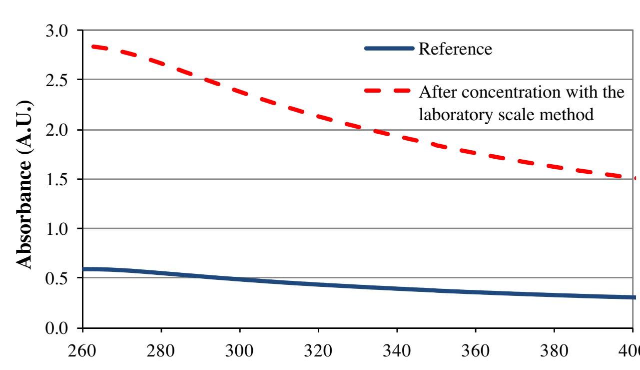

Fig. 3. Optical absorbance spectra of MWCNTs suspensions before and after concentration using the laboratory scale method (swing bucket SW41 rotor).

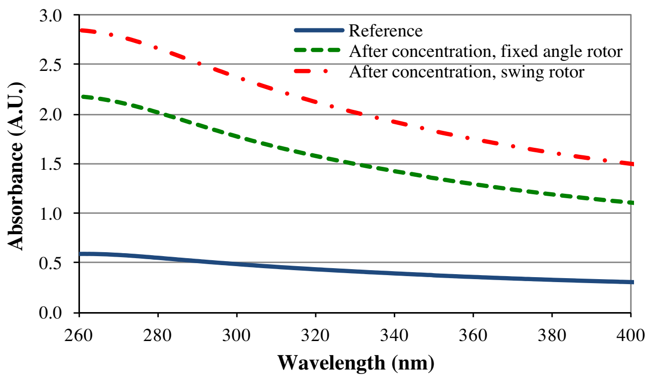

Fig. 4. Optical absorbance spectra of MWCNTs suspensions concentrated using the swing bucket Ti 32 and the fixed angle JLA-16.250 rotors.

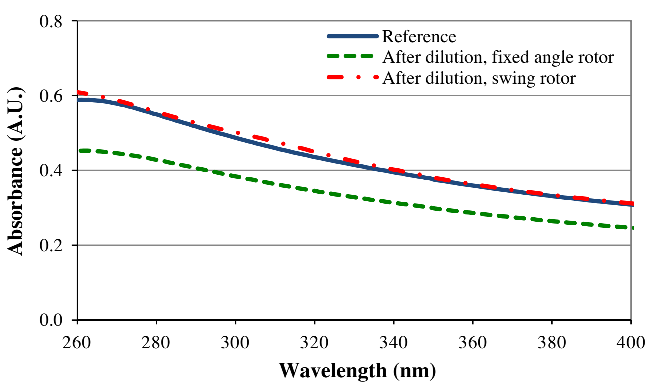

Fig. 5. Optical absorbance spectra of MWCNTs suspensions after dilution that were concentrated using the Ti 32 swing bucket and the JLA-16.250 fixed angle rotors.

The produced admixtures were then diluted with water following the procedure described previously. The absorbance spectra of the samples after dilution compared to the reference suspension are shown in Fig. 5. As observed, the concentrated samples using the swing configuration exhibit the same concentration as the control mix. This implies that no MWCNTs were lost during the concentration procedure and the pellet was fully re-dispersed in the suspension. Results were different in the case of experiments using the fixed angle rotor. Samples prepared with the exact same procedure but using the fixed angle rotor showed lower absorbance after dilution, indicating a lower final concentration of MWCNTs when compared to both the initial suspensions and the concentrated suspensions prepared using the swing bucket rotor.

3.2. Mechanical properties

The effectiveness of the ultracentrifugation concentration method was evaluated by three-point bending tests. Fig. 6 shows typical load-CMOD curves of the investigated samples at the age of 28 days. Fig. 7 depicts the results of the flexural strength and the Young's modulus of nanocomposites with MWCNT that were concentrated using the swing bucket and the fixed angle rotors at different ages. The results of cement paste samples reinforced with the reference suspensions, without concentration and the results of the plain cement paste samples are also depicted for comparison.

In all cases, the MWCNT reinforced nanocomposites exhibit higher flexural strength and Young's modulus when compared to the plain cement paste samples. The samples prepared using the swing bucket rotor show an almost identical flexural strength at all curing ages when compared with the initial reference (non-concentrated) suspensions. The Young's modulus of these specimens after 3 days of hydration is almost the same as the Young's modulus of the non-concentrated samples at the same curing age. However, at 7 and 28 days of hydration the samples reinforced with the highly concentrated/diluted MWCNT suspensions demonstrate a slightly higher Young's modulus than the reference samples. The specimens prepared from the suspensions created using the fixed angle rotor exhibited a lower flexural strength and slightly lower Young's modulus than those prepared by the swing bucket rotor. Previous research using the same type of MWCNTs has shown that nanocomposites with MWCNT at concentrations lower than the concentration used in this study (0.08 wt.% of cement) exhibit lower strength [1,3]. The suspensions prepared using the fixed angle rotor, had a lower concentration of MWCNTs than the suspension prepared using the swing bucket rotor, as shown by the absorbance spectroscopy results (Fig. 5). Therefore, as expected, they exhibit lower flexural strength. This suggests that the swing bucket rotor is more efficient for the concentration of MWCNT suspensions as these suspensions do not lose any CNTs during the admixture preparation process. Consequently, the nanocomposites reinforced with the swing bucket rotor suspensions demonstrate exceptional mechanical properties, similar to the properties demonstrated by the nanocomposites reinforced with the non-concentrated MWCNT suspensions.

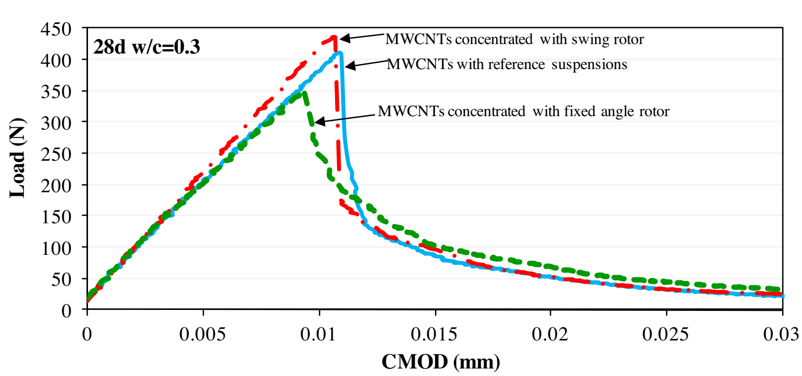

Fig. 6. Typical load-CMOD curves for 28 day cement paste reinforced with the reference non-concentrated suspensions and cement paste reinforced with the concentrated MWCNTs suspensions prepared using the Ti 32 swing bucket and the JLA-16.250 fixed angle rotors, respectively.

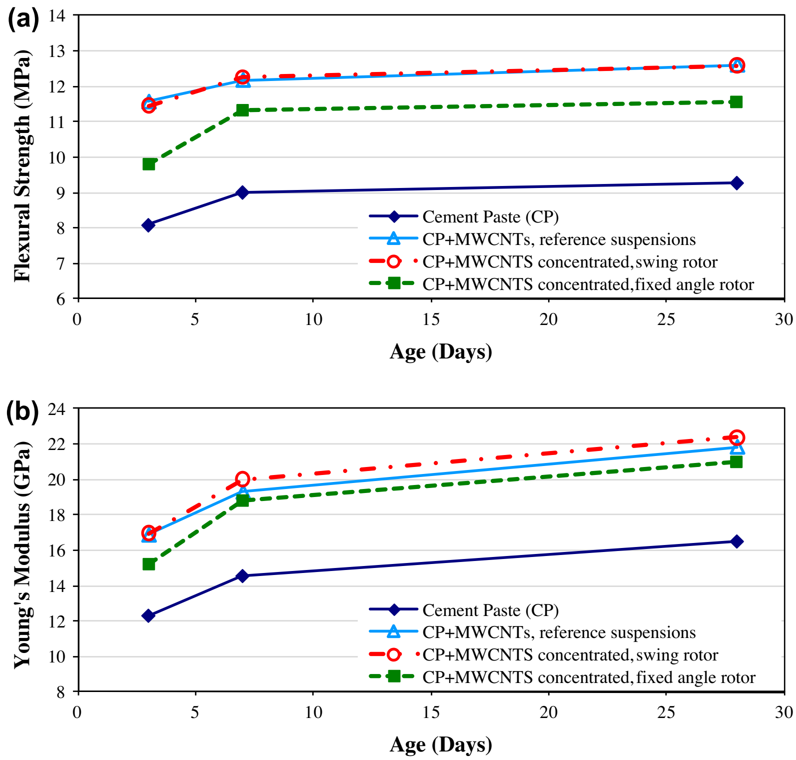

Fig. 7. Effect of admixtures prepared using different ultracentrifugation methods on (a) the flexural strength and (b) the Young's modulus of cement paste (w/c = 0.3).

4. Conclusions

A process for the production of highly concentrated MWCNT suspensions that can be used as an admixture for reinforcing cementitious materials at the nanoscale was developed. The proposed process involves dispersion of the MWCNTs in an aqueous/surfactant solution by ultrasonication, ultracentrifugation of the MWCNT suspension, decantation, and ultrasonication of the remaining suspension. Absorbance spectroscopy results confirmed a five-fold increase in the concentration of the MWCNTs of the suspensions. Mechanical properties test results indicate that the ultracentrifugation concentration method preserves successfully the solubility of the concentrated MWCNT suspensions, without affecting the reinforcing properties of the admixture. Therefore, as demonstrated in this research, the ultracentrifugation concentration method can be utilized for the large scale production of MWCNT admixtures for cementitious materials.

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