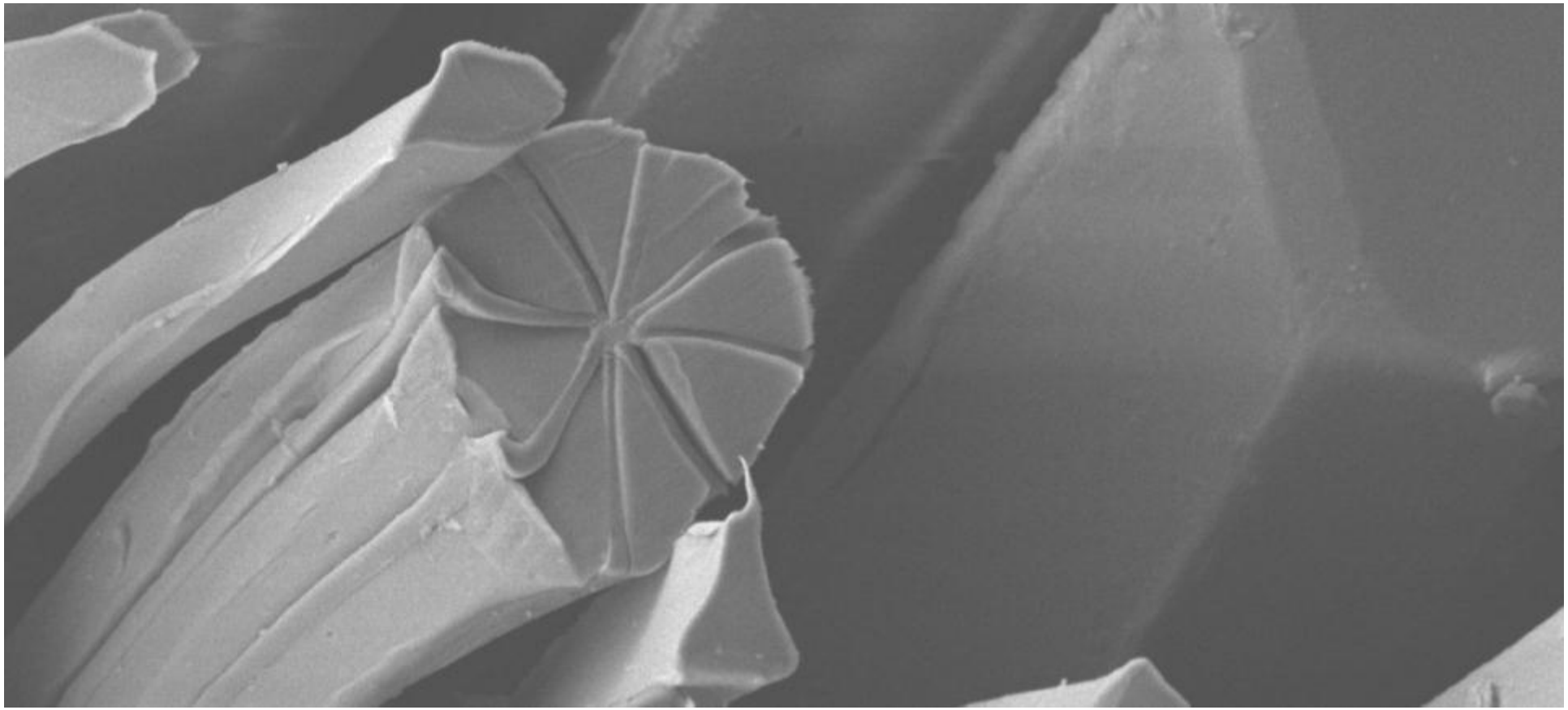


Bio-polymer based fibres & biofunctional coatings

Luc Ruys & Myriam Vanneste,
R&D managers, Centexbel, Belgium

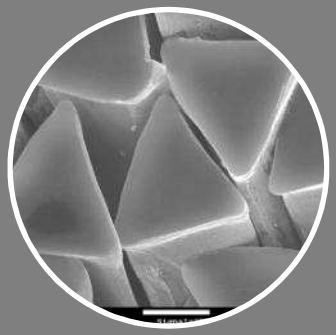
Content

- Centexbel: Textile competence Centre
- Market developments in Biobased polymers
- Examples of Biobased fibres developments
- Examples of Biobased resins & coating formulations
- Conclusions

Centexbel: textile competence centre

- Collective research and technical centre
  - Governed by the industry
- Membership organisation
  - Belgian textile companies
  - Associated (international) member companies and organisations
- Staff
  - 150 skilled and highly educated men and women

Research: Technology Fields

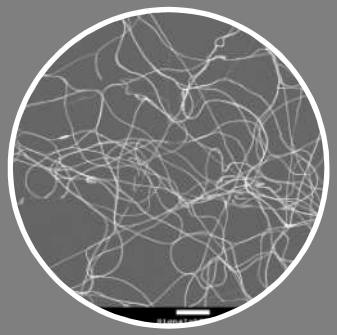


Functional thermoplastic textiles

- Meltprocessing of polymers in textiles and composites

Textile functionalisation and surface modification

- Coating, finishing and surface modification for new and superior functional performances



Health, safety and security

- Textile products for health, safety and security purposes

CENTEXBEL

VKC–Centexbel: plastic competence centre

- VKC, a division of Centexbel, expands our services to the plastic industry
  - Technological advice
    - materials, finished products and recycling
  - Material characterisation
  - Plastic processing platform
    - Compounding, injection moulding, extrusion, thermo-forming
  - Research

Content

- Centexbel: Textile competence Centre
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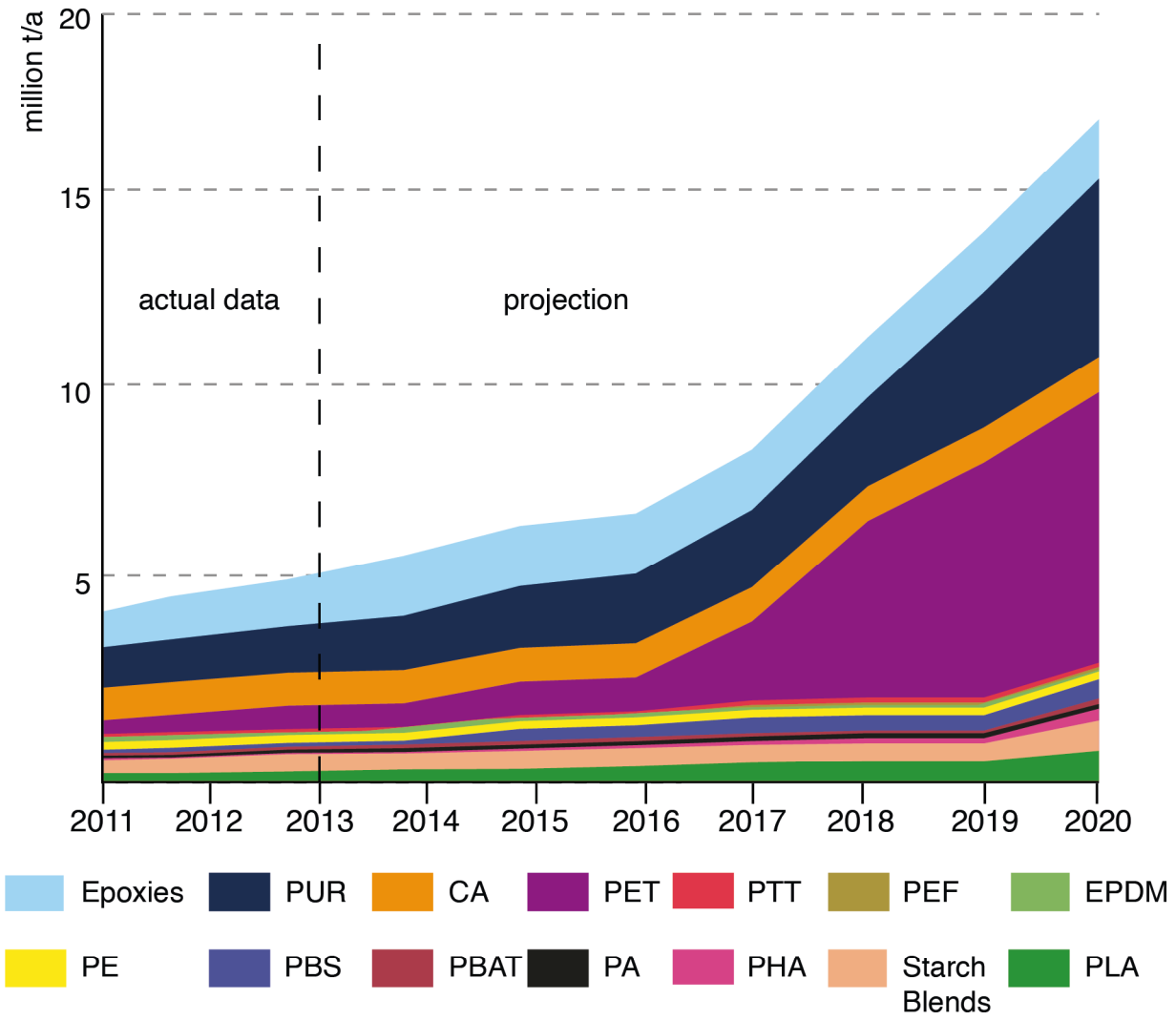
- Conclusions

Market development biobased polymers

- Developments on-going for > 10 years
- A lot of research performed
- Attracts a lot of attention
  - Are expectations fulfilled?
  - Is there suffient process & product development?
  - Large break-through or eye-catcher innovations?
- People are getting somewhat impatient

Bio-based polymers: Evolution of worldwide production capacities from 2011 to 2020



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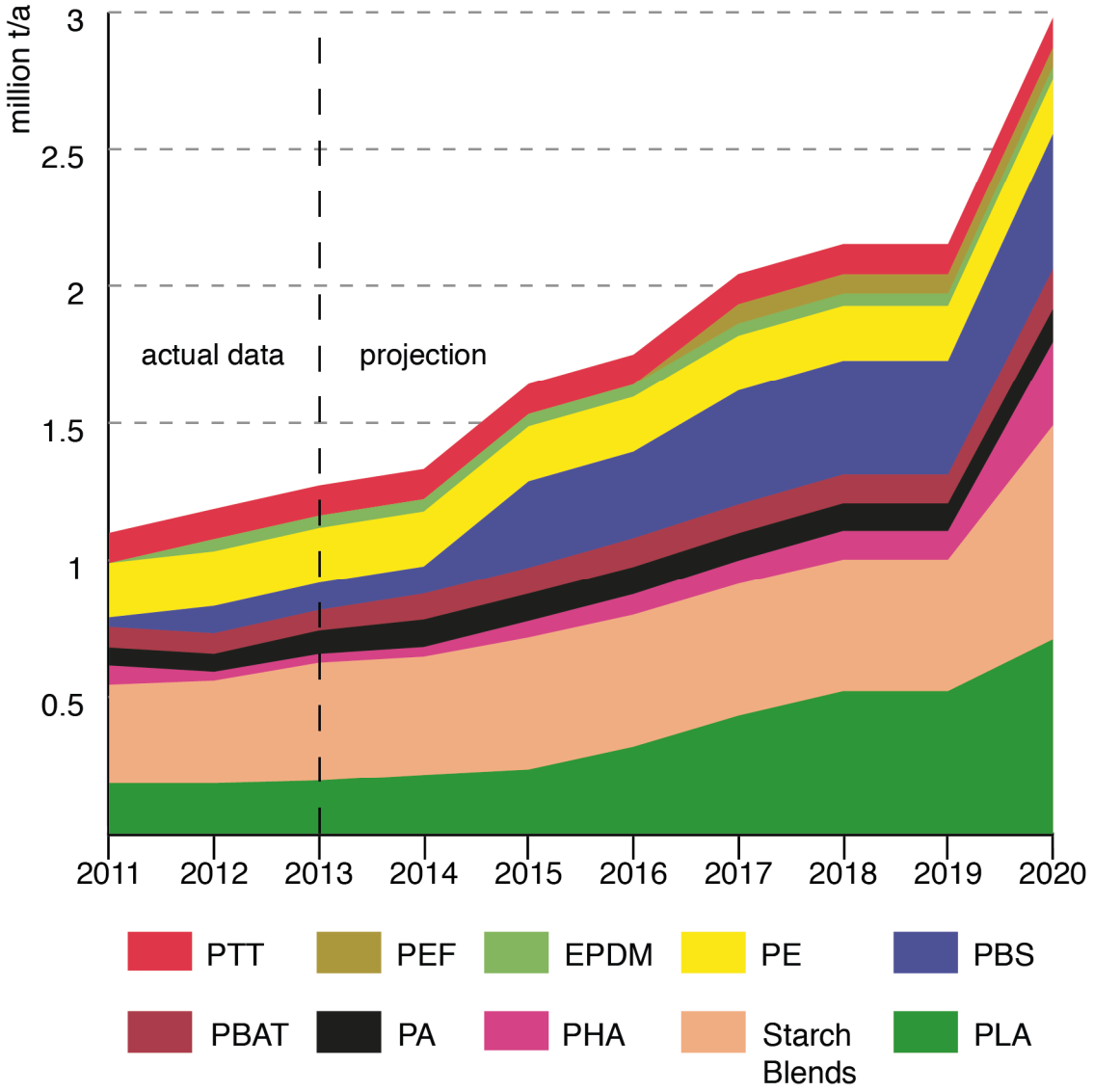
Market development biobased polymers

- Constant Growth
- Positive expectations for coming 5 years:
  > 15 million/year
- Largest growth in drop-in biopolymers:
  - **Bio-PET**, Bio-PE
- Not only thermoplastics
- Also resins and coatings
- Growth in the USA and Asia (except TPS)

Selected bio-based polymers: Evolution of worldwide production capacities from 2011 to 2020



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Market development biobased polymers

- If focus on novel Bio-thermoplastic
  - TPS dominating (limited in textiles)
  - PLA growing in importance – taking the lead
  - Huge growth expected for PBS
  - PHA less pronounced growth
  - PEF – biobased durable aromatic polyester; newcomer with large potential? – first application area plastic bottle

Constant need for research and innovations

Content

- Centexbel: Textile competence Centre
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- Conclusions

PLA: Agrotextiles

- Bioagrotex: FP7-NMP 2007-2012
- Industrial products launched based on PLA
- Groundcovers
  - Needlefelt – DS Textiles: Hortaflex®
  - Woven Tapes – Bonar: Duracover®
  - Insect netting – Texinov: FILBIO®
  - Growing implementation
- Public Procurement France: groundcovers

PLA: Agrotextiles

Hortaflex

Duracover

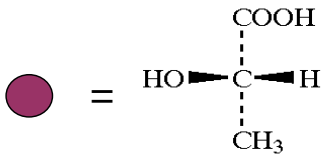
FILBIO

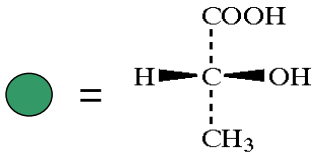
Jute Agrotextiles: **SUSTAFFOR**

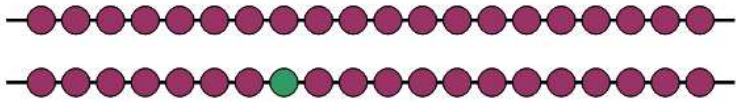
- FP7-SME-2013-606554: **SUSTAFFOR**
- Field tests of groundcovers in forestation action in synergy with soil-conditioners
- Tests in different climate zone in Spain
- On-going project
- Intermediate results show positive effects

Effect of PLA grade

- PLLA with low D content
  - L-lactic acid
  - D-lactic acid





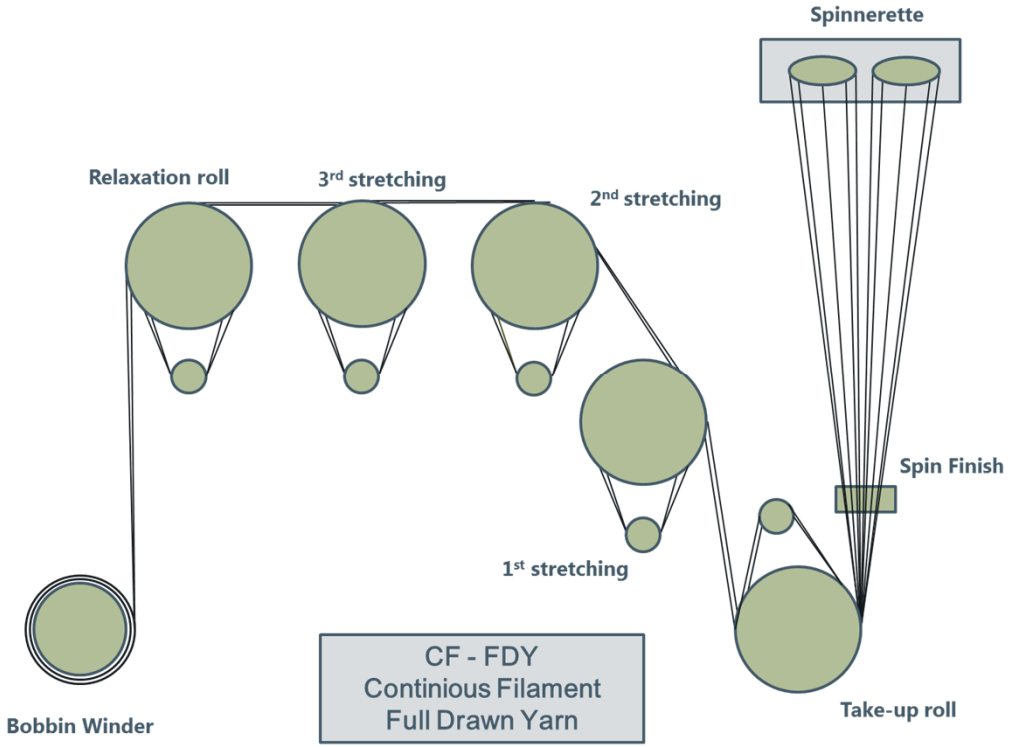


Tm 175 °C
Tm 165 °C

MVR @210°C [cm^3/10min]	%D [wt%]	T_{melt} [°C]
6 | low	2 | high	166
21 | high	0,3 | low	175
12 | medium	<0,1 | low	177
5 | low	<0,1 | low	174
6 | low	<0,1 | low	176

Multifilament extrusion: process

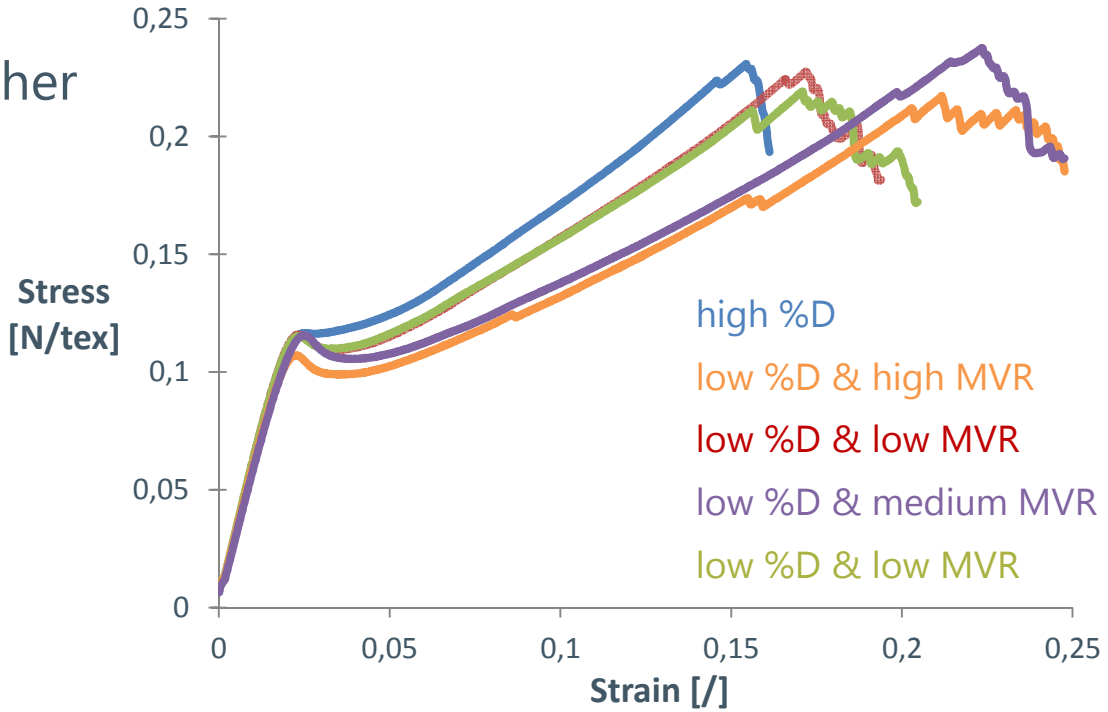
- Process type: Fully Drawn Yarn (FDY)
  - 1 step process: extrusion + 3-step cold drawing



Effect of PLA grade

Grades with low D content

- → still a yield point
- → can be stretched further



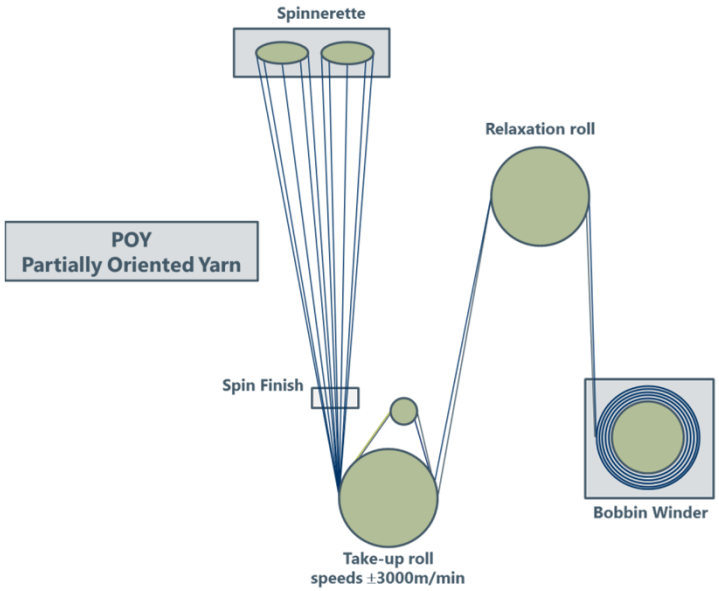
When max. stretching (↑ roll speed) is applied

- → 0,27 N/tex

CEN TEX BEL

POY extrusion: process

- Multifilament extrusion at high take-up speed
  - up to 3500 m/min



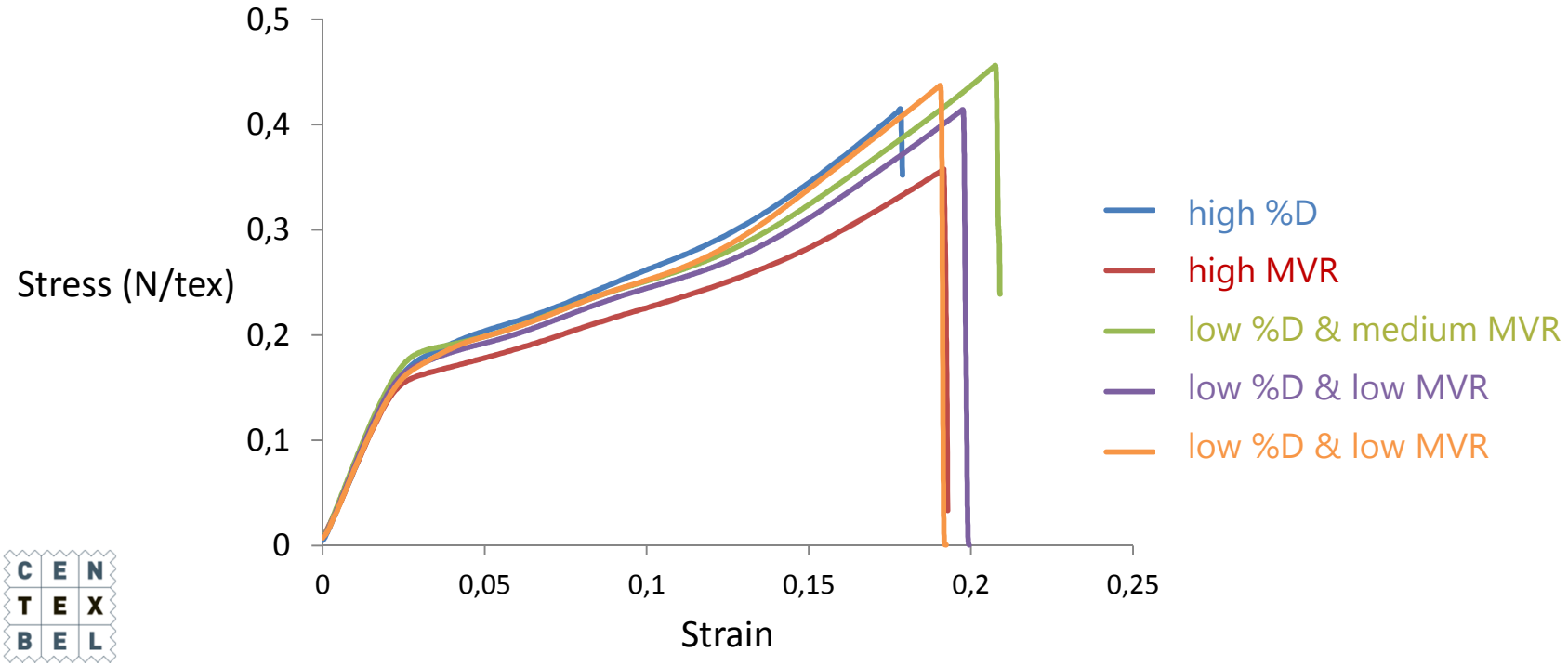
- Fully stretching of yarn on monofilament extrusion line (stretching through oven)

Effect of PLA grade

Best tenacity & stiffness for PLA grades with

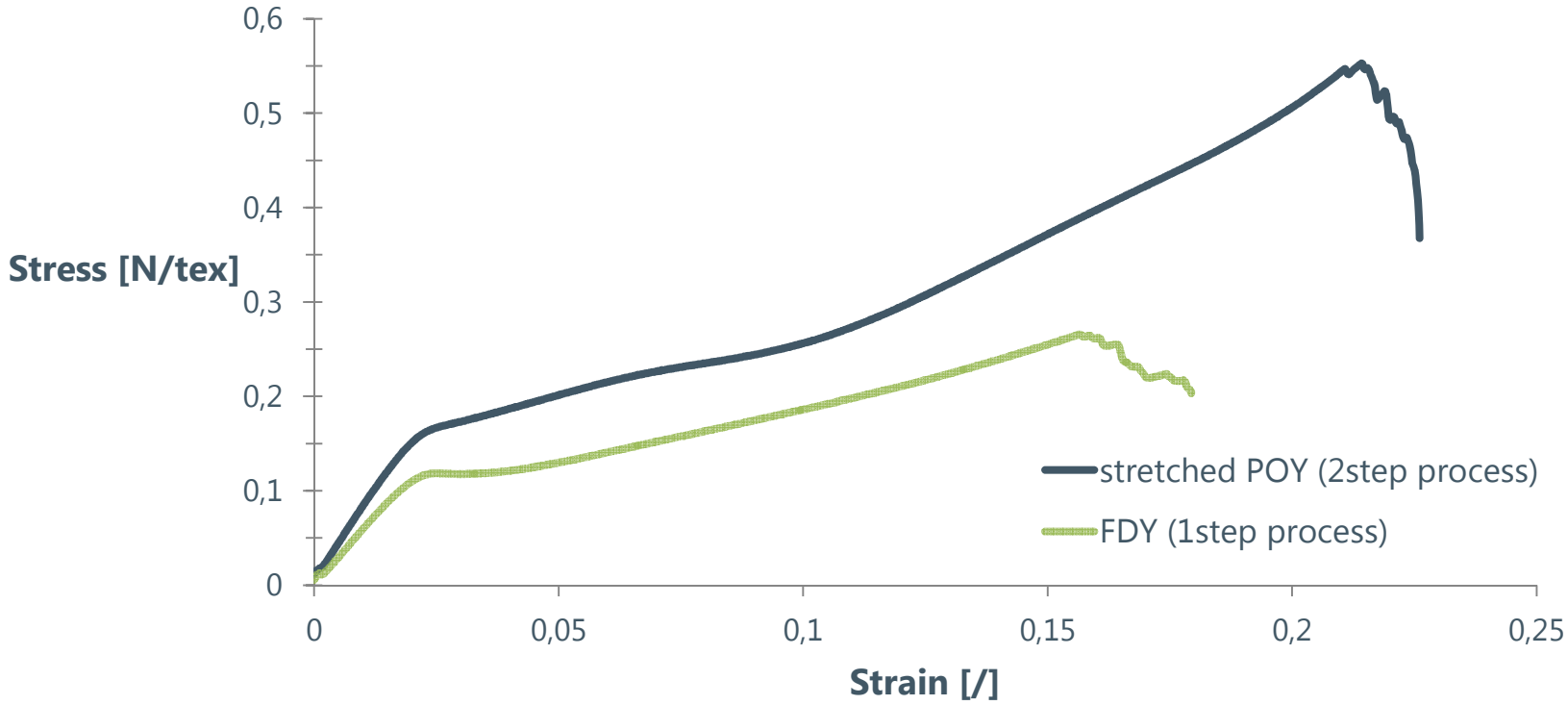
- low to medium MVR
- low D content

→ tenacity 0,45 N/tex & modulus 9,5 GPa



Comparison between stretched POY & FDY

- Very significant increase in tenacity & stiffness thanks to 2-step process
- Offers opportunities in composite applications

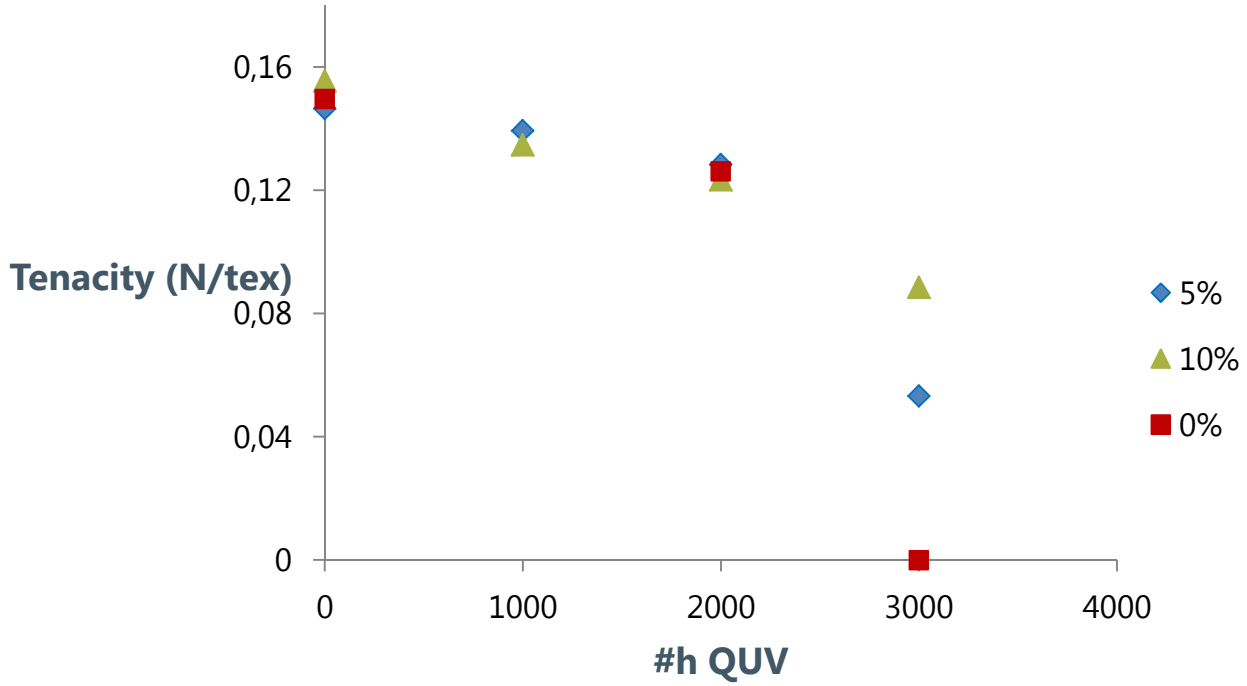


PLA: Improvement of UV stability

- Standard PLA yarns relatively stable under QUV ageing
- Further increase in stability if needed for certain applications
  - via addition of UV-stabilisers
  - realised by stabiliser addition during multifilament extrusion
    - → no effect on processsing
    - → no effect on mechanical properties

PLA: Increase in UV stability

- Addition of 5 and 10% UV stabiliser masterbatch
- Careful selection required.



PLA: stabilisation against hydrolysis

- PLA is stable at high temperature
- PLA less stable at high temp. (80°C) and 80 % rh
- Commercially available stabiliser tested
- 2 types tested
  - monomer-based
    - end capping of PLA chains
    - avoids hydrolysis & increased durability
  - oligomer-based
    - endcapping & crosslinking of PLA chains
    - increased melt viscosity & mechanical properties

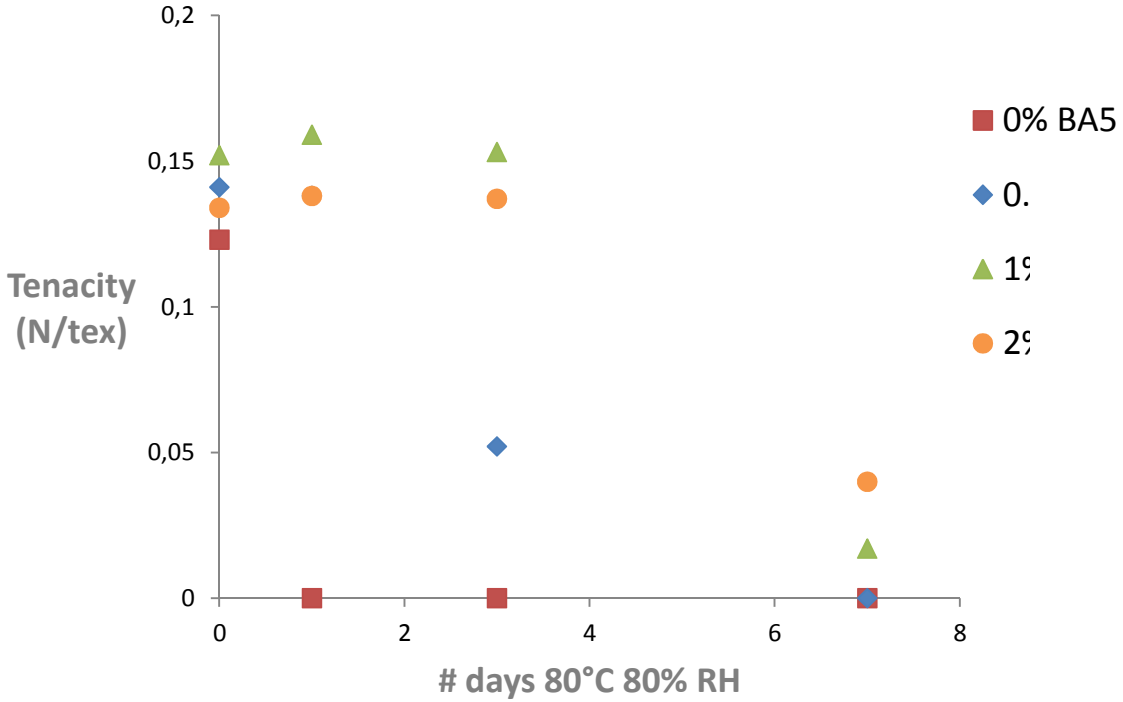
Addition of hydrolysis stabilisers

- Multifilament extrusion
  - possible to extrude
  - monomer based: no changes to process & properties
  - oligomer based: more difficult process & lower max. draw ratio
    - → slight decrease in mechanical properties

- Evaluation of hydrolysis stability
  - in climate chamber at 80 °C & 80% RH

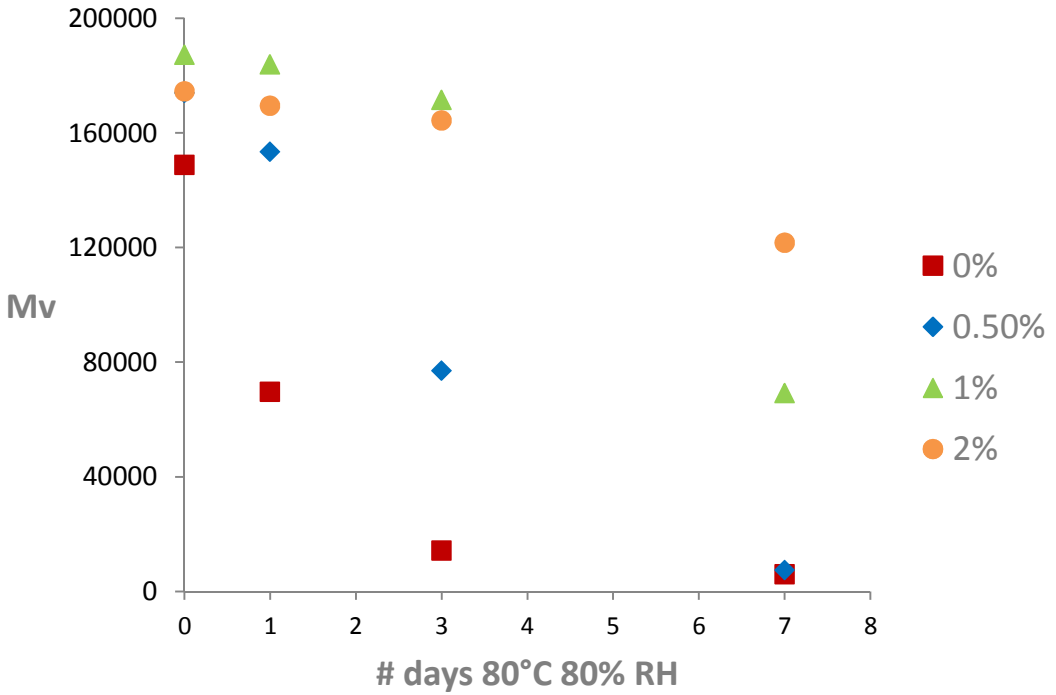
Increase in hydrolysis stability

- Tested in climate chamber at 80 °C & 80% RH
- Reference: after 1 day complete loss of properties
- With stabiliser significant stabilising effect



Increase in hydrolysis stability

- Decrease in molecular weight
  - significant less decrease in molecular weight for hydrolysis stabilised filaments



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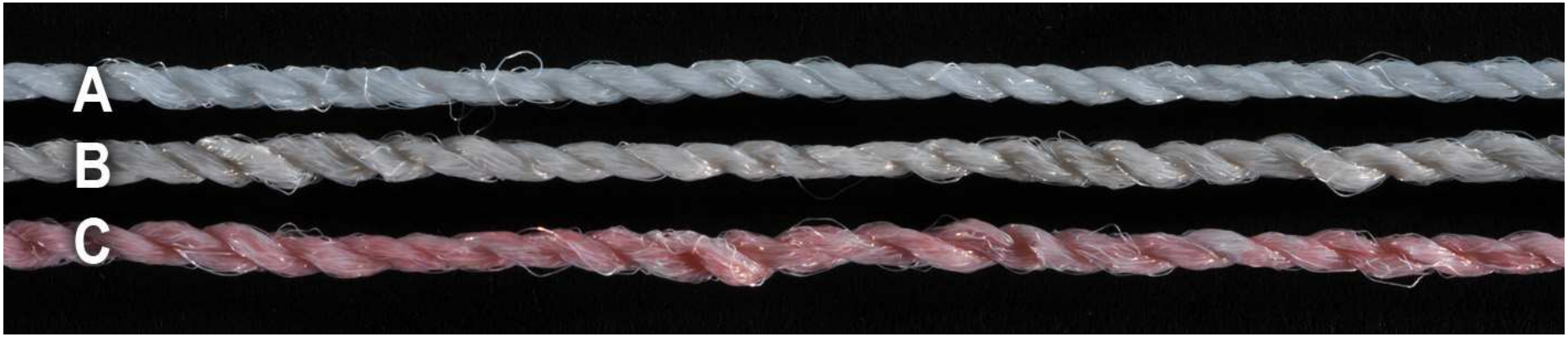
Biopolymers: anti-staining

- Anti-staining: Tannic acids
  - A = untreated PA yarn (not immersed in Cool Aid)
  - B = tannic acid treated PA yarn immersed in Cool Aid and washed with water
  - C = untreated PA yarn immersed in Cool Aid and washed with water



Anti-microbial: Thymol + carvacrol (CTB)

- Water:ethanol (4:1)
- 0.3% thymol + 0.3% carvacrol

S. aureus	**Test specimen**	**ZI (mm)**	**Growth underneath sample**
Side A	1	(9-7) 1**	No
	2	(10-9) 1**	No
Side B	1	(10) 0.5**	No
	2	(11) 1**	No

E. coli	**Test specimen**	**ZI (mm)**	**Growth underneath sample**
Side A	1	(<1) 0	No
	2	(<1) 0	No
Side B	1	(<1) 0	No
	2	(<1) 0	No

Chitosan

- Shake flask test

- Reduction of Gram- (*K. pneumonia*) and Gram+ bacteria (*S. aureus*) after 1, 5 and 24h

	Reduction (%) of *K. pneumoniae*			Reduction (%) of *S. aureus*		
	1h	5h	24h	1h	5h	24h
Co	36.8	-1163.2	-1426.3	-8.4	-8.4	-8.4
Co + 1% chitosan	93.2	99.99	99.9	74.8	96.8	99.9
Co + 5% TCA + 1% chitosan	99.7	99.99	99.99	96.6	99.8	≥99.99

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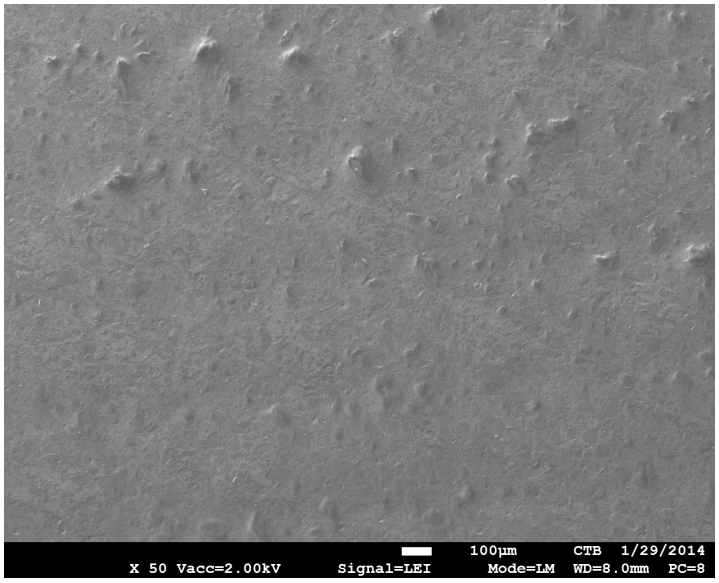
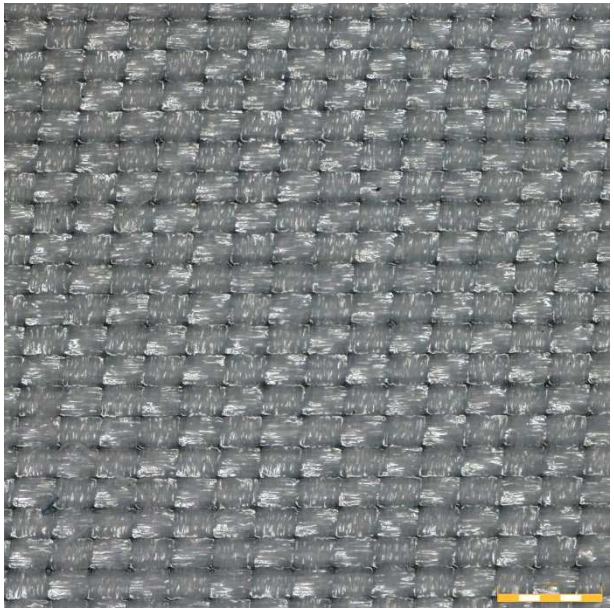
PLA applied as top-coat

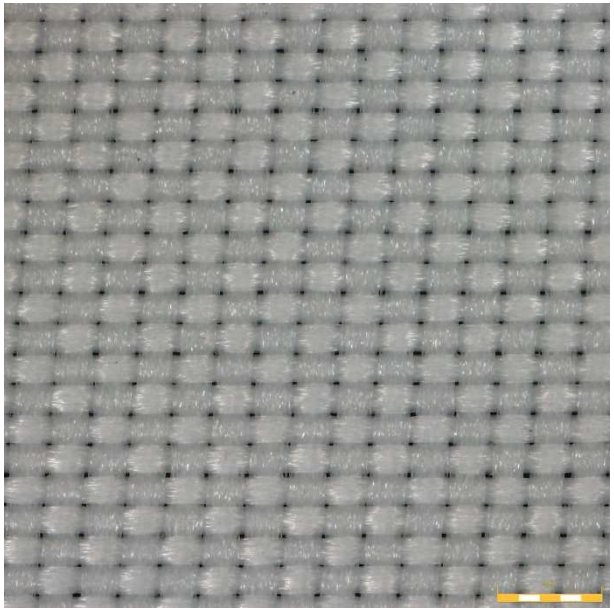
- PLA in topcoat and adhesive layer
- Multiple layers: flexible coating
  - Crumple flex: no cracking after 8 000 cycli
- UV test: OK



PLA applied as top-coat: QUV test

- PLA coating
  - No degradation and not fragile
  - PES fabric: dull white color by UV





Conclusions

- Biobased products: monomers, polymers, resins, finishing agents are still in full development
- Growth potential is still intact.
- More initiatives are needed in Europe especially on production of biopolymers.

More incentives are needed to support the European biobased polymer production

Aknowledgement

- Reported results are linked to several research projects subsidised by Differnt Authorities:
  - IWT: Flanders
  - AIF: Germany
  - Europe: FP7

- THANKS FOR YOUR ATTENTION

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