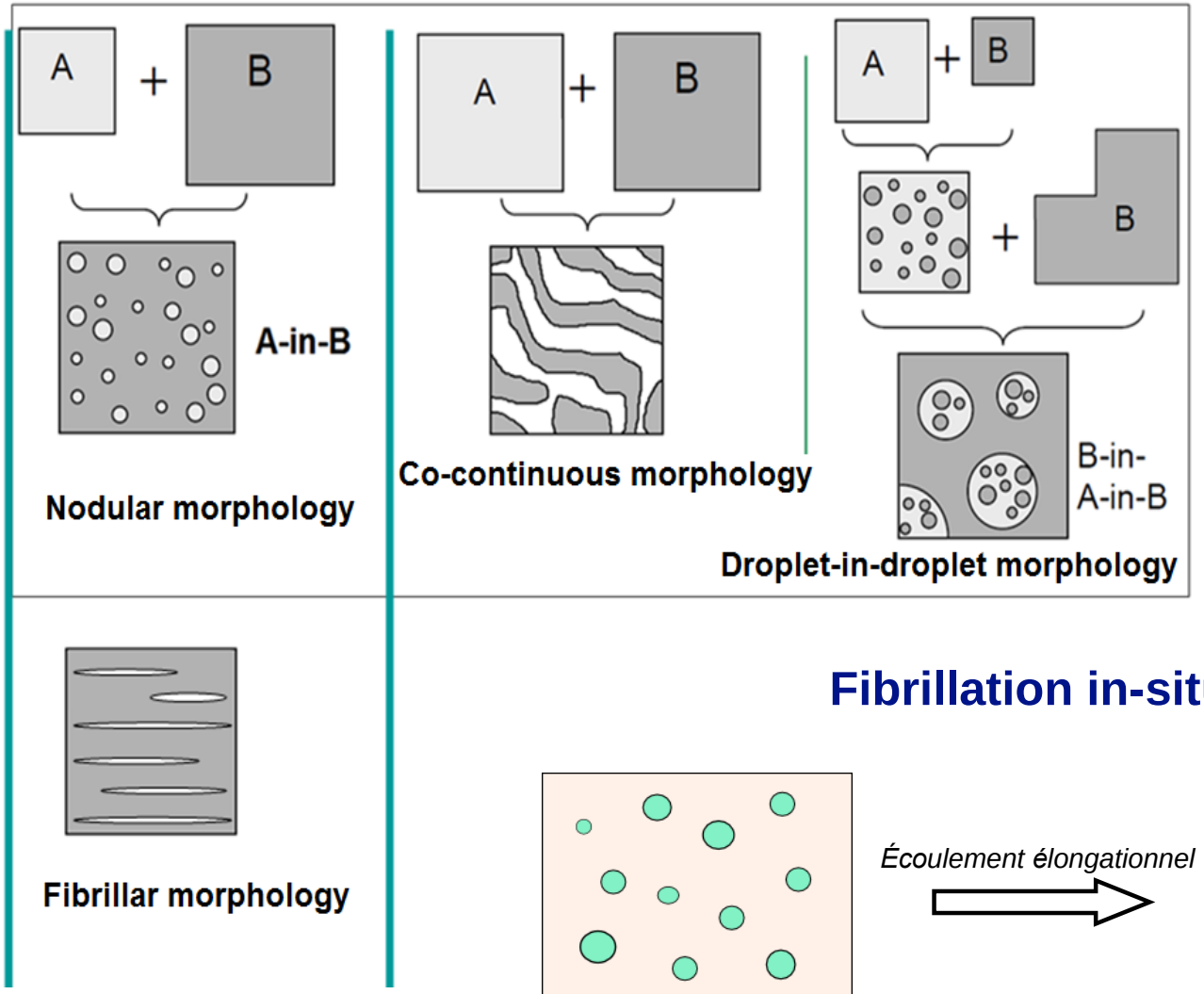
INSTITUT
Mines-Télécom

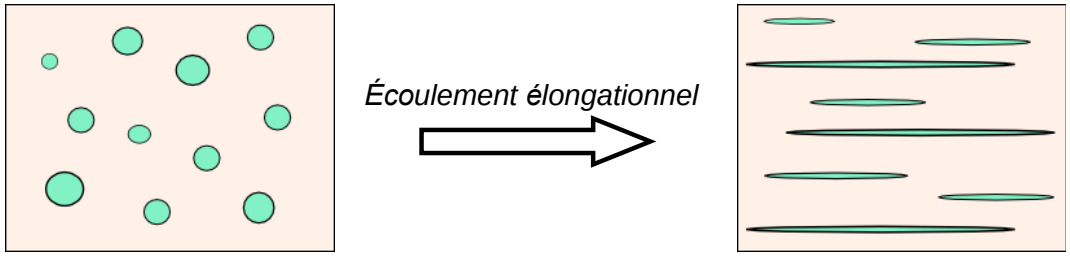
Systèmes polymères multiphasés : des polymères de commodité vers les polymères de performance, par le contrôle des propriétés interfaciales et des procédés de mise en œuvre et mise en forme

Prof. J. SOULESTIN, dpt TPCIM,
Mines Douai

Immiscible polymer blends: various possible morphologies

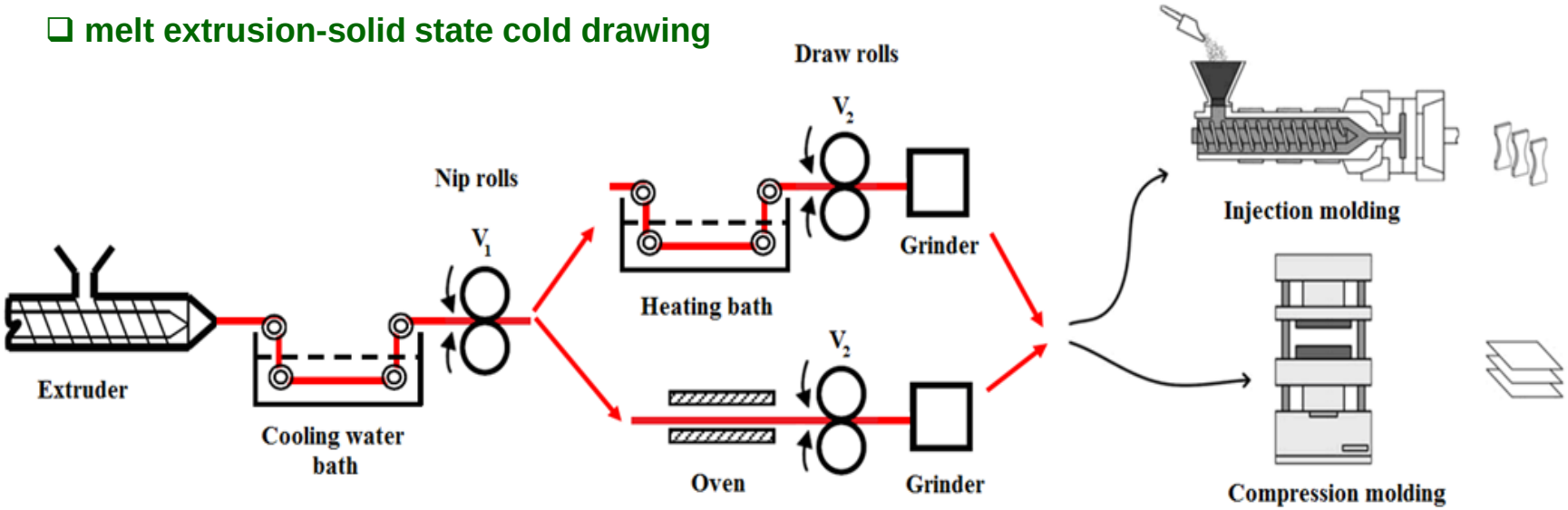


Fibrillation in-situ

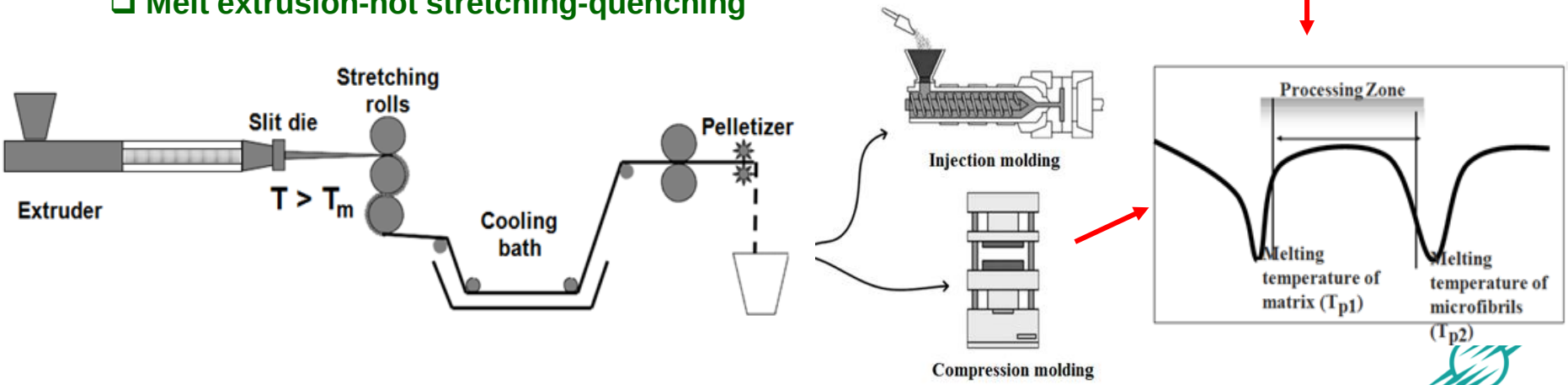


Different industrial approaches to prepare in-situ microfibrillar TP/TP composites

- melt extrusion-solid state cold drawing



- Melt extrusion-hot stretching-quenching

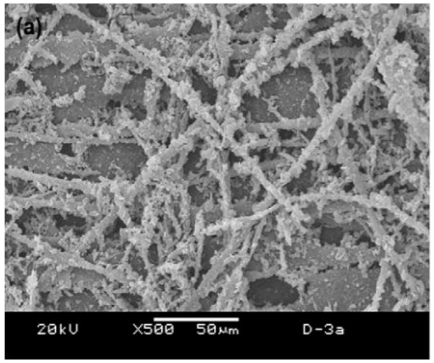


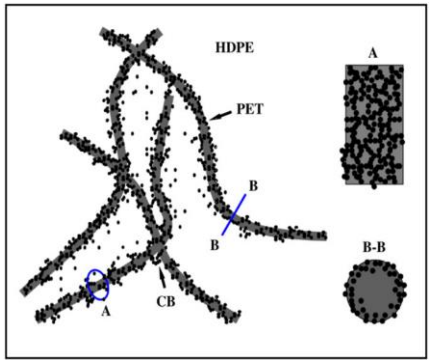
Potential applications of MFC technology

❑ MFC technology for recycling of plastics

MFCs have good application potentials in the car manufacturing industry, particularly in Europe due to the initiation of ecological regulations and legislation such as the *European Union End-of-Life Vehicles regulation*.

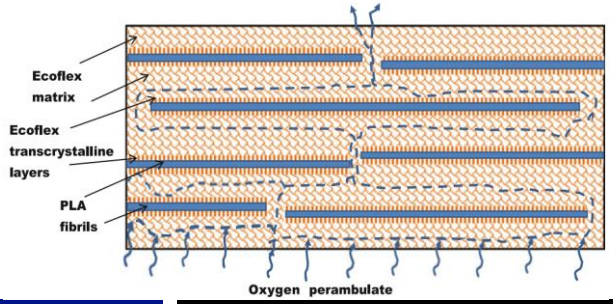
❑ Conducting composites

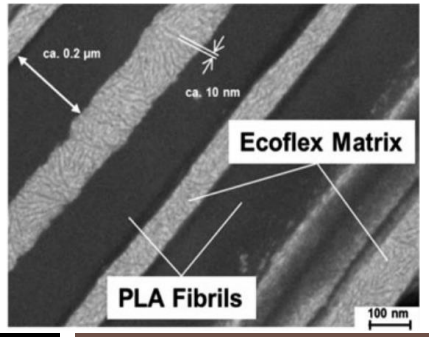




Polymer ***2007****: 48 ; 849.*

❑ Packaging applications

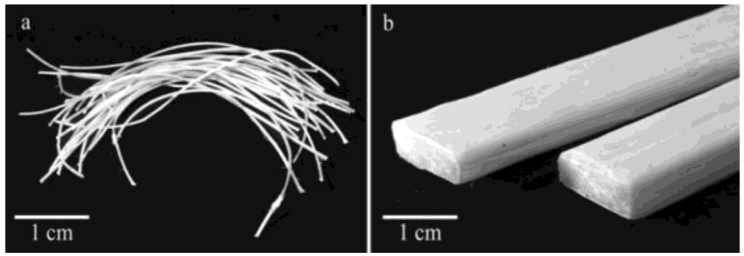




J Mater Sci. ***2013****, 48, 6312.*

Potential applications of MFC technology

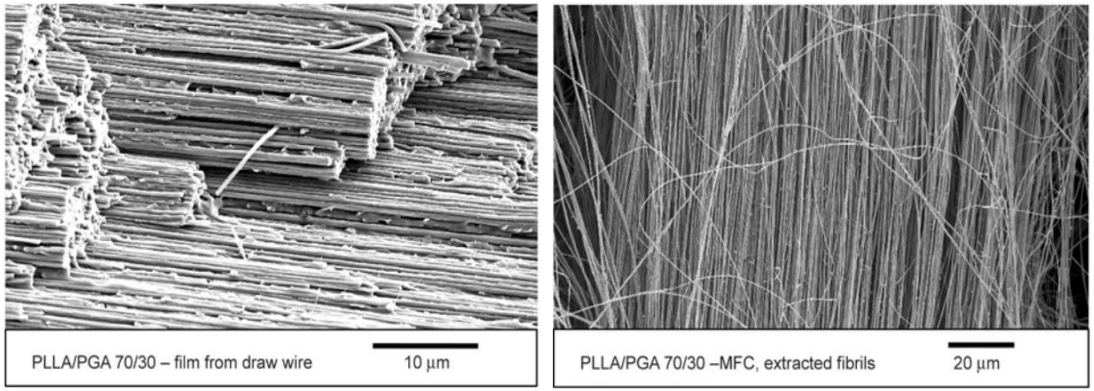
❑ Pultruded products



*Polym.Eng.Sci.**2010,** 50, 402.*

❑ Biomedical application

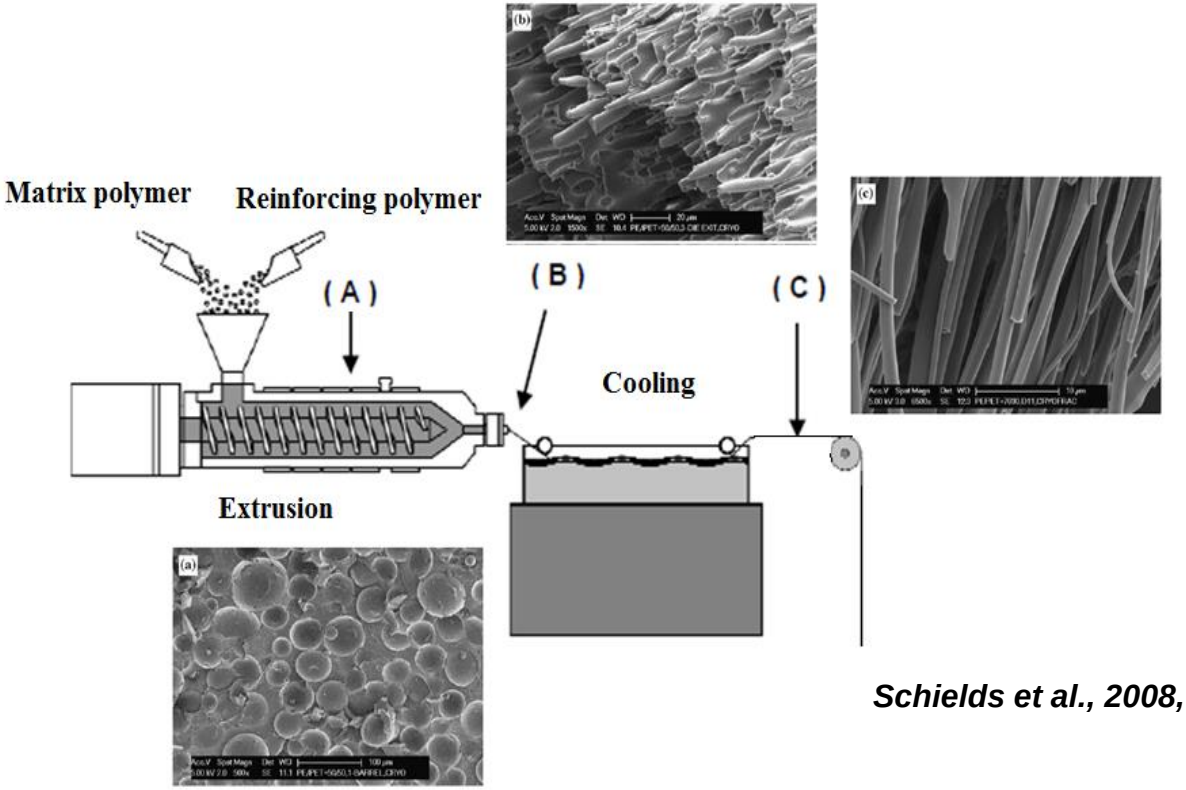
Isolation of bio-microfibrils via selective dissolution of the matrix component offers the potential for their biomedical applications as scaffolds for regenerative medicine or in controlled drug delivery or as biodegradable coronary stents .



Biodegradable microfibrillar polymer-polymer composites from poly(L-lactic acid)/poly(glycolic acid)

*Express Polymer Letters , **2015**, 9, 300*

Morphological evolution of in-situ microfibrillar composites during processing



Schields et al., 2008, J Mater Sci. 2008, 43, 6758

Preparing in-situ fibril–reinforced materials during processing (extrusion or injection molding) requires careful selection of rheological conditions necessary to produce the fibrillation of the minor phase.

Case of Newtonian drop in Newtonian matrix

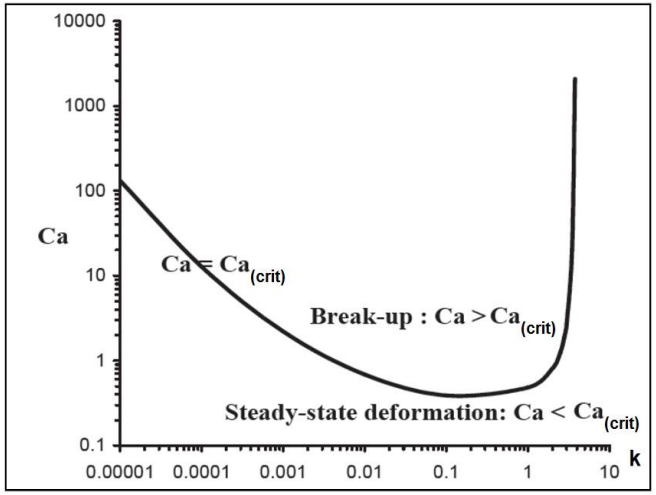
- Critical capillary number $Ca_{(crit)}$ in the case of **Newtonian fluids**

$$Ca = \frac{\eta_m \cdot \dot{\gamma}}{\Gamma / R}$$

G.I. Taylor. Proc. R. Soc. London 1934. A146. 501.

At drop breakup: $\dot{\gamma} = \dot{\gamma}_{(crit)}$

$$\longrightarrow \quad Ca = Ca_{(crit)} = \frac{\eta_m \cdot \dot{\gamma}_{(crit)}}{\Gamma / R}$$

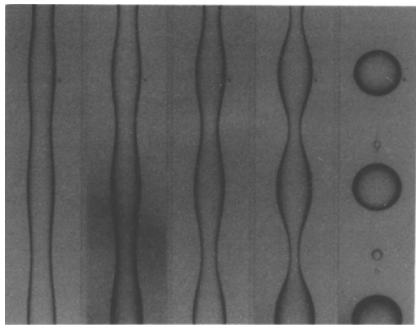


HP. Grace. Chemical Engineering Communications. 1982, 14, 225.

$$\log(Ca_{(crit)}) = -0.506 - 0.0994\log(k) + 0.124(\log(k))^2 - \frac{0.115}{\log(k) - 0.6107}$$

Favorable conditions to obtain a fibrillar morphology

- Viscosity ratio (k) < 4 **(HP. Grace. 1982)**
- Elasticity ratio (k') < 1 **(Mighri et al. 1998)**
- Break-up (tb) >> relaxation time (λ) **(Stegeman., 2002)**
- Break-up time (tb) >> cristallization time ($t_{1/2}$) **(Fulchiron, 2002)**



Sinusoidal distortions on a polyamide 6 thread (diameter 55 µm) embedded in a PS matrix at 230 °C (Elemans et al., 1990).
The photographs were taken at: t = 0, 15, 30, 45, 60 s.

R.A. de Bruijn. PhD thesis, Eindhoven University of Technology, The Netherlands, 1989.

Case of non-Newtonian fluids

- Critical capillary number in the case of **non-Newtonian fluids**

$$Ca_{(crit)} = \frac{\eta_m \cdot \dot{\gamma}_{(crit)}}{\Gamma / R}$$

✓ Elastic effect of the dispersed phase

U. Sundararaj and C.W. Macosko. Macromolecules, 1996,28, 2647.

The break-up will occur when:

Shear stress →

$$\eta_m \cdot \dot{\gamma} - N_{1,d} > Ca_{crit} \cdot \left(2 \cdot \Gamma / D\right)$$

✓ Elastic effect of the dispersed phase and the matrix (continuous phase)

Y. Seo and J. Kim. Polymer, 2001,42, 5029

$$Ca^{Elasttic} = \frac{N_{1,m} - N_{1,d}}{2\,\Gamma / D}$$

Dispersed particles are deformed when **$Ca^{Elastic} > 1$**

P. Ghodgaonkar and U. Sundararaj. Polymer Engineering and Science, 1996,36, 1656.

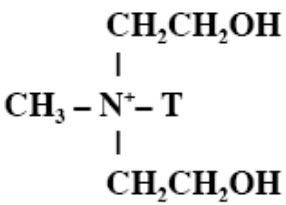
The break-up will occur when:

$$\eta_m \dot{\gamma} + N_{1,m} > \frac{2\Gamma}{D} + N_{1,d}$$

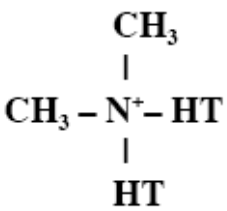
shear forces + matrix elasticity > interfacial forces + droplet elasticity

Elaboration of PP/PA/Clay blends using direct compounding

- MB route: no information on the formulation of the materials
- Influence of the type of surfactant
  - **Cloisite® 15A: better affinity with polyolefins**
  - **Cloisite® 30B: better affinity with polar polymers like PA**



C30B surfactant



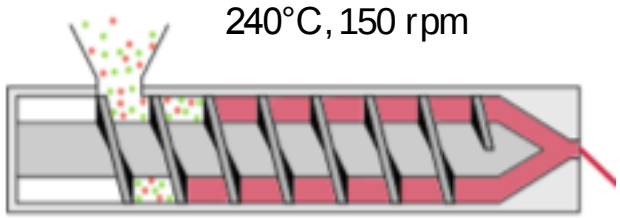
C15A surfactant

- **Processing method**

PP + PA

Cloisite
C15A or C30B

240°C, 150 rpm



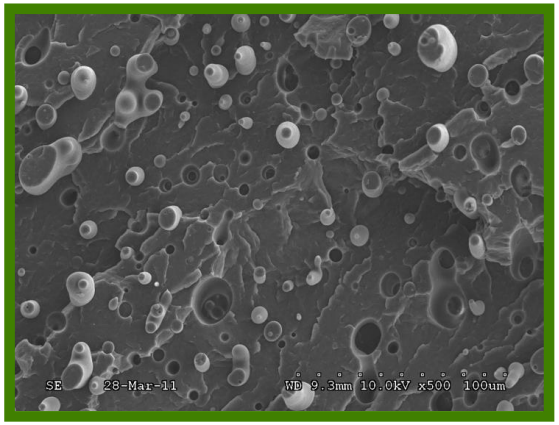
Twin-screw extruder

(80/20 wt%)

PP/PA
PP/PA/C15A
PP/PA/C30B
} 2 wt% Clay

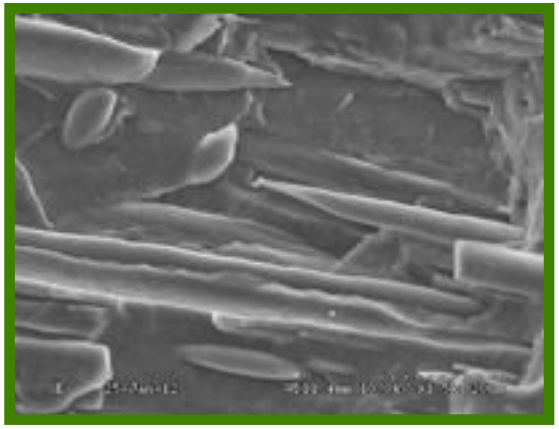
Morphology of PP/PA/Clay blends obtained using direct compounding

PP/PA blend

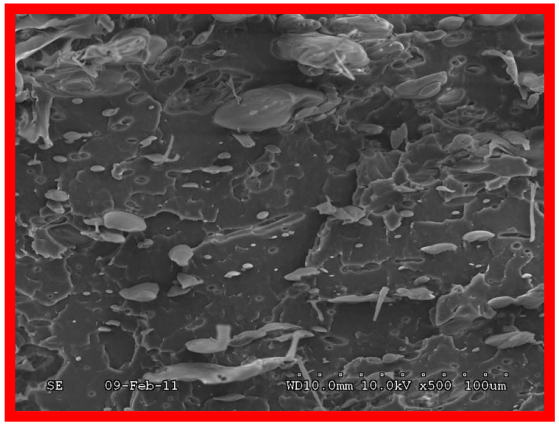


Transverse

Longitudinal

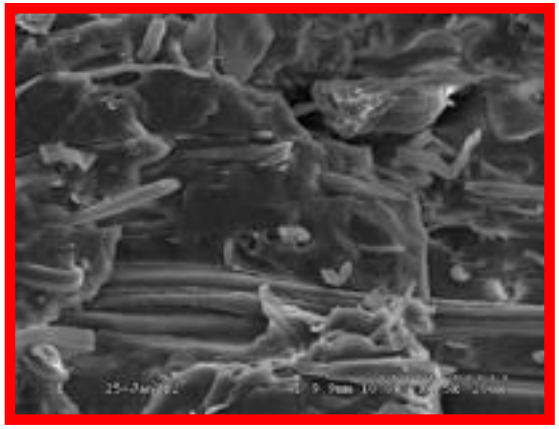


PP/PA/C30B

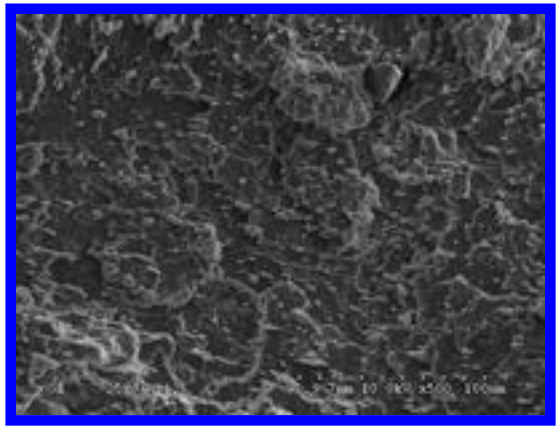


Transverse

Longitudinal

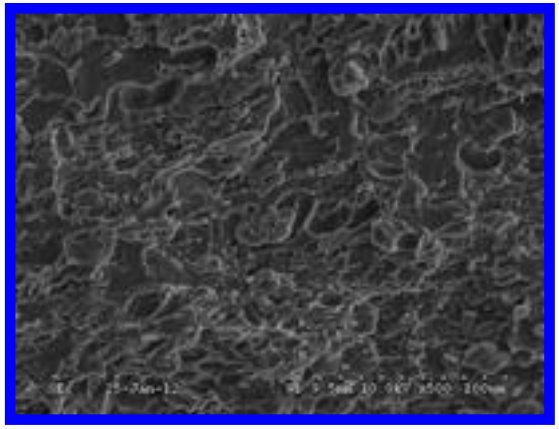


PP/PA/C15A



Transverse

Longitudinal

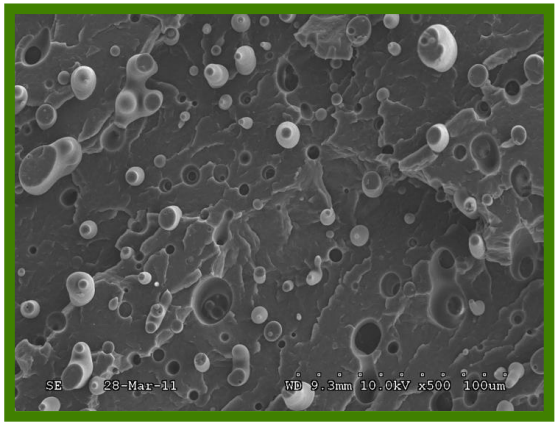


morph. homogeneity

destruction of fibrillar structure with clay

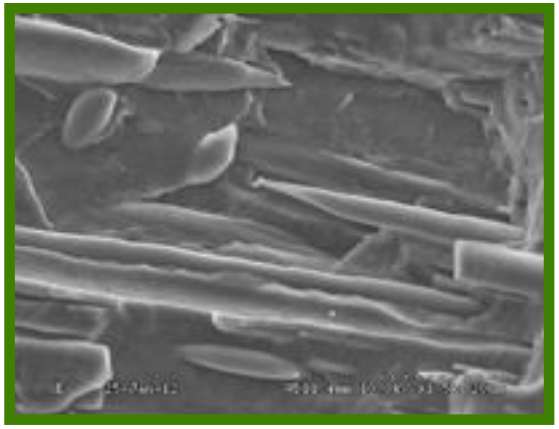
Morphology of PP/PA/Clay blends obtained using direct compounding

PP/PA blend

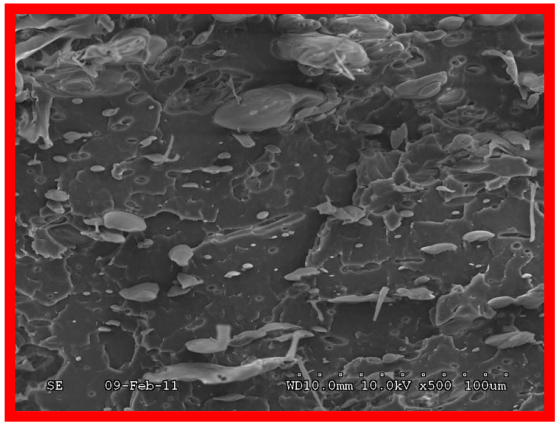


Transverse

Longitudinal

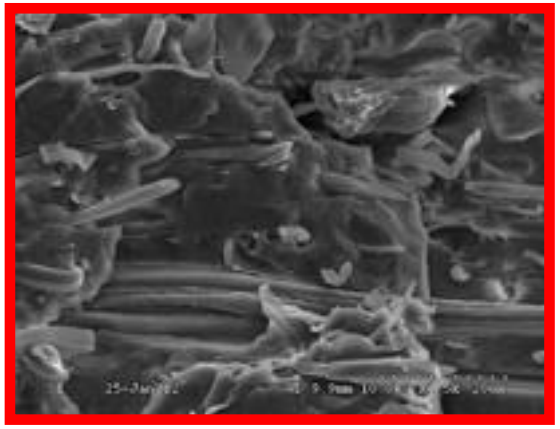


PP/PA/C30B

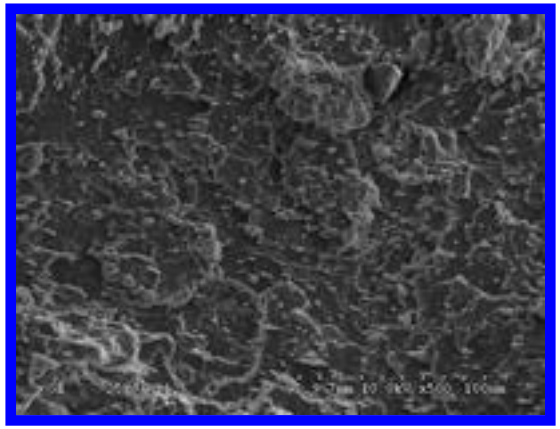


Transverse

Longitudinal

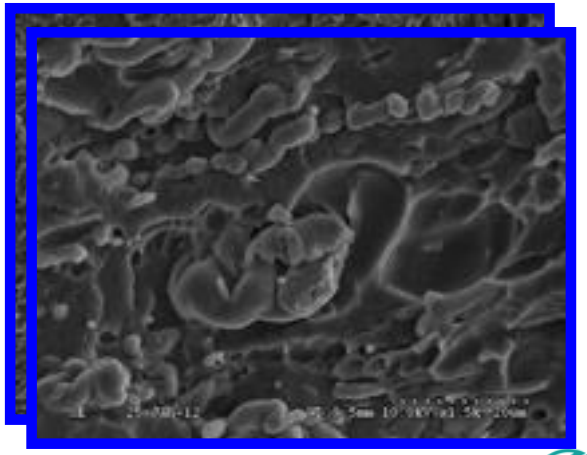


PP/PA/C15A



Transverse

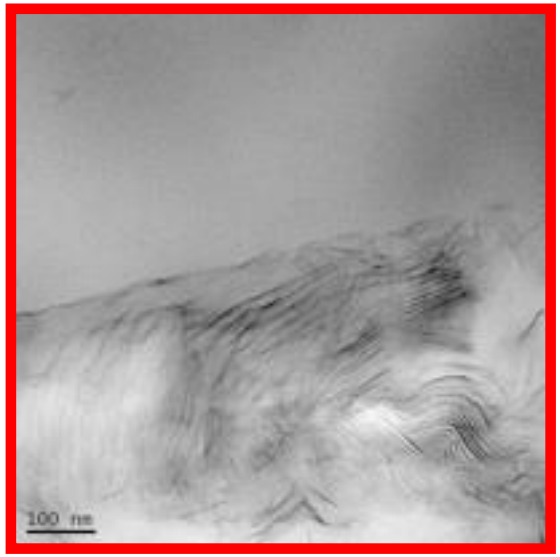
Longitudinal

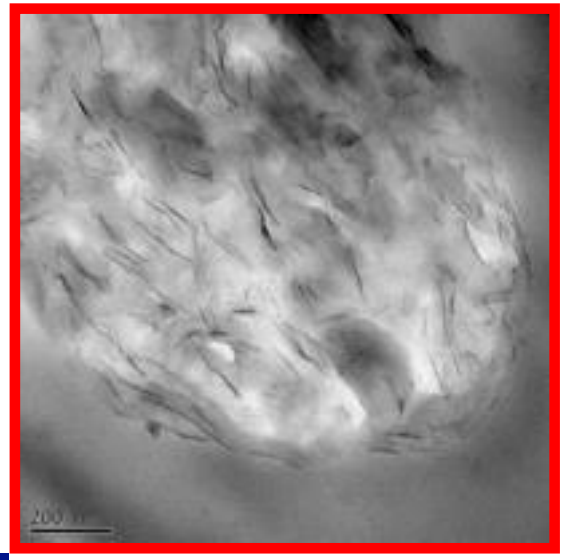


- morph. homogeneity
- destruction of fibrillar structure with clay

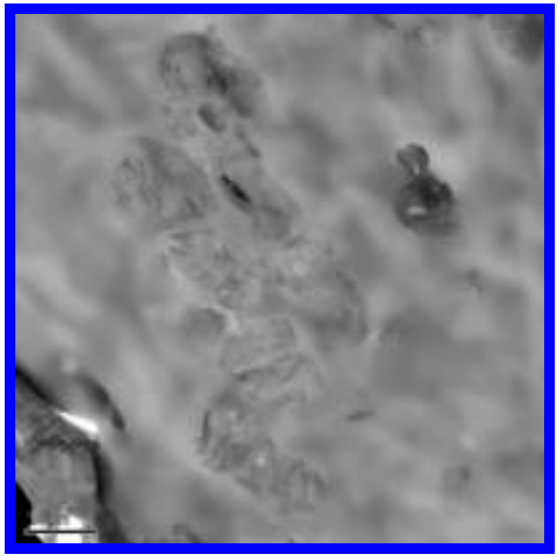
Dispersion and localization of clay in PP/PA/Clay blends obtained using direct compounding

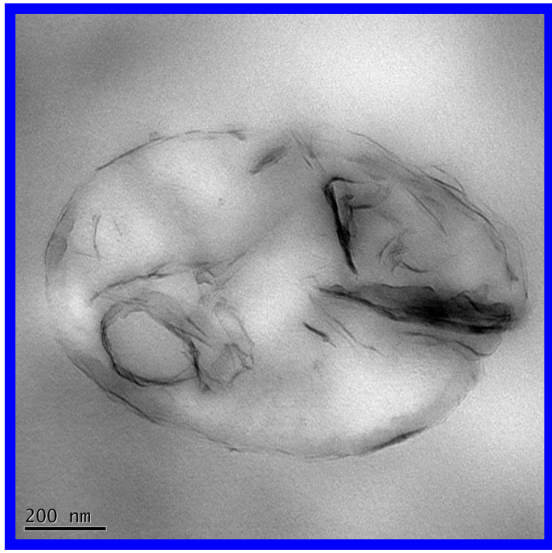
PP/PA/C30B

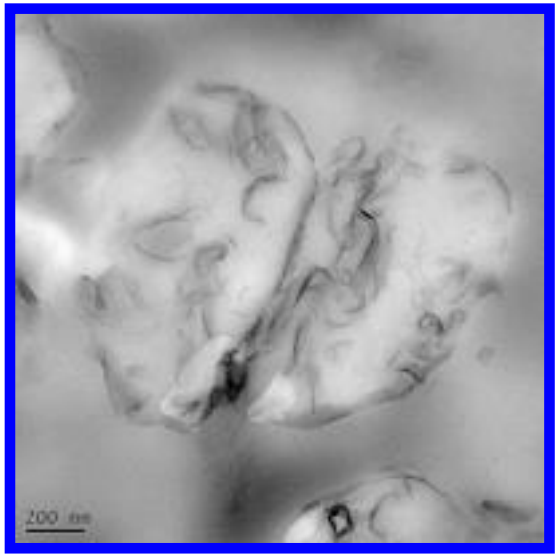


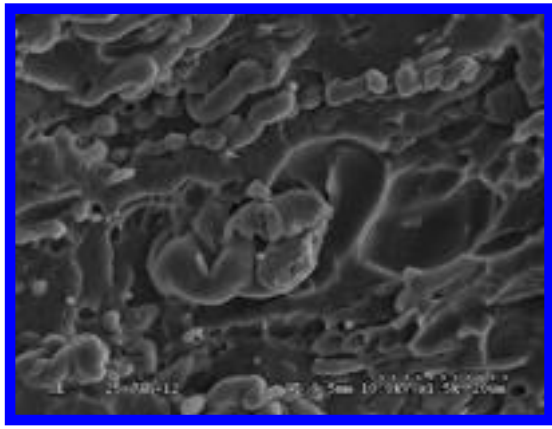


PP/PA/C15A









Localization of clay in PA6 phase for C15A/C30B

Elaboration of polymer/organoclay blends

PP + C15A

or

PA6 + C30B

TWIN-SCREW EXTRUSION

Determination of mineral content by means of calcinations

masterbatch

PP-8.3% C15A

PA6-9.4% C30B

SINGLE-SCREW EXTRUSION

dilution

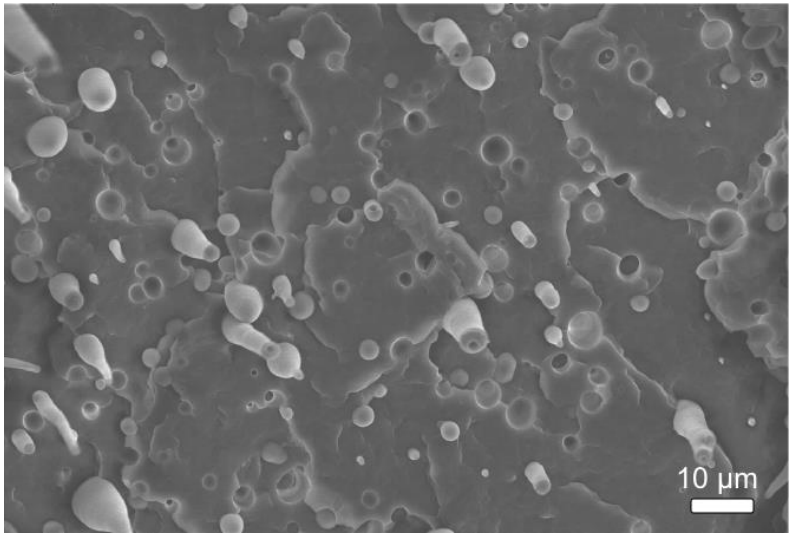
PP-0% C15A	PA6-0% C30B
PP-0.5% C15A	PA6-3% C30B
PP-1.1% C15A	PA6-6% C30B
PP-1.6% C15A	PA6-9% C30B

"% C15A" and "% C30B" stand for % montmorillonite arising from C15A or C30B (i.e. mineral fraction).

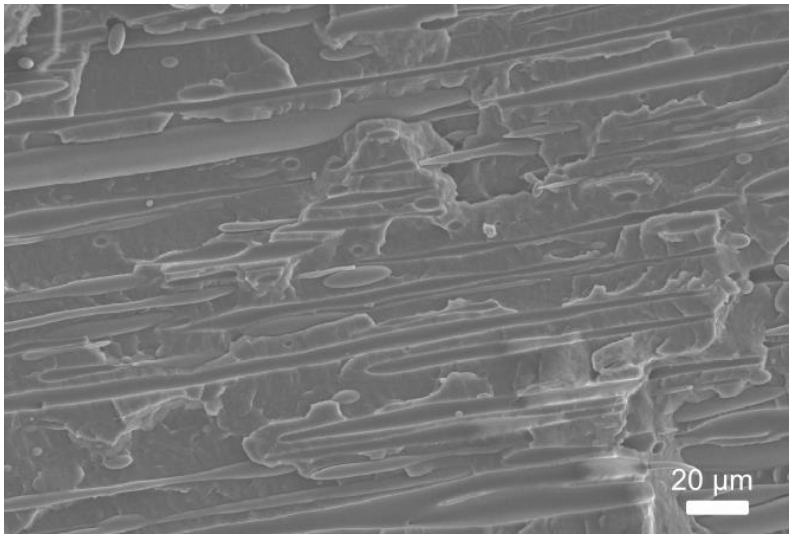
MINES Douai

Morphology: PP/PA6

Transversal



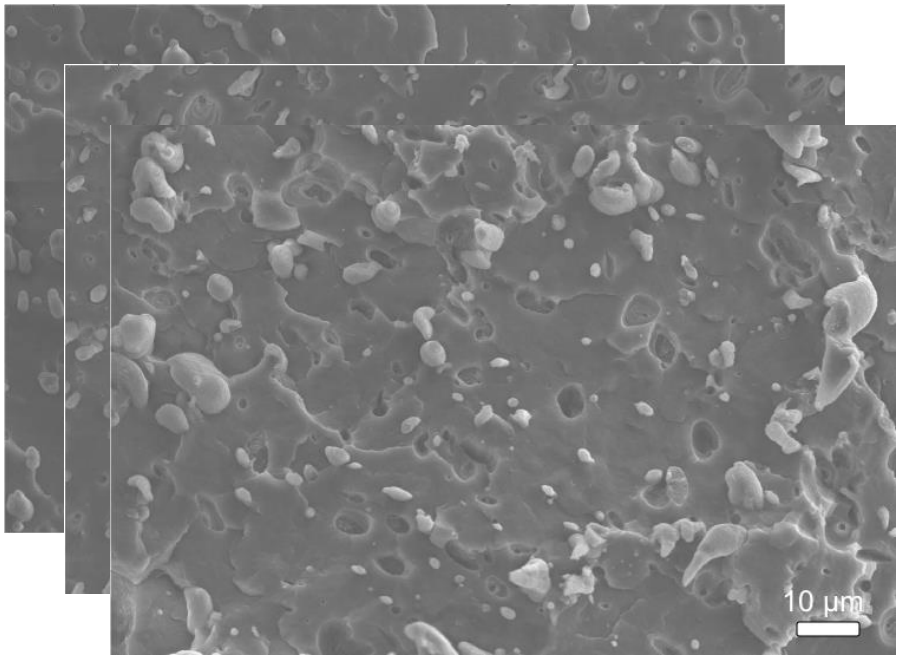
Longitudinal



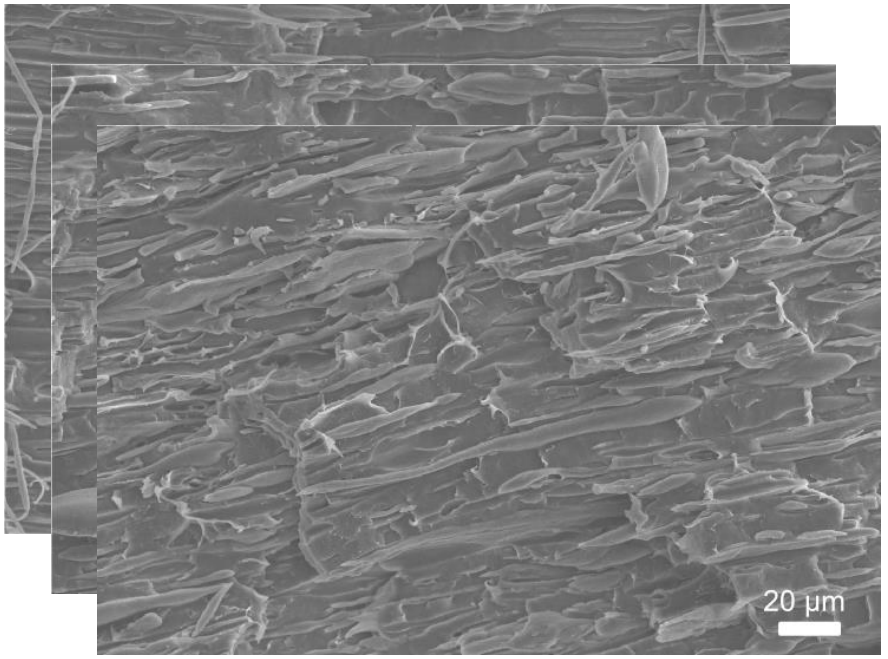
→ Fibrillar morphology with high interfacial tension

Morphology: PP/PA6/C15A

Transversal



Longitudinal



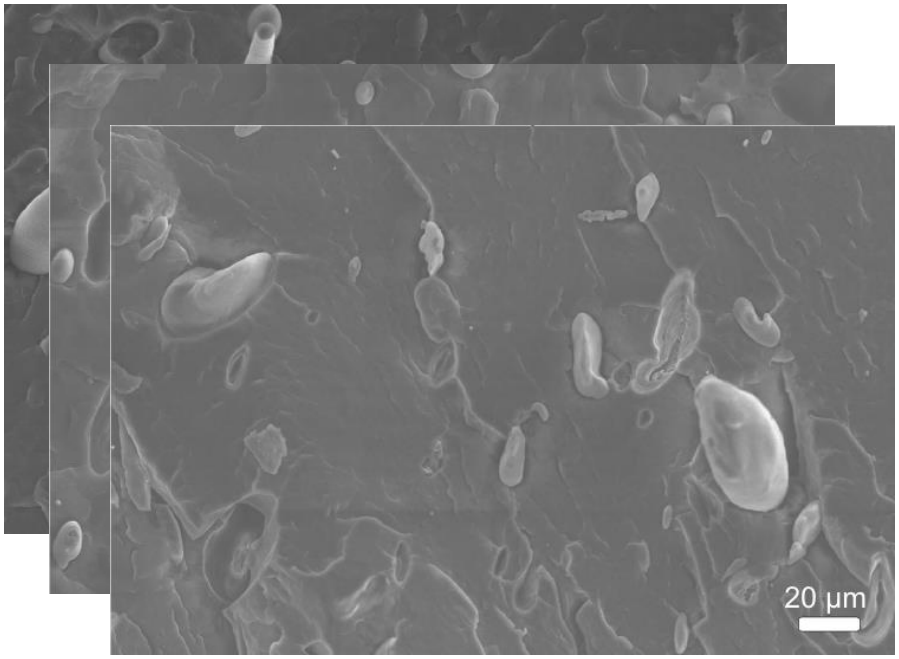
0.45% clay

0.9% clay

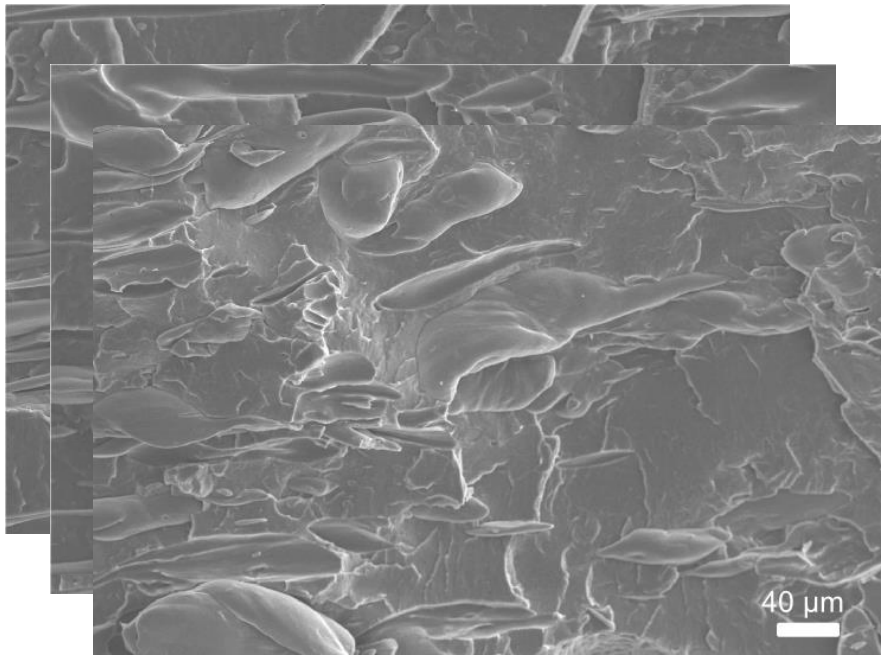
1.35% clay

Morphology: PP/PA6/C30B

Transversal



Longitudinal

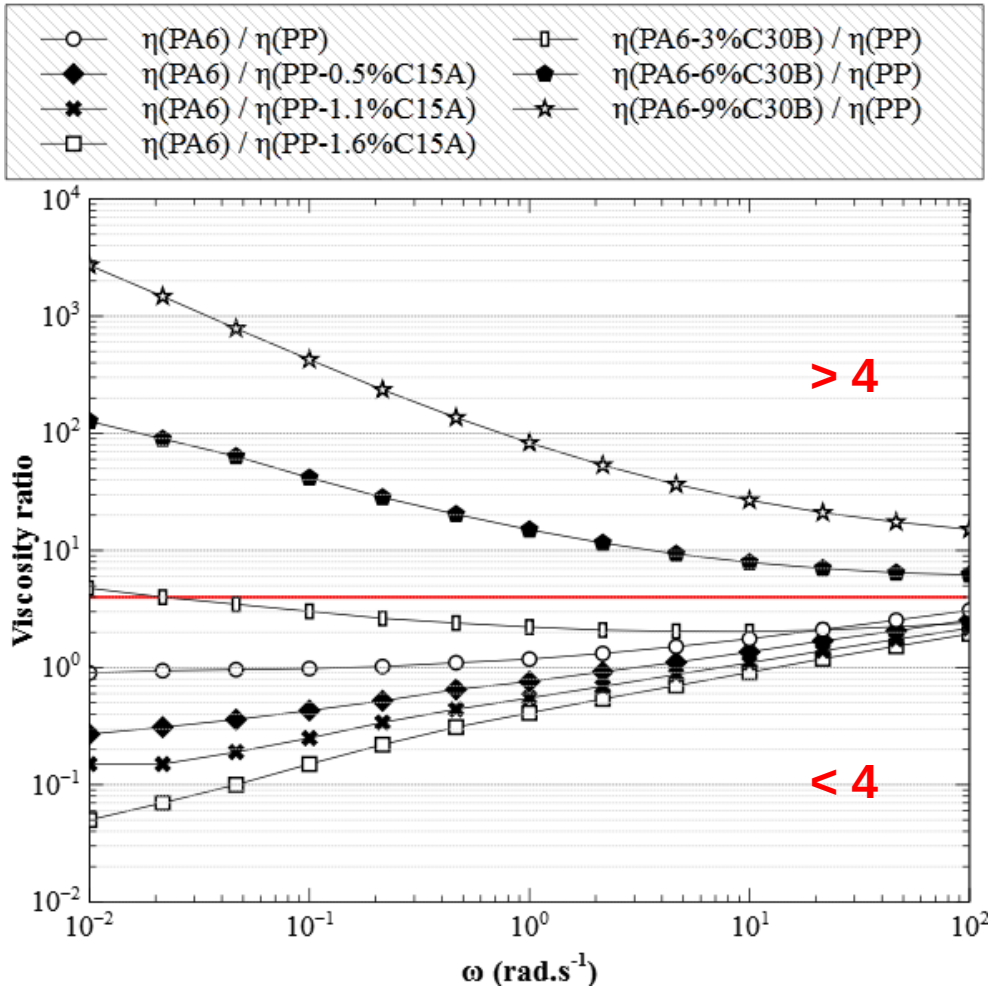


0.45% clay

0.9% clay

1.35% clay

Viscosity ratio



At 100 rad.s^{-1}:	Viscosity ratio
η(PA6) / η(PP)	3.1
η(PA6) / η(PP-0.5% C15A)	2.6
η(PA6) / η(PP-1.1% C15A)	2.2
η(PA6) / η(PP-1.6% C15A)	1.9
η(PA6-3% C30B) / η(PP)	2.4
η(PA6-6% C30B) / η(PP)	6.2
η(PA6-9% C30B) / η(PP)	15.1

→ Having the clay dispersed in the minor phase affects strongly the viscosity ratio.

Elaboration of PLA/PA11 blends with fibrillar morphologies

85 % PLA

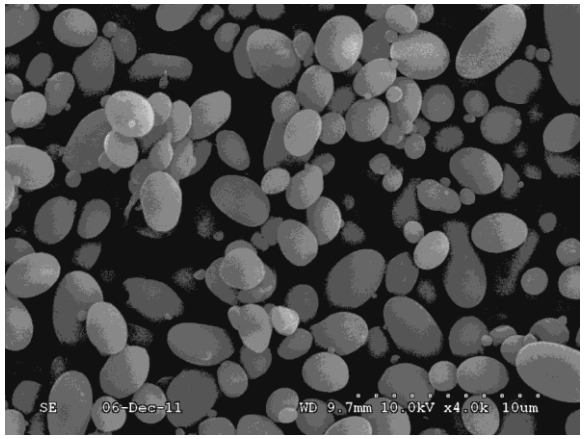
15 % PA11

→ TS Extrusion
150 rpm
200 - 210 °C

→ Stretching
HSR = 6

→ PLA/PA11 Blends

➔ Chemical etching for SEM morphological observations

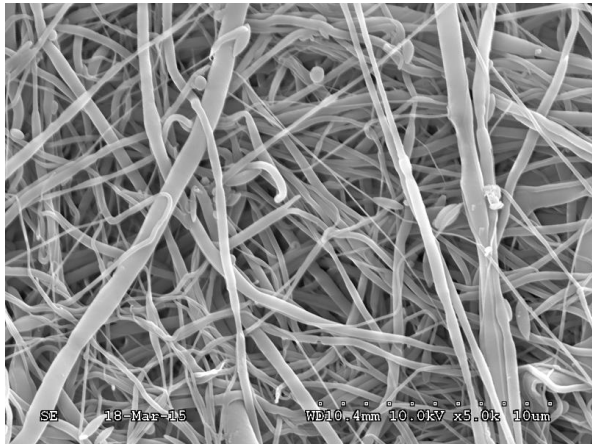


PLA/PA11 nodular morphology

➔ No in-situ fibrillation

PLA/PA11 Decrease of η_{PA11}

➔ Partial fibrillation



PLA/PA11 Increase of η_{PLA}

➔ Fibrillation

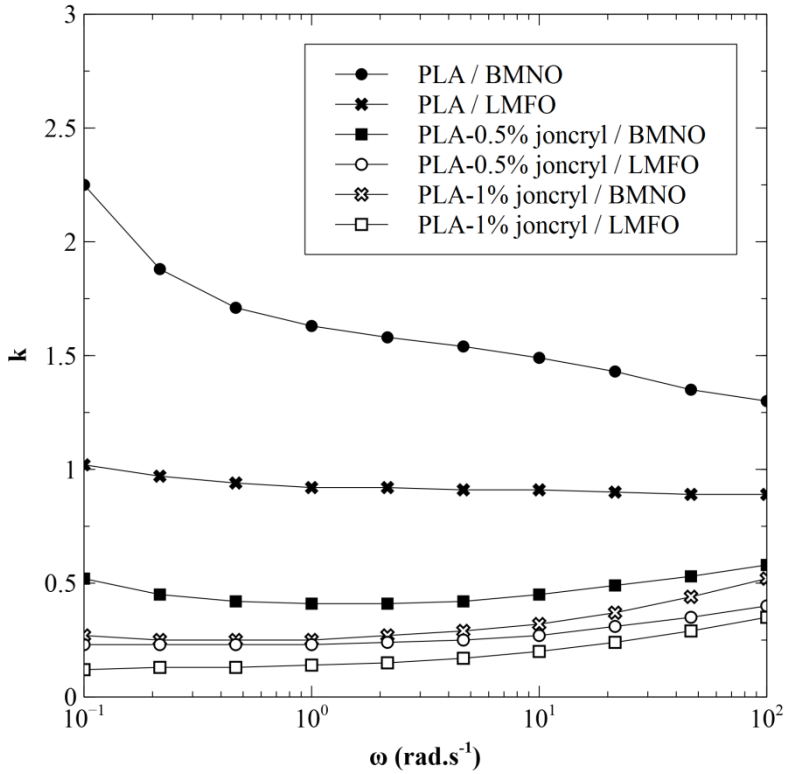
Fibrillation = very high ductility

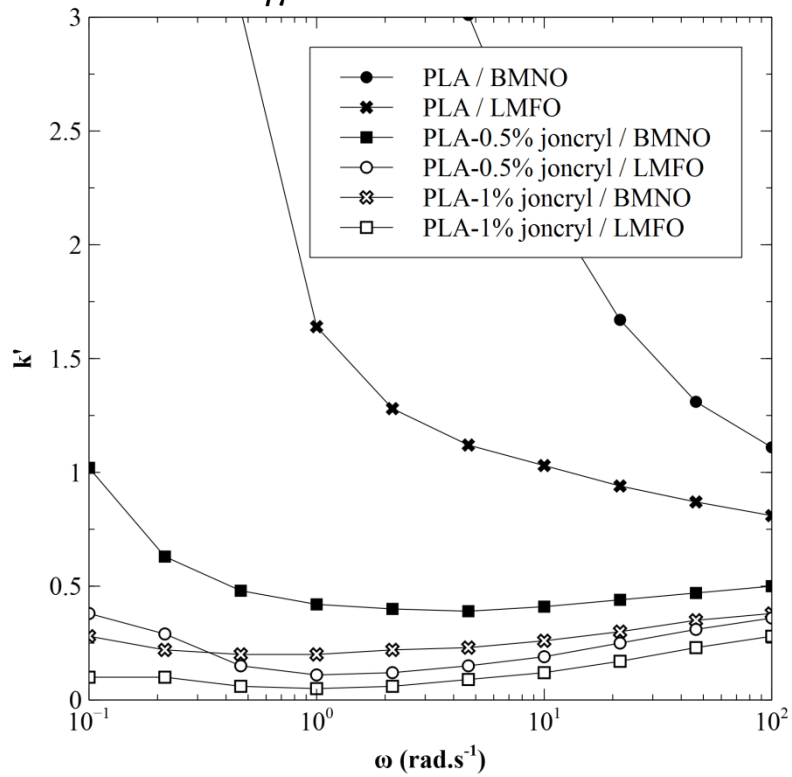
Viscosity and elasticity of PLA/PA11 blends at 200°C

k = | (phase minoritaire) / | (matrice)

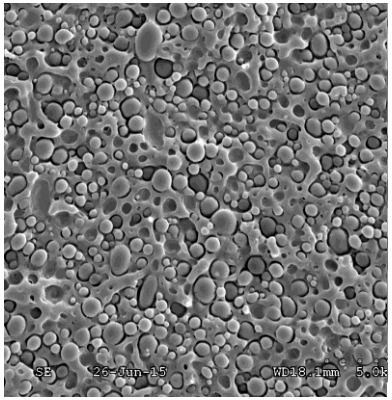
k' = ⌊ (phase minoritaire) / ⌊ (matrice) avec $\lambda = \frac{N1}{2\eta\dot{\gamma}^2}$

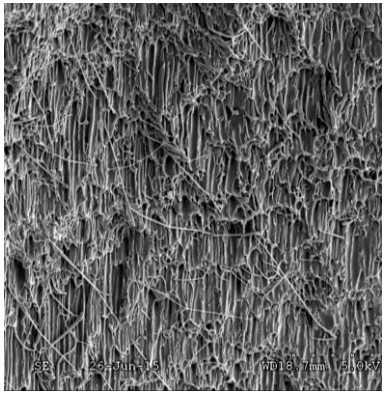
Mighri, Journal of Rheology (1998)





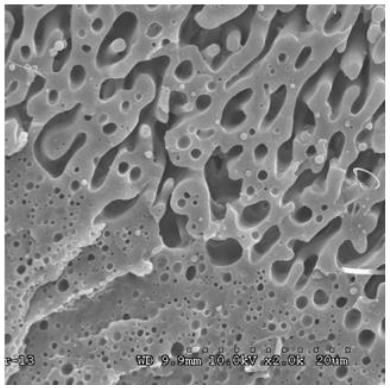
Different blends with k and k': >1; =1; ou <1.





MINES Douai

TPCIM
Technologie des Polymères et Composites & Ingénierie Mécanique



Prof. Patricia Krawczak

Dr. Mohamed Yousfi
Dr. Dimitri Chomat
Dr. David Lemeny
Prof. M-F. Lacrampe
Dr. Eric Lafranche
Dr. Kalappa Prashantha
Dr. Cedric Samuel
Laurent Charlet
Dr. Catherine Douchain
Carlo Angotzi
Thierry Chevalier
Murielle Delsert
Bernard Pauchet
Jean-Michel Pollet