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The investigation of Multi-Walled Carbon Nanotubes dispersion and its influence on the cement systems

1. Einleitung/ Indroduction

The carbon nanotubes (CNT) have a great perspective for modification of cement systems. A number of researches demonstrate a positive effect of nanomodification on mechanical, electrical, thermal and other properties of cement composites [1-4]. For instance, in reference [1] were noticed that modification of cement composites by multi-walled carbon nanotubes (MWCNT) leads to increase of compressive strength up to 40%, the decrease of porosity and the uniform distribution of pores.

The positive effect of nanomodification is not stable due to tendency of nanostructures to agglomeration, therefore the application of nanomodified composites is limited in construction practise [5], [6].

The final properties of nanomodified cement composites are depended on quality of CNT dispersion. The type, geometrical parameters, dosage of CNT, properties of plasticizing admixture, ratio between dosage of CNT and plasticizer, the type and intensity of homogenization are the crucial factors in homogenization of CNT [7-12].

The modification of cement systems by CNT requires a comprehensive approach. Despite the significant number of publications, this topic remains relevant due to unclear mechanisms of interaction between CNT and cement system.

The current research was focused on investigation of MWCNT dispersion properties during storage and its influence on rheological properties of cement pastes.

2. Versuchsdurchführung/ Experimental program
2.1. Ausgangsmaterial/ Raw Materials

The cement CEM I 42.5 R (supplied by "Akmenes Cementas", Lithuania) conforming to EN 197-1 was used as a binder.The mineral composition of the cement is presented in Tab. 1. The physical and mechanical properties of the cement are listed in Tab. 2.

Tab.1: Mineral composition of cement

Component	Amount [%]
Tricalcium silicate (C_3S)	57.9
Dicalcium silicate (C_2S)	15.6
Tricalcium aluminate (C_3A)	7.5
Tetracalcium aluminoferrite (C_4AF)	11.9

Potable water according to EN 1008 was used for preparation of cement pastes.

The MWCNT dispersion was prepared from the masterbatch "Graphistrength CW 2-45" produced by the company "Arkema" (France). The masterbatch contains 45 wt. % of

Tab.2: Physical and mechanical properties of cement

Property	Value
2-day compressive strength, MPa	28±2
28-day compressive strength, MPa	55±3
Initial setting time, min	180
Final setting time, min	225
Volume stability, mm	1.0
Water consumption, %	26.6
Residue on the 90µm sieve, %	1.5
Specific surface, cm^2/g	4000

MWCNT and 55 wt. % of carboxymethylcellulose (CMC). The MWCNT was characterized by filament length equal to 0.1–10 µm and diameter equal to 15–20 nm. The concentration of "Graphistrength CW 2-45" in the dispersion was equal to 1.0%.

2.2. Experimental Process

The MWCNT dispersion (D) was prepared in following way. The masterbatch "Graphistrength CW 2-45" were immersed in hot water with temperature about 75°C and stirred by standard mixer agitation about 1000 rpm during 15 min. Subsequently, dispersion was subjected to ultrasonication for a duration of 6 min. The ultrasonication was performed by Bandelin Sonopuls HD 3400 ultrasonic homogenizer (400W, 20 kHz) with probe VS 200 T (Ø 25mm, amplitude - 82µm).

The quality of dispersion was evaluated by pH-meter Mettler-Toledo EL20 with limits of error ± 0.01 pH; electrical conductivity meter Mettler-Toledo EL30 tests with limits of error ± 0.5 %. The same equipment was used to determine the pH and electrical conductivity of cement pates and assess the influence of MWCNT on cement pastes. Particle size analysis of dispersion was accomplished by particle size and zeta potential analyzer DelsaNano C, Beckman Coulter with resolution of measurements placed from 0.6 nm to 7µm.

The cement pastes with composition presented in Tab. 3 were prepared for rheological test. MWCNT dispersion was dissolved in potable water. Water together with MWCNT dispersion was added to the cement and cement paste was mixed for 180 s at high speed by mixer. Rheological properties of cement pastes were tested in different time after pastes mixing: 5, 30, 60 and 120 min. The rheology tests were carried out at temperature 20±2 °C. The rotational rheometer Rheotest RN 4.1 with coaxial cylinders was used for rheological tests.

Tab.3: Composition of tested cement pastes

Dosage of MWCNT, %	W/C ratio	PL, [% by weight of cement]	MWCNT, [% by weight of cement]	MWCNT dispersion, [% by weight of cement]
0	0.30	0	0	0
0.125	0.30	0	0.00125	0.125
0.25	0.30	0	0.0025	0.25
0.5	0.30	0	0.005	0.5

The scheme of cylinder measuring system of rheometer is presented in Fig. 1a. The assembled measuring cup (1) with coupling is poured by cement paste (3), and fixed in the equipment stand. The rotating cylinder rotor (2) is placed inside the measuring cup (1) with gap between them about 1.5 mm and rotates during the test. Shear rate ranged from 100.0 s^{-1} to 0.1 s^{-1} during testing time. The shear rate mode described by the graph in Fig. 1b was used in the current experiments.

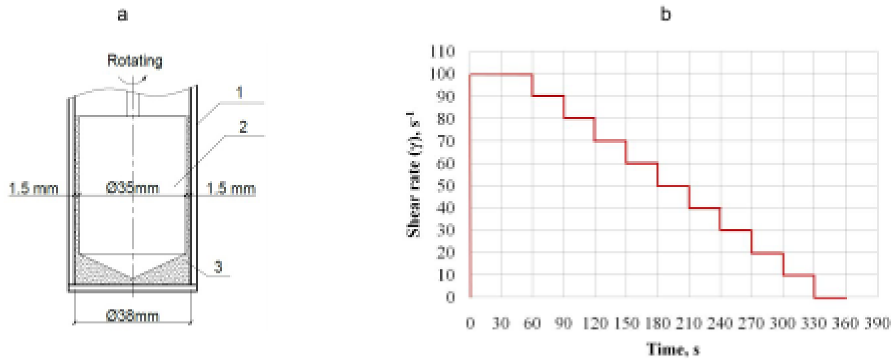

Fig.1: a) scheme of cylinder measuring system Rheotest RN 4.1; b) shear rate mode of rheological test

Cement pastes after mixing between tests were placed in the plastic containers and carried in the laboratory conditions with temperature 20±2 °C and relative humidity not less than 65 %. The cement pastes were premixed before rheological test by hands using metallic scoop for 1 min.

3. Ergebnisse und Diskussion/ Results and discussion

Fig. 2 shows the changes in pH of MWCNT dispersion during the storage, pH level was decreased from 8.89 to 8.02. In other words, the dispersion medium becomes more acidic during the storage.

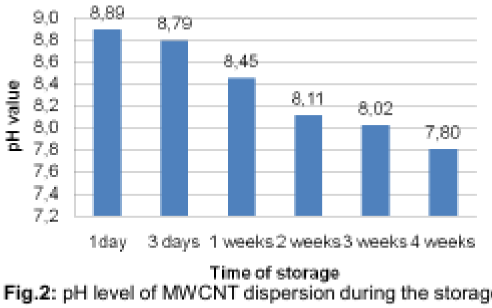

Fig.2: pH level of MWCNT dispersion during the storage

Fig. 3 demonstrates the changes in electrical conductivity of MWCNT dispersion during the storage. Electrical conductivity was increased from 2.00 to 2.75 mS/cm.

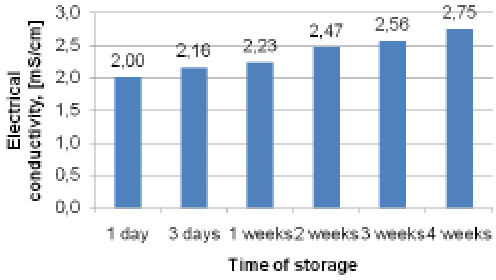

Fig.3: Electrical conductivity of MWCNT dispersion during the storage

The results presented in Fig. 3, 4 can be explained by the influence of MWCNT on the physico-chemical processes which take place in water medium of dispersion.

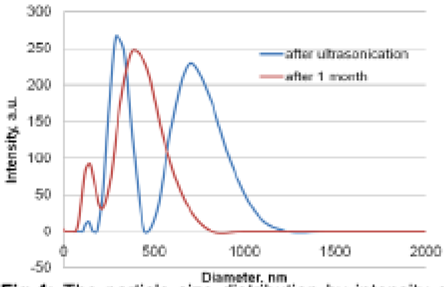

Fig.4: The particle size distribution by intensity of MWCNT dispersion after ultrasonication and after 1 month of storage

The particle size analysis of MWCNT dispersion after the homogenization revealed that the diameter of MWCNT dispersion particles was varied from 119 to 1070 nm. The average diameter of particles was established equal to 294 nm. The diameter of particles for the MWCNT dispersion tested after 1 month of storage showed the variation from 82 to 677nm and average diameter about 270.3 nm. The results of particle size analysis are presented in Fig.4.

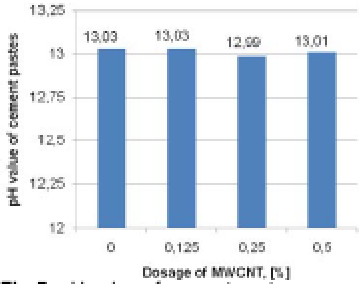

Fig.5: pH value of cement pastes

Fig. 5 and Fig. 6 demonstrate the changes in pH and electrical conductivity of cement pastes modified by MWCNT dispersion in different dosage in 5 min after mixing.

pH value of nanomodified cement paste with different dosage o MWCNT was not changed as it's seen in Fig. 5.

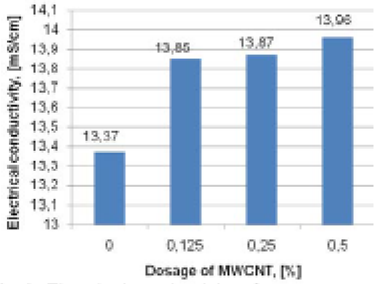

Fig.6: Electrical conductivity of cement pastes

The modification of cement pastes by MWCNT dispersion leaded to the increase of electrical conductivity with the increase of MWCNT dosage. The maximum increase of electrical conductivity by 0.59 mS/cm was reached for cement paste modified by MWCNT dispersion in the dosage of 0.5% by weight of cement.

The experimental rheological flow curves are presented in Fig. 7 and Fig.8 after 5 and 120 min of testing, respectively. The yield stress (τ_0) and plastic viscosity ($\mu_{pl.}$) were determined in the course of linear approximation of flow curve (dependence between shear stress (τ) and shear rate (γ) in the range from 0.1 to 100 s^{-1} based on Bingham model. The Bingham model is more widely used model for description of flow behaviour of cement systems, which is expressed by Equation 1:

$$\tau = \tau_0 + \mu_{pl} \cdot \gamma \quad , \qquad (1)$$

where: τ - shear stress, Pa;
τ_0 - yield stress of the cement paste, Pa;
$\mu_{pl.}$ - plastic viscosity of the cement paste, Pa·s;
γ - shear rate, s^{-1}.

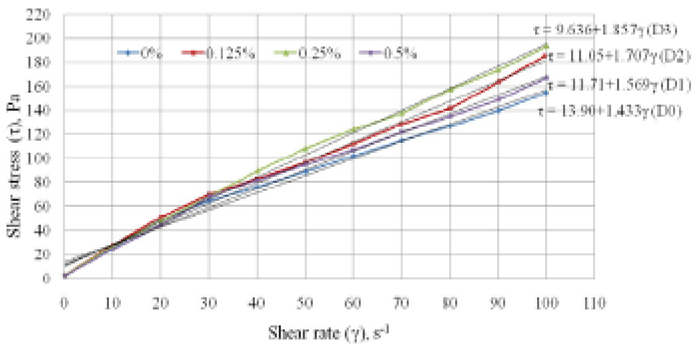

Fig.7: Flow curves of nanomodified cement pastes after 5 min of mixing.

The introduction of MWCNT dispersion changes the flow behaviour of cement pastes. The increase of shear stress and plastic viscosity of nanomodified cement pastes is observed in Fig. 7 in the range of shear rate from 0.1 to 100 s^{-1} for 5 min after mixing. The maximum increase of shear stress was identified for cement paste modified by MWCNT dispersion in dosage 0.25% by weight of cement. The shear-thinning behaviour takes place in the course of modification of cement paste by MWCNT dispersion. At the same time, as it seen in Fig. 8, shear stress and plastic viscosity are not changed for cement pastes in the range of shear rate from 0.1 to 100 s^{-1} for 120 min after mixing for different dosage of MWCNT.

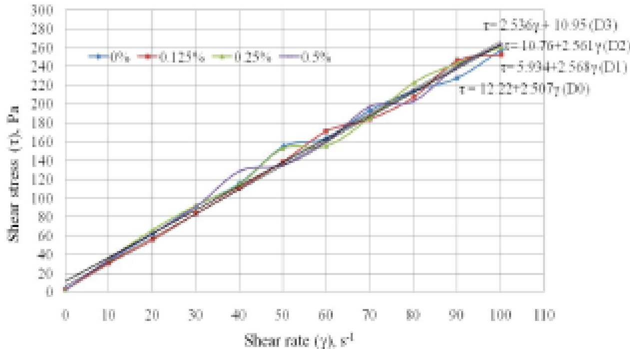

Fig.8: Flow curves of nanomodified cement pastes after 120 min of mixing.

The equations of cement pastes flow behavior according to Bingham model were derived and presented in the Fig. 7 and Fig. 8 together with flow curves of pastes with different dosage of MWCNT dispersion. The yield stress and plastic viscosity values for cement pastes with different dosage of MWCNT for 5 and 120 min after mixing were determined and presented in Table 4.

Tab.4:Values of plastic viscosity and yield stress for nanomodified cement pastes

Dosage of MWCNT dispersion, %	After 5 min		After 120 min	
	Yield stress, Pa	Plastic viscosity, Pa·s	Yield stress, Pa	Plastic viscosity, Pa·s
0	13.90	1.433	12.22	2.507
0.125	11.71	1.569	5.934	2.568
0.25	11.05	1.707	10.76	2.561
0.5	9.636	1.857	10.95	2.536

The maximum decrease in yield stress for 5 min after mixing by 30.7% is observed for cement paste modified by MWCNT dispersion in dosage 0.25% by weight of cement.

The maximum increase of plastic viscosity for 5 min after mixing by 29.6% was establish for cement pastes with MWCNT dispersion in the dosage 0.25% by weight of cement.

4. Zusammenfassung/ Conclusions

The following conclusions are drawn in this study:

1. The MWCNT dispersion for modification of cement pastes with average particle diameter up to 294 nm was obtained in the course of research. The duration of ultrasonication about 6 min, the power equal to 400W was established as optimal parameter of nano dispersion homogenization.

2. The obtained MWCNT dispersion showed the stability for 1 month of storage. The average diameter after 1 month of storage did not increase and was equal to 270.3 nm.
3. The pH level and electrical conductivity of MWCNT dispersion changes in the range from 8.89 to 8.02 and from 2.00 to 2.75 mS/cm, respectively, during the 1 month of storage. The changes in pH and electrical conductivity of MWCNT dispersion during the storage can be caused by physico-chemical interactions between MWCNT and water molecules.
4. The pH level of nanomodified cement pastes are not changed, the maximum increase of electrical conductivity by 0.59 mS/cm was reached for cement paste modified by MWCNT dispersion in the dosage of 0.5% by weight of cement.
5. The introduction of MWCNT dispersion changes the flow behaviour of cement pastes for 5 min after mixing. The MWCNT dispersion does not influence significantly on rheological behavior of cement paste for 120 min after mixing.
6 The maximum decrease in yield stress for 5 min after mixing by 30.7% is observed for cement paste modified by MWCNT dispersion in dosage 0.25% by weight of cement. The maximum increase of plastic viscosity for 5 min after mixing by 29.6% was established for cement pastes with MWCNT dispersion in the dosage 0.25% by weight of cement.

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