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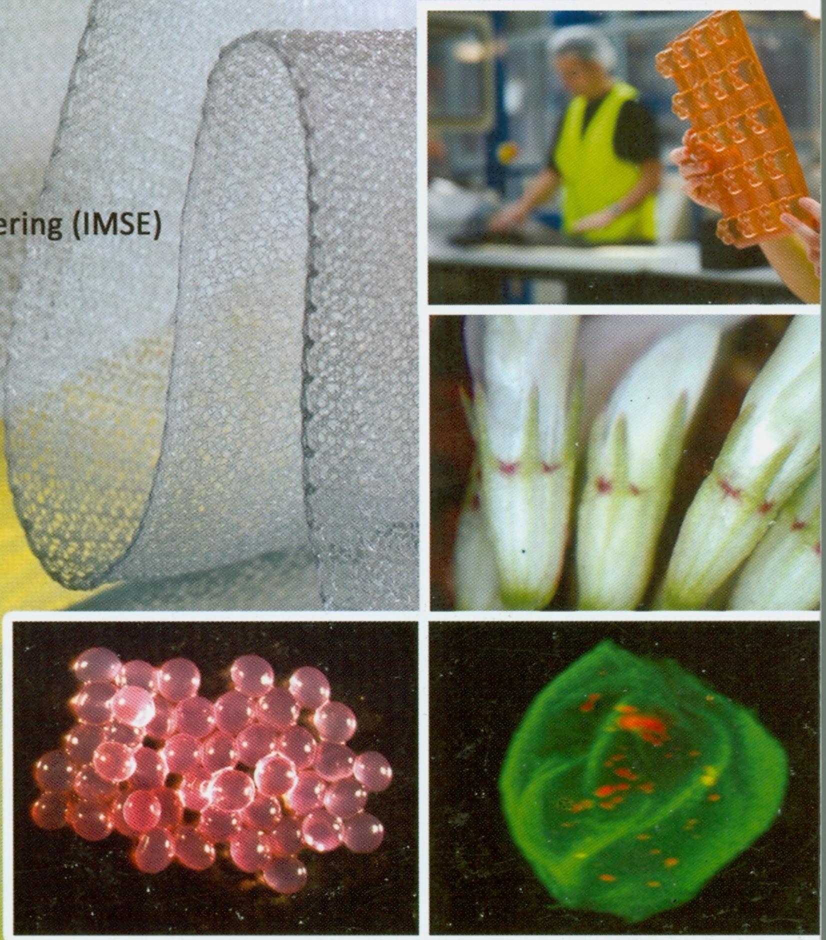

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Biopolymer-Cement Composites for Building Purposes: Performance of Chitosan and Some of Its Derivatives as Cement Admixtures

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Polysaccharides have been reported to be efficient cement additives behaving as viscosity-enhancing admixtures and set retarders. In the present work, chitosans of different molecular weights and several chitosan derivatives have been assessed as cement admixtures. The effect of chitosan incorporation on the rheological properties of a fresh cement paste has been evaluated. For non-modified chitosan polymers, slight variations at fresh state have been found, related to the insolubility of the polymer chain. However, the addition of polymers modified by the introduction of some hydrophilic groups (hydroxypropyl methyl, hydroxyethyl or carboxymethyl) gave rise to relevant changes in the fresh mixture. This fact has been connected with the increased solubility of the polymer. At the alkaline pH of the cement matrix, the carboxymethyl chitosan (CMC) has been proved to be the most efficient rheological modifier, with an outstanding flocculant effect of the fresh mixture at low dosages (as little as 0.3% of CMC addition reduced by half the slump of the fresh mixture). By means of zeta potential and particle size distribution measurements a clear interaction between this chitosan derivative and cement particles has been proved. Biopolymers showing best results have been used to carry out tests in hardened state mortars. Mechanical strengths as well as pore size distribution have been determined: a 0.4% of CMC yielded the minimum loss of strength both in flexural and compressive tests. Among the different assayed water/cement ratios, a 0.55 value has been found to be consistently the best in terms of mechanical performance of the biopolymer-cement composites.

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Biopolymer-cement composites for building purposes: performance of chitosan and some of its derivatives as cement admixtures

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INTRODUCTION

The use of different polysaccharides (sugars, starches, cellulose ethers…) as viscosity-enhancers and set retarders for cement mortars has been previously reported [1, 2]. Cellulose additives have shown certain advantages in connection with workability of mixtures and their use in concretes for underwater construction works.

Chitosan, the deacetylated derivative of chitin, is obtained from chitin which 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 [3, 4].

In the present work, commercial chitosans of three different molecular weights and several chitosan derivatives (carboxymethyl, hydroxyethyl and hydroxypropylchitosan) have been assessed as cement admixtures. Moreover, the effect of the incorporation of chitosan and its derivatives on the rheological properties of the fresh cement pastes has been evaluated.

MATERIAL AND METHODS

An ordinary Portland cement (OPC) (CEM II 32,5 N, supplied by Portland S.A. Olazagutía, Spain) and a standardised siliceous aggregate were used to prepare the mortars. The selected binder:aggregate (B:Ag) ratio was 1:3 by weight and the water:cement ratio was 0.55.

The additives added to the mortar were, in first place, commercial chitosan with three different molecular weights (named as LMW for the one of lower molecular weight, MMW for the chitosan of medium molecular weight and finally, HMW for the polymer of higher molecular weight) from Sigma-Aldrich (Steinheim, Germany) and carboxymethylchitosan (CMC) (Heppe medical chitosan GmbH, Saale, Deutchland). The derivatives hydroxypropyl (HPC) and hydroxyethylchitosan (HEC) were synthesized in the laboratory. These additives were added in six different dosages (0.05, 0.1, 0.2, 0.3, 0.4, and 0.5 of the cement weight) in order to evaluate the influence of the dosage of additive in the properties of the mortars.

Properties of the mortars in fresh state were evaluated through the flow table test, the water retention capacity and the setting time. Measures of particle size distribution and ζ- potential were also carried out in order to asses the results obtained. In hardened state, density, shrinkage, pore size distribution and mechanical strength were measured at 28 days.

RESULTS AND DISCUSSION

The rheological properties of cement pastes both in fresh state and in hardened state have been measured and the effect of the addition of the above-mentioned additives has been evaluated. The unmodified chitosan has shown slight variations in the properties of the fresh state mortar. This is related to the limited solubility of the polymer. Nevertheless, the introduction of hydrophilic groups as hydroxypropyl, hydroxyethyl and carboxymethyl to the biopolymer, makes the mixture to undergo important changes, probably due, in some extent, to the increase of the solubility.

From all the additives assayed, CMC proved to be the most efficient rheological modifier, having a relevant effect on the fresh mortar. This effect reached a maximum at a dosage of 0.3% of polymer, so it can be said that it is effective even at low dosages (Figure 1). Results of water retention and setting time complement this behaviour, as CMC increases the water retention of the mortar and reduces the setting time.

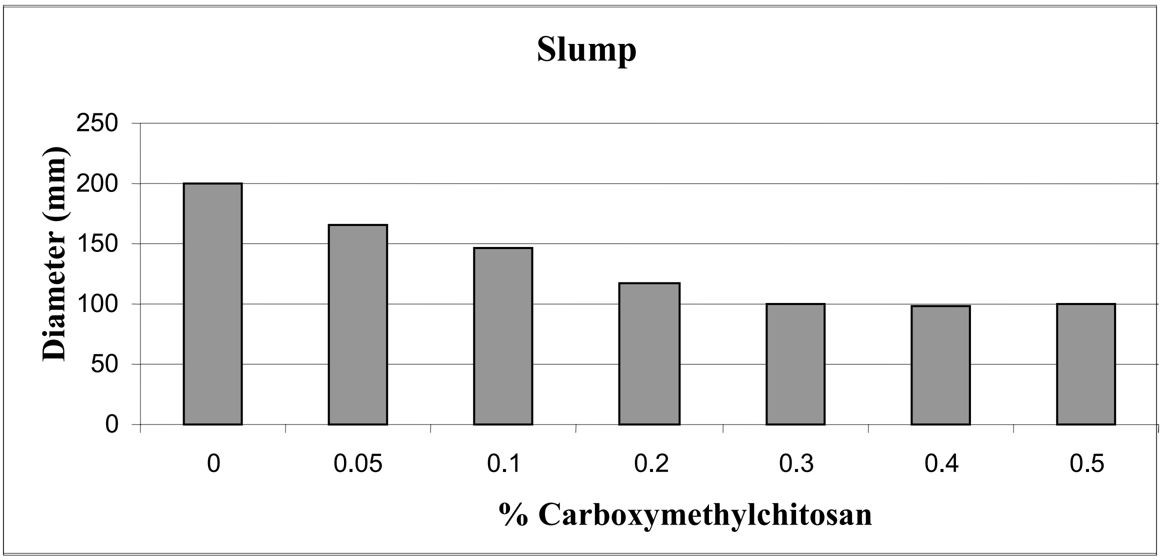

Figure 1: Slump results at increasing dosages of carboxymethylchitosan.

Zeta potential and particle size have been used to asses an interaction between this chitosan derivative and the cement particles. At such alkaline pH, the polymer would be a negatively charged polyelectrolyte owing to its functional groups. This shifts the zeta potential values towards more negative figures, so the polymer is able to interact with positively charged cement particles and allowing an adsorption on the surface of the particles. In that case, the molecules of the polymer could link different cement particles. Figure 2 shows the particle size distribution in solution of cement with different amounts of CMC. The addition of the polymer has a flocculant effect that can be observed by the increasing number of large agglomerates as the dosage increases. This is a consequence of the linking between polymer molecules and cement particles, causing a negative value of the surface potential [5].

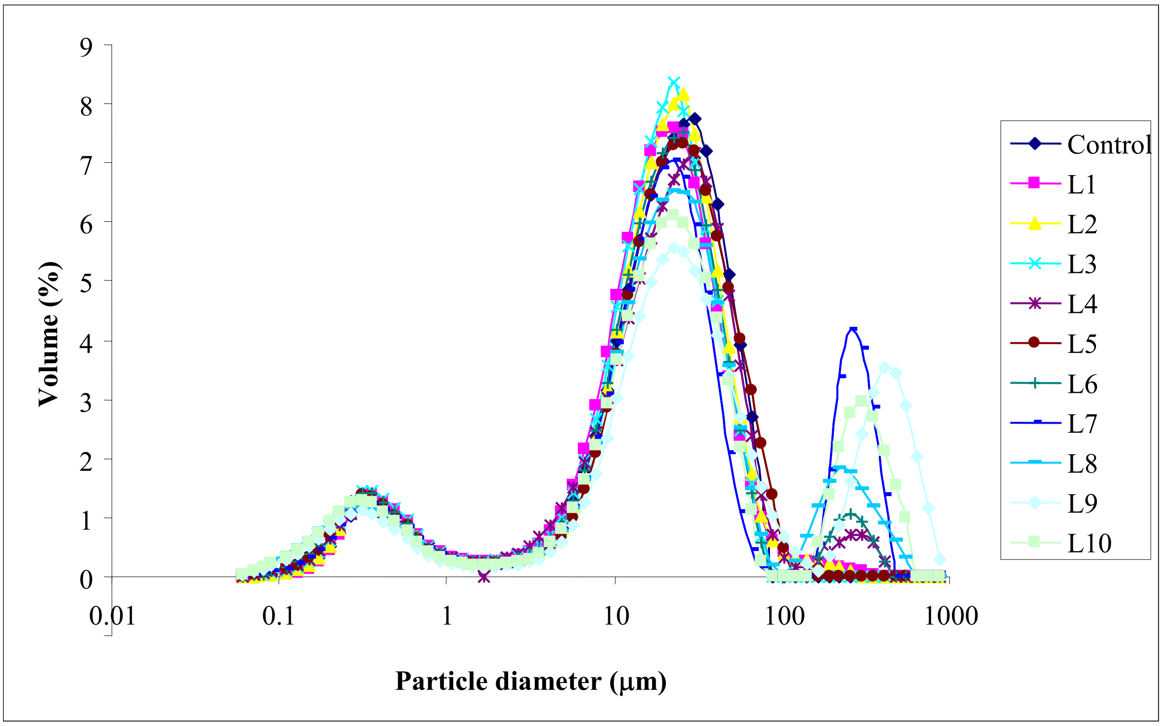

Figure 2: Particle size distribution in cement solutions for increasing CMC concentrations (Control: 0 % CMC; L1 to L10: 0.1% to 1.0% CMC)

Measurements of mechanical strength and pore size distribution have been carried out to test the properties of the mortars in the hardened state after 28 days. The polymers selected for these tests were CMC and HPC. The addition of CMC results in a loss of strength in both flexural and compressive tests, the addition of a 0.4% of the polymer being the quantity that minimises this loss. On the other hand, the addition of HPC has a minimum influence in the mechanical strength of the mortars.

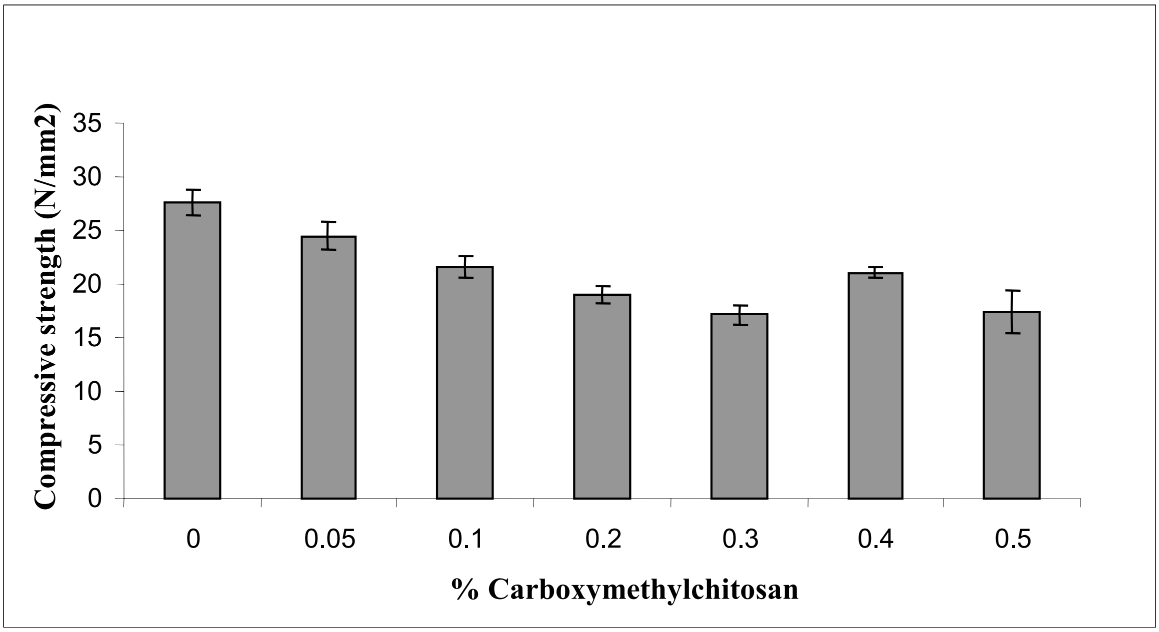

Figure 3: Compressive strength of mortars as a function of %CMC at 28 days.

CONCLUSIONS

Among the polymers assayed, carboxymethylchitosan has been found to be the most efficient rheological modifier.

A clear interaction between this polymer and cement particles has been proved by means of zeta potential and particle size measurements.

In the hardened state, the presence of 0.4% of CMC yielded the minimum loss of strength, in either flexural or compressive tests.

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