

DOI: 10.5604/20830157.1176583

THE INFLUENCE OF SiO₂, TiO₂ AND Al₂O₃ NANOPARTICLE ADDITIVES ON SELECTED PARAMETERS OF CONCRETE MIX AND SELF-COMPACTING CONCRETE

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Abstract. The paper presents the results of own research on 10 series of self-compacting concrete which was modified with different amounts of SiO₂, TiO₂ and Al₂O₃ nanoparticle additives. The study included rheological properties of concrete mixes and mechanical properties of the hardened concrete in the form of compressive strength and bending strength. The obtained results are shown in relation to comparative concrete made without the addition of nanoparticles.

Keywords: self-compacting concrete, modification, nanoparticles, physical and mechanical characteristics

WPLYW DODATKU NANOCZĄSTEK SiO₂, TiO₂ I Al₂O₃ NA WYBRANE PARAMETRY MIESZANKI BETONOWEJ I BETONU SAMOZAGĘSZCZAJĄCEGO SIĘ

Streszczenie. W pracy przedstawiono rezultaty własnych badań 10 serii betonu samozagęszczającego się modyfikowanego różną ilością dodatku nanocząstek SiO₂, TiO₂ i Al₂O₃. Badaniami objęto cechy reologiczne mieszanek betonowych i cechy mechaniczne stwardniałego betonu w postaci wytrzymałości na ścislenie i zginanie. Uzyskane rezultaty przedstawiono na tle betonu porównawczego, wykonanego bez dodatku nanocząstek.

Słowa kluczowe: beton samoagęszczający się, modyfikacja, nanocząstki, właściwości fizyczne i mechaniczne

Introduction

Concrete, as one of the world's most commonly used structural building materials, is constantly being improved. Recently, for this purpose, attempts to modify this composite with various additives in the form of nanoparticles have been undertaken in many countries. Their main objective is to investigate the influence of various nano-additives on the physical and mechanical properties of the composite which is obtained with their participation. Studies to date, despite the fact that they are dispersed and also selective, seem to be promising. Table 1 shows types of used additives in relation to the assessed characteristics of concrete modified with the use of these additives [1, 3-4, 6-16].

Table 1. Summary presenting tested to date characteristics of concrete modified with various additives in the form of nanoparticles ("✓" – tested characteristic, "x" – untested characteristic)

Tested characteristic	Type of additive						
	SiO ₂	Al ₂ O ₃	CuO	TiO ₂	ZnO ₂	Fe ₂ O ₃	Cr ₂ O ₃
Workability of a concrete mixture	✓	✓	x	x	x	x	✓
Porosity	✓	✓	✓	✓	✓	x	✓
Absorptivity	x	x	x	x	x	✓	✓
Water resistance	x	x	x	x	x	x	x
Freeze resistance	x	x	x	x	x	x	x
Phase composition	✓	✓	x	x	✓	x	✓
Compressive strength	✓	✓	✓	✓	x	✓	✓
Tensile strength	✓	x	x	x	x	✓	✓
Bending strength	✓	✓	x	x	✓	✓	✓
Abrasion resistance	✓	✓	x	x	x	x	x
Hardness	✓	x	x	x	x	x	x
Parameters of fracture mechanics	x	x	x	x	x	x	x
Stress level initiating cracking	x	x	x	x	x	x	x
Critical stress level	x	x	x	x	x	x	x

The literature review concludes that particles with a nano-size of 10⁻⁹ m were added to concrete in a wide range from 0.2% to 18% of the weight amount of cement. The available research results show that they adversely affect the rheological parameters of a concrete mix, but have a positive impact on the physical and mechanical characteristics of the obtained composite when they are added. This is confirmed by the data summarized in Table 2 [1, 3-4, 6-16].

Based on the carried out literature review the author has planned, within the framework of a conducted doctoral

dissertation, own research which aims to determine the impact of selected nanoparticle additives on the rheological properties of concrete mixture and on a wide range of physical and mechanical characteristics of hardened self-compacting concrete. The first results of the carried out studies which relate to the workability of concrete mixture and also compressive and bending strength of the hardened concrete are presented below.

Table 2. The influence of an additive in the form of nanoparticles on the rheology of a concrete mix and on selected physical and mechanical properties of hardened concrete ("+" - improvement, "-" - deterioration, "n.d." - no data)

Tested characteristic	Type of nanoparticles						
	SiO ₂	Al ₂ O ₃	CuO	TiO ₂	ZnO ₂	Fe ₂ O ₃	Cr ₂ O ₃
	The content of an additive in the composition of concrete in relation to the weight of cement [%]						
	0,2÷18	0,5÷4	1÷5	1÷5	1÷4	0,5÷10	0,5÷2
Workability of a concrete mix	-	-	n.d.	n.d.	n.d.	n.d.	-
Porosity	+	+	+	+	+	n.d.	+
Absorptivity	n.d.	n.d.	n.d.	n.d.	n.d.	+	+
Freeze resistance	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Compressive strength	+	+	+	+	n.d.	+	+
Tensile strength	+	n.d.	n.d.	n.d.	n.d.	+	+
Bending strength	+	+	n.d.	n.d.	+	+	+
Abrasion resistance	+	+	n.d.	n.d.	n.d.	n.d.	n.d.
Hardness	+	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

1. Description of carried out studies

To make self-compacting concrete mixes for the tests the following were used: Portland cement CEM I 52.5R; superplasticizer Glenium Sky 600 with a density of 1.06 g/cm³ in an amount of 4% of the cement weight; granite aggregate with an average density of 2.67 g/cm³ and fractions of 10-5, 5-2, 2-1, 1.2-0.5 and 0.6-0.1 mm; a fraction with a particle size <0.1 mm acting as a fine filler and also tap water. Three types of nanoparticles in the form of nanopowder (nano-additive) were used as additives, such as: SiO₂ (99,5% trace metal basis) with a particle size of 10-20 nm (Fig. 1) in an amount equal to 0.5%, 2.0% and 4.0% of the cement weight; anatase TiO₂ (99,7% trace metal basis) with a particle size <25 nm in an amount equal to 0,5%, 2.0% and 4.0% of the cement weight and also Al₂O₃ with a particle size <50 nm in an amount equal to 0.5%, 1.0%, 2.0% and 3.0% of the cement weight. All of the nanoparticles were delivered by Sigma-Aldrich Company.



Fig. 1. SiO_2 nanoparticles in the form of nanopowder

Shapes of the nanoparticles were not determined. The W/C ratio of the designed concrete mixes was equal to 0.42.

From the above ingredients, 11 self-compacting concrete mixes were prepared including one mix which was made without the addition of nanoparticles for comparison. A summary of compositions of designed mixes per 1 m^3 is presented in Table 3.

Table 3. Summary of compositions of the designed concrete mixes per 1 m^3

Number of mix	Type of nano-additive and its amount in [%]	Water	Cement	Aggregate	Nano-additive mass	SP
		[kg]	[kg]	[kg]	[kg]	[kg]
1	0	193,2	460	1640	0	18,4
2	SiO_2 - 0,5%	193,2	457,7	1640	2,3	18,4
3	SiO_2 - 2%	193,2	450,8	1640	9,2	18,4
4	SiO_2 - 4%	193,2	441,6	1640	18,4	18,4
5	TiO_2 - 0,5%	193,2	457,7	1640	2,3	18,4
6	TiO_2 - 2%	193,2	450,8	1640	9,2	18,4
7	TiO_2 - 4%	193,2	441,6	1640	18,4	18,4
8	Al_2O_3 - 0,5%	193,2	457,7	1640	2,3	18,4
9	Al_2O_3 - 1,0%	193,2	455,4	1640	4,6	18,4
10	Al_2O_3 - 2,0%	193,2	450,8	1640	9,2	18,4
11	Al_2O_3 - 3,0%	193,2	446,2	1640	13,8	18,4

Homogenization of each mix was carried out in a mechanical mixer in two stages. At first cement with aggregate and the addition of nanoparticles was stirred for 2 minutes in dry conditions and after the addition of water, earlier combined with the superplasticizer, everything was then stirred for a further 2 minutes. The rheological properties of each mix were assessed using an Abrams cone. The subsidence time T_{500} , when the mix coming out of the cone reaches a slump size with a diameter equal to 500 mm, was firstly measured and then also the maximum diameter of the slump as an average of two perpendicular measurements.

From each mix, with a symbol and composition given in Table 3, a series of six cubic samples with a side length of 100 mm was made in order to investigate the compressive strength. To investigate the bending strength, a series of six beams with dimensions of $40 \times 40 \times 160$ mm was made. Cubic and beam samples are presented respectively in Fig. 2 and 3. Strength tests were carried out after 28 and 90 days of the samples curing at a temperature of 20°C ($\pm 1^\circ\text{C}$) and relative humidity of 95% ($\pm 5\%$).



Fig. 2. Cubic samples for compressive strength tests



Fig. 3. Beam samples for bending strength tests

2. Results of studies and analysis

Table 4 presents the results of rheological characteristic studies of all 11 designed self-compacting concrete mixes. It should be noted that an increase in the amount of SiO_2 and Al_2O_3 nanoparticle additives deteriorates the fluidity of a mix which is being assessed on the basis of the measurement of time of obtaining a slump with a diameter equal to 500 mm and also by a measurement of a maximum diameter of a slump. This can be explained by the fact of the large specific surface area of nanoparticles and thus their high water demand [5] and high chemical reactivity which is manifested in e.g. the pozzolanic reaction. However, the influence of TiO_2 nanoparticle additives on the studied rheological properties of mixes is negligible. All the assessed mixes met the requirements for self-compacting concrete given in [2], with the exception of mixes 3, 4 and 11.

Table 4. The results of rheological characteristic studies of concrete mixes with the use of an Abrams cone

Number of mix	Type of nano-additive and its amount in [%]	Time of reaching a slump with a diameter of 500 mm	Slump diameter	Requirements according to [2]	
		T_{500} [s]	r [mm]	T_{500} [s]	r [mm]
1	0	2,9	760	2-5	650-800
2	SiO_2 - 0,5%	3,0	715		
3	SiO_2 - 2%	5,7	565		
4	SiO_2 - 4%	-	370		
5	TiO_2 - 0,5%	2,1	745		
6	TiO_2 - 2%	2,7	775		
7	TiO_2 - 4%	2,6	735		
8	Al_2O_3 - 0,5%	2,4	750		
9	Al_2O_3 - 1,0%	2,9	655		
10	Al_2O_3 - 2,0%	3,2	620		
11	Al_2O_3 - 3,0%	5,5	510		

What is worth to be mentioned, all the prepared concrete mixes were characterized by high deformability and moderate viscosity that are necessary to ensure uniform suspension of aggregates. An exemplary maximal slump flow for the mix number 2 is shown in Fig. 4.

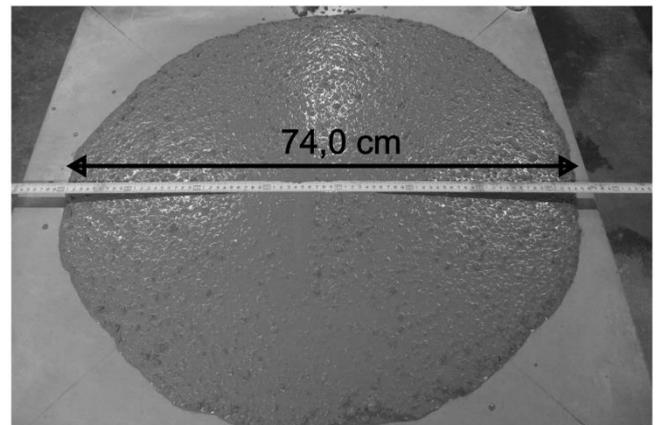


Fig. 4. An exemplary maximal slump flow for the mix number 2

However, Fig. 5 shows the results of the compressive strength studies, and Fig. 6 the results of bending strength studies after 28 and 90 days of curing of concrete made from the designed mixes. The symbols on the horizontal axis in these figures refer to a series of S concrete made of concrete mixes with a number 1 to 11.

When analyzing the obtained results of strength studies a significant increase in the compressive strength tested after 28 days of concrete sample curing for concretes made with the addition of SiO_2 nanoparticles can be noted in comparison to S1 concrete without a nano-additive. Beneficial results are also achieved with the use of the TiO_2 nano-additive in an amount of 2% of the cement weight and Al_2O_3 in an amount of 0.5% and 2.0% of the cement weight in relation to the S1 comparative concrete. A similar tendency is noted regarding the results

of the compressive strength obtained after 90 days of sample curing. The obtained results of bending strength studies show that, only in the case of using the additives of SiO_2 and TiO_2 nanoparticles in an amount of 0.5% of the cement weight, an increase in bending strength occurs after 28 days of concrete curing when compared to the S1 reference concrete. However, it is symptomatic that after 90 days of sample curing none of the concretes made with a nano-additive obtained a higher bending strength in comparison to the S1 comparative concrete.

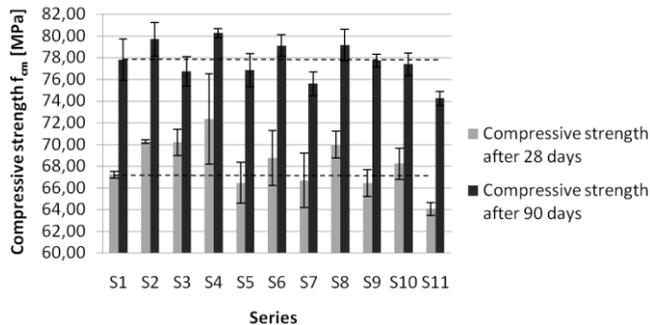


Fig. 5. The average compressive strength f_{cm} of the tested concrete series after 28 and 90 days of curing

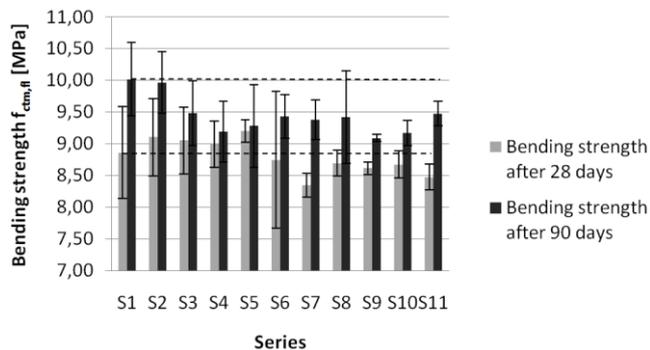


Fig. 6. The average bending strength $f_{cm,fl}$ of the tested concrete series after 28 and 90 days of curing

The mechanism describing the increase of mechanical properties of cement composites due to the use of nanoparticles was included, among others, in papers [1, 4, 15]. These papers conclude that the high chemical reactivity of nanoparticles has a beneficial influence on the formation of the C-S-H phase which is responsible for the strength of concrete. In addition, nano-additives make a concrete structure more compact and uniform.

In turn, as the nanoparticles are not easy to disperse uniformly because of their high surface energy, the decrease in values of mechanical characteristics may be associated with the formation of conglomerates by nanoparticles. That issue according to [3] may be the result of their inhomogeneous distribution throughout the whole volume of the concrete mix.

In contrary to the results presented in other works [3, 7–14] one should be noted, that the obtained results may not unequivocally mean that the nanoparticles addition causes an increase in compressive and bending strength of the self-compacting concrete. It may be caused by many factors, for instance lack of quartz sand in mix composition or inhomogeneous distribution of nanoparticles in concrete mix. Due to above further research is required.

3. Summary

The conducted research of the rheological characteristics of 11 designed self-compacting concrete mixes showed, that depending on the type and the amount of nanoparticle additives which were used to make the concrete, workability of a concrete mix deteriorates. Among the 11 tested mixes, 8 met the requirements for self-compacting concrete given in [2].

The carried out strength studies showed, that the use of SiO_2 nanoparticles as an additive for self-compacting concrete in an amount up to 4% of the cement weight, has a clearly beneficial influence on 28-day compressive and bending strength in relation to the comparative concrete. However, such ambiguity cannot be seen in the case of concrete made with the addition of TiO_2 and Al_2O_3 nanoparticles.

Symptomatic for all tested concretes made with the addition of nanoparticles is that the bending strength after 90 days is clearly lower when compared to the comparative concrete.

In contrary to the results obtained in literature, the addition of nanoparticles to the self-compacting concrete not unequivocally improves its mechanical properties.

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