



## 40 **1. Introduction**

41 Cement is a commonly used binding material for the construction industries. Cementitious  
42 materials or composites possess good compressive properties, but they lack in tensile  
43 strength. There exists another problematic issue with the cementitious materials: the  
44 formation of nano/micro cracks starting from the molding stage; these cracks then conjoin  
45 and form micro/macro cracks in the final composites [1][2]. Cementitious composites have  
46 hierarchical or multi-scale structure consisting of micron and sub-micron scale hydration  
47 products and millimetre scale constituents like sand. As the cracks present within  
48 cementitious composites are in multi-scale dimension, the ideal solution to develop crack free  
49 cementitious composites should also be addressed by multi-scale reinforcements. The  
50 commonly used reinforcements are steel fibres, carbon fibres, poly vinyl alcohol fibres, glass  
51 fibres, etc [3][4][5]. The influence of reinforcing materials on cementitious composites  
52 mainly depends on the scale of reinforcement. Macro fibres (typically defined as the fibres  
53 with diameters greater than 500  $\mu\text{m}$ ) can improve the post-cracking toughness by bridging  
54 macro-cracks. Fine microfibers (typically defined as the fibres with diameter less than 50  
55  $\mu\text{m}$ ), on the other hand, bridge the micro-cracks delaying crack propagation within  
56 cementitious matrix [6]. Nowadays, nanoparticles/nanofibers (diameter in the nanometer  
57 scale) are also used to bridge nano-scale cracks in the cementitious matrix [7][8]. These  
58 nanomaterials can provide additional functionalities to the cementitious composites such as  
59 self-sensing, self-cleaning, thermo-regulation, etc. [9][10][11][12].

60

61 The concept of using two or more different scale (multi-scale) fibres is already well  
62 established in polymeric matrices [13]. These multi-scale or hierarchical polymeric  
63 composites have been developed for advanced applications such as aerospace, automotive,  
64 transportation, electrical and electronic goods, etc. [14]. Multi-scale composites developed  
65 using carbon nanotubes (CNTs) possess several advantageous characteristics; they provide  
66 excellent thermal and electrical conductivity, electromagnetic shielding, piezoresistivity,  
67 improved in-plane mechanical properties, delamination resistance, fracture toughness and so  
68 on [15][16][17]. Due to these interesting properties, multi-scale materials are drawing  
69 tremendous attention worldwide and are the subject of many scientific investigations.

70

71 Nano-scale reinforcements in cement are being explored for a decade now. Nano-  
72 reinforcements are preferred as they can control material behaviours at nano-scale and also  
73 add functional characteristics to the cement matrix [9][10][18]. Researchers have also

74 successfully grown nanomaterials onto cement particles [19][20]. Most of the existing works  
75 in this area are with nano-silica (nano-SiO<sub>2</sub>), nano-titanium oxide (nano-TiO<sub>2</sub>), nano-alumina  
76 (nano-Al<sub>2</sub>O<sub>3</sub>), nano clay, CNTs, etc. [10]. Due to excellent mechanical properties, chemical  
77 stability, high aspect ratio and surface area, CNTs are considered as an effective reinforcing  
78 material of polymeric/cementitious composites. Mechanical performance, workability,  
79 hydration properties, durability, electrical properties and microstructure of CNT reinforced  
80 cementitious composites have been widely investigated [21]. By using optimized  
81 concentrations of CNT (0.007 to 0.5 wt.% with respect to cement) and with proper dispersion  
82 techniques, researchers have achieved strong improvements in flexure strength (up to 269%),  
83 flexural modulus (up to 72%), tensile strength (up to 34.28%), tensile modulus (up to 70.9%),  
84 compressive strength (up to 200%), fracture toughness (up to 149%), fracture energy (up to  
85 63%), Young's modulus (up to 227%) and ductility (up to 130%) [9]. Recently, due to the  
86 growing interest on bio and plant based reinforcing materials, a few studies were also carried  
87 out on microcrystalline cellulose (MCC) /nano cellulose reinforced cementitious composites  
88 [22][23][24][25]. Parveen et al. reported MCC (0.5 wt.%) reinforced cementitious composites  
89 with 31% and 66% improvements in flexural and compressive strength, respectively after 28  
90 days of hydration [22]. The concept of using multi-scale reinforcements in cementitious  
91 composites has also been explored to some extent [1][26][27][28]. For example, multi-scale  
92 cementitious composites were developed by reinforcing cement matrix with carbon nano  
93 spheres (CNS) grown on poly acrylonitrile (PAN) and carbon fibre (CFs). It was observed  
94 that the compressive strength of plain mortar increased by 34.7% after 28 days of hydration  
95 and the developed multi-scale composites exhibited excellent thermal resistance, retaining  
96 98% of the original compressive strength at 600°C. The enhancement of compressive strength  
97 and thermal resistance resulted due to the filling of CF surface by CNS creating a better  
98 interface (due to interlocking of fibres with the matrix) between cement matrix and CFs [29].  
99 The multi-scale approach was also used to develop cement composites by replacing 10% of  
100 cement by nano metakoline (NMK) along with the addition of 2 wt.% (with respect to  
101 cement) of short natural fibres, and this resulted in an increase of flexural strength by 200%  
102 as compared to the plain cement composites. This was attributed to the reinforcing effect of  
103 fibres combined with the pozzolanic effect of NMK [30]. Researchers also used the  
104 combination of carbon nano fibres (CNFs, 0.02 wt.% of cement) with steel micro fibres ( 2  
105 vol.% of cement) to reinforce cement composites and reported enhancement of flexural  
106 strength (40%), tensile strength (45%) and toughness (85%). It was also observed that the  
107 fracture energy increased by 57% as compared to plain cement composites after 27 days of

108 hydration resulting from the higher resistance to crack propagation due to crack bridging at  
109 nano scale by CNFs [31]. In another study, the hybrid cementitious composites developed by  
110 carbon nanofibers and poly vinyl alcohol microfibers showed up to 50% improvement in  
111 flexural strength, 84% improvement in Young's modulus and 33 times (3351%) improvement  
112 in fracture toughness over plain cement matrix[6]. Previous studies by the authors suggested  
113 an excellent improvement of elastic modulus and strength (i.e., pre-cracking behaviour) of  
114 cementitious composites using MCC, which however, did not improve (or even reduced) the  
115 post-cracking, i.e. crack propagation behaviour of composites[22]. As CNT is an excellent  
116 reinforcing material to control the post-cracking behaviour of composite materials, the  
117 present research attempted for the first time to improve both pre- and post-cracking behaviour  
118 of cementitious composites using MCC-CNT hybrid or multi-scale reinforcement. Although  
119 elastic modulus, strength as well as fracture toughness of cementitious composites could be  
120 improved using only CNTs at optimum concentrations[9], the use of MCC in combination  
121 can reduce the amount of toxic and expensive CNTs and also shorten the dispersion  
122 treatment. The dispersability of MCC-CNT combination in aqueous medium, however, has  
123 never been studied till date; therefore, a thorough investigation has been performed in this  
124 research to achieve homogeneous dispersion using two types of surfactants, namely Pluronic  
125 F-127 and cetyltrimethylammonium bromide (CTAB). The developed multi-scale composites  
126 were characterized for mechanical performance (flexural and compressive properties),  
127 porosity, hydration products and fracture morphology, in order to properly understand the  
128 structure and properties of these novel composite materials.

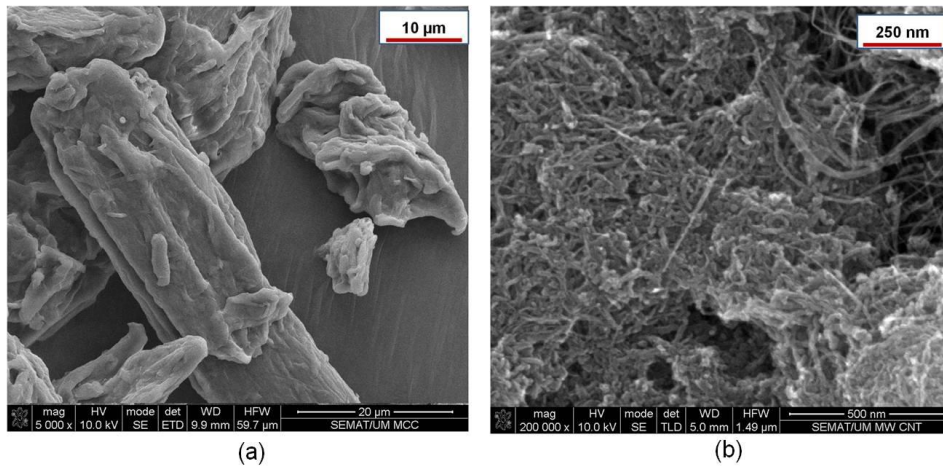
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## 130 **2. Experimental**

### 131 **2.1 Raw Materials**

132 MCC (Avicel<sup>®</sup> PH-101) was purchased from Sigma Aldrich (Portugal). MWCNTs were  
133 supplied by Nanostructured & Amorphous Materials, Inc. (Houston, USA). The morphology  
134 of MCC, as characterized by Scanning Electron Microscopy (FEG-SEM, NOVA 200 Nano  
135 SEM, FEI, acceleration voltage: 10kV, coating: 30 nm Au-Pd), is shown in Fig.1(a).  
136 According to the manufacturer's data, MCC particles have a size range between 2 to 260  
137 micron, Sauter mean of diameter of 49.1 micron, moisture content of ~3 wt%, solid density  
138 of 1.54 g/cm<sup>3</sup> and the particles have various shapes starting from larger fibrous rods to  
139 smaller irregular cuboids. The SEM morphology of MWCNTs, characterized using the above  
140 conditions, is shown in Fig. 1(b) and their properties are listed in Table 1. Pluronic F-127 and

141 CTAB, which were used to disperse MCC-CNT in water, were also supplied by Sigma  
 142 Aldrich (Portugal).



143  
 144 Fig.1 SEM Morphology of: (a) MCC and (b): MWCNT

145  
 146 **Table 1 Physical properties of MWCNT used in the present study**

Type of CNT	Diameter (nm)*		Length (μm)*	Surface Area* (m <sup>2</sup> /g)	Elements (wt. %)**		Impurity (%)**
					C	O	
MWCNT	2-5nm (inner)	<8nm (outer)	10-30	350-420	92.1	7.9	0

147 \* Source: Nanostructured & Amorphous Materials, Inc.

148 \*\* Characterized using Energy Dispersive X-ray (EDX) analysis using Si(Li) detector and 5  
 149 kV accelerating voltage

150  
 151 **Table 2 Properties of surfactants used in the present study**

MCC-CNT conc. (wt.%)		Type of surfactant	Mol. Wt. (gmol <sup>-1</sup> )	Aqueous Solubility	CMC (wt.%)
MCC	CNT				
0.4	0.2	Pluronic F-127	12600*	>10% (25°C)*	0.004 –0.091 (25°C)*
1.0	0.6				
0.4	0.2	CTAB	364.46**	0.3% (20°C)**	0.0364 (20°C)**
1.0	0.6				

152 \* Source: Ref. [32] \*\* Source: Sigma Aldrich

153 Table 2 lists the important properties of these surfactants. A defoamer, tri-butyl phosphate  
 154 (TBP), which was used to suppress the foam formation due to the surfactants, was supplied  
 155 by Acros Organics (Thermo Fischer Scientific). The details of cement and sand used for  
 156 developing cementitious composites are listed in Table 3 and 4, respectively.

157

158 **Table 3 Properties of cement used for fabricating cementitious composites**

Material	Composition	95 – 100% Clinker + 0 – 5% minor additional components
Ordinary Portland Cement (CEM I 42.5 R)*	Loss on ignition	≤ % 5
	Insoluble residue	≤ % 5
	Sulphur trioxide (SO <sub>3</sub> )	≤ % 4.0
	Chloride (Cl <sup>-</sup> )	≤ % 0.1
	Initial setting time	≥ 60 min
	Soundness	≤ 10 mm
	2 days compressive strength	≥ 20.0 MPa
	28 days compressive strength	≥ 42.5 MPa ≤ 62.5 MPa

159 Source: [www.secil.pt](http://www.secil.pt)

160

161 **Table 4 Properties of sand used in the present study**

Sand (NP-EN 196-1)**	Moisture content	≤ % 0.2 %
	Particle size distribution	
	Square mesh size (mm)	Cumulative sieve residue (%)
	2.00	0
	1.60	7 ± 5
	1.00	33 ± 5
	0.50	67 ± 5
	0.16	87 ± 5
	0.08	99 ± 1

162 Source: [www.tecnilab.pt](http://www.tecnilab.pt)

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166

167 **2.2 Methods**

168 **2.2.1 Preparation of Aqueous MCC Suspensions**

169 The aqueous suspensions of MCC-CNT using Pluronic F-127 or CTAB were prepared by  
170 first mixing MCC in water with the help of magnetic stirring for 10 min. The aqueous MCC  
171 suspensions were then stored for 2 days for soaking, and then MWCNT powder was added to  
172 the suspensions along with Pluronic F-127 or CTAB through magnetic stirring for 5 min. The  
173 MCC-CNT-surfactant suspensions were then kept in a bath ultrasonicator (Sonica  
174 Ultrasonicator 3200 S3) operated at 40 kHz frequency and 180W power for 1h. When the  
175 suspensions were used for fabricating mortar specimens (not just for the dispersion study),  
176 TBP was also added while adding Pluronic/CTAB, to suppress the formation of foam. The  
177 defoamer concentration used was the half of Pluronic F-127 concentration and in case of  
178 CTAB, it was used either in the ratio of 1:0.75 or 1:1 with respect to CTAB concentration.

179

180 **2.2.2 Characterization of Aqueous MCC-CNT Suspensions through Optical Microscopy**

181 MCC-CNT suspensions prepared with Pluronic F-127 and CTAB (without adding defoamer)  
182 were characterized for dispersion homogeneity and MCC/CNT agglomerates using optical  
183 microscopy. For this analysis, a drop of the suspension was taken on glass slide and covered  
184 using a glass slip to study under the optical microscope at different magnifications.  
185 Observations were made from the different parts of each suspension and the process was  
186 repeated at least 3 times in order to get a clear idea about the dispersion quality. The overall  
187 homogeneity, presence of individually dispersed MCC/CNT and agglomerated MCC/CNT  
188 were observed and compared for different suspensions. The optical characterization was  
189 performed immediately after the preparation of suspensions.

190

191 **2.2.3 Characterization of Aqueous MCC-CNT Suspensions through UV-Vis  
192 Spectroscopy**

193 MCC-CNT aqueous suspensions prepared with Pluronic F-127 and CTAB (without adding  
194 defoamer) were characterized by UV-Vis spectroscopy (after 24 hours of preparation) to  
195 measure the absorption intensity of prepared suspensions. The suspensions showing lower  
196 absorption intensity indicate lower amount of dispersed particles due to lower stability and  
197 sedimentation. Higher absorption intensity, on the other hand, indicates better dispersion  
198 quality and stability[33]. Suspensions prepared by varying MCC (0.4 wt. % and 1.0 wt. %)  
199 and CNT (0.2 wt.%- 0.6 wt. %) concentrations were studied by UV-Vis spectroscopy, in  
200 order to study the influence of MCC/CNT concentrations on dispersion quality. For each

201 measurement, solutions with same concentrations of Pluronic F-127/CTAB solution (without  
202 MCC-CNT) were used as blank to eliminate the peaks due to surfactants.

203

#### 204 **2.2.4 Fabrication of MCC-CNT Reinforced Cementitious Composites**

205 Fabrication of multi-scale composites was carried out by mixing MCC-CNT suspensions  
206 (225 ml) with cement (450g, cement: water ratio of 0.5) and sand (1350 g) in a Hobart mixer  
207 according to BS EN 196-1:1995 standard. After proper mixing, the samples were moulded in  
208 standard 160 mm x40 mm x40 mm rectangular moulds. The moulded samples were kept in a  
209 moist environment for 48 h before they were demoulded. The demoulded samples were next  
210 kept submerged in water for 28 days and 56 days to complete the hydration process, and also  
211 to investigate the influence of hydration period on the formation of hydration products,  
212 microstructure and mechanical properties of cementitious composites.

213

#### 214 **2.2.5 Characterization of Flow Behaviour of Cement Mortar Paste**

215 The flow behaviour of plain mortar and MCC-CNT-cement mortar paste was measured by  
216 performing the mini slump test. This test was performed to study the influence of MCC, CNT  
217 and surfactants on the flow behaviour of cement paste.

218

#### 219 **2.2.6 Characterization of Dry Bulk Density**

220 Dry bulk density of plain mortar and MCC-CNT cement mortar was characterized following  
221 BS EN 1015-10:1999 standard using Eq.s (1) and (2).

$$222 \quad A = \frac{M_{s,dry}}{V_s} \quad (1)$$

$$223 \quad V_s = \frac{M_{s,sat} - M_{s,i}}{\rho_w} \quad (2)$$

224 Where,  $M_{s,dry}$  is the oven dry mass of specimen of hardened mortar (kg),  $M_{s,sat}$  is the mass  
225 of saturated specimen of hardened mortar (kg),  $M_{s,i}$  is the apparent mass of saturated  
226 specimen of hardened mortar immersed in water (kg),  $\rho_w$  is the density of water ( $\text{kg/m}^3$ ) and  
227  $V_s$  is the volume of specimen of hardened mortar ( $\text{m}^3$ ).

228

#### 229 **2.2.7 Pore size distribution using mercury intrusion porosimetry (MIP)**

230 The pore size and its distribution in plain mortar and selected MCC-CNT mortar composites  
231 were analyzed using mercury intrusion porosimetry (MIP) instrument (Micromeritics  
232 AutoPore IV 9500 V1.07). A pressure range of 0.0007 to 414 MPa was maintained for  
233 measuring pore size ranging from 340  $\mu\text{m}$  to 5 nm. An advancing/receding contact angle of



234 mercury of 30° and surface tension of 0.485 N/m were used in the MIP analysis. The samples  
235 were kept at room temperature after 28 days of hydration and prior to testing, the samples  
236 were dried for 2 days in oven at 60°C.

237

### 238 **2.2.8 Characterization of Mechanical Performance**

239 Plain mortar and MCC-CNT mortar composites were characterized for flexural and  
240 compressive properties according to BS EN 196-1:1995 standard. 3 specimens with 160 mm×  
241 40mm× 40mm dimension were tested for flexural properties at 50 N/s using a preload of 50  
242 N and 6 specimens having 80 mm× 40mm× 40mm dimension were tested for compressive  
243 strength at a speed of 500 N/s.

244

### 245 **2.2.9 Micro-structural Characterization of MCC-CNT mortar composites**

246 Microstructure of MCC-CNT mortar composites was characterized using the fragments of  
247 composite samples (fractured in mechanical testing) by SEM (FEG-SEM, NOVA 200 Nano  
248 SEM, FEI) using secondary electron mode and acceleration voltage of 10kV) after coating  
249 with a thin film (30 nm) of Au-Pd in a high resolution sputter coater (208HR Cressington).  
250 Integrated Energy Dispersive Spectrometer [Si (Li) detector - SEM ultra-thin window  
251 (SUTW) type] was used to measure the wt. % of elements present in the composite samples  
252 at specific locations.

253

### 254 **2.2.10 Characterization of hydration products**

255 The MCC-CNT mortar composites were analysed by Thermogravimetric Analyzer (TGA,  
256 Perkin Elmer) in a nitrogen atmosphere at a heating rate of 10°C/min up to a temperature of  
257 900°C. For the quantitative estimation of different products formed due to hydration such as  
258 C-S-H, Ca(OH)<sub>2</sub>, CaCO<sub>3</sub>, etc, derivative thermogravimetry (DTG) curves of these samples  
259 were recorded and subsequently analyzed.

260

## 261 **Results and Discussion**

### 262 **3.1 Optimized MCC-MWCNT aqueous suspensions**

263 For the preparation of homogeneous and stable MCC-CNT suspensions, optimized  
264 concentrations of the surfactants were used. Pluronic F-127 is a non-ionic surfactant and its  
265 role in dispersing MCC and CNT (separately) in aqueous medium was previously discussed  
266 by Parveen et al[22][34]. However, there is no report on the aqueous dispersion of MCC-  
267 CNT hybrid system using Pluronic F-127. In the present research, the concentration of

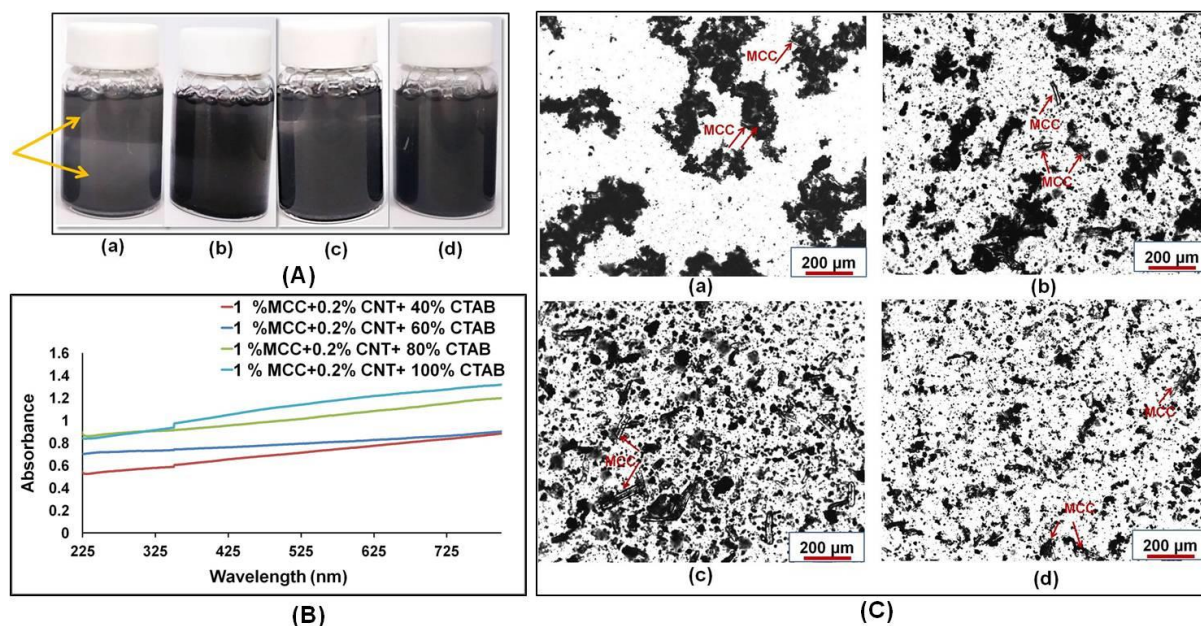
268 Pluronic F-127 used to disperse MCC-CNT hybrid system was 3 wt.% (with respect to  
269 water), which was the previously reported optimized concentration for dispersing CNT in  
270 aqueous medium for developing cementitious composites[35]. As the optimum Pluronic F-  
271 127 concentration for dispersing MCC in aqueous medium (optimum Pluronic: MCC ratio of  
272 1:5 according to Ref.)[22] was much lower than that for dispersing CNT, the later  
273 concentration was used for the hybrid system.

274

275 CTAB, on the other hand, is a cationic surfactant and it was selected due to its cationic head  
276 and hydrophobic tail which are expected to promote proper dispersion of MCC-CNT system  
277 by steric stabilization and coulombic repulsion[36][37]. Many researchers found CTAB as a  
278 preferred surfactant to disperse CNT and nano crystalline cellulose (NCC) separately in  
279 aqueous medium[36][38][37][39]. Previously, a CTAB: CNT ratio of 0.66:1 was found to  
280 produce stable MWCNT suspensions in aqueous medium [40]. However, the optimum CTAB  
281 concentration for dispersing MCC or MCC-CNT hybrid system has never been reported. In  
282 the present study, in order to find the optimum CTAB concentration for the hybrid system,  
283 four CTAB: CNT concentration ratios were studied: 0.4:1, 0.6:1, 0.8:1 and 1:1 (i.e. 40%,  
284 60%, 80% and 100% with respect to CNT concentration) for a fixed CNT (0.2 wt. %) and  
285 MCC (1 wt.%) concentrations. Similar to Pluronic F-127, CTAB concentration was mainly  
286 optimized considering CNT concentration in the hybrid system, as the CTAB concentration  
287 required to disperse MCC is expected to be much lower as compared to that required for  
288 CNTs.

289

290 The prepared suspensions were kept standing at room temperature for 24 h to observe  
291 sedimentation. As can be noticed from Fig. 2 (A) that the optimum CTAB: CNT ratio to  
292 obtain a stable suspension was 1:1, as the suspensions prepared with other CTAB  
293 concentrations exhibited 3 distinct phases (the upper and lower CNT phases, as indicated by  
294 arrows and MCC phase in the middle). This observation was further confirmed by performing  
295 UV-Vis spectroscopy and optical microscopy, as shown in Fig 2(B) and (C).



297

298 Fig: 2. Visual observation (A), UV-Vis spectra (B) and optical micrograph (C) of MCC  
 299 suspensions\*: (a) 1% MCC+0.2% CNT+40% CTAB, (b) 1 % MCC+0.2% CNT+60%  
 300 CTAB, (c) 1% MCC+0.2% CNT+80% CTAB (d) 1% MCC + 0.2% CNT+100% CTAB  
 301 (\*MCC% and CNT% have been reported with respect to water and CTAB% has been  
 302 reported with respect to CNT).

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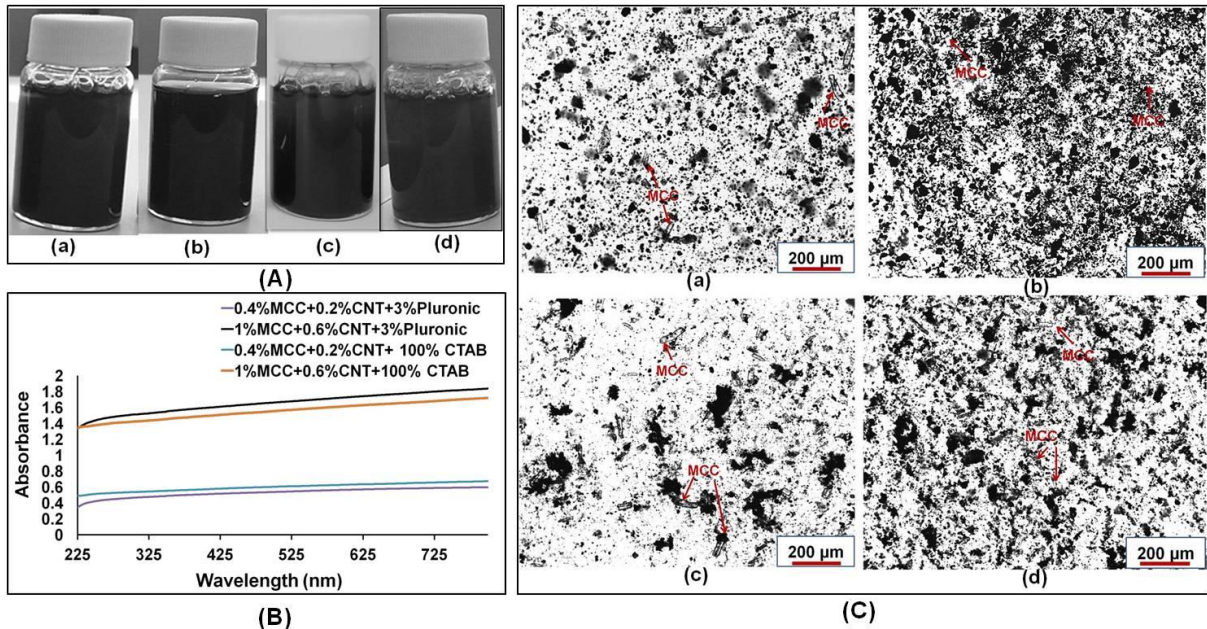
304 As can be seen in Fig. 2(B), the absorbance of the suspensions increased with the increase in  
 305 CTAB concentration and 100% CTAB, i.e. CTAB: CNT ratio of 1:1 exhibited the highest  
 306 absorbance. As only well dispersed particles in the suspensions are active in UV-Vis  
 307 spectroscopy[41], the increased UV absorbance with CTAB concentration reflects higher  
 308 quantity of dispersed particles and better dispersion quality. Further, the optical micrographs  
 309 (Fig. 2C) showed that CNTs were not properly dispersed and formed agglomerates of large  
 310 sizes in case of lower CTAB concentrations. Due to presence of highly agglomerated CNTs,  
 311 MCCs were not visible properly in these suspensions. However, in case of 1:1 ratio of  
 312 CTAB: CNT, the agglomeration of CNTs was reduced drastically and the suspension became  
 313 homogeneous (Fig. 2C-d). All these observations suggested that a CTAB: CNT ratio of 1:1  
 314 can be used as the optimized CTAB concentration for preparing MCC-CNT aqueous  
 315 suspensions.

316

317 Fig. 3 shows the quality of the suspensions prepared for fabricating cementitious composites  
 318 using optimized Pluronic F-127 and CTAB concentrations, as observed visually after 24 h

319 (Fig. 3A), through optical microscopy (Fig. 3B) and UV-Vis spectroscopy (Fig. 3C). It can be  
 320 observed from Fig 3A that all suspensions were quiet stable after 24 h. The optical  
 321 micrographs showed that the homogeneity and agglomeration were similar for Pluronic-127  
 322 and CTAB suspensions, with only slight increase in agglomeration at higher MCC/CNT  
 323 concentrations. The UV-Vis spectra, presented in Fig. 2B revealed an interesting finding that  
 324 the increase in CNT and MCC concentrations significantly increased the absorbance,  
 325 indicating that most of the added CNTs and MCC particles were dispersed without  
 326 sedimentation. Therefore, the chosen surfactant concentrations provided satisfactory results  
 327 in terms of suspension homogeneity, agglomeration, stability and quantity of dispersed  
 328 particles.

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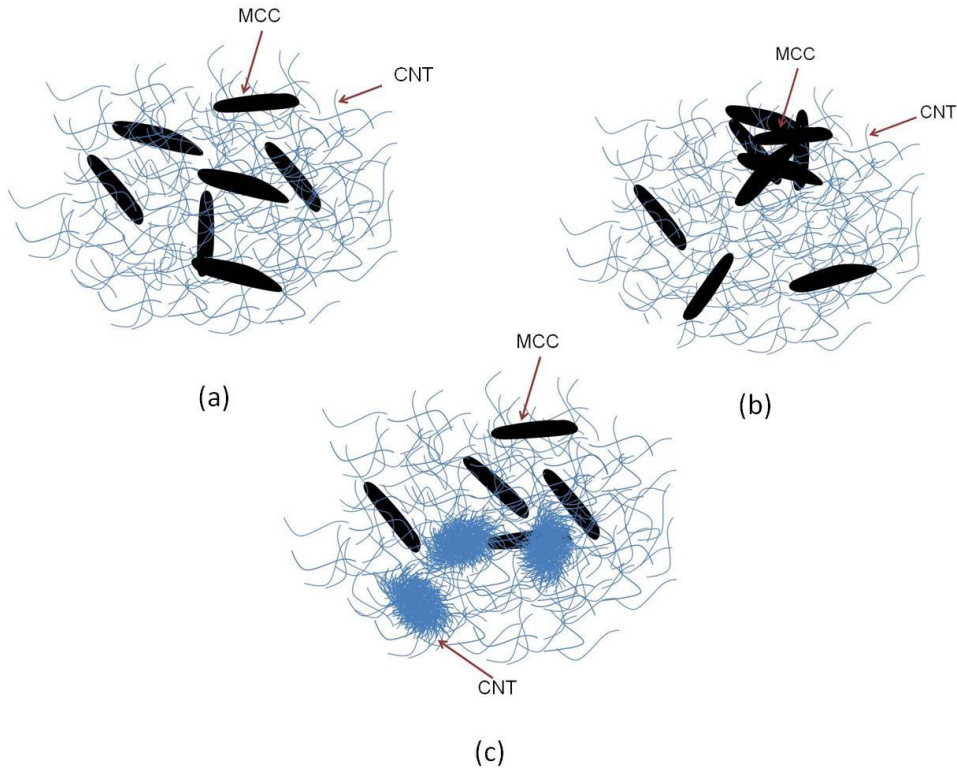
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331 Fig: 3. Visual observation (A), UV-Vis spectra (B) and optical micrographs (c) of MCC  
 332 suspensions\*: (a) 0.4% MCC+0.2%CNT 3% Pluronic, (b) 1% MCC+0.6% CNT 3%Pluronic,  
 333 (c) 0.4% MCC+0.2%CNT+100% CTAB (d) 1% MCC + 0.6% CNT+100% CTAB (\*MCC%,  
 334 CNT% and Pluronic% were reported with respect to water, CTAB% was reported with respect to  
 335 CNT)

336

337 However, it can be expected that the quality of dispersion in the hybrid system could be  
 338 inferior to the aqueous systems containing only CNT or MCC and therefore, mechanical  
 339 property improvements in the hybrid composites could also be lower as compared to CNT or  
 340 MCC based composites. Three possible dispersion scenarios in the hybrid system are  
 341 schematically illustrated in Fig. 4. In the first scenario, which exists in some parts of the

342 suspensions, both CNTs and MCC were dispersed without formation of dense clusters. This  
343 type of dispersion state is expected to be more stable. The stability of MCC or CNT in this  
344 state may also positively influence each other as MCC and CNT are connected as a network.  
345



346  
347 Fig. 4 Schematic illustration of possible dispersion scenarios in MCC-CNT hybrid system:  
348 (a) agglomeration free dispersion, (b) presence of MCC agglomerates and (c) presence of  
349 CNT agglomerates  
350

351 However, agglomeration of CNTs or MCC with time may also occur resulting in the  
352 sedimentation of whole system. In the second scenario, MCC agglomerates are present  
353 within a network of dispersed CNTs and the sedimentation tendency of these agglomerates  
354 can reduce the stability of the hybrid system. Similarly, in the presence of CNT agglomerates  
355 in the third scenario, the stability of the whole system is reduced due to sedimentation  
356 tendency of the CNT agglomerates and their negative influence on the stability of the  
357 surrounding CNTs or MCC.

358

### 359 3.2 Flow Behaviour of MCC-Cement Paste

360 The flow behaviour of mortar pastes containing MCC-CNT suspensions were compared with  
361 those of plain mortar paste in Table 4 (Pluronic % has been reported with respect to cement

weight and CTAB has been used in the ratio of 1:1 with respect to CNT in Table 4 and all subsequent figures and tables). The pastes containing MCC-CNT suspensions showed similar flow values to the recommended flow value of cement mortar (180 mm ± 10 mm), according to EN 1015-3 standard. It was observed in the previous research studies that the presence of MCC reduced the flow value of cement paste due to presence of –OH groups which adhere water molecules through hydrogen bonding[25] and reduce flow values. The maintained flow values of MCC-CNT containing mortar pastes can be explained by the positive influence of surfactant molecules in dispersing cement particles and thereby, improving mortar’s flow properties [42]. Pluronic F-127 has hydrophilic groups (poly ethylene oxide chains) that improve cement dispersion[34]. Author’s previous study also showed similar effect of Pluronic F-127 on mortar flow values. CTAB, on the other hand, is composed of a long alkyl chain (hydrophobic chain) which helps to disperse cement particles by producing air pockets (air-cement-air bridge) around the cement particles, which act as the compressible bearings under shear force [42]. Though previous studies reported lower flow of mortar paste in presence of CNTs, the flow value was maintained in the present research mainly due to the positive effects of the surfactants and also owing to the low concentration of CNTs used in the mixture.

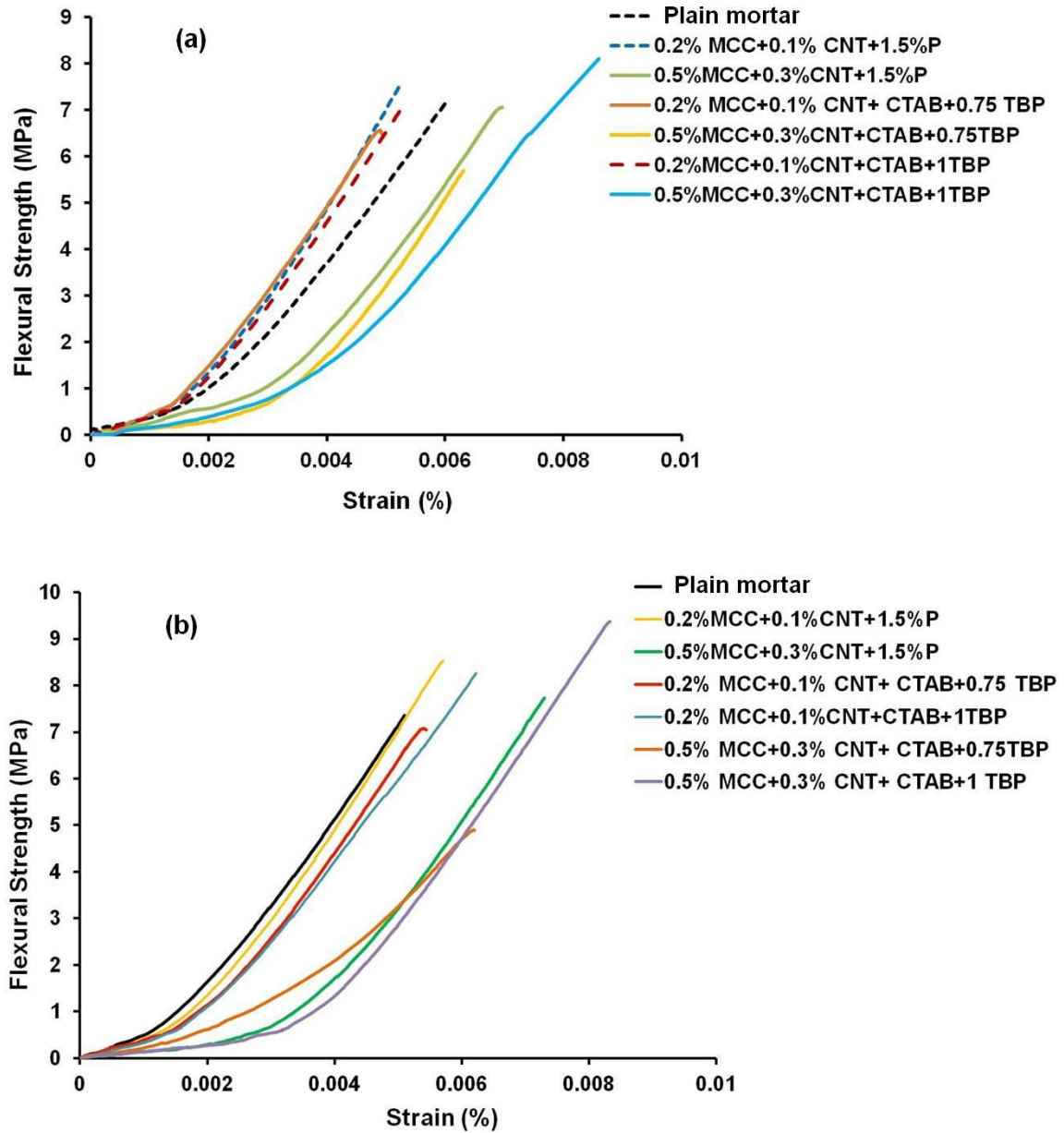
**Table 4 Flow of freshly prepared mortar paste containing different MCC-CNT suspensions**

Samples	Flow Values (mm)	
Plain mortar	189	187
Mortar + 0.2%MCC + 0.1%CNT+ 1.5%Pluronic + 0.50 TBP	195	200
Mortar + 0.5%MCC + 0.3%CNT+ 1.5% Pluronic + 0.50 TBP	200	195
Mortar + 0.2% MCC+0.1% CNT+ CTAB+0.75TBP	170	172
Mortar + 0.5% MCC+0.3% CNT+ CTAB+0.75TBP	220	215
Mortar + 0.2% MCC+0.1% CNT+ CTAB+1TBP	185	190
Mortar + 0.5% MCC+0.3% CNT+ CTAB+1TBP	200	195

385 **3.3 Mechanical Properties of MCC-CNT Multi-scale Composites**

386 Flexural properties were studied for two different hydration periods (28 days and 56 days), to  
387 analyze the effect of hydration time on the flexural properties of reinforced mortar  
388 composites. The results are provided in Fig. 5, Table 5 and 6.

389



390

391

392 Fig. 5 Flexural stress-strain curves of plain mortar and MCC-CNT mortar composites after  
393 (a) 28 days of hydration and (b) 56 days of hydration (P denotes Pluronic F-127).

394

395

396

397 **Table 5 Flexural properties of plain mortar and MCC-CNT mortar composites after 28**  
 398 **days**

Samples	Flexural strength(MPa)	% Increase	Flexural modulus(GPa)	% Increase
Plain mortar	7.10 ± 0.14	-	14.26 ± 0.8	-
0.2%MCC + 0.1%CNT +1.5%P* +0.5 TBP	7.42 ± 0.19	2.9	17.75 ± 0.6	24.1
0.5%MCC + 0.3%CNT + 1.5% P + 0.5 TBP	7.06 ± 0.18	-2.1	14.61 ± 0.9	2.2
0.2% MCC+0.1% CNT+ CTAB+0.75 TBP	6.37 ± 0.23	-11.7	15.11 ± 0.8	5.7
0.5% MCC+0.3% CNT+ CTAB+0.75 TBP	5.22 ± 0.25	-27.7	14.74 ± 0.8	3.1
0.2% MCC+0.1% CNT+ CTAB+1 TBP	7.26 ± 0.35	0.68	15.85 ± 0.5	10.8
0.5% MCC+0.3% CNT+ CTAB+1 TBP	8.10 ± 0.23	12.3	16.12 ± 0.6	12.7

399 \*P denotes Pluronic F-127

400

401 **Table 6 Flexural properties of plain mortar and MCC-CNT mortar composites after 56**  
 402 **days**

Samples	Flexural Strength(MPa)	% Increase	Flexural modulus(GPa)	% Increase
Plain Cement	7.2±0.09	-	14.99±0.7	-
0.2%MCC + 0.1%CNT +1.5%P +0.5 TBP	8.2±0.32	15	15.45±0.5	3
0.5%MCC + 0.3%CNT + 1.5% P +0.5 TBP	7.5±0.26	4.4	13.32±0.7	-11.2
0.2% MCC+0.1% CNT+ CTAB+0.75 TBP	6.8±0.51	-5.6	14.93±0.6	-0.47
0.5% MCC+0.3% CNT+ CTAB+0.75 TBP	4.9±0.54	-32.33	13.39±0.7	-10.73
0.2% MCC+0.1% CNT+ CTAB+1 TBP	8.2±0.12	13	13.26±0.5	-11.6
0.5% MCC+0.3% CNT+ CTAB+1 TBP	8.8±0.07	23.2	16.19±0.4	7.96



403 It was observed that the defoamer (TBP) concentration played an important role on the  
404 flexural properties. Both surfactants, Pluronic F-127 and CTAB produced foam in the cement  
405 mixture if proper percentage of defoamer was not used. To suppress foam, defoamer in the  
406 ratio of 0.5:1 with respect to Pluronic F-127 was used according to author's previous research  
407 [34]. In case of CTAB, two different defoamer ratios were used to suppress foam formation:  
408 0.75: 1 and 1:1 with respect to CTAB concentration. It was noticed that 1:1 ratio of defoamer  
409 to CTAB resulted in better flexural properties as compared to 0.75:1 (Table 5). It can be  
410 explained by the fact that the lower defoamer content could not eliminate the foam formation  
411 completely, which led to more air voids and defects in the cementitious composites and  
412 inferior mechanical performance.

413  
414 Maximum improvement in flexural strength of 12.3% was achieved after 28 days of  
415 hydration through addition of 0.5% MCC-0.3% CNT using CTAB and TBP in the ratio of  
416 1:1. In case of MCC-CNT mortar composites prepared using Pluronic F-127, however, there  
417 was no marked improvement in flexural strength after 28 days. It is noteworthy that after 56  
418 days the improvements in flexural strength for both surfactants were quiet prominent.  
419 Flexural strength increased by ~23% in case of 0.5% MCC-0.3% CNT reinforced composites  
420 with CTAB and by 15% in case of 0.2% MCC-0.1% CNT reinforced composites with Pluronic  
421 F-127. Delayed hydration of MCC based cementitious composites has been previously  
422 reported [22]. MCC retained some quantity of water (which would have been used in the  
423 hydration process otherwise) in the early hydration period due to presence of –OH groups.  
424 This MCC bound water was released slowly due to the ongoing hydration process,  
425 accelerating the hydration in the later stages [22]. Moreover, in case of composites containing  
426 Pluronic F-127, which also possess –OH groups and retained water, delayed hydration could  
427 be observed more prominently and significant strength improvement was only observed after  
428 56 days. In authors' previous study, flexural strength and modulus of mortar composites  
429 increased by 31% and 103%, respectively using Pluronic F-127 through dispersion of 0.5%  
430 MCC, but significant decrease in flexural strain and fracture energy was observed [22]. This  
431 was attributed to the formation of stiffer hydration products in presence of MCC. Although  
432 the hybrid reinforcement used in the present study resulted in lower improvement in flexural  
433 modulus and strength, it also improved the breaking strain and fracture energy, as provided in  
434 Table 7. The fracture energy improved by 85% after 56 days of hydration using 0.5% MCC-  
435 0.3% CNT with CTAB. Previously, MWCNTs, which were dispersed using Pluronic F-127  
436 through the same dispersion route (ultrasonication for 1h), significantly improved the fracture

437 energy, but reduced the mortar's flexural strength[34]. Therefore, the hybrid reinforcement  
 438 investigated here showed better results as compared to only MCC or MWCNTs when both  
 439 strength and fracture energy of mortar are to be improved.

440

441 **Table 7 Fracture energy of plain mortar and MCC-CNT mortar composites after 56**  
 442 **days of hydration**

Samples	Fracture Energy (J)	% Improvement
Plain mortar	0.2608595 ±0.008	-
0.2% MCC+0.1% CNT+ CTAB+0.75 TBP	0.259248284 ±0.005	-0.617656557
0.2% MCC+0.1% CNT+ CTAB+1 TBP	0.297619837 ±0.002	14.17958736
0.5% MCC+0.3% CNT+ CTAB+0.75 TBP	0.190532942 ±0.002	-23.62966076
0.5% MCC+0.3% CNT+ CTAB+1 TBP	0.423218392 ±0.004	85.21302936
0.2% MCC + 0.1% CNT + 1.5% P*+0.5TBP	0.329162369 ±0.003	16.13891793
0.5% MCC + 0.3% CNT + 1.5% P*+0.5TBP	0.298231179 ±0.002	11.35356974

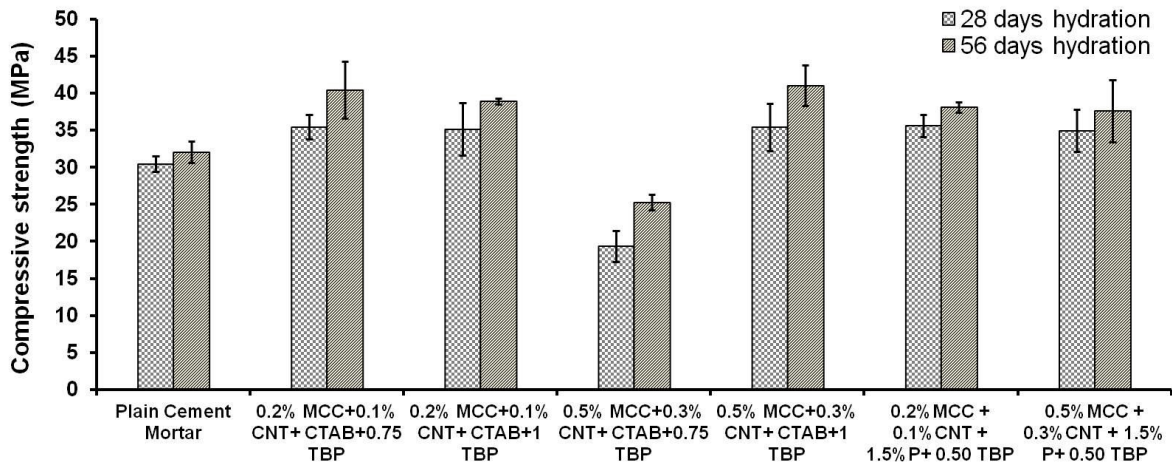
443 \*P denotes Pluronic F-127

444

445 Similarly, it can be observed from the results of compressive strength presented in Fig. 6 and  
 446 Table 8 that the influence of the hybrid reinforcement on compressive strength was quite  
 447 positive and promising. Compressive strength improved considerably in all specimens after  
 448 both 28 and 56 days (except 0.5% MCC+0.3% CNT+ CTAB0.75 TBP) unlike flexural  
 449 properties which showed marked improvement only in some particular specimens. Due to the  
 450 un-optimized defoamer concentration in 0.5% MCC+0.3% CNT+ CTAB0.75 TBP specimen,  
 451 the presence of large number of air voids diminished the positive effect of hybrid  
 452 reinforcements. Compressive strength improved more prominently than flexural properties as  
 453 the former is expected to be less influenced by defects (such as voids, agglomerations, etc.).  
 454 In compressive mode, the air voids and defects get compressed unlike tensile or flexural  
 455 mode (in which the upper surface of the specimen remains under tensile stress) in which the  
 456 defects extend and conjoin to make bigger damages resulting in quick failure of the  
 457 specimens. The composite specimen, 0.5% MCC+0.3% CNT+ CTAB1 TBP exhibited an  
 458 improvement of compressive strength by 16% and 28%, respectively after 28 days and 56  
 459 days of hydration. With Pluronic F-127, maximum improvements of compressive strength by  
 460 17% and 19% were achieved after 28 and 56 days of hydration, respectively in the 0.2%MCC  
 461 + 0.1%CNT +1.5%P composite specimen.

462

463



464

465 Fig. 6. Compressive Strength of plain mortar and MCC-CNT cement composites at 28 and 56  
 466 days of hydration (P denotes Pluronic F-127)

467

468

469 **Table 8 Percentage improvement in compressive strength at different ages of hydration**

Samples	Compressive strength (28 days)	% Increase	Compressive strength (56 days)	% Increase
Plain Cement	30.45±1.04	-----	32.09	-----
0.2%MCC + 0.1%CNT +1.5%P* +0.5TBP	35.62±1.5	16.98	38.08±0.69	18.68
0.5%MCC + 0.3%CNT + 1.5% P +0.5TBP	34.94±0.52	14.75	37.64±1.25	17.28
0.2% MCC+0.1% CNT+ CTAB+0.75 TBP	35.43±1.6	16.35	40.44±3.86	26.01
0.5% MCC+0.3% CNT+ CTAB+0.75 TBP	19.35±2.06	-36.45	25.27±1.01	-21.24
0.2% MCC+0.1% CNT+ CTAB+1 TBP	35.14±3.51	15.4	38.92±0.40	21.27
0.5% MCC+0.3% CNT+ CTAB+1 TBP	35.4±3.15	16.26	41.05±2.73	27.93

470 \* P denotes Pluronic F-127

471 Similar to flexural strength, the multi-scale or hybrid reinforcement resulted in a better  
472 compressive strength of mortar as compared to only MWCNTs (which deteriorated the  
473 compressive strength of plain mortar) when dispersed using the same technique [31].  
474 Nevertheless, the improvement of compressive strength achieved with the multi-scale  
475 reinforcement was lower as compared to that obtained with only MCC dispersed using  
476 Pluronic F-127 [19]. This could be due to inferior MCC dispersion in the hybrid system, as  
477 schematically illustrated in Fig. 4.

478

479 A number of studies have been reported till date to improve mechanical strength, modulus, or  
480 fracture energy and toughness of cementitious composites using various nano/micro  
481 structures [9]. Majority of these studies reported improvement in one of these properties  
482 (either strength/modulus/fracture energy), while other properties were maintained or even  
483 deteriorated in some cases. This was mainly attributed to the fact that most of the used  
484 nano/micro reinforcements could control either pre-cracking (strength and modulus) or post-  
485 cracking (fracture energy and toughness) behaviour of composites depending on their type  
486 and aspect ratio. Among these, CNTs (mainly SWCNTs) could control both these behaviours  
487 effectively due to their exceptionally high strength and modulus combined with very high  
488 aspect ratio, which make them capable of controlling even the post-cracking behaviour  
489 through the crack bridging mechanism [35]. Consequently, SWCNT reinforced cementitious  
490 composites showed high elastic modulus, high flexural and compressive strengths as well as  
491 high fracture energy and ductility[34][35]. MWCNTs, on the other hand, were not found  
492 much effective and the reinforced composites showed either improved strength and modulus  
493 or fracture energy or both (or even deterioration in these properties), according to the used  
494 dispersion methods[34][35]. Well dispersed MWCNTs using superplasticizers, and an  
495 optimized ultrasonication process could improve both strength and fracture energy of  
496 cementitious composites [43][44]. The results presented in this research demonstrated that  
497 both pre- and post-cracking performances of cementitious composites could be improved  
498 significantly using the hybrid reinforcement system through a simple and short dispersion  
499 route without using any additive or expensive materials (e.g. SWCNTs).

500

### 501 **3.4 Dry Bulk Density of MCC-CNT Multi-scale Composites**

502 The dry bulk density results of plain mortar and selected multi-scale cementitious composites  
503 are provided in Table 9. It can be noticed that the addition of 0.2%MCC-0.1%CNT using  
504 Pluronic F-127 and 0.5%MCC- 0.3%CNT using CTAB increased the dry bulk density

505 significantly. Pluronic F-127 and CTAB helped to disperse cement particles through steric  
 506 stabilization during the molding stage. This resulted in proper distribution of water molecules  
 507 within the matrix and therefore, led to well compacted composites. The favourable effect of  
 508 MCC/NCC particles in dispersing cement through steric stabilization has also been reported  
 509 [45]. Due to similar particle size of cement ( $\sim 50\mu\text{m}$ ) and MCC ( $51\mu\text{m}$ ) the process of steric  
 510 stabilization would be more facile [22]. In addition to that, CNT could also improve the  
 511 microstructure and improve bulk density through pore filling mechanism, as reported earlier  
 512 [34]. The dry bulk density in case of hybrid cementitious composites was higher as compared  
 513 to those containing only 0.5% MCC with Pluronic F-127 ( $2158.5 \text{ kg/m}^3$ ), as reported  
 514 previously [22] and this shows the additional advantage of using CNT in improving  
 515 microstructure. All these positive effects were responsible for significant improvement in  
 516 bulk density in multi-scale cementitious composites.

517

518 **Table 9 Dry bulk density of plain mortar and selected MCC-CNT mortar composites**

Samples	Dry Bulk Density ( $\text{Kg/m}^3$ )
Plain mortar	2012.4
0.2% MCC+0.1% CNT+1.5% P*+0.5% TBP	2178.2
0.5% MCC+0.3% CNT+CTAB+1% TBP	2102.8

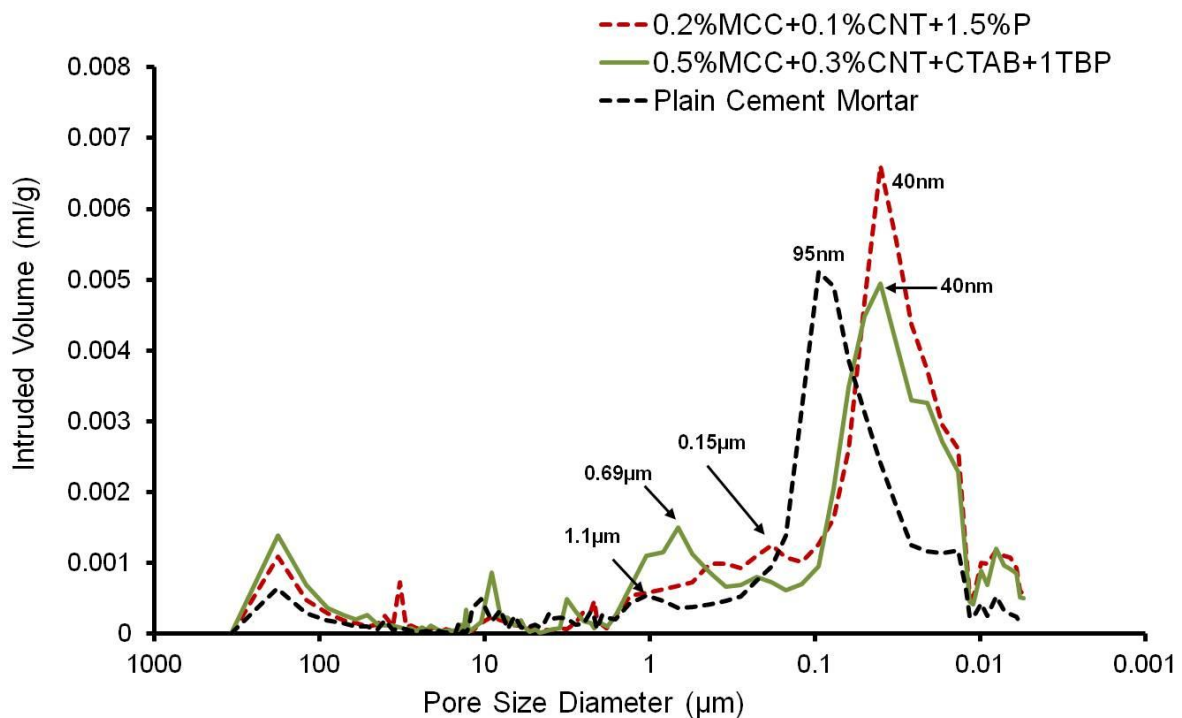
519 \*P denotes Pluronic F-127

520

### 521 3.5 Porosity and Pore Size Distribution

522 The pore size diameter vs intruded volume of mercury was obtained from MIP analysis, as  
 523 shown in Fig. 7. The analysis was carried out to know the effect of MCC-CNT on different  
 524 types of pores in cementitious matrix. The pores present within the cementitious matrix are  
 525 classified as large ( $0.05$  to  $10 \mu\text{m}$ ), small capillary pores ( $10$  to  $50 \text{ nm}$ ) and gel pores ( $0.5$ -  
 526  $10 \text{ nm}$ ) [46]. According to Fig. 7 the maximum volume % of pores in the case of MCC-CNT  
 527 mortar composites were of  $\sim 40 \text{ nm}$  and in case of plain mortar composites were of  $\sim 95 \text{ nm}$ .  
 528 The size of gel pores, on an average, in all analyzed samples (reinforced and plain mortar)  
 529 was  $\sim 8 \text{ nm}$ . This indicates that in the range of gel pores the hybrid reinforcement did not play  
 530 any significant role. But, in the range of capillary pores, the hybrid reinforcement reduced the  
 531 pore size of mortar composites. The average pore size also reduced considerably (see Table  
 532 10), even much lower as compared to the composites developed using only MCC with  
 533 Pluronic F-127 (average pore size in this case was  $39.8 \text{ nm}$  [22]). Nevertheless, the porosity

534 of plain mortar slightly increased due to the hybrid reinforcement mainly due to presence of  
 535 MCC/CNT agglomerates, which could not be removed completely through the dispersion  
 536 process. The possible reason behind the reduction of pore size in case of hybrid cementitious  
 537 composites could be the better dispersion of cement particles due to surfactants [34] and also  
 538 due to MCC and CNT [22][34], well dispersed and well packed hydration products as their  
 539 growth was nucleated and controlled by CNT and MCC[47] [45] [48]as well as filling of  
 540 nano pores by CNTs [49]. Consequently, cementitious composites developed using the  
 541 hybrid system showed lower pore size as compared to only MCC based cementitious  
 542 composites reported earlier.  
 543



544  
 545 Fig. 7 Incremental intrusion volume of mercury versus pore diameter for plain mortar and  
 546 selected multi-scale cementitious composites (P denotes Pluronic F-127)  
 547

548 **Table 10 Average pore diameter and porosity of plain mortar and selected multi-scale**  
 549 **cementitious composites**

Samples	Average Pore Diameter	Porosity (%)
Plain Cement Mortar	47.4 nm	10.5
0.2% MCC+ 0.1%CNT+1.5% P*	28.2 nm	13.9
0.5% MCC+ 0.3%CNT+CTAB+1TBP	30.3nm	12.9

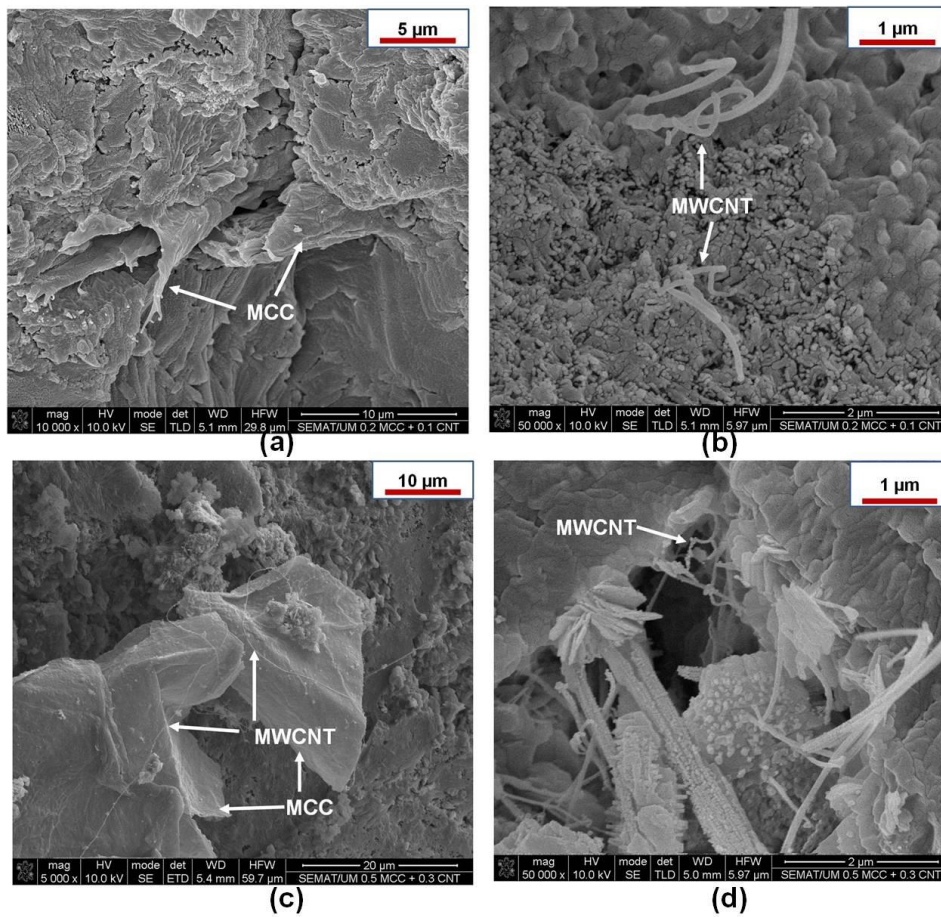
550 \*P denotes Pluronic F-127

551

### 552 3.6 Microstructure of MCC-CNT Multi-scale Composites

553 The fracture morphology of MCC-CNT mortar composites at different magnifications has  
554 been presented in Fig. 8. The fracture surfaces shown in Fig. 8(a) and (b) show the presence  
555 of MCC and CNTs which were well integrated with the cement matrix.

556



557

558 Fig.8. Microstructure of MCC reinforced cementitious composites at different magnifications  
559 showing: (a) presence of MCC, (b) presence of CNT, (c) MCC and CNT and (d) crack  
560 bridging by CNTs

561

562

**Table 11 Elements present in plain mortar and observed micro particles**

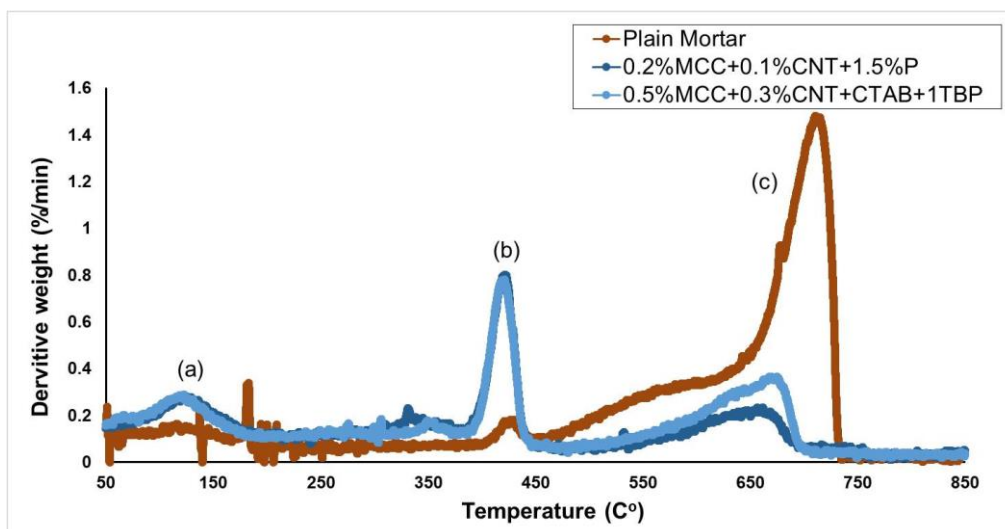
Samples	Elements (Wt.%)							
	C	O	Na	Mg	Al	Si	S	Ca
Plain mortar	11.44	45.59	0.29	0.31	0.77	3.93	0.61	36.25
0.5% MCC+ 0.3% CNT+CTAB+1TBP	42.28	28.24	-	-	1.25	5.47	-	22.75

563 It can be further observed that CNTs were present either individually or in small bundles  
 564 without much agglomeration, as can be seen in Fig. 8(b), 8(c) and 8(d). Good dispersion of  
 565 CNTs in the aqueous suspensions was also maintained within the cement matrix due to the  
 566 stabilizing effect of the surfactants at the optimized concentrations. The presence of MCC  
 567 was confirmed through elemental analysis of the observed particles using EDX, the results of  
 568 which are provided in Table 11. Significantly higher quantity of C (due to cellulose) and  
 569 lower quantity of Ca confirmed that the observed micro particles were MCC. However,  
 570 presence of Ca, Si, Al, etc. indicated that the MCC particles were well coated with the cement  
 571 hydration products. It was interesting to note from the fracture surface morphology in Fig.  
 572 8(c) that CNTs were present on the surface of MCC particles. Possibly, MCC and CNT were  
 573 well connected together as well as with the cementitious matrix. The role of CNTs in  
 574 bridging the cracks of cementitious matrix was also observed in the fracture surface, as can  
 575 be noted in Fig. 8(d).

576

### 577 3.7 Hydration Behaviour of MCC-CNT Multi-scale Composites

578 TGA analysis was performed for selected specimens and DTG curves (Fig. 9) were studied to  
 579 analyse the weight loss due to [25]: (a) removal of water from the porous and amorphous C-S-  
 580 H gel which occurred around 105°C-400°C, (b) removal of water associated with the non-  
 581 porous, crystalline phase of cementitious matrix i.e. calcium hydroxide (CH) that occurred in  
 582 between 400°C and 450°C. (c) decomposition of CaCO<sub>3</sub> that occurred over 600°C (however,  
 583 DTG curves do not provide the exact amount of decomposed CaCO<sub>3</sub>, since it also depends  
 584 upon storage conditions, mainly on the atmospheric CO<sub>2</sub>).



585

586 Fig. 9 DTG curves for plain cement mortar and selected multi-scale cementitious composites

587

(\*P denotes Pluronic F-127)



588 It was observed that both peak (a) and peak (b) were much stronger and sharper in case of  
589 MCC-CNT mortar composites. This indicated the formation of higher hydration products [C-  
590 S-H gel and  $\text{Ca}(\text{OH})_2$ ] in case of hybrid cementitious composites, as also earlier noticed in  
591 case of MCC or CNT reinforced cementitious composites [31][19]. Better hydration in case  
592 of MCC-CNT reinforced composites was mainly attributed to the positive influence of both  
593 CNT and MCC on cement hydration. CNTs could act as the nucleation centre for the growth  
594 of C-S-H gel and  $\text{Ca}(\text{OH})_2$  [47][48]. MCC, on the other hand, controlled the hydration  
595 process by retaining water and releasing it slowly as the hydration proceeded, resulting in a  
596 better hydration process [45]. Properly dispersed reinforcements also helped to diffuse water  
597 (by holding and releasing water from the hydrated to unhydrated phase) and therefore,  
598 accelerated the formation of hydration products [45]. It was also highly interesting to note  
599 that the formation of  $\text{CaCO}_3$  was suppressed tremendously by the hybrid reinforcement. This  
600 finding was also observed previously in case of MCC reinforced cementitious composites  
601 [22].  $\text{CaCO}_3$  may lower the alkalinity of cement structures due to carbonation of CH phase  
602 and lead to degradation of steel reinforcements[50]. Carbonation occurs due to the  
603 penetration of  $\text{CO}_2$  through pores/ cracks and its subsequent reaction with  $\text{Ca}(\text{OH})_2$ . Due to  
604 the lower average pore diameter and dense microstructure of MCC-CNT reinforced  
605 composites,  $\text{CO}_2$  could not penetrate well through the cement matrix to react with  $\text{Ca}(\text{OH})_2$ ,  
606 which was, although, present in much higher quantity in the reinforced composites.  
607 Therefore, the developed hybrid reinforcement could significantly reduce the carbonation  
608 problem of cementitious composites.

609

610 The mechanical properties achieved with the hybrid reinforcement have been compared in  
611 Table 12 with those obtained with CNT in the selected recent literature. In general, most of  
612 the research studies on CNT reinforced cementitious composites have been performed using  
613 MWCNTs, and SWCNTs were rarely used, probably due to higher cost and more difficulties  
614 in dispersing SWCNTs as compared to MWCNTs. It is also evident from Table 12 that there  
615 exists a wide variation in the % improvement obtained in different mechanical properties by  
616 various researchers depending on the CNT type and functionalization, concentration,  
617 dispersion technique and the type of cementitious composites, i.e. cement paste or mortar.  
618 With respect to the dispersion methods, the type of surfactant, type of ultrasonication  
619 treatment (probe type or bath type) as well as its energy and treatment time also had strong  
620 influence on the CNT dispersion and ultimately, on the mechanical performance of resulting  
621 composites.

622

623

624

**Table 12 Comparison of Mechanical Performance with Existing CNT based  
Cementitious Composites**

Type of CNT	Dispersion technique	Influence on the properties	Ref.
Pristine, annealed and functionalized MWCNT, 0.5 wt.%	Using acetone and ultrasonication for 4h	11% and 17% increase in compressive strength of cement mortar with pristine and annealed MWCNTs and 86% decrease with functionalized MWCNTs.	51
MWCNT, 0.5 wt.%	Ultrasonication for 10 min	2% decrease in compressive strength of cement mortar	52
MWCNT, 1.0 wt.%	No. Direct mixing	10% increase in compressive strength of cement	53
MWCNT, 0.26 wt.%	Ultrasonication with surfactant, ultracentrifugation, decantation, and ultrasonication of the remaining suspension	36% and 37% increase in the flexural strength and Young's modulus of cement	54
MWCNT functionalized with COOH, 0.075 wt.%	Ultrasonication	32%, 50% and 63% increase in Young's modulus, flexural strength and fracture energy of cement, respectively.	55
MWCNT, 0.1 wt.%	Ultrasonication with surfactant for 30 min, ultracentrifugation for 30 min, decantation and ultrasonication of remaining solution.	30% and 15% increase in flexural and compressive strength of cement.	44
MWCNTs, 0.05 to 0.1 wt.%	4 h of magnetic stirring, followed by about 30 min of sonication	29% and 23% improvements in flexural and compressive strengths, respectively	56
MWCNTs, 0.1 wt.%	Ultrasonication in presence of surfactant	86.7%, 92.4% and 85.7% increase in flexural strength, elastic modulus and fracture toughness, respectively	57
SWCNTs, 0.1 wt.%	Ultrasonication with surfactant for 1 h	Up to 66%, 6.7%, 19.1% and 109% improvements in flexural modulus, flexural strength, compressive strength and fracture energy of cement mortar, respectively	34
0.5 wt. % MCC-0.3 wt. % MWCNT	Ultrasonication with surfactant for 1 h	12.3% and 16.3% increase in compressive strength and flexural strength, respectively after 28 days. 23.2%, 27.9% and 85.2% increase in compressive strength, flexural strength and fracture energy of cement mortar, respectively after 56 days.	Present study

625

626 A few studies even reported decrease in the mechanical properties of cementitious  
627 composites using CNTs [35, 51, 52] probably owing to inferior CNT dispersion. On the other  
628 hand, a higher improvement in mechanical properties (as compared to those achieved with  
629 the presently studied hybrid reinforcement) obtained in a few studies was attributed to better  
630 CNT dispersion resulting from either a lengthy and complex dispersion route [54, 44, 56],  
631 functionalized CNTs [55], use of superplasticizer [44] or higher energy tip type  
632 ultrasonication process [57]. In contrast to that, in the present study, a good improvement in  
633 the mechanical properties (more noticeable after 56 days of hydration) was achieved using a  
634 short and medium energy bath type ultrasonication process and a non-toxic and  
635 biocompatible surfactant (Pluronic F-127). This simple dispersion process produced highly  
636 stable CNT suspensions, which can be stored for a long time period and therefore, is highly  
637 suitable for application in the construction industry [34, 35]. In our previous research studies,  
638 SWCNTs and MWCNTs were dispersed using this process and although, significant  
639 improvements in strength, modulus and fracture energy were achieved with SWCNTs, a  
640 decrease in the flexural and compressive strengths was noticed in case of MWCNTs  
641 (although fracture energy increased significantly). In the industrial context, however,  
642 MWCNTs are more suitable due to their low cost and higher availability. To overcome this  
643 issue, i.e. to improve the strength and modulus of MWCNT reinforced cementitious  
644 composites, MCC has been added as the third filler in the present research due to high  
645 potential of MCC to improve strength and modulus of cementitious composites [22]. The use  
646 of MCC within cementitious composites is also encouraged looking at the growing interest  
647 on using bio-based materials in the construction sector. However, reduction of fracture  
648 energy due to stiffer and crystalline MCC was found to be a crucial problem [22]. Therefore,  
649 addition of a small quantity of MWCNTs can help to improve the low fracture energy of  
650 MCC based cementitious composites due to their crack bridging effects. Based on this  
651 understanding, to overcome the problems with MWCNT (i.e. reduced strength) and MCC  
652 (lower fracture energy) based cementitious composites, in the present study a combination of  
653 MWCNT and MCC was used to achieve improvements in both pre-cracking behaviour (i.e.  
654 elastic modulus and strength mainly due to MCC) as well as post-cracking behaviour (i.e.  
655 fracture energy mainly due to MWCNTs). The obtained results suggested the positive effects  
656 of using both MCC and MWCNT in the cementitious matrices. In addition to that, the hybrid  
657 reinforcement can provide additional advantages to the cementitious composites such as  
658 increased hydration degree (due to positive influence of both MCC and CNT) and

659 piezoresistivity and sensing property (due to presence of MWCNT), which can further  
660 increase their application potential in the construction sector.

661

#### 662 **4. Conclusions**

663 In the present research, multi-scale or hierarchical cementitious composites using MCC-CNT  
664 hybrid reinforcement has been developed for the first time and characterized for mechanical  
665 performance and microstructure. The dispersion of hybrid reinforcement in aqueous medium  
666 was carried out using two surfactants, namely Pluronic F-127 and CTAB at optimized  
667 concentrations. Good homogeneity and stability of CNT and MCC in the aqueous  
668 suspensions were achieved using Pluronic F-127 concentration of 3 wt.% (with respect to  
669 water) and CNT:CTAB ratio of 1:1. The flow values of prepared mortar pastes containing  
670 MCC-CNT were maintained at the similar level of the plain mortar paste. The mechanical  
671 performance of cementitious composites was strongly influenced by the concentration of  
672 defoaming agent, TBP and TBP: Pluronic F-127 and TBP:CTAB ratios of 0.5:1 and 1:1 were  
673 found suitable for achieving better mechanical performance. Both flexural and compressive  
674 properties improved with the hydration period. After 56 days of hydration, flexural strength  
675 increased by ~23% using 0.5% MCC-0.3% CNT with CTAB and by 15% using 0.2% MCC-  
676 0.1% CNT with Pluronic F-127. The compressive strength also improved by 28% using 0.5%  
677 MCC-0.3% CNT with CTAB and 19% using 0.2% MCC- 0.1% CNT with Pluronic F-127. In  
678 addition, flexural modulus, flexural strain and fracture energy also improved significantly.  
679 The cementitious composites containing the multi-scale reinforcement exhibited higher dry  
680 bulk density and lower average pore diameter as compared to plain mortar suggesting  
681 improved microstructure due to the reinforcements. The formation of hydration products was  
682 also found better in case of reinforced cementitious composites and the reinforcements  
683 showed good integration with the cement matrix and evidence of crack bridging mechanism.  
684 Therefore, these newly developed multi-scale composites can be a superior material for the  
685 construction industry as compared to the conventional cementitious materials due to their  
686 better strength, elastic modulus as well as breaking strain and fracture energy. Furthermore,  
687 due to the presence of CNTs, these composites can be designed to be self-sensing capable of  
688 detecting strains and damages and therefore, can be applied for structural health monitoring  
689 or traffic monitoring.

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