Thixotropy vs wall slip in suspensions

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Papers :

- Dullaert, Mewis : Thixotropy : Build-up and breakdown curves during flow (JoR, 2005)
  - Claimed the first robust stress measurement of the thixotropic system
  - Introduced de-embedding of rheometer's transfer function from the output data
- Dullaert, Mewis : A model system for thixotropy studies (Rheol Acta, 2005)
  - Detailed description on the previous 'robust thixotropic system'
  - Covered various issues which was problematic for previous researches and was reduced with their new compound
  - Covered wall-slip phenomenon and remedy for it

Experiments about thixotropy

- Difficulties in experiments
  - While there are various models & theories about thixotropy, there are few reliable experimental datasets
  - Primary reason for this is the difficulties involved in measuring thixotropic system with enough accuracy
- Main objective of this paper
  - Building robust thixotropic system which supports repeatible & reliable measurements

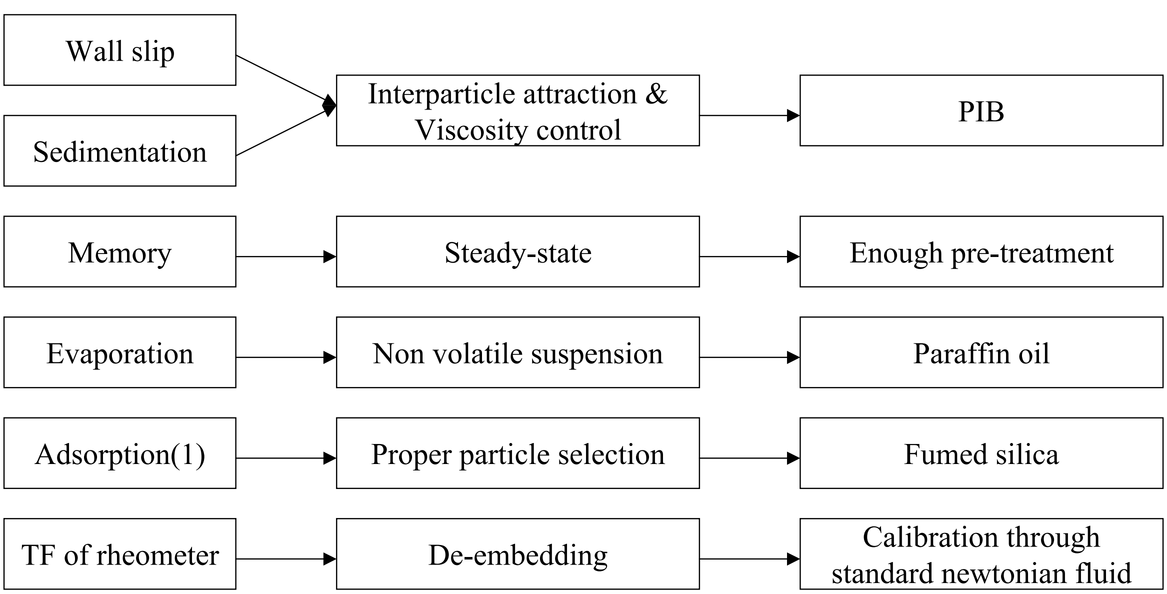
Recall :

- Definition of thixotropy in this paper
  - Change of floc structure resulting in varying viscosity
  - Does not necessarily include viselasticity

Why is measurement difficult?

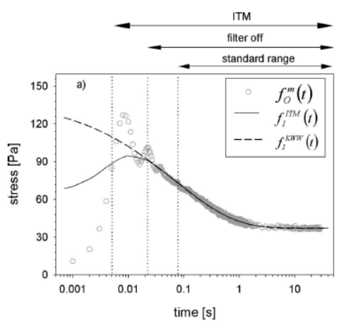
- Implemental artifacts
  - Wall slip
  - Heterogeneous shear rates
  - Gap size effect
  - Rheometer's transfer function
  - Memory of floc's microstructure
  - Evaporation of solvents
  - Particle sedimentation, change in particle's wetting property, adsorption

Plan

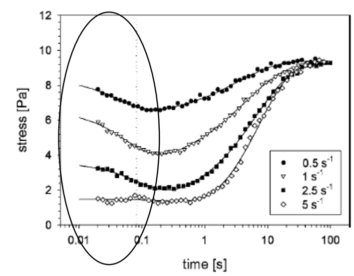


Specifications :

- Rheometer :
  - MCR300 stress controlled Rheometer
    - 12.5mm plate with 0.035 / 0.07 rad (sand blasted to reduce slip)
  - ARES rate controlled Rheometer
    - 12.5mm plate with 0.04 rad
  - Rheometer's transfer function was de-embedded in JoR paper



$$H(s) = \frac{F_O^{me}(s)}{F_I(s)} = \frac{\sum_{i=0}^{c} a_i s^i}{\sum_{j=0}^{d} b_j s^j}$$



Specifications :

- Thixotropic system
  - Fumed silica particles – Aerosil R972
    - Transparent, availability in wide range of surface treatments
    - Hydrophobic, 16nm particles
  - Paraffin oil – Riedel-de Ha e n 18512
    - Non-volatile, 0.16pa s viscosity
  - PIB (Poly(isobutylene)) is added to control viscosity & particle interaction : 27wt%
    - 45pa s own viscosity, 0.65pa s total viscosity
  - Volume fraction of particle : 2.5vol% ~ 3.0vol%
    - Upper limit : wall slip & yielding
    - Lower limit : sedimentation & weakness

Effect of PIB :

- Drastic change in viscosity
- System's recovery time also changes significantly

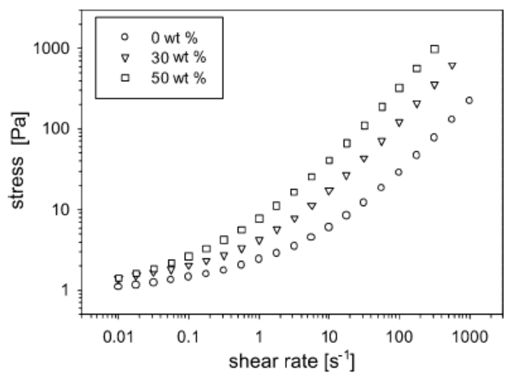


Fig. 1 Effect of PIB on the flow curve of a 1.5 vol% fumed silica dispersion in a mixture of paraffin oil and PIB

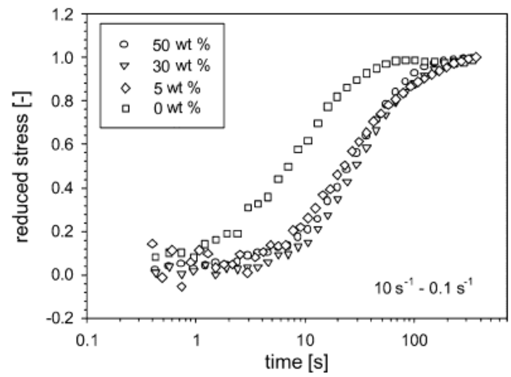
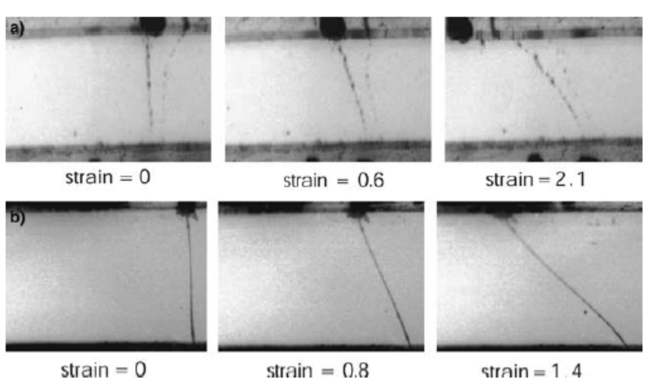


Fig. 2 Effect of PIB on the build-up behaviour after a stepwise reduction in shear rate from 10 s^{-1} to 0.1 s^{-1} on a 1.5 vol% fumed silica dispersion in a mixture of paraffin oil and PIB

Effect of PIB : Slip

- Preparation :
  - $25 s^{-1}$ for 200sec to ensure steady state
  - TiO_2 powder was used as a marker



Without PIB add

With PIB add

Effect of temperature & humidity :

- High temperature changes the adsorption of PIB to silica
- Humidity highly affects the yield stress

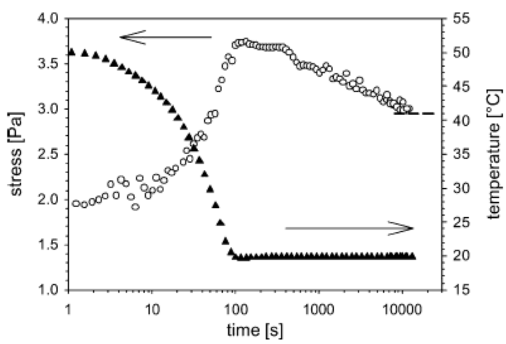


Fig. 3 Stress evolution at a shear rate of 0.1 s^{-1} during a quenching experiment from an initial temperature of 50°C to 20°C at constant relative humidity on a 1.5 vol% fumed silica dispersed in paraffin oil and PIB (50 wt%)

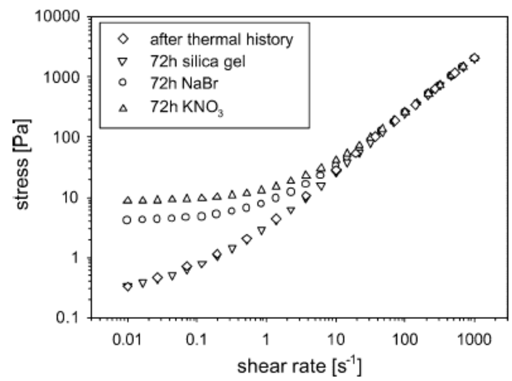
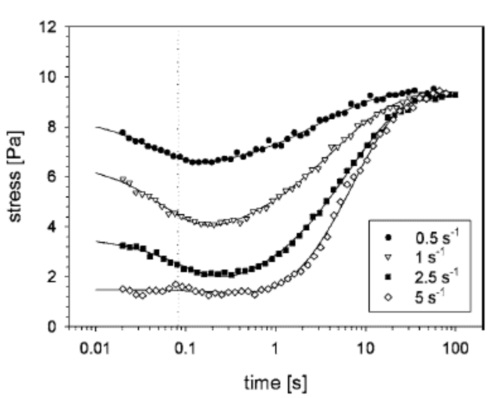


Fig. 5 Effect of thermal history and relative humidity of environment on the flow curve of a 2.7 vol% dispersion of fumed silica in a mixture of paraffin oil and PIB (30 wt%)

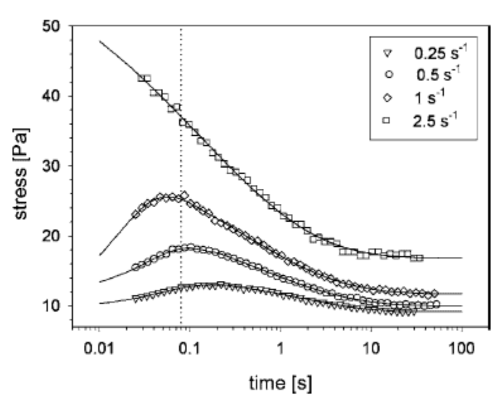
Test result :

- KWW, aka stretched exponential model (1970)

$$\sigma_{\text{dec}}(t) = \sigma_1 \exp\left(-\frac{t}{\tau_1}\right) + \sigma_2\left(1 - \exp\left[-\left(\frac{t}{\tau_2}\right)^m\right]\right) + \sigma_3.$$



Build up



Break down

Effect of de-embedding

- Constant λ curve

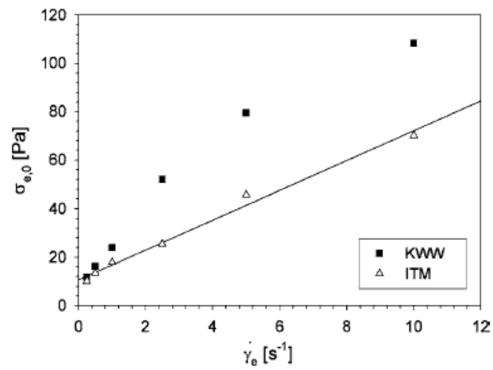


FIG. 6. Constant λ curve for an initial shear rate of 0.05 s^{-1} obtained with either the standard procedure (■) or the present one (△).

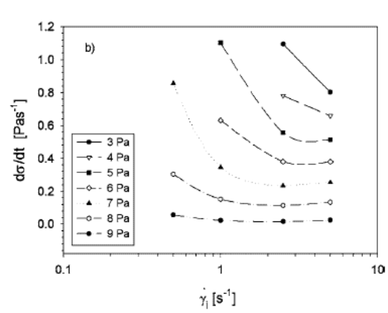
Model evaluation

- Prove or disprove the predictive ability of major models :
  - Cheng's constitutive + single kinetic model (1965)

$$\sigma(t) = F[\dot{\gamma}(t), \lambda(t)]$$

$$d\lambda(t)/dt = G[\dot{\gamma}(t), \lambda(t)].$$

$$\frac{d\sigma}{dt} = \frac{\delta F}{\delta \lambda} G(\dot{\gamma}_e, \lambda) = h(\dot{\gamma}_e, \lambda).$$



Model evaluation

- Prove or disprove the predictive ability of major models :
  - Houska's 1D model (2002)

$$\sigma(\dot{\gamma},t) = \lambda\sigma_{y,0} + \lambda K_{st,0}\dot{\gamma}^n + K_\infty\dot{\gamma}^n$$

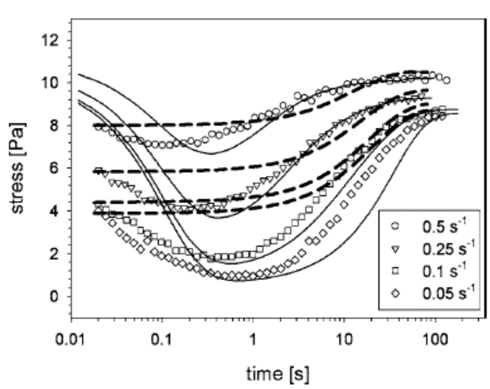
$$\frac{d\lambda}{dt} = -k_1\dot{\gamma}^a\lambda + k_3(1-\lambda)$$

  - Coussot's model (1993)

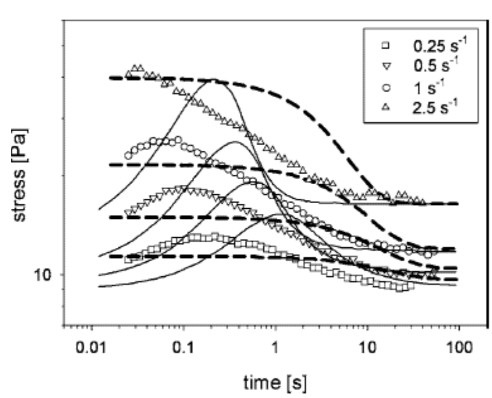
$$\sigma(\dot{\gamma},t) = \sigma_{el}(\dot{\gamma},t) + \eta_\infty\dot{\gamma}.$$

$$\frac{1}{G_0}\frac{d\sigma_{el}}{dt} + \frac{\lambda^{-n}-1}{n}\frac{\sigma_{el}}{\eta_{st,0}} = \dot{\gamma}.$$

Model evaluation



Build up test from 1/s
(Dashed – Houska, solid – Coussot)



Break down test from 0.1/s
(Dashed – Houska, solid – Coussot)

Conclusion

- Reliable & robust thixotropic system was achieved (at least, they say so)
- Major ideas were :
  - De-embedding of rheometer's transfer function
  - Adding of PIB for viscosity & interparticle attraction reduction
- Model evaluation was tried for single exponential model, Houska's 1D model and Coussot model
  - Showed evidence why single exponential can't work
  - Compared strength & weakness of Houska / Coussot model