EVOLUTION OF THE RHEOLOGICAL BEHAVIOUR OF AN AQUEOUS SUSPENSION OF GEOPOLYMERIC PRECURSORS DURING AGEING

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Evolution of the rheological behaviour of an aqueous suspension of geopolymeric precursors during ageing

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Introduction

Context and issue

Geopolymer based glass-ceramic matrix precursors can be processed at room temperature. Cost effective Liquid Composite Moulding processes are therefore conceivable provided that the rheological behaviour of the suspension is suitable to conveniently permeate the fibrous preform, which is not straightforward.

Objective

The aim of this study is to investigate the changes in rheological behaviour during ageing at -18 °C and during the processing window (up to 1 h at ~15°C) and provide an interpretation and a phenomenological model.

Literature

Geopolymeric precursors are suspensions of alumino-silicate particles in an alkaline silicate solution [1]. The hardening roughly acts in three main steps [2]:

- dissolution of the alumino-silicate particles in the alkaline solution
- polycondensation of the dissolved alumino-silicates with the silicates in solution
- development of a gel phase that grows up to the hardening of the precursor.

Materials and methods

The suspension under study is used for manufacturing glass-ceramic matrix composites and is not commercially available as precursor. The composition is thus confidential. The suspension is stored at -18°C. The resin is characterized as manufactured and with an addition of 2wt%, 3wt% and 5wt% of water in order to assess the effect of dilution on rheological behaviour.

Rheological shear tests are performed using a Rheostress 600 (Thermo Electron) rheometer (1° truncated cone-plate with a gap of 0.054 mm). Both cone and plate have a smooth surface and a diameter of 35 mm. Prior to each experiment, the samples are pre-sheared at 70 s^{-1} for 3 minutes and kept at rest 3 other minutes.

Flow tests were carried out at 10°C, 15°C and 20°C, applying an upward and downward strain rate scan between 0.01 s^{-1} and 200 s^{-1}. The stabilized stress (change lower than 5 % during 5 s) is recorded as a function of strain rate. The strain rate scan is repeated 3 times after 10 min at rest to characterize the changes in rheological behaviour.

Results

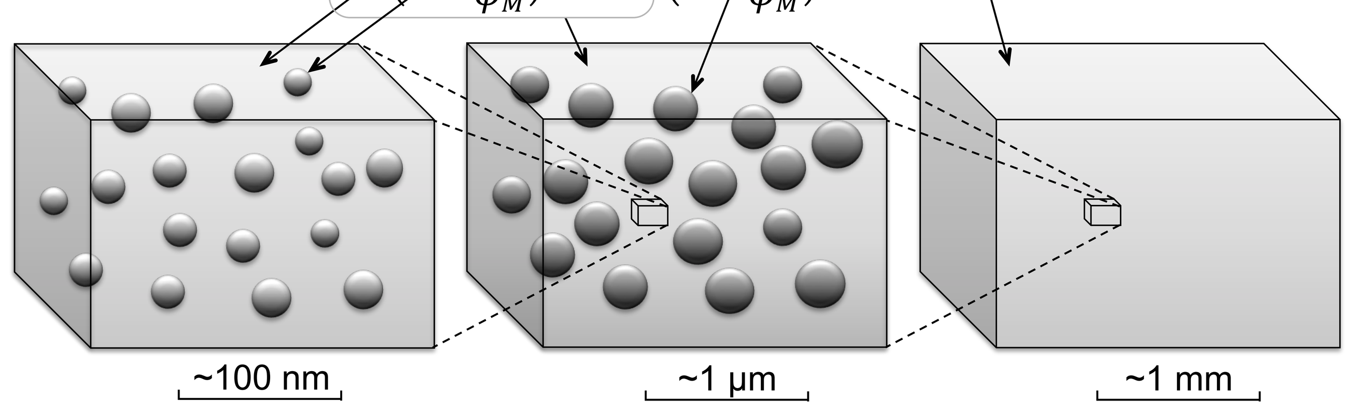
Phenomenological modelling

Provided that the liquid precursor under study is a suspension of alumino-silicate in a silicate solution [1], it is assumed to be composed of:

- a solid fraction ϕ_1 of large alumino-silicate particles dispersed in
- a solution of fine silicate particles of solid fraction ϕ_2 dispersed in
- a fluid phase of viscosity η_f

Assuming a full-scale separation between the scales of both particles populations, two Krieger-Dougherty models can be combined to express the suspension viscosity η:

$$\eta_f\left(1-\frac{\phi_2}{\phi_M}\right)^{-[\eta]\phi_M}\left(1-\frac{\phi_1}{\phi_M}\right)^{-[\eta]\phi_M}=\eta$$



For highly sheared suspensions $\phi_M=\frac{\pi}{3\sqrt{2}}$

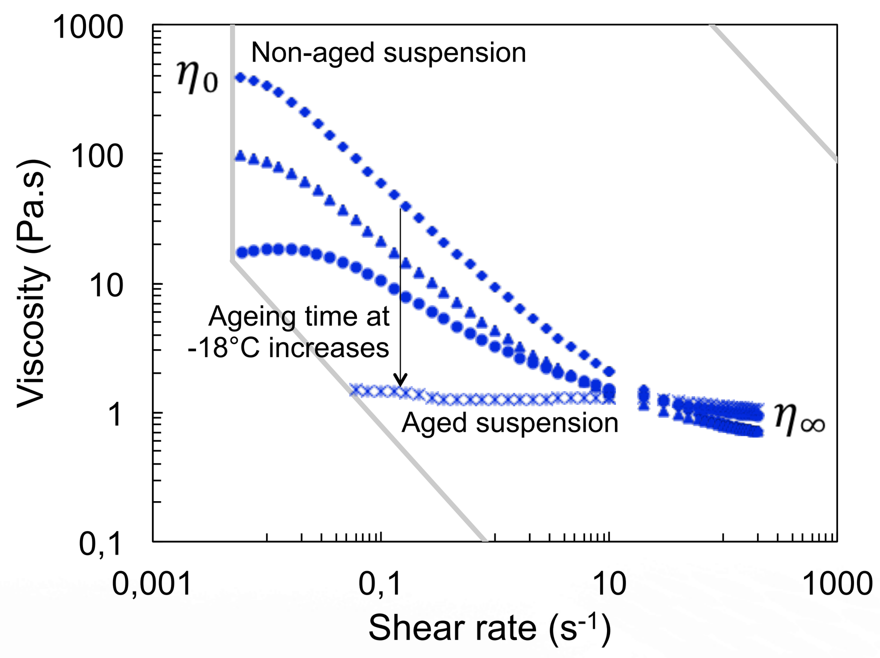
For spherical particles $[\eta]=2.5$

The suspension behaviour is non-Newtonian with

- a high viscosity plateau at low shear rate
- a shear-thinning range
- and an asymptotical low viscosity at high shear rate.

Ageing at -18 °C (storage temperature) results in

- a large decrease of the high viscosity plateau
- a slight increase of the viscosity at high shear rate
- a Newtonian aged suspension



Supported by other rheological results [3], this can be interpreted as the result of dissolution of the large particles in the silicate solution [2]. Therefore

- the silicate solution with dissolved alumino-silicate particles is assumed to be Newtonian
- the non-Newtonian behaviour is related to the presence of large alumino-silicate particles and can be described by an effective solid fraction, function of the microstructure of the suspension.

$$\eta=\eta_f\left(1-\frac{\phi_2}{\phi_M}\right)^{-[\eta]\phi_M}\left(1-\frac{\phi_{eff}}{\phi_M}\right)^{-[\eta]\phi_M}$$

Calibration from rheology results

The effective solid fraction of large particles can be assessed from rheology $\phi_{eff}=\phi_M\left(1-\frac{\left(\frac{\eta}{\eta_f}\right)^{-\frac{1}{[\eta]\phi_M}}}{1-\frac{\phi_2}{\phi_M}}\right)$

At high shear rate the effective solid fraction tends toward the solid fraction ϕ_1

$$\eta_\infty=\eta_f\left(1-\frac{\phi_2}{\phi_M}\right)^{-[\eta]\phi_M}\left(1-\frac{\phi_1}{\phi_M}\right)^{-[\eta]\phi_M}$$

Dissolution of the large particles

Dissolution is assumed to occur at constant volume, i.e. a given volume of large alumino-silicate particles is converted to the same volume of fine particles in solution. The solid fraction of fine particles after an ageing time t is related to the remaining solid fraction in large particles:

$$\phi_2^t=\phi_2+\frac{\phi_1-\phi_1^t}{1-\phi_1^t}(1-\phi_2)$$

At the end of dissolution, all large particles are dissolved and the behaviour is Newtonian $\phi_{eff}^t=\phi_1^t=0$

$$\phi_1=\frac{\phi_2^\infty-\phi_2}{1-\phi_2}$$

The final solid fraction of fine particles in solution can be assessed from rheology.

$$\phi_2^\infty=\phi_M\left(1-\left(\frac{\eta_\infty^\infty}{\eta_w}\right)^{-\frac{1}{[\eta]\phi_M}}\right)<\phi_M$$

η_∞^∞: Newtonian viscosity of the suspension at the end of dissolution

Effect of dilution and test temperature

Temperature is assumed to affect only the fluid phase viscosity and the effective solid ϕ_{eff}

Water dilution of the suspension affects:

- The viscosity of the fluid phase

$$\eta_f=(1-x')\eta_{f0}e^{\frac{E_{aw}}{RT}}+x'\eta_w$$

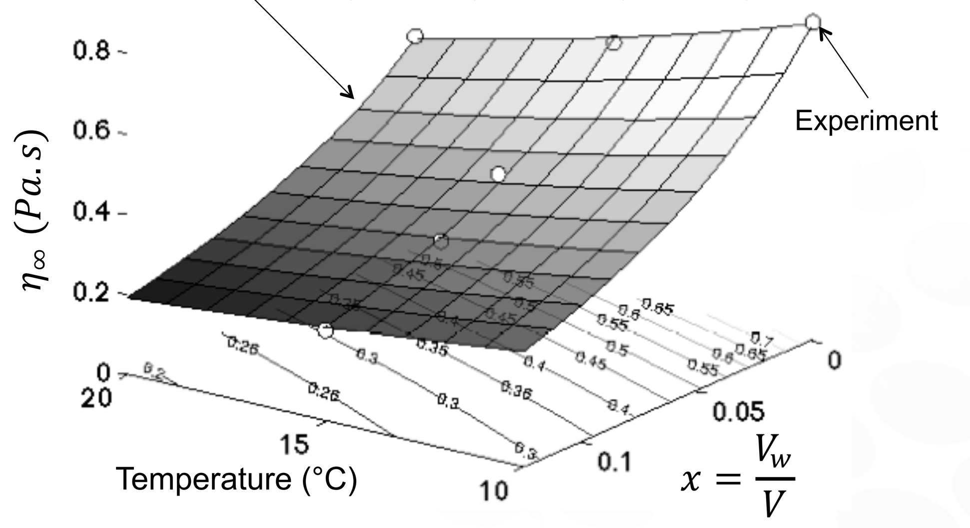
- The solid fraction of both particles populations

$$\phi_1^x=\frac{\phi_1}{1+x}$$

$$\phi_2^x=\phi_2\frac{1-\phi_1}{1-\phi_1+x}$$

$$x'=\frac{V_w}{V_f+V_w}=\frac{x}{x+(1-\phi_1)(1-\phi_2)}$$

$$\eta_\infty=\eta_f\left(1-\frac{\phi_2^x}{\phi_M}\right)^{-[\eta]\phi_M}\left(1-\frac{\phi_1^x}{\phi_M}\right)^{-[\eta]\phi_M}$$



V_w: added volume of water V_f: initial volume of the fluid phase V: initial volume of suspension

Thixotropic behaviour

- A microstructure variable, s, is defined as a function of the effective solid fraction of large particles and can be assessed from rheology measurements.

$$s=\frac{\phi_{eff}-\phi_{eff}^\infty}{\phi_{eff}^0-\phi_{eff}^\infty}=\frac{\eta_\infty^{-\frac{1}{[\eta]\phi_M}}-\eta^{-\frac{1}{[\eta]\phi_M}}}{\eta_\infty^{-\frac{1}{[\eta]\phi_M}}-\eta_0^{-\frac{1}{[\eta]\phi_M}}}$$

- A usual evolution law is proposed that includes a build-up (t_{bu}) and a breakdown (t_{bd}) characteristic time for microstructure change mechanisms.

$$\dot{s}=\frac{\dot{\phi}_{eff}}{\phi_{eff}^0-\phi_{eff}^\infty}=-\frac{s}{t_{bd}}+\frac{1-s}{t_{bu}}$$

- The equilibrium microstructure is given by $\dot{s}=0$

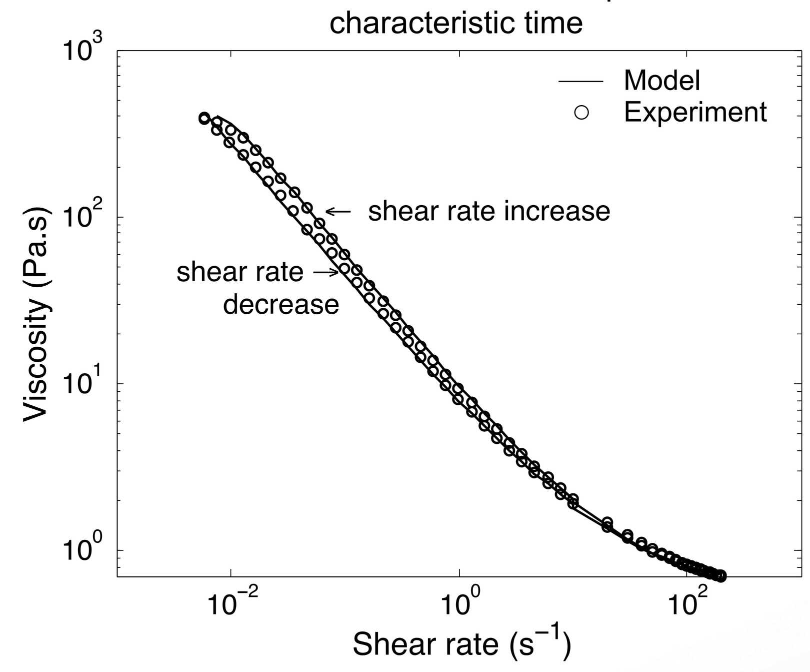
$$\frac{t_{bu}}{t_{bd}}=\frac{1-s_{eq}}{s_{eq}}$$

- The equilibrium microstructure parameter is fitted with a stretched exponential function of strain rate

$$s_{eq}=s_{eq}^\infty+\left(s_{eq}^0-s_{eq}^\infty\right)\cdot e^{-(\tau_S\dot{\gamma})^\beta}$$

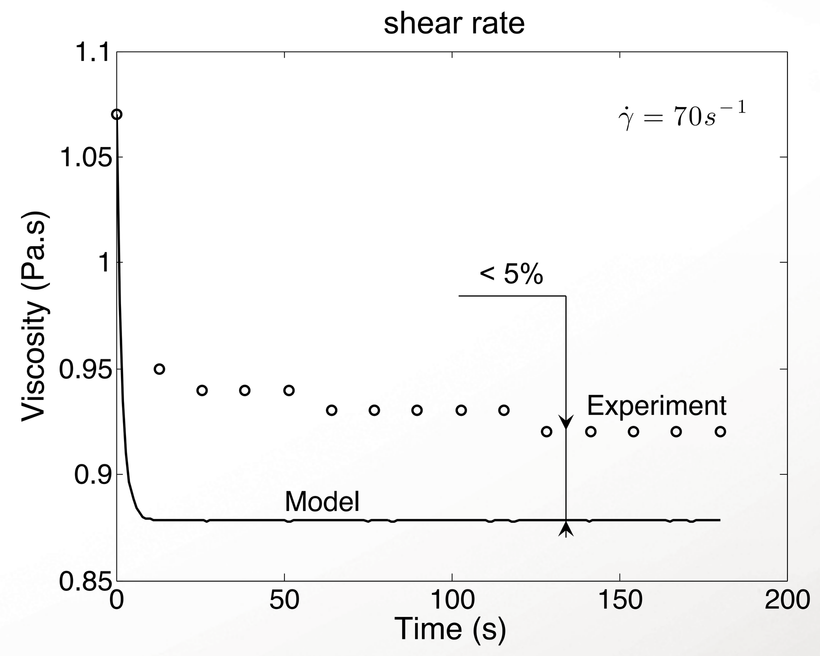
- The build-up characteristic time is assumed to be constant and the break-down characteristic time is introduced as a function of shear rate in order to match the stabilized viscosity.
- The build-up characteristic time is tuned to reproduce the hysteresis of the stabilized viscosity data

Identification of build-up characteristic time



The model accounts for the hysteresis on the equilibrium viscosity as a function of strain rate

Validation test at constant shear rate



The model accounts for the sudden viscosity drop while shearing at 70 s^{-1}. The mismatch for the asymptotical value is lower than 5%.

Conclusion

- A phenomenological interpretation of rheology evolution during ageing at -18°C is provided for a geopolymer precursor suspension.
- Dissolution of large alumino-silicate particles leads to a decrease of viscosity at the Newtonian plateau and a slight increase of the viscosity at high shear rate up to reach a Newtonian behaviour with viscosity of 1.2 Pa.s, more suitable for processing that the behaviour of the non-aged suspension.
- A quite simple phenomenological model is proposed that is able to properly describe the effects of test temperature, water dilution and thixotropic behaviour. A convenient framework is thus available to study the suspension from mainly rheology measurement.

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