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KNRTU-KAI, Kazan, Russia

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THE BASIC OF KNOWLEDGE ABOUT BIOCOMPOSITES AND BIODEGRADABLE MATERIALS

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PK

Course goal

Development of knowledge and skills in the field of environmentally-friendly engineering materials competitive with traditional materials

The course describes traditional materials as well as modern ones and it is focused on biopolymers and their composites (natural and synthetic or modified) obtained from different kinds of biomass feedstock

Learning outcomes

Knowledge of:

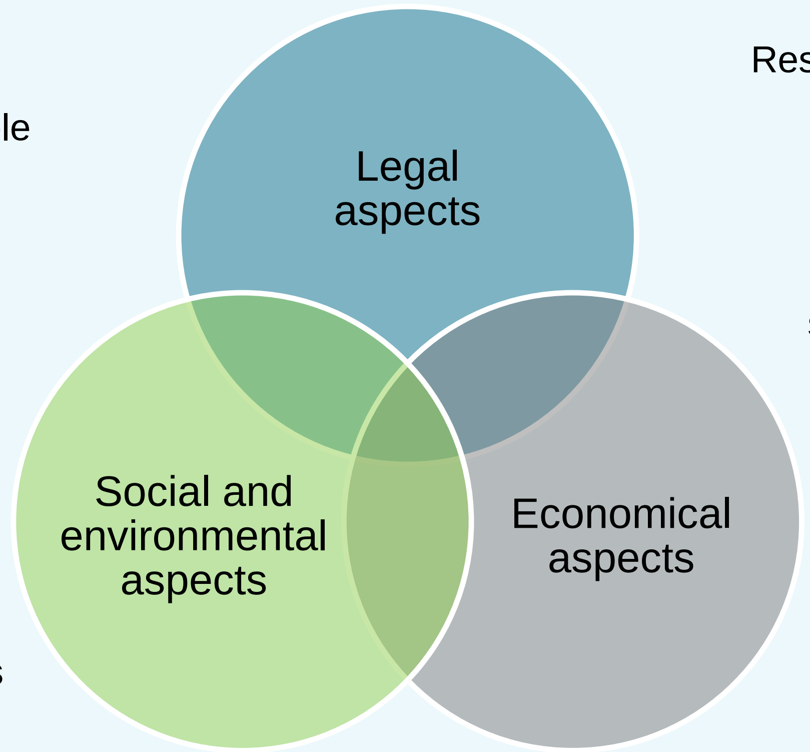
- **basic definitions and classifications connected to materials obtained from renewable sources**
- **advantages and disadvantages of using renewable and non-renewable sources in materials synthesis, processing and use**

Why to teach about it?

Depletion of non-renewable resources

Eco-politics, possibility to get founds, projects, etc.

Eco-fashion, green-thinking consumers



Restrictions on CO_2 emission

Regulations on recycling for packaging, automotive, E&E sectors

Rising prices of raw materials

Green marketing

It is not to compliment biobased materials and deplore non-renewable ones.
It is to make students think on when it may be beneficial to use one or another.

IMPORTANT REMARKS:

- **This subject is mainly on biobased**
  ORGANIC POLYMERIC MATERIALS
  supplied directly or indirectly by nature
  and separated, modified or synthetized by humans.
- It is **not** on energy sources.
- It is current and developing –
  information will need to be supplemented
  with new knowledge up to date.
  Regional aspects should be considered.
- It arises topics which can be disputable.

Content (lecture)

Topic	AH
• Classification of raw materials for materials manufacturing into renewable and non-renewable. Advantages and disadvantages of the use of non-renewable sources in materials synthesis and processing and prospects for the future. Renewable vs. non-renewable materials – how to show which is better? Aspects of LCA (Life Cycle Assessment) analysis. Ecodesign. • Renewable raw sources – biomass (definition), different types of biomass and the possibility of using them in materials engineering.	5
Characterization of traditional materials from renewable sources – the history and developement: • Wood and wood-based products • Natural fibers (plant fibers and animal fibers)	4

AH – academic hour (Total: 25 for lecture)

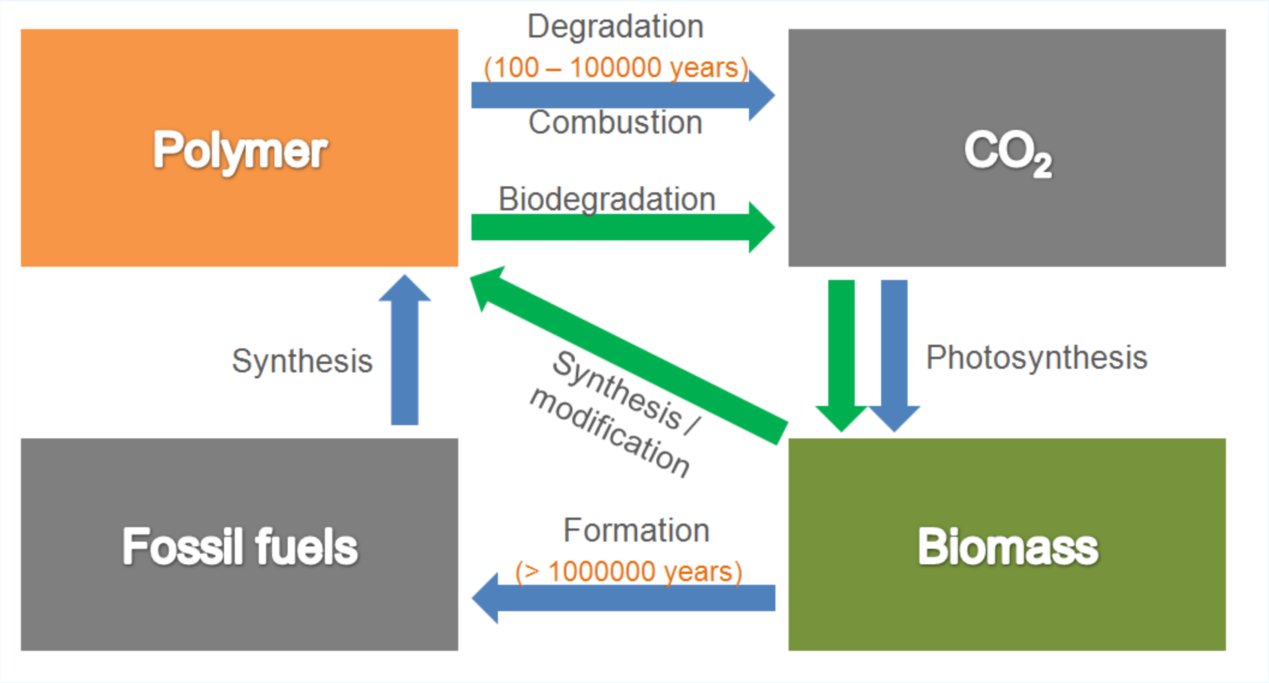
Topic	AH
• Biopolymers – definition and basic division. Biodegradability, organic recycling, composting and methods of assessing the biodegradability of polymers • Biodegradable polymers – division, main examples, properties and applications • Non-biodegradable polymers – examples, properties and applications • Biodegradable vs. oxo-degradable, biodegradable vs. non-biodegradable, thermoplastics vs. thermosets – discussion	6
• Biocomposites – definition. Components: matrices and fillers used • WPC (Wood Plastic Composite) • NFC / NFRC (Natural Fiber Reinforced Composite) • Ashby plots. NFC vs glass-reinforced polymer composites • Processing of biocomposites with short, long fibers, mats, textiles • Ready-to-use compounds, semi-finished products on the market • Applications, advantages and limitations	8
Present and future market for traditional and novel materials obtained from renewable sources, prospects of development	2

Classification of raw materials for materials manufacturing into renewable and non-renewable. Advantages and disadvantages of the use of non-renewable sources in materials synthesis and processing and prospects for the future.

- ! Looking for information: renewable sources – more information about energy sources than engineering materials srouces.
- ! A good opportunity to systematize knowledge on raw sources of main materials groups
- ! Sensitize students on the need for proper use of terms (raw material, resource, reserves, feedstock, etc.)

- ➢ Talk of non-renewable sources of engineering materials, their division, processing, use for materials manufacturing, reserves and consumption. Pros and cons. Give examples.
- ➢ Talk in general of what are renewable sources of engineering materials (mainly organic biomass).
- ➢ Talk of short-term/long-term life cycles

Example of short-therm and logn-therm life cycle



A simplified organic carbon cycle for engineering polymers: biobased and biodegradable polymers (green arrows) and common petrochemical polymers (blue arrows)

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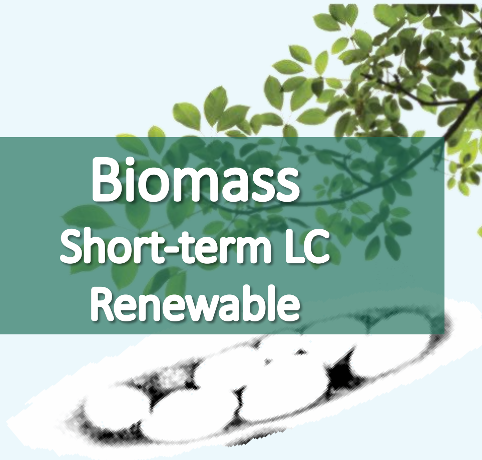
Engineering material sources

Rock, minerals; ores
Long-term LC
Non-renewable

Fossil fuels
Long-term LC
Non-renewable



Biomass
Short-term LC
Renewable

source of metals, glass & ceramics and other inorganic non-metallic materials

used in industry as minerals (e.g.: talc, asbestos, diamond; zeolits) or rocks (e.g.: diatomite, basalt, tuff);

source of polymers and other materials like asphalt, carbon black

source of polymeric materials - living cells mostly rely on macromolecules as their building material and chemical energy reservoir (e.g., cellulose, starch, collagen).

Reserves and consumption
– show exemplary data for ores and fossil fuels

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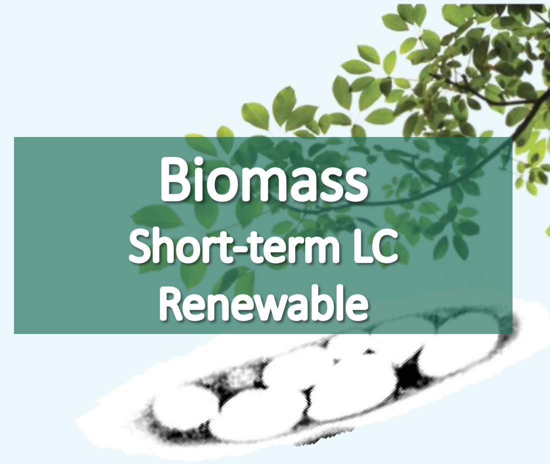
Engineering material sources

ZINC

The main regions where zinc ore is mined: 1. Asia and Australia: 44% 2. America: 43% 3. Europe: 10% 4.Africa: 3%.The ore can be extracted from areas when the zinc concentration exceeds 5%.
Mining resources are estimated at a level of 220 million tons of currently exploitable zinc ore reserves. Annual world consumption of zinc is at present 9,7 million tons. Since recycling accounts for about 39% of zinc consumption, zinc reserves are depleted at a yearly rate of 5,9 million tons.

- VMZINC, www.vmzinc.com/sustainable-building6/ore-reserves.html -

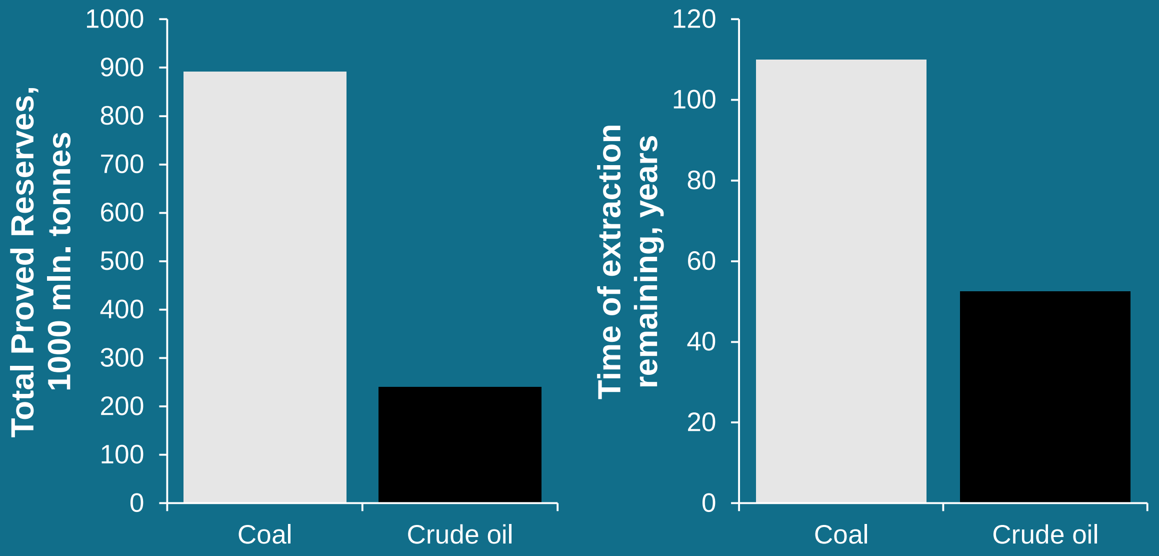
Reserves and consumption
– show exemplary data for ores and fossil fuels



source of polymeric materials - living cells mostly rely on macromolecules as their building material and chemical energy reservoir (e.g., cellulose, starch, collagen).

Engineering material sources

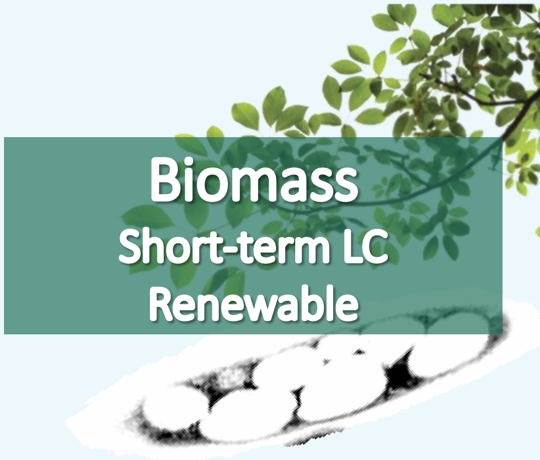
FOSSIL FUELS



- BP (British Petroleum) Statistical Review of World Energy June 2015 -

Reserves and consumption

– show exemplary data for ores and fossil fuels



source of polymeric materials - living cells mostly rely on macromolecules as their building material and chemical energy reservoir (e.g., cellulose, starch, collagen).

Renewable raw sources – biomass (definition), different types of biomass and the possibility of using them in materials engineering. Advantages and disadvantages

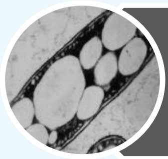
! Renewable sources of materials ~ biomass. Different definitions (many for the purpose of defining energy sources)

- Talk of sources derived from plants, microorganisms, algaes, animals. Examples:

Plant oils
(Used for materials synthesis)

Starch
(Used for fermentation and synthesis or modification)

Lignocellulosic materials
(„Ready to use” after extraction, modified or used for synthesis)



Bacterial, algae polymers
(„Ready to use” after extraction or modified)

Renewable sources - arguable points

- Food crops sourced polymers and the global lack of food crop. Land use.
- Overharvesting
- Biomass material inhomogeneity
- Regional and global avaliability,
- Dependence on climate, weather conditions, insects, plagues
- Costs of cultivation, harvesting and transport
- Development of genetically modified organisms
- Biomass processing: materials from renewable sources – always eco-friendly (e.g.: PA11)?

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Renewable vs. non-renewable materials – how to show which is better? Aspects of LCA (Life Cycle Assessment) analysis. Ecodesign.

! The purpose is not to describe how LCA worsk in detail, but to show when it is useful, when it is misused and what one should take into consideration making the analisys.

- Show that in many cases there is more than one raw source in manufacturing materials and products – what are the factors that favour the use one or another in practice?
- Consider how it influences material choice: materials manufacturing and products manufacturing – usually separate paths (time, place, processess)
- Present differen life cycle stages and variants of LCA
- Show how LCA and similar methods can be responsibly used
- Use this course to talk about ecodesing if its not discussed elsvere with students

LCA – use responsibly. An example

European Bioplastics comments on the study "A Life Cycle Assessment of Oxo-biodegradable, Compostable and Conventional Bags", Bio-based News, 30 Juli 2012

Position paper critizising Intertek-study about working with incorrect and incomplete assumptions

(on-line: news.bio-based.eu/european-bioplastics-comments-on-the-study-a-life-cycle-assessment-of-oxo-biodegradable-compostable-and-conventional-bags):

- „The study is unbalanced and (…) it is full of incorrect, unverified or partial assumptions"
- **„LCAs are increasingly used as a comparative marketing tool using e.g. selected parameters and impact categories favourable to one's product, which cannot and should not be the intent of an LCA"**

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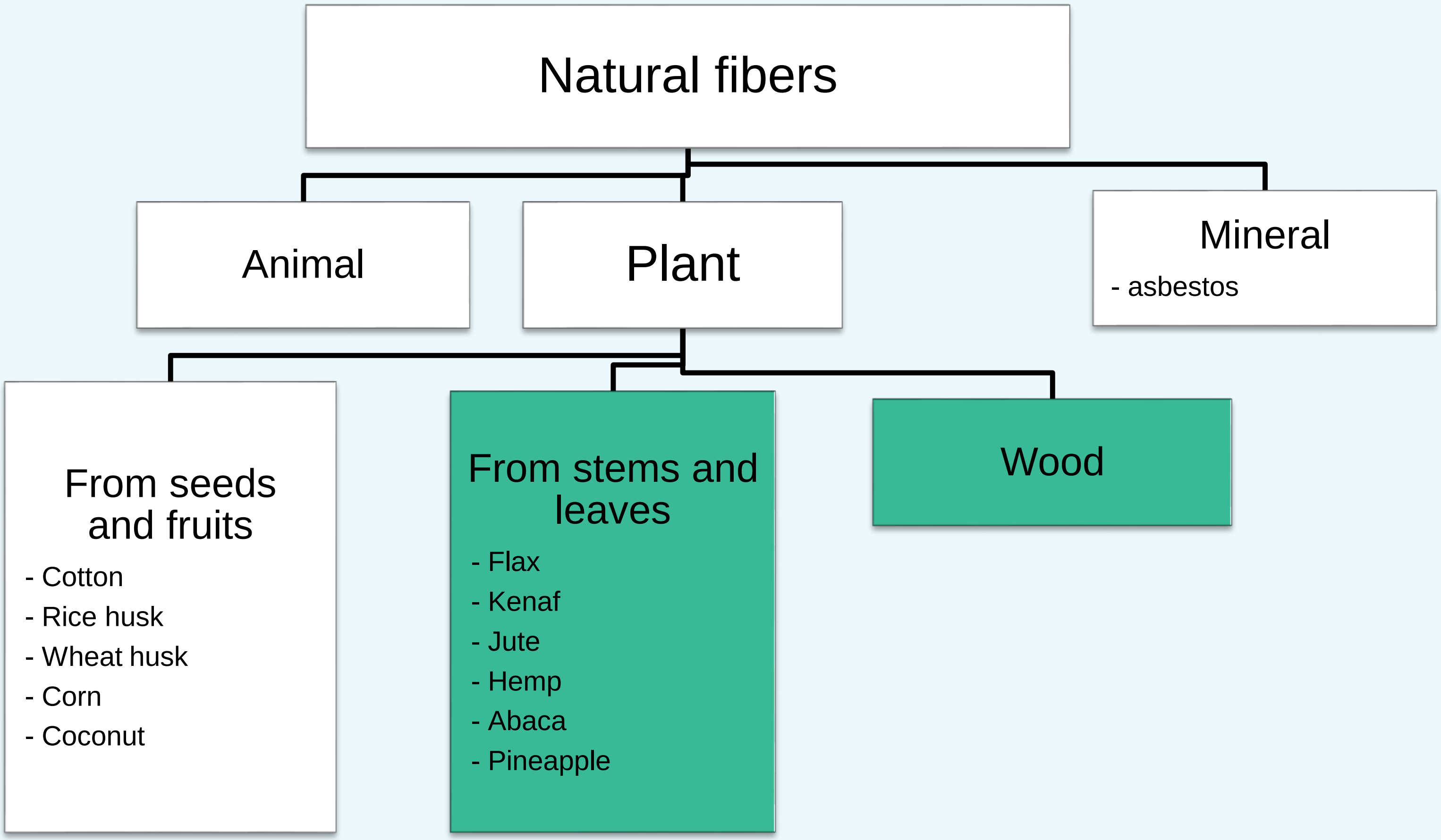
Characterization of traditional materials from renewable sources – the history and developement:
- Wood and wood-based products
- Natural fibers (plant fibers and animal fibers)

! Use native literature

! Remember of regional aspects and potential of your region/country

- Wood – focus on structure-property relationships, characterise the material in view of various applications. Show novel examples of use.
- Natural fibers – show the properties, structure and compare with other fibrous materials. Show the variety! Talk in general of applications, but the application for biocomposites productuion will be further discussed in more detail.
- Use ‘facts and myths’ discussing general opinions of traditional biomass-based materials

Natural fibers - division



Natural fibers - properties

Material	Density [g/cm^3]	Tensile strength [MPa]	Tensile modulus [GPa]	Strain at break [%]
Flax	1.45	500-900	50-70	1.5-4.0
Hemp	1.48	350-800	30-60	1.6-4.0
Kenaf	1.3	400-700	25-50	1.7-2.1
Jute	1.3	300-700	20-50	1.2-3.0
Bambus	1.4	500-740	30-50	ok. 2
Sisal	1.5	300-500	10-30	2-5
Coconut fiber	1.2	150-180	4-6	20-40
Glass fiber E	2.5	1200-1800	72	ok. 2.5
Carbon Fiber	1.4	ok. 4000	235	ok. 2
Kevlar 49	1.44	3600-4100	130	ok. 2.8

Natural fibers vs. glass fibers – not a whole picture. An example

Properties	Natural fibers	Glass fibers
Density	low	higher
Renewable sources	yes	no
Recycling	yes	no
Tool wear during processing	low	high
Health risk if inhaled	low	high
Biodegradability	yes	no

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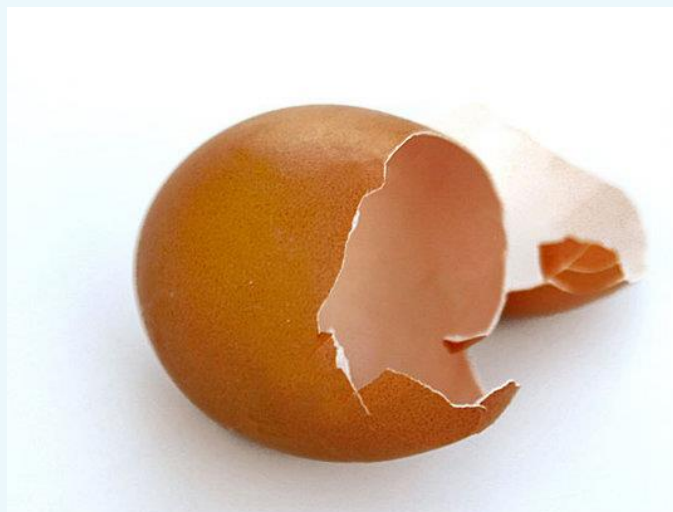
Traditional an novel applications of traditional biobased materials – an example

- Natural fiber applications
  - Textile technology: spinning, weaving, knitting, finishing
  - Cellulose pulp (source of man-made cellulose fiber) and paper
  - Other technical applicatons
    - Composites: polymer biocomposites, concrete filler
    - Mats and geotextiles
    - Raw material for insulation
    - Filters
    - Mats for mechanical vibrations damping and acoustic insulation
  - Energy

Less popular… and not only fibrous


Biopolymers – definition and basic division. Biodegradability, organic recycling, composting and methods of assessing the biodegradability of polymers. Biodegradable polymers – division, main examples, properties and applications. Non-biodegradable polymers – examples, properties and applications.

- ! Use current literature (a lot of books and review articles) and international standards
- ! Sensitize students on the need for proper use of terms

- Give definitions – the terms connected to biopolymers are frequently confused
- Talk of biobased/biodegradable materials certification
- Most of currently produced biodegradable polymers are dedcated for packaging, medicine (e.g. implants) and cosmetics. Talk more of materials which can be also used for structural applications (e.g.: PLA)
- Talk of importance of biobased and non-biodegradable polymers – these are important for technical applications

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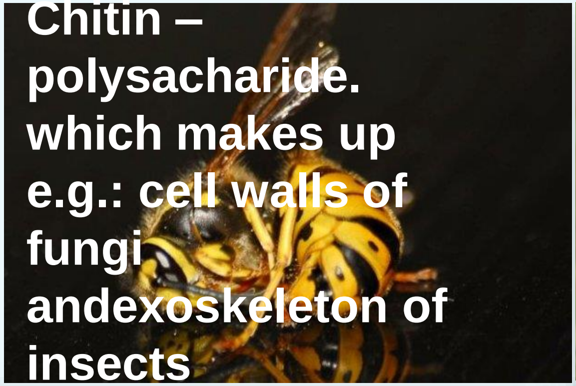
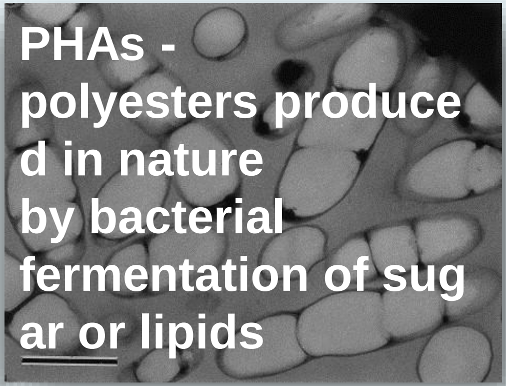
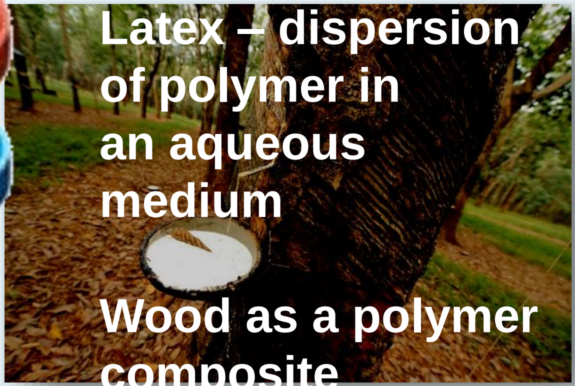
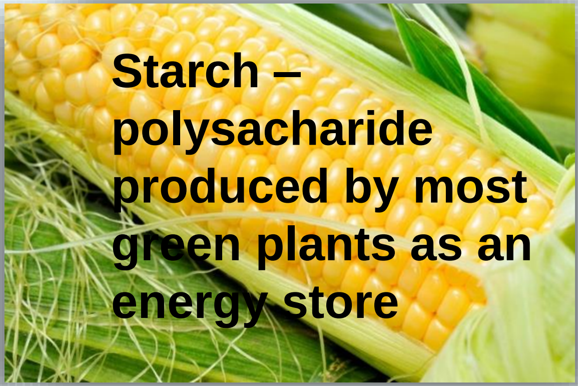
Biopolymers = natural polymers?

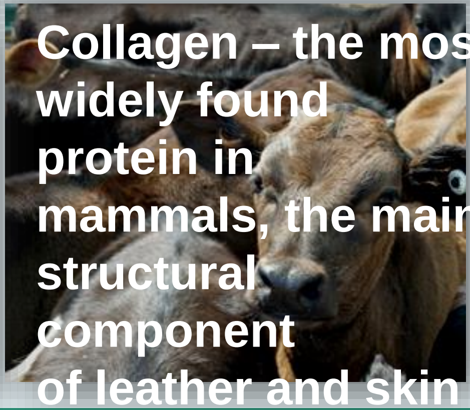
Natural polymers, e.g.: cellulose, starch, DNA, chitosan, collagen, silc, latex.











Biobased and/or biodegradable

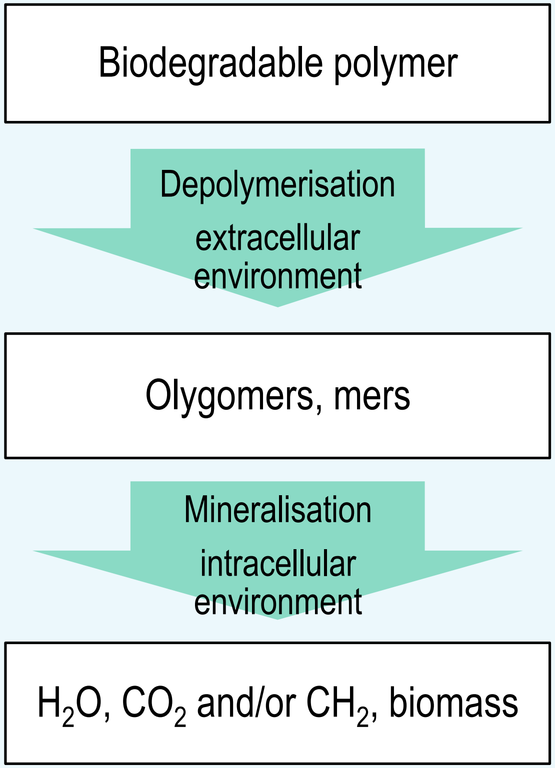
BIODEGRADABILITY	PETROCHEMICAL	BIOBASED
YES	PBS, PCL	TPS, PLA, PHA, cellulose esters and their bledns
NO	PE, PP, PET, PVC, PA, ABS, and other thermoplastic or thermoset traditional plastics	Bio-PE, PA 11, PA 10,10, bio-PET, bio-PP
	FEEDSTOCK	

Biopolymers and the „feedstock → technical material” path possibilities

- Biodegradable polymers
  - Bio-based
    - Synthetized by plants: Polysacharides (starch, cellulose) Proteins (soy proteins)
    - Synthetized by humans: PLA
    - Synthetized by microorganizms: PHA, bacterial cellulose
    - Natural polymer modified by humans: TPS, cellulose esters
  - Petrochemical

Definitions. Example: biodegradable and compostable – it is not the same.

- **Biodegradation**
  conversion of the organic matter into CO_2 (or methane), water and mineral salts due to the action of micro-organism.
- **Biodegradable polymer**
  biodegrade in at least 90% by the time of 6-month composting in controlled conditions
- **Compostable polymer**
  - cannot release toxic breakdown products
  - cannot influence negatively on the composting process,
  - has to disintegrate into fractions indistinguishable in the compost
    (testing acc. to EN 14045)



Traditional and biobased materials - compare

Material feature	**TPS**	**PLA**	**PHA**	**bio-PE**	**bio-PA**
Physical properties					
Density	H	M	M	L	L
Strength and stifness	L	M – H	L – M	L – M	M – H
Thermal resistance	L	L – M	M	M	M – H
Water absorption	H	M	M	L	L
End of life					
Recyclability	L/No	L	L	H	M
Biodegrability	H	M	H	No	No
Market issues					
Price	M	M	H	L – M	H
Avaliability	H	H	L	M	M

Examples of technical applications for biobased biodegradable polymers

PLA used for
Röchling Automotive’s air filter

PLA housing
of a touchscreen computer

Foamed PLA surfboard

Examples of technical applications for biobased non-biodegradable polymers

Biodegradable polymers - arguable points

- The presence of biodegradable plastic carrier bags in the recycling waste stream and the influence on recycling industry
- The properties and price: biodegradable materials vs. traditional plastics
- Fast degradation – advantage or disadvantage
- Garden compost heap – is it a place for biodegradable polymers?

Biodegradable vs. oxo-degradable, biodegradable vs. non-biodegradable, thermoplastics vs. thermosets – discussion

! Use current literature and international standards

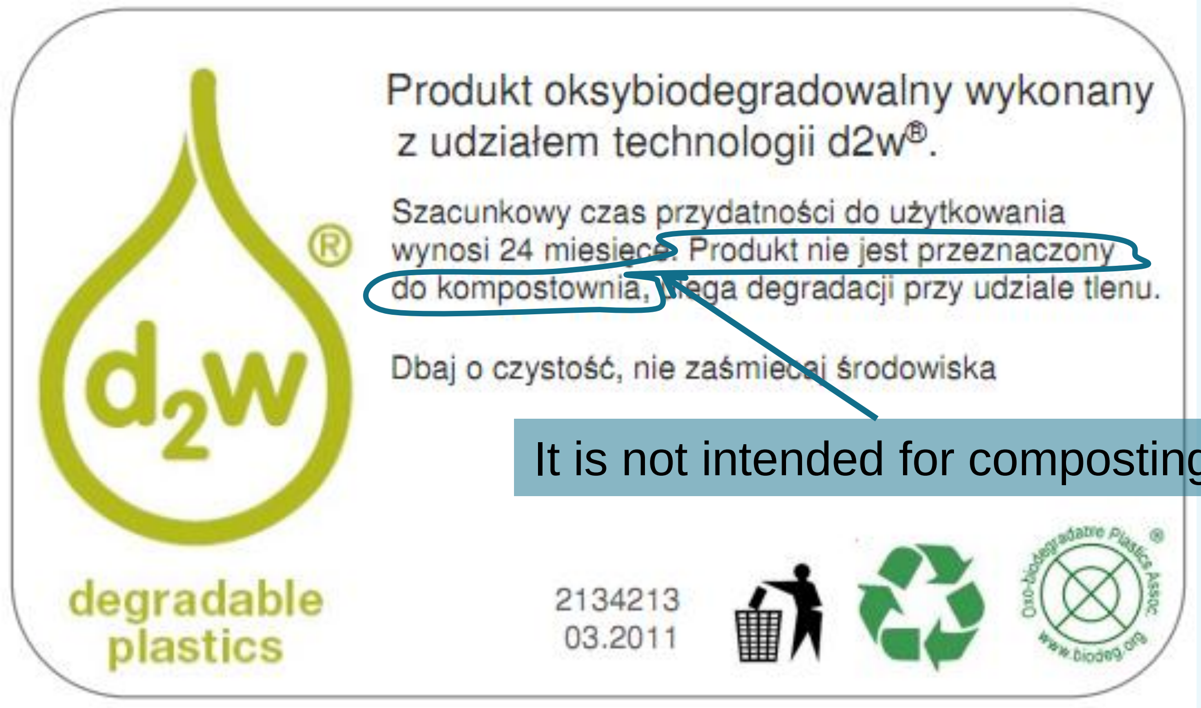
! Read articles on internet portals and check comments – what do people know/thikn and what do they ask for?

! Sensitize students to look for trastful literature

- Define and present the problem; give some pros and cons.
- Give some facts & opinions from scientific literature, popular sience and other magazines / forums.
- Check what do your students think about the topics disussed

Example: biodegradable and/or compostable vs. oxo-biodegradable

compostable
EN13432



It is not intended for composting

Examples:
Advertisement of oxo-biodegradable additive: www.youtube.com/watch?v=niYZeQ2lq74
Biodegradable vs Oxo-Biodegradable vs Compostable: organics.org/biodegradable-vs-oxo-biodegradable-vs-compostable/

Biocomposites – definition. Components: matrices and fillers used WPC (Wood Plastic Composite), NFC / NFRC (Natural Fiber Reinforced Composite). Ashby plots. NFC vs glass-reinforced polymer composites. Processing of biocomposites with short, long fibers, mats, textiles Ready-to-use compounds, semi-finished products on the market. Applications, advantages and limitations

! Use current literature (a lot of books and review articles)

! There are international standards for WPC and NFC products, e.g.: ASTM D7032 – 14, ISO/NP 19821, ISO 16616

- Give definitions – the terms connected to WPC and NFC are frequently confused
- Show division of the fillers (origin, shape and size, other properties) and possible matrices which can be used (biobased and petroleum)
- Talk of processing issues
- Show structure-property relationships, show Ashby plots and compare with other materials and glass fibre reinforced composites
- Pros and cons with the use of different matrices and fillers

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The variety of biocomposites

Filler	traditional *e.g.: glass fiber*	+/-	+	+/-	Traditional composite
	biodegradable non-biobased *e.g.: PBS fiber*	o	o	o	o
	biobased non-biodegradable *e.g.: bio-PA fiber*	o	o	o	o
	Biobased and biodegradable *e.g.: wood flour*	+	+	+/-	+
		Biobased and biodegradable *e.g. polilaktyd*	Biobased non-biodegradable *e.g. bio-PA*	Biodegradable non-biobased *e.g. PBS*	traditional *e.g. PVC*
		Matrix			

Legenda:
+ high importance
+/- lower importance
o few or no research

WPC and NFC – is there a difference?

WPC – Wood Plastic Composite

Wood chips, flour, fibers but sometimes also other similar non-fibrous plant fillers like rice husk

NFC (NFRC) – Natural Fiber (Reinforced) Composites

Usually plant fillers in the form of fiber other than wood

Matrix is also important

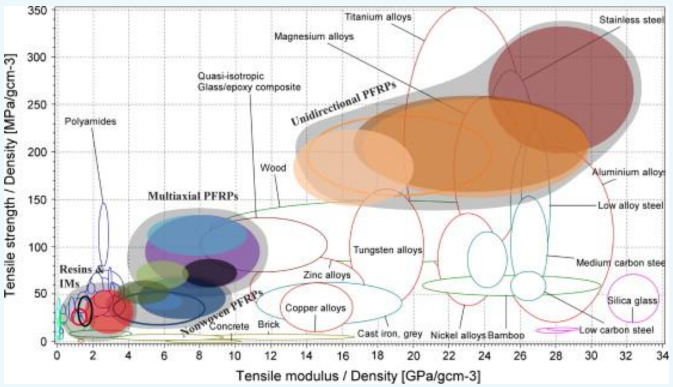
Biobomposies matrices – mainly thermoplastics of low processin temperatures (190 - 230°C) and low viscosity:

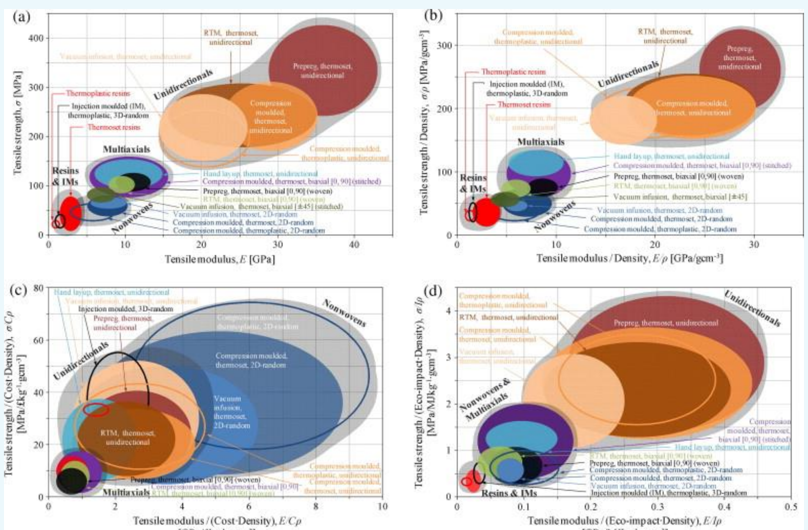
- Non-biodegradable polymers, standard or biobased, also recycled polymers: PP, PEHD, PVC, PS
- Biopolymers (PLA, TPS, PHB, CA)

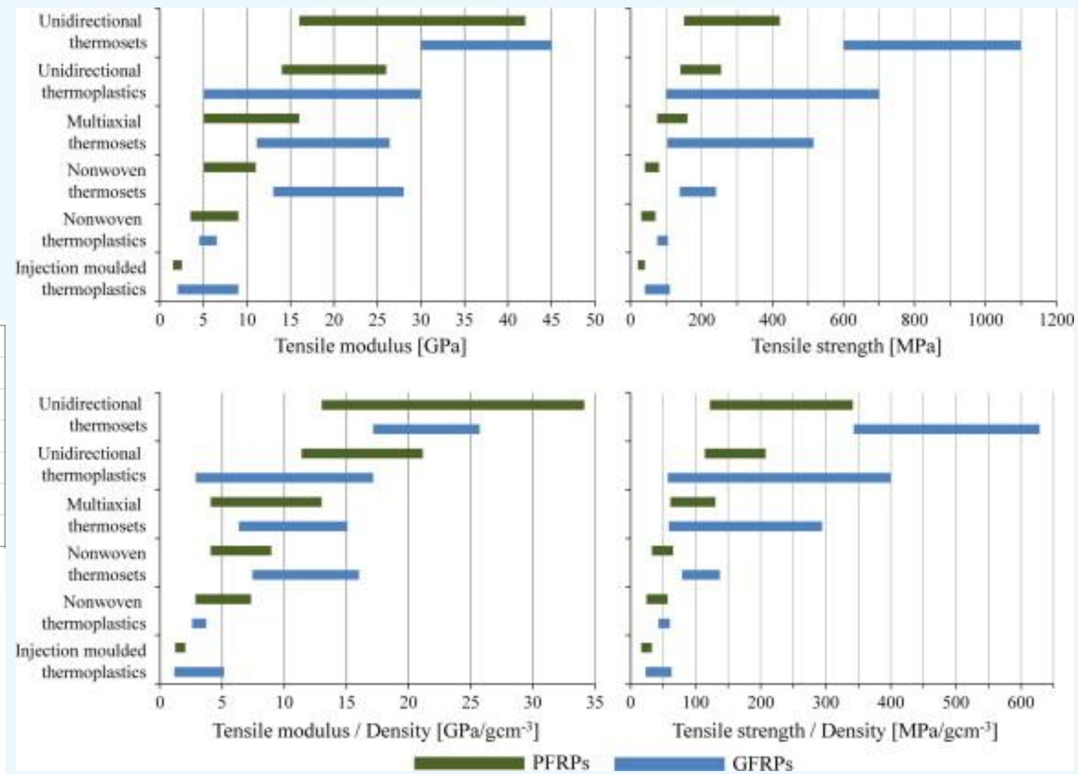
Thermosets: standard petrochemical thermosets or partially biobased

Various matrices → various processing methods

Traditional and biobased materials - compare



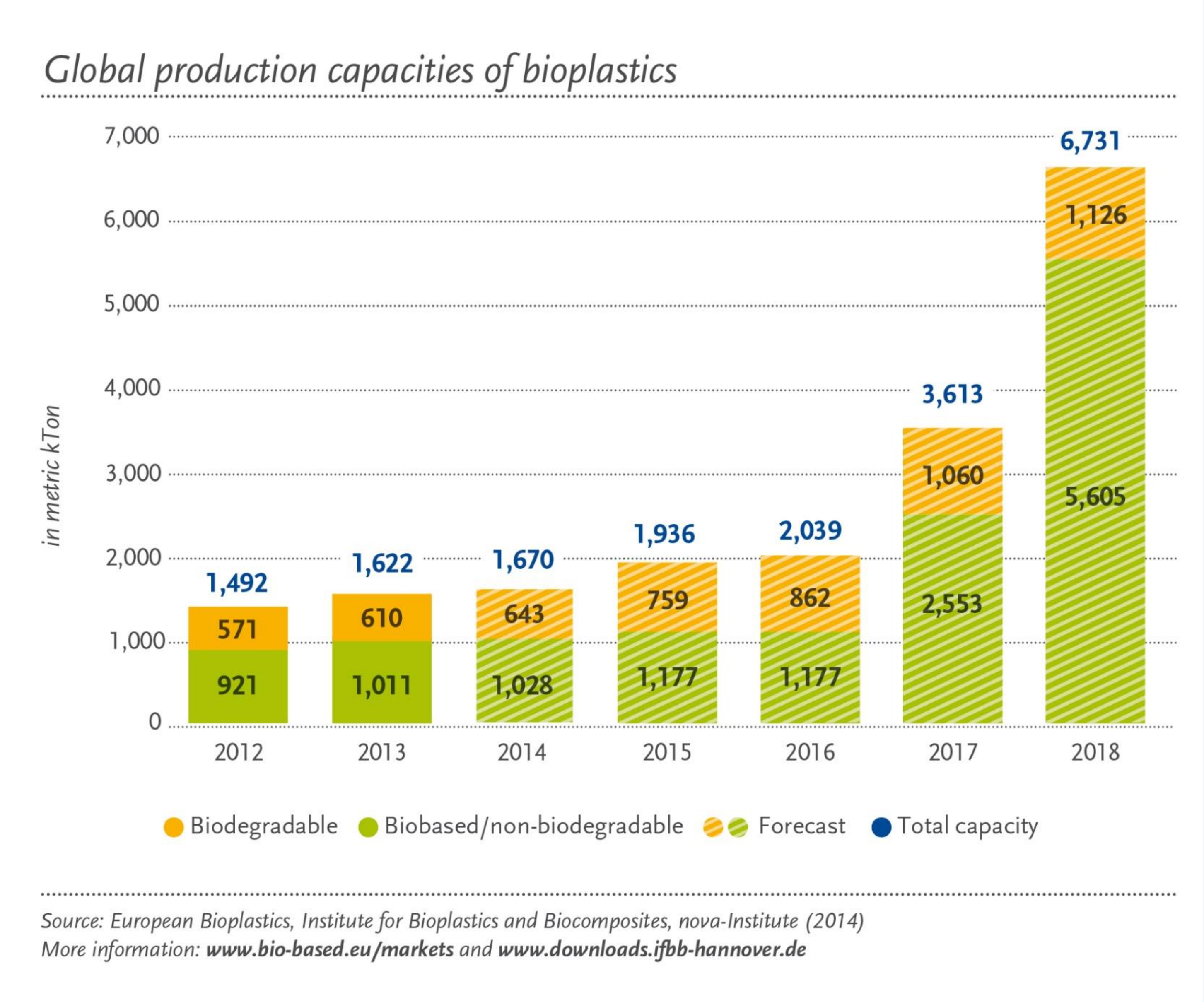




Present and future market for traditional and novel materials obtained from renewable sources, prospects of development

- ! Use current statistic data and examples of the most important, novel and interesting products on the market
- ! Talk about local and global market. Compare.

- Do a summary for traditional and novel materials and show their potential
- Give interesting examples from different industry sectors. Focus on structural appliations but others too.
- Showing the materials & products on the market talk about the „form" of the materials prepared to be processed avaliable, semi-finished products and for what they can be used


Global production capacities of bioplastics
7,000
6,000
5,000
4,000
3,000
2,000
1,000
0
in metric kTon
1,492
571
921
1,622
610
1,011
1,670
643
1,028
1,936
759
1,177
2,039
862
1,177
3,613
1,060
2,553
6,731
1,126
5,605
2012
2013
2014
2015
2016
2017
2018
Biodegradable
Biobased/non-biodegradable
Forecast
Total capacity
Source: European Bioplastics, Institute for Bioplastics and Biocomposites, nova-Institute (2014)
More information: www.bio-based.eu/markets and www.downloads.ifbb-hannover.de

Biocomposites on the market – examples of materials and products

FlexForm

FlexForm Technologies (US)

Natural fibers (kenaf, jute, hemp) + PP

Applications:

- Automotive: Mercedes Benz/Chrysler (DCX) Ford, GM, Honda, Nissan
- Furniture, panels
- Packaging

Fibrolon
FKuR (Germany)

Polyolefins or PLA
+ wood flour

Applications

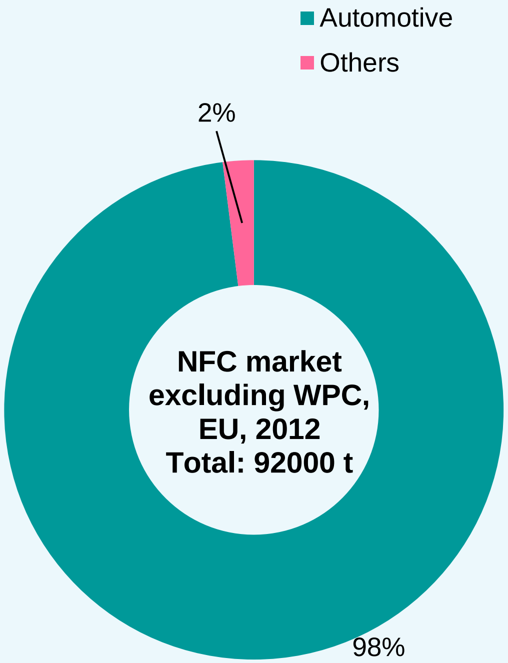
- Injection molded parts and extruded profiles, e.g.: dishes, office supplies, urns, etc.

Kareline® PLMS
Kareline (Finland)

PP, ABS, PS, POM or PLA
+ wood flour

NFC


S-MR 2840


Automotive
Others
2%
NFC market excluding WPC, EU, 2012
Total: 92000 t
98%


Ford
Wheat Straw Bio-Filled Polypropylene
Industry and World-First Usage in Quarter Trim Bins on 2010 Ford Flex
Extrusion Compounding
Injection Molding
Wheat Straw
Wheat Straw / Polypropylene Resin
Wheat Straw Bio-Filled Polypropylene Quarter Trim Bin

Motive Kestrel

(biocomposite: thermoset polymer with hemp fibers)

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BioConcept Car

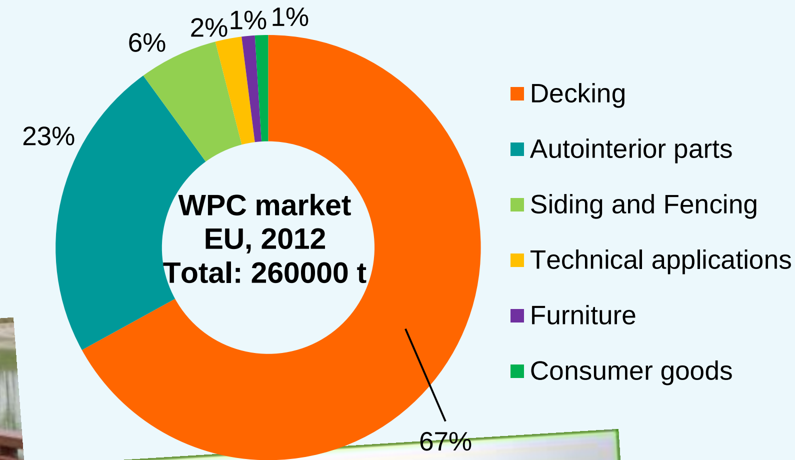
Four Motors GmbH

(biocomposite: thermoset resin with flax, hemp and cotton fibers)

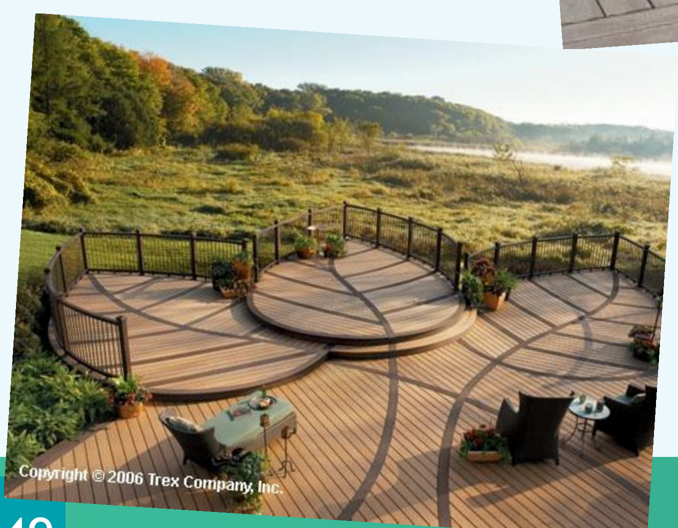
QWIC Electric scooter

(natural fibers and polyester resin biocomposite)

WPC



WPC market
EU, 2012
Total: 260000 t
67%
23%
6%
2%
1%
1%
Decking
Autointerior parts
Siding and Fencing
Technical applications
Furniture
Consumer goods



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NEC, FOMA N701i ECO mobile fone

(PLA + kenaf)

Lecture – summing up

Main topics and general tips	AH
Renewable and non-renewable feedstock and LCA → *Start at the beggening to engage students to think reasonably on many aspects and complexity of the topic*	5
Traditional materials from renewable sources → *Show wood and natural fibers as complex composite materials and their standard and novel applicatbility. Discuss strengths and weaknesses comparing to other materials*	4
Novel biobased materials → *Sensitize students to use correct terms and find proper definitions. Give them a base to form an opinion. Discuss strengths and weaknesses comparing to other materials.*	14
Present and furute market for renewabe materials *Summarize. Use current data and examples of products on the market. Show potential of renewable materials but also be critical talking of demands of the market*	2

Novel biobased materials – where and why?

- Biodegradable: mainly short-life cycle products and biomaterials (packaging, implants in medicine)
- Non-biodegradable: packaging (bio-PE), structural elements for automotive and E&E industry; special applications

- Offer for the consumers searching for „green” products
- Improvement of the company's image (use of renewable resources and reduction CO_2 emission)
- Possibility of applying for projects and funding
- New products and prototypes exhibited at the fairs and taking part in competitions
- Art - interesting textures and patterns of materials with fillers natural, "organic" look

So, what do your your students know and think of biobased materials after the course?

It is a nice idea to make a „survey” on their opinion (and knowledge) before and after the lecture /not for evaluation/

Lecture – summing up

Main topics and general tips	AH
Renewable and non-renewable feedstock and LCA *→ Start at the beggening to engage students to think reasonably on many aspects and complexity of the topic*	5
Traditional materials from renewable sources *→ Show wood and natural fibers as complex composite materials and their standard and novel applicatbility. Discuss strengths and weaknesses comparing to other materials*	4
Novel biobased materials *→ Sensitize students to use correct terms and find proper definitions. Give them a base to form an opinion. Discuss strengths and weaknesses comparing to other materials.*	14
Present and furute market for renewabe materials *Summarize. Use current data and examples of products on the market. Show potential of renewable materials but also be critical talking of demands of the market*	2

Part 2.

Suggestions for the laboratory work with examples

Implementing the course think what your students know about plastics and composites

- What do you teach your students about plastics and polymer composites?
- What kind of equipment can you use?
- What kind of information will your students need?

Content (laboratory work)

Topic	AH
Processing of biopolymers and biocomposites.	3
Composting of biodegradable materials from renewable sources and assessment of biodegradation capability.	3
Water absorption and aging process of biodegradable polymers and biocomposites with natural fibers.	3
Mechanical properties of biopolymers and biocomposites and the influence of water uptake.	3
Structure of wood, natural fibers and natural fiber composites – microscopic observations.	3

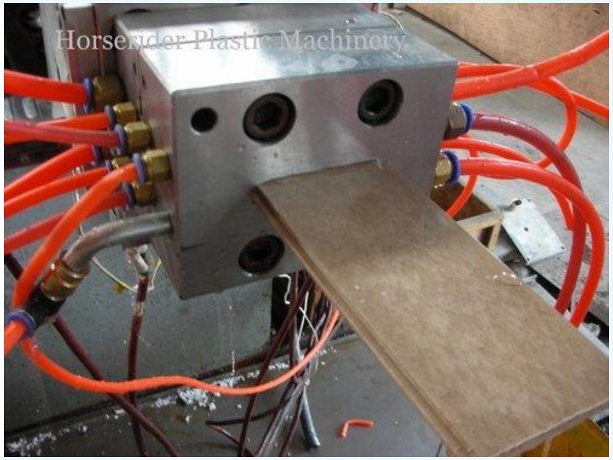
AH – academic hour (Total: 15 for laboratory work)

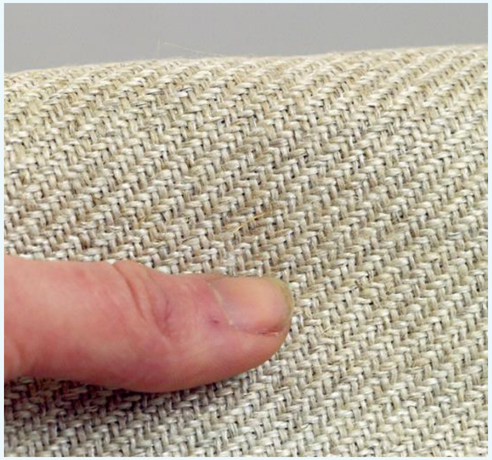
1. Processing of biopolymers and biocomposites.

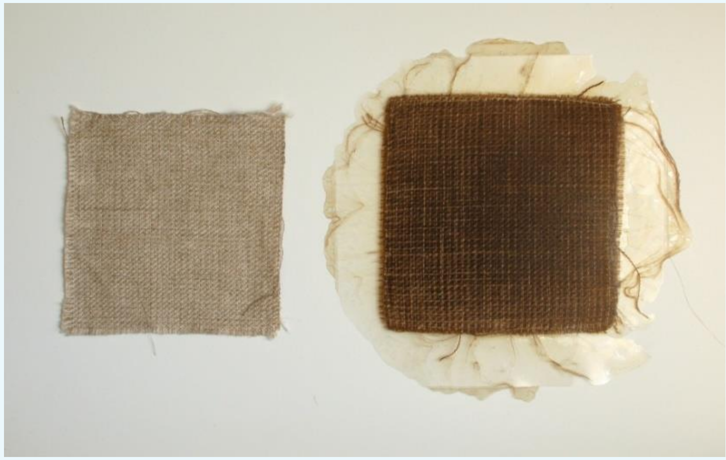
- ! Chose the matrix (thermoplastsic or thermoset) and the amount of filler and adequate method of processing, e.g.: injection molding, extrusion molding (compounding), hand lay-up, infusion, compression molding
- ! Most of biopolymers are thermoplastic

- ➢ Show differences between processing of ‘traditional’ composites and biocomposites (mainly: biodegradable polymers and composites with natural fibers)
- ➢ Talk of preparation of the materials for processing (e.g.: drying, fibers modification)
- ➢ Set and talk about processing parameters
- ➢ Use produced specimens in further tests

Processing of WPC or NFC







Processing of WPC or NFC

Using thermosets

(long fibers, mats, textiles)

- Natural fibers absorb liquid resin and swell. The porosity of the wetted fiber-preform decreases, and hence its permeability, reduces with time.
- Processing usually results in low fiber volume fraction and uncertain void content

Using thermoplastics

(usually short fibers)

- low processin temperatures and short cycles are required: max 190 - 220°C
- Problems with inhomogenity and filler agglomerates
- Low volum fractions for injection molding

Problems with moisture content and moisture absorpbion rate

Problems with fiber-matrix interface

2. Composting of biodegradable materials from renewable sources and assessment of biodegradation capability.

! Chose the environment and method of biodegradation assessment

- Choose aquatic or terrestial environment you can obtain and maintain. Control conditions (as much as you can), mainly: temperature and humidity
- Prepare at least 2 stands with different conditions and vatious materials (e.g.: destillated water vs. natural fresh water | PLA vs. TPS).
- Check the changes in e.g.: solution pH, mechanical properties, colour
- Talk about the influence of the biodegradation process parameters on the rate of biodegradation, additional factors and the difficulties and obstacles in testing biodegradation
- Talk about methods specified for material certification

Environment – a lot to choose from

Environment used for biodegradability assessment:

- Aquatic:
  - Marine
  - Fresh water
  - Sludge
- Terrestial:
  - Soil
  - Compost
  - Landfill

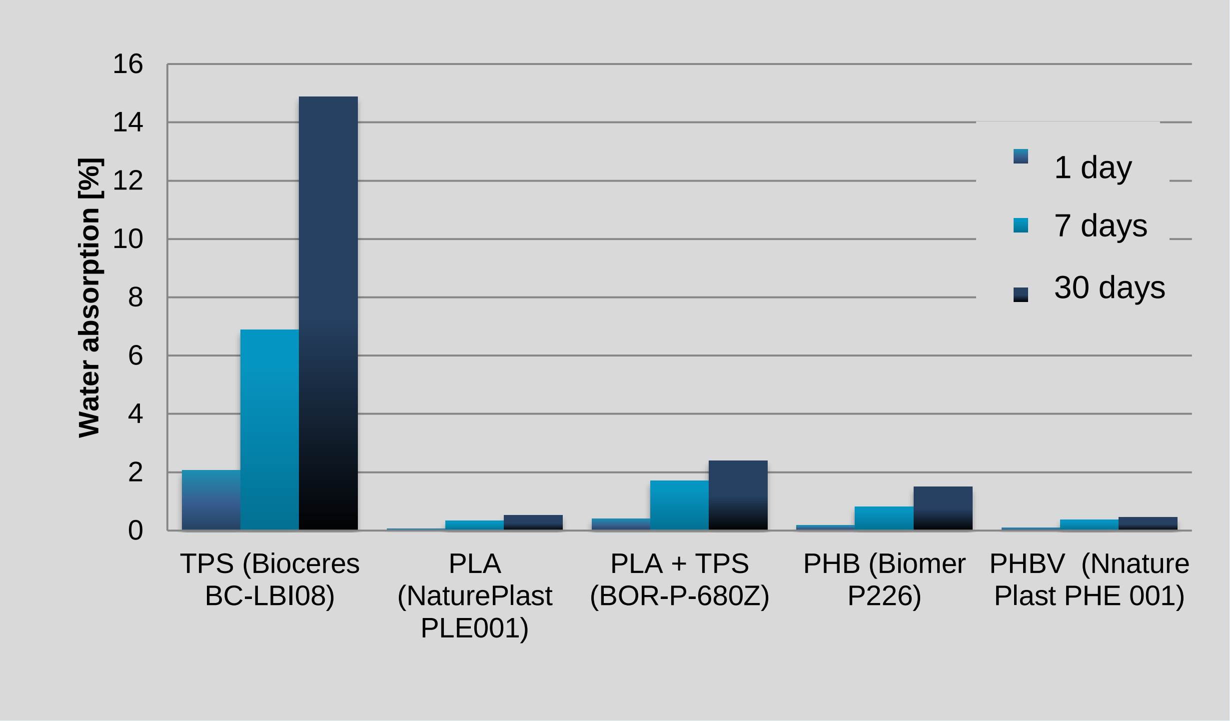
- ISO 14851 - Aerobic biodegradability in aqueous medium by oxygen demand
- ISO 14852 - Aerobic biodegradability in aqueous medium by evolved carbon dioxide
- ISO 16929 - Disintegration under composting conditions in a pilotscale test
- ISO 17556 - Aerobic biodegradability in Soil
- ISO 20200 - Disintegration under composting conditions in a laboratory-scale test
- ISO 14853 - Anaerobic biodegradability in an aqueous system
- ISO 15985 - Anaerobic biodegradability under high-solids conditions
- ISO 14855-1 - Aerobic biodegradability under controlled composting conditions
- ISO 14855-2 - Aerobic biodegradability under controlled composting conditions in a laboratory-scale test
- ISO 10210:2012 - Plastics -- Methods for the preparation of samples for biodegradation testing of plastic materials

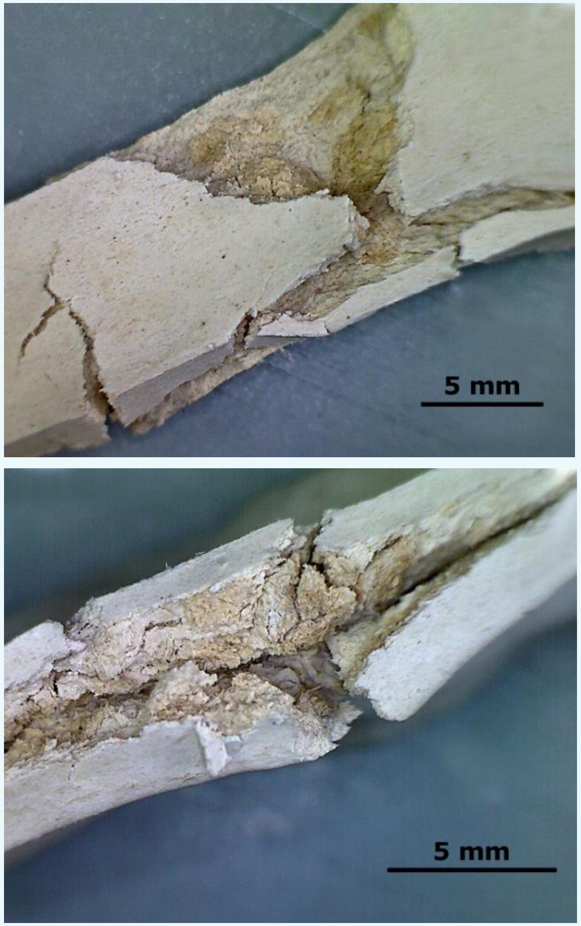
3. Water absorption and aging process of biodegradable polymers and biocomposites with natural fibers.

- ! ISO 62:2008. Plastics -- Determination of water absorption
- ! Chose standard or accelerated method. Remember about water soluble substances.

- Standard method – soak the specimens in water at room temperature for one day or more: prepare your experiment earlier, e.g.: on previous classes (you may measure water absorption after one week of soaking)
- Accelerated method: soak the specimens in boiling water for 0.5 h. Check the influence (some biodegradable specimens may be seriously damaged)
- Do the tests for biodegradable polymers and composites with lignocellulosic fillers.
- Additionally: chech surface rroughness and dimensional changes for biocomposites
- Tell/show students how to reduce water uptake

Water absorption – an example





TPS with wood flour after a month of soaking in water (room temerature)

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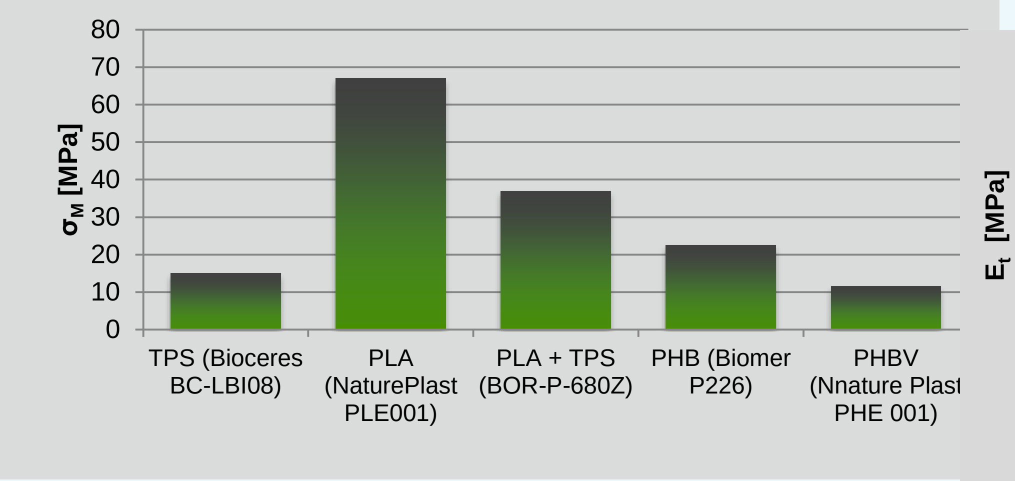
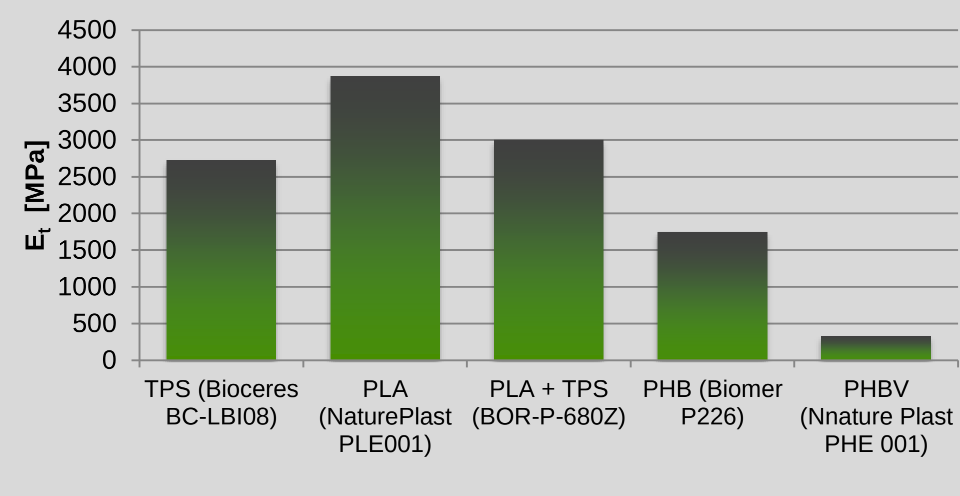
4. Mechanical properties of biopolymers and biocomposites and the influence of water uptake.

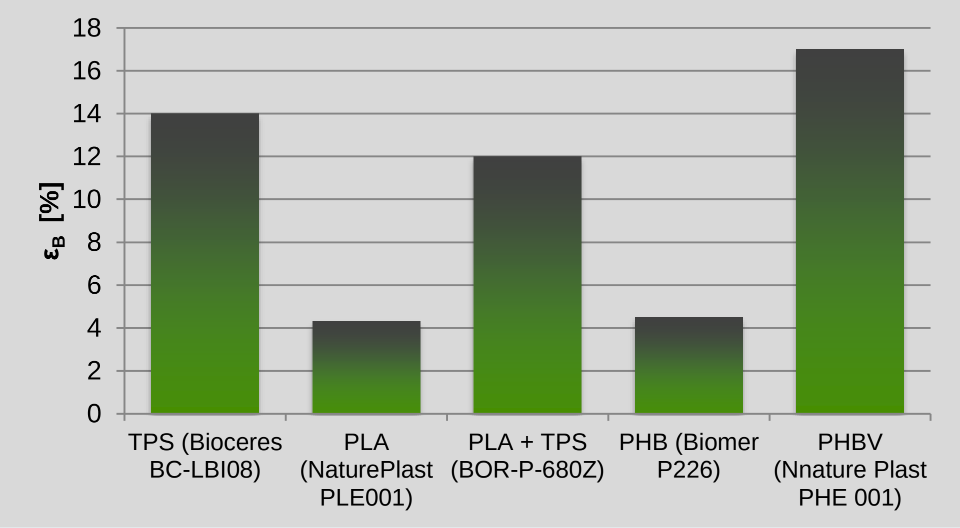
- ! Choose a test method (most often: standard tensile test) and compare various biobased and petroleum materials
- ! Use technical data sheets (TDS)

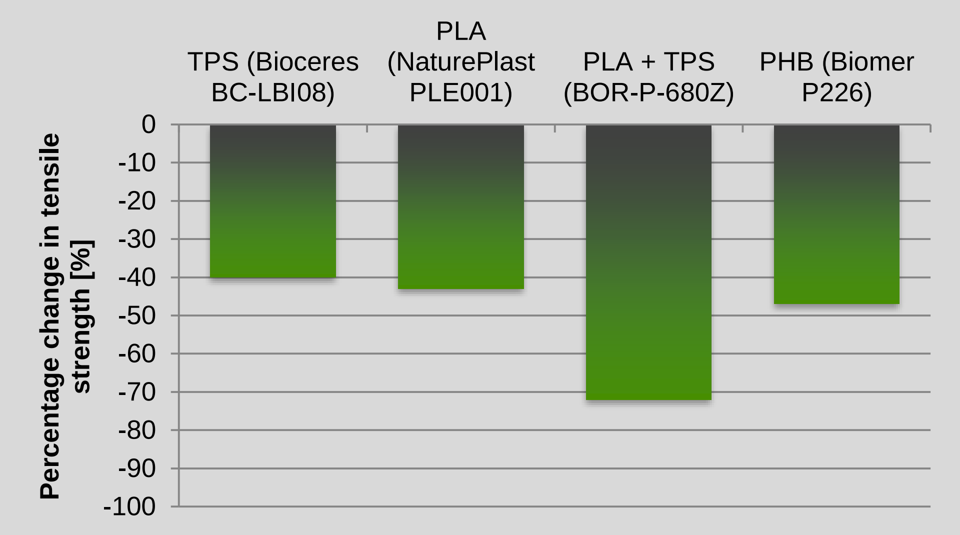
- ➢ Test properties of main biodegradable polymers (PLA, TPS, PHB) as well as of neat matrices and composites with natural fillers. Compare the results with resutls obtained for traditional materials (own experimental data or TDS)
- ➢ Assess water influence - tensile test after soaking specimens in water
- ➢ Properties → applications?

Tensile test results – an example







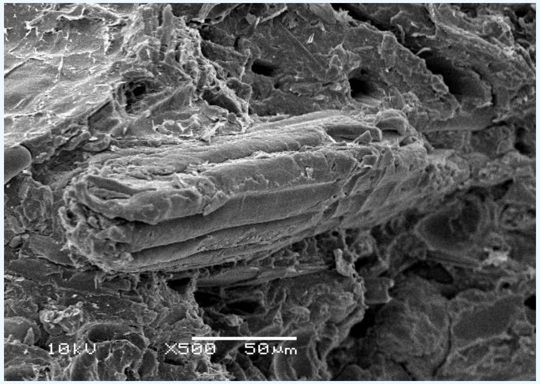


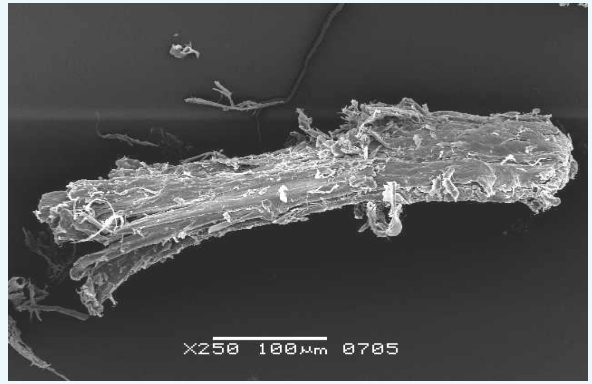
5. Structure of wood, natural fibers and natural fiber composites – microscopic observations.

! Use: SEM, stereo microscope (or optical microscope)

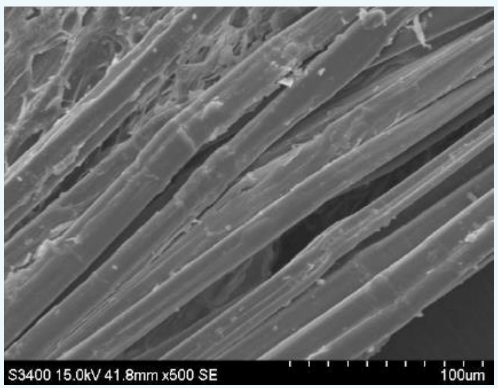
- Show: structure and morphology of wood, morphology and dimensions of the fillers, structure of biocomposites
- Show/talk of preparation of specimens
- Structure – property relationships (it would be the best to show properties of the materials which images you are showing)
- Compare with other ‘traditional’ composites

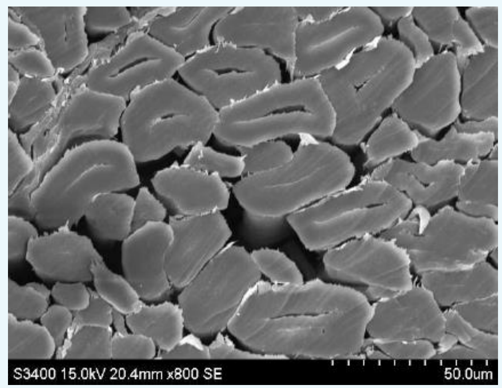
Morphology of plant fillers –examples



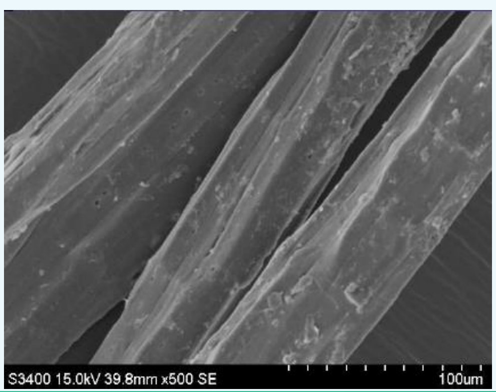


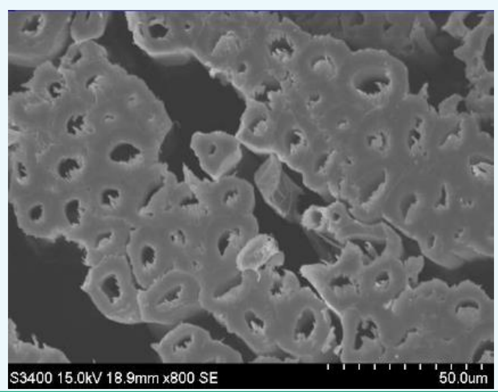
Wood flour





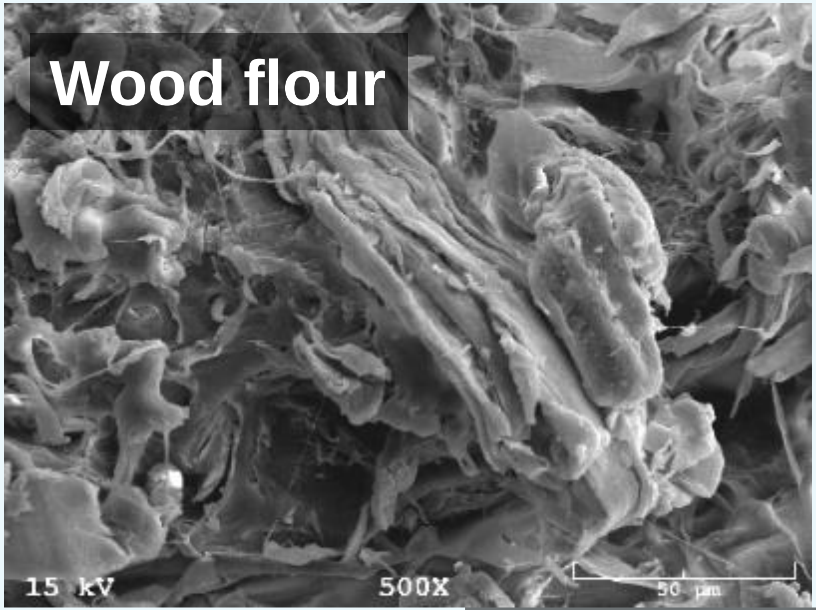
Flax fibers

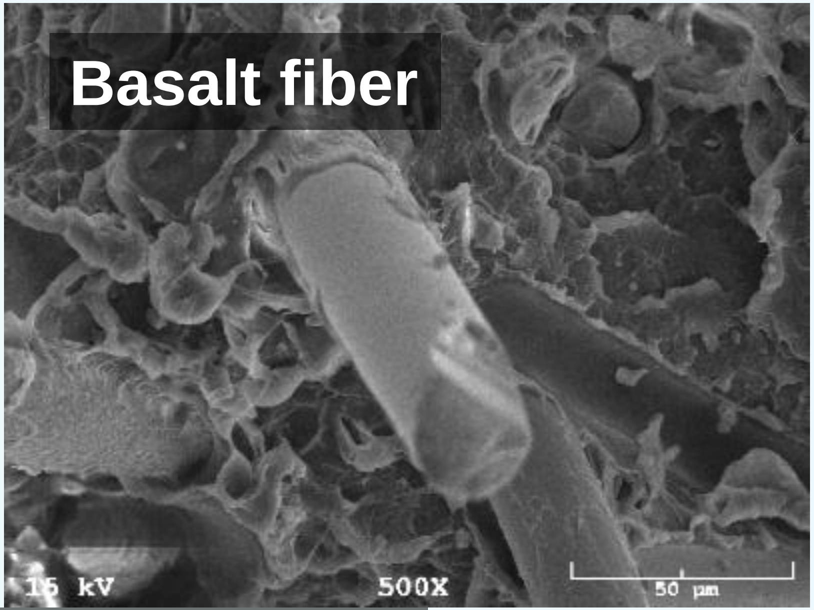


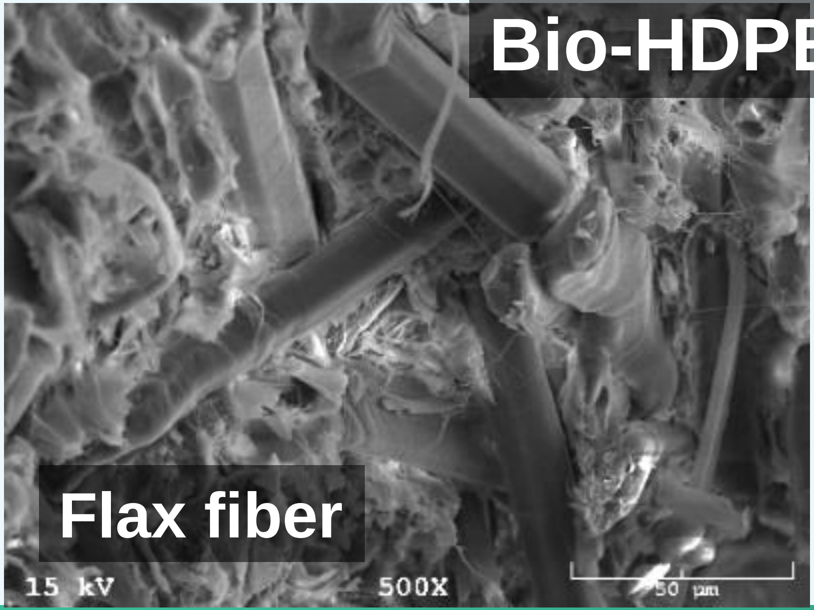


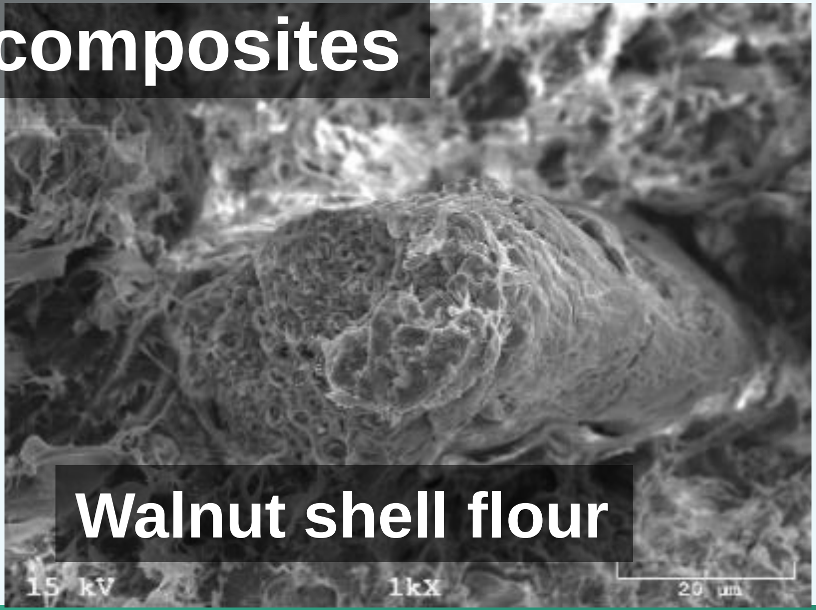
Kenaf fibers

Bio-HDPE composites

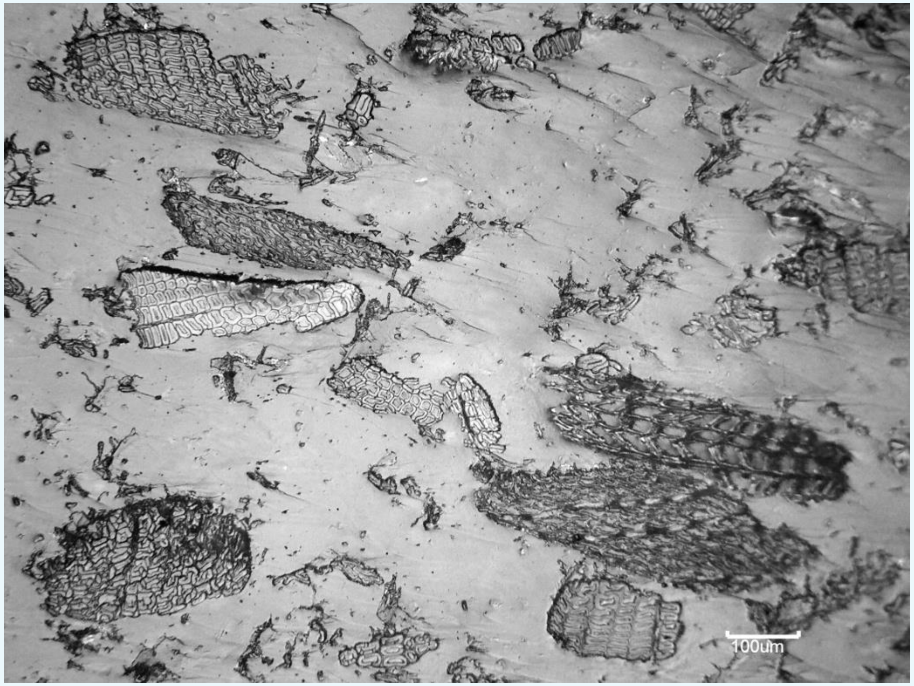


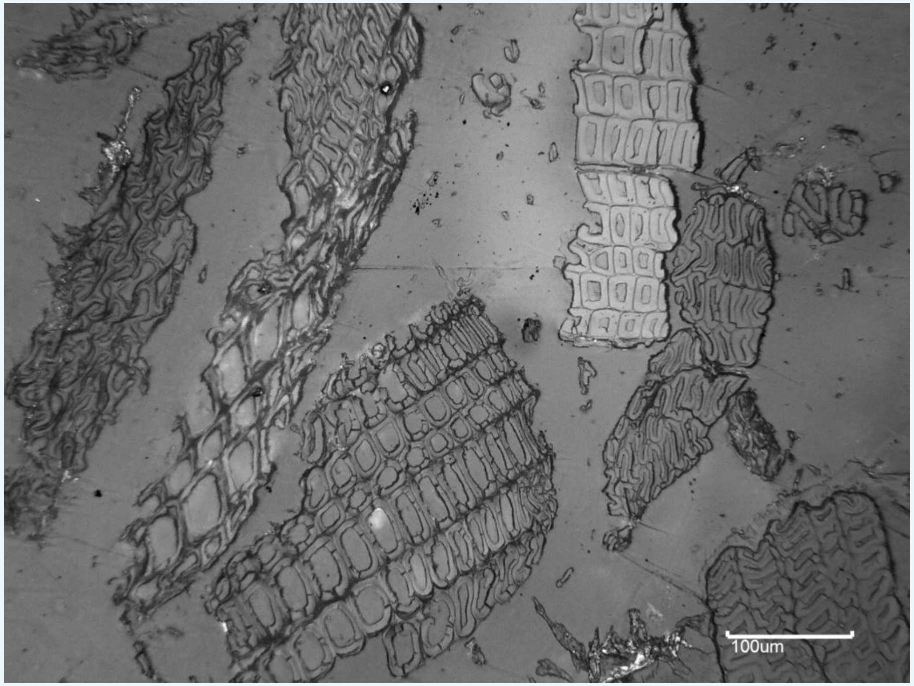






Optical microscope:
Wood flour in bio-PE matrix

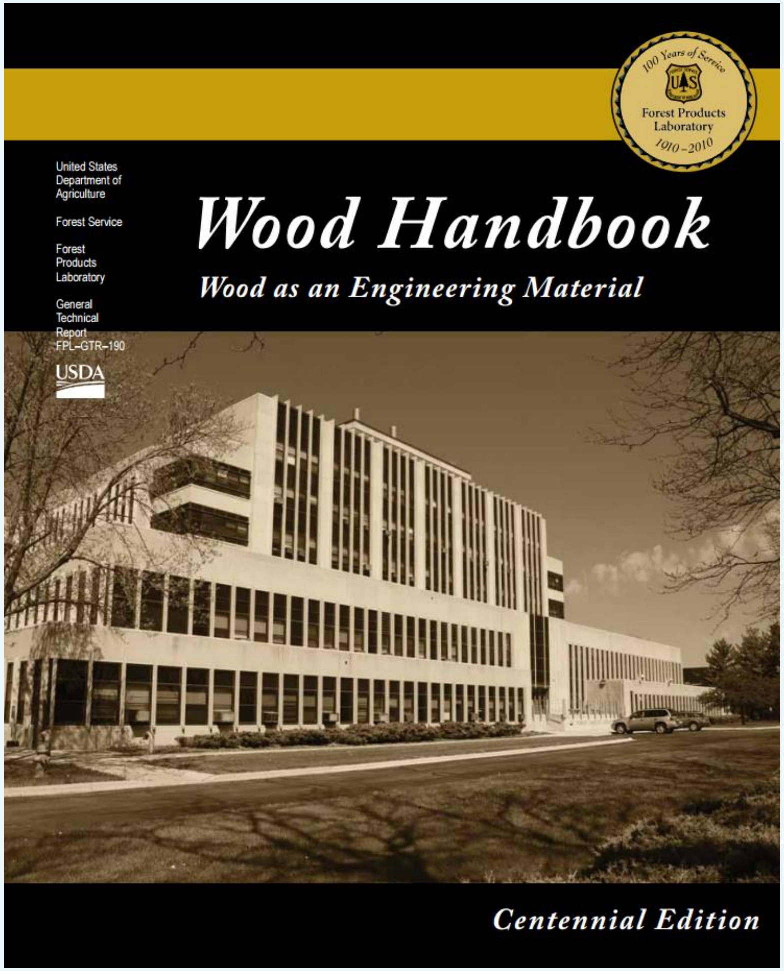




Keywords

Wood flour
Life cycle
LCA
Biomass
Biodegradable
Reserves
PLA, TPS, PHA, bio-PE
Starch
Ecobalance
Finite resource
Sustainable development
Feedstock
Ecodesign
Renewable
Natural fibers
Resource depletion
Cellulose
NFC, NFRC, WPC
Biobased
Raw material
Biocomposite
Biopolmer
Lignocellulosic material
Cradle-to-grave
Plant fillers

Literature - examples



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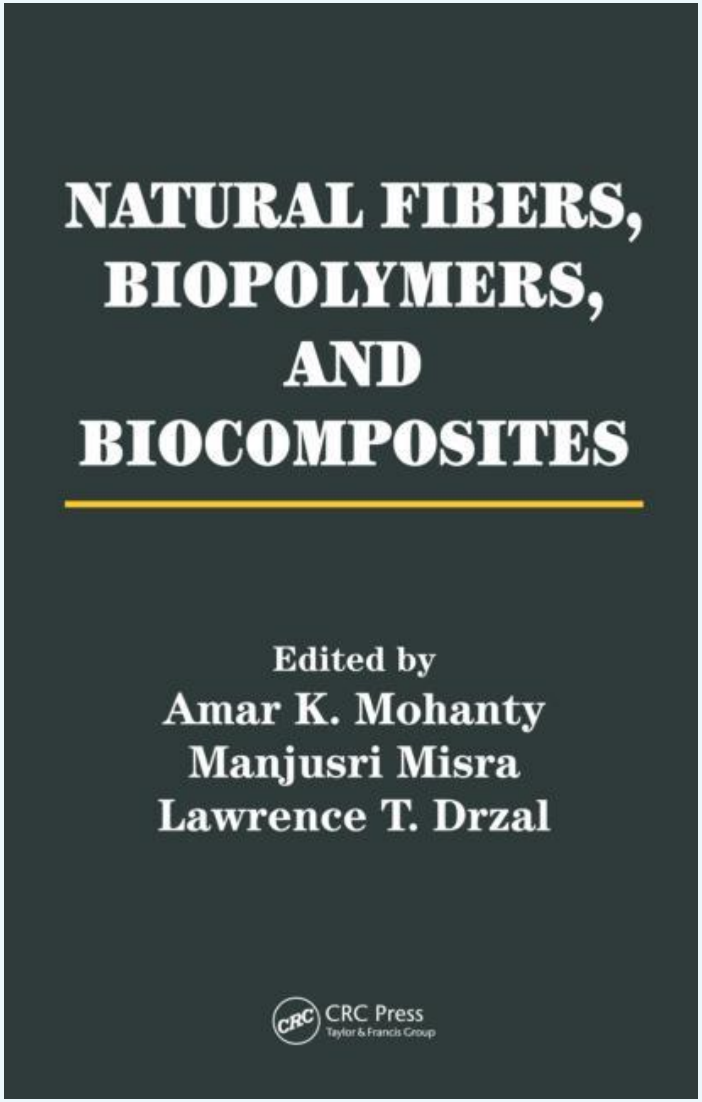

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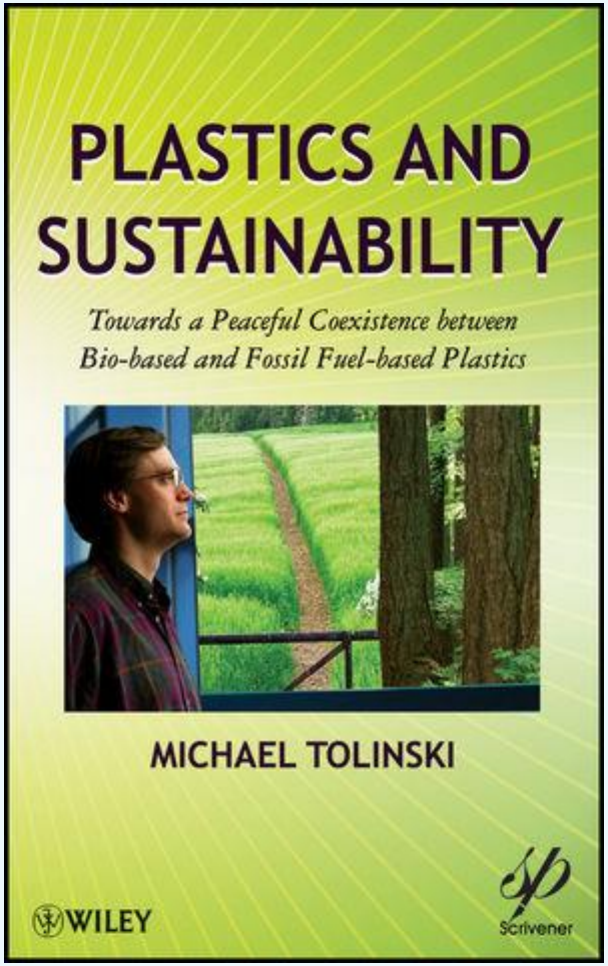

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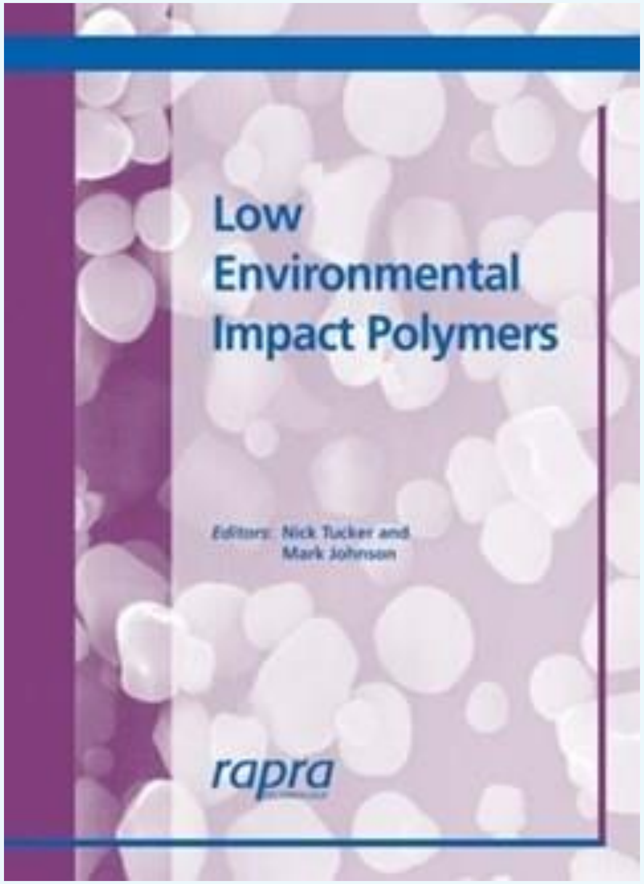

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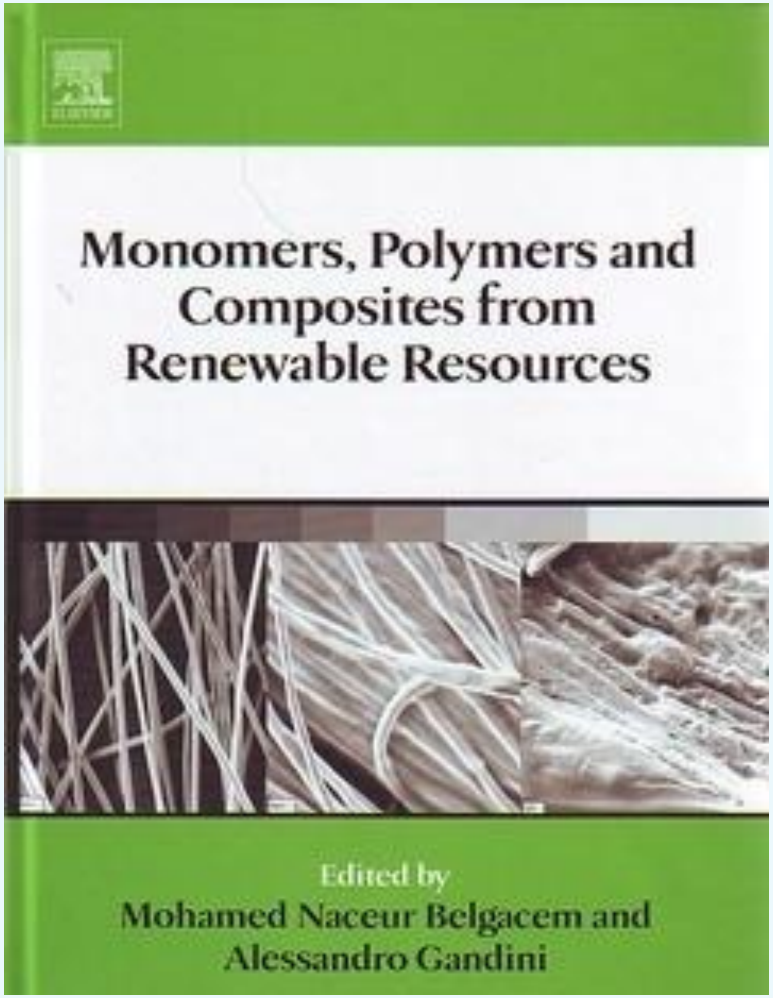

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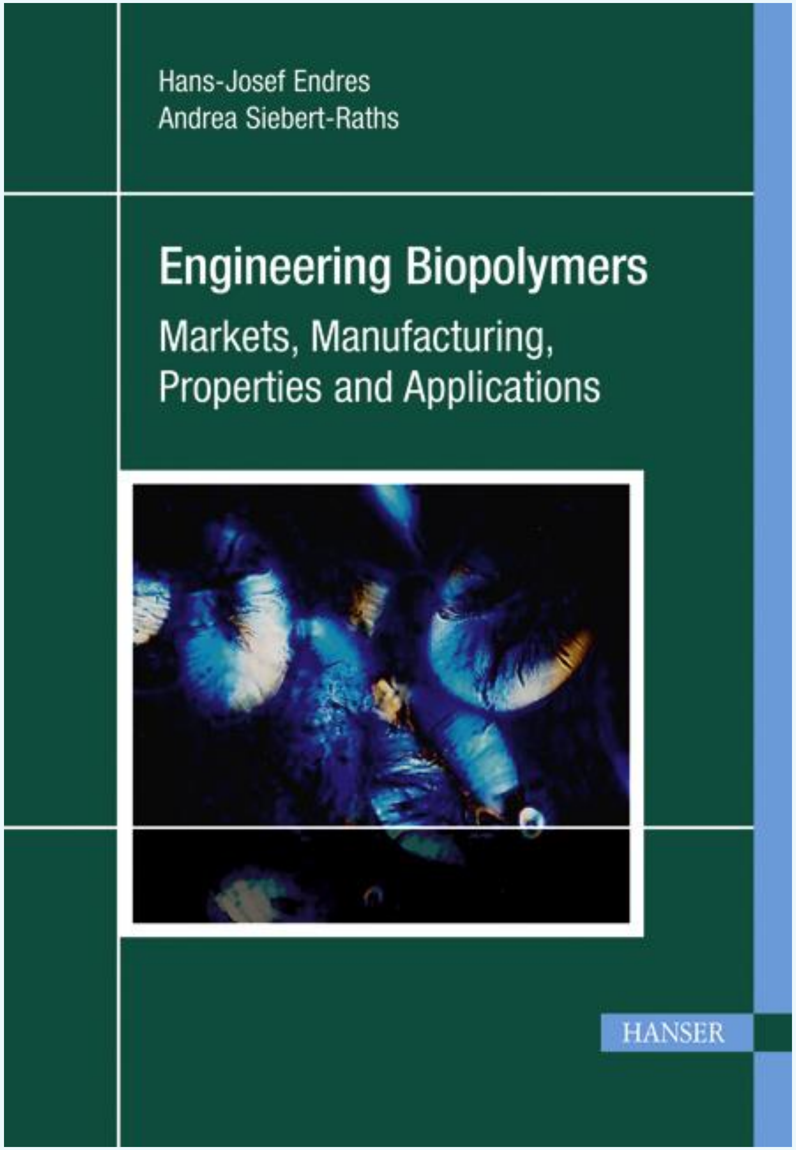

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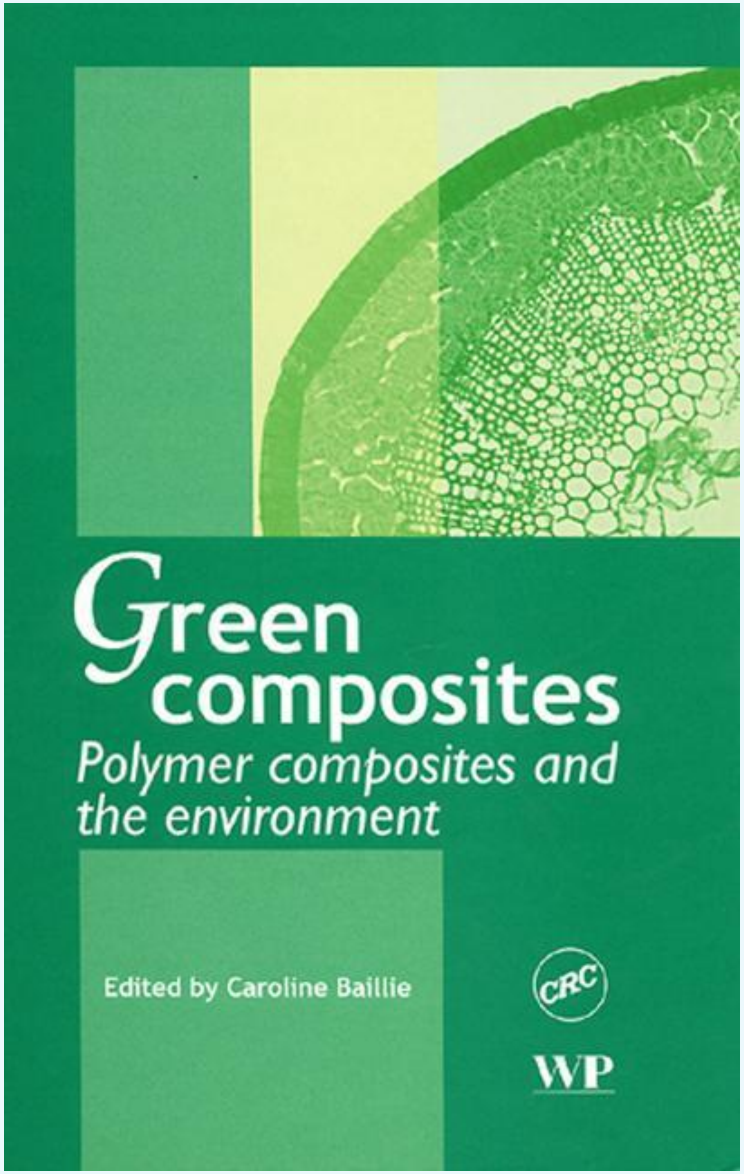

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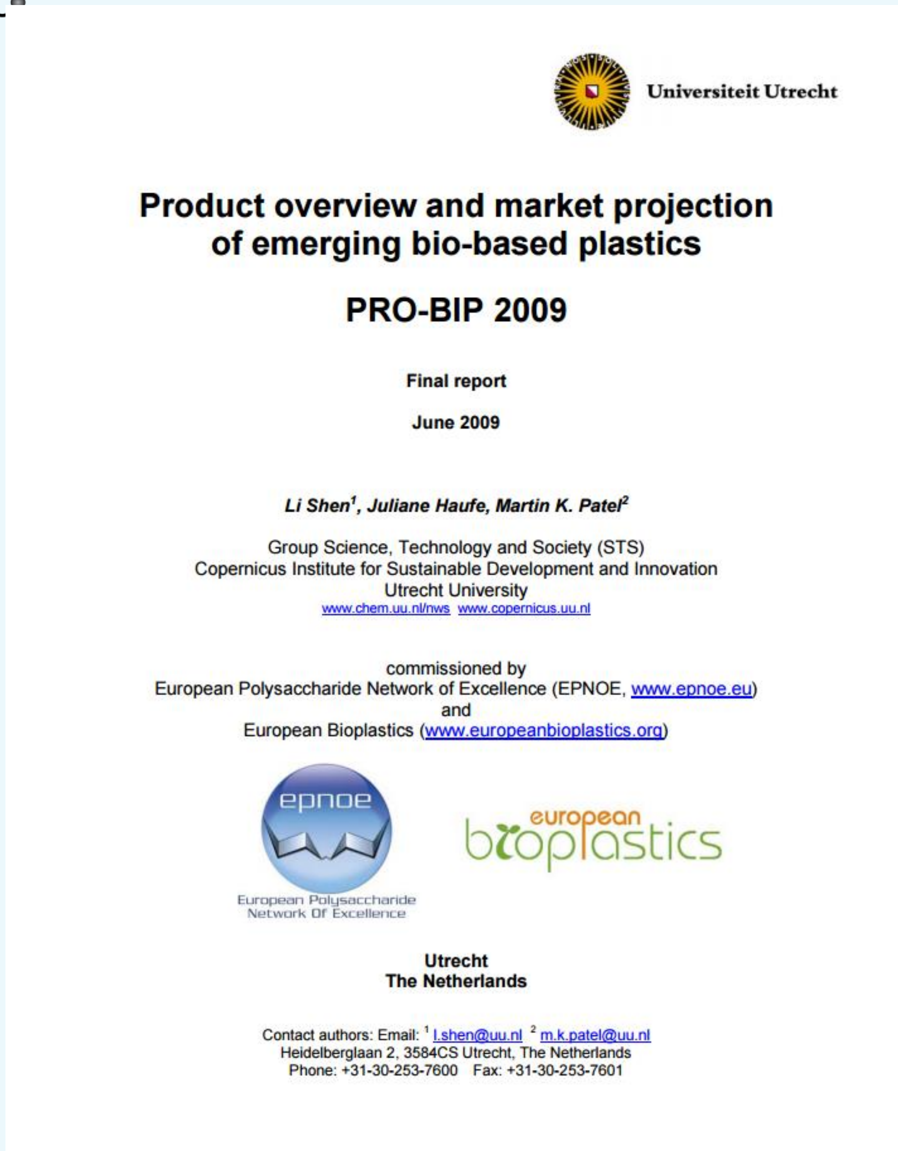

Universiteit Utrecht

Product overview and market projection of emerging bio-based plastics

PRO-BIP 2009

Final report

June 2009

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Review

Green composites: A brief review

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A B S T R A C T

The rising concern towards environmental issues and, on the other hand, the need for more versatile polymer-based materials has led to increasing interest about polymer composites filled with natural-organic fillers, i.e. fillers coming from renewable sources and biodegradable. The composites, usually referred to as "green", can find several industrial applications. On the other hand, some problems exist, such as worse processability and reduction of the ductility. The use of adhesion promoters, additives or chemical modification of the filler can help in overcoming many of these limitations. These composites can be further environment-friendly when the polymer matrix is biodegradable and comes from renewable sources as well. This short review briefly illustrates the main paths and results of research (both academic and industrial) on this topical subject, providing a quick overview (with no pretence of exhaustiveness over such a vast topic), as well as appropriate references for further in-depth studies.

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8. Environmental impact considerations 585
9. Conclusions 586
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1. Introduction

Polymer composites have been widely used for several years and their market share is continuously growing. It is widely known that the use of a polymer and one (or more) solid fillers allows obtaining several advantages and, in particular, a combination of the main properties of the two (or more) solid phases. Among the fillers used, it is worth citing [1] calcium carbonate, glass fibers, talc, kaolin, mica, wollastonite, silica, graphite, synthetic fillers (e.g. PET- or PVA-based fibers), high-performance fibers (carbon, aramidic, etc.).

However, this leads also to one of the main limitations of polymer composites: the two different components make the reuse and recycling quite difficult, to such an extent that it is often preferred to perform the direct disposal in a dump, or incineration [2,3]. This way is often considered to be unsatisfactory (especially in the first case), because of the high costs, the technical difficulties and the environmental impact. The latter is, indeed, a problem of primary importance. Furthermore, it is worsened by the fact that plastics production requires a remarkable consumption of oil-based resources, which are notoriously non-renewable.

These problems have begun to be particularly evident for about 10 years, thus leading the scientific research to look for new alternatives, able to replace traditional polymer composites with substitutes having lower environmental impact and thus often referred to as "ecocomposites" or "green composites". This task can be made easier by the fact that many of the typical applicative fields of these composites do not require excellent mechanical properties (i.e. secondary and tertiary structures, panels, packaging, gardening items, cases, etc.) [2,4].

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Review

Biofibres and biocomposites

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Abstract

This review deals with a recent study of the literature on the various aspects of cellulosic fibres and biocomposites. Cellulosic fibre reinforced polymeric composites are finding applications in many fields ranging from construction industry to automotive industry. The pros and cons of using these fibres are enumerated in this review. The classification of composites into green composites, hybrid biocomposites and textile biocomposites are discussed. New developments dealing with cellulose based nanocomposites and electrospinning of nanofibres have also been presented. Recent studies pertaining to the above topics have also been cited. Finally, the applications of cellulosic fibre reinforced polymeric composites have been highlighted.

Keywords: Biocomposite; Biofiber; Green composite; Textile; Hybrid

1. Lignocellulosic fibres/natural fibres

Natural fibres are subdivided based on their origins, coming from plants, animals or minerals. All plant fibres are composed of cellulose while animal fibres consist of proteins (hair, silk, and wool). Plant fibres include bast (or stem or soft sclerenchyma) fibres, leaf or hard fibres, seed, fruit, wood, cereal straw, and other grass fibres. Over the last few years, a number of researchers have been involved in investigating the exploitation of natural fibres as load bearing constituents in composite materials. The use of such materials in composites has increased due to their relative cheapness, their ability to recycle and for the fact that they can compete well in terms of strength per weight of material. Natural fibres can be considered as naturally occurring composites consisting mainly of cellulose fibrils embedded in lignin matrix. The cellulose fibrils are aligned along the length of the fibre, which render maximum tensile and flexural strengths, in addition to providing rigidity. The reinforcing efficiency of natural fibre is related to the nature of cellulose and its crystallinity. The main components of natural fibres are cellulose (α-cellulose), hemicellulose, lignin, pectins, and waxes.

Cellulose is a natural polymer consisting of D-anhydroglucose ($C_6H_{11}O_5$) repeating units joined by 1,4-β-D-glycosidic linkages at C_1 and C_4 position (Nevell & Zeronian, 1985). The degree of polymerization (DP) is around 10,000. Each repeating unit contains three hydroxyl groups. These hydroxyl groups and their ability to hydrogen bond play a major role in directing the crystalline packing and also govern the physical properties of cellulose. Solid cellulose forms a microcrystalline structure with regions of high order i.e. crystalline regions and regions of low order i.e. amorphous regions. Cellulose is also formed of slender rod like crystalline microfibrils. The crystal nature (monoclinic sphenodic) of naturally occurring cellulose is known as cellulose I. Cellulose is resistant to strong alkali (17.5 wt%) but is easily hydrolyzed by acid to water-soluble sugars. Cellulose is relatively resistant to oxidizing agents.

Hemicellulose is not a form of cellulose and the name is a misnomer. They comprise a group of polysaccharides composed of a combination of 5- and 6-carbon ring sugars. Hemicellulose differs from cellulose in three aspects. Firstly, they contain several different sugar units whereas cellulose contains only 1,4–β-D-glucopyranose units.

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Natural fibre composites: Comprehensive Ashby-type materials selection charts

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ABSTRACT

To aid design engineers in closing the existing gap between current scientific knowledge and actual market applications of plant fibre reinforced plastics (PFRPs), this article provides comprehensive Ashby-type materials selection charts for PFRPs to facilitate product design and development. General tensile mechanical property profiles are presented for a variety of PFRPs to enable the design for (i) optimal stiffness and strength, (ii) minimal weight (i.e. optimal specific properties), (iii) minimal cost, and (iv) minimal eco-impact. A large database is used to capture the range in properties of different (i) reinforcements forms (short fibres: pellets and nonwovens; long fibres: multiaxials and unidirectionals), (ii) polymer matrices (thermoplastic and thermosetting), and (iii) manufacturing techniques (injection moulding, compression moulding, hand lay-up, vacuum infusion, resin transfer moulding and prepregging). As PFRPs are often viewed as alternatives to glass fibre composites (GFRPs), for demonstrative purposes the tensile properties of the various PFRPs are compared with similar GFRPs. Moreover, highlighting that other mechanical parameters may be critical performance indices for specific products and applications, a materials property chart for a fatigue-limited design is also produced.

1. Introduction

Increasing environmental concerns and awareness amongst consumers, tightened environmental and waste management legislations by government, and a deepening reliance on non-renewable resources by industry despite a commitment to social responsibility are key factors that have driven the increasing interest in the use of bio-based materials as replacements to traditional 'man-made' materials in various applications. To alleviate some of the environmental issues associated with using synthetics in fibre reinforced plastics (FRPs), bio-based, if not fully-green, ingredients are being considered to replace both the typically synthetic fibre reinforcement and the petrochemically-derived matrix [1]. Notably, other than the eco-advantage of using bio-based constituents, their typically lower cost and wide availability, and their promising and competitive technical mechanical properties have strengthened the case for bio-based composites as engineering materials [1].

Despite the tremendous interest and vivid research in natural fibre reinforced composites for over two decades, to date, they have been successfully established only in the automotive industry (for interior components) [1,2], and have to a limited extent penetrated the construction (mainly deckings) and consumer goods markets [2]. Parallel to this, in spite of a threefold growth in the use of plant fibres (excluding wood and cotton) in reinforced plastics over the last decade in the EU, only a small percentage of plant fibres have been utilised as reinforcements in composites [1]. A report by the European Industrial Hemp Association [3] claims that in 2012, while hemp fibres represented 10–20% of the market share of plant fibre reinforced plastics (PFRPs) in the EU, the total allocation of hemp for composites applications was 14%; the two primary applications of hemp fibres were for specialty pulp and paper (55%) and insulation (26%). Flax fibres, on the other hand, accounted for >60% of the EU market share of PFRPs, but even their primary application (>75%) lay in textiles [4].

While it is clear that there is great scope for plant fibres to be exploited as composite reinforcements, it is often suggested [1,5–7] that the critical aspects limiting the wide industrial applications of PFRPs relate to:

(i) the variable and often inferior mechanical properties of plant fibres in comparison to synthetic fibres like E-glass,
(ii) the lack of – or at least limited – empirical data on (a) critical atypical loading conditions such as off-axis, multiaxial, high-strain rate, fatigue and creep loading, and (b) the effects of environmental conditions such as humidity/moisture and temperature/fire, and

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