Behaviour, properties and structures of complex fluids upon spreading

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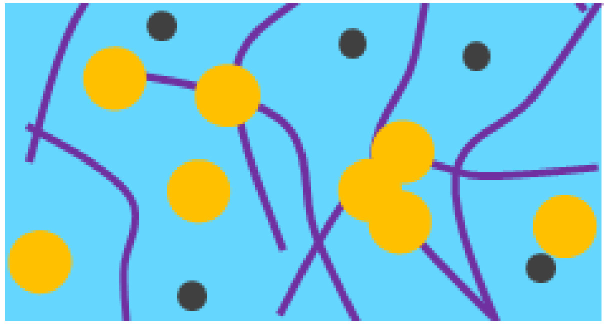
Industrial context

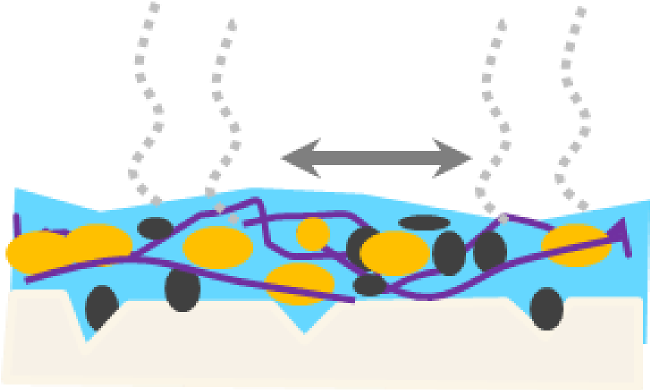
Life cycle of cosmetic products

Packaging, storing



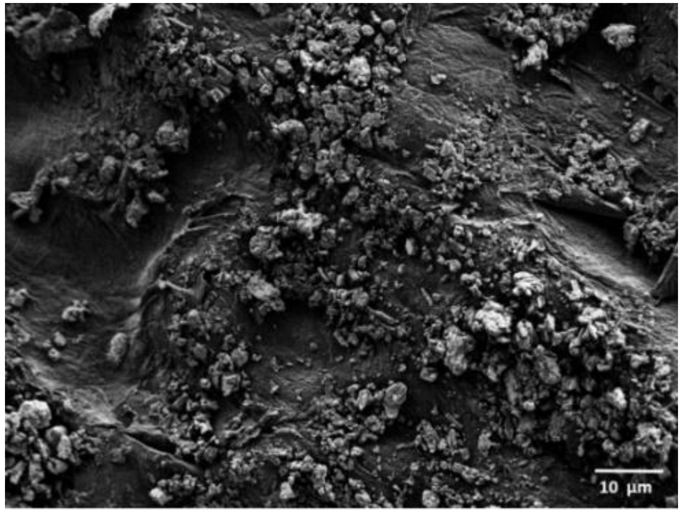
Bulk **stability** of formulations
Stability over time

Application



Spreading dynamic and behaviour of complex fluids under **stress** and during drying

Efficiency, performance



Deposit **characterization**
Distribution of particules

Industrial context

Life cycle of cosmetic products

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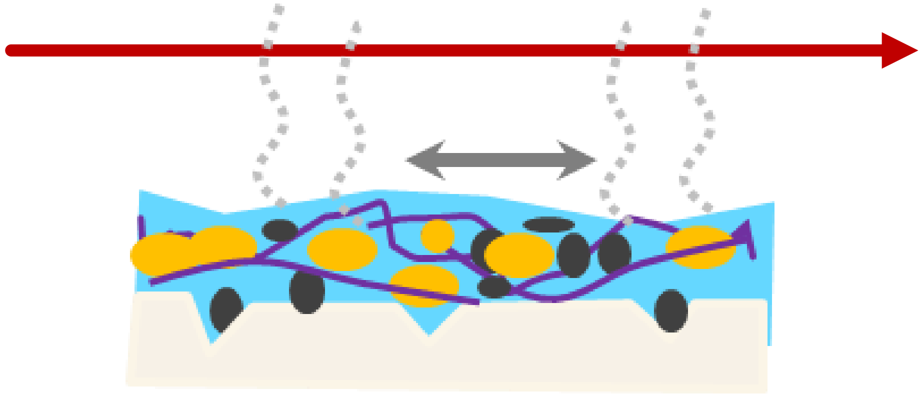
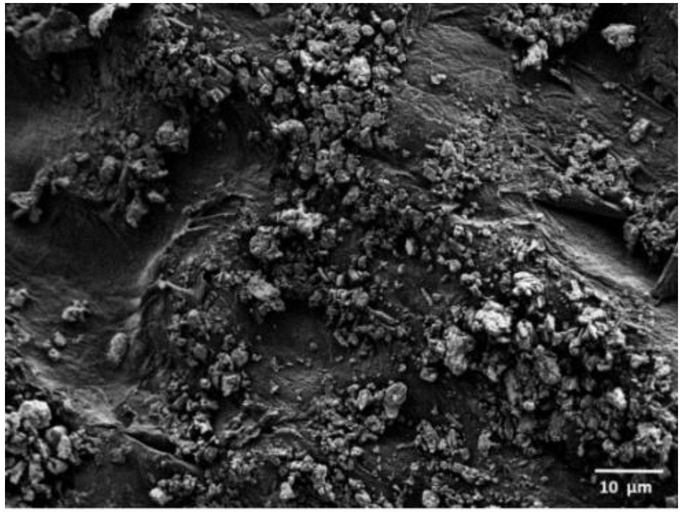
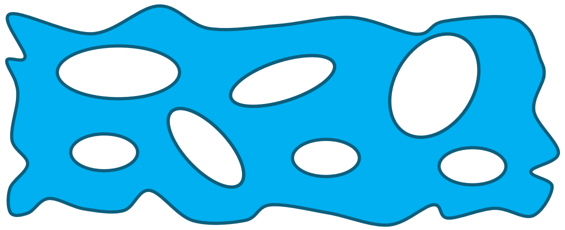
Application



Efficiency, performance



Homogeneous coating



Heterogeneous coating

What can we do to get a **homogeneous coating of cosmetics** on skin ?

What is a cosmetic formulation made of ?

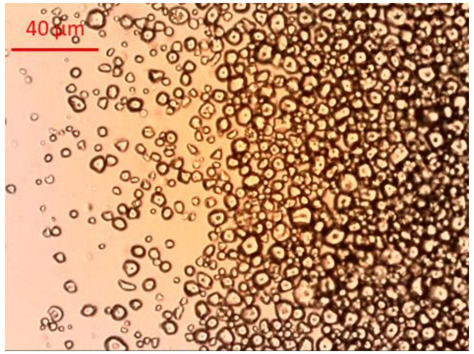
Hundreds of ingredients

Volatil phase (aqueous)	Active non-volatil phase	Texture agents
Water	Glycerol, oils, waxes Pigments, UV filters	Carbopol Particles (starch, silica)

Cosmetics are complex fluids with non-newtonian behaviours

Cosmetics are **complex fluids** with **non-newtonian behaviours**

Yield stress fluids



Shear-thickening fluids

Introduction to non-Newtonian behaviours

Newtonian fluids (simple fluids)

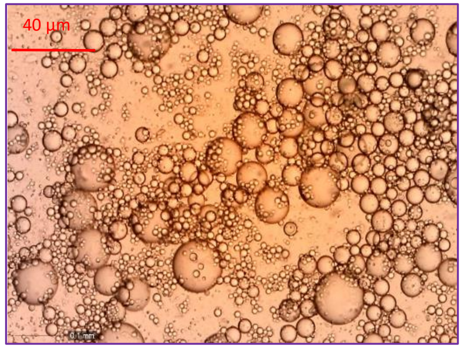
Monophasic

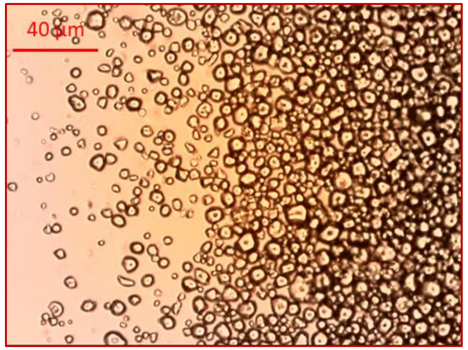
$\eta(\dot{\gamma}) = cst$

Their **viscosity is constant** whatever the shear they undergo

Complex fluids

Multiple phases





$\eta(\dot{\gamma}) \neq cst$

Their **viscosity varies** with the shear they undergo

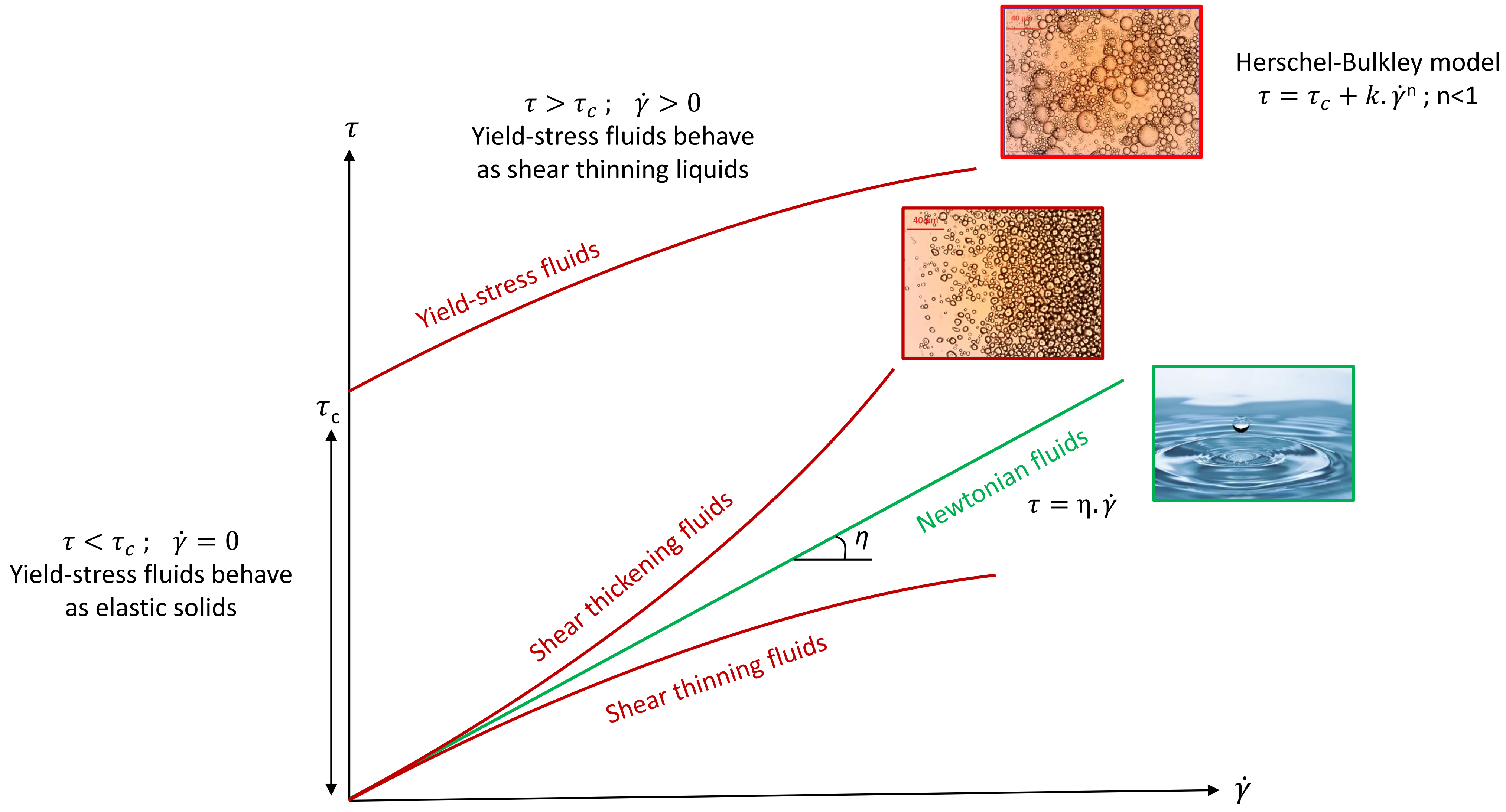
Non-Newtonian behaviour

Structure-Flow coupling

Yield stress fluids

Shear-thickening fluids

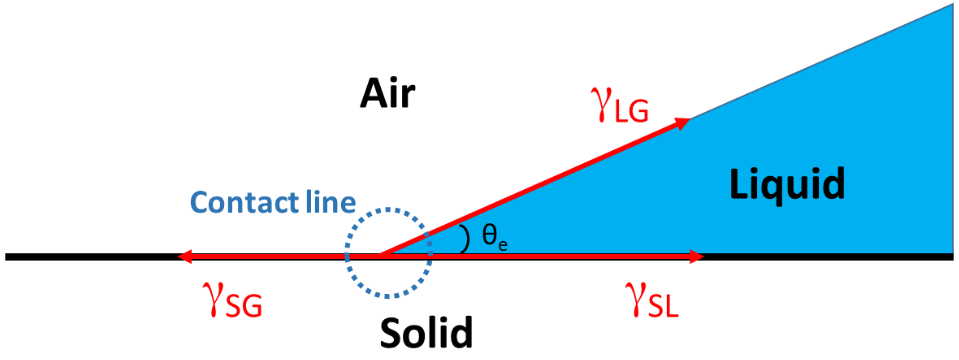
Introduction to non-Newtonian behaviours



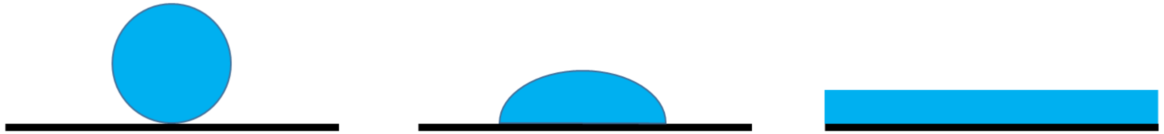
Spreading of non-Newtonian fluids is new: interesting for academic research

Everyday problem

Spontaneous spreading of fluids: wetting properties



Young's law $\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos\theta_e$



Non-wetting $\Theta_e = 180°$

Partial wetting $0° < \Theta_e < 180°$

Total wetting $\Theta_e = 0°$

Spreading coefficient $S = \gamma_{SG} - \gamma_{LG} - \gamma_{SL}$

Spontaneous spreading of **Newtonian fluids** well **understood**

Young, T. An Essay on the Cohesion of Fluids. *Philos. Trans. R. Soc. London* **95,** 65–87 (1805).
Harkins, W. D. & Feldman, A. Films. The Spreading Of Liquids And the Spreading Coefficient. *Am. Chem. Soc.* **44,** (1922).
Zisman, W. A. Relation of the Equilibrium Contact Angle to Liquid and Solid Constitution. *Adv. Chem. Ser.* (1964).
Bergeron, V., Fagan, M. E. & Radke, C. J. Generalized entering coefficients: a criterion for foam stability against oil in porous media. *Langmuir* **9,** 1704–1713 (1993).

Forcing the spreading of a non-wetting fluid

Forcing the spreading of a non-wetting fluid

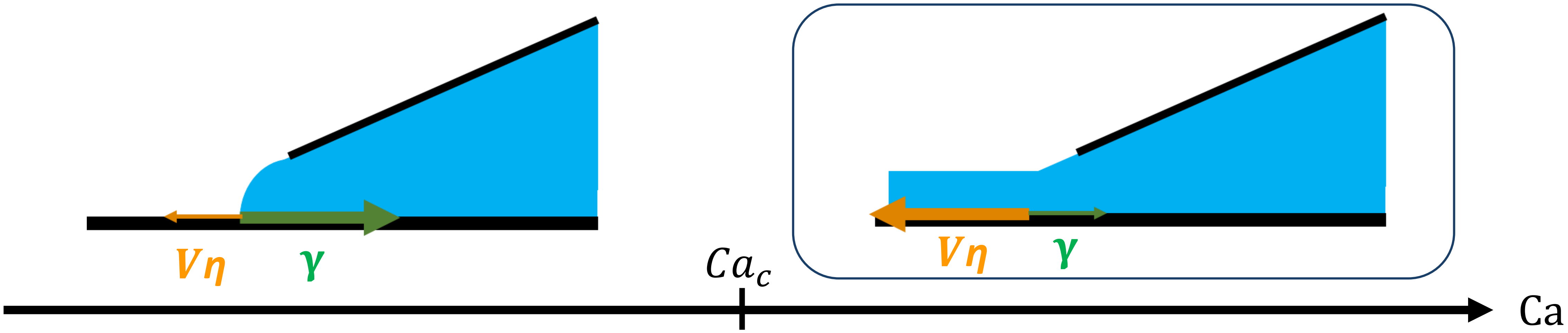
$$\mathrm{Ca} = \frac{V\eta}{\gamma}$$

U : Spreading velocity
η : Viscosity of the fluid
γ : Liquid/air surface tension

$$Ca_c = \frac{\theta_e{}^3}{9 \ln \frac{l_c}{l'}}$$

θ_e : Equilibrium contact angle
l_c : Capillary length
l' : Molecular length

Comparison between
viscous stress and **surface tension**



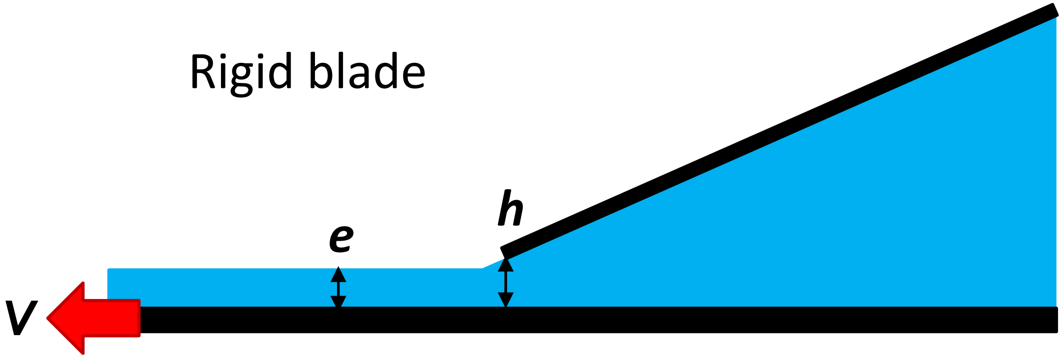
What fixes the thickness of the formed film ?

Snoeijer, J. H. & Andreotti, B. *Annu. Rev. Fluid Mech.* **45,** 269–292 (2013).
Deblais, A., Harich, R., Colin, A. & Kellay, H. *Nat. Commun.* **7,** 12458 (2016).

Spreading of Newtonian fluids

Blade-Coating using rigid and soft blades

Rigid blade



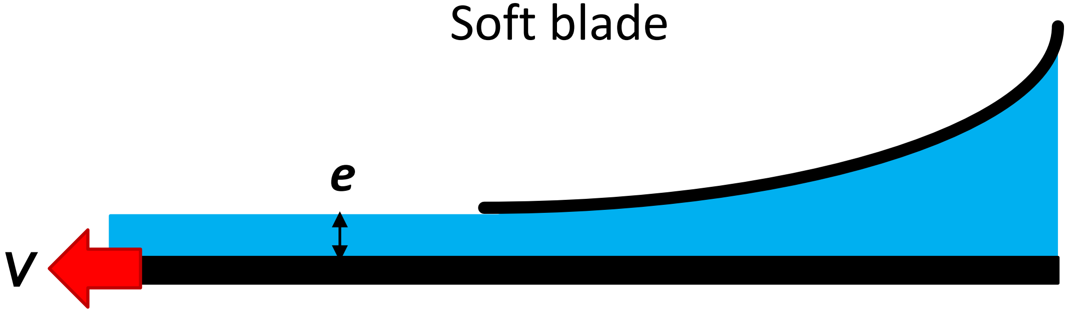
No slip and small angle

Only depends on the geometry

$$e \sim h/2$$

Greener, Y. & Middleman, S. Blade-coating of a viscoelastic fluid. *Polym. Eng. Sci.* **14,** 791–796 (1974).

Soft blade



Coupling flow-geometry

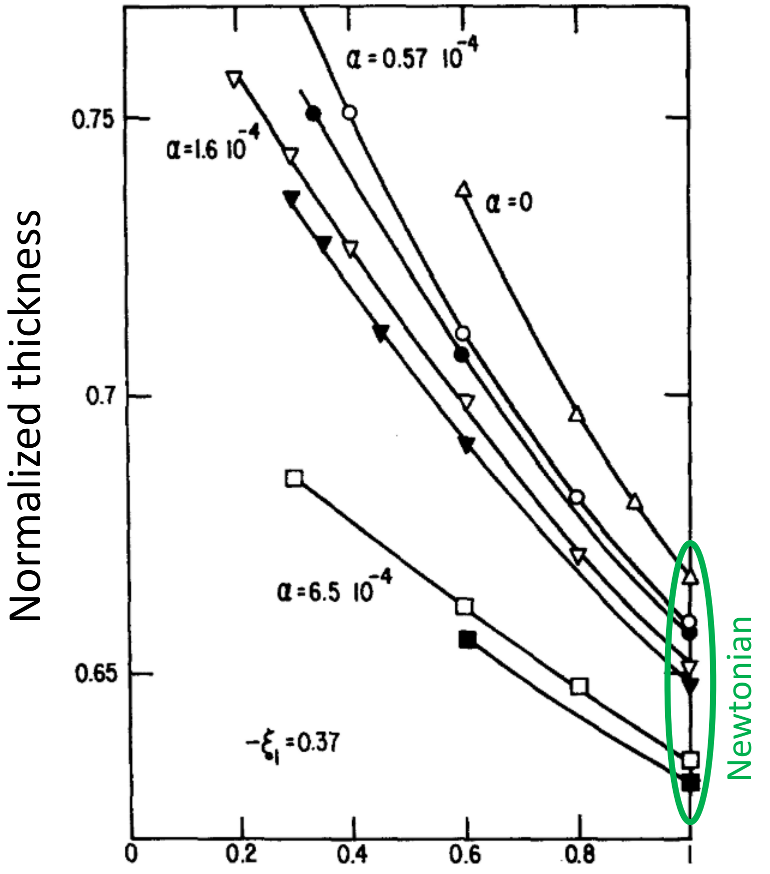
$$e \sim L\left(\frac{\eta V L^2}{B}\right)^{3/4}$$

V : Spreading velocity
η : Viscosity of the fluid
L : Length of the blade
B : Rigidity of the blade

Seiwert, J., Quéré, D. & Clanet, C. Flexible scraping of viscous fluids. *J. Fluid Mech.* **715,** 424–435 (2013).

Spreading of non-Newtonian fluids

Blade-Coating using rigid blades



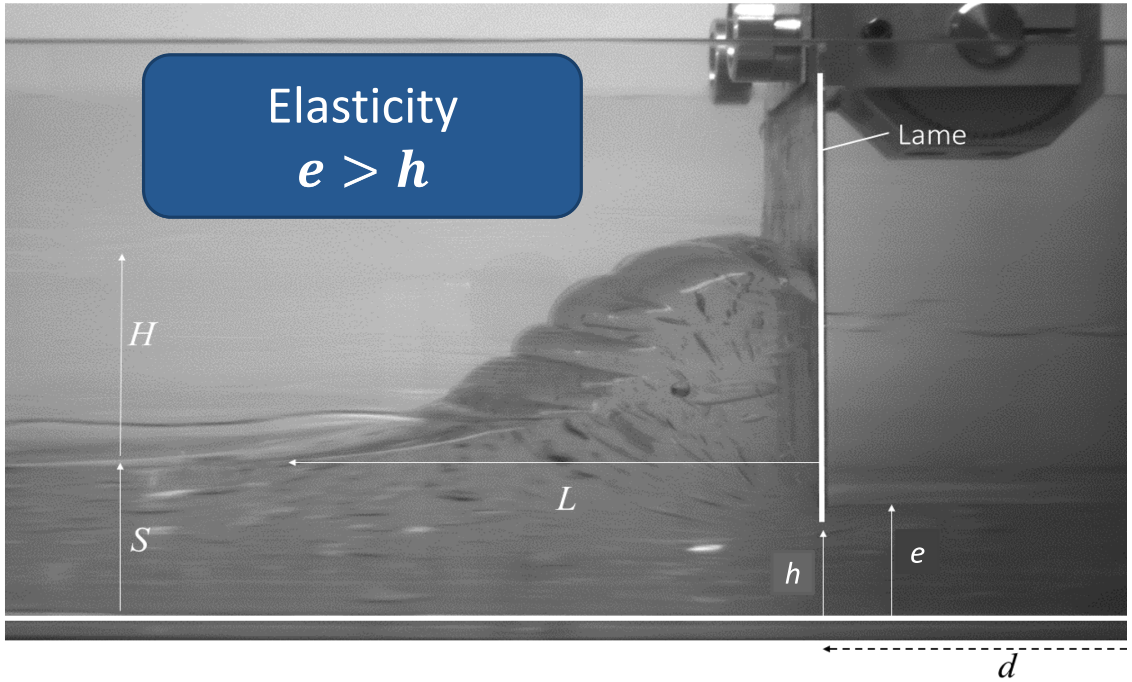
Films are thicker than those made of newtonian fluids

$e > h/2$

e **increases with shear thinning behaviour**

e **decreases for increasing** ***V***

Carbopol gel

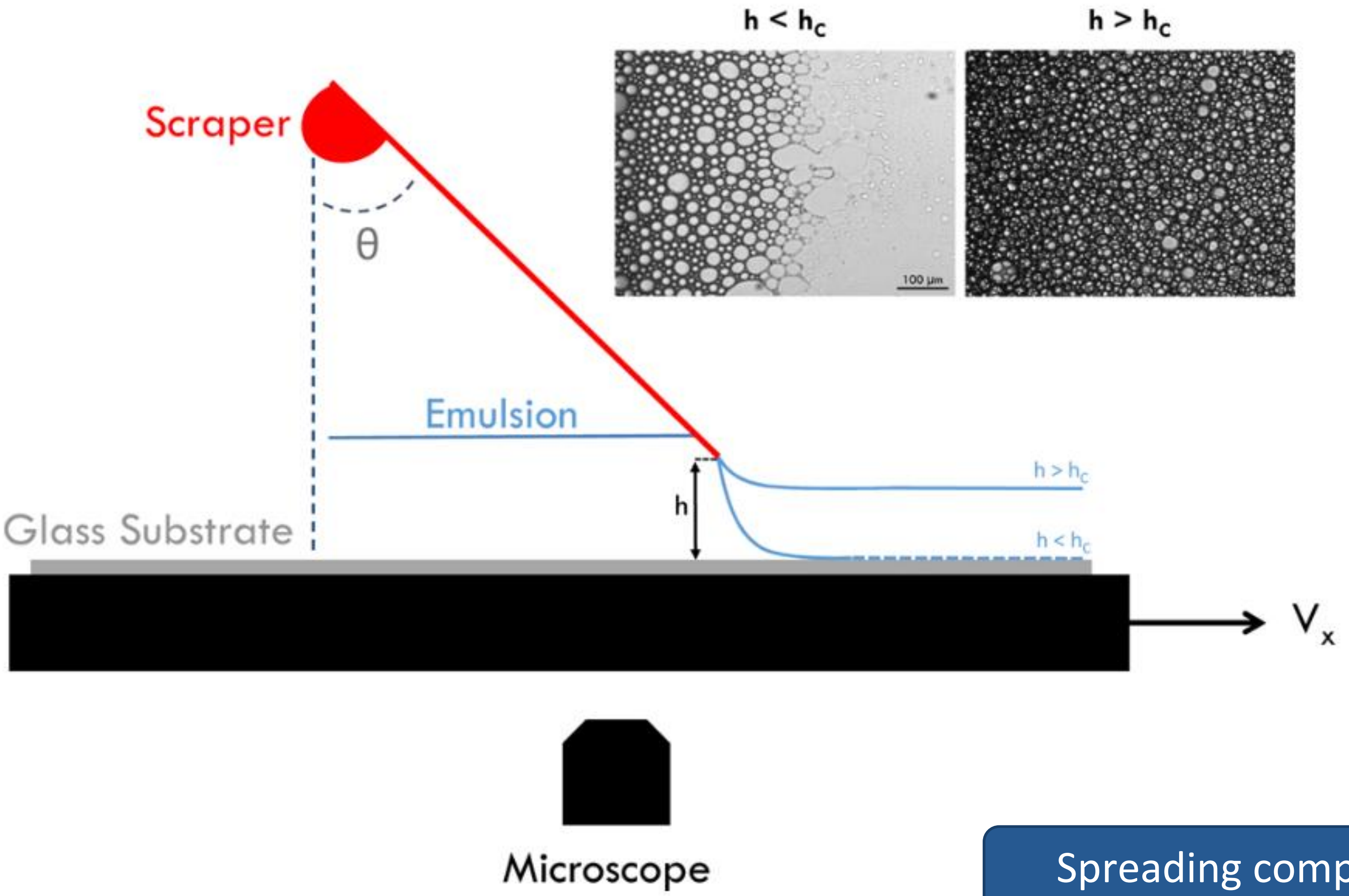


Maillard, M. Étalements de fluides à seuil. (2016).

Middleman, S., Greener, J. & Malone, M. *Fundamentals of polymer processing.* (1977).
Sullivan, T., Middleman, S. & Keunings, R. *AIChE J.* **33,** 2047–2056 (1987).
Sullivan, T. M. & Middleman, S. *J. Nonnewton. Fluid Mech.* **21,** 13–38 (1986).
Hsu, T. C., Malone, M., Laurence, R. L. & Middleman, S. *Journal Non-Newtonian Fluid Mech.* **18,** 273–294 (1985).

Spreading of non-Newtonian fluids

Blade-Coating using rigid blades

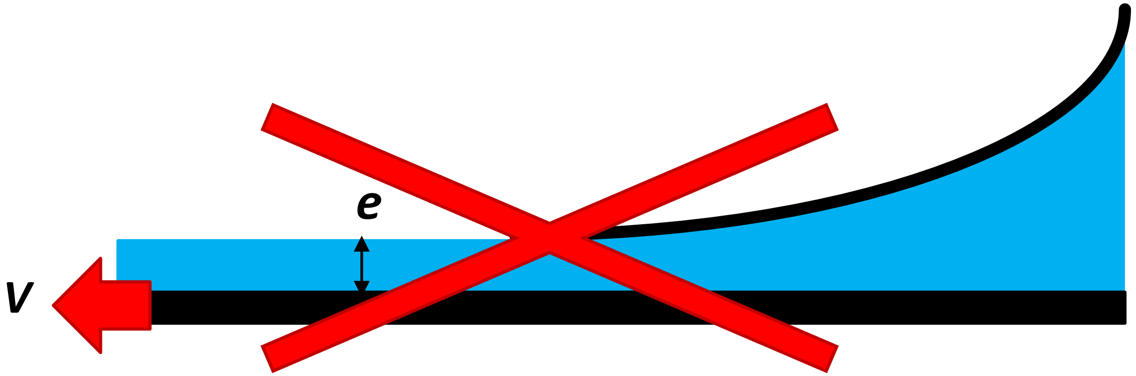


Deblais, A., Harich, R., Bonn, D., Colin, A. & Kellay, H. *Langmuir* **31,** 5971–5981 (2015).

Spreading complex fluid is **not harmless**

Spreading of non-Newtonian fluids

Blade-Coating using soft blades



No study to predict the thickness of non-Newtonian fluids

Clear **academical interest**

And industrial

Main questions and strategy

How are films formed using an elastic blade?

- Setting a precise blade-coating experimental set-up
- Observing films using microscopy and profilometry

How can we predict film thickness for complex fluids?

- Carrying coating experiments using different parameters
  - *Spreading velocity*
  - *Rheology of the fluid*
  - *Nature of the substrate*
- Describing the flow under the blade with Stokes' equations

Part 1

What do I get if I spread very complex fluids?

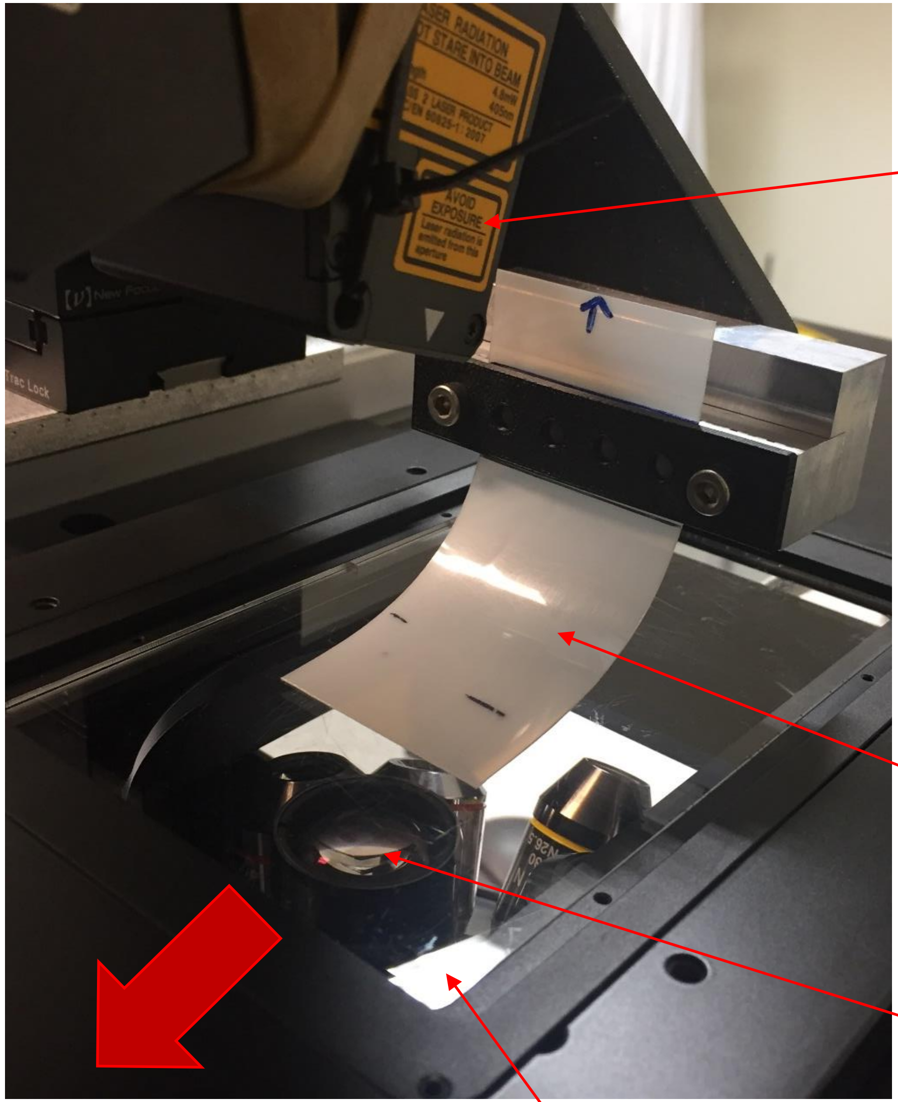
- Preparation of a simple cosmetic models
- Study the impact of non-volatile phases and the presence of solid particles on rheological behaviour and spreading
- Setting a more realistic spreading experimental set-up

Part 2

Part 1:
Blade-coating: Spreading a yield-stress fluid

Blade Coating under microscopy

Experimental set-up



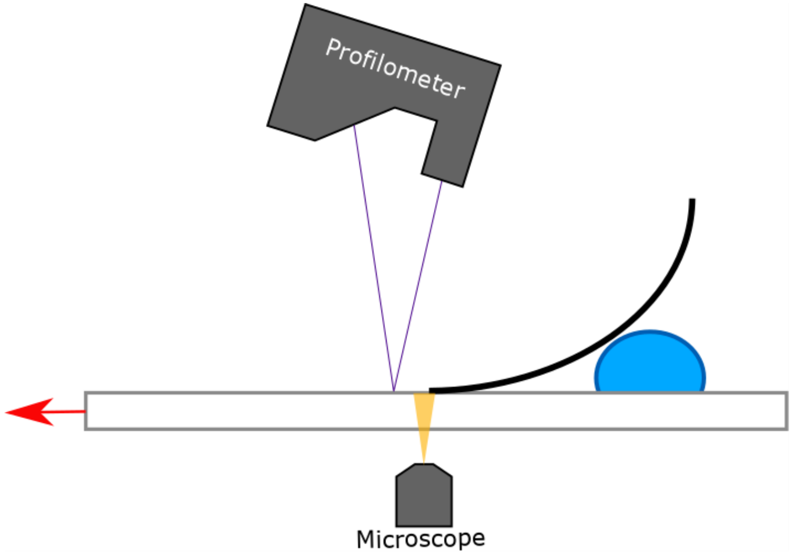
Profilometer

Static Soft Mylar blade
Length = 5.7 cm; thickness = 125 µm;
Width = 4 cm

Microscope

Motion of the stage

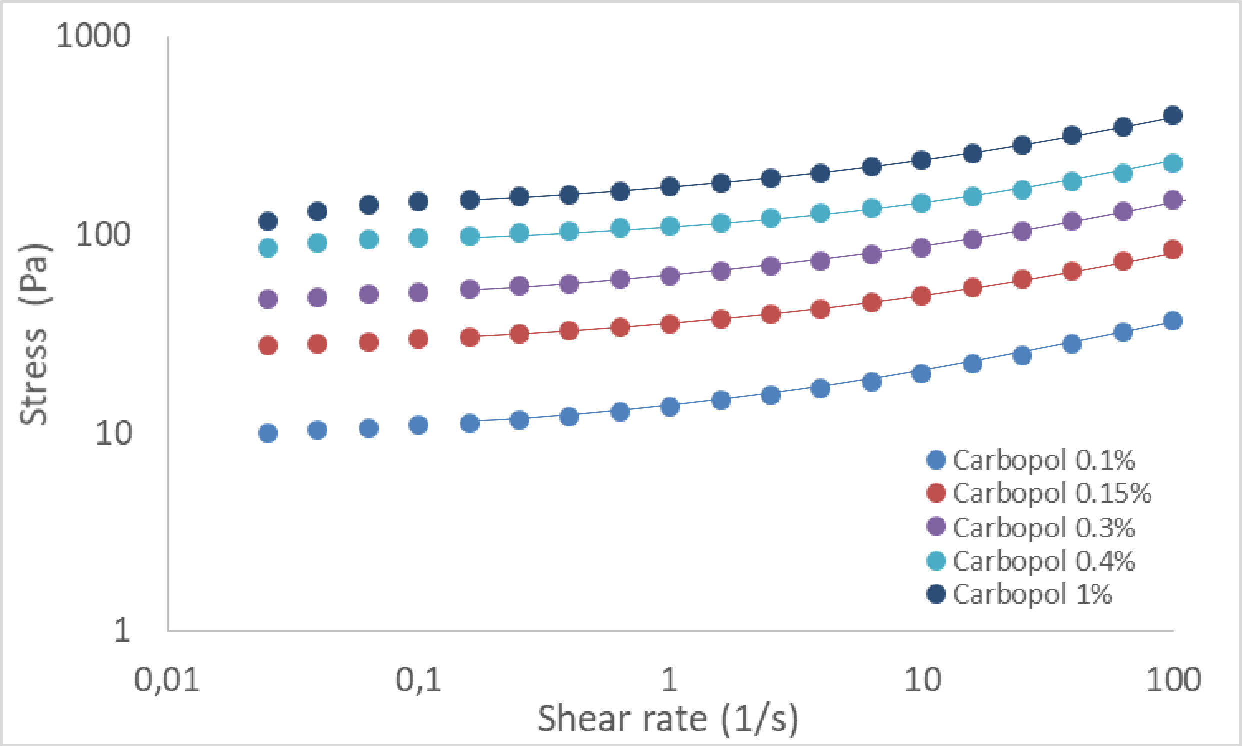
PMMA substrate



Easily tunable : Force, surface tension, …

Allows to **observe the film formation** and to **measure the film thickness**

Yield stress fluids used



Flow sweep

Carbopol gels = model system of yield stress fluid
= used often in cosmetic applications

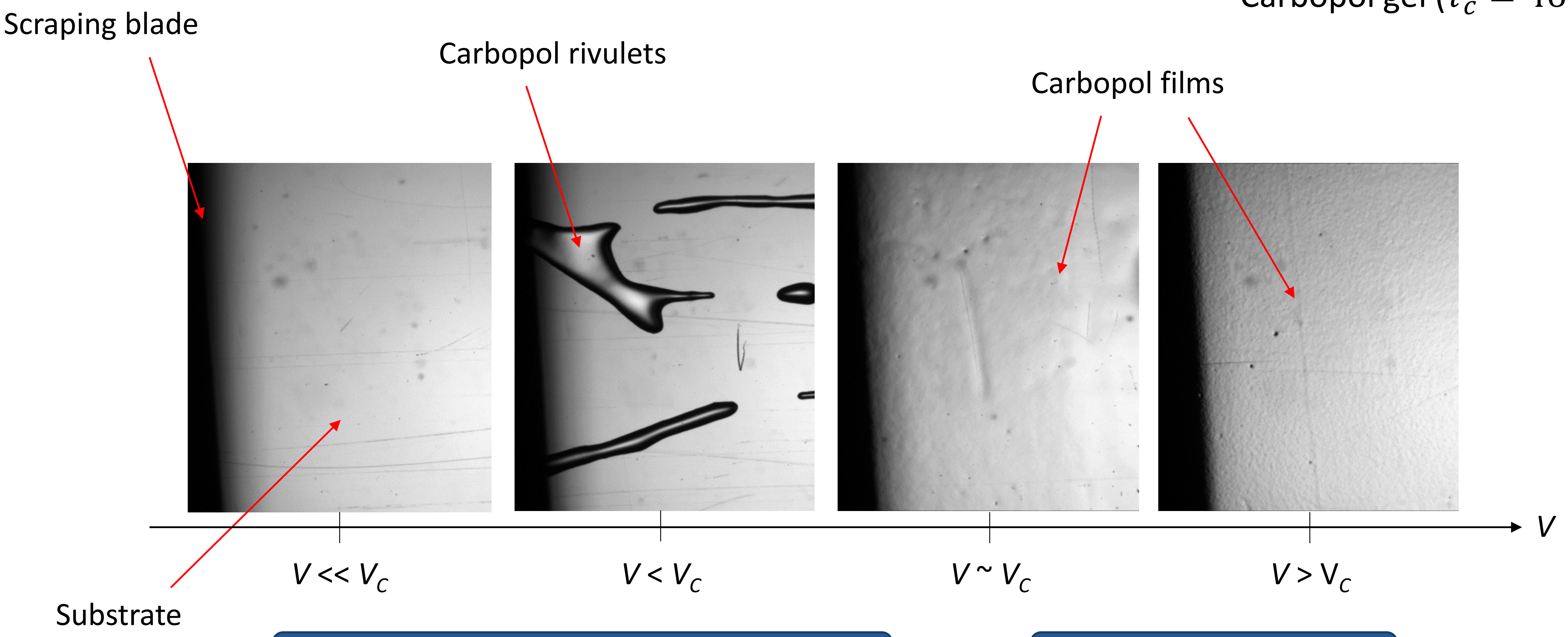
Fitted by a Herschel-Bulkley model: $\tau = \tau_c + k\dot{\gamma}^n$

Blade Coating of carbopol gels

Spreading of carbopol gels on a smooth PMMA plate

Non-wetting system in slippery conditions

Carbopol gel ($\tau_c = 46$ Pa)

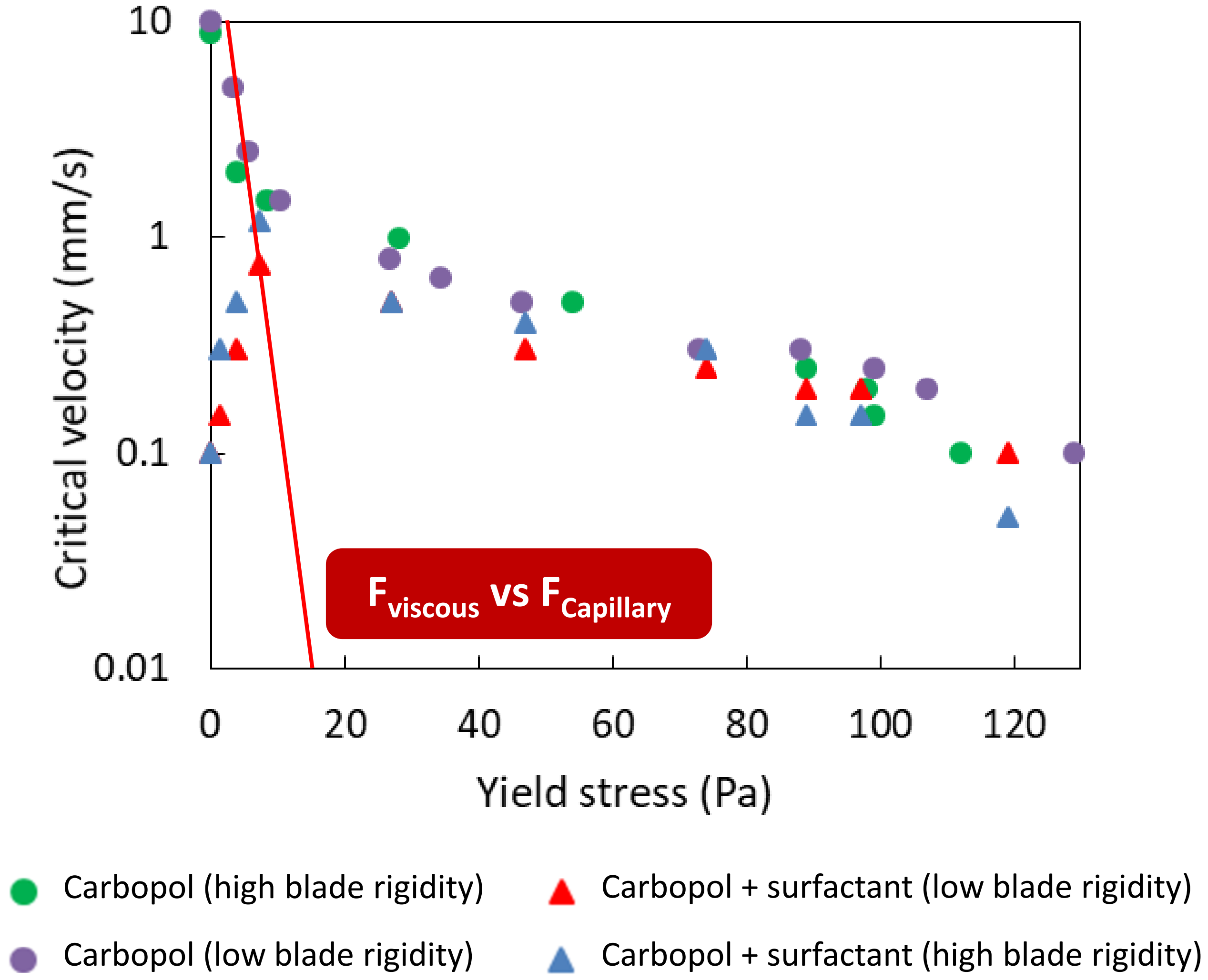


Spreading occurs only if $V > V_C$

What does fix V_C ?

Blade Coating of carbopol gels

Spreading of carbopol gels on a smooth PMMA plate



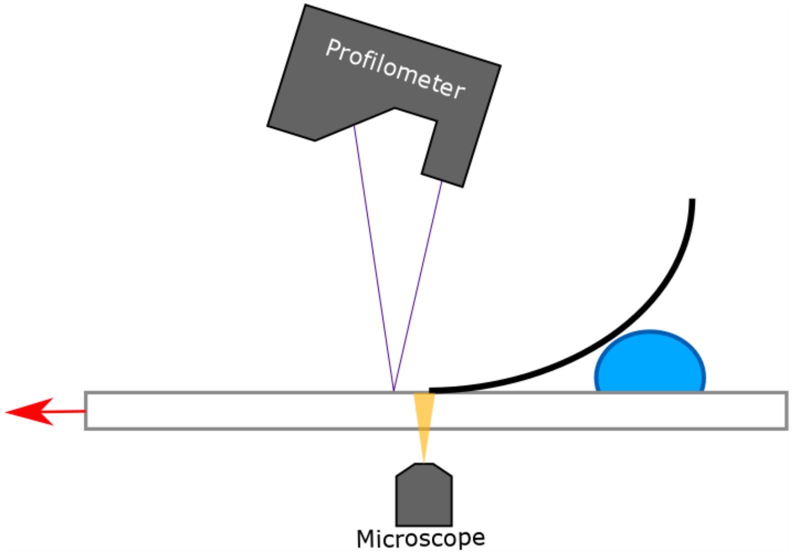
- Yield stress decreases V_C
- Rigidity of the blade : no impact
- Surface tension : no impact for τ_c > 15 Pa

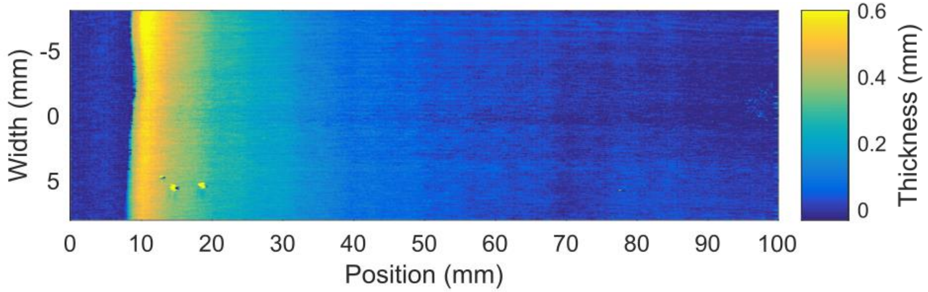
V_C linked to slippery effect
Different from what we described before

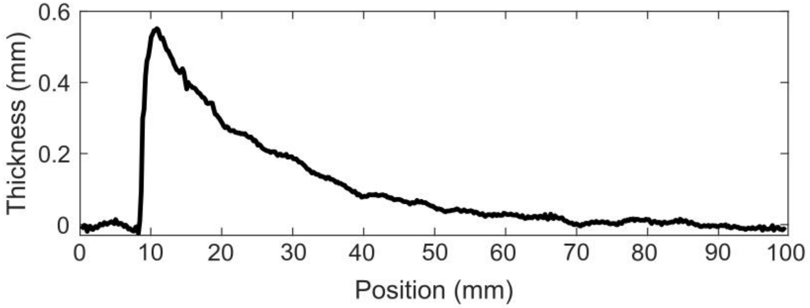
Rough plates = simpler systems
Easier to observe the science of spreading

Blade Coating of carbopol gels

Spreading on a plasma treated PMMA rough plate



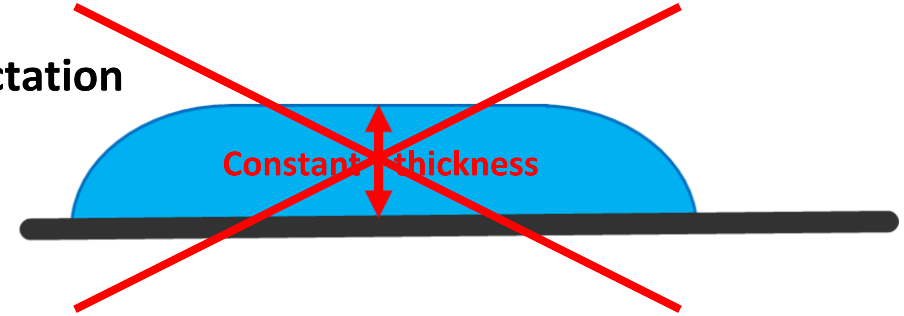




Wetting system in no slip conditions

Film forms whatever is the spreading velocity

Expectation



Reality

*Due to the **finite mass** of the coated **sample***

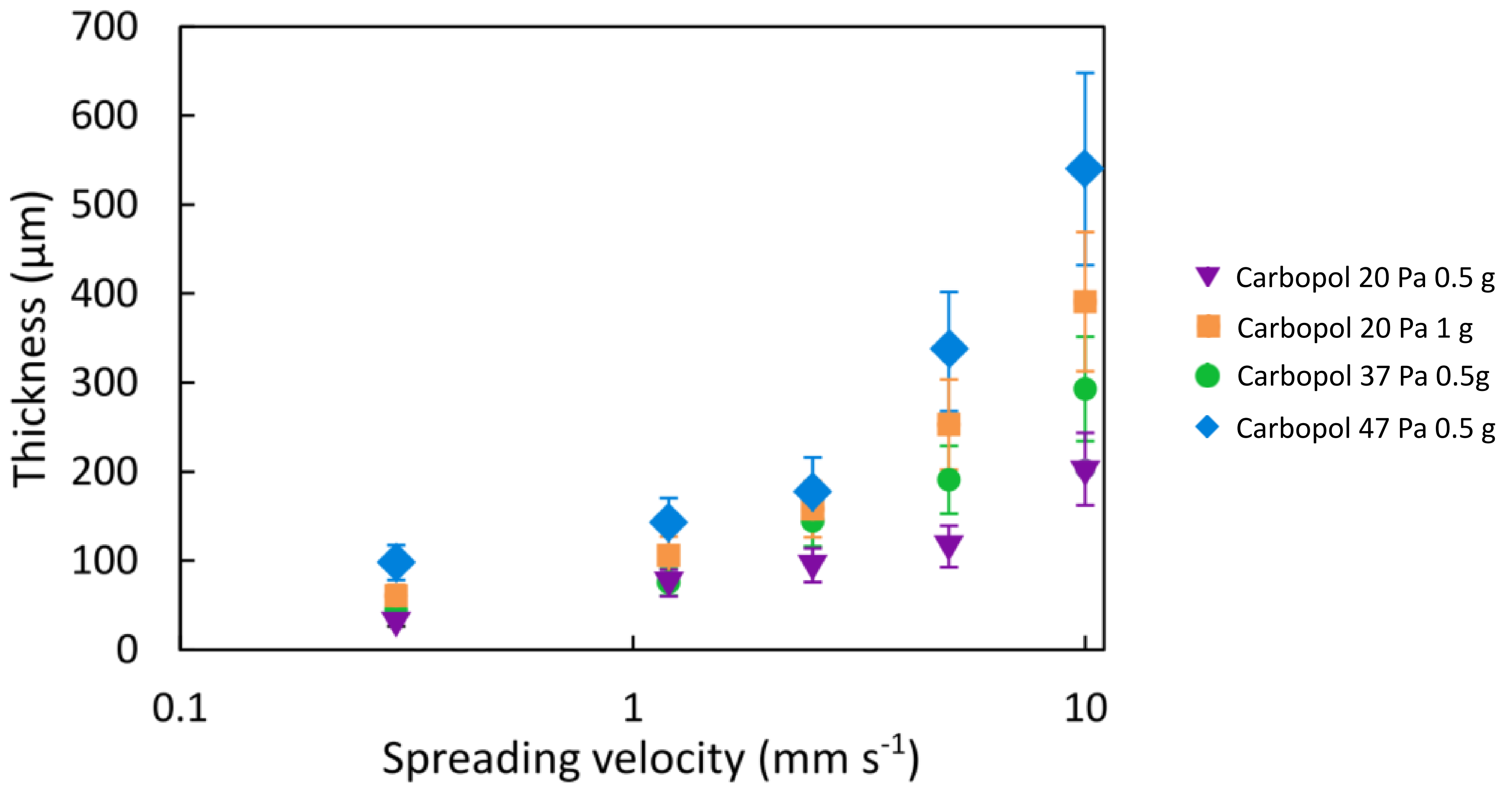
What are the **main parameters** that **fix** the **thickness** of the film ?

Blade Coating of carbopol gels

Prediction of the film thickness

Spreading of carbopol gels on a plasma treated PMMA rough plate

Wetting system in no slippery conditions



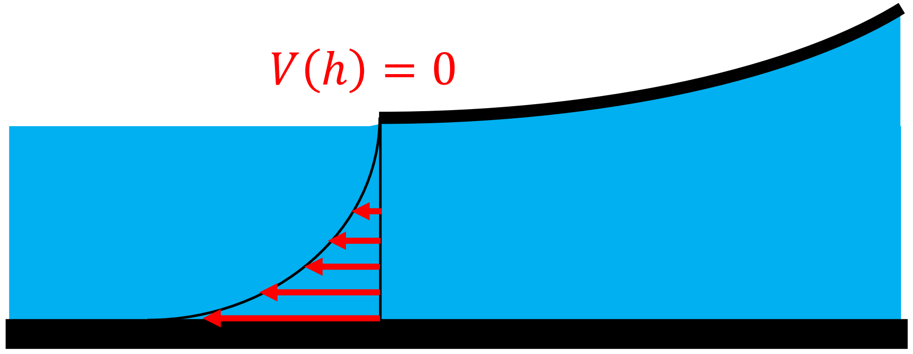
***e* increases with *V*, τ_c and the mass of sample**

Blade Coating of carbopol gels

Prediction of the film thickness

Spreading of carbopol gels on a plasma treated PMMA rough plate

Initial condition :
Raising of the blade in no slip conditions



$$\tau(h) \approx -\tau_c$$

$$\tau(0) = -\tau_c - k\dot{\gamma}^n$$

Stokes' equation under the blade

$$\tau(h) = \frac{\partial P}{\partial x} h - \tau(0)$$

Viscous forces of the fluid = elasticity of the blade

Seiwert (2013) : $\frac{\partial P}{\partial x} = \frac{B}{h^{2/3} R_c^{10/3}}$

$$\boldsymbol{h \propto \left(\frac{kV^n R_c^{10/3}}{B}\right)^{1/(n+\frac{1}{3})}}$$

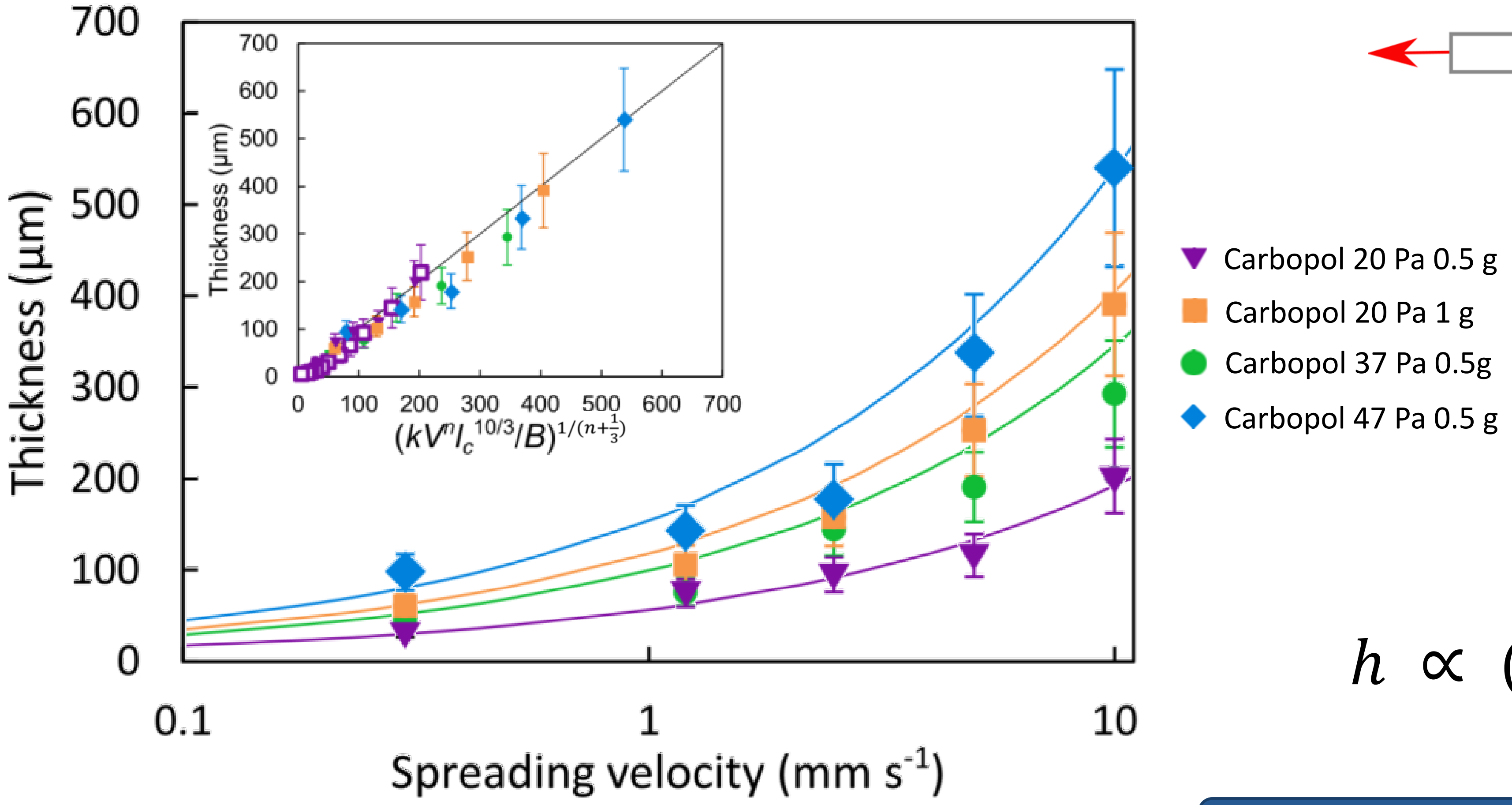
R_c : Curvature radius of the blade
B : Rigidity of the blade

k : Viscosity parameter
V : Spreading velocity

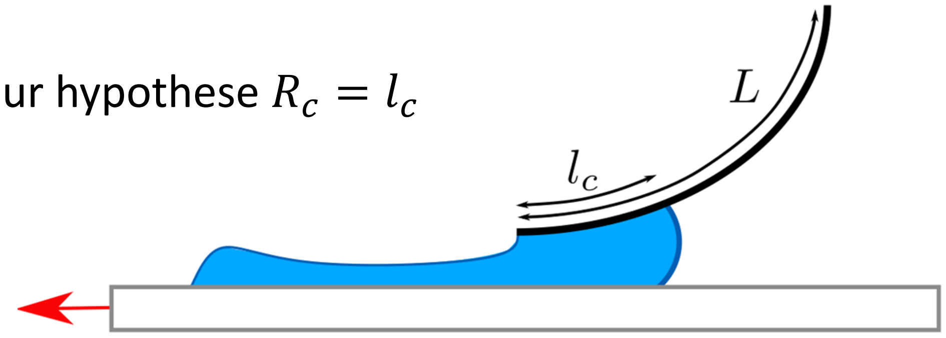
Seiwert, J., Quéré, D. & Clanet, C. Flexible scraping of viscous fluids. *J. Fluid Mech.* **715,** 424–435 (2013).

Blade Coating of carbopol gels

Prediction of the film thickness



Our hypothese $R_c = l_c$



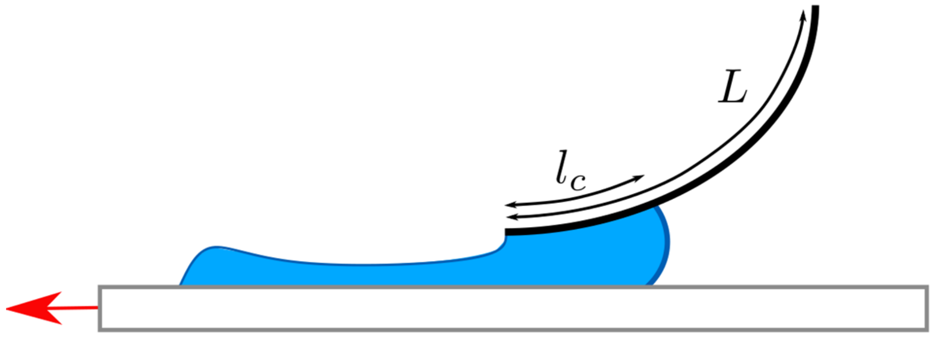
$$h \propto \left(\frac{k\,V^n l_c^{10/3}}{B}\right)^{1/(n+\frac{1}{3})}$$

Modelling **consistent** with the experiments

Blade Coating of carbopol gels

Prediction of the film thickness

$$h \propto \left(\frac{k\,V^n R_c^{10/3}}{B}\right)^{1/(n+\frac{1}{3})}$$



Newtonian case : n = 1 (Seiwert)

$$e \sim L\left(\frac{\eta V L^2}{B}\right)^{3/4}$$

Not consistent with experiments

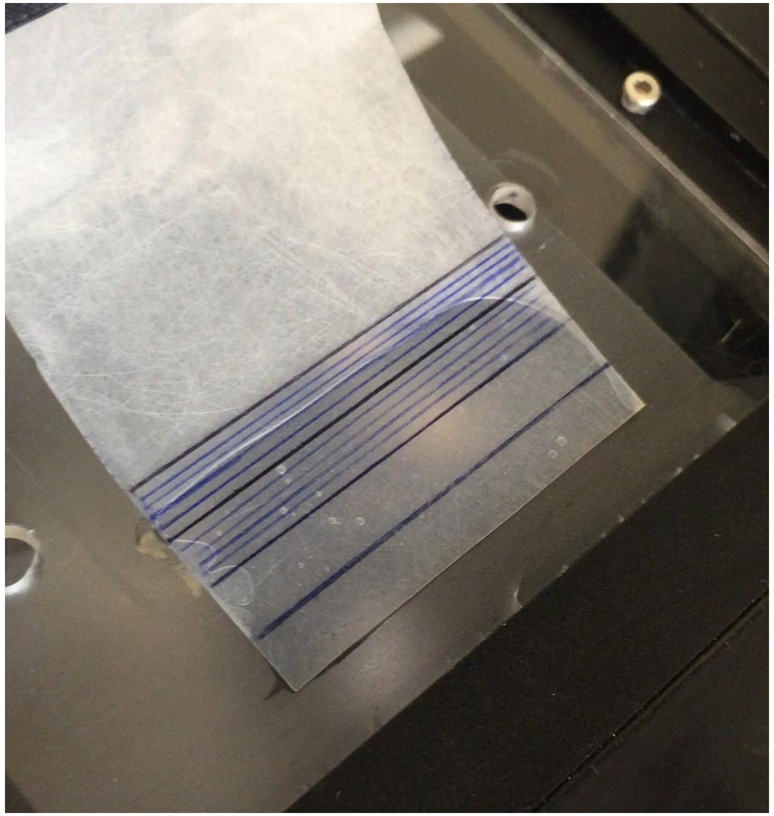
$R_C = L$ for Seiwert's model

Cannot explain the **thickness evolution** during the spreading process

Blade Coating of carbopol gels

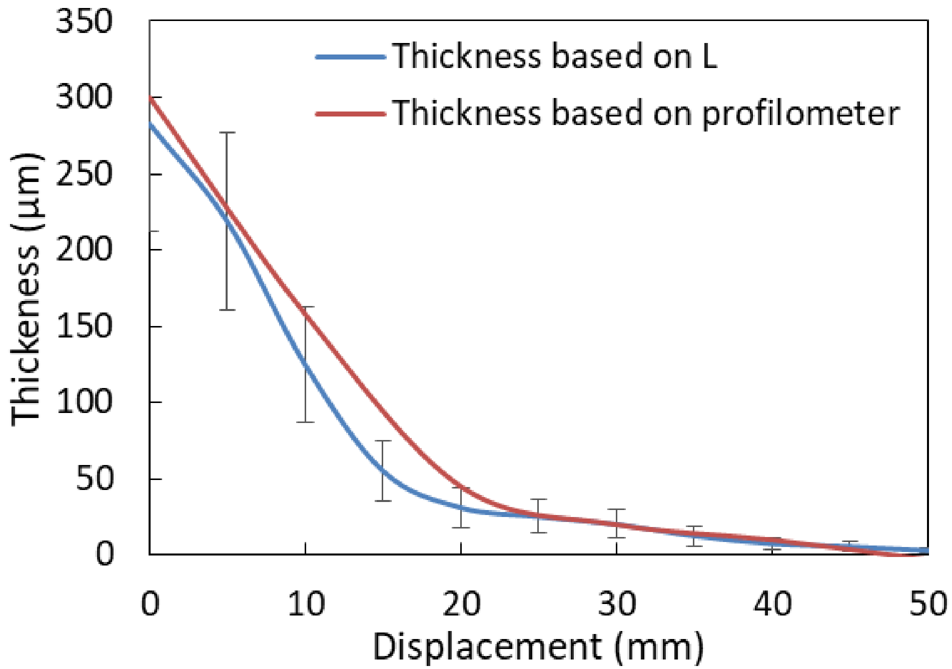
Prediction of the film thickness

$$h \propto \left(\frac{k\, V^n l_c^{10/3}}{B}\right)^{1/(n+\frac{1}{3})}$$



Variable thickness due to the evolution of L during spreading

Decreasing of the thickness explained only if $R_c = l_c$

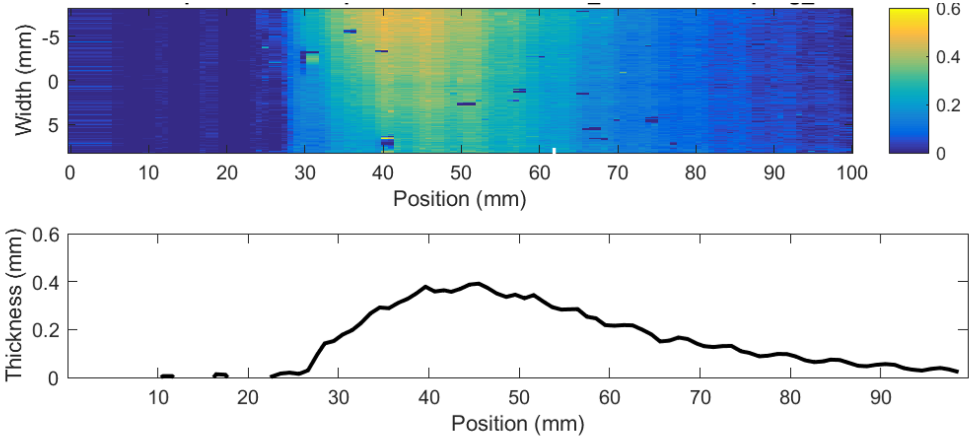


Consistent with the use of $R_c = l_c$

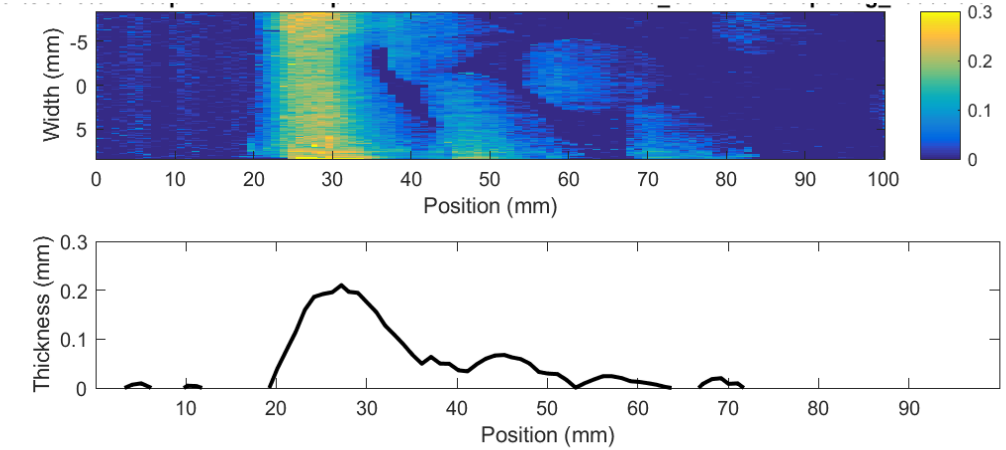
Blade Coating of carbopol gels

Heterogeneity within the film

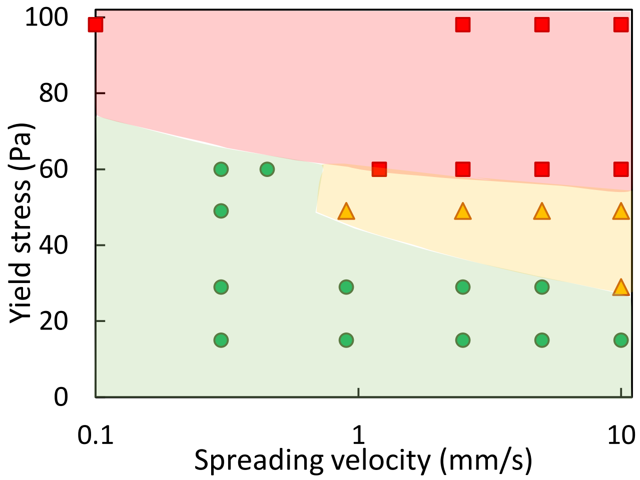
Carbopol 15 Pa; V = 10 mm/s

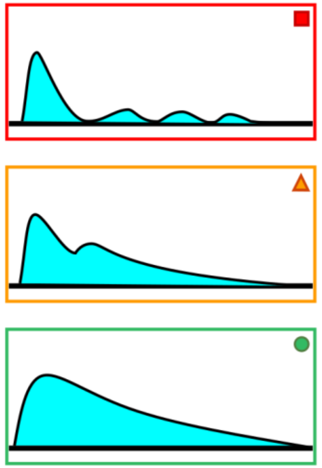


Carbopol 60 Pa; V = 10 mm/s

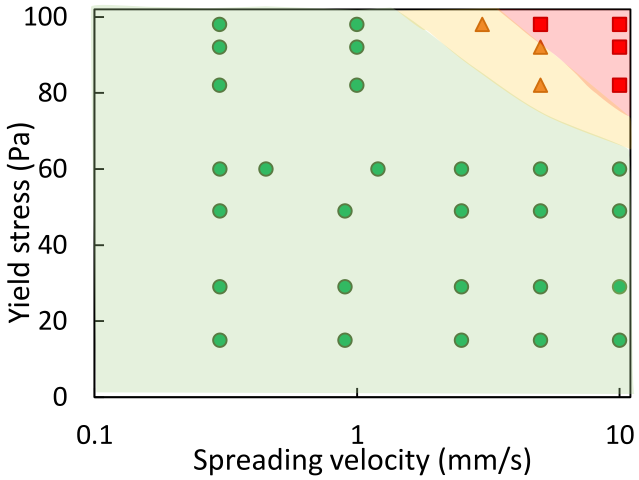


Low blade rigidity





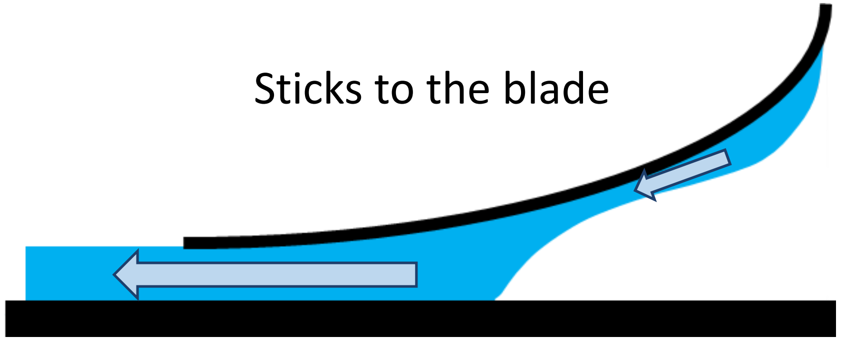
High blade rigidity

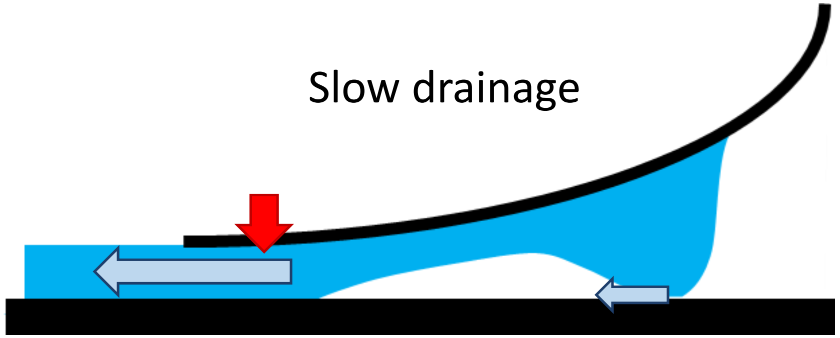


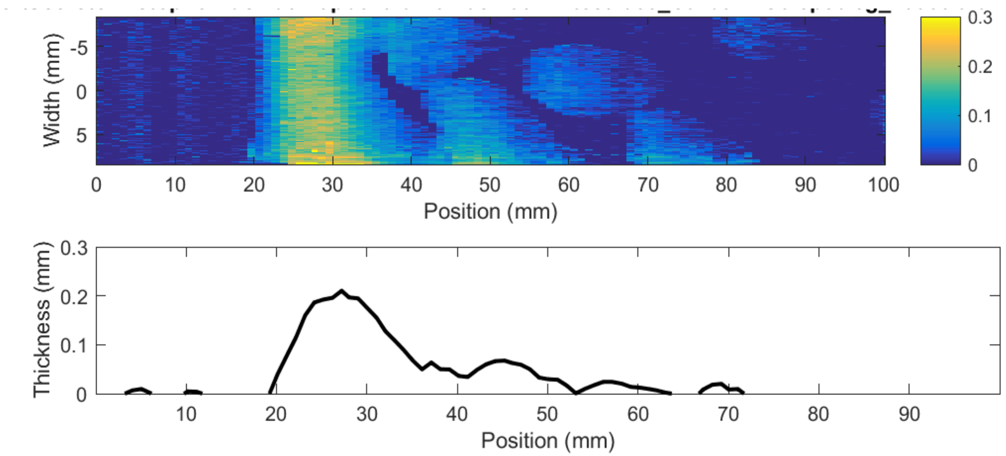
High spreading velocity and **yield stress** induce **heterogeneity**

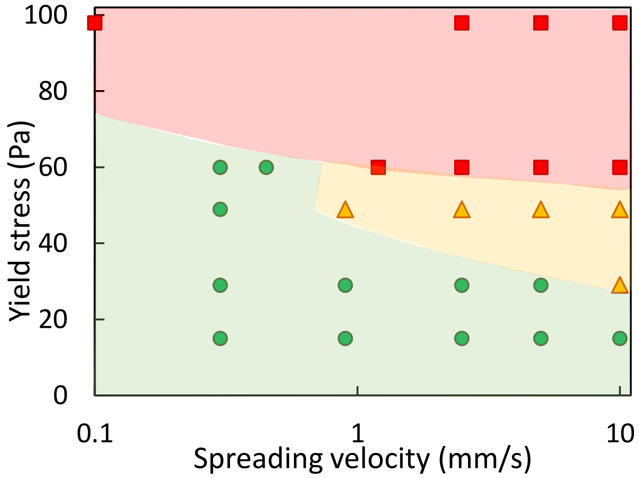
Blade Coating of carbopol gels

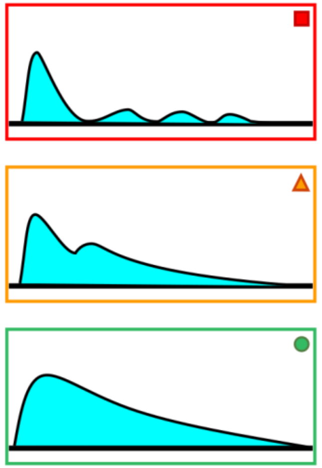
Heterogeneity within the film





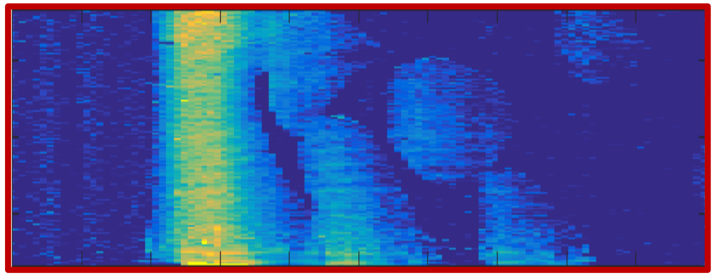


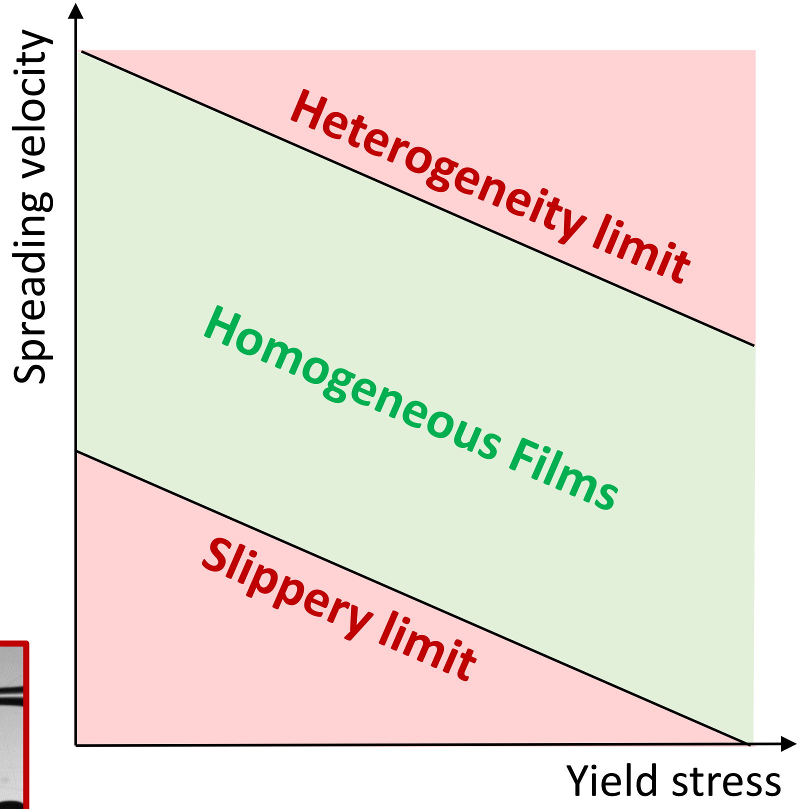


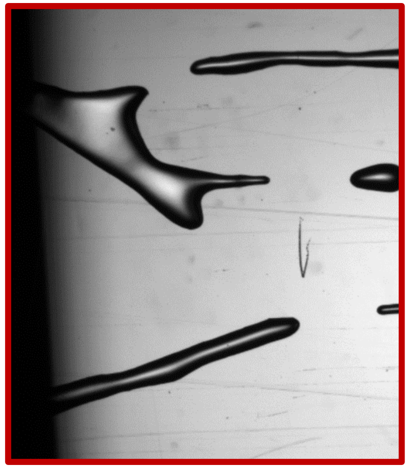


Conclusion

The skin is neither smooth nor a perfect wetting system







Specific to a formulation on a substrate

Gives formulation limits

$$h \propto \left(\frac{k\,V^n l_c^{10/3}}{B}\right)^{1/(n+\frac{1}{3})}$$

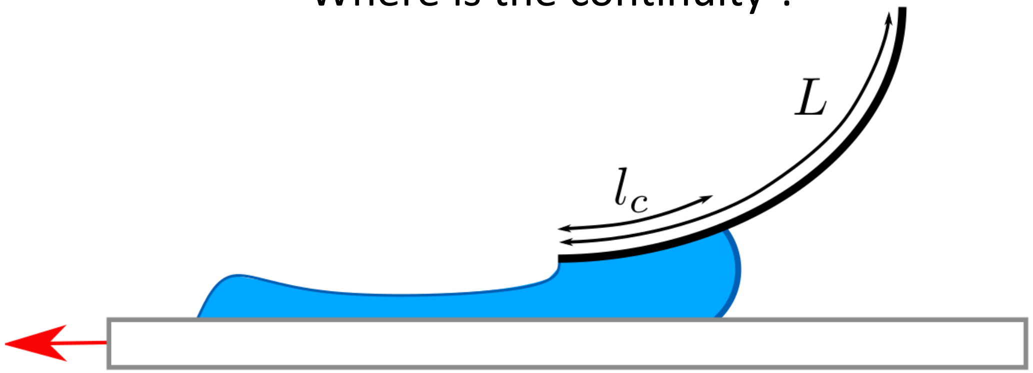
Able to **predict the film thickness anytime** during spreading using **Stokes' equation** and **geometrical parameters**

Outlooks

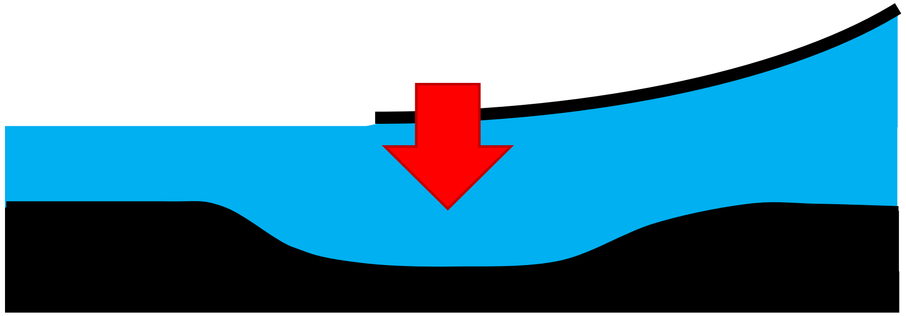
Seiwert R_c = L_{blade}

Us R_c = l_c

Where is the continuity ?



Spreading on soft substrate



Part 2:
Complex formulations: spreading defects

Preparation of a model cosmetic formulation

Hundreds of ingredients

Volatil phase (aqueous)	Active non-volatil phase	Texture agents
Water	Glycerol, oils, waxes Pigments, UV filters	Carbopol Particles (starch, silica)

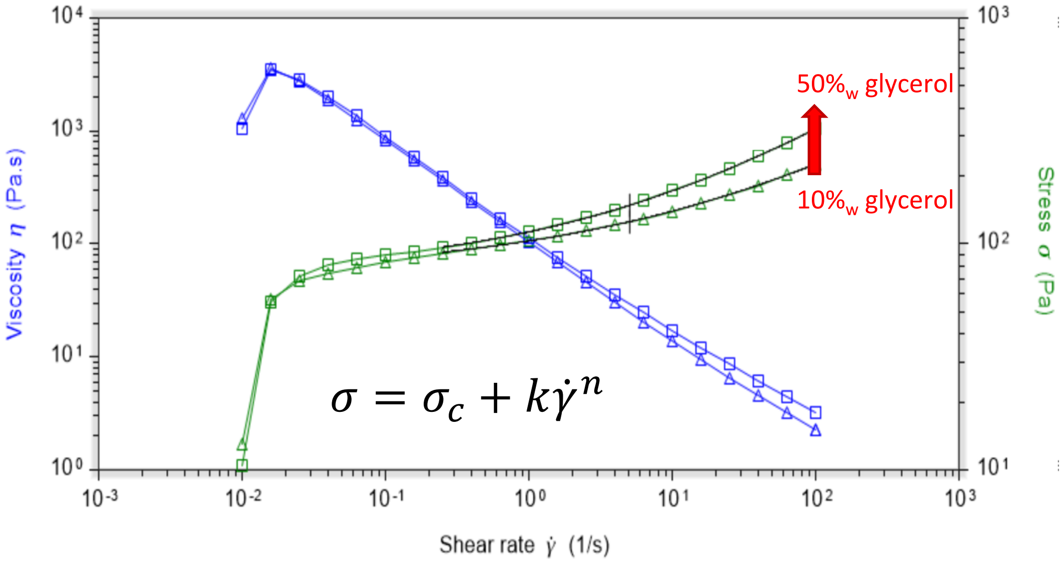
Carbopol	**0.3 $\%_w$**
Water/Glycerol	**50-50 or 90-10**
Starch	**6-13$\%_v$**

Impact of glycerol and cornstarch

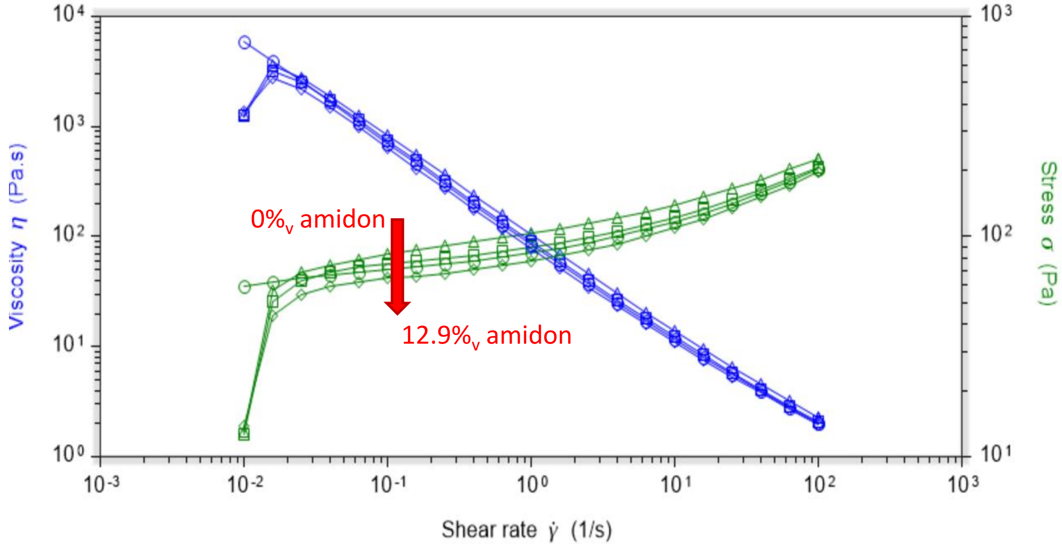
Formula	$\%_w$ carbopol (in liquid phase)	$\%_v$ starch (global volume)	$\%_w$ glycerol (in liquid phase)	τ_y (Pa)	k ($Pa.s^{1/n}$)	n	φ_{starch} (In the dry film)
1		6.4		50.8	18.4	0.40	0.46
2		9.3	10	48.3	16.9	0.42	0.56
3	0.3	12.0		44.0	16.0	0.44	0.63
4		6.9		46.8	29.1	0.44	0.14
5		10.0	50	41.5	27.4	0.45	0.20
6		12.9		37.6	25.7	0.47	0.25

Starch particles unstable in water
Experiments carried within 1 week

Highest and lowest volume fraction



The glycerol increases the viscosity of the media

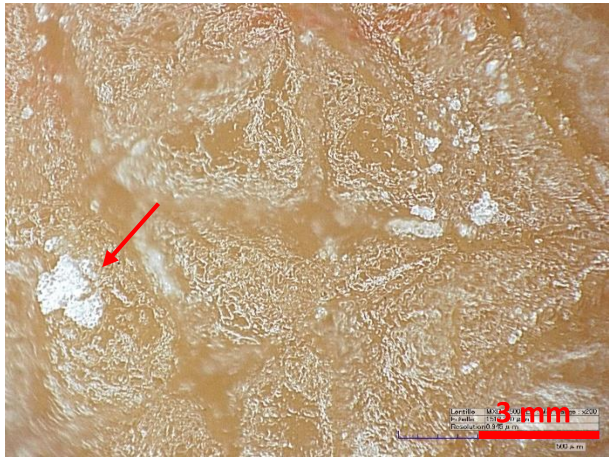
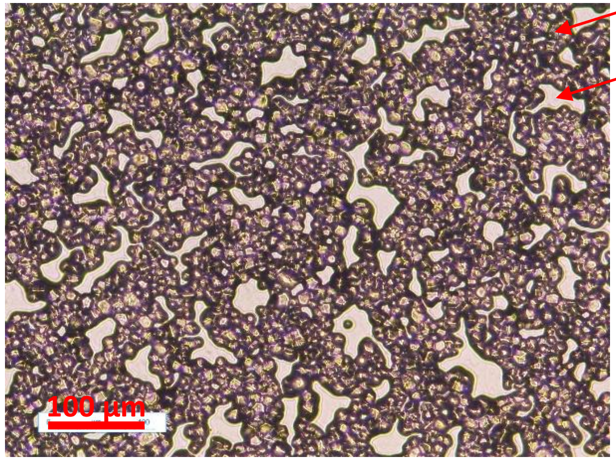
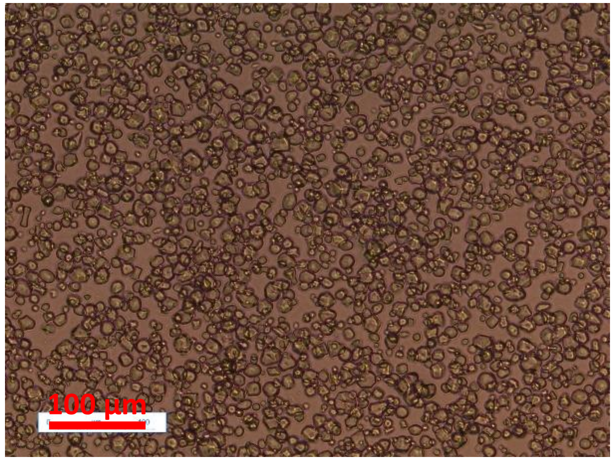


The starch decreases the yield stress of the media

Impact of glycerol and cornstarch

Structure of a dry deposit

Formula	$\%_w$ carbopol (in liquid phase)	$\%_v$ starch (global volume)	$\%_w$ glycerol (in liquid phase)	φ_{starch} (In the dry film)	τ_y (Pa)	k (Pa.s$^{1/n}$)	n
1	0.3	6.4	10	0.46	50.8	18.4	0.40
2		9.3		0.56	48.3	16.9	0.42
3		12.0		0.63	44.0	16.0	0.44
4		6.9	50	0.14	46.8	29.1	0.44
5		10.0		0.20	41.5	27.4	0.45
6		12.9		0.25	37.6	25.7	0.47

	Spreading on artificial skin	*Single-layer coating on a glass plate*
φ_{starch} (dry) = 0.63		
φ_{starch} (dry) = 0.14		

Particles

Air

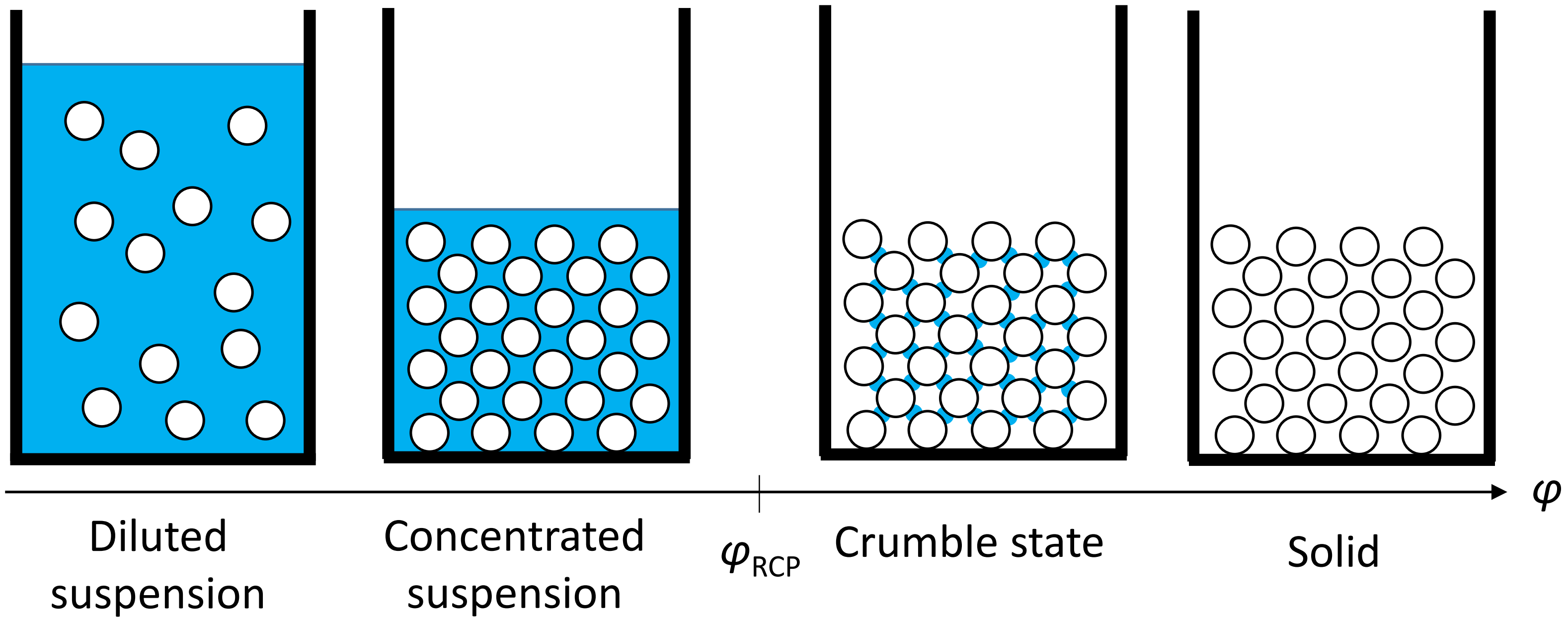
Capillary bridges formed by glycerol
Formation of Aggregates !

Starch particles **still dispersed** in the remaining glycerol

Aggregates are formed at **high volume fraction** of particles

The volume fraction in the dry film, a key parameter

What does a formula look like as a function of the particle volume fraction?

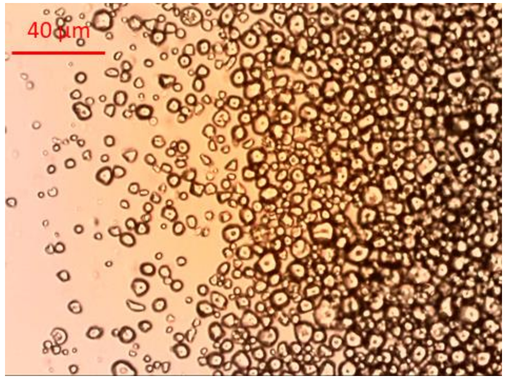


$\varphi_{\text{Close packing}}$ (perfect spheres) = 0.74

$\varphi_{\text{Random close packing}}$ (perfect spheres) = 0.64

- Shape of particules
- Polydispersity

- Nature of the solvent
- Friction coefficient of particles



Has to be determined more precisely

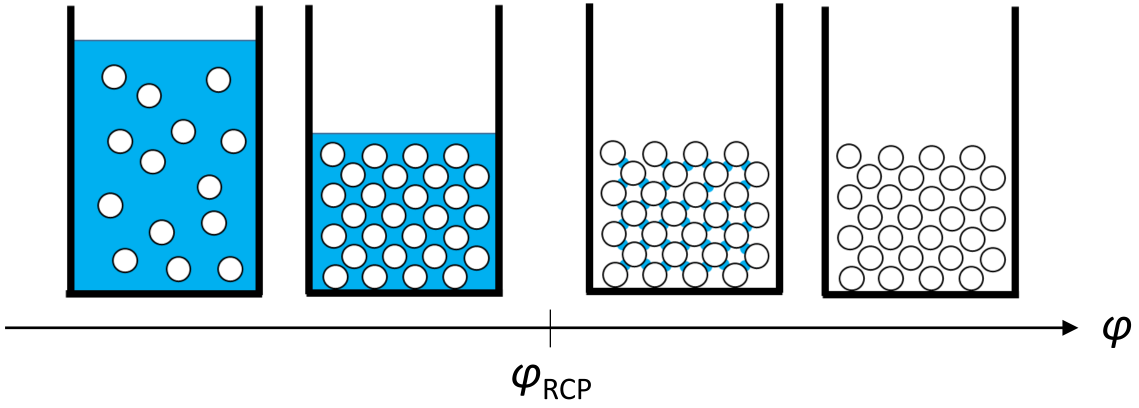
Kansal, A. R., Torquato, S. & Stillinger, F. H. Diversity of order and densities in jammed hard-particle packings. *Phys. Rev. E* **66,** (2002).

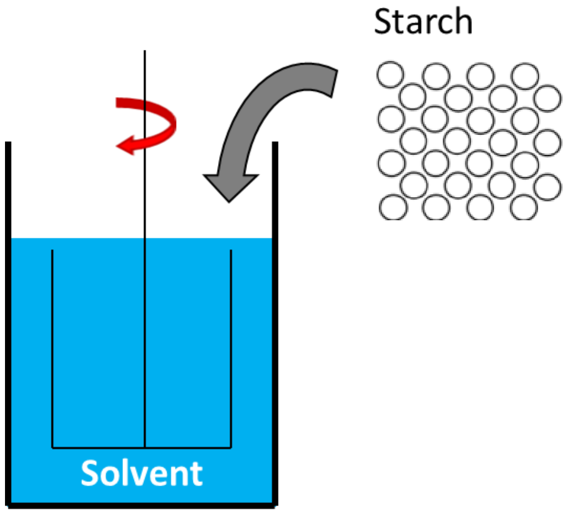
Kansal, A. R., Torquato, S. & Stillinger, F. H. Computer generation of dense polydisperse sphere packings. *J. Chem. Phys* **117,** 8212 (2002).

Mari, R., Seto, R., Morris, J. F. & Denn, M. M. Shear thickening, frictionless and frictional rheologies in non-Brownian suspensions. *Cit. J. Rheol.* **58,** 1693 (2014).

The volume fraction in the dry film, a key parameter

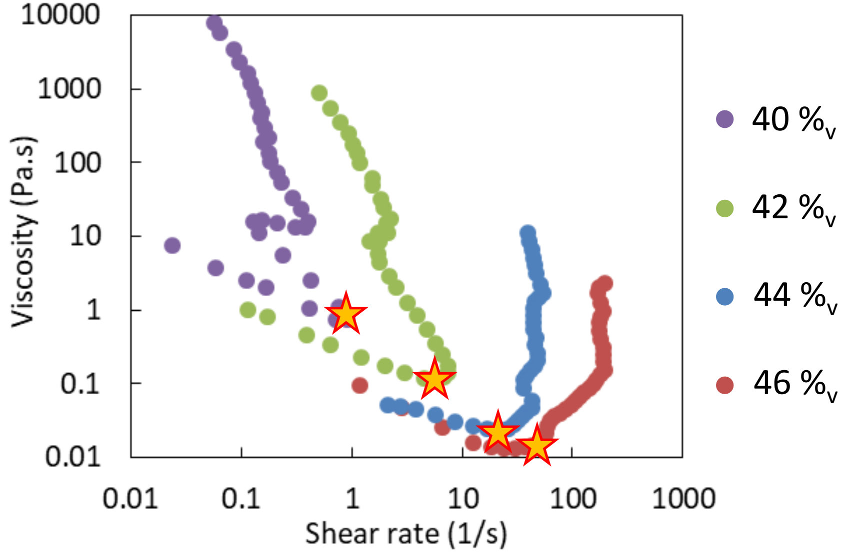
How do we measure φ_{RCP} ? Two methods

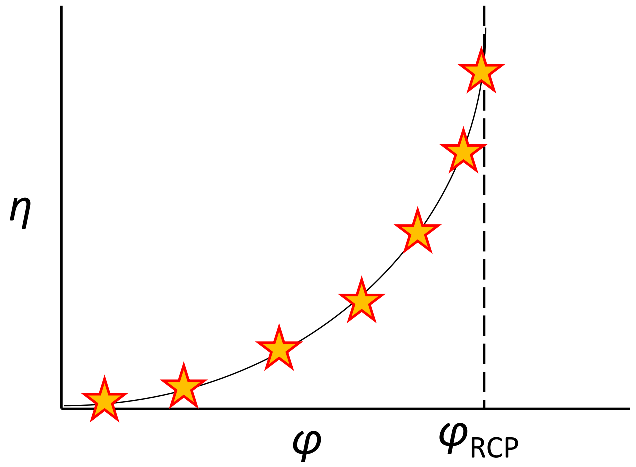




φ_{RCP} (water) = 50 $\%_v$ φ_{RCP} (glycerol) = 56 $\%_v$

Important tool in formulation science





Krieger-Dougherty model

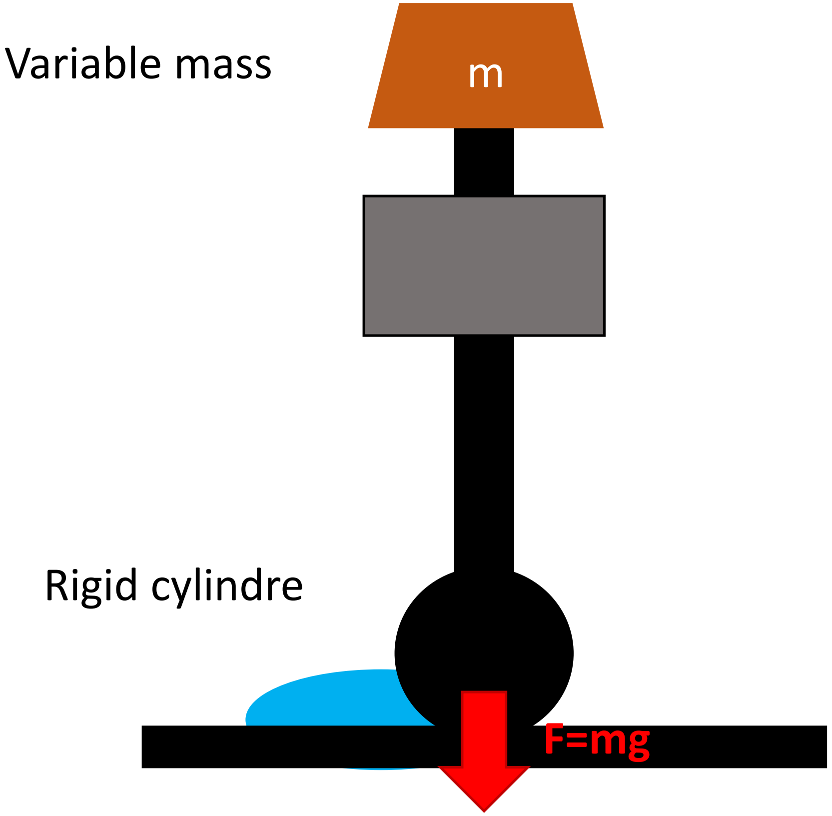
$$\eta = \eta_0 \left(1 - \frac{\varphi}{\varphi_{RCP}}\right)^{-[\eta]\varphi_{RCP}}$$

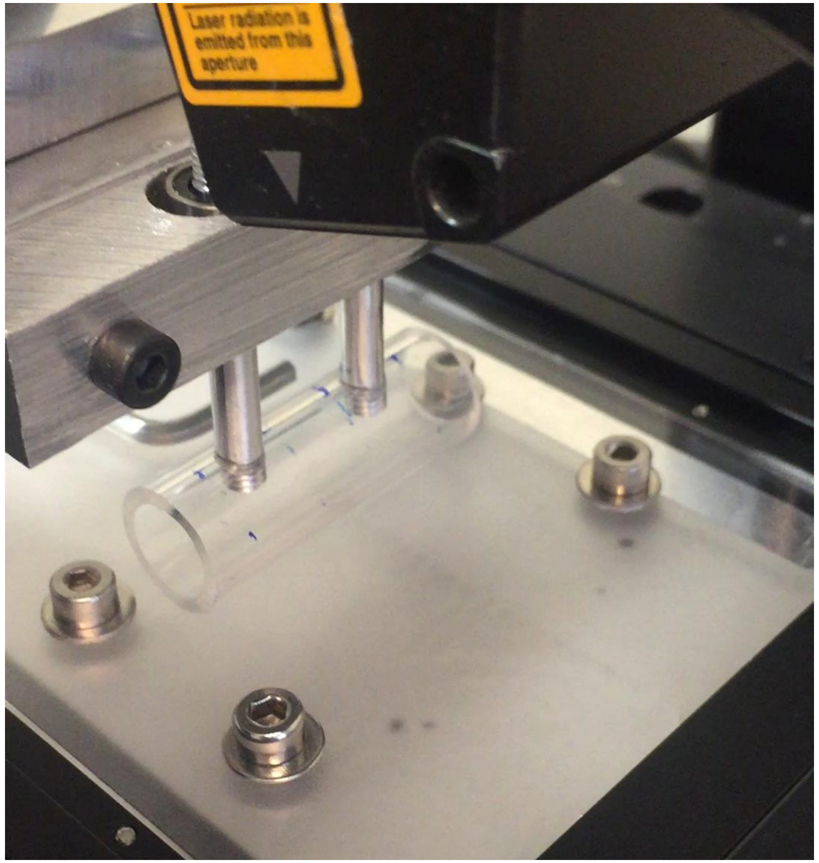
$[\eta]$: Intrinsic viscosity
η_0 : Viscosity of the solvent

Mari, R., Seto, R., Morris, J. F. & Denn, M. M. Shear thickening, frictionless and frictional rheologies in non-Brownian suspensions. *Cit. J. Rheol.* **58,** 1693 (2014).

Carrying more relaistic spreading experiments

Evolution of the experimental set-up



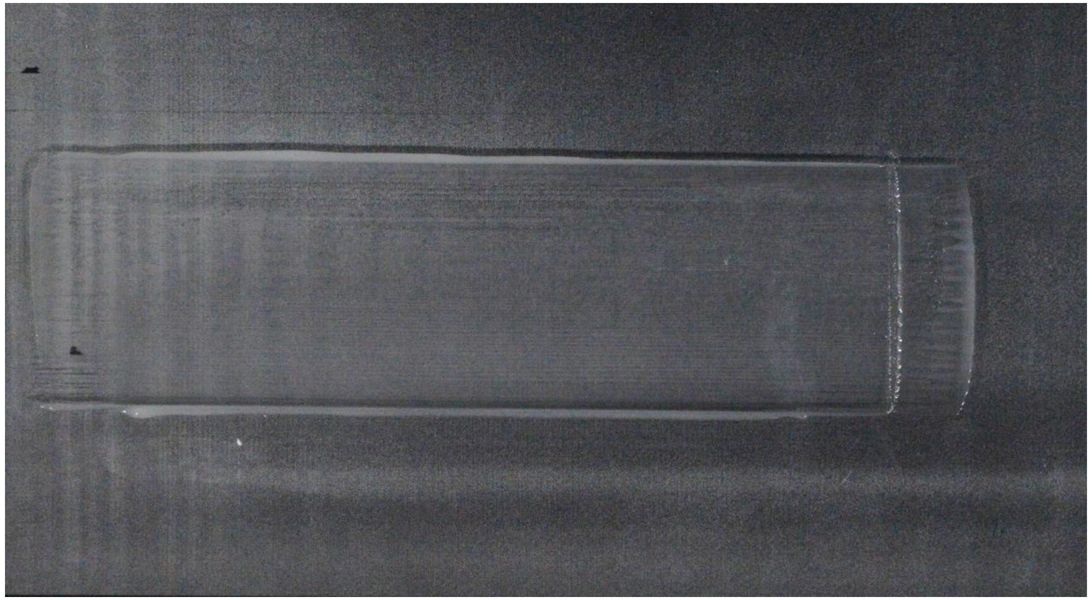


Carrying more relaistic spreading experiments

New spreading experiment

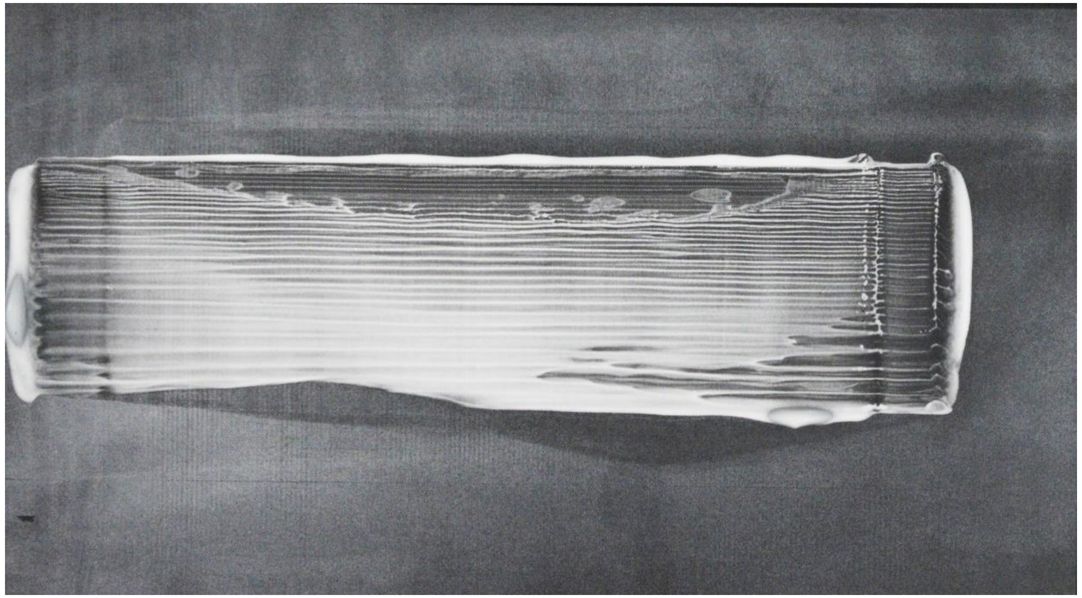
m sample = 0,5g
Application force = 63mN → (15 Back and forth, V = 10 mm/s → 5 min drying) x2

φ_{starch} (dry) = 0.14



Fluid and homogeneous coating

φ_{starch} (dry) = 0.63



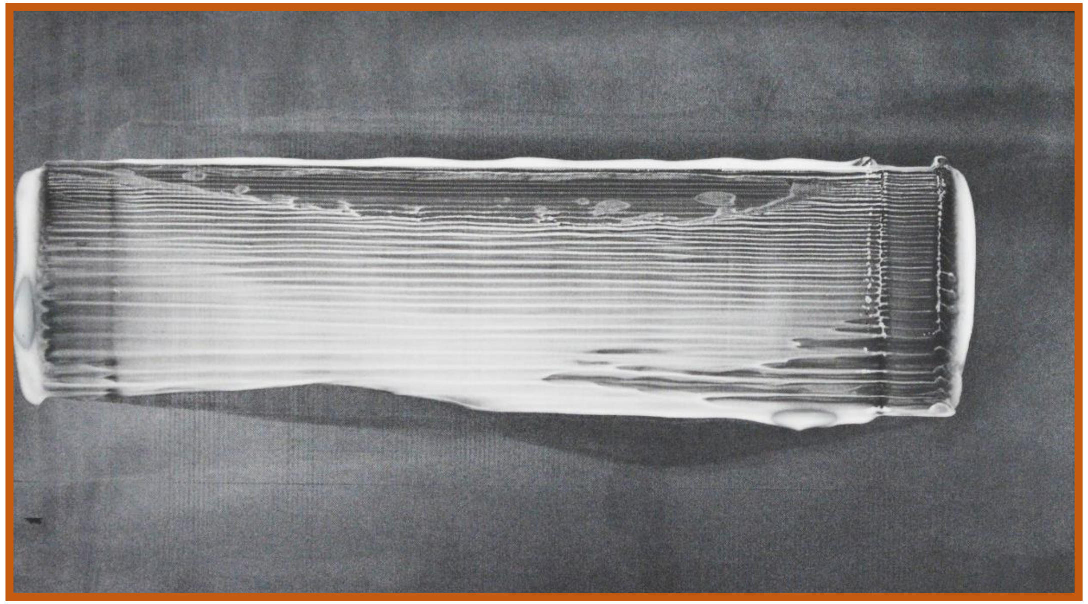
Dry and heterogeneous coating

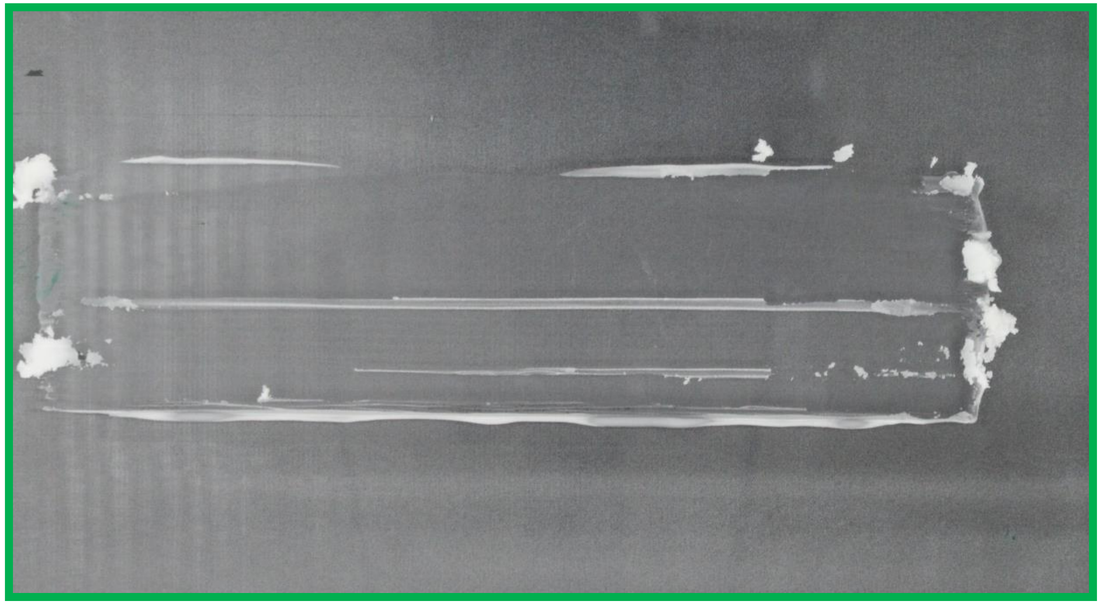
Impact of φ highlighted

Carrying more relaistic spreading experiments

New spreading experiment

φ_{starch} (dry) = 0.63





Coating peeled off through successive back and forth movements

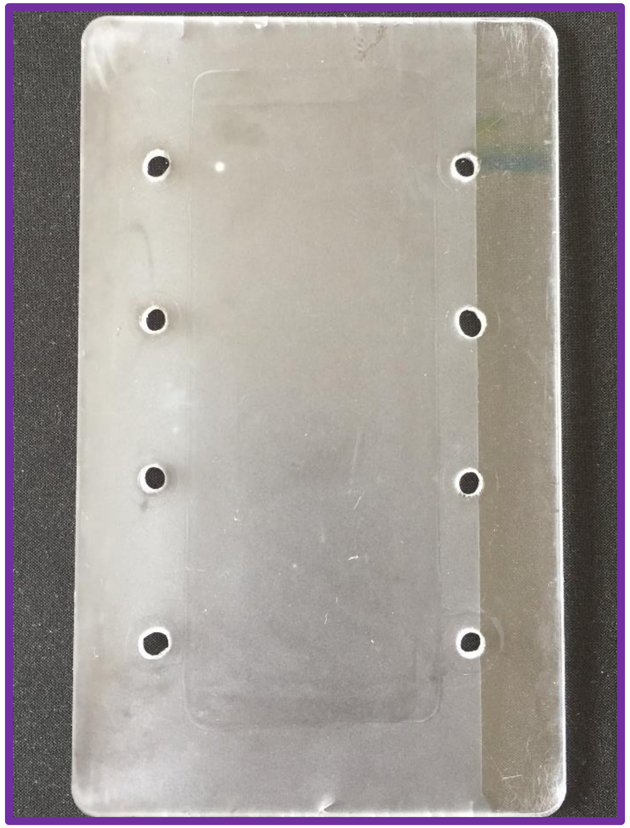
m sample = 0,5g
Application force = 63mN → (15 Back and forth
V = 10 mm/s → 5 min drying) x2 → Higher application force [63 ; 17x10^{-3} mN] (F_i x270)
15 Back and forth

Pre-coat

Carrying more relaistic spreading experiments

Three materials

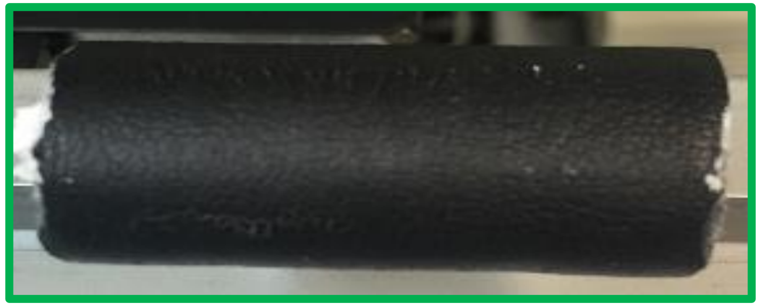
Smooth PMMA



Rough PMMA

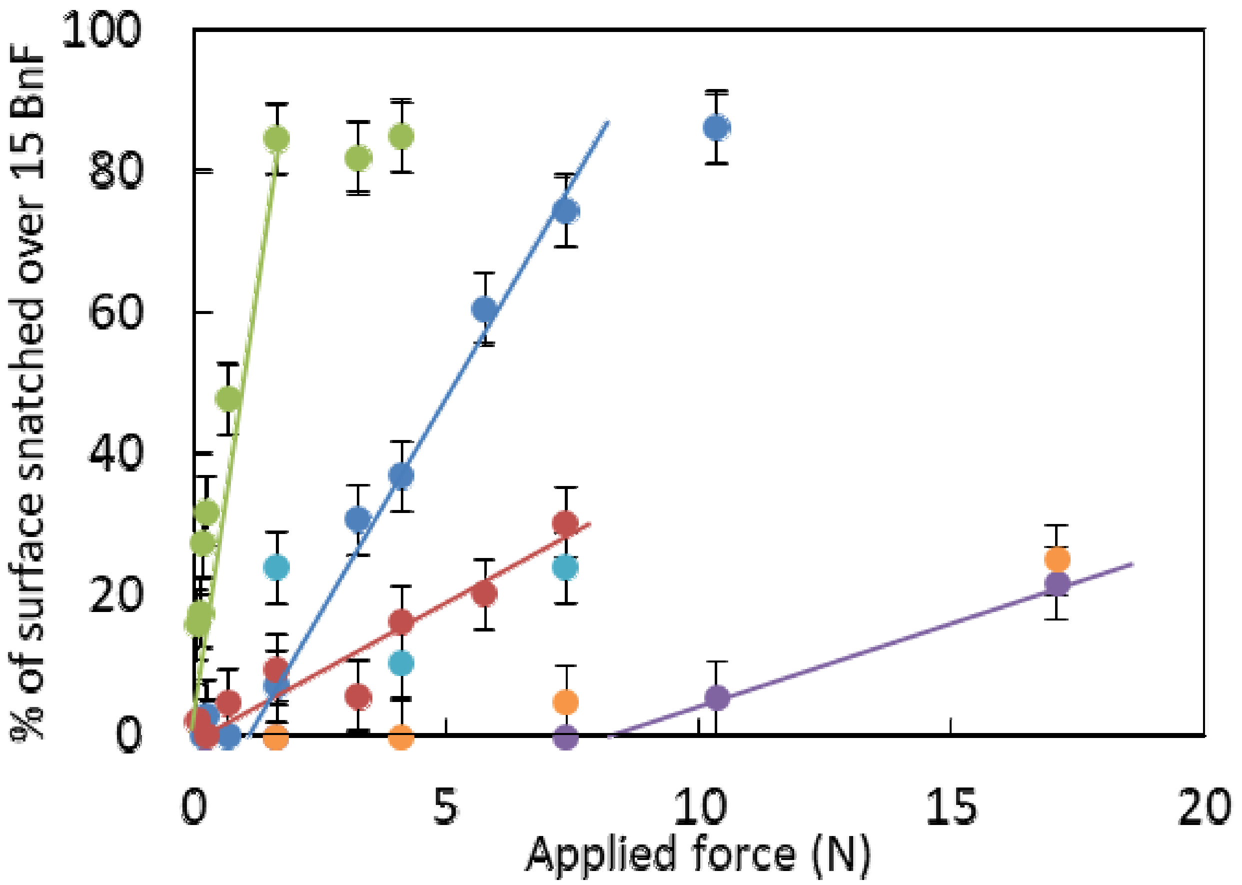
Artificial leather

Checking the impact of roughness and softness



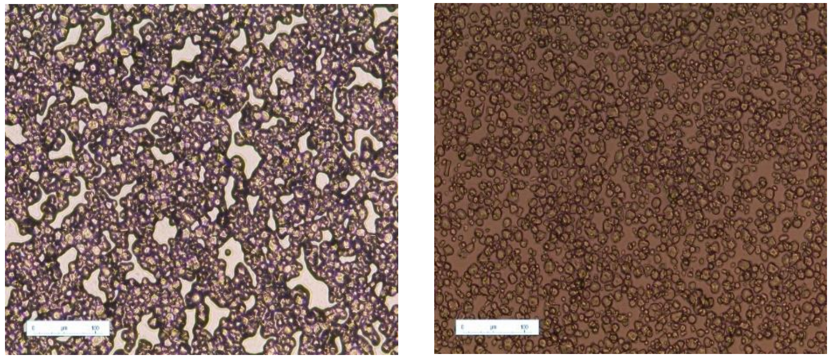
Carrying more relaistic spreading experiments

Impact of the materials on the spreading defects



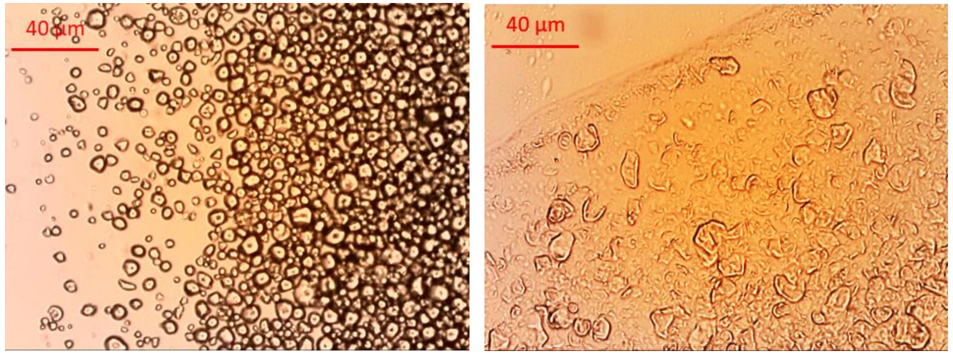
- *Smooth PMMA/Smooth PMMA*
- *Artificial leather/Artificial leather*
- *Artificial leather/Smooth PMMA*
- *Artificial leather/Rough PMMA*
- *Smooth PMMA/Rough PMMA*
- *Smooth PMMA/Artificial leather*

Conclusion and outlooks

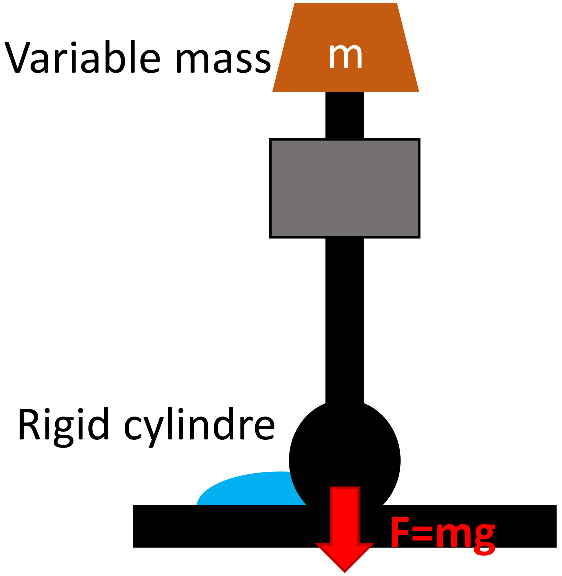


Impact of φ
Critical parameter φ_{RCP}

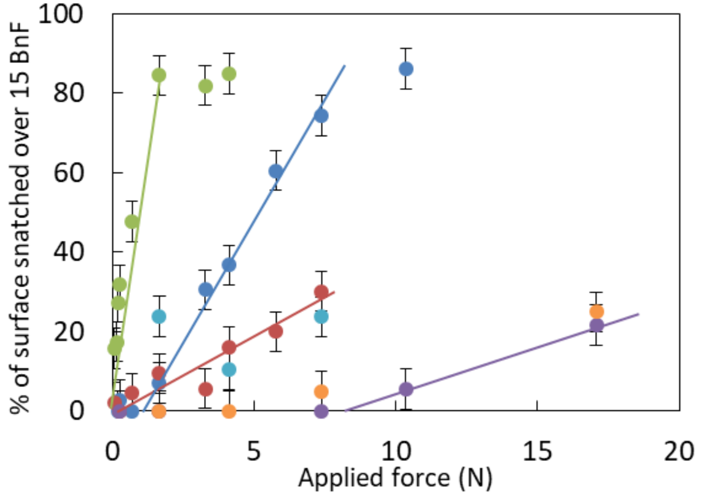
Evolution of φ overtime



Starch before and after ageing in water



More realistic spreading set-up



Impact of the substrate and applicator on spreading defects

Upgrade experimental set-up
- xyz force captor (stress)
- use even more realistic materials
- adapt the gesture

Conclusion et perspectives

How are films formed using an elastic blade?

How can we predict film thickness for complex fluids?

What do I get if I spread very complex fluids?

Aknowledgments

Jury members: Catherine Barentin, Guillaume Ovarlez, José Bico, Daniel Bonn

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