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Impact of the charge density on the behaviour of polycarboxylate ethers as cement dispersants

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HIGHLIGHTS

- Polycarboxylate ethers prepared by esterification experience partial degradation.
- Temperature-driven degradation results in charge densities lower than expected.
- Polycarboxylate ethers with same structure and different charge behave diversely.
- Charge density rules the adsorption and affects the whole dispersant performance.

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ABSTRACT

The charge density of polycarboxylate ethers (PCEs) is the driver for adsorption of these polymers on the surface of hydrating Portland cement, which is the necessary step for the PCE to disperse and plasticise Portland-based materials. The charge density of a PCE is commonly considered the result of a certain molecular architecture and the complement of the sidechain density, regardless the synthetic route chosen to produce the comb polymer. Hence, its effect is normally masked by the impact of different structures. In this work, three sets of three polymers each have been prepared by esterification of three similarly sized but different in constitution polyacrylic acids. Within each set, the reaction conditions have been tuned to promote a more or less accentuated acid function loss. The resulting PCEs all bear the same structure and conformation but substantially differ in charge density. The so-isolated molecular feature has been studied through its impact on adsorption extent and rate, chemical stability, calorimetric and rheological characteristics of cement paste. It is shown that the charge density has a wide impact on the performance of PCEs as superplasticisers. Its modification heavily affects the adsorption behaviour and can turn the same structure to behave as either strong water reducer or workability extender, with a limited effect on the heat signature of the cement paste. Furthermore, some insights are disclosed regarding reactivity of polyacrylic acids towards esterification, selectivity of ester formation and resulting chemical stability.

1. Introduction

Polycarboxylate ethers (PCEs) are the most powerful and flexible superplasticisers used today in concrete manufacture. This class of products is globally employed to reduce the amount of water necessary to produce workable Portland-based materials. Furthermore, PCEs are unavoidable if highly flowable, self-compacting, high-strength concrete is required. Discovered in the 80s, PCEs provided a quantum leap in performance compared to the former generations of superplasticisers based on synthetic polycondensates (polynaphthalenes and polymelamines) or waste product from paper making (lignosulphonates) [1–3]. Unlike the previous chemistries, PCE superplasticisers introduced an alternative dispersion mechanism based on steric repulsion [4,5]. Plus, PCEs can be modified during their synthesis to achieve different structures and hence tailor the performance according to the user's need [6,7]. A typical polycarboxylate ether is composed by a negatively charged backbone, responsible of the necessary drive for molecule adsorption on cement particles; a series of hydrophilic lateral chains depart from the backbone, giving a "comb" shape to the structure and inducing sterical repulsion among the coated cement grains thus eliminating their natural tendency to clump together [5,6,8–10]. Most structural features can be modified upon

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Nomenclature

$\%_t^{mPEG}$	Mass fraction of mPEG at time t [–]
$\%_{t=0}^{mPEG}$	Initial mass fraction of mPEG (purity) [–]
$\%_t^{PCE}$	Mass fraction of PCE at time t [–]
$\%_{t=0}^{PCE}$	Initial mass fraction of PCE (purity) [–]
C_{PCE}^f	Final mass concentration of PCE [mg L^{-1}]
C_{PCE}^i	Initial mass concentration of PCE [mg L^{-1}]
ED	Esterification degree [–]
h	Initial adsorption rate [mg g^{-1} min^{-1}]
K	PCE adsorption constant [–]
k_1	Adsorption kinetic constant [g mg^{-1} min^{-1}]
m_{BB}^{dry}	Dry mass of acrylic backbone [g]
m_{SC}^{dry}	Dry mass of sidechains [g]
MP	Molecular weight at peak [Da]
MW	Molecular weight [Da]
M_W	Weight average molecular weight [Da]
MW_{BB}	Molecular weight of backbone [Da]
$\overline{MW}_{mon}$	Weight average molecular weight of monomers [Da]
MW_{PCE}^{cal}	Final molecular weight of PCE [Da]
MW_{SC}	Molecular weight of side chains [Da]
N	Constitutional repeating units of backbone [–]
n	Equivalent cores of the comb polymer chain [–]
n_{COOH}	Moles number of acid sites [mol]
n_{COOR}	Moles number of ester sites [mol]
P	Constitutional repeating units in a sidechain [–]
PDI	Polydispersity index [–]
q	Specific capacity of adsorption [mg g^{-1}]
q_{max}	Maximum specific capacity of adsorption [mg g^{-1}]
t	Time [min]
V_i	Initial volume of pore solution [L]
W_0	Mass of binder [g]
X_A	PCE alkaline degree of conversion [–]
x_{mon}^{COOH}	Number of acid groups per monomer [–]
X_{mPEG}	Degree of mPEG conversion [–]
z	Charge per backbone monomer [–]
η	Adsorption efficiency [–]
ρ_{BB}^{theo}	Theoretical charge density of the backbone [mol g^{-1}]
ρ_{PCE}^{cal}	Expected charge density [mol g^{-1}]
ρ_{PCE}^{meas}	Measured charge density [mol g^{-1}]

synthesis, resulting in PCEs with different backbone length, branching density and size of sidechains. The chemistry can be also changed to some extent [11]. The result is a powerful dispersing effect, which allows great concrete water reduction and, consequently, high strength and durability. Among the drawbacks, lower early strength, concrete tackiness and viscosity, and compatibility with certain binders and clays have been reported along the years. However, all these issues have been studied and partially addressed [12,13].

Since the PCEs discovery, many modifications and features have been proposed to enhance the performance or to remedy the few shortcomings of this chemistry [11]. Nonetheless, most commercial products still rely on acrylic/methacrylic backbones, polyglycols as sidechains and ester linkages between the two. The polymer form-factor ranges in a limited window, which results in conformation regimes of “Flexible Backbone Worm” and “Stretched Backbone Worm” as first described by the work of Gay and Raphaël (in the following, also “G–R”) [14]. This general design complies with most of the applications and matches the demand in terms of price and availability. Many articles described in detail the phenomenology of the PCE action but, despite the maturity of the technology, the research is still very active and is devoted to further comprehension and refinement of this relevant class of polyelectrolytes.

This article focuses on the analysis of an important molecular feature, the charge density, which is responsible of occurrence, rate and extent of PCE adsorption onto the hydrating cement particles. The adsorption determines the performance of a polycarboxylate ether as superplasticiser in terms of either sheer power or workability retention. Commonly, the charge density is seen as a consequence of the chosen PCE design as it is mostly the complement of the grafting density. In this work, the charge density has been isolated during the synthesis of nine similarly structured PCEs based on three different backbones. The backbones possess different constitution but comparable size. All the resulting PCEs share the same form-factor and conformation and have been prepared through esterification of acrylic backbones with mPEG (polyethylene glycol monomethyl ether). Altering the reaction temperature, a more or less severe degradation of the PCE’s backbone has been induced thus resulting in nine polymers with same structure but different charge density. The reactions have been monitored through gel permeation chromatography (GPC) and titration, while the performance as dispersant has been measured through studies of rheology of cement paste, adsorption, calorimetry and chemical stability. The adsorption extent and occurrence has been related to the adsorption constant, a parameter firstly proposed in the work by Marchon et al. [15]. Finally, an attempt to describe the kinetics of the adsorption process has been carried out through the model of Ho and McKay [16].

2. Experimental

2.1. Materials, reactions and PCE characterisation

The three backbones (termed PAAC73, PAAC55, PAAC28) were experimental products provided by several European chemical companies. They were based on acrylic acid (AA)/methacrylic acid (MAA) in relative molar ratio 70/30 (PAAC73), 50/50 (PAAC55) and 20/80 (PAAC28). mPEG 1000 was supplied by Sasol. Sodium hydroxide was used as catalyst and was purchased from Sigma-Aldrich. All the reagents were used without further purification. Table 1 reports the specifications of all reagents. Purity, molecular weight (weight average M_W and molecular weight at peak MP) and polydispersity index (PDI) were determined by GPC, through a Waters Breeze 2 GPC apparatus comprising an isocratic pump, an autosampler and a refractive index detector. Three columns (Ultrahydrogel 120, 250 and 500) connected in series were used to separate the compounds; sodium nitrate 0.1 M at pH = 11 was used as eluent. Relative calibrations were based on narrow standards of PEG and polyacrylic acid. The theoretical charge density, calculated through Eq. (1) (see below), is reported as well. All the titrations were performed with an SI Analytics automatic DET (dynamic endpoint titration) apparatus.

The procedure for direct esterification involved the loading of all the reagents in a 350 mL glass reactor equipped with oil thermal bath, mechanical stirrer, 65 mm half-moon Teflon stirrer shaft, Graham condenser, digital vacuum pump and digital on-off thermal loop controller. The catalyst amount ranged from 1.5×10^{-4} to 2×10^{-4} mol per g of backbone according to the substrate. 60 mbar vacuum was applied to the system and heating started. After removal of the reagents water, the temperature was set at the chosen value and quickly reached thanks to the small size of the