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MICROTEACHING ESR 9

SOLVENT TECHNIQUES FOR CLOSED-LOOP RECYCLING OF PLASTICS

Rita Kol - 25/10/2021

Supervisor: Prof. Steven De Meester
Co-Supervisor: Prof. Dimitris Achilias

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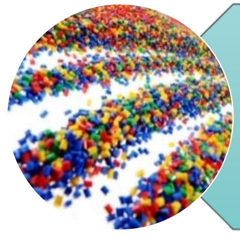
ARISTOTLE UNIVERSITY OF THESSALONIKI

C-PlaNeT CIRCULAR PLASTICS NETWORK FOR TRAINING

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No. 859885

CONTENT

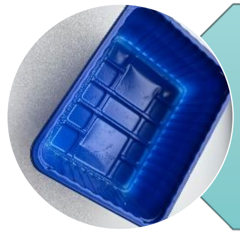
Challenges in plastic recycling



Plastic additives

Solvent-based recycling
Dissolution-precipitation technique

Rheology and viscosity of polymer solutions



Filtration process for removal of colorants

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CHALLENGES IN PLASTIC RECYCLING

CHALLENGES IN PLASTIC RECYCLING

Unknown composition

Different types of plastic

Degraded polymers

Additives

Multilayer structures

Contaminants

PLASTIC ADDITIVES

ADDITIVES IN PLASTICS

Functional additives	Flame retardants, antistatic agents, stabilizers, plasticizers, antioxidants, lubricants, slip agents, foaming agents and biocides
Fillers	Increase bulk of plastic and modify properties such as hardness, chemical resistance, impact and tensile strength. Examples: Calcium carbonate, graphene, talc
Reinforcements	Increase mechanical strength and stiffness. Example: Glass fibres, carbon fibres
Colorants	Aesthetic purposes, increase heat resistance and as reinforcement. Two groups: Dyes, pigments

ADDITIVES IN PLASTIC RECYCLING

However

- Migration → Brominated flame retardants, phthalates
- Degradation → Metal containing additives
- Emission/Leaching → Phthalates, brominated flame retardants, Bisphenol A, lead, etc.
- Unwanted effects on recycled plastic → Colour pigments

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SOLVENT-BASED RECYCLING

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SOLVENT-BASED RECYCLING

- **Solvent-based recycling** (physical recycling):

  Composition of the polymer is not changed ≠ chemical recycling

- **Advantages:**
  - Removal of impurities;
  - 'Virgin-grade' granulates;
  - Prevention of operational problems, such as corrosion.

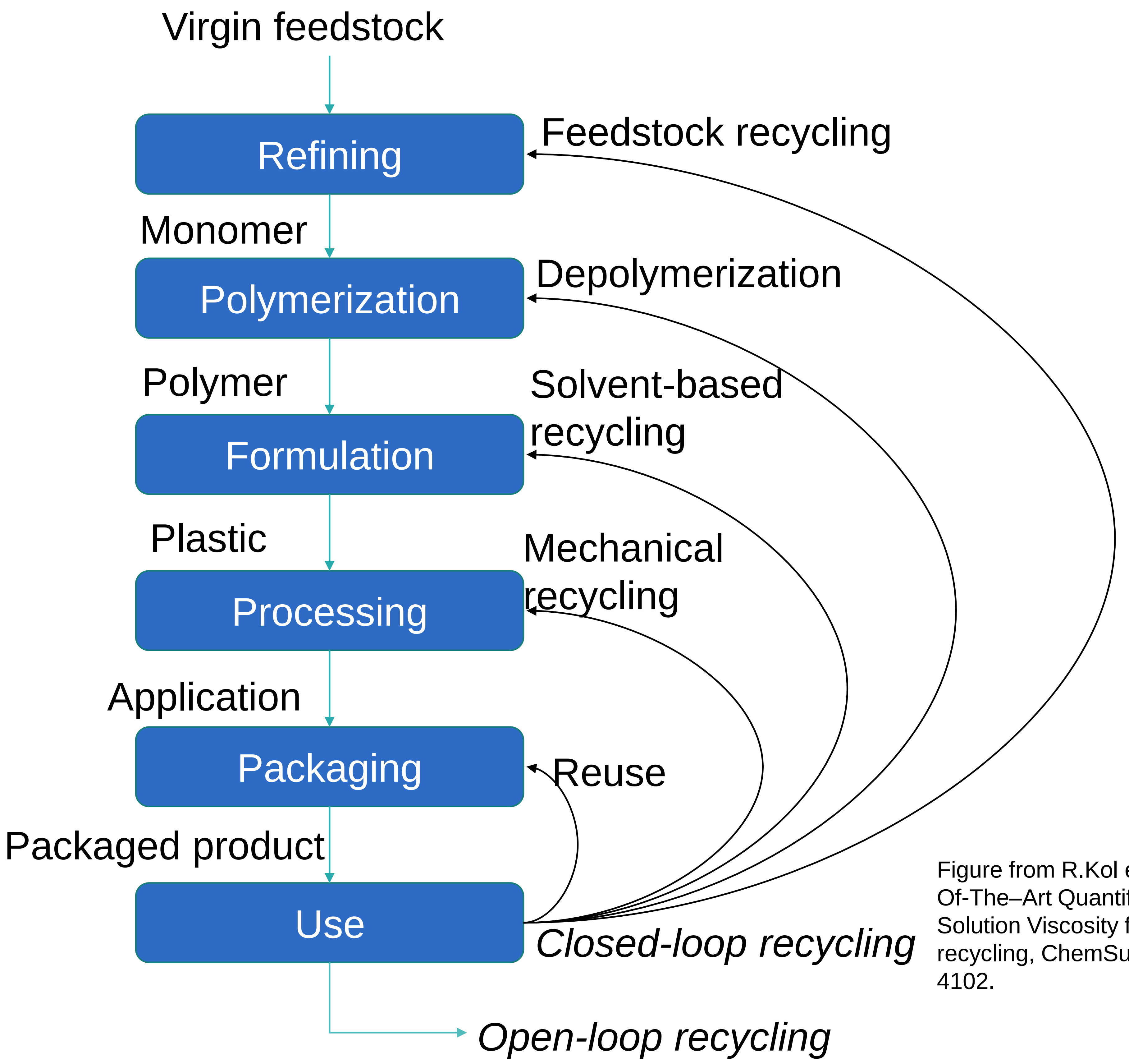

Figure from R.Kol et al.(2021) State-Of-The–Art Quantification of Polymer Solution Viscosity for Plastic Waste recycling, ChemSusChem, 14, 4071-4102.

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SOLVENT-BASED TECHNIQUES

Solvent-based techniques

- Solid-liquid extraction
- Dissolution-precipitation

Shake-flask, Soxhlet, Ultrasonic extraction, Microwave assisted extraction, Supercritical fluids extraction, Accelerated solvent extraction

Chapter Intechopen, 2021

Recent Advances in Pre-Treatment of Plastic Packaging Waste

Rita Kol, Martijn Roosen, Sibel Ügdüler, Kevin M. Van Geem, Kim Ragaert, Dimitris S. Achilias and Steven De Meester

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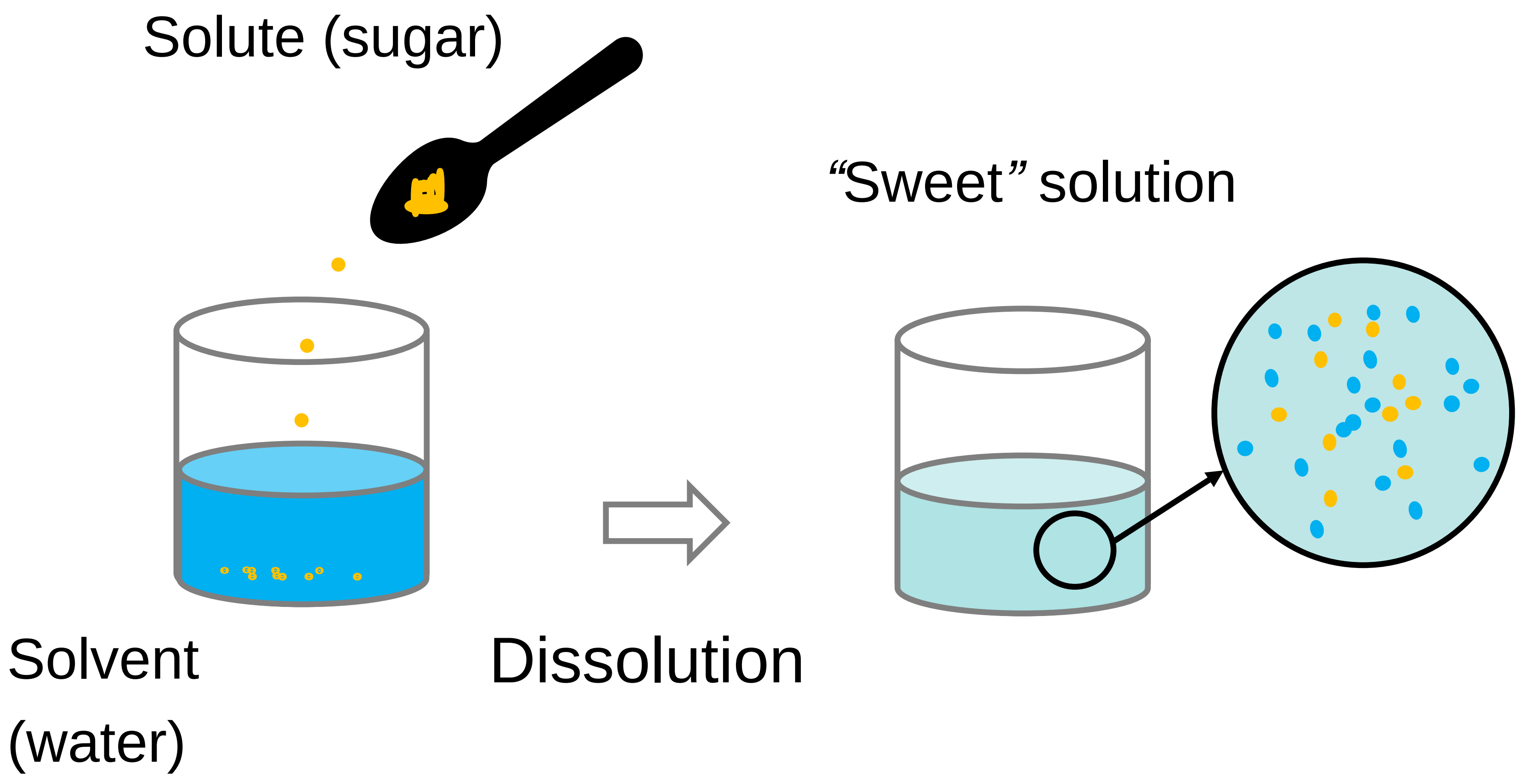
DISSOLUTION-PRECIPITATION TECHNIQUE

DISSOLUTION-PRECIPITATION TECHNIQUE

- Example: Sugar and water
- Solvent: A fluid that dissolves a material (called solute).
- During dissolution: Solute molecules (sugar molecules) separate from each other and are surrounded by solvent molecules.

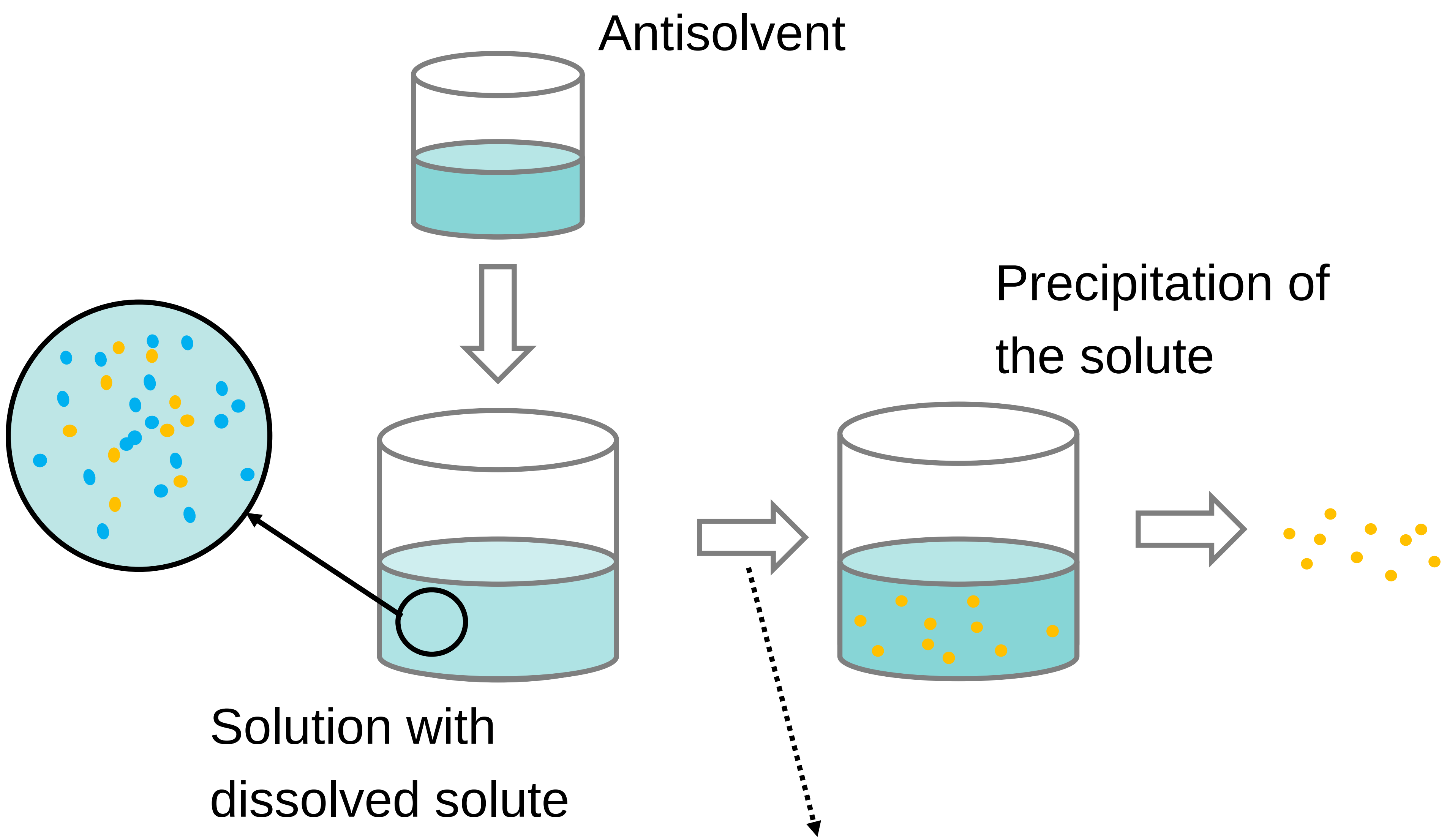


- Temperature
- Stir

⇨ Faster dissolution

DISSOLUTION-PRECIPITATION TECHNIQUE

- Antisolvent: Liquid that is miscible with the solvent, and it will reduce the solubility of the solute in the solution, leading to precipitation of the solute (polymer).



DISSOLUTION-PRECIPITATION TECHNIQUE

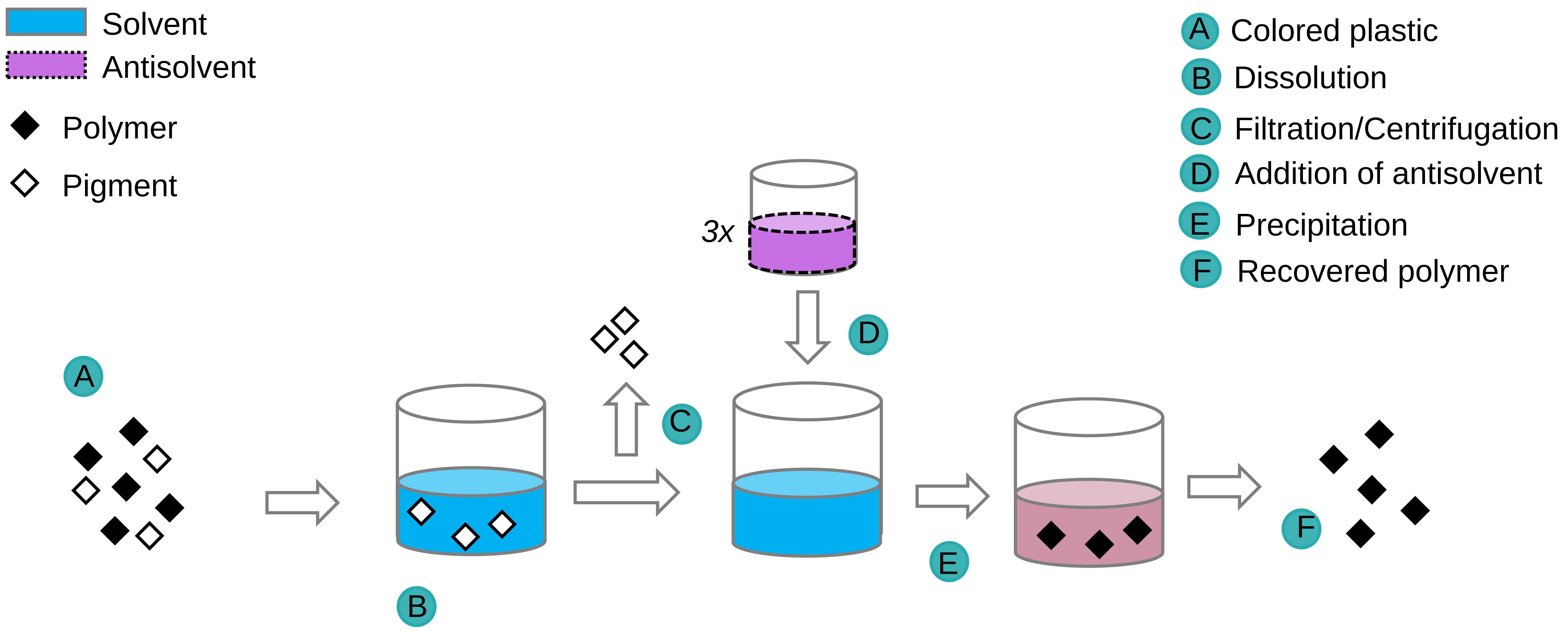


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Figure redrawn and adapted from J. Sherwood (2020) Closed-loop recycling of polymers using solvents. Johnson Matthey Technology Review. pp. 4-15

SELECTIVE DISSOLUTION

Separation of different polymers

- ❑ Changing solvents
- ❑ Temperature
  - Xylene @25°C for PS
  - Xylene @85°C for LDPE
  - Xylene @150°C for HDPE

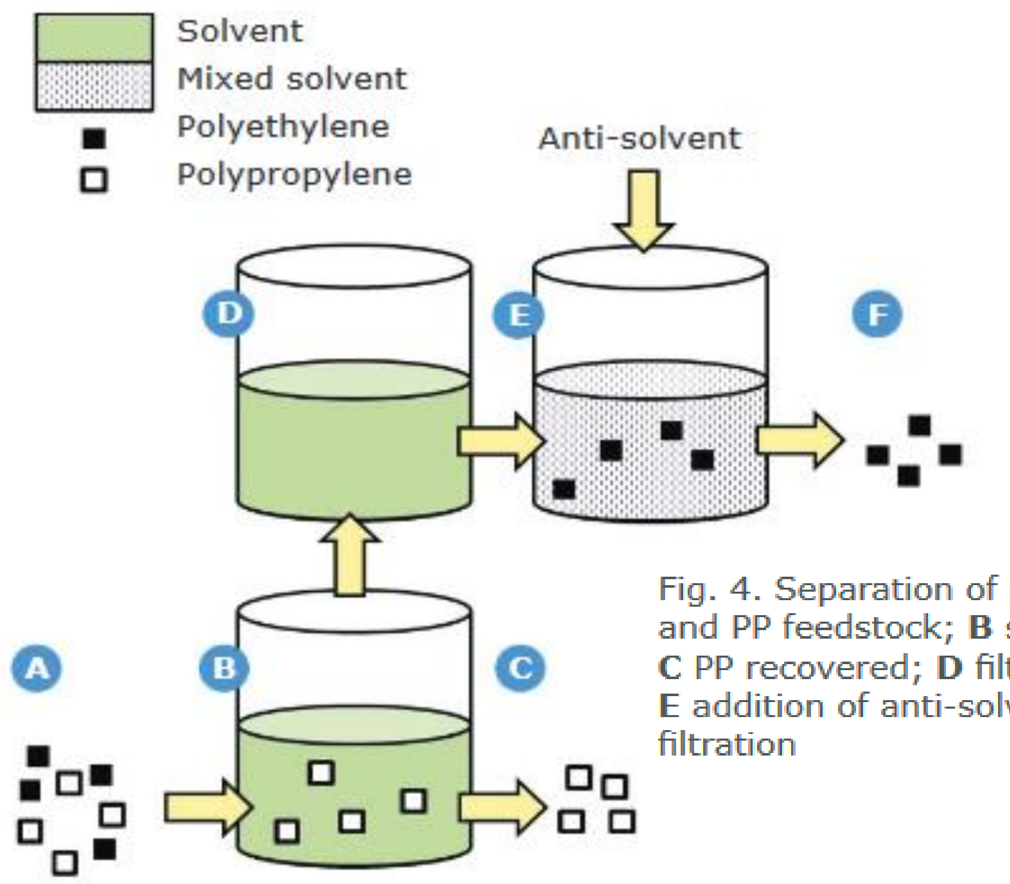

Fig. 4. Separation of polyolefins; **A** mixed PE and PP feedstock; **B** selective dissolution of PE; **C** PP recovered; **D** filtration to give a PE solution; **E** addition of anti-solvent; **F** isolation of PE by filtration

Figure from J. Sherwood (2020) Closed-loop recycling of polymers using solvents. Johnson Matthey Technology Review. pp. 4-15

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OVERVIEW OF (OPERATIONAL) PLANTS

Technology	Principle	Current state and capacity	Current application	Source
VinyLoop® & Texyloop®	Dissolution and precipitation of flexible PVC	Italy: pilot scale at 10.000 tons/year (closed in 2018)	Recycling of flexible PVC.	(VinylPlus)
Polyloop®	Dissolution and precipitation of PVC	Mobile (container) solution, treating 300kg in 3h intervals. Sales planned to start in 2021.	Recycling of PVC composite materials, continuing from Texyloop®	(Polyloop, 2020), (Ferrari, 2021)
CreaSolv® Technology, PolyStyreneLoop	Dissolution and precipitation of PS	The Netherlands: pilot scale at 3.000 tons/year starting 2020	Removal of banned, legacy flame retardant HBCDD.	(PolyStyreneLoop, 2020)
CreaSolv® Technology, Unilever Sachet Recycling	Dissolution and precipitation of PE	Indonesia: pilot scale at 30 tons/day	Separation of multilayer sachets.	(Crippa et al., 2019)
CreaSolv® Technology, Lober	Dissolution and precipitation of PE and PP from multilayer laminates	Germany: pilot scale at 5 m^3 per day, with 15x industrial up-scaling in a second phase	Separation of multilayer laminates	(CreaCycle, 2018a)
PureCycle Technologies℠, P&G	Dissolution and precipitation of PP	The United States: industrial-scale demonstration plant at 119 million pounds (≈ 54.000 tons) per year by 2021	Removal of colour, odour and other contaminants.	(PureCycle Technologies, 2019)
Newcycling®, APK AG	Dissolution and precipitation of PE multilayer films	Germany: pilot scale at 8.000 tons/year	Separation of multilayer films (PE/PA). Additional separation of PP, PET, PS, PLA and aluminium fractions possible.	(Niaounakis, 2020), (Wohnig, 2018), (Coker, 2019)

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DISSOLUTION-PRECIPITATION TECHNIQUE

Economical balance: amount of solvent

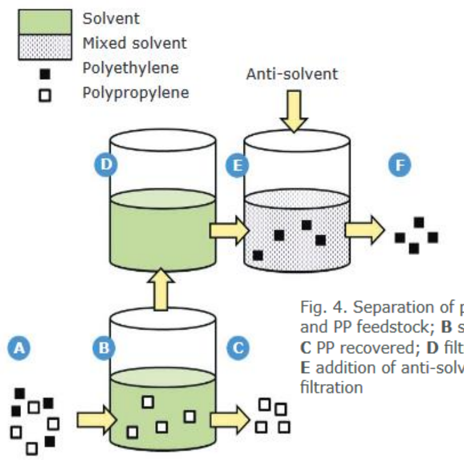

Fig. 4. Separation of polyolefins; **A** mixed PE and PP feedstock; **B** selective dissolution of PE; **C** PP recovered; **D** filtration to give a PE solution; **E** addition of anti-solvent; **F** isolation of PE by filtration

High amounts of solvents

- ✓ Less viscous solutions
- ✗ High amount of antisolvent (typical ratio: 3:1)
  Higher costs (also for S/AS treatment)

Low amounts of solvents

- ✓ Low amount of antisolvent
  Lower costs (also for S/AS treatment)
- ✗ More viscous solutions

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RHEOLOGY AND VISCOSITY OF POLYMER SOLUTIONS

RHEOLOGY

- *Rheology:* Study of deformation and flow of materials under an applied force.
    - Shear flow
    - Extensional flow

- *Viscosity:* Measure of a fluid resistance to flow.

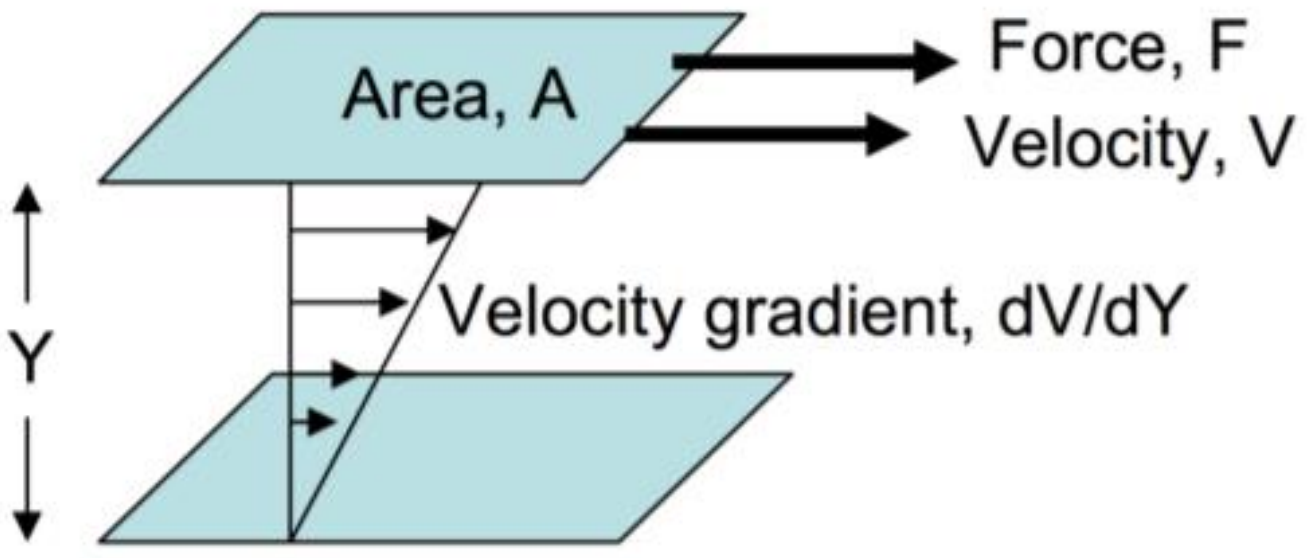
Figure from Anton Paar, https://wiki.anton-paar.com/en/basics-of-rheology/.

SHEAR FLOW

- *Shear rate*, $\dot{\gamma}$: Velocity gradient, which is the rate of change of deformation with time.

- *Shear stress*, σ: External applied force that acts on the fluid.

Two-plate model



$\dot{\gamma} = v/y$ [1/s]

$\sigma = F/A$ [Pa]

$\eta = \sigma/\dot{\gamma}$ [Pa·s]

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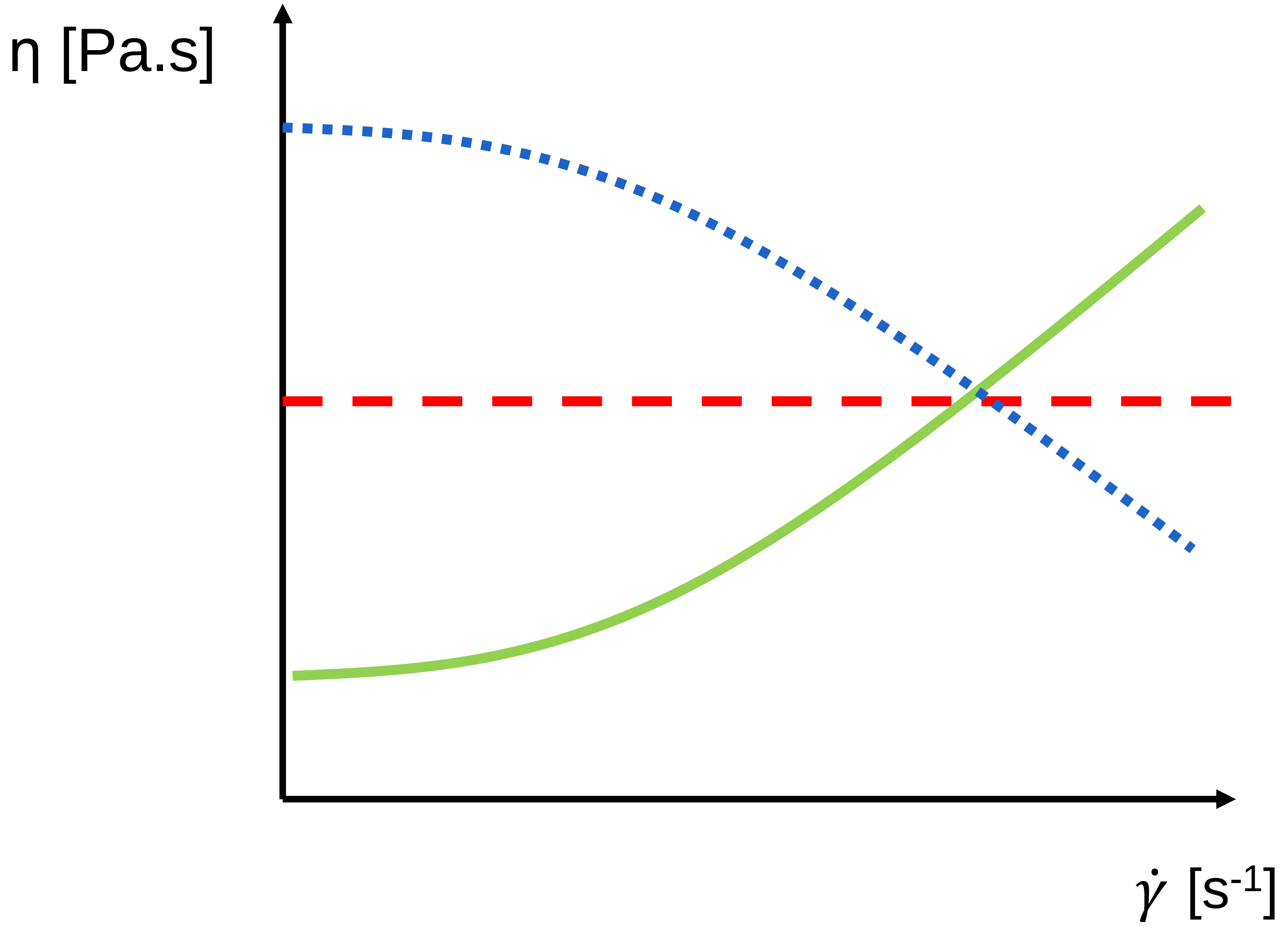
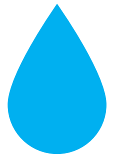
Figure from B. Hasanzadeh (2017) Testing and modeling of the thixotropic behavior of cementitious materials. Electronic Theses and Dissertations. Paper 2868.

FLOW CURVE



Non-Newtonian: shear-thickening fluid

Newtonian fluid



Non-Newtonian: shear-thinning fluid

Polymer solutions

There are also:

- Bingham fluids
- Time-depend fluids: thixotropic, rheopectic
- Viscoelastic behaviour

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SHEAR RATE RANGES

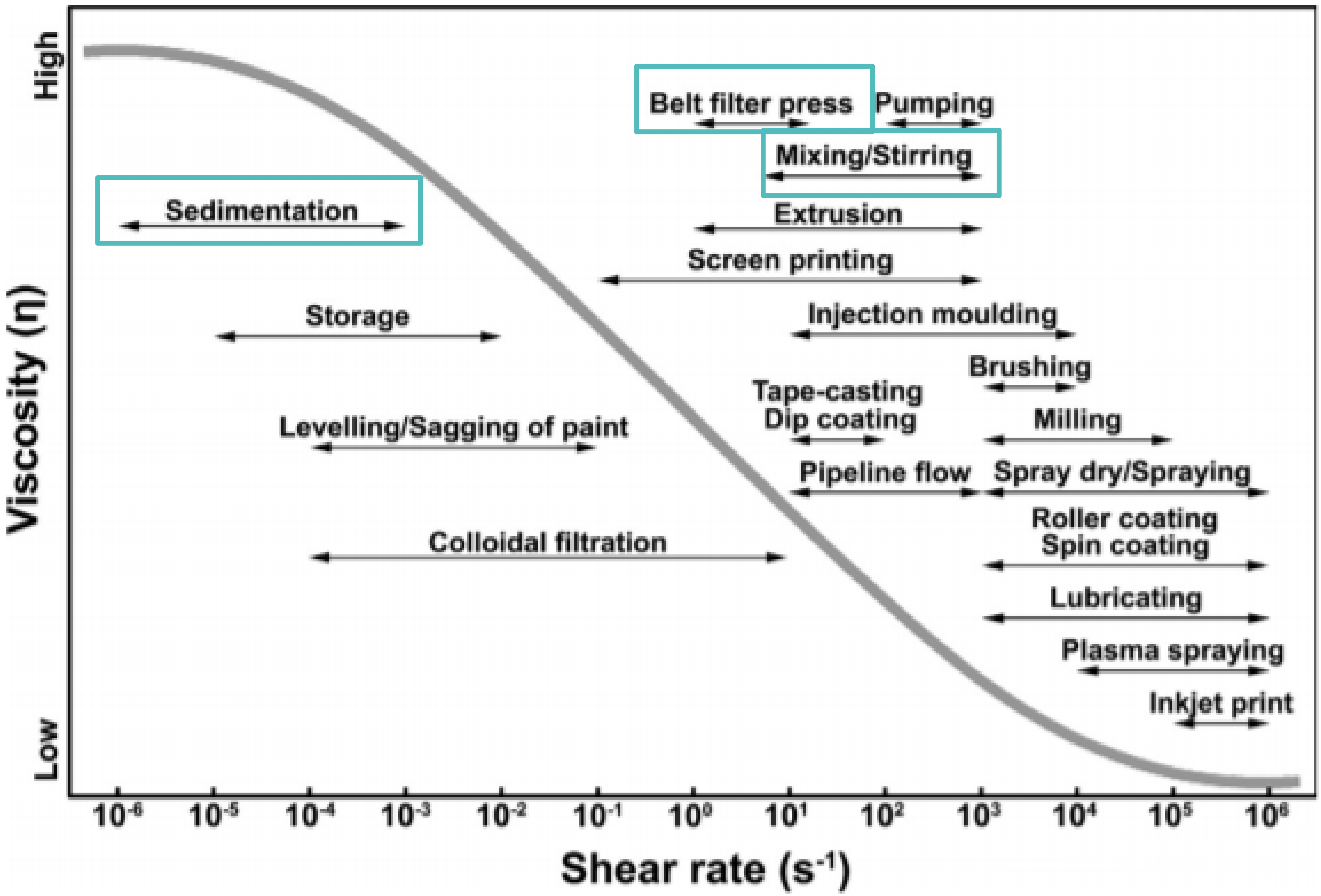
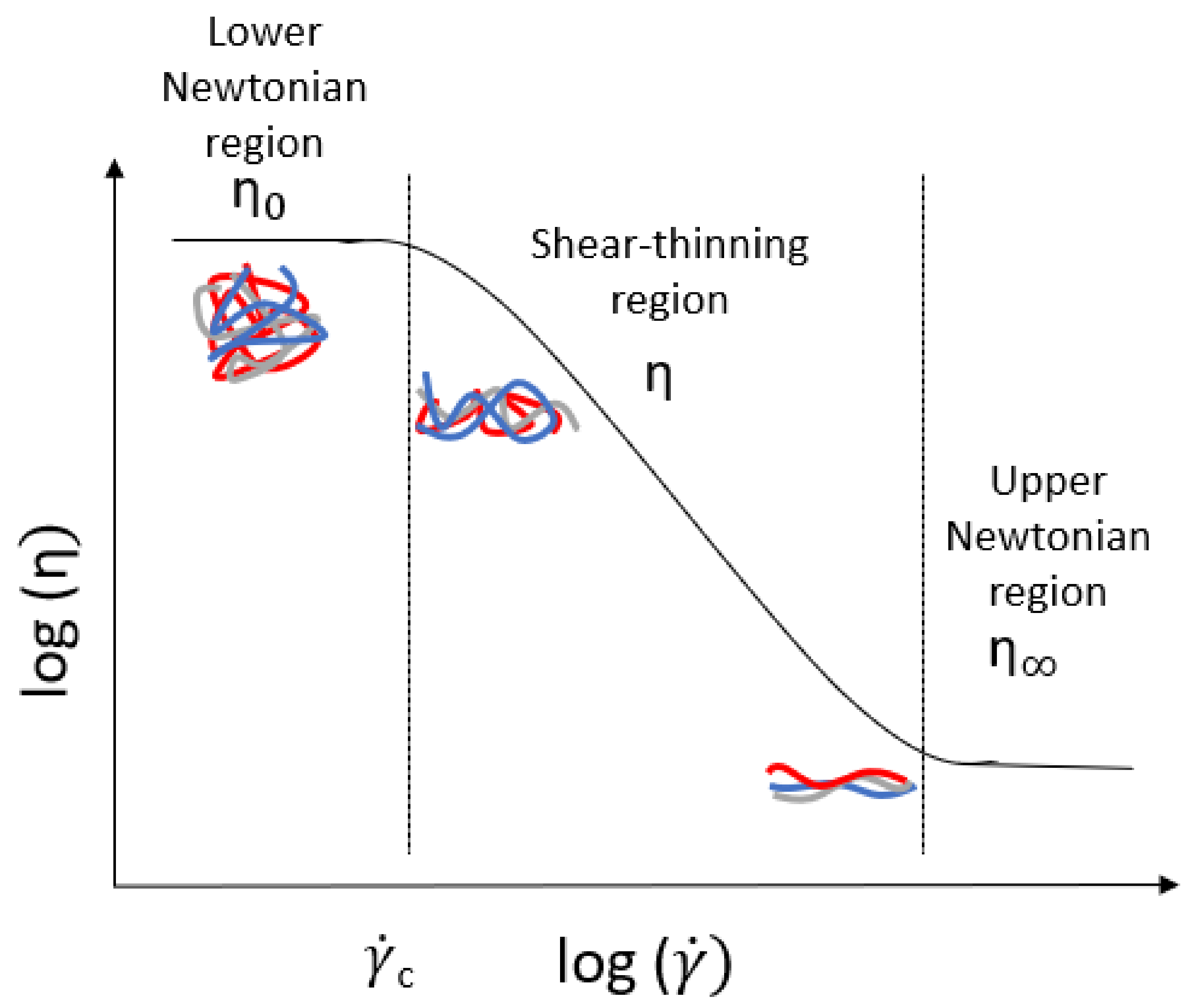


Figure from V. Carnicer et al. (2020), Open Ceramics 5,100052.

RHEOLOGY OF POLYMER SOLUTIONS



Rheological behavior of polymer solutions is influenced by:

- ❑ Concentration
- ❑ Molar mass
- ❑ Temperature
- ❑ Pressure
- ❑ Solvent interactions
- ❑ Others, such as branching, dispersity, conformation

$\dot{\gamma}_c$ - critical shear rate
η_0 – Zero-shear viscosity
η – Non-Newtonian viscosity
η_∞ - Infinite shear viscosity

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Figure from:


ChemSusChem
Chemistry–Sustainability–Energy–Materials
Chemistry Europe
European Chemical Societies Publishing

Review | Open Access

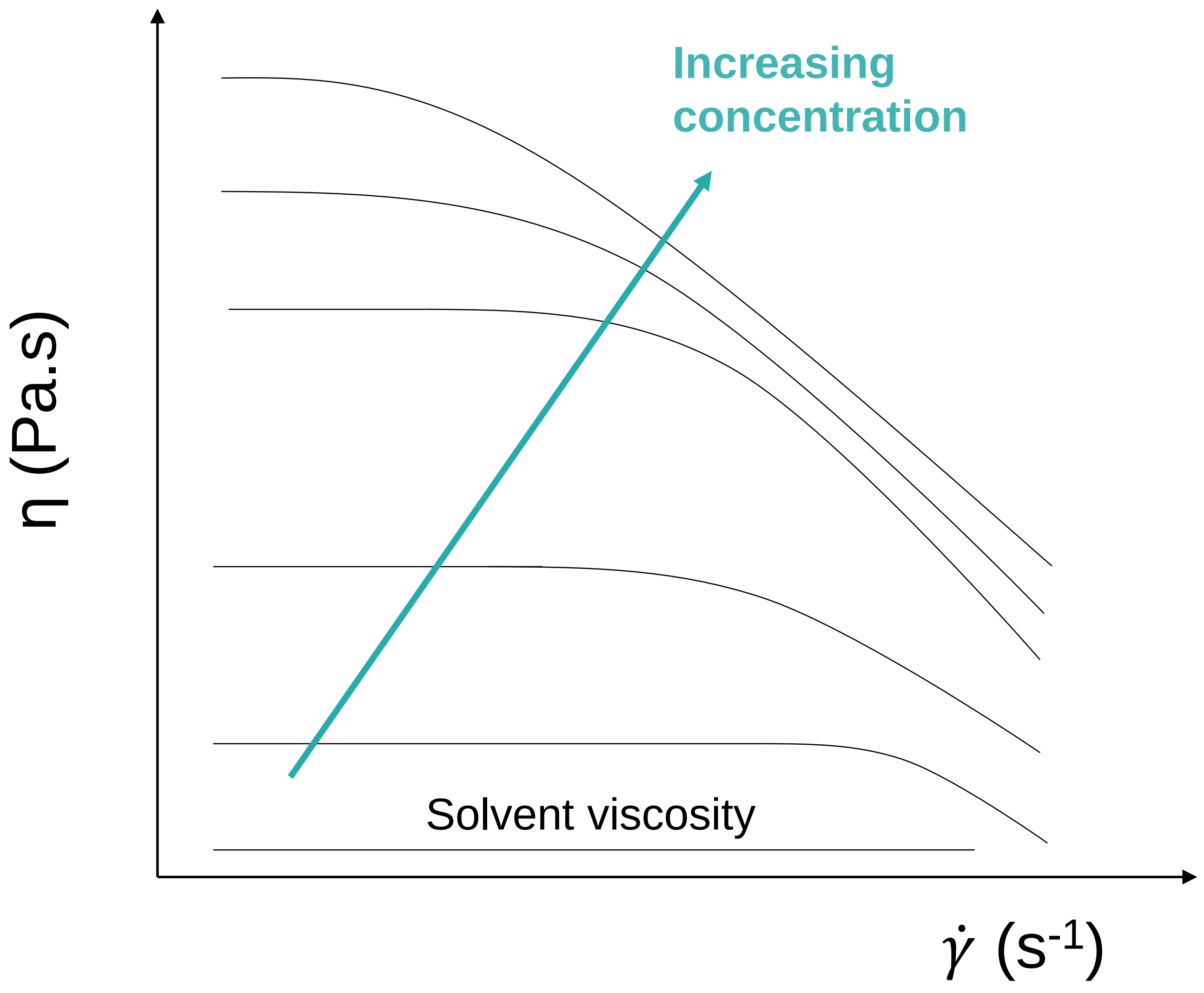
State-Of-The-Art Quantification of Polymer Solution Viscosity for Plastic Waste Recycling

Rita Kol, Tobias De Somer, Prof. Dagmar R. D'hooge, Fabian Knappich, Prof. Kim Ragaert, Prof. Dimitris S. Achilias, Prof. Steven De Meester

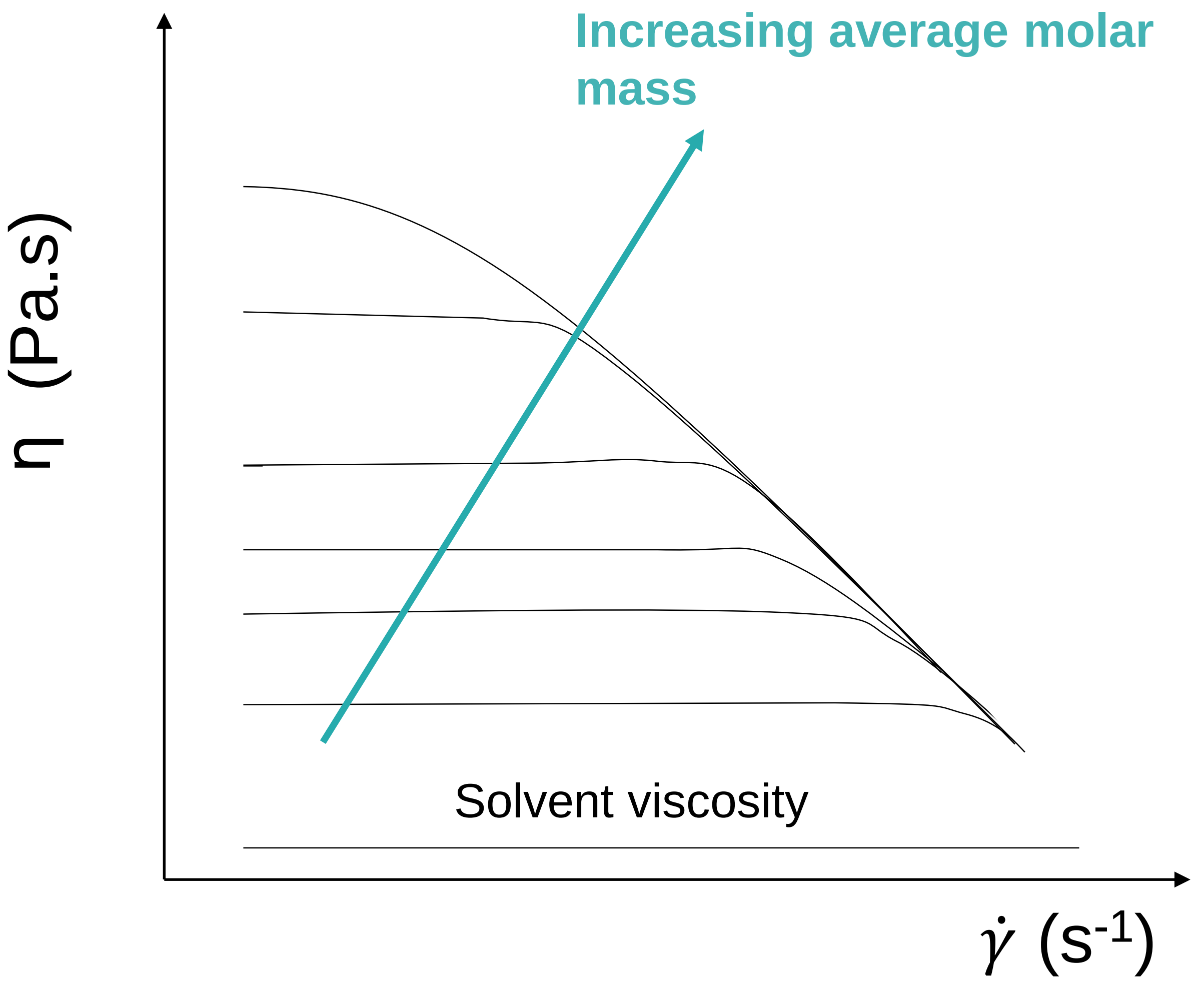
First published: 29 July 2021 | https://doi.org/10.1002/cssc.202100876

NEWTONIAN AND SHEAR-THINNING

- Concentration



- Molar Mass



Figures from R.Kol et al.(2021) State-Of-The–Art Quantification of Polymer Solution Viscosity for Plastic Waste recycling, ChemSusChem, 14, 4071-4102.

NEWTONIAN AND SHEAR-THINNING

- Temperature
- Pressure

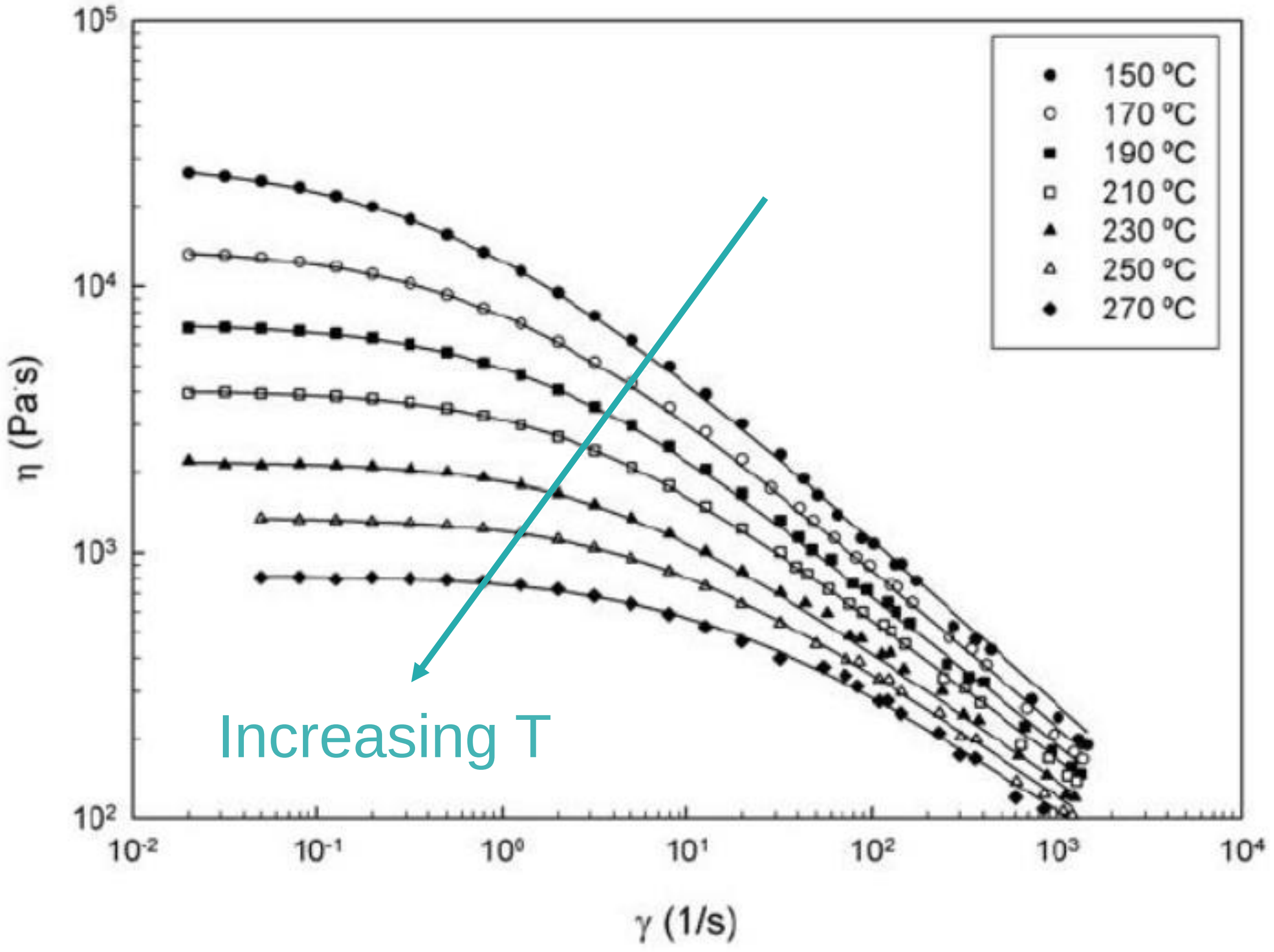


Figure from J.R. Robledo-Ortiz,et al. (2006) Journal of Plastic Film&Sheeting, 22, 287-314

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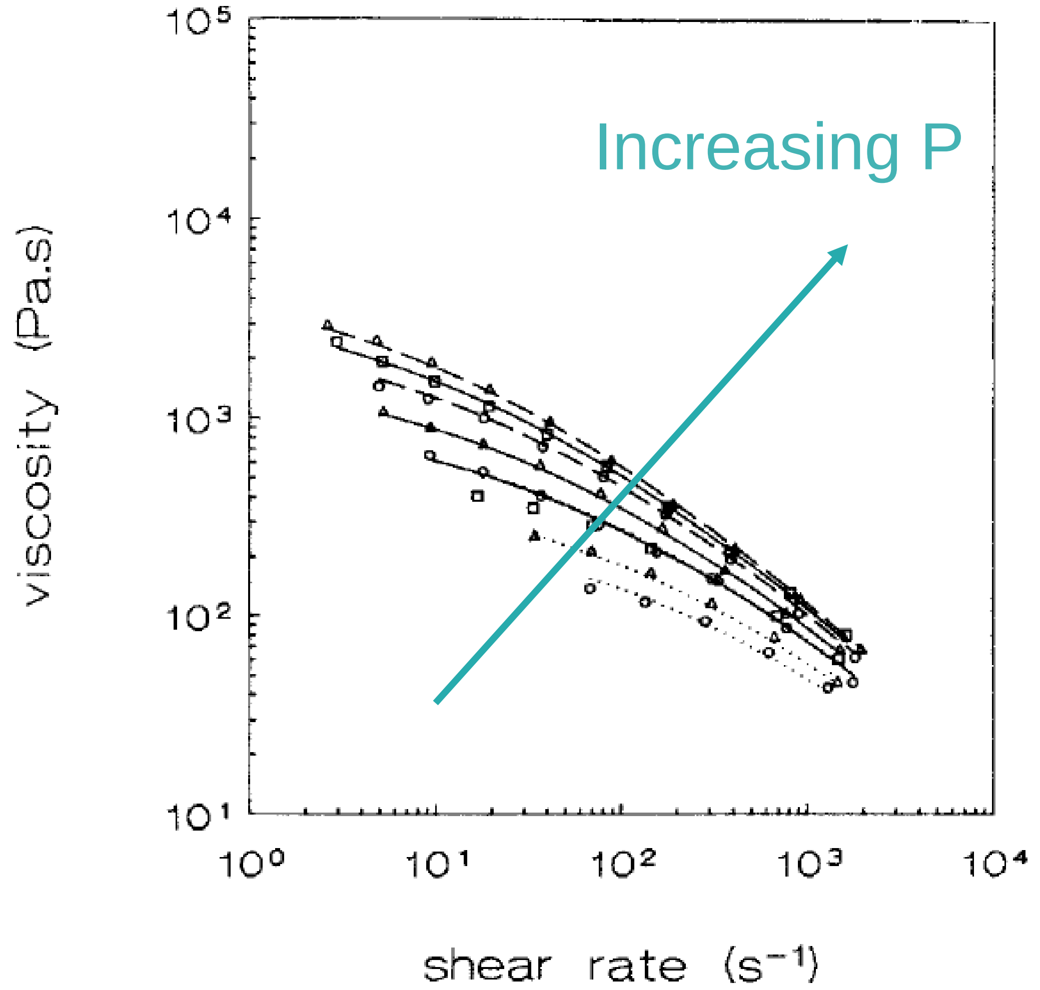

Fig. 6. Viscosity of PP vs. the shear rate (after Weissenberg-Rabinowitsch correction) at pressure levels of 200 bar (circles), 500 bar (triangles), and 1000 bar (squares) at temperatures of 180°C (broken lines), 230°C (solid lines), and 300°C (dotted lines). The drawn curves are fits of the six-parameter WLF-Cross-Carreau model ($\beta = 0$, $T_r = 0$).

Figure from S. E. Kadijk , B. H. A. A. Van Den Brule (1994) Polymer Engineering and Science, 34, 1535-1546.

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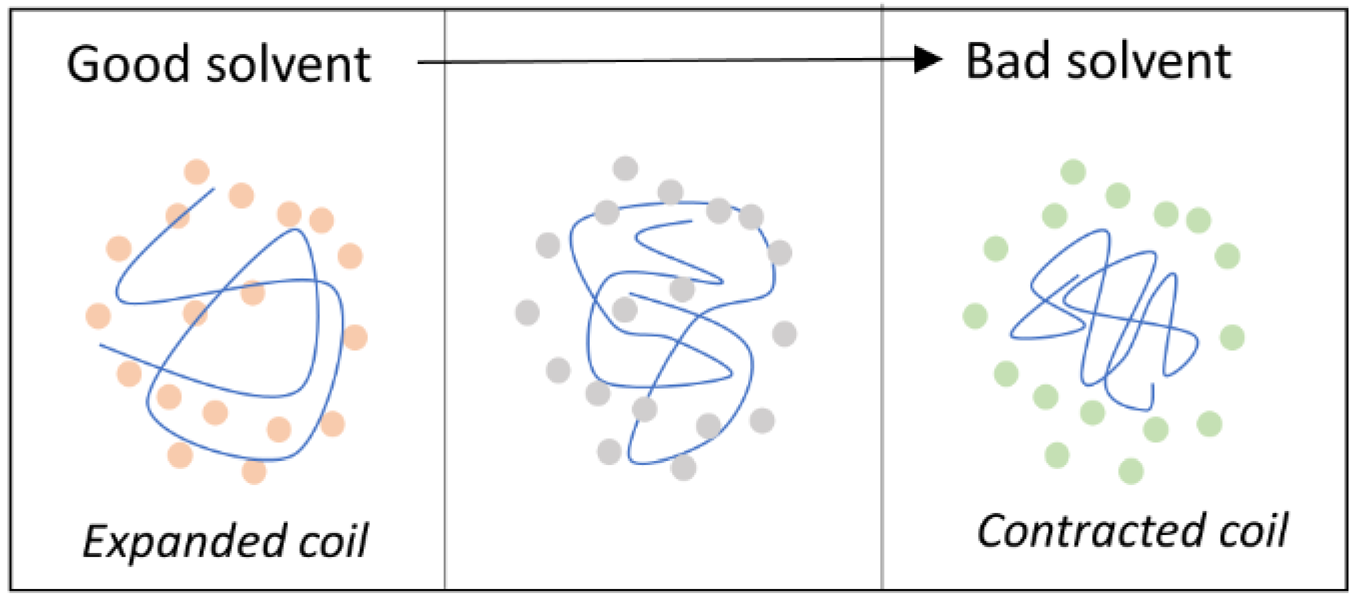
NEWTONIAN AND SHEAR-THINNING

- Solvent interaction



Viscosity is lower than in 'bad solvent'

Figures from R.Kol et al. (2021) State-Of-The–Art Quantification of Polymer Solution Viscosity for Plastic Waste recycling, ChemSusChem, 14, 4071-4102.

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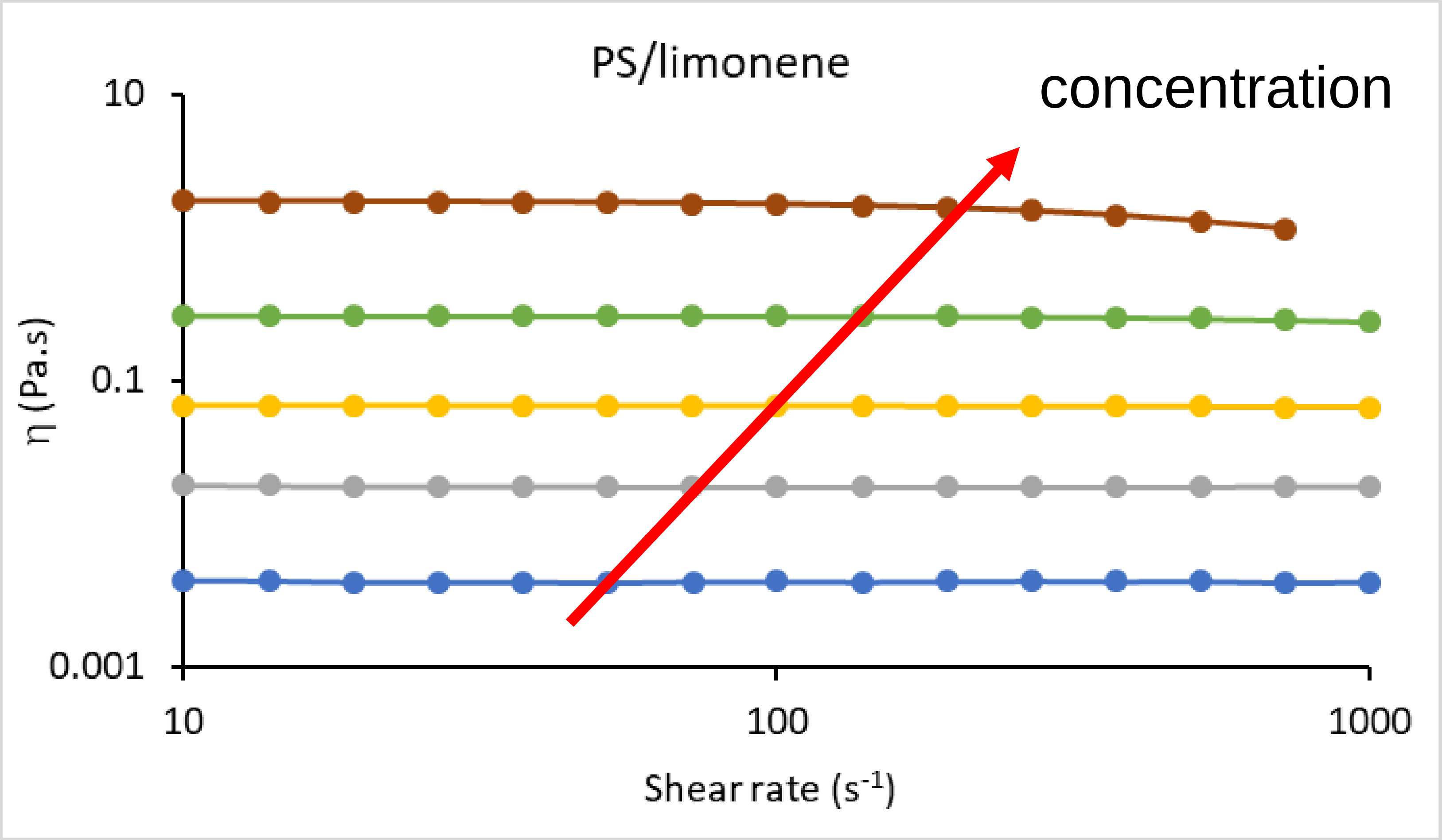
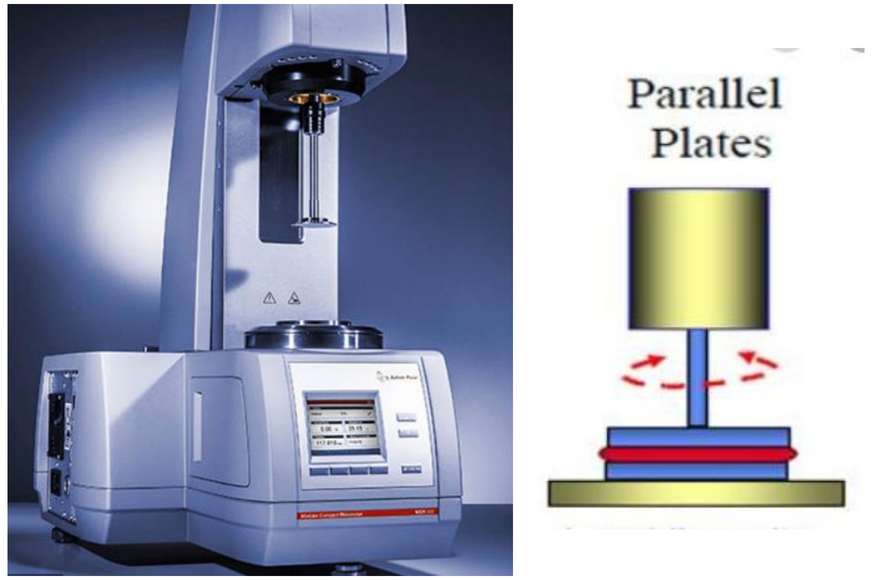
RHEOLOGICAL RESULTS

PS in limonene (L) at concentrations ranging from 5 – 35 wt%





- ❑ Mostly Newtonian behaviour.
- ❑ Higher concentrated solutions (>25 wt%) start to show non-Newtonian behaviour at higher shear rates.

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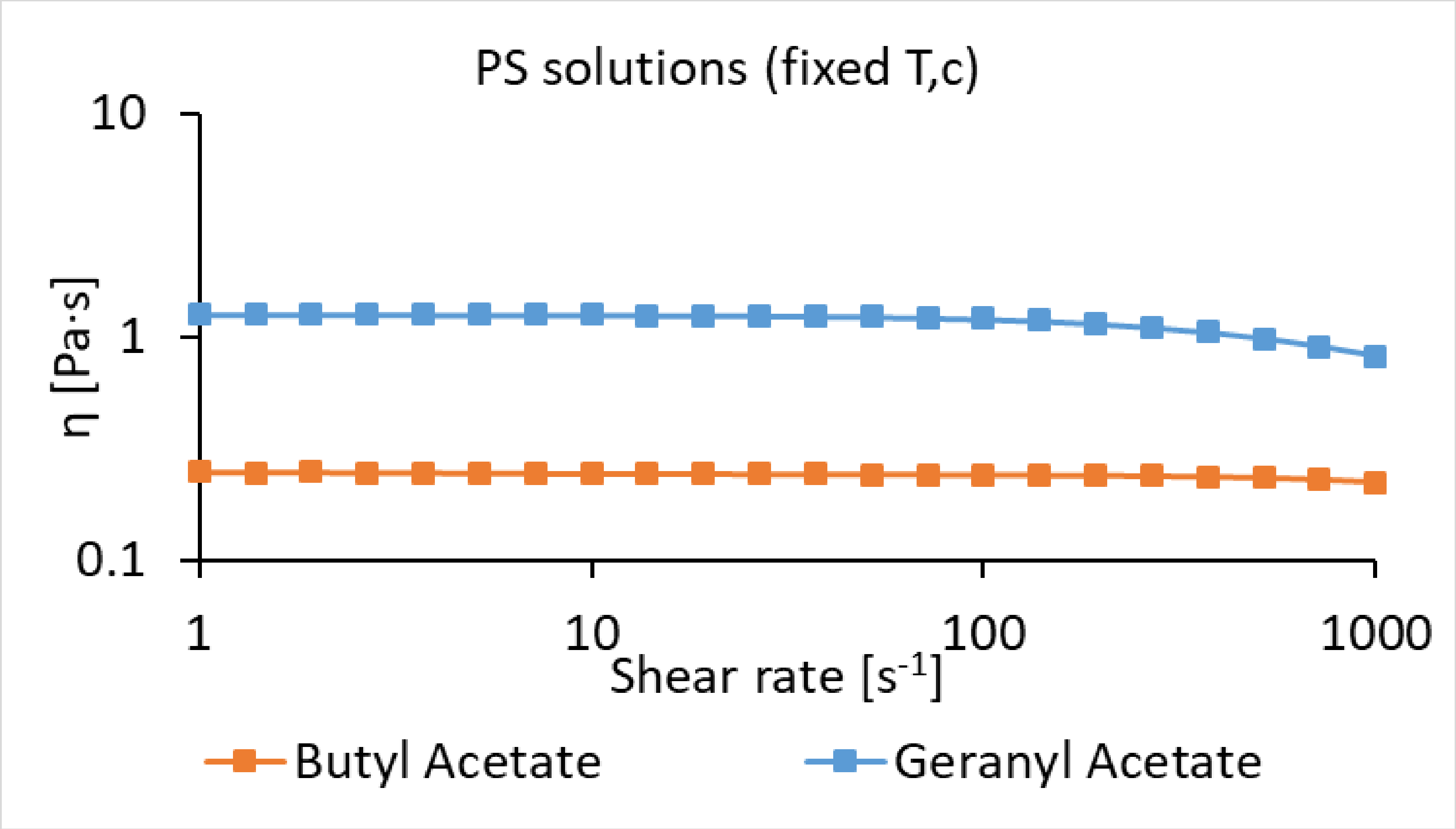
RHEOLOGICAL RESULTS

PS solutions with different solvents



	η_0 (mPa.s)
Butyl – acetate	0.68
Geranylacetate	2.30

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HANDLING WITH POLYMER SOLUTIONS

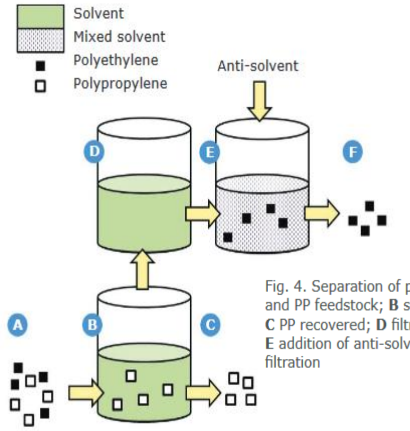
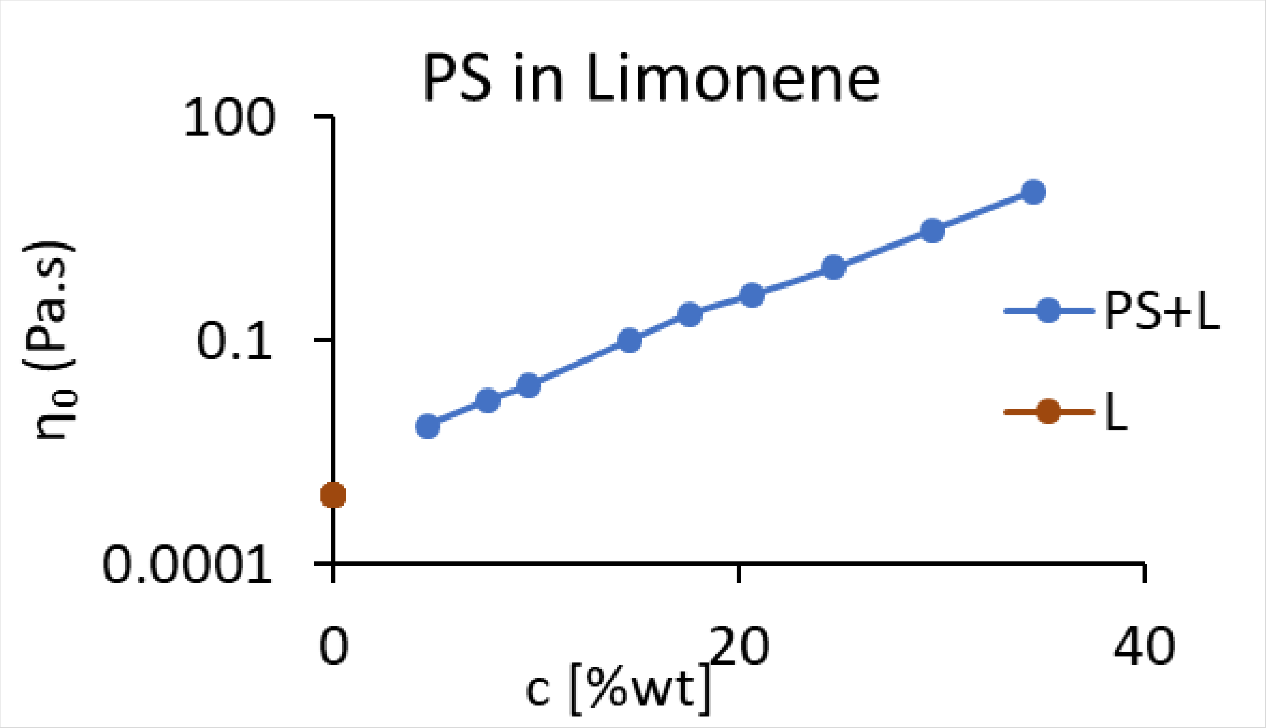


Fig. 4. Separation of polyolefins; **A** mixed PE and PP feedstock; **B** selective dissolution of PE; **C** PP recovered; **D** filtration to give a PE solution; **E** addition of anti-solvent; **F** isolation of PE by filtration

- ❑ Increase of concentration of the polymer in solution → increase in viscosity



Viscosity of a 5 wt% is 8.5 times higher than viscosity of solvent

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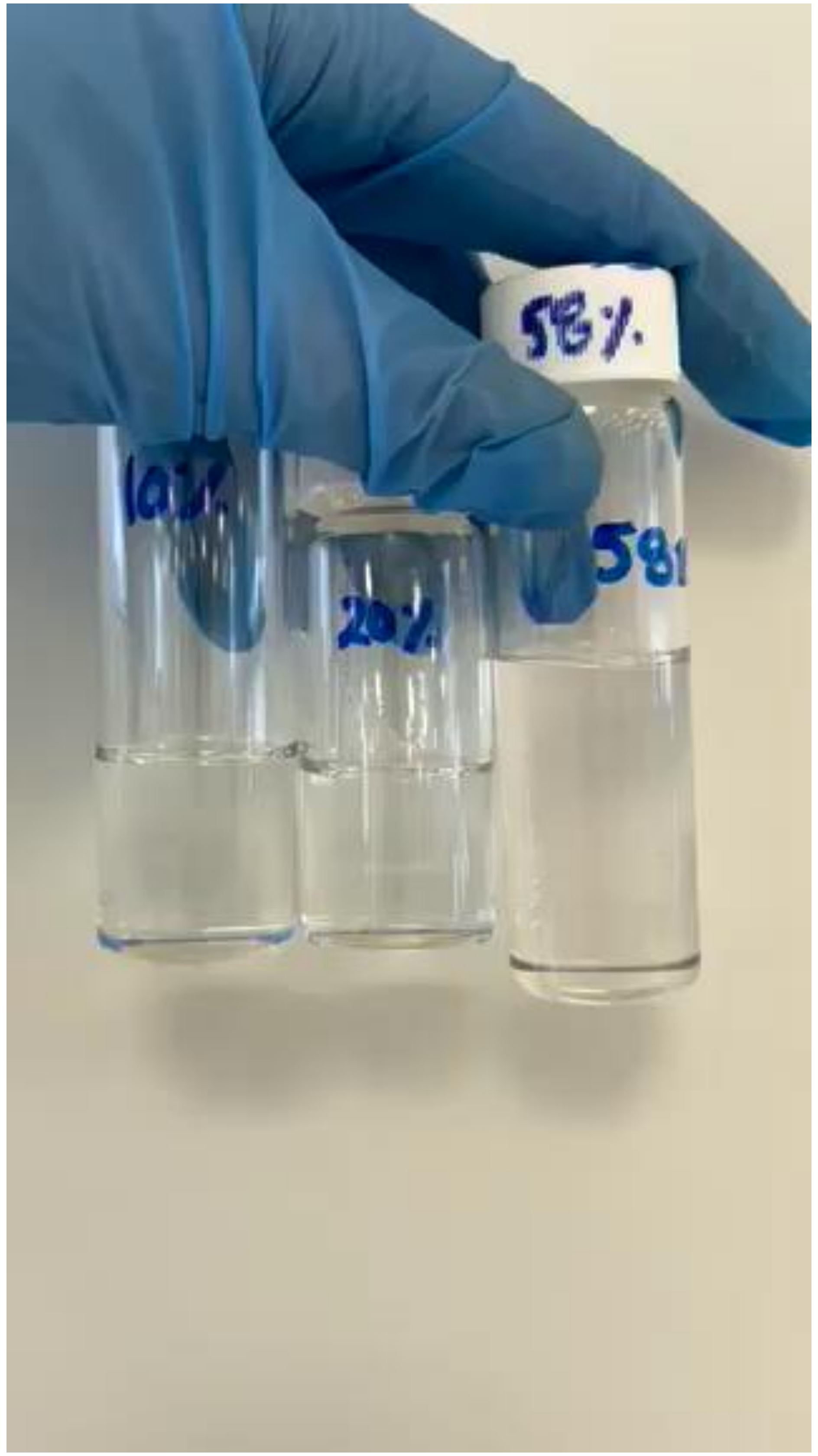
HANDLING WITH POLYMER SOLUTIONS



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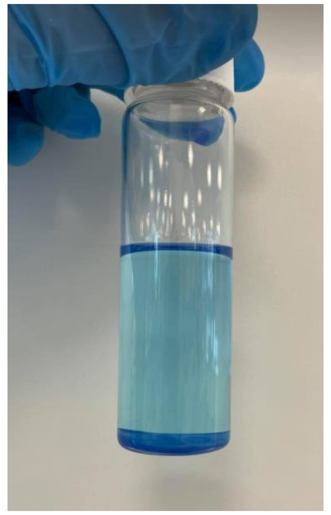
FILTRATION PROCESS FOR REMOVAL OF COLORANTS

FILTRATION OF PIGMENTS

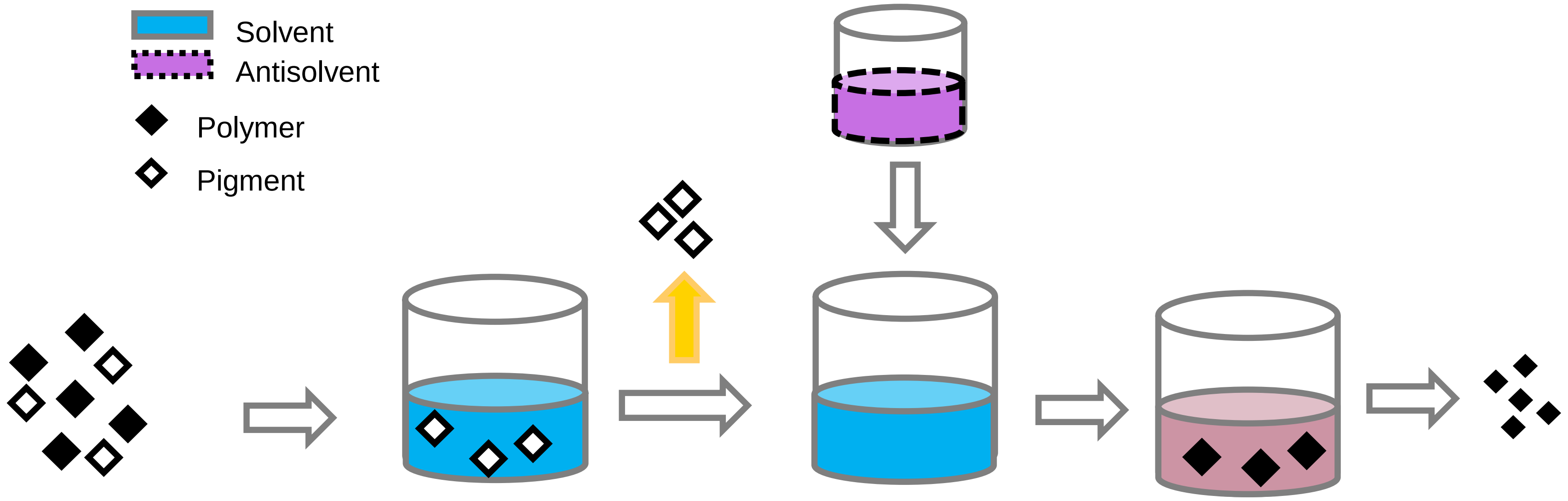
- Pigments do not dissolve in the medium ≠ dyes

Pigment



Dye

- Separate from the polymer with a solid-liquid separation process (e.g. filtration, centrifugation)



FILTRATION OF PIGMENTS

Cake filtration

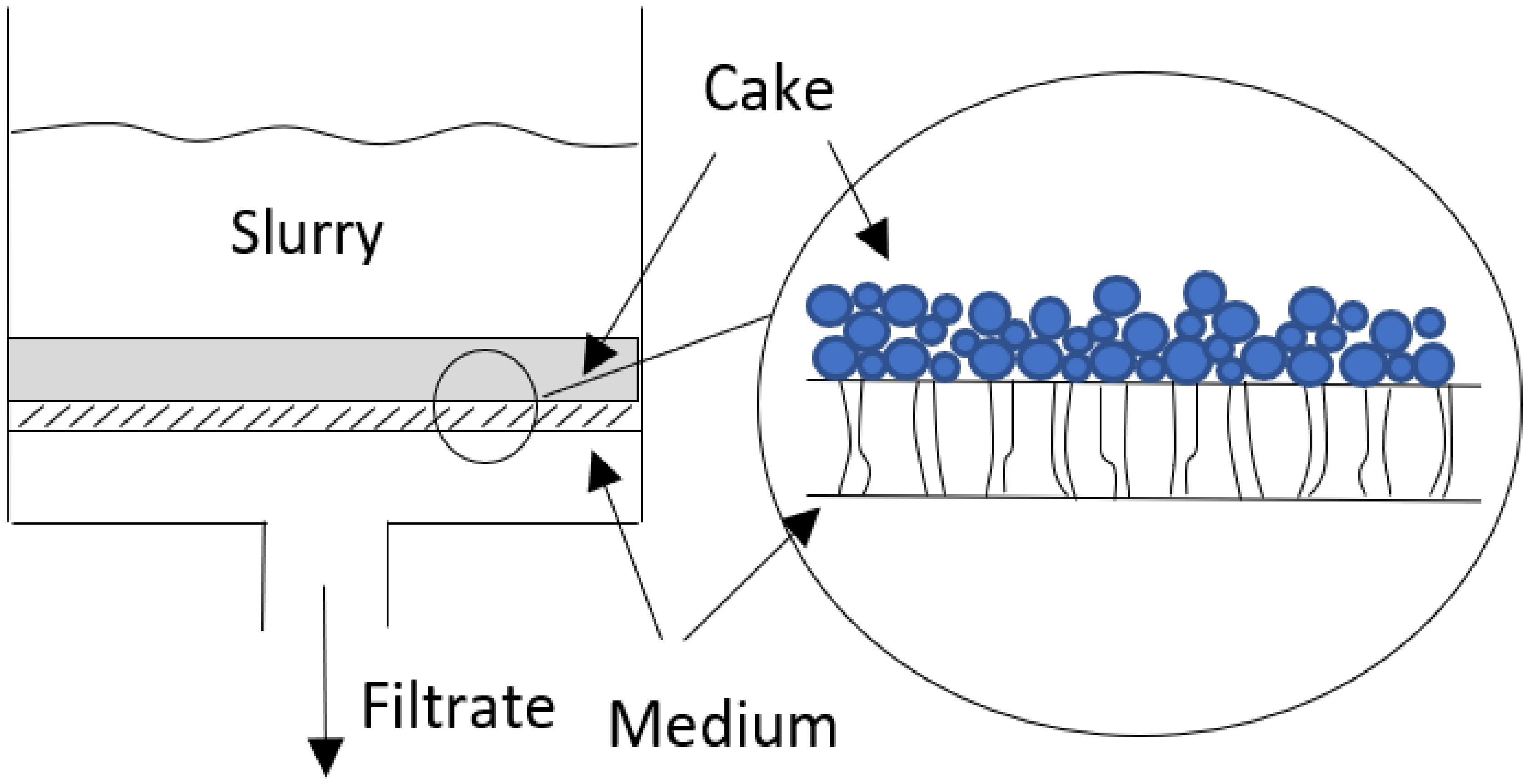


Figure from R.Kol et al.(2021) State-Of-The–Art Quantification of Polymer Solution Viscosity for Plastic Waste recycling, ChemSusChem, 14, 4071-4102.

FILTRATION OF PIGMENTS

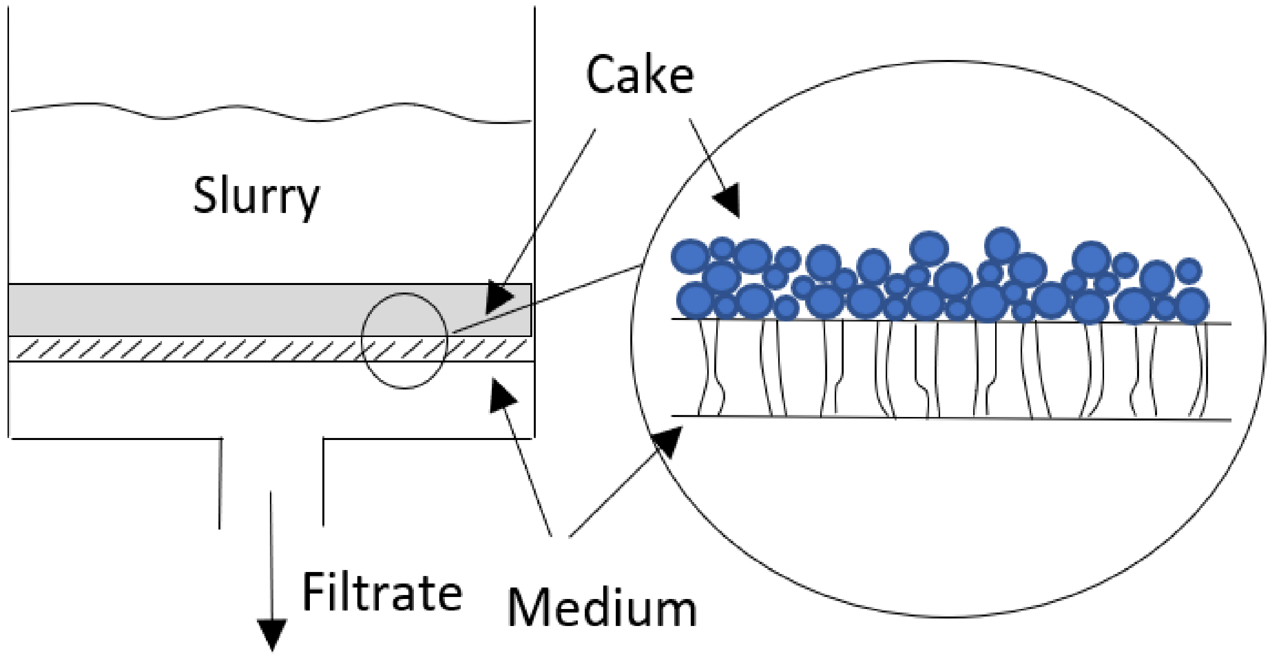
Cake filtration, constant pressure

Flow rate

$$\frac{dV}{dt} = \frac{A\Delta P}{\eta_0 (R_C + R_M)} = \frac{A\Delta P}{\eta_0 \left(\frac{\alpha c_m V}{A} + R_M \right)}$$

Viscosity

Resistance of the cake and filter medium



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FILTRATION OF PIGMENTS

How the viscosity of polymer solutions will influence the filtration?

Changing the polymer solution viscosity, how much pressure has to be applied in order to obtain the same flow rate?

- ❑ Assumption:
  - ○ Newtonian behaviour
  - ○ $R_m << R_c$

- ❑ PS/styrene solution containing 0.5 wt% TiO_2

$$\frac{\Delta P_2}{\Delta P_1} = \sqrt[1-s]{\frac{\eta_{0,2} c_{m,2}}{\eta_{0,1} c_{m,1}}}$$

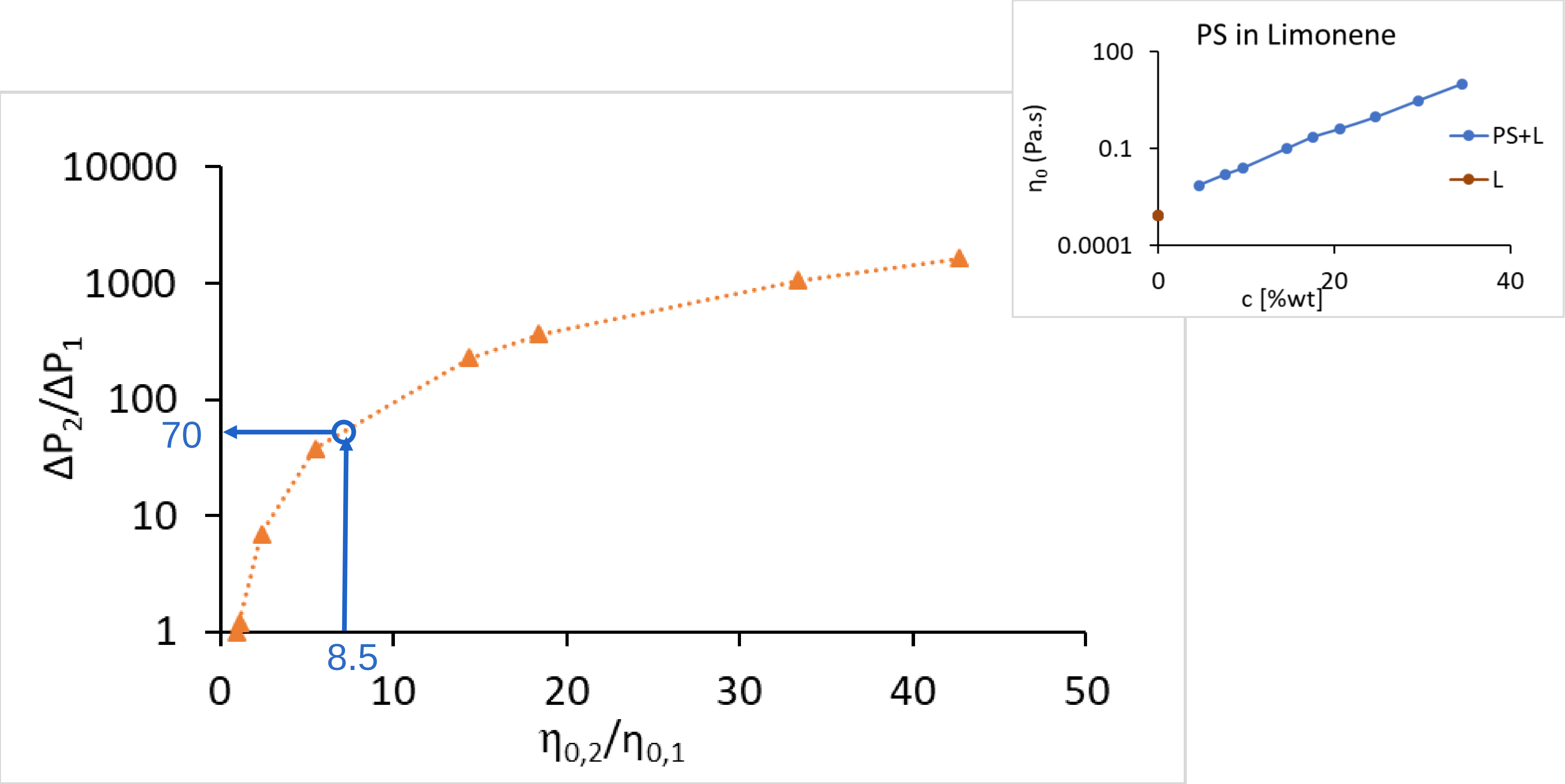

Figure adapted from R.Kol et al.(2021) State-Of-The–Art Quantification of Polymer Solution Viscosity for Plastic Waste recycling, ChemSusChem, 14, 4071-4102.

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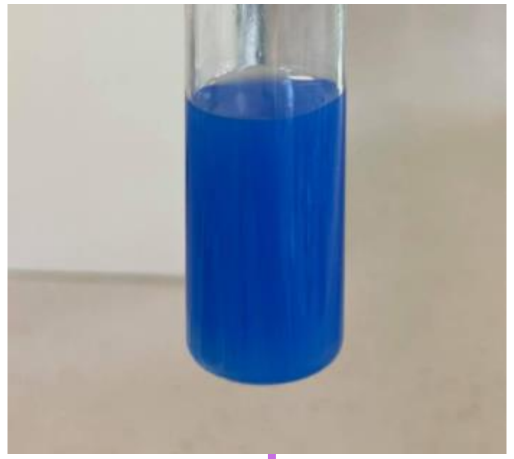
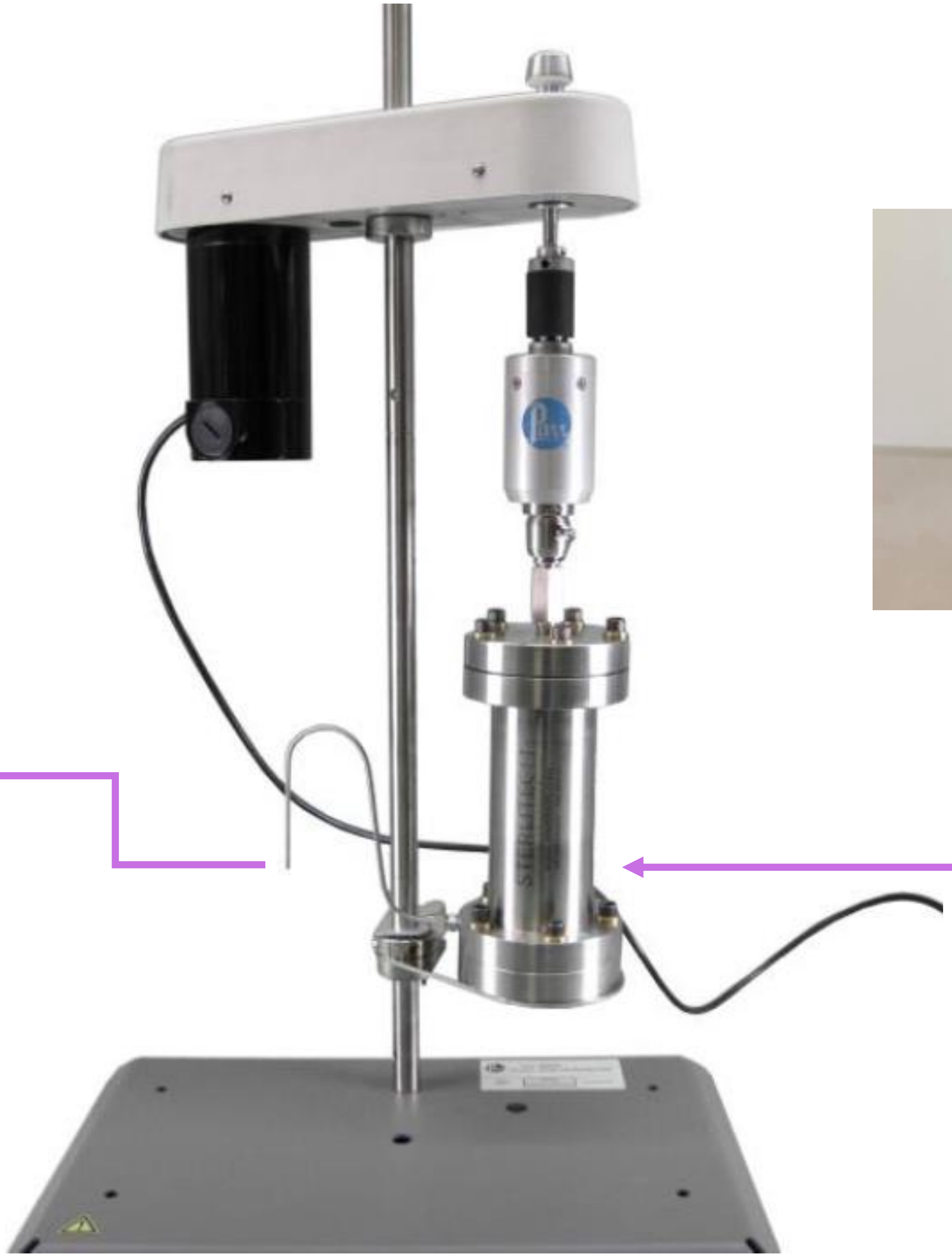
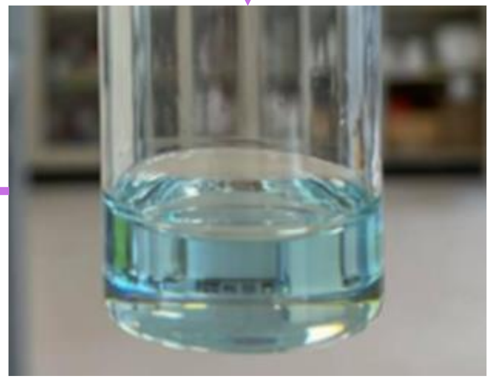
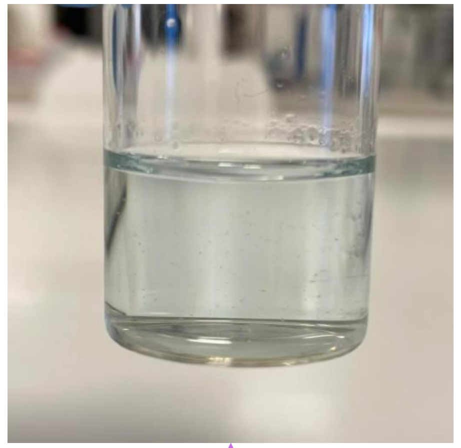
DISSOLUTION OF MUSHROOM BOX









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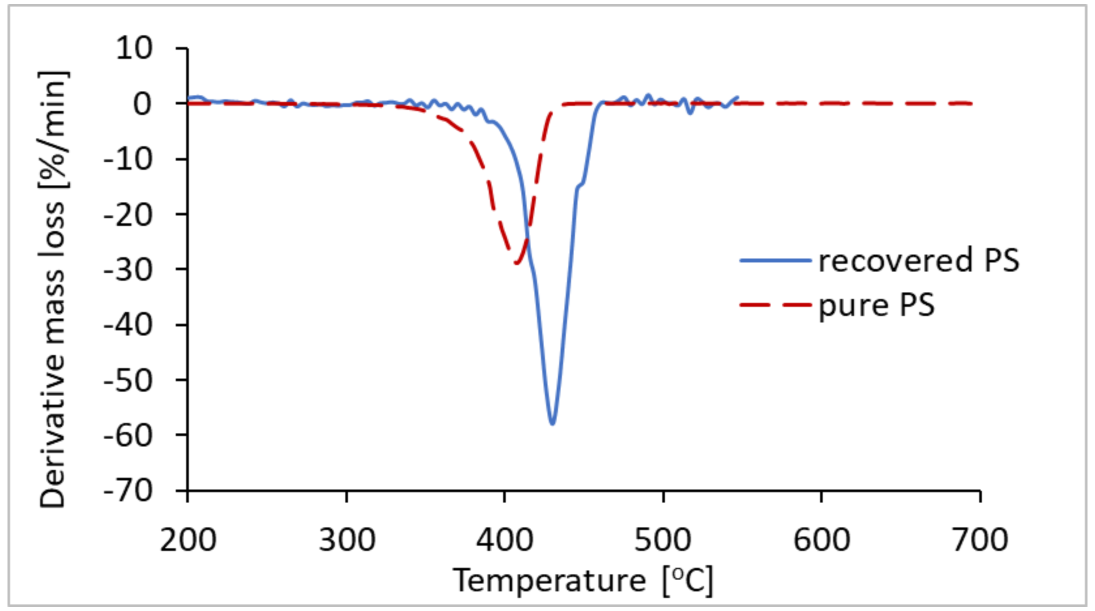
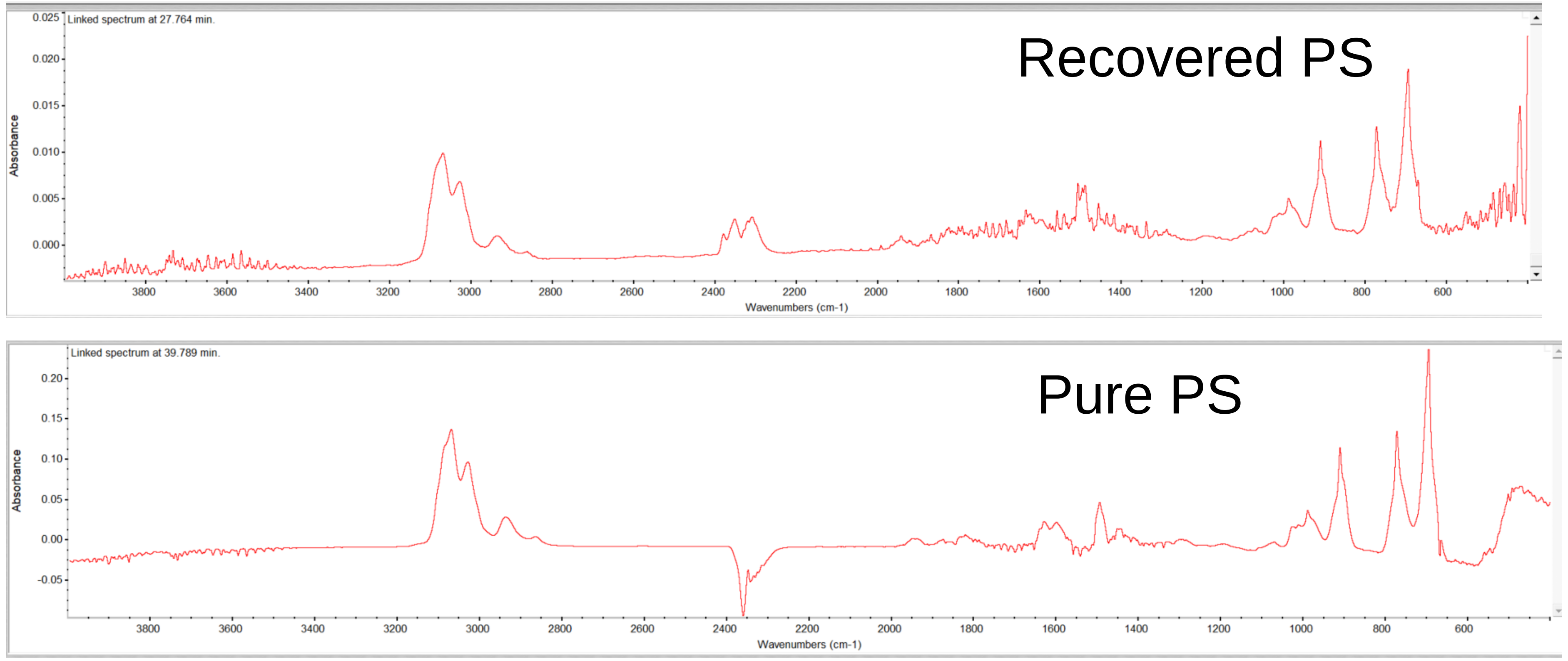
RECOVERED POLYMER FROM BLUE BOX

- Filtration and drying after addition of antisolvent

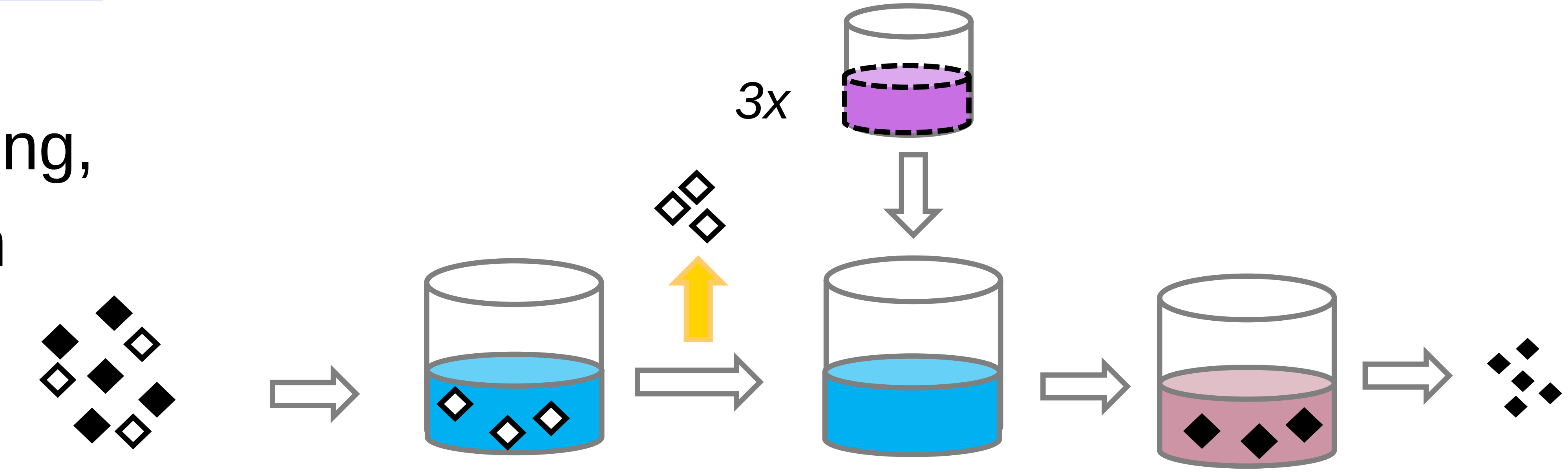


- Filtration residue contains polystyrene



FINAL CONCLUSIONS

- ❑Working on solvent-based recycling, using the dissolution-precipitation techinque.



- ❑Focus:
  - ❑Study of the rheology of polymer solutions to analyse its influence on solid-liquid separation processes for the removal of colourants.
  - ❑Optimization of a solid-liquid separation process for the removal of contaminants from plastic waste.

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Chapter Intechopen, 2021

Recent Advances in Pre-Treatment of Plastic Packaging Waste

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ChemSusChem
Chemistry-Sustainability-Energy-Materials

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State-Of-The-Art Quantification of Polymer Solution Viscosity for Plastic Waste Recycling

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First published: 29 July 2021 | https://doi.org/10.1002/cssc.202100876

FACULTEIT BIO-INGENIEURSWETENSCHAPPEN

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No. 859885

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C-PlaNeT CIRCULAR PLASTICS NETWORK FOR TRAINING

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Figure slide 37:

Image from Sterlichtech, Stirred Cell Assembly and Operation Manual.

Figure slide 36:

Dye in solution, a courtesy from the colleague Kim Phan.

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