Rheology of natural hydraulic lime pastes modified by non-traditional biopolymeric admixtures

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Abstract
Viscosity enhancing admixtures, widely used to improve characteristics of concrete and ready-mix mortars, are mainly different derivatives of cellulose. Due to the nature of cellulose processing, the environmental-friendly alternatives should be studied in order to reduce the impact of the building industry on the environment. The rheological study of natural hydraulic lime (NHL) grouts modified by four different biopolymers is carried out to investigate their behaviour in the NHL-based mortars.

The biopolymers studied are of seaweed (sodium salt of alginic acid (ALGNA) and carrageenan (CG)) and microbial (diutum gum (DG) and xanthan gum (XG)) origin. The effect of addition of these admixtures in the doses of 0.1%, 0.5%, and 1% was studied using hybrid rheometer with DIN concentric cylinders geometry. The flow properties as well as viscoelastic properties were studied. The addition of any of the admixtures led to the increase in yield stress, with DG being the most effective admixture. Desirable increase in consistency coefficient was observed within the pastes with CG and DG addition having growing dosage dependency, the ALGNA addition also increased the coefficient noticeably, but it was furtherly decreased with growing dose of admixture. The fluidity index lower than 1 expressed shear-thinning behaviour of studied pastes, except the pastes with highest dose of admixtures, and all of the XG pastes. The addition of CG and DG supported the stability of the grout expressed as the increase in critical strain, thus prolongation of linear viscoelastic region. The flow strain was increased by all of the studied admixtures promoting the gel-like behaviour of the pastes. Complex modulus and viscosity measured at 1Hz frequency were unaffected by the DG addition while they were increased notably by addition of other admixtures with ALGNA and XG supporting the resistance to deformation of the grouts studied. Correspondingly to complex modulus increase, the loss tangent is diminished, reporting more elastic behaviour of the material.

All of the admixtures studied increased the yield stress, and the influence of most of them had similar trends within other properties. Noticeable differences in efficiency and dosage-dependency were observed. The xanthan gum was overall the worst performing admixture. This was mainly due to higher sensitivity of xanthan to the concentration of bivalent ions in the solution.

Keywords: natural hydraulic lime, rheology, flow properties, viscoelastic properties, biopolymeric admixture

1. Introduction
The viscosity enhancing admixtures (VEAs) are used to modify the fresh state properties of building materials, mainly mortars and self-consolidating concrete (SCC) [1, 2]. The VEAs are often of polysaccharidic origin, currently most used are cellulose ethers, but a range of natural gums (e.g. welan gum, guar gum, gum arabic, etc.) is being studied. This study is focused on two biopolymers of microbial origin (xanthan (XG) and diutan gum (DG)), and two obtained from seaweeds (sodium salt of alginic acid (ALGNA) and carrageenan (CG)). These VEAs have been scarcely studied for the use in cementitious material, especially in SCC, and are mainly used in the food industry as gelling and thickening agents and stabilisers [2–4].

The microbial XG and DG are partially in use in building industry, where they reduce segregation and bleeding of SCC mixtures [2, 3, 5]. Xanthan gum, with slump-reducing side effect in utilization in SCC, proposes shear-thinning behaviour [6] in cementitious compositions [2, 7]. While used in the aerial lime-based [8, 9] mortars, the efficiency of XG addition was lower than the expectations based on the results from cement mixtures. This discrepancy is probably caused by a cationic sensitivity of XG, especially in the case of bivalent (e.g. Ca$$^{2+}$$) ions [10]. In the other types of materials, xanthan gum based stabilizer has been successfully used to improve the stability of fly ash-metakaolin geopolymer binary system [11]. The DG is of similar use and properties to XG with even less sensitivity to the conditions such as pH, temperature and salinity [10, 12]. DG is more efficient in the modifying of rheological properties.
of aqueous solution, thus having more dosage-dependent effect [10]. The improved stability of SCC by the DG addition is achieved by the increase in yield stress of the mixture [1]. The ALGNA, acquired from brown seaweed, has properties comparable with the commercially available super-absorbent polymers (SAP) [13]. The impure brown seaweed extract, containing 10–40% of dry weight of alginate was used by León-Martínez et al. as a VEA for SCC with interesting results, the properties of the extract are comparable with the pure sodium alginate, especially in higher concentrations, both, the sodium alginate as well as algae extract express the shear-thinning behaviour of aqueous dispersions [14]. The addition of sodium alginate to either aerial or hydraulic lime mortar leads to the increase in yield stress and promotion of shear-thickening behaviour of the pastes [8, 15]. Carrageenan (CG) is, as well as more famous gelling agent agar, obtained from red seaweed. There exists a wide range of carrageenan types with different degree of sulfatation, which influences mainly the solubility and gel strength [16]. The CG addition improves the mechanical properties of fly-ash based geopolymers, mainly by creating more condensed structure [17, 18]. The short-term strengths of lime mortars have not been notably improved in the case of hydraulic lime [19] and significantly decreased in the strengths of lime mortars have not been notably improved in the case of aerial lime [9], but with the difference diminishing with further ageing. The aerial lime pastes rheology is improved by increase in yield stress and consistency coefficient, and also by prolongation of period of gel-like behaviour observed by study of viscoelastic properties.

The presented paper studies the influence of the above-mentioned biopolymers on the flow and viscoelastic properties of natural hydraulic lime (NHL) based grouts focusing on the dosage-dependency of the biopolymer addition.

2. Materials and methods

2.1 Materials and sample preparation

All the grouts studied were prepared by dry mixing of natural hydraulic lime of NHL 3.5 class according to EN 459-1 (Zement- und Kalkwerke Otterbein GmbH & Co. KG, Germany) and biopolymeric admixture (summary of admixtures used, and their characteristics are stated in Table 1) in the dosage of 0.1%, 0.5%, and 1% of the binder weight. Water was then added using constant water:binder ratio of 0.7 and the paste was prepared by mixing for one minute. The grout was then introduced into measuring cup of Discovery HR-1 hybrid rheometer by TA instruments using DIN concentric cylinders measuring geometry tempered to 20°C. The measurement was started by a 60 s preshear at 100 s⁻¹, which begun 5 minutes after water introduction into the dry mixture, followed by 60 s resting time. The curves were analysed using TRIOS 4.0.2.30774 software.

2.2 Methods of measurement

The measuring procedure has been described in detail in previous publication [8], thus only the basic description follows.

### Table 1

| Abbrev. | Chemical composition | Commercial name | Viscosity (1% aq. solution, 20°C) [mPa s] | Manufacturer |
|---------|----------------------|-----------------|---------------------------------------|--------------|
| ALGNA   | sodium alginate      | –               | 14.5                                  | Sigma-Aldrich, Co. |
| CG      | carrageenan          | Genuvisco CG–131| 72.1                                  | CP Kelco     |
| DG      | diutan gum           | Kelco-Crete DG–F| 13 363.8                              | CP Kelco     |
| XG      | xanthan gum          | Kelzan AP–AS    | 7 633.3                               | CP Kelco     |

2.2.1 Flow properties

The results obtained by procedure described in [8] were expressed graphically as flow curves (shear rate vs shear stress) and the downward curves were analysed using Herschel-Bulkley model (Eq. 1) to obtain the variables describing behaviour of the samples.

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

(1)

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 the length of linear viscoelastic region (LVR), characterized by the critical strain \( \gamma_c \), and flow point \( \gamma_f \), described as the equilibrium between loss \((G'')\) and storage \((G')\) modulus, the small amplitude oscillation test at 1 Hz frequency was carried out. The strain value from the LVR of all samples was chosen to execute the frequency sweep test (0.1 Hz – 10 Hz) in linear conditions. The results were expressed as complex modulus \(G*\) and loss tangent \(\tan(\delta)\) as defined by equations 2 and 3 respectively.

\[ G* = \sqrt{(G'\gamma_c)^2 + (G''\gamma_c)^2} \]

(2)

\[ \tan(\delta) = G''/G' \]

(3)

3. Results and discussion

3.1 Flow properties

The measurement data were expressed as shear rate vs shear stress diagram. For the illustrational purposes, the downward curves of pastes with ALGNA addition are shown in Fig. 1. The transition from pseudoplastic (shear-thinning, \( n < 1 \)) to dilatant (shear-thickening, \( n > 1 \)) behaviour is observed as a change of shape of curves from convex (REF, ALGNA 0.1% and 0.5%) to concave (ALGNA 1%). The values of yield stress \( (\tau_f) \), consistency coefficient \( (k) \), and fluidity index \( (n) \) for all the pastes are compared in Fig. 2. The admixture addition increases the yield stress of pastes with further growth with increasing dosage, which is typical for the VEAs in traditional building materials [8, 9, 20–22]. The non-monotonicity of CG and XG addition was observed and described by Cappellari et al. [20] on the cementitious mortars modified by hydroxypropyl...
guaran (HPG) and methylhydroxyethyl cellulose, and it is also reported on the NHL pastes modified by HPG with low degree of substitution and hydroxypropyl methyl cellulose [9]. The non-monotonicity is supposed to be caused by the competition between the lubricating and dispersing effect of the admixtures [20]. The most effective admixtures in the lowest dose are CG and XG, while DG is the most efficient admixture in higher doses. The increase in consistency coefficient (k) is connected with improvement of adhesive and anti-sagging properties of grouts. The reversed dosage-dependency of ALGNA is contrary to the aerial lime results [8], and also the inefficiency of XG is much clearer. The extreme drop of k value for CG and DG in highest dosage is probably caused by the high thickness of the tested samples. Lower doses of ALGNA and CG, as well as DG, may be potentially beneficial for the use to modify e.g. tile adhesives. The value of fluidity index, as stated earlier, describes whether the mixture's behaviour is shear-thinning or shear-thickening. The shear-thinning behaviour is more common and mostly desired in the case of building materials [8, 9, 15]. The transition from shear-thinning to shear-thickening behaviour is due to water-retentive function of biopolymers [9] that causes a decrease in liquid phase content in the grout, which is basically a suspension of NHL particles in water/water-biopolymer environment, thus the paste draws to the state of "thick suspensions of particles in a liquid", which is the typical example of dilant fluid [23]. The alginate and DG addition in lower dosage promotes the shear-thinning behaviour of the paste, while high doses of biopolymers and XG in general promote dilatancy of the pastes. A. Azzizi and P. F. G. Banfill [15] observed an opposite trend with the ALGNA addition but using much lower concentrations. Based on the comparison of the two results, it can be assumed that somewhere between the dosage of 0.035% (the highest dose in [15]) and 0.5% of binder weight lies a dose of alginate, at which the thixotropy of the NHL based paste is the most promoted. The studied biopolymers behave differently in comparison to hydroxypropyl derivatives of guar gum, chitosan or cellulose [24] (the same experimental setup on the same measuring device).
3.2 Viscoelastic properties

3.2.1 Amplitude sweep test

The critical strain $\gamma_c$ determines the length of LVR, thus also the stability of the paste (the longer the LVR, the more stable the paste). The moduli curves in the modulus/oscillation strain system for ALGNA, alongside with the examples of the critical and flow strain values ($\gamma_c$ and $\gamma_f$ respectively) are shown in Fig. 3, while in Fig. 4, the strain values for all mixtures are compared. The addition of CG and DG in lowest dose do not affect the value of critical strain, which is furtherly increased with growing dosage of admixture, whereas the CG is more efficient in the dosage of 1%. This behaviour is similar to the one of hydroxypropyl derivatives of guaran, chitosan and cellulose [24], out of which cellulose ether are currently one of the most common VEAs used. The ALGNA decreases the value of $\gamma_c$ thus the ALGNA-modified pastes behave differently than cementitious pastes modified by marine brown algae extract in which the alginates are present [14]. The XG slightly decreases grouts stability in low dosage and improves it with growing dosage, which is in correspondence with the behaviour of XG aqueous solution in different concentrations [6].

The second parameter studied, the flow strain $\gamma_f$, marks the point of transition from solid viscoelastic behaviour ($G’ > G’’$) to liquid behaviour ($G’ < G’’$). The addition of admixtures markedly increases the flow strain value as seen in Fig. 4. In the case of CG and DG, the highest increase is within the lowest dosage (0.1%) and with growing dosage, the flow strain value decreases. This trend is similar to hydroxypropylmethyl cellulose (HPMC) and hydroxypropyl guaran (HPG) [24] on the same instrumental setup but CG and DG seem to be more efficient. In the case of DG 0.1% the moduli did not intersect in the studied strain range, thus the paste retains viscoelastic properties. The growth of $\gamma_f$ for ALGNA up until dosage of 0.5% is in accordance with results of León-Martínez et al [14], where the increase in flow stress was observed. The XG is in efficiency of affecting the $\gamma_f$ inferior to the three other admixtures with unclear dosage-dependency.

3.2.2 Flow sweep test

The test was carried out at 0.005% strain, which ensures that all the pastes are in the LVR. The data obtained were visualised using charts similar to Fig. 5 and the values of complex shear modulus ($G^*$), and loss tangent (tan $\delta$) at 1 Hz frequency were recorded for comparison and are presented in Fig. 6. The growth of resistance to deformation of the samples represented by increasing value of $G^*$ in combination with decrease in loss tangent corresponds with the results of amplitude sweep tests. The values of tan $\delta$ indicate prevailing elastic behaviour of samples with storage modulus being 4-10 times higher than loss modulus. The extremely low tan $\delta$ value of DG 0.1 % may be interpreted as behaviour of ideally elastic material. The decrease in loss tangent with addition of VEA has been observed also with HPG and chitosan derivatives in lime mortars [25, 26], and hydroxypropyl derivatives of several biopolymers in NHL pastes [24]. On the other hand, HPG and HPMC in cementitious paste did not cause a decrease and starch ether in initial dose caused increase in loss tangent [20]. The gradual increase in tan $\delta$ with growing dosage, observed especially in the case of CG and DG where the trend
corresponds with the growth of flow strain, is also described in aforementioned literature within different admixtures in several binder systems. The studied biopolymers, previously used in aerial-lime pastes [8], exhibited opposite trends in both binder systems, with exception of XG, where the trends are unclear in both cases.

4. Conclusion

The study informs about influence of addition of biopolymeric admixtures on the rheological properties of natural hydraulic lime pastes.

The addition of biopolymers increased the yield stress of the pastes with growing dosage dependency. The sodium salt of alginate acid, carrageenan and diutan gum increased the consistency coefficient, which is connected with adhesive and anti-sagging properties of mixture, but alginate had dosage-dependency trend opposite to the other two admixtures. Addition of these three biopolymers in the dosage of 1% lead to transition of the behaviour of the pastes from pseudoplastic to dilatant, while xanthan gum modified paste showed shear thickening characteristics even in the lowest dose of 0.1%. The study on viscoelastic properties of the modified pastes showed improvement of stability of the grouts modified by carrageenan and diutan gum by prolonging the linear viscoelastic region. The promotion of gel-like behaviour has been observed for all biopolymers but xanthan gum was inferior in efficiency to the other three admixtures. The beneficial effect of the admixtures on the stability of the grouts was also observed by flow sweep tests. The values of complex strain modulus and especially loss tangent support the conclusions.

The use of xanthan gum in natural hydraulic lime pastes is limited due to low efficiency and unclear trends within some of the studied properties. The diutan gum and carrageenan were the admixtures which showed the greatest similarity in behaviour with the hydroxyethylpropyl cellulose, one of the most spread viscosity enhancing admixture in commercial use.

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References

[1] Van Der Vurst, F. – Grünewald, S. – Feys, D. – Lesage, K. – Vandewalle, L. – Vantomme, J. – De Shutter, G. (2017): Effect of mix design on the robustness of fresh self-compacting concrete. Cem Concr Compos 82. http://dx.doi.org/10.1016/j.cemconcomp.2017.06.005
[2] Plank, J., (2004) Application of biopolymers and other biotechnological products in building materials. Appl Microbiol Biotechnol 66. http://dx.doi.org/ 10.1007/s00253-004-1714-3
[3] Singh, N. K. – Mishra, P.C. – Singh, V.K. – Narang, K.K. (2003) Effects of hydroxyethyl cellulose and oxalic acid on the properties of cement. Cem Concr Res. 33. http://dx.doi.org/10.1016/S0008-8846(03)00060-7
[4] Rinaudo, M. (2008) Main properties and current applications of some polysaccharides as biomaterials. Polym Int 57. http://dx.doi.org/10.1002/pi.2378
[5] Isik, I.E. – Ozkul, M.H. (2014) Utilization of polysaccharides as viscosity modifying agent in self-compacting concrete. Constr Build Mater 72, http://dx.doi.org/10.1016/j.conbuildmat.2014.09.017
[6] Martín-Alfonso, J.E. – Cuadri, A.A. – Berta, M. – Stading, M. (2018) Relation between concentration and shear-extensional rheology of xanthan and guar gum solutions. Carbohydr Polym 181. http://dx.doi.org/10.1016/j.carbpol.2017.10.057
[7] Vazquez, A. – Pique, T.M. (2016), Biopolymers and Biotech Admixtures for Eco-Efficient Construction Materials, Woodhead Publishing, Duxford.
[8] Žižlavský, T. – Vyšvařil, M. – Rovnaníková, P. (2018) Rheological characteristics of aerial lime-based pastes with biopolymers. IOP Conf Ser Mater Sci Eng 385 http://dx.doi.org/10.1088/1757-899X/385/1/012067
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