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# Effect of MWCNT and PCE plasticizer on the properties of cement pastes

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**Abstract.** Polycarboxylate ether (PCE) plasticizer possesses by high water-reduction capability of about 30-40%. Despite the superior water reduction capability, the high dosages of PCE may cause the bleeding in cement systems, which is not suitable for high workability and self-compacting concrete. The current research is devoted to the studying of multi-walled carbon nanotubes (MWCNT) suspension prepared in combination with PCE plasticizer on the rheological properties of cement pastes. The bleeding of cement pastes modified by different dosages of MWCNT was estimated as well. The increase of yield stress in 3.7 and 3.5 times was obtained for cement paste modified by MWCNT suspension in dosage of 0.12% by weight of cement (bwoc) in 5 and 120 min after cement paste mixing, respectively. The increase of plastic viscosity in 2.95 and 1.55 times was obtained for cement paste modified by MWCNT suspension in dosage of 0.12% bwoc in 5 and 120 min after cement paste mixing, respectively. Modification of cement pastes by MWCNT suspension in the dosage of 0.24 % bwoc led to the decrease of bleeding water volume by 21.7% in comparison with cement pastes modified only by PCE plasticizer.

## 1. Introduction

Application of high workability and self-compacting concrete requires the usage of plasticizing admixtures with high water reduction capability [1]. The last generation of comb-shaped copolymers discovered in the mid-1980s possesses by high water reduction capability and enables to decrease amount of water in cement systems up to 40%. The comb-shaped copolymers consist of backbone presented by carboxylic groups and non-ionic polyether side chains, which are attached to backbone. Mainly, this type of plasticizing admixtures called as polycarboxylate ethers, polycarboxylate esters or polycarboxylates (PCE).

Electrostatic and steric hindrance effects underlie the action mechanism of PCE plasticizers. The negatively charged backbone provides the adsorption of plasticizer onto the positively charged cement particles. Steric hindrance effect is provided by non-adsorbing side chains. The combination of electrostatic and steric hindrance effect makes the action mechanism of PCE plasticizers more efficient in comparison with other types of polymer plasticizers.



The chemical nature of the backbone, length and chemical nature of the side chains, distribution of the side chains along the backbone, anionic charge density and binding between backbone and side chain play an important role in performance of PCE plasticizers [2].

The number of researches are devoted to the investigation of the correlation between molecular structure of PCE plasticizers and fluidity of cement pastes and concrete mixtures [3-5].

Authors of research [3] designed and synthesized the PCE plasticizer with star-shaped topological molecular structure and compared it with PCE of comb-shaped structure. The star-shaped PCE presented the better fluidity and water reduction capability. Researchers [4] established that PCE plasticizers with higher molecular weight, lower side chain densities and shorter side chains have the stronger adsorption properties. Besides the adsorption properties of plasticizers, the critical micelle concentration determines the efficiency of PCE plasticizer in cement systems as well. The addition of PCE plasticizer higher than critical micelle concentration provides the low yield stress and high flowability [5].

The PCE plasticizers require their improvement in terms of avoiding bleeding in cement systems at high dosages of plasticizer. Nowadays, the application of different types of viscosity modifying agent (VMA) such as welan gum, cellulose ethers, polyethylene oxides, polyacrylamide, polysaccharides and some others can be applied for this purpose [6,7].

Nanoadditives with nanometer dimensions of particles, high aspect ratio and unique physical, chemical, electrical properties may be used as a perspective tool to improve the stability of concrete mixture [8,9]. E. Garcia-Taengua et. al. observed the increase of viscosity of fresh mortar modified by 2% of nano-silica [8]. M.R. Du et.al. investigated the effect of MWCNT and methylcellulose on stability of cement pastes [9].

Nowadays, concrete is produced with application of different types of mineral, chemical and nano additives and admixtures simultaneously. For example, the researchers [10, 11] investigated the effect of different surfactants on the properties of MWCNT suspension and cement systems. O.A. Mendoza et.al. highlighted the incompatibility between dosage of surfactant used to obtain an adequate dispersion degree of MWCNT suspension in water and dosage of surfactant necessary to obtain adequate rheological properties of cement system [11]. For this reason the combine effect of additives and admixtures is required to be studied for better understanding of their complex action mechanism and subsequent effect on cement systems.

The present research is focused on the studying of multi-walled carbon nanotubes (MWCNT) suspension prepared in combination with PCE plasticizer on the rheological properties of cement pastes and bleeding of cement pastes modified by different dosages of MWCNT.

## 2. Materials and Methods

### 2.1. Materials

The Portland cement without mineral additives CEM I 42.5 R conforming to EN 197-1 with water consumption 26.6% and fineness by Blain of 3552 cm<sup>2</sup>/g was used as a binder.

**Table 1.** Composition of MWCNT suspensions.

Specimen	MWCNT in volume of suspension, %	PCE in volume of suspension, %	Ratio between MWCNT and PCE	Time of ultrasonication, min
D1	0.015	3.8	1:256	6
D2	0.030	3.8	1:128	6
D3	0.060	3.8	1:64	6
D4	0.120	3.8	1:32	6
D5	0.240	3.8	1:16	6
D6	0.048	3.8	1:8	6
D7	0.096	3.8	1:4	6

The MWCNT suspension was prepared from the masterbatch pellets "Graphistrength CW 2-45" produced by the company "Arkema" (France). The masterbatch contains 45 wt. % of MWCNT and 55 wt. % of carboxymethylcellulose (CMC). The MWCNT was characterized by filament length of 100 – 10000 nm and diameter of 15–20 nm.

Distilled water was used as dispersion medium for MWCNT. The polycarboxylate ether of MPEG type (PCE) with specific gravity 1.100 g/cm<sup>3</sup>, pH up to 5 at 20 °C and dry content equal to 50.5% was applied in the research as dispersant to distribute the nanotubes in the volume of suspension. The compositions of generated MWCNT suspensions are presented in Table 1.

## 2.2. Methods

The MWCNT suspension was prepared in the following way. The masterbatch pellets "Graphistrength CW 2-45" were immersed in hot water with temperature about 75 °C and stirred by standard mixer agitation about 1000 rpm during 5 min.

After that the MWCNT suspension was subjected to ultrasonication for a duration of 6 min. The ultrasonication was performed by Bandelin Sonopuls HD 3400 ultrasonic homogenizer (400 W, 20 kHz) with probe VS 200 T (Ø 25mm, amplitude – 82µm).

The prepared MWCNT suspension was characterized by pH, electrical conductivity tests, measurements of surface tension, particle size analysis and measurements of zeta potential.

pH test was performed by pH-meter Mettler-Toledo EL20 with limits of error ± 0.01 pH. The electrode with gel electrolyte was used.

Electrical conductivity was measured by Mettler-Toledo EL30. The measurement range of it is 0.1 to 199.1 mS/cm with limits of error ± 0.5 %. The electrode for medium to high conductivities (10 µS/cm ... 500 mS/cm) was applied.

Surface tension of MWCNT suspension was measured based on stalagmometric method by stalagmometer Traube with measurement accuracy 1 mN/m. The stalagmometric method consists in determination of drops number which are formed in the course the flowing of liquid from capillary tube of known volume. The surface tension of studied liquid is calculated based on Equation (1):

$$\sigma_x = \sigma \cdot \frac{N}{N_x} \cdot \frac{d_x}{d} \quad (1)$$

where:  $\sigma$ - surface tension, mN/m; N - number of drops; d - density, g/cm<sup>3</sup> of water;  $\sigma_x$ ,  $N_x$ ,  $d_x$ - the same for studied liquid.

Particle size analysis and zeta potential measurements of MWCNT suspension were performed by particle size and zeta potential analyser Delsa Nano C, Beckman Coulter. Particle size analysis was based on the principle of photon correlation spectroscopy with resolution of measurements placed from 0.6 nm to 7 µm and measurement accuracy of 0.05 nm.

**Table 2.** Content of materials for 1 m<sup>3</sup> in tested cement pastes.

Specimen	Cement, kg	Water, kg	W/C ratio	MWCNT, % bwoc <sup>a</sup>	PCE, % bwoc <sup>a</sup>
REF	935	280	0.30	0	0
PCE	935	234	0.25	0	1.0
PCE+0.00375	935	234	0.25	0.00375	1.0
PCE+0.0075	935	234	0.25	0.0075	1.0
PCE+0.015	935	234	0.25	0.015	1.0
PCE+0.030	935	234	0.25	0.030	1.0
PCE+0.060	935	234	0.25	0.060	1.0

<sup>a</sup>bwoc -by weight of cement

Zeta potential measurements was based on the electrophoretic light scattering principle with range of measurement from -150 mV to +150 mV and measurement accuracy of 0.005 mV.

The cement pastes with composition presented in Table 2 were prepared for rheological test. The MWCNT suspensions with composition presented in Table 1 were used as mixing liquid and mixed together with cement for 180 s at high speed by standard mixer according to EN 196-1. Rheological properties of cement pastes were tested in different time after pastes mixing: 5, 60 and 120 min. The rheology tests were carried out at temperature  $20 \pm 2$  °C. The rotational rheometer Rheotest RN 4.1 with coaxial cylinders was used for rheological tests. Shear rate ranged from 100.0 s<sup>-1</sup> to 0.1 s<sup>-1</sup> during testing time. Cement pastes after mixing between tests were placed in the plastic containers and carried in the laboratory conditions with temperature  $20 \pm 2$  °C and relative humidity not less than 65 %. The cement pastes were premixed before rheological test by hands in plastic container using metallic scoop for 1 min. The yield stress ( $\tau_0$ ) and plastic viscosity (K) were determined in the course of approximation of flow curve (dependence between shear stress ( $\tau$ ) and shear rate ( $\gamma$ ) in the range from 0.1 to 100 s<sup>-1</sup> based on Herschel-Bulkley model. The Herschel-Bulkley model is more widely used model for description of flow behaviour of cement systems with shear thinning or shear thickening effect, which is expressed by the Equation (2):

$$\tau = \tau_0 + K \cdot \gamma^n \quad (2)$$

where:  $\tau$  - shear stress, Pa;  $\tau_0$ - yield stress of the cement paste, Pa; K- plastic viscosity, Pa·s;  $\gamma$  - shear rate, s<sup>-1</sup>; n - shear thinning or shear thickening index if  $n < 1$  or  $n > 1$ , respectively.

Amount of bleeding water was determined according the following method. 50 g of MWCNT suspension was pour into the 100 ml container, after that 50 g of cement was added for 1 min. Subsequently, MWCNT suspension and cement were mixed continuously for 4 min in the container and were poured into a graduated cylinder of 30 ml. The graduated cylinder with cement paste was placed onto the table and the initial volume of cement paste was written. The graduated cylinder was standing without moving and shaking during the test. The volume of sedimented cement in cement paste after water bleeding was determined after 2 hours since the reference point and every 30 min after it. The observation of water bleeding was performed till the moment when the volume of cement paste did not changed. Water separation (water bleeding) was calculated according the Equation (3):

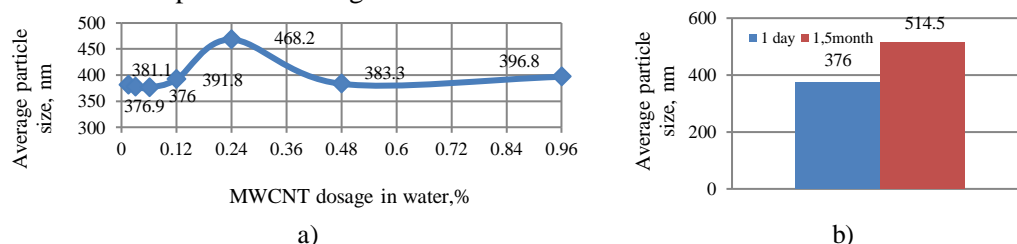
$$K = \frac{a-b}{a} \cdot 100 \quad (3)$$

where: K –coefficient of water bleeding, %; a - initial volume of cement paste, cm<sup>3</sup>; b - volume of sedimented cement, cm<sup>3</sup>.

### 3. Results and Discussion

#### 3.1. Analysis of MWCNT suspension homogeneity

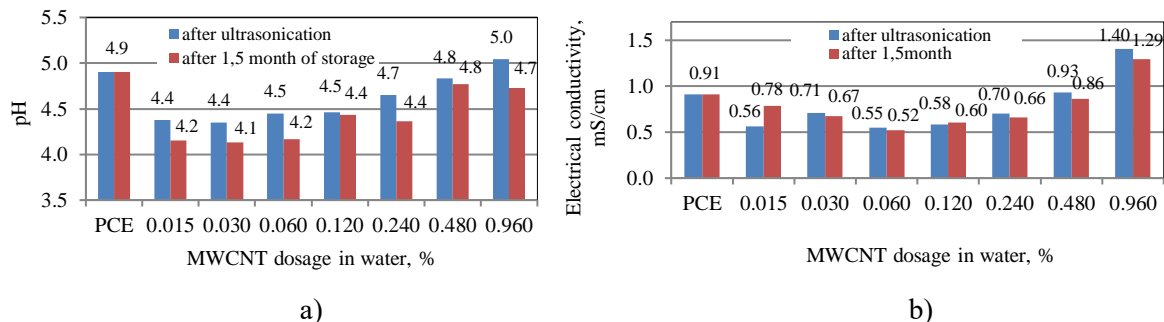
The results of particle size analysis of MWCNT suspensions with PCE plasticizer subjected to ultrasonication are presented in Fig. 1.



**Figure 1.** Particle size analysis of MWCNT suspension after ultrasonication (a) and particle size analysis of MWCNT suspension with 0.06% of MWCNT in water after 1.5 month of storage (b).

The graph in Fig.1a presents the particle size analysis of MWCNT suspension after ultrasonication. The average diameters of particles are placed on the same level. The minimum average diameter of particles was achieved of 376 nm for suspension with MWCNT dosage equal to 0.06% in water. The suspension with 0.06% of MWCNT was tested after 1.5 months of storage. It is revealed the increase of average particle size up to 514.5 nm, caused by coagulation processes in MWCNT suspension (Fig.1b).

The MWCNT suspension was characterized by pH, electrical conductivity, zeta potential and surface tension measurements as well.



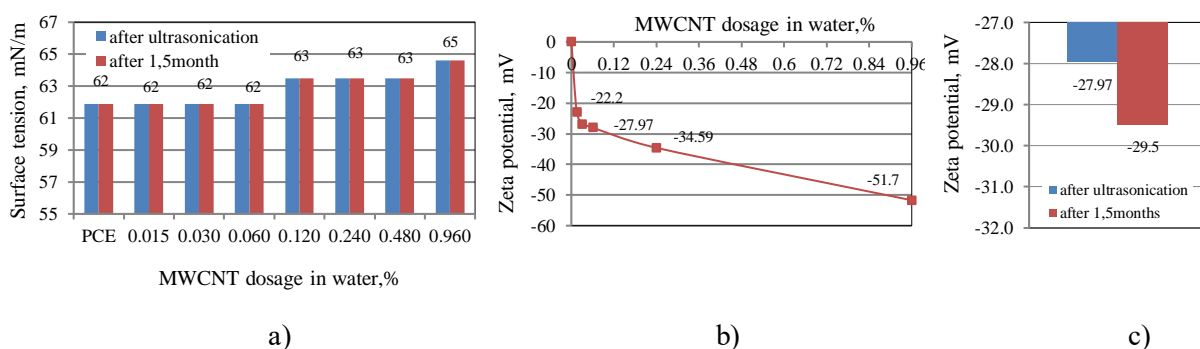
**Figure 2.** pH of MWCNT suspension (a); electrical conductivity of MWCNT suspension (b).

Fig.2a demonstrates the changes in pH level of suspensions with different MWCNT dosage after ultrasonication and 1.5 months of storage. Increase of MWCNT dosage changes the pH level of the suspensions not significant. pH of MWCNT suspensions slightly decreased in the process of storage. This process can be explained by coagulation processes which take part in MWCNT suspensions during the time.

Test of electrical conductivity revealed that increase of MWCNT dosage to 0.96% increase electrical conductivity from 0.91 to 1.40 mS/cm as it is seen in Fig. 2b. Changes in electrical conductivity during the 1.5 months of storage did not observed. The dimensions of electrical conductivity for suspensions with MWCNT dosage from 0.015 to 0.24% demonstrated smaller electrical conductivity in comparison with sample without MWCNT, which can be caused by the electrostatic interactions between MWCNT and plasticizers.

Fig.3a shows that the surface tension of MWCNT suspensions increased with increase of MWCNT dosage in water. Increase of MWCNT dosage up to 0.96% led to the increase of surface tension from 62 to 65 mN/m.

Zeta potential of MWCNT suspension increased with the increase of MWCNT dosage to 0.96% as it seen in Fig.3b. Fig.3c shows that zeta potential did not changes significantly during 1.5 months of storage.



**Figure 3.** Surface tension of MWCNT suspension (a); zeta potential of MWCNT suspension after ultrasonication (b); zeta potential of MWCNT suspension with MWCNT dosage of 0.06% in water after 1.5 months of storage (c)

The results of MWCNT suspension analysis confirmed that usage of MWCNT suspension is more suitable after ultrasonication process when degree of coagulation is not high.

3.2. Rheological properties and bleeding of cement pastes with MWCNT suspension

The Fig.4, 5 present the changes in rheological behaviour of nanomodified cement pastes with different dosage of MWCNT in 5 and 120 min after cement pastes mixing, respectively.

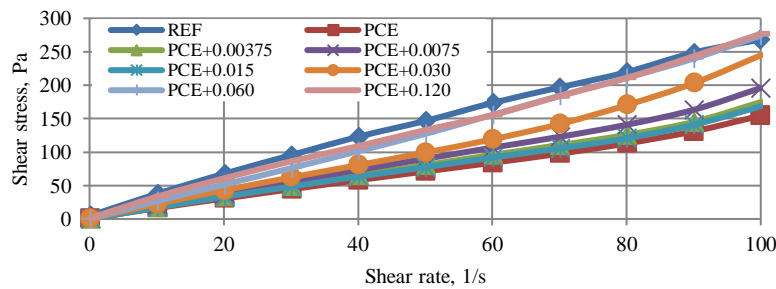


Figure 4. Flow curves of nanomodified cement pastes in 5 min after cement paste mixing.

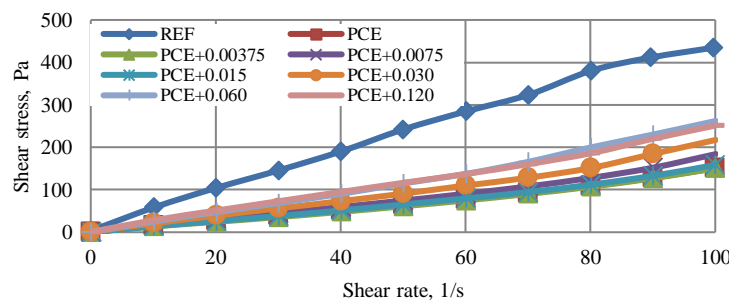
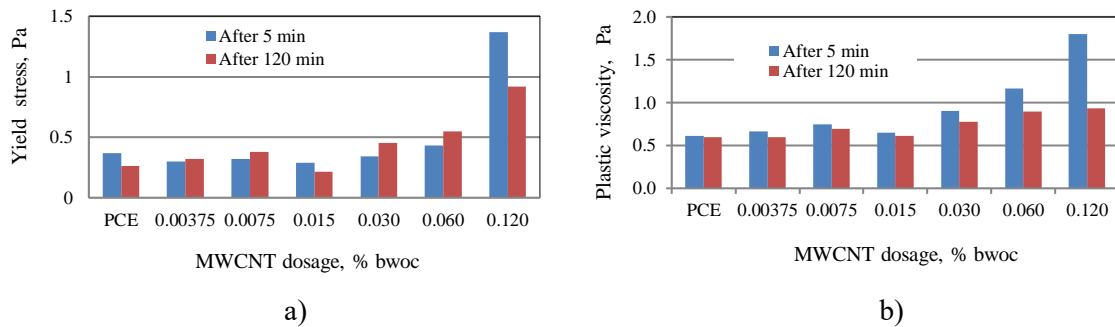


Figure 5. Flow curves of nanomodified cement pastes in 120 min after cement paste mixing.

Rheological behaviour of cement pastes modified by PCE plasticizer changes from the shear thinning to shear thickening. Addition of MWCNT at the dosage 0.060 and 0.012% by weight of cement (bwoc) make the behaviour of cement paste closer to shear thinning. However, this effect did not observed in 120 min after cement paste mixing. Modification by MWCNT suspension more than 0.030% bwoc increases the plastic viscosity of cement pastes in 5 and 120 min after cement pastes mixing. The experimental flow curves were approximated by Herchel-Bulkley model. The obtained equations and thixotropy indexes are available in Table 3.

Table 3. Equations based on Herschel-Bulkley model and thixotropy indexes of cement pastes.

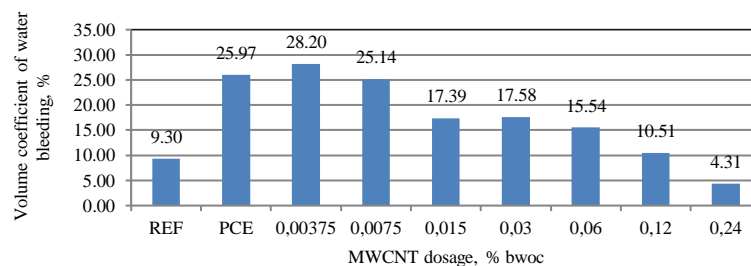
Specimen	Flow curves equations		Thixotropy Indexes	
	After 5 min	After 30 min	After 5 min	After 30 min
REF	$\tau=4.97+3.470\gamma^{0.940}$	$\tau=4.2+3.750\gamma^{1.050}$	0.940	1.050
PCE	$\tau=0.37+0.610\gamma^{1.197}$	$\tau=0.26+0.600\gamma^{1.190}$	1.197	1.190
PCE+0.00375	$\tau=0.30+0.663\gamma^{1.200}$	$\tau=0.32+0.600\gamma^{1.190}$	1.200	1.190
PCE+0.0075	$\tau=0.32+0.750\gamma^{1.200}$	$\tau=0.38+0.698\gamma^{1.193}$	1.200	1.193
PCE+0.015	$\tau=0.29+0.650\gamma^{1.230}$	$\tau=0.212+0.610\gamma^{1.190}$	1.230	1.190
PCE+0.030	$\tau=0.34+0.900\gamma^{1.200}$	$\tau=0.45+0.780\gamma^{1.190}$	1.200	1.200
PCE+0.060	$\tau=0.43+1.163\gamma^{1.100}$	$\tau=0.55+0.895\gamma^{1.230}$	1.100	1.230
PCE+0.120	$\tau=1.37+1.178\gamma^{1.090}$	$\tau=0.92+0.930\gamma^{1.210}$	1.090	1.210



**Figure 6.** Yield stress (a) and plastic viscosity (b) of cement pastes with different MWCNT dosage.

The changes of yield stress and plastic viscosity for cement pastes with different dosage of MWCNT in 5 and 120 min after cement pastes mixing are presented in Fig. 6a and Fig. 6b, respectively. Addition of MWCNT at the dosage more than 0.03% bwoc increases the yield stress. The maximum increase was observed for cement paste modified by 0.120% bwoc. The yield stress was increased by 3.7 and 3.5 times in 5 and 120 min after cement paste mixing, respectively.

Fig. 6b demonstrates the changes of plastic viscosity for cement pastes modified by different MWCNT dosage. The MWCNT dosage more than 0.030% bwoc increases the plastic viscosity. The maximum increase of plastic viscosity was established for cement paste modified by 0.120% bwoc. The plastic viscosity increased by 2.95 and 1.55 times in 5 and 120 min after cement pastes mixing, respectively.



**Figure 7.** Water bleeding of nanomodified cement pastes.

The water bleeding test of nanomodified cement pastes revealed the decrease of bleeding water with modification of cement pastes by MWCNT as it is seen in Fig.7. The maximum decrease by 21.7% was obtained for cement paste modified by MWCNT of 0.24% bwoc in comparison with sample modified only by PCE plasticizer.

#### 4. Conclusions

The following conclusions are drawn in this study:

1. The MWCNT suspension with average diameter of particles of 376 nm was established. The results of MWCNT suspension analysis confirmed that usage of MWCNT suspension is more suitable after ultrasonication process when degree of coagulation is not high.

2. The flow behavior of cement pastes modified by MWCNT suspension with PCE plasticizer changed from shear thinning to shear thickening in comparison with reference cement paste without admixtures.

3. The increase of yield stress in 3.7 and 3.5 times was obtained for cement paste modified by MWCNT suspension in dosage of 0.12% bwoc in 5 and 120 min after cement paste mixing, respectively. The increase of plastic viscosity in 2.95 and 1.55 times was obtained for cement paste modified by MWCNT suspension in dosage of 0.12% bwoc in 5 and 120 min after cement paste mixing, respectively. The increase of yield stress and plastic viscosity during time for cement pastes



modified by MWCNT suspensions with different ultrasonication treatment may be caused by Van-der-Waals, electrostatic and steric forces, which appear between cement particles in the course of modification by plasticizer and MWCNT.

5. Modification of cement pastes by MWCNT suspension in the dosage of 0.24 % bwoc led to the decrease of bleeding water volume by 21.7% in comparison with cement pastes modified only by PCE plasticizer.

6. Effect of MWCNT suspensions on yield stress, plastic viscosity and bleeding may give the opportunity to use them as effective viscosity modifying agent for high workability and self-compacting concrete.

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