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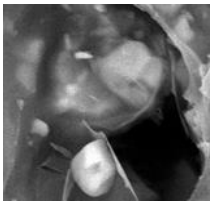

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Comparison of hardening kinetics by small amplitude oscillatory rheometry in the case of alkali activated kaolinitic clays

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Abstract. In this study, the rheological behaviour of geopolymeric inorganic binders were determined. These binders were synthesized by alkaline activation of aluminosilicate material. Five kaolinite clays were chosen for investigation and as an alkaline activator of hardening process, the potassium silicate solution with silicate module of 1.61 was used. For increase of reactivity, the kaolinite clays were calcined by heat treatment at 600 °C for 4 hours and converted to metakaolin state. The particle size of individual materials was determined by measurement of laser light scattering. The rheological properties were determined in accordance to flow properties by measurements on Ford viscosity cup and by strain controlled small amplitude oscillatory rheometry measurements at 30 °C isotherm and the hardening process evolution was documented by measurement of complex viscosity. The effects of granularity and accessory minerals on flow and hardening properties are discussed.

1. Introduction

The inorganic polymeric binders, Davidovits introduced as a pioneering work on alkali-activated binders based on calcined clays [1,2] and entitled them as "geopolymers" because of theirs polymer like structure. Geopolymers are products of chemical reaction between aluminosilicate material and liquid alkaline environment where chemical cleavage of the Si-O and Al-O bonds in parent material leads to saturation of liquid solution and subsequent polycondensation of amorphous aluminosilicate matrix [3-5]. Geopolymers can be synthesized from thermally activated clays and coal fly ashes and can be modified by slags with consideration of mechanical and rheological properties [6,7].

In this experimental research we examined rheological properties of different kaolinitic clays. Five clays were selected from local resources and calcined to metakaoline state at 600 °C [8-10]. The flow properties and early age of consolidation process were documented after initiation of geopolymerizaton process by measuring through flow time on Ford viscosity cup and by the small amplitude oscillatory rheometry measurements respectively [10-12].

2. Materials

Five selected kaolinite clays were examined as a binder. These materials were supplied by Sedlecky kaolin a. s, Czech Republic and chemical compositions of individual materials are presented in Table 1 according to data provided by supplier. Obtained materials were thermally activated by transformation of kaolinite content into the metakaoline state. The heat treatment comprised of heating to the 600 °C

by the rate of 3 °C/min and of dwell time of 4 hours. After the dwell time the material was cooled to room temperature naturally.

For alkaline activation of geopolymerization reaction an aqueous solution of potassium silicate with silicate module 1.61 was used. The morphology of individual clays after heat treatment taken by scanning electron microscope (SEM) are presented in Figures 1-5. The overall granularity curves were measured by laser light scattering and are presented in Figure 6. The main accessory mineral is mica in the case of T-79, MK and MK3 clays and in the case of Sedlec Ia and OT 82 it is combination of mica and quartz minerals.

Table 1. Chemical composition of raw materials [mass %]

Composition	SiO_2	Al_2O_3	CaO	MgO	TiO_2	Fe_2O_3	K_2O	LoI
SedlecIa	47	37	0.3	0.2	0.2	0.8	0.9	13
T 79	47	37	0.3	0.3	0.2	1.2	1.2	13
OT 82	46	37	0.3	0.2	0.7	1.3	0.8	13
MK	50	34	0.1	0.2	0.5	1.5	1.6	11
MK 3	48	36	0.2	0.2	1.5	1.6	1.0	12
Activator	17.6	-	-	-	-	-	17.1	65.3

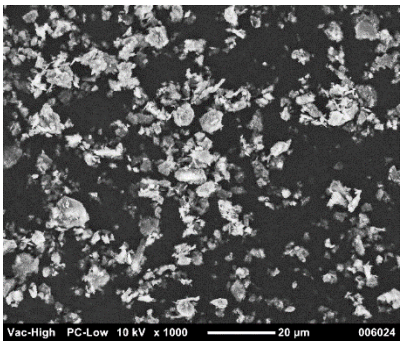

Figure 1. SEM image of calcined clay Sedlec Ia.

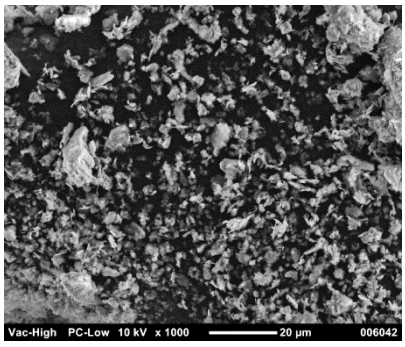

Figure 2. SEM image of calcined clay T 79.

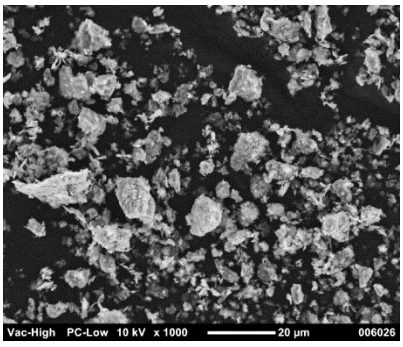

Figure 3. SEM image of calcined clay OT 82.

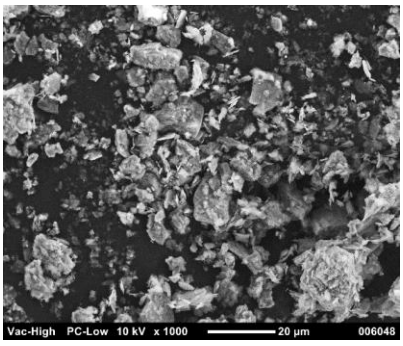

Figure 4. SEM image of calcined clay MK.

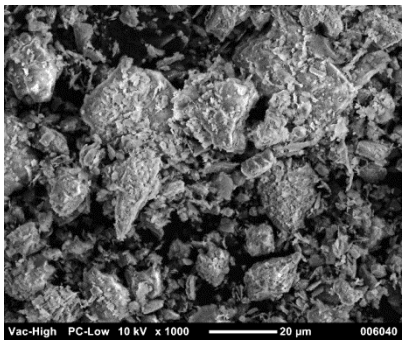

Figure 5. SEM image of calcined clay MK 3.

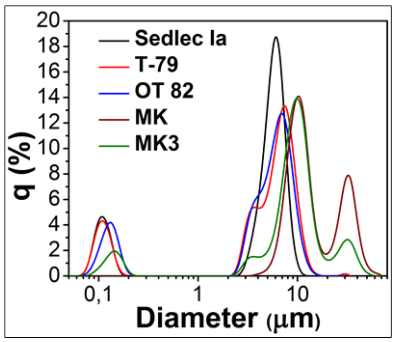

Figure 6. Particle distributions of individual calcined clays.

3. Procedures and results

3.1. Preparation of individual binders

In the case of individual materials after thermal treatment the geopolymerization process was activated by mixing of 100 weight parts of metakaolin powder with 100 or 120 weight parts of potassium silicate activator in laboratory vacuum mixer for period of 5 minutes and then subjected to analysis.

3.2. Flow properties

The flow properties were determined immediately after mixing by measurements on Ford viscosity cup with diameter of 6 mm and the results can be seen in Figure 7 and 9 described as time required to flow through the viscosity cup. In the case of 100:100 weight percent compositions only the materials MK and MK 3 exhibited measurable flow. It is because of considerably higher amount of coarse particles and lower specific surface. However, MK material exhibited slightly higher viscosity which can be attributed to higher content of mica particles around 30 μm. In relation, all 100:120 compositions exhibited measurable flow where MK and MK 3 materials exhibited lowest viscosity. It can be concluded that amount of potassium silicate solution was sufficient for liquefaction of all studied materials. The effect of different mineral composition can be deduced from different viscosities of T-79 and OT 82 materials. The main accessory mineral of T-79 is mica and the viscosity is almost twice as high as of OT 82 which contains also quartz. Although granularities are almost identical the different shape of accessory minerals strongly influences the flow properties [13].

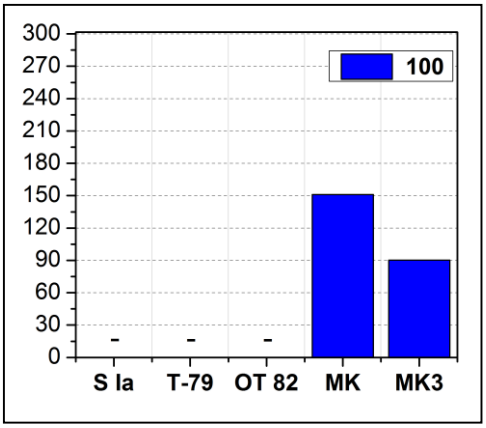

Figure 7. Time to flow of mixture 100:100 through 6 mm Ford cup.

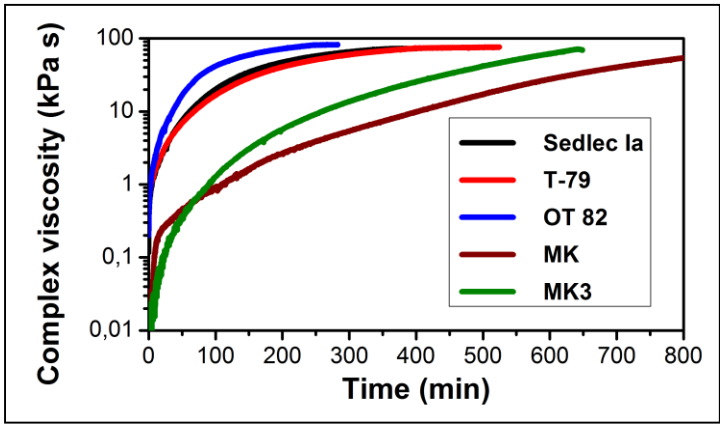

Figure 8. Complex viscosity at beginning of hardening process for mixtures 100:100.

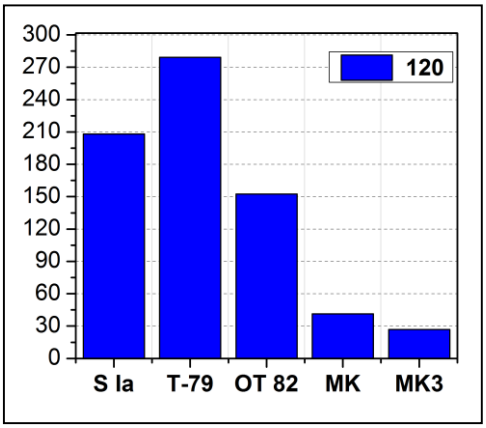

Figure 9. Time toflow of mixture 100:120 through 6 mm Ford cup.

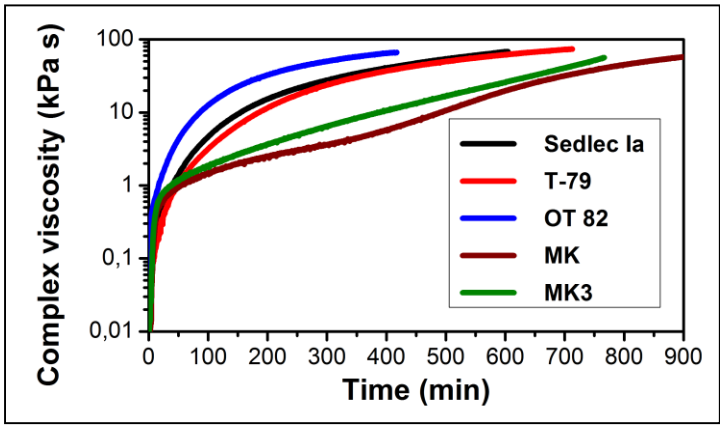

Figure 10. Complex viscosity at beginning of hardening process for mixtures 100:120.

3.3. Complex viscosity measurements

Changes of complex viscosity in the beginning of hardening process was determined by time-resolved oscillatory rheometric measurements with small amplitude on a strain controlled rheometer TA Instruments Ares G2 in plane-plate geometry of 40 mm in diameter. Measurements were performed after 15 minutes from beginning of mixing. The radial velocity of 10 rad/sec and strain 0.01% were applied to ensure a minimal influence on the hardening process. The results of 100:100 and 100:120 compositions expressed as complex viscosity can be seen in Figure 8 and 10 respectively. The changes of complex viscosity measured by low strain oscillations describe two processes. In the early time of measurement the particles in suspension come to equilibrium position after high shear mixing procedure and it contributes to fast increase of initial viscosity. In the later time, the subsequent rising of viscosity can be attributed to dissolution and polycondensation process which leads to hardening of mixture. Comparing Figure 8 and 9, it can be clearly seen that increasing content of activator solution leads to delay in saturation and polycondensation process, because of increasing the liquid to solid ratio. In both concentrations the MK and MK 3 materials exhibited lower reactive rate due to lower content of reactive metakaolin where it can be expected that mica under these conditions do not contribute to the geopolymerization process [14, 15]. From results the OT 82 can be evaluated as the most reactive material in this study and the reactivity of T-79 and Sedlec Ia is almost the same.

4. Conclusions

In this study the effect of mineral composition and granularity on geopolymerization process and flow properties of prepared suspensions were investigated in the case of five calcined kaolinite clays. It can be concluded that content of coarse particles in clays have beneficial effect on flow properties and reduction of viscosity and it can be attributed mainly to the content of accessory minerals which are in this study mica and quartz. On the contrary, these minerals do not contribute to the geopolymerization reaction and to the hardening process. In the case of this study the clay marked OT 82 represents best compromise between hardening kinetics and flow properties in the range of investigated conditions.

Acknowledgments

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