Rheological study on influence of hydroxypropyl derivatives of guar gum, cellulose, and chitosan on the properties of natural hydraulic lime pastes

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Abstract. Viscosity enhancing admixtures are widely used to improve properties of concrete and ready-mix mortars. Guar gum derivatives and chitosan ethers are reported to have water-retaining effect, which is beneficial for the adhesion of the mixture as well as for the hydration of hydraulic particles in the binder phase of concrete or natural hydraulic lime (NHL) mortars. Influence of addition of admixtures in doses of 1, 5, and 10‰ of the binder weight has been studied on NHL based pastes with constant water:binder ratio. The measurements were carried out on the Discovery HR-1 rheometer with DIN concentric cylinders geometry. The flow properties and viscoelastic properties were studied on the specified mixtures. Pastes expressed shear-thinning behaviour with thixotropic character of flow curves. Admixture addition caused increase of yield stress, fluidity index and consistency coefficient varying on the amount and type of the admixture. Differences in the effectivity of admixtures were observed, the dosage-dependency of the admixtures varied.

1. Introduction
In the building industry the viscosity enhancing admixtures (VEAs), especially the cellulose-based ones are widely used to improve properties of ready-mix mortars and reduce the risks of bleeding and segregation in concrete [1]. Nowadays different biopolymeric admixtures such as guar gum derivatives, diutan gum, and xanthan gum have occurred [2–4]. Most of these admixtures are currently mainly used in the food industry, where they are used as stabilisers, thickeners and emulgators. The studies on their use, especially in concrete, are lately being published [1–6].

The main focus of the paper is on rheological properties of NHL-based pastes (grouts) modified by addition of hydroxypropyl- derivatives of three different biopolymers: cellulose, chitosan, and guar gum. Even though the usage of cellulose ethers is widely spread, the studies of effect of its addition on the properties of grout, or mortar based on non-cementitious binder are scarcely to be found. Water retaining admixtures are in general reported to have a thickening effect, thus increasing the yield stress of the mixture [7–16]. The exceptions of this statement occur in the literature, namely the hydroxypropylnmethyl cellulose (HPMC) is reported to decrease yield stress with growing dosage after initial increase in low dose of admixture while used in cement based [12, 14, 15] as well as lime based [8, 17] mixtures. On the contrary, the hydroxypropyl guar (HPG) derivatives act as expected from the general conclusions [15, 16], increasing the yield stress with growing dosage of admixture in cement [11–13, 15] and also lime [10, 17] mortar. There are very few studies on chitosan derivatives found, it seems, that chitosan addition acts similarly to other VEAs in cementitious environment [18],
whereas in the lime mortar, hydroxypropyl chitosan (HPCH) decreases the yield stress in low doses followed by increase with growing amount of admixture from the certain dosage [9]. All of the admixtures showed thixotropic behaviour.

2. Materials and methods

2.1. Materials and mixing procedure
The dry mixture consisted of commercial natural hydraulic lime (Otterbein Calcidur) of the NHL 3.5 class according to EN 459-1, and the admixture of dosage 1‰, 5‰, and 10‰ of binder weight. The admixtures used and their specifications are presented in table 1. Dry mixture of lime and admixture was prepared, and then the specified amount of water (water/binder ratio of 0.7:1) was added. All constituents were mixed together for one minute. Then the paste was introduced into the measuring cup.

Table 1. Properties of biopolymeric admixtures used.

| Abbrev. | Chemical composition         | Degree of substitution | Viscosity (1% solution, 20°C) [mPa s] | Manufacturer                  |
|---------|------------------------------|------------------------|--------------------------------------|-------------------------------|
| HPG H   | hydroxypropyl guar medium/high| 1654                   | Lamberti s.p.a                        |
| HPG L   | hydroxypropyl guar low       | 3668                   | Lamberti s.p.a                        |
| HPCH    | hydroxypropyl chitosan high  | 22                     | Kraeber & Co GmbH                    |
| HPMC    | hydroxypropylmethyl cellulose| 3904                   | Lotte Fine Chemicals Co. Ltd         |

2.2. Methods of rheological measurements
Rheological measurements were executed on the hybrid rheometer Discovery HR-1 from TA instruments. The DIN concentric cylinders geometry has been chosen for all the measurements. The measuring apparatus with sample was tempered to 20°C. The results should not be reproduced quantitatively.

2.2.1. Flow properties. Five minutes after the start of mixing pre-shear was performed for 60 s at 100 s\(^{-1}\) to re-homogenize the sample. After pre-shear the sample rested for another 60 s, after that the measuring procedure was carried out. The detailed description of procedure has been published lately [19]. The results have been expressed as flow curves (shear rate vs. shear stress) and the Herschel-Bulkley model was applied to downward curves to describe rheological behaviour:

\[
\tau = \tau_0 + k\dot{\gamma}^n
\]  

where \(\tau\) - shear stress, \(\dot{\gamma}\) - shear rate, \(\tau_0\) - yield stress, \(k\) - consistency coefficient and \(n\) - fluidity index which characterizes shear-thinning \((n < 1)\) or shear-thickening \((n > 1)\) behaviour of a material.

2.2.2. Viscoelastic properties. To determine viscoelastic properties of lime pastes, the small amplitude (0.005%) oscillation tests at 1 Hz frequency was carried out. Using this method the critical strain \(\gamma_c\) which determines the end of the linear viscoelastic region (LVR), where the decrease in \(G'\) is observed, and the flow point \(\gamma_F\), where \(G'=G''\) (from this point onward the sample shows the character of a liquid without a consistent chemical or physical network-of-forces [20]) were measured. The frequency sweep tests in linear conditions (strain value was set to be lower than the critical strain of any of tested samples) were conducted. The material behaviour was observed by increasing the frequency from 0.1 Hz to 10 Hz. The results were expressed as complex modulus \(G^*\) and loss tangent \(\tan(\delta)\) defined by following equations:

\[
G^* = \sqrt{(G')^2 + (G'')^2}
\]
\[ \tan(\delta) = \frac{G''}{G'} \]  

(3)

3. Results and discussion

3.1. Flow properties

Downward flow curves of pastes with different amount of HPG H are shown in figure 1. The shape of expressed curves indicates pseudoplastic (shear-thinning, \( n < 1 \)) behaviour of NHL-based pastes, which was also observed on the lime and cement-based mortars [10–13]. The presented curves were analysed using TRIOS software and Herschel-Bulkley (1) analysis to obtain values for yield stress \( (\tau_0) \), consistency coefficient \( (k) \), and fluidity index \( (n) \). The data obtained are compared using bar charts in figure 2.

![Figure 1. Downward flow curves of NHL pastes with different HPG H addition.](image)

The admixture addition caused increase of yield stress followed by further growth of its value with increasing dosage. The non-monotonic behaviour of HPG L and HPMC was reported by Cappellari et al. [15] on HPG and methylhydroxyethyl cellulose (MHEC) and is supposed to be caused by the competition between two effects of biopolymers, the dispersing and lubricating effect, which becomes dominant within high dose of HPG L and HPMC, and the associative property which predominates in the other cases. The yield stress increase was reported for most of the applications of water-retaining agents in traditional building materials [8–19], the non-monotonic behaviour seems to be typical for most cellulose derivatives in all types of environments [8, 14, 15]. The increase of consistency coefficient \( (k) \) values shown in figure 2 is desirable, because it improves the adhesive and anti-sagging properties of the grout/mortar. Growth with higher doses in most cases with exception of HPCH, the especially significant increase in the case of HPMC was expected, for the main application of this product according to the manufacturer should be for tile adhesives. These results are in accordance with the ones obtained on cementitious materials [14, 15] and contrary to the ones observed on lime mortars [8]. This is due to a different concentration of Ca(OH)\(_2\) in the binder solution, where cellulose ethers have a great ability to be adsorbed on Ca(OH)\(_2\) crystals [17, 21, 22]. The fluidity index \( (n) \) describes shear-thinning \( (n < 1) \) or shear-thickening \( (n > 1) \) behaviour of the material. Most of the studied pastes showed shear-thinning characteristics, which is typical and desirable for building materials. The value for HPG H in lowest dosage is close to 1, which means, that it’s almost Newtonian fluid. The lowering value of fluidity index with the growing dosage of admixture is common for most of the VEAs on cementitious materials [11, 13–15] while lime mortars exhibit increase of flow index with addition of VEA [8–10]. The notable increase its value within the lowest dosage was observed also by Cappellari et al. [15] on MHEC.
3.2. Viscoelastic properties

3.2.1. Amplitude sweep test. Oscillation test was carried out to determine the end of the linear viscoelastic region (LVR), which is represented as critical strain ($\gamma_c$). The critical strain is represented by the end of horizontal part of the storage modulus ($G'$) curve on figure 3.

The critical strain of the tested pastes overcome the value of reference paste in most cases, so the biopolymer addition increase the stability of the paste (the LVR is the same or longer as reference), this effect is dosage-dependent as can be seen either in figure 3 or 4, with increasing dosage of admixture grows the stability of the paste. The HPMC showed same non-monotonous behaviour as was observed within flow properties. All the pastes tested had the storage modulus values ($G'$) larger than the loss modulus ($G''$), which means that the material consists of a strongly multi-connected network of elements; this is quite typical for lime or cement based pastes but also for aqueous solutions of some of the biopolymers [9, 10, 20, 23, 24]. The flow strain $\gamma_F$ expresses how hard it is to make the sample become liquid. It is represented by the intersection of the moduli curves in figure 3, thus the point of equivalence between the moduli. In figure 4, there can be two basic dosage-dependent trends observed. HPG H and HPCH with growing dosage increase the flow strain, thus making it more difficult to make sample liquid, while HPG L and HPMC decrease the strain; taking into account the critical strain results, the addition of HPG H and HPCH widens the region in which the sample has gel-like behaviour, while HPMC and HPG L are making this region shorter. The flow strain results correlate with the degree of substitution of used admixtures (table 1).
3.2.2. Frequency sweep test. Frequency sweep test at 0.005% strain was performed to determine the viscoelastic properties of pastes. In figure 5 complex modulus, complex viscosity ($\eta^*$), and $\tan(\delta)$ of HPMC are presented depending on frequency, while in figure 6, the charts show the values of complex modulus ($G^*$) and loss factor ($\tan(\delta)$) of the tested samples measured at 1 Hz frequency. The trends of $G^*$ in the tested pastes are similar as for the flow strain, reporting the increasing resistance to deformation of the tested materials for HPG H and HPCH. The trend is opposite for HPG L and HPMC. The growing $G^*$ corresponds with the decreasing loss tangent, whereas the trends are not so clear as for the flow strain. The diminishing loss tangent reports more elastic behaviour of the material, thus greater resistance to external interference [15]. The results obtained are comparable to the ones of lime mortars in the case of HPG, but contrary to the ones of HPCH [9, 10]. Generally, results and mainly the trends, obtained on NHL 3.5 pastes, correspond more likely with the results obtained on cementitious mixtures [12, 14, 15].
Figure 5 Results of frequency sweep test for NHL paste with HPMC.

Figure 6. Complex modulus ($G^*$) and loss factor ($\tan(\delta)$) comparison of tested pastes.

4. Conclusions
The study reports the influence of derivatives of chitosan, cellulose, and guar gum containing hydroxypropyl group on rheological properties of natural hydraulic lime based pastes.

The addition of hydroxypropyl derivatives of above mentioned biopolymers led to an increase of yield stress of tested paste, the hydroxypropyl guar and hydroxypropylmethyl cellulose, which both have low degree of substitution, expressed non-monotonic behaviour while yield stress of paste with highest dosage was inferior to the one of the paste with lower dose. The admixture addition led to increase of consistency coefficient, which is closely connected with the adhesive and anti-sagging properties of the mortars. All the pastes with exception of hydroxypropyl chitosan and hydroxypropylmethyl cellulose in the lowest dose reached fluidity index $n < 1$ which implies their shear-thinning behaviour.

The influence on viscoelastic properties mostly copied the flow properties. Addition of the admixtures with exception of hydroxypropyl guar with high degree of substitution led to an extension of linear viscoelastic region thus increased the stability of tested paste. Addition
of biopolymeric admixture led to an increase of flow strain with two different dosage-dependent dependencies. Hydroxypropyl guar and hydroxypropylmethyl cellulose (admixtures with low degree of substitution) showed decreasing trend of flow strain value with growing dosage of admixture, but still reaching higher values than the nonadmixed paste. The other two admixtures, with high degree of substitution, increased the flow strain value accordingly to the growth of admixture dosage. The complex modulus expressed the same trends as the flow strain.

The behaviour of the studied natural hydraulic lime pastes was analogous to the cementitious pastes, so similar effects can be anticipated to the ones on the cementitious mixes while using these admixtures in the natural hydraulic lime materials.

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