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The effect of multi-walled carbon nanotubes on the rheological properties and hydration process of cement pastes

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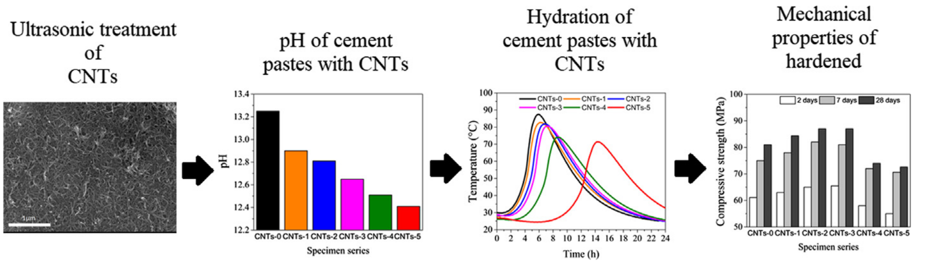
HIGHLIGHTS

- Dispersed CNTs (from 0.00005 to 0.005%) improve properties of cementitious materials.
- CNTs amounts above 0.005% decreased pH and viscosity of the fresh cement pastes.
- Lower values of pH lead to a retardation of setting and exothermic reaction time.
- Mechanical properties of specimens decreased, as well as water absorption increased.

GRAPHICAL ABSTRACT



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ABSTRACT

The properties of cementitious materials can be noticeably improved by the addition of carbon nanotubes (CNTs). It is important to detect the effects of the pellets containing multi-walled CNTs, dispersed in carboxyl-methyl cellulose, on the hydration process of fresh cement pastes, and physical or mechanical properties of hardened cement paste specimens, obtained without the use of commercially available surfactants and plasticisers, in order to use CNTs in cementitious materials more effectively. The influence of dispersed CNTs in different amounts (from 0 to 0.5%) on the pH and electrical conductivity values of water solutions and fresh cement pastes, as well as on the rheological properties, setting time and exothermic reaction of fresh cement pastes or on the physical and mechanical properties of hardened cement paste specimens was analysed in this work. It can be stated, that 0.005% is the marginal amount of CNTs, as amounts above 0.005% deteriorate the hydration parameters of cement pastes. This was confirmed by decreased values in electrical conductivity (approximately 17%), pH (approximately 6.8%) and dynamic viscosity (approximately 3 times) tests. Lower pH values lead to a significant retardation of the dissolution of cement minerals and this process is reflected in the setting time (prolonged by 110–130%) and maximum time (extended by 148%) or temperature (decreased by 18.4%) of exothermic reaction. Consequently, the mechanical properties of hardened cement paste specimens (after 28 days) decreased about 10%, as well as water absorption increased up to 10.6%.

1. Introduction

Nowadays, the use of nano additives is one of the ways suggested to enhance physical and mechanical characteristics of cementitious materials. The size of nanoparticles, due to enormous specific surface area, produces a greater effect on the filler compared to micro based materials [1]. CNT is an allotrope of carbon with cylindrical nanostructure. CNT have the length-to-diameter ratio of up to 132 000 000:1, significantly larger than any other material. These cylindrical carbon molecules have unusual properties, which are valuable for nanotechnology, electronics, optics and

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other fields of materials science and technology [2–5]. CNTs are categorized as single-walled nanotubes and multi-walled nanotubes. Individual nanotubes naturally align themselves into 'ropes' held together by van der Waals forces [6,7]. Cementitious materials are generally defined as quasi-brittle materials with low tensile strength and low toughness, which lead to the development of undesirable cracks in structures [8]. The use of nanotechnologies to improve the properties of cementitious systems is a rapidly developing area. Reinforcement of cementitious materials with different kind of fibres (such as polypropylene and nylon), natural cellulose (such as hardwood and softwood pulps), and inorganic fibres (such as steel, glass and carbon) is a common method to control the cracking processes [9]. That is why CNTs are potential candidates for use as resistance to crack propagation additive [10,11]. CNTs have gained the interest of researchers for their noticeable high mechanical and tensile strength, thermal and unique electrical and chemical properties [12–20]. Researchers [18,19] 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 [20]. A significant reduction of the average pore diameter was observed in the specimens. A study [21] 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 fibres. The results obtained by other authors [22] showed that the flexural strength of cement paste specimens containing short (0.2% by weight of cement) and long (0.1% by weight of cement) CNTs increased approx. 26.9% and 65% respectively after 28 days of curing compared to plain cement paste specimens. A study [23] showed that the index of flexural toughness increased up to 57.5%, when CNTs (0.08% by weight of cement) was used. Changes in the morphology of new formations with ultra-small amount (within 0.02%–0.0025% by weight of cement) of CNTs were evaluated and it was stated that such changes lead to a significant increase of mechanical strength in cementitious materials [1,24,25]. Authors [26] argue that the addition of CNTs (0.15%) to cementitious systems improve their compressive strength by 8%. CNTs are the best nano additives in terms of improving flexibility and enhancing the strength of ultra-high performance concrete [27].

Poor dispersion of CNTs is the main difficulty to incorporate them in cementitious materials. It leads to several defects in cementitious materials, decreases the reinforcing effect of CNTs [28–30]. Proper dispersion and mixing methods are known to be the major factors having an effect on the performance of such materials. Chemical and physical modifications are the methods that are commonly used for the dispersion of CNTs. The functional groups are introduced on the surface of CNTs using chemical agents, surfactants, high energy discharge, UV radiation or other processes [30,31] in chemical modification. Sometimes such treatment shows side-effects. The study [32] reported incompatibility issues during the hydration phase between cementitious material and the surfactants used for improving CNTs dispersion. There is still considerable disagreement with regard to the strength improvements in cementitious materials achieved by using CNTs [33–35].

Physical modification employs mechanical stress through processes such as crushing and ultrasonic treatment to activate the surface of CNTs [36]. Carboxylation procedure was used [11,17] to improve the bonding behaviour between CNTs and the cement paste, resulting in increased flexural (25%) and compressive (19%) strengths. Microscopy results revealed the bonding of cement paste hydration products by carbon nanotubes and bundles, as well as crack bridging when CNTs (2% by weight of cement) were dispersed in isopropanol using ultrasonic treatment [10]. In the study [24] it was established that CNTs could accelerate the hydration reaction of C_3S in Portland cement pastes. Other authors [10] argue that CNTs can affect early-age hydration and a strong bond is possible between cement paste and CNTs. The addition of nano additives can also decrease the initial and final setting time as reported in [37], and also makes the paste thicker, increases water demand, an thus makes the paste more cohesive [38]. Higher amount (1%) of CNTs, as reported in [39,40], did not affect the rate of hydration reaction. The above mentioned findings confirm that smaller amounts of CNTs (up to 0.2%) certainly improve the hydration and physical properties of cementitious materials, but the effect of a larger amount of CNTs is still poorly understood.

CNTs production methods and forms (pellets, solutions or powders) can definitely affect the rheological properties of cementitious materials. In general, plasticisers in cementitious materials with CNTs additive are used. For this reason the influence of CNTs on cement hydration process is not clear and can be obscured. For more effective use of CNTs in cementitious materials and to improve their compatibility with plasticizers it is important to detect the effects of pure CNTs on cement hydration process. This aspect is very relevant and is one of the main factors for the successful use of CNTs in cementitious materials. Few researchers have addressed the effect of CNTs (in the form of pellets) dispersed in water in different amounts (using ultrasonic treatment) on the dynamic viscosity and pH values of water solutions and fresh cement paste with no addition of plasticizer. 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 the pH and electrical conductivity values of water solutions and fresh cement pastes, and also on rheological properties, setting time and exothermic reaction of fresh cement pastes and physical or mechanical properties of hardened cement paste specimens. It is important to determine the optimal amount of CNTs to be added to cement pastes in order to improve the properties listed above.

2. Materials and methods of testing

2.1. Materials

Portland cement CEM I 42.5 R (PC) from UAB AKMENES CEMENTAS (Lithuania), with a specific surface of 3190 cm^2/g was used. Mineral composition of clinker (in %): C_3S – 63.98; C_2S – 7.74; C_3A – 6.38; C_4AF – 12.68.

GRAPHISTRENGTH CW2-45 pellets containing multi-walled CNTs of >90%, purity at 45% concentration (by weight), dispersed in carboxyl-methyl cellulose at 55% content (by weight) provided by ARKEMA company were used (Fig. 1).

2.2. Preparation of water solutions, forming mixtures and samples

For the preparation of water solutions, the pellets containing the necessary amount of CNTs – 0.0, 0.002, 0.02, 0.2, 2 and 20 g (this corresponds to the percentage content of the compositions in Table 1) were immersed in 100 ml of hot (95–100 °C) distilled water (characterized by pH of 5.8 and electrical conductivity of $5{\cdot}10^{-4}$ S/m) for 10 min without mixing. Afterwards, CNTs were subjected to ultrasonic treatment by the ultrasonic disperser UZDN-2T (frequency 22 kHz, power 480 W) for 5 min in 200 ml capacity cylinder. Prepared CNTs solutions were diluted with 1100 g of distilled water (this quantity was calculated according to the cement paste composition and the final amount resulted in 1200 g), and mixed with a mixer. Experimental water solutions

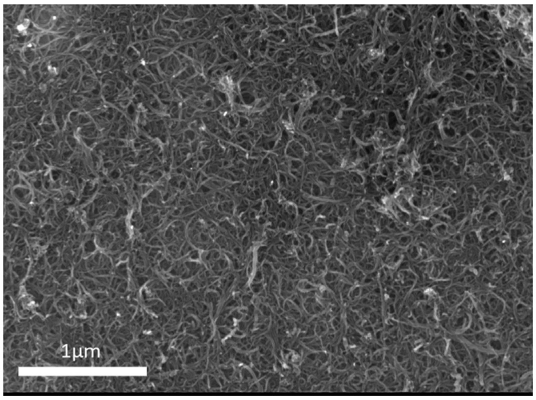


Fig. 1. Pellets, containing multi-walled CNTs, dispersed in water solution.

Table 1
The amount of CNTs in the cement paste compositions with constant W/C ratio – 0.3.

Specimen series	PC, %	Multi-walled CNTs, %
CNTs-0	100	0.0
CNTs-1	100	0.00005
CNTs-2	100	0.0005
CNTs-3	100	0.005
CNTs-4	100	0.05
CNTs-5	100	0.5

with CNTs were cooled to room temperature (20 °C), and then pH, electrical conductivity and dynamic viscosity were measured. The same water solutions with CNTs were used for the preparation of fresh cement pastes (Table 1). Water to cement ratio (W/C) in all specimens was the same (0.3). The amount of CNTs in the forming mixture varied from 0.00005 to 0.5% (by weight of cement). Such amounts of CNTs were selected basing on the experience of other authors [1,10,18,19,24,25]. The specimens were made and cured in compliance with EN 12390-2:2009. The specimens of 40 × 40 × 160 mm dimensions were kept in moulds for 1 day in normal conditions and then hardened in water at 20 °C temperature for 27 days.

2.3. Methods of testing

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 min. Electrical conductivity and pH tests for CNTs water solutions and for fresh cement pastes modified with CNTs were measured with the Mettler Toledo MPC 227 pH/conductivity meter: pH electrode INLAB 410 with measuring accuracy of 0.01, electrical conductivity electrode INLAB 730 with measuring range from 0 to 100 S/m.

The hydration characteristics of fresh cement paste were followed by an exothermic profile in accordance with ALCOA methodology [41]. The heat generated in exothermic reactions of cement minerals in fresh cement paste was measured at 20 °C using 1.5 kg specimens placed in an insulated 10 × 10 × 10 cm textolite mould. A thermocouple (type T) was embedded in the specimen and linked to data capture system to record temperature as a function of time.

The development of specimen structure was evaluated by means of ultrasonic pulse velocity (UPV) method using the tester Pundit 7. The values of UPV were obtained after hardening and drying of the specimens. Specimens were placed between two ultrasonic transducers (transmitter and receiver) operating at the frequency of 54 kHz. The transducers were pressed against the specimens at two strictly opposite points. Vaseline was used to ensure a good contact. The ultrasonic pulse velocity (V) was calculated using the Eq. (1):

$$V = \frac{l}{\tau} \cdot 10^6 \tag{1}$$

here l is a distance between cylindrical heads, τ is time of pulse spread.

Compressive 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.

3. Research results and discussion

3.1. Properties of water solutions

3.1.1. Dynamic viscosity

Dynamic viscosity measurements of water solutions (Table 2) showed that smaller amounts (0.002–0.2 g) of CNTs reduce the dynamic viscosity down to the 15% compared to the viscosity of pure distilled water. Higher (2.0 g) and the highest (20 g) amounts of CNTs increased the dynamic viscosity up to 30% or by 4.7 times compared to the dynamic viscosity of pure distilled water. 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 (0.002–0.2 g) amounts of CNTs opposite processes occur and the dynamic viscosity of the solution decreases.

3.1.2. pH and electrical conductivity

In order to better understand the behaviour of CNTs in water solutions, electrical conductivity and pH measurements were taken. It is known that electrical conductivity values depend on the amount of ions in water solution. Research results presented in Table 2 prove the influence of CNTs on the electrical conductivity of the solution. With higher amounts of CNTs in water solutions, electrical conductivity values increased from $15{\cdot}10^{-4}$ to $245{\cdot}10^{-4}$ S/m (16.3 times), whereas pH values dropped from 6.89 to 5.70 respectively. It is important to note that pure distilled water not subjected to ultrasonic treatment has pH of 5.8. It means that ultrasonic treatment changes water pH from 5.80 to 6.89.

Presumably, CNTs pellets are not absolutely inert. It is possible that after ultrasonic treatment in hot water, CNTs binding material (carboxyl-methyl cellulose) present in the pellets passes into water solution and influences electrical conductivity and pH of the solution. According to research findings [42], carboxyl-methyl cellulose is a weak acid able to reduce pH of water solution.

Table 2
Dependence of dynamic viscosity, pH and electrical conductivity of water solutions on the amount of CNTs after ultrasonic treatment.

Amount of CNTs in water (1200 g) solution, g	Dynamic viscosity, mPa·s	pH	Electrical conductivity, S/m
0	0.74	6.89	$15{\cdot}10^{-4}$
0.002	0.68	6.75	$83{\cdot}10^{-4}$
0.02	0.65	6.6	$98{\cdot}10^{-4}$
0.2	0.63	6.42	$125{\cdot}10^{-4}$
2.0	0.96	6.07	$159{\cdot}10^{-4}$
20.0	3.5	5.78	$245{\cdot}10^{-4}$

3.2. Properties of fresh cement pastes

3.2.1. Dynamic viscosity

Usually, researchers provide the brand names of surfactants, but do not indicate how CNTs should be used. Surfactants have an effect on pH values of the solution and thus can also affect the rheological properties of cement paste [17,20–22,26,43–46]. The initial dynamic viscosity in control specimen (CNTs-0) reached 610 mPa·s after mixing and after 30 min it increased until the highest value 2100 mPa·s. When minimal amounts of CNTs (0.00005 and 0.0005%) were used in fresh cement pastes, the initial dynamic viscosity decreased to 400 mPa·s (approximately 20%), see Fig. 2. Practically, there was no difference in the dynamic viscosity between both fresh cement pastes within 20 min. During the last 10 min of the experiment, the dynamic viscosity in specimen CNTs-1 reached 1.610 mPa·s, and 1.870 mPa·s in specimen CNTs-2. The lowest dynamic viscosity was observed in specimen CNTs-3. The change in dynamic viscosity during 30 min was from 390 to 570 mPa·s.

The results obtained by some other researchers [19] reveal the same tendencies. Opposite results are reported in some papers [47] showing that relatively small (0.038 and 0.075%) amounts of CNTs by weight to cement paste mixture had worsened rheological properties of the paste. Presumably, the difference of the results is influenced by the type of CNTs surfactants used. Tests with two different types of surfactants used for CNTs dispersion, namely Pluronic F127 and sodium dodecylbenzene sulfonate (SDBS) (pH 7–10) [48] revealed that the use of SDBS resulted in more agglomerates of CNTs, even at lower CNT concentration. Pluronic is more effective in reducing the size of CNT clusters. Authors of the paper note that the chemical structure of Pluronic F-127 contains polyethylene oxide (PEO) side chains similar to commonly used polycarboxylate super plasticizers responsible for the dispersion of cement particles and the fluidity of mortar. It is well known that polycarboxylate super plasticizers produce acidic pH in water solution and thus have a greater effect compared to SDBS producing alkaline pH.

In the mixes containing 0.05% and 0.5% of CNTs (CNTs-4 and CNTs-5) the dynamic viscosity increased from 480 and 675 mPa·s to 720 mPa·s and 940 mPa·s after 30 min. These results are confirmed by other researchers [49] who found that the addition of CNTs in amounts of 0.1–2% by weight of cement leads to the reduction in the workability and viscosity [43] of cement pastes, because of CNTs agglomeration. It should be noted that in general the studied amounts of CNTs had lowered the dynamic viscosity of fresh cement pastes.

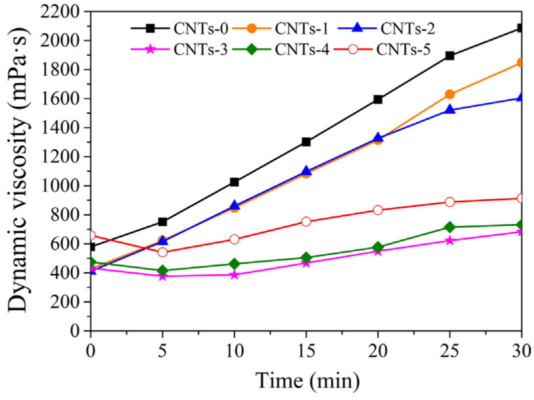


Fig. 2. Dependence of dynamic viscosity of fresh cement pastes on the amount of CNTs in the composition.

3.2.2. pH and electrical conductivity

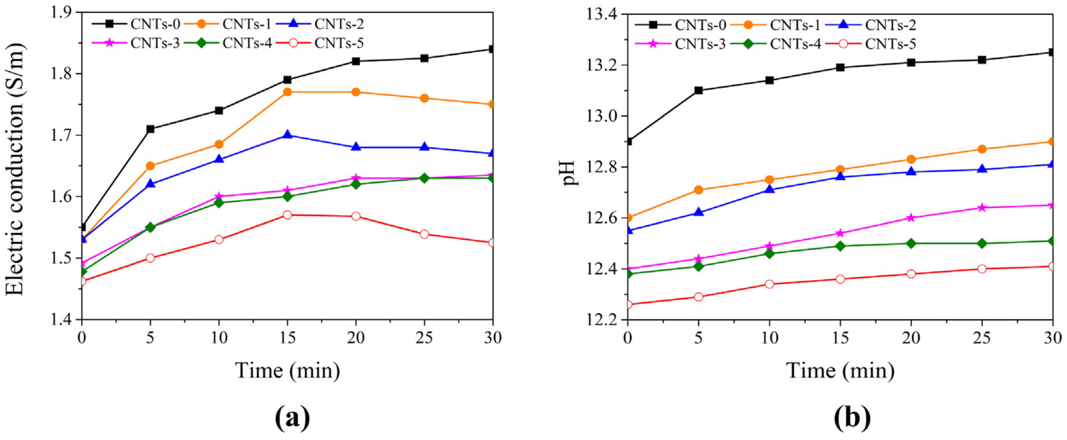
Electrical conductivity and pH measurements in cement pastes can help to characterize the progress of cement hydration in the presence of CNTs. Tests were performed within 30 min because significant and fast increase of electrical conductivity during this period describes the process of cement minerals dissolution and penetration of ions into the solution. Additives have the greatest effect at this specific stage because in later stages electrical conductivity is stabilized by the appearance of crystal germs. The growth of hydrates and reduction of electrical conductivity started at the point where stable electrical conductivity values were achieved.

Within 30 min of the measurement, electrical conductivity values of control specimen (CNTs-0) changed from 1.55 to 1.84 S/m (Fig. 3). The increased amount of CNTs in cement paste from 0.00005 to 0.5% slightly reduces the initial electrical conductivity values from 1.53 to 1.46 S/m. Lower amounts of CNTs (0.00005 and 0.0005%) have less significant influence, whereas higher levels reduce electrical conductivity values approx. 5% – to 1.46 S/m. Test results showed that the smaller amounts of CNTs in cement paste were used, the higher electrical conductivity values after 30 min were achieved. The difference in electrical conductivity between the control specimen and the specimen with the highest amount of CNTs was 0.32 S/m (approximately 17%). These results show that CNTs lowered electrical conductivity of fresh cement pastes, influenced dissolution of cement minerals and in such a way retarded the hydration process.

The test showed that pH values in control specimen CNTs-0 increased from 12.9 to 13.3 within 30 min (Fig. 3). Like in electrical conductivity tests, lower amounts of CNTs (0.00005 and 0.0005%) have less influence on the initial pH in the fresh cement paste. Noticeable changes were observed when higher amounts of CNTs were added. Similarly to electrical conductivity tests, pH test results revealed that the lower amount of CNTs was used in fresh cement pastes, the higher pH values were obtained after 30 min. In fresh cement pastes CNTs act in the same way as in water solutions, where CNTs lower pH values (see Table 2). The highest amount of CNTs can reduce the pH of fresh cement paste to 6.8%. Apparently, CNTs retard the hydration of cement minerals because they decrease electrical conductivity and pH of fresh cement pastes. In general, all measurements of dynamic viscosity, pH and electrical conductivity of fresh cement pastes correlate. However, the dynamic viscosity decreases only to a certain limit (the same tendency was observed in water solutions with CNTs). Presumably, this reduction is influenced by carboxyl-methyl cellulose, characterized by acidic pH value.

3.2.3. Setting time of fresh cement paste

The results of initial and final setting times of fresh cement pastes are presented in Table 3. The analysis of obtained results showed that lower amounts of CNTs in fresh cement pastes practically do not have any influence on the initial setting time. When CNTs amount in fresh cement paste reaches 0.005%–0.5%, the initial setting time increases to 190, 228 and 357 min. The percentage change in the initial setting time was calculated in specimens with CNTs and compared to the initial setting time of the control specimen for better understanding of the effect of CNTs amount on the initial setting time. Higher CNTs amount prolongs the initial setting time as follows: 0.00005% by 3.2%, 0.0005% by 6.45%, 0.005% by 25.1%, 0.05% by 47% and 0.5% by 130%. Some researchers [50] state the opposite reporting that the addition of 0.05%–0.5% CNTs by weight to mortar mixes cause the initial setting time to reduce. The tested mixes modified with CNTs required almost 25% less time to set compared to the plain mixture. Presumably the results obtained by other authors [47,49] may be influenced by different characteristics of the surfactant used in the mix.



(a)

(b)

Fig. 3. Dependence of electrical conductivity and pH of fresh cement pastes on the amount of CNTs in the composition.

Table 3
Dependence of initial and final setting times of fresh cement pastes on the amount of CNTs in the composition.

Specimen series	CNTs-0	CNTs-1	CNTs-2	CNTs-3	CNTs-4	CNTs-5
Initial setting time, min	155	160	165	194	228	357
Final setting time, min	200	220	225	259	288	420
Increase (*) of the initial setting time, %	–	3.20	6.45	25.1	47.0	130
Increase (*) of the final setting time, %	–	10.0	12.5	29.5	44.0	110

[*] Calculations of the percentage changes in initial and final setting times were compared to the control specimen of fresh cement paste.

The final setting time measurement results showed that the increased amount of CNTs up to 0.05% in fresh cement pastes gradually increases the final setting time (prolongs it from 200 to 290 min). The final setting time increased to 420 min when CNTs was added at 0.5%. The same calculations of the percentage change in the final setting time between the control specimen and specimens with CNTs show that amounts from 0.00005% to 0.005% prolong the final setting time by 29.5%, 0.05% by 44% and 0.5% by 110%. Research results showed that CNTs amount above 0.005% may significantly retard the hydration of cement minerals.

3.2.4. Maximum temperature and time of exothermic reaction

Fresh cement pastes with different amounts of CNTs were tested to estimate whether the heat released during cement hydration has an effect on the temperature of specimens. Detailed research into the thermal profiles of hydration process in fresh cement pastes with CNTs reflects the change in the maximum temperature and time of exothermic reaction. The test results showed that the increase of CNTs in cement mix composition gradually reduces the mix temperature from 30 to 26 °C. Changes in specimen CNTs-0 hydration temperature (Fig. 4) showed that the duration of induction period is 4 h, time of exothermic reaction appears at 5.8 h and the maximum temperature of exothermic reaction reaches 87.5 °C. When the amount of CNTs in fresh cement paste is increased (from 0.00005% to 0.5%), the duration of induction period prolongs from 4.2 to 10 h and the time of exothermic reaction prolongs from 6.1 to 14.4 h (Fig. 4). The maximum temperature of exothermic reaction decreases from 82.5 to 71.6 °C. For better explanation how CNTs amount can impact the hydration reaction, the percentage increase in time of exothermic reaction was calculated and compared to time of exothermic reaction in the control specimen (Table 4). The calculations showed that CNTs in amounts 0.00005%–0.005% prolonged the time of exothermic reaction by 19%, 0.05% of CNTs prolonged it by 36.2% and 0.5% of CNTs prolonged it by 148.3%. Calculations of the percentage reduction of the maximum temperature of exothermic reaction in comparison to the control specimen showed that 0.00005%–0.005% of CNTs reduced the temperature by 7.8%; 0.05% of CNTs reduced it by 15.28% and 0.5% of CNTs reduced it by 18.4%.

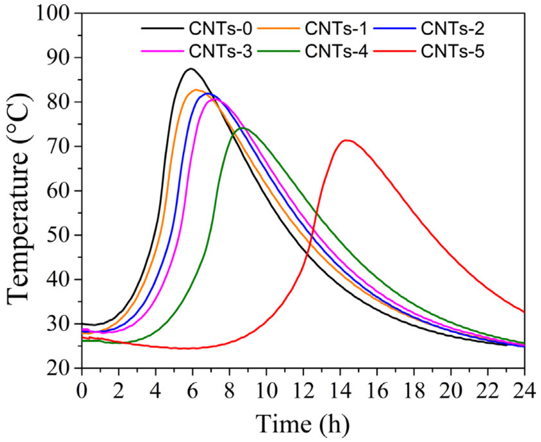


Fig. 4. Dependence of temperature and time of exothermic reaction of fresh cement pastes on the amount of CNTs in the composition.

3.3. Properties of hardened specimens

3.3.1. Compressive strength

Tests after two days of curing showed that the compressive strength of specimen CNTs-0 reached 61 MPa. 7.3% growth in strength was observed in specimens, where CNTs amount in the mix was increased up to 0.005% (Fig. 5). The same tendency was indicated by other authors [20–26,51]. When CNTs amount in the mix reaches 0.05% and 0.5%, the compressive strength of the specimens drops by 5% and 10% compared to the strength of specimen CNTs-0. The same trends were observed after 7 days of curing. The increase of CNTs amount within 0.00005%–0.005% limits increases the compressive strength up to 9.3%, compared to the strength of the control specimen (75 MPa). Higher amounts of CNTs (0.05% and 0.5%) reduce the compressive strength by 4% and 6.7%. After

Table 4
Dependence of temperature and time of exothermic reaction of fresh cement pastes on the amount of CNTs in the composition.

Specimen series	CNTs-0	CNTs-1	CNTs-2	CNTs-3	CNTs-4	CNTs-5
Maximal temperature of the exothermic reaction, °C	87.4	82.6	81.5	80.6	74.1	71.3
Maximal time of the exothermic reaction, h	5.80	6.10	6.60	6.90	9.10	14.4
Reduction ([*]) of temperature of the exothermic reaction, %	–	5.49	6.70	7.80	15.3	18.4
Increase ([*]) in maximal time of the exothermic reaction, %	–	5.20	13.8	19.0	56.9	148

[*] Calculations of the percentage changes in temperature and time of exothermic reaction were compared to the control specimen of fresh cement paste.

28 days of curing the compressive strength of specimens containing 0.00005%–0.005% of CNTs by 6.5% and 7.4% compared to the control specimen, whereas higher amounts of CNTs (0.05% and 0.5%) reduce the compressive strength by 8.7% and 9.8%. These results indicate that during the hardening period of 2–28 days, smaller amounts of CNTs (up to 0.005%) increase the compressive strength by 7%–9%, whereas higher amounts of CNTs reduce the compressive strength by 7–10%. The same trends for smaller amounts of CNTs (0.025, 0.05 and 0.1%) were observed in other studies [51]. The addition of 0.025%, 0.05% and 0.1% CNTs increased the 7-days compressive strength by 9.4%, 18.32% and 21.78%, respectively, whilst the 28-days compressive strength increased by 6.25%, 12.73% and 14.62%, respectively. Other authors [9,52,53] obtained that higher amounts of CNTs (0.3%–1%) decreased the compressive strength from 7% to 13.18% after 28 days of curing. Higher levels of surfactant may also produce a negative effect caused by air bubbles in the mix. The air bubbles lead to a large decrease of the compressive strength of CNTs reinforced cement-based composites. The influence of dispersants on the properties of CNTs reinforced cement-based materials was also observed by other authors [54]. Researchers [55] indicated that SEM images of specimens with higher CNTs indicated the appearance of micro-cracks in the microstructure was obtained. In addition to micro-cracks, the agglomeration of CNTs around cement grains was observed. These agglomerates lead to partial hydration of cement grains and produce hydrated product having weak bond. The aforementioned results and references lead to the conclusion that if the amount of the CNTs in composition of the mix exceeds 0.005%, a reduction in compressive strength can be predicted.

3.3.2. Flexural strength

Similar trends were observed in flexural strength testing results. 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 strengtht decreased 3.4% and 13.3% compared to the control specimen (Fig. 6). After seven days of curing the difference in flexural strength between the control specimen and specimens containing smaller amounts of CNTs sometimes reached 19.5%, whereas the flexural strength of specimens containing higher amounts of CNTs was 1.5% and 9% below the flexural strength of the control specimen. After 28 days of curing the above mentioned difference for the specimens containing smaller amounts of CNTs reached 17.8%, whereas for specimens containing bigger amounts of CNTs the flexural strength was 2.8% and 8.3% below the flexural strength of the control specimen. The same trends for smaller amounts of CNTs (0.025%–0.1%) were observed in the study [43,44,47] and for higher amounts of CNTs (1%) with decrease in flexural strength in the study [52]. The addition of 0.08% CNTs exhibited the optimum content [23]. 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 bigger than the gain in compressive strength.

3.3.3. UPV

UPV tests revealed the compaction of specimens and structure development during the setting (Fig. 7) [56] and essentially confirmed the results of compressive strength tests. The UPV in the control specimen was 3820 m/s after two days of curing. The increase of CNTs amount in the mix up to 0.005% gradually increased the UPV to 3860 m/s. In specimens with higher amounts of CNTs (0.05% and 0.5%) the UPV values reached 3805–3790 m/s. A significant increase of the UPV value from 4050 to 4110 m/s was recorded in specimens containing smaller amounts of CNTs after seven days of curing. This can be attributed to the fact that CNTs can fill in the pores between the hydration products of Portland cement [55]. In specimens with higher amounts of CNTs UPV values reached 3930 and 3900 m/s, showing 0.8% and 1.52% reduction of UPV compared to the control specimen.

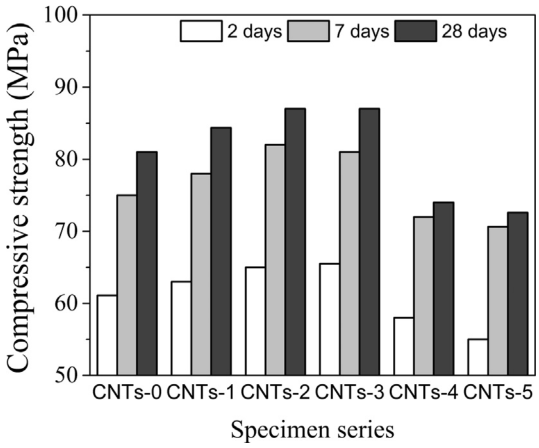


Fig. 5. Dependence of compressive strength of hardened specimens on the amount of CNTs in the composition.

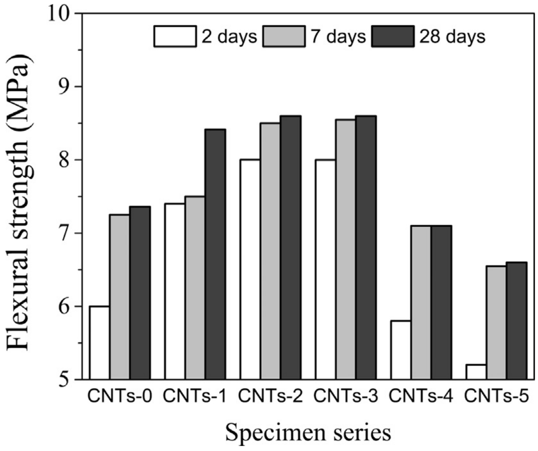


Fig. 6. Dependence of flexural strength of hardened specimens on the amount of CNTs in the composition.

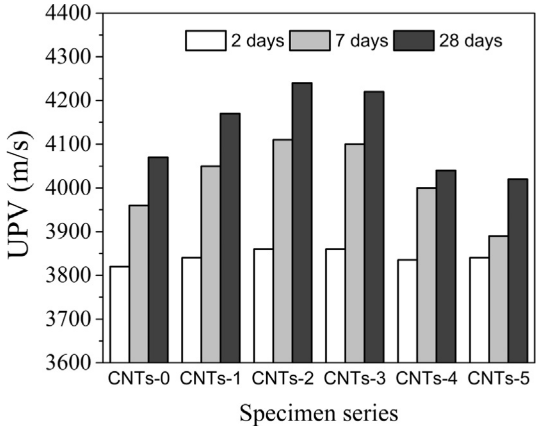


Fig. 7. Dependence of UPV of hardened specimens on the amount of CNTs in the composition.

Longer curing time (28 days) promotes the compaction of specimen structure and in specimens with the minimum amount of CNTs the UPV values were 4170–4240 m/s, representing a 4.2% increase compared to the control specimen. In specimens higher amounts CNTs the UPV value increased to 4040 and 4020 m/s, i.e. 0.73% and 1.23% less compared to the control specimen.

3.3.4. Water absorption

Observations of water absorption kinetics in the specimens revealed the reduction in the rate of water absorption during the testing time (28 days). The analysis of water absorption kinetics (Fig. 8) showed that CNTs content up to 0.005% in specimens cured for 2 days reduced water absorption values by 11.4%, 1.8%, 3.1% and 7.6% after 30, 60, 90 min and 24 h in comparison to the control specimen. In specimens containing 0.5% of CNTs water absorption values grew by 1.6%, 1.2%, 9.8% and 8.7%. After 28 days of curing, the decrease in water absorption values followed a similar trend (Fig. 9). Compared to the control specimen, the increase of CNTs content up to 0.005% in fresh cement paste composition resulted in 6.8%, 8.1%, 8.2% and 10% lower water absorption values after 30, 60, 90 min and 24 h, whereas at 0.5% content of CNTs in fresh cement paste the water absorption values increased by 2.7%, 10.5%, 8.2% and 10.6%.

The results of water absorption tests with smaller amounts of CNTs up to 0.005% in specimens are confirmed by other researchers [55,57] who state that CNTs reduce the total pore volume and act as the filler of voids; that explains why the addition of 0.015%–0.045% of CNTs leads to the reduction of water absorption. Alternatively to the findings with higher amounts of CNTs in our study, other researchers [58] report that higher amounts of CNTs (0.5%, 1% and 1.5%) caused a decrease in water absorption. I our case higher amounts of CNTs (0.05% and 0.5%) produce porous structures with voids and thus reduce the strength properties of the specimens.

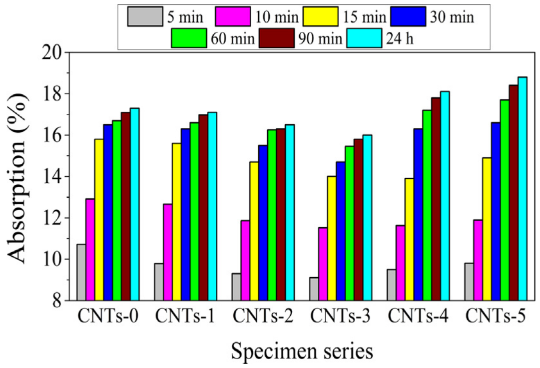


Fig. 8. Dependence of water absorption of hardened specimens on the amount of CNTs in the composition after 2 days of curing.

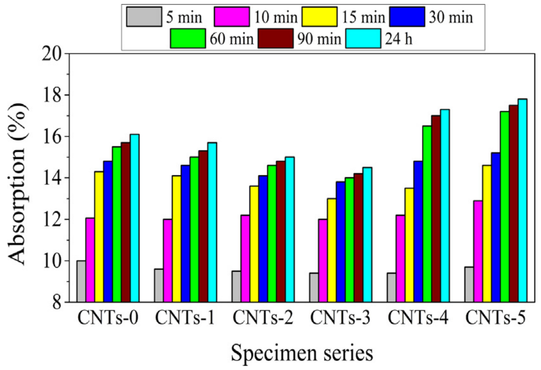


Fig. 9. Dependence of water absorption of hardened specimens on the amount of CNTs in the composition after 28 days of curing.

4. Conclusions

The effects of multi-walled CNTs, dispersed in carboxyl-methyl cellulose using ultrasonic treatment, on the properties of water solutions, fresh cement pastes and hardened specimens were investigated.

CNTs dispersed in carboxyl-methyl cellulose gradually increase the electrical conductivity and decreases the pH of water solutions. Lower amounts of CNTs (0.00005%–0.005%) 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. CNTs in fresh cement paste reduce the electrical conductivity of the paste (down to 17%), impede the penetration of ions to the solution, decrease pH (down to 6.8%) and viscosity (by 67.5%) of the paste. Lower pH significantly retards the dissolution of cement minerals, which is reflected in more than twice longer initial and final setting times of the cement paste, almost three times longer exothermic reaction time and temperature drop by 18.4%. It can be stated that 0.00005%–0.005% amounts of CNTs have an insignificant effect on the rheological properties of cement paste (retard cement hydration period not more than 19%), increase the compressive strength of hardened cement paste by 7.3%, 9.3% and 7.4% and the flexural strength by 33.3%, 19.5% and 17.8% after 2, 7 and 28 days of curing respectively, make the structure more compact (after 2, 7 and 28 days of curing the UPV values increase by 1%, 3.8% and 4.2% respectively), and lead to the reduction of water absorption up to 10% in the specimens cured for 28 days.

The test results proved that 0.05%–0.5% 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 of CNTs significantly deteriorate cement paste hydration parameters, structure development and produce a voided porous structure with poorer strength properties.

Conflict of interest

None.

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