A novel type of mixer/reactor based on elongational flows: application to the elaboration of new polymeric materials

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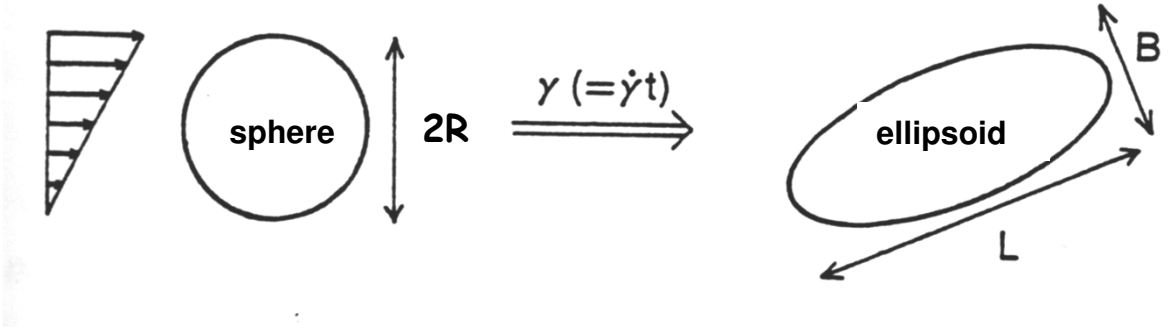
Deformation and breakup of liquid droplets in a liquid matrix



Viscous shear stress : $\eta_m \dot{\gamma}$ enhances deformation

Interfacial stress: $\frac{\sigma}{R}$ stabilizes drop shape

(dimensionless) Capillary number: $Ca = \frac{\eta_m \dot{\gamma} R}{\sigma}$ controls the drop shape

Critical capillary number for droplet breakup *(Taylor, 1934)*

If $Ca < Ca_c$ the drop shape stabilizes in the flow

If $Ca > Ca_c$ the drop deformation increases until breakup

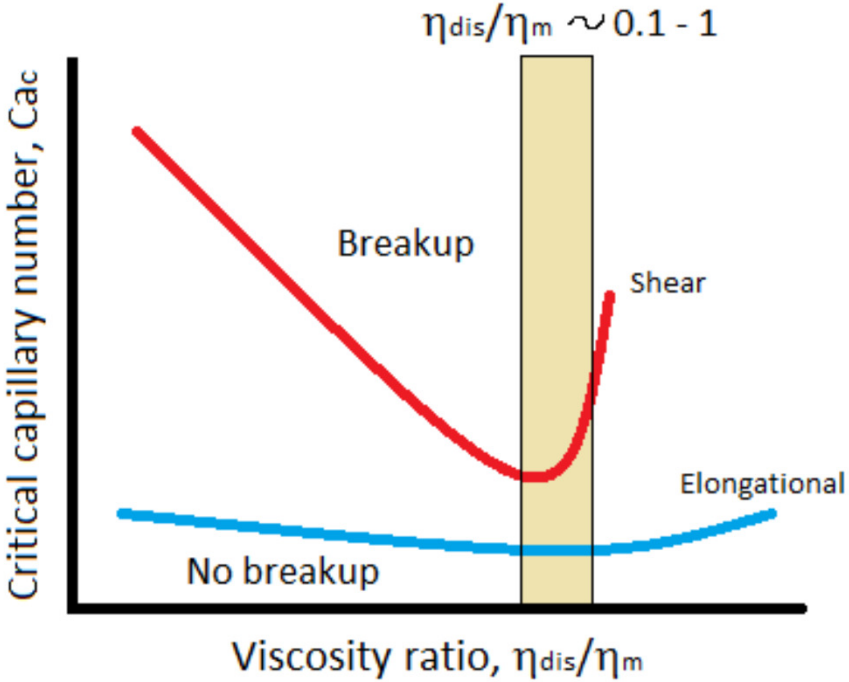
Ca_c depends:

on the viscosity ratio: $p = \frac{\eta_d}{\eta_m}$

on the type of flow: $\dot{\gamma}$, $\dot{\varepsilon}$

$Ca_c \cong 0,2$

(elongation)



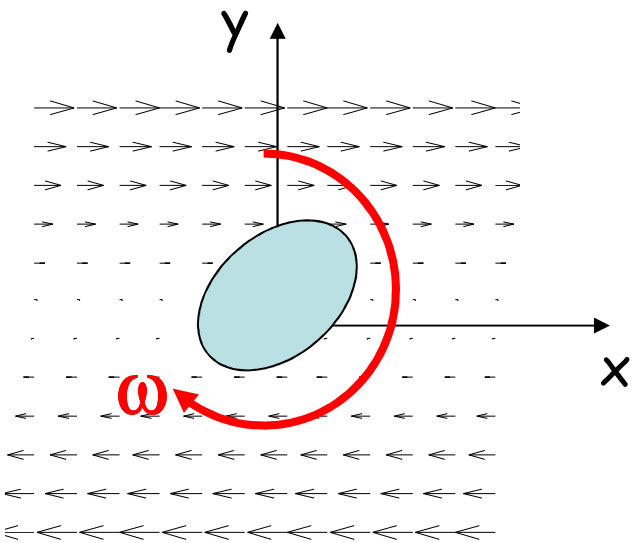
H.P. Grace, *Chem. Eng. Commun.*, 14, 2225 (1971)

If p>4:

No breakup in shear whatever the shear rate

Breakup remains possible in elongation

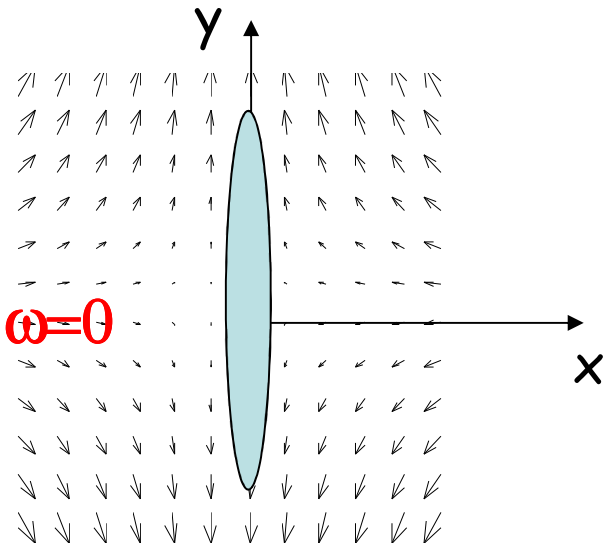
Rotational component in shear flow



Deformation and rotation of drop

For high viscosity drops (p>4), small and periodic deformation

Pure elongation: irrotational flow



Drop deforms without rotation.

Deformation will eventually increase and breakup occur even for highly viscous drops

OUTLINE

Principle of operation of RMX

Results for polymer blend morphology

Results for monomer emulsification

In-situ polymerization

Flow visualization and numerical simulation

Perspectives

Main types of laboratory mixers:

Brabender type (batch)

Rheomix (batch)

Twin-screw microcompounders (batch or continuous)

Single or twin-screw extruders (continuous)

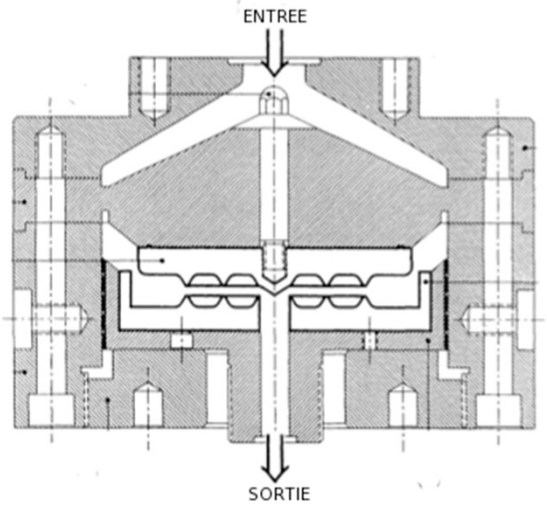
Main limitations or drawbacks:

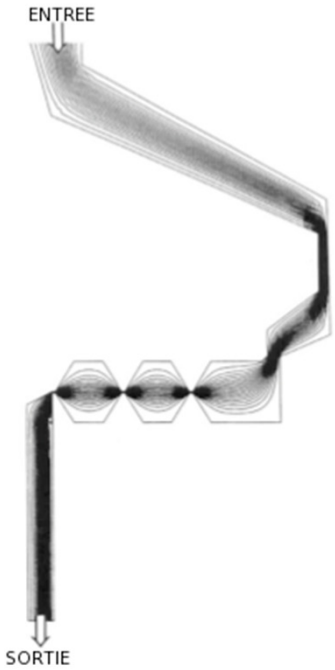
Difficulty to control elongational vs. shear flow

Uneasy recovery of specimens (additional molding step)

Difficulty to work under controlled atmosphere (evaporation, ..)

Attempts to promote extensional flow:





"Extensional flow mixer"

X.Q. Nguyen and L.A. Utracki,
U.S. Patent, 5, 451, 106, 19 (1995)

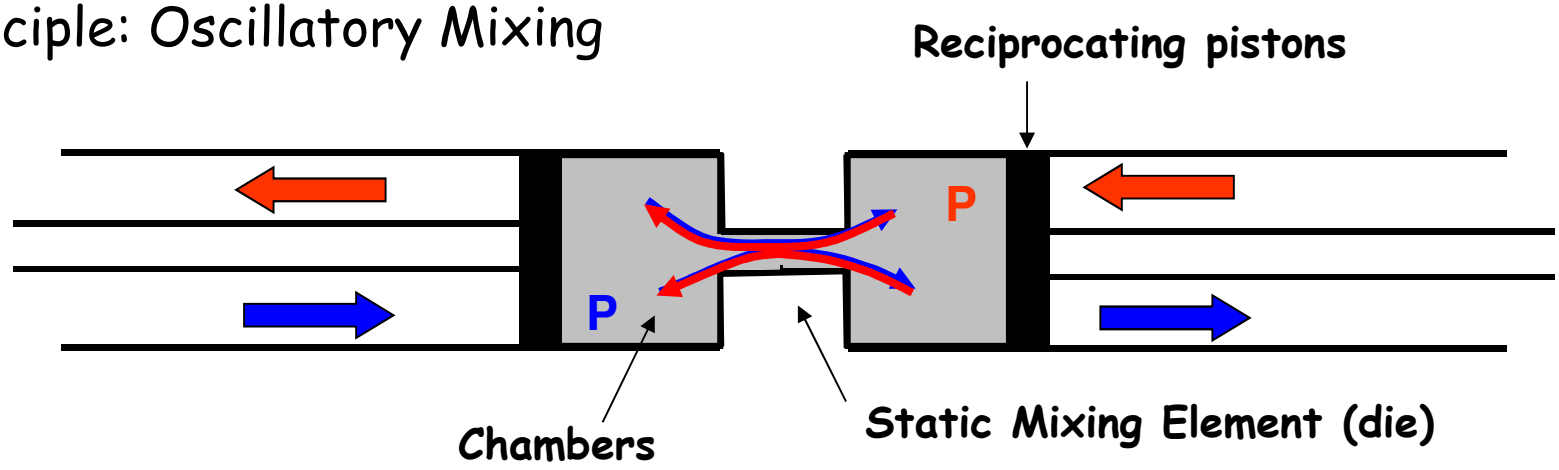
Limited number of contractions
(High pressure drop)

Multi-pass rheometer: Cambridge group (M. Mackley)

Use of multi-pass idea for mixing: US patent(1960)

Development of a new Mixer/Reactor

Principle: Oscillatory Mixing



Importance of elongational vs. shear flow

elongation through contraction factor

shear through die dimensions

Reorientation of material at each cycle

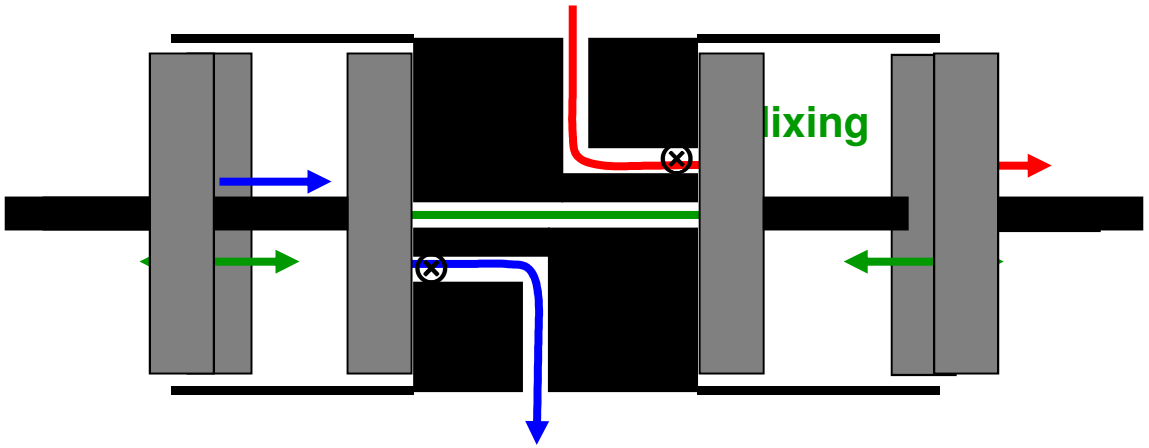
Tightness – operation under pressure (volatile products and reactives)

Design of Mixing Element

Criteria:

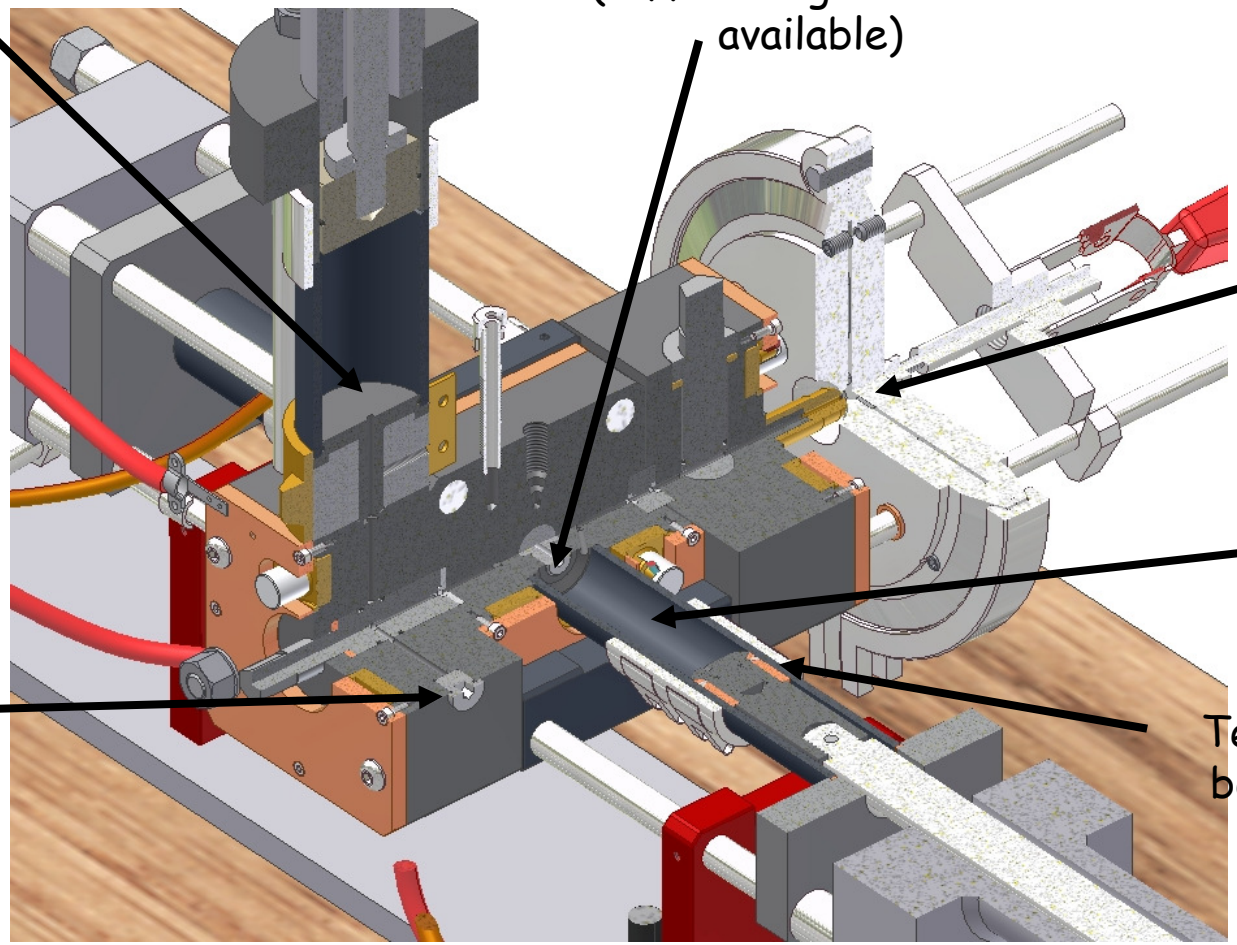
Feeding of components (including liquids under pressure)
Easy recovery and shaping of specimens
Liquid- and gas tightness
Fitting to extruder or second mixing unit

Feeding of melt or liquid

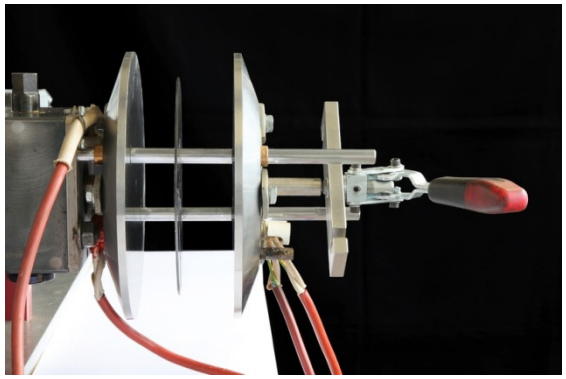


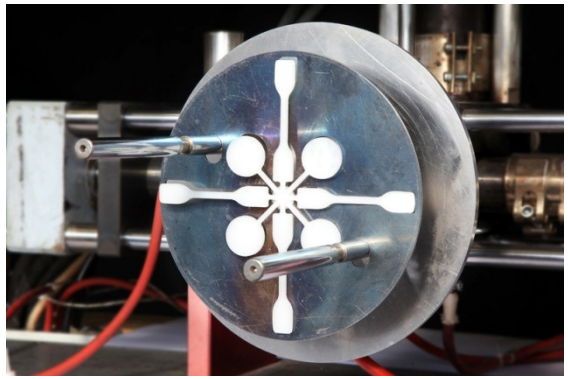
To mould, inlet of second unit, …

Schematic view of mixer



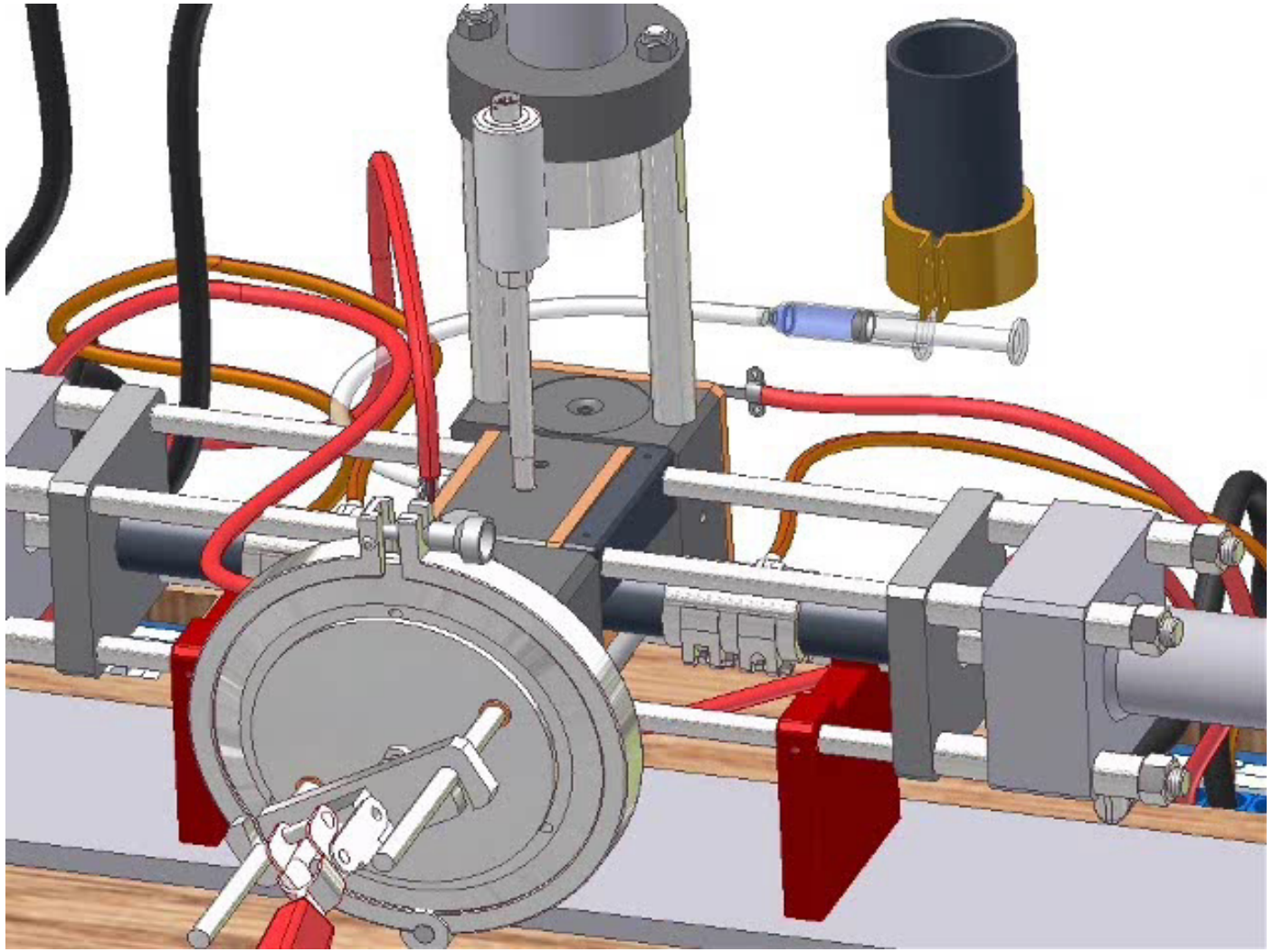
Hydraulic version of RMX (polymer melts)





- Variable mixing volume (5 to 100cm^3) depending on piston displacement
- Hydraulically driven pistons: power of hydraulic pump: 2kW
- Maximum pressure in chambers: 300 bars
- Typical frequency at 100 bars: 1 cycle in 2s

Principle of Operation



Model polymer blends: PS/PMMA

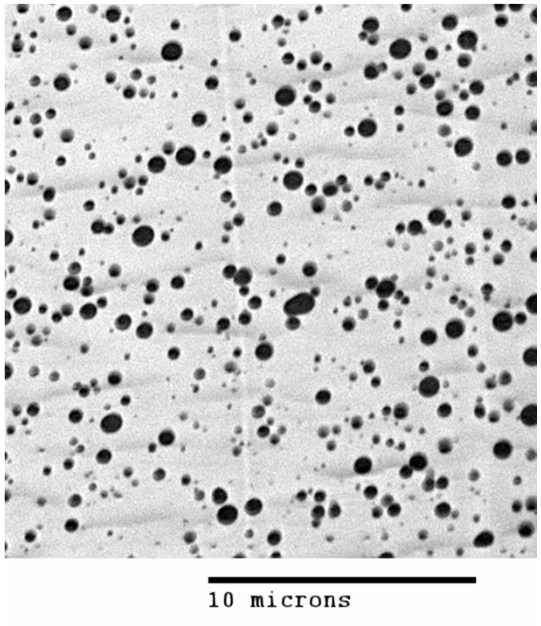
Low viscosity inclusions in high viscosity matrix:

PS / PMMA 10/90

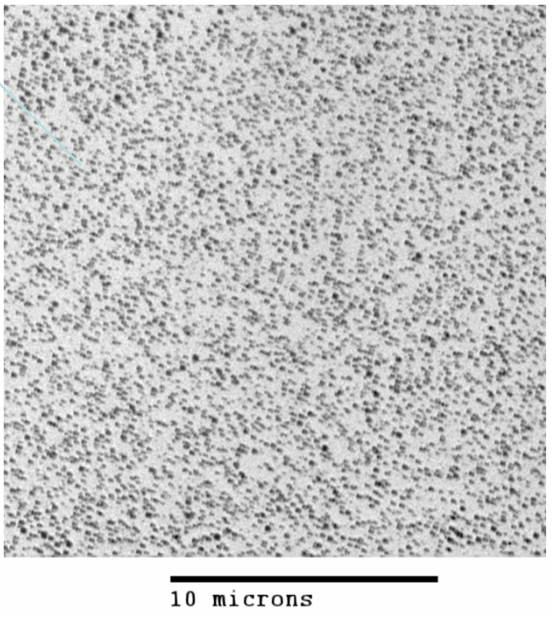
η(PS)/η(PMMA) ≅ 0,2

T=210°C

Piston speed: 10 mm/s



a



b

a: Rheomix Haake 630 J/g

b: RMX (30 cycles) 200 J/g

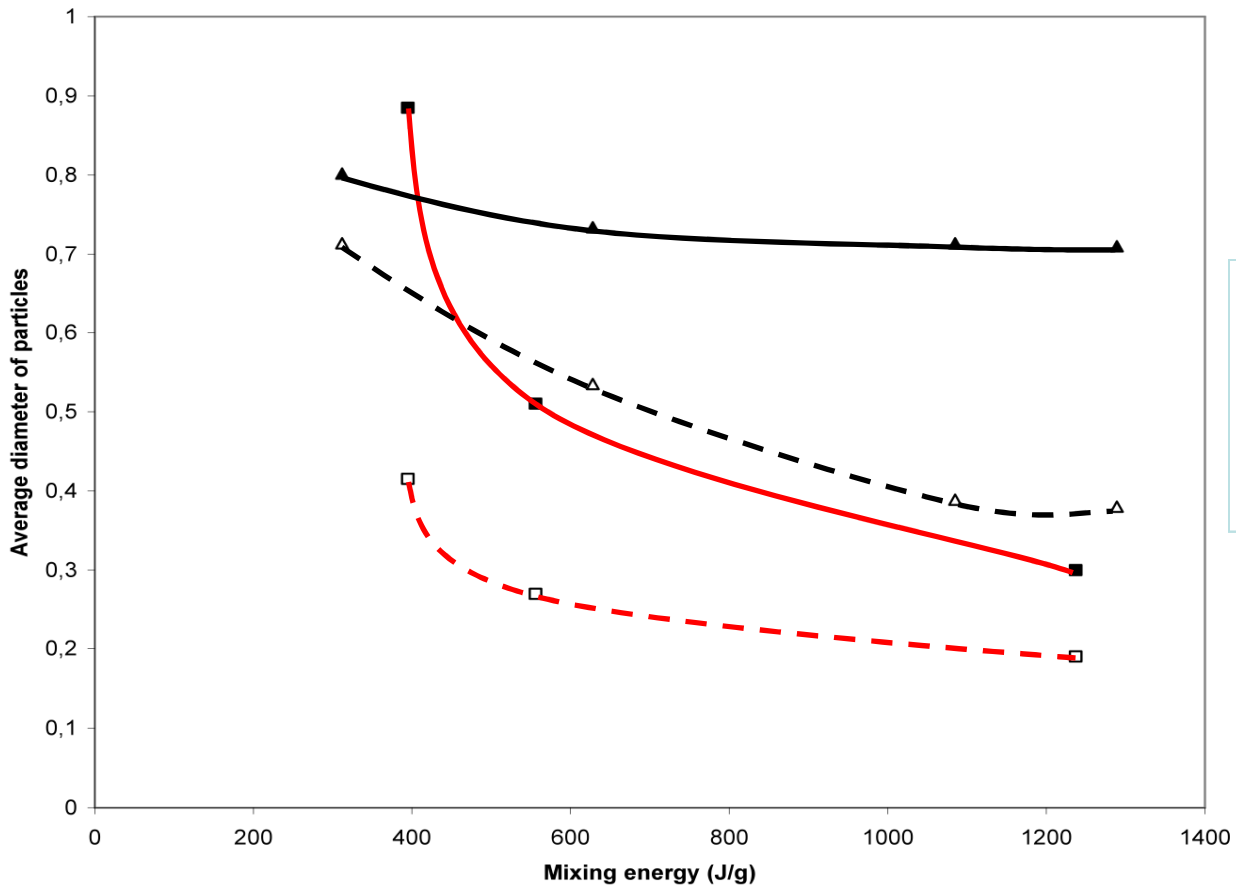
High viscosity inclusions in low viscosity matrix

PS / PMMA 90/10

η(PMMA)/η(PS) ≅ 5

T=210°C

Piston speed: 10 mm/s



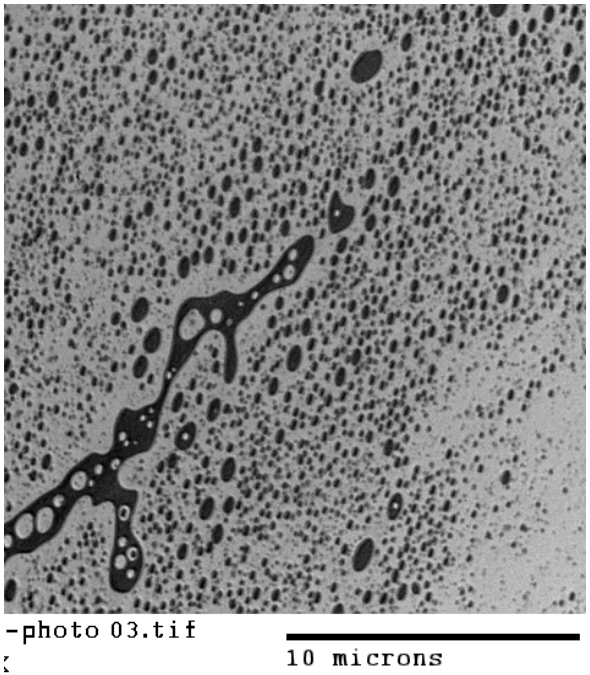
Influence of number of mixing cycles

PS / PMMA 10/90

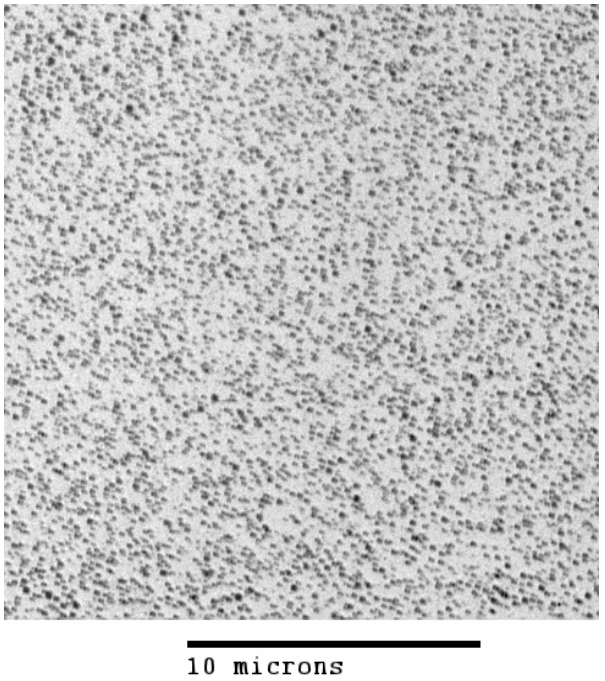
η(PMMA)/η(PS) ≅ 5

T=210°C

Piston speed: 10 mm/s



a

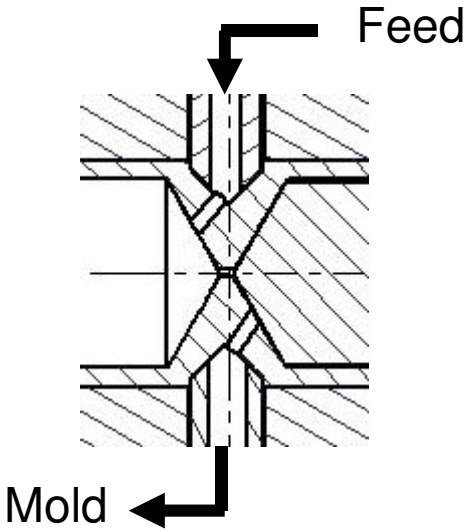


b

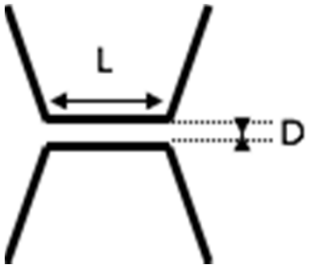
a: 10 cycles

b: 30 cycles

Mixing elements



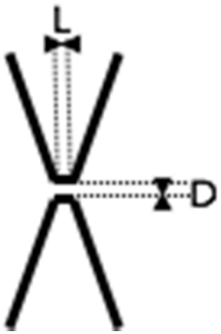
Long die mixing element



L=15 mm
D=3mm

L/D=5

Short die mixing element



L=2 mm
D=2mm

L/D=1

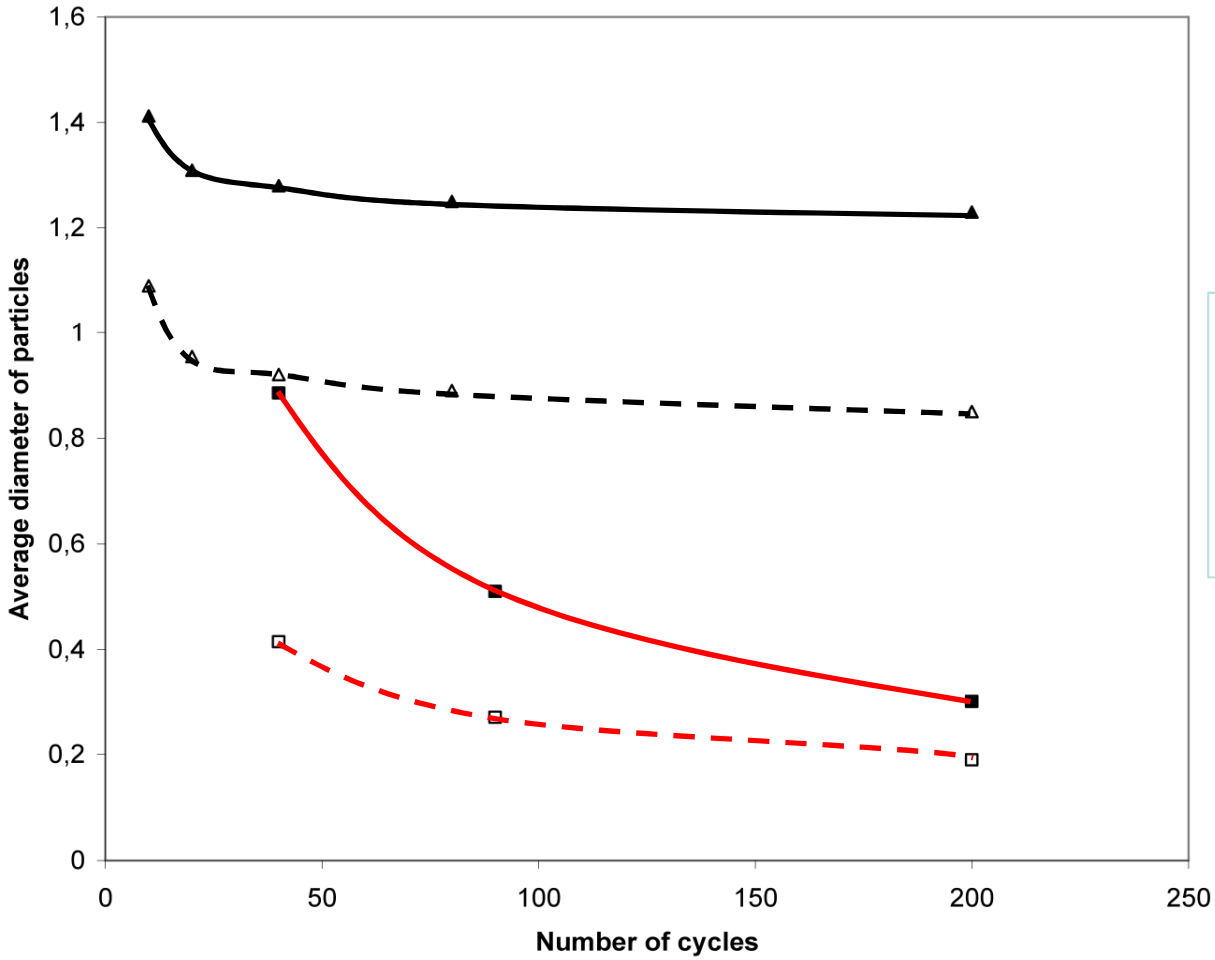
Influence of geometry of mixing element

PS / PMMA 10/90

η(PS)/η(PMMA) ≅ 0,2

T=210°C

Piston speed: 10 mm/s



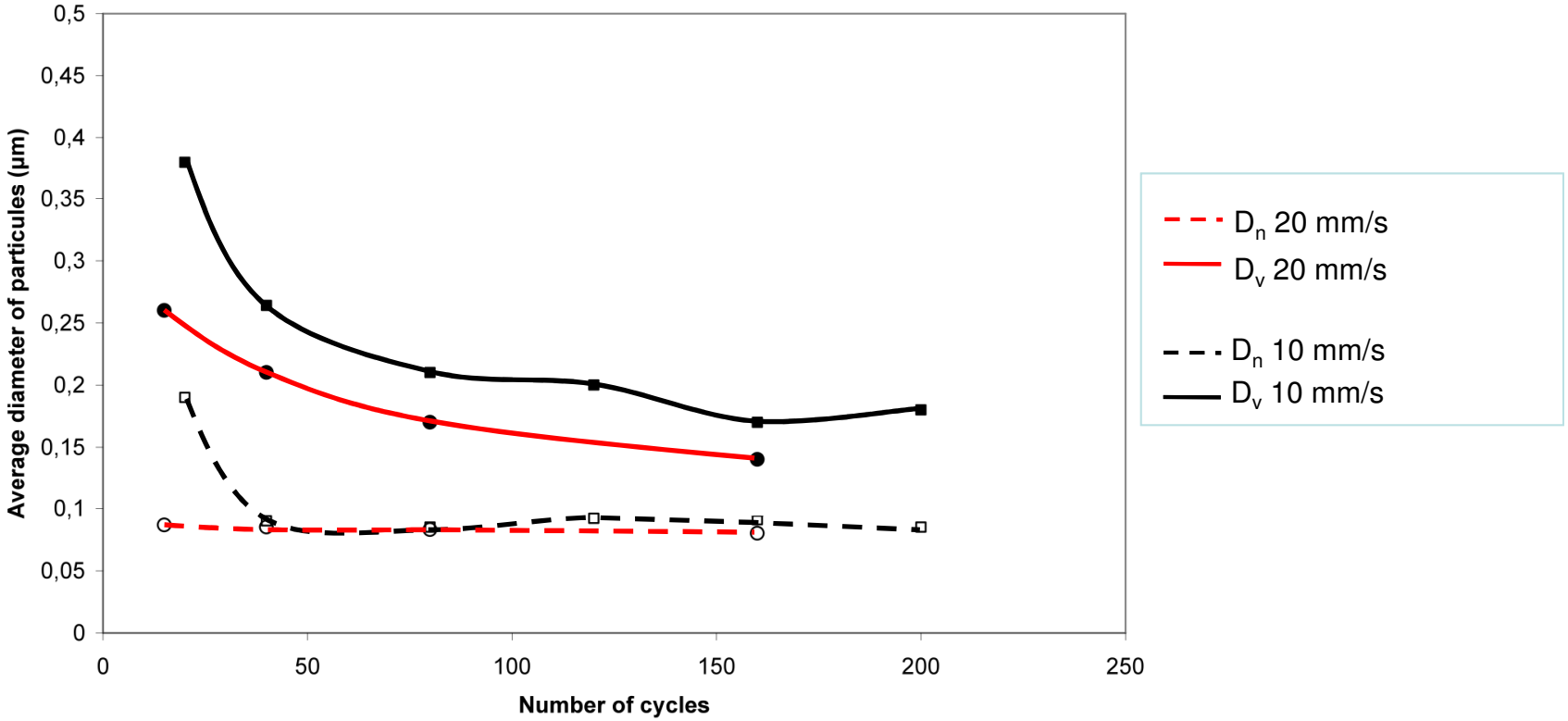
Influence of flow rate (piston speed)

PS / PMMA 10/90

η(PS)/η(PMMA) ≅ 0,2

T=210°C

Long die mixing element



Application to recycling: "model" waste polymer blend

50 HDPE / 40 PP / 10 PS (w/w)

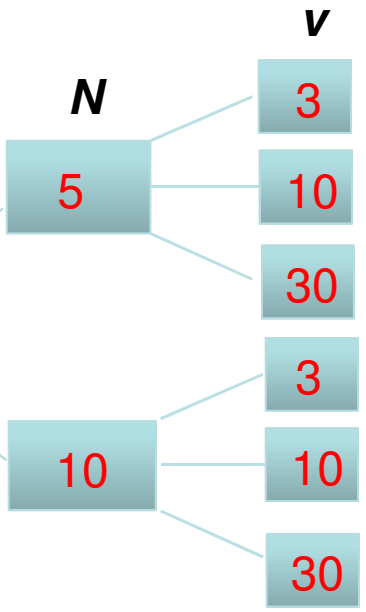
Polymer	Supplier	Reference	MFI (g/10min)
PP copo	BRASKEM	C715-12 NPH	12 (230°C)
HDPE	TOTAL PETROCHEMICAL	HDPE 5502	0.3 (190°C)
PS	TOTAL PETROCHEMICAL	STYRON 678E	11 (200°C)

Compounding in twin-screw extruder

Reprocessing in RMX

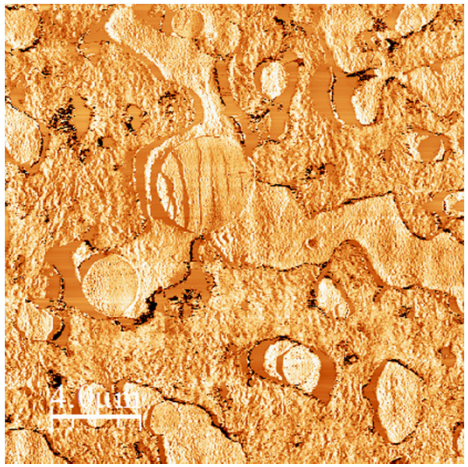
Mixing element

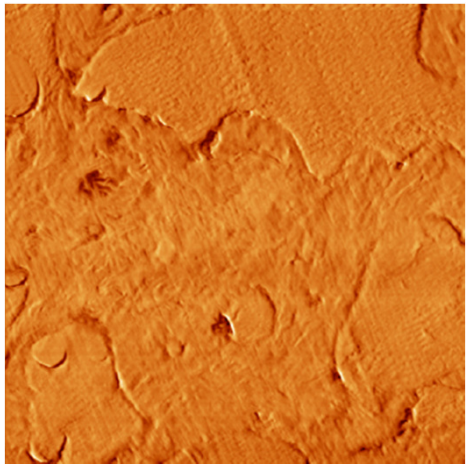
Ø = 2 mm, Ø = 4 mm



AFM RESULTS

Extruded sample





Reprocessed sample (RMX)

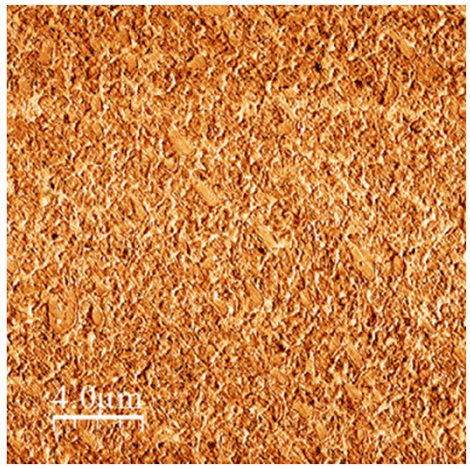
Ø = 2 mm

3mm/s,

5 cycles

$\dot{\gamma}$=4500 s^{-1}

$\dot{\varepsilon}$=110 s^{-1}

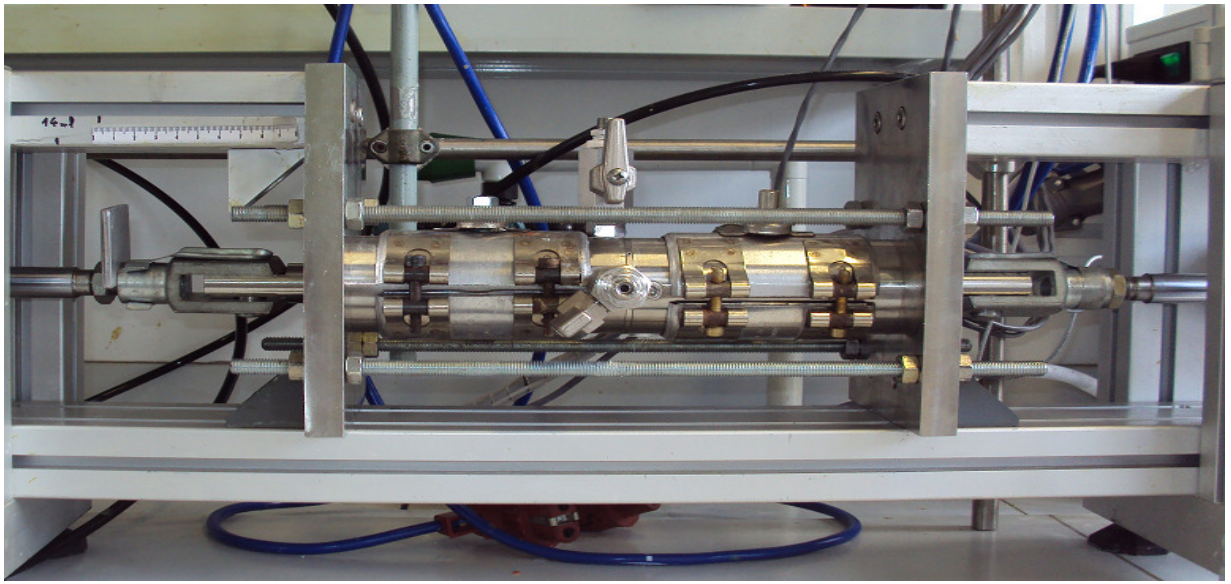


First results on monomer emulsification

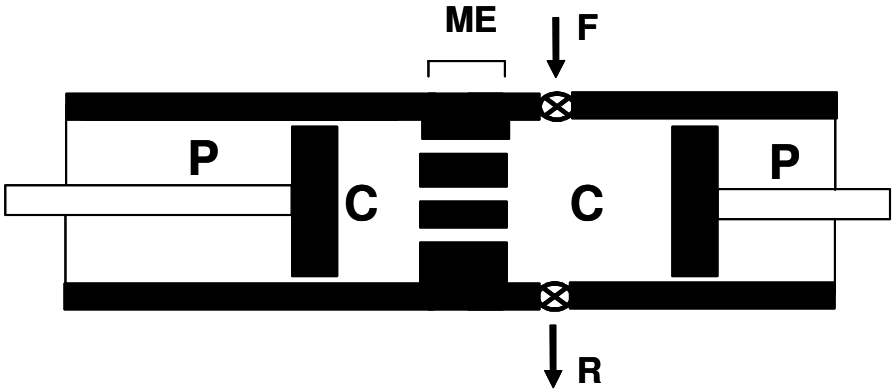
Pneumatic device

Controlled pressure

Low pressures (<25 bars)

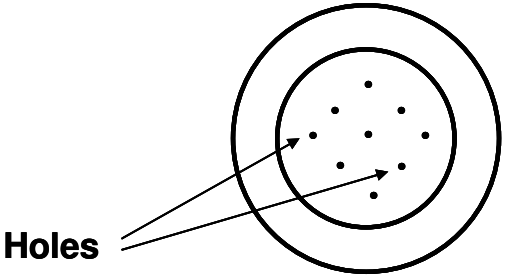


1a



Specific mixing element

1b



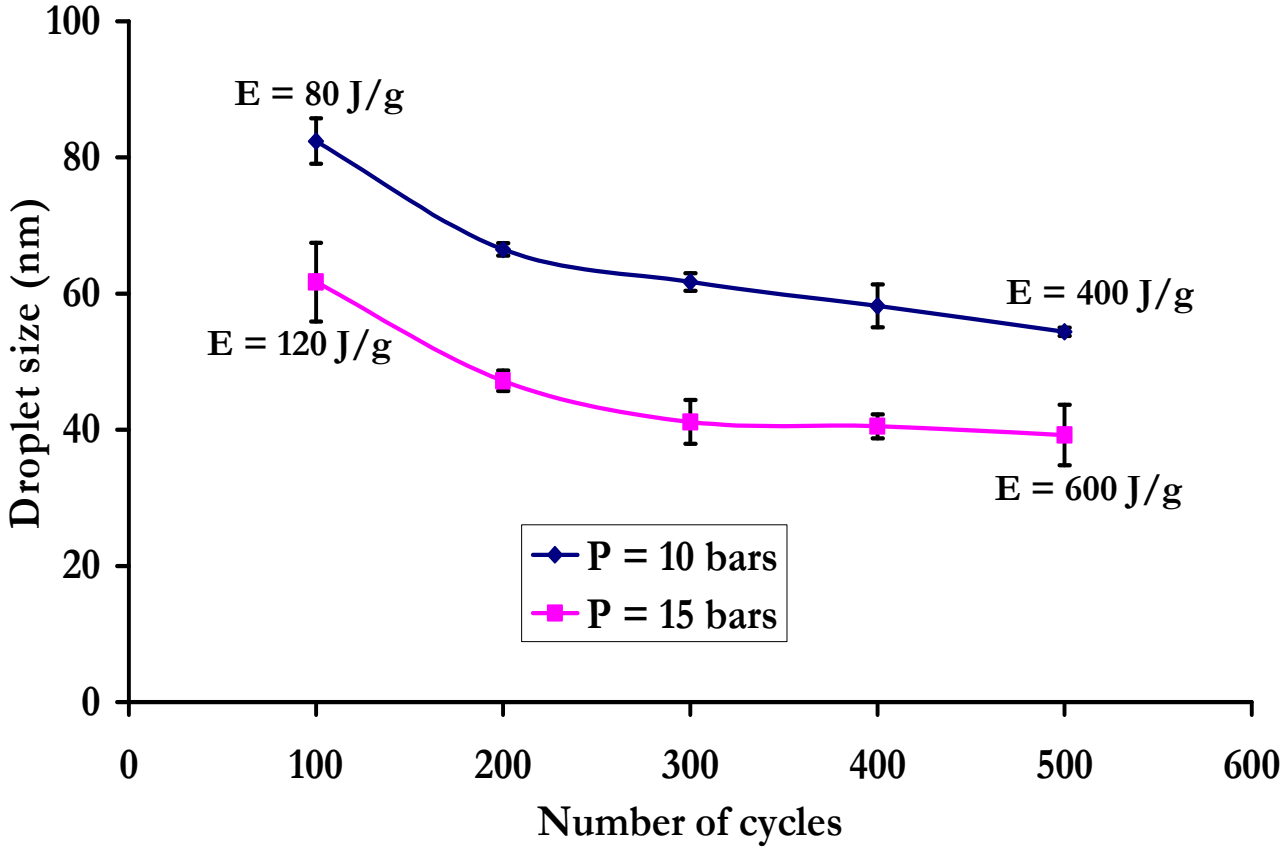
Number of holes : between 1 and 30

Diameter of holes : between 0,2 mm and 1 mm

1a. Schematic representation of the RMX device: P pistons; C mixing chambers; ME mixing element; F: feeding channel; R: sampling and recovering channel.

1b: Front view of a typical mixing element, Holes; number of holes between 1 and 30, diameter of holes between 1 mm and 0.2 mm.

Influence of the number of cycles (mixing energy)



85% Water

15% MMA

[SDS] = 4 g/l

[HD] = 4% wt./MMA

Pressure

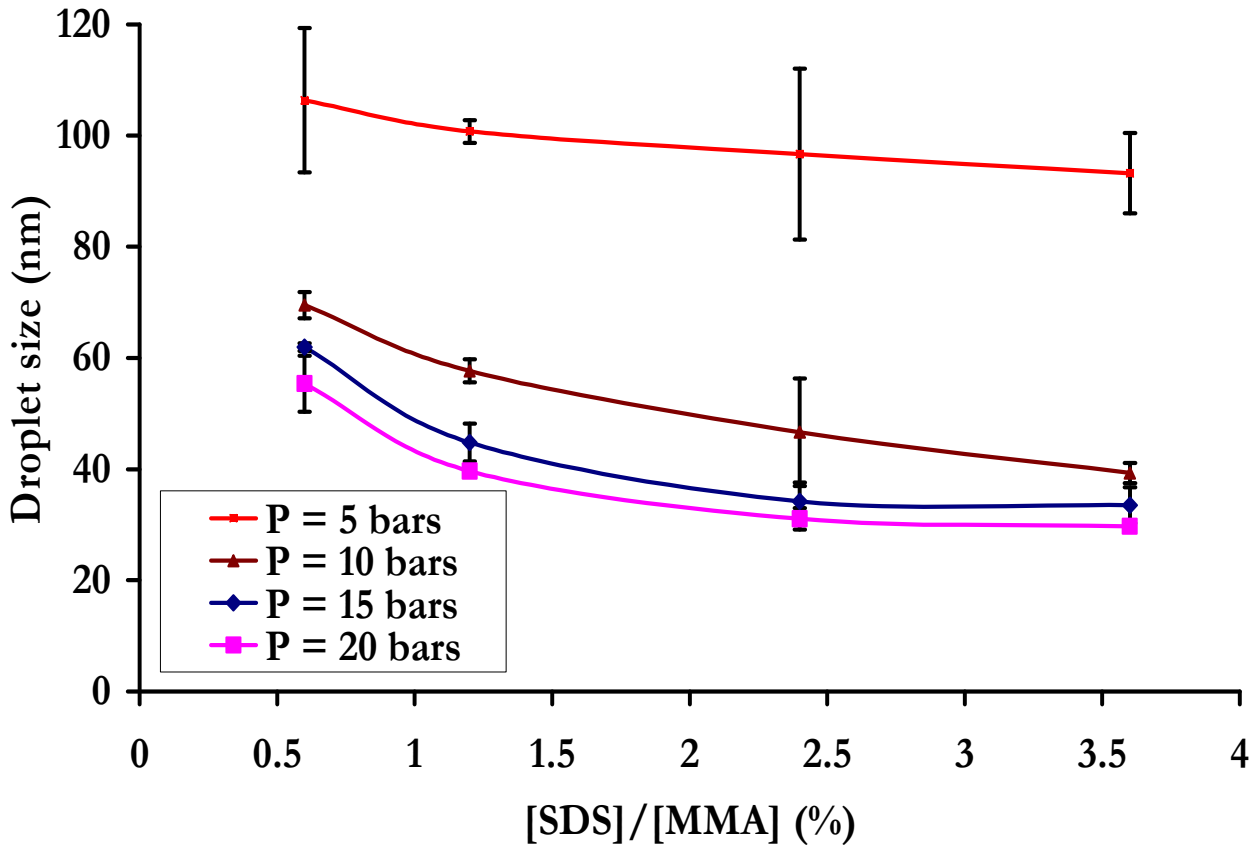
Number of cycles

ME: 3 holes of 500 µm

➔ Decrease in size with mixing time/energy

➔ No variation in size above 300 cycles

Influence of SDS concentration



85% Water

15% MMA

[SDS]

[HD] = 4% wt./MMA

Pressure

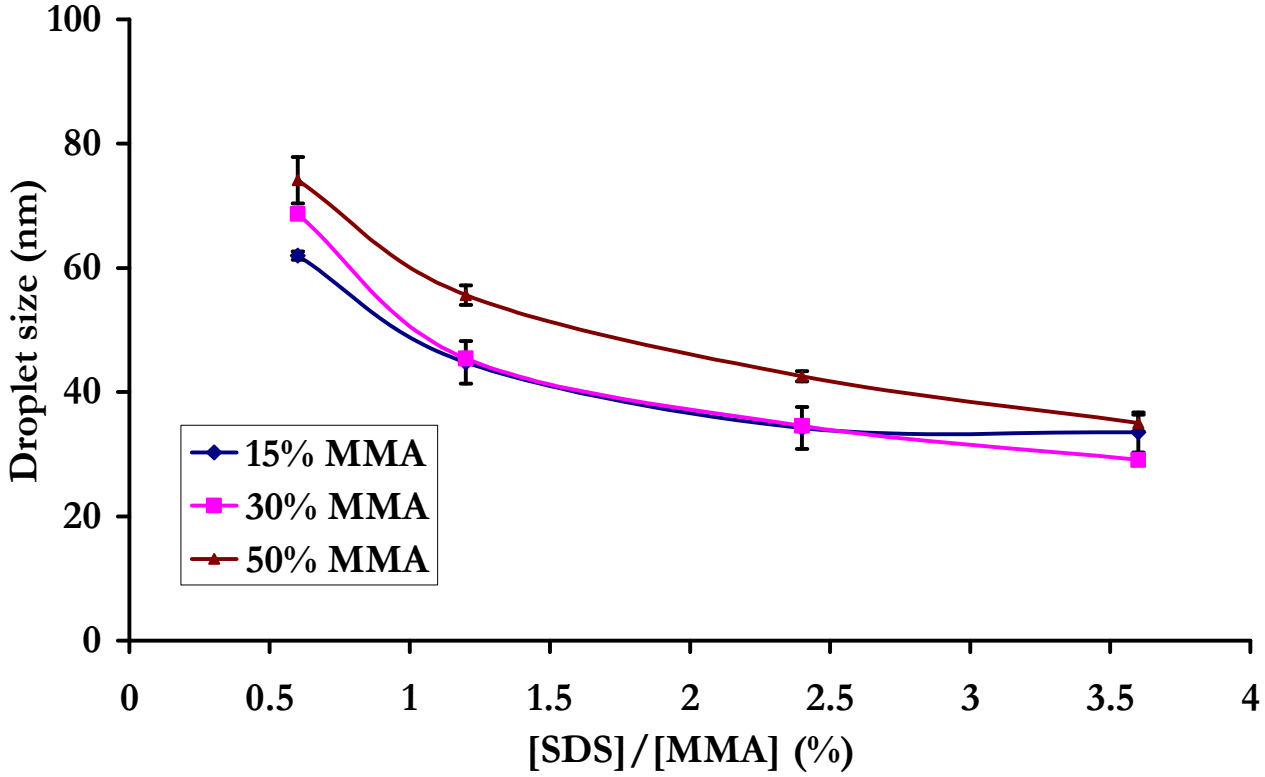
500 cycles

ME: 3 holes of 500 µm

➔ Decrease of droplet size by increasing [SDS]

➔ A limit is reached at about [SDS]/[MMA] = 2.5%

Influence of MMA concentration



Water

MMA

[SDS]

[HD] = 4% wt./MMA

P = 15 bars

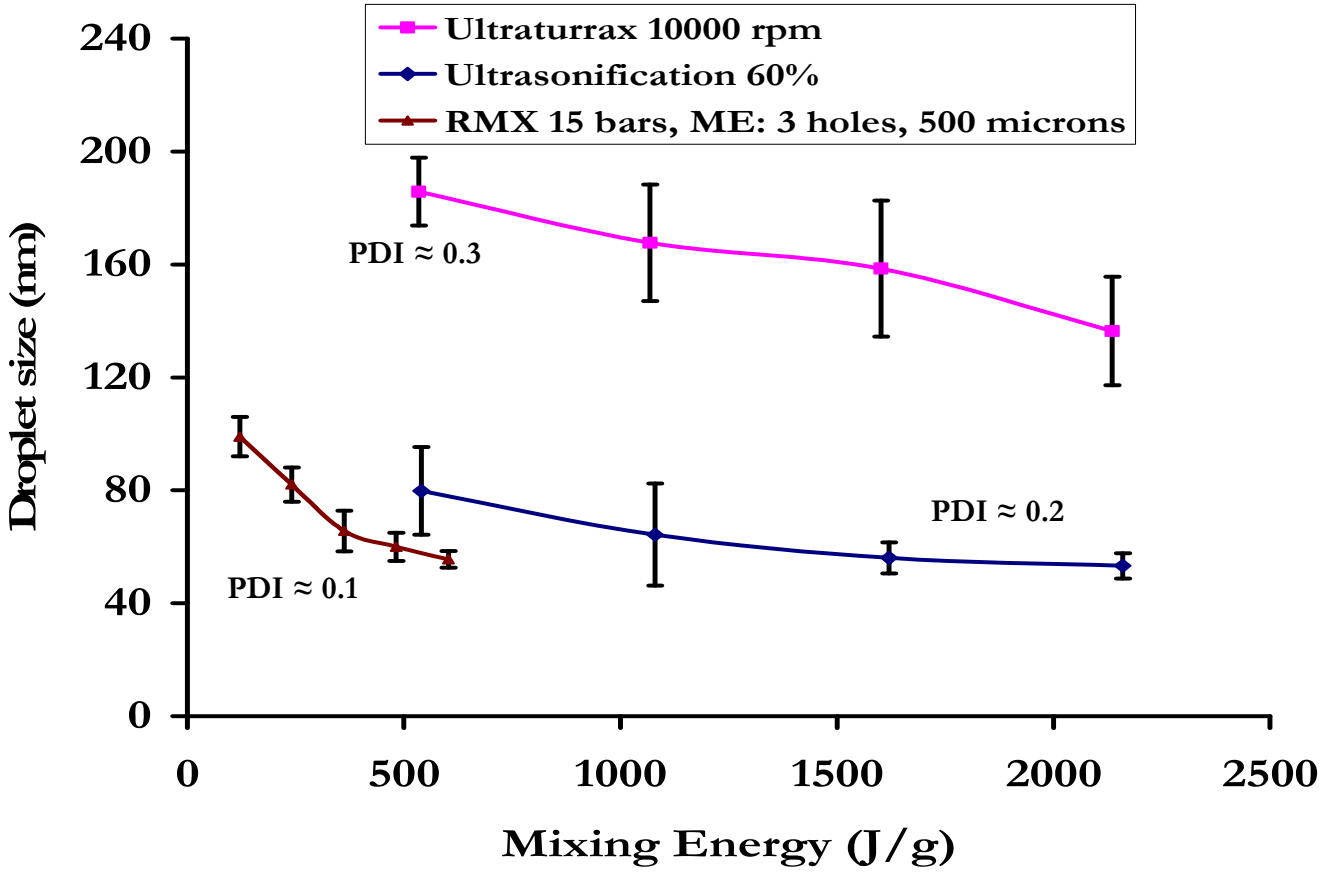
500 cycles

ME: 3 holes of 500 µm

➔ Small droplet size even at high monomer fractions

BUT lower emulsion stability

Comparison between ultrasonification, ultraturrax and RMX



85% Water

15% MMA

[SDS] = 4 g/l

[HD] = 4% wt./MMA

➔ **Efficiency of RMX:**

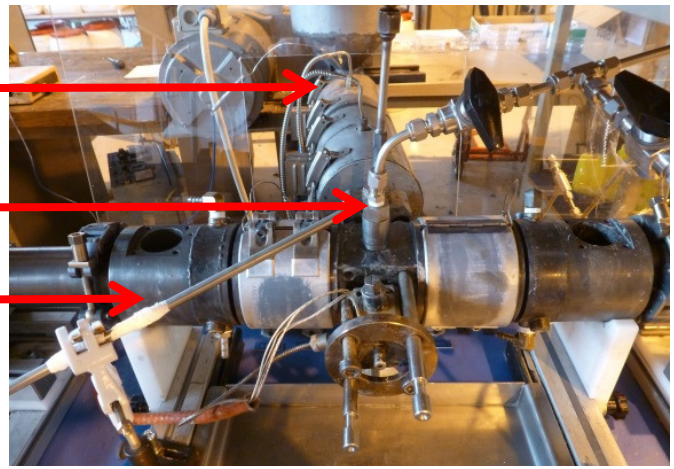
- small size with lower mixing energy, low PDI
- better reproducibility

- Adaptation du mélangeur à la polymérisation in-situ
  - RMX®

Extrudeuse: polymère fondu

Pompe: Monomères + amorceurs

Système de refroidissement par air



- **Système étudié**
  - **PMMA/styrène**
    - **Par polymérisation radicalaire à T=190°C**
  - **Variables du procédé**

Extrusion:
- **Composition en styrène (10-55%m)**
- **$t_{1/2}$**
- **Vitesse des pistons**
- **Mode: statique ou dynamique**
- **Température**

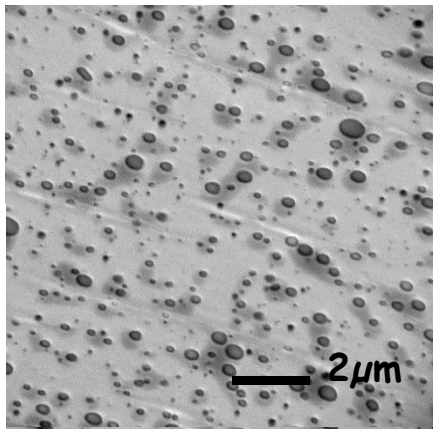
Nom commercial	Nom scientifique	$t_{1/2}$ à 190°C (s)
Luperox DI (Sigma)	Peroxyde de tert-butyle	35
Trigonox 311 (AksoNobel)	3,3,5,7,7-pentamethyl-1,2,4-trioxepane	226

- Influence du temps de séjour
  - Polymérisation "dynamique" dans le RMX

18%$_{vol}$ styrène; L/D=0,3; vit.=150cm/mn; 40 cycles; 2%m LupDi

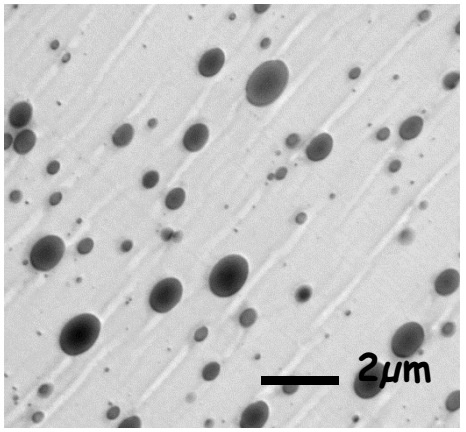
20mn

$\overline{R_n}$ = 60 nm
$\overline{R_v}$ = 270 nm
Mn=6500
IP=1,9



+30mn statique

$\overline{R_n}$ = 75nm
$\overline{R_v}$ = 400 nm
Mn=6000
IP=1,9

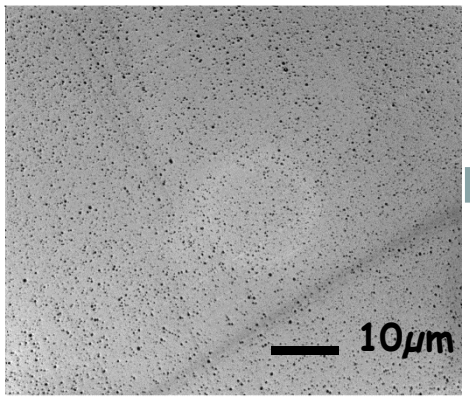


Composition constante dans tout l'échantillon (mélange distributif)
Evolution de la taille des particules en fonction du temps (coalescence)
PS = 10% de la surface et non 18%

- Influence du nombre de cycle
  - Polymérisation "dynamique" dans le RMX

13%$_{vol}$ styrène; L/D=5;vit.=100cm/mn; 2%m LupDi

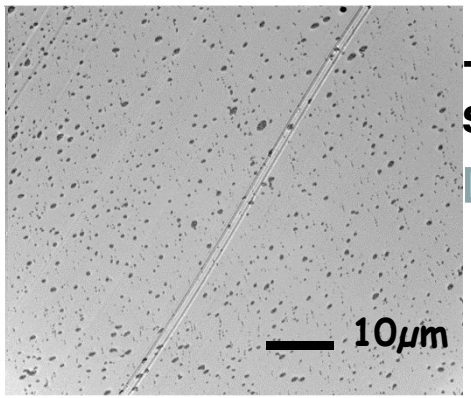
$\overline{R_n}$ = 60 nm $\overline{R_v}$ = 140 nm
Mn=5000 IP=1,9 %$_S$= 5



a: 10c 2mn

+30c

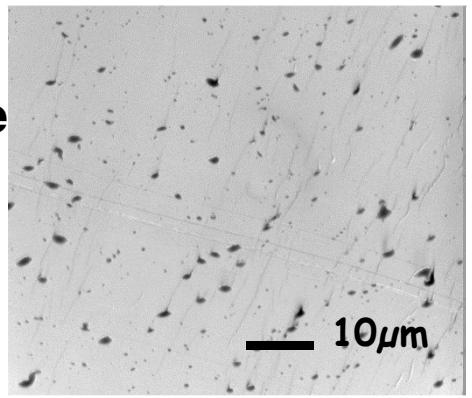
$\overline{R_n}$ = 100 nm $\overline{R_v}$ = 530 nm
Mn=5000 IP=1,9 %$_S$= 5



b:40c 10mn

+10mn statique

$\overline{R_n}$ = 170 nm $\overline{R_v}$ = 630nm
Mn=5000 IP=1,9 %$_S$= 5



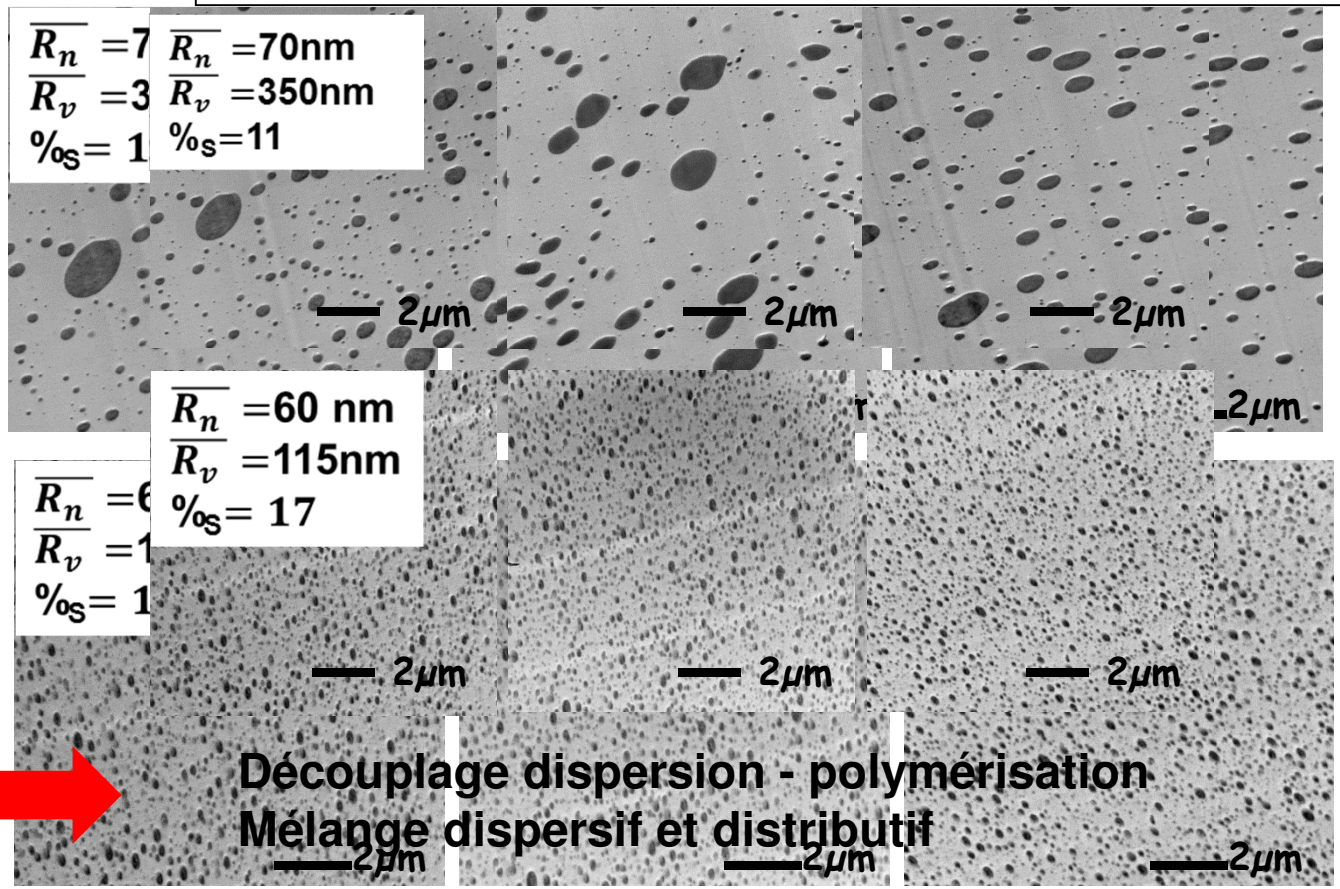
c:40c 20mn

Composition constante dans tout l'échantillon (mélange distributif)

Evolution de la taille des particules en fonction du temps

- Influence du procédé de polymérisation
  - Polymérisation sous écoulement vs poly. statique puis dispersion

22%vol; L/D=5; vit.=100cm/mn; 90 cycles; 33mn; 1%m Trigo311



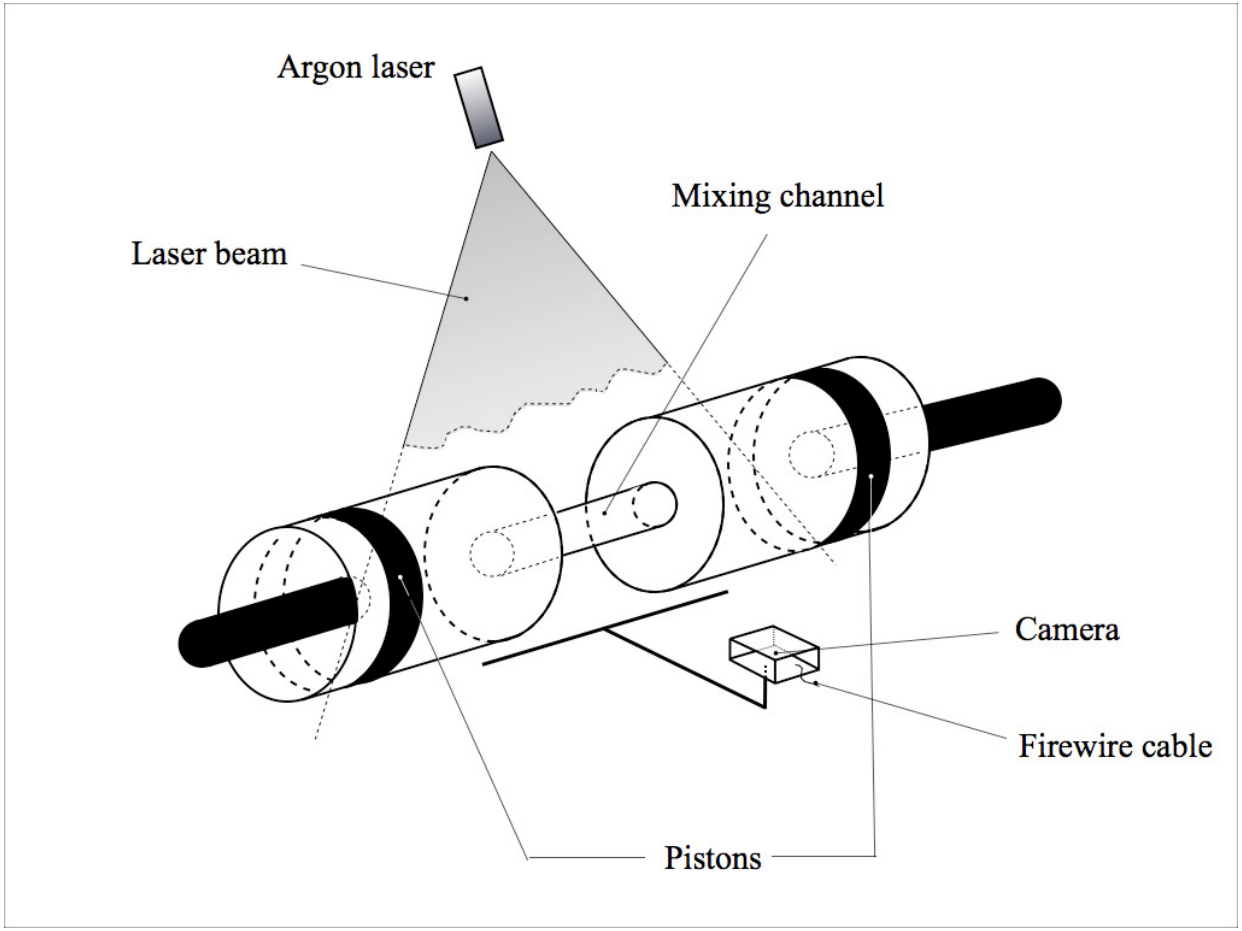
1: Statique 20mn
2: Dynamique 90cycles (13mn)

1: Dynamique 90 cycles (13mn)
2: Statique 20mn

Flow visualization

Transparent chambers

Fluorescent fluid

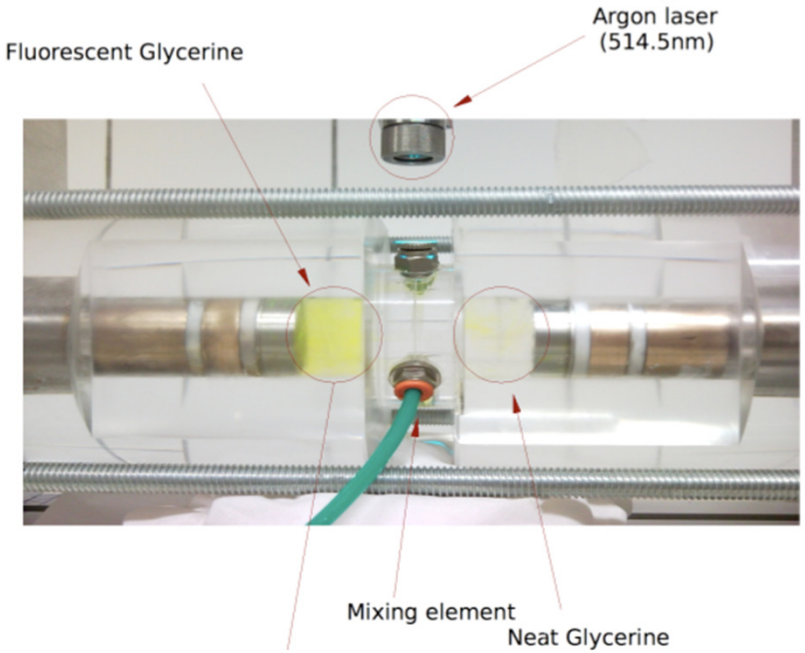


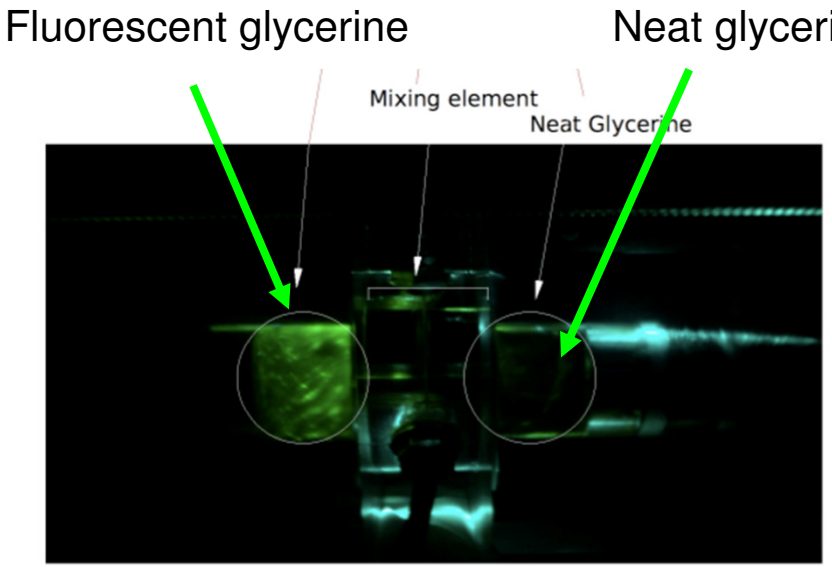
Flow visualization

PMMA chambers

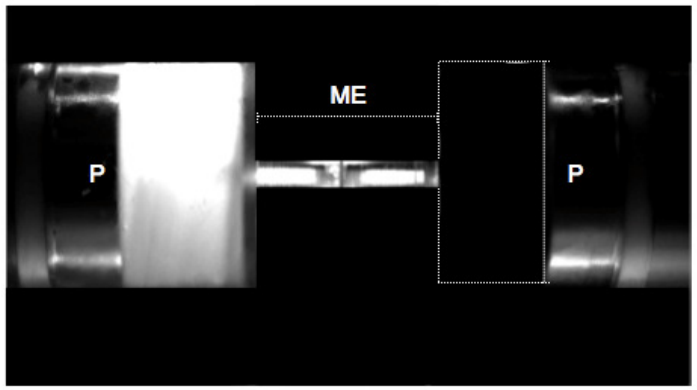
Linear laser vertical beam

Same fluid in both chambers but in one of the chambers contains fluoresceine

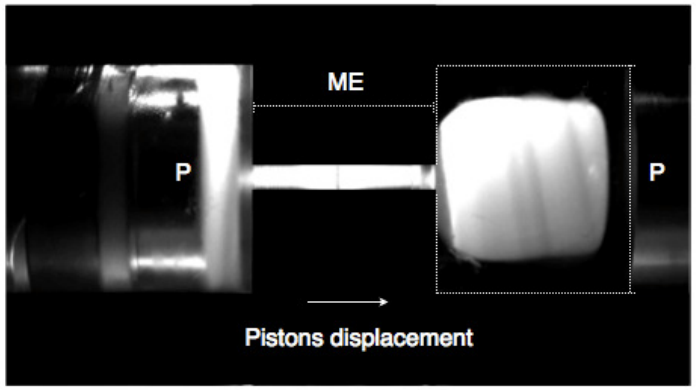




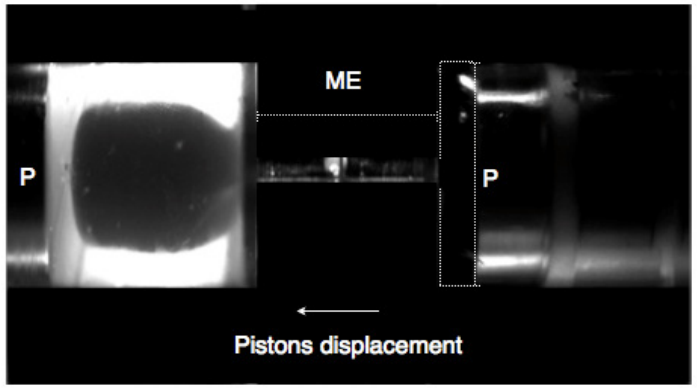
Creeping flow (Re≅0.001): newtonian, low viscosity fluid: experiments



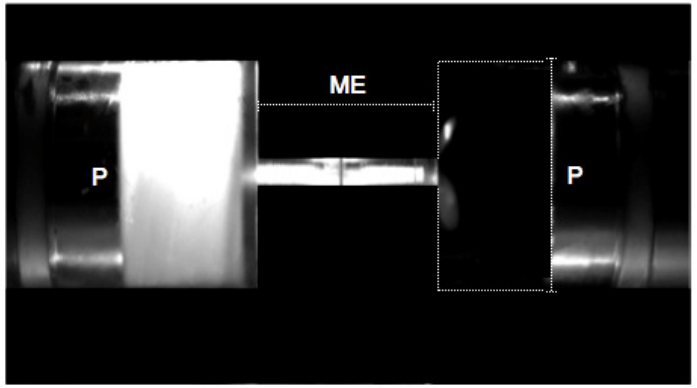
a



b

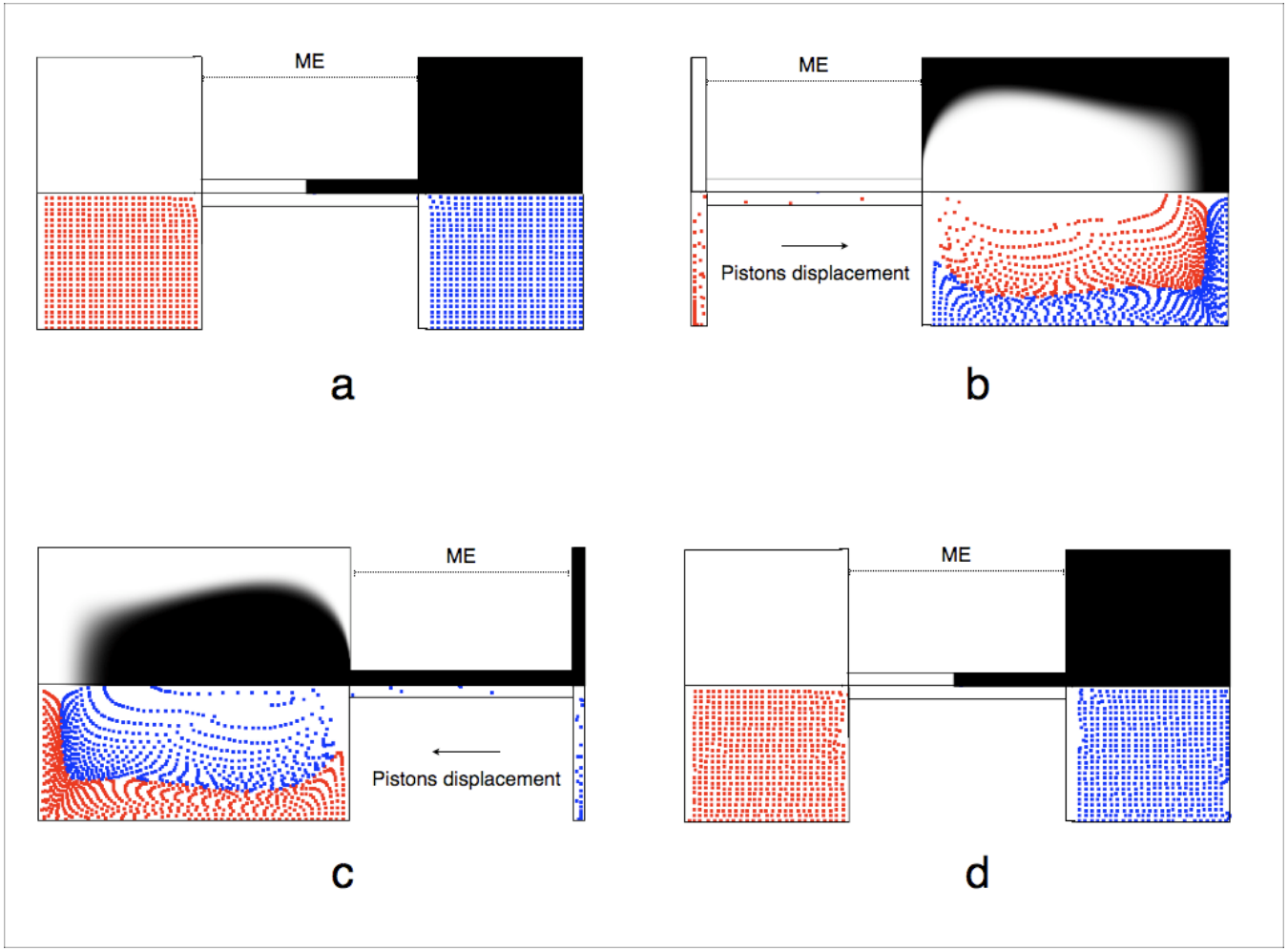


c



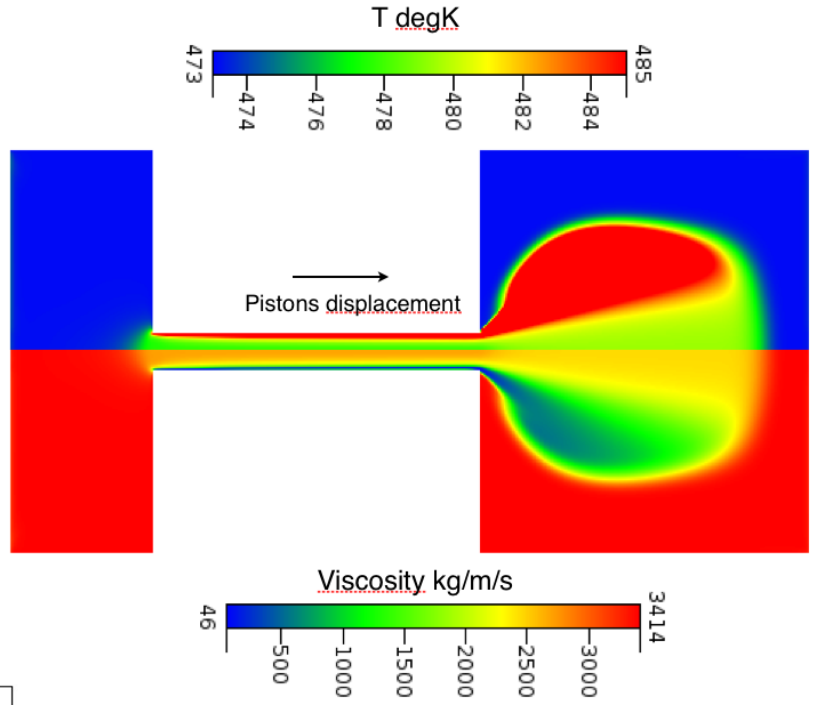
d

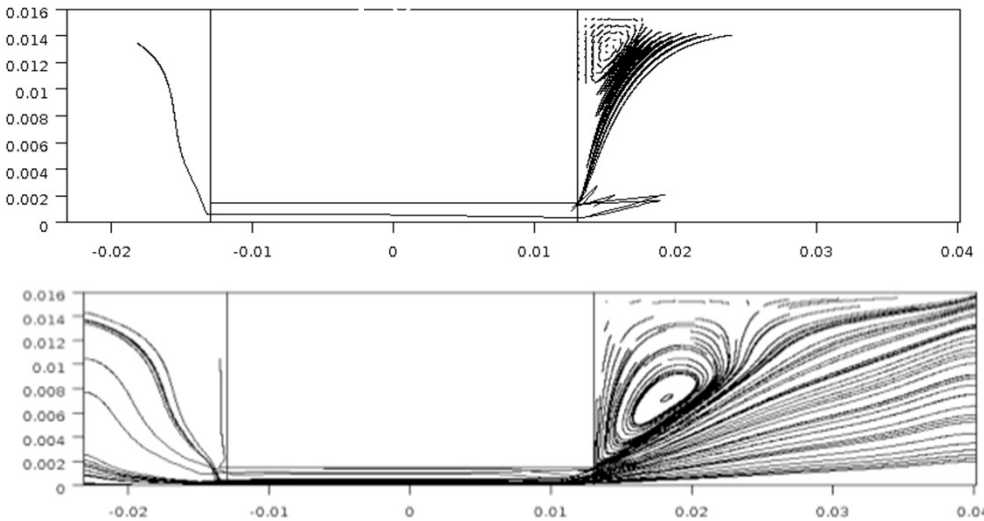
Creeping flow (Re=0.001): newtonian fluid: isothermal simulation



Creeping flow (Re≅0.001):

Simulation for
newtonian fluid
and solving energy equation

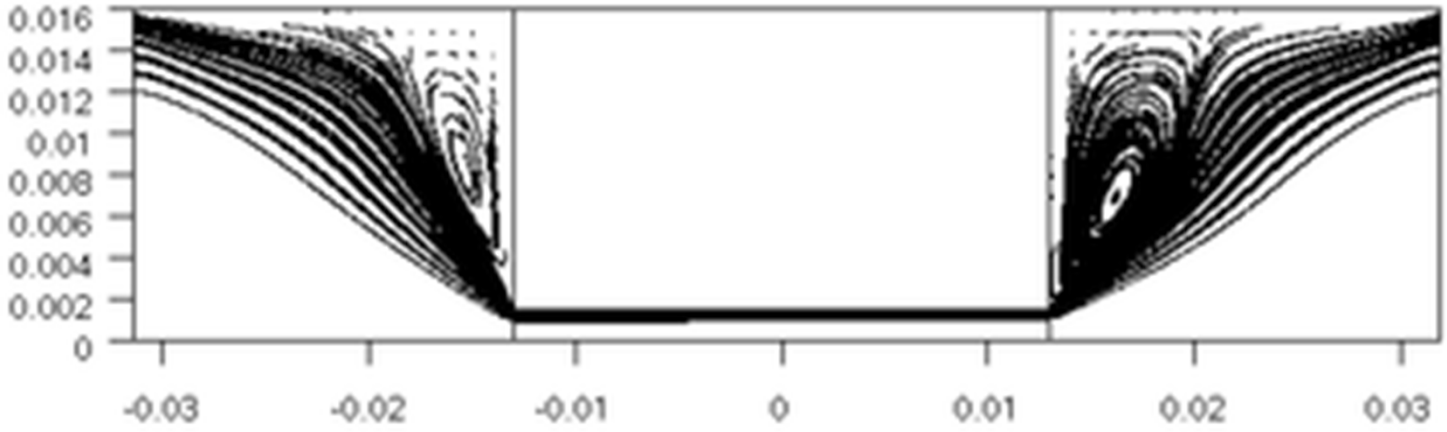


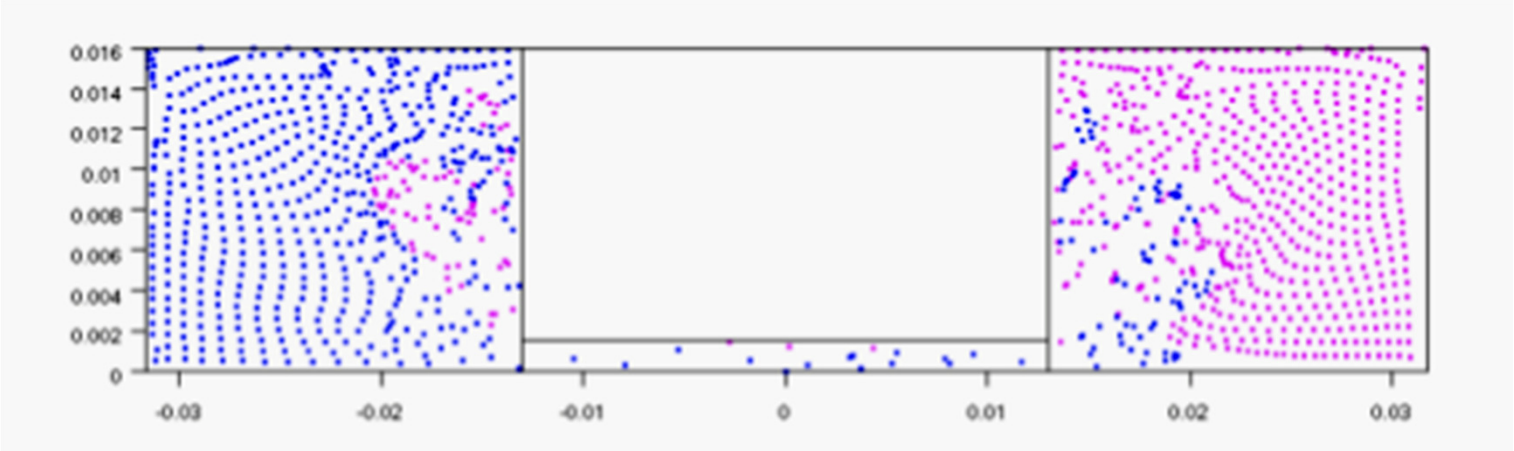


Low viscosity

High viscosity

Creeping flow (Re≅0.001): newtonian fluid: high viscosity





Dimensionless parameters

Reynolds Number $$Re = \frac{\rho U d}{\mu}$$

Re<0.1: creeping flow

Re>0.1: inertial flow

Astarita parameter $$\chi = 2\frac{|\Omega_{rel}|}{|\Omega_{rel}| + |D|}$$

D: rate of deformation tensor
Ω: vorticity tensor
W: eigenvectors of D
$\Omega_{rel}=\Omega-W$

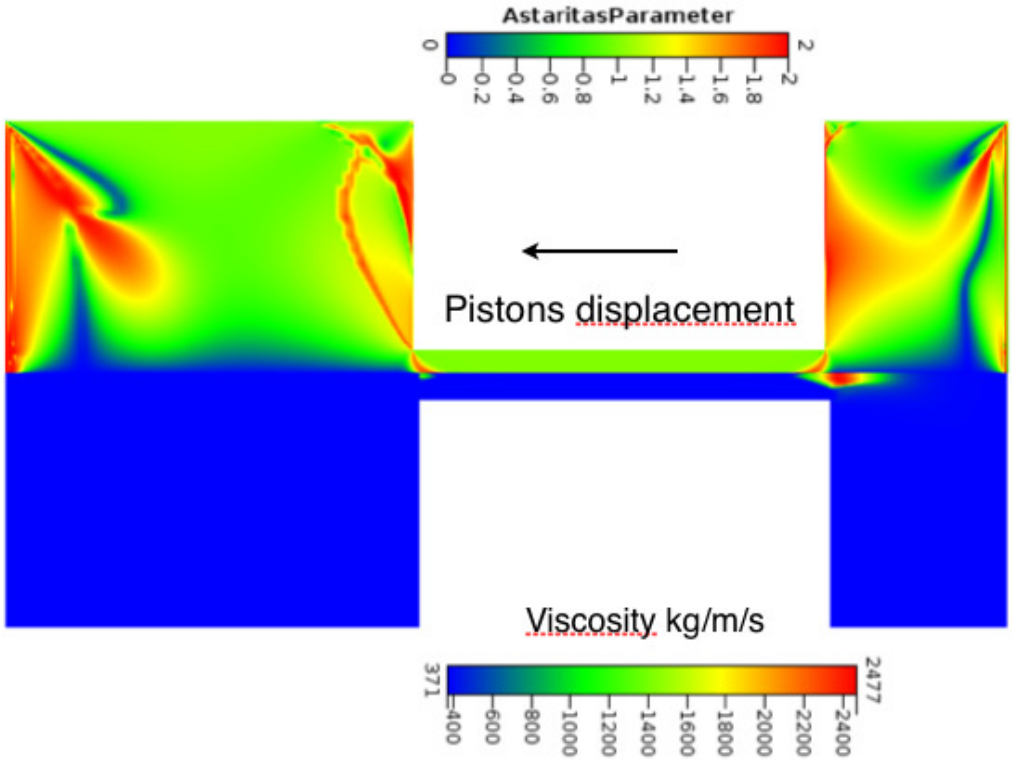
χ=2: blocking flow
χ=1: shear flow
χ=0: elongational flow

Creeping flow (Re≅10^{-5}): non-newtonian flow simulation

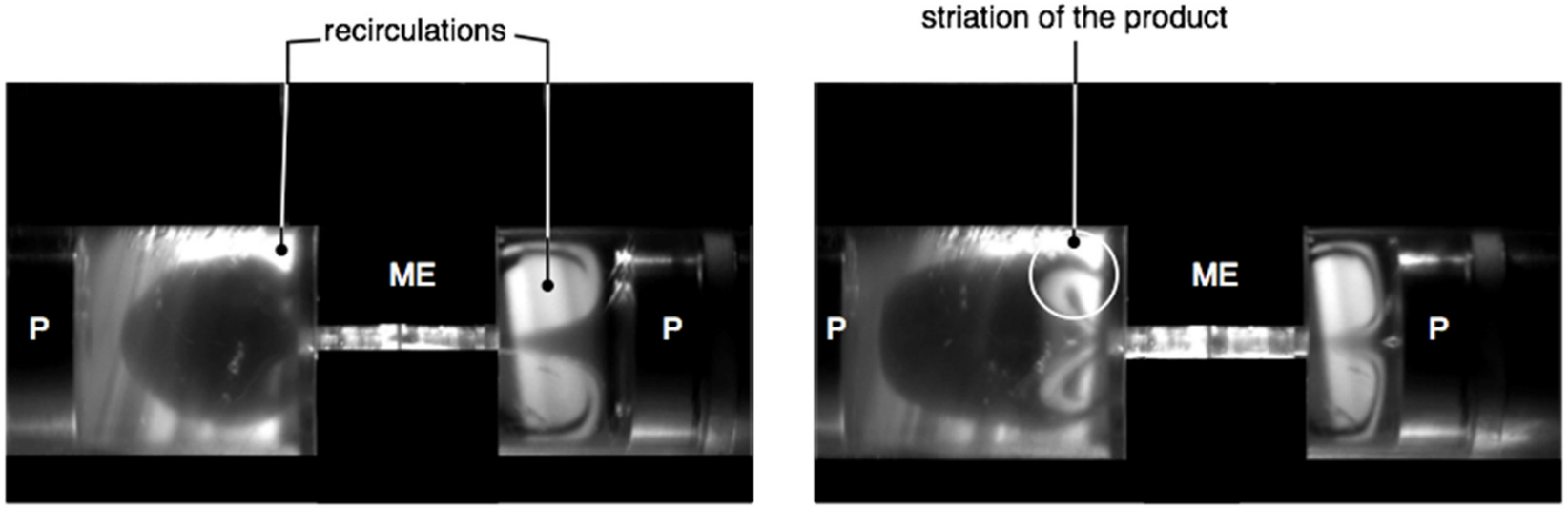
$$\mu = f(\chi)\mu_s + (1 - f(\chi))\mu_e$$

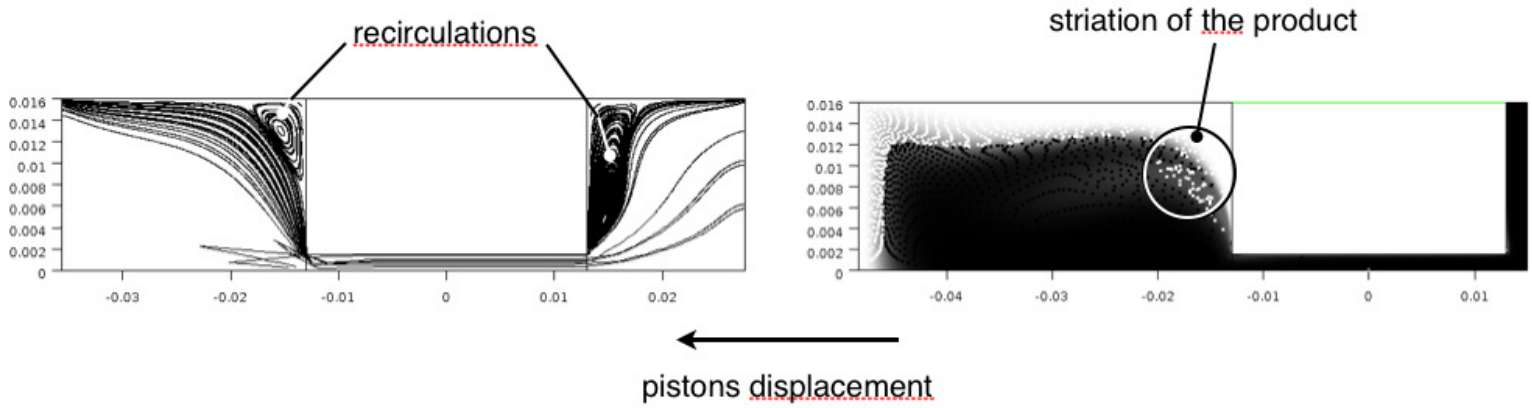
Geometric parameter χ

Viscosity μ

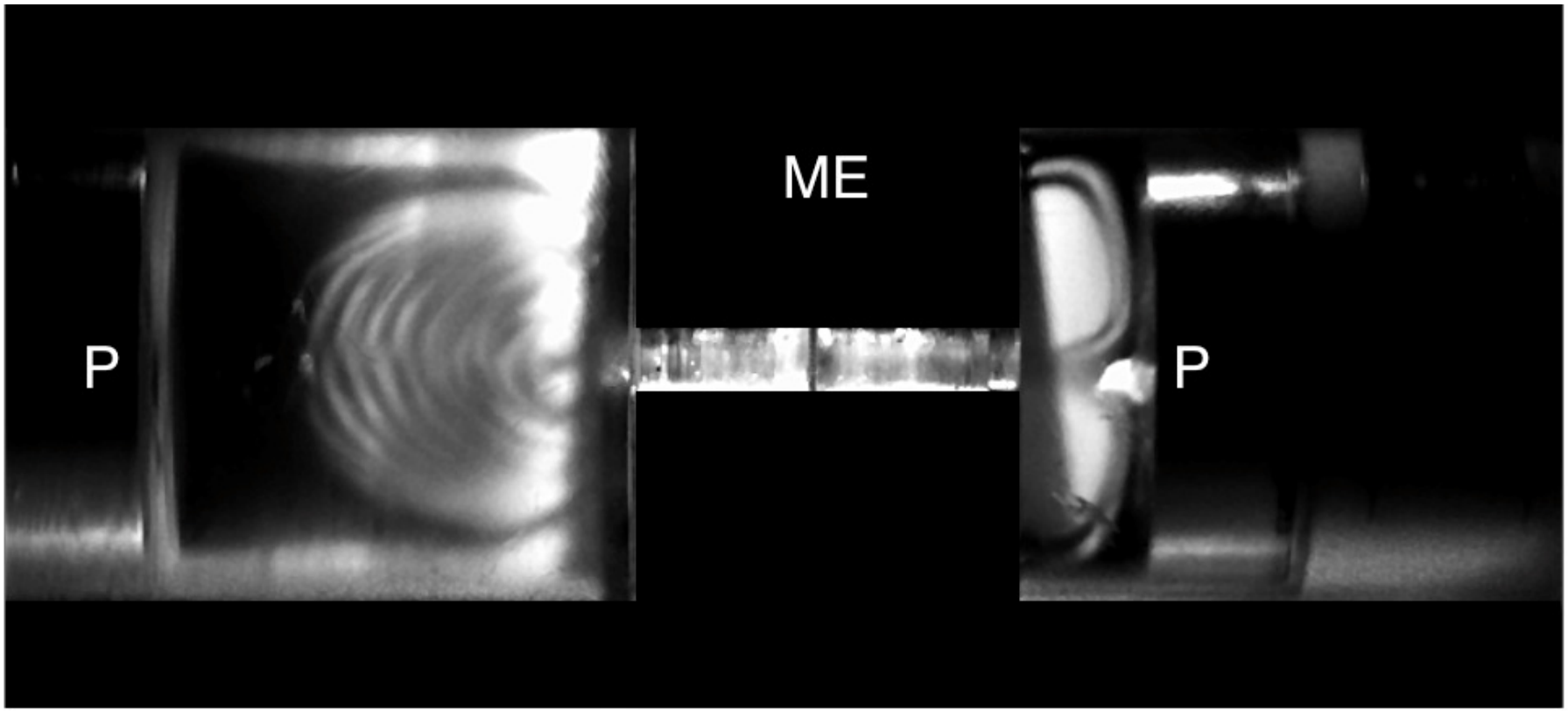


Viscoelastic flow simulation versus experiment



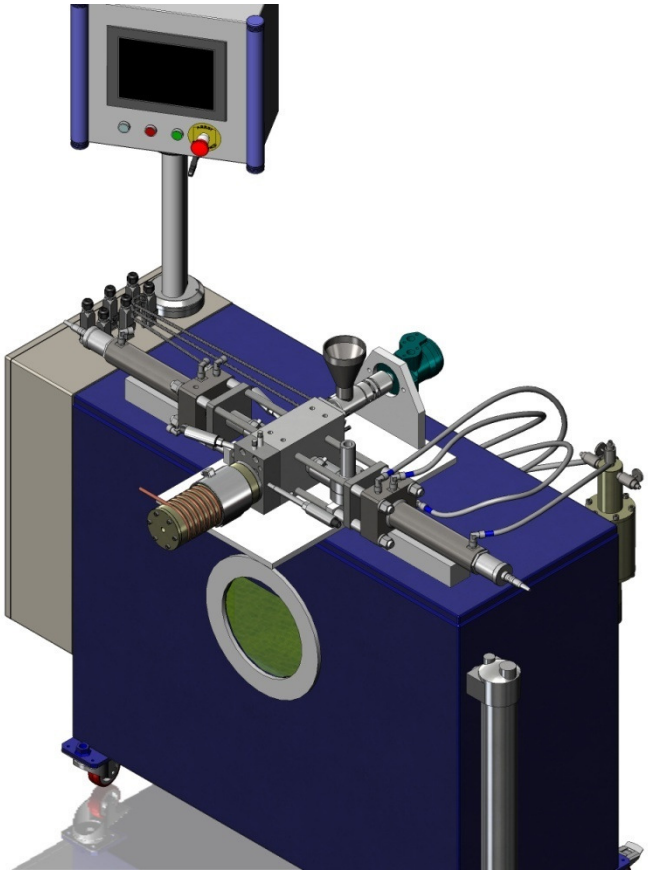


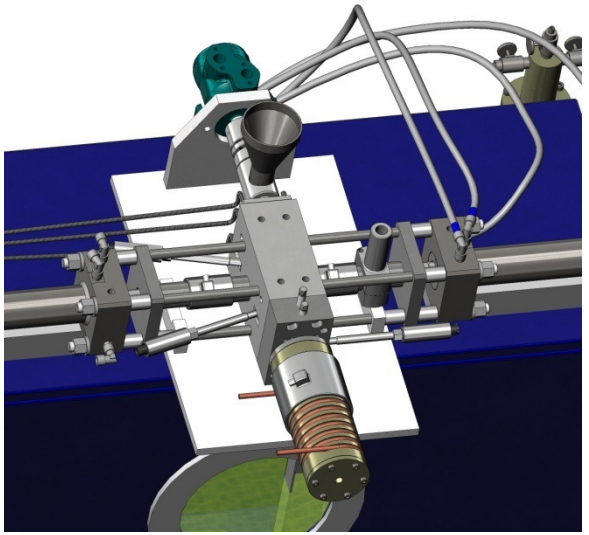
Creeping flow ($Re \cong 10^{-4}$): viscoelastic flow experiment

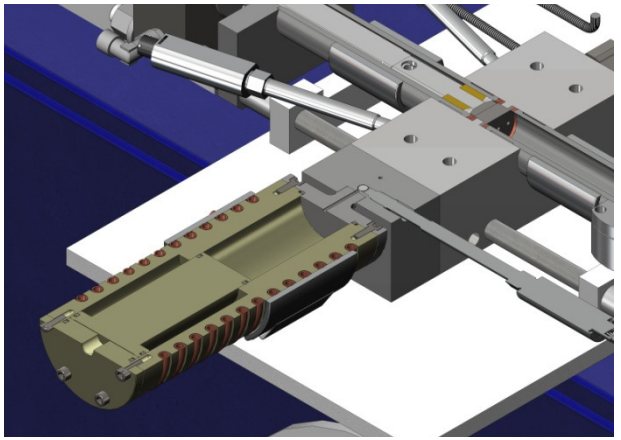


Recent developments

Screw-feeding, special moulds (foams)







In - line process characterization

- Continuous in-line monitoring of fluid viscosity through force transducers mounted on pistons or power of electric jacks in batch or continuous modes

-Possibility to adapt optical, dielectric or spectroscopical sensors on mixing element in batch mode or on connection elements in continuous mode.

- In-line rheological characterization with instrumented die at outlet or on connection element.

Thank you for your kind attention!