Effect of Inorganic SiO$_2$ Nanofibers in High Strength Cementitious Composites

Lenka Bodnarova$^1$, Rudolf Hela$^1$, Daniel Sedlacek$^2$

$^1$Brno University of Technology, Faculty of Civil Engineering, Veveri 95, 602 00 Brno, Czech Republic
$^2$Universität Innsbruck, Institut für Konstruktion und Materialwissenschaften, Arbeitsbereich Materialtechnologie, Technikerstraße 13, A-6020 Innsbruck, Austria

Abstract. The paper deals with the verification of the effect of the addition of inorganic SiO$_2$ nanofibers to cement composites. In the first stage, a stable suspension of SiO$_2$ nanofibers was prepared in an aqueous medium. It is important to distribute nanofibers so that the nanofibers do not appear in the form of clumps and at the same time do not get damaged during the dispersion process. The ultrasonification process was used for dispersion. The dispersed suspension of SiO$_2$ nanofibers and water was dosed together with the superplasticizing admixtures into the dry components of the cement composite and the components were homogenized. The properties of the cement composite with SiO$_2$ nanofibers have been tested – compressive strength, flexural strength, density. Composites with the addition of SiO$_2$ nanofibers at a dose of 0.008 % by weight of cement exhibited an increased compressive strength of up to 33 % and a 19 % greater flexural strength at doses of 0.016 and 0.032 % of cement weight than the reference sample without nanofibers. The presence of SiO$_2$ nanofibers in the composite was monitored by scanning electron microscopy (SEM).

1 Introduction

Concrete is the most widely used building material worldwide. Concrete is quasi-brittle material with high compressive strength, low tensile strength and low toughness, which in the end can result in cracks, especially in the stretched areas of concrete structures. This can largely be prevented by the application of fibers that act as dispersed reinforcement in the cement matrix and, if the fibers have a greater modulus of elasticity than the matrix, they capture a portion of internal stress [1-4]. Although macro and micro fibers can slow the development of cracks, they cannot prevent them from forming. The application of nanoparticles, especially nanofibers can theoretically achieve greater control over the distribution of internal stress at the nanoscale, thus preventing the forming of the cracks [5-6]. However, the use of nanofibers has its own disadvantages over macro and microfibers. Due to their small dimensions and the large ratio between the length and the diameter, large aggregates are formed, which have to be disassembled before being used in the matrix. Another condition without which nanofibers would not fulfill their purpose is the strength of the fiber-matrix transit zone (ITZ – interfacial transition zone). This zone is analogous to the transit zone at the aggregate-matrix interface and, as is known, that is the weakest place in the concrete structure. Other problems the application of nanofibers is facing are the inability of nanofibers to „attach“ in portlandite crystals and also the relatively large porosity of ordinary concrete. It is possible that a great deal of these pitfalls can be circumvented by at least suppressing the use of ultraviolet concrete due to its dense structure, lower content of portlandite, higher content of C-S-H gel and better transit zone properties. Another reason to use ultra high strength concrete is purely economic. In ordinary concrete technology, we generally try to reduce the production costs and use of waste materials, which does not correspond to the potential use of expensive nanofibers. Conversely, ultra high strength concrete is an advanced high-tech material in which the use of nanofibers makes sense [7]. Therefore, the research work focused on the use of nanofibers for high strength cement composites.

2 The objective of the experimental work

The aim of the experimental work was to verify the efficiency of the addition of inorganic SiO$_2$ nanofibers in the cement composite.

In the first stage of preparation, it was necessary to create a stable suspension from SiO$_2$ nanofibers so that the nanofibers did not form clumps and it was possible to disperse nanofibers in the entire volume of the cement composite. The simple addition of nanofibers
without dispersion into the cement matrix does not produce a positive effect [8-9]. The ultrasonification process was used for dispersion. The dispersed suspension of SiO$_2$ nanofibers and water was dispensed together with superplasticizing admixtures into the dry components of the cement composite. The properties of the cement composite with SiO$_2$ nanofibers have been tested – compressive strength, flexural strength, density. Using the scanning electron microscopy (SEM), the presence of SiO$_2$ nanofibers in the composite was monitored.

3 Mix design and materials used

The proposed mix design contained standard components for high strength composite, namely CEM I 52.5 N cement, microsilica, siliceous powder, silica sand, superplasticizing admixtures and water. The ratio of cement, siliceous powder and microsilica was 100:50:25. The water-cement ratio w/c was 0.28. As a residual porosity, 2 % was chosen for the design of the mixture [10].

The composition of the cement composite per 1 m$^3$ is given in Table 1.

Table 1. Mix design of cement composite per 1 m$^3$

| Component                        | Weight [kg] |
|----------------------------------|-------------|
| Cement CEM I 52.5 N C3A frei     | 690         |
| Siliceous sand 0.1-0.4            | 927.5       |
| Siliceous powder QuarzwerkeGruppe| 345         |
| MicrosilicaElkem 940 Undensified  | 172.5       |
| BASF MasterGlenium ACE 430       | 31          |
| BASF MasterSure 911              | 13.8        |
| BASF MasterFinish DF 370         | 1           |
| Water                            | 160.5       |
| SiO$_2$ nanofibers (dose from the weight of cement) | 0.004, 0.008, 0.016, 0.032, 0.064 % |

3.1 Nanofibers

Inorganic nanofibers from SiO$_2$ produced by Pardam were used. Nanofibers from silica are a type of ceramic material. The fibers consist only of amorphous silicon dioxide, with a small proportion of porous particles of the same chemical composition [11]. Amorphous silicon dioxide nanofibrous material is represented by fine fibrous structure and high specific surface area. This material is produced by Centrifugal Spinning technology which enables to produce very thin fibers 100 – 300 nm in diameter with narrow distribution of fiber diameters.

Table 2. Selected parameters of SiO$_2$ fibres NnF CERAM® produced by Pardam, Czech Republic [11].

| Fiber structure          | Amorphous nanofiber |
|--------------------------|---------------------|
| Typical fiber diameter   | 100 - 300 nm        |
| Fiber length             | 2 to hundreds of μm (can be modified by milling) |
| Specific area            | 50-500 m$^2$/g      |
| Crystal phase            | Amorphous SiO$_2$   |
| Physical form            | White powder        |
| Melting point            | 1665 °C             |
| Thermal conductivity     | 1.3 W/mˑK           |

3.2 Cement

Cement CEM I 42.5 N C3A frei Mannersdorf, producer company Lafarge was used for experimental work. The cement has low amount of C$_3$A. The C$_3$A, is connected to the initial setting and hardening of cement, and hydration heat release. Another important aspect is the fact that the C$_3$A is linked to sulphate attack resistance when the sulphate is coming from the environment. Properties of cement are in Table 3.

Table 3. Properties of cement CEM I 42.5 N C$_3$A-frei [12].

| Properties                  | Guide values | Standard requirement EN 197-1 |
|-----------------------------|--------------|-----------------------------|
| Density [kg/dm$^3$]         | 3.14         | -                           |
| Compressive strength [N/mm$^2$] 1 day | 12          | -                           |
| 2 days                      | 24           | ≥ 10                        |
| 7 days                      | -            | -                           |
| 28 days                     | 51           | ≥ 42.5 ≤ 62.5               |
| Tensile strength [N/mm$^2$]  | -            | -                           |
| Grinding fineness [cm$^2$/g] | 3200        | -                           |
| Bleeding [cm$^3$] after 120 minutes | 15          | -                           |
| Heat development [J/g] after 15 hours | 200         | -                           |
| Initial setting time [min]  | 160          | ≥ 60                        |

3.3 Microsilica

ElkemMicrosilica® Grade 940 U (Undensified) is microsilica supplied in a undensified form. The microsilica behaves physically as microfiller and chemically as a strongly reactive pozzolan. The properties of microsilica are shown in Table 4.
Table 4. Chemical and physical properties of Elkem Microsilica® Grade 940 Undensified [13].

| Properties                  | Specification |
|-----------------------------|---------------|
| SiO₂ [%]                    | > 90          |
| Retention on 45μm sieve [%] | < 1.5         |
| H₂O (when packed) [%]       | < 1.0         |
| Bulk Density [kg/m³]        | 200 - 350     |

3.4 Siliceous powder QuarzwerkeGruppe

Table 5. Properties of siliceous powder QuarzwerkeGruppe [14].

| Properties                  | Specification |
|-----------------------------|---------------|
| Density [kg/m³]             | 2650          |
| Retention on 45μm sieve [%] | 19            |
| Retention on 63μm sieve [%] | 3             |
| SiO₂ content                | 97            |
| Al₂O₃ content               | 1.6           |

3.5 Silica sand

Siliceous sand of 0.1-0.4 mm fine particle was used as filler, resulting in a high homogeneity of the mixture.

3.6 Superplasticizing admixtures

A combination of 3 chemical admixtures - BASF MasterGlenium ACE 430, BASF MasterSure 911 and BASF MasterFinish DF 370 were used to prepare the UHPC.

3.6.1 BASF MasterGlenium ACE 430

It is a superplasticizing admixture based on polycarboxylate ethers. It allows a high flow rate and greater initial strength. The recommended dosage is 0.2 – 3 % by weight of cement. In our case, a dosage of 4.5 % by weight of cement was used due to the high content of microsilica and silica powder [15].

3.6.2 BASF MasterSure 911

It is a polycarboxylate ether based plasticizer with delayed effect used to maintain consistency. The effect starts after approximately 15 – 25 minutes; the effect lasts at least 90 minutes. It is used in combination with a conventional superplasticizing admixture [15].

3.6.3 BASF MasterFinish DF 370

Liquid admixture with a strong bleeding action, the recommended dosage is in the range of 0.75 – 1 kg/m³ of fresh concrete. When used with the MasterGlenium superplasticizing admixture, it improves the flow rate even though it does not have the liquefying properties itself [15].

4 The process of preparing cement composite with SiO₂ nanofibers

The first step was the dispersion of nanofibers. Perfect and stable dispersion of nanoparticles in aqueous solution and then in the concrete mix is a prerequisite for the successful use of nanofibers for the transfer of tension across the matrix.

The process of preparing the dispersion of nanofibers was designed based on our experience in preparing nanoparticle suspensions, in particular carbon nanoparticle suspensions [8-9, 16, 17]. The nanofibrous suspension was prepared by ultrasonification; the ultrasonic cavitator performance was 100 W. SiO₂ nanofibers were centrifuged for 1 minute. The nanofibers were dosed at concentrations of 0.004, 0.008, 0.016, 0.032 and 0.064 % by weight of cement. The suspension was then filled with liquid admixtures - BASF MasterGlenium ACE 430, BASF MasterSure 911 and BASF MasterFinish DF 370.

The dry components of the mixture (cement, silica sand, siliceous powder and microsilica) were weighed on laboratory scales with 0.1 g accuracy. The dry mixture was homogenized for a minute using a cordless drill with a stirrer extension at 400 rpm. After the 10 seconds of mechanical mixing of the liquid components, a liquid portion was added while stirring the dry mixture at a rate of 400 rpm. The time of application of the liquid portion was 30 – 40 s, for the best possible homogeneity. The total stirring time at 400 rpm was 1 minute. Higher speed was not used due to turbulence of the dry mix at higher speeds. After 1 minute, the dry and liquid portions of the mix water were homogenised to the extent that higher rates of 1300 rpm could be used. This speed was maintained for the next 2 minutes. The resulting mixture was then filled into moulds and test specimens were made.

5 Experiment results and discussion

5.1 Characteristics of cement composites with SiO₂ nanofibers

The properties of the cement composites with SiO₂ nanofibers were verified after 28 days – compressive strength, flexural strength, density. Cement composites with SiO₂ nanofibers showed virtually identical values of bulk weights as composites as reference samples without nanofibers. However, the differences were reflected in the mechanical properties of the composites with SiO₂ nanofibers that increased in flexural strength by up to 19 % at 0.016 and 0.032 % concentrations and a compressive strength of 33 % at a concentration of 0.008% of the fiber by weight of the cement. The results are shown in the following Table 6 and in Fig. 1 and Fig. 2.
Table 6. Changes in compressive and flexural strength after 28 days relative to the strength of the reference sample without the addition of SiO2 nanofibers.

| SiO2 nanofibers content of weight of cement [%] | Changes in compressive strength after 28 days [%] | Changes in flexural strength after 28 days [%] |
|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| 0                                            | --                                           | --                                           |
| 0.004                                        | 12                                           | 1                                            |
| 0.008                                        | 33                                           | 9                                            |
| 0.016                                        | 19                                           | 19                                           |
| 0.032                                        | -4                                           | 18                                           |
| 0.064                                        | -13                                          | -6                                           |

The bulk density of the reference cement composite without nanofibers was 2240 kg.m$^{-3}$. The bulk density of composites with nanofibers ranged between 2240 and 2250 kg.m$^{-3}$.

The reference mixture without nanofibers had a tensile strength of 14.0 MPa. For composites with SiO2 nanofibers, a flexural strength of 16.7 MPa at a 0.016 and 16.5 MPa concentration at 0.032 % was achieved, then dropped to 13.1MPa at a concentration of 0.064 %. Even in the case of compressive strength (Fig. 4), some dependence on the concentration of nanofibers can be seen. Compared to a reference mixture with strength of 96.6 MPa, it progressively increased to 108.6 MPa at a concentration of 0.004 % and 128.3 MPa at a concentration of 0.008 %. With increasing concentration, the strength gradually decreased to 84.2 MPa.

5.2 Direct observation of nanofibers with SEM

The presence of SiO2 nanofibers in the composite was monitored using scanning electron microscopy (SEM). Sample fragments of cement composites with SiO2 nanofibers at a concentration of 0.064 % after the compression strength test were subjected to direct observation of nanofibres in the structure. There samples were chosen because of the high concentration of nanofibers, allowing their easier finding. The scanning electron microscope FEI was used for observation. After initial unsuccessful attempts to find them, the specimens were treated so that they were immersed in 5% HCl solution for 3 minutes due to breakage of the cement matrix on the surface and eventual detection of nanofibers. This procedure proved to be successful. The SiO2 nanofiber in the cement matrix is shown in Fig. 3.
6 Conclusions

The aim of the research was to verify the possibility of using inorganic SiO\textsubscript{2} nanofibers in high strength cement composites.

Our previous researches in this area [9, 16-17] were mainly focused on inert carbon nanofibers and nanotubes, the verification of the effect of inorganic nanofibers from silica is a new direction of our research.

The experiments carried out confirmed the successful application of SiO\textsubscript{2} nanofibers to the cement composite.

Different concentrations of SiO\textsubscript{2} nanofibers were tested. Concrete density, compressive strength and flexural strength were determined. The positive effect of SiO\textsubscript{2} fibers in certain concentrations on the resulting mechanical properties of cement composites was found. SiO\textsubscript{2} nanofibers in the cement composite were detected using a scanning electron microscope.

As a further direction of the research, a suspension with SiO\textsubscript{2} nanofibers for the production of ultra high strength concrete (UHPC) will be tested. Nanofibers are a currently relatively expensive material, so its use is useful in special types of concrete such as HPC and UHPC. Any further significant improvements to the HPC and UHPC properties may be justified even if the price increases.

Acknowledgement

This study was a part of the project MPO TRIO FV 20019, supported by the Ministry of Industry and Trade and Project FAST-S-18-5410, supported by Brno University of Technology.

References

1. N. Banthia, M. Criswell, P. Tatnall, K. Folliard, SP-216: Innovations in fiber-reinforced concrete for value (ACI, 2003). ISBN: 9780870311260.
2. T. Komarkova, J. Lanik, O. Anton, Evaluation of Selected Physicomechanical Properties of SFRC according to Different Standards (Advances in Materials Science and Engineering) (2018) https://doi.org/10.1155/2018/7098065
3. L. Bodnarova, M. Fialova, D. Kopkane, T. Moravek, P. Stahel, M. Cernak, Importance of polypropylene fibers as a reinforcement in concrete (Chemicke listy) 106 1427-1430 (2012)
4. J. Ciganek, A. Materna, J. Brozovsky, Optimization of the fibre-concrete mixture, Fibre concrete 2009: Technology, design, application, Ed. by: A. Kohoutkova, 71-77 (2009)
5. M.S. Konsta-Gdoutos, Z.S. Metaxa, S.P. Shah, Multi-scale mechanical and fracture characteristics and early-age strain capacity of high performance carbon nanotube/cement nanocomposites (Cement and Concrete Composites) 32 (2) 110-115 (2010). https://doi.org/10.1016/j.cemconcomp.2009.10.007
6. P. Reiterman, Influence of Metakaolin Additive and Nano-particle Surface Treatment on the Durability of White Cement Based Concrete (European Journal of Environmental and Civil Engineering) (to be published) https://doi.org/10.1080/19648189.2018.1504235
7. F. Sanchez, K. Sobolev, Nanotechnology in concrete – A review (Construction and Building Materials) 24 (11) 2060-2071 (2010) https://doi.org/10.1016/j.conbuildmat.2010.03.014
8. J. Foldyna, V. Foldyna, M. Zelenak, Dispersion of carbon nanotubes for application in cement composites, Procedia Engineering, 149 94-99 (2016) https://doi.org/10.1016/j.proeng.2016.06.643
9. T. Jarolim, T., M. Labaj, R. Hela, K. Michnova, Carbon Nanotubes in Cementitious Composites: Dispersion, Implementation, and Influence on Mechanical Characteristics (Advances in Materials Science and Engineering) (2016) https://doi.org/10.1155/2016/7508904
10. D. Sedlacek, Studying the effect of the application of inorganic nanofibers in high strength concretes, Master thesis, Supervisor L. Bodnarova, Brno University of Technology (2017)
11. Pardam, Technical sheet, http://www.pardam.cz/, http://www.nano4fibergroup.cz/downloads/SDS_CERAM_SiO2_(ELSP)_web.pdf
12. Lafarge, Technical sheet, http://www.lafarge.at/zement/produkte/derecontragress-425-n/
13. Elkem, Technical sheet, https://www.elkem.com/silicon-materials/products-and-markets/fibre-cement-additive/elkem-microsilica-grade-940-for-fibre-cement/
14. Quarzwerke Gruppne, Technical sheet, https://www.quarzwerke.com/en/products/high-performance-fillers/
15. BASF, Technical sheet, https://www.master-builders-solutions.basf.at/de-at/products/
16. R. Hela, L. Bodnarova, A. Florian, L. Sevelova, High strength concrete with carbon nanotubes, Proc. Of SEC 2013 - 7th International Structural Engineering and Construction Conference: New Developments in Structural Engineering and Construction, 583-587 (2013)
17. L. Bodnarova, T. Jarolim, Study the effect of carbon nanoparticles in concrete (Journal of Physics: Conference Series) (to be published)