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

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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

1. Wall slip → Interparticle attraction & Viscosity control → PIB
2. Sedimentation
3. Memory → Steady-state → Enough pre-treatment
4. Evaporation → Non volatile suspension → Paraffin oil
5. Adsorption(1) → Proper particle selection → Fumed silica
6. TF of rheometer → De-embedding → Calibration through standard newtonian fluid
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

- Thixotropic system
  - Fumed silica particles – Aerosil R972
    - Transparent, availability in wide range of surface treatments
    - Hydrophobic, 16nm particles
  - Paraffin oil – Riedel-de Haen 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 200 sec to ensure steady state
  - TiO₂ 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

Test result:

- KWW, aka stretched exponential model (1970)

\[ \sigma_{\text{dec}}(t) = \sigma_1 \exp\left(-\frac{t}{\tau_1}\right) + \sigma_2 \left(1 - \exp\left[-\left(\frac{t}{\tau_2}\right)^n\right]\right) + \sigma_3. \]
Effect of de-embedding

- Constant \( \lambda \) curve

![Graph showing \( \sigma_\alpha \) vs. \( \dot{\gamma}_\alpha \)](image)

FIG. 6. Constant \( \lambda \) 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)

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

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

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

![Graph showing \( \sigma_\alpha \) vs. \( \dot{\gamma}_\alpha \)](image)
Model evaluation

- Prove or disprove the predictive ability of major models:
  - Houska’s 1D model (2002)
    
    \[ \sigma(\dot{\gamma}, t) = \lambda \sigma_{\gamma,0} + \lambda K_{\mu,0} \dot{\gamma}^\alpha + K_\infty \dot{\gamma}^\mu \]
    
    \[ \frac{d\lambda}{dt} = -k_1 \dot{\gamma}^\alpha \lambda + k_3 (1 - \lambda) \]
  - Coussot’s model (1993)
    
    \[ \sigma(\dot{\gamma}, t) = \sigma_c(\dot{\gamma}, t) + \eta_\infty \dot{\gamma} \]
    
    \[ \frac{1}{G_0} \frac{d\sigma_c}{dt} + \frac{\lambda - \frac{n}{\eta_\infty}}{n} = \frac{1}{\eta_{\mu,0}} \frac{d\sigma_c}{dt} = \dot{\gamma} \]

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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