Rheology of microgel-based supramolecular double-networks

Supervisor: Michel Cloitre

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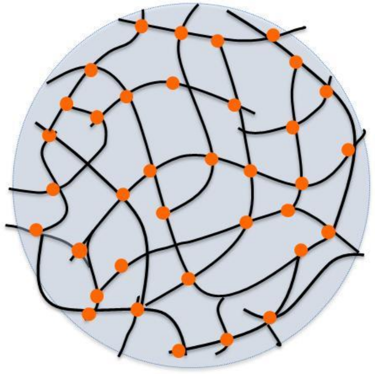
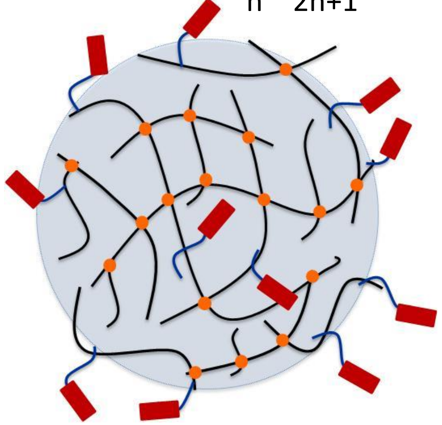


Repulsive



Associative

INITIAL TRAINING NETWORK

ESPCI PARIS | PSL

Outline of activities

Research Projects

- **Transient rheology of soft glasses**
- **Rheology of industrial microgels for applications**
- **High frequency rheology of soft glasses**

In collaboration with Dimitris Vlassopoulos and Thanasis Athanasiu.

Dissemination

Publications:

- F. Khabaz et al. « Transient dynamics of soft particle glasses in startup shear flow. Part I: Microstructure and time scales » Journal of Rheology **65**, 241 (2021)
- BF Di Dio et al. « Transient dynamics of soft particle glasses in startup shear flow. Part II: Aging and mechanical memory (being finalized)

Oral communications:

- Bruno Di Dio, Fardin Khabaz, Roger T. Bonnecaze, Michel Cloitre, "Transient yielding of soft particle glasses". Society of Rheology Conference (2021; Bangor, Maine, USA)
- Bruno Di Dio, Fardin Khabaz, Roger T. Bonnecaze, Michel Cloitre, "Yielding transitions in Soft Particle Glasses during startup flow". International Rheology Conference (2020; Rio de Janeiro, Brazil)
- DoDyNet meetings: July 2020 ; September 2020 ; February 2021

Training

Courses:

- « Éthique de la recherche et Intégrité scientifique » (7h)
- Scientific mediation (7h)
- Soft skills workshop (8h)
- Rheology at microscopic scale and laser light scattering (6h)

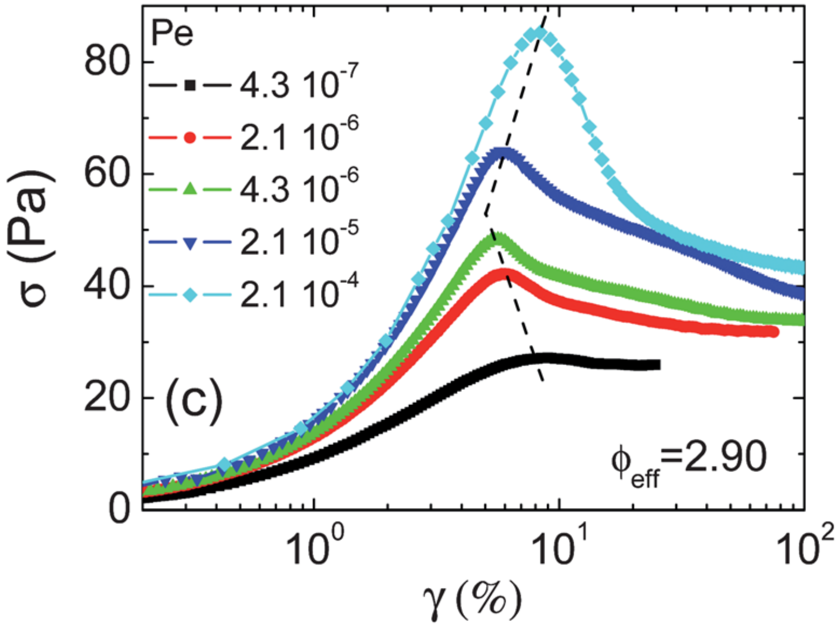
Secondments:

- Secondment at FORTH University in December 2021 (3 weeks)

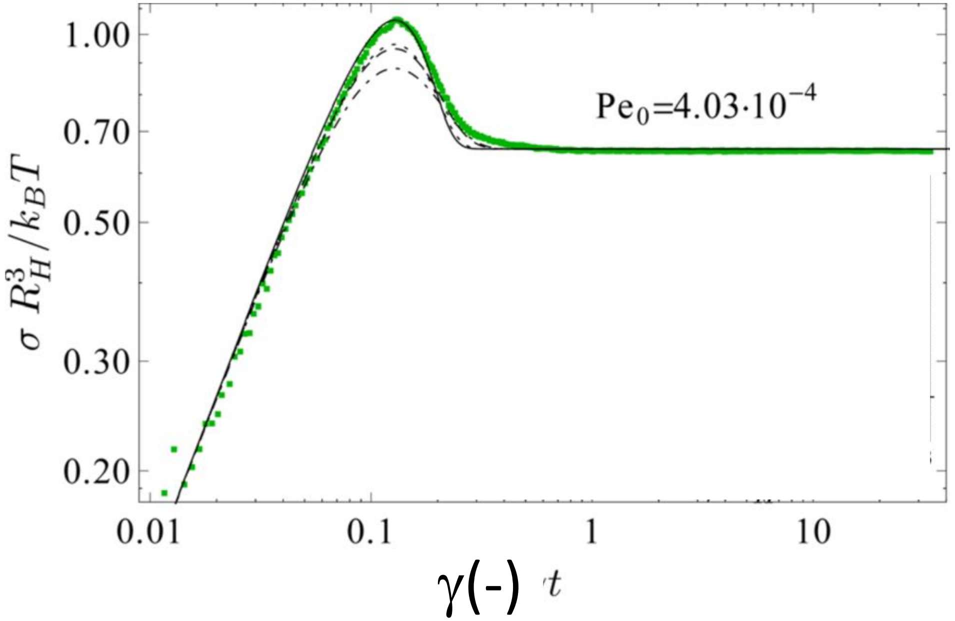
From December 2020 to May 2021 the access to the lab was limited to 25% of full capacity

Yielding of soft particle suspensions from rest

Star-like micelles



PS-PNIPAm core-shell colloids



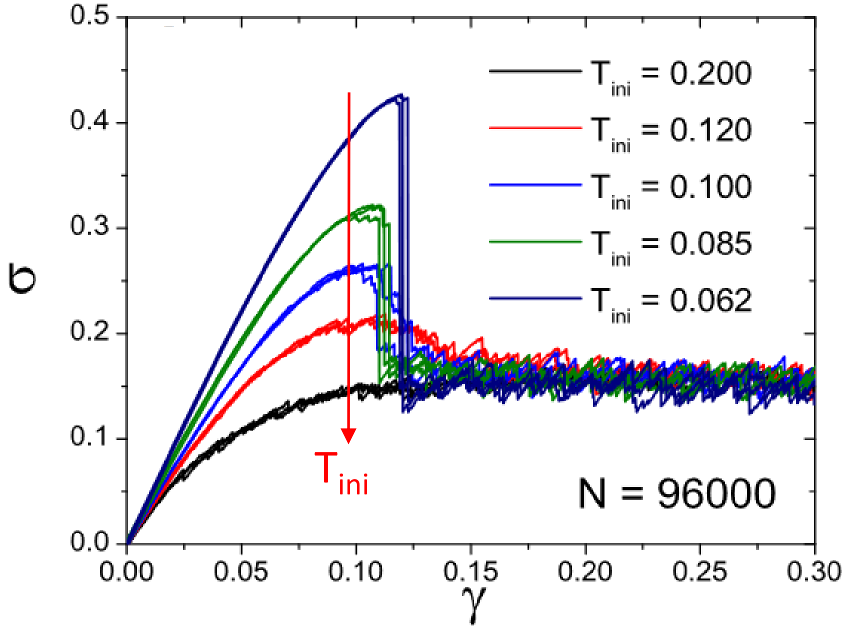
Stress overshoots are also ubiquitous in material science: metallic glasses, silica glasses, hard spheres, polymer melts and solutions…

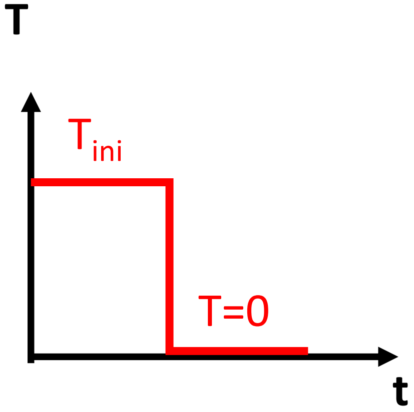
N Koumakis, A Pamvouxoglou, A S Poulos, G Petekidis, *Soft Matter* 8, 4271 (2012)

C. P. Amann, M Siebenbürger, M Krüger, F. Weysser, M Ballauff, M Fuchs, *J. Rheol.* 57, 149 (2013)

Brittle-to-ductile yielding transition of amorphous materials

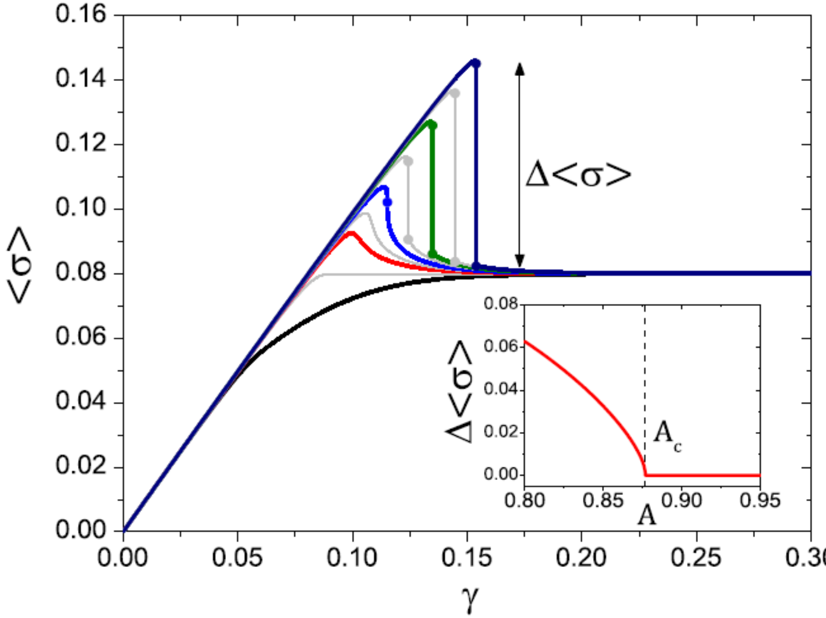
Flow simulations of thermally annealed glasses





- The system is first equilibrated at T_{ini} then quenched at T=0° and deformed

Mean-field elasto-plastic model

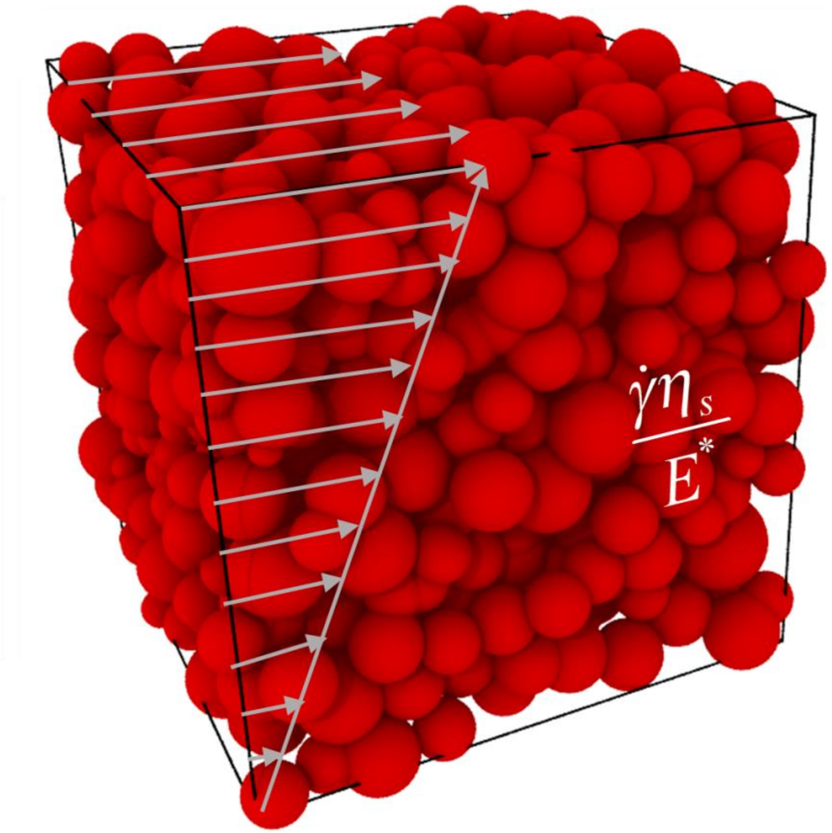


- The system is decomposed in mescoscopic blocks i={1,…,N}, each at a local stress σ_i
- The initial distribution of stresses $P_{\gamma=0}(\sigma)$ encodes the degree of annealing, which is parametrized by A (role of T_{ini})

- Three yielding behaviors: monotonic, with overshoot, brittle
- Elasto-plastic model and simulations predict different macroscopic yielding scenarios, but do not bridge the gap with the microscopic dynamics behind.

M.Ozawa, L. Berthier, G. Biroli, A. Rosso, G.Tarjus, *PNAS* 115 (2018)

Micromechanical model of soft particle glasses



Jammed suspensions of elastic and deformable particles interacting through elastic forces and lubrication forces:

$$\vec{\mathbf{v}}_\alpha = \dot{\gamma} y \vec{\mathbf{e}}_x + \bar{\bar{\mathrm{M}}}_\alpha \sum_\beta \left[\vec{\mathbf{f}}^{\,e}_{\alpha\beta} + \vec{\mathbf{f}}^{\,\mathrm{lub}}_{\alpha\beta} \right]$$

η_s : solvent viscosity

E^* : $\cong$ particle Young modulus

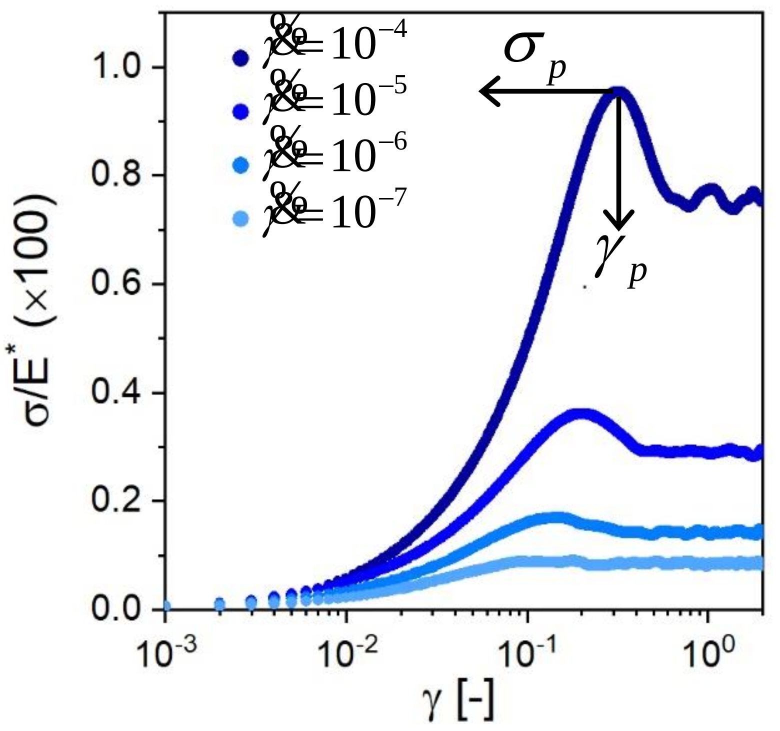
$\tilde{\dot{\gamma}} = \frac{\dot{\gamma}\eta_s}{E^*}$: non-dimensional shear rate

Initially, the suspension is fully equilibrated with zero force and torque on each particle
Then a constant shear rate is applied at *t* = 0

F. Khabaz, F. B. Di Dio, M. Cloitre, R. T. Bonnecaze, *J. Rheol.* 65, 241 (2021)
J. R. Seth, L. Mohan, C. Locatelli, M. Cloitre, R. T. Bonnecaze, *Nature Materials* 10, 838 (2011)

Startup flow response of model soft particle glasses

Volume fraction: 0.8



Simulations reproduce the behaviors found in experiments

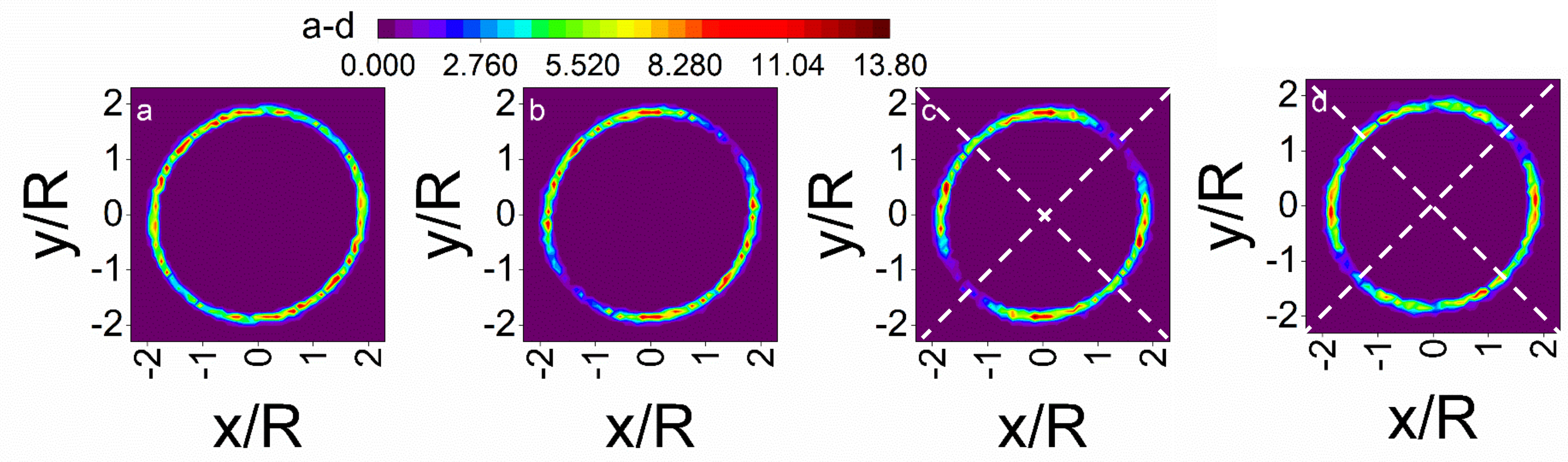
σ_p and γ_p are the static yield stress and stain, respectively

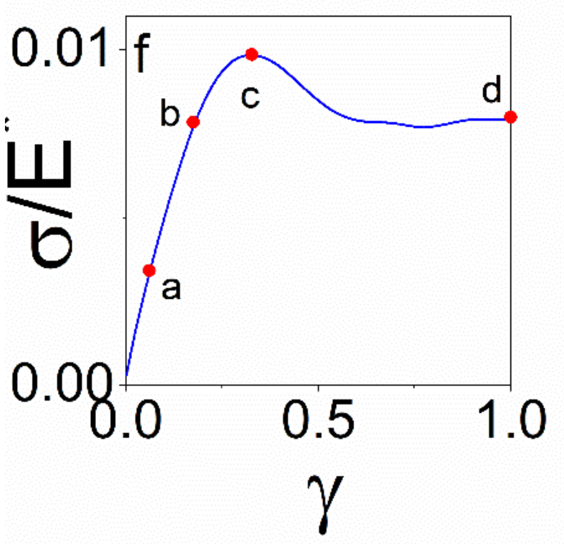
Simulated results correspond to experiments:

- monotonic at low shear rates
- stress overshoot at high shear rates

F. Khabaz, B.F. Di Dio, M. Cloitre, R. T. Bonnecaze, *J. Rheol.* **65**, 241 (2021)

Yielding at the microscopic scale





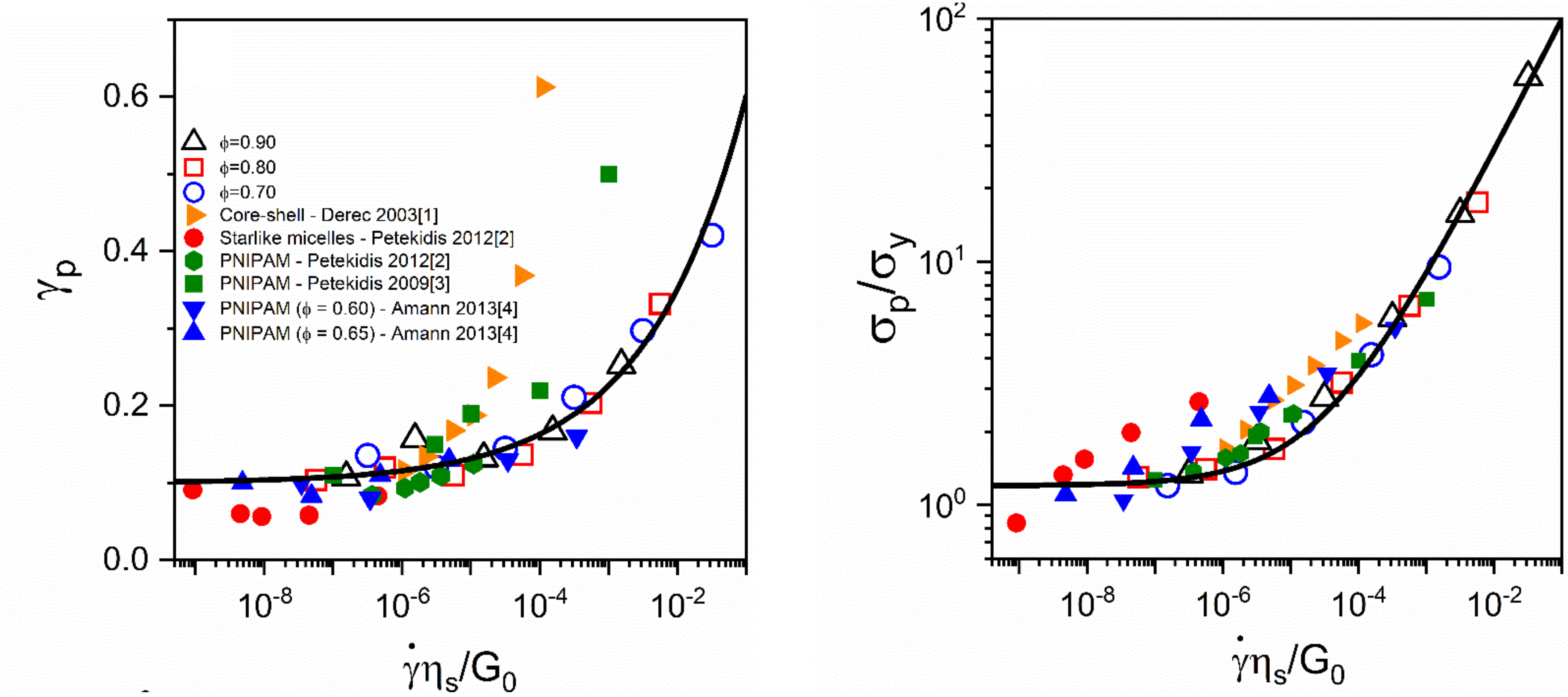
The peak overshoot and the stress at steady-state are controlled by the asymmetry of the pair distribution function

At the stress overshoot there is an extra asymmetry which is released as the particles rearrange and gets more compressed

The asymmetry slowly relax after flow cessation

F. Khabaz, B.F. Di Dio, M. Cloitre, R. T. Bonnecaze, *J. Rheol.* 65, 241 (2021)
L. Mohan, M. Cloitre, R. T. Bonnecaze, *J. Rheol.* 59, 63 (2015)

Comparison with data from literature

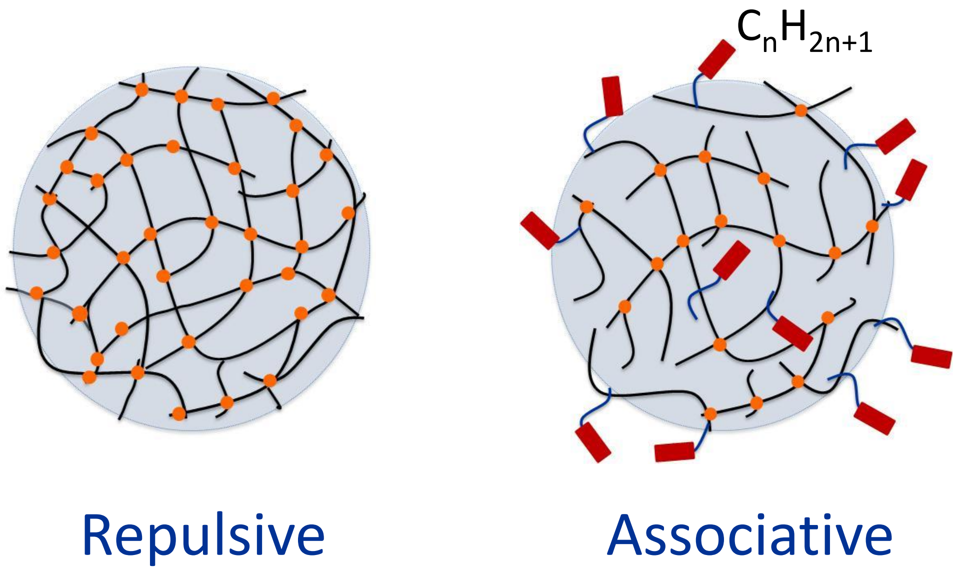


Systematic well-controlled experiments are needed

Stimuli-responsive microgels

Stimuli responsive (pH)

Semi-batch synthesis
Continuous
Starved conditions

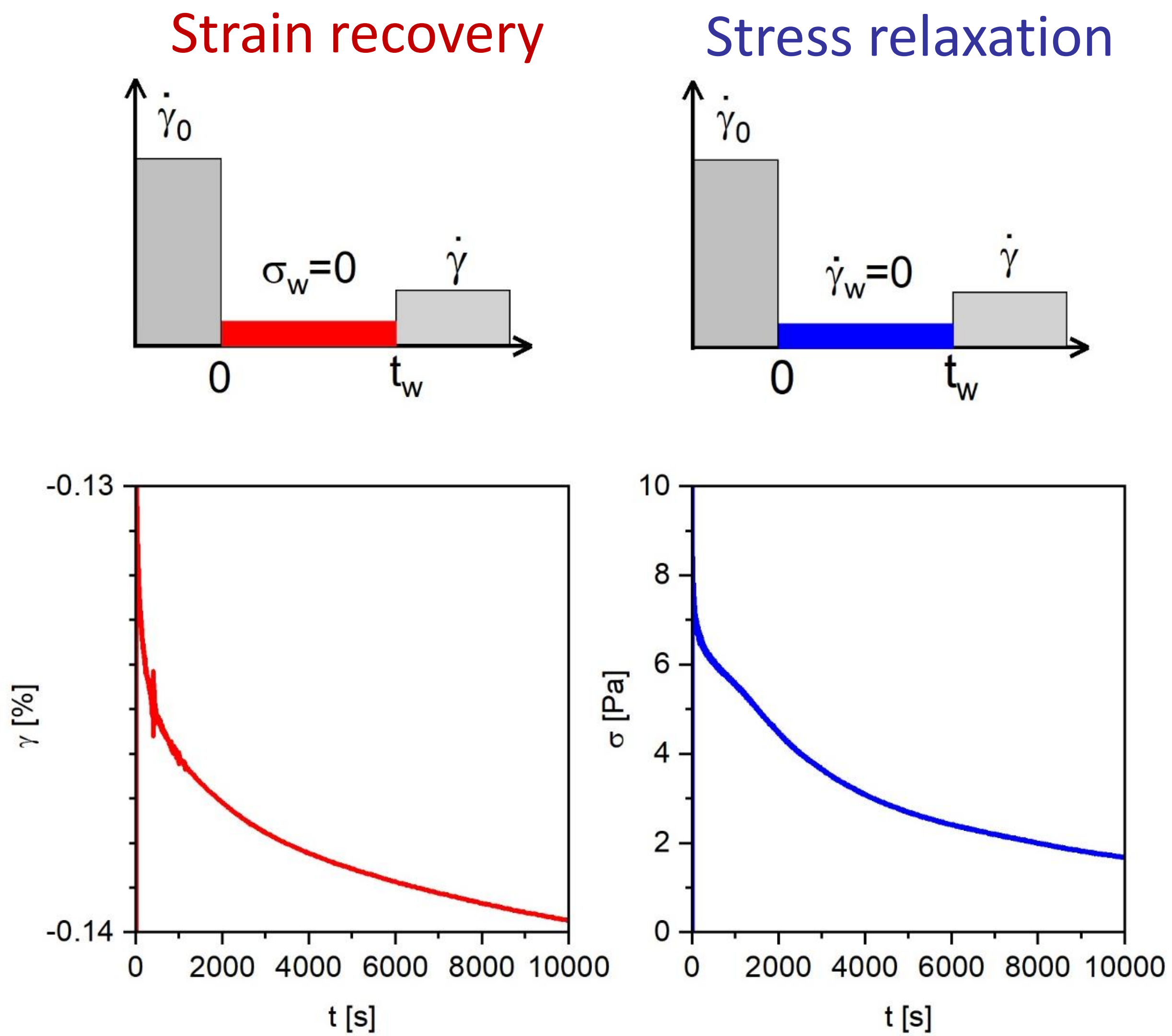


Particles swollen with water (99%)
$R_H \cong 200$ nm
No dangling ends

Parameters:

- nature and quantity of crosslinker
- spatial distribution of crosslinks

Effect of preparation protocol

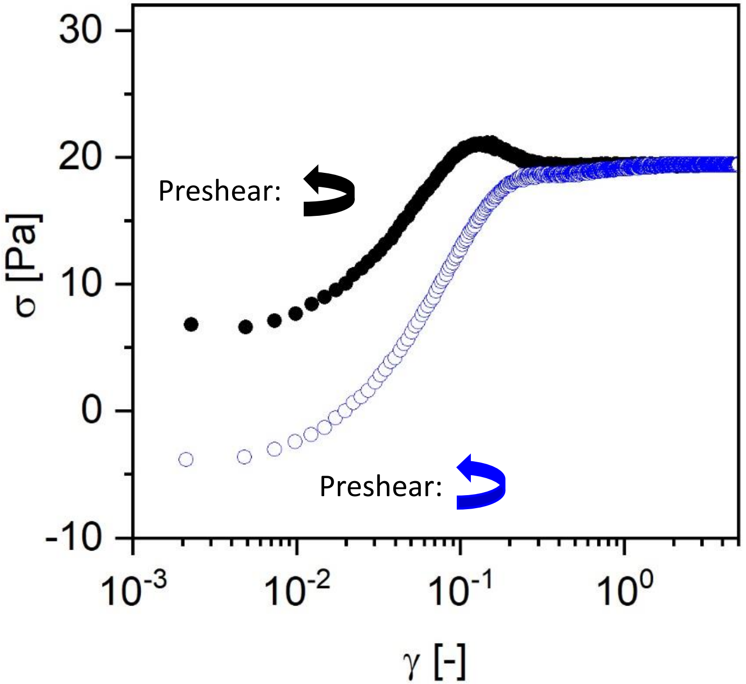


Preshear prepares the suspension in a reproducible state but …. subsequent measurements probe out-of-equilibrium materials

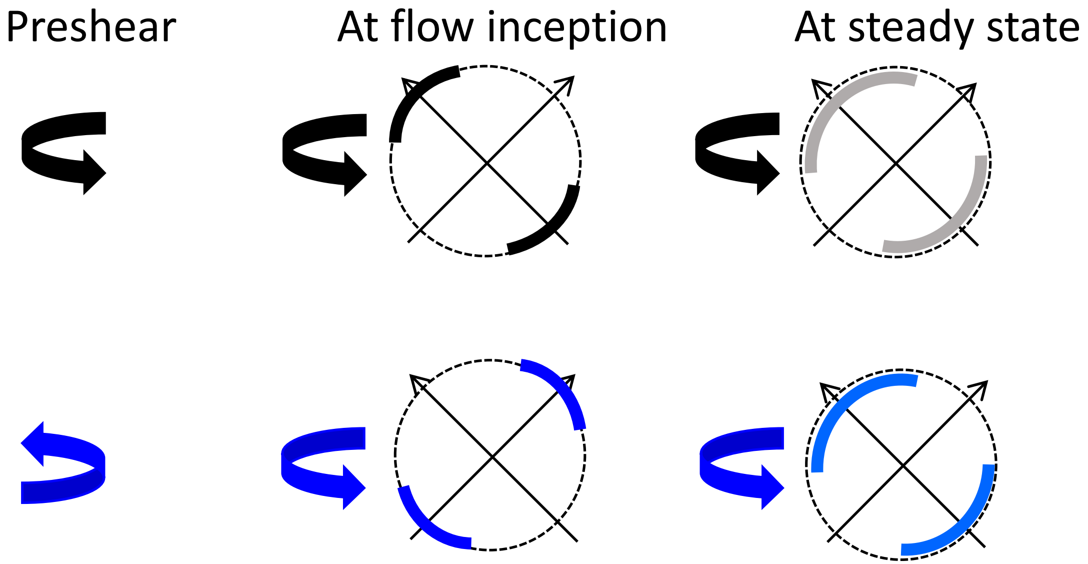
L. Mohan, R. T. Bonnecaze, M. Cloitre, *Phys. Rev. Lett.* 111, 268301 (2013)
L. Mohan, M. Cloitre, R. T. Bonnecaze, *J. Rheol.* 59, 63 (2015)
M. Cloitre, R. Borrega, L. Leibler, *Phys. Rev. Lett.* 85, 4819 (2003)

I : Mechanical memory: quantifying the mechanical bias

$\dot{\gamma}_w = 0$



Distortions of the pair correlation function



Long-lived distortions of the pair correlation function imprints directional memory inside SPGs

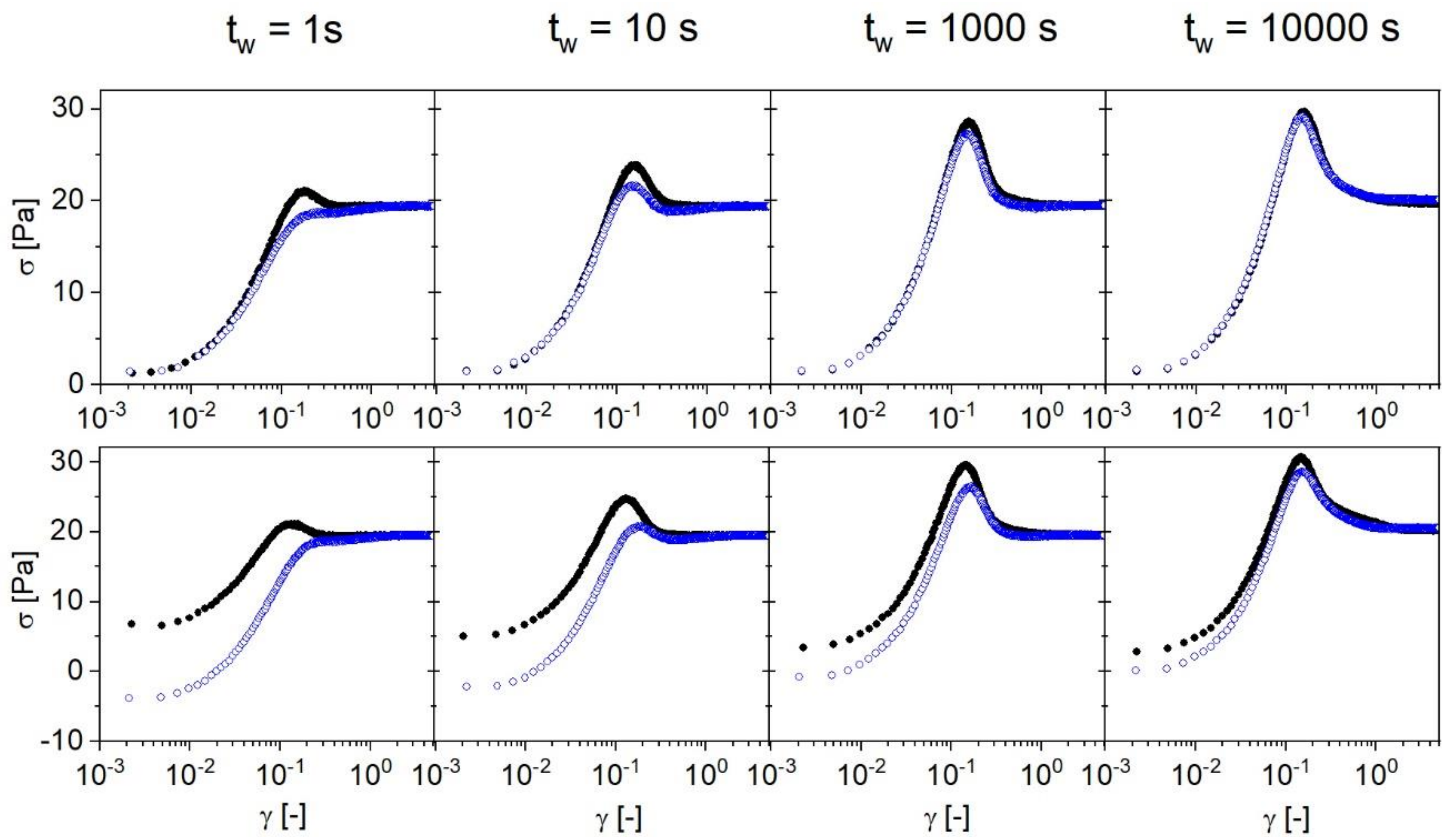
The response is not reversible when the preshear direction is reversed

See also: W. Letwimolnun, B. Vergnes, G. Ausias, P.J. Carreau, *J. Non-Newtonian Fluid Mech.* 141, 167 (2007)
J. Choi and S. A. Rogers, *Rheol. Acta* 59, 921 (2020)

Erasing directional memory

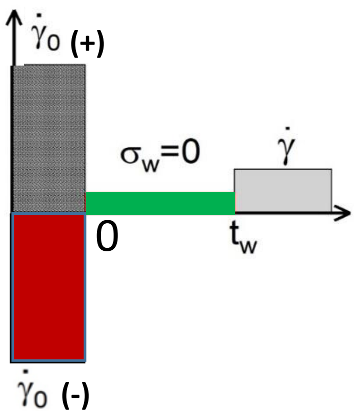
$\sigma_w = 0$

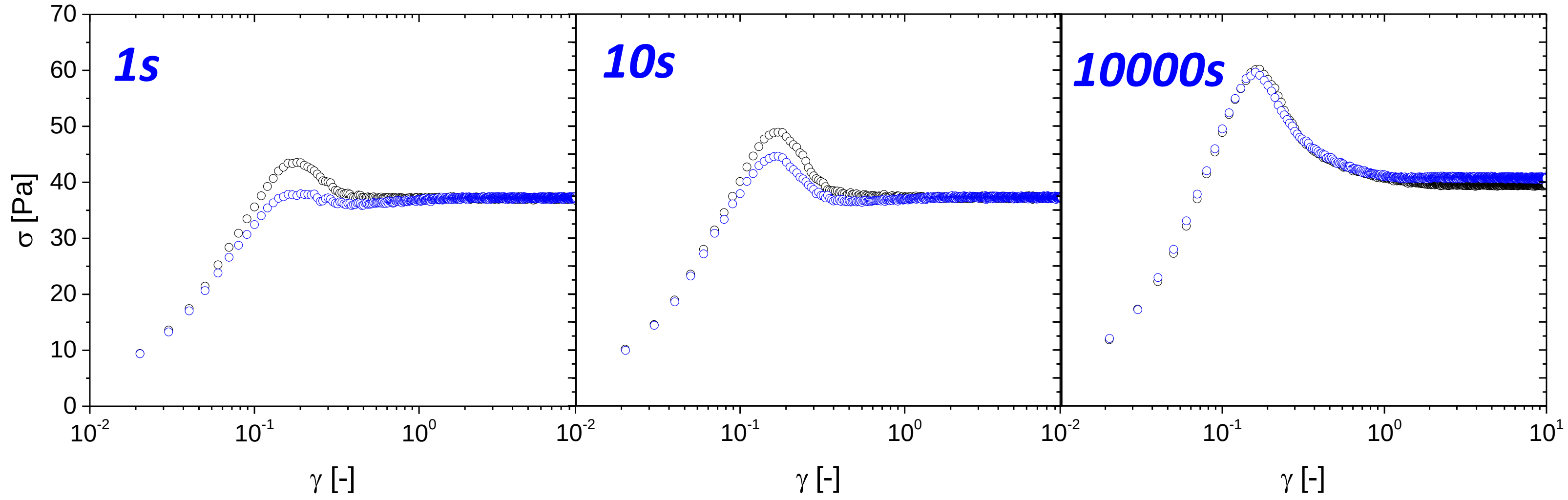
$\dot{\gamma}_w = 0$

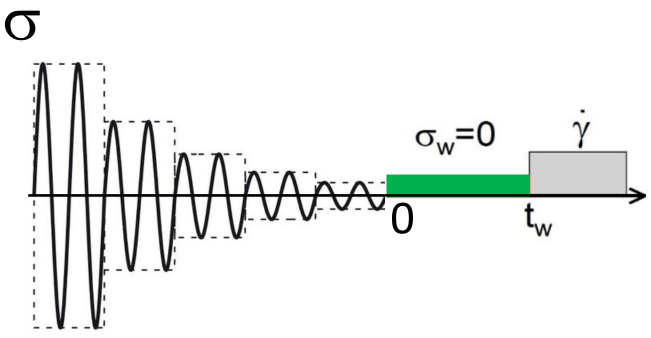


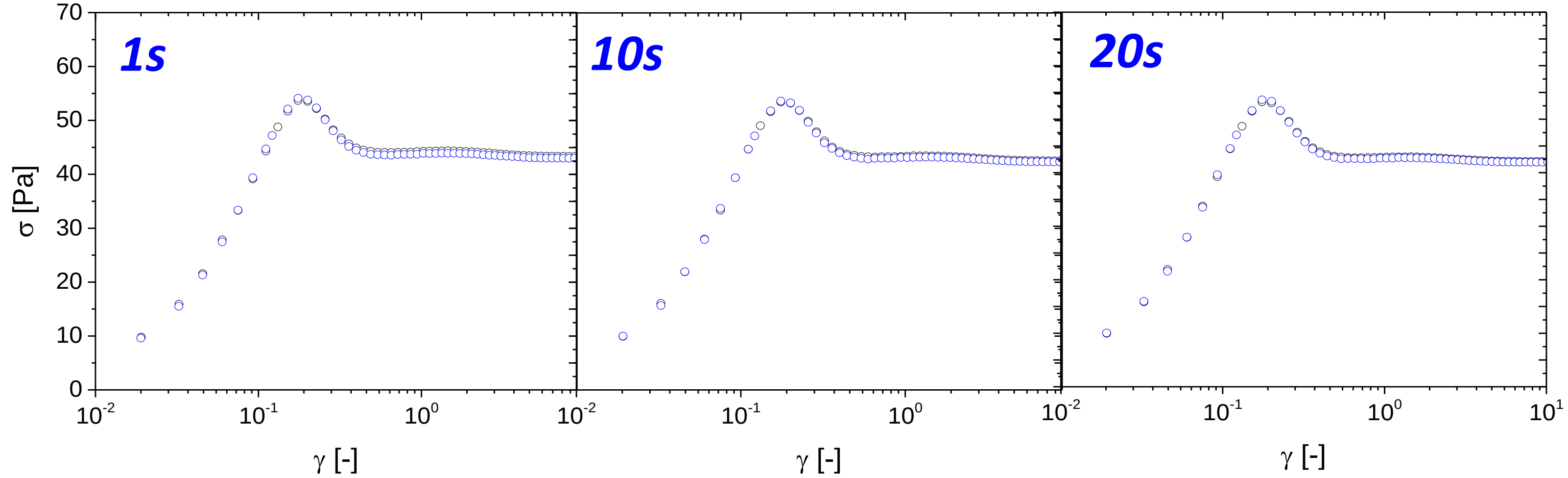
Imposing $\sigma_W = 0$ after preshear for long enough t_w ensures reversibility, i.e. erase the directional memory

Erasing directional memory… more







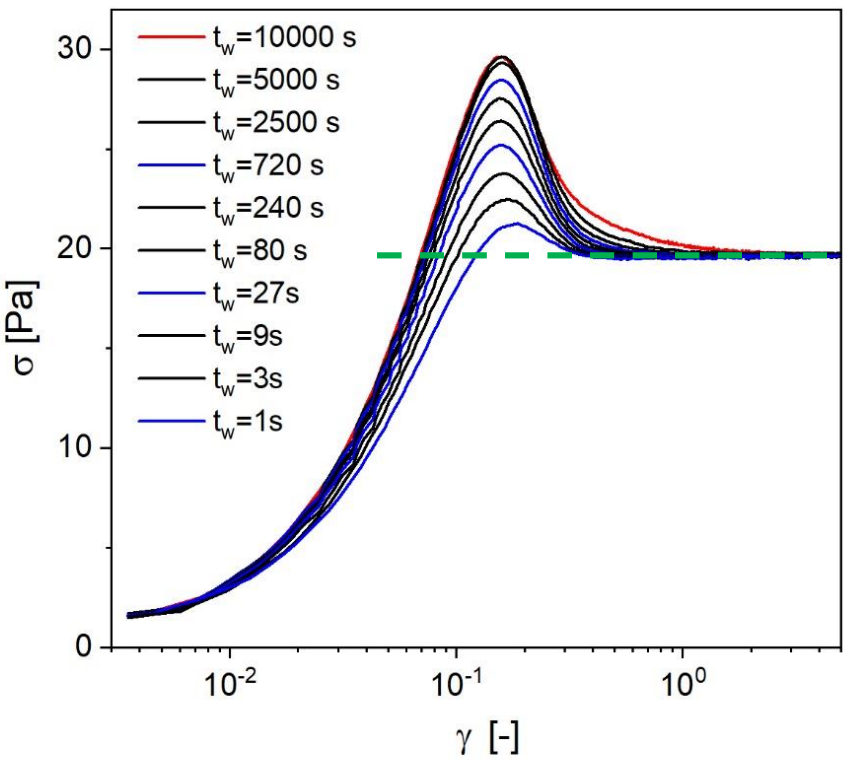


Stress-controlled oscillatory preshear with a decreasing amplitude ensures reversibility even at short t_w

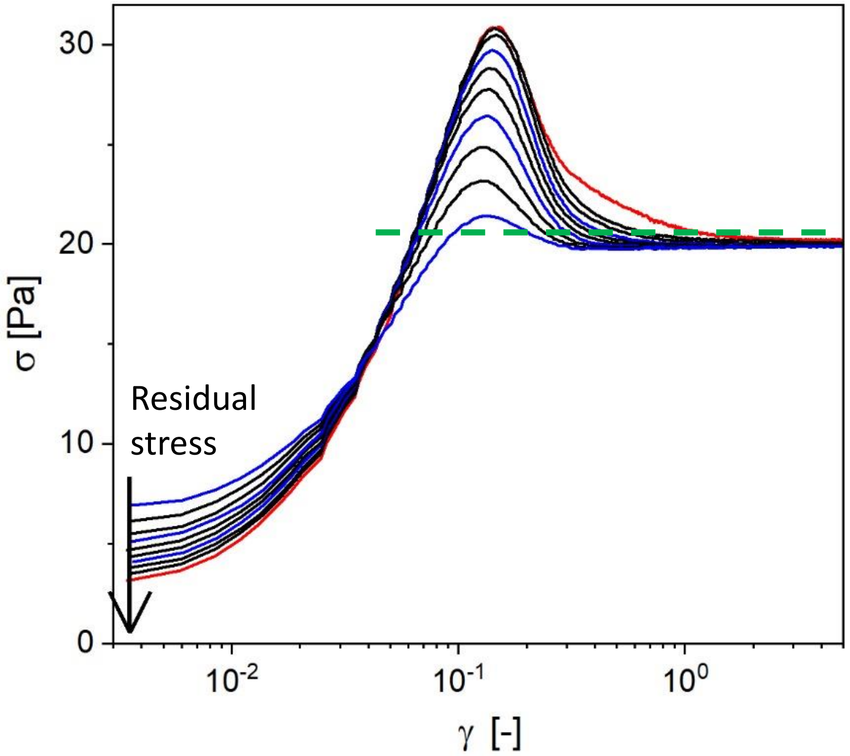
With Paolo Edera – ESPCI (ongoing work)

II : Aging

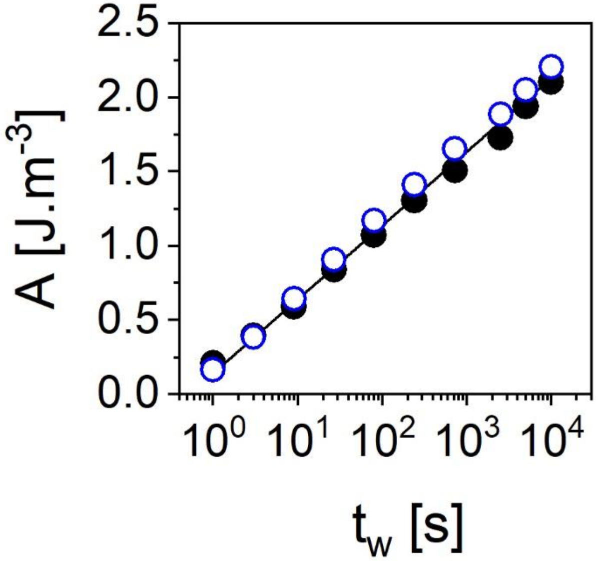
$\sigma_w = 0$



$\dot{\gamma}_w = 0$



$$U = \frac{1}{2}\int_{peak} \sigma(\gamma)d\gamma$$



Yielding energy is a logarithmic function of time

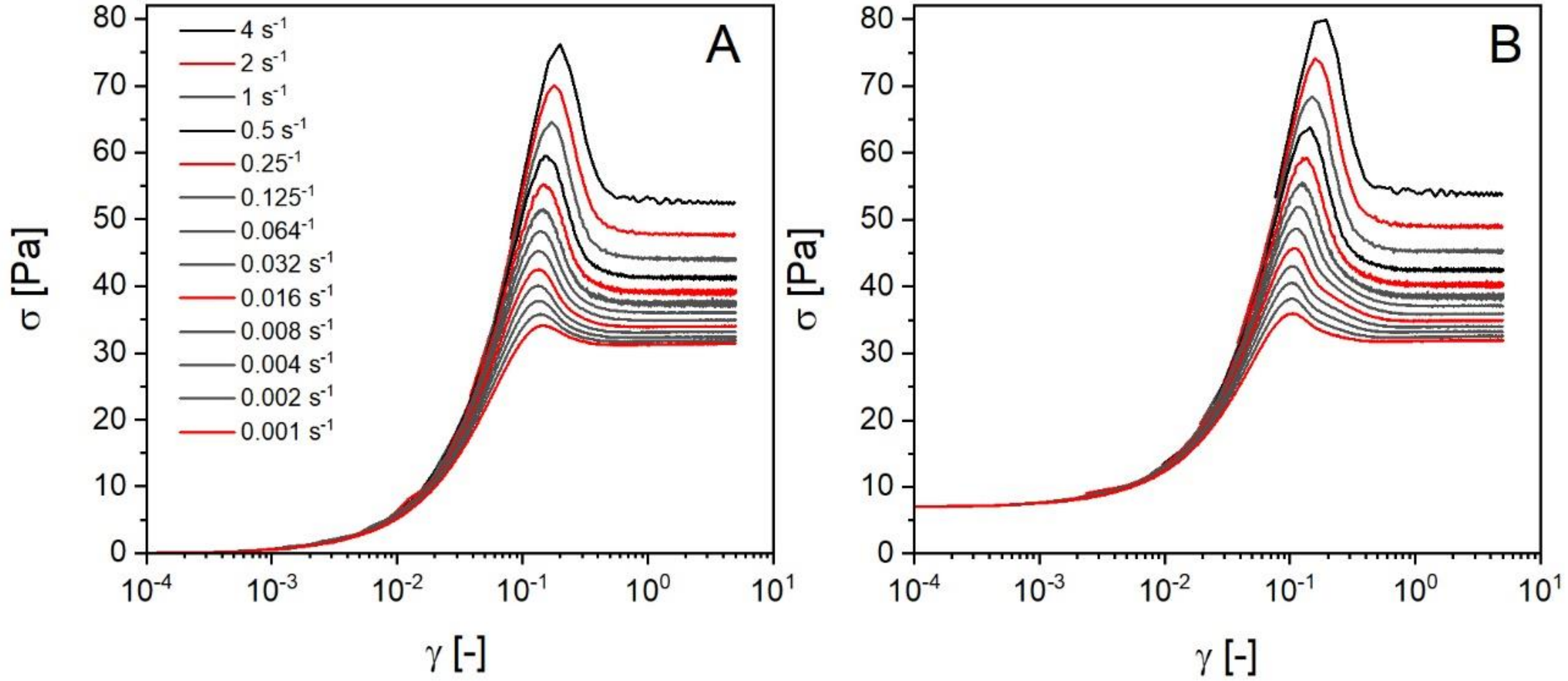
Strain recovery or stress relaxation slightly matters

Aging takes place even if there is no (macroscopic)residual stress

M. A. Lomholt, L. Lizana, R. Metzler, T. Ambjörnsson, Phys. Rev. Lett. 110, 208301 (2013)

Yielding at different shear rates (t_W=1000 s)

$\sigma_w = 0$ $\qquad\qquad$ $\dot{\gamma}_w = 0$

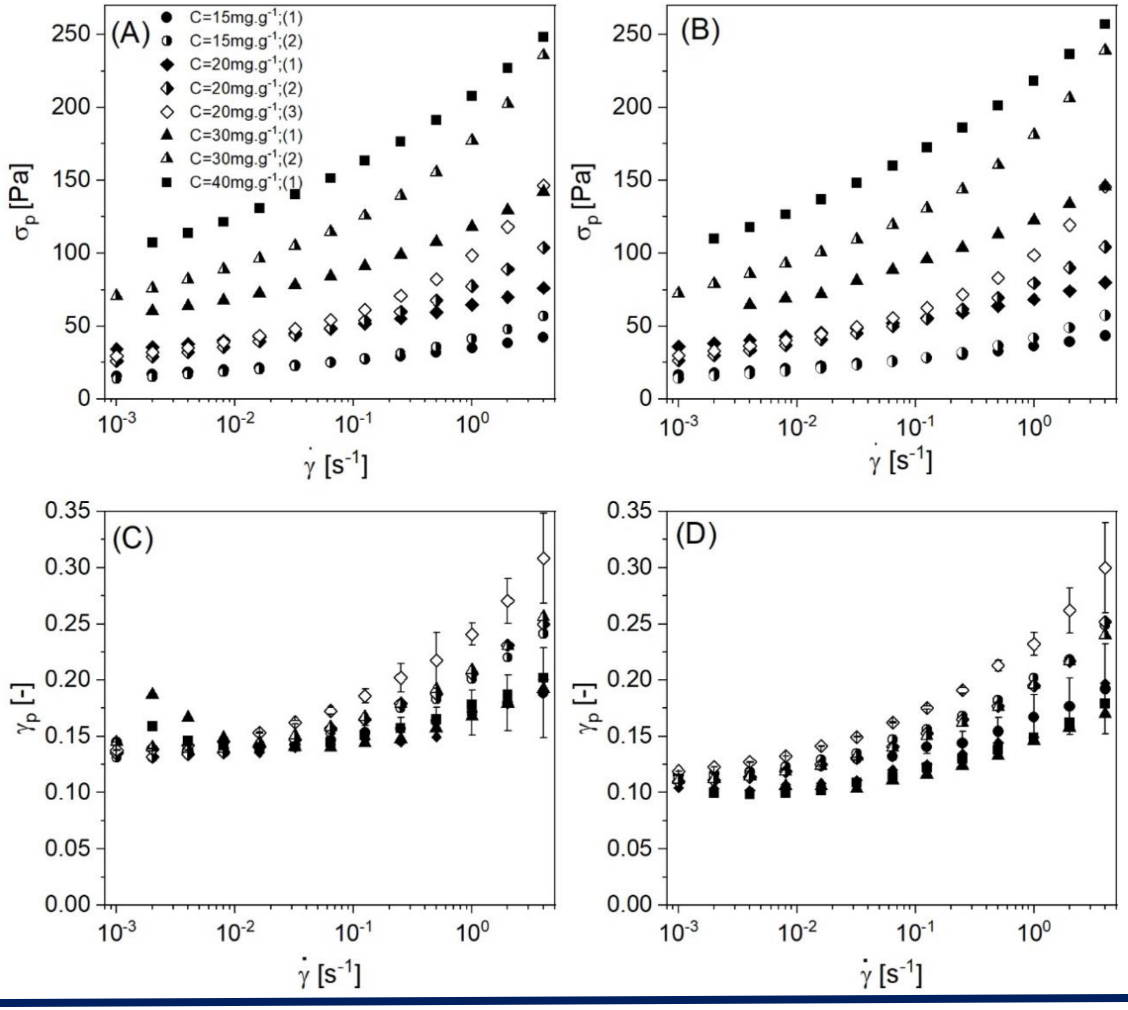


Yielding is monotonous for low applied shear rates

Static yield point exists at high enough shear rates

Yield stress and yield strain variations

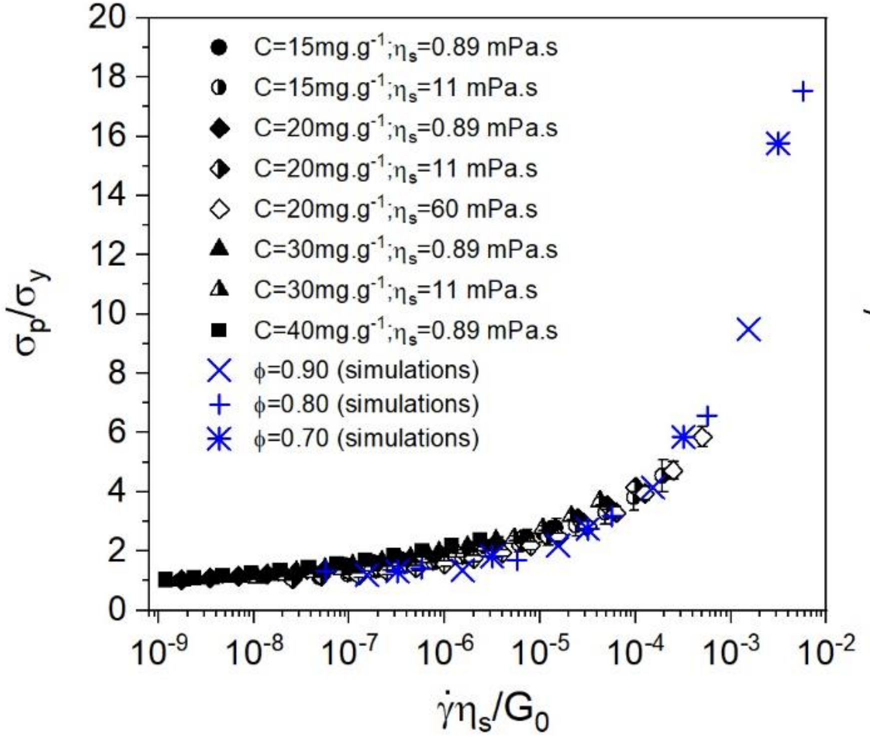
$\sigma_w = 0$ $\dot{\gamma}_w = 0$



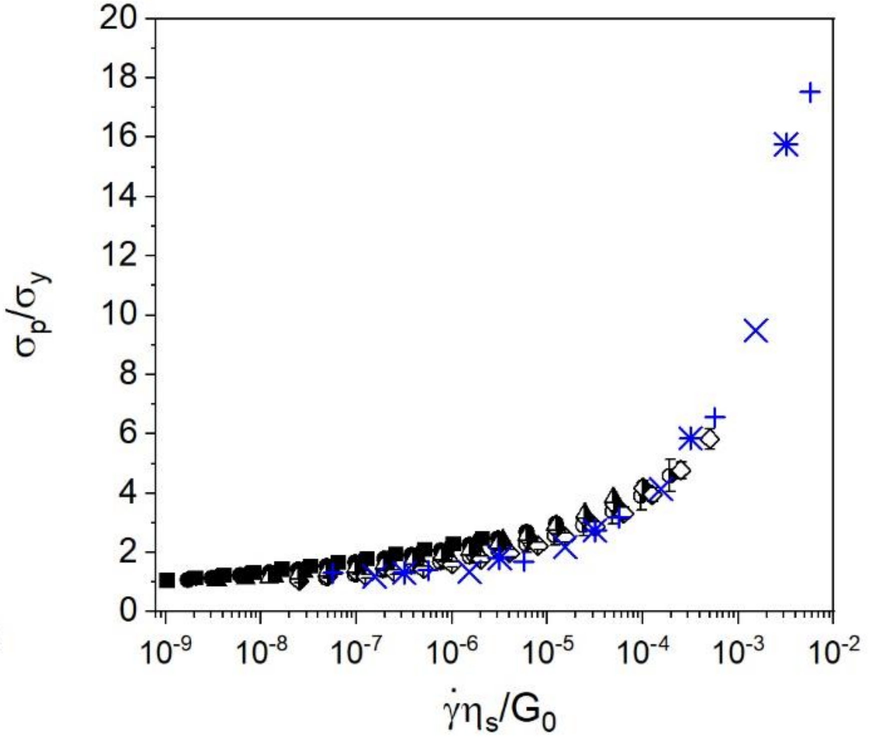
Concentration and suspending fluid viscosity are varied

Scaling of the static yield stress

$\sigma_w = 0$



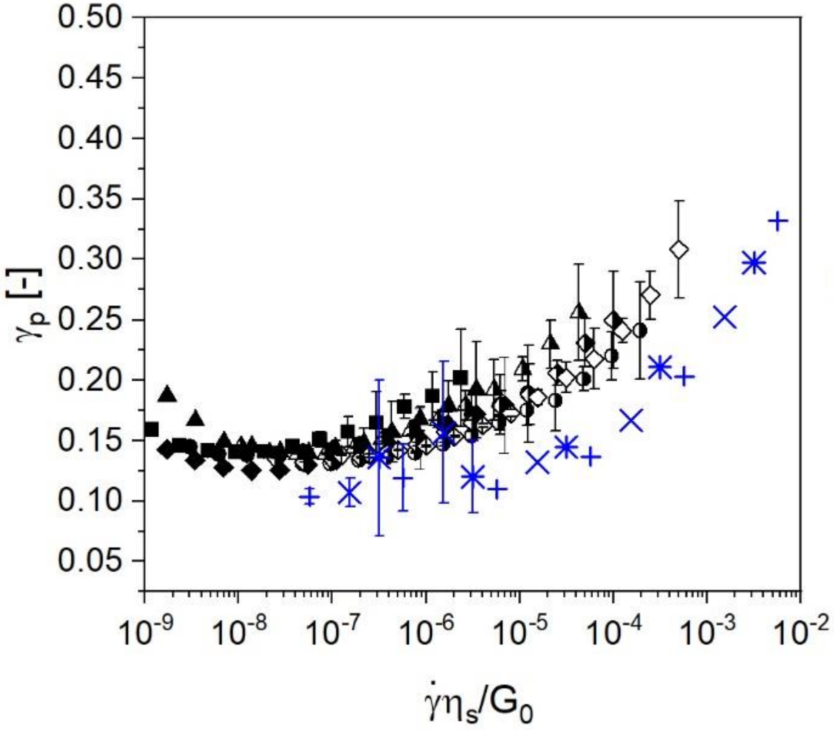
$\dot{\gamma}_w = 0$



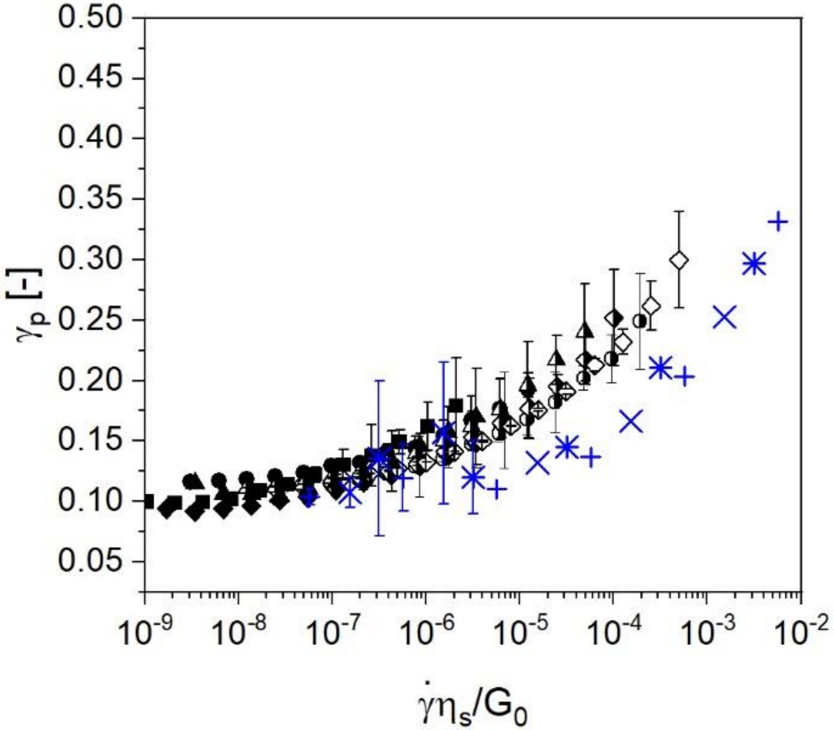
The non dimensional variable $\dot{\gamma}\eta_s / G_0$ successfully collapses the data. The predictions of the micromechanical model agree with the experiments

Scaling of the static yield strain

$\sigma_w = 0$

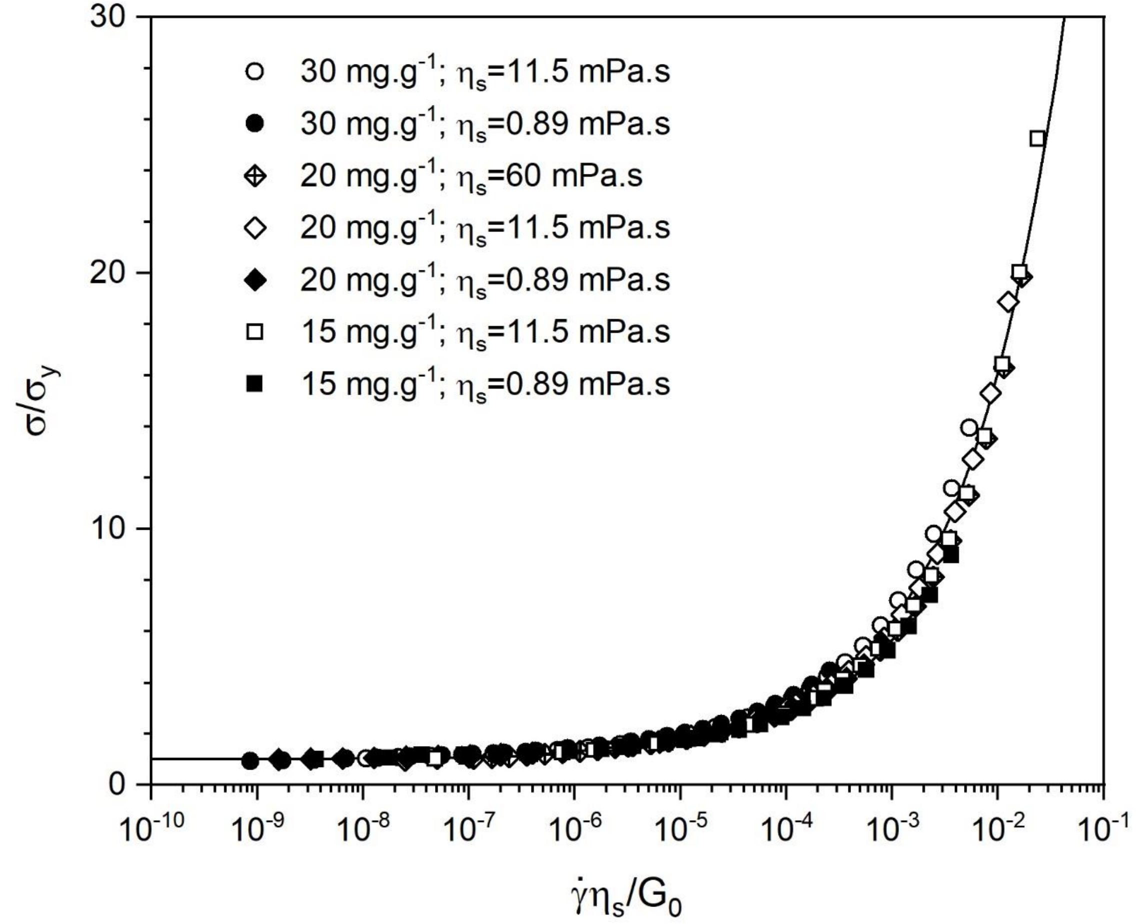


$\dot{\gamma}_w = 0$



The non dimensional variable $\dot{\gamma}\eta_s / G_0$ successfully collapses the data but the predictions of the micromechanical model slightly underestimates experiments
The mechanical preparation makes difference (still a memory of the preshear?)

Steady-flow mechanisms



Particles are trapped in cages. Flow proceeds through particle rearrangements. The duration of a rearrangement varies like η_s / G_0

$\dot{\gamma}\eta_s / G_0 \ll 1$: cages plastically deform and break intermittently. Stress build-up is monotonic

$\dot{\gamma}\eta_s / G_0 \gg 1$: cages respond elastically and break. There is a static yield stress

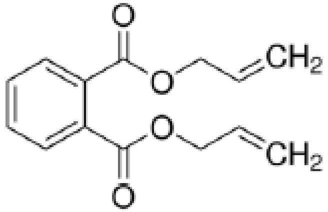
T. Liu, F. Khabaz, R. T. Bonnecaze, M. Cloitre, *Soft Matter* 14, 7064 (2018)
F. Khabaz, M. Cloitre, R. T. Bonnecaze, *J. Rheol.* **64**, 459 (2020)

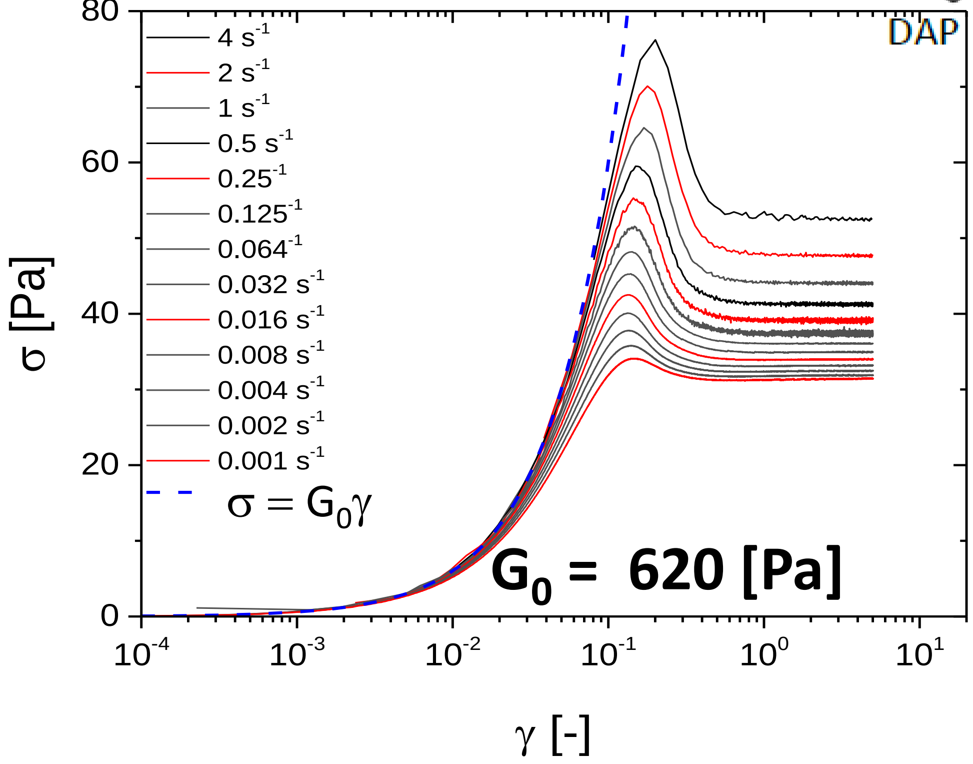
M. Cloitre, R. Borrega, F. Monti, L. Leibler, *Phys. Rev. Lett.* **90**, 068303 (2003)

Effect of microstructure on yielding behavior

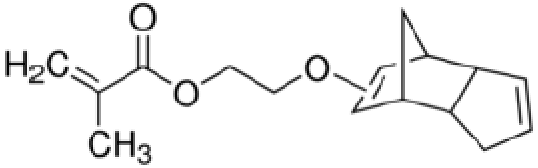
Same synthesis but different crosslinkers

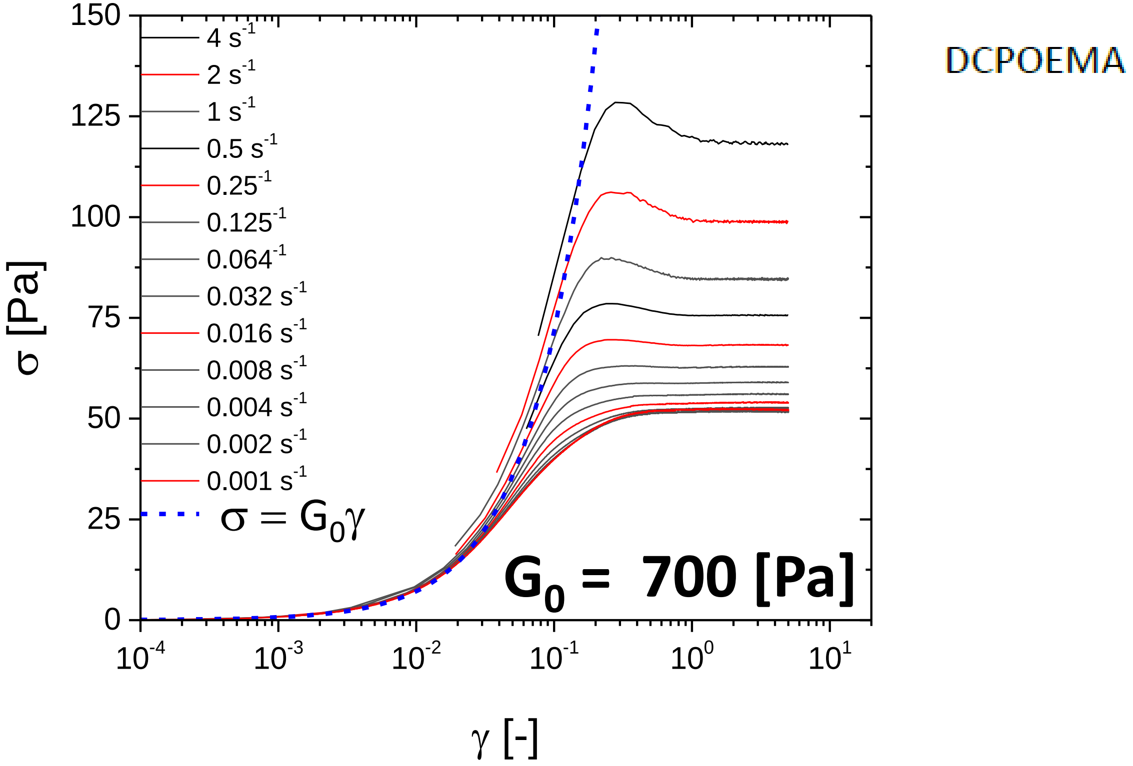
Crosslinker: 0.4% mol





Crosslinker (0.4% mol):

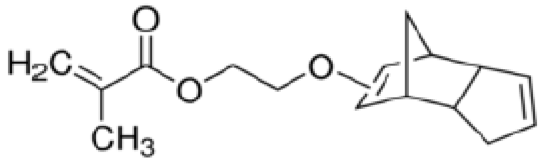


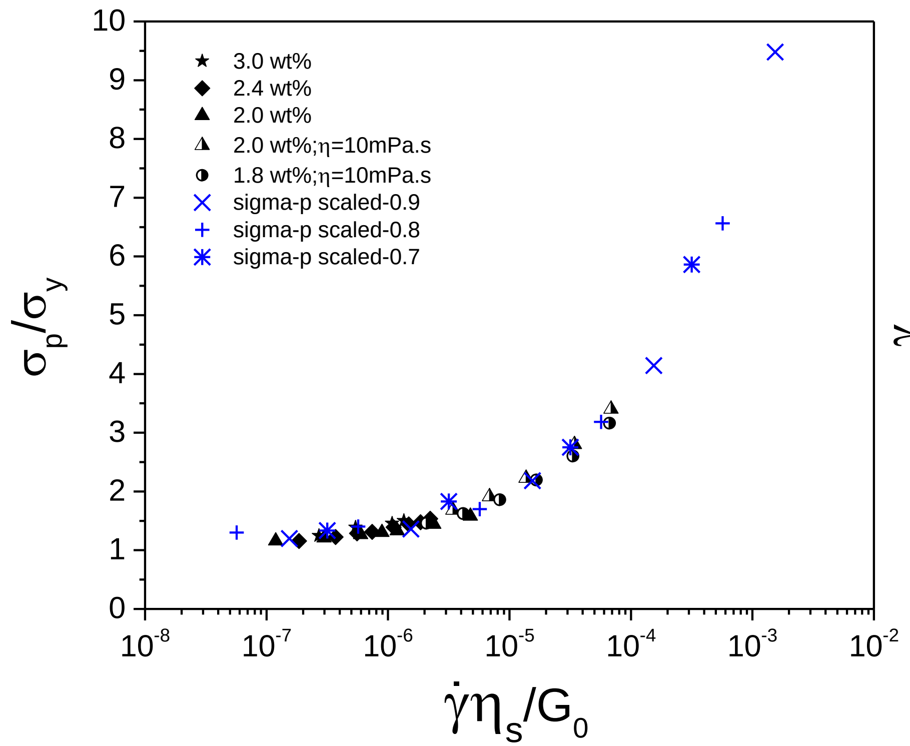


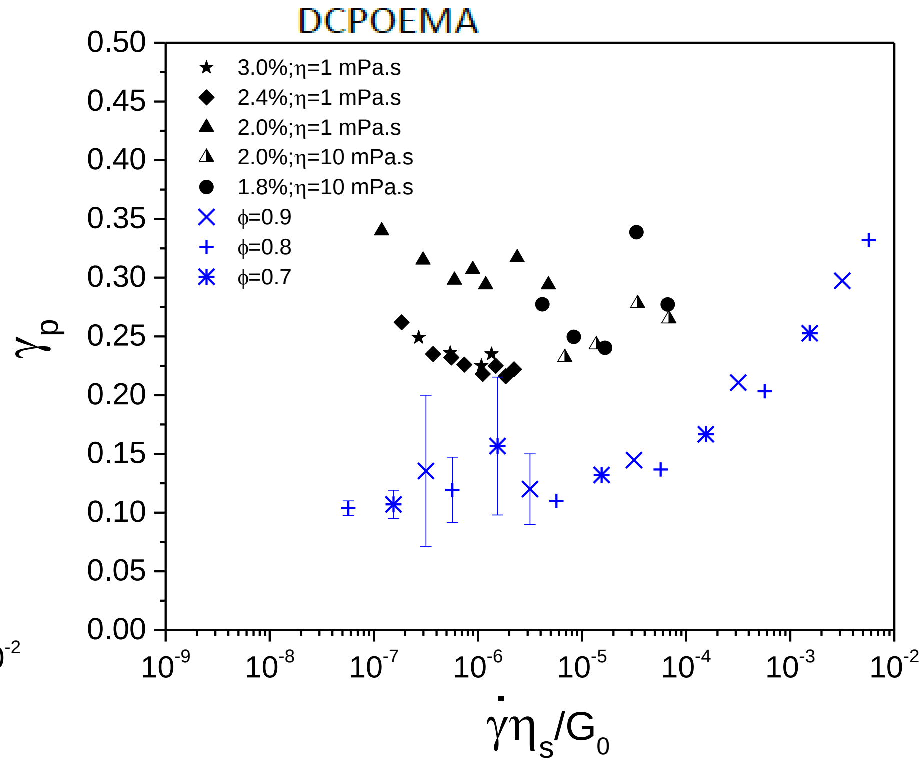
Changing the synthesis/crosslinker, and consequently the microstructure, makes difference: a clear monotonic to non-monotonic yielding is observed when the shear rate is increased in the case of particles crosslinked with DCPOEMA

Effect of microstructure on scaling of properties

Crosslinker (0.4% mol):

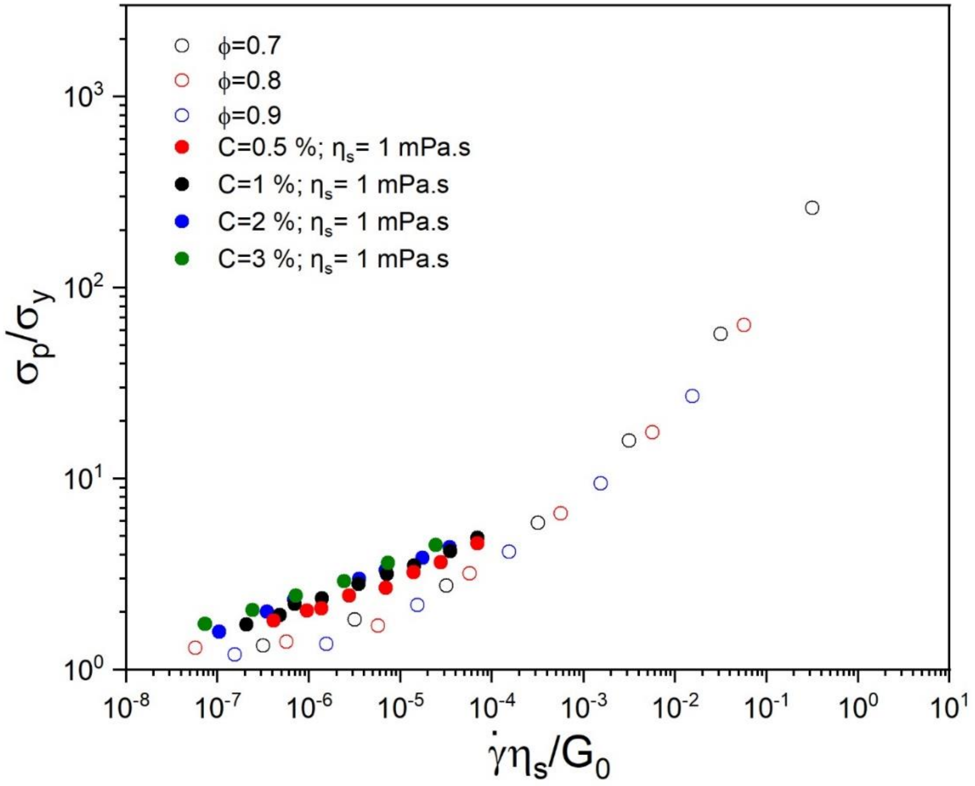


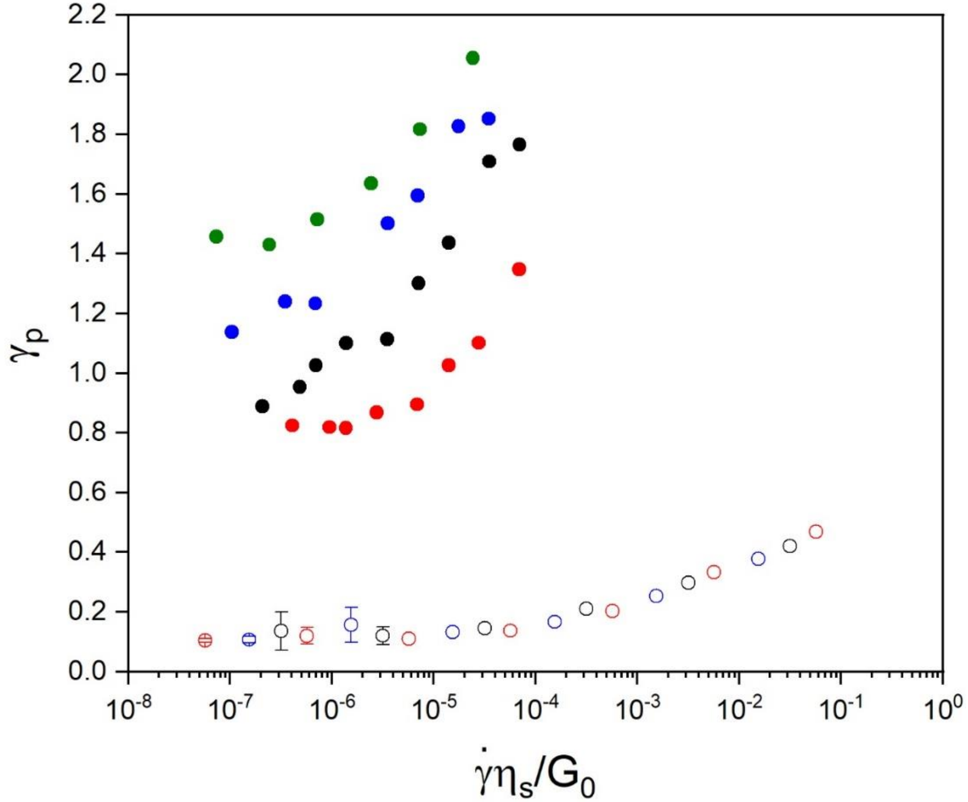




- Need for analysis of microstructure (SAXS)
- Investigation of simpler particles: concentrated emulsions

Comparison with recent data from the literature

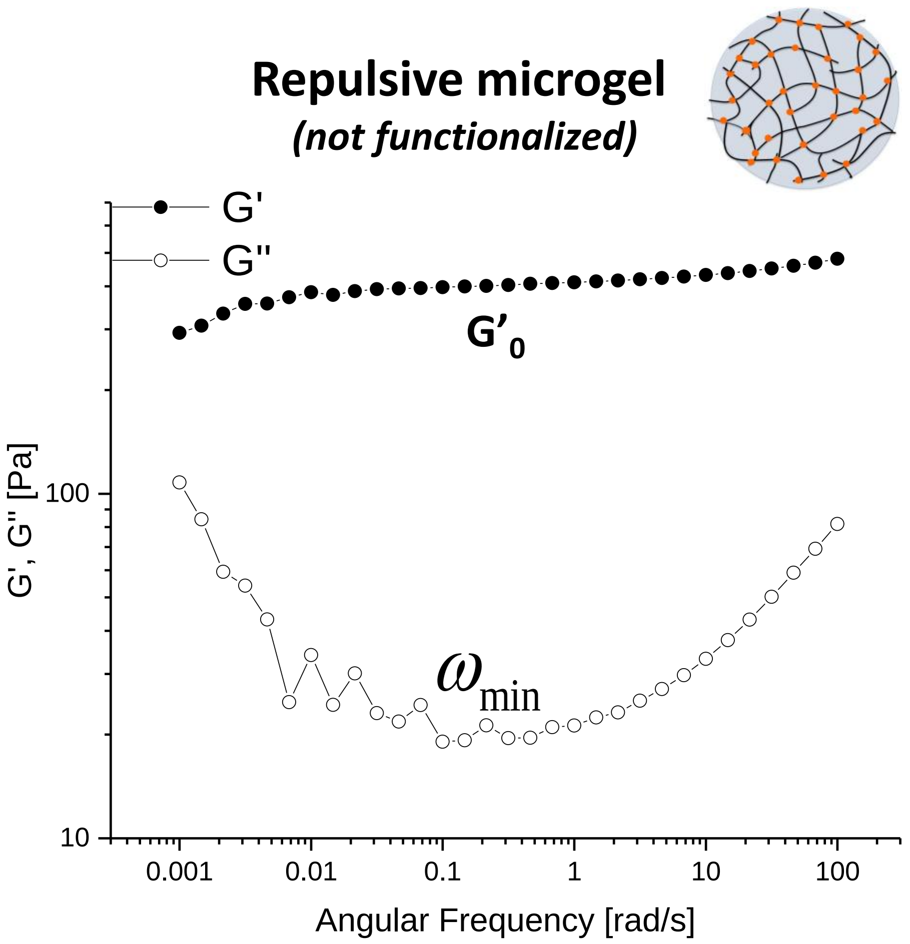


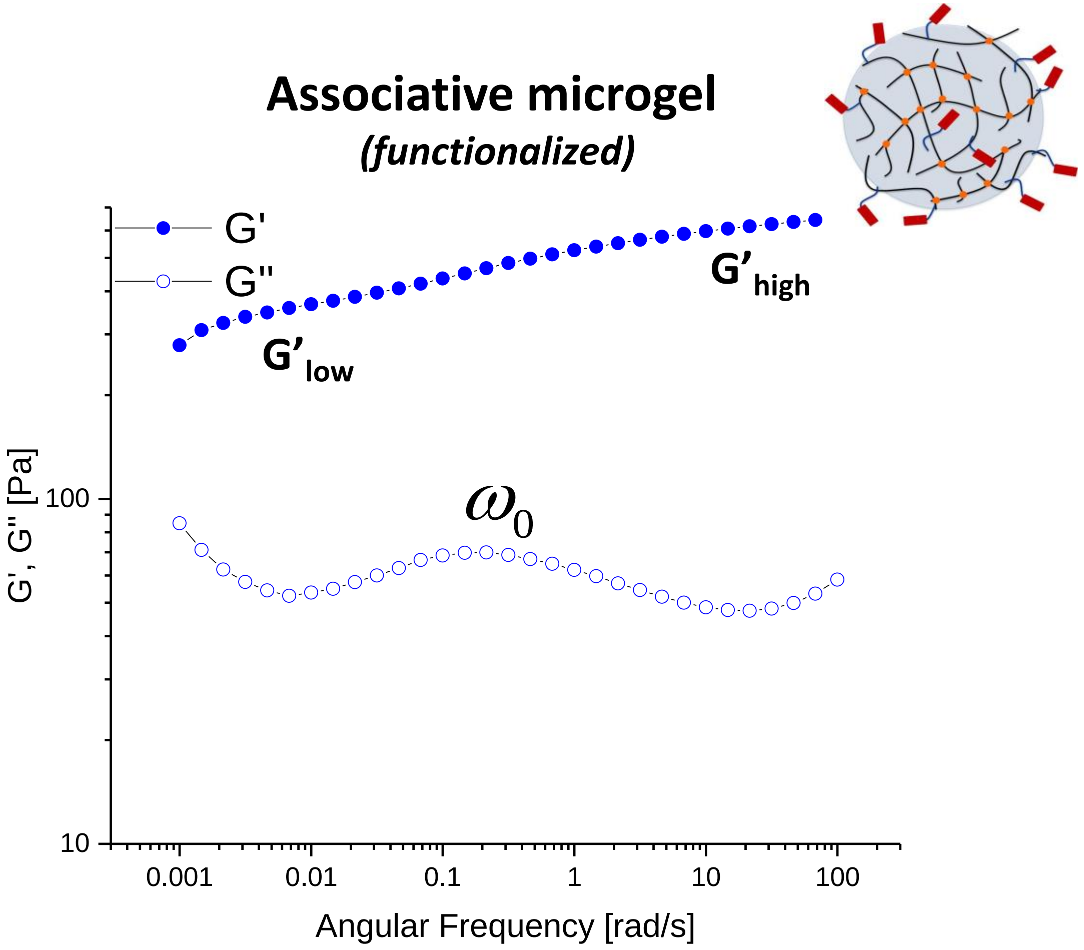


The non dimensional variable $\dot{\gamma}\eta_s / G_0$ successfully collapses the yield stress data
Strong disagreement between the static yield stress data in simulations and Carbopol
The values of γ_p for Carbopol are much larger than expected for colloids (structure of Carbopol particles?)

R. Benzi, T. Divoux, C. Barentin, S. Manneville, M. Sbragaglia, and F. Toschi, *Phys. Rev. Lett.* 127, 148003 (2021)

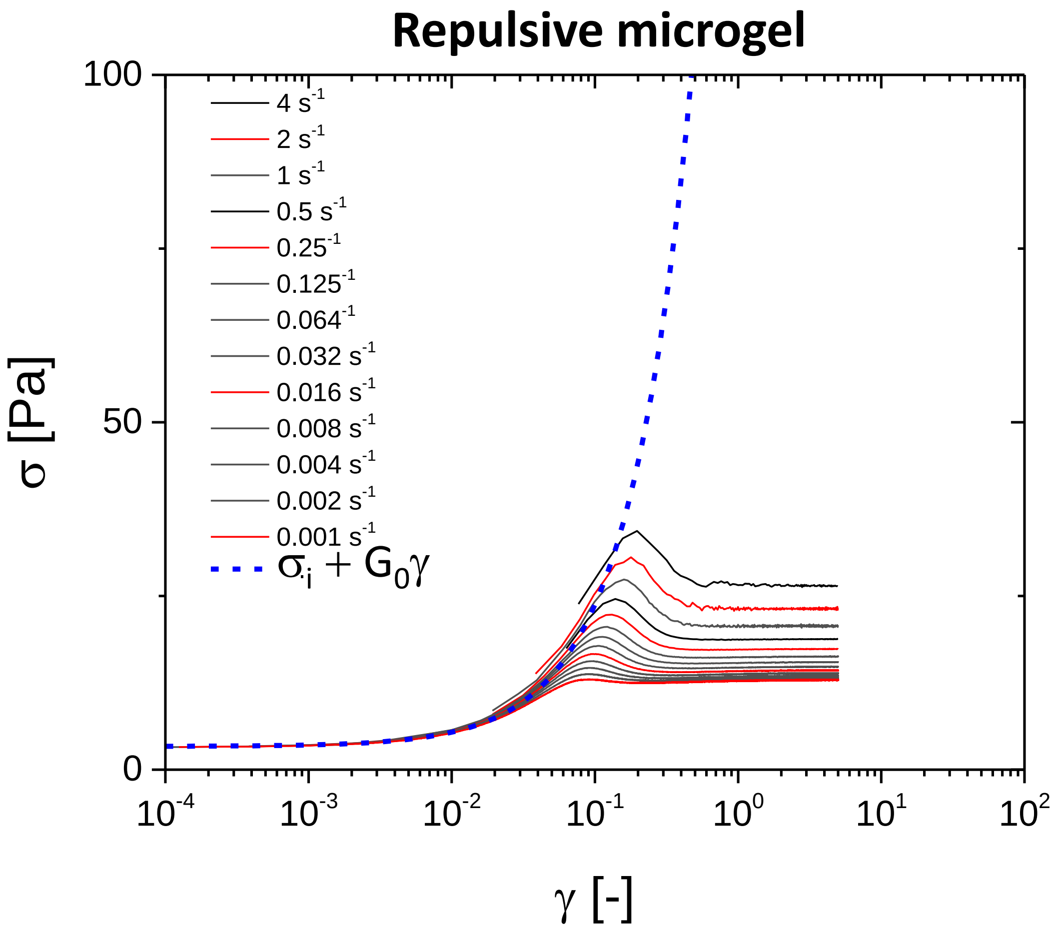
Effect of inter-particle interactions: linear viscoelasticity

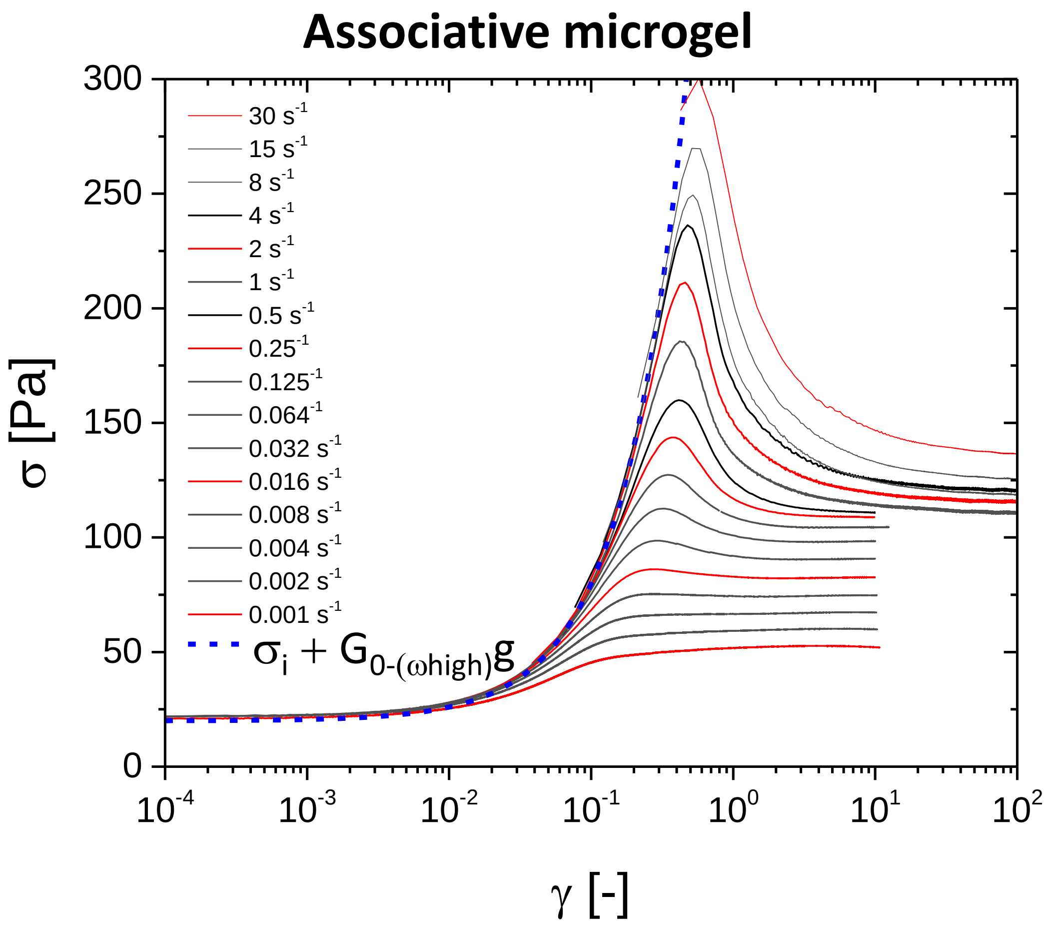




- Same particle but different functionalization
- Both suspensions behave as a viscoelastic solid (G'>>G'')
- Associative microgel suspensions are characterized by two elastic moduli: $G_{\omega high}$ and $G_{\omega low}$

Effect of inter-particle interactions: startup flow





- Linear elastic response ~ $\gamma G'_{high\_\omega}$ at high shear rates (gel vs. glass)
- The values of γ_p for associative microgels are much larger than for repulsive particles
- At shear rates tested, the cooperative in-cage associations are effective

Conclusions

The static yield stress and the stress at steady-state have a common microscopic origin. The consequence is that they exhibit similar scaling properties

The static yield strain seems to depend on the nature of interaction between particles

It is essential to implement a preparation protocol that minimizes directional memory

The amplitude of the peak stress increases with the age of the system and (slightly) depends on the annealing protocol

The local relaxation time η_s/G_0 controls the static yield stress and the stress at steady-state scaling, whose data can be fully collapsed by the non dimensional shear rate $\dot{\gamma}\eta_s/G_0$

Adknowoldgements

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Fardin Khabaz

Stefano Aime
Paolo Edera

Jean-Marc Suau