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## Effect of linkage bond between backbone and side chain in comb-like copolymer dispersants on early properties of concentrated cement suspensions

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### Abstract

Comb-like copolymer, consists of backbone with ionizable group and charge neutral poly(ethylene oxide)-based “teeth” side chain grafted onto the backbone at frequent intervals, has been widely used as superplasticizer in concrete industry due to its unique properties compared to traditional polyelectrolyte dispersants, such as lower dosages, outstanding water reduction, excellent workability retention and lower shrinkage. It is easy to modify and adapt this molecular structure in order to maximize the targeted properties and also meet specific properties for different applications. However, modification attempts usually focused on the side-chain length and charge density. In fact, the linkage bond between backbone and side chain has greatly influence on the early behavior of cement suspensions due to copolymers with different linkage bond have different structure stability under the strong basic environment. In this study, two comb-like copolymer dispersants with different linkage group (ester and ether) were produced. The effects of the type of linkage bond in comb-like copolymers on the adsorption characteristics and hydration behavior of concentrated cement suspensions, were investigated by means of Total organic carbon analyzer(TOC), DSC-TG and calorimetric device and Environmental Scanning Electron Microscope(ESEM). Test results showed that the comb-like copolymer with ester linkage bond, has lower initial adsorbed amount, and thus not only accelerate the hydration rate, but also change its crystal shape of hydrated cement. This will help in the understanding of the structure-property relationship of comb-like copolymer and in the designing the molecular structure of new functional superplasticizer.

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*Keyword:* Comb-like copolymer; Linkage bond; Adsorption; Structure stability; Early hydration

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## 1. Introduction

Comb-like copolymers are relatively more efficient and new types of cement dispersants with a very flexible chemical structure. It is easy to modify and adapt this molecular structure in order to maximize the targeted properties and also meet specific properties for different applications. Thus it has attracted significant attention and been extensively studied in the recent 20 years [1, 2]. These comb-like copolymers are composed of a polyelectrolyte backbone and nonionic poly (ethylene oxide)-based “teeth” side chains grafted onto the backbone at frequent intervals. The polyelectrolyte backbone provides anchoring group while the long side chain provides the steric hindrance effect resulting from the extension of this side chain away from the cement surfaces in the solution [3].

Recently, many reports about the chemical structure modifications concerning comb-like copolymers have been published [4-8]. However, modification attempts usually focused on the effects of the molecular structure (i.e. side-chain length, charge density, polymerization degree of backbone) on the adsorption and dispersion behavior. It is rather surprising that the literature documents have seldom reported that the effects of the chemical structure of comb-like copolymers on the early hydration of cement suspensions, which is very important for early strength development or slump loss of concrete. Our previous paper focused on the impacts of length of side chain in comb-like copolymers on the early hydration of cement [9]. In fact, the linkage bond between backbone and side chain in comb-like copolymers has greatly influence on the early behavior due to copolymers with different linkage bond have different structure stability under the strong basic environment.

The present study aims to develop a full understanding of impact of the type of linkage bond in comb-like copolymers on the early hydration of cement suspensions. Towards this purpose, two comb-like copolymer dispersants with different linkage group were produced. The effects of the type of linkage bond in comb-like copolymers on the adsorption characteristics, heat of hydration and hydration process of concentrated cement suspensions were investigated systematically. The information generated should help develop structure-property relationships that will provide new insights in the designing the molecular structure of new functional dispersants.

## 2. Materials and Methods

### 2.1. Materials

**Cement.** The P-II 42.5 Portland cement, complying with the Chinese National Standard GB 175–1999, was purchased from Xingfa Cement Ltd. in Beijing. The cement composition was determined by x-ray fluorescence and Bogue analysis. The particle size analysis using a Helos-Sucell Laser particle size analyzer (SYMPATEC Instruments, German) shows the volume average mean particle size (VMD) is about 25  $\mu\text{m}$ , and the median diameter  $d_{50}$  is about 20  $\mu\text{m}$ . The Blain surface area is 316.4  $\text{m}^2.\text{kg}^{-1}$ . Table 1 shows the characteristics and compositions of the cement.

Table 1 Phase composition and physical properties of the cement

Phase composition <sup>a</sup> /%				Percent volume diameters/ $\mu\text{m}$				Blain surface
C <sub>3</sub> S	C <sub>2</sub> S	C <sub>3</sub> A	C <sub>4</sub> AF	d <sub>10</sub>	d <sub>50</sub>	d <sub>90</sub>	VMD <sup>b</sup>	area/ $\text{m}^2.\text{kg}^{-1}$
52.17	21.16	7.49	8.21	3.74	19.82	52.05	25.04	361.4

<sup>a</sup>C<sub>3</sub>S, tricalcium silicate, C<sub>2</sub>S, dicalcium silicate, C<sub>3</sub>A, tricalcium aluminate, C<sub>4</sub>AF, tetracalcium

aluminate ferrite; <sup>b</sup> VMD, volume average mean particle size.

**Comb-like copolymers.** The two comb-like copolymers (herein after called PCE) with different linkage group (Fig. 1) were prepared and characterized as described elsewhere [10]. The composition of PCE was estimated by <sup>1</sup>H-NMR spectroscopy. The molecular weight of PCE was determined using a Wyatt Technology miniDAWN® static three-angle laser light scattering detector (MALLS) equipped with TSK-GELSW (TOSOH) columns. The PCE architectures used and their molecular characteristics are shown in Table 2.

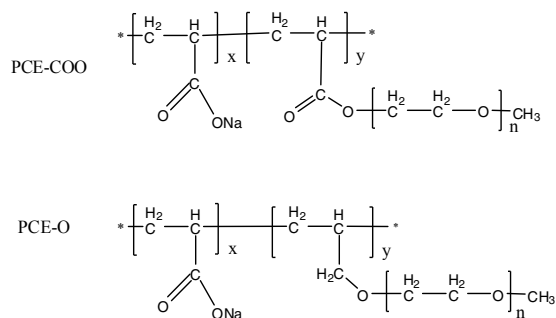


Fig. 1 Schematic illustration of molecular structure of comb-like copolymer dispersants

$x$ —Molar composition of sodium of acrylic acid unit in copolymer;  
 $y$ —Molar composition of acrylic ester unit in copolymer;  $n$ —moles of ethylene oxide.

Table 2 Molecular characteristics of PCE comb-like copolymer dispersants

	Linkage bond	Side chain length ( $n$ )	Molar composition /%		$M_w$
			$x$	$y$	
PCE-O	Ether -O-	26	67	33	33490
PCE-COO	Ester -COO-	26	64.66	35.34	36300

$M_w$  is mass average molecular mass.

## 2.2. Methods

**Adsorption** --The amount of comb-like copolymer adsorbed was determined by means of a total organic carbon analyzer (TOC), Multi N/C3100 (analytikjene AG, Germany). 20 g of solution containing 0.2g of dispersant and 10 g of cement were mixed by a magnetic stirrer at 250 rpm for different time (5, 15, 30, 60 min) at 20°C. The sample solution was separated by suction filter. The aqueous phase was separated by centrifugation at 13,000 rpm for 5 min and the supernatant was immediately decanted and diluted with deionized water for TOC measurements. The difference in the concentration before and after contact with the cement is attributed to the adsorbed comb-like copolymer.

**Isothermal calorimetry**-- The heat flow during hydration of the cement pastes was determined by means of isothermal conduction calorimetry (TAM 08Isothermal Calorimeter) at 20 °C. For each sample 10.00 g of cement were weighted into a flask and 2.9 mL of water dispersant solution (0.20%, by cement mass) were added. The cement paste was then mixed by a stirrer for 2 min. Then, the flask was capped

and placed into the calorimeter. The heat flow was recorded over the first 72 h.

**Differential scanning calorimetry–thermo-gravimeter (DSC-TG)** --Cement pastes were prepared at a water cement ratio of 0.29 by adding the tap water with the defined amount of dispersant dosages (0.20% by cement mass). DSC–TG curves of the specimens cured at different ages were obtained using a TA Instruments SDT Q600 simultaneous thermal analyzer at a uniform heating rate of 20°C/min in a nitrogen atmosphere in a flowing rate of 80 mL/min. The amount of calcium hydroxide formed at different hydration periods was determined by measurement of the mass loss of calcium hydroxide on decomposition.

**Environmental scanning electron microscope (ESEM)** -- The morphology of the hydration products was determined using an environmental scanning electron microscope (PHILIPS XL–30 ESEM). Water cement ratio and dosages of dispersants were the same as described in DSC–TG analysis.

### 3. Results and Discussion

The impacts of the type of linkage bond in comb-like copolymers on adsorption characteristics and hydration process of concentrated cement suspensions were investigated systematically in detail.

#### 3.1. Adsorption behavior

As an important index of the comb-like copolymer, the adsorption curves of the two copolymers on the cement particles are shown in Fig. 2. For the copolymers, all the molecular weight of the side chains was about 1000 and the molar ratio between the carboxylic acid groups and polyether side chains was about  $x/y=2$  ( as shown in Fig. 1). The curves showed that the linkage group of the copolymer had great influence on its adsorption ability. For PCE-O, the adsorption ratio just after 5 min could reach to 49% and further increased with increasing time. The adsorption ratio increased up to 63% after 1h. For PCE-COO, however, increasing the adsorption time caused a slight decrease in the adsorption ratio. The ester bond which connected to the backbone for PCE-COO would hydrolysis under the strong basic environment ( $pH>12$ ) as shown in Fig. 3[7, 11]. The hydrolysis product polyethylene glycol would dissolve into the pore solution of cement which was reason of the decreased adsorption ratio. For PCE-O, compared with PCE-COO, the ether bond which connected to the backbone (-O). So, as the time passed, the adsorption ratio of PCE-COO decreased slightly. The previous research has also proved that the increased adsorption ratio would be very small for the comb-like copolymer containing ester bond [7].

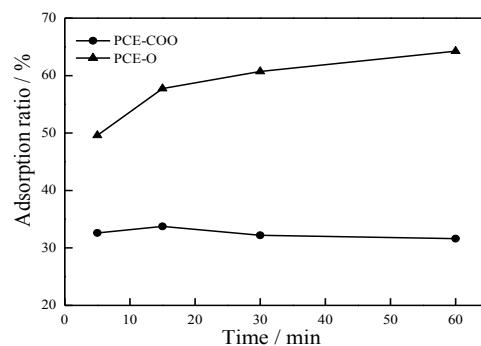


Fig. 2 Effect of the type of linkage bond in comb-like copolymer on adsorption kinetics on cement particles

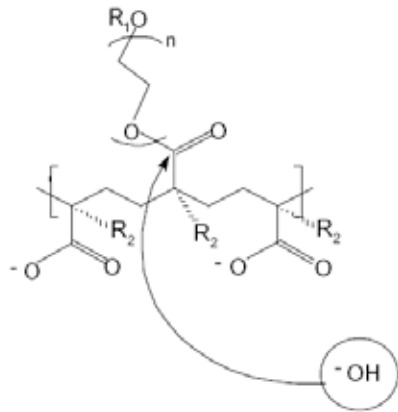


Fig. 3 Hydrolysis of the ester group on the PCE-COO. Notes:  $R_1$  represents H or  $\text{CH}_3$ ;  $R_2$  represents H or  $\text{CH}_3$

### 3.2. Hydration behavior

The effects of the type of linkage bond in comb-like copolymer on heat evolution of concentrated cement suspensions are presented in Fig.4. From Fig.4 a, It seems that the PCE-COO has a higher initial peak than PCE-O(Fig.4 a). It can be also seen that from Fig.4 b the accelerated hydration peak due to the calcium silicate hydrate (C-S-H) formation occurred earlier for the cement mixtures containing dispersant with ester bond (PCE-COO), compared to the mixture containing dispersant with ether bond (PCE-O). The accelerating effect for PCE-COO on cement hydration shows that the shortening of induction period and shifting of the main heat evolution peak is evident.

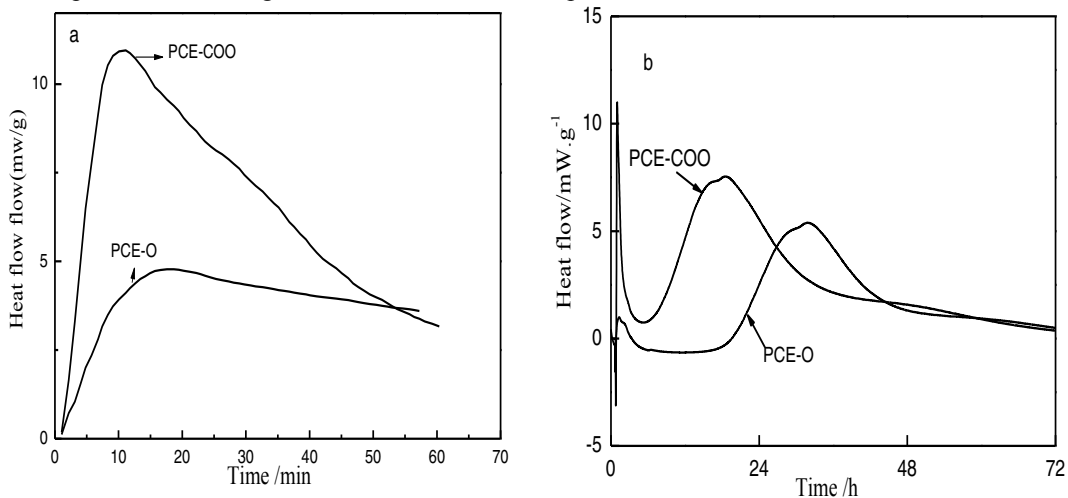


Fig. 4 Heat evolution curves of cement pastes containing comb-like copolymer with different linkage bond at early age

The hydration degree in the Portland cement system containing dispersants with different linkage bond between backbone and side chain was measured by DSC-TG thermal analysis (Fig.5). For two dispersants, The decomposition peak of  $\text{Ca}(\text{OH})_2$  is between  $420^\circ\text{C}$  and  $460^\circ\text{C}$ . The hydration degree at 4h of cement containing PCE-COO was 3.52%; In contrast, the hydration degree for PCE-O was just

3.32% (Table 3). These results are agreement with the heat evolution curve of cement pastes.

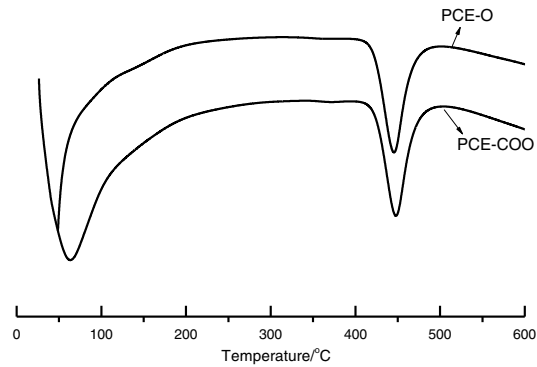
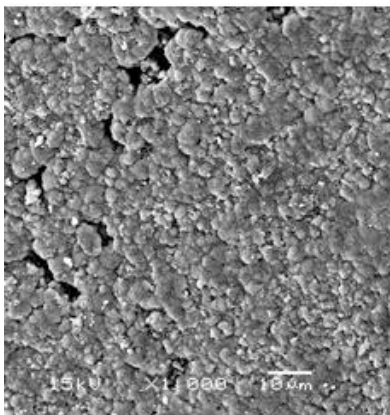


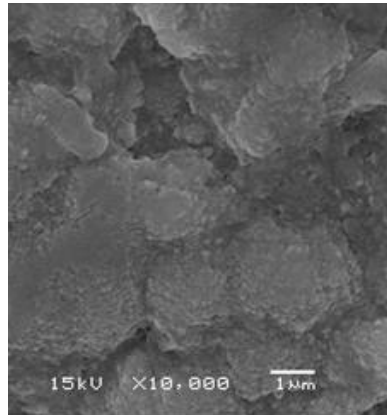
Fig. 5 Effects of the type of linkage bond in comb-like copolymer on DSC curve of cement hydration at 4 h

Table3. Ca(OH)<sub>2</sub> content of hydrated cement pastes containing dispersants with different linkage bond at 4 h

Sample	Mass fraction of Ca(OH) <sub>2</sub> /%
PCE-COO	3.52
PCE-O	3.32



(a) PCE-COO



(b) PCE-O

Fig. 6 Effects of the type of linkage bond in comb-like copolymer on ESEM micrographs of cement suspensions (w/c=0.29), cured at 20°C for 15min)

To discern the effect of linkage bond in comb-like copolymer on the morphology of hydrated phases, an ESEM investigation was performed on diluted suspensions of cement at an age of 4h. Fig.6 shows the ESEM micrographs of hydrated cement containing dispersants with different linkage bond cured for

15min. The ESEM observations are a good supplement to the calorimetric and DSC-TG measurements. It was observed that the microstructure of hydrated cement at early age is largely dependent on type of linkage bond in the comb-like copolymer. For PCE-COO with ester bond, the plate-like C-S-H and needle like type of ettringite crystals appeared. These differences in the morphological structures of the crystals maybe are due to the interaction of the hydrolysis product (polyethylene glycol and sodium polyacrylate ) with the C-S-H. Polyethylene glycol and sodium polyacrylate can increase silicate polymerization degree and nano-structure of C-S-H[12-13].

#### 4. Conclusion

The impacts of the type of linkage bond in comb-like copolymer dispersants on adsorption characteristics and hydration process of concentrated cement suspensions were investigated by using TOC, DSC-TG, and ESEM systematically. The results indicate that the linkage bond in comb-like copolymer dispersant has a great effect on cement hydration at early age. The comb-like copolymer with ester bond not only accelerates the hydration of cement, but also changes the crystal shape of hydrated cement. These results would have important implications in the design of the molecular structure of new superplasticizer with the ultra high early strength or high slump retention. Further research about the effect of linkage bond in comb-like copolymer on the microstructure formation during hydration is needed.

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