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Experimental study of the behaviour of cement pastes in the presence of carbon nanotubes

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Abstract. One of the methods recently applied for the noticeably improvement of properties of cementitious materials is the use of the single or multi-walled carbon nanotubes (CNTs) as nano-reinforcements in cementitious materials. The positive action of CNTs highly depends not only on its nature, length and amount, but also on previous treatment of CNTs and quality of CNTs dispersion. It is important to obtain the effects of multi-walled CNTs, dispersed only in carboxyl-methyl cellulose – commercially available pellets without the use of any commercially available surfactants or plasticizers. The influence of dispersed CNTs on the rheological properties of fresh cement pastes and physical and mechanical properties of hardened specimens was analyzed in this work. Compared to the dynamic viscosity of pure distilled water smaller amounts of CNTs (0.00005–0.005%) reduce the dynamic viscosity down to the 15% whereas higher amounts of CNTs (0.05–0.5%) increase the dynamic viscosity from 1.3 to 4.7 times. Mechanical tests of hardened for 28 days cement paste specimens showed that smaller amounts of CNTs (0.00005–0.005%) increase the compressive and flexural strengths by 38.07– 42.3% and 40.1– 44.6%, whereas higher amounts of CNTs (0.05–0.5%) increase these strengths just by 21.11–18.82% and 18.33–6.6% respectively.

Keywords: multi-walled carbon nanotubes, fresh cement paste, dynamic viscosity, hardened cement paste, mechanical strength.

Introduction

Carbon nanotubes are a form of carbon which was first discovered in 1952 in Russia, but mostly ignored, then rediscovered in the 1991 at NEC's Fundamental Research Lab in Japan as a minor by-product of fullerene synthesis (Sumio, 1991). The structure of CNTs consists of nano-dimensions made up of rolled sheets of graphite. There are many ways of which a sheet of graphite is rolled up to form a tube such as zigzag, chiral and armchair are the names given to different types (Esawi & Farag, 2007). Verities of CNTs include single-walled nanotubes and multi-walled nanotubes. Single-walled nanotubes were discovered in 1993, they have only one wall which constitutes a tube, whilst multi-walled nanotubes have multi walls which can slide against other. The diameter of CNTs are on the scale of 1–100 nm, which are small that 50 000 of them could reach the diameter of one human hair. The surface area typically is in the range of ~100 000–700 000 m^2/kg (Peigney, Laurent, Flahaut, Bacsa, & Rousset, 2001). For single-walled nanotubes, the diameters of tubes in the range of few nanometers (1–10 nm), whilst they reached several tens of nanometers (5–100 nm) in the case of multi-walled nanotubes because their structure consists of many concentric cylinders held together by van der Waals forces (He, Kitipomchai, & Leiw, 2005), but they are less effective than those of single-walled nanotubes. The multi shell structure of multi-walled nanotubes is stiffer than the single-wall ones, especially in compression. Multi-walled nanotubes usually maintain the inter shell spacing close to that of the graphite inter-layer spacing of 0.335 nm (Lavin, Subramoney, Ruoff, Berber, & Tománek, 2002). Another advantage of multi-walled nanotubes over those of single-walled nanotubes is that large-scale synthesis can be easily achieved by performing several enhanced chemical vapor deposition method (Bandow et al., 2002). It is worth mentioning that multi-walled nanotubes are less expensive and more readily available than those of single-walled nanotubes. CNTs are widely considered to be the one of the prospective materials of the 21st century and bring new patterns to structural integrity (Liu, Zheng, Wang, & Jiang, 2005), cement-based materials (Sobolev & Shah, 2015) and other fields (Bandaru, 2007; Malarkey & Parpura, 2007; Harrison & Atala, 2007).

The use of nanotechnologies to improve the properties of cementitious systems is a rapidly developing area. Reinforcement of cementitious materials with different kind of fibers (such as polypropylene and nylon), natural cellulose (such as hardwood and softwood pulps), and inorganic fibers (such as steel, glass and carbon) is a common method to control the cracking processes (Musso, Tulliani, Ferro, & Tagliaferro, 2009). That is why CNTs are potential candidates for use as resistance to crack propagation additive (Makar, Margeson, & Luh, 2005; Li, Wang, & Zhao, 2007). CNTs have gained the interest of researchers for their noticeable high mechanical and tensile strength, thermal and unique electrical and chemical properties (Ajayan, 1999; Salvetat et al., 1999; Srivastava, Wei, & Cho, 2003; Makar & Beaudoin, 2003; Campillo, Dolado, & Porro, 2003; Li, Wang, & Zhao, 2005; Cwirzen et al., 2009; Cwirzen, Habermehl-Cwirzen, & Penttala, 2008; Yakovlev, Keriene, Gailius, & Girniene, 2006). Researchers (Cwirzen et al., 2009, 2008) have reported the increase (approx. 50%) in compressive strength of cement paste specimens when 0.045–0.15% of CNTs (by weight of cement) was added to the forming mixture. Approximately 70% (from 0.18 to 0.306 MPa) increase in compressive strength of cementitious foamed concrete specimens was obtained when 0.05% of CNTs (by weight of cement) was used in the forming mixture (Yakovlev et al., 2006). A significant reduction of the average pore diameter was observed in the specimens. A study (Laukaitis, Keriene, Kligys, Mikulskis, & Lekunaite, 2012) reports a considerable increase of crystallinity and compressive strength as well as decrease of thermal deformation in autoclaved aerated concrete specimens upon the addition of 0.1% (by weight of binder) of crushed carbon fibers.

CNTs production methods and forms (pellets, solutions or powders) can definitely affect the rheological properties of cementitious materials. In general, plasticizers in cementitious materials with CNTs additive are used. The aim of this paper was to estimate the influence of CNTs, used in different amounts (0% to 0.5% by weight of cement) on rheological properties of the fresh cement paste and physical or mechanical properties of the hardened cement paste specimens. It is important to determine the optimal amount of CNTs to be added to fresh cement pastes in order to improve the properties listed above.

Materials and methods of testing

GRAPHISTRENGTH CW2-45 pellets containing multi-walled CNTs of about 90% purity at 45% concentration (by weight), dispersed in carboxyl-methyl cellulose at 55% content (by weight) provided by ARKEMA company were immersed in 100 ml of hot (95–100 ºC) distilled water for 10 min (without mixing) and subjected to ultrasonic treatment for 5 min (disperser UZDN-2T). Prepared CNTs water solutions were diluted (according to the fresh cement paste composition) and measured. The same CNTs water solutions were used for preparation of fresh cement pastes. Ordinary Portland cement (OPC) CEM I 42.5 R, specific surface of 3190 cm^2/g was used. Mineral composition of clinker (in.): C3S – 63.98; C2S – 7.74; C3A – 6.38; C4AF – 12.68. Water to cement ratio in all specimens was the same (0.3). The amount of CNTs in the forming mixture varied from 0.00005 to 0.50000% (by weight of OPC) (see Table 1). The specimens were made and cured in compliance with EN 12390-2:2009. The specimens of 40×40×160 mm dimensions were kept in molds for 1 day in normal conditions and then hardened in water at 20 °C temperature for 27 days.

Table 1. The amount of CNTs in the water solutions (a) and fresh cement pastes with constant water to cement ratio (b)

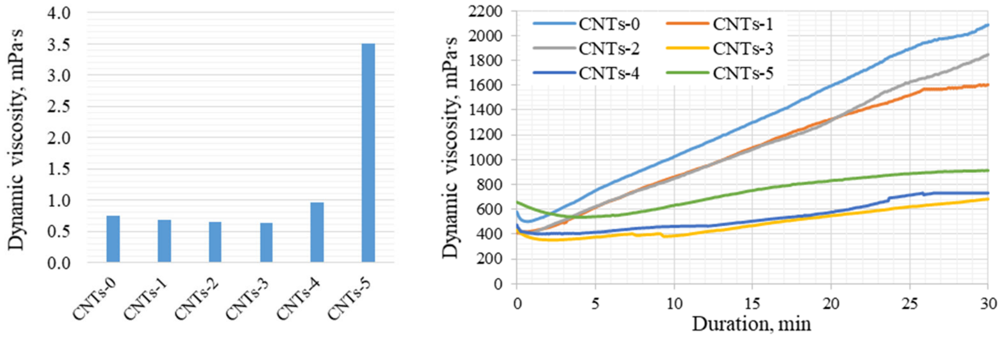
Specimen series	OPC, %	(a) CNTs, %	(b) CNTs, %
CNTs-0	100	0.00000	0.00000
CNTs-1	100	0.00017	0.00005
CNTs-2	100	0.00170	0.00050
CNTs-3	100	0.01700	0.00500
CNTs-4	100	0.1700	0.05000
CNTs-4	100	1.7000	0.50000

The effect of different amounts of CNTs on the dynamic viscosity of water solutions and fresh cement pastes was tested using the vibro-viscometer SV-10 (capacity – up to 12.000 mPa·s, accuracy – 0.01 mPa·s). The dynamic viscosity of water solutions and fresh cement pastes was measured immediately after the preparation and during 30 minutes.

Strength tests were performed with ALPHA 3-3000 S testing machine. Arithmetic averages of each 5 successful measurements are presented in the paper. The conventional tests were done in compliance with the following standards: EN 12390-3:2009, EN 12390-7:2009, EN 196-6:2010, EN ISO 1927-1:2012, EN 1402-6.

Research results and discussion

The studies of dynamic viscosity of water solutions have been carried out. The measurements of water solutions (Figure 1a) showed that smaller amounts (0.00017–0.017%) of CNTs decrease the dynamic viscosity down to the 15% compared to the viscosity of pure distilled water. In case when higher (0.17%) and the highest (1.7%) amounts of CNTs were used increased the dynamic viscosity of water solutions up to 30% and by 4.7 times compared to the dynamic viscosity of pure distilled water were observed. This increase may have been influenced by carboxyl-methyl cellulose, used in the production of the pellets containing CNTs. It is known that carboxyl-methyl cellulose acts as a thickener in water solutions. However, in water solutions with small (0.00017–0.017%) amounts of CNTs opposite processes occur and dynamic viscosity of the solutions decreases.

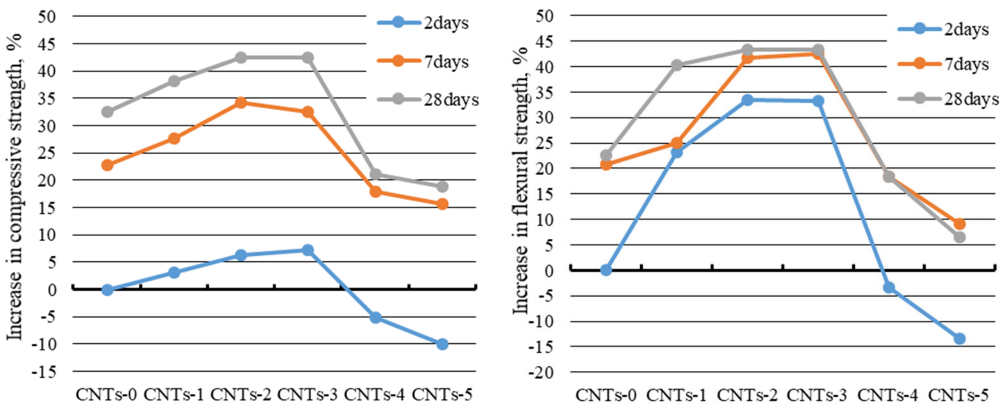


a) b)

Figure 1. Dynamic viscosity: (a) water solutions; (b) fresh cement pastes

It was determined that the initial dynamic viscosity in control paste (CNTs-0) rose to 610 mPa·s after mixing, and within 30 minutes, it increased until the highest value – 2100 mPa·s. When smaller amounts of CNTs (0.00005 and 0.00050%) were used in fresh cement pastes, the initial dynamic viscosity decreased to 400 mPa·s (approximately 20%). Practically, there was no difference in the dynamic viscosity between both fresh cement pastes within 20 minutes. During the last 10 minutes of the experiment, the dynamic viscosity in pastes CNTs-1 and CNTs-2 reached 1.610 mPa·s, and 1.870 mPa·s respectively. The lowest dynamic viscosity was observed in paste CNTs-3, where the change in dynamic viscosity during 30 minutes was from 390 to 570 mPa·s (Figure 1b).

Tests after two days of curing (see Figure 2a) showed that the compressive strength of specimen CNTs-0 reached 61 MPa (0%). 7.2% growth in compressive strength was observed in specimens, where CNTs amount in the mix was increased up to 0.005%. When CNTs amount in the mix reaches 0.05000% and 0.50000%, the compressive strength of the specimens drops accordingly by 5% and 10% compared to the strength of specimen CNTs-0. The same tendencies were observed after 7 days of curing. The increase in CNTs amount within range 0.00005–0.00500% increases the compressive strength up to 27.66 to 32.57%, compared to the strength of the control specimen (22.7%). Higher amounts of CNTs (0.05000% and 0.50000%) increase the compressive strength just by 17.84% and 15.6% respectively.



a) b)

Figure 2. Increase in strength: (a) compressive; (b) flexural

After 28 days of curing the compressive strength of specimens containing 0.00005–0.0005% of CNTs increases by 38.07% and 42.39% compared to the control specimen, whereas higher amounts of CNTs (0.05000% and 0.50000%) increase the compressive strength just by 22%. These results indicate that during the hardening period of 2–28 days, smaller amounts of CNTs (up to 0.00500%) significantly increase the compressive strength whereas higher amounts of CNTs does not have a significant impact on the compressive strength. The same tendency for smaller amounts of CNTs (0.025%, 0.05% and 0.1%) was observed in other research (Xu, Liu, & Li, 2015). The aforementioned results and references lead to the conclusion that if the amount of the CNTs in composition of the mix exceeds 0.00500%, a reduction in compressive strength can be predicted.

The same tendencies were observed in testing results of flexural strength (see Figure 2b). After two days of curing the flexural strength in specimens containing smaller amounts of CNTs increased up to 33.3%, whereas in specimens with higher amounts of CNTs, the strength decreased by 3.4% and 13.3% compared to the control specimen. After seven days of curing the difference in flexural strength between the control specimen (20%) and specimens containing smaller amounts of CNTs sometimes reached 42.5%, while the flexural strength of specimens containing higher amounts of CNTs was increased just by 17% and 9% compared to the strength of specimen CNTs-0. After 28 days of curing the above mentioned difference for the specimens containing smaller amounts of CNTs reached 44.6%, while for specimens containing higher amounts of CNTs the flexural strength was increased just by 18.3% and 6.6% compared to the strength of specimen CNTs-0. The results obtained in our study indicate that the trends of changes in flexural strength correspond to the changes in compressive strength, but the gain in flexural strength was higher than the gain in compressive strength.

Conclusions

The effects of multi-walled CNTs, dispersed in carboxyl-methylcellulose using ultrasonic treatment, on the properties of water solutions, fresh cement pastes and hardened specimens were investigated. It can be stated that 0.00005%–0.00500% amounts of CNTs have an insignificant effect on the rheological properties of fresh cement paste – decrease the dynamic viscosity of water solutions approximately 15%, whereas higher amounts of CNTs (0.05% and 0.5%) increase the dynamic viscosity from 1.3 to 4.7 times. It can be stated that 0.00005%–0.00500% amounts of CNTs increase the compressive strength of hardened cement paste by 38.07%, 42.2% and 42.39% and the flexural strength by 40.1%, 41.9% and 44.6% respectively after 28 days of curing. The test results proved that 0.05000–0.50000% of CNTs have a significantly negative effect on rheological and mechanical properties. These amounts of CNTs are marginal for cement paste compositions because higher amounts significantly deteriorate cement paste hydration parameters.

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