Effects of polycarboxylate superplasticizers with different molecular structure on the hydration behavior of cement paste
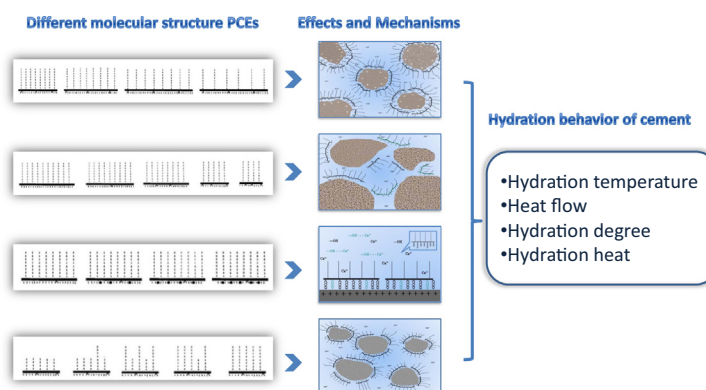
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HIGHLIGHTS

- Stronger retardant effect was obtained from PCEs with more COO^- and shorter side chains.
- Hydrolysis of ester groups in PCEs result in the co-retardation effect.
- The PCEs with high Mw will lead to cement particles' agglomerate, then hydration delay.

GRAPHICAL ABSTRACT

ABSTRACT

Effects of polycarboxylate (PCE) superplasticizers with different densities of carboxylate groups, functional group contents, molecular weight, and side chain polymerization degrees on the hydration behavior of Portland cement were investigated in this study. The experiments were conducted by using semi-adiabatic calorimeters equipped with a temperature measurement system. The water cement ratio (W/C) was 0.4, and the PCE dosage used was 0.3%. Besides, the Total Organic Carbon (TOC) experiments were taken to further study the delaying mechanism of different PCE on cement hydration. The ability to delay hydration increased in PCEs with high densities of carboxylate groups, short side chains, and high molecular weight and the copolymerization of methyl acrylate (MA) monomers decreased the heat flow peak. Nevertheless, the main hydration temperature peak and the maximum elevated temperature decreased when the density of the carboxylate groups increased. Moreover, PCEs with only a moderate molecular weight had the lowest hydration degree. The main hydration peak decreased but appeared in advance when the amount of MA monomers copolymerized with PCEs was increased; the hydration degree also decreased. PCEs only polymerized by methyl allyl polyethenoxy ether (TPEG400) macromonomer had a hydration degree of 69.46%. Absorption amount results indicate that PCEs affect the hydration of cement paste by absorbing PCEs on the surface of cement particles or encapsulating some cement particles to restrain cement hydration. PCEs grafted with MA hydrolyzed to carboxylic and hydroxyl groups, which can both restrain the hydration of cement paste.

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1. Introduction

Since their discovery in the 1980s, polycarboxylate superplasticizers (PCEs) have gradually become important concrete admixtures [1,2]. Comb-like polycarboxylate copolymers consist of two main parts: carboxylic groups as the backbone and polyethylene oxide (PEO) as the side chains [3]. Carboxylic groups, acting as anchors, are adsorbed on cement particles. PEO-grafted side chains extend from the cement particle surface into the pore solution to produce steric hindrance and prevent cement particle agglomeration [4]. Thus, PCEs retards cement hydration. More interestingly, owing to the variability of PCEs' molecular structures, it might exert different effects on the cement performance and hydration. [5–7].

Several recent studies have focused on cement hydration, which is a complex physical and chemical process with constant heat release [8]. With the hydration process going on, both the hydration temperature and the hydration degree of cement paste would change till the end of hydration [9]. The change in temperature during cement hydration can reflect the hydration degree of cement; hydration heat curves also depict the effects of additives on cement hydration. PCEs with various molecular configurations have been widely used, but most investigations on the early hydration behavior of cement focused on admixtures with a single type of molecular structure [10–13]. The molecular structure of PCEs and their effects on the hydration behavior of cement remain poorly understood. The current study aims to investigate the effects of PCEs with different densities of carboxylate groups, functional groups, molecular weights, and side chain polymerization degrees on the hydration behavior of cement.

2. Experimental

2.1. Raw materials

2.1.1. Cement
The cement used in this study was standard Portland cement (Chinese standard GB 8076-2008) supplied by Qvfu cement plant, China. The chemical and mineral compositions of this material are presented in Table 1.

2.1.2. Organic materials
Analytical-grade acrylic acid (AA) (Tianjin Chenfu Chemical), ammonium persulfate (APS) (Guangzhou Chemical), sodium hydroxide (Guangdong Xilong Chemical), and methyl acrylate (MA) (Tianjin Damao Chemical) were used in the experiments. Sodium methallyl sulfonate (MAS) (>98% purity) was provided by Aladdin. Industry-grade allyl polyethenoxy ether (TPEG) macromonomers with molecular weights of 400 and 2400 were provided by Liaoning Aoke Chemical and Letian Chemical, respectively. Deionized water was used throughout the experiment.

2.2. Synthesis and characterization of the PCEs

2.2.1. Synthesis of PCEs
Four series of self-synthesized PCEs were used in this study. Series A is PCEs with long side chains with different densities of carboxylate groups. Series B is PCEs with different molecular weights. MA monomers were copolymerized with the PCE backbone as the functional group for Series C. PCEs with different side chains lengths comprised Series D. All PCE series were synthesized via free radical polymerization reactions with APS as the initiator. A 30% sodium hydroxide solution was used to neutralize the polymer solution. The chemical structure and schematic of the PCEs are shown in Fig. 1. Details of the monomer ratios are shown in Tables 2–5. To facilitate annotation and description, PCEs polymerized by AA, TPEG2400, and MAS monomers with the same molar ration of 3.5:1:0.08 were numbered as A2, B2, C1, and D5.

2.2.2. Gel permeation chromatography (GPC)
The average molecular weight and molecular weight distribution of PCEs were determined through Waters 1515 gel permeation chromatography with an ultrahydrogel chromatographic column and a Waters 2414 refractive index detector. The samples were analyzed using a 0.1% NaN3 aqueous solution as an eluant at a flow rate of 0.6 mL/min. Glucans with different molecular weights were used as calibration standards. The results are shown in Tables 2–5.

2.3. Testing methods and calculation of hydration parameter

2.3.1. Measurement of cement paste hydration temperature
The change in temperature during cement hydration was measured by using semi-adiabatic calorimeters equipped with a temperature measurement system. The schematic of the measurement system is illustrated in Fig. 2. The test was carried out for 72.0 h. The mass of the cement sample was 300 g with a W/C of 0.4 and a PCE dosage of 0.3%. Ambient temperature was controlled at 20 ± 1 °C.

The heat dissipation constant K [J/(h °C)] and heat capacity C [(J/°C)] of the semi-adiabatic calorimeters were calculated in accordance with the Chinese standard GB/T 12959-2008 "test methods for heat of hydration of cement" respectively.

2.3.2. Calculation of hydration heat of cement paste
Each mineral and chemical composition of cement has specific hydration heat. The total hydration heat of cement can be calculated as

$$H_0 = 500w(C_3S) + 260w(C_2S) + 866w(C_3A) + 420w(C_4AF) + 624w(SO_3) + 1186w(fCaO) + 850w(MgO)$$

H_0 – the total hydration heat of each unit weight of cement paste (J/g).
w_i – the weight ratio of the i-th compound in terms of the total cement content.

According to Table 1, the H_0 of the standard Portland cement used in this study was 475.41 J/g.

The cement hydration heat can be calculated as

$$H(t) = \frac{K \int_0^t T_t + C_p(T_t - T_0)}{m}$$

T – hydration age of cement paste (h).
$H(t)$ – per mass of cement hydration heat at t (J/g).
K – heat dissipation constant of the semi-adiabatic calorimeter J/(h °C).
C_p – heat capacity of the semi-adiabatic calorimeter (J/°C).
T_t – temperature of cement paste at t (°C).
T_0 – initial temperature of cement paste (°C).
m – quality of cement paste (g).

2.3.3. Calculation of hydration degree
After the cement particles mix with water, a series of physical and chemical reactions occurs with large amounts of heat release. Hydration heat release correlates with hydration degree and hydration age. Therefore, the degree of hydration can be determined on the basis of the hydration heat of the cement sample as follows:

$$\alpha_{72} = \frac{H_{72}}{H_0}$$

α_{72} – hydration degree of cement paste at 72.0 h.
H_0 – final hydration heat of unit mass cement (J/g).
H_{72} – hydration heat of unit mass cement at 72.0 h (J/g).

2.3.4. Calculation of heat flow of cement paste
The heat flow can be calculated as

$$R(t) = \frac{dH(t)}{dt}$$

$R(t)$ – cement heat flow at t [J/(g h)].

Table 1
Chemical and mineral compositions of cement (wt/%).

Chemical composition (%)										Mineral composition (%)			
SiO$_2$	Fe$_2$O$_3$	Al$_2$O$_3$	CaO	MgO	SO$_3$	fCaO	Cl$^-$	Na$_2$Oeq	LOSS	C$_3$S	C$_2$S	C$_3$A	C$_4$AF
20.560	3.230	4.600	62.560	2.570	2.950	0.870	0.011	0.530	2.040	57.340	18.900	6.470	11.250