Supramolecular double-networks based on microgels with reversible covalent interactions

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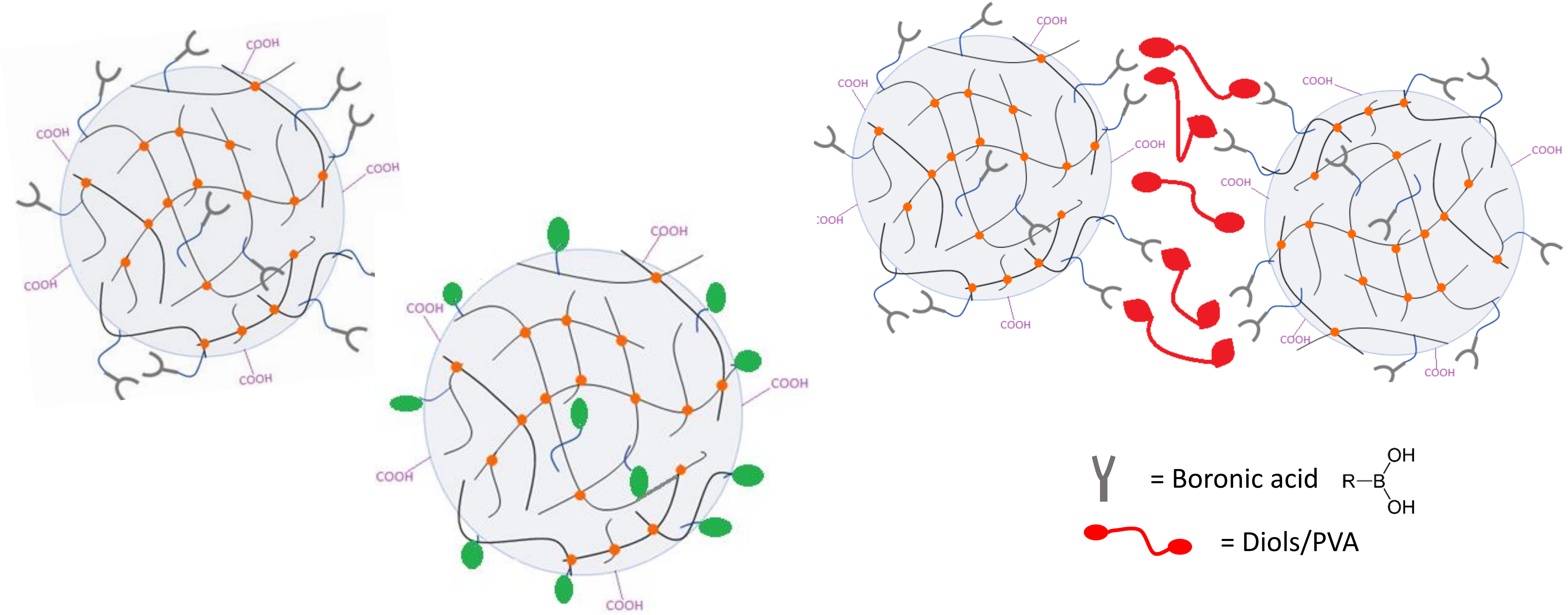
Outline

- Objective of the project
- Methods
- Repulsive microgels
  - Linear viscoelastic properties
  - Flow properties
  - Shear start-up flow
  - Ageing: waiting time-dependence
- Interpretation

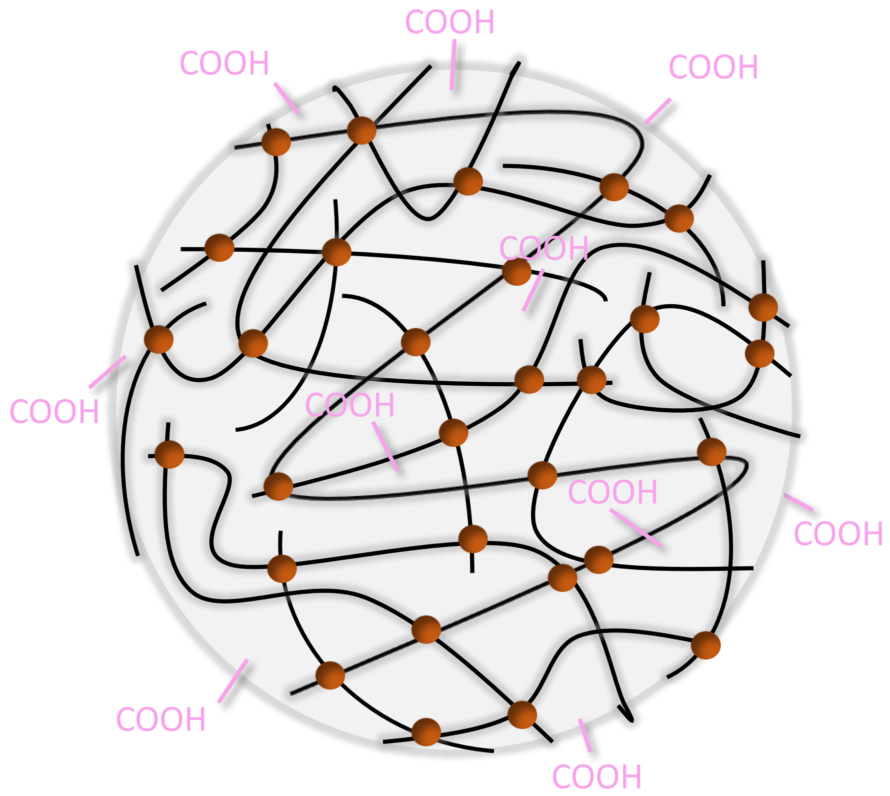
Objective of the project

Supramolecular networks from building blocks interacting through complementary reversible covalent bonds



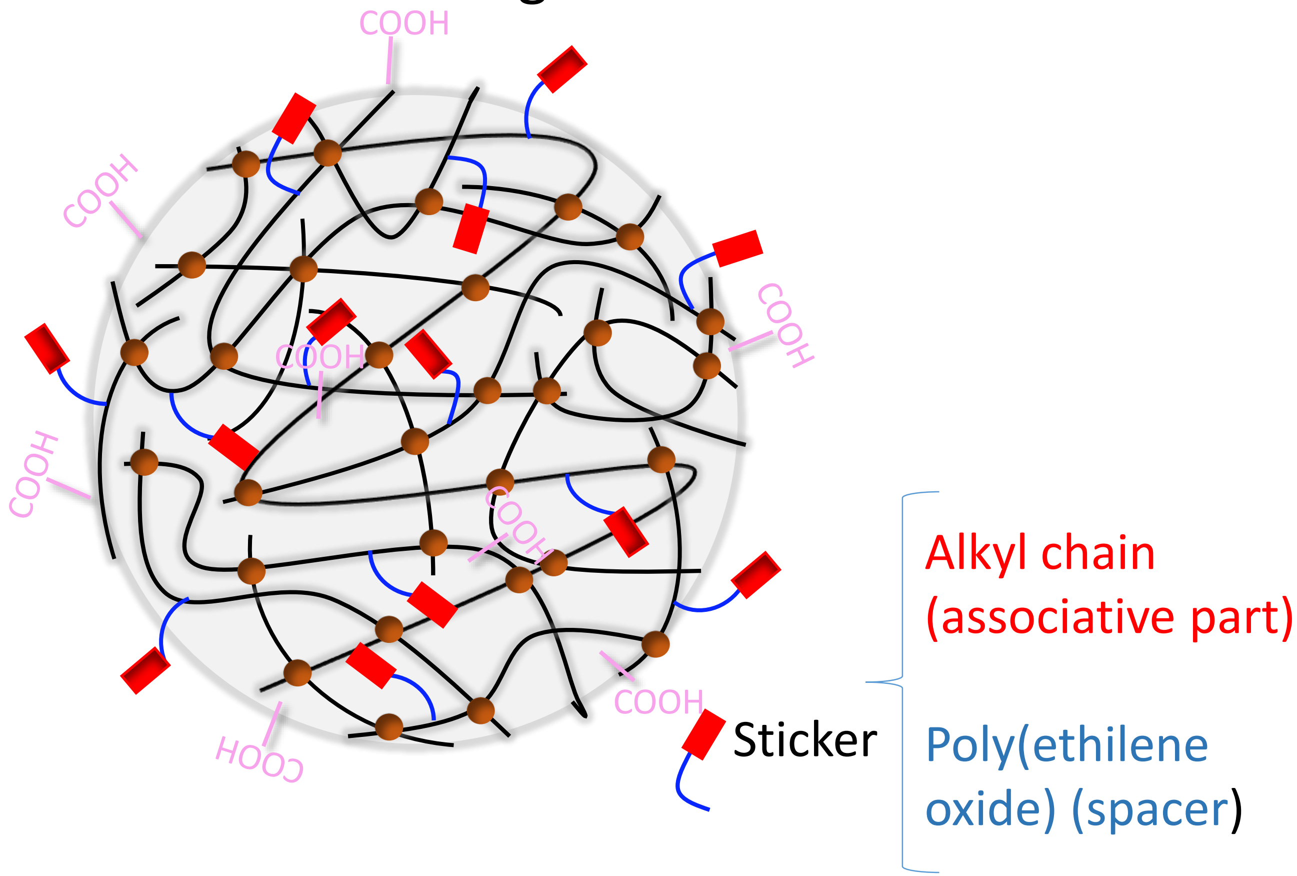
Objective of the project: microgels as building blocks

Repulsive microgels



EA (%mol)	MMA (%mol)	TPMTA (%mol)
59.5	39.7	0.8

Associative microgels



EA (%mol)	MMA (%mol)	TPMTA (%mol)	Sticker formula
59	40.1	0.8	$-C_{22}H_{45}$

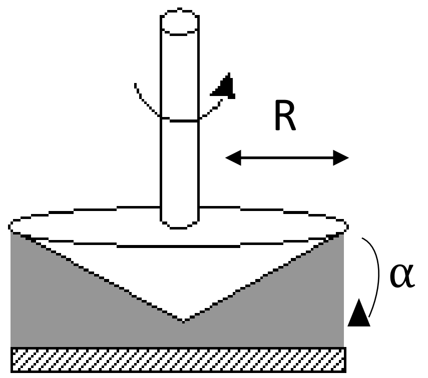
Microgels synthetized by COATEX

Methods

Rheometer

- Stress-imposed rheometer
- Solvent trap to avoid vaporitation

Geometry



Cone-plate
R=25 mm
α= 2°

Linear rheology

Sinusoidal imposed oscillation:

$\gamma = \gamma_0 \sin(\omega t)$

γ_0 constant and small (1%)

ω change logarithmically [0.001-100] $^{rad}/_{s}$

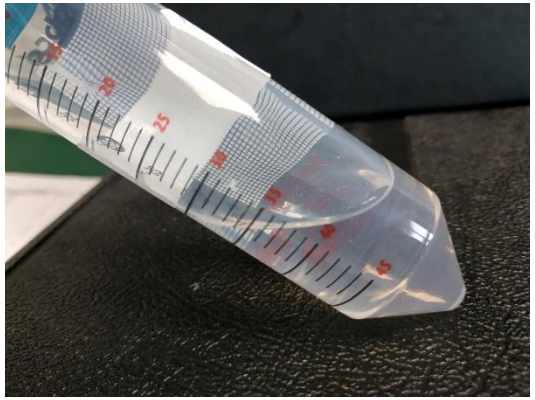
Non-linear rheology

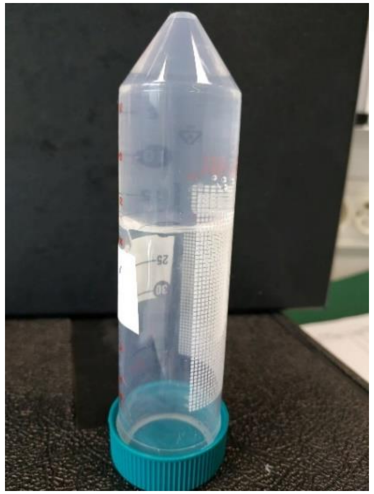
Start-up shear test:

$\dot{\gamma}$ applied constant

Repulsive microgels: linear viscoelastic properties

Viscous

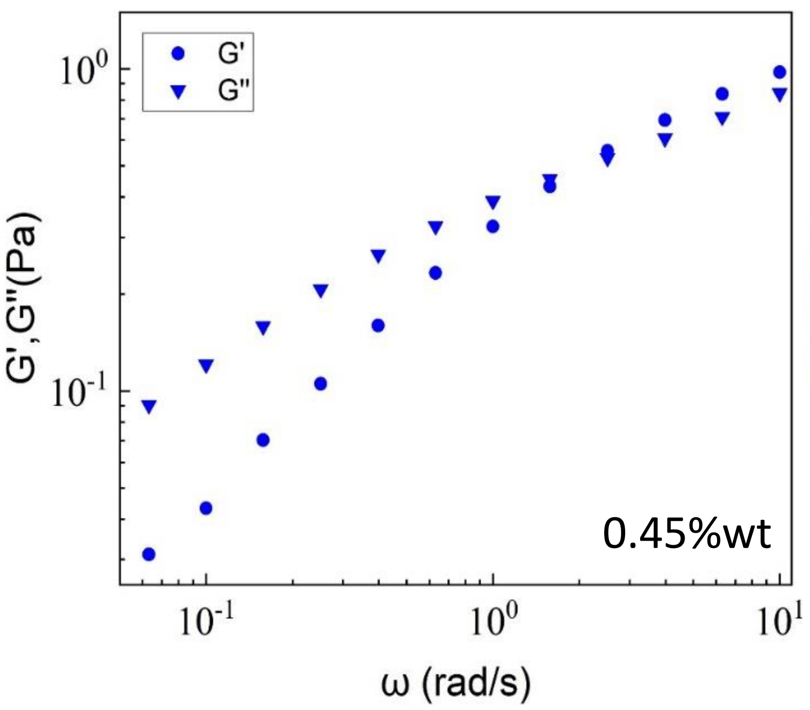


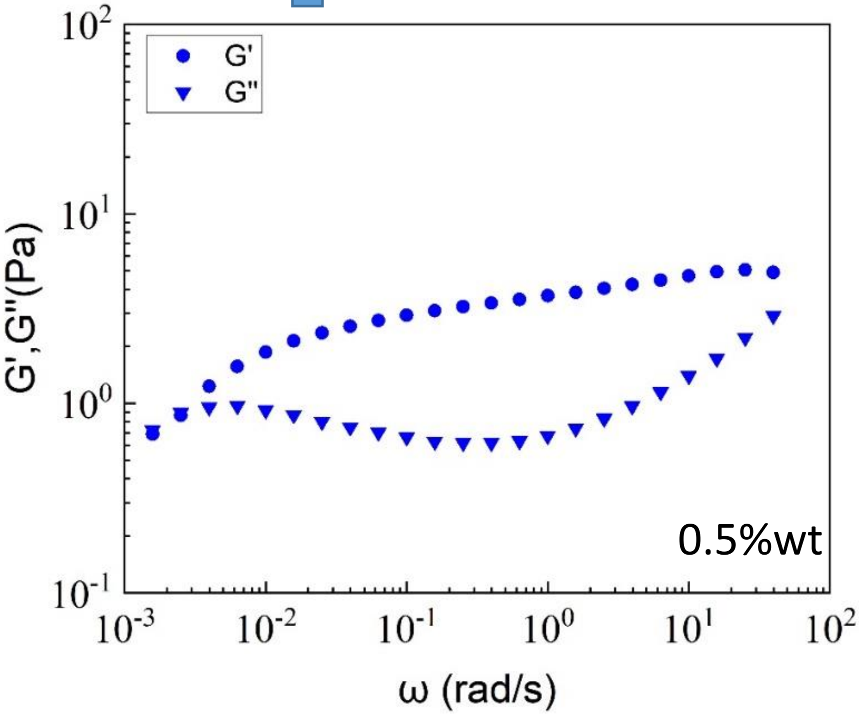


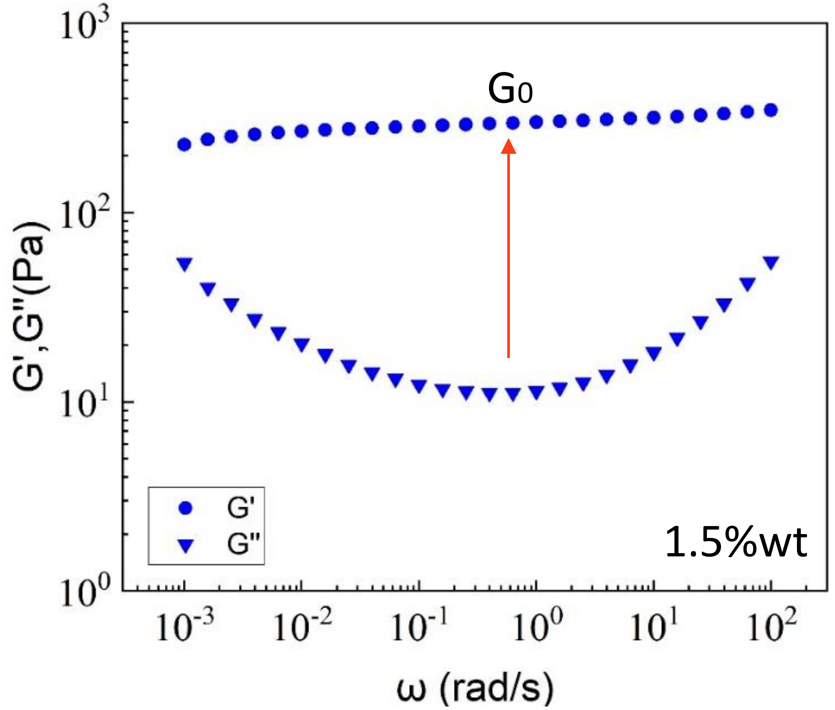
Solid

Transition

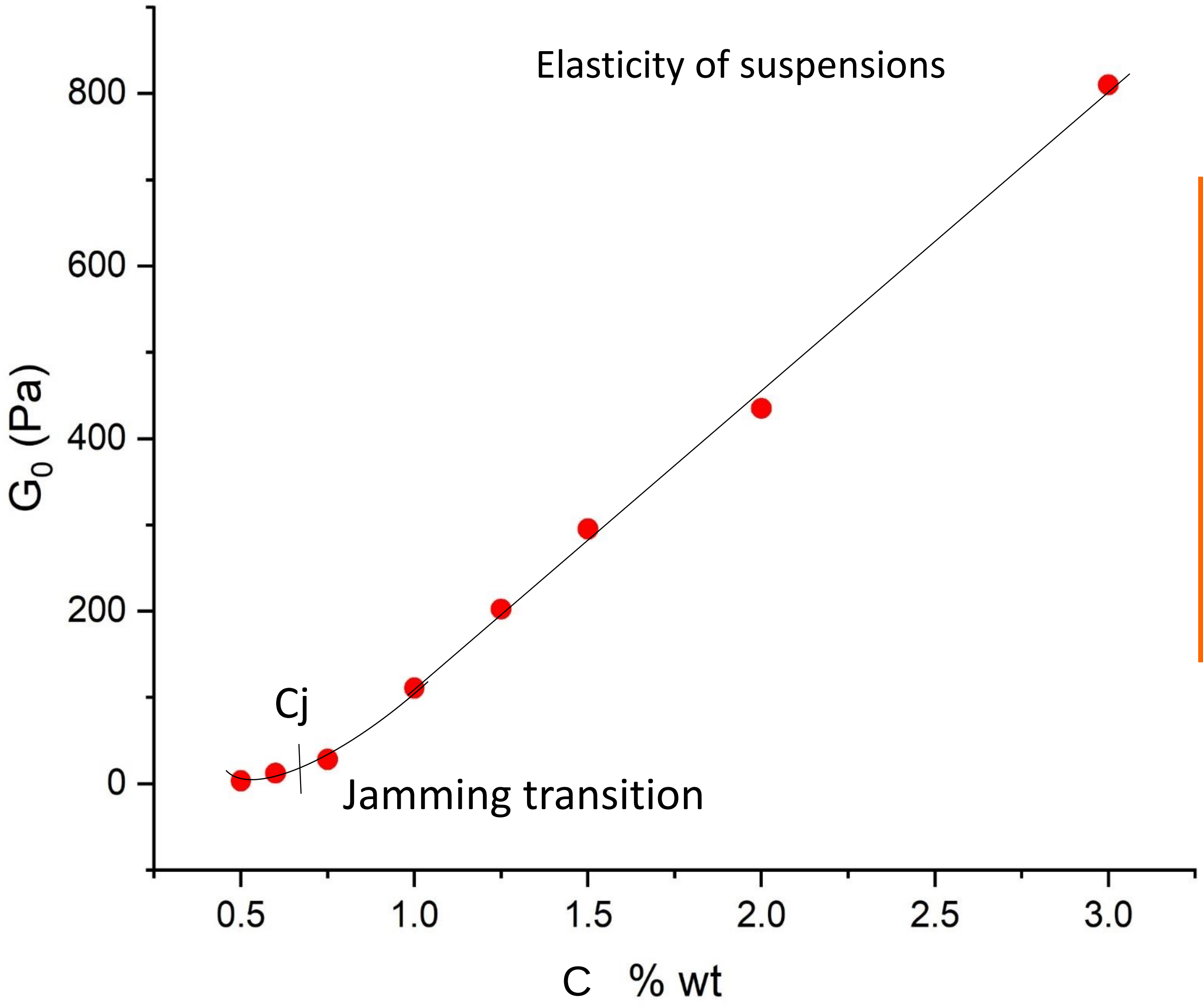
C



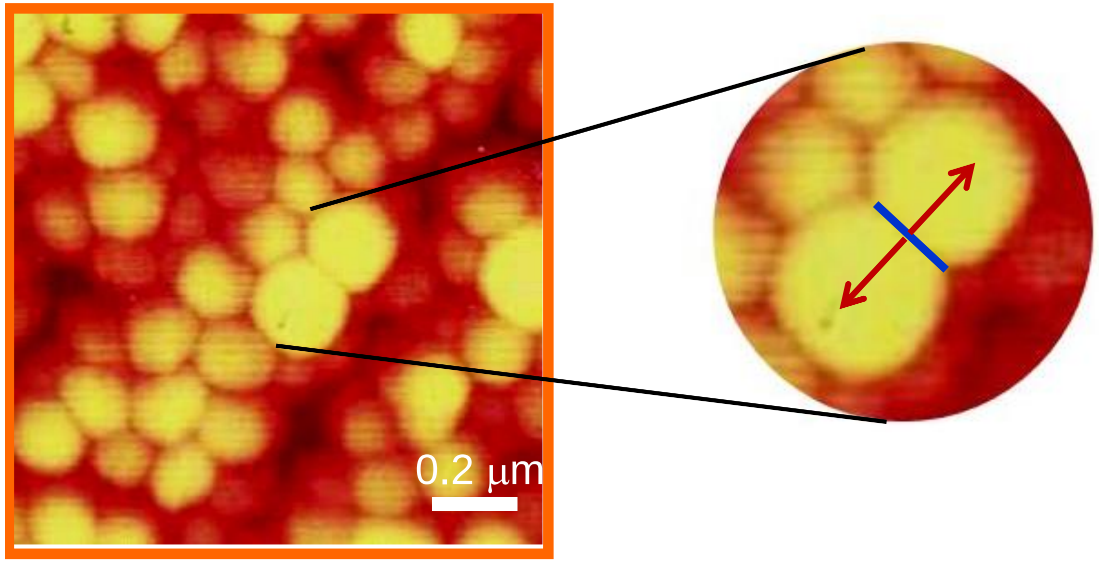




Repulsive microgels: linear viscoelastic properties



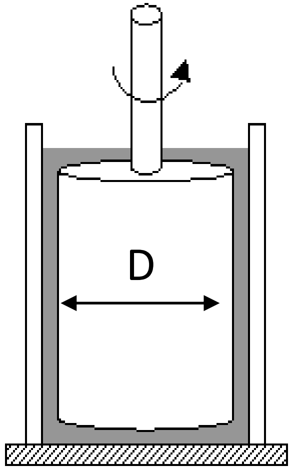
Particles are trapped in ''cages''



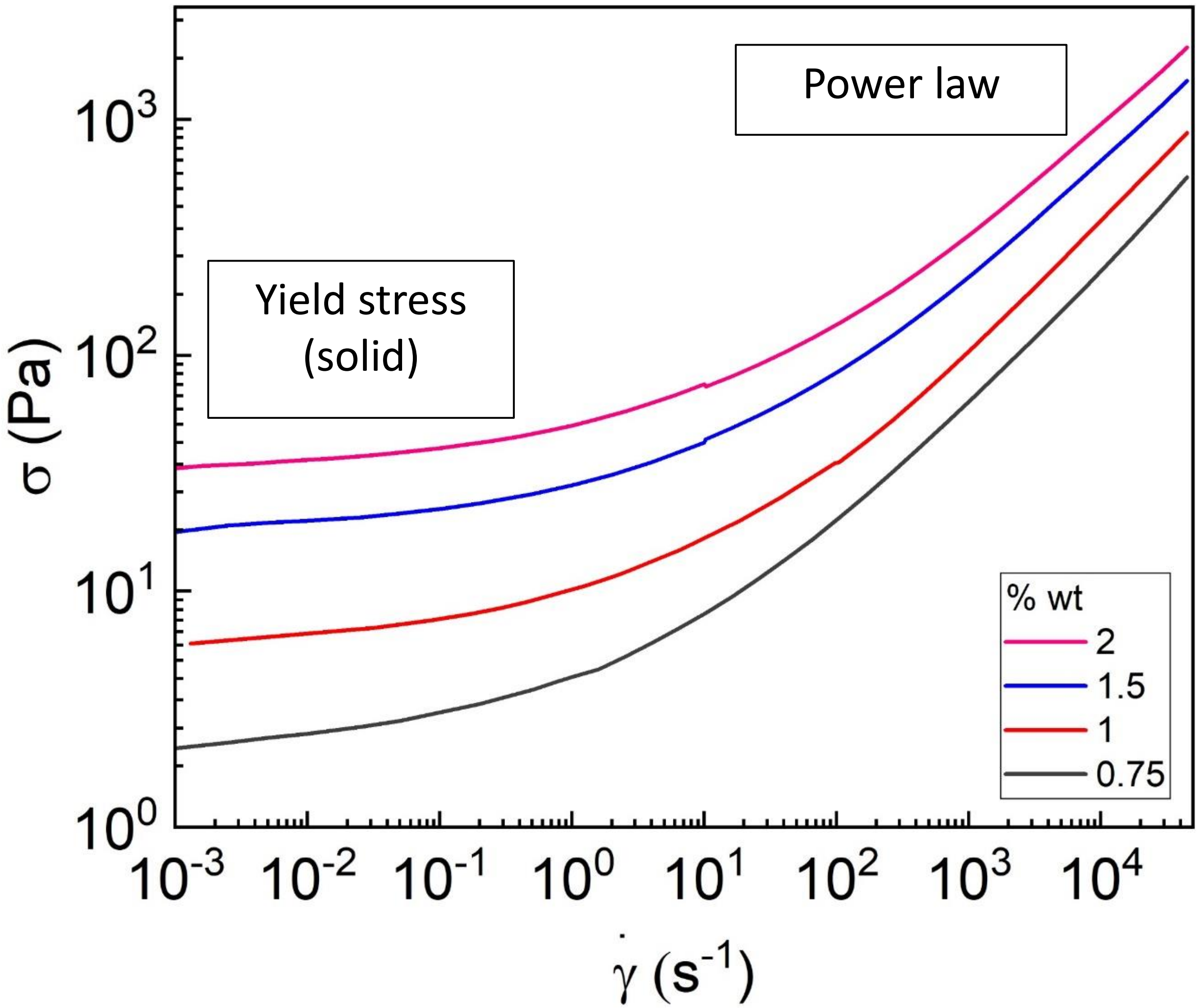
Elasticity → Repulsive interaction forces

Flow properties

Specificity: flow curve at high shear rate



Couette cell
D=28.7 mm
Gap=0.099 mm

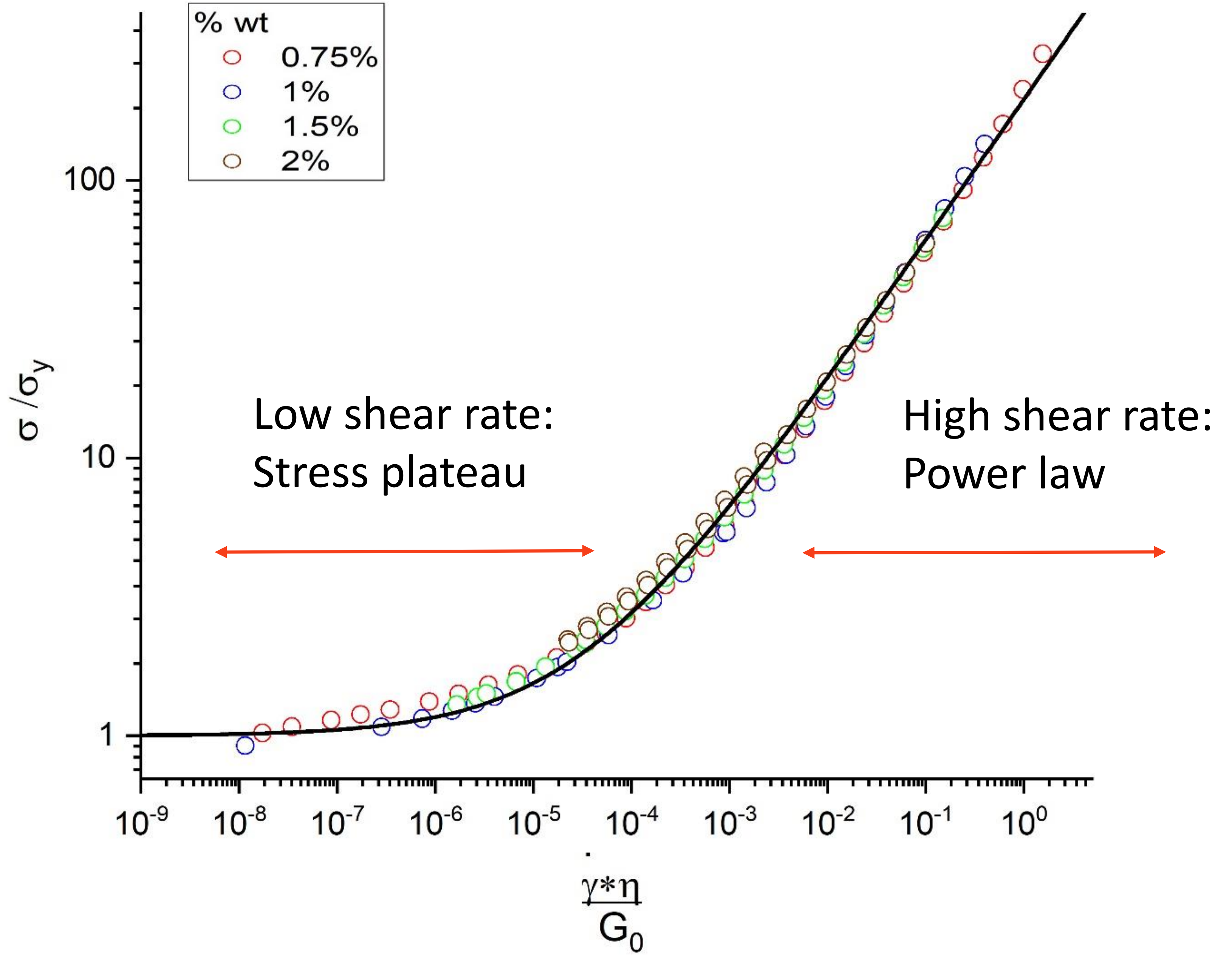


Fitted to Herschel Bulkley equation:

$$\sigma = \sigma_y + k\dot{\gamma}^n \qquad n < 0.5$$

- ❖ Asymptotic behavior at high shear rates
- ❖ Rilevant to applications

Flow properties: Master curve



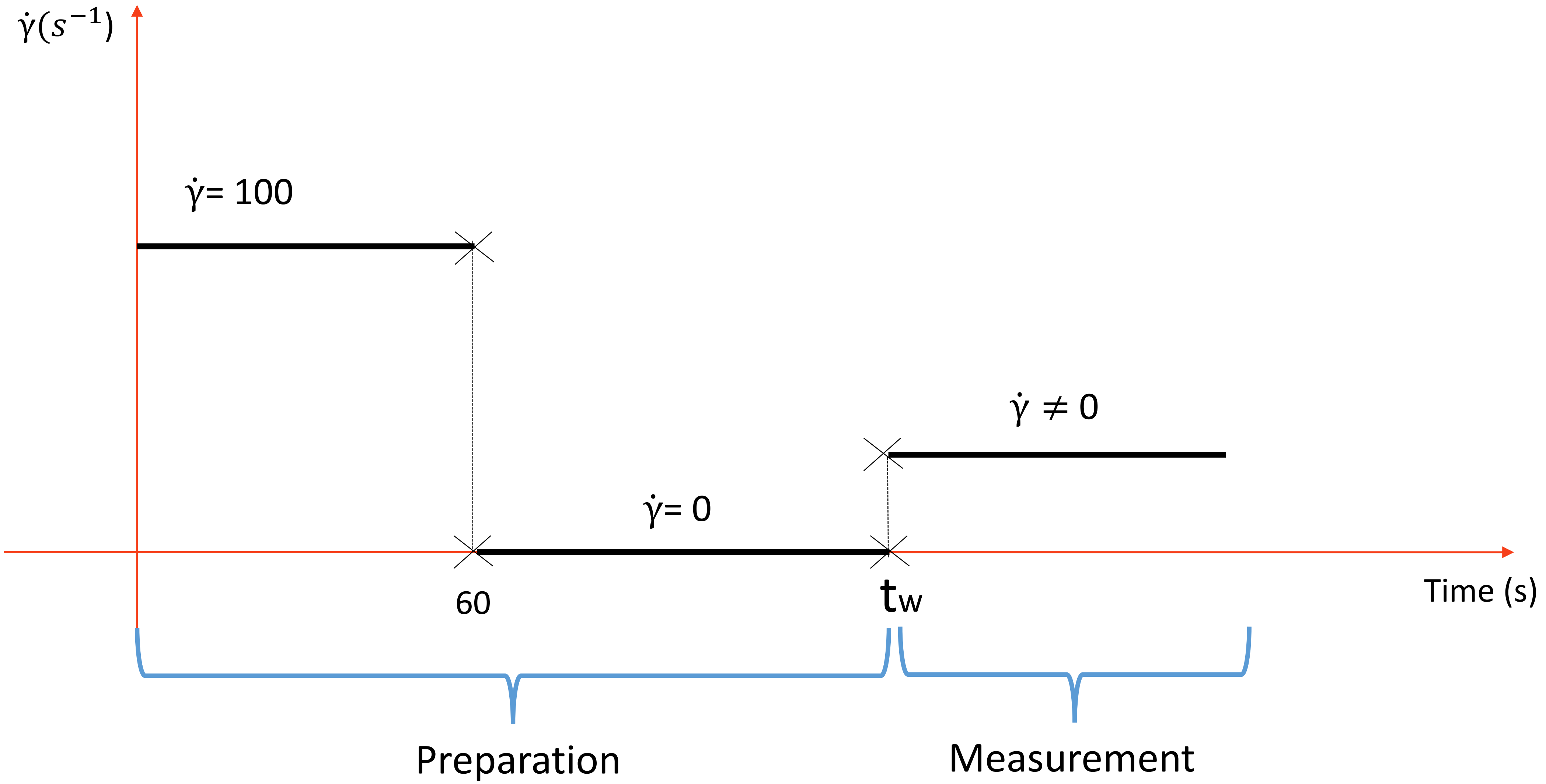
Collapse of flow curve in

a master curve:

$$\sigma/\sigma_y = 1 + 185(\dot{\gamma}\eta/G_0)^{0.51}$$

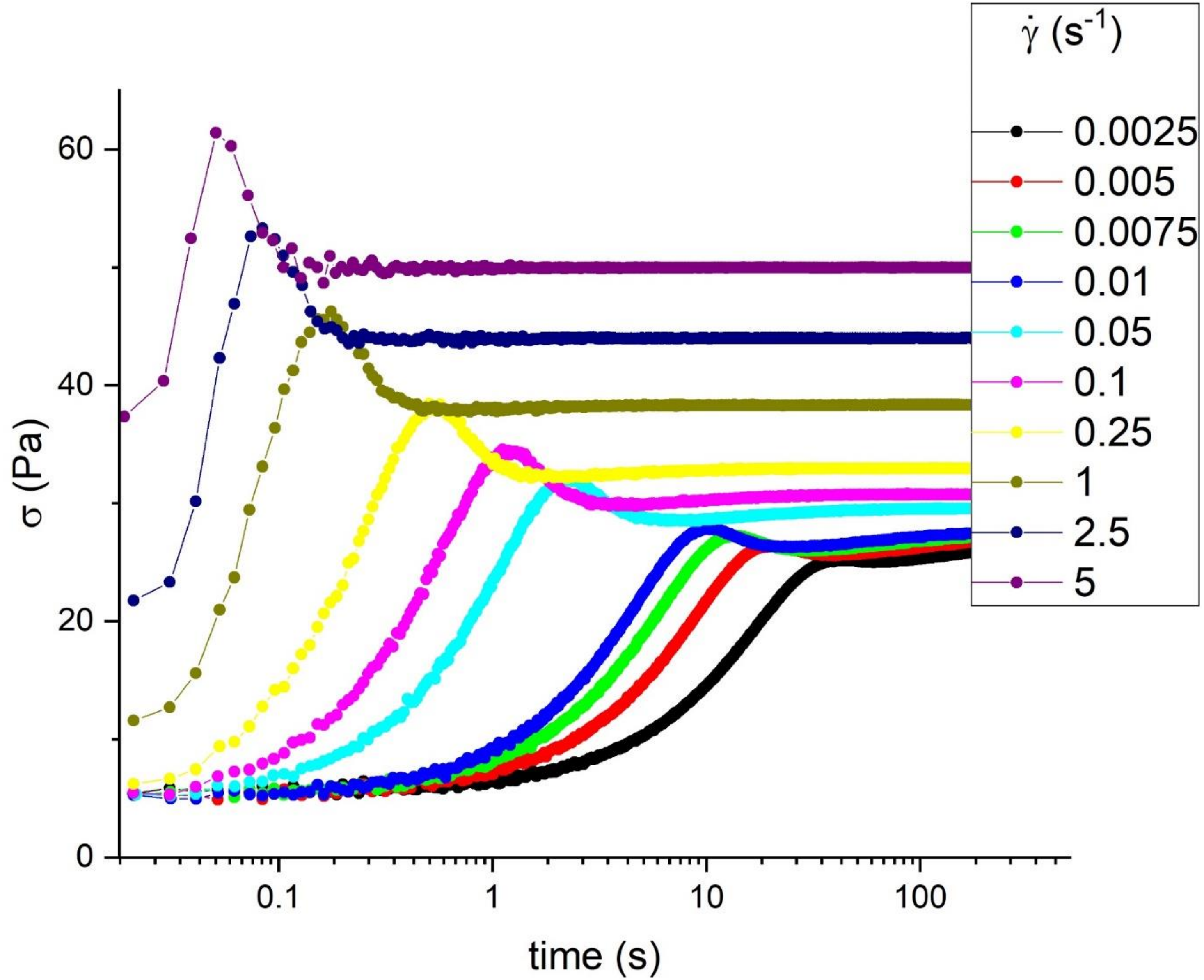
Shear start-up flow

How do repulsive microgels fail?



Shear start-up flow

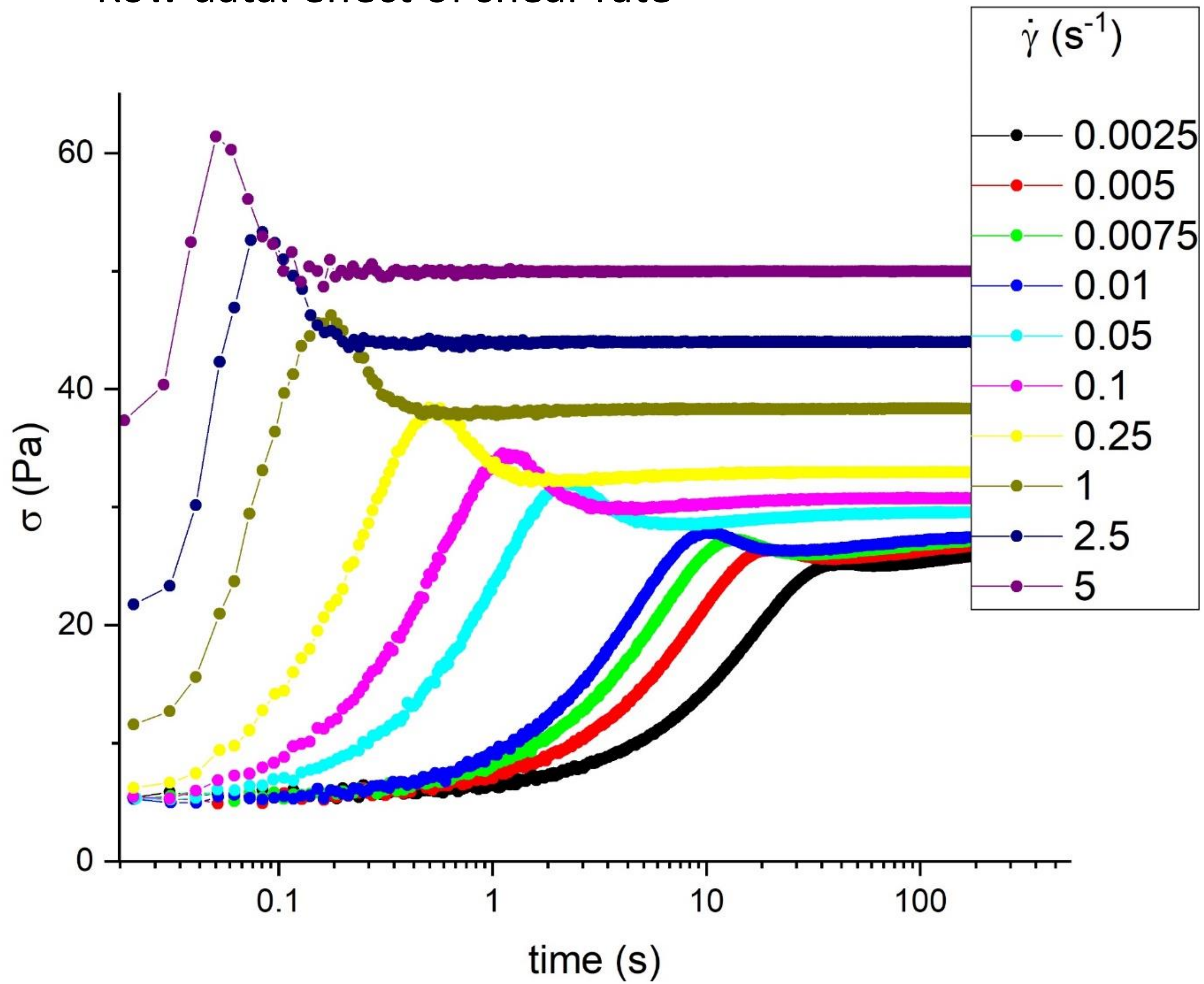
Row data: effect of shear rate



Stress overshoots which increase with shear rate

Shear start-up flow

Row data: effect of shear rate



Stress overshoots which increase with shear rate

Two regimes:

- **Low** $\dot{\gamma}$: no overshoot

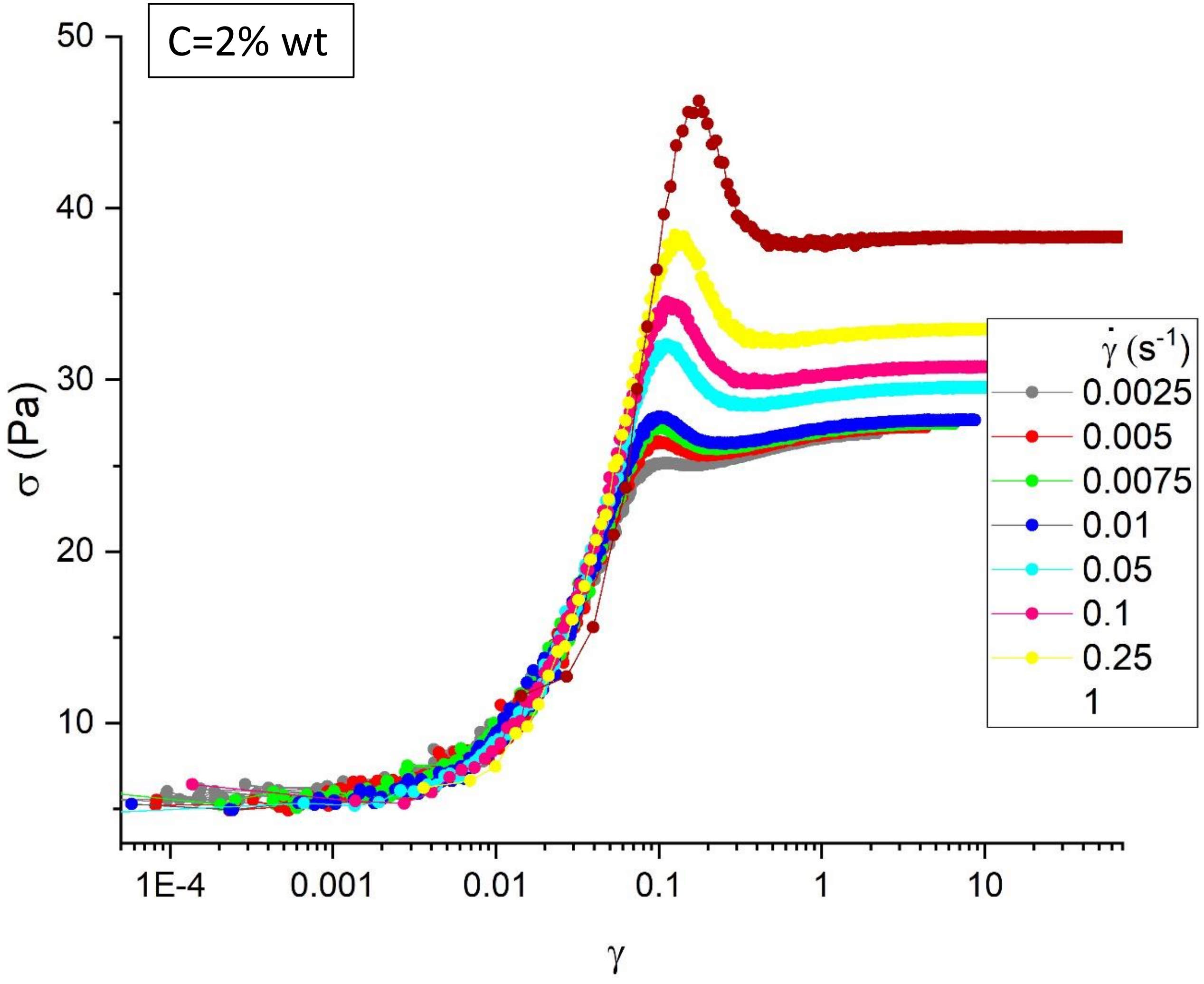
  Ductile material

- **High** $\dot{\gamma}$: overshoot

  Fragile

Shear start-up flow

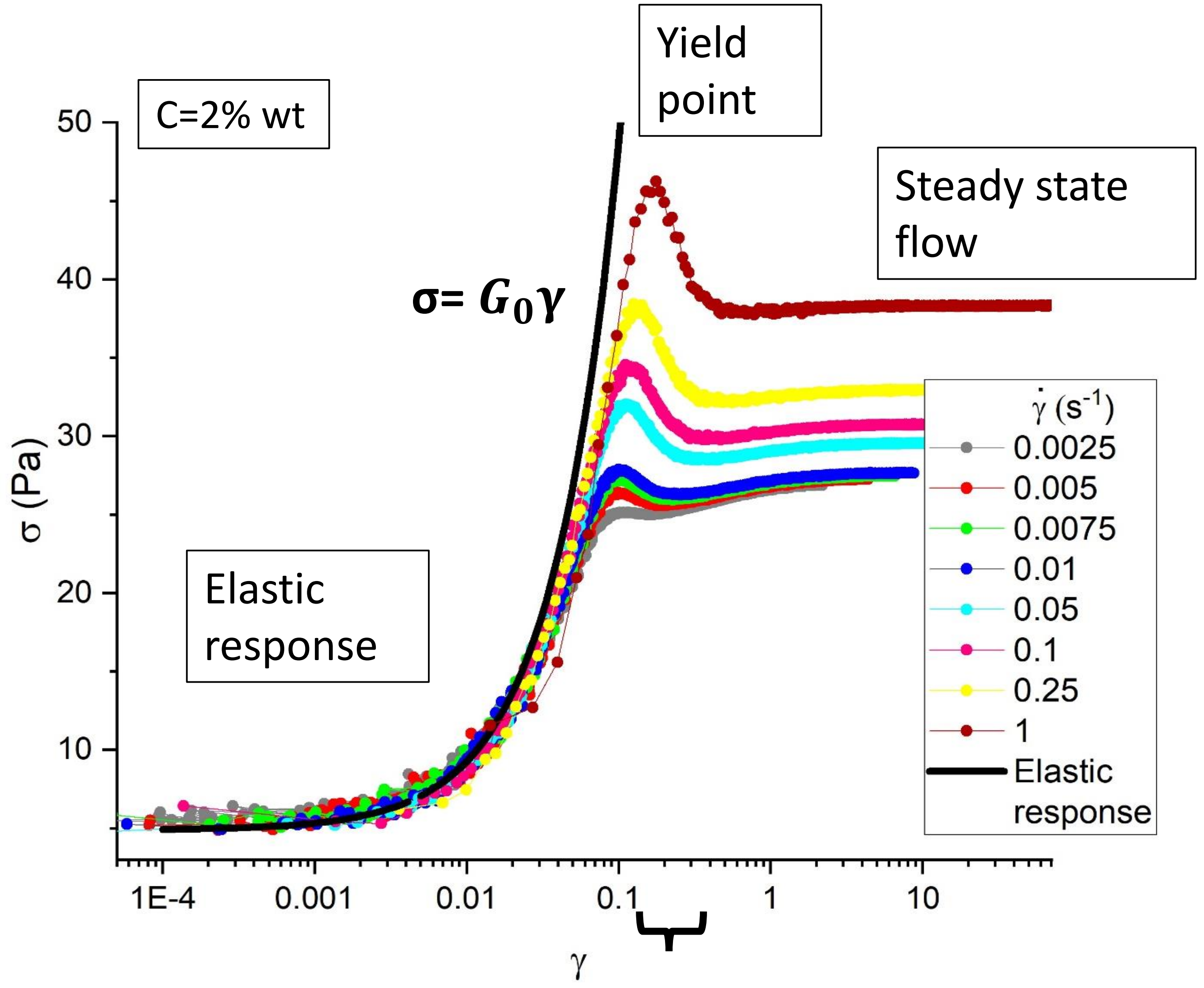
Scaling and interpretation



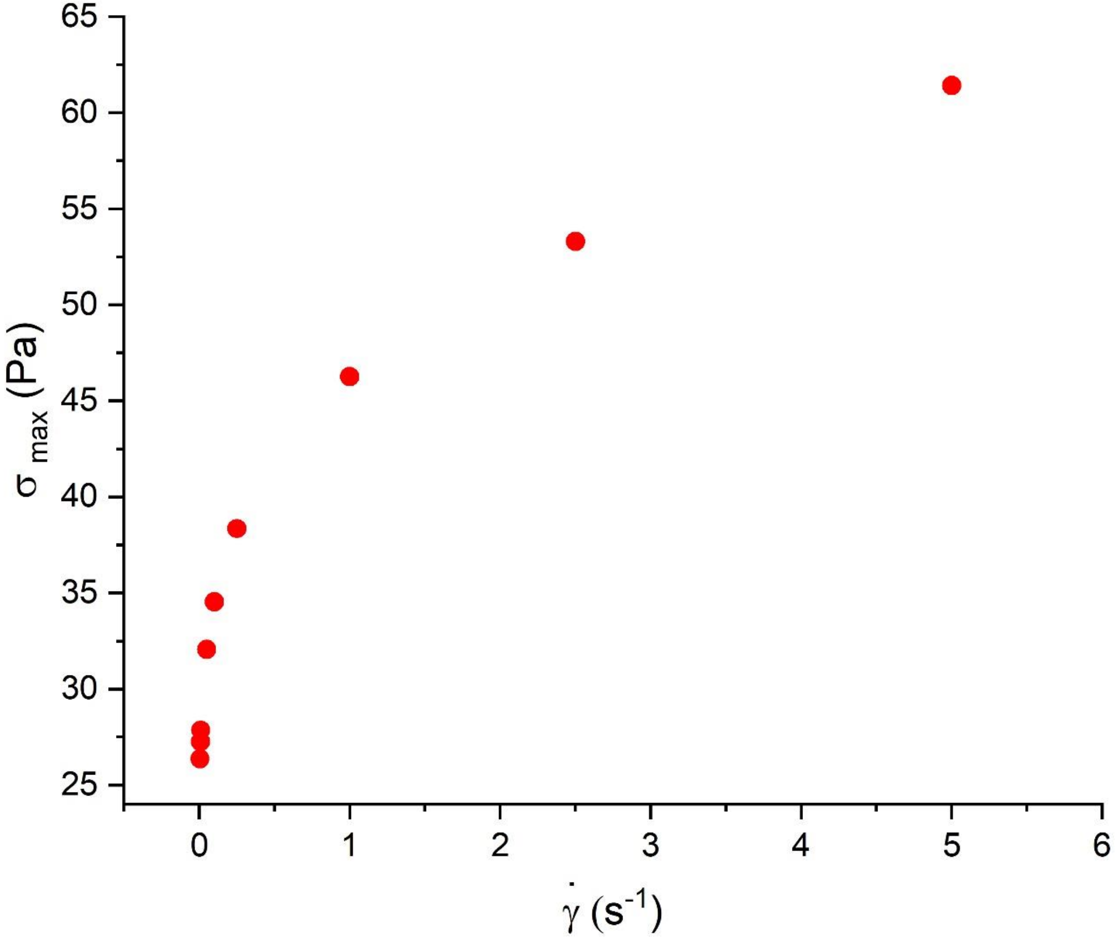
Shear start-up flow

Scaling and interpretation

σ_{MAX} increase with $\dot{\gamma}$

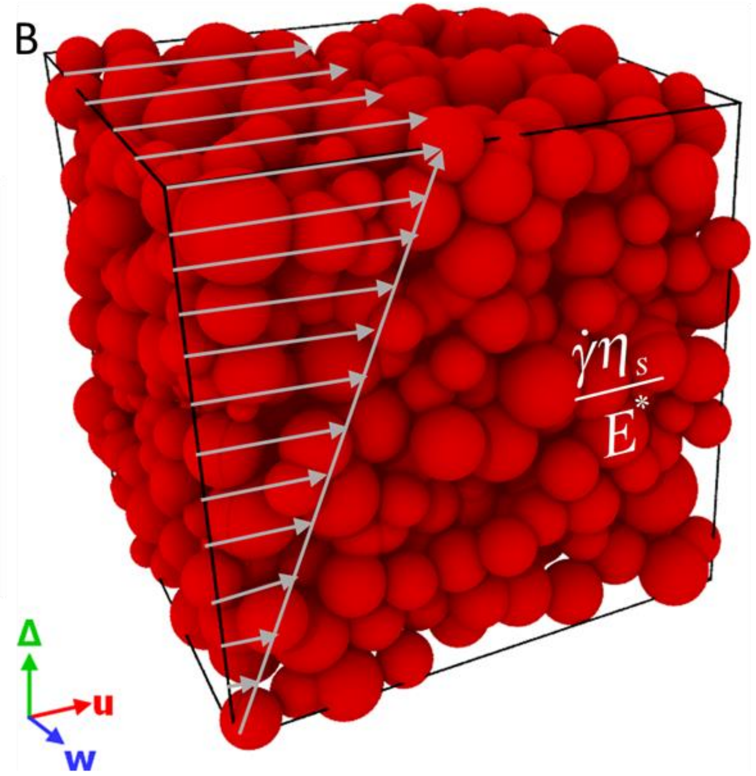


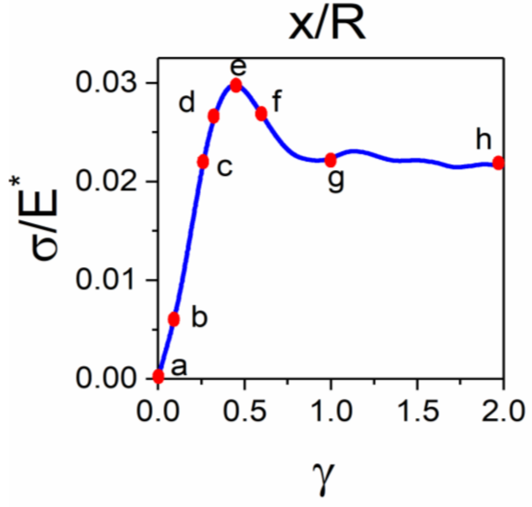
γ_{MAX}=0.10 – 0.12



Modelling

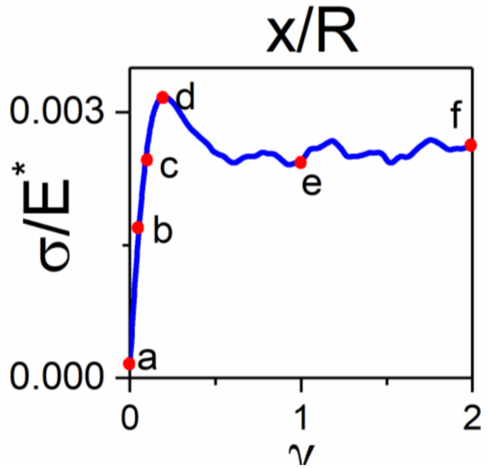
Three-dimensional particle-dynamics simulation

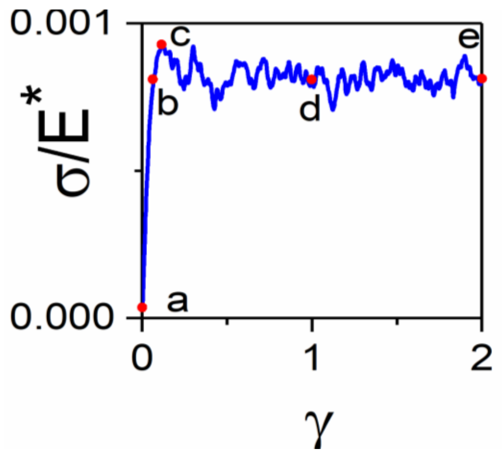




Low shear rate

Intermediate shear rate





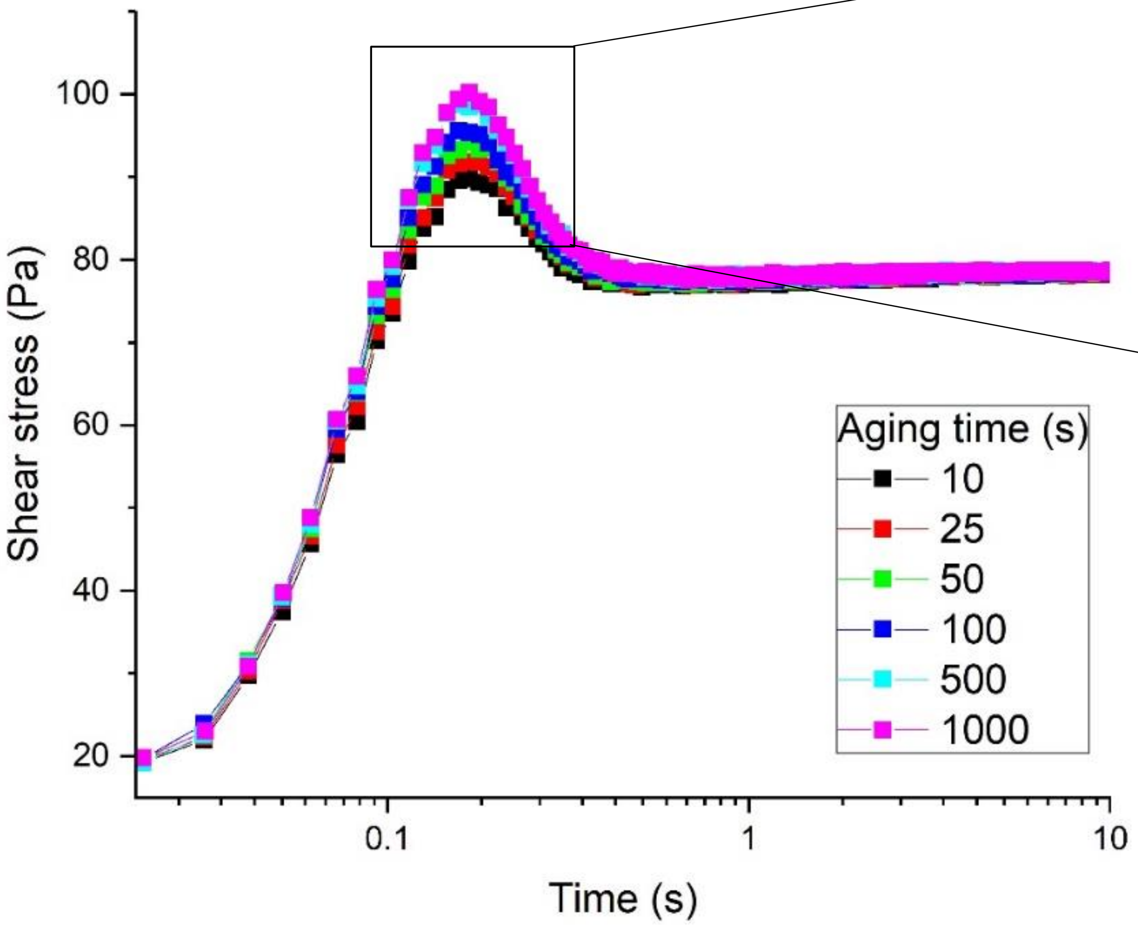
High shear rate

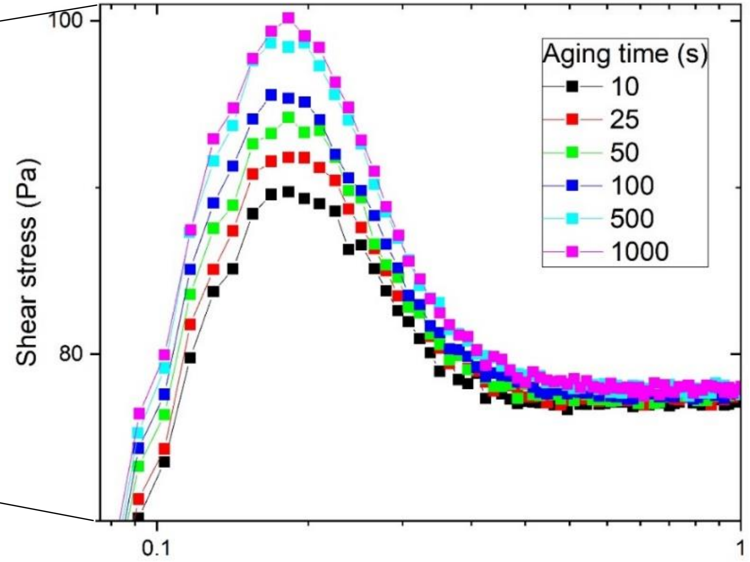
THE UNIVERSITY OF TEXAS AT AUSTIN

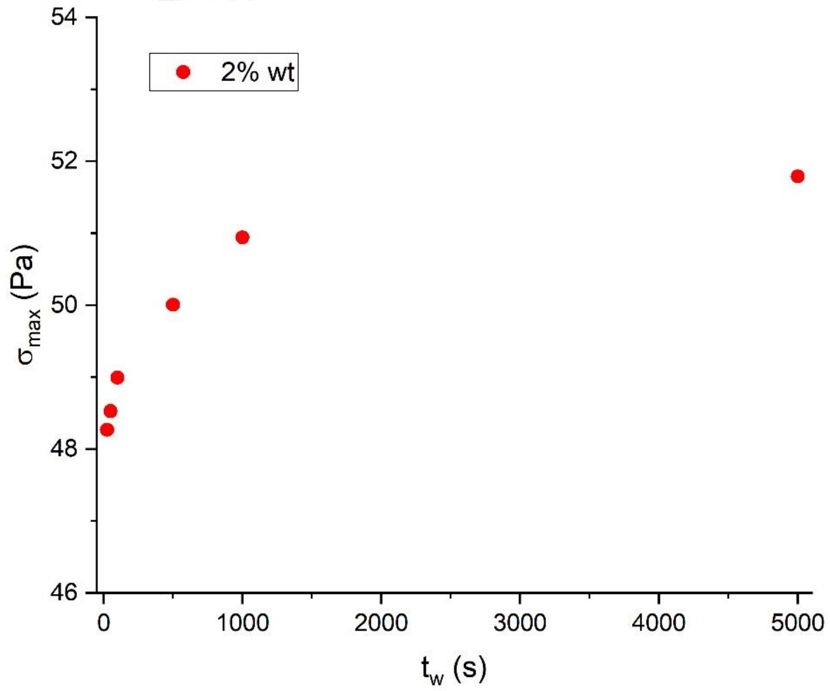
Roger T. Bonnecaze, Fardin Khabaz

Ageing: waiting time-dependence

Shear rate =1



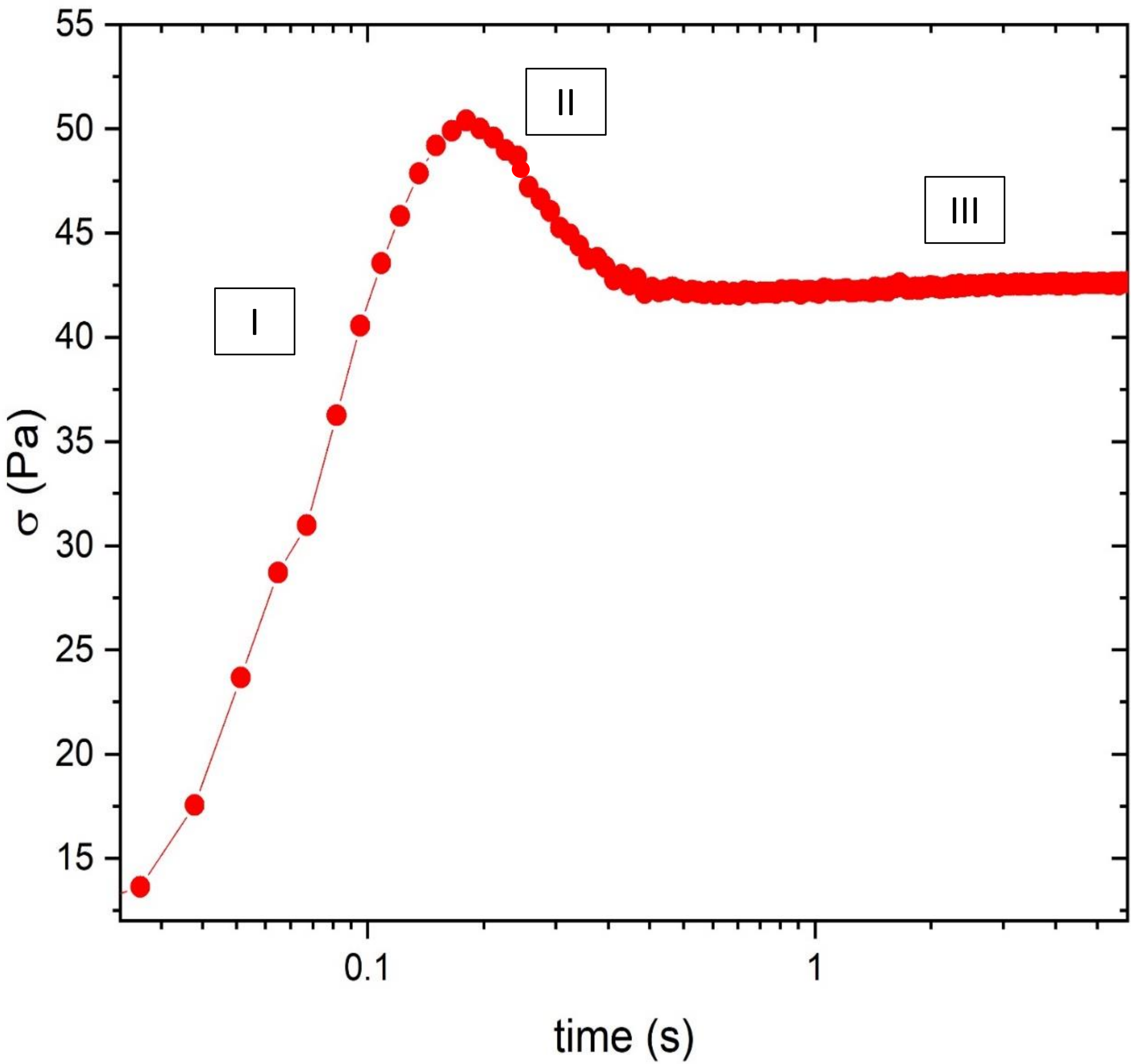




tw

stiffness

Interpretation



I) Elastic response:

The cage deforms elastically reversible

II) Failure

III) Build-up of a structural rearrangement:

steady-state value as a function of the shear strain

Acknowledgement

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Dodynet group

Thank you for your attention