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Synthesis of novel polymer nano-particles and their interaction with cement

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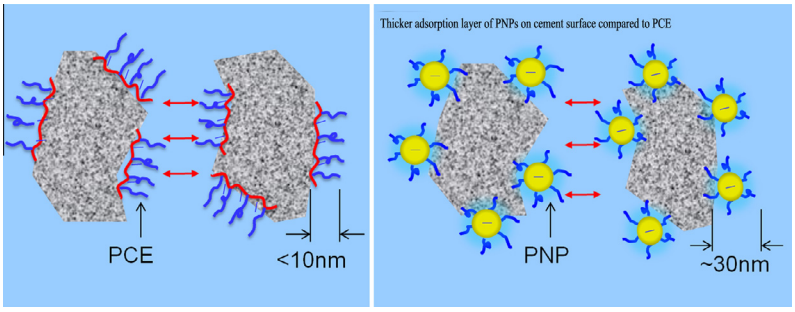
HIGHLIGHTS

- A novel superplasticizer, polymer nano-particle (PNP) was put forward and synthesized.
- PNP can adsorb on cement surface and improve the fluidity of fresh cement pastes.
- PNPs' retardation effect on cement hydration is less significant than traditional PCEs.
- PNPs reduce the connectivity of micro-pores in hardened cement pastes.

GRAPHICAL ABSTRACT



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ABSTRACT

Polymer nano-particles (PNPs) with particle size range of 29.4–52.7 nm were synthesized via emulsion polymerization. The mini-cone tests were conducted to evaluate the dispersion capability of PNPs in fresh cement pastes (fcps). Interactions of PNPs with cement were studied by measurements of total organic carbon, zeta potential, transmission electron microscopy, calorimetry and mercury intrusion porosimetry. Results show that the prepared PNPs can be adsorbed on to cement surface and improve fluidity of fcps effectively. The addition of PNPs leads to lesser retardation effect on cement hydration than popularly used polycarboxylate superplasticizers and reduces pore connectivity of micro-pores in hardened cement pastes.

1. Introduction

Concrete technology has undergone rapid advancement in the last decades. Workability and durability of concrete are gaining more and more emphasis [1]. With the intensive development of chemical admixtures, a large variety of polymers are being used in concrete formulations in forms of water soluble polymers, polymer fibers, polymer dispersions and redispersible powders, etc. to achieve desired properties [2].

The use of superplasticizers has drastically changed the properties of concrete nearly in all aspects including workability, strength, impermeability and durability due to the lowered water to cement ratio. The development of superplasticizers experiences the first generation of lignosulfate, the second generation of polycondensate (poly (melamine sulfonate), poly (naphthalene sulfonate)) to the late generation of polycarboxylate (PCE) type. PCE superplasticizers are comb-like water soluble polymers, which are usually composed of polycarboxylate main chains and polyethylene oxide as side chains. The main chains usually contain anionic anchor groups such as $-COO^-$, $-SO_3^-$ to allow the molecules to adsorb onto surfaces of cement and hydrates. Adsorption of PCE on the cement surface

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generates the electrostatic repulsion force and steric hindrance, and consequently leads to better dispersion of cement grains in water medium. This unique mechanism makes PCE have more robust dispersing power than polycondensates [3,4].

On the other hand, polymer latexes have been widely applied in cementitious systems to improve important properties of fresh and hardened mortars and concretes such as adhesion, cohesion, flexural strength, impermeability, water-proofing and durability [5–8]. Since many years, it has been a field of intense research to demonstrate the properties of the polymer modified mortar (PMM) and concrete (PMC), to disclose the mechanism of PMM and PMC and to describe the microstructural formation and evolution of PMM and PMC. Several models have been put forward to illustrate the mechanism of PMM and PMC including the most famous Ohama theory [2] and Puterman model [9].

PCE superplasticizers are usually fully water soluble polymers and the hydraulic radius of PCE molecule is about 10 nm in aqueous solution [10]. Casein, a biopolymer has been known as cement dispersant for a long time [11–13]. Thanks to its excellent plasticizing effect and self-healing effect on the surface of the grout, casein is widely used in self-leveling underlayments. Casein is composed of protein molecules and calcium phosphate clusters. When casein is dispersed in water, it forms colloidal particles usually with diameter of 90–140 nm, which are built of submicelles with size in the range between 12 nm and 15 nm in diameter. Plank et al. have studied the working mechanism of casein as superplasticizer for cement. They suggested that casein particles dissociate into submicelles with size of 10–20 nm in alkaline solution. The smaller submicelles show higher adsorption on cement surface and produce better superplasticizing effect [11].

Due to the special bio-resource and fluctuant quality for different batches, the application of casein in concrete is limited compared to the industrially synthesized products such as PCE superplasticizers. Our question is then, 'Is it possible to synthesize nano-particle dispersions that may serve as superplasticizer for cement?' If yes, we will have a chance to obtain similar superplasticizing effect as casein, and even to combine the functions of water soluble superplasticizers like PCE and the polymer latex dispersions.

Some researchers have studied the effects of polymer latexes on properties of fresh cement mortars and the interaction between latex particles and cement. Plank found that both cationic and anionic polymer latex particles can adsorb onto the inorganic binder surface due to the heterogeneous charge distribution developed by the mineral phases in cement and the cement hydrates [14]. Some literatures reported that addition of polymer latexes influences the flowability as well as workability of cement mortars. Some are beneficial while some are detrimental to the workability of fresh cementitious mixtures [15–17]. Rheological study on fresh cement asphalt paste conducted by Zhang found that both anionic and cationic asphalt emulsion improve the flowability of the pastes and the anionic asphalt emulsion is more effective than the cationic type due to its favorable adsorption [18].

However, all literatures above mentioned are dealing with polymer latexes with relatively big particle size of several hundreds of nanometers or with asphalt emulsions having particles size as big as several microns. Emulsion polymerizations including mini-emulsion polymerization, traditional emulsion polymerization and micro-emulsion polymerization enable to produce polymer dispersions with finely tuned particle size from 20 nm to hundreds of nanometers. In this paper, we used semi-batch emulsion polymerization to synthesize anionic polymer nano-particle (PNP) dispersions with particle size around 30–50 nm. We have chosen polystyrene dispersion as a model system to explore the possibility that the PNPs can be functioning as cement dispersant similar to the PCE superplasticizers. Influences of the structural parameters of the synthesized PNP dispersions on the fluidity of fresh cement pastes (fcps) were firstly investigated. After that, interaction of a selected PNP dispersion with cement was specifically studied by means of adsorption measurement, zeta-potential measurement, isothermal calorimetry, transmission electron microscopy (TEM) as well as mercury intrusion porosimetry (MIP). Adsorption of the PNPs on the cement grains was investigated by total organic carbon (TOC) tests on the supernatant that was separated by centrifuging the cement pastes. Zeta potentials of cement pastes with water to cement ratio (w/c) of 0.5 were measured at various dosages of PNP dispersions. Isothermal calorimetry was adopted to study the impacts of the PNPs on cement hydration. Pore structure of the hardened cement pastes (hcps) with varied contents of PNP was characterized by MIP with the expectation that addition of PNPs can modify the pore structure of hcps and consequently enhance the impermeability and durability of cementitious materials.

2. Materials and methods

2.1. Materials

Analytical grade of styrene (St), acrylic acid (AA), sodium dodecyl sulfate (SDS), sodium methyl acryl sulfonate (SMAS) and sodium persulfate (SPS) were used as received (all >98% purity). Marco-monomer, methoxy polyethylene glycol methacrylate (MPEGMA, 85%), was prepared via esterification reaction of methacrylic acid and polyethylene glycol whose weight average molecular weight is about 1300 at 130 °C. Emulsifier MS-1 ($C_8H_{17}C_6H_4O(CH_2CH_2O)_{10}COC_3H_6$-$SO_3Na$, 40 wt% aqueous solution) and emulsifier OP-10 ($C_8H_{17}C_6H_4O(CH_2CH_2O)_{10}H$, 40 wt% aqueous solution) were provided by Haian petrochemical factory. A home-made PCE superplasticizer was used to benchmark the plasticizing effect of the PNPs in cement pastes. The PCE used is a co-polymer of AA, MPEGMA and SMAS with monomer molar ratio of 2.12:1.00:0.29. The weight average molecular weight of the PCE used is 9.08×10^4 which was measured by gel permeation chromatograph.

Ordinary Portland cement classified by P.O.42.5 and compliant with the Chinese National Standard GB8076-1997 was used to prepare the cement pastes. Chemical composition and mineral composition of this cement are presented in Table 1.

2.2. Preparation and characterization of the polymer nano-particle dispersions

PNP dispersions were prepared by micro-emulsion polymerization in a 1000 mL three-neck glass flask equipped with a mechanical stirrer, dosing units for both the water-soluble monomers and the oil-soluble monomer. A water bath with tuned temperature of 85 °C was used to ensure the constant temperature during polymerization. Firstly, 10% of the total amount of St, 80% of the total emulsifiers, 10% of initiator (SPS) and ~190 g de-ionized (DI) water were well mixed by a high-shear mixer and then charged into the flask. The pre-charge was heated up to 85 °C under stirring and pre-polymerized for 10 min. The pre-emulsion, which was prepared by mixing all the rest of monomers, emulsifiers and 100 g DI water, and the aqueous solution of the rest initiator SPS with concentration of 4.45% were then separately dosed into the flask at constant dosing rates. The dosing time of pre-emulsion and the initiator solution were 2.5 h and 3.0 h respectively. After polymerization, the obtained polymer dispersion was cooled down to the room temperature. Recipes for preparation of PNP dispersions are shown in Table 2.

Solid content of the prepared polymer dispersion was measured by drying a portion of the dispersion at 80 °C until constant weight was reached. The solid content of all the prepared polymer dispersions was in a range of 18–20%. The dried polymer was then dissolved in tetrahydrofuran (THF) and closely kept under stirring for 24 h. Afterwards, the insoluble part of the polymer was separated by using a copper mesh filter and the filtrate was used to determine the molecular weight of polymer by gel permeation chromatograph (GPC) (Shimadzu, LC-20AD, Japan). Tetrahydrofuran (THF) was used as the eluent and the flow rate was 1 mL/min. During emulsion polymerization, cross-linked polymers may be produced due to chain transfer reaction and they are not any more soluble in solvent [19]. This insoluble part of polymer is called gel. Gel content as well as the molecular weight distribution of the soluble part of polymer was listed in Table 3. The results confirm the successful polymerization for those samples studied in this paper. Particle size of the polymer particles in PNP dispersions was determined by dynamic light scattering (DLS) with a Malvern Zetasizer 3000hs (UK). The characterization results of the synthesized PNP dispersions are presented in Table 3.

2.3. Mini-cone tests

The mini-cone test was conducted according to the Chinese National Standard GB/T 8077-2000 to evaluate the fluidity of fcps. The mixing procedure of the cement paste was as follows: Water and PNP dispersions were first added into the mixer. 300 g cement was gradually introduced over a time span of 2 min into the mixer