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Effect of geopolymer composition on the mechanical and rheological properties

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Abstract. Coating systems, not only in the building industry, have historically their irreplaceable role. Modern times, however, take on increasing responsibility for both the environment, the versatility of product use, and the reduction of production costs. The development of the new multifunctional geopolymer coating, therefore, clearly covers all of these global aspects. In this paper, the mechanical and rheological properties of various geopolymer pastes were investigated. The geopolymer mixtures were composed of metakaolin and various dosage of water glass solution with three different $\text{SiO}_2/\text{Na}_2\text{O}$ ratios. The best mechanical properties were achieved for the mixture with content 90% of water glass and $\text{SiO}_2/\text{Na}_2\text{O}$ ratio of 1.4. The rheological measurements showed high thixotropy of all mixtures and very low yield stress values.

1. Introduction

Protective coatings play an irreplaceable role in protection of a very wide range of construction and building materials. They provide the substrates with the required properties and protect them in particular against their degradation due to weather and operating influences. The role of them is growing as the range of protected substrates (especially steel, zinc and aluminium alloys, wood, concrete, masonry and mineral materials) is constantly expanding. A new option for the protect of these substrates can be materials with higher utility properties than conventional protective coatings, namely geopolymers [1]. In addition to environmental, durability and applicability advantages over conventional coating systems, geopolymers also exhibit high temperature resistance of up to 800 degrees Celsius [2] and are thus destined to be used on structures to be protected against high temperatures.

Geopolymers are materials composed predominantly of amorphous substances with minimal occurrence of crystalline phase. At higher temperatures, the amorphous structure is microcrystalline [3]. For the production of geopolymers, aluminosilicate materials such as metakaolin, blast furnace slag or fly ash are commonly used and these are activated with a suitable alkaline activator. The most commonly used reagent to start the geopolymerization reaction is water glass. Water glass is a colloidal solution of alkaline silicates produced by dissolving alkaline silica glass (mostly sodium) in water. Soluble silicates are essentially a combination of alkali metal oxide of Na_2O , SiO_2 and water. The base formula is $x\text{SiO}_2 \cdot \text{Na}_2\text{O} \cdot z\text{H}_2\text{O}$, where x is the degree of polymerization and z is the number of water molecules. Sodium silicate is defined by the molar ratio of $\text{SiO}_2/\text{Na}_2\text{O}$, also referred to as the silicate modulus (M_s) [4].

The pH of the alkali silicate solution is dependent on the $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio, but also on the concentration of alkalis. The pH of the solution is between 10.9 and 13.5; value is a very important characteristic determining the stability of high modulus silicate solutions, i.e. their tendency to gelation



or coagulation. The stability of alkaline silicate solutions increases with increasing pH [4].

The optimum silicate modulus is variable depending on the raw material and aging conditions. In the case of insufficient alkaline activation of the aluminosilicate by the activator, a lower modulus is preferred. Otherwise, a higher silicate modulus is preferred [5], especially because of easier and more friendly handling of the fresh geopolymer mixture.

Sodium water glass was chosen as an alkaline activator. The most commonly used and most available alkaline activators are sodium activators mentioned above ($\text{Na}_2\text{O} \cdot n\text{SiO}_2$ silicates, NaOH hydroxides). Some potassium activators, such as potassium hydroxide KOH or $\text{K}_2\text{O} \cdot n\text{SiO}_2$ potassium hydroxide (the properties of sodium and potassium compounds are very similar) were used in laboratory studies, however their use is greatly limited by their availability and cost. For the purposes of this work, sodium water glass with different silicate modulus 1.2; 1.4; 1.6 was used.

The metakaolin (Mefisto L05) was used as a basic component. Metakaolin is aluminosilicate material produced by the burning of kaolin, kaolin clay in the temperature range 600–900°C. The basic component of kaolin is the kaolinite mineral ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) resulting from the weathering of feldspars. Metakaolin can be used as an active admixture for concrete to improve physical and mechanical properties. It increases strength, improves water absorption and reduces efflorescence [6].

table 1 shows the chemical and physical properties of the metakaolin.

Table 1. Chemical and physical properties of Mefisto L05 [7].

Component	Typical value (%)	Guaranteed value
Al_2O_3 content	40.1	min. 38.0
SiO_2 content	54.1	max. 57.0
K_2O content	0.8	max. 0.9
Fe_2O_3 content	1.1	max. 1.80
TiO_2 content	1.8	max. 2.00
MgO content	0.18	max. 0.4
CaO content	0.13	max. 0.2
Loss of ignition (%)	2.2	0.3 - 0.4
Humidity (%)	0.5	-
Specific surface (m^2/g)	12.69	-
Pozzolan activity ($^\circ\text{C}$)	4.3	min. 4.0
Degree of whiteness (%)	60	-

The most important properties of the coating compositions are their viscosity, which is closely related to the flow properties. Rheological properties affect how the mixture will behave, how it will be transferred to the substrate and spread over its surface. We are interested not only in technology, but also in energy. To measure the rheological properties, the rotary rheometer with concentric cylinders' geometry was used. This geometry is optimal for the measurement of building binders because it provides almost no free surface of the measured material and hence, it prevents the mixing water from evaporation which would otherwise influence the measurement. The basic rheological parameters, plastic viscosity and yield stress, were determined from the decreasing branches of the measured flow curves using a Bingham model. The thixotropic parameter was determined as a surface area between increasing and decreasing branches of the flow curve. The flowing test were performed again only on the mixtures with 90% content of alkaline activator and different silicate modulus.

The fundamentals of the research are focussed on the formulation of a universal coating system that will be applicable to all building materials, non-flammable, UV stable, breathable for water vapour,

resistant to weathering and frost, resistant to the effects of dilute acids and alkalis, and is insoluble in water.

The benefit of this work will be a new, durable painting universal system, its advantages will be simple applicability, independence from petroleum products in its production, and ecological production compared to conventional coating systems.

2. Material and sample preparation

Geopolymer mixtures were prepared from metakaolin and sodium water glass was used as an alkaline activator. The metakaolin was supplied by ČLUŽ company Czech Republic. The activating solution was prepared by mixing 1000 g of commercial sodium water glass with an $\text{SiO}_2/\text{Na}_2\text{O}$ ratio of 1.6 and 30 g of NaOH p.a, in order to adjust the $\text{SiO}_2/\text{Na}_2\text{O}$ value to 1.4, and mixing 1000 g of commercial sodium water glass with an $\text{SiO}_2/\text{Na}_2\text{O}$ ratio of 1.6 and 70 g of NaOH, in order to adjust the $\text{SiO}_2/\text{Na}_2\text{O}$ value to 1.2. The chemical composition of water glasses is given in table 2.

Table 2. Chemical composition of water glass (wt. %).

Component	Water glass 1.6	Water glass 1.4	Water glass 1.2
SiO_2	26.43	25.66	24.70
Na_2O	16.61	18.38	20.59
H_2O	56.96	55.96	54.71

The L05 material granulometry can be represented as a percentage of the cumulative representation where the particle size of the d_{50} is about 3 μm and with the d_{90} is around 10 μm . The particle size distribution of aluminosilicate precursor (metakaolin) was determined by laser granulometry measurement and the distribution curves are presented in figure. 1. The d_{50} and d_{90} value indicates that 50% and 90% all grains are smaller than a given value.

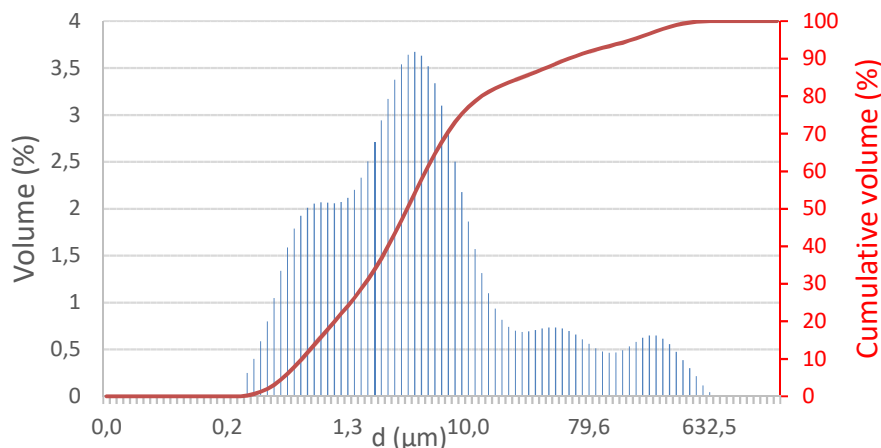


Figure 1. Particle size distributions of metakaolin L05 determined by laser granulometry measurement.

Rheological properties were determined for the pastes, which were composed of 40 g of metakaolin and 70%, 80%, 90% a 100% of water glass of a different silicate modulus by weight of metakaolin. The water coefficient was determined as the amount of water in which two spherical perpendicular measurements were taken on average $100 \text{ mm} \pm 10\%$ when the individual mixtures were spilled onto the substrate. Water content of all mixtures is showed in table 3.

The specimens prepared for the mechanical testing were cast in steel moulds (40 x 40 x 160 mm) and sealed with PE foil. After 48 h were demoulded and stored in plastic bags under laboratory condition. The mixtures were made and stored at ambient temperature $22 \pm 2^\circ\text{C}$ and relative humidity $60\% \pm 10\%$. After 28 days of curing were the specimens under mechanical tests (flexural strength and compressive strength).

Table 3. Water content of individual samples.

Sample	Water glass (silicate modulus)	Content of water glass from metakaolin (%)	Water content (ml)
1	1.6	70	5.5
2		80	3.5
3		90	3.0
4		100	1.5
5	1.4	70	5.0
6		80	3.5
7		90	3.0
8		100	1.5
9	1.2	70	6.0
10		80	4.0
11		90	2.0
12		100	2.0

3. Experimental and methods

Rheological measurements of the pastes were performed by means of a Discovery HR-1 (TA Instruments) hybrid rheometer and TRIOS 4.0.2.30774 software was used for data evaluation. The measurements were performed in a Peltier Concentric Cylinder system with a DIN rotor at 25°C . The standard gap for the DIN cylinder system (5.917 mm) was employed. The rheological measurements were started after a period of rest of 60 s. Paste properties were estimated from the flow curves determined for increasing and decreasing values within the shear stress range from 0.1 to 100 s^{-1} . Yield stress values and plastic viscosities were determined from the decreasing branch of the flow curve using the Bingham model [8].

Mechanical properties were tested using prismatic specimens with dimensions of 40 x 40 x 160 mm at the age of 28 days. Flexural strengths were determined using a standard three point bending test and compressive strengths were measured on the far edge of each of the two residual pieces obtained from the flexural test according to the EN 196-1 standard. For each mixture a set of three specimens was used.

4. Results and discussion

4.1. Mercury intrusion porosimetry

Pore size was carried out by mercury intrusion porosimetry. This is method for the study of the structure of porous substances, based on the phenomenon of capillary depression. Pore size distribution was determined only for the mixtures with 90% content of water glass which appeared to be the most promising activator dosage from the viewpoint of the mechanical properties. The results of the porosimetry measurements are presented in figure 2 and figure 3, showing the comparison of cumulative pore volume vs. pore diameter and differential pore volume vs. pore diameter, respectively, for different silicate modulus of alkaline activator.

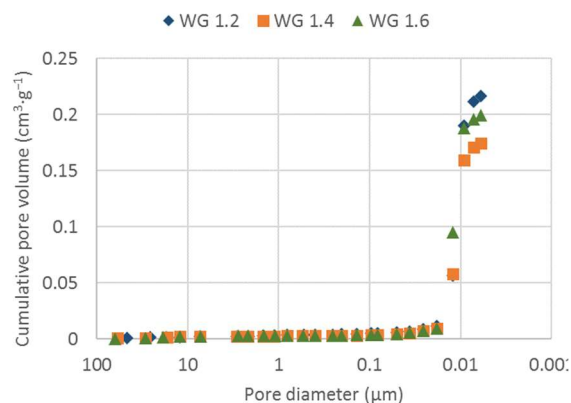


Figure 2. Cumulative intruded volume vs. pore diameter for the mixtures with 90% content of water glass having different silicate modulus.

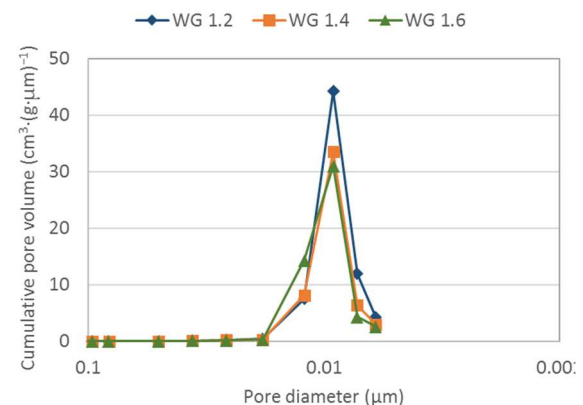


Figure 3. Differential pore volume vs. pore diameter for the mixtures with 90% content of water glass having different silicate modulus.

A cumulative pore distribution showed that the maximum of the pore volume is associated with small pores below 20 nm, which is common for metakaolin based geopolymers [9]. The lowest value of the total intruded volume was achieved for the mixture with $M_s = 1.4$ and the highest one for $M_s = 1.2$. These results clearly correspond to the trend observed for the compressive strength. The curves of the differential pore volume show that the dominant pore size in all three tested mixtures is ca. 10 nm. However, the number of pores is higher almost by one half when the activator with $M_s = 1.2$ was used.

4.2. Mechanical properties

The compressive strength of the geopolymer mixtures with various silicate modulus of water glass ratios are presented in figure 4. The tests were performed at samples geopolymer paste ages 28 days. The lowest 28 days compressive strength (47.5 MPa) was achieved for the mixture with 70% content of water glass and silicate modulus 1.6, the highest 28 days compressive strength (81.9 MPa) was achieved for the mixture with 90% content of water glass a silicate modulus 1.4. On the other hand, the lowest 28 days flexural strength (1.2 MPa) was achieved for the mixture with 80% content of water glass and silicate modulus 1.4, the highest 28 days flexural strength (5.7 MPa) was achieved for the mixture with 90% content of water glass a silicate modulus 1.2.

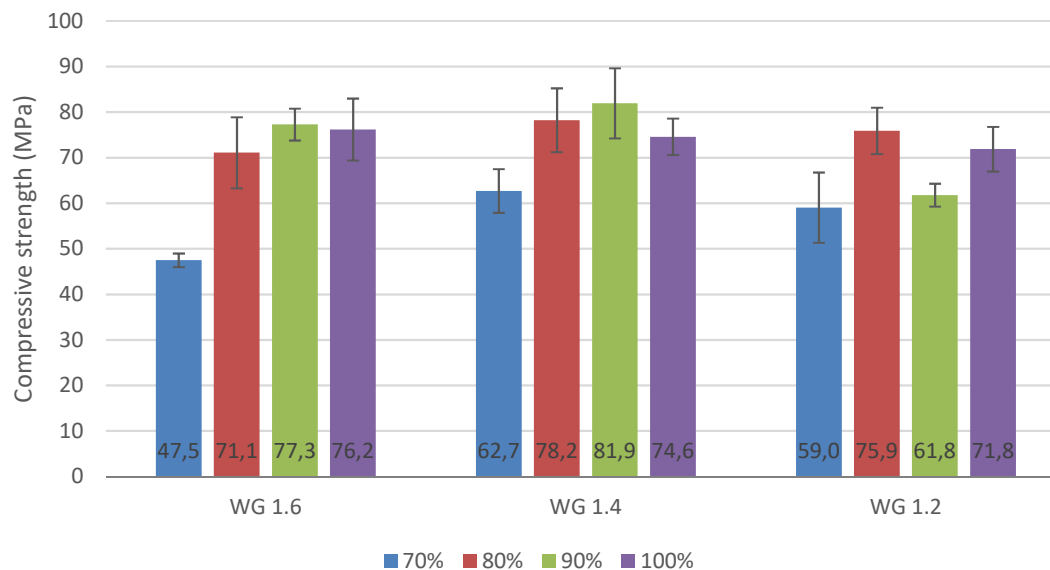


Figure 4. Compressive strengths of geopolymers with various ratio of water glasses.

It is difficult to find any trend for flexural strengths because the standard deviations of the results are very high. This is caused mainly by the absence of any aggregates that usually prevent the binder from propagation of microcracks. If any microcracks appears in the binder, e.g. due to drying shrinkage, it acts as a stress concentrator and the failure of the beam occurs at lower applied stress. This phenomenon can also explain the paradox that the mixtures with $M_s = 1.4$ show the lowest flexural strengths although the compressive strengths are the highest ones.

4.3. Rheological properties

The results of the assessed rheological parameters are summarized in table 4. The plastic viscosity increased with decreasing silicate modulus of water glass. This effect can be generally attributed to the alkaline activating solution because the decreasing silicate modulus is associate with higher alkaline content. Especially, sodium ions are extremely hydrophilic and adsorb a lot of water in the solvating layer. It causes a reduction of free rheological water and rise in viscosity. The same trend was also observed for the yield stress values but with respect to the flow curves presented in figure 5 and literature data [10], it is assumed that all tested mixtures show practically very low yield stress.

Table 4. Rheological parameters of samples with 90% content of water glass.

	Viscosity (Pa·s)	Yield stress (Pa)	Thixotropy (Pa·s ⁻¹)
WG 1.6	5.43	5.59	4588
WG 1.4	7.56	13.83	5404
WG 1.2	12.54	25.60	14654

For non-Newtonian fluids, the internal structure changes due to deformation, which is reflected in the macroscopic behaviour of the liquid. A mechanical decrease in viscosity over time with constant mechanical stress may occur and such fluid are called thixotropic. The thixotropic parameter of tested geopolymer mixtures considerably increased with lowering silicate modulus (table 4). While thixotropic parameter for higher modulus (1.6 and 1.4) are almost similar, the shear thinning behaviour of mixture with $M_s = 1.2$ was more pronounced as the value of the thixotropic parameter increased almost three times.

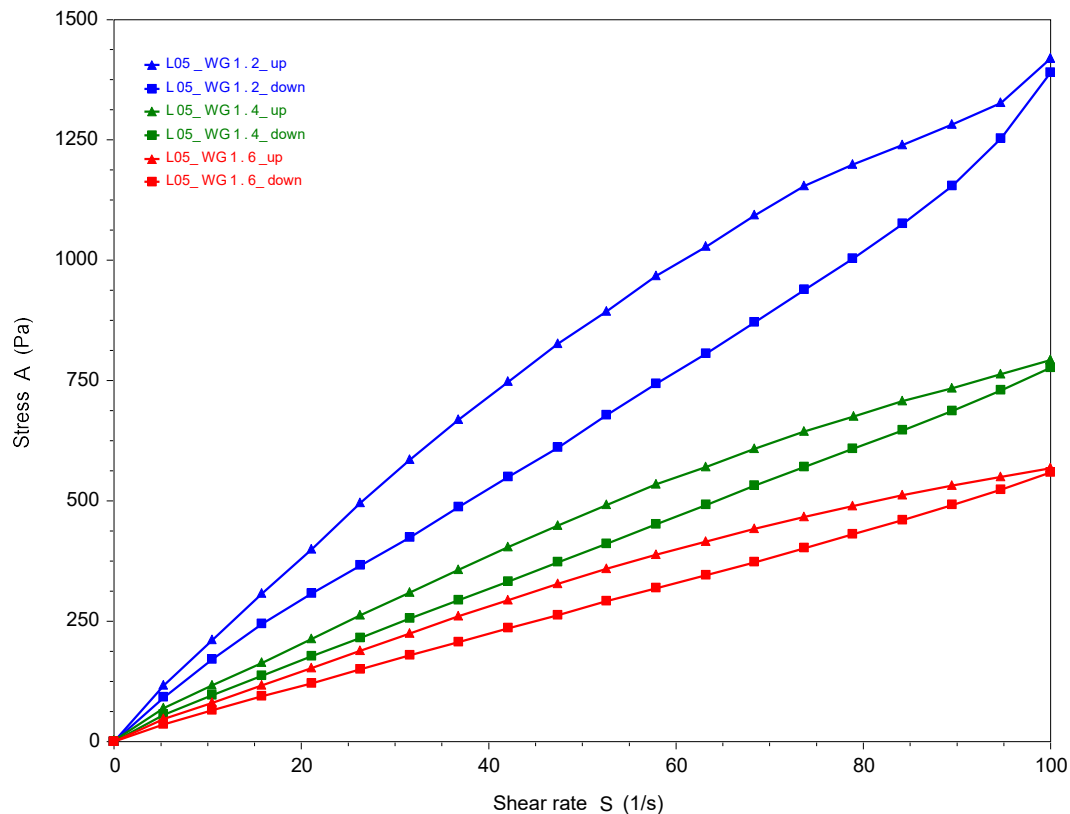


Figure 5. Flow curve of geopolymer with 90% of water glass having different silicate modulus.

5. Summary

Four different geopolymer mixtures with metakaolin and sodium water glass with various silicate modulus were tested for their mechanical and rheological properties.

This paper evaluates the mechanical and rheological properties of the geopolymer composition by applying sodium water glass as an alkaline activator with different silicate modulus – 1.6; 1.4 and 1.2. The best effect on mechanical properties was obtained for the samples with content 90% of water glass with respect to the weight of metakaolin. This trend manifested itself in both compressive strengths and flexural strengths.

For rheological measurements, all samples exhibited thixotropic behaviour which increased with lower silicate modulus of water glass. For all samples very low yield stress and relatively plastic viscosity was observed. However, the viscosity increased when the silicate modulus was lowered.

Acknowledgements

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