The effect of nanosilica on the mechanical properties of polymer-cement composites (PCC)

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Abstract

In the last decade nanomaterials due to their unique physical and chemical properties, have attracted the interest of researchers to fabricate new building materials with novel functions. One of the most referred to and used cementitious nanosized materials is nanosilica (nSiO\textsubscript{2}). Although the number of publications devoted to the influence of nanosilica on the properties of cementitious composites has increased over the course of the last decade, the field of polymer-cement composites (PCC) has remained under-studied. Therefore, this paper will deal with the potential application and the influence of nanosilica (nSiO\textsubscript{2}) on the mechanical properties of PCC.

In this study the influence of diameter (100 nm and 250 nm) and quantity (1%, 3%, 5% by weight of cement) of nSiO\textsubscript{2} on the consistency and mechanical properties of polymer-cement mortars (PCC) have been examined. Moreover, the hydration of cement compounds was followed by X-ray diffraction (XRD).

Studies have shown that the addition of nanosilica has great potential to accelerate the pozzolanic reaction, thus reacting more with the CH and increasing conversion of C-S-H, and having the potential to improve mechanical properties of PCC. The obstacle overcome is the high water demand of nanosilica particles, leading to significant deterioration of consistency. Finer particles of nSiO\textsubscript{2} seem to be more effective and cause fewer problems with the consistency of fresh mortars.

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1. Introduction

Even though cement mortar and concrete are the most popular building materials, and production is increasing day by day, there are still a few disadvantages caused by the nature of the material: low tensile strength, low bonding strength in repair application, and low chemical resistance. Modern admixtures and additives are the solution to improve a variety of properties and overcome some of the disadvantages. Materials that attract the attention of researchers are those that, due to their unique physical and chemical properties, enable them to fabricate new materials with novel functions, such as polymers and nanomaterials. The incorporation of polymers can contribute to improve durability and mechanical properties (especially flexural and tensile strength) of cementitious composites. However, Czarnecki and Łukowski [1] and Ramachandran [2] report that the effect of polymers on the compressive strength is often unremarkable or even negative. Decrement of the compressive strength is associated with the retardation of cement hydration caused by polymer and surfactants presence in the mix - Van Gemert [3].

One of the most referred to and used cementitious nanosized material is nanosilica (nSiO2). Horszczaruk et al. [4] reported that nanosilica addition increases the compressive strength and reduces the overall permeability of hardened concrete due to the pozzolanic properties, resulting in finer hydrated phases (C-S-H gel) and densified microstructure – Horszczaruk et al. [5] and Quercia et al. [6].

Previous studies held by Horszczaruk et al. [4] and Horszczaruk et al. [5] have shown that the presence of nanosilica contributed to the densification of the interfacial transition zone (ITZ) and the improvement of the compressive and flexural strength by 27% and 8% respectively.

Despite the interesting properties and high application potential, the incorporation of nanosilica deteriorate consistency of cementitious composites as a result of high water demand of nanoparticles (effect of high surface area to volume ratio of nSiO2). Czarnecki and Łukowski [1] reported that the use of polymers even in small amounts have a positive affect on the rheological properties of the cementitious composites, and in turn, diminish the negative impact nSiO2 has on the consistency.

Although the number of publications devoted to the influence of nanosilica on the properties of cementitious composites has increased over the course of the last decade, the field of polymer-cement composites (PCC) has remained under-studied. Therefore, this paper will deal with the potential application and the influence of nanosilica (nSiO2) on the mechanical properties of PCC.

In this study the influence of diameter (100 nm and 250 nm) and quantity (1%, 3%, 5% by weight of cement) of nSiO2 on the consistency and mechanical properties of polymer-cement mortars (PCC) have been examined. Moreover, the hydration of cement compounds was followed by X-ray diffraction (XRD).

2. Materials and methods

2.1. Synthesis of nanosilica spheres (nSiO2)

Solid nanosilica spheres (nSiO2) were synthesized by the modified Stöber method with use of precursor of nanosilica - tetraethyl orthosilicate (TEOS), ammonia acting as a catalyst, water, and ethanol. By controlling the pH and temperature of the solution, it was possible to obtain desired diameter of nanosilica spheres. In the presented study, two nanosilica structures with diameter of 100 nm and 250 nm have been synthesized. The
detailed description of the synthesis of silica nanospheres was reported by Cendrowski et al. [7] and Stober et al. [8].

2.2. Composition of cement mortars

Rapid Hardening Portland Cement (RHPC) type I 42.5R conforming to EN 197-1 was used as received. The fine aggregate of quartz sand with grains finer than 2 mm conforming to EN 196-1 was used for this study. Acrylic polymer dispersion containing 38 wt% of solid material and density of 1.25 kg/dm³ was used.

Six series of specimens containing nanosilica in the amounts of 1%, 3%, and 5% by mass of cement and 10 wt% of polymer content were prepared. The control samples without admixture of nanosilica were prepared.

Cement mortar components were mixed according to the EN 196-1 procedure. Nanosilica was applied as a dry powder and mixed mechanically with cement. Polymer dispersion was stirred with the mixing water at high speed for 1 min in order to obtain uniform dispersion. After mixing of components, the consistency of fresh mortars was determined by a flow table method (EN 1015-3). Afterwards, six specimens of each series with 40x40x160 mm were prepared in accordance with the requirements of PN-EN 196-1. The specimens were demolded after 24 hours and cured for five days in a standard water bath at temperature of 20±2°C. Afterwards, specimens were stored in laboratory conditions (95% RH at 20±2°C) up to 28 days of curing. The compressive and flexural strength were determined in accordance with PN-EN 196-1.

A range of composites were prepared based on variations of the composition as follows:

- R: reference sample,
- N-1-100, N-1-250: samples containing 1 wt% of nSiO₂ in diameter of 100 nm and 250 nm,
- N-3-100, N-3-250: samples containing 3 wt% of nSiO₂ in diameter of 100 nm and 250 nm,
- N-5-100, N-5-250: samples containing 5 wt% of nSiO₂ in diameter of 100 nm and 250 nm.

The water to cement (w/c) ratio was fixed to 0.5 to enable reasonable mortars workability. In order to test the properties of material itself, nanosilica structures were applied without help of any dispersing agents. The composition of cement mortars is shown in Table 1.

<table>
<thead>
<tr>
<th>Sample designation</th>
<th>Unit weight [kg/m³]</th>
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<tbody>
<tr>
<td></td>
<td>Cement</td>
</tr>
<tr>
<td>R</td>
<td>519</td>
</tr>
<tr>
<td>N-1-100</td>
<td>519</td>
</tr>
<tr>
<td>N-1-250</td>
<td>519</td>
</tr>
<tr>
<td>N-3-100</td>
<td>519</td>
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<tr>
<td>N-3-250</td>
<td>519</td>
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<tr>
<td>N-5-100</td>
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<tr>
<td>N-5-250</td>
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</table>
3. Results and discussion

3.1. Characteristics of nanosilica (nSiO₂)

To characterize the morphology of the silica nanostructures, a high-resolution transmission electron microscope with a dispersive X-ray spectrometer EDS (FEI Tecnai F20) was used. Properties of synthesized nanosilica structures are presented in the Table 2. Transmission electron micrographs (TEM) presented in Figure 1 show the solid and relatively similar diameter of nanostructures.

Table 2. The properties of nanosilica spheres (nSiO₂).

<table>
<thead>
<tr>
<th>Sample designation</th>
<th>Diameter [nm]</th>
<th>Purity [%]</th>
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<tbody>
<tr>
<td>NS100</td>
<td>100±10</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td>NS250</td>
<td>250±25</td>
<td>&gt;99.9</td>
</tr>
</tbody>
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EDS spectrum of nanosilica spheres proves the effectiveness of the synthesis method presented in Figure 1. Weak signal from nickel and copper comes from TEM grid.

Fig. 1. TEM micrographs of synthesized nSiO₂ - 100 nm diameter (a), 250 nm diameter (b) and EDS diagram (c) of solid silica nanospheres (nSiO₂).

3.2. Consistency of cement mortars

Results of a consistency test determined by flow table according to EN 1015-3 are presented in Figure 2. Note that mortar containing low dosage of nanosilica (regardless of diameter) did not affect the workability of fresh mortar. With the increased content of nanosilica (3 wt% and 5 wt%) there is noticeable decrease of consistency. Moreover, there is remarkable difference between mortars containing nanosilica with diameter of 100 nm and 250 nm. Nanomaterials, due to their high surface area to volume ratio, can noticeably decrease liquidity and cause difficulties in achieving a desired blend of workability.

Specimen containing 5 wt% of 250 nm nanosilica exhibits reduced consistency by 40%, while specimen containing 5 wt% of 100 nm nanosilica reduced consistency of mortar by 18%. This phenomenon can be probably associated with the hydrophobic properties of nanosilica. With the increase of silica diameter the hydrophobic character is decreasing, therefore structures with greater diameter exhibit higher water demand. Hence, less free water is available to provide sufficient workability of cement mortar.
3.3. Mechanical properties

Results of flexural strength determination are displayed in Figure 3. Studies have shown that nanosilica particles of smaller diameter (100 nm) did not affect the flexural strength of specimens. In case of 250 nm nanosilica noticeable deterioration of flexural strength was observed when higher content of nanosilica (3 wt% and 5%wt) was applied.

Compressive strength test results are presented in the Figure 4. Results have shown that application of 3 wt% of nanosilica (regardless to diameter) improved the compressive strength of tested mortars. Small amounts of nSiO$_2$ did not affect the strength significantly as well as high amounts (5 wt%), but this phenomenon can be linked with unsatisfactorily compacted structure due to significant decrement of consistency.
3.4. X-Ray Diffraction analysis

XRD analyses were conducted to investigate the mineralogical composition of specimens after 7 days of hydration. For XRD analysis samples that exhibited the highest improvement of compressive strength have been chosen (NS-3-100 and NS-3-250). For comparison, the peak of CH at 18° (2θ) and the peak of C-S-H at 29.2° (2θ) as suggested by Aly et al. [10] and Kim et al. [11] have been selected. As presented in the Figure 5, a sharp CH peak is observed which is released from the hydration of cement. It can be noticed that the intensity of the CH peak is decreased by adding nanosilica, which reflects the consumption of CH by pozzolanic reaction. At the same time, the intensity of the C-S-H peak increased in specimens containing nanosilica. From the following results in can be concluded that nanosilica (irrespectively of diameter) exhibits certain pozzolanic activity and accelerates the hydration process.

Fig. 4. Compressive strength of specimens after 28 days of curing.

Fig. 5. XRD pattern of target mortars: (a) CH peaks, and (b) C-S-H peaks.
4. Conclusions

From the preliminary studies on the effect of nanosilica on the mechanical properties of polymer-cement composites (PCC) the following conclusions can be drawn:

- Despite relatively good initial consistency, attributed to polymer presence in the mortars, nanosilica due to its properties can highly decrease the consistency of cement mortars, leading to lowering the strengths of PCC.
- Finer nanosilica particles due to their higher pozzolanic activity seem to be more effective and have a positive impact on the PCC performance.
- To optimize the performance of nanosilica in PCC, the use of dispersing agents seems to be necessary.
- Based on the XRD analysis and mechanical properties results it can be concluded that nanosilica can find potential application in PCC to improve its mechanical properties and hydration process. The addition of nanosilica has great potential to accelerate the pozzolanic reaction, thus reacting more with the CH and increasing conversion of C-S-H.

References