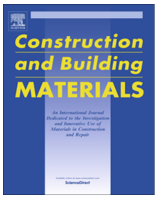
Construction and Building Materials 140 (2017) 282–292

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat



Effects of synthetic C-S-H/PCE nanocomposites on early cement hydration

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HIGHLIGHTS

- A “co-precipitation” method was used to synthesize C-S-H/PCE nanocomposites.
- A Box-Behnken design was employed to design the experiments.
- PCE polymers were adsorbed on surface or chemically incorporated into C-S-H structure.
- C-S-H/PCE nanocomposites accelerated hydration and lowered porosity of cement paste.
- C-S-H/PCE nanocomposites was conduce to early strength improvement of the mortar.

ARTICLE INFO

Article history:
Received 9 October 2016
Received in revised form 31 January 2017
Accepted 15 February 2017
Available online 3 March 2017

Keywords:
C-S-H
Polycarboxylate
Nanocomposites
Cement
Hydration

ABSTRACT

This work investigates the influence of synthetic C-S-H/polycarboxylate(PCE) nanocomposites (CPNs) on the hydration and properties of hydrated cement pastes. HPEG-PCE copolymers exhibiting side chain length of 45 ethylene oxide (EO) units was utilized to synthesize CPNs by precipitating C-S-H from Na_2SiO_3 and $Ca(NO_3)_2$ in the PCE solution. A Box-Behnken Design (BBD) for the Response Surface Methodology (RSM) was employed to statistically optimize the sizes of the resultant. The prepared CPNs were characterized by particle size distribution (PSD), X-ray diffraction (XRD), Fourier transform infrared spectra (FT-IR) and thermo gravimetric/derivative thermo gravimetric (TG/DTG) analyses. The influence of CPNs on the hydration properties of cement were assessed and discussed in terms of hydration kinetics, mechanical properties, phase composition and pore structure analysis. The experimental results showed that the optimum synthetic parameters, an experimental temperature of 30.1 °C, reactant flow velocity of 0.63 ml/min and initial volume of PCE solution of 28.5 ml, produced CPNs with a minimum size of 329.12 nm. It was demonstrated that PCE polymers were either grafted on the surface or partially intercalated in the interlayer regions of C-S-H, and their introduction also increased the distance between C-S-H interlayers. Cement hydration was significantly promoted as a result of an increased heat release, even at low CPNs content. The early compressive strength of the mortar significantly improved with increasing CPNs content due to the accelerated cement hydration of the CPNs: the 0.6 wt.% CPNs content improved the compressive strength by 18.97%. Moreover, the inclusion of CPNs is advantageous for pore modification: the total porosity decreased by 25.77% after 3 days. Finally, phase composition analysis confirmed that no new crystalline phase was produced upon CPNs addition.

1. Introduction

Recent progress in nanotechnology has brought technological innovation and industry transformation to the traditional cement industry [1]. The application of nanomaterials, a product of nanotechnology, to construction has attracted considerable scientific interest in recent years and appears to be a promising approach towards the development of new classes of cement-based materials with superior properties [2–5]. However, due to their high specific surface areas and surface energies [1], nanoparticles tend to agglomerate easily, dramatically decreasing their efficiency in cement-based materials [6,7]. Thus, the use of a dispersant, especially a superplasticizer, is a common solution to improve the dispersion property of nanoparticles in cement-based materials [8,9].

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http://dx.doi.org/10.1016/j.conbuildmat.2017.02.075

Calcium silicate hydrates (C-S-H) are the principal hydration products (approximately 60% by mass) and primary binding phases in hydrated Portland cement [10]. The nanostructure of the C-S-H phase is a primary contributor to important properties such as strength and shrinkage in the hardened cement paste [11]. In the past, synthetic C-S-H particles were often used to as seeds promote the development of C-S-H gels produced from the hydration of silicate phases in cement-based materials [12–17]. Owens et al. reported an increase in early strength development with 2 wt.% C-S-H addition, where both the initial and final setting times decreased by approximately 50% [17]. Thomas et al. studied the early hydration kinetics by partially replacing Portland cement and pure C_3S with pure C-S-H at different weight percentages. The addition of C-S-H was found to accelerate the main hydration rate peak times and increase the amount of hydration by seeding the hydration process [18].

Despite success in improving the efficiency of C-S-H in accelerating cement hydration, it was also found that this effect in early age either was either only minor or didn't show at all, especially at relatively low dosages of less than 1 wt.% [19,20]. Since the extent of nucleation and acceleration often depends on the surface area of the added fine particles [21], the minor acceleration effect may be due to a lowed surface area caused by agglomeration of C-S-H particles, which do not retain in their original size during synthesis. Recently, the preparation of inorganic/organic nanocomposites has been reported and seems to be a more effective approach to solving the problem of agglomeration [22,23]. Because of the layered silicate structure in C-S-H, C-S-H/polymer nanocomposites are excellent candidates for the manipulation and control of properties through the intercalation of organic molecules [12,24–27]. In fact, C-S-H stabilized by the addition of comb-like copolymers demonstrates low aggregation [28]. Polycarboxylate superplasticizers (PCEs), which are comb-like copolymers, adopt a comb-like structure with polymer backbones containing anionic groups (including carboxylic groups, sulfonic groups, and phosphate groups) and grafted long side chains (e.g., poly(ethylene glycol) with terminal hydroxyl or methyl group). The anionic groups serve as adsorption groups through electrostatic interactions with nanoparticles, while the side chains provide steric hindrance to prevent nanoparticles from agglomerating [29]. Plank concluded that PCE polymers produced smaller particle sizes for CPNs than C-S-H and that the synthesized CPNs can contribute to significant increases in the early compressive and flexural strength of the mortar [30]. However, research into the modification effect of CPNs incorporated in cement-based materials is still in its infancy. Moreover, detailed studies are needed on the effects of the synthetic conditions on CPNs size and on the CPNs effects on the hydration properties need and are missing in the literature.

To remedy this inadequacy, the first aim of the present study was to synthesize CPNs using a "co-precipitation" method, considering the experimental temperature, initial volume of PCE solution and reactant flow velocity as the primary synthetic variables, which are shown, after a series of preliminary tests, to have a direct impact on the particle size of C-S-H. To this end, a Box-Behnken design, a type of experimental design for the response surface methodology, was used to establish the relation between the primary synthetic variables and the resultant CPNs particle size. The second aim of this study was to partially substitute these synthetic materials in Portland cement to explore their influence on the hydration properties of Portland cement in terms of hydration kinetics, mechanical properties, phase composition and pore structure. The outcomes of this study may help to inspire new ideas and provide a theoretical guide for the effects of nano-modification of nanomaterials on cement-based materials.

2. Experimental section

2.1. Materials

The Portland cement used in this study was of type II-52.5 according to Jiangnan Onoda. Its chemical composition and physical properties are given in Table 1. Calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$), sodium silicate ($Na_2SiO_3{\cdot}9H_2O$) and sodium hydroxide (NaOH) were purchased from Aladdin Reagent Co. Ltd, which were used without further purification. A commercially available HPEG-PCE exhibiting side chain length of 45 ethylene oxide (EO) units (with 40% solid content and pH value of 6.75) was used as a dispersant during the synthesis of C-S-H to help stabilize its original size.

2.2. Preparation of CPNs

A co-precipitation method was utilized to synthesize CPNs in this experiment, and the molar ratio of CaO/SiO_2 in the starting materials was 1.5. The specific synthetic procedure was performed mainly according to the published literature [30] with some modifications, as schematically shown in Fig. 1. First, a 1.31 mol/L Na_2SiO_3 solution, a 1.97 mol/L $Ca(NO_3)_2$ solution and a 30 wt.% NaOH solution were prepared. Next, the prepared Na_2SiO_3 and $Ca(NO_3)_2$ solutions were added to the PCE solution at a given speed using a precision pump over a time period of 30 min with continual stirring using a magnetic stirrer at a certain temperature and speed. The pH of the suspension during synthesis was maintained at 11.6 ± 0.1 by adding NaOH solution. After 7 days of stirring, the as-prepared CPNs suspension was freeze-dried in a lyophilizer for 48 h. Then, the powders were washed twice with deionized water in order to remove the remaining reactants and freeze dried again in the lyophilizer for 48 h. The final powders were characterized using PSD, XRD, FT-IR and TG/DTG analysis.

2.3. Response surface methodology (RSM)

Box-Behnken Design (BBD) for RSM is a commonly used design method to statistically assessing the mathematical relationship between the independent variables and the responses [31]. As a tool for multivariate optimization, Box-Behnken design is a class of rotatable or nearly rotatable second-order designs based on three-level incomplete factorial designs. Compared with central composite design (CCD) [32,33], BBD adapts to the test area of the spherical domain and is especially suitable for areas in which the cube vertices are unable to provide data. For 3 factor design, the design principle is illustrated in Fig. 2, a cube is created that

Table 1
Chemical composition and physical properties of OPC.

Oxides	Percent (%)
Calcium oxide, CaO	65.47
Silicon dioxide, SiO_2	19.82
Aluminium oxide, Al_2O_3	4.66
Sulphur trioxide, SO_3	2.87
Ferric oxide, Fe_2O_3	3.03
Magnesium oxide, MgO	0.84
Potassium oxide, K_2O	0.64
Sodium oxide, Na_2O	0.10
Titanium oxide, TiO_2	0.16
Loss on ignition	3.34
Density	3.2 g/cm^3
Specific surface area	355 m^2/kg
Average particle size	18.54 μm