SPREADING OF COMPLEX FLUIDS: DEPOSITION LAW AND ANALYSIS OF SPREADING DEFECTS

PhD defense

04/10/22

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Industrial context

Product spreading: a key step in cosmetics life

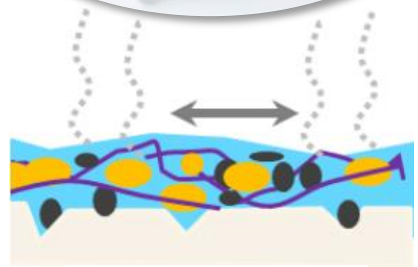
Storage *Application* *Deposit*

Product spreading: a key step in cosmetics life

Impacts

Sensory perception

Efficiency Performances



Application

Physics at stakes

Evaporation

Solid mechanics

Rheology

Substrate impregnation

Tribology Friction

Wetting

Many physics involved:

- **Complex modeling**
- **Interdependance** of phenomena

⇨ **Lack of understanding**

COSMETIC CREAM FORMULATION

Volatile phase	Non-Volatile phase		
	Texture agents	**Actives**	**Preservatives**
Water *…*	*Polymers (Carbopol, Xanthan…)* *Solid particles (starch, silica)…*	*Glycerol, UV filters, waxes, oils, Pigments, Mattifying particles (cellulose beads, silica)…*	*Phenoxyethanol* *…*

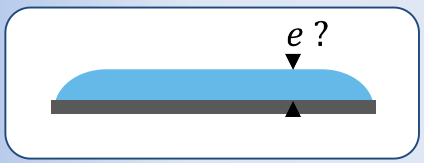
My PhD subject

UNDERSTAND THE PARAMETERS THAT GOVERN SPREADING AND THE PHENOMENA RESPONSIBLE FOR SPREADING DEFECTS

FOCUS ON 2 MAIN ASPECTS

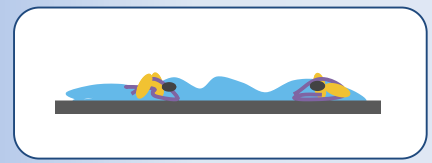
« Simple » fluids

Thickness of spreading

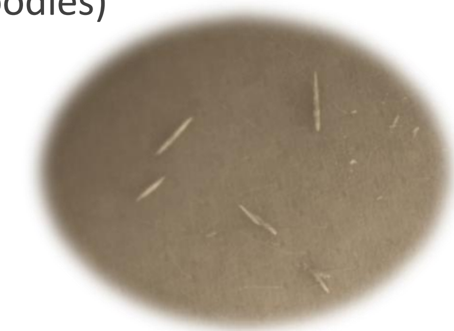


Filled polymeric gels

Spreading defects



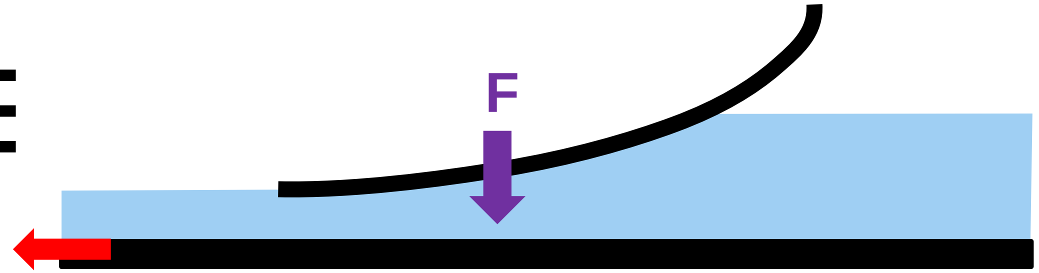
Aggregates formation
(Noodles)



What governs the spreading thickness?

Model studied: soft blade coating

≡



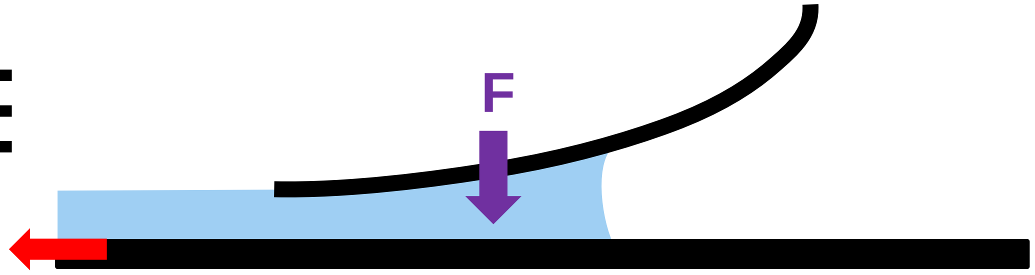
Seiwert & Quéré (2013)
Trinh & Stone (2013)
Pranckh & Scriven (1990)

⇨ Elasticity-capillary analogy

Dip coating

Landau-Levich (1942)
Derjaguin (1943)
de Ryck & Quéré (1998)
Smit (2021)
Spiers (1975)

MODEL STUDIED: SOFT BLADE COATING



Seiwert & Quéré (2013)
Trinh & Stone (2013)
Pranckh & Scriven (1990)

⇒ Elasticity-capillary analogy

- **Finite** reservoir + **emptying**
- Newtonian and **complex fluids**

Initially adressed by C. Kusina (2019) for yield stress fluids

Dip coating

Landau-Levich (1942)
Derjaguin (1943)
de Ryck & Quéré (1998)
Smit (2021)
Spiers (1975)

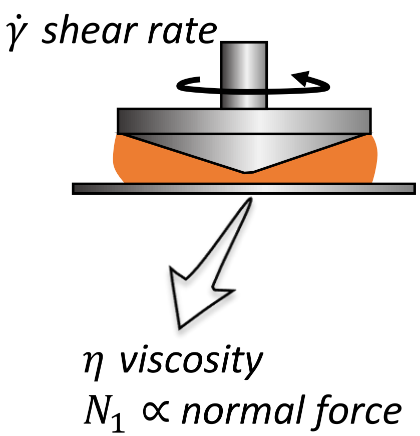
How does a finite reservoir influence the spreading dynamics ?
What is the impact of rheology ?

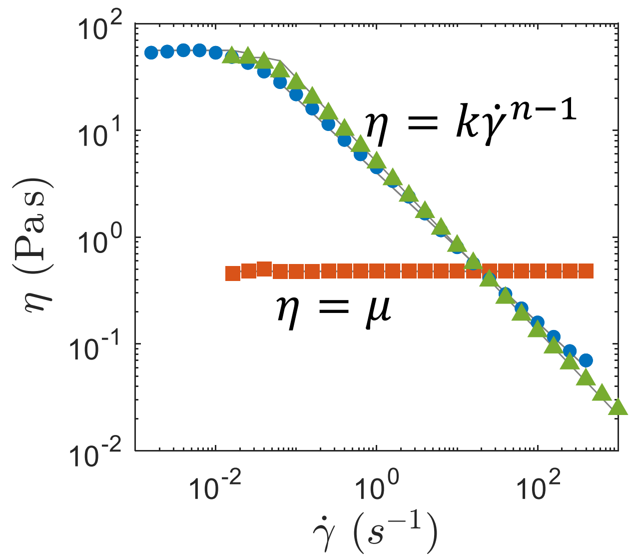
Fluids of interest

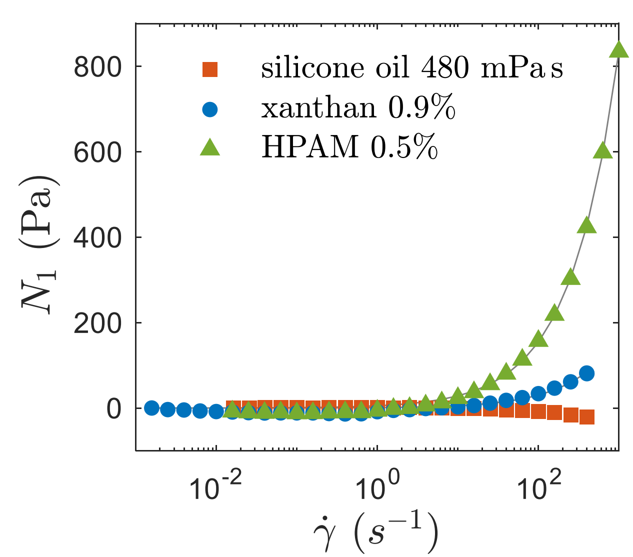
Newtonian fluids $\tau = \mu\dot{\gamma} \longrightarrow$ ***Silicone oil***

Shear-thinning fluids $\tau = k\dot{\gamma}^{n} \longrightarrow$ ***Xanthan gel***

+ Normal stress $N_1 = \alpha\dot{\gamma}^{m} \longrightarrow$ ***HPAM solution***

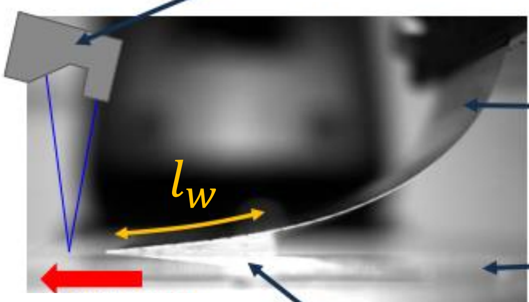






Experimental setup

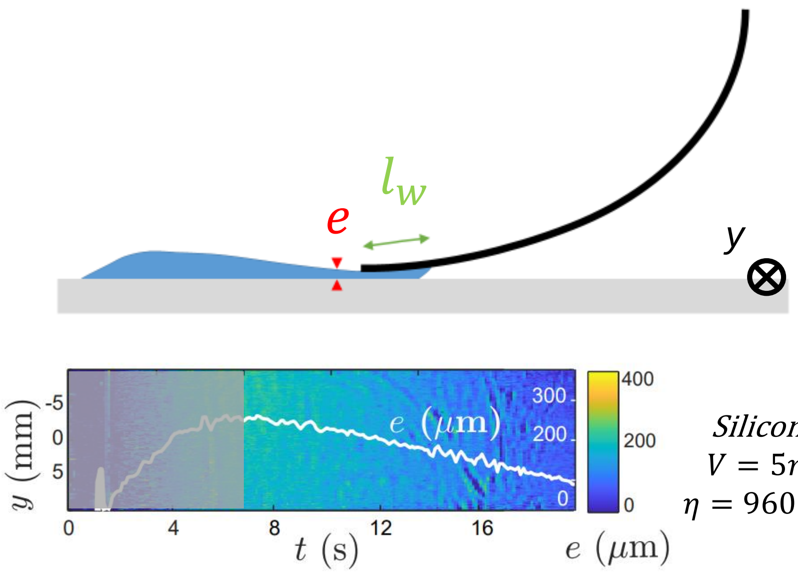
Based on Kusina's PhD setup



Simultaneaous recording :

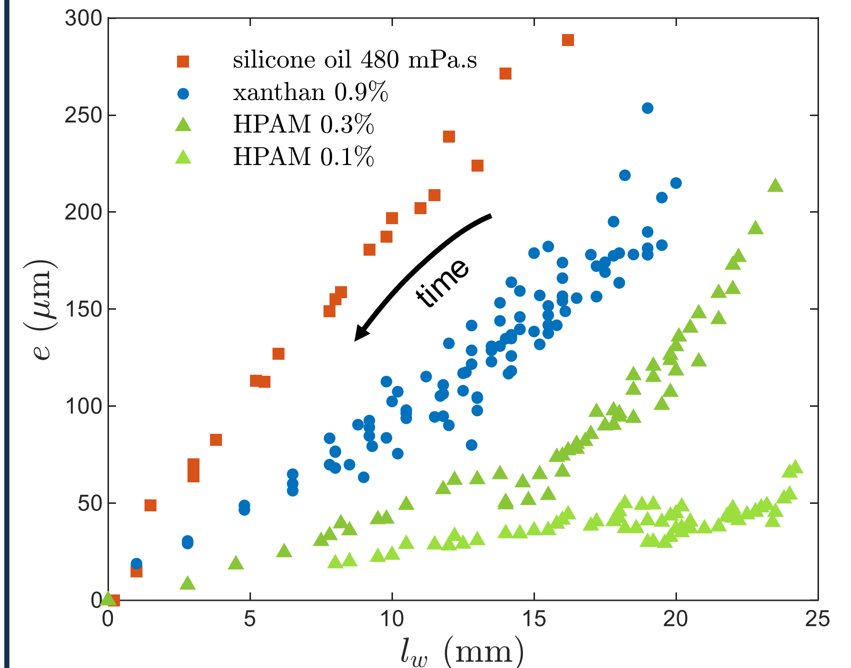
- **Deposited thickness** e (profilometer)
- **Wetting length** l_w (cameras)

SOFT BLADE COATING EXPERIMENT



Silicone oil
$V = 5mm/s$
$\eta = 960\ mPa.s$

Evolution $e = f(l_w)$ for 3 types of fluids

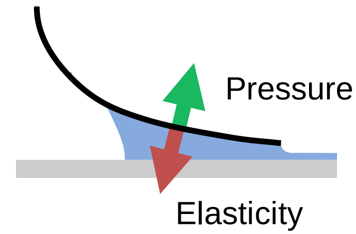


e **not constant** ➔ deposit of decreasing thickness as l_w decreases

What governs the spreading thickness ?

Physical law for film thickness

- *Blade elasticity* $\Gamma_{dry} \sim E^* I \dfrac{d\theta}{ds} \sim \dfrac{E^* I}{L - l_w}$
- *Lubricating pressure* $p \sim \eta \dfrac{V}{e^2} l_w$ —Torque→ $\Gamma_{wet} \sim \eta \dfrac{V}{e^2} b {l_w}^2 (L - l_w)$



Balance of viscous and elastic torques:

Shear thinning ($n = 1$ →) **Newtonian**

Shear thinning	Newtonian
$\eta = k\dot{\gamma}^{n-1}$	$\eta = \mu$ (cte)
$e \sim \left(l_w \sqrt{\dfrac{k V^n L^2 b}{E^* I}} \left(1 - \dfrac{l_w}{L}\right) \right)^{\frac{2}{n+1}}$	$e \sim l_w \sqrt{\dfrac{\mu V L^2 b}{E^* I}} \left(1 - \dfrac{l_w}{L}\right)$
Krapez et al., PRF 2022	*Krapez et al., PRL 2020*

fluid:
- *e thickness of fluid*
- *V velocity of the blade*
- *l_w wetting length*
- *k flow consistency*
- *n flow behaviour index*
- *μ dynamic viscosity*

blade:
- *b width of the blade*
- *L length of the blade*
- *I geometric parameter*
- *E* young modulus (incl. Poisson ratio)*

Scaling law :
- **Dependence** on l_w
- e ↗ with fluid **viscosity**, spreading **velocity**
- e ↘ with **blade rigidity**

WHAT GOVERNS THE SPREADING THICKNESS ?

PHYSICAL LAW FOR FILM THICKNESS

Shear thinning

$$\eta = k\dot{\gamma}^{n-1}$$

$$e \sim \left(l_w \sqrt{\frac{kV^n L^2 b}{E^* I}\left(1 - \frac{l_w}{L}\right)} \right)^{\frac{2}{n+1}}$$

Krapez et al., PRF 2022

$n = 1$

Newtonian

$$\eta = \mu \text{ (cte)}$$

$$e \sim l_w \sqrt{\frac{\mu V L^2 b}{E^* I}\left(1 - \frac{l_w}{L}\right)}$$

Krapez et al., PRL 2020

e thickness of fluid
V velocity of the blade
fluid:
l_w wetting length
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b width of the blade
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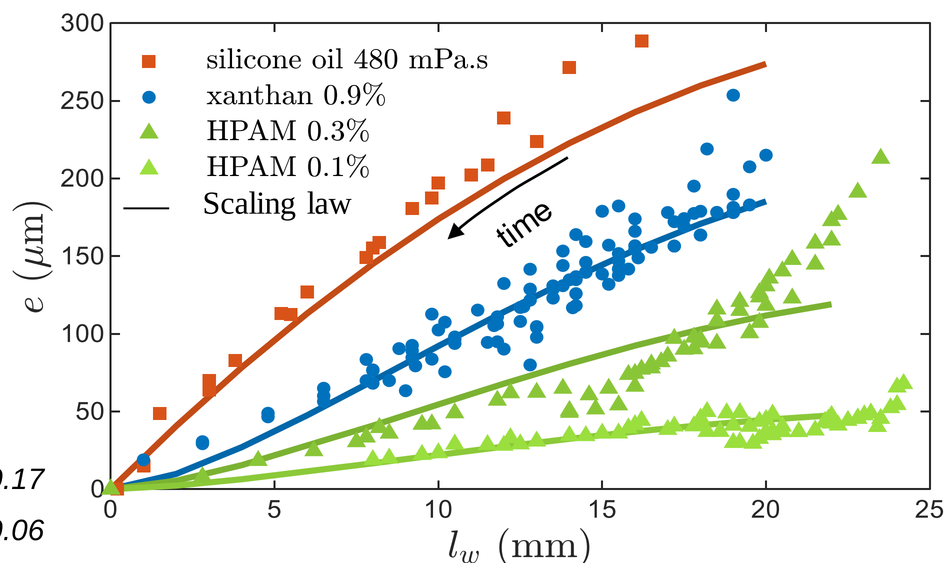


Prefactor 0.17
Prefactor 0.06

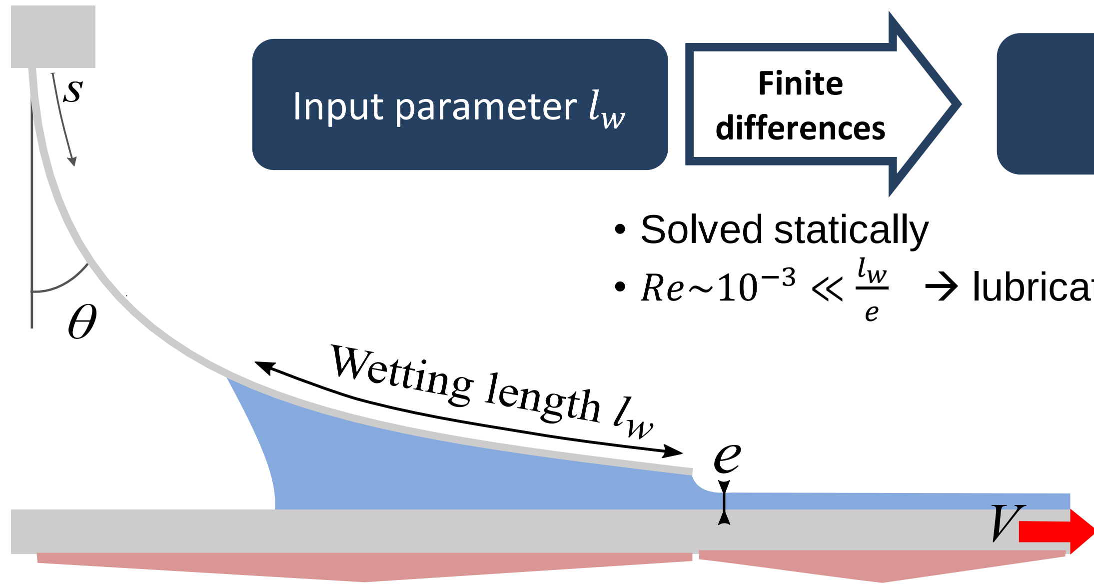
Film thickness **predicted by scaling law**

Thickness **increases** with **viscosity** and spreading **velocity**

New numerical study

Input parameter l_w → **Finite differences** → Corresponding thickness e

- Solved statically
- $Re \sim 10^{-3} \ll \frac{l_w}{e}$ → lubrication approximation



Fixed mounting $\theta(0) = 0$
No torque at tip $\left.\frac{d\theta}{ds}\right|_{s=L} = 0$

Horizontal $\lim_{x \to +\infty} \theta = \frac{\pi}{2}$
Laplace $\left.\frac{d\theta_l}{ds}\right|_{s=L} = -\frac{p_L}{\gamma}$

Blade

$$E^* I \frac{d^2\theta}{ds^2} = b \int_s^L f_v \sin(\theta(s) - \theta(s')) - p \cos(\theta(s) - \theta(s')) ds'$$

Euler Elastica — Viscous drag force — Lift from fluid pressure

Free surface

Laplace pressure

$$\frac{d^2\theta}{ds^2} = -\frac{1}{\gamma}\frac{dp}{ds}$$

Governing equation for the shape (θ)

$$\frac{d^2\theta}{ds^2} + S(s, \theta(s)) = 0$$

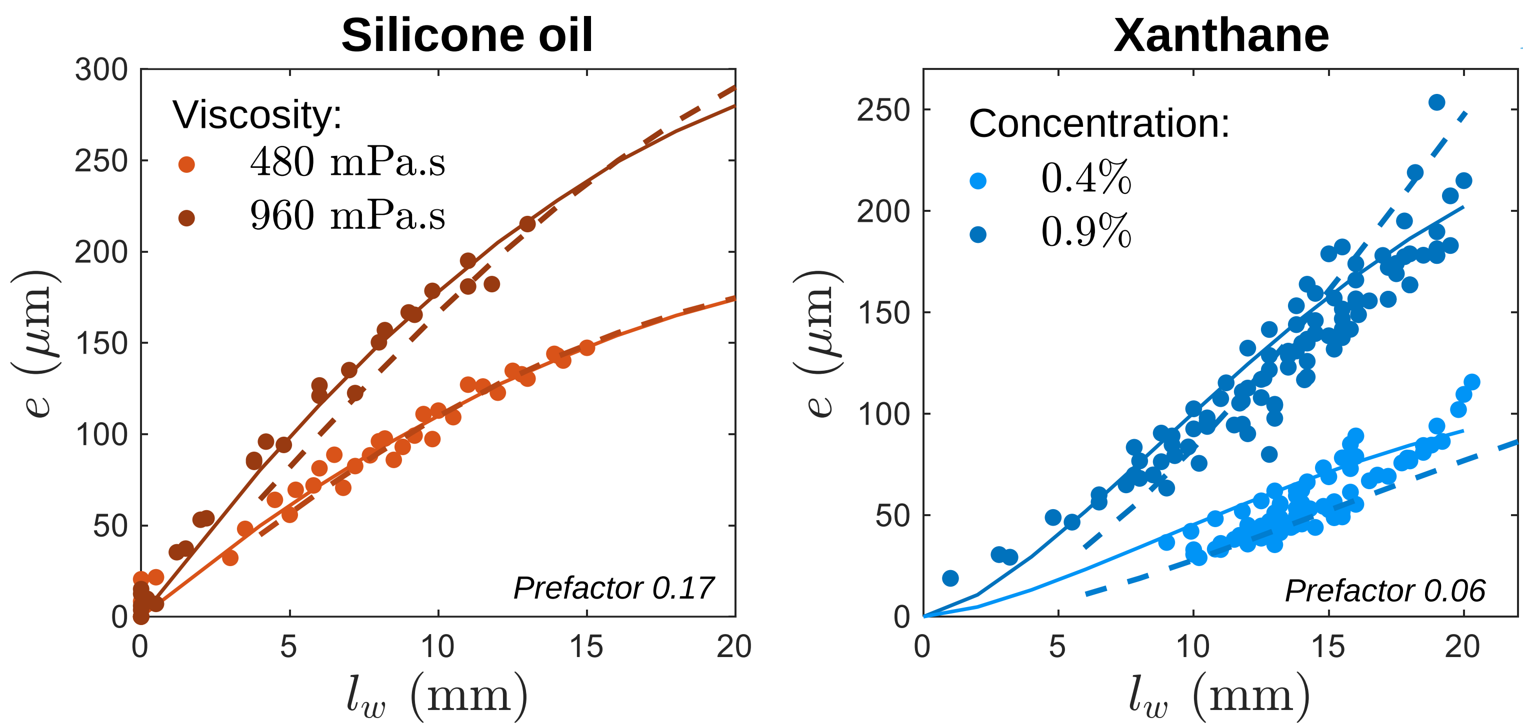
⇒ Analogy heat equation $\frac{\partial\theta}{\partial t} = \frac{\partial^2\theta}{\partial s^2} + S$, $\frac{\partial\theta}{\partial t} \to 0$

Validation of the model

Thickness as a function of the wetting length:

● Experiments
— Scaling law
- - Numerical computation

(No adjustable parameters)



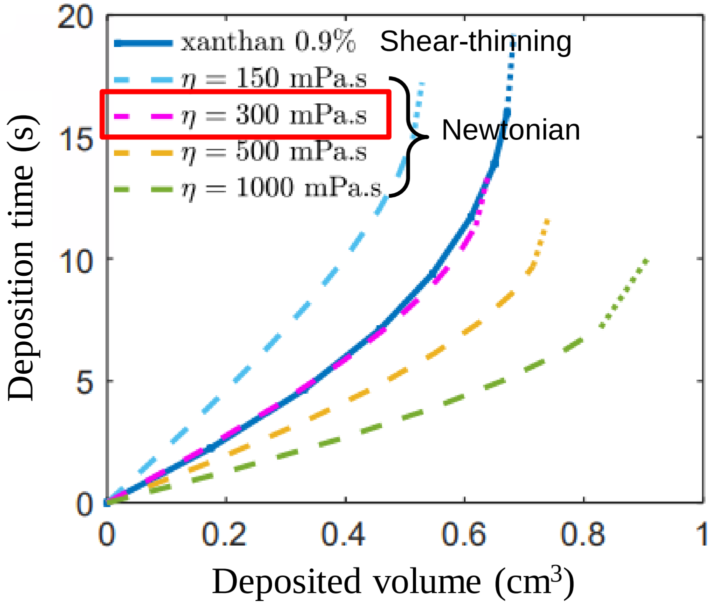
Agreement of scaling law & numerical computation with experimental data

Comparison : Newtonian & shear-thinning fluids

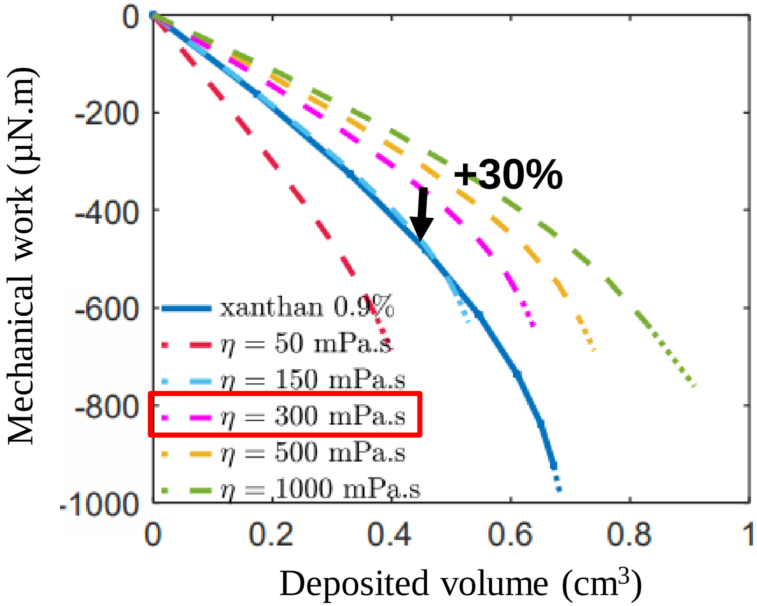
Choice of Newtonian equivalent

Same volume of fluid spread in the **same time** (identical velocity and initial wetting length)

$V = 10$ mm/s
$l_w(t=0) = 18$ mm



Energy needed to spread the fluid



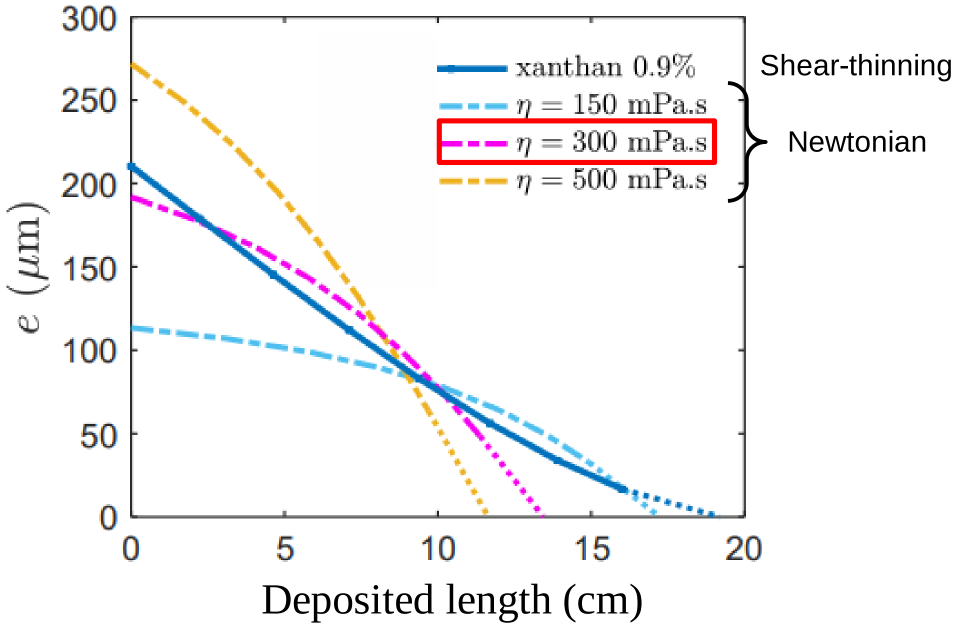
Krapez et al., PRF 2022

A **higher mechanical work** is needed to spread a **shear-thinning** fluid compared to its Newtonian equivalent (300 mPa.s)

Comparison : Newtonian & shear-thinning fluids

Shape of fluid deposit

$V = 10$ mm/s
$l_W(t = 0) = 18$ mm

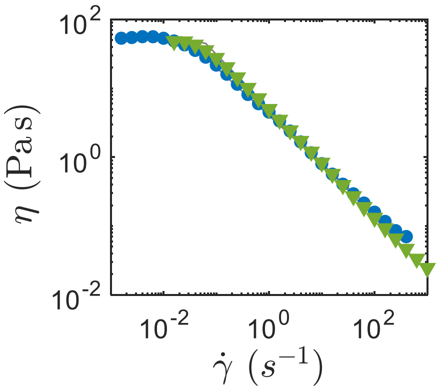


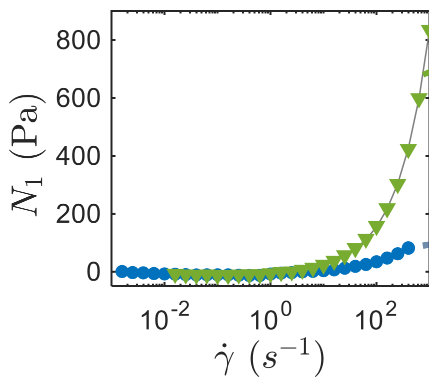
Different curvatures

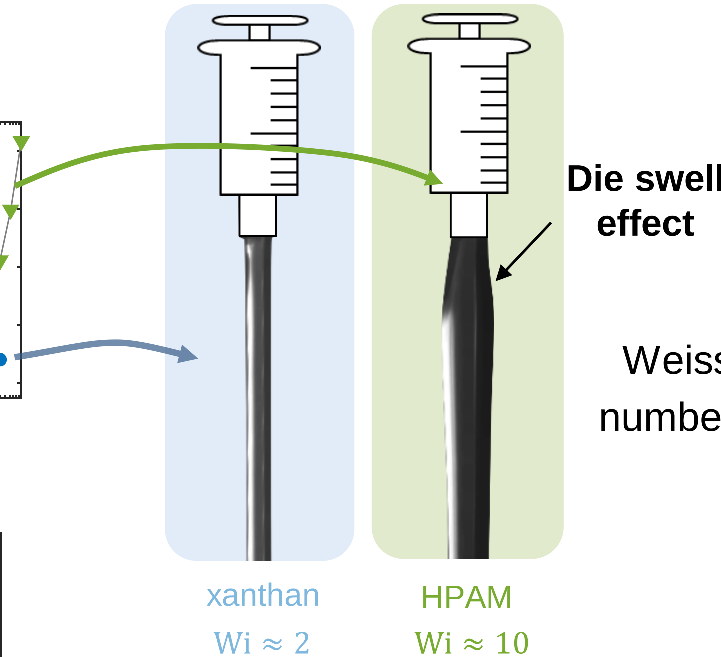
Greater film **homogeneity** for **low viscosity Newtonian** fluid

Normal stress fluids

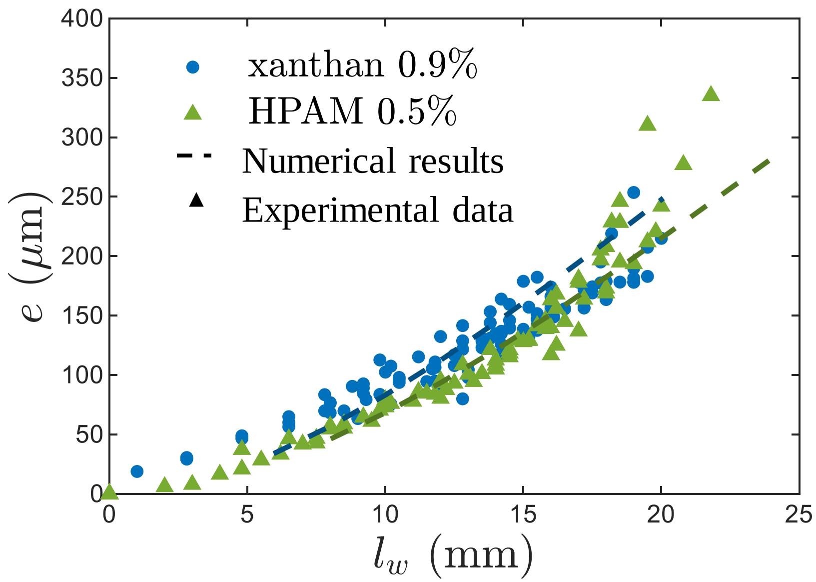
Normal stresses impact







Weissenberg number $\mathrm{Wi} = \frac{N_1}{\tau}$



Krapez et al., PRF 2022

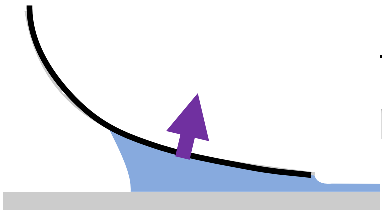
Film thickness increased by factor 2 to 8 in dip coating

de Ryck & Quéré 1998

No effect of normal stress

Normal stress fluids

Why is there no effect of normal stress?



Total pressure:
$p = p_l + p_N$

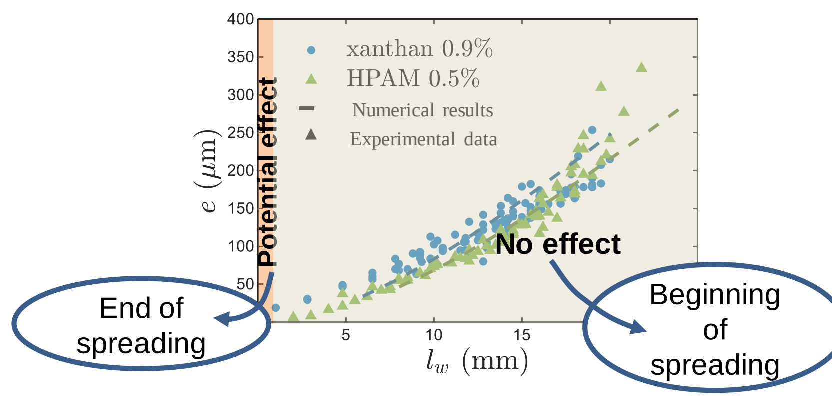
- Lubricating pressure: $p_l \sim \frac{lw}{e}\tau$
- Pressure due to normal stress: $p_N \sim N_1$

$$\frac{p_N}{p_l} \sim \frac{N_1}{\tau}\frac{e}{l_w} \sim Wi\,\frac{e}{l_w}$$

→ **Geometric factor** that counterbalances the high Weissenberg number

Negligible while:

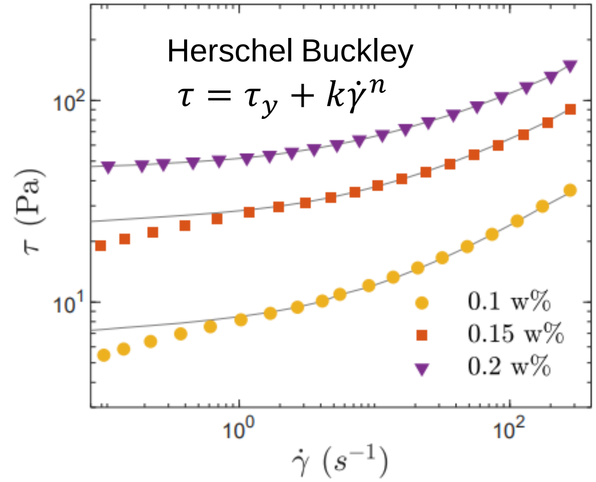
$$\frac{p_N}{p_l} \ll 1 \;\Leftrightarrow\; \boldsymbol{l_w} \gg$$ **0.05 mm** (HPAM 0.5%)



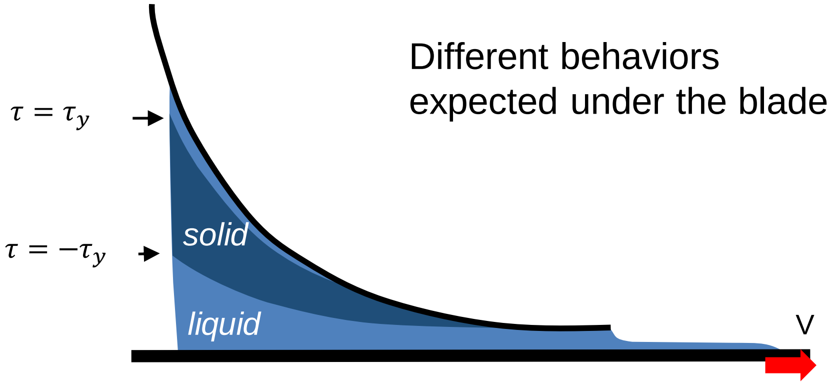
Soft blade coating of yield stress fluids

Carbopol gel in water

Rheology



Theoretical representation



Large **discrepancy** of the data

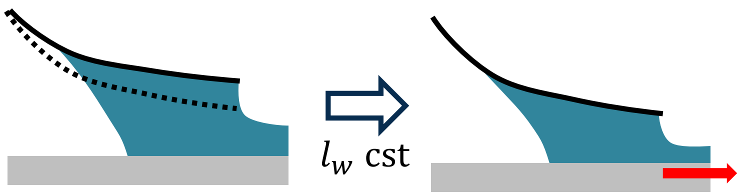
Do not follow the scaling law

⇨ At least **two limiting phenomena** identified

LIMITS WITH YIELD STRESS SPREADING

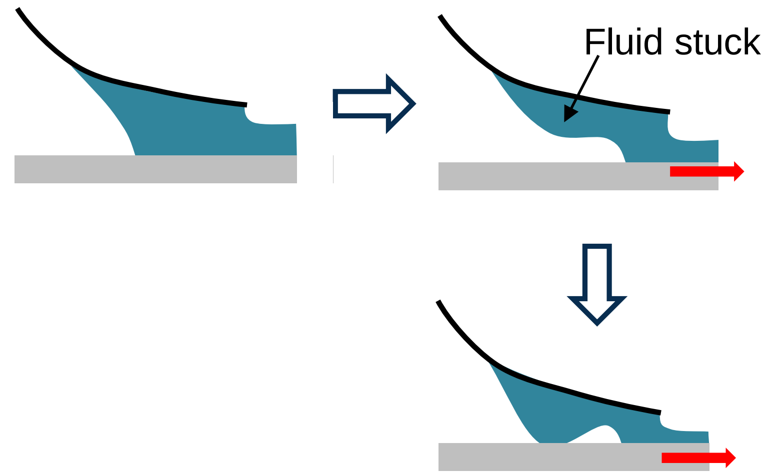
INITIAL ELASTIC FORCES

Elastic forces induced by Carbopol not taken into account in the blade shape



- e varies **independantly** from l_w

FLUID STUCK UNDER THE BLADE



- **Non monotonous** deposit (bumps)
- l_w **?** → no longer properly defined

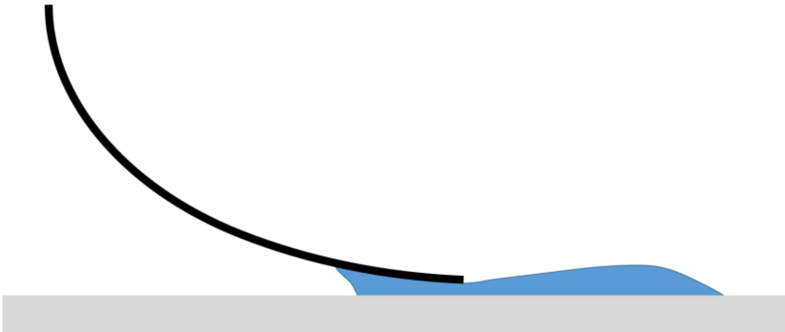
Situations **not described** in our model !

Solution : Fixed blade (*Maillard 2016*)

Out of our study scope

Conclusions

Analogy with finger coating



Key points:

- **Non uniform coating** is expected for **Newtonian and shear thinning fluids**
  → **Solution** : **infinite reservoir** of fluid
- Adding polymers to obtain **normal stress** has **no impact** on the thickness **at the begining of spreading**.
- To get **longer** and more **homogeneous** deposit **reduce spreading velocity** or **viscosity** (side effect: it leads to overall **thinner** deposit)
- **Limits** to describe **yield stress** spreading

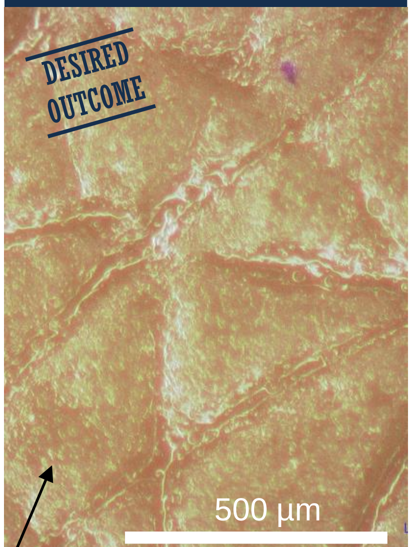
Spreading of formulation with **solid particles** ?

THE IMPACT OF PARTICLES IN SPREADING DEFECTS

Observations:

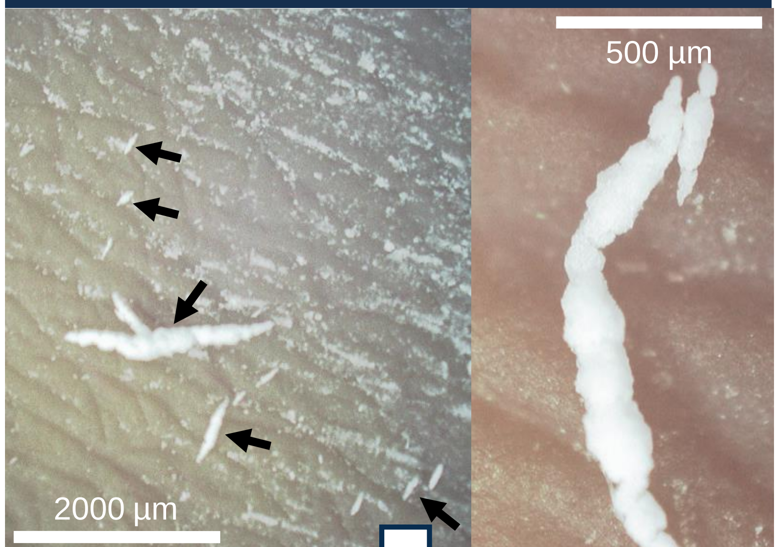
Different types of results at the end of spreading a cosmetic cream :

Liquid film

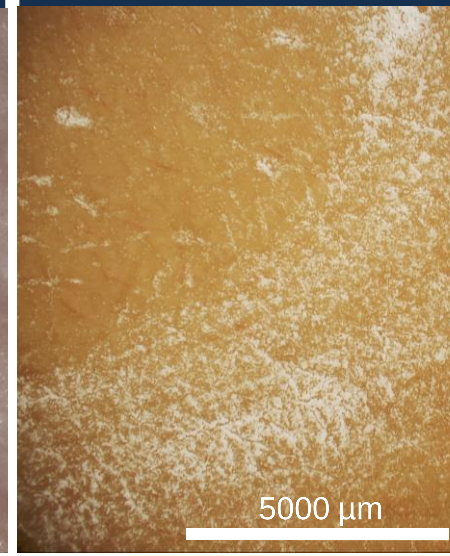


Artificial skin

Aggregates



Powdery deposit

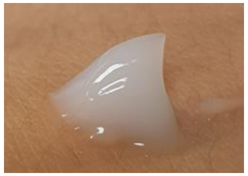


- Induce **unpleasant sensation** upon spreading on skin
- **Reduce the efficiency** of cosmetic product

What are the parameters involved ?
How to explain aggregate formation ?
How to avoid them ?

Challenge to switch to biobased products (ex : cellulose)

FORMULATION



CHOICE OF THE FORMULATION BASIS :

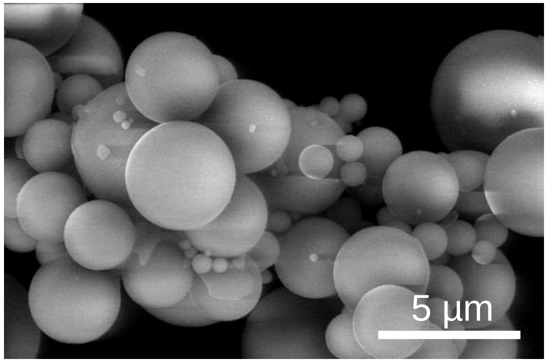
- ➔ Characteristic **rheological behaviour**
- ➔ As **simple** as possible

- ❑ Carbopol gel in water: mechanical resistance (yield stress)
- ❑ Glycerol : residual film (10 wt%)
- ❑ Preservatives

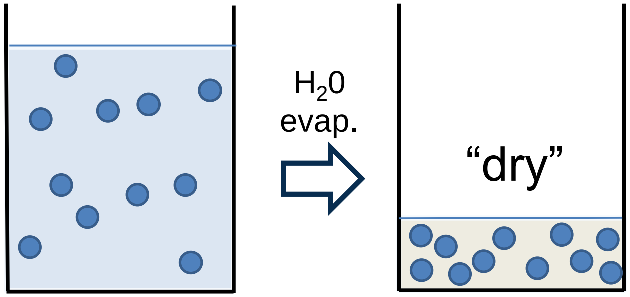
CHOICE OF THE PARTICLE :

MODEL : SILICA BEADS

- ➔ Spherical
- ➔ Non porous
- ➔ Rigid and smooth



EVOLUTION:

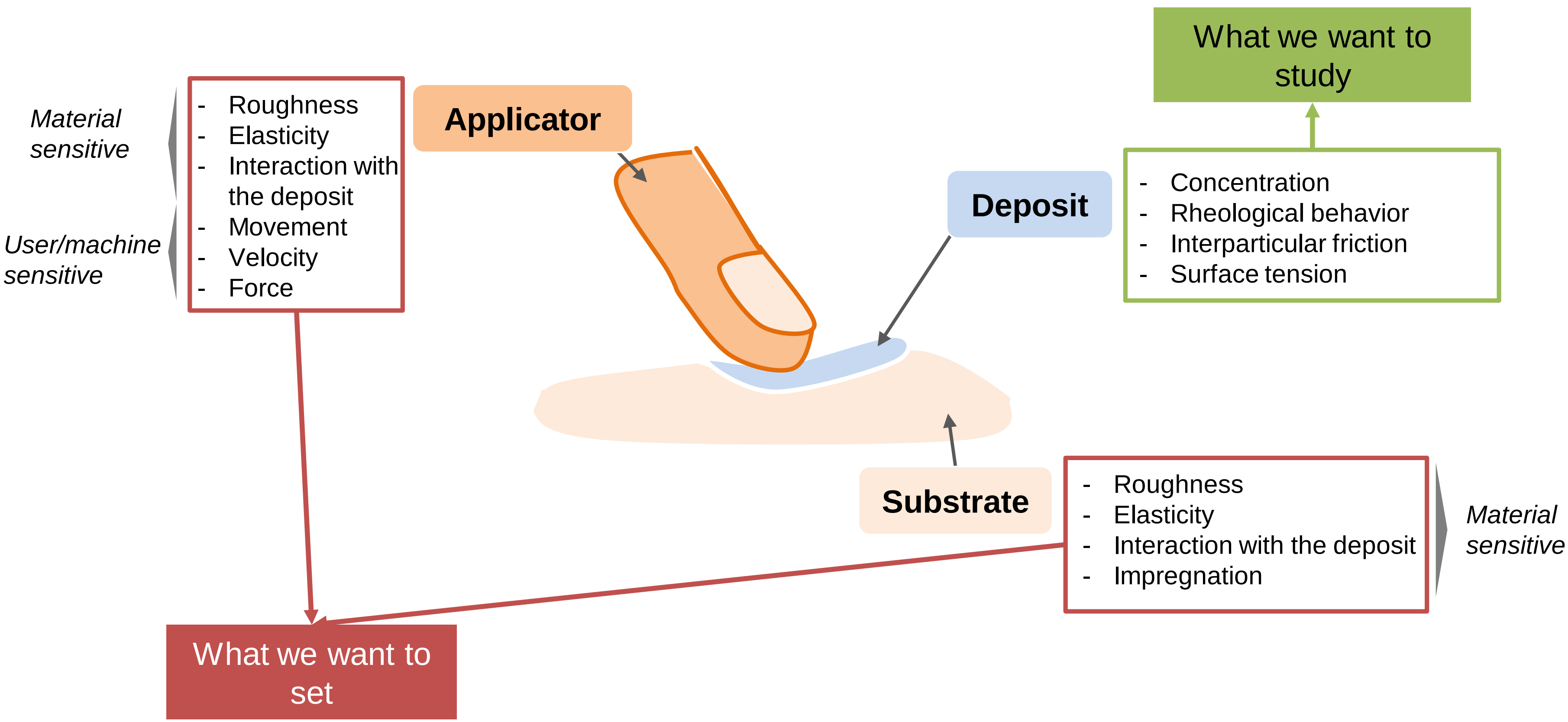


Concentration (volume fraction) of particule in the **non-volatile** phase :

$$c_v = \frac{V_{solid\,particles}}{V_{solid\,particles} + V_{glycerol}} . 100$$

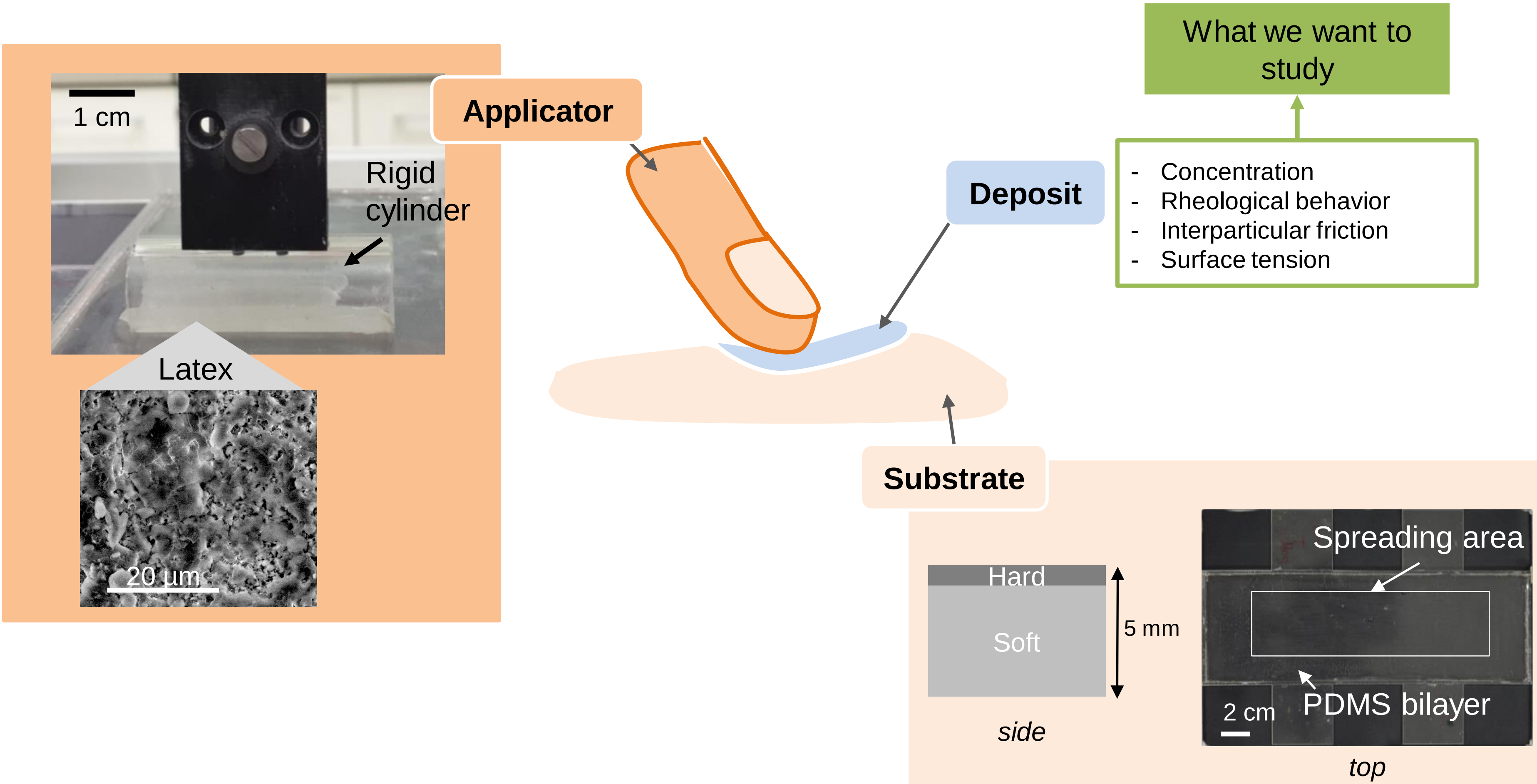
Scope of the study

Factors that MIGHT influence the emergence of aggregates:



Scope of the study

Factors that might influence the emergence of aggregates:

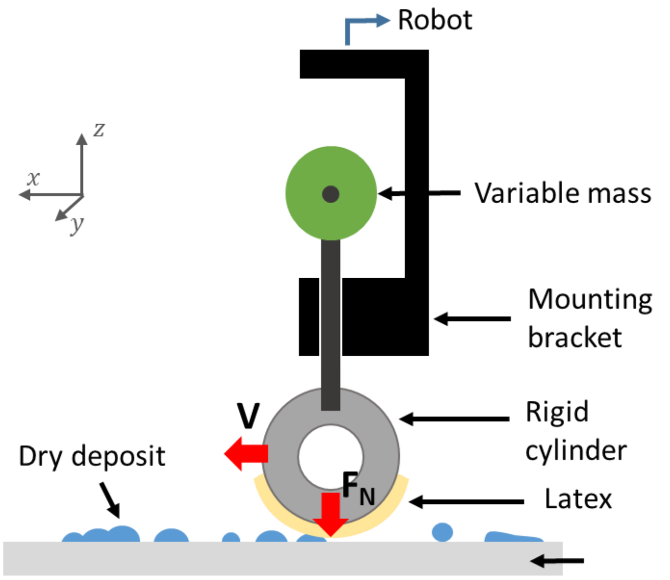


Experimental setup & Protocol

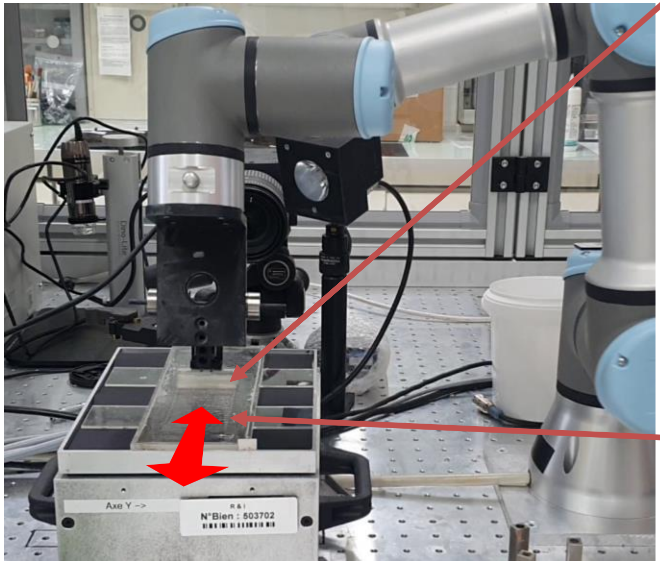
Protocol

- **Spreading** around 0.1-0.2 g of formulation with the applicator
- **Drying** on a heated plate at 40°C for 20min

⇨ **Dry** deposit = glycerol, carbopol and solid particles



Applicator



Substrate

- **2 Back and forth** movement with **the applicator moved by the robot**

Role of discontinuity

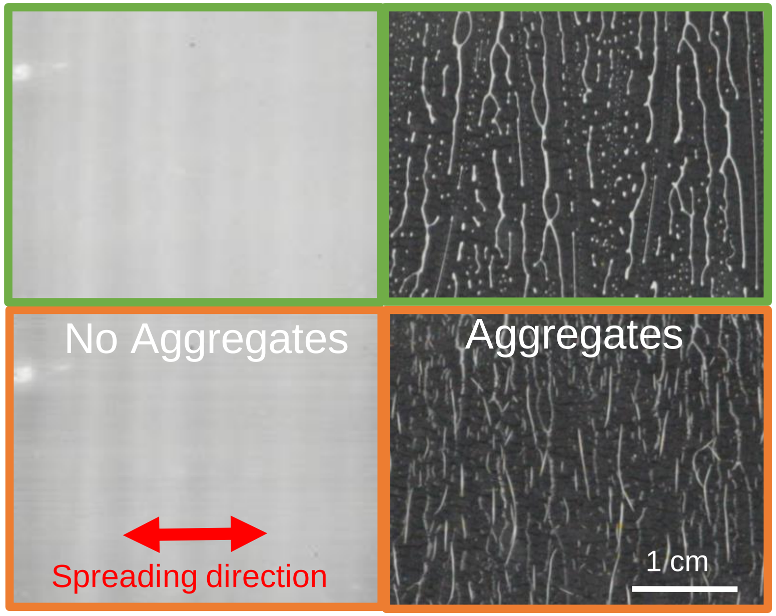
Continuous deposit :

Discontinuous deposit (dewetting)

≠ *amount*

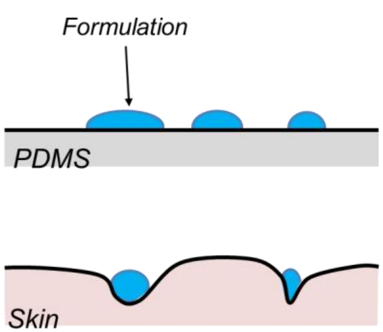
Initially:

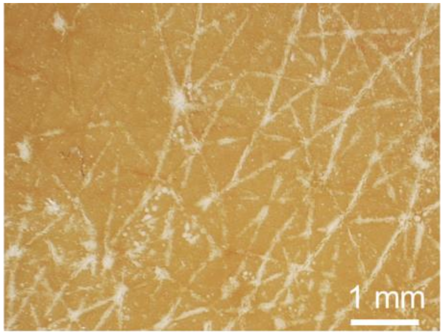
After 4th run:



Discontinuity is at the origin of aggregates formation

Parallel with spreading on skin



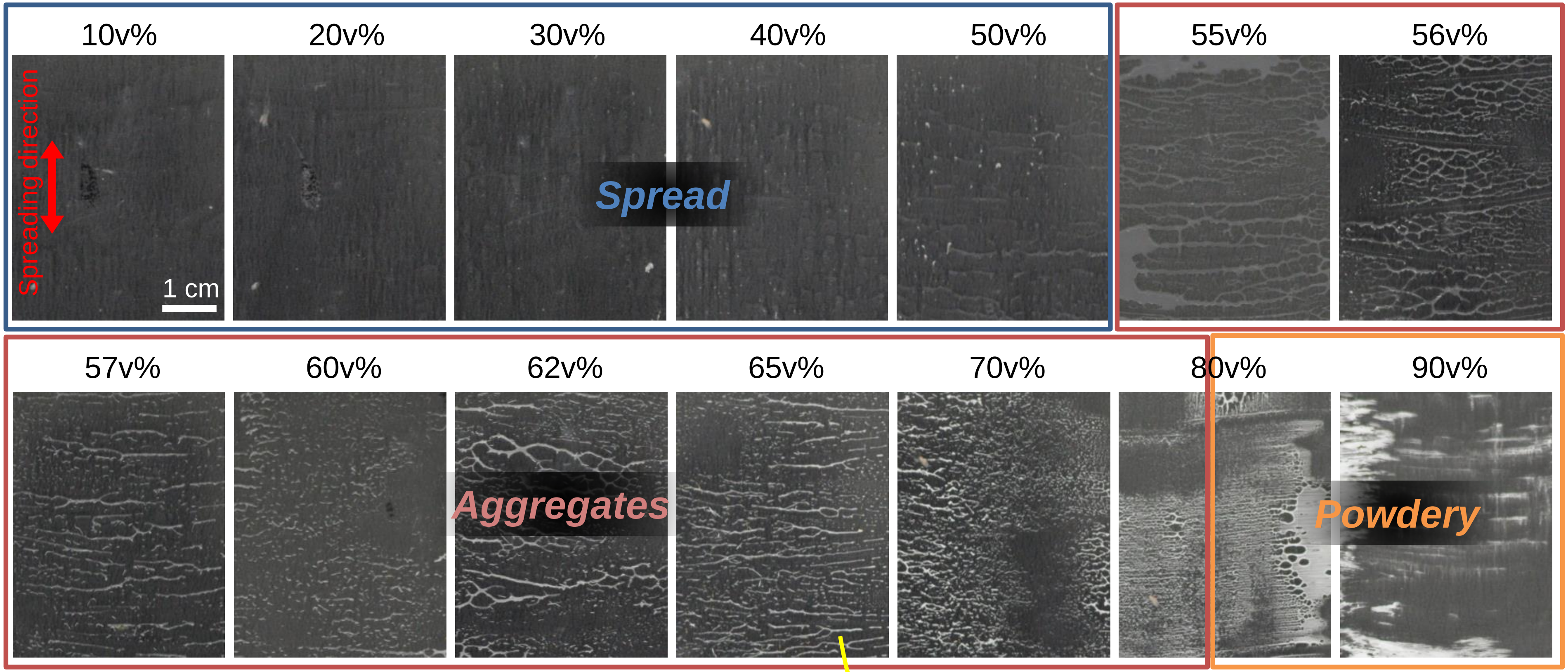


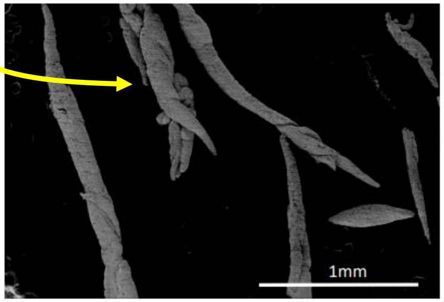
The spreading of cosmetics on the skin also causes a discontinuity in the deposit

- **Choice of discontinuous deposit for the experiments**

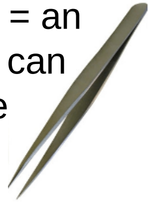
Impact of particle concentration

After the **1st run** :



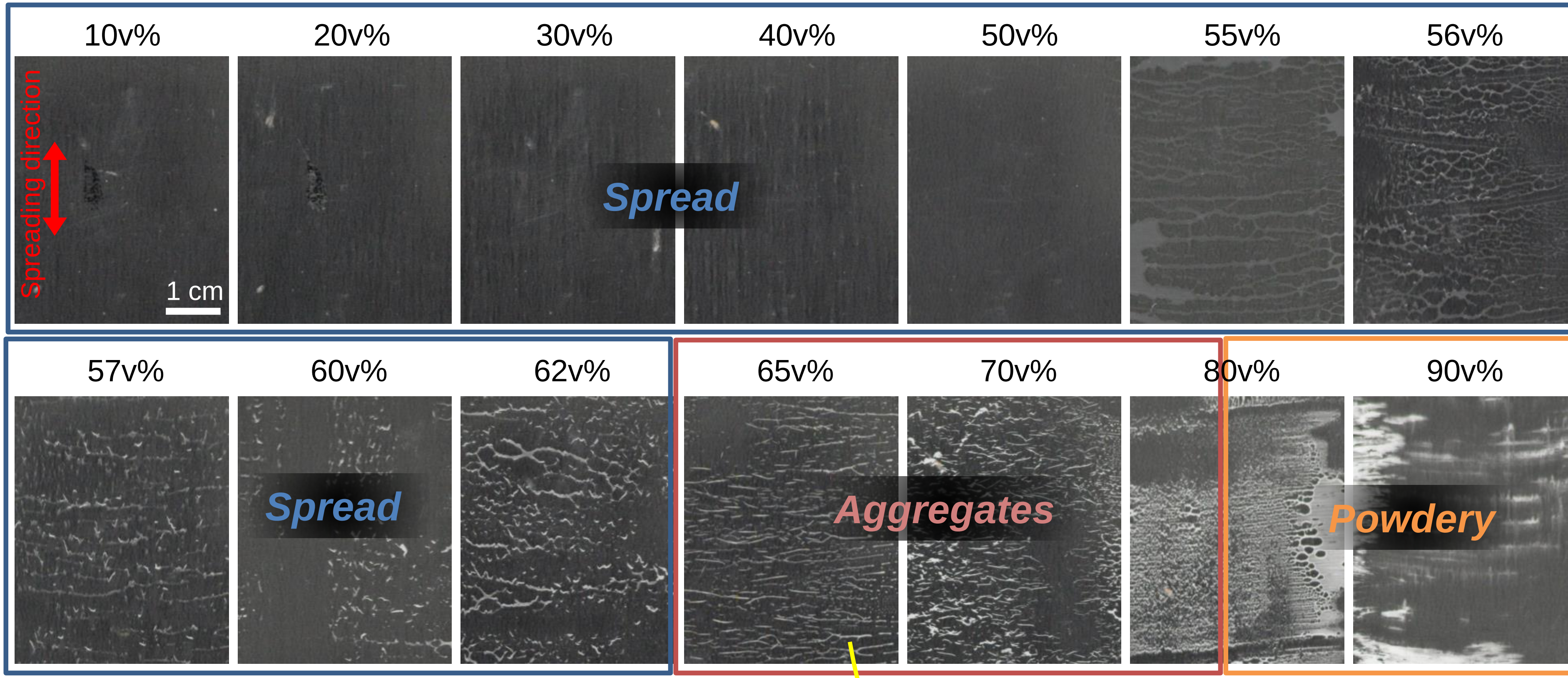


Aggregate = an object you can manipulate



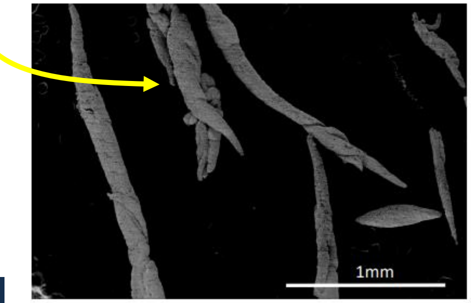
IMPACT OF PARTICLE CONCENTRATION

After the **4th run** :



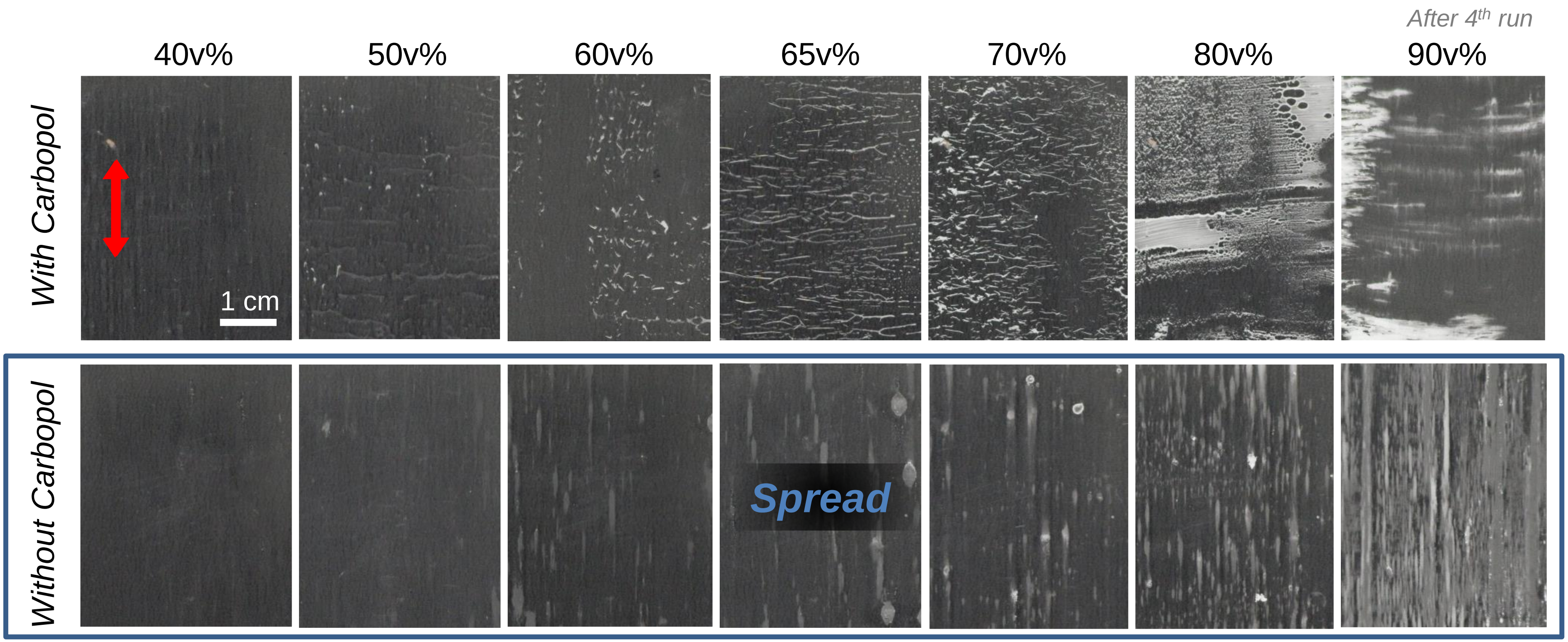
Aggregates formation **depends on particle concentration** in glycerol:

- Low c_v= spread
- Intermediate c_v= **aggregates**
- High c_v = powdery deposit



Aggregate = an object you can manipulate

IMPACT OF CARBOPOL IN THE FORMULATION

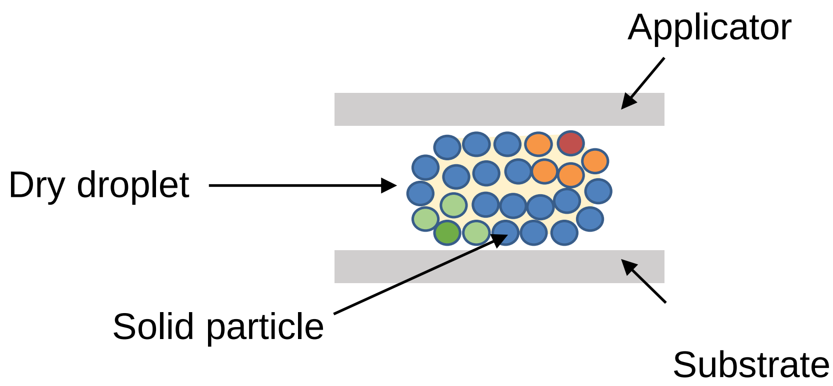


Without carbopol the samples do **not form** aggregates

Mechanism of aggregates formation

Formation mechanism

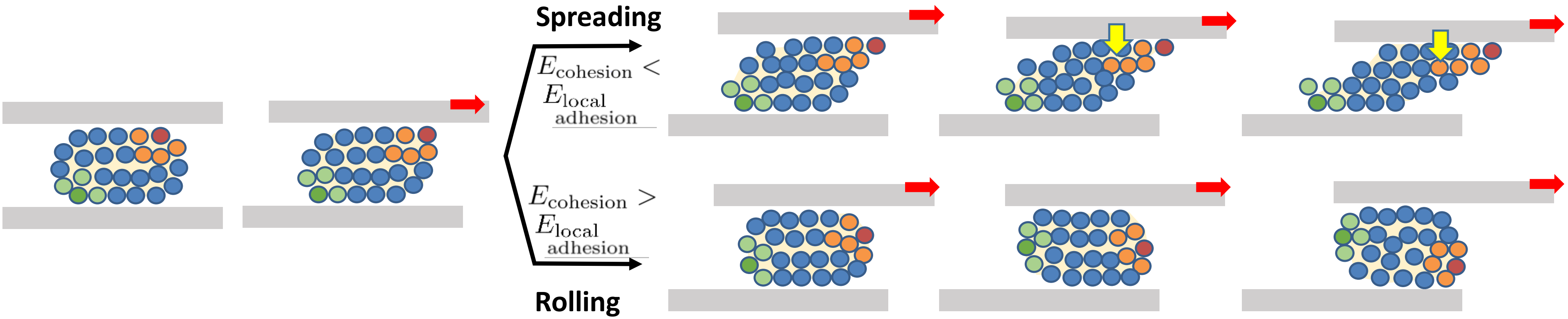
Proposal for a microscopic mechanism



+ ***No slip*** at the wall

Formation mechanism

Proposal for a microscopic mechanism



Aggregates forms if: $\boldsymbol{E}_{\textbf{cohesion}} > \boldsymbol{E}_{\textbf{local adhesion}}$ (+ no slip)

$\downarrow$

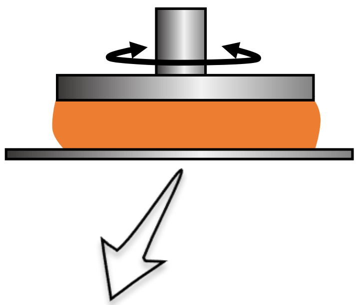
$\sim G'$

Validation of the model : Rheology

Principle

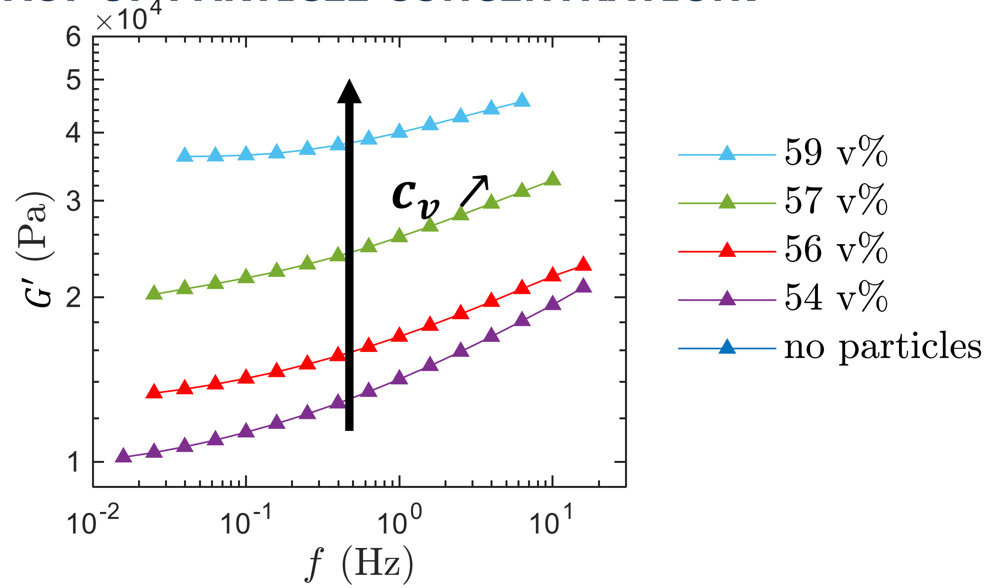
In oscillation

$\hat{\gamma}$ *strain*
f *frequency*

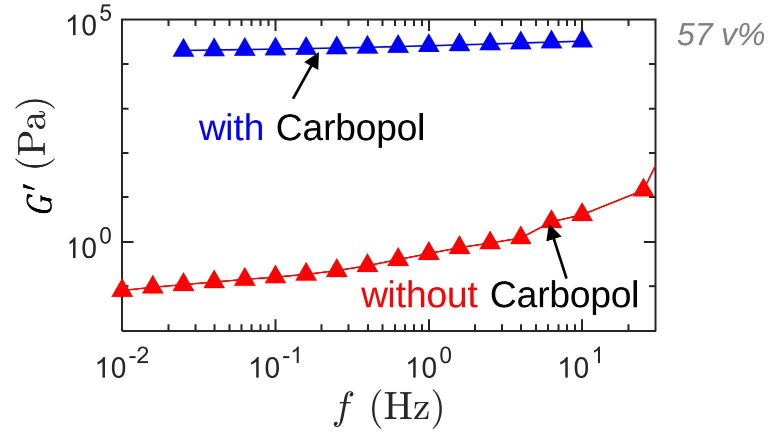


G' Elastic modulus
G'' Viscous modulus

Impact of particle concentration:



Impact of carbopol:

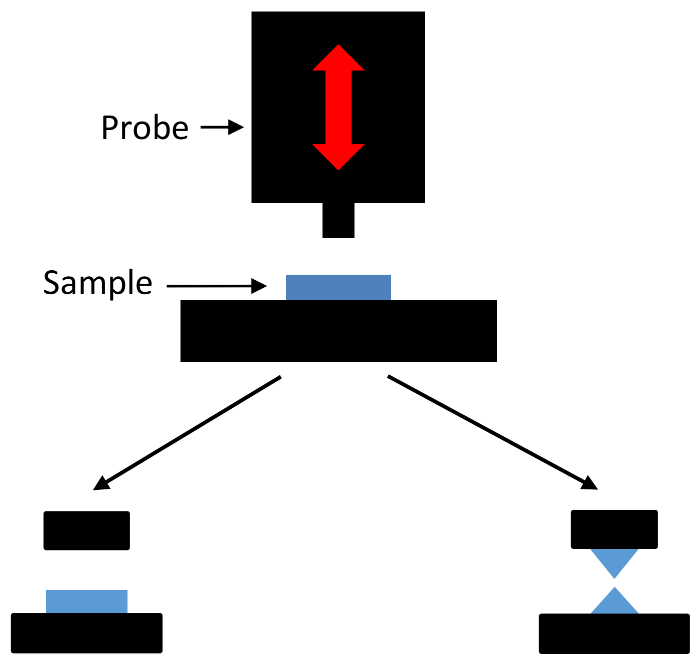


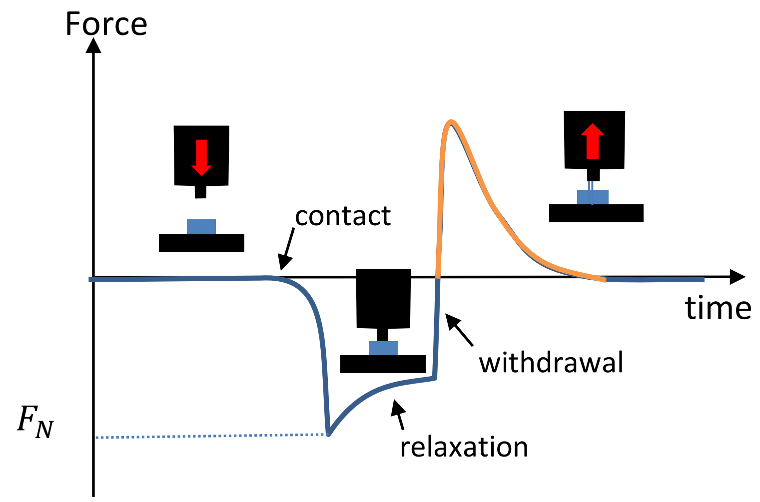
Elastic modulus G' **increases** with:
- **particle concentration** c_v
- **Carbopol** presence
- **frequency**

↳ **Consistent with aggregates formation**

Validation of the model: Probe Tack test

Principle





Adhesive failure

$E_{\text{cohesion}} > E_{\text{adhesion}}$

Aggregates expected

Cohesive failure

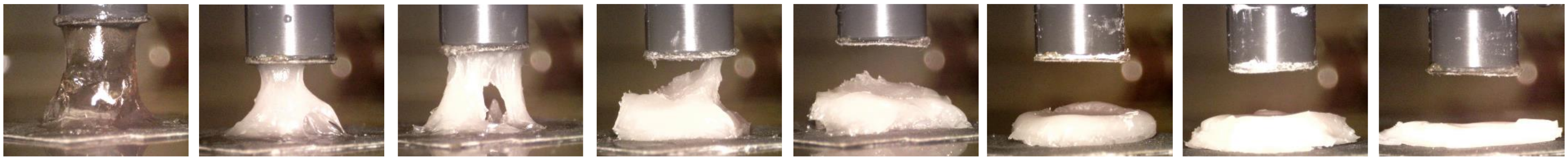
$E_{\text{cohesion}} < E_{\text{adhesion}}$

Spreading expected

Validation of the model: Probe Tack test

Impact of the solid particle concentration

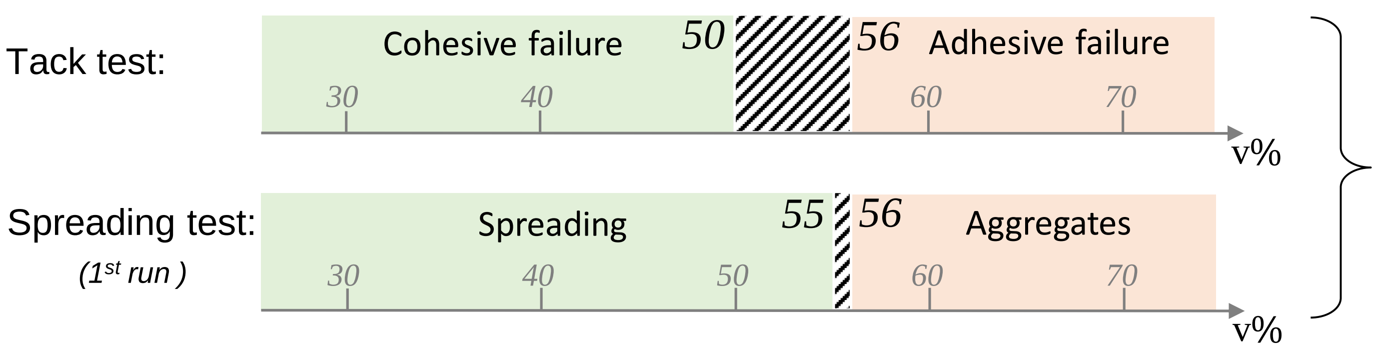
$c_v = 0$ % | 40 % | 50 % | 54 % | 56 % | 57 % | 59 % | 65 %



Cohesive failure (0 % – 54 %) | *Adhesive failure* (56 % – 65 %)

$c_v \geq 54\% \Rightarrow$ Adhesive failure is observed,
$E_{\text{cohesion}} > E_{\text{adhesion}}$ and aggregates are expected

Comparison with spreading test

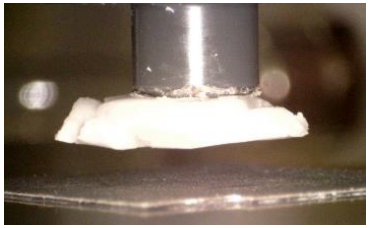


Tack test gives **good match** between **adhesive failure** and **aggregates**

VALIDATION OF THE MODEL: PROBE TACK TEST

IMPACT OF CARBOPOL

with Carbopol



Removing Carbopol

without Carbopol

60 v%

Adhesive failure

$$E_{\text{cohesion}} > E_{\text{adhesion}}$$

Cohesive failure

$$E_{\text{cohesion}} < E_{\text{adhesion}}$$

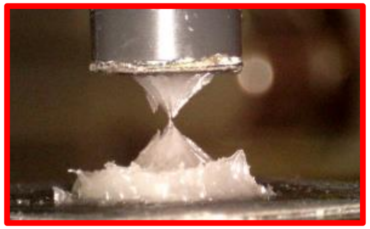
Consistent with the absence of aggregates

Validation of the model: Probe Tack test

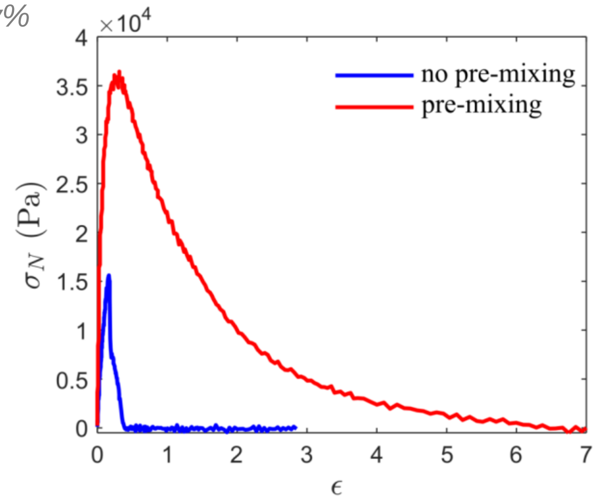
Impact of Pre-mixing

No pre-mixing

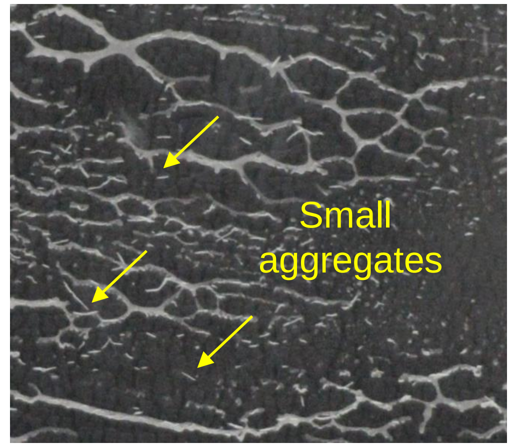
Pre-mixing



57v%

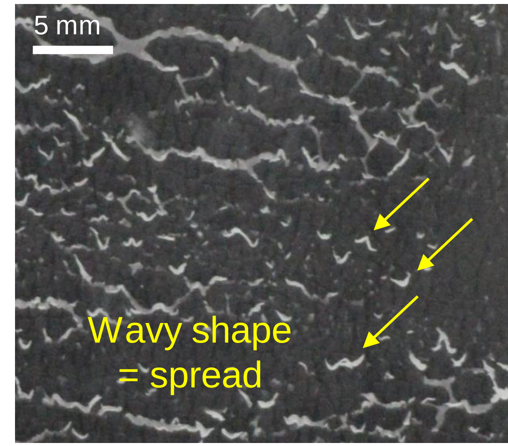


After 1[st] run



After 4[th] run

62v%

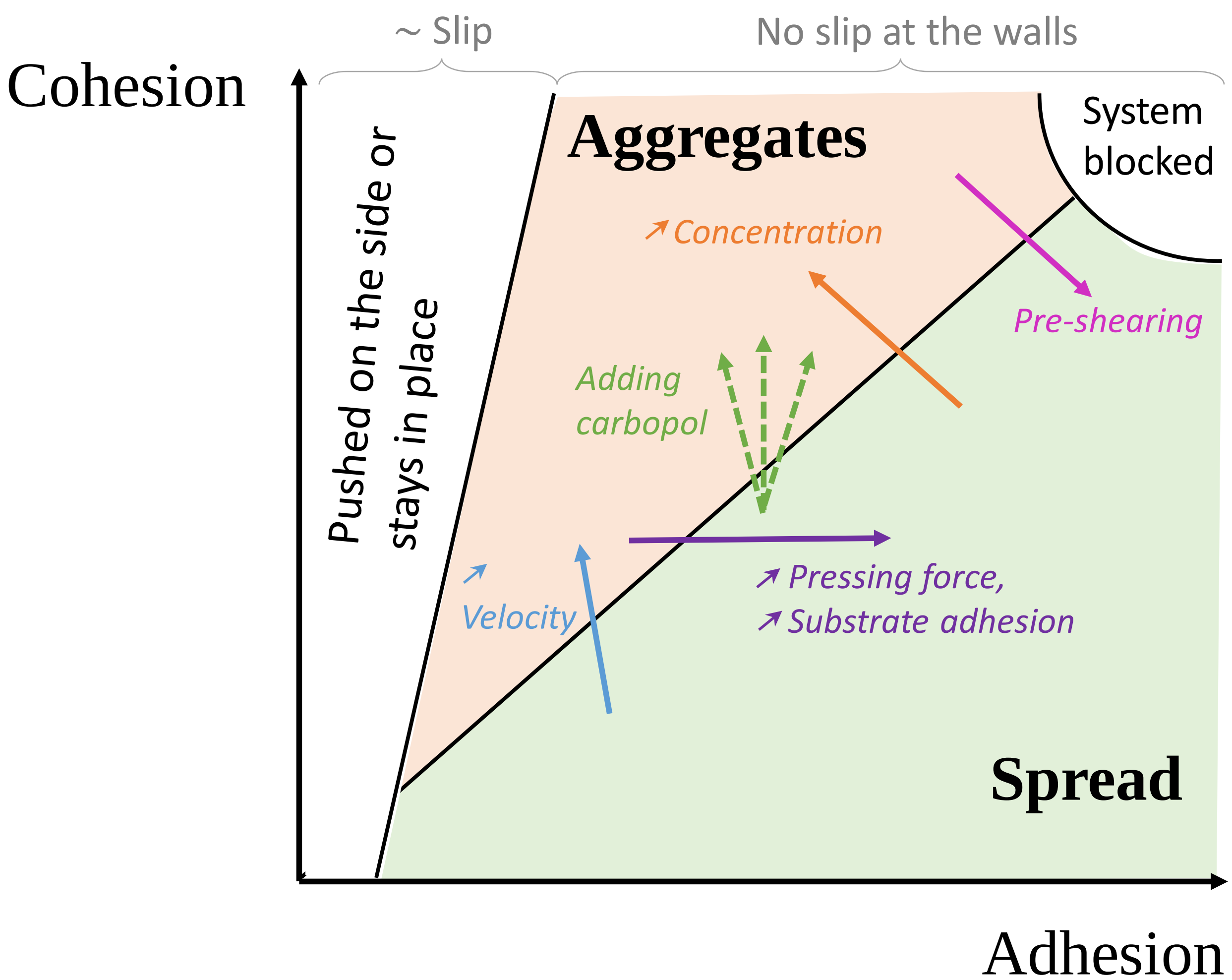


Spreading of aggregates by successives runs ≃ premixing

With **pre-mixing** ➔ $E_{cohesion} > E_{adhesion} \Rightarrow E_{cohesion} < E_{adhesion}$
➔ **cohesive failure** for $c_v \leq 57\%$ (instead of 54%)

Explain the spreading of aggregates after the first run (at some c_v)

SUMMARY

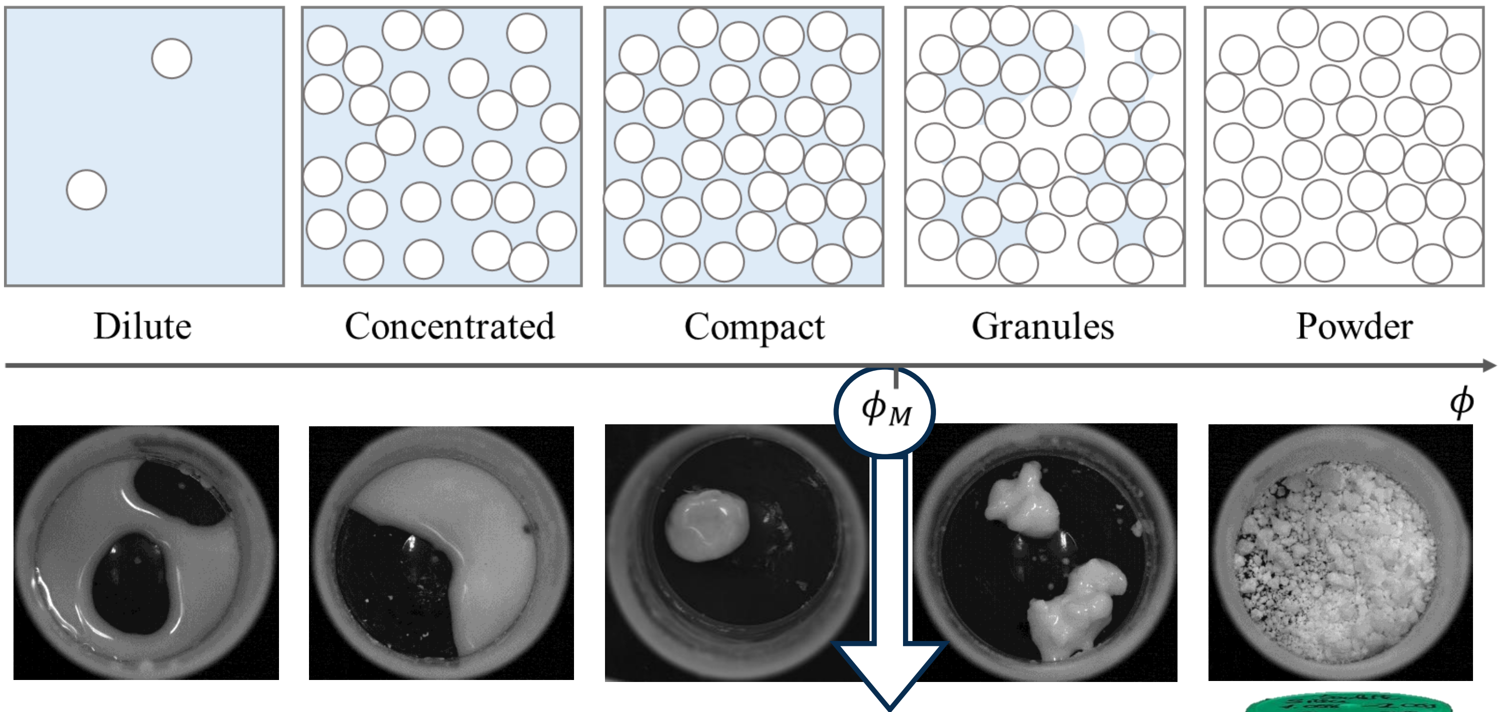


~ Slip
No slip at the walls
Cohesion
Pushed on the side or
stays in place
Aggregates
System
blocked
↗ Concentration
Pre-shearing
Adding
carbopol
↗
Velocity
↗ Pressing force,
↗ Substrate adhesion
Spread
Adhesion

What would be a safe range of concentration?

For carbopol/glycerol based formulations

Jamming packing fraction

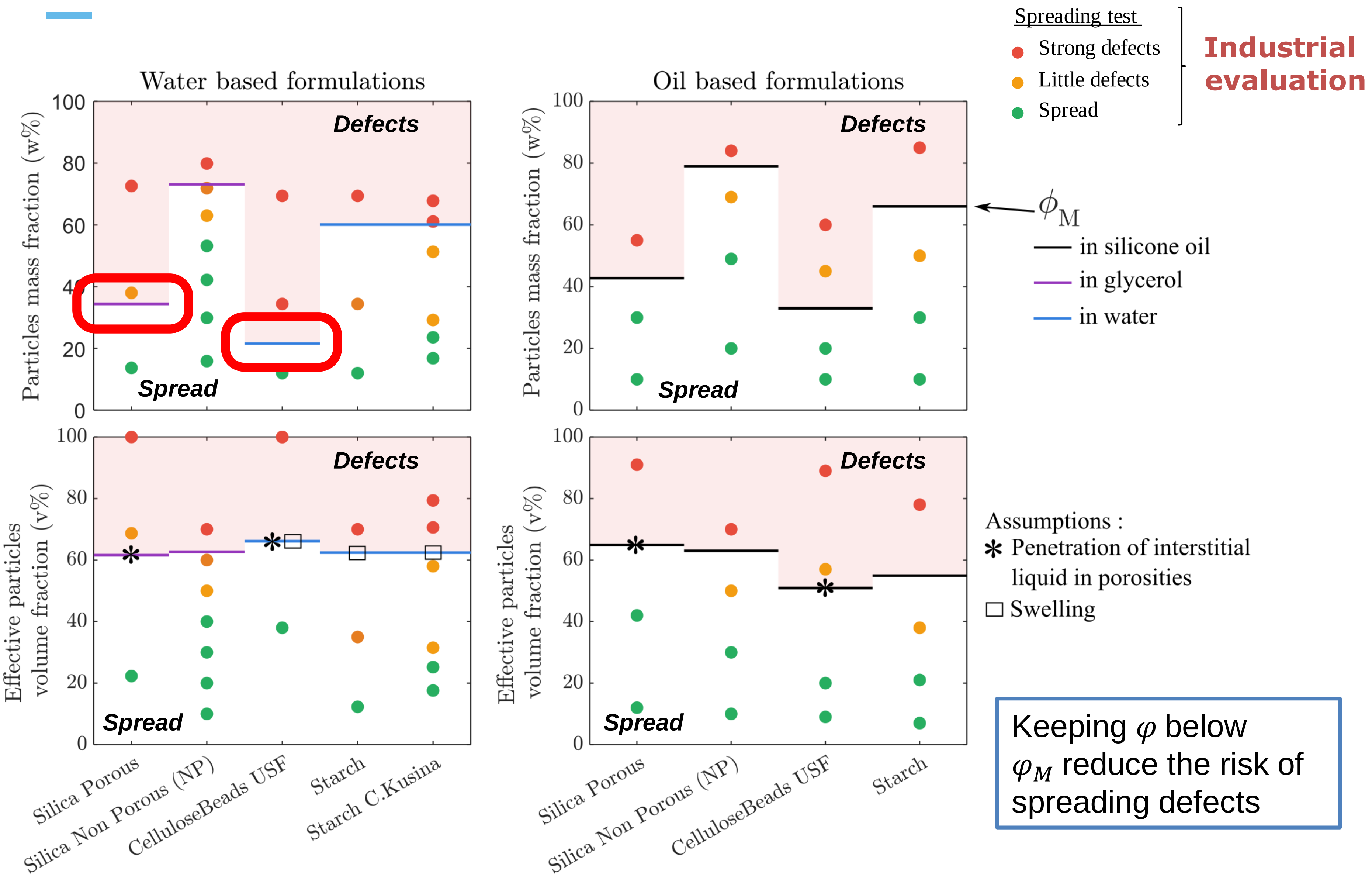


Estimated through the
« Small ball test »

Above this limit in the <u>non volatile phase,</u>
aggregates are expected to occur after drying

Ball representing
the limit $\boldsymbol{\varphi_M}$

Comparison with aggregates test

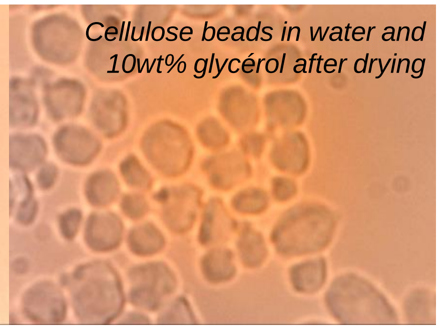


Keeping φ below φ_M reduce the risk of spreading defects

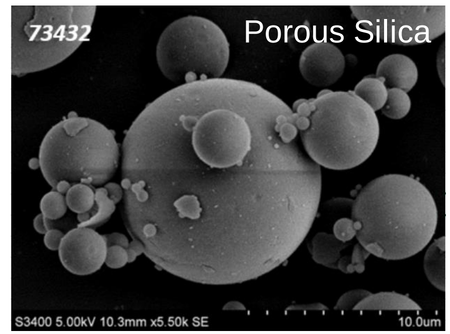
Extension to other particles

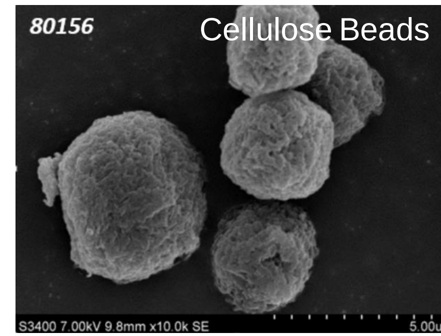
Two corrective effects on the volume fraction:

SWELLING



POROSITY



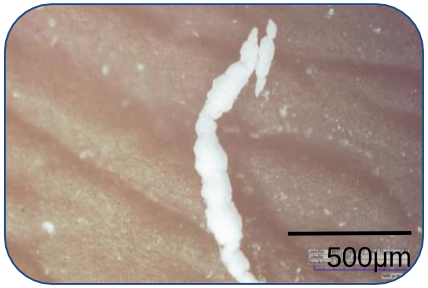


Effect on the volume of particule and volume of interparticulate liquid

The jamming packing fraction is reached for **low mass fraction** of particles if they are **porous** or **swell** in solvent

CONCLUSIONS

AGGREGATES OF PARTICLES



Key points:

- **New set-up** with robot & **artificial skin** to study aggregate formation
- **Several** factors indentified as impacting aggregates formation: **particle concentration, Carbopol …**
- Aggregates form when **cohesion** of the material is stronger than adhesion on the walls.
- Good match between **tack test** and spreading test results. Easier experiment to predict aggregates.
- To reduce the risk of aggregates keep $\phi < \phi_M$
- Warning: **swelling & porous particles** have low maximum mass fraction.

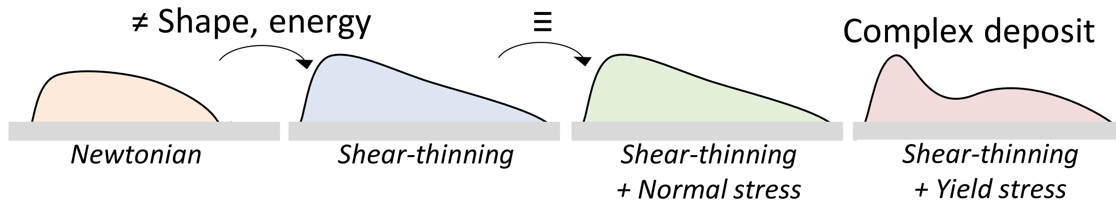
Conclusion and perspectives

Conclusion and Perspectives

Soft substrate influence ?
Rigid blade for yield stress ?

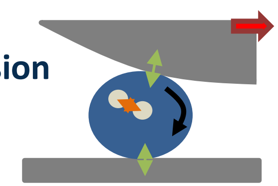
How does a finite reservoir influence the spreading dynamics ?

What is the impact of rheology ?



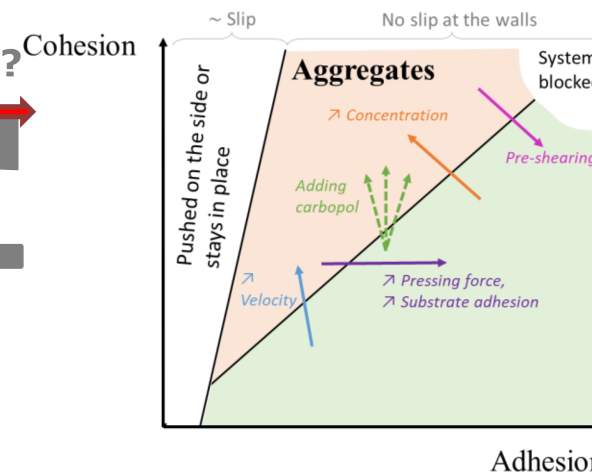
What are the parameters involved in aggregates formation ?

How to explain their formation ? **Cohesion** VS **adhesion**



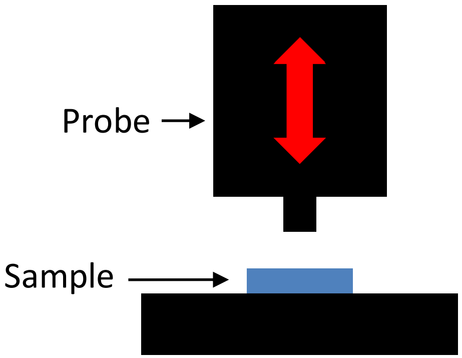
How to avoid them ? $\phi < \phi_M$

<u>& Spreading if :</u>
- Low cohesion in the material
- Strong adhesion to the walls



Quantitative validation ?
Improve equivalence spreading test & tack test (material, movement) ?
Skin topography ?

PERSPECTIVE: TACK TEST



Use:

Prediction of aggregates formation for a given formulation (dried)

Advantages:

- Quick
- Easy to implement in industry

To dig deeper:

- Probe surface material
- Test conditions (pull-back velocity…)

Acknowledgments

Jury: Marie-Caroline Jullien, Ludovic Pauchard, Guillaume Ovarlez, David Quéré, Jean-François Joanny

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Thank you for your attention

Questions ?