



Preparing hyperbranched polycarboxylate superplasticizers possessing excellent viscosity-reducing performance through in situ redox initialized polymerization method



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ABSTRACT

Significant improvements to modern concrete have emerged in recent years, primarily due to application of various polycarboxylate dispersant with designed structure. However, self-compacting or high strength concrete characterized by a low water-to-cement ratio (w/c) pose challenges for their viscosity and pumpability. Here we propose a strategy so called in situ redox polymerization method to synthesis hyperbranched polycarboxylate superplasticizers. By adopting a unique monomer Dimethylaminoethyl Methacrylate, acting as monomer as well as initiator, hyper-branched structure are obtained through this one-pot synthesis procedure. In contrast to their conventional counterparts, that is, comb-like polycarboxylate, hyperbranched structure is shown to cut down the viscosity of pore solution and alleviate the shear thickening behavior of cement paste, leading to a 30% reduction in viscosity of paste. Moreover, owing to the ease of industrial manufacture, our approach, in situ redox polymerization method, show broad prospects and great potential for development.

1. Introduction

Due to their outstanding water reduction and tune-able slump retention performances, polycarboxylate superplasticizers (PCEs), composed of a linear backbone of carboxylate and long side chains of ether group or ester group, are recognized as an important class of chemical admixtures. They are added to modern concrete, which are characterized by a reduction of cement contents, a utilization of more supplementary cementitious materials and a low water-to-cement ratio (w/c), to improve their workability [1–6]. However, these optimized concrete mixes tend to be more “sticky”, which negatively influences its pumpability, place ability, surface finishing, and therefore increases the time and cost required in construction [7–9].

This stickiness is probably associated with the energy dissipation in the flowing of concrete, resulting from its viscosity. Hot [10] suggested that the macroscopic viscosity comes from the pronounced increase in the local viscosity of the interstitial fluid between neighboring particles. This increase could be correlated with either the adsorbed or non-adsorbed polymer coils and depend on the polymer molecular structure. Zhang [11] compared the effect of different PCEs on the viscosity of mortar with low water-binder ratio and found that the apparent

viscosity of mortars with different PCEs is probably related to the water film thickness of cement particles, and more closely to the viscosity of aqueous solutions containing unadsorbed PCEs. Besides, a few authors have reported that the use of superplasticizers acting by steric hindrance exhibit high shear thickening response, which could induce unexpected consequences on concrete workability, compared with those acting by electrostatic repulsion [12–14].

Considering the apparent viscosity of mortars is closely linked to the viscosity of pore solutions containing the residual PCEs, water soluble hyperbranched polymer exhibiting lower intrinsic viscosity, which is at the origin of a more branched and dense structure, would show a different rheology behavior [15–17]. At the end of 19th century, Berzelius [18] firstly reported the hyperbranched structures based on an $A_2 + B_3$ approach. In 1952, Flory [19] developed the theory that highly branched polymers can be synthesized by polycondensation of a monomer containing one A functional group and two or more B functional ones capable of reacting with A (AB_y monomer, $y \geq 2$). Finally, Kricheldorf [20] and Frechet [21,22] obtained hyperbranched polymers by copolymerization of AB and AB₂ type monomers. However, synthesis and influence of hyperbranched PCEs on the viscosity of cement paste have rarely been investigated in the literature.

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In this article we proposed a distinctly novel strategy to fabricate polycarboxylate superplasticizers possessing hyperbranched structure. Copolymers were formed through an in situ redox initialized polymerization in our system. Dimethylaminoethyl Methacrylate (DMAEMA) was introduced to copolymerize with acrylic acid (AA) and Isobutyl alcohol polyoxyethylene ether (IPEG) as a soluble vinyl monomer which additionally bears an initiating group. The obtained copolymers were intensively characterized by Fourier-transform infrared (FT-IR) spectroscopy, H nuclear magnetic resonance ($^1\text{H NMR}$) spectroscopy and size exclusion chromatography (SEC/GPC) to confirm the formation of hyperbranched structure. The influences of hyperbranched and conventional comb-like PCEs on the dispersing ability, adsorption conformation, as well as rheological behavior of cement paste were investigated by the mini-slump, adsorption layer thickness, flow velocity and rheology test respectively. Last but not least, the acting mechanism of hyperbranched PCEs on the rheological behavior of cement paste is fully discussed.

2. Material and methods

2.1. Material

Acrylic acid (AA), dimethylaminoethyl methacrylate (DMAEMA), ascorbic acid (Vc), potassium persulfate (KPS) and mercaptopropionic acid (MPA) were purchased from Sinopharm Chemical Reagent Co., Ltd. Isobutyl alcohol polyoxyethylene ether (IPEG) with a molecular weight of 2400 were purchased from Jiangsu Sobute New Materials Co., Ltd. AA and DMAEMA were distilled prior to use. Unless stated otherwise, all reagents were used as received. Deionized water was used throughout all the experiments.

Ordinary Portland cement P II 52.5 according to Chinese Standard GB175-2007 was purchased from Jiangnan Onoda Co., Ltd. (Nanjing, China) to perform cement paste, adsorption and mortar mini V-funnel test. The composition of cement is illustrated in Table 1. River sand with 2.66 g/cm^3 specific gravity was used in this study.

2.2. Synthesis of hyperbranched and comb-like PCEs

Unless otherwise stated, all the following reaction mixtures were degassed by nitrogen bubbling before the adding of initiator solution. All the reactions were performed under nitrogen atmosphere.

In a typical procedure, the hyperbranched PCEs was synthesized as follows: IPEG (120.00 g) and deionized water (120.00 g) were added into a four-necked round-bottom flask with a mechanical stirrer, a nitrogen inlet tube, a nitrogen outlet tube and a rubber stopper. The mixture was mixed at 350 rpm, and the temperature was gradually raised to 45°C . Acrylic acid (AA, 14.43 g), Dimethylaminoethyl Methacrylate (DMAEMA, 0.98 g) and mercaptopropionic acid (MPA, 0.66 g) were dissolved in deionized water (50.00 g) to obtain mixed monomer solution. Potassium persulfate (KPS, 1.35 g) was dissolved in deionized water (20.00 g) to obtain oxidant solution. After all the species were dissolved, the monomer solution was added dropwise into the reaction flask for 2 h. Meanwhile, the oxidant solution was added dropwise for 2 h. Afterwards, the temperature was kept at 45°C for 2 h. Then the reaction was cooled to room temperature and neutralized to $\text{pH} = 7$ by 32 wt% aqueous NaOH solution. Deionized water (16.13 g) was then used to dilute solid content to 40%.

In a typical procedure, the conventional comb-like PCEs were synthesized as follows: IPEG (120.00 g) and deionized water (120.00 g)

were added into a four-necked round-bottom flask with a mechanical stirrer, a nitrogen inlet tube, a nitrogen outlet tube and a rubber stopper. The mixture was mixed at 350 rpm, and the temperature was gradually raised to 45°C . Acrylic acid (AA, 14.43 g), ascorbic acid (VC, 0.13 g) and mercaptopropionic acid (MPA, 0.66 g) were dissolved in deionized water (50.00 g) to obtain mixed monomer solution. Potassium persulfate (KPS, 1.35 g) was dissolved in deionized water (20.00 g) to obtain oxidant solution. After all the species were dissolved, the monomer solution was added dropwise into the reaction flask for 2 h. Meanwhile, the oxidant solution was added dropwise for 2 h. Afterwards, the temperature was kept at 45°C for 2 h. Then the reaction was cooled to room temperature and neutralized to $\text{pH} = 7$ by 32 wt% aqueous NaOH solution. Deionized water (14.86 g) was then used to dilute solid content to 40%.

2.3. Characterization of PCEs

The resultant product was purified by dialysis using a 3500 Da cellulose cut-off membrane (Spectra/Por 6 dialysis tubing, 3.5 K MWCO) for further measurements. All the Fourier transform infrared (FT-IR) spectra were collected by a Nicolet Avatar 370 spectrometer. Nuclear magnetic resonance ($^1\text{H NMR}$) spectra were recorded in D_2O solutions on a Bruker AVANCE 500 MHz NMR spectrometer. The molecular weight, PDI (Mw/Mn), intrinsic viscosity and hydrodynamic radius of the synthesized PCE samples were determined by gel permeation chromatography (GPC) using a Viscotek GPCmax system equipped with the A6000 M*2 columns and differential refractive index (RI), viscometer (VIS), and laser light scattering (LS) triple detectors. A d_n/d_c of 0.135 mL/g for poly (ethylene oxide) was used, 0.1 mol/L NaNO_3 , at $\text{pH} = 12$ adjusted with NaOH was used as eluent. The hydrodynamic radius was determined by dynamic light scattering (DLS, ALV/CGS-3, Germany), where the wavelength of laser was set at 633 nm and the test angle was fixed at 173° . All the tested samples were prepared as follows: to prepare a solution of polymer with deionized water and adjust concentration to 1.0 mg/mL, then clarified with 220 nm filters (Millipore) to remove dust.

3. Performance measurements of PCEs

3.1. Fluidity and flow velocity of cement paste

A cement paste blender (NJ-160 A, Wuxi Jianyi Instrument & Machinery Co., Ltd, Wuxi, China) was used for mixing. All cement pastes were prepared by weighing 300 g of cement into the mixing bowl and by adding aqueous solution of PCEs (the w/c ratio was set at 0.29 and 0.22 respectively, the PCE dosages were shown in Fig. 3). The admixtures were dissolved in the mixing water. The mixing procedure was set to 2 min of mixing at stage I ($62 \pm 5 \text{ r/min}$) and 2 min of mixing at stage II ($125 \pm 10 \text{ r/min}$). Then the mixed paste was quickly injected into a mini slump cone (60 mm high, top diameter 36 mm, and bottom diameter 60 mm), which was lifted vertically. The paste flow value was the mean value of the maximum diameter with perpendicular directions to each other. Each flow test was video recorded using a digital camera, and the spread change over time was plotted as described in the literature [23].

3.2. Mini V-funnel test

The mortars with cement-sand ratio of 0.63 and w/c ratio of 0.32

Table 1
Chemical composition of cements.

Al_2O_3 (%)	CaO (%)	Fe_2O_3 (%)	K_2O (%)	MgO (%)	Na_2O (%)	SO_3 (%)	SiO_2 (%)	TiO_2 (%)
4.94	63.05	2.92	0.66	1.33	0.15	3.83	19.95	0.27

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