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The Multi-Walled Carbon Nanotubes Effect on the Physical-Mechanical Characteristics of Lightweight Concrete

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Abstract

Obtaining high-strength and high-quality concrete with a complex of mechanical and operational properties is successfully solved by modifying its structure with additives of various functional purposes. This article presents the results of a study of the effect of modifiers based on carbon nanotubes (CNTs) on the strength characteristics of lightweight concrete. It was found that the introduction of low concentrations of modifiers based on carbon nanotubes significantly accelerates the curing of cement stone and concrete, especially in the early stages of hardening. The use of nanostructural modifiers in building composites, in particular in light concrete compositions, will not only provide improved characteristics, but will also reduce the consumption of initial components while maintaining the physicomechanical characteristics of light concrete.

Keywords

Carbon nanotubes (CNTs); lightweight concrete; compressive strength; tensile strength, modifiers.

Introduction

Today, science offers a wide range of additives to improve the quality of concrete. In this case, it is assumed that while maintaining strength, while maintaining or saving binder consumption, the strength of concrete increases and the workability of the concrete mix improves. The cost of the most famous additives, i.e. plasticizers, superplasticizers, etc. varies widely in the country and abroad. High prices for the most famous domestic and foreign additives increase the cost of the final product; therefore, not all manufacturers seek to use these additives [1].

In recent decades, nanosized particles have been used to modify cement composites, as well as chemical and mineral additives from nanowires made from fullerene nanotubes to quantum dots and quantum corals [2].

The use of certain nanosized particles as a modifier of various building materials depends on the composite structural formation, conditions for increasing the operational properties and composite structure parameters [3].

Concrete is a brittle material having a binder in the form of a cement mortar having a porous structure including micropores and mesopores. The nature of the concrete mix and its changes are mainly determined by cement hydration [4].

In most cases, the use of carbon nanotubes (CNTs) in cement composites is intended to create a reinforcing effect and increase the strength and performance characteristics. In addition, the well-known advantages of these materials include extremely high strength [5], Young's modulus [6], elasticity index [7], favorable electronic properties [8], and heat resistance [9]. In the mesoporous structure of concrete, nanosized particles can be used as a filler, and contribute to a denser structure of the material, as well as prevent the cracks' development in the early stages of hardening and improve the quality of the interfacial structure of the aggregate matrix as a whole. Therefore, with the help of carbon nanotubes it is possible to obtain more durable and rigid concrete [10 – 12].

Most researchers have focused on nanoparticle distribution methods compatible with Portland cement chemistry. The main approach is to use universal modifiers, such as super- and hyperplasticizers as dispersing agents [13].

Typically, the mechanical properties of concrete, such as (compressive strength and tensile strength), are low, especially when the age of the concrete is less than 14 days, the cement is not fully hydrated, and the strength properties of concrete are much lower than the strength characteristics of concrete in 28 days [14]. In addition, during the first 14 days of the concrete hydration process, shrinkage causes significant deformations and tensile stresses that lead to cracking [15].

Researchers have developed a number of methods to prevent early cracking of concrete, such as using shrink mixes for internal hardening or adjusting the mix ratio [16]. However, these methods are not universal and have a great effect on the strength of concrete for 28 days. Fiber concrete is an alternative because adding fibers can increase the strength properties of concrete to mitigate cracking problems. The use of carbon nanotubes of CNTs is considered one of the most promising options, due to their high strength, as well as unique chemical, thermal, and electrical properties [17]. Since the first mention of CNTs in literary sources, more and more researchers have been dealing with the problems of using cement materials reinforced with carbon nanotubes [18].

There are two main technical barriers to the use of CNTs in a wider range of applications, because of the aggregation of nanotubes due to van der Waals forces, and the hydrophobic nature of nanotubes, which could jeopardize their adhesion to cement materials. The physical and chemical treatment of CNTs is used to speed up the process of distribution and binding of CNTs with cement materials, but the results of increasing the strength characteristics are rather contradictory [19 – 22].

It was experimentally found that CNTs affect not only mechanical properties, but also heat resistance and shrinkage. Strength increase occurs. mainly due to the effect of cross-linking of nanotubes in concrete microcracks. On the other hand, CNTs form a denser microstructure of concrete as a fine filler.

In addition, until now, studies of the strength of concrete with the addition of nanomaterials have been carried out mainly on concrete samples at the age of 28 days. The set of concrete strength at an earlier date is not well understood. However, it is reported that the increase in strength depends on the level of cement hydration. It was reported that the use of nanosilica increases the compressive strength of concrete by 26 % in 3 days, 12 % in 7 days and 3 % in 28 days. In addition, the deformation properties of early concrete reinforced with nanomaterials are equally important for the crack resistance of concrete structures and therefore should be studied [23].

This study focuses on the effect of CNTs (Taunit-24), at very low concentrations, on the physic-mechanical characteristics of lightweight concrete in the early stages of hardening.

Materials and methods

The following materials were used in the experiments: Portland cement type (M500), taken from (Eurocement, Belgorod / Russia), and gradient sand as a fine aggregate. The water/cement ratio was (0.4). In addition, a foaming agent (MAXPEN, Russia) was used to produce (LWFC). CNTs Taunit-24 were manufactured at LLC NanoTech Center (Tambov, Russia). Table 1 shows the properties of this material, and Figure 1 presents the SEM image of its structure obtained using a scanning electron microscope. Polyvinylpyrrolidonewas used as a surfactant for better distribution of CNTs in the dispersion.

In the experiment with nanomodifiers of lightweight concrete based on carbon nanotubes, the following materials were used: Portland cement (M500), (Eurocement, Belgorod/Russia), gradient sand as fine aggregate and also ordinary tap water was used; the water/cement ratio was (0.4), as well as foaming agent (MAXPEN, Russia) used for production (LWFC) and carbon nanotubes of the Taunit-24 type manufactured at LLC NanoTech Center (Tambov, Russia). Table 1 shows the properties of CNTs, and Figure 1 shows the SEM of CNTs Tanit-24. Polyvinylpyrrolidone (PVP) was used as a surfactant to prepare the dispersion.

Table 1

CNTs (Taunit-24)

Parameters	Value
Outer diameter, nm	20–50
Inner diameter, nm	10–20
Length, microns	≥ 2
Total impurities, %:	
initial	≤ 10
after purifying	≤ 1
Specific surface area, m^2/g	≥ 160
Bulk density, g/cm^3	0.3–0.6

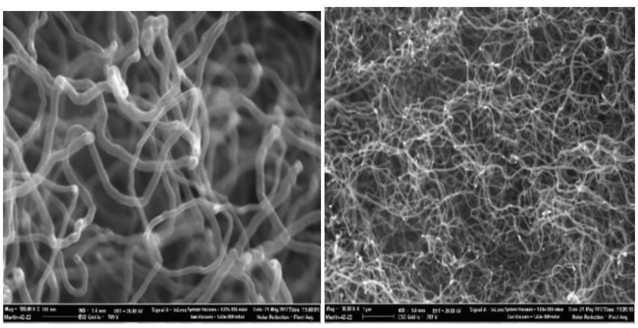

Fig. 1. SEM of CNTs Taunit-24 [24]

Table 2

Mix preparations

Mix No.	CNTs (%*)
Mix 0	0
Mix 1	0.0004
Mix 2	0.0006
Mix 3	0.0008
Mix 4	0.0010
Mix 5	0.0012

* By mass of cement mass.

The water-cement ratio was selected depending on two parameters: the density of the samples and compressive strength. Polyvinylpyrrolidonewas dissolved in 100 ml of water and stirred with a magnetic stirrer for 10 minutes. Then, CNTs were added and mixed manually for 5 minutes in a glass beaker. Ultrasonic treatment of the solution was carried out for 15 minutes with a frequency of 60 kHz.

Cement and sand were mixed in a 1 : 1 ratio, then mixing water was added to prepare the concrete. A dispersion of CNTs was added to the concrete mixture at the concentrations indicated in Table 2. After this, a foaming agent was added to the mixture to obtain lightweight concrete. The components of the mixture (cement and sand in an amount of 1200 g), a foaming agent (6 g) were used in all samples. Table 2 shows the carbon nanotubes concentration.

After mixing the components, the mixture was molded in the form of rolls with dimensions 40 × 40 × 160 mm. Samples in 24 hours after casting were further kept in water (1, 3, 7, 14, 28 days) until curing at a temperature of (23 ± 2) °C in accordance with GOST 31108-2016. Strength characteristics were tested according to the average of three samples in accordance with GOST 310.4-76, bending strength was first determined, and then the halves of the prism samples were tested for compression at a curing time of 28 days. Testing of the samples was carried out on a press (IP-M testing machine) with a load of 2000 kN, the loading rate was 0.4 MPa/s.

Results and discussion

The test results for the strength of light concrete samples modified with nanostructured CNTs (Taunit-24) additives at the age of 1, 3, 7, 14 and 28 days are shown in Table 3. These tables show that the introduction of even a low concentration of the CNTs Taunit-24 modifier into concrete mix can significantly increase the strength of concrete, especially in the early stages of hardening. The increase in strength is especially evident in the hardening period of 14 days for all samples with the addition of CNTs Taunit-24. A possible reason for this effect is that tube agglomerates uniformly distributed in the matrix of the building composite due to the introduction of surfactants fill the pore space between the grains of cement during hydration and reduce capillary porosity.

To assess the effectiveness of the impact of modifiers based on carbon nanostructures on the strength characteristics of lightweight concrete, we used one of the methods of multi-criteria analysis of solutions (TOPSIS method). The specified method is used to achieve the desired level of the mixture to obtain acceptable compressive strength, and tension at low concentrations of carbon nanotubes (CNTs). The TOPSIS method combines all identified system performance values into one value, which can be used as a single performance indicator in optimization questions with several answers [25 – 27].

Table 3

Effect of CNT concentrations on the properties of lightweight concrete at different hardening times

Concentrations of CNTs, %	Hardening time, Days									
	Compressive strength, MPa					Tensile strength, MPa				
	1	3	7	14	28	1	3	7	14	28
0	0.5	1	3	4.5	11.25	0.1	0.12	0.12	1.4	3.5
0.0004	1	2	4.6	5.7	11.37	0.1	0.14	0.143	1.43	3.63
0.0006	1.7	1.9	4.9	7.9	12.65	1	1.3	1.7	1.9	3.98
0.0008	2.3	4	7	12.8	18.9	1.2	1.4	2	2.7	4.68
0.0010	2	4	7.1	11.7	17.5	1.2	1.3	2	2.8	4.2
0.0012	1.9	3	6.3	10	16.4	1.2	1.4	2	3	4.02

Table 4
Decision matrix

Mix No.	R1	R2	R3
M0	0	11.25	3.50
M1	0.0004	11.37	3.63
M2	0.0006	12.65	3.98
M3	0.0008	18.90	4.68
M4	0.0010	17.50	4.20
M5	0.0012	16.40	4.02

R1 is the content of CNTs, R2 is the compressive strength, and R3 is the bending strength.

In accordance with the TOPSIS method, we perform the following actions:

Step 1: create a decision matrix (**M**): the matrix consists of m alternatives and n criteria, in our case $m = 6$.

The decision matrix is presented as Table 4. The solution, created in accordance with the data in this table, and expressed in a matrix format is as follows:

$$\mathbf{M} = \begin{matrix} 0.0000 & 11.25 & 3.50 \\ 0.0004 & 11.37 & 3.63 \\ 0.0006 & 12.65 & 3.98 \\ 0.0008 & 18.90 & 4.68 \\ 0.0010 & 17.50 & 4.20 \\ 0.0012 & 16.40 & 4.02 \end{matrix} .$$

Step 2: we establish a weighted matrix of normalized decisions (n): each row in the matrix will be normalized using the following equation, which eliminates the deviation with different units and scales in many multi-criteria decision problems:

$$v_{ij} \frac{m_{ij}}{\sqrt{\sum_{i=1}^{16} m_{ij}^2}} . \quad (1)$$

The decision matrix with normalized weight is calculated by multiplying the importance weights of the evaluated criteria and the decision matrix with the norms, as shown below:

$$n_{ij} = w_j \cdot v_{ij} , \quad (2)$$

where $w_{ij} = \sum_{j=1}^{6} w_{j=1}$.

The weights of the importance of the evaluation criteria (w_j) in this study are 0.2 for R1, R2, and R3, for R1 and 0.4 for R2 and R3, therefore, the weighted normalized decision matrix n is expressed as follows:

$$n = \begin{matrix} 0.000000 & 0.122552 & 0.142170 \\ 0.042163 & 0.123860 & 0.147451 \\ 0.063244 & 0.137803 & 0.161668 \\ 0.084326 & 0.205888 & 0.190102 \\ 0.105407 & 0.190637 & 0.170604 \\ 0.126489 & 0.178654 & 0.163293 \end{matrix} .$$

Step 3: define the worst alternative A_w and the best alternative A_b . The criteria R1, R2 and R3 indicate that the more n, the better

$$A_{b=} \{ (\min n_{ij} \mid j \in H), (\max n_{ij} \mid j \in S) \};$$
$$A_{w=} \{ (\max n_{ij} \mid j \in H), (\min n_{ij} \mid j \in S) \}; \quad (3)$$

$$A_b = (0.126489, 0.205888, 0.190102);$$

$$A_w = (0, 0.122552, 0.14217).$$

Step 4: calculate the distance to the best and worst ideal reference points (d_{ib} and d_{iw})

$$d_{ib} = \sqrt{\sum_{j=1}^{6} \left(n_{ij} - A_{jb}\right)^2} ; \quad (4)$$

$$d_{iw} = \sqrt{\sum_{j=1}^{6} \left(n_{ij} - A_{jw}\right)^2} . \quad (5)$$

Step 5: calculate the proximity coefficient r from the distance to the best ideal control point and the distance to the worst ideal control point

$$r_i = \frac{(d_{iw})}{(d_{ib}) + (d_{iw})} ; \quad (6)$$

$$r = \begin{bmatrix} 0 \\ 0.253583 \\ 0.411374 \\ 0.752044 \\ 0.798273 \\ 0.785536 \end{bmatrix} ;$$

M4 > M5 > M3 > M2 > M1 > M0.

M4 is chosen as a positive ideal solution. Multi-criteria decision making allows you to choose the best alternative from a finite set of alternative solutions in terms of many commonly conflicting criteria.

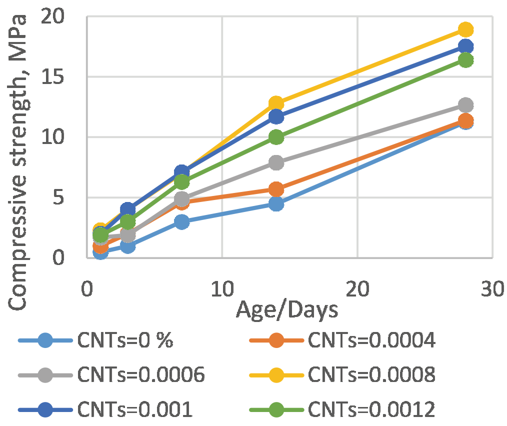

Fig. 2. Nanomodified strength kinetics lightweight concrete

Analysis of the data presented on the Fig. 2 shows that the strength gain of samples with the addition of a modifier based on carbon nanotubes in comparison with control samples is much more intensive, especially in the early stages of hardening. Nanomodified samples of lightweight concrete in the early stages of hardening gain compressive strength 3 times faster, and less than 70 % with a curing time of 28 days, due to the influence of the nanoscale effect.

Conclusion

The presented results of an experimental study of the effect of modifying additives based on carbon nanotubes (CNT Taunit-24) show a significant increase in the strength characteristics of lightweight concrete even at very low modifier concentrations. The use of the experimental research data processing method (the TOPSIS multicriteria analysis method) made it possible to determine the optimal concentration of the nanomodifier at which the physicomechanical and operational characteristics of lightweight concrete increase significantly. An intensive set of strength of lightweight concrete is observed, especially in the early stages of hardening, which is important in modern high-tech construction methods. The use of modifying additives with carbon nanotubes in lightweight concrete will not only improve their properties, but also significantly reduce the consumption of binders while maintaining the strength characteristics of the composite.

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