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Modification of cement systems by carbon nanotubes

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ABSTRACT

The nanoparticles and nanostructures such as nano silica, nano metakaolin, titanium dioxide and aluminium oxide nanoparticles, graphite nanomaterials, carbon nanotubes are used for modification of composite materials in construction industry. The considerable attention of researchers is focused on the investigation of cement systems modified by carbon nanotubes (CNT). The present research describes the generalized data about modification of cement systems by CNT suspension in fresh and hardened state. The influence of carbon nanotubes on setting time of cement paste, rheological and mechanical properties of nanomodified cement systems are demonstrated in the present research.

keywords: carbon nanotubes; suspension; cement paste; cement composites.

1. Introduction

Application of nanoparticles and nanostructures contributes to the generation new matrix materials with advanced properties in medicine, energy sector, electronics, metallurgy and other fields. The number of researches present the changes in properties of nanomodified materials in construction industry as well [1-5]. For example, authors of research [1] established the decrease of flow-ability of ultra-high strength concrete (UHSC) modified by nano-CaCO₃ and nano-SiO₂ and identified the optimal dosage for improvement of flexural and compressive strength of UHSC. The optimal dosages were in the range from 1.6 to 4.8 % and from 0.5 to 1.5% for nano-CaCO₃ and nano-SiO₂, respectively. The modification of concrete by nano metakaolin in the dosage 1% led to the strength development due to filling effect on 3-7 days and the pozzolanic reaction which took place after 14 days of storage [2]. Modification of cement composites by nano-TiO₂ and nano-Al₂O₃ separately and in combination with other additives changes the technological, rheological properties of cement systems and improves the mechanical properties of cement composites [3, 4].

Along with nano additives described above, the number of researches are devoted to the modification of cement matrix by carbon nanotubes (CNT). The outstanding mechanical, electrical, optical, thermal properties of carbon nanotubes make their investigation and future application perspective in terms of generation of concrete with advanced properties in fresh and hardened state [6-12]. The increase of compressive strength of nanomodified cement pastes by 40% was obtained by the researchers [6]. The research [7] demonstrates the improvement of porosity, compressive strength and electrical properties of cement composites modified by CNT. Despite on the ability of CNT to improve the properties of cement composites, their application in real practice are constrained due to not clear mechanisms of their action, particularly, in combination with other concrete additives and admixtures. The modification of cement systems by CNT associated with number of challenges, mainly, with distribution of CNT in the volume of aqueous suspension and into cement systems. The preparing of CNT suspension requires to pay attention to the type and concentration of used CNT, type and concentration of plasticizer used to distribute nanotubes, parameters of homogenizer etc. [13-15].

The aim of current research was focused on the investigation of influence of CNT on setting time of cement pastes, their rheological properties and mechanical properties of hardened cement mortar modified by CNT.

2. Experimental program

2.1 Materials

Portland cement without mineral additives CEM I 42.5 R conforming to EN 197-1 was used as a binder. Mineral composition of the cement is presented in Table 1.
Sand with fraction of 0/4 mm was applied as a fine aggregate conforming to the requirements of EN 12620. Potable water according to EN 1008 was used for preparation of cement pastes.

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tricalcium silicate (C₃S)</td>
<td>57.9</td>
</tr>
<tr>
<td>Dicalcium silicate (C₂S)</td>
<td>15.6</td>
</tr>
<tr>
<td>Tricalcium aluminate (C₃A)</td>
<td>7.5</td>
</tr>
<tr>
<td>Tetracalcium aluminoferrite (C₄AF)</td>
<td>11.9</td>
</tr>
</tbody>
</table>

Table 1. Mineral composition of cement.

The polycarboxylate ether (PCE) of MPEG type with specific gravity 1.100 g/cm³, pH up to 5 at 20°C and dry content equal to 50.5% was applied as plasticizer.

![Figure 1: Particle size analysis of MWCNT suspension.](image)

The MWCNT suspension was prepared from the masterbatch "Graphistrength CW 2-45" produced by the company "Arkema" (France). The masterbatch contains 45 wt. % of multi-walled carbon nanotubes (MWCNT) and 55 wt. % of carboxymethylcellulose (CMC). The MWCNT filament length is equal to 0.1–10 μm and diameter is equal to 15–20 nm. The concentration of "Graphistrength CW 2-45" in the suspension was taken equal to 1.0%. The procedure of homogenization of MWCNT suspension was consisted in the following. 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, the suspension 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 particle size distribution of MWCNT suspension, provided by analyzer DelsaNano C, Beckman Coulter with resolution of measurements placed from 0.6 nm to 7μm, after homogenization is presented in Figure 1. The dimension of MWCNT suspension particles was varied from 119 to 1070 nm with the average size up to 397.4 nm.

2.2 Methods

The cement pastes were prepared according to EN 480-1. The water to cement ratio for pastes was set to be 0.275. The amount of MWCNT suspension was equal to 0.5% by weight of cement (bwoc). The setting time test was carried out according to EN 480-2 by standard Vicant apparatus at temperature 20±2°C during the test.
Rheological test of cement pastes was performed in the following order. Primarily, MWCNT suspension was dissolved in potable water. After that, water together with MWCNT suspension was added to the cement. Cement paste was mixed for 180 s at high speed by using a mixer. Rheological properties of cement pastes were controlled in different time periods after paste mixing: 5, 30, 60, and 120 min at temperature 20 ± 2°C. The rotational rheometer Rheotest RN 4.1 with coaxial cylinders was used for rheological tests. Figure 2 presents the scheme of cylinder-measuring system of the rheometer. 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 a gap between them of about 1.5 mm and rotated during the test. Shear rate ranged from 100.0 s⁻¹ to 0.1 s⁻¹ during testing time.

![Figure 2: Scheme of cylinder measuring system Rheotest RN 4.1.](image)

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 yield stress (τ₀) and plastic viscosity (µ_pl) were determined based on linear approximation of flow curves (dependence between shear stress (τ) and shear rate(γ)) in the range from 0.1 to 100 s⁻¹ based on the Bingham model, expressed by following equation:

\[
\tau = \tau_0 + \mu_{pl} \cdot \gamma,
\]  

(1)

where τ - shear stress, Pa; τ₀ - yield stress of the cement paste, Pa; µ_pl - plastic viscosity of the cement paste, Pa·s; γ - shear rate, s⁻¹.

Water to cement ratio during the rheological test of cement pastes was set to be 0.30 for pastes modified only by MWCNT suspension and 0.24 for cement pastes modified MWCNT suspension and PCE, added in the amount of 0.6% by weight of cement (bwoc). The dosage of MWCNT suspension varied from 0.125 to 0.5% bwoc.

Standard prisms of size 40×40×160mm for determination the density, flexural and compressive strength were prepared with reference to EN 480-1 and EN 196-1. The mixtures with water to cement ratio equal to 0.5 and cement to sand ratio of 1:3 were produced. The MWCNT suspension was introduced in the amount of 0.5% bwoc. The density and strength of cement mortar were tested according to EN 1015-10, EN 1015-11, respectively. The dosages of MWCNT suspension was chosen according to the previous research [16].

3. Results and discussion

The results of setting time test of cement pastes are presented in Figure 3. The setting time test revealed the increase of setting time by 40 min for cement paste modified by MWCNT suspension in the dosage 0.5% bwoc. The significant changes in final setting time was not observed.
The flow curves (dependence between shear stress and shear rate) were obtained in the course of rheological test within 5, 30, 60, 120 min after mixing of cement pastes. The flow curves for cement pastes modified by MWCNT suspension with and without PCE within 5 and 120 min after mixing are presented in Figure 4 and 5, respectively. The flow curves for 30, 60 min are omitted due to not significant difference in comparison with rheological data for 120 min after mixing.

Figure 4: Flow curves of cement paste with dosage of MWCNT suspension 0.125, 0.25, 0.5% bwoc: a- within 5 min, b- within 120 min after mixing.

Figure 5: Flow curves of cement paste with dosage of MWCNT suspension 0.125, 0.25, 0.5% bwoc and PCE: a- within 5 min, b- within 120 min after mixing.

Approximation of experimental flow curves were performed according to Bingham model mentioned above. The rheological parameters, such as plastic viscosity and yield stress were expressed from these equations. The equations are presented in Table 2. The changes in plastic viscosity and yield stress for nanomodified cement pastes with and without PCE after 5 and 120 min of mixing are presented in Figure 6 and 7, respectively.
The plastic viscosity of cement pastes was increased with modification by MWCNT suspension. The maximum increase by 0.43 Pa·s (30.1%) was observed for 0.5% of MWCNT suspension bwoc in comparison with reference sample within 5 min after mixing. The plastic viscosity within 120 min after mixing did not change significantly. The combine modification of cement paste by PCE and MWCNT suspension was not revealed the significant changes within 5 and 120 min after mixing as well.

Figure 6: Plastic viscosity of cement pastes within 5 and 120 min after mixing.

The yield stress was decreased with modification by MWCNT suspension within 5 min after mixing and was not presented the significant changes within 120 min after mixing. The maximum decrease by

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**Table 2. Flow curves equations based on Bingham model.**

<table>
<thead>
<tr>
<th>MWCNT suspension content, % bwoc</th>
<th>After 5 min</th>
<th>After 120 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>τ=13.90+1.433γ</td>
<td>τ=12.22+2.507γ</td>
</tr>
<tr>
<td>0.125</td>
<td>τ=11.71+1.569γ</td>
<td>τ=10.934+2.568γ</td>
</tr>
<tr>
<td>0.25</td>
<td>τ=11.05+1.707γ</td>
<td>τ=10.76+2.561γ</td>
</tr>
<tr>
<td>0.5</td>
<td>τ=9.636+1.857γ</td>
<td>τ=10.95+2.536γ</td>
</tr>
<tr>
<td>0+ PCE</td>
<td>τ=13.09+2.112γ</td>
<td>τ= -12.89+2.311γ</td>
</tr>
<tr>
<td>0.125+ PCE</td>
<td>τ= -4.732+2.051γ</td>
<td>τ= -13.32+2.217γ</td>
</tr>
<tr>
<td>0.25+ PCE</td>
<td>τ= -14.22+1.991γ</td>
<td>τ= -7.926+2.160γ</td>
</tr>
<tr>
<td>0.5+ PCE</td>
<td>τ= -4.156+1.903γ</td>
<td>τ= -12.15+2.039γ</td>
</tr>
</tbody>
</table>

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**Figure 7: Yield stress of cement pastes within 5 and 120 min after mixing.**
4.3 Pa (30.9%) was obtained for cement paste modified by 0.5% bwoc of MWCNT suspension within 5 min after mixing. The introduction of PCE with and without MWCNT suspension contributes to the decrease of yield stress till 0 Pa within 5 and 120 min after mixing of cement pastes.

The test of hardened cement mortar revealed the enhancement in density, flexural and compressive strength.

**Figure 8:** Density of hardened cement mortar after 28 days of curing.

![Density of hardened cement mortar after 28 days of curing.](image)

**Figure 8** presents that the density of cement mortar modified by 0.5% of MWCNT suspension bwoc was increased by 51 kg/m³. **Figure 9a** demonstrates the increase of flexural strength of cement mortar with 0.5% of MWCNT suspension bwoc by 12.2% and 8.4% in comparison with reference sample in 7 and 28 days of curing, respectively. The compressive strength of cement mortar for the same dosage of MWCNT suspension bwoc was increased by 6.9 and 10.0% in 7 and 28 days of curing, respectively (Figure 9b).

**4. Conclusions**

The following conclusions are drawn in this study:
1. The setting time test revealed the increase of setting time by 40 min for cement paste modified by MWCNT suspension in the dosage 0.5% bwoc. The significant changes in final setting time was not observed. The retartartion effect of MWCNT may be explained by the possible physical interaction between them and cement particles.

2. The introduction of MWCNT suspension led to the changes in rheological properties of cement pastes. The plastic viscosity of cement paste modified by 0.50% of MWCNT suspension bwoc was increased by 30.1% in 5 min after mixing of cement paste and did not change in 120 min after mixing. The additional introduction of PCE was not revealed the significant changes in plastic viscosity of cement pastes.

3. The yield stress was decreased by 30.9% for cement paste modified by 0.50% of MWCNT suspension bwoc within 5 min after mixing. The changes of yield stress within 120 min after mixing of nanomodified cement pastes were insignificant. The introduction of PCE with and without MWCNT suspension led to the decrease of yield stress till 0 Pa.

4. The possible reason of observed changes in rheological properties of nanomodified cement pastes may be explained by quite small size of nanostructures and their steric interactions with cement particles, changes in zeta potential and value of surface tension in cement paste.

5. The density of hardened cement mortar with MWCNT suspension increased up to 51 kg/m³ in the dosage of 0.5% bwoc. The MWCNT suspension in the dosage 0.5% bwoc increased the flexural and compressive strength of hardened cement mortar by 8.5 and 10.0 %, respectively, in 28 days.

6. The changes in density, flexural and compressive strength of hardened cement mortar are caused by changes in its microstructure with modification by solid particles of MWCNT, which play role of crystallization center for cement hydration products.

**Conflict of Interest**

No conflict of interest was reported by the authors.

**References**


