Journée Technique : Substitution dans la filière textile
23 novembre 2021

Lignine : élément biosourcé aux propriétés prometteuses pour la fonctionnalisation en voie fondue des textiles synthétiques

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ENSAIT,

Une grande école, une des meilleures écoles textiles d'Europe

Personnel

37 enseignants
30 à **40** enseignants vacataires
22 ingénieurs et techniciens
33 personnels administratifs

Etudiants

400 élèves ingénieurs (dont **75** apprentis)
130 diplômés par an
20 étudiants en Master
40 doctorants

Bibliothèque de l'ENSAIT

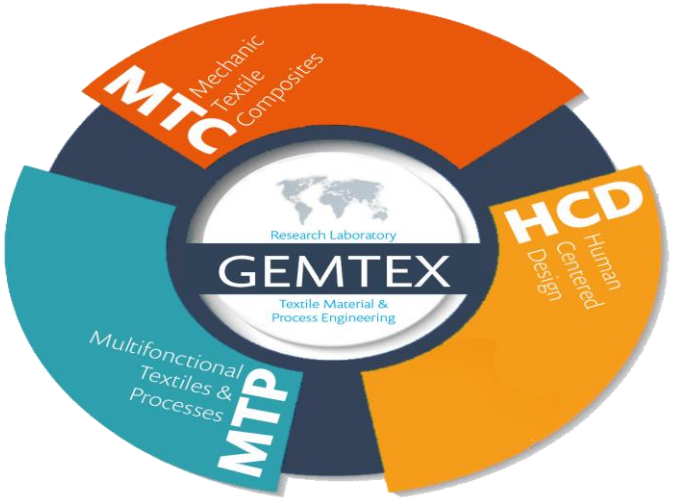
Le laboratoire GEMTEX

Professeurs **12**

Maitres de conférence **19**

Techniciens et ingénieurs **10**

Attaché temporaire d'enseignement et de recherche **3**



Crée en
1992

Directeur :
Pr. Xianyi ZENG

57 Doctorants en 2019

55 Programmes de recherche collaboratifs dep 2013

12 Brevets depuis 2013

1 Programme Erasmus Mondus

Domaines d'applications:

aéronautique, transport, médical , Bien-être, sport & loisir, bâtiment, habillement



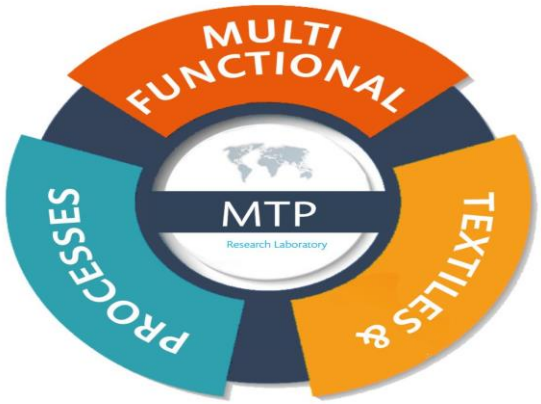


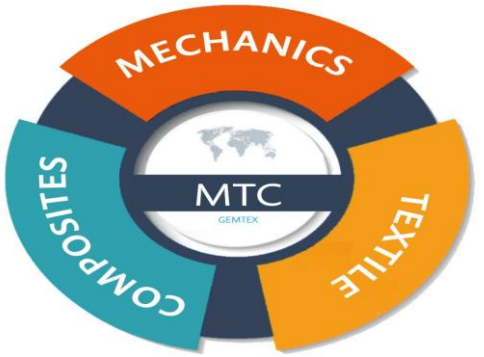




Le laboratoire GEMTEX : 1 équipe en 3 groupes

Customisation de masse, analyse sensorielle, textile intelligent, gestion de la chaine logistique, aide à la décision, modélisation paramètres techniques/critères marketing.



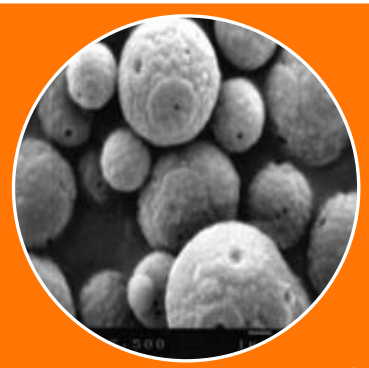


Comportement et caractérisation mécanique, modélisation, simulation éléments finis, conception, milieux fibreux, composites, procédés de fabrication, fibres naturelles

Procédés de mises en œuvre des polymères et systèmes complexes, Procédés textiles, Matériaux nanostructurés, Physico-chimie des polymères, Fonctionnalisation de surface, Encapsulation, Interaction entre surfaces et interfaces, Relations structure propriétés, Eco-conception, Durabilité, Caractérisation multi-échelle, Métrologie textile.

Les compétences du groupe MTP

Systèmes complexes à propriétés fonctionnelles



Formulation de systèmes complexes

En voie fondue :
- -mélange de polymères
- - nanocomposites

En solution (apprêt, diffusion):
- - ajouts de molécules
- - ajouts d'enzymes

Synthèse de microcapsules

Caractérisation

Positionne

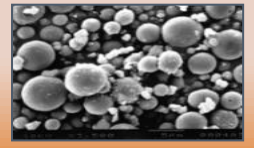
Plateforme Textiles Multifonctionnels

Formulation de systèmes polymères complexes

En voie fondue :
Extrudeuse bi-vis, malaxeur, presse chauffante, …

En solvant :
réacteur de formulation (8l), cuve ultra-son,…

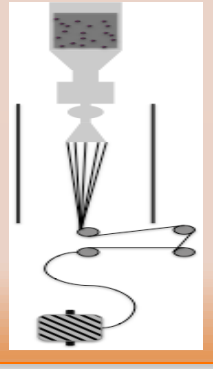
Caractérisation :
Rhéomètre, melt flow index, DMA, DSC ATG, granulomètre, potentiel zêta électrophorèse, IRTF, spectroscopie UV-visible, …

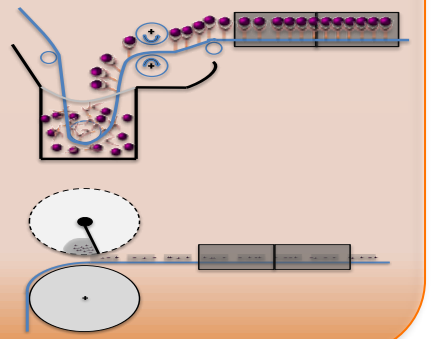


Mise en œuvre des systèmes complexes

Filage mono-vis, imprimante 3D FDM, autoclave, imprimante jet d'encre, foulard, ligne enduction, table impression, plasma atmosphérique, brodeuse

Caractérisation:
Tensiomètre, potentiel zêta à potentiel d'écoulement, profilomètre, hot disk, spectroscopie ATR …





Procédés Textiles

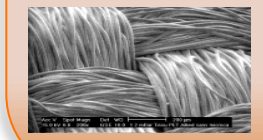
Filature : DREF, mini-carde, mini-aiguilleteuse, broche creuse, twistec, open end, …

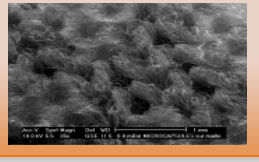
Tissage : métiers à tisser armurés et Jacquard, …

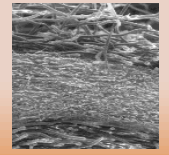
Maille : Métiers maille circulaire, rectiligne automatique et maille jetée double fonture,…

Tressage : Tresseuses

Caractérisation : banc de traction, banc de perforation, hot disk, perméabilimètre à l'air et l'eau, profilomètre, tensiomètre, banc de filtration, banc acoustique







Collaborations avec d'autres plateformes : CETI, CENT, CREPIM, …

Propriétés / domaines d'application

Protection

- Equipement de protection individuel (EPI), Filtration et séparation, Ignifugation, Isolation

Médical

- Régénération osseuse, Chauffant, Thérapie photodynamique

Bien-être

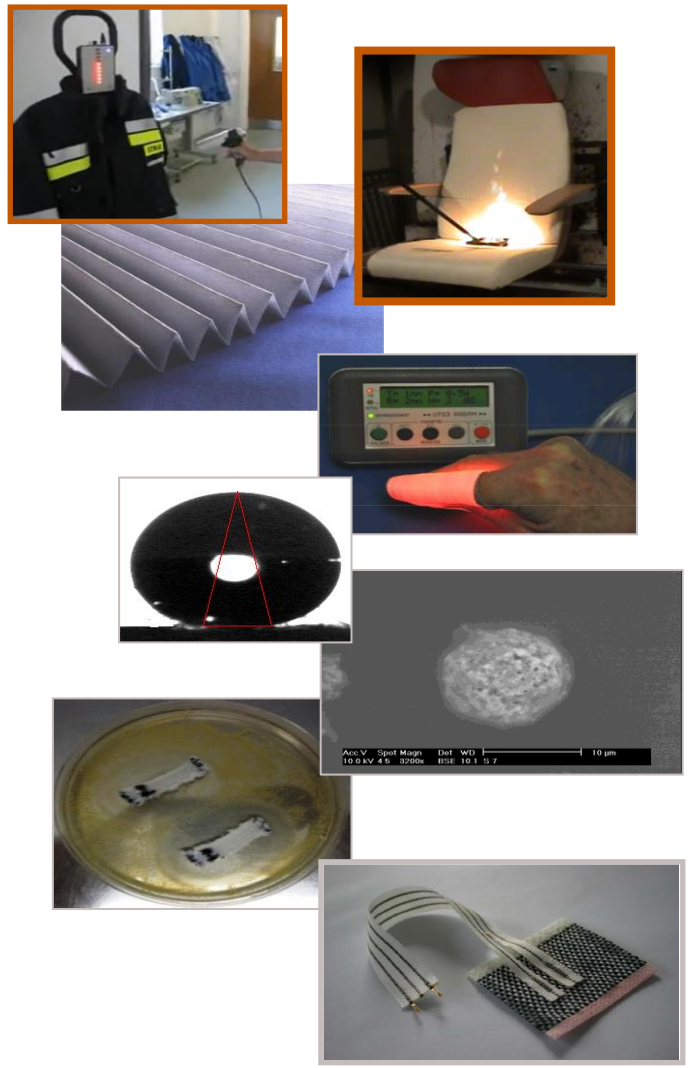
- Cosméto-textile, Antibactérien, Confort thermique

Alerte

- Capteurs (température, solvants, mécaniques), Actionneur

Energie

- Piezoélectricité, récupération RF



Context

Textile functionalization with sustainable development ?

Antimicrobial Textile

Building *Clothing* *Medical*

Flame retardant Textile

Transportation *Furniture* *Building*

Silver particles, …

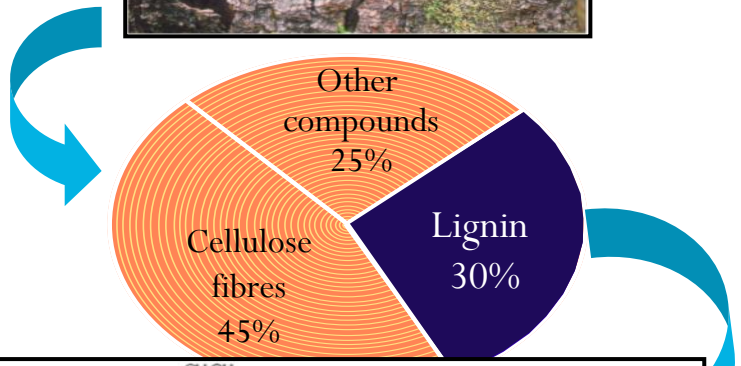
Current addtives for synthetic fibers versus environmental concerns and/or REACH regulation

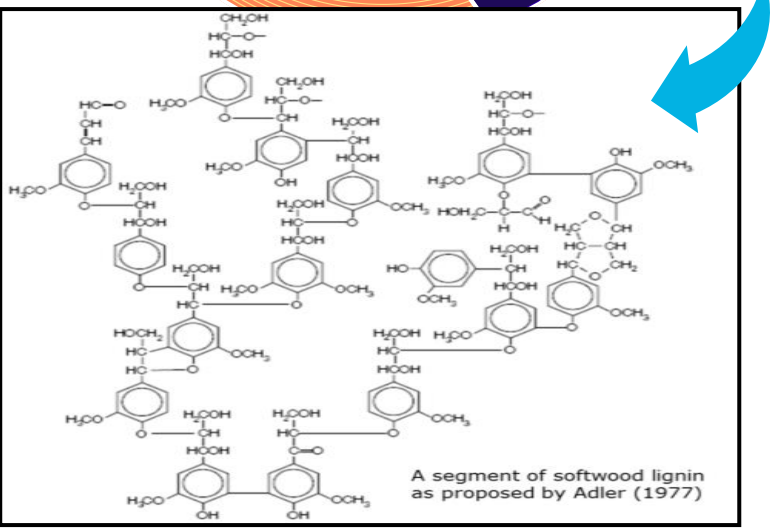
Halogenated Additives, …

use sustainable fillers

LIGNIN ?

Lignin advantages





- Most abundant polymer from biomass based on aromatic units
- By-product of wood pulping & paper industries
- Blending compatibility with other thermoplastic polymer
- Previously studied for FR and antimicrobial properties

2 kind of commercial kraft lignin tested

From Sigma Aldrich : **Kraft Lignin (KL)**

From UPM Biochemicals : **Domtar Lignin (DL)**

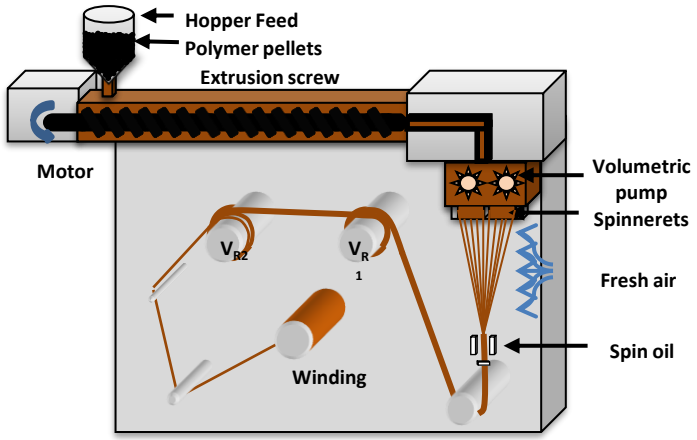
Process: functionalized synthetic fabric

Extruder
+
Granulator

Monofilament Pellets

Characterization of pellets

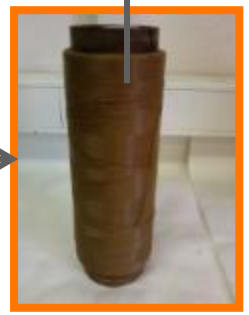
Melt spinning



Knitting machine

Knit fabric

Study of the functionalization



Characterization of multifilament

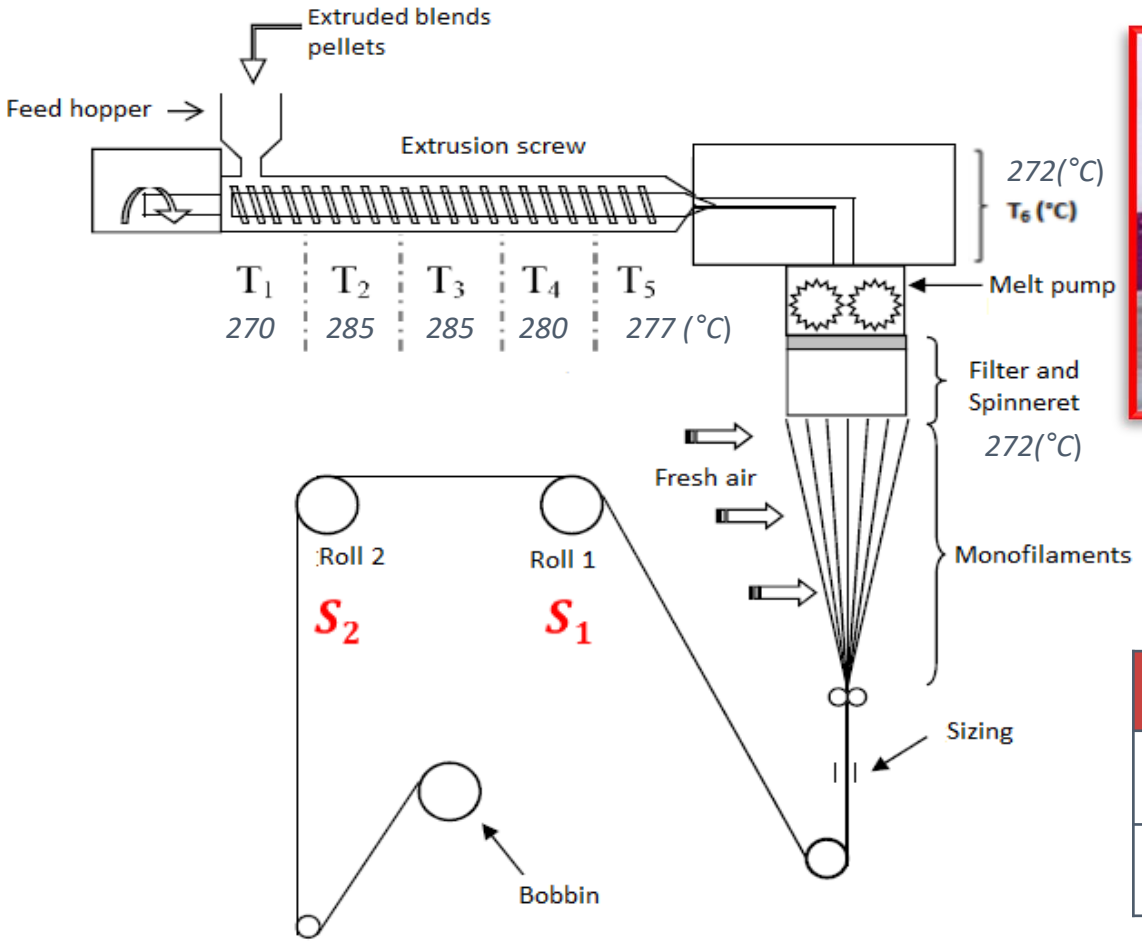
Materials

Polyester : PolyEthylene Terephthalate [PET]: the most synthetic fiber used

Additives

- From Sigma Aldrich : **Kraft Lignin (KL)**
- From UPM Biochemicals : **Domtar Lignin (DL)**
- As antimicrobial reference : **TiO_2** from KRONOS® 1071

Process : Spinning



Machine : Spinboy I

- Single screw extruder
- Pump speed: 10 rpm

Draw ratio:

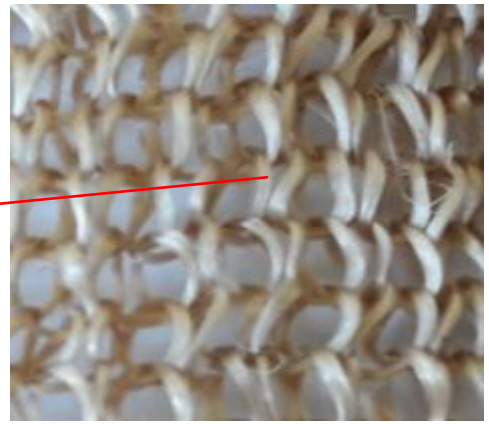
$$DR = \frac{S_2}{S_1}$$

% filler	KL	DL	TiO_2
1	DR= 2	DR= 2&4	DR= 2&4
2	DR= 2	DR= 2&4	DR= 2&4

DR=4 Not spinnable because of dispersion

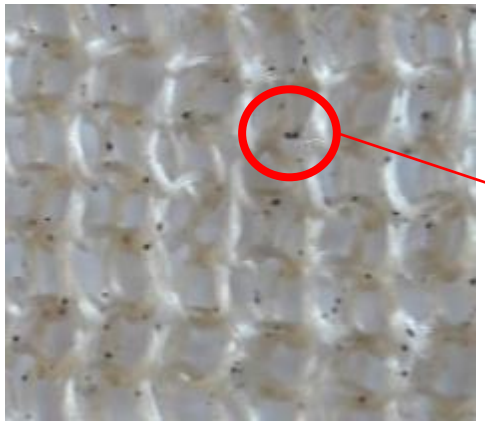
Filler dispersion (optical characterization)

- First sighting



No agglomeration

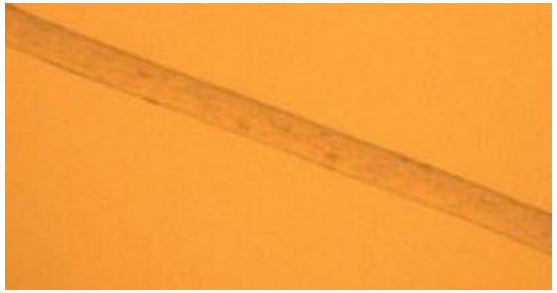
Knit: PET + 2wt.% DL



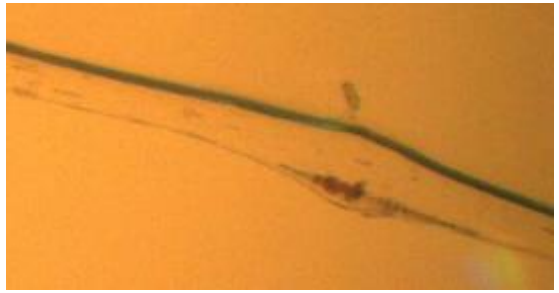
KL agglomerates

Knit: PET + 2wt.% KL

- Optical microscope : Microscope B1 Advanced Series de MOTIC



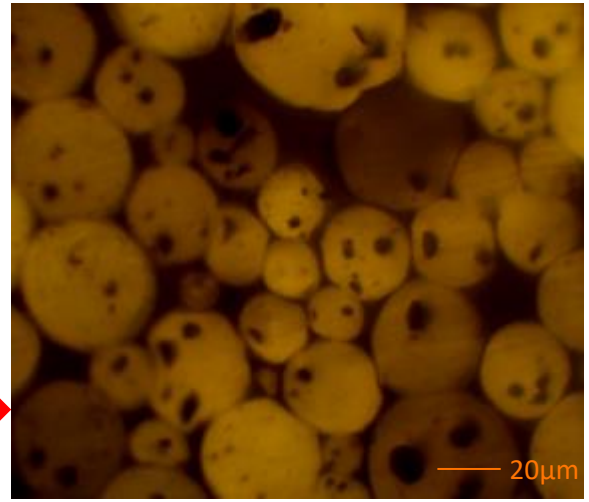
PET + 2 wt.% DL DR=2
Magnification X10



PET + 2 wt.% KL DR=2
Magnification X10

- Well dispersion of DL in the PET, not KL

Cross section



PET + 2 wt.% KL DR=2
Magnification X40

Filler dispersion (tension surface study)

Surface tension of Lignin

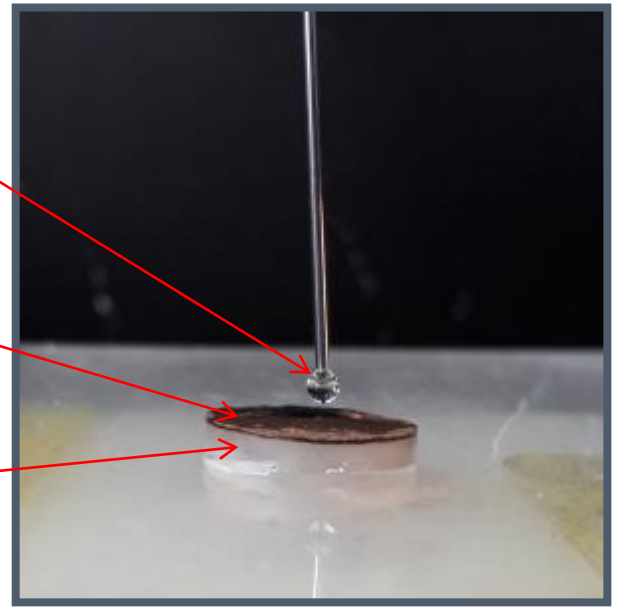
Machine : DigiDrop

(mN/m)	γ_s	γ_s^p	γ_s^d
KL	55,4	30,1	25,3
DL	53,8	37,9	15,9
PET	39,3	29,7	9,6

$$\gamma_{x/PET} = \gamma_X + \gamma_{PET} - \frac{4\,\gamma_X^{\,d}\,\gamma_{PET}^{\,d}}{\gamma_X^{\,d} + \gamma_{PET}^{\,d}} - \frac{4\,\gamma_X^{\,p}\,\gamma_{PET}^{\,p}}{\gamma_X^{\,p} + \gamma_{PET}^{\,p}}$$

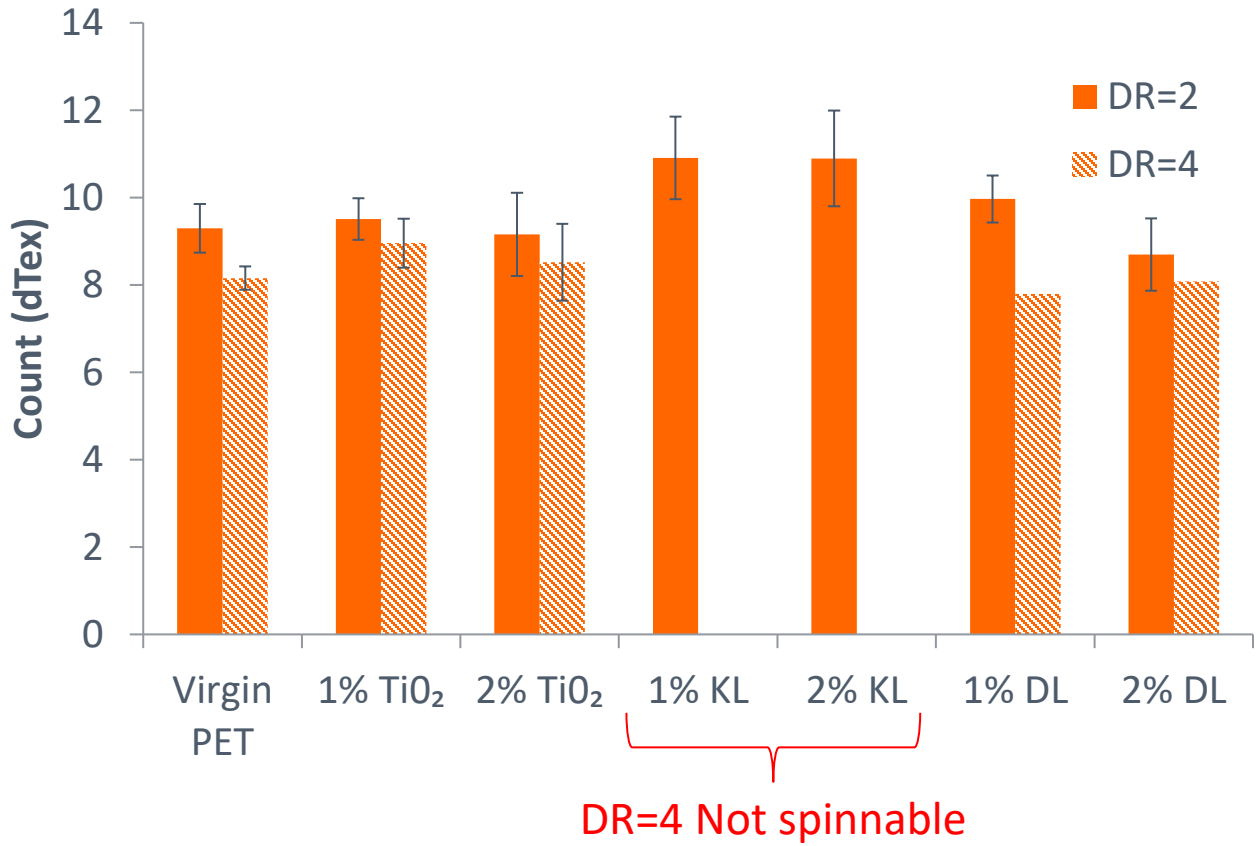
(mN/m)	$\gamma_{X/PET}$
$\gamma_{KL/PET}$	7,0
$\gamma_{DL/PET}$	2,5

$\gamma_{DL/PET} < \gamma_{KL/PET}$



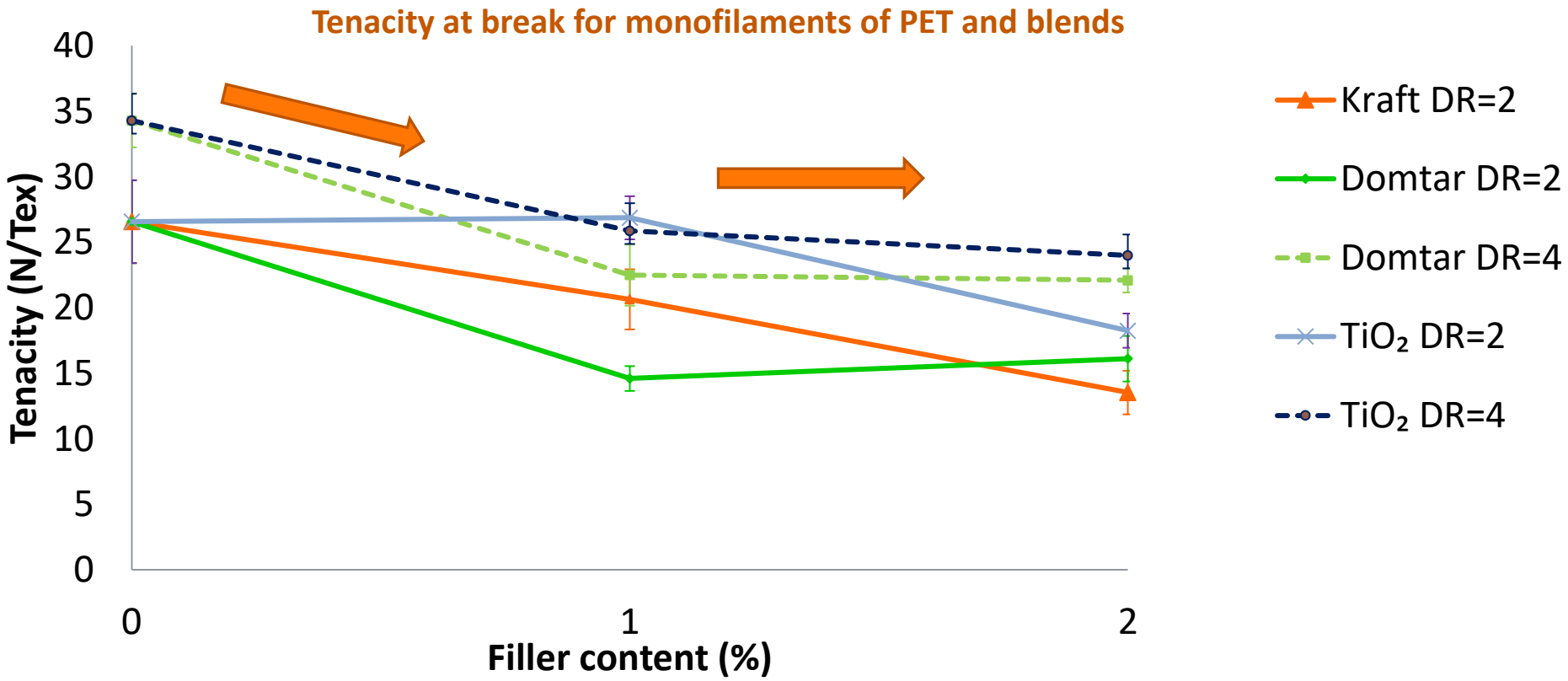
Physical characterizations of filaments

- Vibroskop LENZING INSTRUMENTS, 10 samples



Physical characterizations of filaments

- Zwick machine, Standard NF EN ISO 5079, Sample size : 20 mm, deformation rate : 20 mm/min



- KL and DL fillers increase the fragility of the PET by almost 40% but the multifilament can be transformed in textile structure
- When DR = 2 the material is less resistant than DR=4

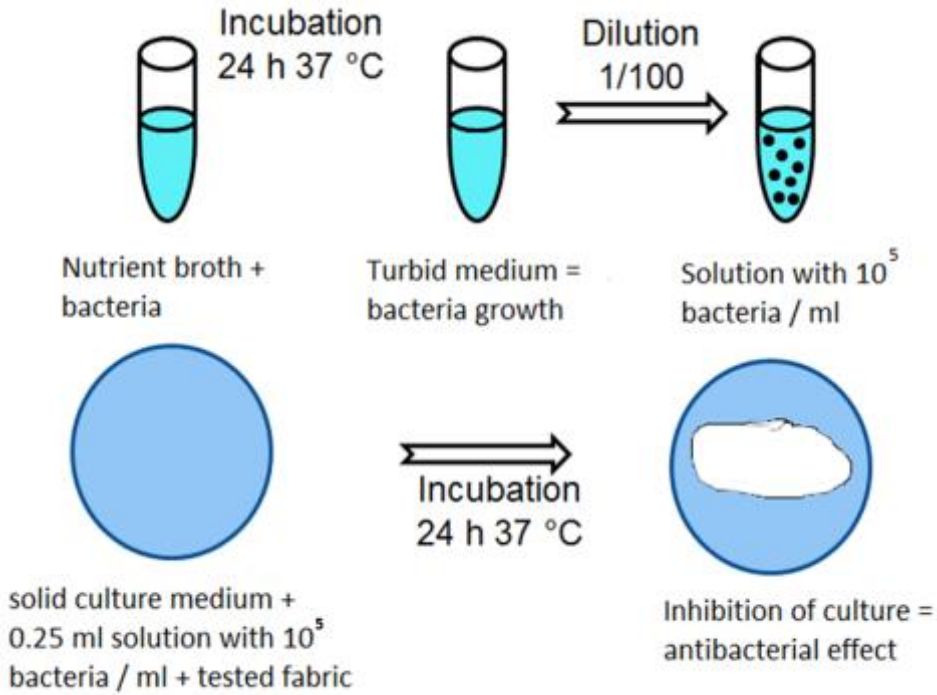
Antibacterial Test

- Desizing : knit fabrics with Soxhlet
- Sterilization : 15-20 min at 120°C
- Qualitative test : Agar Diffusion Test
- Bacteria :
  - Staphylococcus Epidermidis

Present in large amounts on the human skin constantly in contact with clothing textiles

  - Escherichia Coli

Present mainly in the intestines of mammals



Antibacterial Test

	Kraft Lignin (2% ; DR=2)	Domtar Lignin (2% ; DR=2)
Gram-positive bacteria Staphylococcus Epidermidis		
Gram-negative bacteria Escherichia Coli		

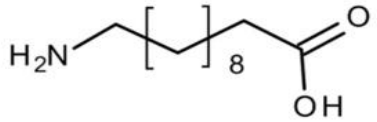
Antibacterial halo

- Both lignins have antibacterial activity more especially Domtar lignin

Materials

Rilsan® PA11 [PA]: Bio-polyamide available commercially and used in textile areas

Castor oil



11-amino undecanoic acid

Polycondensation at 220-250°C → **Polyamide 11**

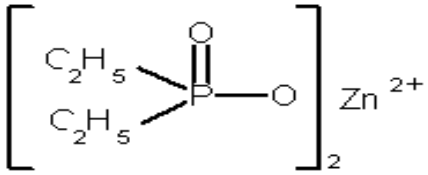
RILSAN by ARKEMA

- Low Density
- Greater Tensile strength
- Good resistance against chemical & abrasion

- Oxidation at high temperature
- Bad UV resistance
- **Low flame retardancy**

FR additive:

- **Zinc phosphinate [ZnP], Exolit OP950 (Clariant),** fusible coumpound appropiate for melt spinning



- **DCL200 Lignin from Domtar (Alkali kraft lignin) [DL]** (more comptatible than [KL])

Fire Retardant Formulations

- Additive amount set at 20 wt-%
- Study of the ratio Domtar Lignin / Zinc Phosphinate

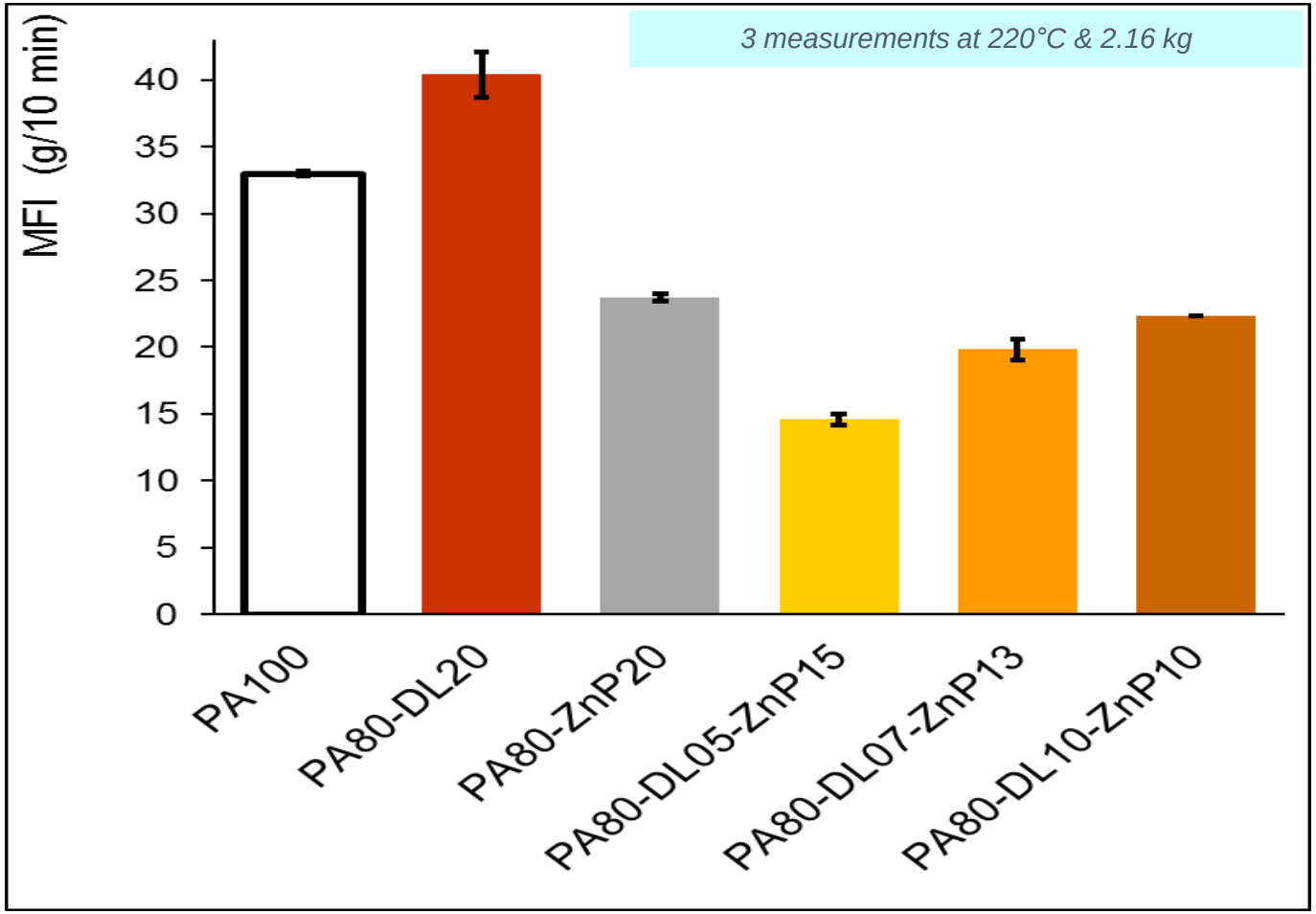
Sample	PA (wt-%)	Domtar Lignin (wt-%)	Zn Phosphinate (wt-%)
PA100	100	0	0
PA80-DL20	80	20	0
PA80-ZnP20	80	0	20
PA80-DL05-ZnP15	80	05	15
PA80-DL07-ZnP13	80	07	13
PA80-DL10-ZnP10	80	10	10

Fluidity (MFI) Measurement

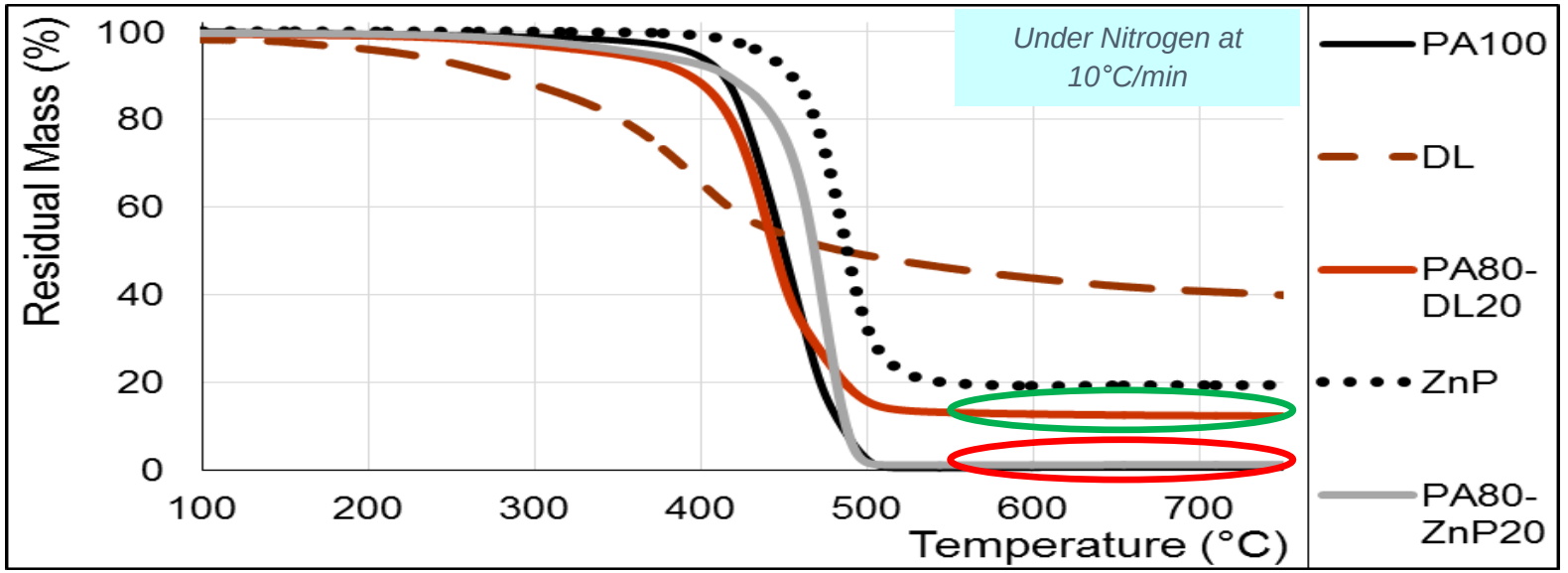
- Melt Flow Index (MFI) :
  Key parameter to get indication for the melt spinning

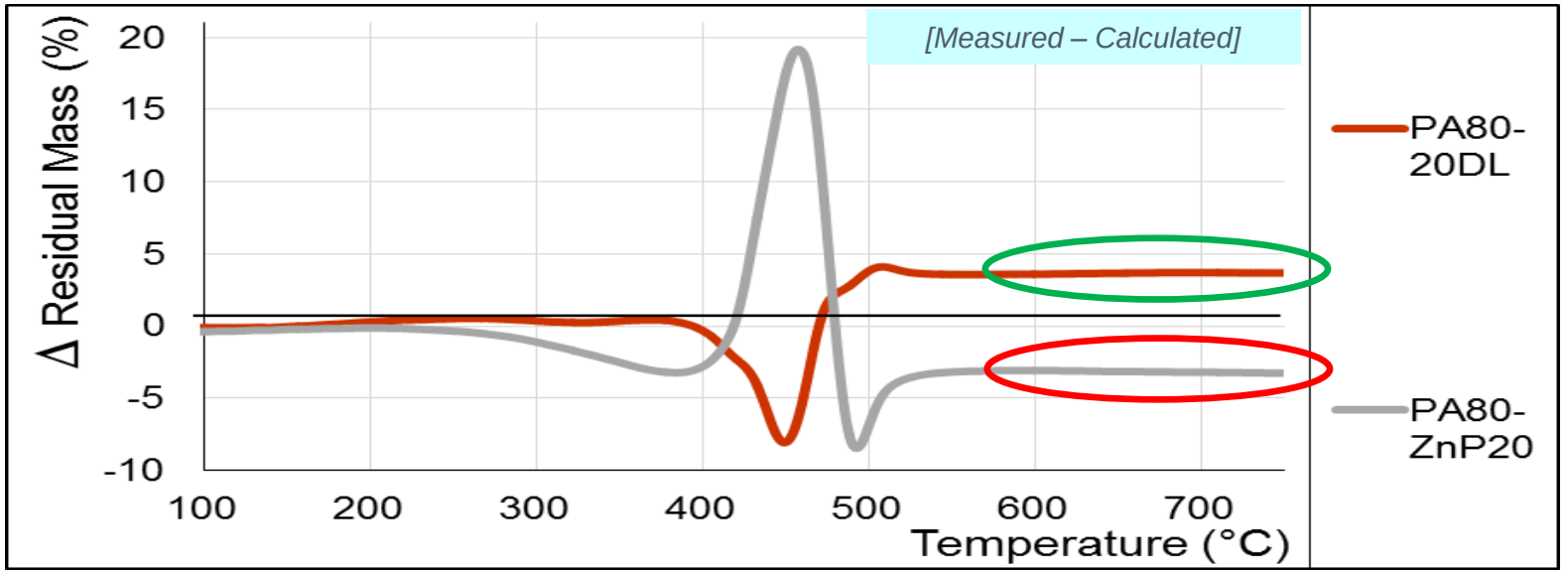
$$\text{Fluidity (MFI)} \propto \frac{1}{\text{Viscosity}}$$

- **Addition of Domtar lignin** leads to higher fluidity
- **Addition of ZnP** leads to higher viscosity
- **Ternary blends** keep MFI compatible with spinning process (15-30 g/10 min)



Thermal degradation analysis





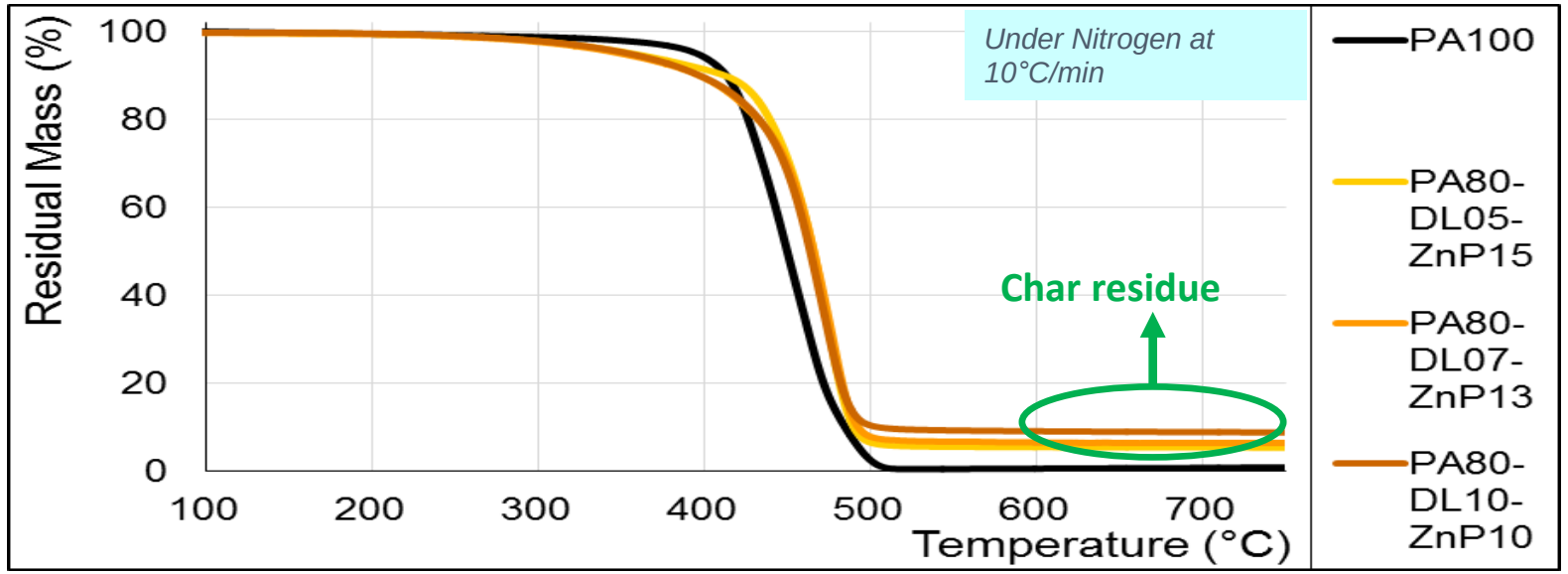
- **Phosphinate addition in PA**

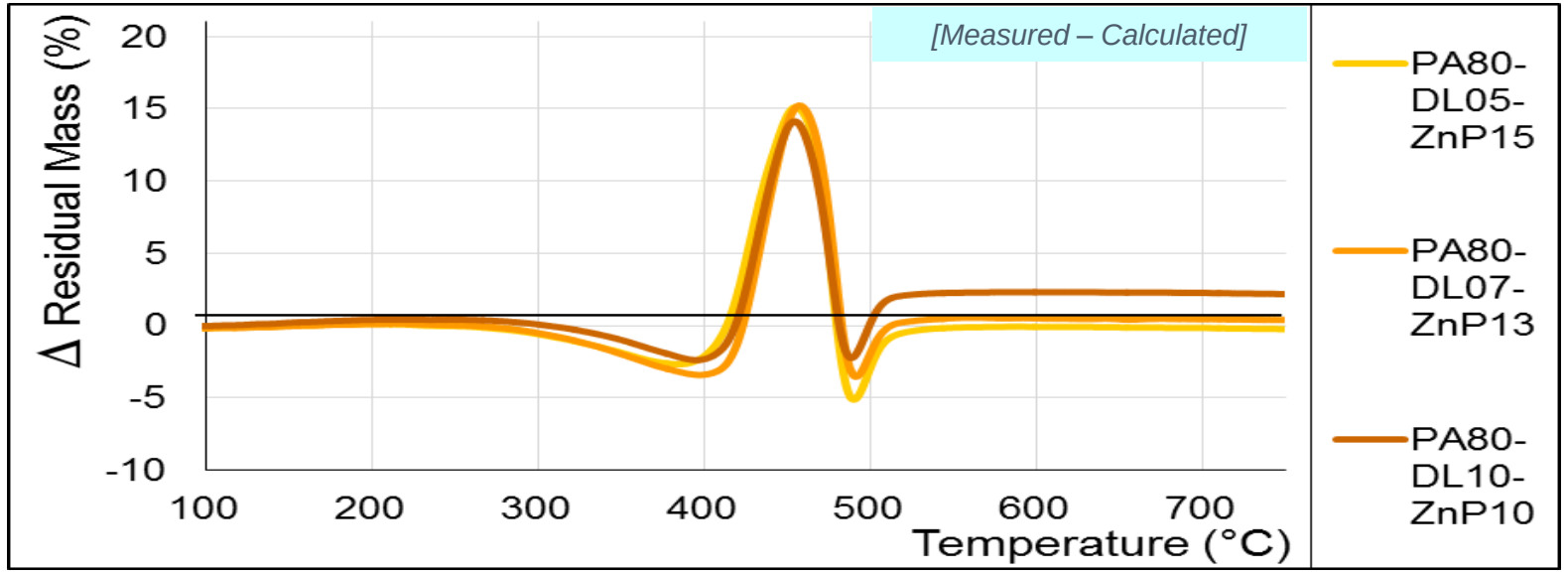
  Shift of main degradation step but no residue

- **Lignin addition in PA**

  High charring efficiency, significant amount of char after 500 °C

Thermal degradation analysis

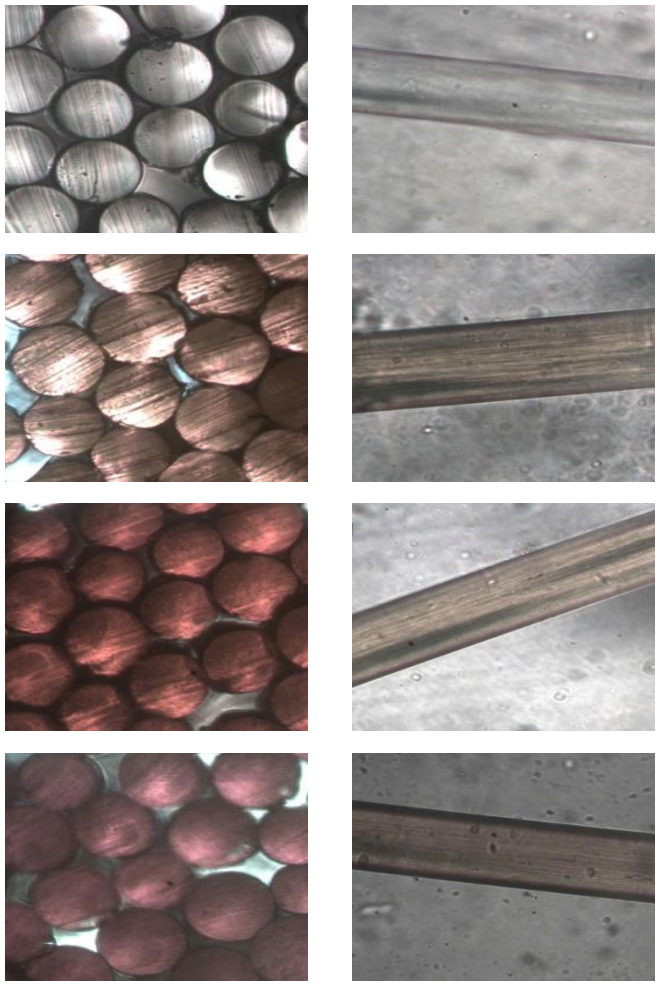




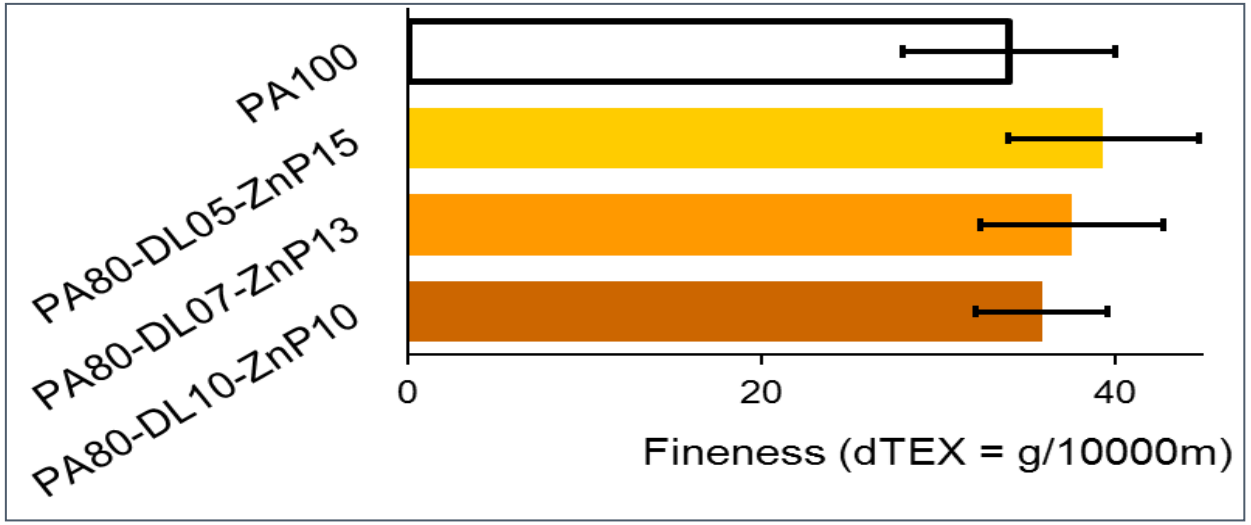
- ✓ ***PA blends in combination with phosphinate and lignin***
  - Interaction of lignin and phosphinate initiate degradation before PA11
  - Thermal stability of blends shifts towards higher temperature by 50 °C
  - Noticeable char residue between 600 – 700 °C

Physical characterizations of filaments

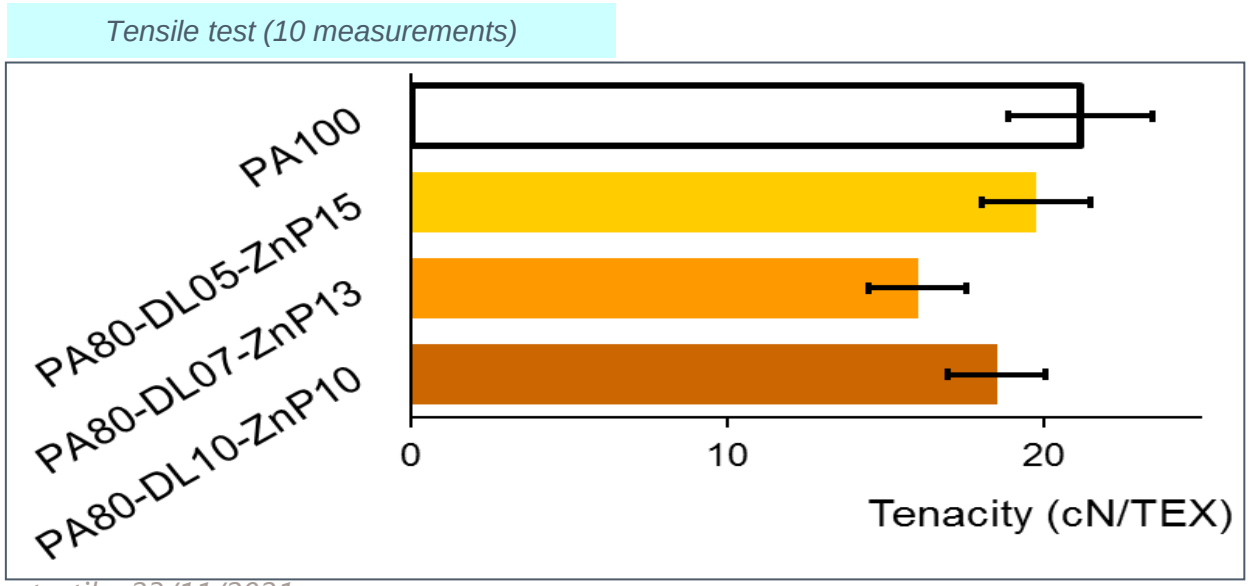
Optical microscopy (x20)
cross section & longitudinal view



Vibroscope (10 measurements)



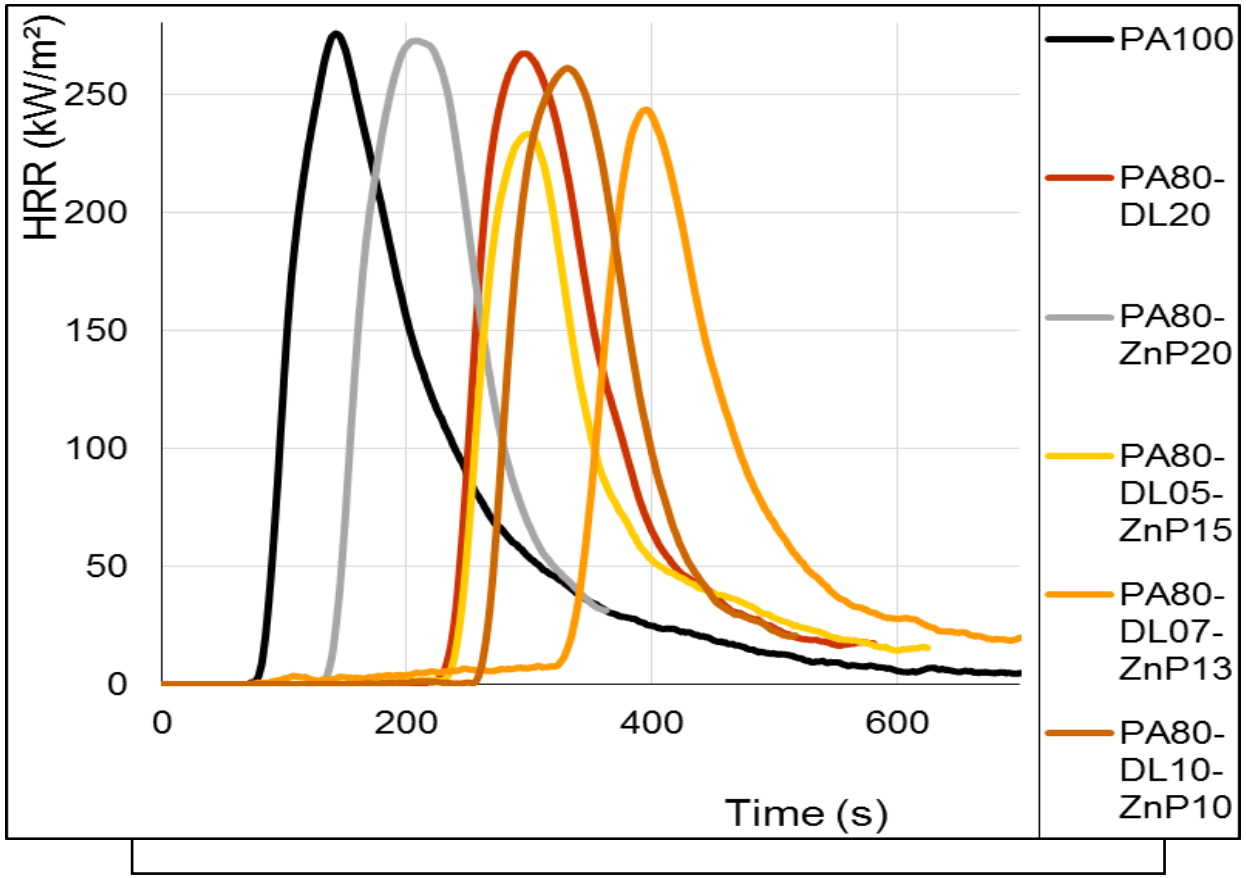
Tensile test (10 measurements)

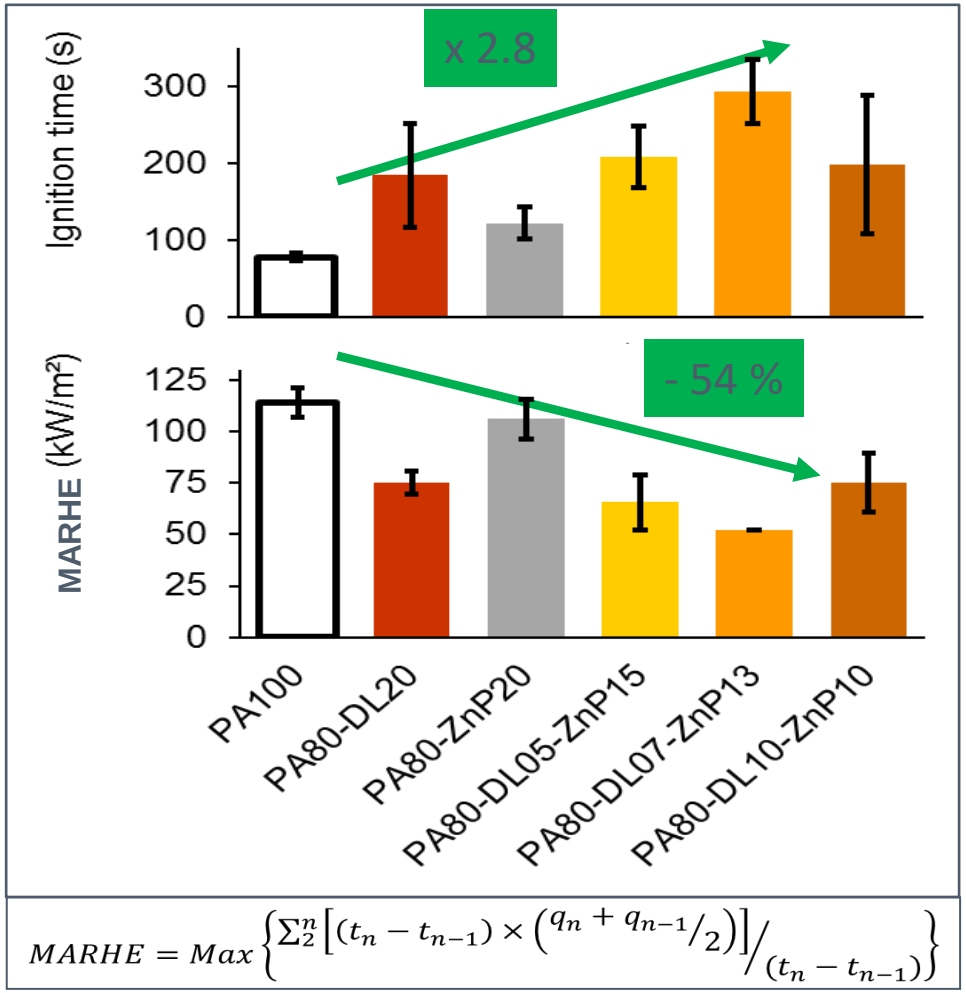


Fire behavior analysis (cone calorimeter)

Characteristic of samples : knitted fabrics 1400 g/m² (± 100 g/m²)

Under external heat flux 35 kW/m² & specimen size 100x100x3 mm³ with grid





$$MARHE = Max\left\{\Sigma_2^n\left[(t_n - t_{n-1}) \times \left(q_n + q_{n-1}/2\right)\right]/(t_n - t_{n-1})\right\}$$

Best FR action with 7% lignin – 13% ZnP

Fire behavior analysis (cone calorimeter)

PA100

PA80-ZnP20

PA80-DL20

PA80-DL05-ZnP15

PA80-DL07-ZnP13

PA80-DL10-ZnP10

- ✓ Noticeable quantity of residue (charring effect) only in presence of lignin
- ✓ Obvious intumescence effect for ternary blends : ignition delayed by the intumescent char layer but not enough strong in order to have a significant HRR decrease

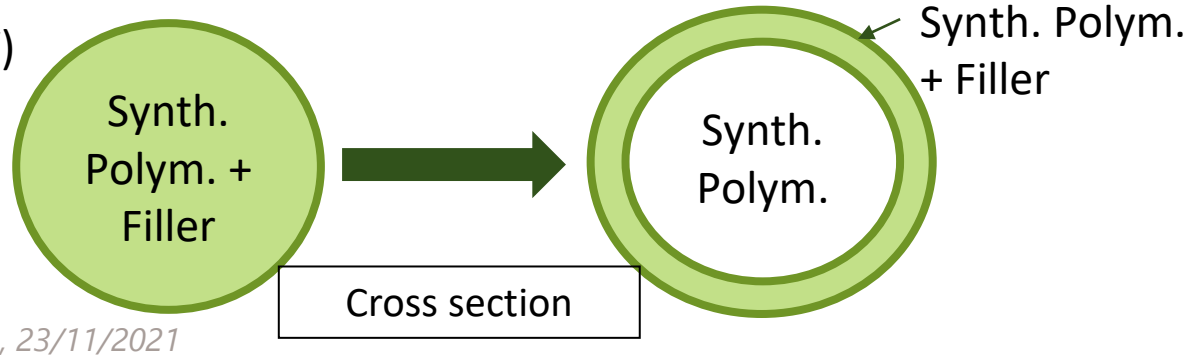
Conclusions & Perspectives

Conclusions:

- Domtar Lignin has better dispersion and antibacterial properties than Kraft lignin
- Both lignins decrease the mechanical properties but multifilament can be transformed in textile structure
- Domtar lignin improves the fire reaction with charring effect and a lower loading content of phosphorus additive

Perspectives :

- Studying the antibacterial and flame retardant properties on a fabric with a unique lignin formulation
- Testing the durability of anti-bacterial and flame retardant properties
  - > Washing (rain)
  - > Weather conditions (temperature, humidity, UV)
- Bi-component filament



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