Clay-cement suspensions based on Belchatow and Patoka polymineral clays – rheological characteristics

E Litwinek-Rozbicka*, P Izak, ŁWójcik, J Mastalska-Popławska
AGH University of Science and Technology, Faculty of Materials Science and Ceramics, Krakow, Poland

E-mail: litwinek@agh.edu.pl

Abstract. The results of studies concerning freshly prepared clay-cement sealing suspensions based on Belchatów and Patoka polymineral clays, Portland cement and the addition of sodium water glass as the initiator of the hydration process were reported. Flow curves were determined in a coaxial cylinder system. On their basis, power of destruction and rebuilding of the thixotropic structure was calculated. Changes of the elasticity modulus $G’$ and viscosity modulus $G’’$ were determined by oscillatory measurements in the plate - plate system at variable frequencies. The influence of the type of clay mineral and its content on the tendency to form a thixotropic structure was defined.

1. Introduction
Clay-cement suspensions are mainly used in the construction and renovation of hydrotechnical facilities and flood protection. They are viscoplastic compositions (water-clay suspensions) to which structure agent (cement) and setting time regulator (water glass) are added. The formation of a reversible structure (related to the content of clays) and the formation of an irreversible structure (related to cement hydration) take place simultaneously. The suspensions in the entire bonding range behave like viscoplastic fluids - no rigid crystalline structure is created. As a consequence, the combination of suspension with rock or soil does not devastate their structure. Moreover, the formation of the internal structure with the expected rheological characteristics regulated during time is possible. Therefore, the suspension does not scour out of the gaps [1-6].

One of the aspects affecting the application of suspensions are their rheological properties in the liquid state. They determine the possibility of pressing the suspension into the soil, filling gaps and cracks in it, and then – cross-linking. As a consequence – the suspension function in the form of an anti-filtration barrier. The rheological properties of suspensions change with time. As a consequence of cement hydration, these changes are irreversible. The suspension in the liquid state became solid. To indicate the moment of transformation of the liquid state to the solid state, the storage (elasticity) modulus $G$ (which characterizes the stored deformation energy) and loss (viscosity) modulus $G’’$ (which concerns the deformation energy lost through internal friction during flowing) are determined. When the value of ratio $G/G’’>1$, the solid state properties dominate in the material as a consequence of existing links inside it, for example physical-chemical interactions (formation of agglomerates) or chemical bonds (cement hydration). For viscoelastic liquids, the value of ratio $G/G’’<1$ because bonds between the individual molecules are weak [7-10].
The aim of this study was an attempt to explain the mechanism of bonding of clay and cement suspensions in the aspect of rheology. The results of studies concerning freshly prepared clay-cement suspensions based on Belchatow and Patoka polyminal clays, Portland cement and the addition of water glass as the initiator of the hydration process were presented. Flow curves were determined in a coaxial cylinder system. On their basis, power of destruction and rebuilding of the thixotropic structure was calculated. The changes of the storage $G'$ and loss $G''$ moduli were determined by oscillatory measurements in the plate - plate system at variable frequencies. The influence of the type of clay mineral and its content on the tendency to form a thixotropic structure was defined.

2. Experimental section

2.1. Samples preparation

Samples of clay-cement suspensions were made based on the following raw materials:
- water-clay suspension based on Belchatow polyminal clay, containing beidellite,
- water-clay suspension based on Patoka polyminal clay, containing kaolinite and illite,
- CEM I 42.5 R Odra Opole cement,
- modifier - sodium water glass R-145.

For each raw material two series of samples were prepared: variable content of cement and variable content of clay mineral. The compositions of the suspensions are presented in Table 1.

| Series        | Density of water-clay suspension [g/cm$^3$] | Content of water-clay suspension [wt%] | Content of cement [wt%] | Content of water glass [wt%] |
|---------------|---------------------------------------------|---------------------------------------|--------------------------|-------------------------------|
| Variable      | 1.20                                        | 94.5                                  | 5.0                      | 0.5                           |
| content of cement | 92.0                                      | 7.5                                   |                          |                               |
|               | 89.5                                        | 10.0                                  |                          |                               |
|               | 87.0                                        | 12.5                                  |                          |                               |
|               | 84.5                                        | 15.0                                  |                          |                               |
|               | 82.0                                        | 17.5                                  |                          |                               |
|               | 79.5                                        | 20.0                                  |                          |                               |
| Variable      | 1.18                                        | 89.5                                  | 10.0                     |                               |
| content of clay | 1.22                                       |                                       |                          |                               |
| mineral       | 1.25                                        |                                       |                          |                               |
|               | 1.28                                        |                                       |                          |                               |

At the first step, the cement was added to the water-clay suspension and they were mixed for 2 minutes. Thereafter, water glass was added to the clay-cement suspension and they were mixed for another 2 minutes. The samples were rheologically tested immediately after their preparation.

2.2. Methods of investigation

The flow curves were determined on the Brookfield R/S plus rheometer in a in a coaxial cylinder system. Measurements were carried out at shear rates from 2 s$^{-1}$ to 50 s$^{-1}$ for 20 minutes with intervals every 2 s$^{-1}$.

The changes of the $G'$ and $G''$ moduli were determined by the use of the oscillatory measurements using the Anton Paar MCR-301 rheometer in the plate-plate system at variable frequencies (1-100 Hz). The measurement time was 90 minutes. On their basis, the proportion of the storage and loss modulus $G'/G''$ was calculated. The gap was 0.2 mm.

All the measurements were carried out at room temperature.
3. Results and discussion
The flow curves of clay-cement suspensions were presented in Figures 1-4. The course of curves was pseudo-thixotropic. For both clay minerals at low shear rate range (2-7 s⁻¹) the shear stress increased rapidly (the durable structure was formed). At higher shear rate range, the course of flow curves for both clay minerals was different. In case of suspension based on Belchatow clay, at the shear rate range 7-50 s⁻¹ the shear stress decreased gradually (the structure was easily destroyed). However, in case of suspension based on Patoka clay, at the shear rate range 7-50 s⁻¹ the shear stress still increased (the structure was more durable and was not damaged in wider shear rate range).

![Figure 1](image1.png)

**Figure 1.** Flow curves of the suspensions based on the Belchatow clay (1.2 g/cm³) and water glass (0.5%) with a variable proportion of cement

![Figure 2](image2.png)

**Figure 2.** Flow curves of the suspensions based on the Belchatow clay, cement (10.0%) and water glass (0.5%) with a variable proportion of clay mineral
The course of changes of the proportion in the ratio of $G'/G''$ moduli for the initial 30 minutes of measurement are presented in Figures 5-8. Suspensions based on Belchatow clay exhibited the proportion of $G'/G''$ moduli higher than 1 only at the early stage of measurement, what may indicate the formation of weak structures easily damaged by shearing. Later, the properties characteristic of the liquid dominated. Dissimilar properties showed suspensions based on Patoka clay. They exhibited the proportion of $G'/G''$ moduli higher than 1 at the whole measurement range, what may indicate the presence of links in the suspension that may be the consequence of cement hydration.
Figure 5. The influence of the density of the suspensions based on the Belchatow clay on the proportion of the storage modulus and loss modulus $G'/G''$ with 10.0% content of cement.

Figure 6. The influence of the content of cement on the proportion of the storage modulus and loss modulus $G'/G''$, suspensions based on the Belchatow clay (density 1.2 g/cm$^3$).
4th International Conference on Rheology and Modeling of Materials (ic-rmm4)  
Journal of Physics: Conference Series  1527 (2020) 012011  doi:10.1088/1742-6596/1527/1/012011

Figure 7. The influence of the density of the suspensions based on the Patoka Clay on the proportion of the storage modulus and loss modulus $G'/G''$ with 10.0% cement content

Figure 8. The influence of the content of cement on the proportion of the storage modulus and loss modulus $G'/G''$, suspensions based on the Patoka Clay (density 1.2 g/cm$^3$)

4. Conclusions
Some general conclusion can be drawn as follow:
1. These studies confirmed that the viscoelastic properties of clay – cement suspensions depend on the type of clay mineral and cement. In the case of their application, measurements of flow curves, storage and loss moduli should be carried out.
2. Belchatow clay (containing beidellite) slows down the cross-linking effect of the suspension. The ratio of G'/G'' moduli at low shear rates is higher than 1 – the weak structure is created (easily damaged by shearing).

3. Patoka clay (containing kaolinite and illite) catalyses the cross-linking effect of the suspension. The ratio of G'/G'' moduli was greater than 1 throughout the entire measuring range – the strong structure is created.

4. To sum up, sealing suspensions based on Patoka clay exhibit different viscoelastic properties than suspensions based on Belchatow clay and this can be related to the type of clay mineral.

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