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Assessment of the interaction of polycarboxylate superplasticizers in hydrated lime pastes modified with nanosilica or metakaolin as pozzolanic reactives

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HIGHLIGHTS

- Two low MW polycarboxylate ethers were fully characterised as plasticizers.
- Flowability of air lime pastes was enhanced by the use of PCE superplasticizers.
- Star-shaped PCE, despite being poorly adsorbed, provided best plasticizing effect.
- NS with large area and “inactive” adsorption sites yielded large SP consumption.
- Steric hindrance was ascertained as the main dispersion mechanism.

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ABSTRACT

Two polycarboxylate ether copolymers were assessed as superplasticizers (SPs) for hydrated lime pastes modified with two reactive compounds, nanosilica (NS) and ceramic metakaolin (MK). Characterization of the molecular structure of the SPs by Size Exclusion Chromatography, XRD, FTIR and MALDI-TOF (Matrix Assisted Laser Desorption Ionization Time-of-Flight) mass spectrometry was performed. The structures of the polymers were seen to be star- and worm-like shapes. A close relationship was found between the molecular architecture and the flowability of the pastes, being the star-shaped plasticizer the most efficient. Zeta potential assessment allowed us to elucidate a steric hindrance as the main action mechanism for these polymers. The large specific surface area of nanosilica led to a large SPs consumption as compared with metakaolin with lower surface area. However, SPs in MK–lime samples were attached favourably on the C–S–H and aluminate hydrates, so that the dispersing action was greater with respect to NS–lime suspensions.

1. Introduction

The use of plasticizing admixtures in order to improve the handling of cement-based media has been extensively reported [1,2]. High-range water reducers or superplasticizers (SPs) act reducing the water demand and enhancing the flowability of the fresh mortars, yielding workable materials [3]. SPs present different chemical compositions, such as lignosulfonates, sulfonated melamine-based polymers or polycarboxylate-based compounds (PCE) [4]. The latter are belonging to the last generation of SPs and consist of a main linear backbone (polymethacrylic acid) with carboxylate groups, some of them grafted with side chains with ether functionalities (polyethylene oxide units) [5]. The length of both backbone and side chains can be variable, thus giving rise to a different effectiveness. In general, PCEs have been reported to show a comb-shaped, worm-shaped or even star-shaped molecular architecture structure, always as a function of their ratio between the main backbone and the side chain length [6]. In high alkaline pH systems (such as cement- or lime-based binders), carboxylic groups of these SPs are expected to be deprotonated as carboxylate groups. The extent of the plasticizing action as well as the dispersion maintaining ability is strongly ascribed to structural factors, such as the length of the backbone and of the lateral chains [7]. At the same time, an increase in the molecular weight is

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expected to enhance the adsorption of the PCE on the binding particles as well as its performance [8,9].

Besides these aspects, the interaction of PCEs with the binding phases can induce several changes in the nucleation and growth of crystals, since PCEs can form complexes with Ca^{2+} ions, modifying the crystallization of Ca-rich compounds [10]. In addition, the dispersive effect inhibits the hydration kinetics leading to changes in the microstructure of the mortars. All these issues are related to the adsorption and compatibility between the admixture and the binder [9].

So far little attention has been devoted to the study of the performance of PCEs in lime-bearing pastes and mortars [11–13]. Lime-based dispersions can be used to obtain hydraulic mortars, which can be prepared either by the use of a natural hydraulic lime or by the incorporation of materials with pozzolanic activity, like metakaolin or nanosilica [14–16]. These two last compounds have shown the enhancement of several properties of air-lime based pastes and mortars: compressive strength, setting time and reduced microcracking, as a result of their filler effect and their reaction with $Ca(OH)_2$ yielding C–S–H phases (for NS and MK additions) [14,17] or aluminate-based compounds such as C_2ASH_8 and C_4AH_{13} (just for MK additions) [18]. The widespread use of hydrated lime and pozzolan-hydrated lime pastes for paints, consolidant products, soil treatments and the obtaining of repair mortars and grouts, especially for architectural monuments of the Cultural Heritage, supports the interest of these materials. In the case of grouts, one of the most relevant features is to achieve a suitable flowability that allows the grout to fill voids providing a good continuity of the masonry system [19]. In order to design suitable hydrated lime pastes and mortars, the use of compatible and effective SPs seems to be imperative.

Therefore, to gain a better understanding on the behaviour of PCEs in lime-bearing pastes and mortars, the goal of this work is the assessment of the interaction between two different PCE admixtures and both plain hydrated lime and hydrated lime pastes modified upon the addition of pozzolans: nanosilica or metakaolin. The adsorption behaviour, the effectiveness of the polymeric admixtures in the increase of fluidity of these systems and the dispersion maintaining ability over the time will be evaluated and related to the polymer characteristics.

2. Materials and methods

2.1. Materials

Both pozzolanic and pozzolan-free pastes were prepared by using a dry slaked lime (class CL 90-S according to European standard [20], supplied by CALINSA, Spain). The first pozzolan used was a colloidal silica suspension, nanosilica (NS; pH = 9.68, with a solid/liquid ratio of 0.28) as supplied by ULMEN Europa S.L. (Spain), with a specific surface area of 500 $m^2\,g^{-1}$ and an average particle size of 50 nm, as shown in the TEM micrograph of Fig. 1. This NS was selected because it was a superplasticizer-free suspension. The second pozzolan was metakaolin (MK), supplied by METAVER, with a specific surface area of 20 $m^2\,g^{-1}$ and an average particle size of 4.5 μm, as depicted in the TEM images in Fig. 1. This is made of a calcined kaolinite so that this fact guarantees a high reactivity. Different weight percentages (0, 6, 10 and 20 wt.% with respect to the weight of lime) of the pozzolans were added to obtain pastes in which the flowability and other properties were assessed.

Two different commercially available PCE-based superplasticizers were added in percentages of 0%, 0.25%, 0.50%, 0.75%, 1.00%, 1.25% and 1.50% with respect to the weight of lime. These copolymers were obtained by grafting side chains of poly(ethyleneoxide) in a main backbone of polymethacrylate [21,22]. Both copolymers were of similar and relatively low molecular weight in order to study the influence of the molecular architecture of the polymers on the performance of the tested admixtures.

Given that the assayed additives were expected to have a strong influence on the fluidity of the fresh pastes, the water/lime ratio that provided a good workability in the control sample, was then chosen as a fixed ratio for all the remaining samples.

2.2. Methods

2.2.1. Pastes preparation

Lime, pozzolan (MK) and dry PCE admixture, when necessary, were blended for 5 min using a solid admixtures mixer BL-8-CA (Lleal S.A.). Water (and, when required, the other pozzolan as a nanosilica suspension) was then added and mixed for 90 s at low speed, in a Proeti ETI 26.0072 mixer.

2.2.2. Experimental measurements

The characterization and structural elucidation of SPs were carried out by elemental analysis, conductometric titration, X-ray diffraction, Fourier transform infrared–attenuated total reflectance (FTIR–ATR) spectroscopy, refractive index size exclusion chromatography (RI-SEC) and MALDI-TOF (Matrix Assisted Laser Desorption Ionization Time-of-Flight) mass spectrometry.

Elemental analysis (weight percentages of C, H and N) was performed with a LECO CHN-900 analyser. The carboxylate groups population present in each PCE was determined by conductometric titration. The conductivity measurements were carried out by means of an Orion 4-Star benchtop pH/conductivimeter (Thermo Scientific) using a 0.1 M NaOH solution. The anionic charge density supplied by carboxylate sites of assayed SPs was expressed in terms of meq per g of polymer.

A Bruker D8 Advance diffractometer was used for XRD analysis, under conditions of a step size of 0.02° and 1 s time/step, from 2° to 80° (2θ) with a Cu Kα_1 radiation. FTIR spectra were recorded with a Nicolet-Avatar 360 FTIR spectrometer equipped with Golden Gate ATR accessory and temperature control (20–200 °C). Spectra were collected over a range 4000–600 cm^{-1} with a resolution of 4 cm^{-1}. Each spectrum was the result of averaging 100 scans.

The molecular weight distribution of SPs was determined using size exclusion chromatography (SEC) coupled to refractive index (RI) detector (Optilab-TRex, Wyatt). Polymer solutions (5 $g\,L^{-1}$) were filtered through a 0.45 μm filter and injected to a series of three Waters columns (Waters, Milford, MA), Ultrahydrogel 2000, 250, and 120 with exclusion limits of 7.10^6, 8.10^4, and 5.10^3 $g\,mol^{-1}$, respectively. A 0.1 M NaCl aqueous solution was used as eluent. A calibration with conventional standards of polyethylene oxide (PEO) and polyethylene glycol (PEG) covering a wide molecular weight range from 615 to 318,000 $g\,mol^{-1}$ was employed.

MALDI-TOF mass spectra were recorded by using UltrafleXtreme III MALDI-TOF system (Bruker-Daltonics) operated in positive-linear mode (m/z range of 100–7000 Da). The matrix used was composed of 10 $\mu g\,\mu L^{-1}$ of α-cyano-4-hydroxycinnamic acid (HCCA) in 50% (v/v) acetonitrile (ACN). A sample/matrix solution (1 μL, ratio 1:1 v/v) was deposited onto the MALDI sample probe.

To determine the consistency of the suspensions either viscosimetry or mini-slump flow test can be used. The latter was selected to assess the flowability of the pastes. A truncated metallic cone was filled with the sample; then, the metallic cone was removed and the cone-shaped sample was vertically lifted (15 strokes of the flow table) so that the gravity allowed the sample to slump down and a quantitative measure of the slump was recorded [23,24]. In order to assess the dispersion maintaining ability over the time, this test was additionally carried out after 0, 30, 60, 90, 120 and 150 min after the preparation of the suspensions. The setting time of the pastes was calculated according to the norm [25].

All sorption experiments for assayed SPs in both individual compound pastes (1 g per 25 mL of water) and in lime–pozzolan systems (5 g of lime and pozzolanic additive at 6, 10 and 20 wt.% with respect to lime in 25 mL of water) were conducted in batch reactors. The mixtures were stirred for 1 h in order to reach equilibration and, subsequently, were centrifuged at 8000 g for 15 min and the supernatant was collected and filtered through 0.45 μm PTFE filters for the measurement of the remaining polymer. The amount of SPs adsorbed onto the particles was determined by difference between initially added and final remaining concentration of the superplasticizer found in the equilibrium solution, as quantified by ultraviolet–visible spectrophotometry. The Freundlich model ($q = K{\cdot}C^{1/n}$) were used to fit the adsorption data, where, q represents the amount of PCE sorbed by the solid phase ($mg\,g^{-1}$), C is the concentration of PCE in the solution ($mg\,L^{-1}$) after equilibration, while K and $1/n$ are the Freundlich constants.

The interaction between the superplasticizer additive and the lime and/or pozzolans was studied by means of the measurement of the zeta potential in the solid/liquid interface [4,26,27]. To this aim, individual (25 g per 140 mL of water) or multicomponent suspensions (7 g of lime and 25 g of either NS or MK per 140 mL of water that were allowed to react for 30 min to ensure the pozzolanic reaction to take place) were prepared. When necessary, 1% w/v PCE solutions were used as titrants. An electroacoustic-based zeta potential analyser (ZetaProbe of Colloidal Dynamics), which allows to accurately measure the zeta potential of concentrated pastes, was used [28].

3. Results and discussion

3.1. Characterization of the polycarboxylate ester copolymers

The structural and compositional characteristics of the two superplasticizers were investigated. Size-exclusion chromatography data allowed us to obtain the weight-average molecular