

Synthesis of Nanoscale Calcium Silicate Hydrate for Strength Enhancement of Cement Paste

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Calcium silicate hydrate-polycarboxylate (C-S-H-PCE) nanocomposites can greatly increase the hydration speed of cement paste. To obtain the optimal synthesis condition for smaller particle size, C-S-H-PCE was prepared by adding $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ solution into PCE dispersion solution under high speed stirring, and the effects of reaction temperature, drip flow rate, aging time, C-S-H content and molecular weight of PCE on the particle size distribution of C-S-H were studied. Dynamic light scattering (DLS) and transmission electron microscopy (TEM) were employed to conduct the analysis of particle size and morphology of the prepared C-S-H-PCE. The application performance of the nano composite was characterized by testing the compressive strength of cement paste added with C-S-H-PCE. The experimental results showed that at 25 °C, C-S-H-PCE synthesized with lower PCE molecular weight, slower drip flow rate, and smaller C-S-H content had better performance. The compressive strength of cement paste with C-S-H-PCE cured under low temperature condition was tested. It turned out that the prepared nanocomposites can remarkably enhance the early strength of cement paste for up to 63.8 % and 24.2 % after 1 d and 3 d.

1. Introduction

Cement is the most widely used material in the construction industry. The cement production process is currently responsible for approximately 8 % of the world's CO₂ emissions (Singh et al., 2013). As we know, the hydration of cement is delayed when it is used in cold climate, which results in the decrease of early strength (Pedrosa et al., 2020). In this case, more cement is generally required in the sprayed concrete due to the increased rebound ratio. Therefore, it is highly desirable to develop active admixture for the strength enhancement of cement under low temperature.

Generally, 50~70 % of the products from cement hydration are nanoscale calcium silicate hydrate (C-S-H) (Bullard et al., 2011). It plays a role of nucleation promoting in the process of cement hydration (John et al., 2018), and thus contribute to strength development at different age, especially at the early stage (Bost et al., 2016). C-S-H nanoparticles have high specific surface area and high surface energy, thus they are easy to agglomerate. This instability greatly limits its use as cement admixture (Kong et al., 2013). To improve the stability of C-S-H nanoparticles, the stabilizer is often used. The organic polymers such as polycarboxylate superplasticizer (PCE) can be adsorbed on the surface of nano C-S-H, which hinders the collision between particles, reduces the tendency of agglomeration (John et al., 2019), and plays the role of stabilizing nanoparticles. For example, Kanchanason and Plank (2017) investigated the influence of pH on the structure, composition and morphology of C-S-H in the presence of PCE. It is found that the smallest size of the foil-like nanocomposites was obtained at pH=11.7. Additionally, the long side chain of the PCE molecule is conducive to the formation of small-sized nanoparticles (Plank et al., 2018). Except for the pH and side chain, we speculated that the particle size of C-S-H and the strength enhancement of cement is related to drip flow rate,

reaction temperature, molecular weight of PCE, aging time, C-S-H content, and so on. However, there was few researches on this subject.

In this study, the effect of drip flow rate, reaction temperature, PCE molecular weight, aging time and C-S-H content on the size distribution of C-S-H-PCE was systematically investigated. The correlation between particle size of the C-S-H and strength enhancement of cement paste was revealed. Finally, the early strength of cement paste in the presence of C-S-H-PCE was tested under low temperature curing conditions.

2. Materials and methods

2.1 Materials

Calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) and nitric acid (HNO_3 , 65 wt.%) were purchased from Damao Chemical Reagent Factory (Tianjin, China). Sodium metasilicate pentahydrate ($\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$) was purchased from Shanghai Macklin Biochemical Co., Ltd (China). Sodium hydroxide (NaOH) was purchased from Aladdin (China). Ordinary Portland cement (P.O-42.5) obtained from Tangshan Tianlu Cement Co., Ltd (China). Two different PCEs were obtained from Tianjin Rumi Novel Materials Co., Ltd (China). The product information of the PCEs is summarized in Table 1.

Table 1: Molecular properties of PCEs

PCE Sample	M_w (g/mol)	M_n (g/mol)	PDI (M_w/M_n)	Solid content (%)
PCE-88 k	88,304	28,364	3.11	40
PCE-36 k	36,826	21,025	1.75	40

2.2 Preparation of C-S-H-PCE nanocomposites

The C-S-H-PCE nanocomposites were prepared using the solution precipitation method. Aqueous solution of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were dripped into the diluted PCE solution. Specifically, 105 g of the PCE solution were diluted with 425 g of water and the pH of this PCE solution was adjusted to 10.0 ± 0.5 by adding aqueous solution of NaOH (30 wt.%). The initial Ca / Si ratio was 1.0. The pH value of the system was maintained at 11.7 ± 0.5 during the reaction. When the dripping was finished, aging was then carried out by stirring at room temperature.

2.3 Characterization

Particle size of C-S-H-PCE nanocomposites was measured by dynamic light scattering (DLS) using a Zetasizer Nano ZS apparatus (Nano ZS, UK). The samples were diluted with pure water at a concentration of 0.1 g/L, and ultrasonically treated for 15 min prior to measurement.

Morphology of the C-S-H-PCE samples was observed by transmission electron microscope (TEM) performed on a JEOL JEM 1400 FLASH (JEOL, Japan). The C-S-H-PCE suspensions were diluted with pure water at a concentration of 0.01 g/L and ultrasonically dispersed with a power of 390 W for 1 min. The dispersed samples were then dropped on a 200 Cu mesh with carbon support films.

2.4 Compressive strength test of cement paste

The compressive strength of cement paste was tested following the Method of testing cements-Determination of strength (GB/T 17671-1999). In the preparation of the test sample, the cement usage was 1.6 kg (or 1.7 kg), the water/cement ratio was 0.325 (or 0.315), and the proportion of C-S-H-PCE sample to cement was 0.05 (or 0.04). The mixture of cement paste and C-S-H-PCE was poured into $70.7 \times 70.7 \times 70.7$ mm molds and cured at room temperature in a closed room. The compressive strength of cement paste was tested after aging 3 d, 7 d and 28 d.

3. Results and discussion

3.1 Morphology of C-S-H-PCE nanocomposites

Figure 1 shows the TEM images of the synthesized C-S-H-PCE nanocomposites. In the presence of PCE, the composites have a globular core-shell structure. The core of nanocomposites is C-S-H, which is cladded by PCE layer. The nanocomposites have an average diameter of ~ 200.0 nm. At high PCE loading, the postponement of the transition from nano-spherical particles to nano-flakes is obvious (Wang et al., 2019). After 7 d, the spherical C-S-H-PCE can still be observed. The result is probably attributed to the large amount of PCE adsorbed on the surface of C-S-H particles, forming a thicker polymer layer (Schönlein and Plank, 2018).

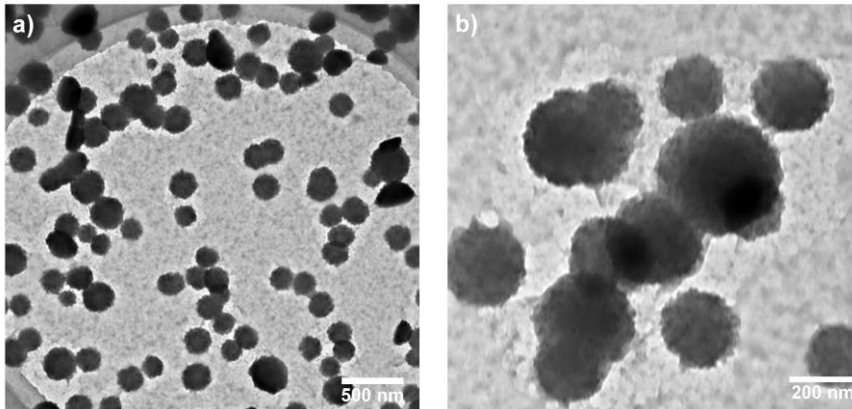


Figure 1: TEM images of C-S-H precipitation in the presence of PCE (PCE-36 k, 25 °C)

3.2 Effect of drip flow rate on particle size and the strength of cement paste

Figure 2a shows the particle size of the C-S-H-PCE nanocomposites prepared with different drip flow rates. It has little effect on the particle size of C-S-H. The compressive strength of cement with C-S-H-PCE samples is shown in Figure 2b. It is demonstrated that the strength of cement paste was highest when using the C-S-H-PCE nanocomposites with a drip flow rate of 2.2 mL/min. Additionally, the C-S-H-PCE prepared by drip flow rate of 8.6 mL/min had a negative effect on the long-term strength of cement paste.

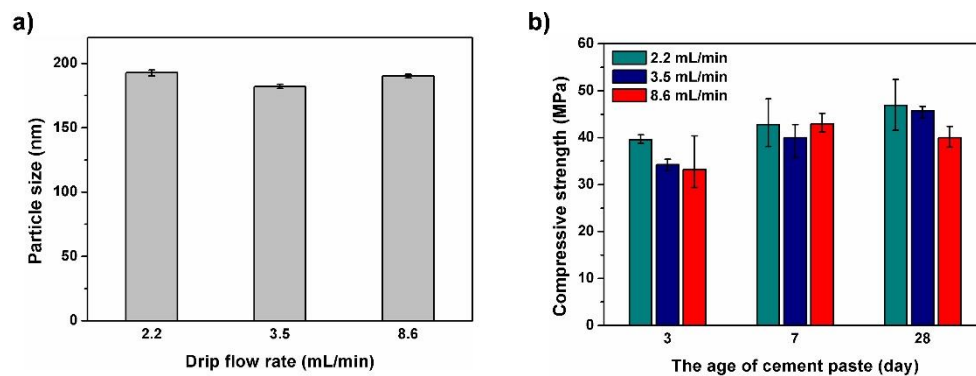


Figure 2: a) Particle size of the C-S-H-PCE composites synthesized with different drip flow rates; b) The compressive strength of cement mixed with C-S-H-PCE composites synthesized with various drip flow rates

3.3 Effect of reaction temperature on particle size and the strength of cement paste

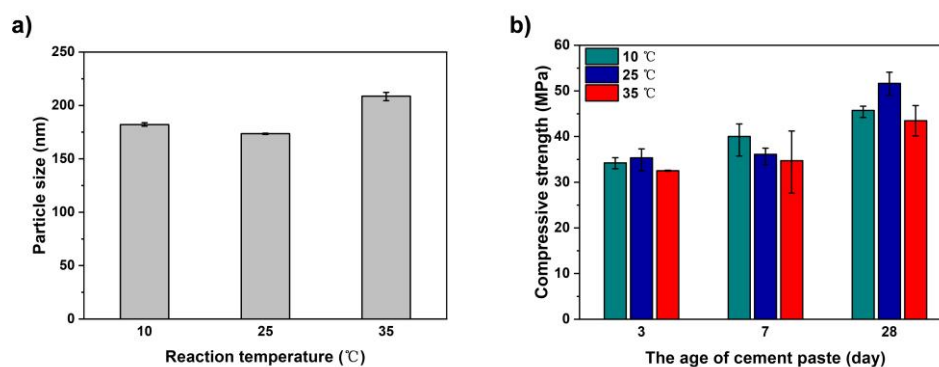


Figure 3: a) Particle size of the C-S-H-PCE composites synthesized with different reaction temperatures; b) The compressive strength of cement mixed with C-S-H-PCE composites synthesized with various reaction temperatures

The particle size of C-S-H prepared with different temperature is shown in figure 3a. The minimum particle size was 173.9 nm, which was achieved under the reaction temperature of 25 °C, and it can induce the biggest seed effect for cement hydration. The 3 d compressive strength of the group with 25 °C reaction temperature was 42.80 MPa, which was 3.2 % and 8.7 % higher than that of 10 °C and 35 °C, respectively. Moreover, the superiority of compressive strength remained after 28 d. When the reaction temperature was 35 °C, the particle size of C-S-H was the biggest, and the enhancement effect on cement compressive strength was the lowest.

3.4 Effect of molecular weight of PCE on particle size and the strength of cement paste

The particle size of the C-S-H-PCE synthesized with different molecular weight PCE is illustrated in Figure 4a. The C-S-H-PCE-88 k had an average particle size of 182.1 nm, while that for C-S-H-PCE-36 k was 230.7 nm, which was 26.7 % larger than the former. With higher molecular weight, the PCE can provide greater steric hindrance when its main chain is adsorbed to the surface of C-S-H, thus C-S-H particles size is smaller. On the other hand, PCE with higher molecular weight can cause gelation of the nanocomposites, and the fluidity of the cement paste is insufficient, which is not favorable for the strength enhancement of cement paste. The compressive strength of cement paste is shown in figure 4b. C-S-H-PCE-36 k performed better than C-S-H-PCE-88 k, which increased by 12.6 %, 20.8 %, 19.9 % after aging 3 d, 7 d and 28 d, respectively. With lower molecular weight, the main chain adsorbed to the surface of C-S-H provided relatively smaller steric hindrance, thus larger C-S-H spherical particles were obtained. In this circumstance, the paste has better fluidity, the seed can be dispersed in the cement paste more effectively, so the compressive strength of cement is enhanced significantly.

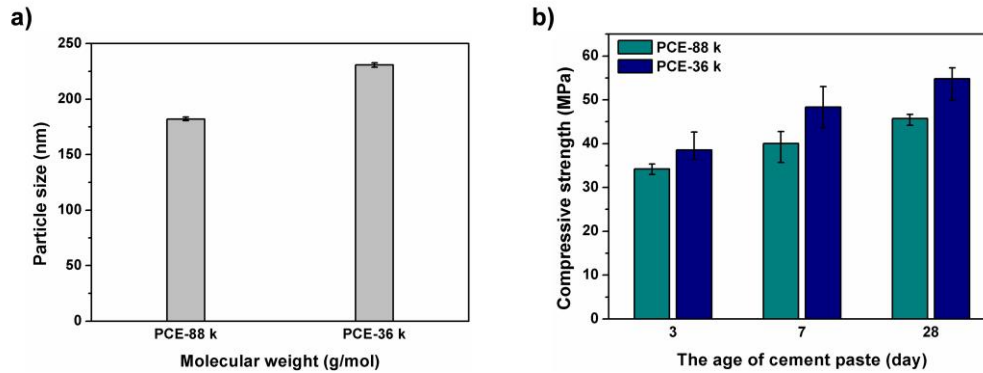


Figure 4: a) Particle size of the C-S-H-PCE composites synthesized with PCE of different molecular weight; b) The compressive strength of cement mixed with C-S-H-PCE composites synthesized with various molecular weight of PCE

3.5 Effect of aging time on particle size and the strength of cement paste

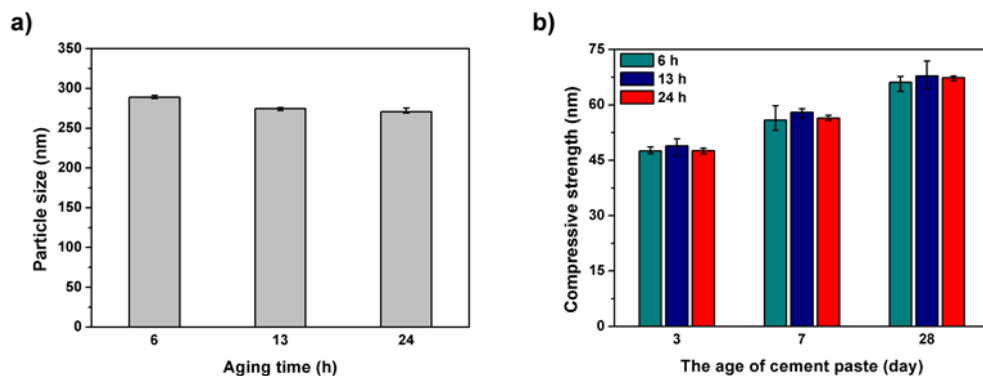


Figure 5: a) Particle size of the C-S-H-PCE composites synthesized with different aging time; b) The compressive strength of cement mixed with C-S-H-PCE composites synthesized with various aging time

The particle size of C-S-H synthesized with different aging time is shown in Figure 5a. The particle size of C-S-H aged for 6 h was the largest, which was 288.9 nm, and the particle sizes for 13 h and 24 h aging time were close at approximately 270.0 nm. The results indicate that the growth process of C-S-H particles becomes stable

after a certain period of aging time. During the first 6 h of the aging process, the C-S-H particles were still growing, and the reaction was unfinished yet. After 13 h of aging, the particle size changes slowly, and the growth of C-S-H particles tended to be stable. Figure 5b shows the strength of corresponding cement paste, and the C-S-H-PCE aged for 13 h performs well on improving compressive strength of cement paste. In general, the C-S-H-PCE prepared with different aging times have no significant difference on the compressive strength of cement paste.

3.6 Effect of C-S-H content on particle size and the strength of cement paste

Figure 6a shows the particle size data of C-S-H particles synthesized with different C-S-H content. With the rise of C-S-H content, the particle size increases. When the C-S-H content was 0.18 mol, the synthesized C-S-H-PCE had the smallest particle size. The low content of C-S-H can abate the increase in particle size caused by the collision of C-S-H nanoparticles. With the combined action of the polymer adsorbed to the surface, the particle size of the nanoparticles was restricted to a lower level. Figure 6b shows the effect of C-S-H particles synthesized with different C-S-H content on compressive strength of cement paste. Interestingly, the samples with high C-S-H content did not have the highest enhancement effect. Instead, the samples with the lowest content had the best enhancement effect. To achieve remarkable improvement of the early strength of cement-based materials, the C-S-H crystal seed should have a very small size on the premise of satisfying the good fluidity of cement paste, so as to produce the largest seed promoting effect on cement hydration reaction. After 28 d curing, the compressive strength achieved a certain increase, which indicated that there is no adverse effect on long-term compressive strength of cement paste (John et al., 2019).

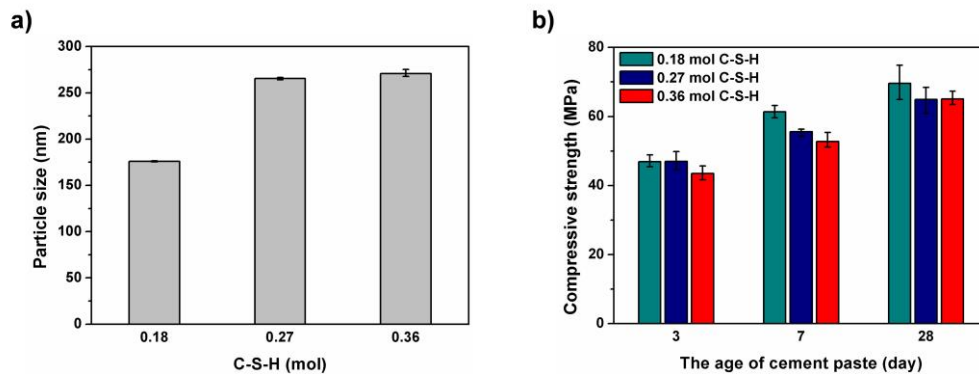


Figure 6: a) Particle size of the C-S-H-PCE composites synthesized with different C-S-H content; b) The compressive strength of cement mixed with C-S-H-PCE composites synthesized with various C-S-H content

3.7 Compressive strength test of cement paste under low temperature curing conditions

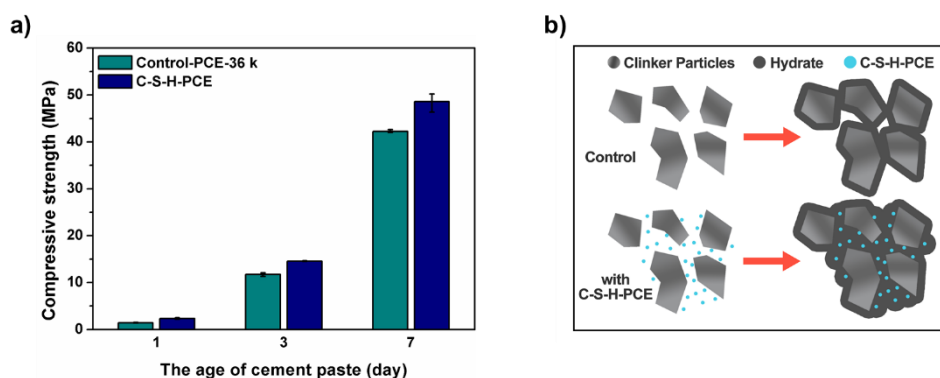


Figure 7: a) The early compressive strength of cement pastes with C-S-H-PCE; b) Schematic representation of cement hydration and the influence of nucleation seeding with C-S-H-PCE

To verify the enhancement of the early strength of cement paste added with C-S-H-PCE at low temperature (4 °C), C-S-H-PCE was synthesized when the reaction temperature was 25 °C, the molecular weight of PCE was 36,826 g/mol, and the content of C-S-H was 0.18 mol. The compressive strength of cement paste is shown in Figure 7a. The prepared C-S-H-PCE was compared with the control sample (PCE-36 k). After 1 d, 3 d and 7 d,

the compressive strengths of cement pastes with C-S-H-PCE added were 63.8 %, 24.2 %, 15.0 % higher than that of control samples (PCE-36 k), respectively.

When cement is used in cold climates, its hydration is delayed, leading to a significant decrease in early strength (Kanchanason and Plank, 2017). Adding CSH-PCE can be used as a secondary nucleation or growth site for cement hydration (Figure 7b), reducing the supersaturation required for the precipitation of hydration products, lowering the nucleation barrier, and accelerating the hydration reaction (Kanchanason and Plank, 2019); the hydration products grow on the seeds, away from the surface of clinker particles, which avoids problems such as hydration products hinder the dissolution of cement clinker ingredients (Nicoleau, 2010). With the addition of C-S-H-PCE, the degree of cement hydration increases, the hydration products are more dispersed, and the cement paste structure is denser and greatly enhance compressive strength of cement paste at the early stage.

4. Conclusions

In summary, the optimized synthetic parameters for C-S-H-PCE nanocomposites were successfully obtained. It was demonstrated that the compressive strength of cement paste at low temperature was significantly enhanced by the C-S-H-PCE nanocomposites prepared under the optimized conditions. The main conclusions are as follows:

- (1) The molecular weight of PCE and the C-S-H content had an important influence on the particle size of C-S-H and the compressive strength of cement paste.
- (2) When the reaction temperature was 25 °C, molecular weight of PCE was 36,826 g/mol, C-S-H content was 0.18 mol, the synthesized C-S-H-PCE had the smallest average particle size of 176.0 nm. The compressive strength after aging 3 d, 7 d, and 28 d were 46.94 MPa, 61.34 MPa and 69.57 MPa.
- (3) Under low temperature curing conditions (4 °C), C-S-H-PCE nanocomposites had 63.8 %, 24.2 %, 15.0 % of strength enhancement of cement paste than the control sample after 1 d, 3 d, 7 d.

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