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Effect of chitosan ethers on fresh state properties of lime mortars

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Abstract. The fresh state properties of mortars are eminently important since determine the material workability and also have a great influence on its hardened state characteristics. In this paper, the behaviour of fresh lime mortars modified by etherified derivatives of chitosan (hydroxypropylchitosan (HPCH) and carboxymethylchitosan (CMCH)) is assessed with the purpose of exploring a new application of such derivatives as lime mortar admixtures. The rheological parameters (relative yield stress, consistency coefficient and fluidity index) and viscoelastic properties were correlated with flow table tests, relative density measurements, water retention abilities of mortars and air content in mortars. Results were seen to be strongly dependent on substituents of the chitosan. Non-ionic derivative (HPCH) had a plasticizing influence on the mortars; the ionic CMCH showed the thickening effect. The effect of chitosan ethers was found to be dosage-dependent. CMCH had low impact on water retention, while HPCH displayed high water retention capability. It was concluded, that the ionic derivative (CMCH) is very similar by its viscosity enhancing effect to starch ether.

1. Introduction

Organic thickening admixtures are widely used in the new types of cement-based or lime-based ready-mix render mortars. Viscosity-enhancing admixtures (VEAs) increase the viscosity, cohesion and stability of fresh mortars. Most VEAs are water-soluble biopolymers with high molecular weight. Biopolysaccharides used nowadays as VEAs include cellulose ethers, welan gum, diutan gum, guar gum, xanthan gum and starch ether [1,2].

Chitin, the raw material of chitosan, is a skeletal polysaccharide in many organisms in nature. This polymer and its derivatives have been used as biomaterials because of their biocompatibility, biodegradability, and biological activities [3]. Chitosan, poly(2-amino-2-deoxy-D-glucopyranose), is obtained by base-catalyzed deacetylation of chitin. In contrast of chitin, chitosan is soluble in water and acidic solutions, however it is insoluble in alkaline media, which limits its applications in cement and lime mixtures [4,5]. Etherification of chitosan makes the derivatives more soluble. Non-ionic hydroxyalkyl chitosans are obtained on reacting chitosan with epoxides and glycidol [6]. The introduction of ionic carboxylic groups onto the amino groups of chitosan gives rise to water soluble, amphoteric polyelectrolytes, carboxyalkyl chitosan derivatives [7]. Recent studies on the use of chitosan and chitosan ethers indicate that their addition increases the viscosity of cement-based mortars, retards the setting time and increases the number of coarse pores. Non-ionic chitosan ethers does not significantly affect the fresh state properties of mortars, but the ionic ethers show a marked effect [8,9]. The role of chitosan on the fresh state properties of lime mortars have not been investigated thus far.

There is a sufficiency of rheological studies of cement based mortars; on the other hand, the rheological characterization of lime based mortars is still very incipient [10–13]. Several rheological studies of lime mortars with VEAs were solely reported. Starch ether-based thickening admixture influences the fresh properties of lime mortars in different ways qualitatively according to the starch dosage interval. The admixture displays thickening effects at low dosage rates and dispersing effects at high dosage rates [14,15]. Izaguirre et al. performed a comparative study between cellulose ether-based and guar ether-based admixtures in lime-mortars [16]. Cellulose ether was found to be much less effective regarding water retention than guar ether. This was attributed to the adsorption of cellulose ether onto the lime particles. From hitherto studies, it seems that the effects of thickening admixtures are qualitatively different for lime-mortars and cement-mortars.

In this paper, the behaviour of fresh lime mortars modified by two different chitosan ethers (hydroxypropylchitosan and carboxymethylchitosan) is assessed with the purpose of exploring a new application of these biopolymers as lime mortar admixtures.

2. Materials

The mortars consisted of commercial-hydrated lime powder (CARMEUSE CZECH REPUBLIC, s.r.o.) of the class CL90 S according to EN 459-1, normalized siliceous sand (EN 196-1, with constant granulometry 0–4 mm) and one of chitosan ethers. The assayed chitosan derivatives were hydroxypropylchitosan (HPCH) and carboxymethylchitosan (CMCH) and they were supplied by Kraeber & Co. GmbH. Some of the molecular parameters of chitosan ethers are given in table 1; they were provided by the manufacturer. The lime/aggregate ratio selected for this study, was 1:1 by volume. In order to compare the effect of the addition of polymers to the mortar, all the samples were prepared with the same water:lime ratio, 1.15. The ethers were added in five different dosages (0.05%, 0.1%, 0.25%, 0.5%, and 1% of the lime weight) with the purpose of evaluating the influence of the additive dosage in the properties of the mortars. The mortars have been prepared following the standard mixing procedure (mixing of the dry components at low speed for 30 s, addition of the required quantity of kneading water, mixing at low speed for 30 s, scraping down the sides of the mixer bowl, mixing at low speed for 30 s).

Table 1. Properties of the chitosan ethers used, as provided by the manufacturer.

	Viscosity (1% solution in water, 20 °C) (mPa s)	Degree of substitution (%)	*pH* (-)
HPCH	16	86.8	5.8
CMCH	12	83.2	9.8

3. Experimental procedure

3.1. Water retention, air content, density and consistency

Water retention was determined by weighing absorbent materials placed on the fresh sample before and after 5 min of contact. Density was recorded using a receptacle of 1 dm^3 previously weighed, which, after being filled with fresh mortar, was weighed again. In a specific device, the entrained air was removed and replaced by a measurable amount of introduced water, which allowed determining the air content. Consistency was obtained through the flow table test, by measuring the slump. All of these characterizations of mortars were set following the standard EN 459-2.

3.2. Rheological properties

A rheological investigation included the characterization of the flow properties and viscoelastic properties of mortars. The rheological measurements were performed on the stress-controlled rheometer Discovery HR-1 from TA Instruments. In order to avoid the wall slippage the Building Material Cell and the paddle type rotor was adopted. The gap thickness was chosen to be large enough (20 mm) for the mortar suspension. All the measurements have been done at 20 °C. The results should not be reproduced quantitatively if one uses for instance another type of rheological set-up, therefore those quantities should be referred to as “apparent”.

3.2.1. Flow properties. The mortar was introduced into the measurement system at the end of the mixing cycle. At 5 min, the mortar was pre-sheared for 60 s at 100 s^{-1} in order to re-homogenize the sample and to eliminate its shear history. After a period of rest of 60 s, the rheological measurements were started. The testing routine comprised a shear rate increase (from 0.1 to 100 s^{-1}) applied through 30 steps with 15 s of measuring time at each shear rate followed by a decrease of shear rate on the same conditions. The results were expressed as shear rate vs. shear stress (flow curves) and the Herschel-Bulkley model (1) was applied to downward flow curves to fit the experimental data and used to describe mortars rheological behaviour:

$$\tau = \tau_0 + k\dot{\gamma}^n \tag{1}$$

where τ is the shear stress, $\dot{\gamma}$ is the shear rate, τ_0 corresponds to the yield stress, k is the consistency coefficient and n is the fluidity index which characterizes shear-thinning or shear-thickening behaviour of mortar.

3.2.2. Viscoelastic properties. The viscoelastic properties of lime mortars were evaluated by small amplitude oscillation tests measuring dynamic moduli, G' and G''. Experimental data can also be reported in terms of complex modulus, G^*, and loss tangent, tan (δ), defined as follows:

$$G^* = \sqrt{(G')^2 + (G'')^2} \tag{2}$$

$$\tan(\delta) = G''/G' \tag{3}$$

Storage modulus G' reflects the strength and the density of the network of connected microstructures making up the material. Loss modulus G'' represents the viscous behaviour of the material. Oscillation strain sweep tests, at 20 °C and 1 Hz frequency, were carried out to determine the linear viscoelastic region (LVR) ending at a critical strain γ_{LVR} at which the decrease of G' is observed. The rheological characterization was completed by frequency sweep tests, at 20 °C, in linear conditions (adopted critical strain values are reported in table 2) by increasing the frequency from 0.1 Hz to 10 Hz with the aim of investigating the material behaviour more in detail.

4. Results and discussion

4.1. Water retention, air content, density and consistency

Figure 1 represents the evolution of water retention versus chitosan ethers dosage rate. After a small decrease of water retention up to a dosage rate of 0.1 %, water retention increases with dosage rate. The CMCH derivative showed smaller influence on water retention than HPCH, this is out of accord with previously reported results on cement-based mortars [9], and it is conformable to water retention of starch ether [17].

In figure 1, there is also depicted a change of mortar density according to chitosan ethers dosage rate. It can be seen that CMCH almost did not affect the density of mortars. Low air content in these mortars (figure 2) could explain the small decrease in the density. The incorporation of HPCH led to an increase in the air content of the mortars. The percentages of entrained air are higher than those obtained while using other VEAs [15,18]. It might have been considered that the higher the amount of HPCH, the larger the entrained air and the higher water retention of lime mortars. The mortars with CMCH are characterizes by a significantly lower air content; this indicates that CMCH has lower surfactant activity than HPCH.

Figure 2 shows the slump results of lime mortars modified by the incorporation of the chitosan ethers. As proved by the slump reduction, both of the chitosan ethers had a thickening effect; these results are again out of accord with those reported for cement-based mortars [9]. The consistency in both cases turned out to be dosage dependent. The ionic derivative, CMCH, showed a more marked effect on the properties, acting as a thickener at high dosage of 1%. The reduction of slump is much more effective than in the case of cellulose ether or starch ether [14–16].

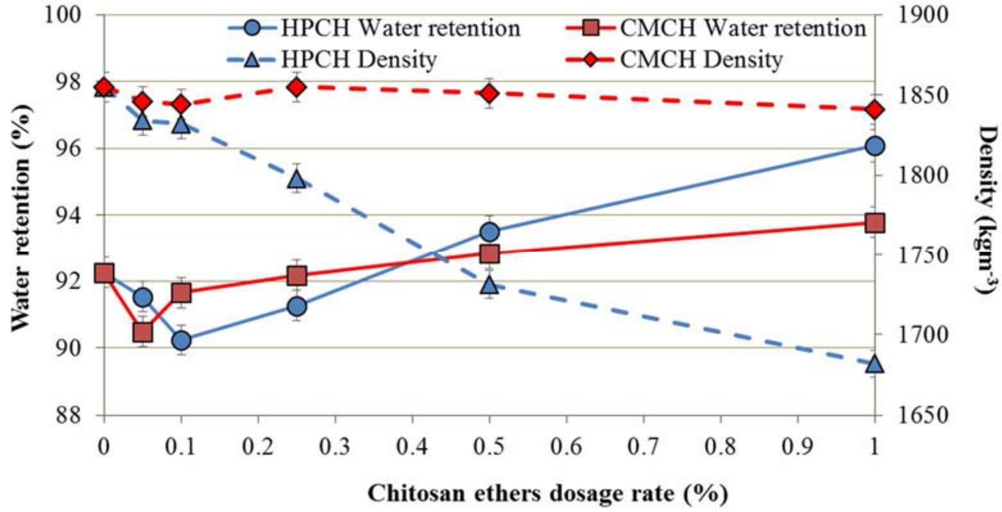

Figure 1. Water retention and mortar density versus chitosan ethers dosage rate.

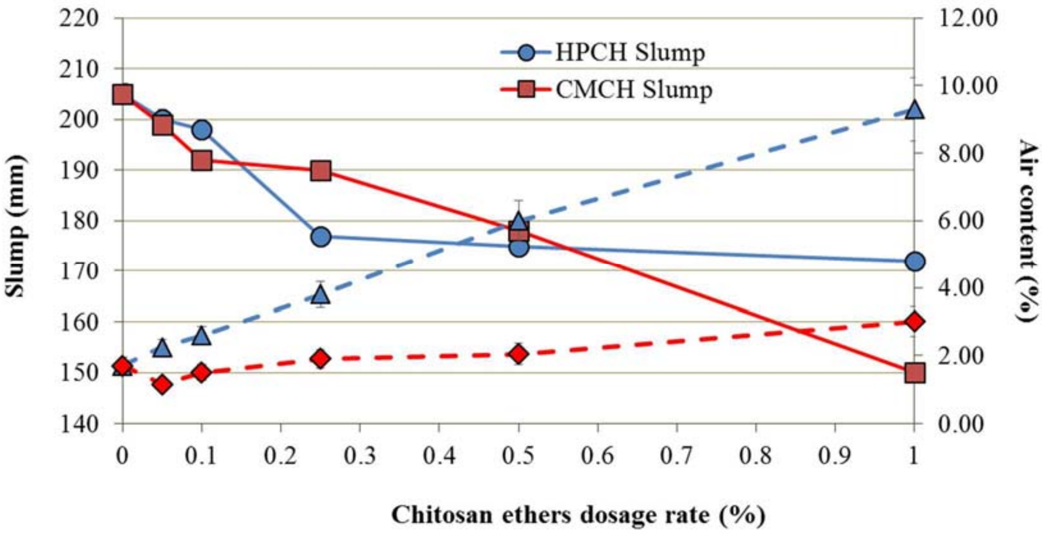

Figure 2. Effect of the addition of chitosan ethers on the slump values and air content of fresh mortars.

4.2. Rheological properties

4.2.1. Flow properties. Figure 3 illustrates the downward flow curves of lime mortars with HPCH. The mortar without any chitosan derivatives (REF) exhibits the shear-thinning behaviour. The addition of HPCH causes the shear-thickening behaviour of lime mortars. It is apparent that the yield stress of mortar decrease with increasing dosage of HPCH to 0.25%. At high dosage rates (0.5% and 1 %), a slightly higher yield stress of the mortars become evident (table 2). As reported Cappellari et al. [17], the non-monotonic behaviour of the yield stress vs. admixture content is caused by the competition between two opposing effect of biopolymers. Dispersing and lubricating effects decrease the yield stress, an associative property should increase the yield stress. In case of HPCH, the dispersive and lubricating effects become dominant. We must also take into account the effect of HPCH on air-entrainment which should contribute to the decrease of yield stress.

The flow curves of the mortars with CMCH are represented in figure 4. It can be seen that the flow curves are qualitatively different from those of HPCH mortars. All the mortars exhibit the shear-thinning behaviour. In spite of it, CMCH causes dramatically growth of the yield stress and the consistency coefficient of mortars (table 2). Generally, the mortars with CMCH are more plastic and thixotropic. This behaviour is in accordance with the behaviour of chitosan-modified cement-based mortars [2].

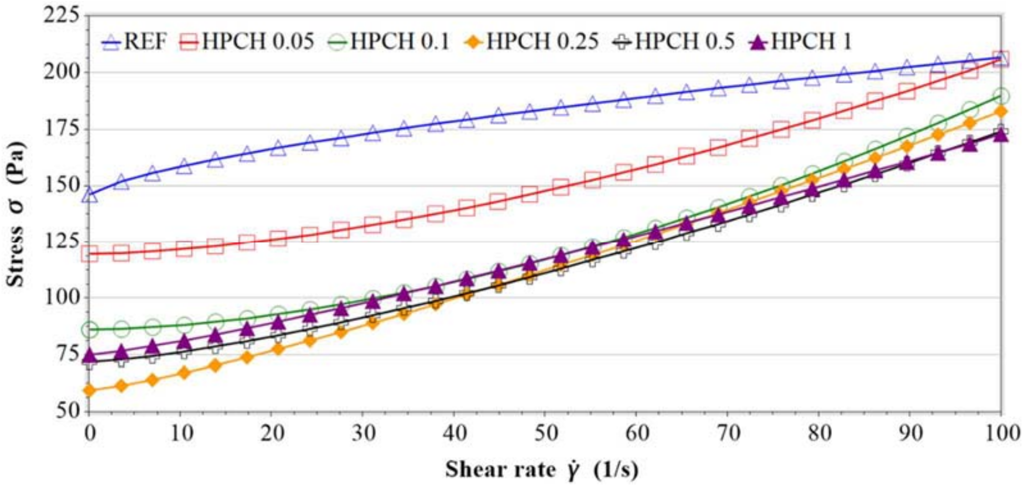

Figure 3. Downward flow curves of the mortars with HPCH.

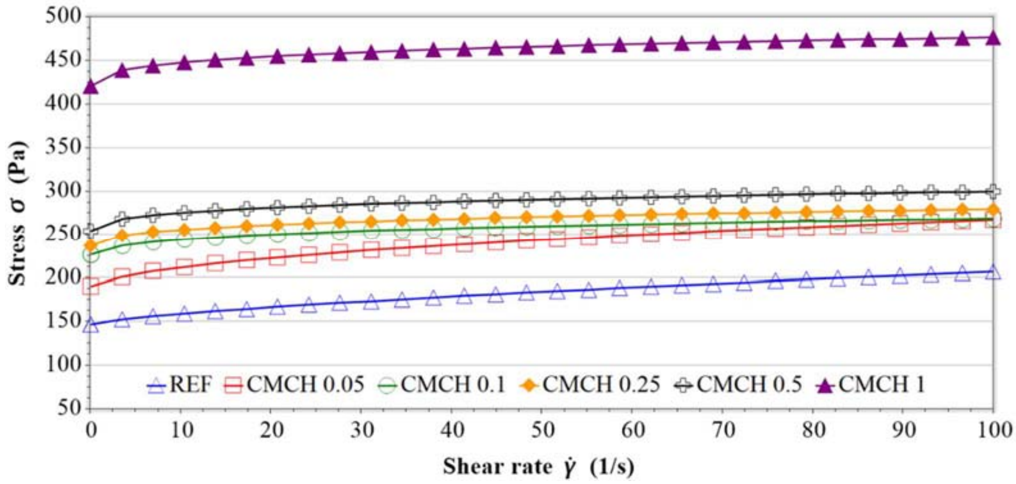

Figure 4. Downward flow curves of the mortars with CMCH.

The evolutions of yield stress (τ_0), consistency coefficient (k), fluidity index (n), complex modulus (G^*) and loss tangent (tan δ) as a function of chitosan ethers dosage rate are presented in figure 5. A certain correlation among the values of yield stress, consistency coefficient and fluidity index can be observed. The fluidity indexes of mortars with HPCH are higher than 1, which characterized these mixes as a shear-thickening, while the mortars with CMCH have fluidity indexes below 1 (shear-thinning).

Table 2. Rheological parameters of mortars with chitosan ethers.

	T_0 (Pa)	k (Pa s)	n (-)	γ_{LVR} (%)	G^* (1 Hz) (kPa)	δ (1 Hz) (°)	tan δ (1 Hz) (-)
REF	145.6	2.73	0.67	0.013	58.36	8.9	0.16
HPCH 0.05	119.6	0.05	1.62	0.007	60.68	6.4	0.11
HPCH 0.1	86.1	0.04	1.74	0.005	62.94	6.6	0.12
HPCH 0.25	59.3	0.45	1.22	0.008	51.96	8.9	0.16
HPCH 0.5	71.8	0.18	1.38	0.008	27.97	10.4	0.18
HPCH 1	74.8	0.38	1.21	0.015	25.03	11.2	0.20
CMCH 0.05	187.0	7.73	0.51	0.006	62.98	7.7	0.13
CMCH 0.1	220.6	11.59	0.31	0.006	66.12	7.5	0.13
CMCH 0.25	230.5	12.80	0.29	0.008	62.24	8.5	0.15
CMCH 0.5	244.7	16.63	0.27	0.011	60.06	8.7	0.15
CMCH 1	406.3	24.06	0.23	0.013	67.31	7.0	0.12

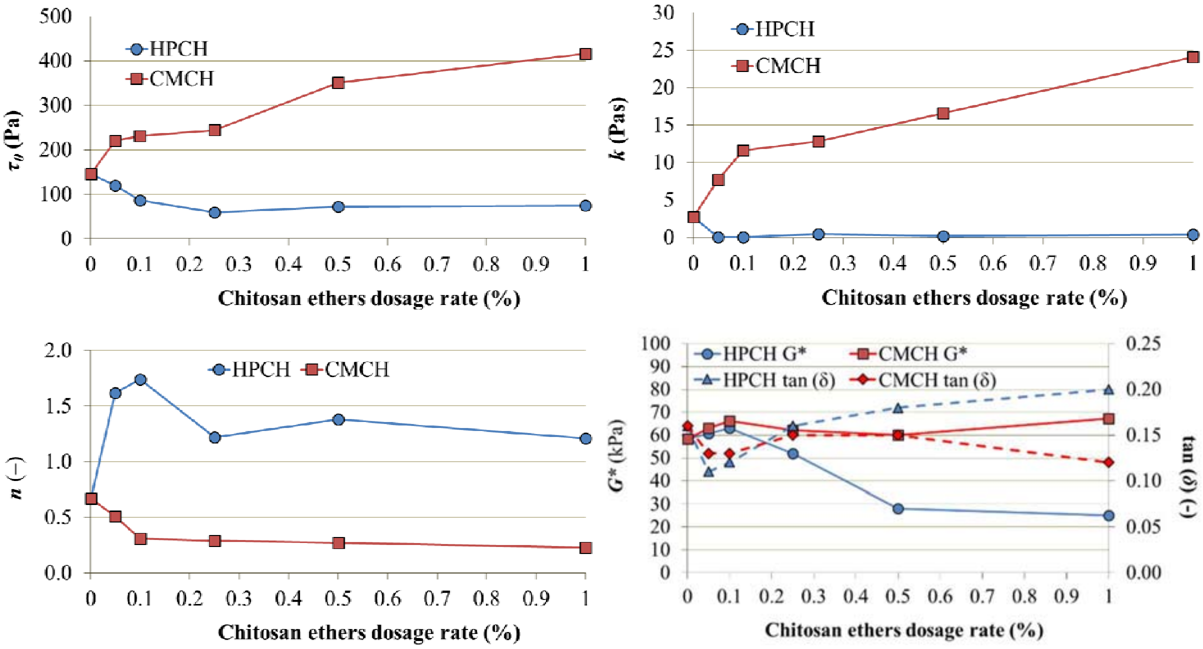

Figure 5. The evolutions of yield stress (τ_0), consistency coefficient (k), fluidity index (n), complex modulus (G^*) and loss tangent (tan δ) as a function of chitosan ethers dosage rate.

4.2.2 Viscoelastic properties. In the first step, the linear viscoelastic region (LVR) was determined for all the mortars by applying varying oscillatory strain amplitude and measuring the dynamic moduli (figures 6 and 7). The critical strains (γ_{LVR}) of the samples are registered in table 2. The sample HPCH 1 exhibits the largest linear region, but the variations are quite small. All samples exhibit G' greater than G'' in the LVR, where the structure of the system is not disturbed; this indicates that the mortars are composed of a strongly multi-connected network of microelements. Adding high dosage of HPCH (0.5% and 1 %) leads to a decrease of the storage modulus. This is quite unexpected since an associative polymer should give more connectivity to the system. This may results from dispersing and lubricating effects of HPCH, similarly to what accounts for a decrease in the yield stress. The decrease of G' may reflect the fact that the mineral particles network is significantly stronger than that of the polymer pore solution. The addition of CMCH leads to an increase of the storage modulus, indicating an increase of the material cohesion. The results for G' are consistent with those of the yield stress.

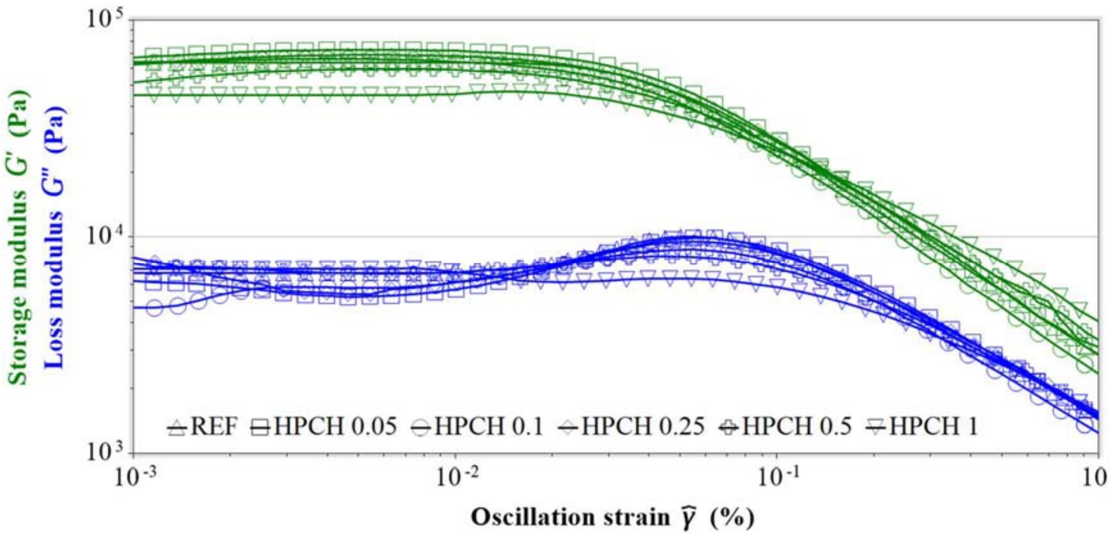

Figure 6. The evolution for G' and G'' as a function of strain amplitude for the mortars with HPCH.

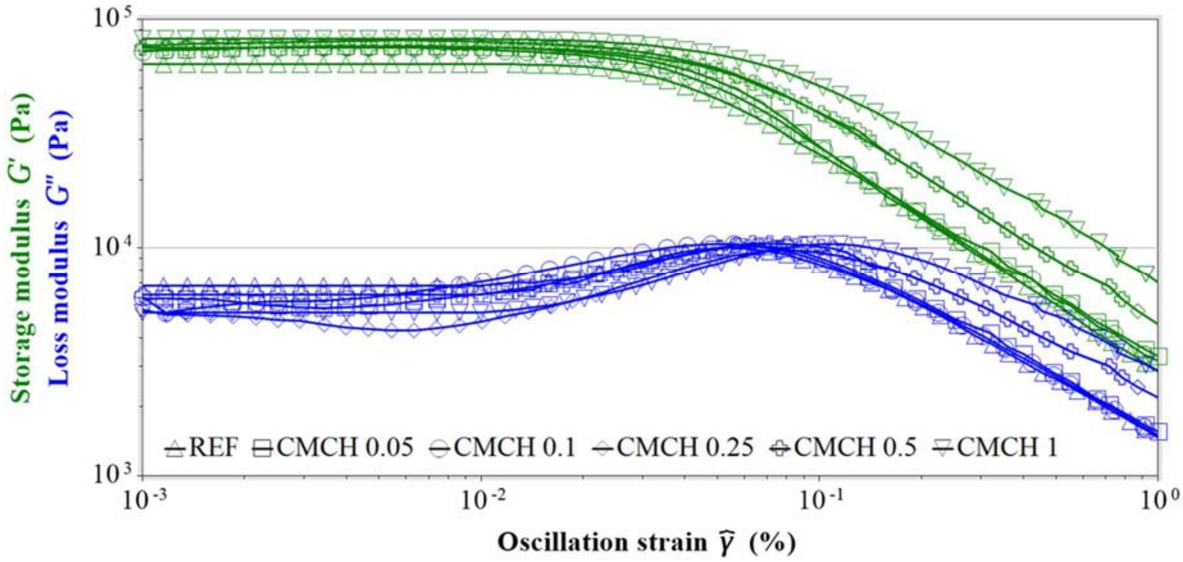

Figure 7. The evolution for G' and G'' as a function of strain amplitude for the mortars with CMCH.

Viscoelastic materials such as fresh lime-based mortars react with a temporal delay, which is expressed by a phase shift angle δ. Since $0 \leq \delta \geq 90°$, phase angles of 0° and 90° indicate purely elastic and viscous materials, respectively. The δ (1 Hz) as a function of chitosan ether dosage rate is presented in table 2. The mortars with high dosage rate of HPCH exhibit a larger liquid-like behaviour than the mortars with CMCH. If the ratio between viscosity and elasticity is considered (loss tangent), the behaviour of lime mortars with low dosage rate (to 0.25%) of the chitosan ethers is similar (figure 5); above this value, HPMC increases the loss tangent while CMCH leads to a decrease. The CMCH mortars are getting more elastic with increasing amount of CMCH.

5. Conclusions

This paper has focused on the effect of hydroxypropylchitosan (HPCH) and carboxymethylchitosan (CMCH) on the fresh state properties of lime mortars. In the first part, water retention, air content, density and consistency of the mortars were compared. In the second part, the rheological properties of mortars were studied under rotational and oscillatory shear test. The main conclusions are follow:

- The more the chitosan ethers displayed surfactant activity by increasing air content, the more it enhanced water retention.
- In steady-shear test on lime mortars, increasing the amount of added HPMCH produced a decrease of yield stress and consistency coefficient; in spite of the dilatant behaviour of the mortars. CMCH increased the yield stress and consistency; the mortars with CMCH were plastic and thixotropic.
- CMCH had larger impact on cohesion (yield stress, storage modulus) than on viscous dissipation (loss modulus) resulted in a decrease in loss tangent. This kind of admixture is expected to have low impact on water retention.
- HPCH increased the loss tangent, indicating that it increased the gel feature of the mortar. This admixture displays high water retention capability.
- It seems that the ionic derivative (CMCH) is very similar by its viscosity enhancing effect to starch ether.

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