The effect of nano-SiO$_2$ on concrete properties: a review

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Abstract: In recent years, the addition of nanometer materials to concrete materials has attracted a group of increasing number of scholars' research interests, and nano-SiO$_2$ is one of the research hotspots. In this paper, we briefly introduce the influence of nano-SiO$_2$ on setting time, slump, shrinkage, durability and mechanical properties of concrete. In addition, this review also includes the microstructure measured by scanning electron microscope (SEM) and the content of various hydration products obtained by X-ray diffraction (XRD). The result shows that the setting time of nano-SiO$_2$ concrete is shortened, the slump is reduced and the shrinkage is improved owing to the high activity and nucleation of nano-SiO$_2$. The improvement effect of nano-SiO$_2$ on concrete is remarkable, especially in the aspect of enhancing the durability of concrete. It should be noted that nano-SiO$_2$ shows limited improvement in the mechanical properties of concrete. In the end, this literature summary explains the macro performance of nano-silica modified concrete through microstructure.

Keywords: nano-silica modified concrete; setting time; slump; shrinkage; durability; mechanical properties

1 Introduction

Concrete is one of the most important materials in modern civil engineering structures. Apart from meeting the requirement of high compression and tension-resistance, concrete is easy to construct, and its high strength, toughness and impermeability can maintain for a long time. Nano-silica modified coating is applied on the surface of concrete, which can prevent the degree of carbonization of concrete. The reason is that the nano-SiO$_2$ particles reduce the microscopic defects in the concrete and the damage to the polymer molecules caused by ultraviolet rays [1]. Ma et al. [2] found that within a certain dose range, the mass of hydrated calcium silicate gels (C-S-H) and ettringite crystal (AFt) gradually increased with the increase of nano-SiO$_2$ content. The incorporation of nano-SiO$_2$ can optimize the pore structure of recycled aggregate concrete and limit the diffusion capacity of chloride ions [3]. Adding nano-SiO$_2$ to the cementing system can accelerate the early hydration of concrete, which is very beneficial for strengthening the early strength of concrete [4]. Li et al. [5] tested the flexural strength of the composite through a three-point bending test. With the incorporation of nano-SiO$_2$, the bending strength of the composite was increased, but its brittleness was also increased. Although the addition of nano-SiO$_2$ particles does not significantly improve the mechanical properties, it can dramatically reduce the penetration of chloride ions and help to prevent the corrosion of steel bars in concrete [6]. Surface protection materials can be prepared by using nano-SiO$_2$ and silica fume modified mortar. When this material is coated on the concrete surface, the concrete shows good impermeability [7]. Nano-silica particles are also valuable in enhancing the strength of mortar, because nano-SiO$_2$ can not only fill the pores in the matrix, but also act as an activator to promote pozzolan reaction [8]. The synergy effect of nano-SiO$_2$ and silica fume makes the concrete more dense and dense and also makes up for insufficient silica fume activity [9]. Prashanth et al. [10] demonstrated the positive effects of adding nano-SiO$_2$ to concrete. The size and distribution of pores in Nano-silica modified concrete show that nano-SiO$_2$ helps to finely divide the pore size and reduce the permeability of concrete. The weakest area in concrete is the interface between the cement matrix and the aggregate. Adding an appropriate amount of nano-SiO$_2$ to the concrete can enhance the interface strength and refine the pores, which can effectively reduce the water permeability of concrete [11]. Nano-silica can also optimize the microstructure of recycled concrete. Silica particles promoted the hydration reaction to produce more dense gel materials, which can improve the interface strength between waste concrete and cement slurry [12]. Singh et al. [13] compared the improvement effect of colloidal nano-SiO$_2$ and powdered nano-SiO$_2$ on the mechan-
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The mechanical properties of concrete, and found that powdered nano-SiO$_2$ promoted the generation of more C-S-H in mortar. Therefore, nano-SiO$_2$ powder is more effective to improve the mechanical properties of concrete. The pore volume of cement slurry prepared by replacing part of cement with nano-SiO$_2$ can be reduced by 13.4%, and it does not adversely affect for the porosity and permeability of cement slurry [14]. Chen et al. [15] investigated the axial compressive properties of nano-SiO$_2$-reinforced concrete filled round stainless steel short columns. It was found that the influence of nano-SiO$_2$ dosage on the axial bearing capacity of nano-SiO$_2$-reinforced concrete filled round stainless steel short columns was discrete. When the nano-SiO$_2$ content was 1%, the axial bearing capacity was highest. Lin et al. [16] found that the number of freeze-thaw cycles had little effect on the bearing capacity of circular nano-silica concrete filled stainless steel tube stub columns. He et al. [17] found that the load bearing capacity and initial stiffness increased as the nano-silica concrete compressive strength of the specimens increased.

2 Properties of nano-SiO$_2$

Nano-SiO$_2$ is a white fluffy powder composed of high purity amorphous silica powder. Because of its small particle size, nano-SiO$_2$ had the advantages of large specific surface area, strong surface adsorption, large surface energy, high chemical purity and good dispersion. Nano silica played an irreplaceable role in medicine, physics, chemistry and biology and other fields because of its unique properties [18–53]. According to the different hydrophilicity of nano-SiO$_2$, it can be divided into hydrophilic nano-SiO$_2$ and hydrophobic nano-SiO$_2$. Among them, the nano-SiO$_2$ used in concrete was mainly hydrophilic nano-SiO$_2$. This was mainly due to the good dispersion of hydrophilic nano-SiO$_2$ in water. The particle size of nano-SiO$_2$ used in the experiment is mainly about 15 nm.

3 Setting time

As for the measurement of setting time, scholars at domestic and foreign mainly use Vicat method needle to determine. The initial setting time of different types of concrete was about 4-7 hours, and the final setting time was about 6-10 hours, as shown in Figure 1. By comparison, it was found that the addition of Nano-SiO$_2$ helped to reduce the setting time of concrete [54]. Litfivy et al. [55] also found a similar rule. Figure 2 shows the coagulation time of the mixture measured in the experiment. This is because the addition of nano-materials accelerates the hydration of tricalcium (C3S) silicate and dicalcium silicate (C2S), which accelerates the formation of C-S-H gel, thereby shortening the setting time of the sediment [56, 57]. Compared with the control concrete, the initial setting time and final setting time of the mixture with nano-SiO$_2$ content of 1.0% were reduced by about 20 minutes. However, when the silica content is 2%, the initial setting time and final setting time of the cementitious materials were shortened by 90 minutes and 100 minutes, respectively [58]. The specific surface area of nano-SiO$_2$ particles with smaller size is larger. Along with the addition of nano-SiO$_2$ particles, the solidification time was greatly shortened. The decreased of nano-particles size made its surface energy increased [59, 60].
4 Slump

Slump denotes the average diameter of the concrete after releasing the standard slump cone, and is one of the important indexes to measure the plasticizing performance of concrete [61]. Björnström and Quercia et al. [62, 63] found that the slump value of Nano-silica modified concrete is between 80mm-100mm, which is 40%–60% lower than that of ordinary concrete. A small amount of water was observed to bleed out from the fresh concrete during the slump test [64, 65]. When the cement is replaced with nano-SiO₂, the nano-SiO₂ has super high reaction capacity because of its high specific surface area and a large number of unsaturated bonds, which makes it easier to attract surrounding water molecules to form chemical bonds. Therefore, there is no water segregation or obvious exudation from the mixture with nano-SiO₂ [69] also hold that because the specific surface area of silica particles is larger than that of cement, and it absorbs more water and reduces the slump of concrete. According to Li et al. [70], when the nano-particles are uniformly dispersed in the concrete matrix, the hydration products of the cement contain huge surface energy during the hydration process. These hydrates accumulate around the nano-SiO₂ dioxide with the nano-SiO₂ dioxide particles as the core. Because of its high activity, nano-SiO₂ can further promote the hydration process. Therefore, in order to ensure the workability of concrete, an appropriate amount of high-efficiency water reducing agent should be incorporated to the concrete.

5 Shrinkage of concrete

Shrinkage is a common phenomenon in cement-based grouting, which is caused by water loss. Shrinkage leads to the development of cracks and further affects the bond strength between aggregates. Wang et al. [71] found that the incorporation of nano-SiO₂ improved the shrinkage of lightweight aggregate concrete, especially the later shrinkage of lightweight aggregate concrete. Li et al. [54] tested the shrinkage of different cement pastes, and found that the shrinkage of cement increased with the increased of cement curing age. The shrinkage of cement paste after 28 days is 0.28%-0.70%. The hydration of C2S and C3S in cement was continuously promoted due to the high activity of nano-SiO₂, and the compactness of concrete was constantly improved. As a result, the cement slurry continues to shrink.

6 Durability properties

Said et al. [72] measured the penetration depth of chloride ion by colorimetry, and found that the penetration depth of chloride ion in concrete with 6% nano-SiO₂ content was lower than that in concrete without nano-SiO₂. Furthermore, as the silicon oxide content increased, the charge and physical penetration depth decreased. Under the pressure of 0.5 MPa, the penetration depth of concrete with a nano-SiO₂ content of 3.8% was less than 5 mm. Although the total porosity did not change much, nano-SiO₂ divides the larger pores in the concrete into smaller pores, which greatly improved the permeability of the concrete. This indicates that Nano-silica modified concrete had great potential in improving the permeability resistance [73]. When nano-SiO₂ and fly ash are mixed into the fresh concrete at the same time, the pore size in the concrete becomes smaller and the porosity decreases after a short time of curing. One reason is the high activity and nucleation of nano-SiO₂ and the secondary hydration promoted by fly ash. Another reason is the filling effect of nano-SiO₂ and fly ash. Moreover, as the curing time increases, the pore size of all types of concrete samples decreases [74]. By testing the durability of concrete with nano-SiO₂ content of 0.3% and 0.9%, it was found that low-dose of nano-SiO₂ can also provide excellent impermeability, because small doses of nano-SiO₂ are more easier to disperse [75].

7 Mechanical properties

7.1 Compressive strength

The addition of nano-SiO₂ is beneficial to the compressive strength of concrete. The compressive strength of nano-SiO₂ modified concrete increases with increased nano-SiO₂ content toward the threshold content. Above the threshold value, a higher amount of nano-SiO₂ leads to a decrease of the compressive strength. Nano-silica concrete with a nano-SiO₂ content of 1.5% provides the highest compressive strength. The compressive strength of Nano-silica modified concrete increases by 16%-25% at 7 days and 12%-17% at 28 days, compared with ordinary concrete. The main reason for the improvement of concrete compressive strength is the pozzolanic reaction from nano-SiO₂ and calcium hydroxide, which promotes the formation of hydrated calcium silicate. However, concrete without nano-SiO₂ can only rely on cement to hydrate to a small amount of calcium silicate hydrate. Hydrated calcium silicate is one of the important elements that provide strength.
Therefore, the compressive strength of concrete without nano-SiO$_2$ is low [76, 77]. Jalal and Abdellahi et al. [78, 79] found that the early strength improvement effect of Nano-silica modified concrete is more obvious, which was due to the higher pozzolan activity of nano-SiO$_2$ particles [80–83]. However, with the delay of the curing time, the nano-SiO$_2$ particles used for pozzolanic reaction gradually decreased, which led to a reduction in the later-stage compression improvement effect of Nano-silica modified concrete [84–90].

Ibrahim et al. [91] studied the compressive strength of nano-SiO$_2$ concrete after high temperature treatment. The experimental results showed that the concrete containing nano-SiO$_2$ had a more prominent effect on the improvement of compressive strength at 400°C. This is because when the temperature reached 400°C, more high-density calcium silicate hydrate was produced in the concrete matrix and the reaction activity of nano-SiO$_2$ was improved, which promotes its hydration process and increases the compressive strength of concrete.

7.2 Flexural strength

The flexural strength of Nano-silica modified concrete showed a similar trend to compressive strength. Due to different water-cement ratios, there are also differences in the optimal content of nano-SiO$_2$, which resulted in different effects on improving the flexural strength of concrete [92–97]. Li et al. [55] found that when the nano-SiO$_2$ content increased from 3% to 10%, the flexural strength of the mortar increased. Rong et al. [76] found that when the nano-SiO$_2$ content was 3%, the nano-SiO$_2$ modified mortar provided the highest flexural strength at curing for 3 days, 7 days, 28 days and 90 days. Figure 3 shows the flexural strength of the mortar at 3 days, 7 days, 28 days and 90 days. Li et al. [98] found that the optimal content of flexural strength of UHPC was 1.0%. When the water-binder ratio was 0.16, the flexural strengths of UHPC were 23.2 MPa and 25.8 MPa at 7 days and 28 days, respectively. Wu et al. [99] studied the flexural strength of nano-SiO$_2$ carbon fiber-reinforced concrete (NSCFRC) at 25°C, 375°C, 575°C and 775°C. It is found that NSCFRC prepared of 1wt% nano-SiO$_2$ and 0.15vol% carbon fiber provided the highest flexural strength at room temperature, and the residual flexural strength of NSCFRC with different content of nano-SiO$_2$ is improved to different extent than that of carbon fiber concrete (0.15% carbon fiber) at 375°C, 575°C and 775°C. This shows that the improving effect of nano-SiO$_2$ on the flexural properties of carbon fiber reinforced concrete after high temperature treatment is very significant. Beigi et al. [69] found that the optimal content of nano-SiO$_2$ was 4%. Compared to ordinary concrete, the flexural strength of concrete with 4% carbon fiber content was increased by 40%. When nano-SiO$_2$ was synergistic with different fibers (0.3% steel fiber, 0.2% polypropylene fiber and 0.2% glass fiber), the bending strength of nano-SiO$_2$ modified fiber reinforced concrete increased by 67%, 53% and 75%, respectively, compared to that of ordinary concrete. This is mainly because the nano-SiO$_2$ filler and pozzolanic effect improved the structural properties and adhesion between the fiber and the interface region.

7.3 Split tensile strength

As expected, nano-SiO$_2$ can improve the split tensile strength of concrete. By testing the splitting strength of different particle size nano-SiO$_2$ dioxide added to concrete, Alireza Khaloo et al. [80] found that the improvement effect of 12 nm nano-SiO$_2$ on the splitting tensile strength of concrete was stronger than that of 7 nm nano-SiO$_2$. They detected that nano-SiO$_2$ with lower specific surface area was easier to disperse in water. Fallah et al. [100] tested the splitting tensile strength of nano-SiO$_2$ concrete. When 3% nano-SiO$_2$ replaced cement, the tensile strength of Nano-silica modified concrete was improved by 16.10% than that of ordinary concrete. Compared with the addition of nano-SiO$_2$ into concrete, the strengthening effect of adding silica fume on the splitting tensile strength of concrete was more effective.

Compared to the ordinary concrete, the split tensile strength of nano-SiO$_2$ modified concrete with 4% nano-SiO$_2$ was increased by 35%. When 4% nano-SiO$_2$ was used together with 0.3% steel fiber, 0.2% polypropylene fiber and 0.2% glass fiber, the split tensile strength of nano-SiO$_2$
Figure 4: SEM micrographs of control group concrete: (a) 10,000× and (b) 5000× [102]

Figure 5: SEM micrographs of paste containing nano-SiO$_2$ particles 10,000× and (b) 5000× [102]

Figure 6: Micro shape and appearance of different test piece [103]
modified carbon fiber concrete increased by 90%, 57% and 77%, respectively, compared to the control concrete. The reason for this phenomenon is that nano-SiO₂ improves the interface strength between the concrete matrix and the aggregate [69]. Adding nano-SiO₂ to concrete not only plays a nano-reinforcement role, but also acts as a filling agent, which fills the pores in the concrete matrix [56, 101].

8 Microstructure

8.1 Scanning electron microscope

The effect of nano-SiO₂ on the durability, rheological properties and mechanical properties of concrete can be explained by microstructure. Figures 4 and 5 are the SEM of nano-SiO₂ modified mortar and the control group, respectively. It was found that the addition of nano-SiO₂ affected the hydration process of the concrete matrix [102]. By comparing the microstructures of Nano-silica modified concrete and control group concrete, it was found that nano-SiO₂ not only filled the gaps between the particles in the concrete matrix, but also promoted the chemical reaction and also generates C-S-H gel to fill the pores of the concrete slurry. That is why the micro silica fume improved the durability and mechanical properties of concrete. Figures 6 and 7 showed the interface of the sample containing nano-SiO₂. It can be seen from the figures that the concrete without nano-SiO₂ was more likely to form larger crystals and pores, and the whole structure was more incompact. When nano-SiO₂ was added to concrete, the size
of pore and crystal becomes smaller, and the coupling between the crystals becomes tighter, which makes the microstructure more compact [103–106]. Ghafari et al. [107] also found that the structure of concrete was more optimized with the addition of nano-SiO$_2$. As the content of nano-SiO$_2$ increased, the volume of capillary pores in the concrete matrix decreased continuously.

8.2 X-ray diffraction (XRD)

Zhang et al. [56] tested the product in cement slurry by X-ray diffraction. It can be seen from Figure 8 that one day later, the peak of portlandite (CH) in cement slurry with nano-SiO$_2$ was higher than that in ordinary cement slurry. However, the silicate peak was decreased significantly at 28 days. This indicates that the high activity of nano-SiO$_2$ consumed part of the silicate in the process of promoting hydration. Rong et al. [76] found that when the hydrogel was relatively low, the mixture contained a large amount of unhydrated cement before 7 days. After 7 days, the content of major hydration products changed slightly, and among them, the content of calcium hydroxide is very small. As time and the content of nano-SiO$_2$ increase, the content of calcium hydroxide decreased. The reason is that nano-

![Figure 8: XRD patterns [56]](image-url)
SiO$_2$ promotes the reaction between calcium hydroxide and pozzolanic materials.

9 Nano-silica challenges

Nano concrete shows excellent performance because nano-SiO$_2$ has a large surface area. At the same time, some problems in the research have also received the attention of scholars. For example, although high specific surface area makes concrete show more excellent performance, nano-SiO$_2$ aggregates because of its high specific surface area, which affects the dispersion effect in water. The introduction of ultrasonic technology improves the dispersion of nano-SiO$_2$ in water, but it is still an important direction of improving the dispersion effect of nano-SiO$_2$ [108]. In addition, the colloidal silica sol containing monodisperse nanoparticles is easy to form flocules and coatings on the surface of cement particles after combining with cement. These flocules can retain more free water, which is more obvious than the improvement of the hydration effect of nano-SiO$_2$. Therefore, the application of colloidal silica sol in concrete deserves attention [109, 110].

10 Conclusion

The effects of nano-SiO$_2$ on the setting time, slump, shrinkage, durability, and the mechanical properties of concrete are described in detail in the review, and the strengthening mechanism of nano-SiO$_2$ is explained by microstructure. Reviewing the previous research on nano-SiO$_2$ concrete, the following conclusions can be drawn:

1. When nano-SiO$_2$ is used to replace part of the cement, the high activity of nano-SiO$_2$ helps to promote the hydration reaction of concrete, which shortens the setting time of nano-SiO$_2$. 

2. Nano-SiO$_2$ has a large specific surface area because of its small particle size. In the process of concrete mixing, a large number of unsaturated bonds promote the nano-SiO$_2$ to absorb more water molecules, which leads to the decrease of concrete slump. 

3. On one hand, nano-SiO$_2$ promotes the degree of hydration of concrete, making the concrete matrix to produce more C-S-H gel, which fills the pores in the concrete matrix. On the other hand, inactive nano-SiO$_2$ plays a filling role. Nano-SiO$_2$ can reduce the pore volume and make the concrete more compact through these two aspects. Therefore, nano-SiO$_2$ modified concrete exhibits excellent durability.

4. Nano-silica has higher pozzolanic activity. In the early stage, the early strength improvement effect of nano-SiO$_2$ concrete is more obvious due to the more sufficient pozzolanic reaction. As the curing time increases, the nano-SiO$_2$ particles become smaller and the pozzolan response becomes weaker. Therefore, the improvement effect of nano-SiO$_2$ on concrete strength in the later period is reduced.

5. The incorporation of nano-SiO$_2$ resulted in changes in the content of hydration products generated during the hydration process, etc. For example, silicate content decreased and hydrated calcium silicate gel increased, etc. The changes of these hydration products content optimized the microstructure of concrete and made the concrete more compact. The changes of these surround layers led to changes in macroscopical performance.

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