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Effect of the addition of chitosan ethers on the fresh state properties of cement mortars

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ABSTRACT

The effect of two non-ionic chitosan derivatives (hydroxypropyl (HPCH) and hydroxyethyl (HECH) chitosans) and one ionic derivative (carboxymethylchitosan, CMCH) on the fresh-state properties of cement mortars was studied. Zeta potential measurements and particle size distribution were carried out in order to elucidate the action mechanism of the admixtures. Results were seen to be strongly dependent on substituents of the chitosan. Non-ionic derivatives had a weak dosage-related influence on the fresh-state properties. The ionic CMCH showed the more marked effect: it was found to act as a powerful thickener and to reduce the workable life of the fresh mixtures, whereas it caused a delay in the hydration of the cement particles. CMCH reduced the slump by 50% while commercial viscosity enhancers exhibiting larger molecular weights (hydroxypropylmethylcellulose, HPMC, and hydroxypropyl guaran, HPG) only reduced it by ca. 25%. The negative values of zeta-potential and the strong flocculating effect point to an adsorption of CMCH onto the positively charged cement particles. Optical microscopy and TEM observations showed the polymer giving rise to interlinking between cement particles.

1. Introduction

Development of new admixtures to be added to cement-based materials has been the object of extensive research, polysaccharides being one of the most widely investigated and used group of products [1]. The effects of adding sugars, starches, and cellulose ethers to cement-based materials have been reported [2,3].

Chitin, the raw material of chitosan, is the second most abundant natural polysaccharide after cellulose. This polymer and its derivatives have been used as biomaterials because of their biocompatibility, biodegradability, and biological activities [4]. Chitosan is mainly obtained from chitin and is made up of glucosamine and acetylglucosamine units, the proportion between these units being called the degree of deacetylation. This parameter, in addition to the molecular weight (M_W), is the main feature affecting the properties and conformation of chitosan.

The use of chitosan as an additive that improves the mechanical properties of many biocements, dental biocements, and cements for bone repair, has already appeared in the bibliography [5]. When present, chitosan (i) enhances the injectability of these composites; (ii) increases the setting time in a way similar to cellulose derivatives in cement–polymer systems and (iii) acts as a cohesion-improving agent in calcium phosphate cement for the repair of bones [6].

The effect of the addition of native chitosan to a Portland cement mortar has been previously reported [7]. This polymer has been proved to increase viscosity and, consequently, to cause a decrease in the fluidity of the mixture, the effect being scarcely influenced by the dosage. The larger the molecular weight, the greater the thickening effect detected, as caused by increased entanglement and cross-linking between chains in a calcium-rich system. Setting time, at low dosages, was seen to be mainly influenced by the molecular weight of the polymer, whereas the degree of deacetylation turned out to be the main controlling factor at high dosages. A set-retarding role for chitosans in cement mortars, as a consequence of an interaction of the polymer with the cement particles, has also been claimed.

However, the insolubility of the chitosan in alkaline media limits its applications in cement mixtures [8,9]. Etherification arises as a simple but excellent way of improving its properties by making it more soluble. Among other etherified derivatives, non-ionic hydroxyalkyl chitosans are obtained on reacting chitosan with epoxides and glycidol [10]. It has also been reported that the introduction of ionic carboxylic groups onto the amino groups of chitosan gives rise to water soluble, amphoteric polyelectrolytes, carboxyalkyl chitosan derivatives. Depending on the synthetic route, N, O, both N and O, and even N,N-carboxyalkyl derivatives can be obtained [11,12].

In the present paper, the behavior of fresh cement mortars modified by etherified derivatives (non-ionic and ionic ones) of chitosan is assessed with the purpose of exploring a new application of such

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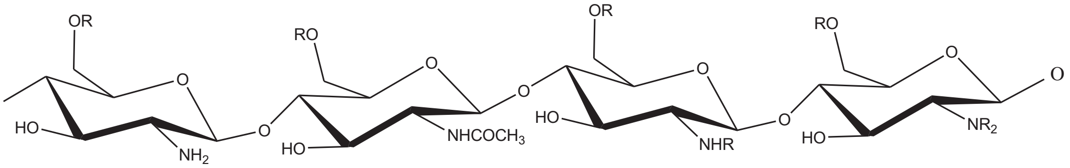

For HPCH derivative: R = -H, -$(CH_2)_3OH$; for HECH derivative: R = -H, -$(CH_2)_2OH$; for CMCH derivative: R = -H, -CH_2COOH

Scheme 1.

derivatives as cement admixtures. A comparison between the performance of these chitosan derivatives and that of the commercial rheological cement-mortar modifiers is also presented.

2. Materials and methods

2.1. Materials

An ordinary Portland cement (OPC) (CEM II 32,5 N, supplied by Portland S.A. Olazagutía, Spain) and a standardized siliceous aggregate were used to prepare the mortars. Mineralogical characterization and grain size distribution of the aggregate were previously reported [13]. The binder:aggregate ratio (B:Ag) selected was 1:3, by weight. In order to compare the effect of the addition of polymers to the mortar, all the samples were prepared with the same water:cement ratio, 0.50.

The assayed chitosan derivatives were hydroxypropylchitosan (HPCH), hydroxyethylchitosan (HECH) and carboxymethylchitosan (CMCH), whose chemical structures are shown in Scheme 1.

The first two derivatives were synthesized in the laboratory as reported by Peng et al. [14] and Xie et al. [15]. The latter was supplied by Heppe Medical Chitosan GmbH, Saale, Germany). Table 1 reports the characterization of the three chitosan derivatives as well as the initial chitosan. The FTIR spectra of the polymers (Fig. 1) exhibited absorption peaks around, 1080, 1030 and 900 cm^{-1} that were assigned to the saccharide moiety. The initial chitosan (a high molecular weight chitosan, from Sigma–Aldrich, Ref. 419419, with a deacetylation degree (DDA) of 75.6%, according to the data from the supplier) showed its characteristic peaks at 3455 cm^{-1} (O—H stretch), 2867 cm^{-1} (C—H stretch), 1154 cm^{-1} (bridge-O-stretch), and 1094 cm^{-1} (C—O stretch) [16–18]. The peaks at 1654 and 1598 cm^{-1} in the initial chitosan were attributed to the carbonyl stretching $\upsilon(C{=}O)$ of the secondary amide and primary amine bending $\delta(N—H)$, respectively [19].

FTIR spectrum of the hydroxypropyl chitosan resembles the one previously reported in the reference used for the synthesis method [14]. It can be observed increased absorption peaks at 1380 and 2980 cm^{-1} corresponding to the C—H stretching and bending of the CH_3 group compared to the spectra of native chitosan, indicating hydroxypropylation of the initial chitosan [14,20]. In addition, the absorption peaks at 1030 and 1160 cm^{-1}, which were attributed to νC—O of 3-OH and 6-OH of chitosan, respectively, nearly disappeared, implying that the substitution occurred at both 3-OH and 6-OH groups. The absence of the peak related to the secondary amide (1654 cm^{-1}) evidenced that essentially complete deacetylation occurred during the basification and alkylation of the chitosan, in agreement with previously reported data on this derivative [19].

With regard to the hydroxyethyl derivative, differences from the native chitosan were evidenced by the enhancement of $\upsilon(C—O—C)$ at 1090 cm^{-1} and $\upsilon(—CH_2)$ at 2950 cm^{-1} [21]. Given that the peaks attributed to the secondary amide and primary amine (1654 and 1598 cm^{-1}) were clearly reduced, it can be inferred that the alkylation process resulted in an almost full deacetylation of the polymer (as in the case of the HPCH) and that a significant substitution took place on the —NH_2 group. A peak at 1030 cm^{-1} (3-OH group) was observed, while the band at 1160 cm^{-1} (6-OH group) was absent, so the substitution on the alcohol groups occurred on the C-6.

Finally, Na salt of the CMCH gave rise to an infrared spectrum that showed an intense band at ca. 1600 cm^{-1}, related to the peak of —COONa (1598 cm^{-1}) (instead of —COOH which should appear at 1741 cm^{-1}) and overlapped with N—H bend [22]. The band at 3400–3500 cm^{-1} (O—H stretch) decreased, thus indicating a OH molar ratio drop owing to the carboxymethylation of alcohol groups. The initial chitosan band at 1654 cm^{-1} disappeared, pointing to a reduction of the secondary amide band: as a consequence of the carboxymethylation process, the resulting chitosan derivative was fully deacetylated [19]. The occurrence of a moderate band at 1411 cm^{-1} (asymmetric axial deformations of COO) confirmed the introduction of the carboxymethyl groups in the polymer chain [11,23]. Compared with the peaks of a native chitosan, the peaks of CMCH at 1599 cm^{-1} and 1324 cm^{-1} increase, thus indicating that carboxymethylation has occurred on both the amino and hydroxyl groups of chitosan [24].

The degree of substitution (DS, average number of substituents introduced on each sugar residue) was obtained by means of elemental analysis (C/N molar ratios in Table 1). Taking into account the number of carbon introduced after chitosan modification, the DS values (Table 1) were calculated by means of an equation published elsewhere [25]. These DS values were proved to be consistent with the ones obtained by additional ^{1}H NMR analysis (graphs not shown). This analysis also allowed us to calculate DDA values in accordance with a published procedure [26], showing almost fully deacetylated chitosan derivatives in good agreement with FTIR results (Table 1).

Molecular weight of each one of the polymers was obtained by means of viscosimetric measurements following a previously proposed method [27]. The results in Table 1 showed chitosan derivatives having similar low molecular weights owing to the degradation of the chitosan chain during the synthesis of the derivatives [14]. It was proved, by means of UV–vis spectroscopy measurements [11], that all the derivatives showed solubility in alkaline media. Since all the assayed derivatives were obtained in chloride-bearing solutions and chloride may interfere with the cement hydration, the amount of residual chloride was also determined by potentiometric titration. The data in Table 1 indicated that the contents of chloride were always very low. As will be reported later, the highest dosage of the admixtures (0.5% of the cement weight) would supply a maximum of ca. 4 ppm of chloride in the cement weight. Therefore, these negligible amounts of chloride allow us to conclude that the used admixtures were chloride-free [28].

In order to compare the results obtained, all the measurements were also carried out with two commercial viscosity enhancers and water retainers, that is, hydroxypropylmethylcellulose (HPMC, Hercules HPMC HK 15 M®, M_W = 770 kDa) and hydroxypropyl guar gum (HPG, Lamberti Quimica S.A., ESACOL HS-30®, M_W = 750 kDa). The latter admixture is a hydroxypropyl derivative of the guaran, a

Table 1
Characteristics of the native chitosan and etherified derivatives.

Compound	C/N molar ratio[a]	Degree of substitution (DS)	Degree of deacetylation (DDA)	Molecular weight (kDa)	Residual chloride (ppm)
Native chitosan	6.50	-	75.6[b]	835	n.d.
HPCH	11.24	1.74	97.2	119	320
HECH	6.74	0.37	95.8	190	<40
CMCH	9.78	1.84	99.1	51	740

n.d.: Not determined.
[a] From the elemental analysis.
[b] According to the data from the supplier.

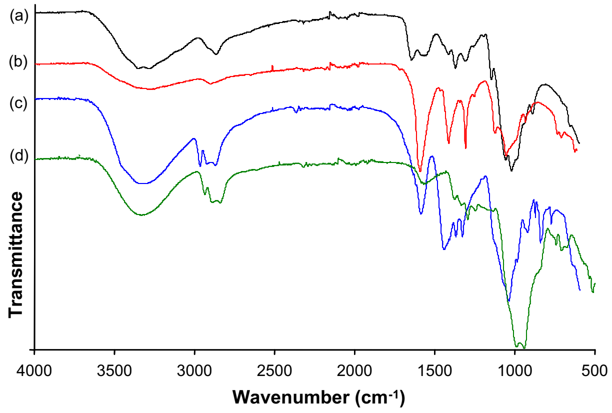

Fig. 1. FTIR spectra of chitosan and chitosan derivatives: (a) native chitosan, (b) carboxymethylchitosan (CMCH), (c) hydroxypropylchitosan (HPCH) and (d) hydroxyethylchitosan (HECH).

polygalactomannan heteropolymer formed by units of mannose linearly linked, with lateral links of galactose, with a ratio of 2:1 mannose:galactose. According to the suppliers' data, the two commercial polymers were of high M_W and showed a large degree of polymerization. With a view to testing the relationship between the consistency of the mortars and the measurements of the particle size distribution of cement–admixture solutions, a commercial superplasticizer was also used (Melflux 2651 F, BASF). This admixture is of a polycarboxylate ether type (PCE), from the supplier's data.

The admixtures were added in six different dosages (0.05%, 0.1%, 0.2%, 0.3%, 0.4%, and 0.5% of the cement weight) with the purpose of evaluating the influence of the additive dosage in the properties of the mortars.

2.2. Mortar preparation

Cement, aggregate and additive (when necessary) were blended for 5 min with a solid mixer BL-8-CA (Lleal S.A.). Then, water was added and mixed for 90 s at low speed, in a Proeti ETI 26.0072 mixer. In order to let the additive take effect, mortars settled for 10 min before the tests. The fresh properties were determined as described below.

2.3. Tests

2.3.1. Fresh state properties

The evaluation of the properties of the mortars in fresh state was carried out by various methods, namely the flow table test, the water retention capacity and the setting time, according to several standardized procedures. In order to measure consistency, the flow table test was used by measuring the slump of the mortar after 15 strokes on a specific compacting table (EN 1015-3, 2000) [29]. The water retention capacity is determined by weighing, before and after 5 min, absorbent materials placed on the fresh sample under pressure (UNE 83-818, 1993) [30]. The workable life progression was obtained from a specific device provided with a bradawl that pushes the fresh sample until the strength exerted exceeds 15 N (EN 1015-9, 2000) [31].

2.3.2. Study of the cement hydration by thermal analysis

The thermal analyses were performed in a simultaneous TG-DTA 851^{e} Mettler Toledo. An isothermal drying step (2 h at 28 °C) was first used to avoid interference by the non-reacted residual water. Nitrogen (100 mL min^{-1}) was employed as purge gas to dry the sample. This procedure had been previously endorsed as a more effective and less time-consuming method than other conventional drying procedures [32]. All samples achieved constant weight after carrying out the drying process, proving the validity of the method. The measurement step was designed from room temperature to 1000 °C, with a heating rate of 10 °C min^{-1}, in alumina crucibles, with 20 mL min^{-1} of N_2 as purge gas. Cement pastes, with 0.5 water/cement ratio and, when necessary, with admixture (0.4% of the cement weight), were prepared and kept in sealed plastic bags during storage. Measurements were carried out after 1, 5, 10, 24, 48 h and 1 week of hydration. The hydration of the cement pastes was assessed taking into account the contents of gypsum, water bound to calcium silicate hydrates (CSHs) and calcium hydroxide. The reported amounts were calculated from the weight losses measured from the thermogravimetry curves (TGs) between the initial and final temperatures of the corresponding DTG peaks (derivative thermogravimetry). The weight losses were attributed to the dehydration of the gypsum (dihydrated calcium sulfate) (110–145 °C), loss of water bound to CSH (in the absence of gypsum, from ambient temperature to 370 °C) and calcium hydroxide dehydroxylation (at ca. 450 °C), according to a previous work [32].

2.3.3. Zeta potential measurements

Specific mixtures of cement, water and additive were prepared to assess the zeta potential. Following a previously proposed and assayed method [33–35], solutions with different concentrations of admixture (10 different percentages w/w from 0.025 to 0.60) were prepared. Cement was added with a solute/liquid ratio of 0.0025. The solutions, after 5 min of stirring, were separated by centrifuge and the supernatants were analyzed with a Zeta Potential Analyzer ZETA PLUS (Brookhaven Instruments Corporation, New York, USA) following the method proposed. The average of twenty measurements was regarded as the zeta potential of the cement particles.

2.3.4. Particle size distribution

For particle size distribution measurements, 20 g of cement were added to 100 g of solutions with different quantities of admixture in water, the resulting admixture/cement ratios ranging from 0% to 1%. Manual stirring (1 min) was carried out and then the particle size distribution of the solutions was determined using a Malvern Mastersizer (Malvern Instruments, Ltd., UK).

2.3.5. Microscopy observations

Optical microscopy observations were carried out in the solutions described for particle size distribution measurements with an optical microscope, Olympus CH40, with Color view-soft imaging systems camera.

In addition, solutions of 5 g L^{-1} of cement with a 1% of admixture were analyzed by Transmission Electron Microscopy (TEM). One drop of these suspensions was placed on a copper grid and subsequent examinations were carried out with and without contrast (phosphotungstic acid) in a LIBRA 120 energy-filtering TEM (Zeiss) operated at 80 kV.

3. Results and discussion

3.1. Fresh state properties

Fig. 2 shows the slump results of cement mortars modified by the incorporation of the different admixtures (0% polymer data correspond to reference cement mortar). As proved by the slump reduction, non-ionic HECH and HPCH derivatives had a slight thickening effect, these results being in line with those reported for native chitosan [7]. The consistency in both cases turned out to be dosage dependent. When HECH was incorporated, lower results of slump than the plain mortar were always obtained. These values showed a decreasing tendency up to a dosage of 0.3%, beyond which a slight change in the trend could be observed since the slump increased again, although it did not reach the slump obtained for the reference mortar at any dosage. The addition of HPCH at low dosages (less than 0.2%) increased the flowability of the mortar by 3.5%, while with dosages between 0.2% and 0.4% the polymer acted as a thickener. The highest addition gave as a result slump values similar to the reference mortar.

However, the ionic derivative, CMCH, showed a more marked effect on the properties, acting as a thickener to a greater extent. The slump reduction reached a maximum with such a low dosage as 0.3% of the polymer. As the slump obtained from this dosage is the minimum measurable by the flow table test, beyond 0.3% of added polymer the measured consistency remained constant. Comparing these results to the values obtained for commercial rheological modifiers of high M_W, HPMC and HPG, it can be said that the three additives reduced the flowability of the mortars. However, the carboxymethylchitosan (with the lowest M_W) had a much more marked effect: when considering a dosage of 0.1% of polymer, the addition of the commercial products in the fresh mortar caused around 5% of fluidity reduction for the cellulosic derivative and ca. 18% of reduction for HPG, while 26% was determined if CMCH was added. When a dosage of 0.3% of polymer was added, the ability of CMCH to reduce the slump of the mortar went as far as to double that of the commercial admixtures (50% slump decrease for CMCH compared with 25% decrease for HPG and 21% for HPMC). Very slight variations in the slump were measured for the commercial polymers beyond the dosage of 0.3%, keeping the same trend in terms of flowability.

Regarding the water retention ability in Fig. 3, the HPCH derivative showed no significant influence on the water retention of the mortar (a variation of the retained water lower than 1.5%, which may fall within the experimental error), while the behavior of HECH was once again influenced by the dosage. For low dosages, the HECH derivative showed augmented water retention (nearly 8% of increase in the retained water) but beyond this dosage, the water retention decreased to values close to the reference mortar data (i.e. a reduction of ca. 5% in the retained water from the 0.3% dosage to the 0.5% dosage). This dosage-dependent effect may be related to the action mechanism of this polymer, as explained below.

It is noteworthy that CMCH is, among the assayed chitosan derivatives, the more effective in retaining water, reaching values nearly 95% of retention in the higher dosage, which involves an increase of around 11% compared with the polymer-free mortar. Nevertheless, HPMC and HPG still play a leading role as water retainers, with water retention values near 100% (around 16% rise in the retained water). These additives retain water, creating a gel through the hydrophilic groups fixing the mixing water by hydrogen bonds [36]. They also reduce the free water and expand their chains in the solution. Due to divergence in the influence in water retention, another mechanism of action is proposed below for the CMCH derivative.

Fig. 4 shows the progression of the stiffening or workable life of the fresh mortars, expressed as setting time versus increasing dosages of the additives. These measurements were also carried out to contribute to elucidating the fresh state properties of the additives assayed. HPCH and HECH derivatives showed limited influence on the stiffening evolution, and only a small reduction of the setting time was observed at the largest dosage: the workable life was shortened by 60 min for HPCH samples, while only 18 min of reduction were measured for HECH samples. As can be seen in Fig. 4, the behavior of HECH also showed a point of inflection at a 0.3% dosage, which was found to have the most noticeable drop (around 30 min of cutting, i.e. ~9% compared with the workable life of the polymer-free mortar).

Once again, the effect of CMCH on the properties of the mortar was distinct, reducing the workable life to a larger extent than the other chitosan derivatives, this effect being more considerable as the dosage increased (the measured setting time was shortened by 75 min for a dosage of 0.1%, while 285 min of reduction were determined when the used dosage was 0.3%). Indeed, with 0.5% of carboxymethylchitosan, the stiffening process only took very few minutes (7 min, which involved a reduction in the time of almost 98% in comparison with the reference mortar). This reduction in the stiffening time may be related to the aforementioned thickening effect of the CMCH derivative: as it reduced the flowability of the fresh mortar by increasing the degree of compactness of the mortar, the progression of the stiffening of the mortar may have been accelerated as determined by the experimental procedure. According to the European Standard (EN 1015-9, 2000) [31], the experimental test carried out registered the resistance to the pen-

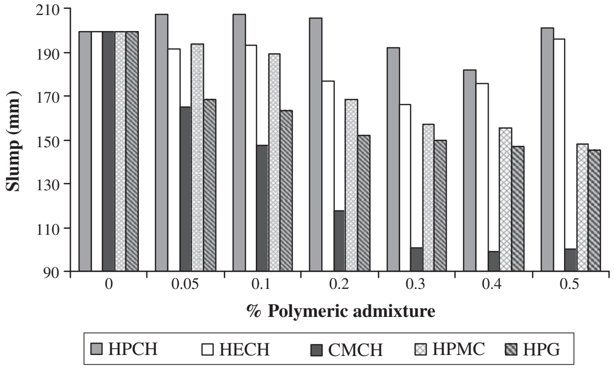

Fig. 2. Effect of the addition of different admixtures on the slump values of fresh cement mortars.

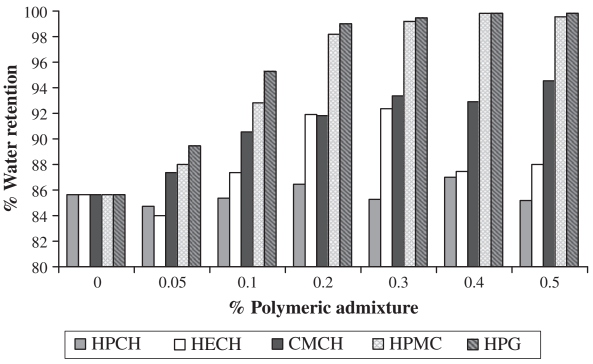

Fig. 3. Effect of the addition of different admixtures on the water retention ability of fresh cement mortars.

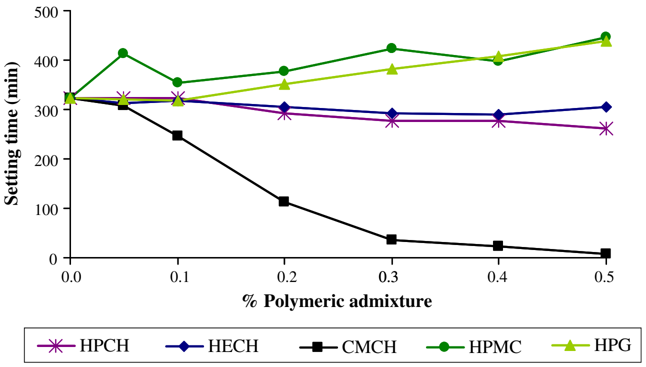

Fig. 4. Workable life evolution of different admixture–cement mortars vs. increasing amounts of admixture.

etration of a bradawl and showed the gradual change from fresh or plastic mortar to setting or set mortar.

The workable life data obtained from the modified mortars agreed with the setting time evolution (EN 196-3, 2005) [37] monitored in cement pastes and CMCH: at low doses (0.05%), the addition of CMCH accelerated the initial setting time from 230 min for the polymer-free cement to 190 min in the CMCH-modified cement paste.

In order to elucidate if the increase in the rate of the stiffening was due to any kind of interaction with the cement hydration, TG-DTA studies on fresh cement pastes were carried out in the early and middle stage of the hydration. Fig. 5 shows the evolution of the contents, calculated on the basis of the final ignited mass of each sample, of the main compounds that underwent changes during the cement hydration over 48 h. Results showed that the behavior of the free-admixture cement paste matched the one previously reported by Dweck et al. [32]: a rapid cement hydration over the first 24 h, proved by increasing percentages of water bound to cement hydrates (hydration of the cement phases yielding CSH gel, tobermorite, as the main compound) and $Ca(OH)_2$ (secondary product also obtained as a result of the CSH formation). In addition, the weight loss (110–145 °C) attributed to the regenerated dihydrated calcium sulfate sharply reduced after 10 h of hydration, in agreement with the data by Dweck et al. [32], who indicated that this compound is continuously consumed to form ettringite in about 16 h. In contrast to these values, the addition of CMCH hindered the hydration of the cement phases, as can be observed in the lower percentages of water related to the formation of CSH and of $Ca(OH)_2$ in comparison with the plain cement paste. The hydration of the cement paste when CMCH was added turned out to be specially impeded over the first 24 h after the water addition, as was also confirmed by the sustained amount of regenerated dihydrated calcium sulfate. The increasing values of water bound to cement hydrates and $Ca(OH)_2$ at 48 h as well as the drop of $CaSO_4{\cdot}2H_2O$ proved that, solely after 24 h, the hydration of cement proceeded in a significant way. Therefore, the addition of CMCH, while increasing the rate of the stiffening of a fresh cement paste, gave rise to a delay in the hydration of the cement particles. The data showing a workable life reduction must be related to the stiffening of the fresh cement paste as a consequence of the thickening action of the CMCH polymer. The mechanisms for these actions (thickening and also delay of cement hydration) deserve a detailed explanation, which is provided below.

This tendency to accelerate the stiffening rate shown by the CMCH derivative is opposite to that for the commercial HPMC and HPG, as they were expected and proved to enlarge the workable life (Fig. 4): when dosages of 0.3% were added, HPMC caused a delay of 102 min in the setting time while HPG delayed it by 59 min. At the largest dosage of polymer (0.5%), both polysaccharide derivatives provoked a similar delay of 2 h (i.e. a 37% increase in the workable life). The workable life changes in the two above-mentioned commercial polymers can be related to their reported water retention ability, which is in agreement with the above results and with some previously published works [38–43]. These additives are able to gelify an aqueous solution, so that both the viscosity and the water retention may be enhanced.

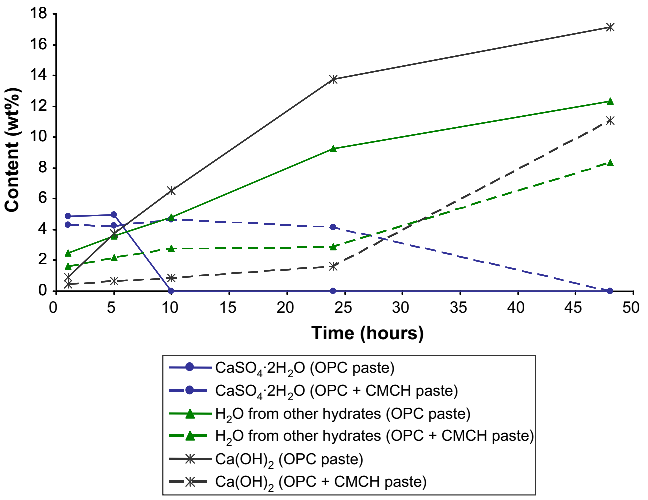

Fig. 5. Composition data for cement pastes as a function of hydration time over 48 h obtained by means of TG analysis. Solid lines: admixture-free cement pastes. Dotted lines: CMCH cement pastes.

Taking into account the different experimental collected data, the rationale is that CMCH might be acting through a different mechanism, as it did not create a gel in pure water to such an extent as the assayed commercial polymers, but nor did it act as an outstanding water retainer. It must be considered that the commercial polymers (HPMC and HPG) showed large M_W, whereas CMCH was proved to have a markedly lower M_W. As will be assessed later with measurements of particle size distribution and zeta-potential, CMCH showed a strong interaction with the cement particles, also reinforcing the idea of a different action mechanism. As far as the results obtained in this section are concerned, among the chitosan ethers, CMCH has been found to be a powerful modifier of the fresh-state properties of cement mortars.

3.2. Assessment by zeta potential and particle size distribution measurements of the interaction between cement particles and chitosan ethers. Optical microscopy and TEM observations

Zeta-potential measurements of samples with different amounts of the polymers were carried out in order to elucidate possible interactions between the cement particles' surface and the admixtures. In spite of the fact that experimental conditions and techniques have been reported to have an influence on the zeta potential values, cement without additives tends to have weakly negative values of zeta-potential [44]. If any adsorption of the charged polymer (i.e. an anionic polyelectrolyte) onto the cement particle surfaces took place, these values would change towards more negative values. In Fig. 6 it can be observed that the addition of HPCH and HECH derivatives caused, if any, very little displacement of the zeta-potential: as a result of their non-ionic nature, these polymers are negligibly ionized at the alkaline pH of the cement media, thus showing scarce interaction with the cement particles. The addition of the commercial polysaccharide derivatives (cellulosic and guar gum products) also showed a little variation in the measurements. These slight departures from the polymer-free cement solution may also be related to their non-ionic composition, which agrees with some previously reported data [45].

In the alkaline pH of the solution, it is supposed that CMCH would be negatively charged because of its functional carboxylic groups. This fact might shift the zeta potential data towards more negative figures. Experimental results, in Fig. 6, confirmed these assumptions, showing marked negative zeta potential values for CMCH–cement solutions in a polymer dosage-dependent behavior.

Combining the abovementioned strong consistency increase and workable life modification of CMCH (Fig. 4) with these significant changes in the zeta potential values, a hypothesis can be set up suggesting that molecules of the polymer could link the cement particles, interacting with cement particles with positively charged surfaces and consequently explaining the experimental results. Polymer molecules, when adsorbed onto the cement particles, might prevent them from hydration, thus explaining the delay in the formation of hydrated cement phases observed by thermal analysis.

Particle size distribution assessment was executed to clarify the mechanism of action of the polymers. In Fig. 7a, polymer-free cement mixture presented two main peaks: the smallest corresponds to particle between 0.1 and 1 μm (average value of 0.3 μm) and the larger one between 10 and 100 μm (average value around 20 μm). The chitosan derivatives, HPCH and HECH (Fig. 7b and c, respectively), and the commercial admixtures HPMC and HPG (Fig. 7d and e, respectively) also showed, in general, a bimodal distribution. However, HECH presented a dosage-dependent distribution behavior, with the largest percentages of agglomerates of around 20 μm for the intermediate dosages, whereas the highest dosages acted reducing the agglomerates of ca. 20 μm and increased the percentage of particles of diameter 0.3 μm. These facts may be correlated with the dosage-dependent performance of this polymer: a thickening action, proved by the slump reduction, with raising dosages up to intermediate amounts of HECH (0.3%) (formation of big agglomerates in the particle size distribution) and a plasticizing action beyond this dosage, shown by the slump increase. In the presence of large amounts of polymer, steric repulsions between the chains of the HECH could take place, resulting in its plasticizing action and in the increase in the surrounding free water, which entailed a water retention ability reduction.

When HPMC and HPG admixtures were added to cement solutions, these showed a bimodal particle size distribution (around 0.3 and 20 μm) (Fig. 7d and e), but with a small percentage of large agglomerates that only appeared at the highest dosages (diameter of the agglomerates ranging from 190 to 300 μm). Optical microscopy (Fig. 8) allowed us to observe some agglomerates of cement particles at the largest dosage of these admixtures, in agreement with the PSD results (Fig. 8d and e). However, many single cement particles can also be seen and identified as scattered, small dark dots, showing a very limited flocculating action. Although in-depth research on the water retention and viscosity enhancing mechanisms of these commercial admixtures is beyond the scope of this work, from these results and from the zeta potential evolution, it is tenable that their viscosity-enhancing and water-retaining actions cannot essentially be related to the interaction with cement particles, but rather to other factors. Patural et al. [46] have recently reported that the chain length of backbone (molecular weight) has a strong influence on the consistency of mortars modified by cellulosic ethers: the entanglement of polymer chains has been said to be responsible for a mortar's viscosity increase. In the same study, related to the water retention mechanisms, it is reported that consistency variations are not always responsible for water retention evolutions. In the case of the present work, the molecular weights of the assayed chitosan ethers are approximately in the same order of magnitude and all of them were seen to be lower than the initial chitosan as a result of the polymer chain degradation during the alkylation process. As a matter of fact, the chitosan derivative showing the largest thickening effect (CMCH) exhibited the lowest molecular weight. Commercial polysaccharides (HPMC and HPG) showed the largest M_W, but their thickening or viscosity enhancing ability of the fresh cement mixtures did not yield values as large as those measured for the CMCH. Therefore, molecular weights of the assayed polymers did not account for differences in the experimental results of the chitosan derivatives.

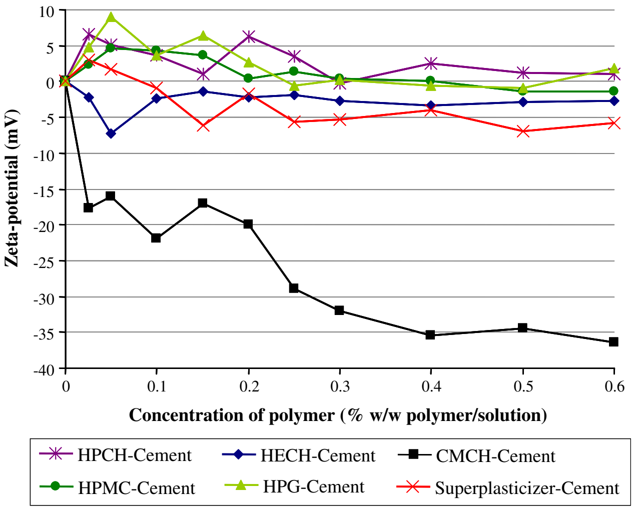

Fig. 6. Zeta potential evolution of cement solutions vs. increasing amounts of polymeric admixtures.

The particle size distribution of all these non-ionic polymers contrasted with the trimodal distribution of cement–CMCH mixtures. With the addition of increasing dosages of the polymer, the peak intensity at ca. 0.3 μm increased while the peak at ca. 20 μm decreased, as depicted in Fig. 7f. However, more outstanding is the appearance of a new population with mean values ranging from 300 to 400 μm, indicating a clear agglomeration of cement particles as a result of the polymer addition in a dosage-dependent way. This fact can help to confirm the previous hypothesis set up to explain the behavior of the assayed polymer, which is expected to have a mechanism of action involving an interaction with the cement particles. As proved by the shift of the zeta potential values towards more negative figures, this polymer, acting as a negatively charged polyelectrolyte, interacted and adsorbed onto positively charged cement particles. Owing to the high number of carboxylate groups (DS value of 1.84, which entails more than one carboxylate group per monomeric unit of the polymer), different segments of the molecules of the polymer could in that case link different cement particles and the addition of the polymer would have a flocculating effect (proved by the strong slump reduction and the increase of the stiffening rate that resulted in a workable life reduction). The number of large agglomerates that arose with increasing dosages of polymer in the particle size distribution study upheld this theory (Fig. 7f). In support of this action mechanism, it has also been reported that oppositely charged polyelectrolytes can give rise to attractive interactions between charged cement particles [47] and chitosan-based polyelectrolytes have been reported to give rise to bridging flocculation of similar charged particles (kaolin) [48]. Furthermore, optical microscopy observations (Fig. 8f) obtained from these solutions reinforced this assumption. As can be seen, when CMCH was added, the cement particles flocculated giving rise to large agglomerates by comparison with the smaller agglomerates observed in polymer-free cement solutions (Fig. 8a).

These results were confirmed by TEM observations of large agglomerates of cement particles (Fig. 9a). Fig. 9b depicts the bridging effect of both needle and round-shaped cement particles

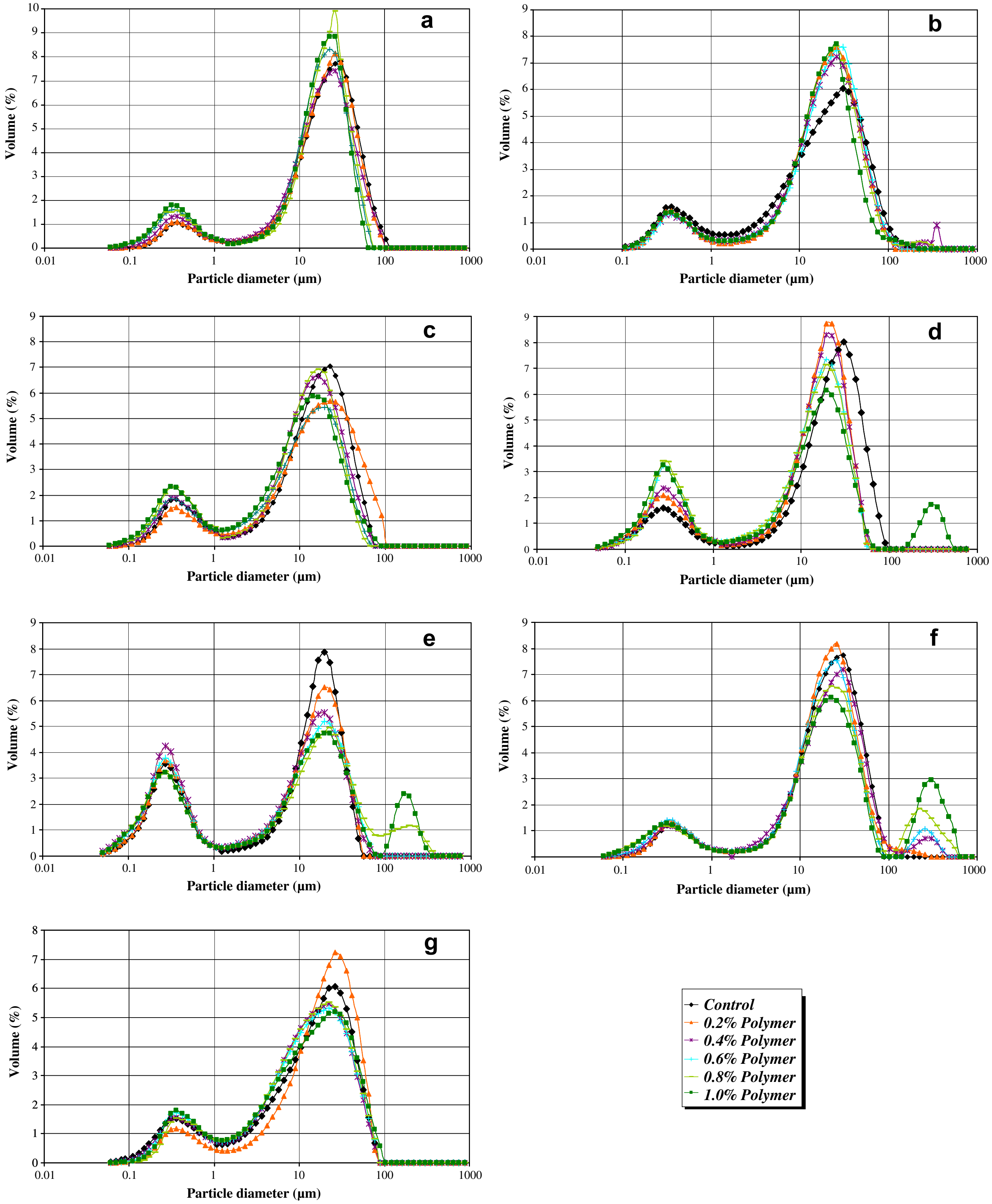

Fig. 7. Effect of the increasing polymer concentrations on the particle size distribution in cement solutions (control: 0% polymer; 0.2%, 0.4%, 0.6%, 0.8% and 1.0% polymer). The graphs correspond to (a) polymer-free, (b) HPCH, (c) HECH, (d) HPMC, (e) HPG, (f) CMCH and (g) superplasticizer.

induced by the CMCH polymer as identified by the smaller darkened areas onto which the contrast agent has adhered. Furthermore, Fig. 9c and d showed a semi-transparent thin and smooth film of CMCH located in some areas embedding the cement particles. Similar polymeric films have been previously reported for other polysaccharide ethers [49].

Measurements of particle size distribution of the commercial superplasticizer admixture were provided for comparison purposes.

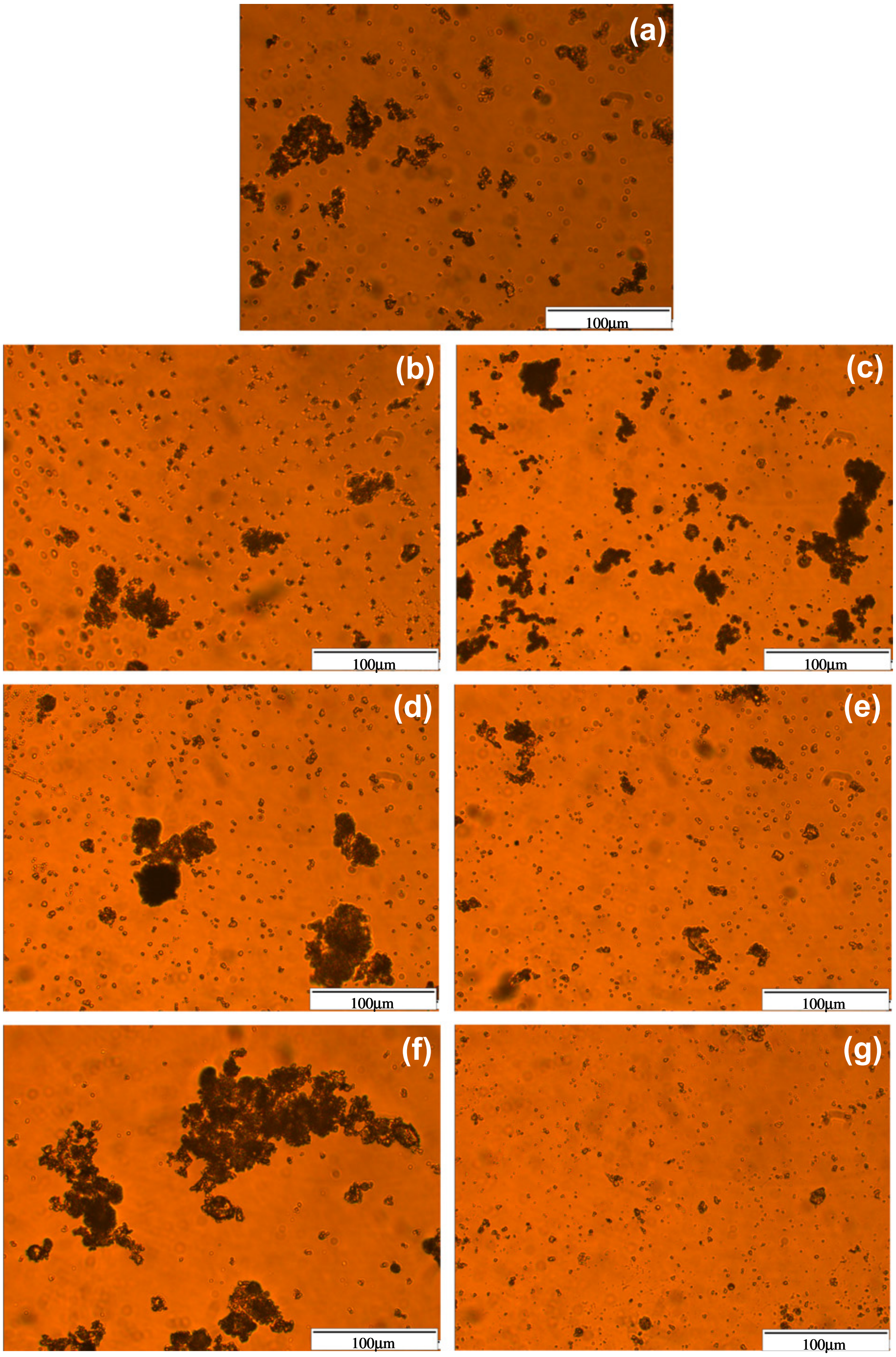

Fig. 8. Optical microscopy images of (a) polymer-free (b) HPCH, (c) HECH, (d) HPMC, (e) HPG, (f) CMCH and (g) superplasticizer cement solutions.

The aim was to prove the relationship of the PSD and the consistency of the fresh mortar. It is reported that superplasticizers are polymers that improve the flow of the mortar by reducing the degree of flocculation of the system [50–52]. These polymers are adsorbed onto the surface of the cement particles, separating them and releasing the trapped water [53,54]. As depicted in Fig. 7g, no large agglomerates of cement particles can be observed in the measurements of particle size distribution. In addition, with higher dosages of the superplasticizer, the main peak (between 10 and 100 μm) decreased while the peak of lower particle size (between 0.1 and 1 μm) increased, corroborating thus the expected deflocculation action of these polymers. Besides, due to its poly-anionic nature, negative values of zeta-potential were expected for cement solutions modified by the superplastizicer addition [55]. The experimental results obtained (Fig. 6) confirmed the previous assumptions as well as the connection of both methods, particularly the particle size distribution, with the rheological performance of the cement mortar. Optical microscopy photographs demonstrated the deflocculating performance of this additive, avoiding the formation of agglomerates of cement particles and provoking the separation between the single cement particles (Fig. 8g).

The noteworthy differences observed between CMCH and other low $M_{W,}$ anionic polyelectrolytes that behave as superplasticizers (polycarboxylate ethers, PCE, such as the one tested in the current work or low M_W starch derivatives, as those reported by Vieira et al. [1]) require further investigation into their mechanism. While

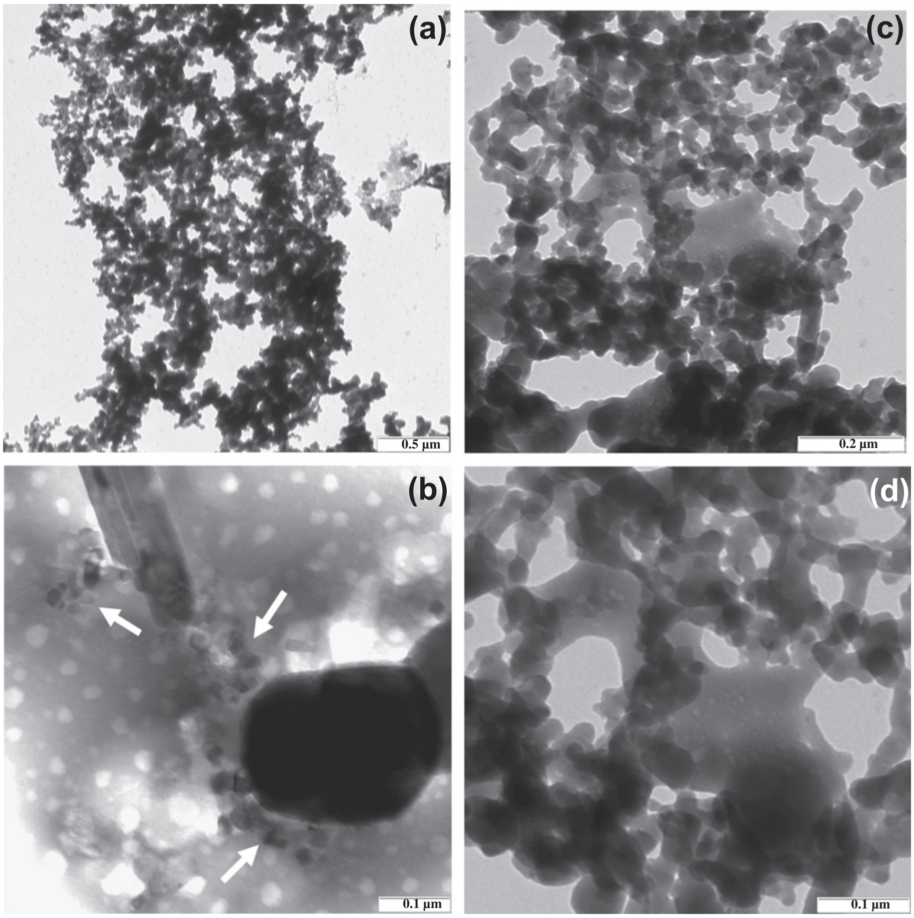

Fig. 9. TEM micrographs of the CMCH–cement solutions: (a) agglomerate of the cement particles; (b) micrograph in the presence of contrast agent showing the bridging effect between needle and round-shaped cement particles caused by the CMCH. The polymer is identified by the smaller darkened areas (denoted by arrows) onto which the contrast agent has adhered; (c) semi-transparent thin and smooth film of CMCH located in some areas embedding the cement particles; (d) detailed film of CMCH embedding cement particles.

superplasticizers have been reported to give rise to negative values of zeta potential and deflocculating action [44,45,53], CMCH acted as an outstanding flocculant, while increasing the negative values of the zeta potential. Since it has been reported that the anionic charge density of a polycarboxylate macromolecule determines the electrostatic interaction with cement [56], a role would be expected to be played by the substitution degree (DS, which was calculated by the molar ratio of carboxymethyl acid groups to monosaccharide units [57]. In fact, Vieira et al. [1] reported that some PCE's have a polymer backbone with anionic substituents, but with substantially lower charge density than some carboxymethyl starch derivatives, due to the fact that the anionic groups are found exclusively on the main polymer chain. Besides, the steric accessibility of the $-COO^-$ functionalities has been related to differences in performance among PCE's [56]. As far as the CMCH used in the present paper is concerned, the facts that (i) it did not show anionic charge reduction, (ii) its linear structure does not present any steric hindrance towards the carboxylate moieties and (iii) the DS is large (1.84), justify the ability of CMCH macromolecule to strongly and simultaneously interact with different cement particles in a different way from that seen for PCEs.

4. Conclusions

Non-ionic and ionic chitosan ethers were tested as admixtures for OPC mortars. The behavior of the polymers, all of them of low M_W, was found to be strongly influenced by the main substitution group of the chitosan derivatives. Hydroxyethylchitosan (HECH) and hydroxypropylchitosan (HPCH) have introduced weak changes in the fresh properties of the mortars. Both polymers showed a dosage-dependent behavior, especially HECH. When up to 0.3% of HECH was added, a thickening action (proved by slump reduction) was observed as confirmed by the formation of large agglomerates, which were inferred from the particle size distribution and observed under optical microscopy examinations. Beyond this dosage, the polymer exhibited a plasticizing action, which was related to steric repulsions that might take place between the chains of the polymer. Consequently, an increase in the free surrounding water, evidenced by a reduction of water retention ability, occurred. For HECH and HPCH, slight interaction with cement particles was found due to their non-ionic nature that made them be negligibly ionized under the alkaline pH of the cement media.

The ionic derivative, carboxymethylchitosan (CMCH), showed a strong effect on the properties of fresh mortars, acting as an effective thickener and reducing the workable life of the fresh paste. Clear interaction with cement particles was proved by the largely negative values of zeta-potential, the flocculating effect denoted in particle size distribution and the delay in the hydration of the cement phases assessed by TG. CMCH caused a bridging effect between cement particles, as was observed by microscopy examinations (optical and TEM). High M_W commercial hydroxypropylmethylcellulose (HPMC) and hydroxypropyl guaran (HPG) showed very limited flocculating action (lower consistency increase) and weak interaction with cement particles in comparison with the much more marked effect of CMCH.

As the assayed CMCH has been found to be a powerful modifier of the fresh-state properties of cement mortars, further studies will be carried out focusing on practical applications of this admixture (thickener and workable life modifier), as well as on the development of new chitosan derivatives based on this polymeric structure, by modifying and investigating the influence of the substitution degree, molecular weight and new functionalities that could be introduced.

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