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Effect of incorporation route on dispersion of mesoporous silica nanospheres in cement mortar

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HIGHLIGHTS

- Mechanical properties of cement mortars modified silica nanoparticles were tested.
- We investigated two routes of incorporating mesoporous silica nanospheres into cement.
- The sample consisting of acetone has better compressive strength.
- We report a photo of agglomerates of mesoporous silica nanoparticles.

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ABSTRACT

It was shown that the uniform dispersion of nanoparticles into a cement matrix is a key issue in their application in the field. Therefore, here we compare two methods of incorporation of mesoporous silica nanospheres into cement using acetone (method A) or water (method B) as a dispersant, to reveal its influence on the mechanical properties of the formed composite. It was proven that in both cases, small amounts of silica nanoparticles agglomerates does not affect the mechanical properties of the cement mortars. However, the addition of mesoporous silica nanospheres to cement in an acetone solution is more effective and results in higher compressive and flexural strength than the sample of the composite formed from water solution of silica nanoparticles and cement.

1. Introduction

The positive influence of silica nanoparticles on the mechanical properties of cement mortars and concretes is widely confirmed by many researchers. Since 2004 (Hui Li) many studies have been done [1,2]. Reports have shown that silica nanoparticles can significantly influence the compressive, flexural and tensile strength of samples [2–7]. It was also shown that silica nanoparticles have influenced the drying shrinkage, durability and water permeability of concrete samples [3,8,9]. The application of nanoparticles of silica in HPC (High Performance Concretes) and SCC (Self-compacting concretes) seems more effective than the addition of conventional silica fume [3,5,7,10,11]. Calcium silicate hydrate gel (C–S–H), the result of cement hydration determines the mechanical properties of the concrete. C–S–H in cement paste forms a truss nanoparticles; that is why smaller silica nanoparticles more precisely fills the voids of C–S–H gel. This leads to a densification of the concrete internal structure [3,9]. Industrial production and incorporation of silica nanoparticles into concrete is undoubtedly the future of modern concrete technology. First of all, silica nanoparticles are environmentally friendly and do not affect the health issue. It can help to create novel, sustainable and advanced concrete structures resulting in lowering the use of cement and decreasing the costs of the final work [5,11]. There are already few commercial products offered by companies to produce high-volume concretes. In addition, due to the high cost of silica nanoparticles, the widespread availability of these products is still reduced [5,11,12].

Even though the silica nanoparticles are becoming very important and potentially a good component to apply there are still some inconveniences when incorporating them into cement mortar. The authors suggest different the application of different amount of the silica nanoparticles [4,6,9,11]. However, the concentration reaching up to 10 wt% can cause problems with well-dispersion of the

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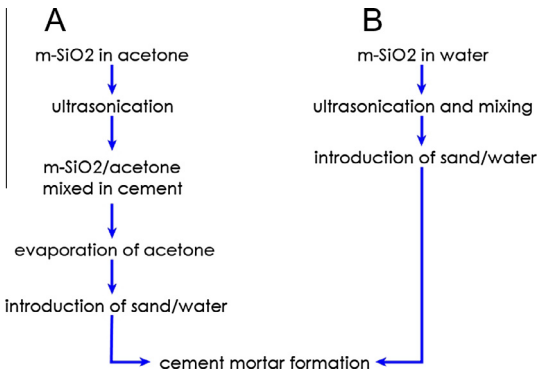

Fig. 1. Schematic presentation of the incorporation methods of m-SiO_2 to cement.

nanomaterial in the final product. The researchers stated that high amount of silica nanoparticles cannot be easily dispersed in water leading to the creation of weak zones in concrete [7,13]. Conversely, other researchers found that small amounts of poorly dispersed silica nanoparticles might not affect the strength properties of the samples [2]. It was found that the main reason of dispersion problem is due to the high surface area of silica nanoparticles. This parameter leads to a higher water demand of the cement mortar. This results in a decrease in the fluidity of the sample. In the case of a low water/cement ratio, the porosity of the CSH gel decreases which affects the enhancement of the strength of cement mortar [9]. The proposed way to overcome this obstacle is through the use of superplasticizers which help to disperse silica nanoparticles uniformly in a cement matrix and increase consistency of the mortars [3,8,14,15]. However, it is still a huge need to propose a technology which will offer the concrete material with well-dispersed nanoparticles in its volume resulting in a homogeneous material.

There are already various ways of introducing silica nanoparticles into a cement. First, and the most common method, is stirring a mixture of nanoparticles, water and a superplasticizing agent (if applicable) for 1–5 min with a high speed and then adding it to the dry components [2,4,6–8,12,16,17]. Another method is to implement the silica nanoparticles into the cement with acetone and then drying it in the oven [10]. Alternatively, silica nanoparticles can be ultrasonicated in water and then added to the dry components or even added in the form of powder directly to cement [18]. Here, in this work we compare two methods of incorporating silica spheres with solid core and mesoporous shell into the cement: using acetone as a dispersant **(method A)**, and using water as a dispersant **(method B**). The created composites were studied in order to reveal their mechanical properties and the mechanisms behind its improvement in respect to the standard cement.

2. Materials and methods

2.1. Synthesis of silica nanospheres with mesoporous shell (m-SiO_2)

The detailed description of the synthesis of silica nanospheres with a mesoporous shell has been reported elsewhere [19]. Briefly, solid silica nanospheres were synthesized by the Stöber method with the use of a precursor of nano-silica – tetraethyl orthosilicate (TEOS). **In order to induce the formation of a porous shell around the solid core** Hexadecyltrimethylammonium bromide **(CTAB)** and TEOS were added. The morphology of the sample was investigated by means of scanning electron microscopy – SEM – (Hitachi SU80020) and transmission electron microscopy – TEM – (FEI Tecnai F20 model with energy dispersive X-ray spectrometer EDS).

2.2. Incorporation methods of m-SiO_2 in cement mortar

Portland Cement (OPC) CEM I 42,5R, conforming to PN-EN 197-1, standard was used as purchased. The sand was natural with particles smaller than 2 mm. The two incorporation methods of the nanoparticles into the cement mortar is schematically presented in Fig. 1. In both procedures 3 wt% of silica nanoparticles were introduced to create the final samples of the cement mortar. In the procedure A (sample M3A), silica nanoparticles were dispersed in acetone, added to the cement and subsequently the solvent was evaporated. Next, the obtained material was grounded in a mortar to get a fine powder and then added to the mixture of water and sand. According to the procedure B (sample M3B), the m-SiO_2 was dispersed in water with the assistance of ultrasounds and then mixed with the cement and sand particles. Next, the samples obtained in procedures A and B, respectively, were poured into oiled molds to form samples with a size of $40 \times 40 \times 160$ mm in accordance with the requirements of PN-EN 196-1. The samples were demolded after 24 h and then cured for 28 days in a standard water bath at a temperature of 20 ± 2 °C. After 28 days of curing, the samples were examined. To compare the results two, series or reference samples, were prepared. The first sample is plain cement mortar (sample C). The second sample, designated as CA, is a sample consisting of cement which was mixed with acetone and afterwards evaporated. Compressive and flexural strength tests were performed in accordance with PN-EN 196-1. The composition of the cement mortars is presented in Table 1.

The silica nanospheres and obtained samples of cement mortar were characterized via high resolution transmission electron microscope (HR-TEM, FEI Tecnai F20 model with energy dispersive X-ray spectrometer EDS) and a scanning electron microscope (Hitachi SU80020). The specific surface area adsorption was measured by BET isotherm with a Quantachrome Instruments analyzer.

3. Results and discussion

Preliminary study has shown (data not presented due to difference in mortar composition) that the highest compressive and flexural strength of cement mortar samples is observed in samples containing 3 wt% of mesoporous silica nanospheres (m-SiO_2) in the cement. The addition of 3 wt% m-SiO_2 also did not influence significantly the consistency of the cement mortar. Therefore, the presented data will focus on the cement mortar modified with 3 wt% of m-SiO_2.

3.1. Characteristics of silica nanospheres

The detailed morphology of silica nanospheres with a mesoporous shell has been presented elsewhere [19]. Briefly, the structure has a spherical shape and a clear shell around a solid core. The SEM (Fig. 2) and TEM (Fig. 3) analyses of the samples indicate that the diameter of the m-SiO_2 was 350 ± 50 nm. The mesoporous shell is presented in the inset of this figure and it exhibits a thickness of about 50 nm. The huge advantage of these studies is very narrow particle size distribution (Fig. 4).

3.2. Flexural strength

The results of flexural strength testing are summarized in Table 2. The data show that nanomaterials incorporated according to the procedure with water as a dispersant slightly improves the flexural strength of the cement mortar. In contrast, M3B – sample with acetone as a dispersant, does not indicates the strength enhancement. In the samples made following the method B

Table 1
Compositions of cement mortars, kg/m^3.

Type of sample	Cement	Water	Sand	m-SiO_2	Nanoparticles, cement mass, %
M3A, M3B	490	279	1519	14.7	3
C, CA	490	279	1519	–	–