Yield stress and thixotropy: on the difficulty of measuring yield stresses in practice

Review and Discussion

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http://web.mit.edu/nnf
• Yield stress fluids can sustain shear stresses without flowing.
  - Differ from Newtonian fluids which flow for any applied stress

• There are at least two important problems with this perception and the H-B model.
  1) The value of the yield stress for a particular fluid is difficult to measure consistently.
    - Dependent on history of the fluid
  2) H-B model assumes that all steady-state shear rates are achievable.
    - Shear banding occurs for low shear rates.

• By considering thixotropy these problems disappear.
  - “Thixotropy can be defined as a (reversible) decrease of viscosity of the material in time when the material is made to flow.”
  - Yield Stress and thixotropy are believed to be caused by the same fundamental physics.

\[
\sigma = \sigma_y + f(\gamma) \quad \text{if} \quad \sigma > \sigma_y \\
\text{and} \quad \gamma = 0 \quad \text{if} \quad \sigma \leq \sigma_y
\]

Herschel-Bulkley (H-B) model
\[
\sigma = \sigma_y + a\gamma^n
\]
The problems with *the* yield stress

- Theoretically the yield stress is defined to be the stress at which the viscosity changes between being infinite to being finite.
  - Requires an infinitely long experiment to be conducted – not efficient definition for experimentalists
  - Experimentalists define it as the highest stress at which there is no flow detectable.
    \[ \Rightarrow \text{Dependent on patience of experimentalist} \]
- The yield stress is not necessarily a material constant but many choose to use it as such.
  - Its value may vary by more than one order of magnitude depending on measurement technique.
- Yield stresses obtained via experiment often incorrectly predict the conditions under which a fluid will flow.
The problems with the yield stress – shear banding

• The H-B model as well as others suggest all steady-state shear rates are possible.
  - There exists a range of steady-state shear rates which are not attainable.

• Experimentation has shown that there is a critical shear rate.
  - Below: flow is localized in a region close to the shearing wall.
  - When increased, the shear rate in this region does not increase, but instead the size of
    the sheared region grows filling the entire gap at the critical shear rate.

• Only a small amount of material flows while the rest remains solid – shear banding (localization).
Thixotropic fluids

- Thixotropic fluids have a viscosity that is a function of time.
  - At high shear rates it decreases with time.
  - At low or zero shear rates it increases with time.
- Thixotropy and the observed variation in viscosity is caused by the microstructure of the fluid.
  - Broken down with time when sheared; rebuilds when left to rest
Relationship between yield stress and thixotropy

- The inclined plane test is used to demonstrate the interplay between yield stress and thixotropy.
  - For bentonite, once the critical slope is reached, the sample starts to flow.
    ⇒ Thixotropy leads to a decrease in viscosity and the flow accelerates – avalanche.
  - H-B model predicts the fluid move only infinitesimally – inadequate in accounting for thixotropy.
- Aging – reverse avalanche – viscosity increases...shear rate decreases...aging becomes easier (at low shear rates)
- Range of shear rates are not accessible – between no flow and critical shear rate
- Critical shear stress is dependent on aging history.
- Discontinuity in viscosity at critical stress– drops from being infinite to a low finite value

![Diagram showing relationship between yield stress and thixotropy](image)
Yield stress model including thixotropy

• $f$ is the structural parameter and describes the degree of interconnection among the microstructure of the fluid.
  - Viscosity increases with increasing $f$.

$$\frac{d\lambda}{dt} = \frac{1}{\tau} - \alpha \lambda \dot{\gamma} \quad \text{when solved, } \lambda = (\lambda_0 - \lambda_{ss}) \exp(-\alpha \dot{\gamma} t) + \lambda_{ss}$$

where $\lambda_{ss} = \frac{1}{\alpha \eta_0 \dot{\gamma}}$

$\tau$ is the characteristic time of the build-up of the microstructure
$\alpha$ and $n$ are parameters that are specific for a given material

$\eta_0$ is the limiting viscosity at high shear rates
$\eta = \eta_0 (1 + \beta \lambda^n)$
$\sigma = \eta \dot{\gamma}$
$\beta$ is a parameter of the fluid

• For $n > 1$ a yield stress is exhibited by the model - Apparent critical stress and shear rate
Yield stress model including thixotropy

Moller, Mewis, and Bonn Model

\[ \lambda_0 > \lambda_{ss} \]
Yield stress model including thixotropy

\[ \lambda_0 < \lambda_{ss} \]
Do MWCNT solutions exhibit thixotropy?

- MWCNT’s do in fact exhibit an alteration in floc size and therefore packing density.
Do MWCNT solutions exhibit thixotropy?

- Rebuilding time is on the order of 5 hours.
- Data exhibits a “yield stress” of about 0.5-0.7 Pa.