Powder Technology 335 (2018) 334–343

Contents lists available at ScienceDirect

Powder Technology

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

Diphosphonated comb-like copolymers synthesis as suspensions dispersants and their resistance to ionic competition phenomenon

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ARTICLE INFO

Article history:
Received 1 December 2017
Received in revised form 16 March 2018
Accepted 18 April 2018
Available online 8 May 2018

Keywords:
Superplasticizers
Calcite suspension
Adsorption
Dispersion
Amino-bisphosphonic acid
Ionic competition

ABSTRACT

The dispersive action of synthesized comb-like copolymers including phosphonated or diphosphonated functions has been investigated using rheology and stability measurements. These investigations were performed by using calcite suspensions able to mimic the early-age behavior of cement paste. In addition, adsorption measurements were conducted to relate the adsorbed amount of copolymer to the effects on dispersion. The effectiveness of the studied copolymers was evaluated in different ionic media. It appears that diphosphonated structures with the shortest chain length are the most effective even in the context of ionic competition phenomenon.

1. Introduction

Superplasticizers or high range water reducers (HRWR) are used as admixture for cementitious materials. These admixtures allow increasing the workability of fresh concrete without increasing the water content and thus improving durability and mechanical behavior of hardened concrete [1,2].

Polycarboxylates (PCEs) are the most effective water reducer used in concrete. Their structure consists of a main chain bearing carboxylic acids and poly(ethylene oxide) (PEO) side chains. Carboxylic acids are assumed to be fully deprotonated in highly alkali environment but anionic moieties, which are negatively-charged, adsorbs on the positively charged surface of cement particles. Furthermore, PEO side chains generate steric repulsion improving the dispersion of particles and avoiding their agglomeration. In fact, the formation of agglomerates tends to trap some of the water that will no longer be available to improve the fluidity of the fresh material.

Despite a high dispersive action, these superplasticizers may, however, lose their effectiveness in certain media [3–5], and lead to undesired side effects such as retardation of cement hydration [6]. For example, it was found that superplasticizer can react with cement phases to form organo-mineral phases (OMP) [5,7]. Furthermore, the adsorption of superplasticizer can be reduced due to the ionic competition phenomenon induced by high concentration of ions such as sulfates [8].

By tailoring macromolecular parameters such as side chain length monomers ratio and their distribution along carbon backbone [9], it is possible to design copolymers able to maintain their dispersive action in different media [10]. In addition, it has been shown that comb-like copolymers including phosphonic acids moieties are less sensitive to the loss of adsorption efficiency induced by sulfates [11]. Amino-bisphosphonic acid such as the commercial superplasticizer from Chryso referred as Optima 100 is among copolymers containing biphosphonic acids. This copolymer seems to have high dispersive action and to reduce the side effects related to admixture/cement incompatibilities. Despite these considerations and the fact that amino-bisphosphonic is relatively more efficient than conventional PCE [12,13], this pattern has never been transposed onto a comb-like copolymer structure.

The aim of this paper is to investigate the dispersive action of synthesized comb-like copolymers bearing amino-bisphosphonated moieties. The dispersive action is evaluated using rheology measurements and colloidal stability with Turbiscan. The amount of adsorbed polymer is determined by total organic carbon analysis (TOC) to relate it to effects on dispersion. The resistance to ionic competition is investigated by using different sulfate and nitrate concentrations. The results of this paper will help to understand the effect of superplasticizers on the dispersion of mineral suspensions, especially in the presence of ionic competition phenomenon.

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https://doi.org/10.1016/j.powtec.2018.04.049
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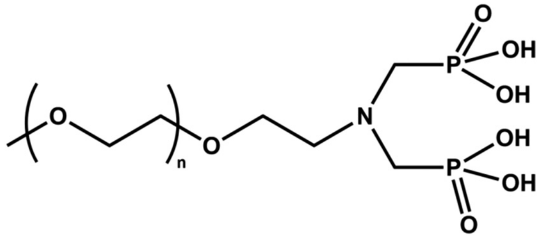

Fig. 1. Chemical structure of commercial superplasticizer (Optima 100).

2. Experimental

2.1. Materials

The synthesis of copolymers was performed by using different reagents. Poly(ethylene glycol) methyl ether methacrylate of 950 g/mol "MAPEG$_{950}$" and 4,4′-Azobis(4-cyanovaleric acid) (ACVA) were purchased from Sigma-Aldrich. Dimethyl(methacryloyloxy)methyl phosphonate (MAPC1(OMe)) was purchased from Specific Polymers. Thioglycolic acid (TA) was provided by Acros. Reagents were used as received without any further purification. Dimethyl(methacryloyloxy) methyl phosphonate (MAPC1(OMe)) was hydrolyzed into (methacryloyloxy)methyl phosphonic acid MAPC1(OH) and Tetramethyl (((2-hydroxyethyl)azanediyl)bis(methylene))bis(phosphonate) (methacrylate monomer bearing amino-bisphosphonic acid) "MANP2" was synthetized according to Chougrani procedure [14].

A pure commercial superplasticizer (optima 100) provided by Chryso was used as reference copolymer. The chemical structure of this copolymer consists of a single poly(ethylene oxide) chain terminated by a diphosphonated function [15] (Fig. 1).

The new synthesized superplasticizers were tested on calcite suspensions in different ionic media by adding sodium sulfate or sodium nitrate. The calcite BL was supplied by OMYA France. Sodium nitrate and calcium hydroxide were provided by Panreax AppliChem, and sodium sulfate was purchased from Prolabo. The measured density of calcite was of about 2.75 g/cm3 and specific surface area was 1.25 m^2/g. Calcite particles are of monomorphic angular shape. The particle size

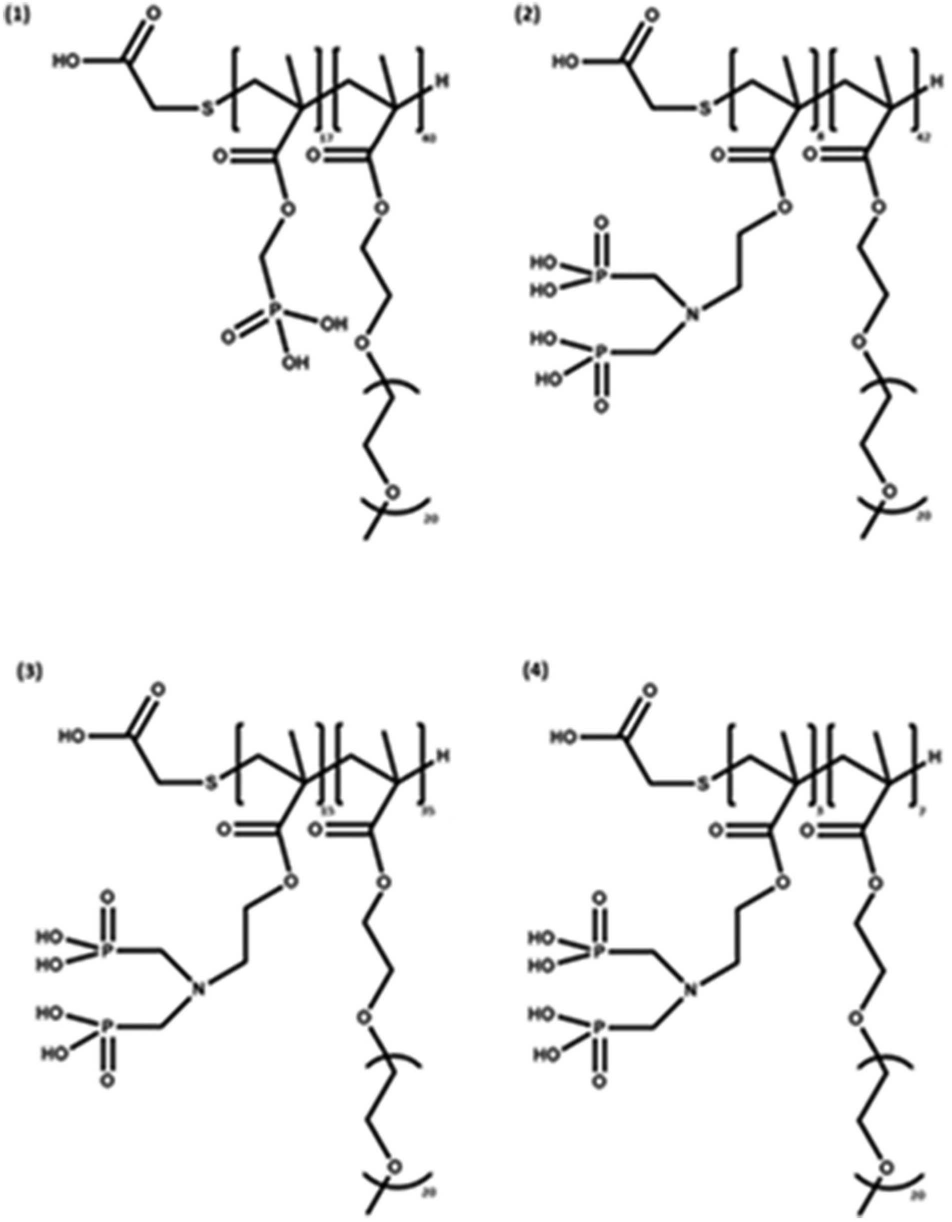

Fig. 2. Chemical formulae of random copolymers: Stat PCE-30P (1), Stat PCE-15 diNP (2), Stat PCE-30 diNP (3), Stat PCE-30 diNP DPn 10 (4).