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Effect of oak tannin and iron chloride on the rheological properties of clay pastes

Large worldwide consumption of concrete has brought a critical environmental impact to the earth, such as CO_2 emissions, energy and resources consumption. Due to these concerns, the construction industry is pushed to propose sustainable construction materials and solutions. Without transport and with infinite recycling possibilities, earth is one of the most local and available construction material with the lowest environmental impact (Hugo Houben 1994) and represents the best example of a closed material flow loop: from excavation site to construction elements. However, despite the numerous advantages of earth, its mass application as mainstream construction material is hindered by the time required to build with it, its low strength and its high water sensitivity. Overcoming these weaknesses, without the use of cement or lime, are needed to enlarge and promote the field of applications of earth building materials in an environmentally friendly way.

Natural additives have lowest environmental impact since many of them can be extracted easily and used directly. Mixing natural additives with clay to improve the strength and water resistance is not an entirely new development in earth construction. Various additives have been recorded in the traditional construction recipes (Anger 2013) and some of them have been studied thoroughly in literature. Among those additives, tannin stands out because of its wide availability and high efficiency. Tannins are the polyphenolic secondary metabolites of higher plants, and can be found mainly in the barks, leaves, stems, seeds and roots of plants (Barbehenn and Constabel 2011). Huge structural variation of tannins, with the molar mass between 300 and 3000, have been identified (Khanbabaee and van Ree 2001). The use of tannins to protect the earthen structure surface from rain can be found in some traditional recipes of vernacular construction techniques and in some local practices in Africa (Schreckenbach et al. 1983). Tannins can be oxidized into insoluble substances when exposed to the atmospheric oxygen and resulting in an increase of the degree of polymerization and molecular weight (Vernhet et al. 2011). The effect of tannin regarding strength and water resistance improvement can be enhanced with the help of iron compounds (Keita et al. 2014; Sorgho et al. 2014). Combining tannin and iron compound help to improve the water resistance of clay materials, but the mechanisms of interactions with clay particles are not well understood.

In this work, a natural additive, oak tannin (OT), and iron chloride ($FeCl_3$) were combined to modify the clay properties. The influence of OT addition and different OT/$FeCl_3$ ratio on the rheological behavior of clay paste, including yield stress, critical strain, and shear viscosity, were investigated. The reaction between OT and $FeCl_3$ and its interaction with clays were studied based on the results.

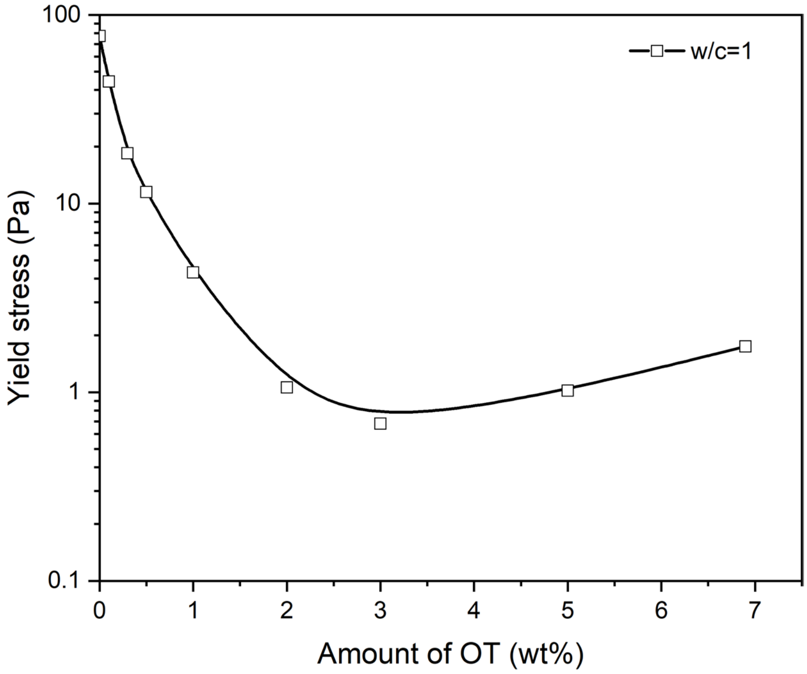
Experimental

Raw materials

A pure kaolinite clay (FP80, Dorfner, Germany) with a density of 2.62 g/cm^3 and a specific surface area of 9.10 m^2/g was used in this study. The average particle size of kaolinite is 8.7 μm determined with laser particle-size analyzer. A commercial oak tannin (OT), extracted from lightly toasted French oak (Quercus robur and Quercus petraea) and sourced from Agrovin (France) was used. The main components of this product is hydrolysable tannins. Ferric chloride (reagent grade, 97%) sourced from Sigma-Aldrich (Switzerland) and water at 20°C was used for the sample preparation.

Mixing process

Different clay pastes were prepared with different dosages of tannin up to 6.9 wt% (by mass of clay) to



01 Yield stress of clay pastes prepared with different amount of tannin

study its effect on the rheological behavior of clay. To produce a homogenous paste, tannin in powder form was dissolved into the water before mixing with kaolinite. The mixture was then mixed with a mechanical stirrer (Heidolph Instruments, Switzerland) equipped with a cross-blade impeller, at 700 rpm for 3 min. In a second step, varying amount of iron chloride (0; 0.095; 0.19; 0.57; 0.95 wt% by mass of clay) were added into the clay paste initially dispersed with 2 wt% of tannin by mass of clay: the paste was mixed at 700 rpm for 2 min before the introduction of iron chloride and mixed again for 2 min.

Rheological measurements

Yield stress

The rheology measurements were conducted using a stress controlled rheometer Kinexus Lab+ (Malvern Instruments, Switzerland), equipped with a Vane geometry. During the measurement, the setup was kept at a constant temperature of 23 ± 0.1°C by a thermostatic bath. An increasing shear rate ramp from 0.1 s^{-1} to 300 s^{-1} was applied for 300 s followed by a decreasing shear rate ramp from 300 s^{-1} to 0.1 s^{-1} for 300 s. Only the decreasing ramps are analysed for the value of the yield stress, extrapolated at low shear rates through a linear regression according to the Herschel-Bulkley model, $\tau = \tau_0 + \eta_p \gamma^n$ where τ is the shear stress, τ_0 the yield stress, η_p the consistency index, γ the shear stress, n the flow index.

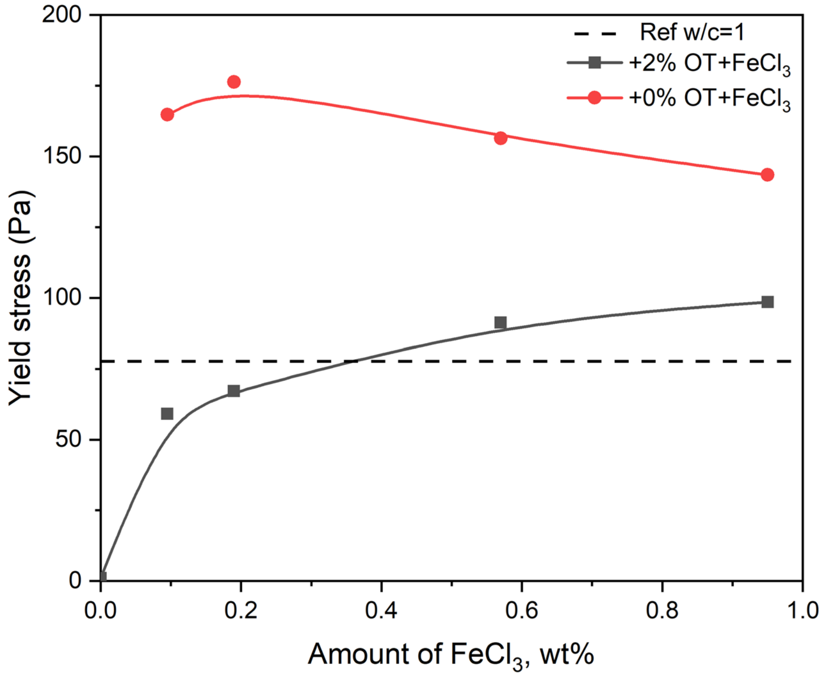
Results and Discussion

The influence of tannin on clay paste rheological behavior

The yield stress of kaolinite pastes prepared with different amount of tannin are shown in Fig. 1. An increasing amount of OT strongly decrease the yield stress and tune the pastes from coagulated state to a highly dispersed state. Above 3 wt% of OT, the yield stress starts to slightly increase, even if the yield stress remains low, maintaining a deflocculated state. The decrease in yield stress is due to the acidic and positively charged characters of tannin. As the clay rheological behaviour is controlled by their surface charge, introduced tannin can adsorbed onto kaolinite particles surface and thus increase the charge density of particles. However, higher amount tannin will increase the concentration of electrolyte, which will compress the double layers between clay particles (Landrou et al. 2018), thus slightly increase the yield stress.

The influence of iron chloride on tannin-dispersed clay paste rheological behavior

In Figure 2, the yield stress of the clay paste with or without OT is plotted as a function of the amount of iron chloride introduced in the mixture. After using iron chloride, the clay pastes changed from a deflocculated state to a coagulated state, even just with small amount of iron chloride. The yield stress of pastes increase to a value similar to the reference



02 Yield stress of clay pastes prepared with and without OT and different amount of $FeCl_3$.

sample, but lower than the pastes containing only $FeCl_3$. This shift may be attributed to the complexation between tannin and iron chloride, which can remove the disperse effect of tannin from kaolinite particles.

Conclusion

The results show that it is possible to control the rheological properties of clay material in an environmentally friendly way by combining the tannin and iron chloride. The deflocculation is related to the nature of tannin while the coagulation is attributed to the complexation between tannin and iron ions. However, more research still need to be done on these additives to completely master their use in earth materials, especially regarding their ability to reduce their sensitivity to water, as used in the practice.

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