

Rheological characteristics of aerial lime-based pastes with addition of biopolymers

T Zizlavsky, M Vysvaril and P Rovnanikova

Faculty of Civil Engineering, Brno University of Technology, Veveri 331/95, Brno 602 00, Czech Republic

Abstract. Viscosity enhancing admixtures are widely used to improve the properties of concrete and ready-mix mortars. This study focuses on the influence of biopolymer (sodium salt of alginic acid, carrageenan, diutan gum, gellan gum, and xanthan gum) in doses of 1, 5, and 10 ‰ on the rheological properties of aerial lime-based pastes. The measurements were carried out on the Discover HR-1 hybrid rheometer with DIN concentric cylinders geometry. On the pastes the flow properties as yield stress, fluidity index and consistency coefficient as well as the viscoelastic properties (complex modulus, loss tangent, critical and flow strain) were studied. All pastes studied expressed shear-thinning behaviour and the flow curves indicated rheopectic character of samples. The significant differences in effectivity of admixtures used were observed. Xanthan and gellan gums were found less effective than the three others in influencing the rheology of aerial lime-based paste while diutan gum was so effective, that the future research with lower doses of the admixture are recommended to better explain its impact on the rheological properties.

1. Introduction

The viscosity enhancing admixtures (VEAs) are widely used in building industry to reduce bleeding and segregation in concrete [1] and to improve properties of ready-mix mortars. The most frequently used ones are the cellulose derivatives-based admixtures. Recently other biopolymer-based admixtures such as guar gum derivatives, diutan gum, and xanthan gum have occurred [2-4]. Most of these admixtures originate from 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 paper deals with the impact of addition of five less-known biopolymers on the rheological properties of aerial lime-based mortars. The sodium salt of alginic acid (ALGNA), a seaweed biopolymer that in cementitious materials surpassed commercial superabsorbent polymers (SAP) and met nominative strength requirements even though higher water demand [5, 6]. Carrageenan (CG) is the second seaweed biopolymer used in these experiments. CG used in fly ash geopolymers considerably increased strengths, and allowed the creation of a more condensed structure [7]. In cement-based materials the use of carrageenan was only reported as the foam-stabiliser for preparation of a high porosity cementitious foam, where the CG addition did not affect the hydration of cement binder [8]. CG is reported to create more densely formed gels in CaCl_2 solution in comparison with gels prepared solely in water, thus we can assume that $\text{Ca}(\text{OH})_2$ solution in the case of lime pastes could have similar effect [9]. The other three admixtures used are of microbial origin. Xanthan gum (XG) is used in SCC as VEA to reduce bleeding and segregation with slump-reduction side effect, thus the XG behaviour should be thinning-thickening [2-4, 10, 11]. The use of gellan gum (GeG) in building industry is mainly studied as a soil-stabilising agent. The application of GeG with cement or



other building binders is reported only as a base for a hydrogel slurry used to create cementitious porous materials [12]. Diathan gum (DG) has the same backbone as GeG but different substituents on the side chain, thus different properties. DG is used in SCC in similar applications as XG. DG is independent on temperature and concentration of ions, making it more suitable for use in building materials due to the higher concentration of Ca^{2+} cations. DG stabilises SCC by increasing the yield stress of the mixture [1, 2-4, 13].

This work studies the behaviour of the above-mentioned biopolymers in various doses in the lime-paste environment.

2. Materials and methods

2.1. Materials and mixing procedure

The dry mixture consisted of commercial dry hydrated lime (Carmeuse Czech Republic) of the CL 90 S class according to EN 459-1, and the admixture of dosage 1‰, 5‰, and 10‰ of binder weight. The admixtures used were: sodium salt of alginic acid (Sigma-Aldrich, Co.), diutan gum (Kelco-crete DG-F, BASF Construction Solutions GmbH), xanthan gum (Kelzan AP-AS), carrageenan (Genuvisco CG-131), and gellan gum (Kelcogel CG-LA) three last named biopolymers supplied by Biesterfeld Silcom s.r.o. but all with the exception of alginate being products of CP Kelco. The lime and admixture were mixed together with the specified amount of water (water/binder ratio of 1:1) for one minute. Then the paste was introduced into the measuring cup.

2.2. Methods of rheological measurements

Rheological measurements were carried out on the hybrid rheometer Discovery HR-1 from TA instruments. The DIN concentric cylinders geometry has been chosen with the gap of 5.917 mm for all the measurements. The testing was executed at 20 °C. The results should not be reproduced quantitatively.

2.2.1. Flow properties. After 1 minute of mixing the paste was introduced into the measurement system. 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 following measuring procedure was carried out. Shear rate increase from 0.1 to 100 s^{-1} was applied through 30 steps consisting of 5 s of equilibration and 10 s of averaging. After reaching the highest shear rate similar procedure was performed with decreasing shear rate within the same values. 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:

$$\tau = \tau_0 + k\dot{\gamma}^n \quad (1)$$

where τ - shear stress, $\dot{\gamma}$ - shear rate, τ_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.

2.2.1. Viscoelastic properties. To determine viscoelastic properties of lime pastes, the small amplitude (0.005%) oscillation tests at 1 Hz frequency, measuring the storage modulus G' and G'' were carried out. Using this method the critical strain γ_C which determines the end of the linear viscoelastic region, where the decrease in G' is observed, and the flow point γ_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 [14]) 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:

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

$$\tan(\delta) = G''/G' \quad (3)$$

3. Results and discussion

3.1. Flow properties

The flow curves of lime paste with different amount of XG added were chosen for the illustrational purposes (figure 1). The shape of expressed curves indicates rheopectic (time-dependent thickening) character and shear-thinning (pseudoplastic) behaviour of aerial lime-based pastes, which was also observed on the lime-based mortar [15, 16]. Because of large amount of data, the simple comparison using bar charts (figures 2 to 4) was chosen. The DG 10 lime paste prepared with selected water-binder ratio was so dense that it was not possible to introduce it properly to the measuring instrument, thus none of the measurements was carried out on this mixture.

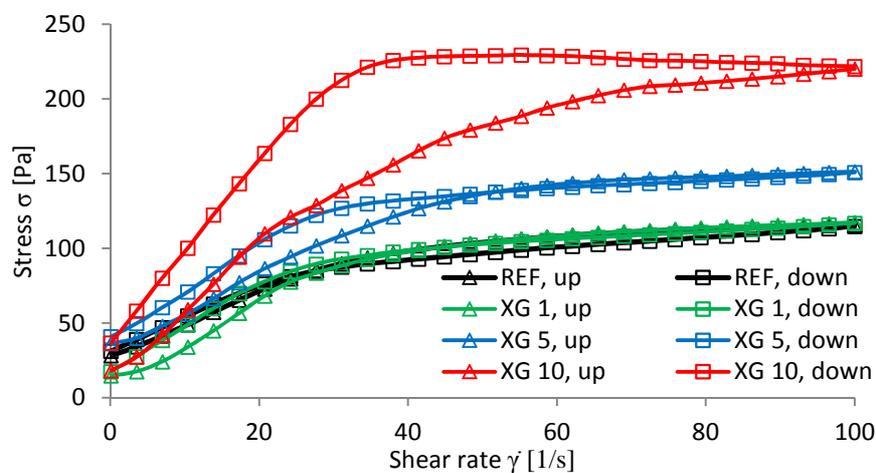


Figure 1. Flow curves of lime pastes with different XG addition.

The addition of biopolymers caused the decrease in yield stress in most cases, but with exception of GeG, the increasing dose of admixture caused the growth of yield stress. This, as reported by Cappellari et al. [17], is caused by the competition between two effects of biopolymers, the dispersing and lubricating effect, which is in this case dominant within low dose of admixture, and the associative property which prevails within the high doses of ALGNA, CG, and DG. The yield stress increase was reported also for carboxymethyl chitosan (CMCH) added to both lime and cement, and guar gum derivatives, hydroxypropyl guar (HPG) and carboxymethylhydroxypropyl guar (CMHPG) [15, 16, 18]. Worse results of XG are probably caused by high concentration of Ca^{2+} ions which is reported to notably influence the XG performance [13]. The consistency coefficient (k) values are also shown in figure 2. The higher doses of ALGNA, CG, and DG reached really high values. Most of the pastes came up to higher values than the reference one. The increase in consistency coefficient is desirable, because it improves the adhesive effect of the paste. The fluidity index (n), which describes shear-thinning ($n < 1$) or shear-thickening ($n > 1$) behaviour of the pastes reached not higher than 0.57 in the case of ALGNA 10, thus we can say that all of the tested pastes expressed the shear-thinning behaviour, and the shape of all the curves is similar to the ones presented in figure 1.

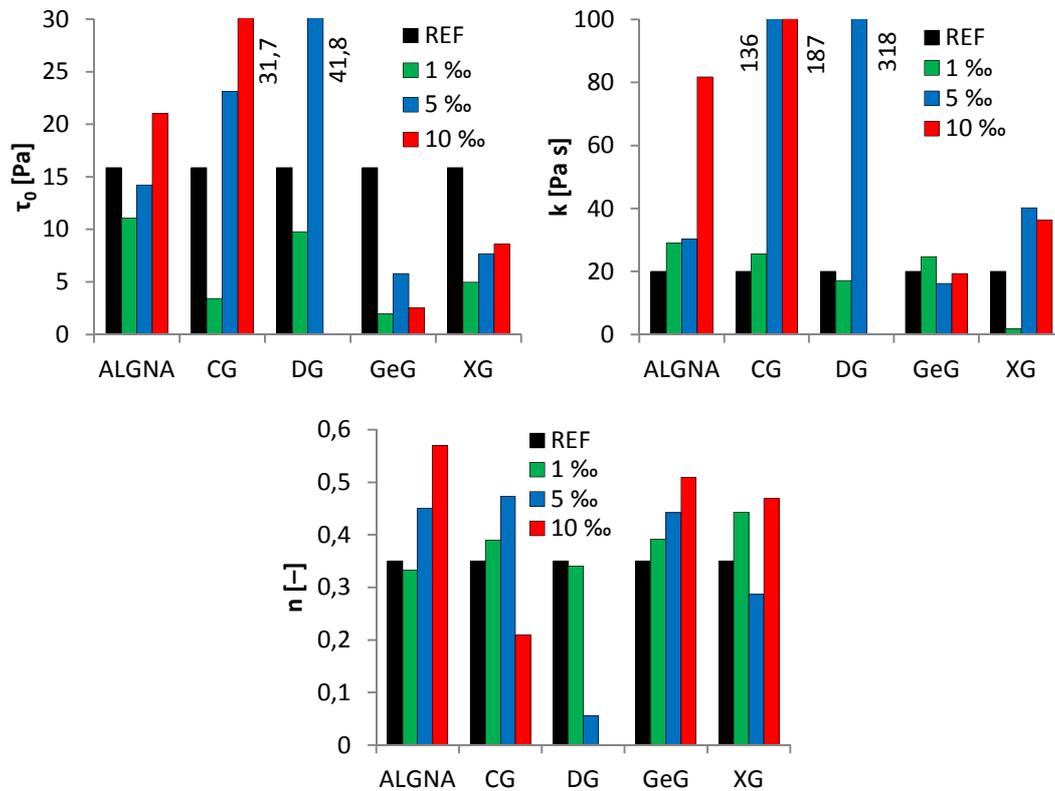


Figure 2. Comparison of yield stress (τ_0), consistency coefficient (k), and fluidity index (n) of lime pastes with biopolymer admixtures.

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 (γ_c). From this point onwards the sample until now behaving as a solid starts to act as a gel. The tests carried out in the linear conditions are non-destructive to the microstructure of the material. The critical strain of the tested pastes does not overcome the value of reference paste (CG 5 and 10, and DG 5 reached similar value), so the biopolymer addition does not increase the stability of the lime paste (the LVR is the same or shorter as reference). Higher dosage of ALGNA or XG furtherly shortened the LVR whereas CG and DG with increasing dose improved stability in comparison with lower doses. All the samples 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 [14-16, 18, 19]. The flow strain γ_f tells us how hard it is to make the sample become liquid. With increasing dosage of CG and DG, the value of flow strain increases significantly; in the case of DG 5 the curves of the dynamic moduli did not intersect in the studied range of oscillation strain, thus being probably much higher than the value of CG 10. Uncertain dosage dependence was observed in the case of ALGNA and XG, where in the first case the 5% addition caused the lowest flow point of the doses studied, and in the case of CG the value was the highest. The addition of CG decreases the flow point value.

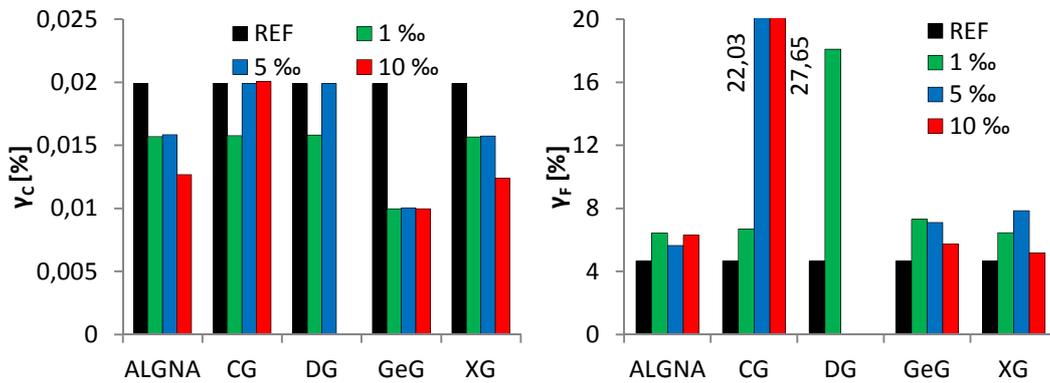


Figure 3. Comparison of critical strain (γ_c) and flow strain (γ_F) values of tested samples.

3.2.2. *Frequency sweep test.* Frequency sweep test at 0.005% strain was performed to determine the viscoelastic properties of pastes. In figure 4, the charts show the values of complex modulus (G^*) and loss factor ($\tan(\delta)$) of the tested samples measured at 1 Hz frequency. The uprising trend of G^* in all tested pastes reports the increasing resistance to deformation of the tested materials. The growing G^* corresponds to the decreasing loss tangent, where the diminishing loss tangent reports more elastic behaviour of the material, thus greater resistance to external interference. The dropping loss tangent value with the growing admixture dosage was also reported for CM derivatives of guar gum and chitosan added to lime mortar as well as starch ether added to the cementitious mortar [15, 16, 18-20]. On the other hand cellulose ethers, the most common VEAs, cause the increase in loss tangent value thus loss of elasticity of materials [17].

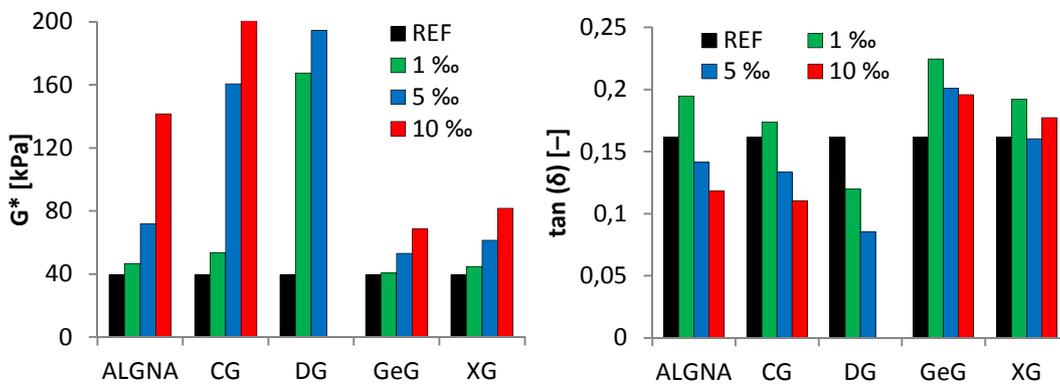


Figure 4. Complex modulus (G^*) and loss factor ($\tan(\delta)$) comparison of tested lime pastes.

4. Conclusions

The paper studies the influence of the addition of biopolymers, which are non-traditional in building industry in various doses on the rheological characteristics of aerial lime-based pastes. All the biopolymers tested fostered the rheopectic character and shear-thinning behaviour of aerial lime-based paste. The addition of xanthan gum and gellan gum was found to be far less effective than the addition of other three biopolymers. The yield stress decrease at low dosage was observed followed by improvement with increasing dosage. Only the most effective admixtures (CG and DG in higher doses) did not shorten the linear viscoelastic region, thus they did not reduce the stability of lime paste. The two aforementioned admixtures also significantly increased the value of flow strain making the specimen more difficult to become a liquid.

The increasing complex modulus with rising dose of any admixture reports the growing resistance to deformation, which is caused by developing elasticity of the materials represented by decreasing

loss tangent. The xanthan and gellan gums were far less effective in the improvement of complex modulus mainly due to the increase in loss tangent.

The xanthan and gellan gums were found not very effective in influencing the properties of lime pastes in current doses. The sodium salt of alginic acid was found well useful if a small decrease in paste stability would be taken into account. Carrageenan and diutan gum were really effective in influencing lime pastes rheological characteristics but for better understanding, the future research on the addition of lower doses with finer differences between them should be conducted at least for these two admixtures.

Acknowledgements

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