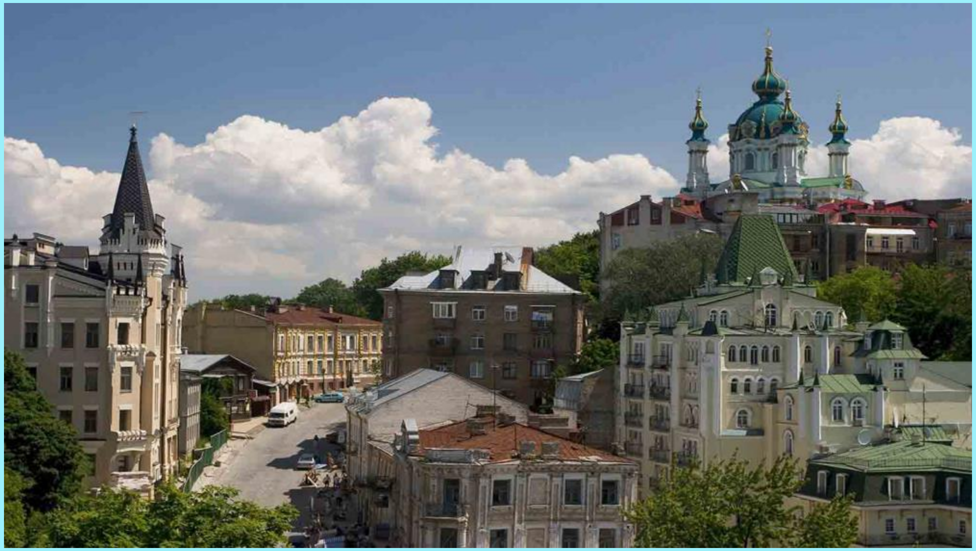
NTUU-KPI, Kiev, Ukraine



THE BASIC OF KNOWLEDGE ABOUT BIOCOMPOSITES AND BIODEGRADABLE MATERIALS

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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:

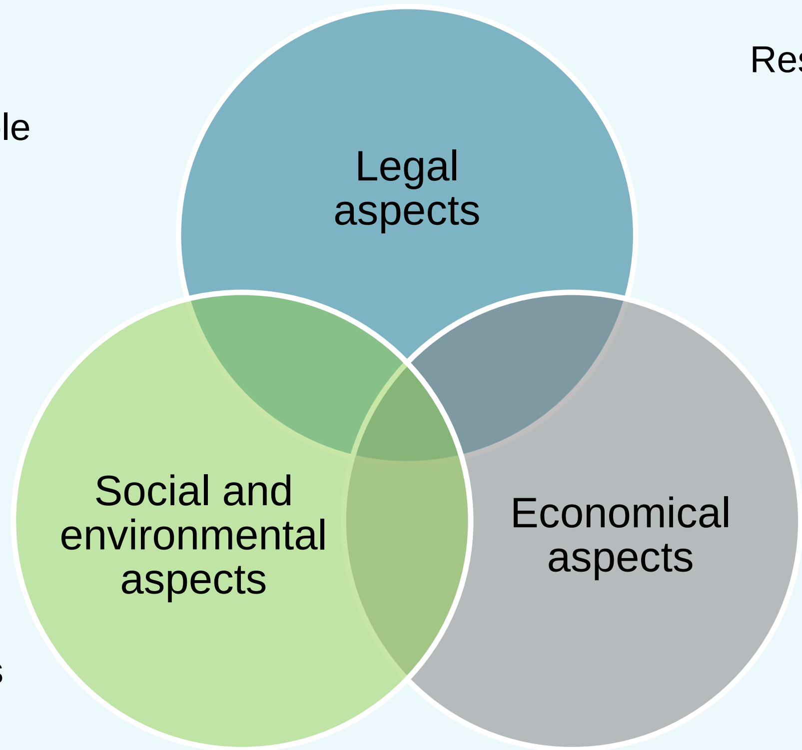
- **basic definitions and classifications connected to materials obtained from renewable sources**
- **advantages and disadvantages of using renewable and non-renewable sources in materials synthesis, processing and use**

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.

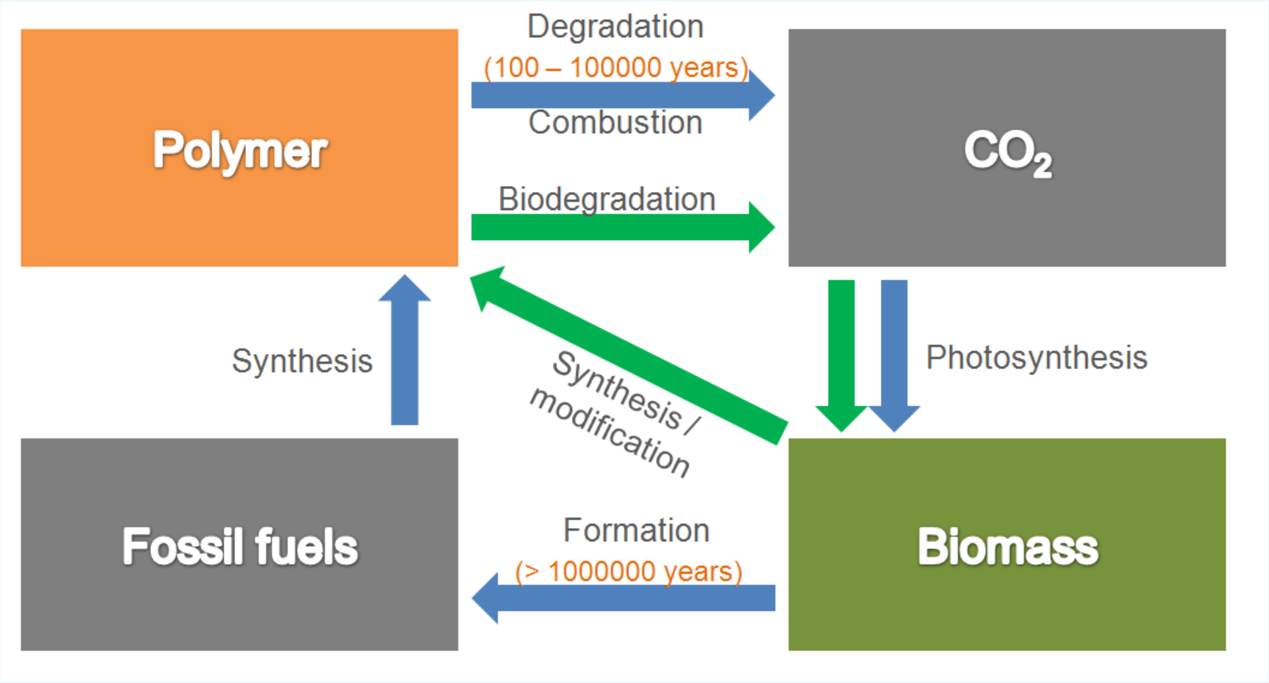
Content (lecture)

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

Example of short-therm and logn-therm life cycle

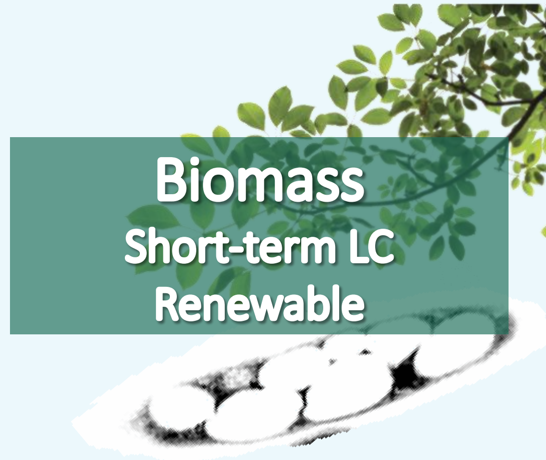


A simplified organic carbon cycle for engineering polymers: biobased and biodegradable polymers (green arrows) and common petrochemical polymers (blue arrows)

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

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

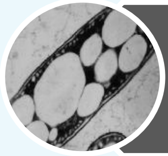
! Renewable sources of materials ~ biomass. Different definitions (many for the purpose of defining energy sources)

- 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)?

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

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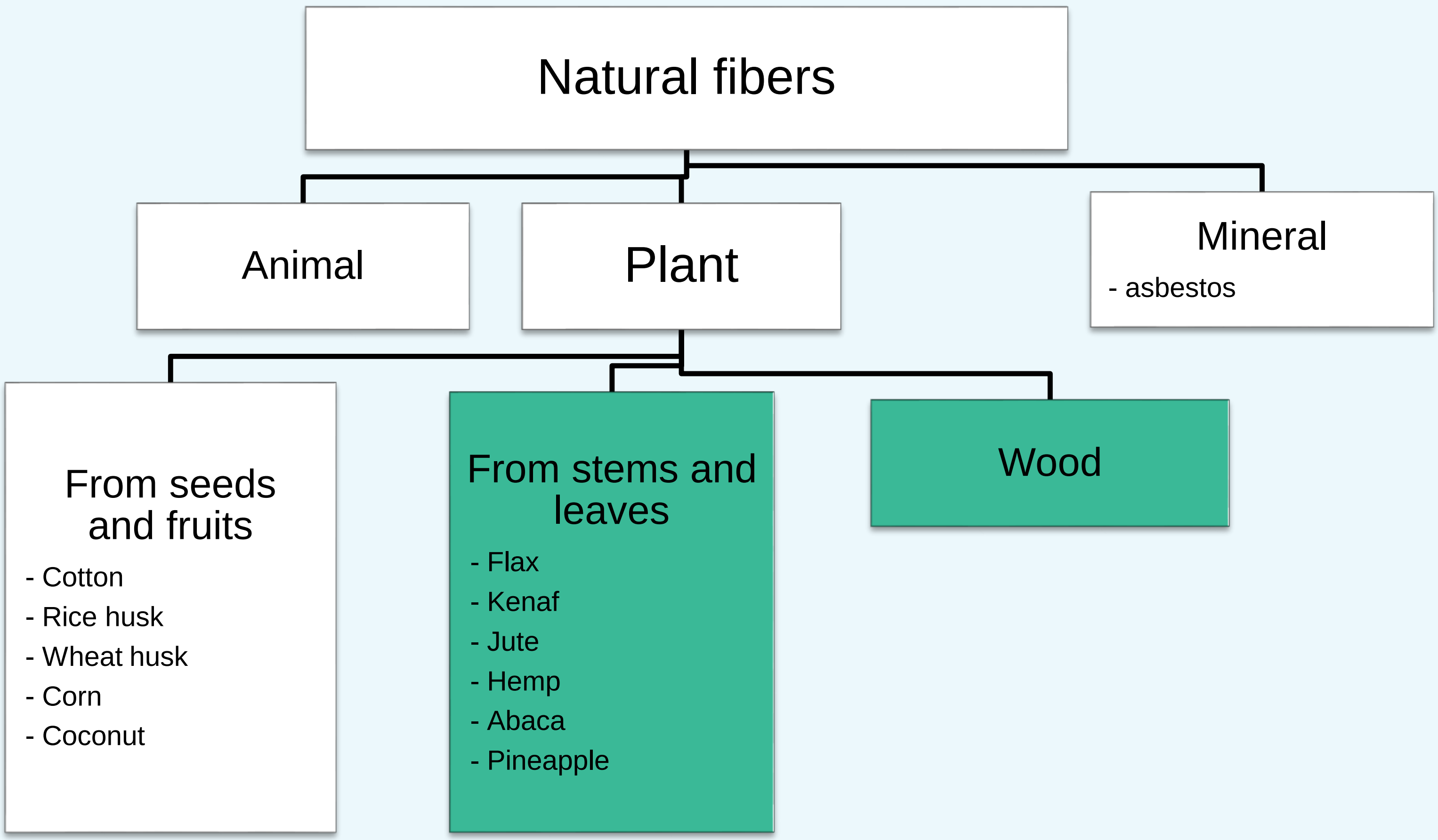
Characterization of traditional materials from renewable sources – the history and developement:
- Wood and wood-based products
- Natural fibers (plant fibers and animal fibers)

! 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



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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

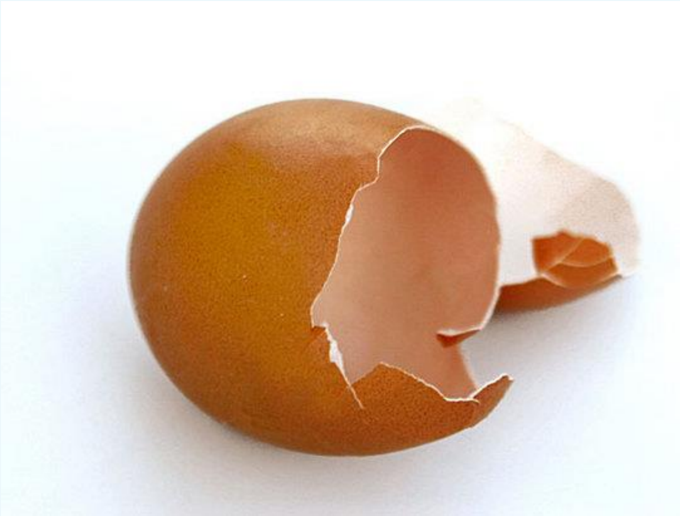
Natural fibers vs. glass fibers – not a whole picture. An example

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

Traditional an novel applications of traditional biobased materials – an example

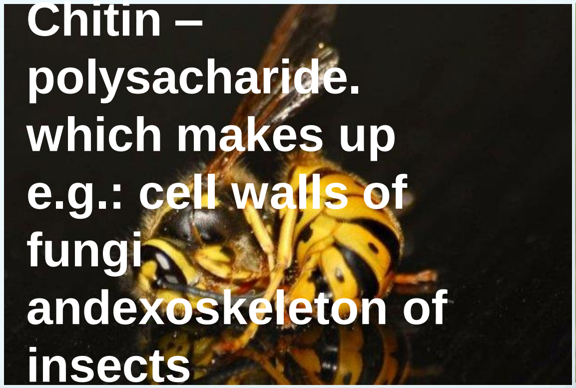
- **Natural fiber applications**
  - Textile technology: spinning, weaving, knitting, finishing
  - Cellulose pulp (source of man-made cellulose fiber) and paper
  - Other technical applicatons
    - Composites: polymer biocomposites, concrete filler
    - Mats and geotextiles
    - Raw material for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

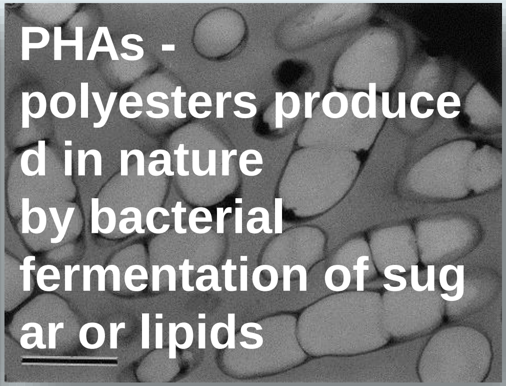
Less popular… and not only fibrous

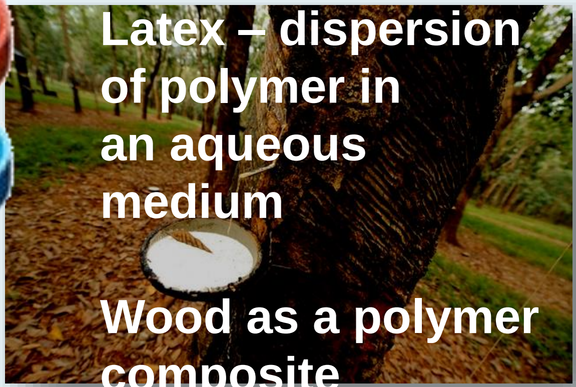


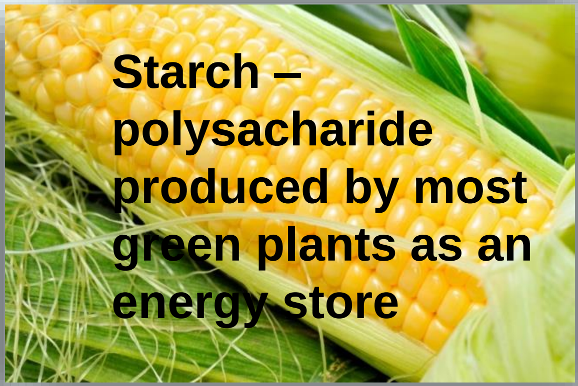
Biopolymers = natural polymers?

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







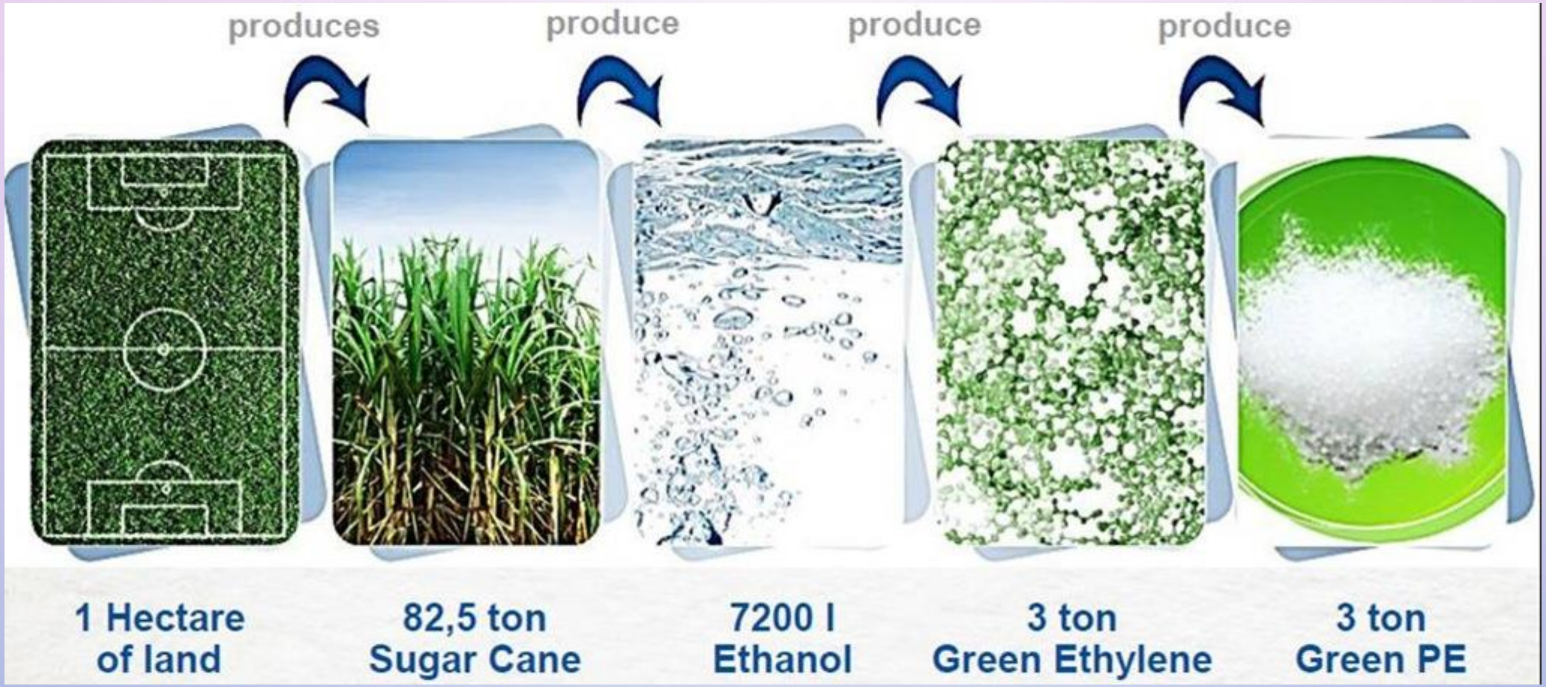


Biobased and/or biodegradable

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

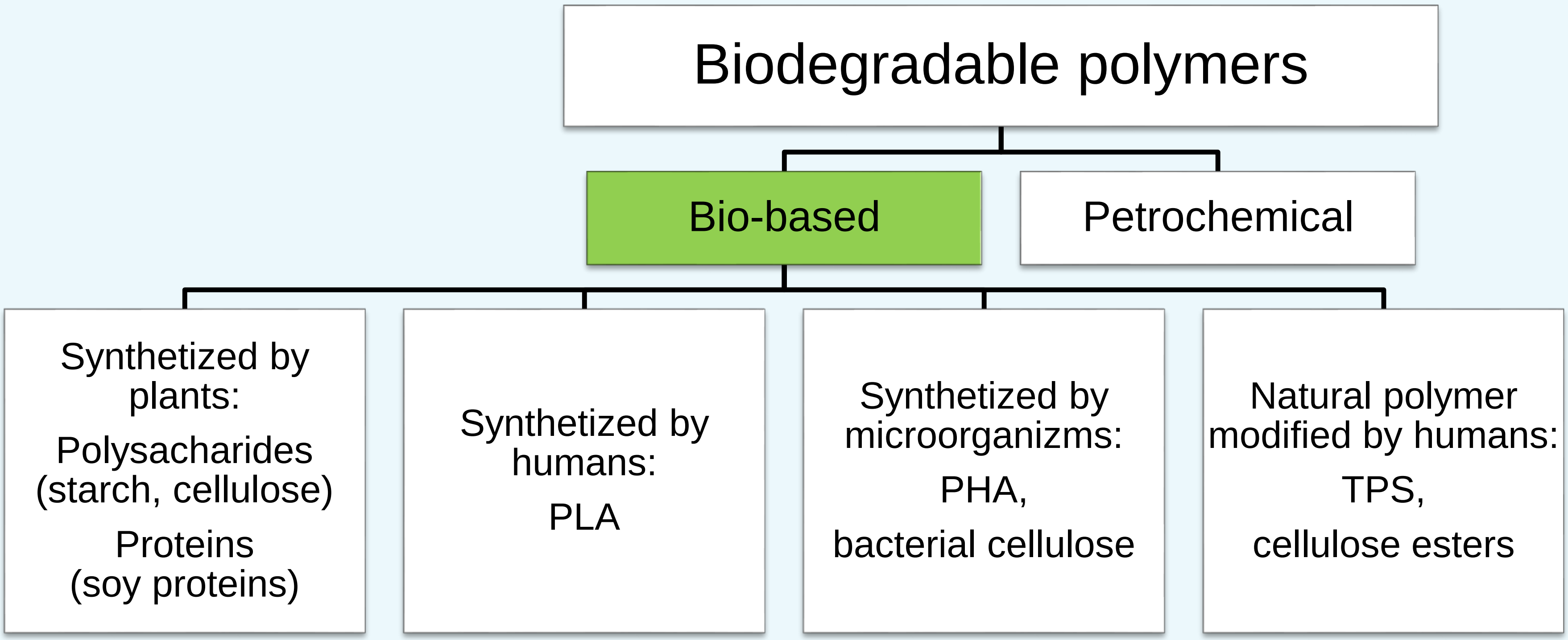
BIODEGRADABILITY

FEEDSTOCK



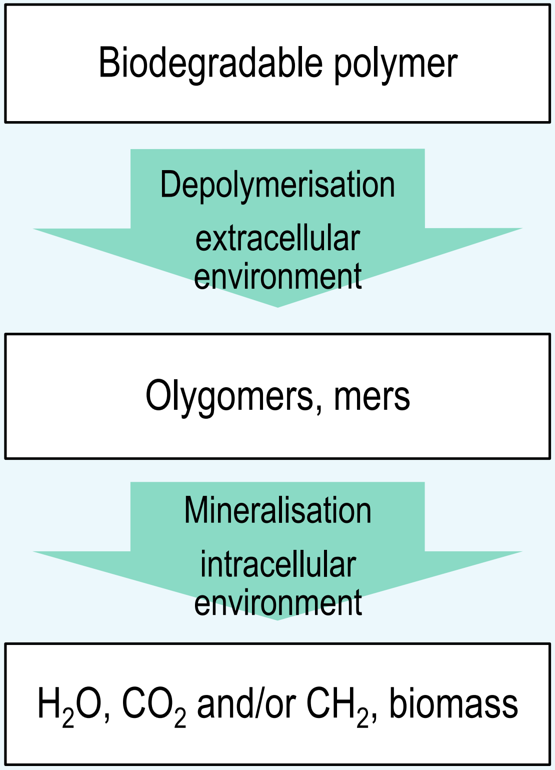
Bio-ethanol is produced from sugar cane using a fermentation process. The bio-ethylene monomer can then be used in traditional polyethylene polymerization processes to make the various grades of PE (HDPE, LDPE, LLDPE).

Biopolymers and the „feedstock → technical material" path possibilities



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 housing
of a touchscreen computer

PLA used for
Röchling Automotive’s air filter

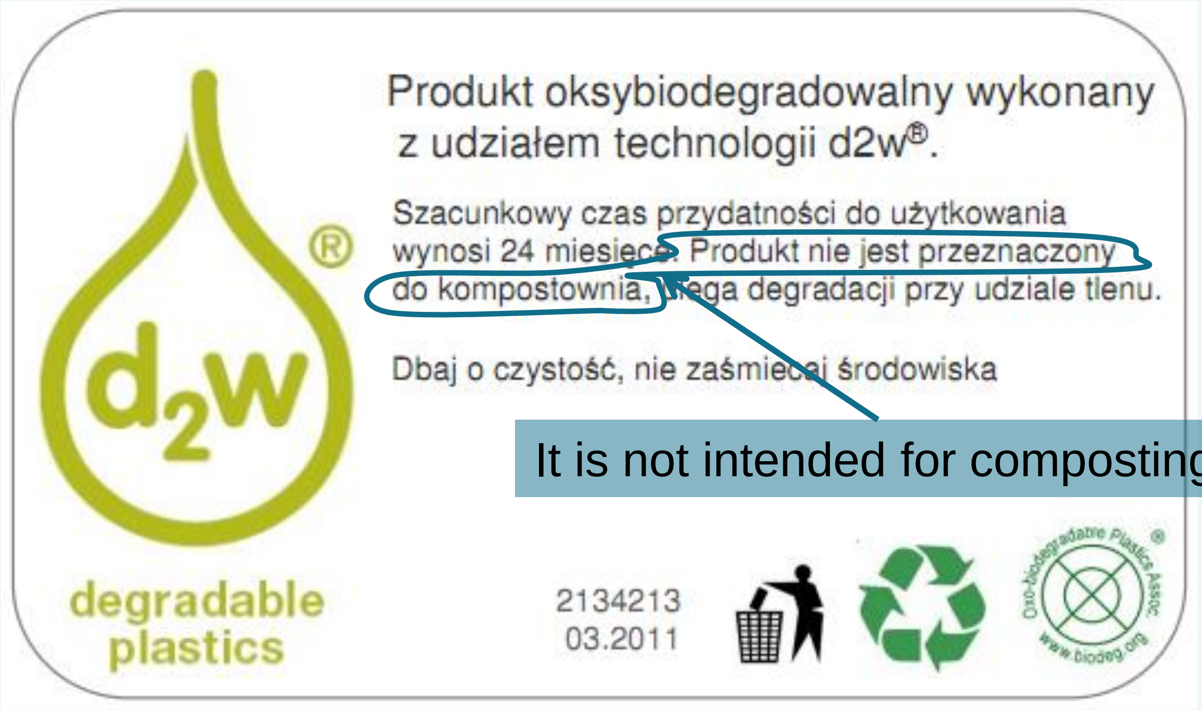
Foamed PLA surfboard

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?

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



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

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

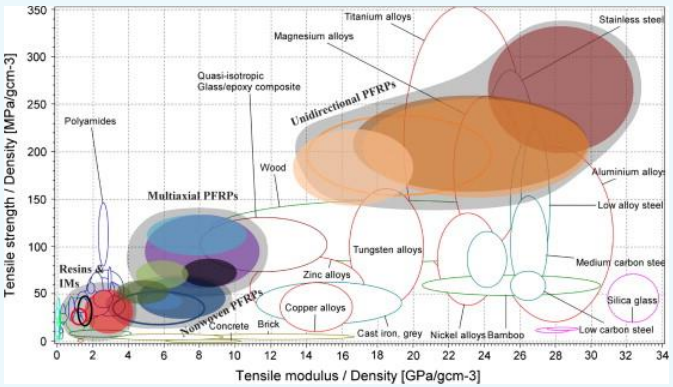
Biobomposies matrices – mainly thermoplastics of low processin temperatures (190 - 230°C) and low viscosity:

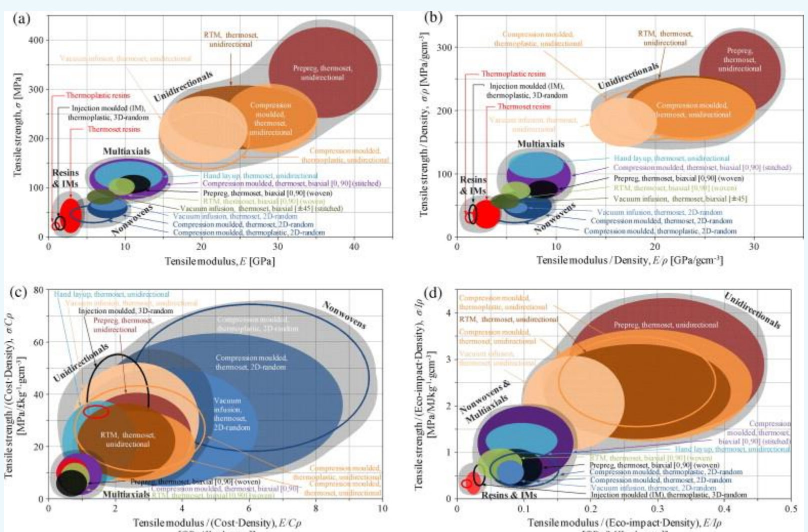
- Non-biodegradable polymers, standard or biobased, also recycled polymers: PP, PEHD, PVC, PS
- Biopolymers (PLA, TPS, PHB, CA)

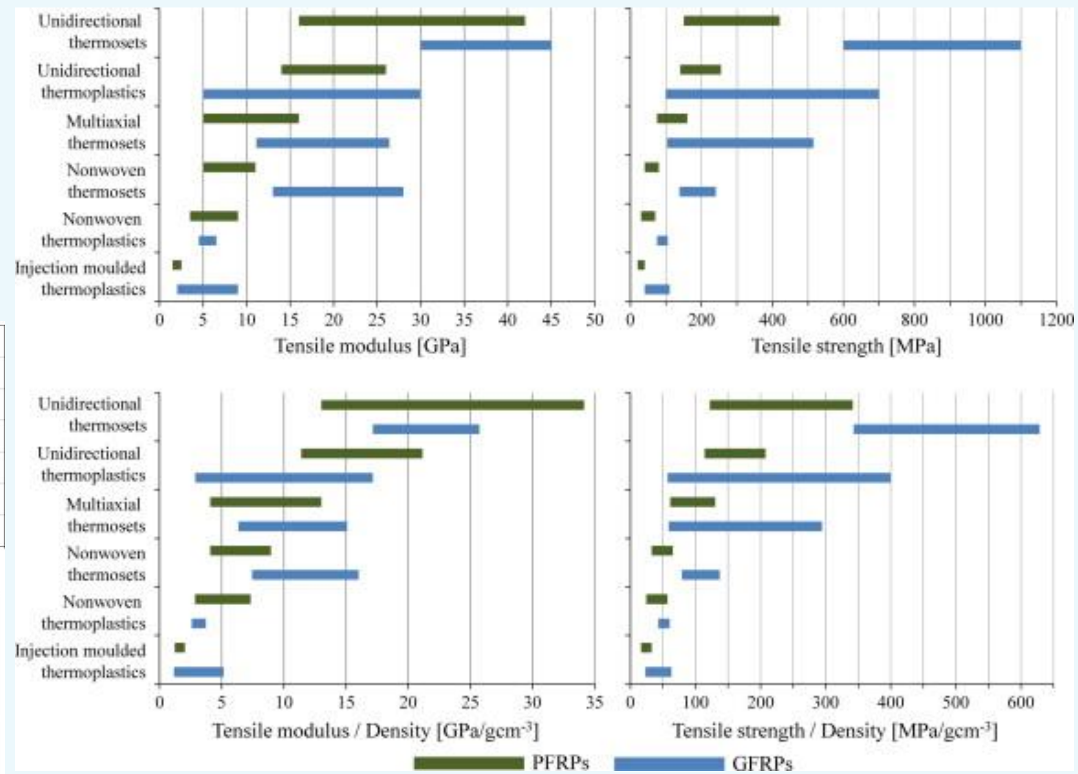
Thermosets: standard petrochemical thermosets or partially biobased

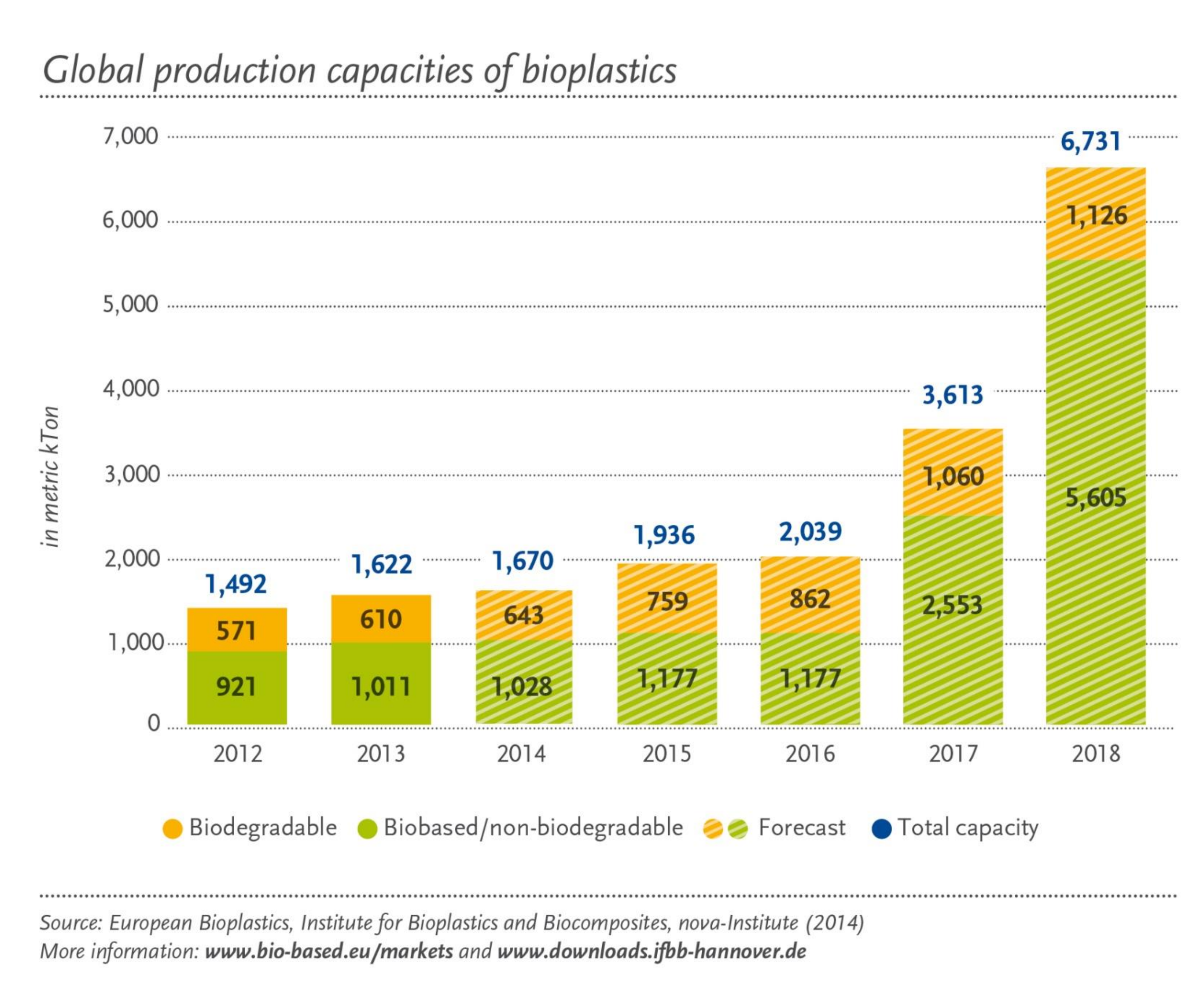
Various matrices → various processing methods

Traditional and biobased materials - compare



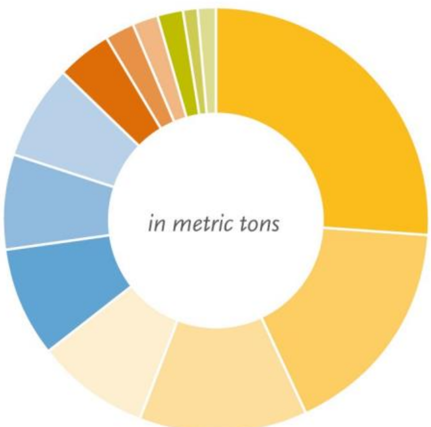






Biocomposites on the market – examples of materials and products

Biopolymers production capacity 2015 (by type)



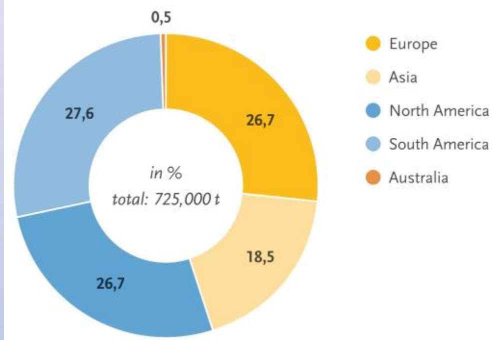
Bio-PE	450.000	26 %
Bio-PET	290.000	17 %
PLA	216.000	13 %
PHA	147.100	9 %
Biodegradable Polyesters	143.500	8 %
Biodegradable Starch Blends	124.800	7 %
Bio-PVC	120.000	7 %
Bio-PA	75.000	5 %
Regenerated Cellulose[1]	36.000	2 %
PLA-Blends	35.000	2 %
Bio-PP	30.000	2 %
Bio-PC	20.000	1 %
Others	22.300	1 %
Total	**1.709.700**	100 %

[1] *only hydrated cellulose foils*

Source: European Bioplastics | University of Applied Sciences and Arts Hanover

european bioplastics -F|-| Fachhochschule Hannover University of Applied Sciences and Arts

Production capacity of biopolymers in 2010 (by region)



Source: European Bioplastics | University of Applied Sciences and Arts Hanover

european bioplastics -F|-| Fachhochschule Hannover University of Applied Sciences and Arts

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

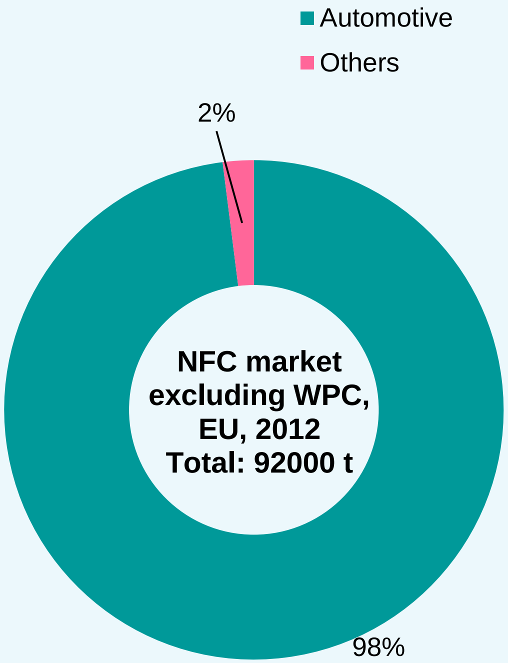
Applications

- 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


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

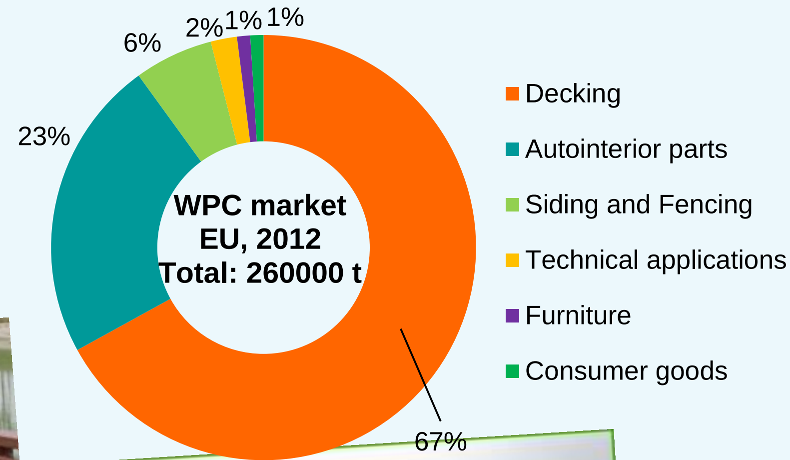
Four Motors GmbH

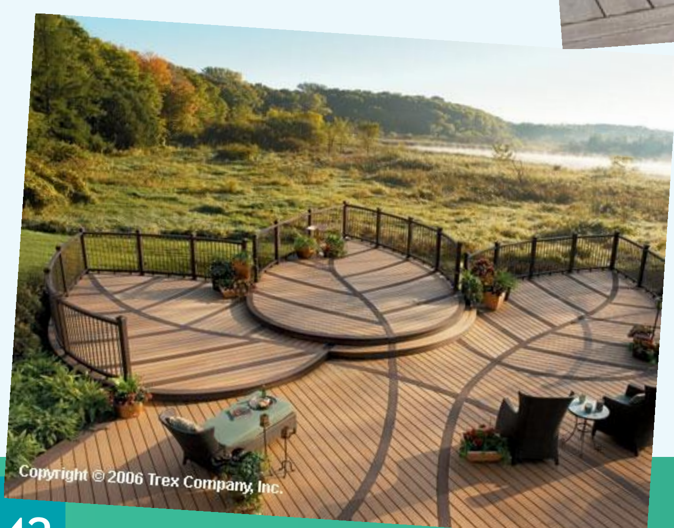
(biocomposite: thermoset resin with flax, hemp and cotton fibers)

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)

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

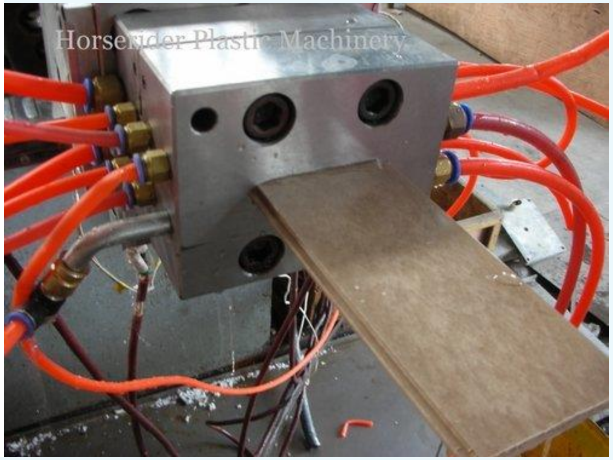
AH – academic hour (Total: 15 for laboratory work)

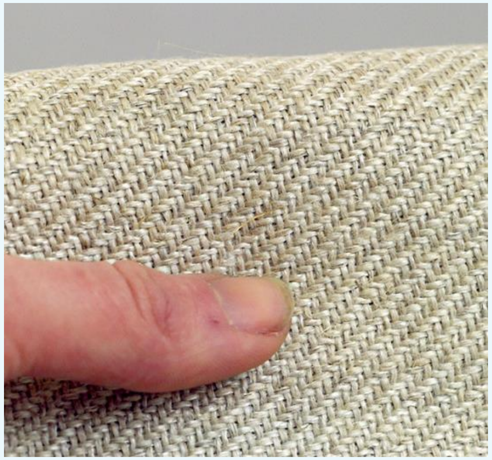
1. Processing of biopolymers and biocomposites.

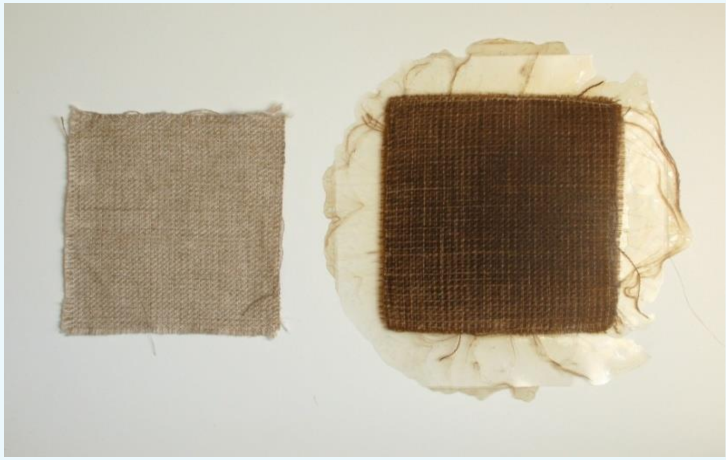
- ! Chose the matrix (thermoplastsic or thermoset) and the amount of filler and adequate method of processing, e.g.: injection molding, extrusion molding (compounding), hand lay-up, infusion, compression molding
- ! Most of biopolymers are thermoplastic

- 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

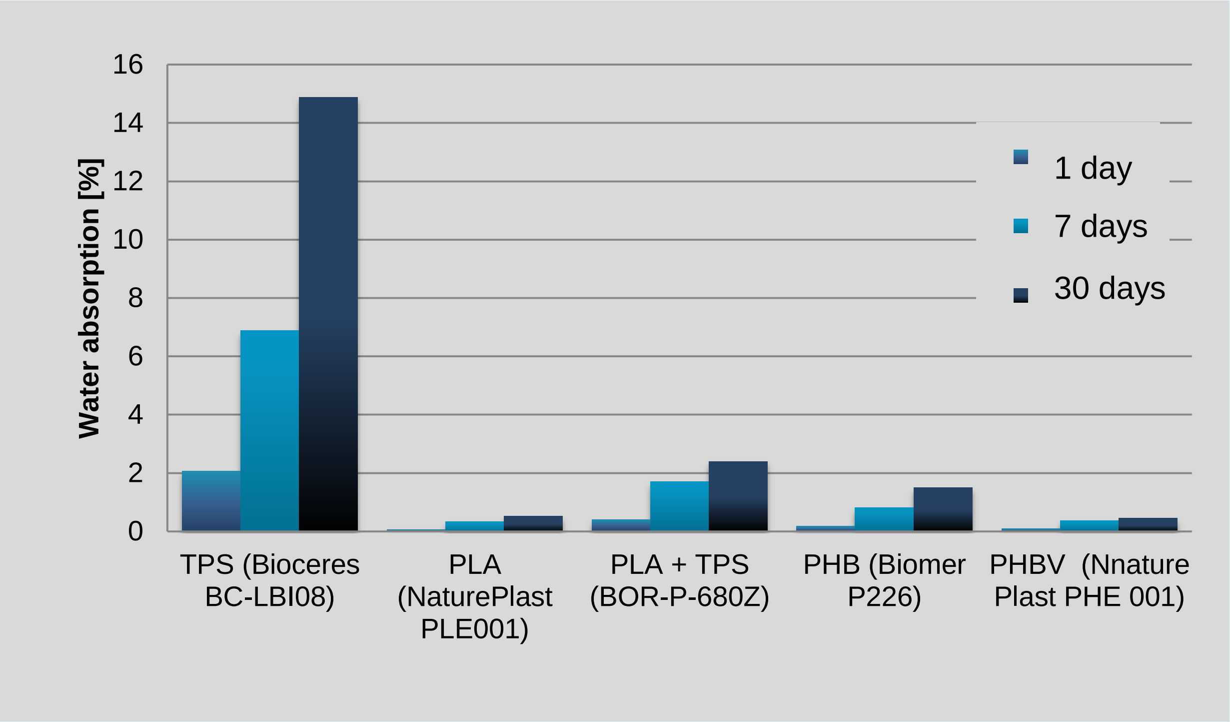
Environment – a lot to choose from

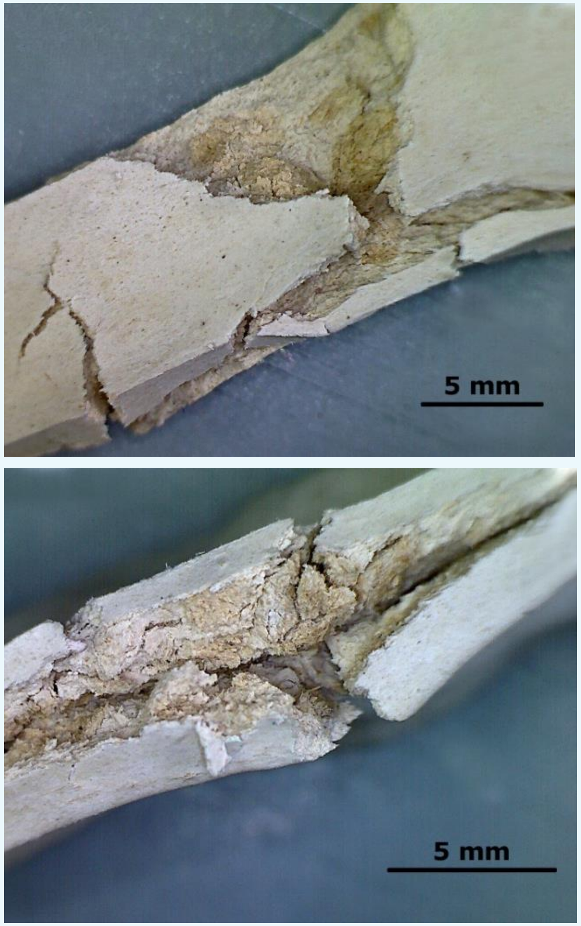
Environment used for biodegradability assessment:

- 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

Water absorption – an example





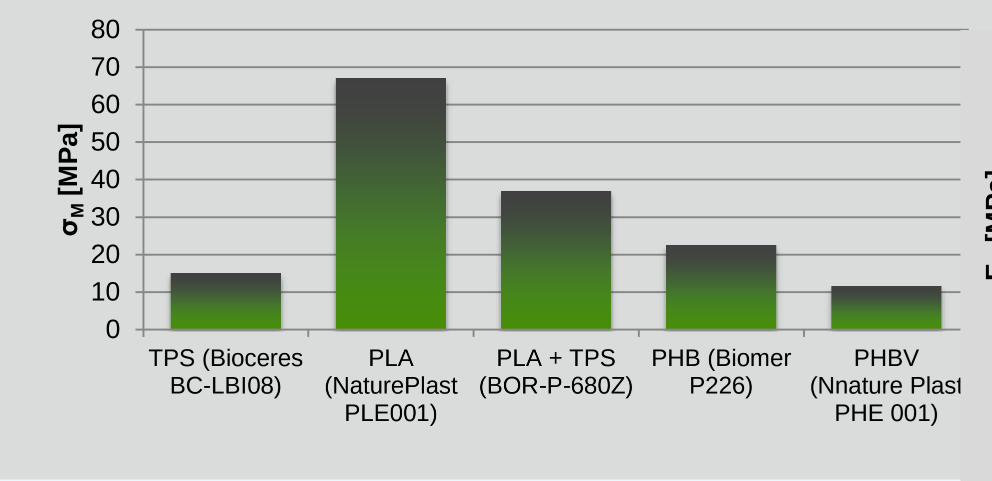
TPS with wood flour after a month of soaking in water (room temerature)

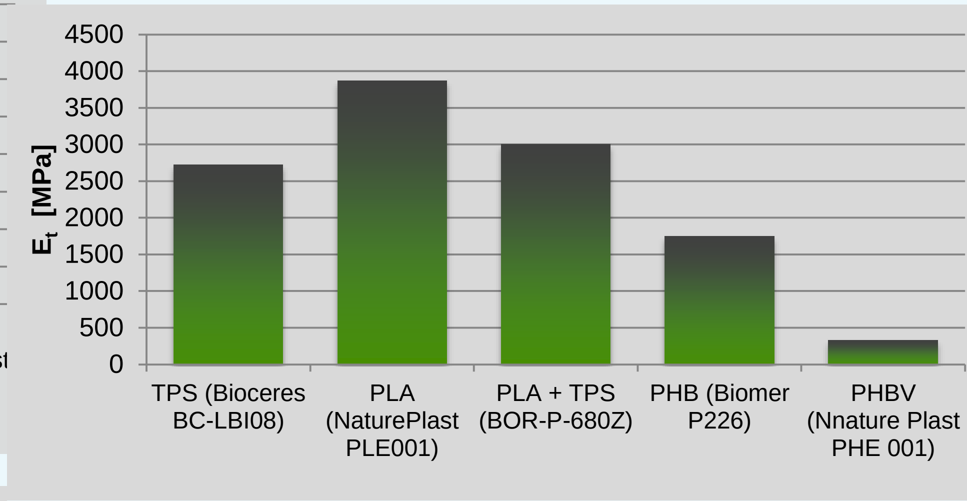
4. Mechanical properties of biopolymers and biocomposites and the influence of water uptake.

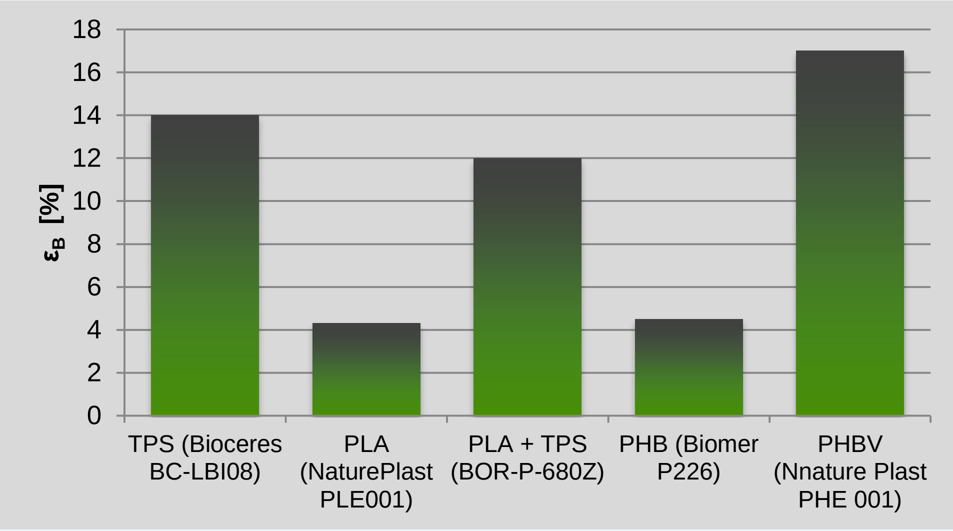
- ! Choose a test method (most often: standard tensile test) and compare various biobased and petroleum materials
- ! Use technical data sheets (TDS)

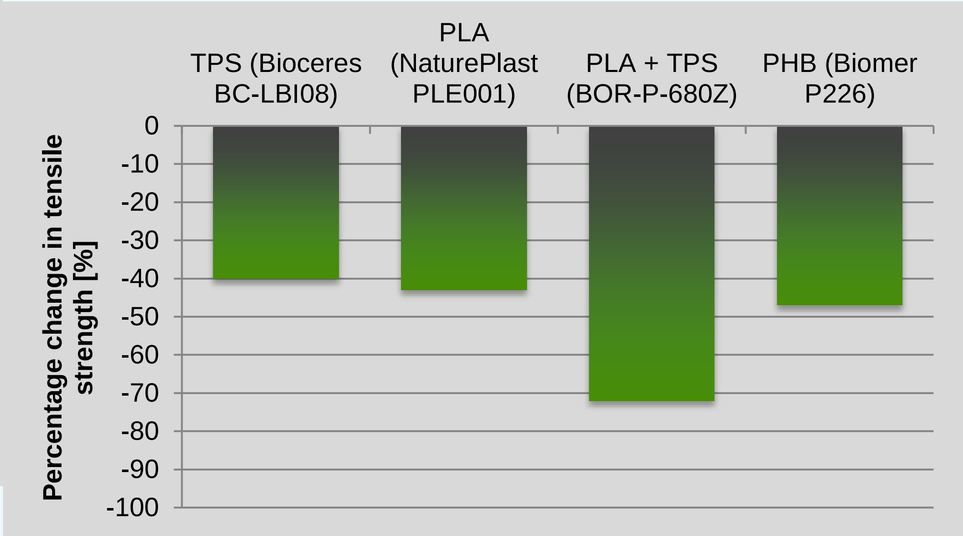
- Test properties of main biodegradable polymers (PLA, TPS, PHB) as well as of neat matrices and composites with natural fillers. Compare the results with resutls obtained for traditional materials (own experimental data or TDS)
- Assess water influence - tensile test after soaking specimens in water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

Tensile test results – an example

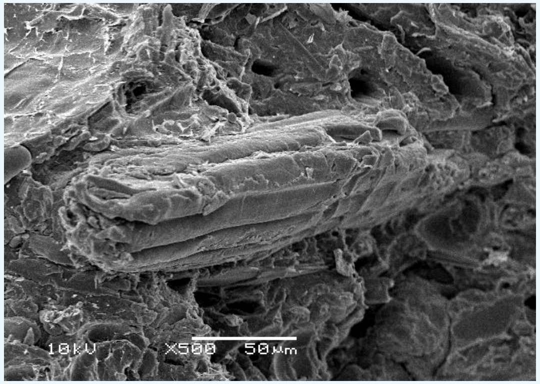


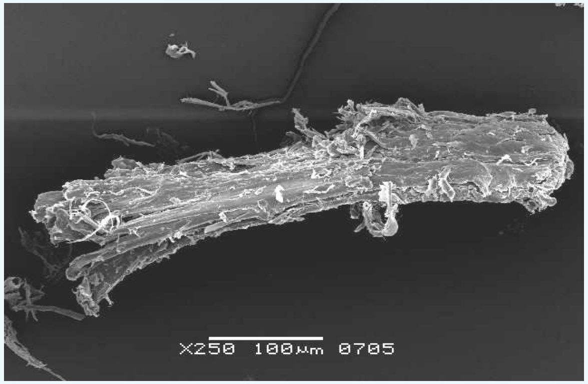




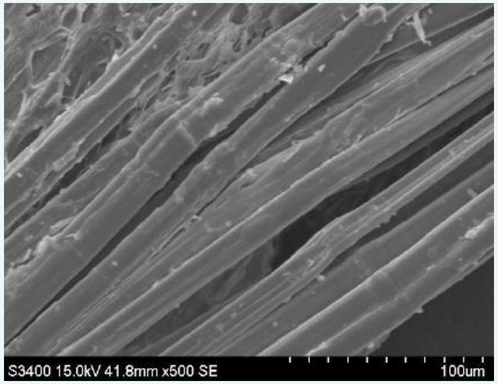


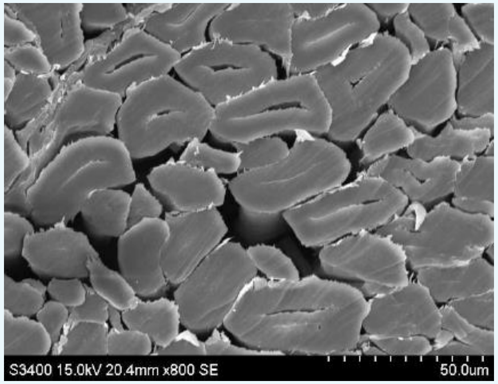
Morphology of plant fillers –examples



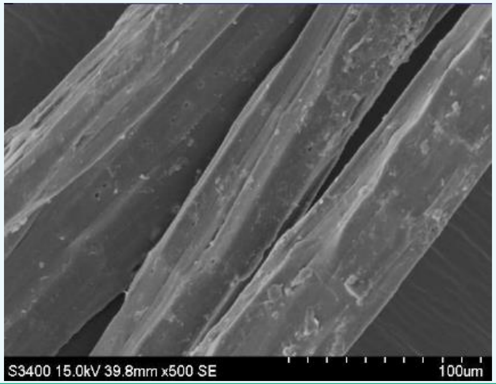


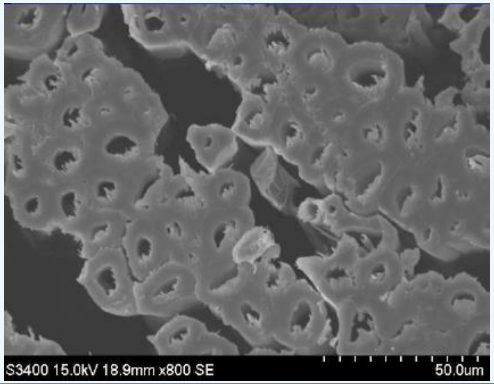
Wood flour





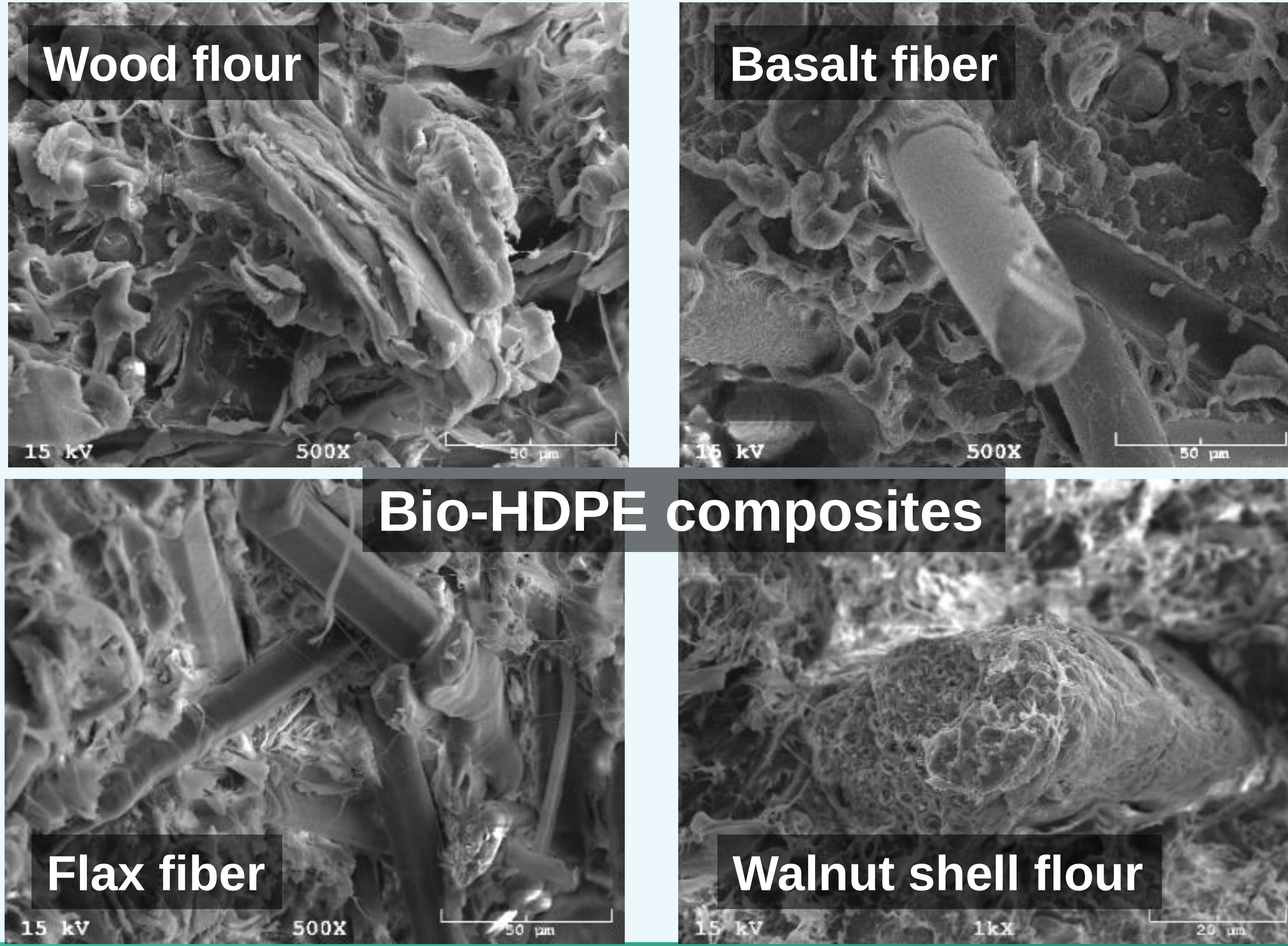
Flax fibers

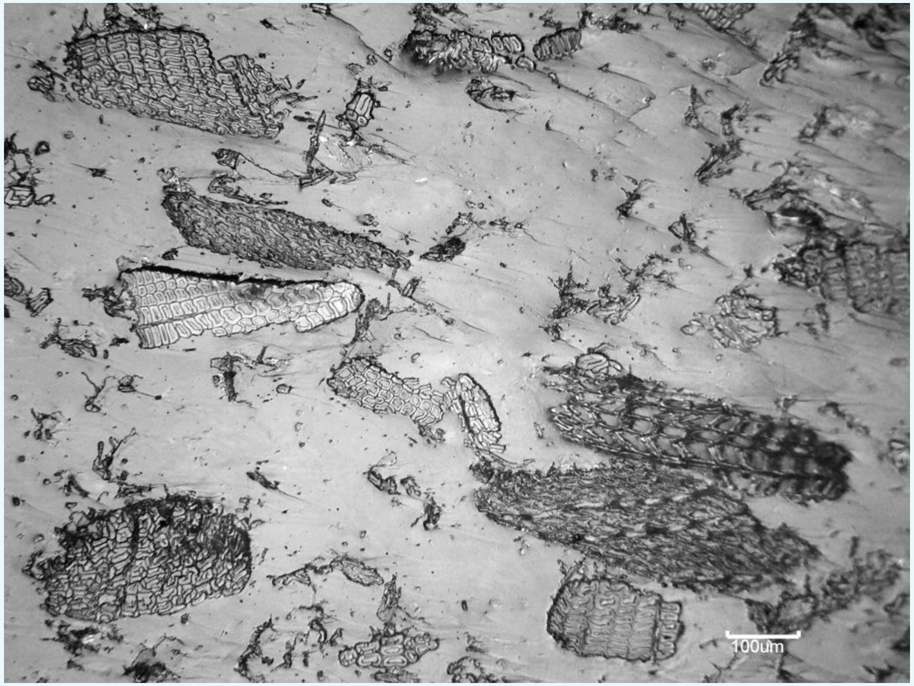




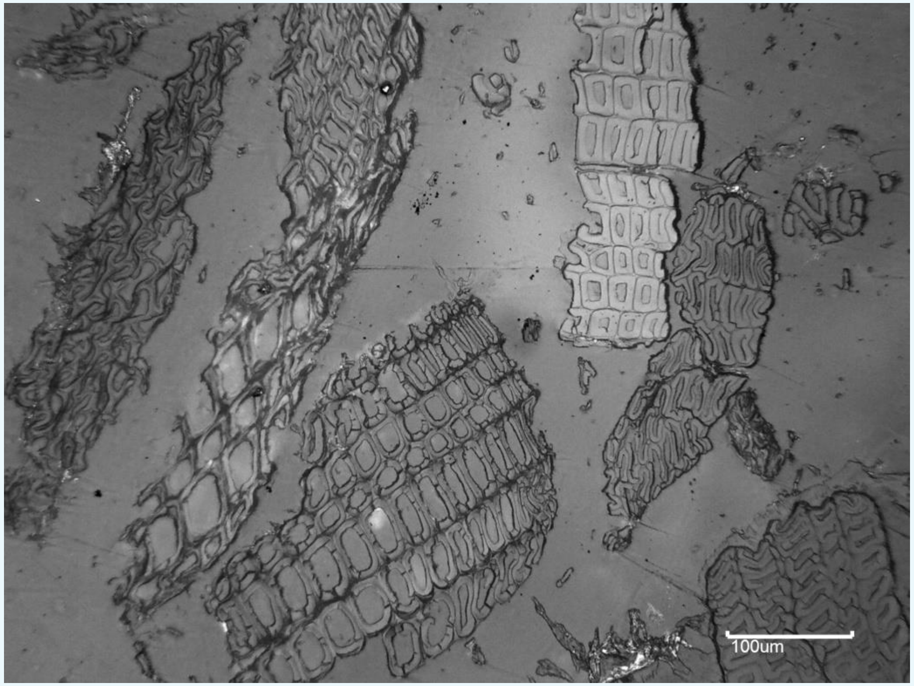
Kenaf fibers

Bio-HDPE composites





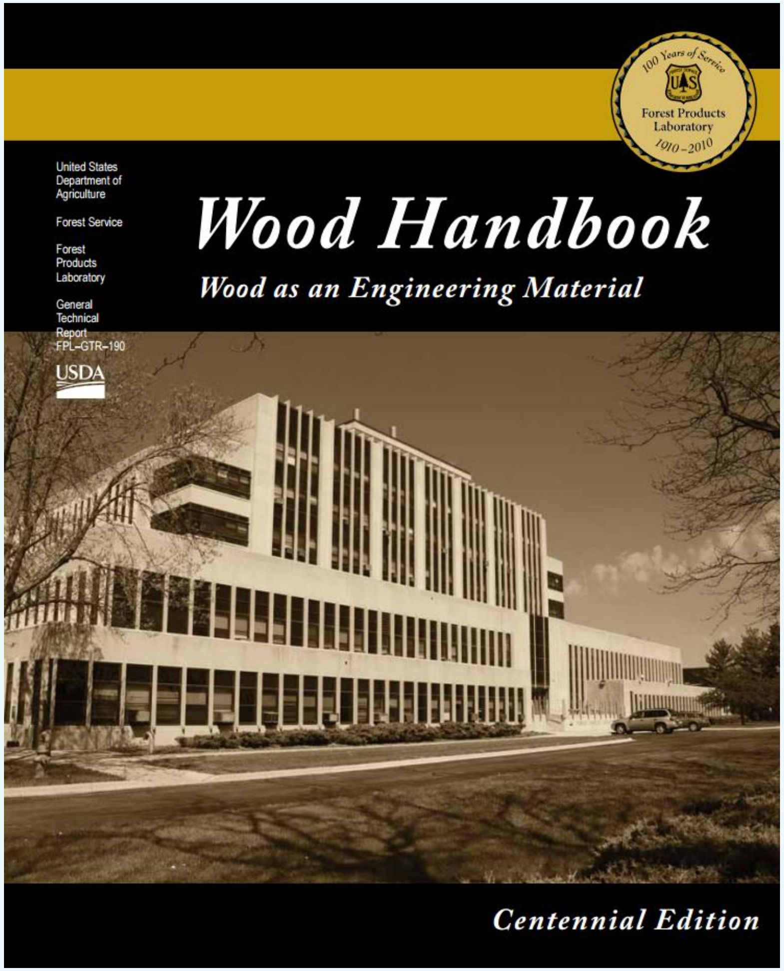
Optical microscope: Wood flour in bio-PE matrix



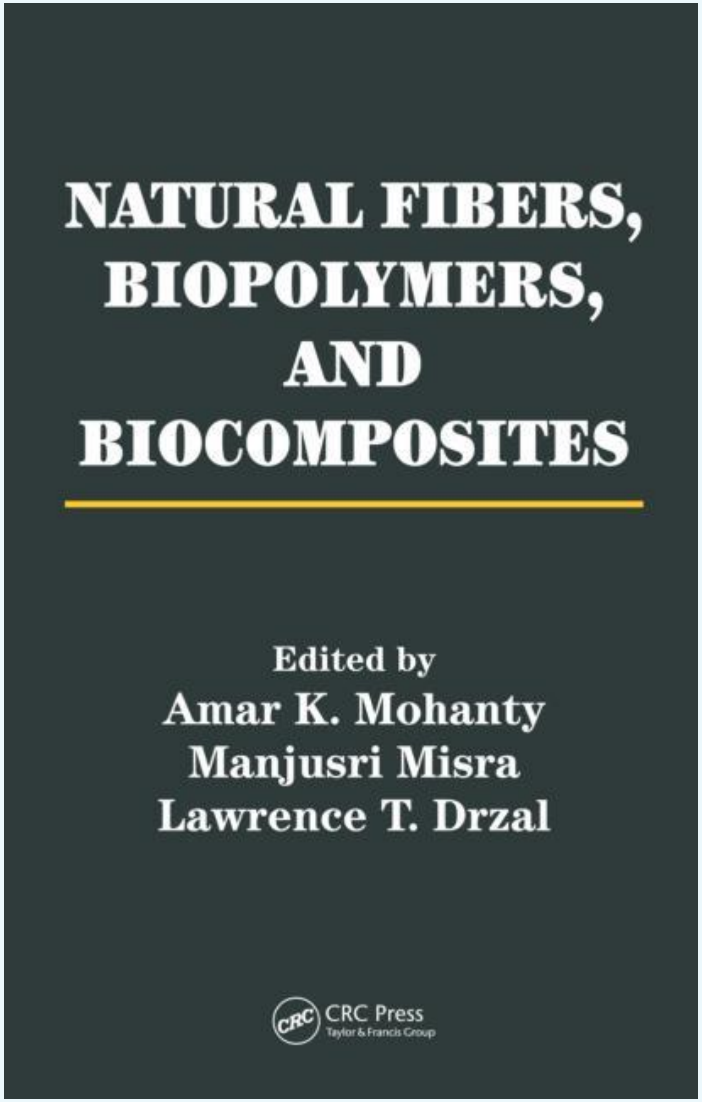
Keywords

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
Lignocellulosic material
Biopolmer
Cradle-to-grave
Plant fillers

Literature - examples



Forest Products Laboratory. Wood handbook: Wood as an engineering material. General Technical Report FPL-GTR-113. Madison, 1999



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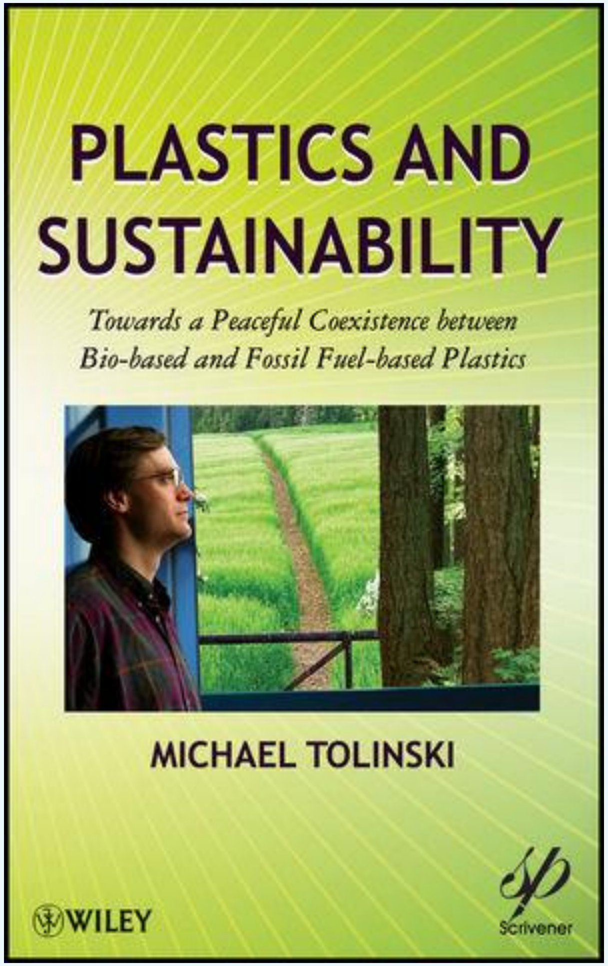
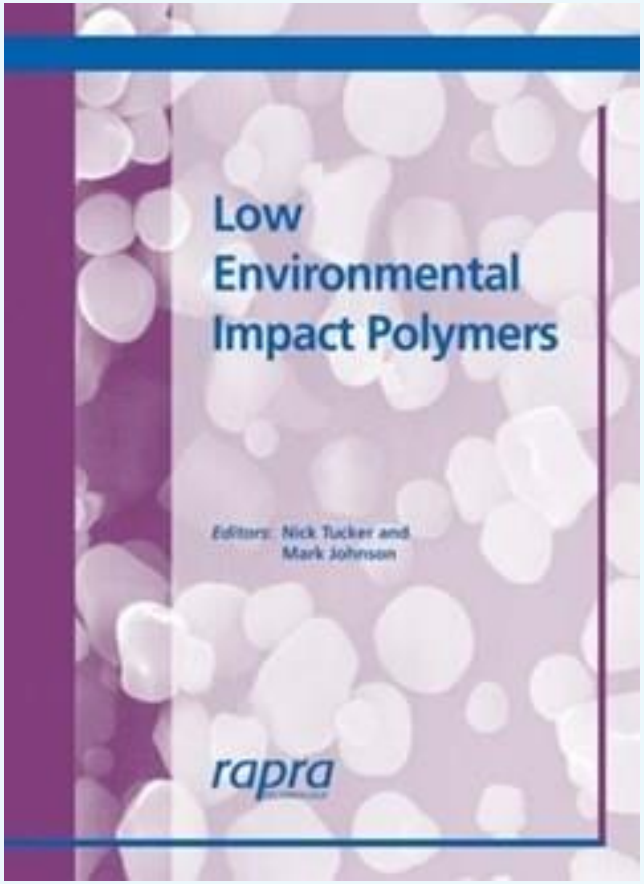


Tolinski M., Plastics and Sustainability: **Towards a Peaceful Coexistence between Bio-based and Fossil Fuel-based Plastics**, Hoboken, N.J.: John Wiley & Sons, 2012



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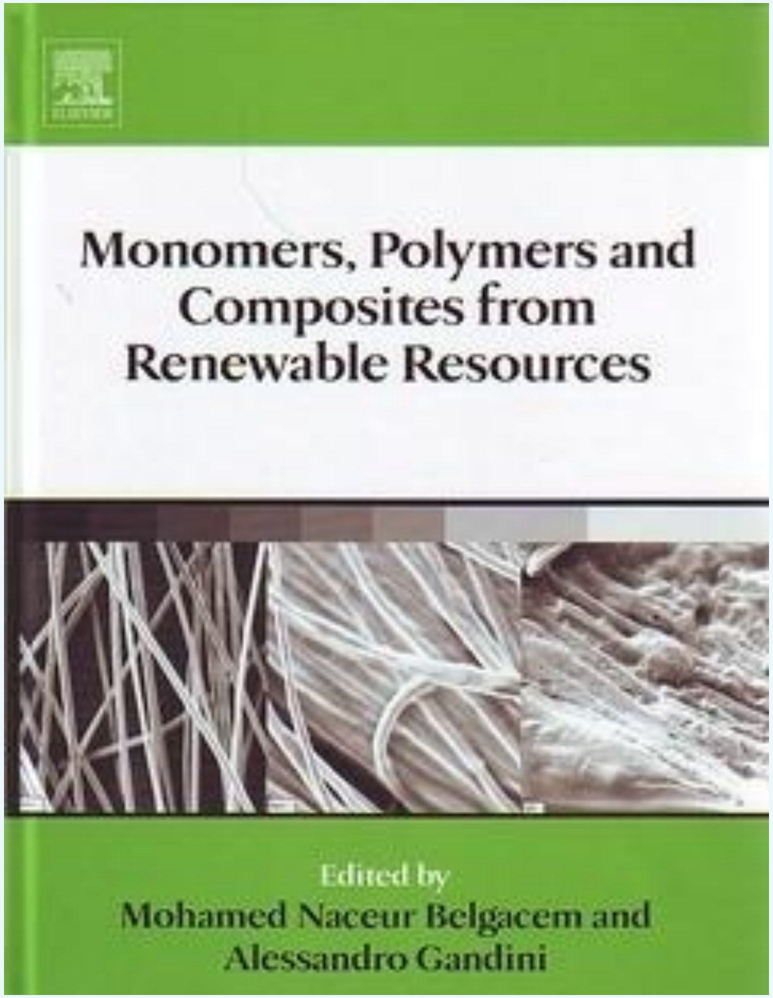
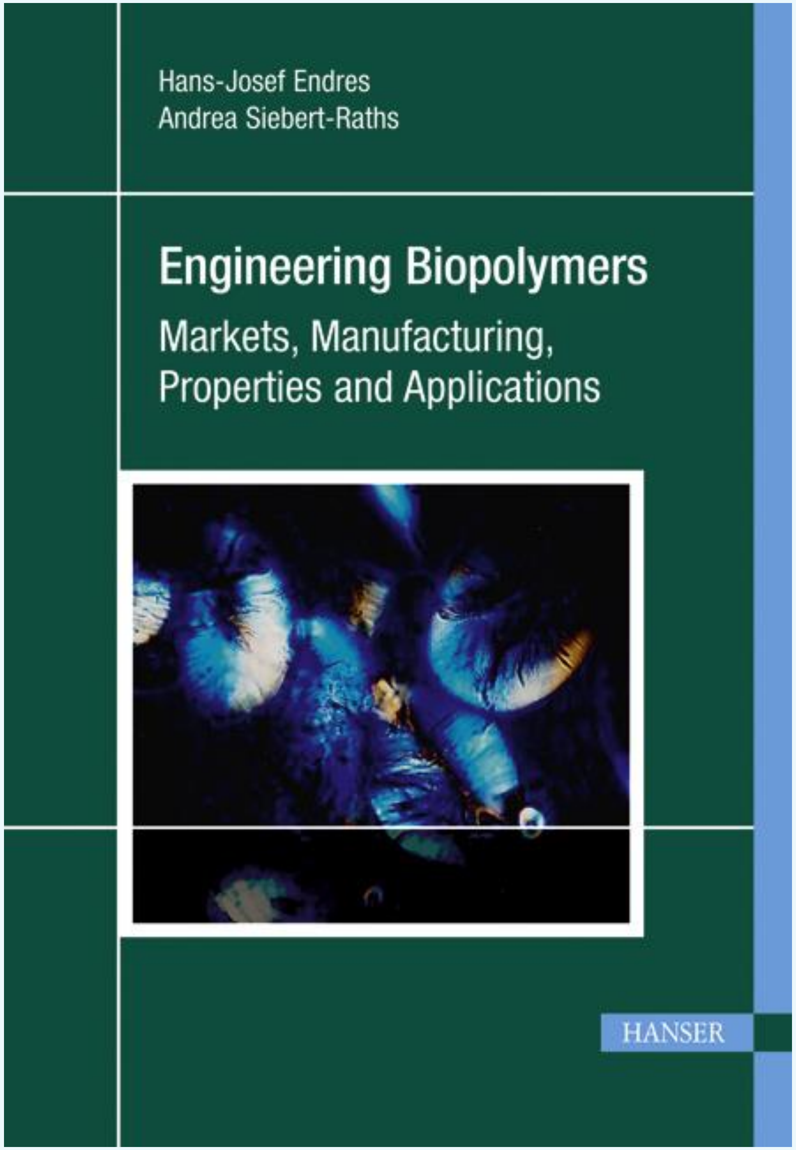
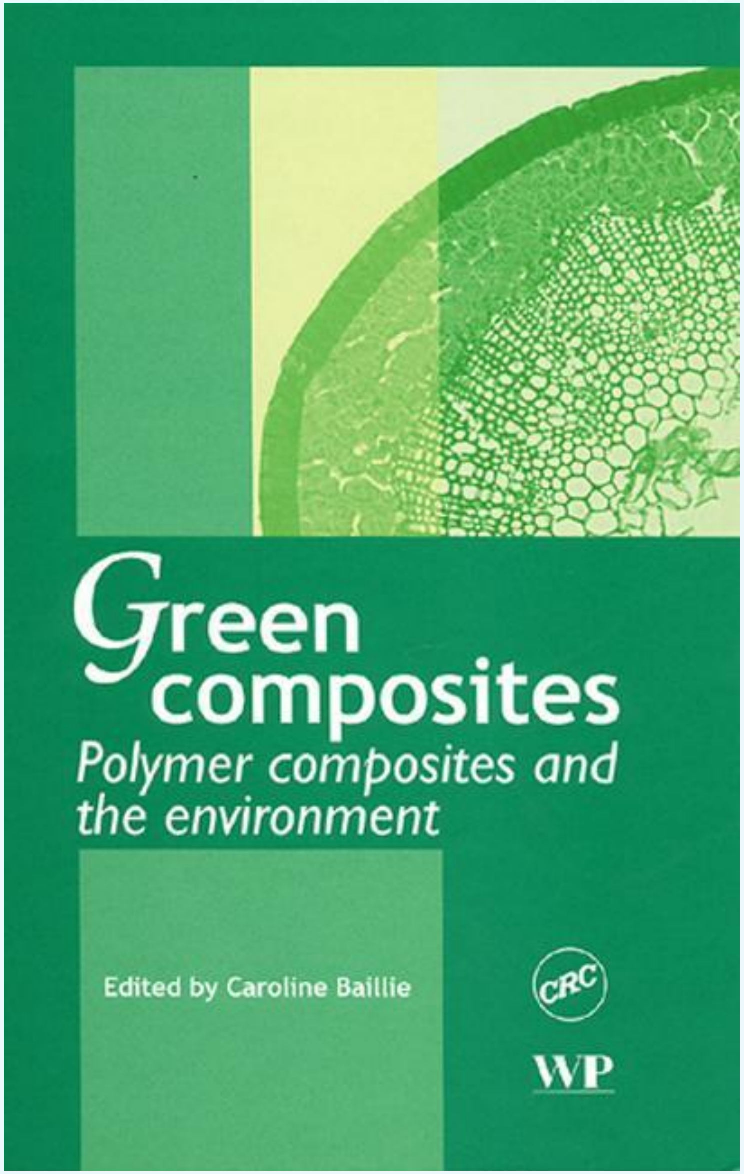


Belgacem M.N., Gandini A., **Monomers, polymers and composites from renewable resources**, Amsterdam: Elsevier, 2008, pp. 243–271



Endres H.J., Siebert-Raths A. **Engineering Biopolymers. Markets, Manufacturing, Properties and Applications**. Hanser, 2011



Baillie C., **Green Composites: Polymer Composites and the Environment**, Woodhead Publishing 2005

Example of tests and reserch programme

Flax fiber

(*Linum usitatissimum* L.): Temida

Flax fibers with diameter of 15-40 μm and length of 15-20 cm were provided by Experimental Station LENKON: Institute of Natural Fibres and Medicinal Plants in Poznań

Fibers after grinding on Retsch mill machine have approximately 40-50 μm and length 200-300 μm.

Biopolymers on matrix

BioCeres BC-LBI08 produced by FuturaMat

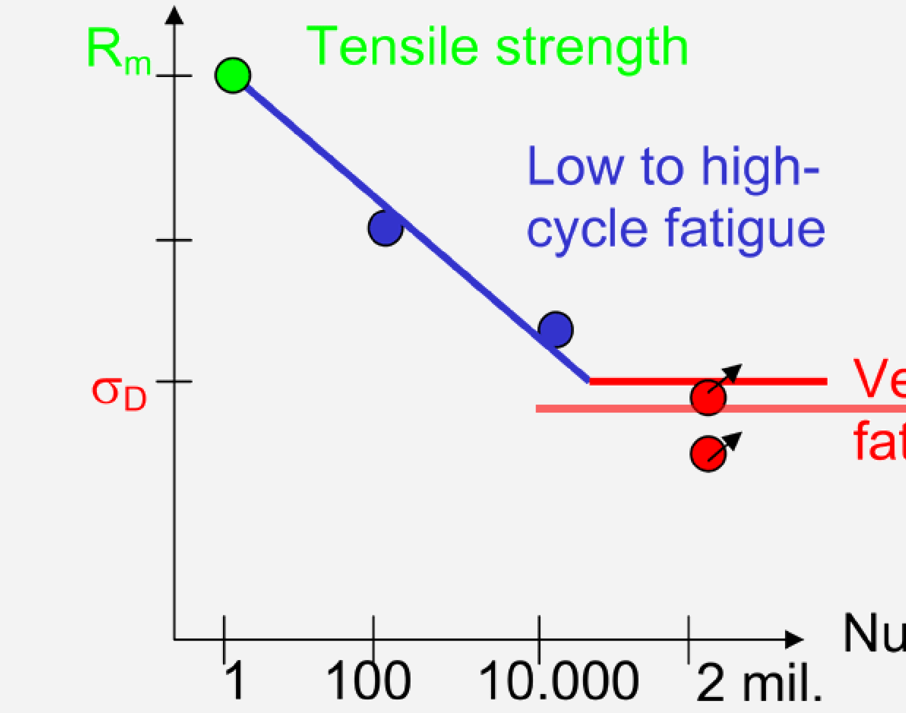
The BioCeres is a wheat flour-based product – thermoplastic starch. BC-LBI08 is an agromaterial descending from the BioCeres range It is a white flour based product. 100% biodegradable and from renawable sources

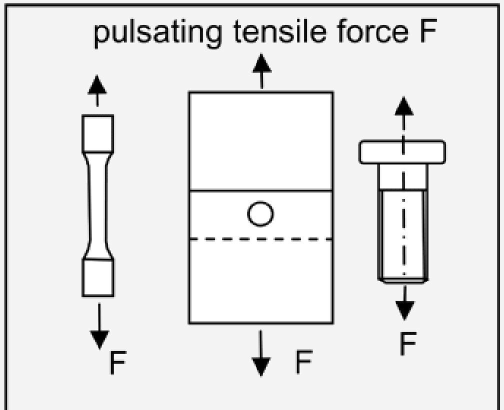
Bio-Flex® F 6510 produced by FKuR® Plastics

BIO-FLEX® F 6510 is trade name indicates blends of co-polyester and poly(lactide) (PLA) with, depending on the particular grade, a very high contend of natural resource material. Bio-Flex® does not contain any starch or starch derivatives This more rigid grade is ideally used for injection moulding and blow moulding. Cast sheet extrusion and subsequent thermoforming are also possible.

Research focus – fatique test

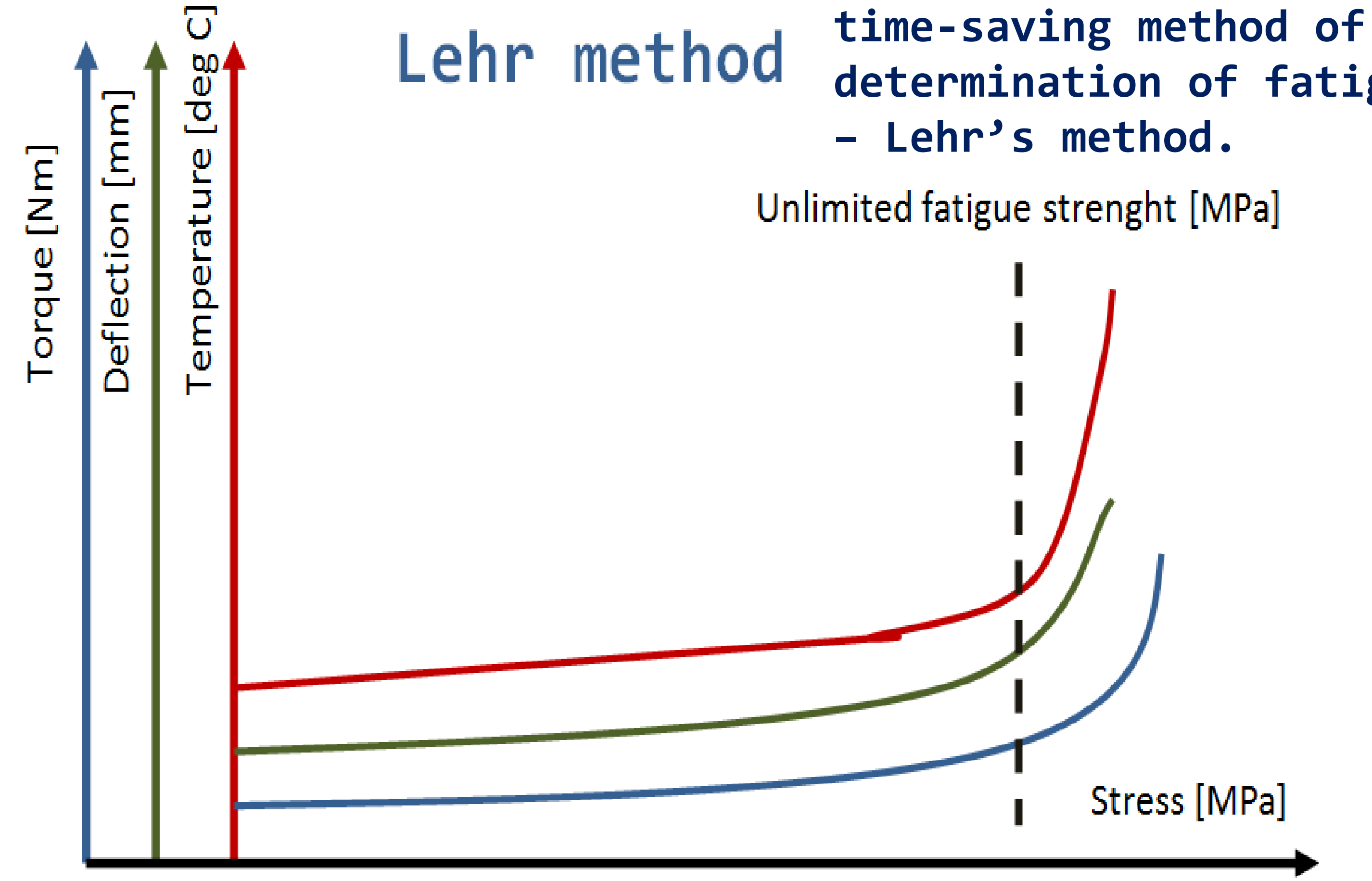
August Wöhler (22 June 1819 - 21 March 1914) was a German engineer, best remembered for his systematic investigations of metal fatigue.





Examples of possible specimen shapes

In our research we used simplified time-saving method of determination of fatigue strength – Lehr's method.



This method is used for metals and is based on the observation that fatigue strength is connected with local plastic strains which start to appear after exceeding fatigue strength in individual grains of metal. However, plastic yield strain of whole specimen is not exceeded. As a consequence, work that must be used for fatigue strain is increasing apparently.

Result of this is increase of torque, temperature and deflection. Measuring all these parameters or just selecting a few of them and plotting them as a function of stress we can obtain approximately fatigue strength.

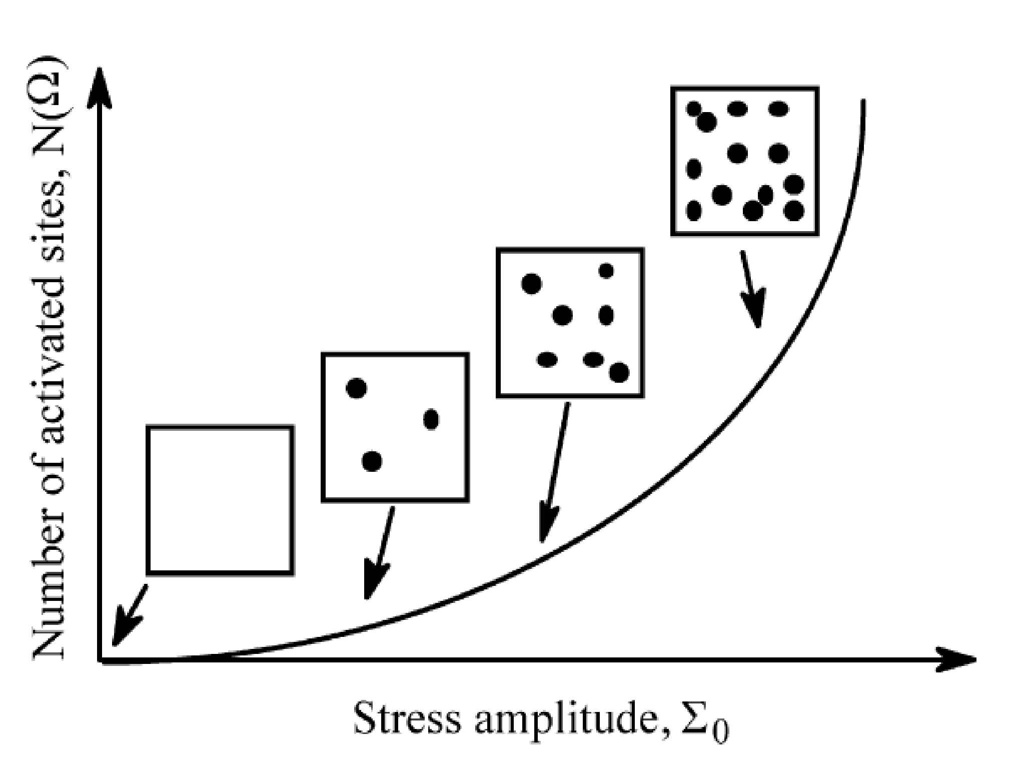
Fatigue – many reasons and aspects:

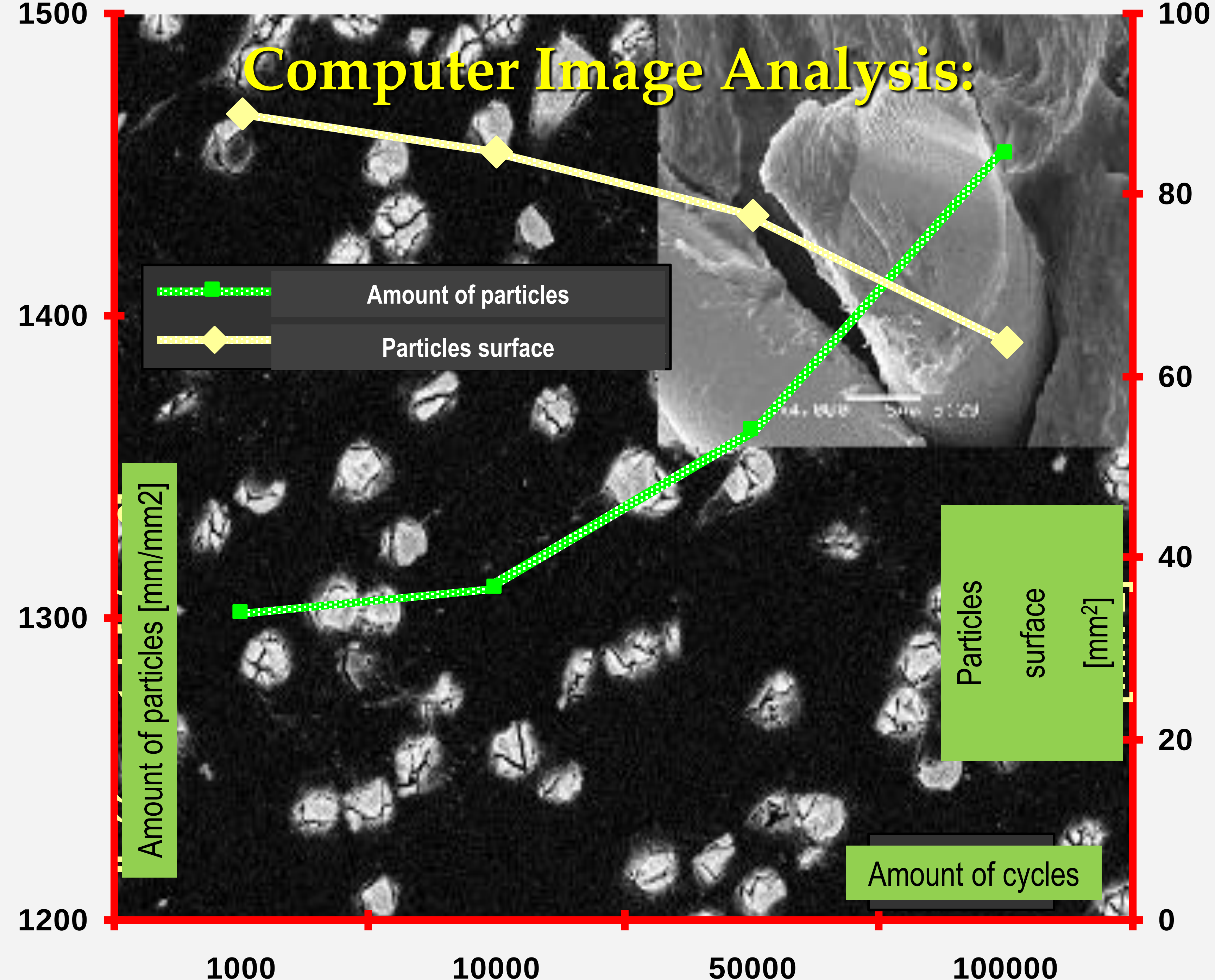
-Elastoviscosity heating – ex. for polymers plastic matrix

-Cracking matrix (brittle polymer PMM or PC)

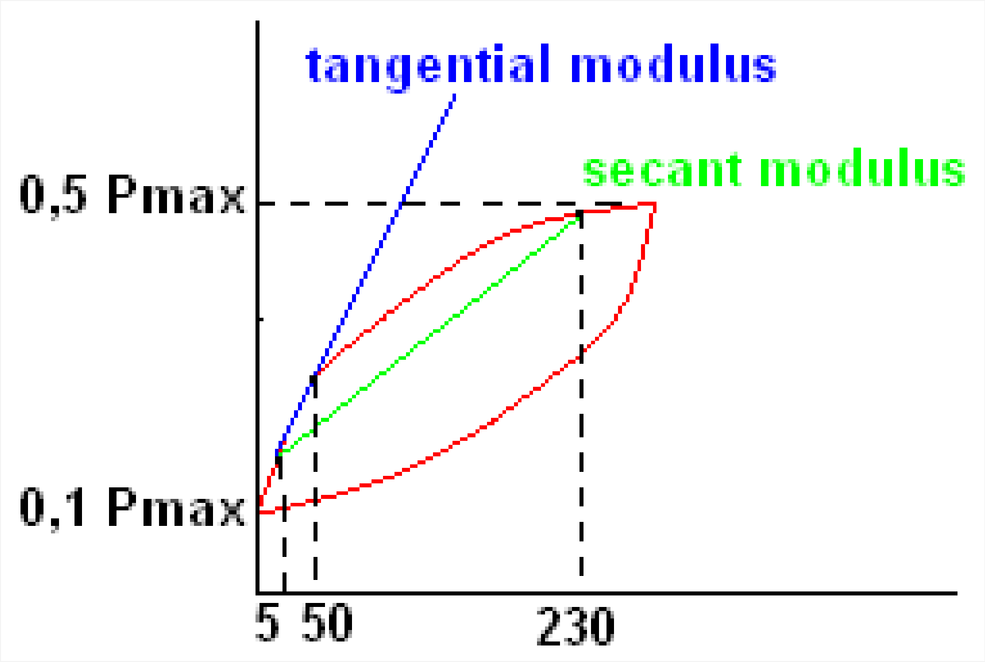
-Cracking of fibers due to fatigue process

Activation process of micro-plastic sites - probabilistic two-scale model





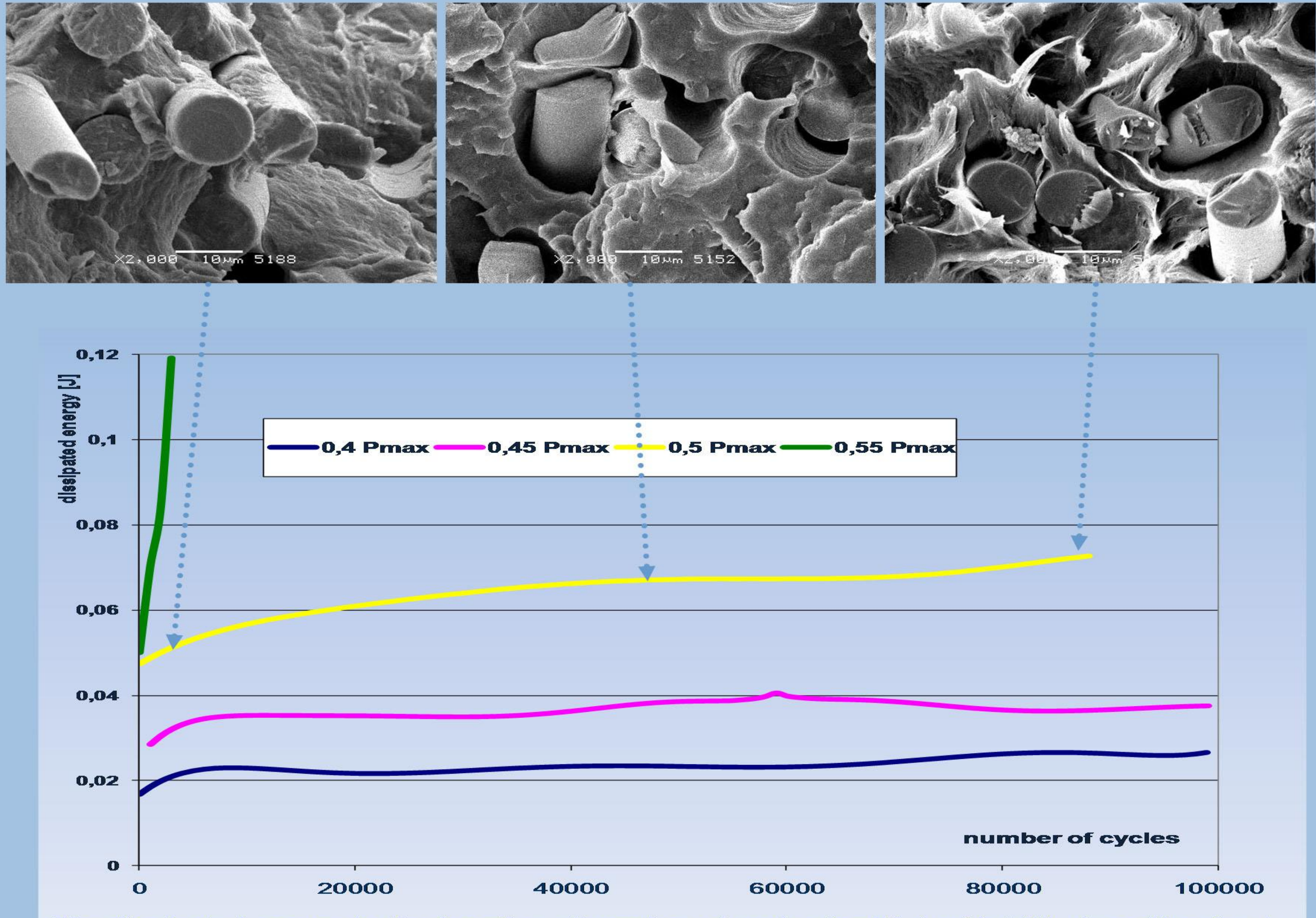
Computer Image Analysis:
Amount of particles
Particles surface
Amount of particles [mm/mm2]
Particles surface [mm2]
Amount of cycles
1500
1400
1300
1200
100
80
60
40
20
0
1000
10000
50000
100000



One cycle measures 500 points (250 points for the loading and 250 for the unloading). The tangential modulus is calculated between the points 5 and 50. The secant modulus of elasticity is calculated between the points 5 and 230.

Properties under dynamic loading were tested on dynamical machine in tensile test (Instron type 8511.20) on the level of frequency - 5 Hz for maximum 100 000 cycles ("load-unload"). Cyclic loading was within the range 0,1 - 0,5 of average maximum force reached in the tensile test – for content of glass fiber 25% Pmax=5,2 kN, for content of glass fiber 50% Pmax=7,9 kN (tab. 2).

Computer program was created to convert numerical data from tensile machine and calculate mechanical properties including modulus of elasticity, elongation, creep effects and mechanical energy of dissipation during sequence of hysteresis loops.

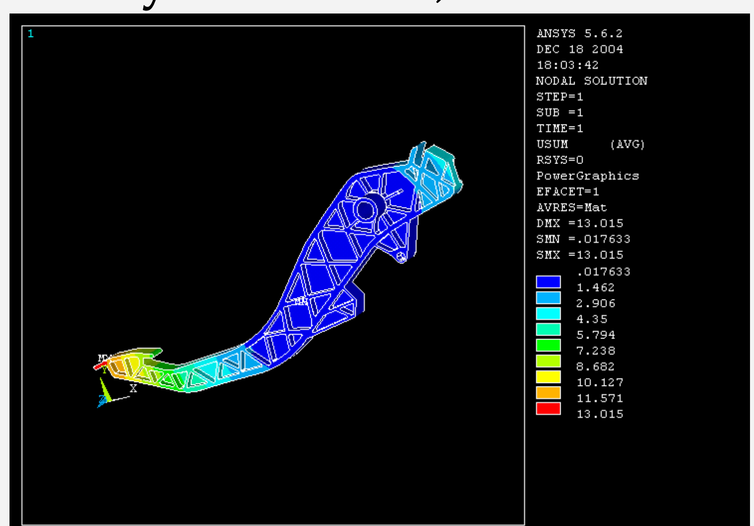


The dissipated energy in the function of number of cycles for PA 6 with 25% glass fiber for 4 increasing levels of load. SEM images of composite under load 0,5

Along with raising the value of load, we can observe increase of strain and energy of dissipation, especially up to 1 000 cycles of load. Modulus of elasticity decreased under cyclic loading of about 15% in comparison to modulus obtained in static test.

For the level of load corresponding to a half value of tensile strength of composites, number of cycles causing fracture was 88 000 for PA 6 with 25% glass fibre and 10 000 for PA 6 with 50% glass fibre. It indicates that relative fatigue strength is much lower for the composite with higher fibre content.

For the high level of load and fracture of composite after small number of cycles (about 10 000), the dominate mechanism of fracture is cracking of matrix and fibres. For lower levels of loads and high number of cycles we can additionally observe the effect of disconnection between matrix and fibres. The character of fracture changed from brittle (after about 1 000 cycles of load) to ductile after fatigue fracture.

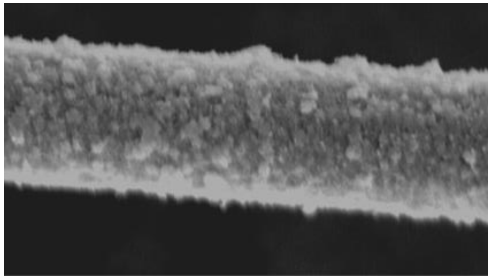


Basalt fiber

Basalt fiber is made from a single material, crushed basalt. The manufacture of basalt fiber requires the melting of the quarried basalt rock at about 1,400 °C (2,550 °F). The molten rock is then extruded through small nozzles to produce continuous filaments of basalt fiber. The fibers typically have a filament diameter of between 9 and 13 µm. They have a high elastic modulus, resulting in excellent specific tenacity—three times that of steel.

Properties	Basalt fiber	Glass fiber	Carbon fiber
Tensile strenght [GPa]	4,84	4,5	3,6-6,0
Elastic moduls [GPa]	89	85,5	400
Elongation at break [%]	3,2	5,6	1,5
Maximum operating temperature[°C]	650	300	500
Density [g/cm^3]	2,7	2,49	1,5
Lenght fibers [µm]	7-22	5-20	6-9
Melting point[°C]	1050 do 1460	850 do 1000	3500
Indicator of thermal insulation[W/m^{2}K]	0,031-0,038	0,034-0,4	0,20
Short term operating temperature[°C]	750	600	1650

Basalt fiber - Fiberbet™

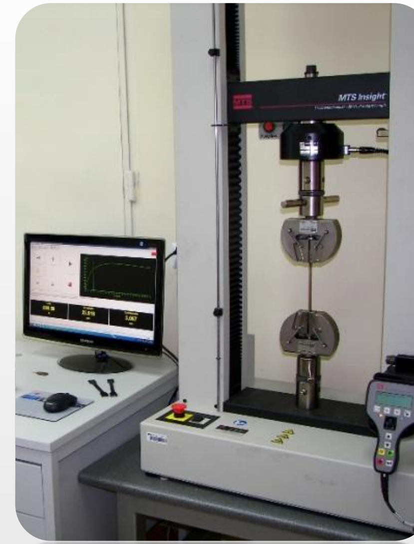


Dispersed FIBERBET™ basalt reinforcement is made as a result of cutting basalt roving (string) TEXBASTM 240 tex into sections ranging from 15 to 24 mm, and basalt roving is made of ultra thin basalt fibers of elementary thickness from 10 to 16 μm.

Due to the fact that basalt fibers and products made from them are natural products created as a result of melting down congealed volcanic lava and exposing the gained raw material to appropriate technological process, it can be included in ecological products undergoing easy and full utilization, 100% harmless to human beings and natural environment.

Basalt fiber for concrte with surface polymeric modification (Maleic Anhydride)

TESTS METHODS



- Tensile tests acc. PN-EN ISO 527
  (Criterion 30 MTS with MTS axial extensometer)
- Instron temperature chambre (-80 – 300 C°)
- Charpy impact tests (Zwick HIT5.5P)
- Sorption of water (20°C) determination after 1, 7, 30, 240 days of soaking, acc. PN-EN ISO 62:2000.
- **Vicat softening temperature (VST)** was measured according to ISO 306 under 50 N loading and with 50ºC/h heating rate using CEAST machine
- The surface roughness average (R_a) measurement
  (Mitutoyo SJ-301)
- DSC model Mettler Toledo
  with computer software for test analysis
- SEM/EDS observations (JEOL JSN5510LV)

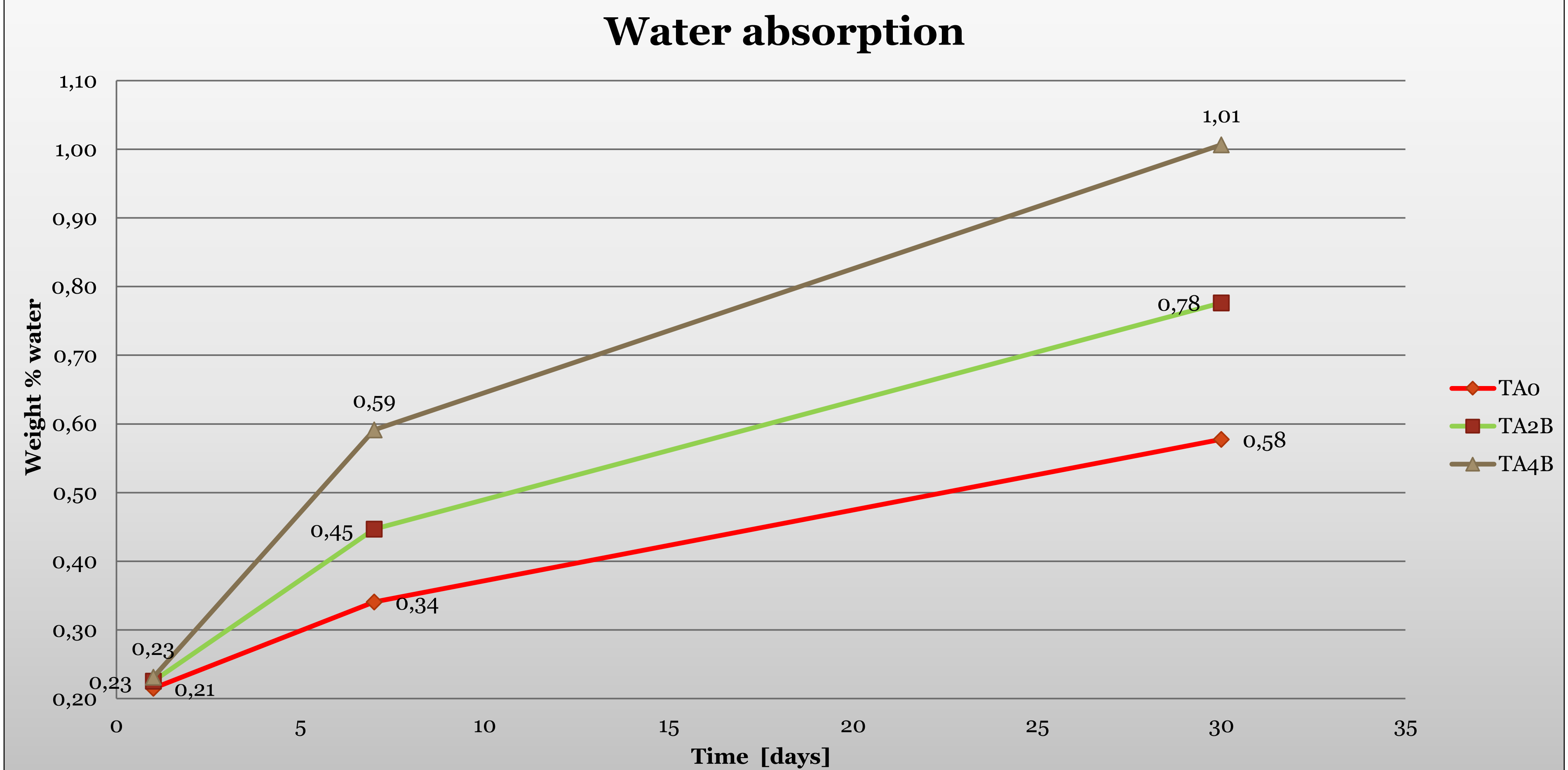
Samples

sort of composites	marked as	density [g/cm3]	s_n
TARNOFORM 400	**TA0**	**1,3954**	0,001
TARNOFORM 400 + 20% basalt fibers	**TA2B**	**1,5393**	0,025
TARNOFORM 400 + 40% basalt fibers	**TA4B**	**1,6748**	0,057

Standard dumbbell type specimens (10 x 4 x 150 mm) were produced by injection molding in Zaklady Azotowe in Tarnow using Engel ES 200/40 HSL. The parameters of the injection process were the following: injection temperature 210°C, mold temperature 80°C, injection pressure 80 MPa, cycle time 25 s (cooling time 20 s).

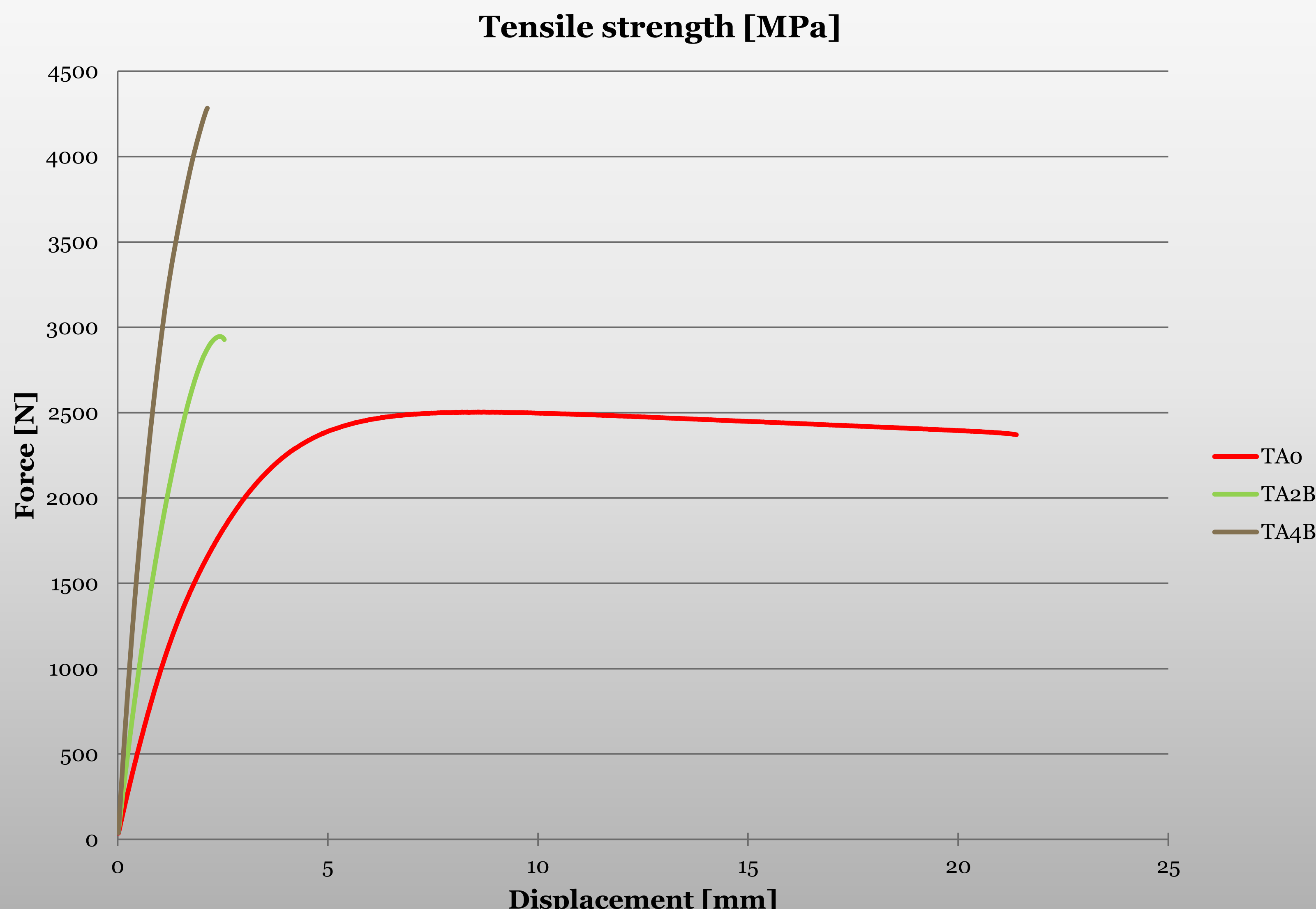
The results were obtained without compauding and manufacturing granules. In conclusion, the potential use of new composites is indicated.

Results – Water absorption:

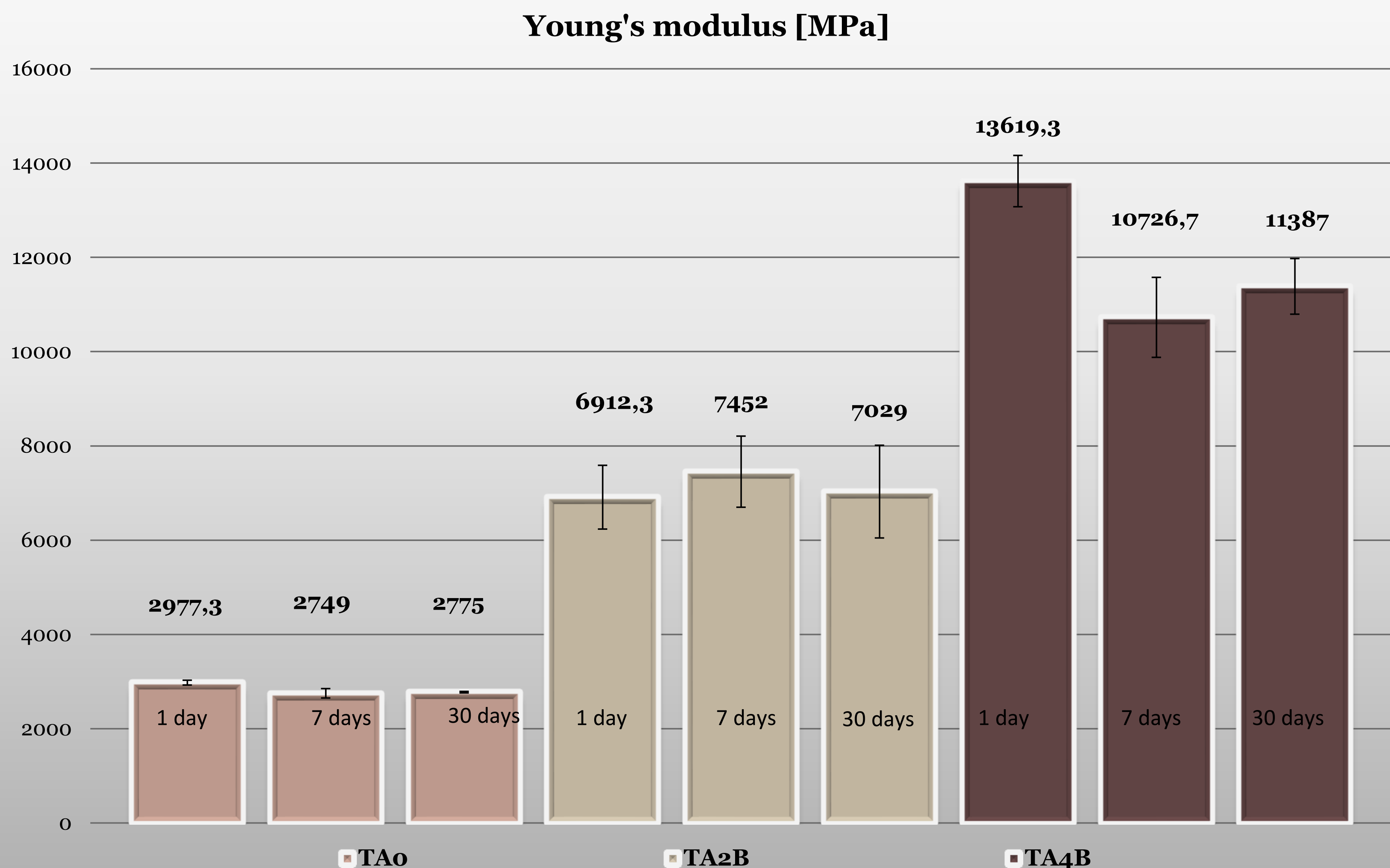


Weight % water			
Time [days]	**1 day**	**7 days**	**30 days**
TA0	0,21	0,34	0,58
TA2B	0,23	0,45	0,78
TA4B	0,23	0,59	1,01

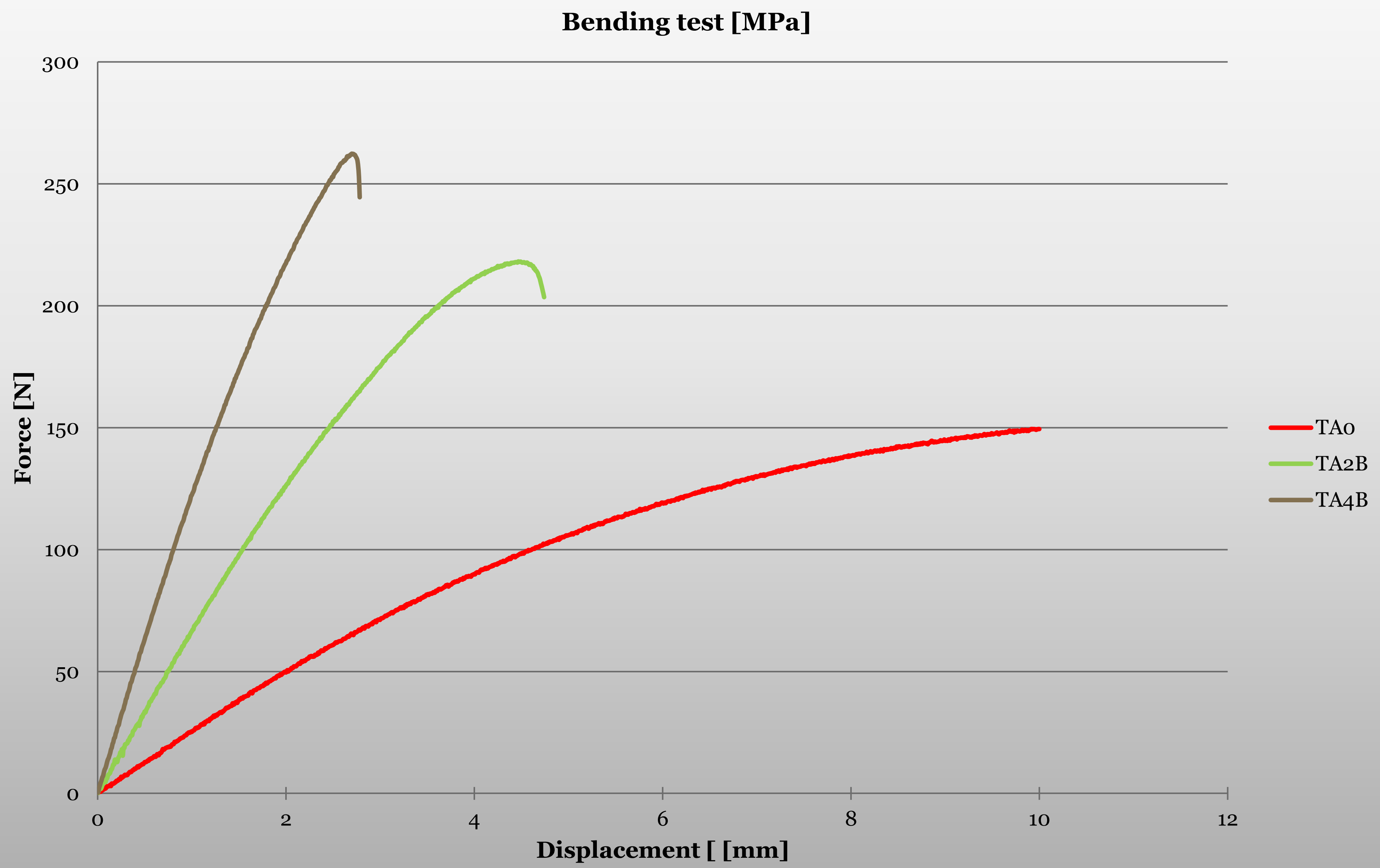
Results of test – Static tensile test



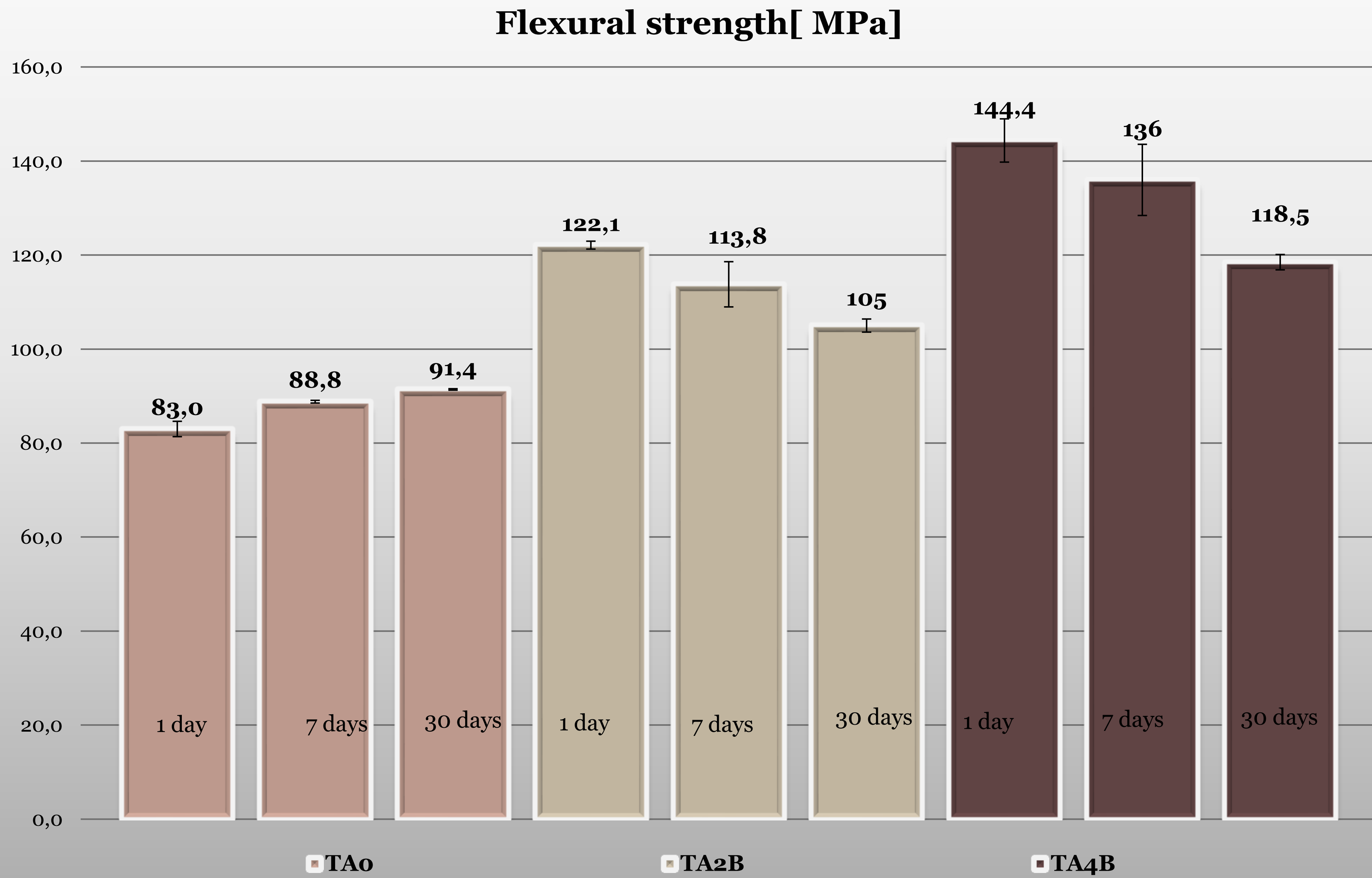
Results – Static tensile test :



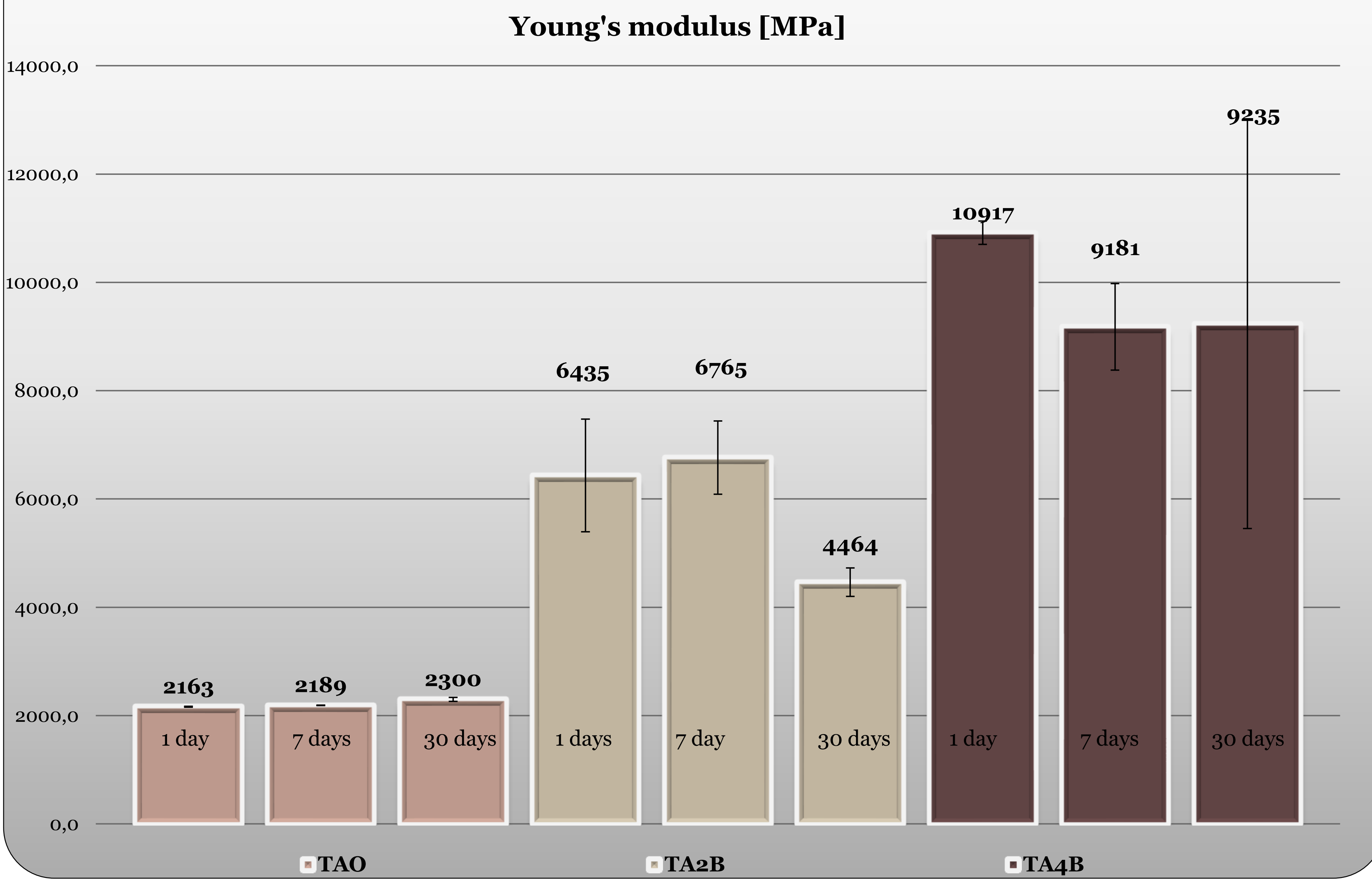
Results – Static bending test :



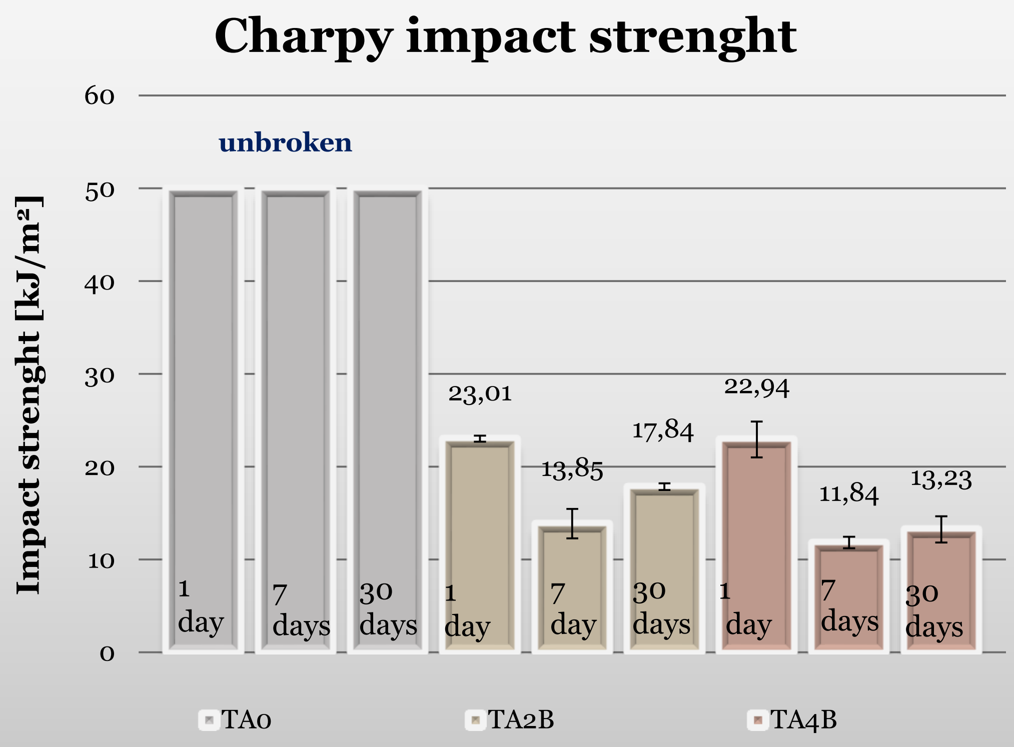
Results – Static bending test :



Results – Static bending test :

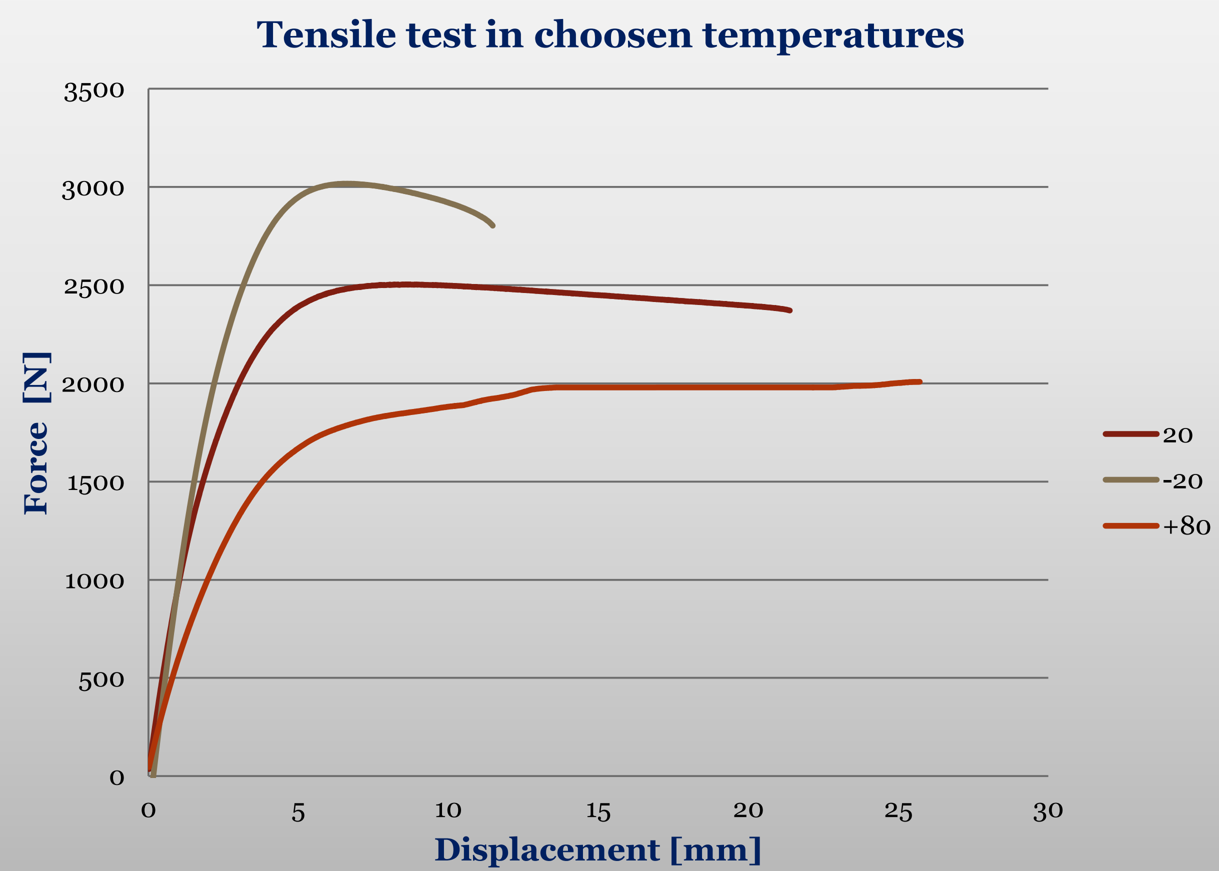


Charpy Impact test :

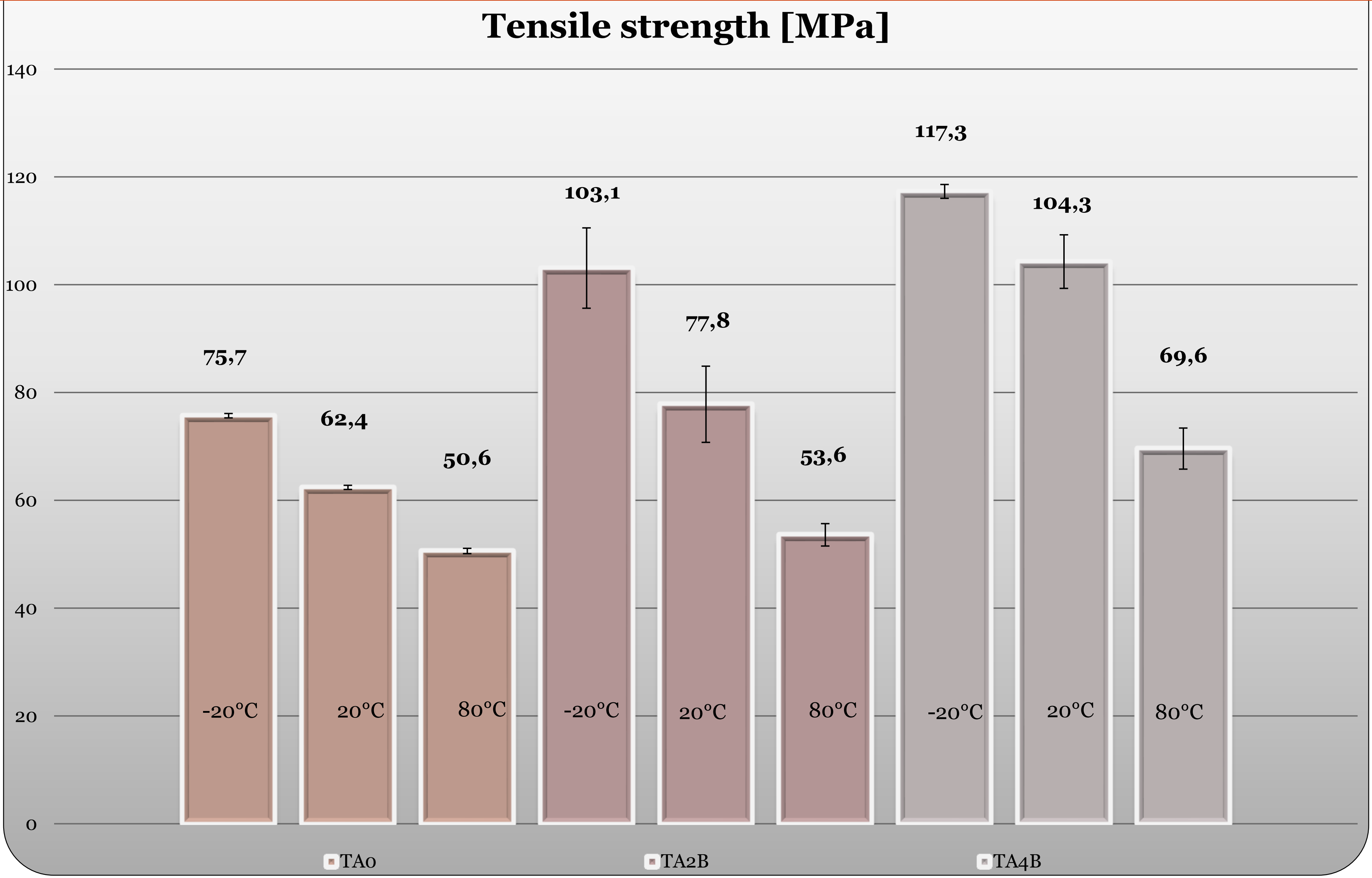


Influence of soaking in water for unnotched impact test

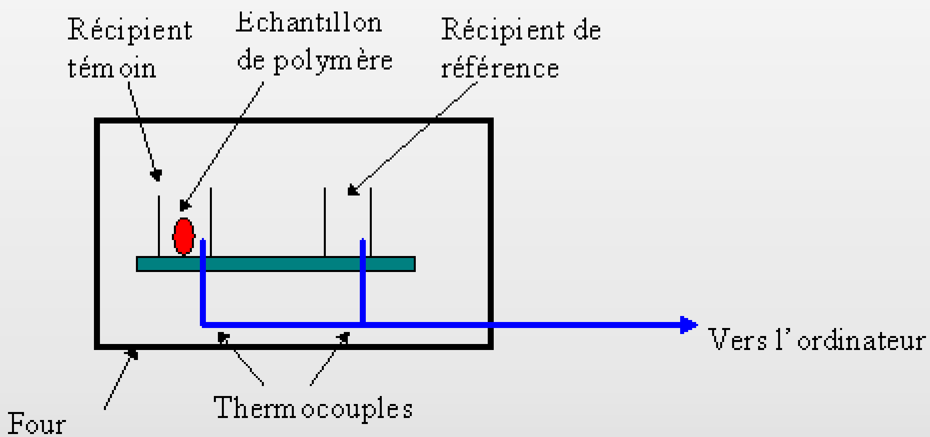
Tensile test in choosen temperatures:



Results - Static tensile test at temperatures:



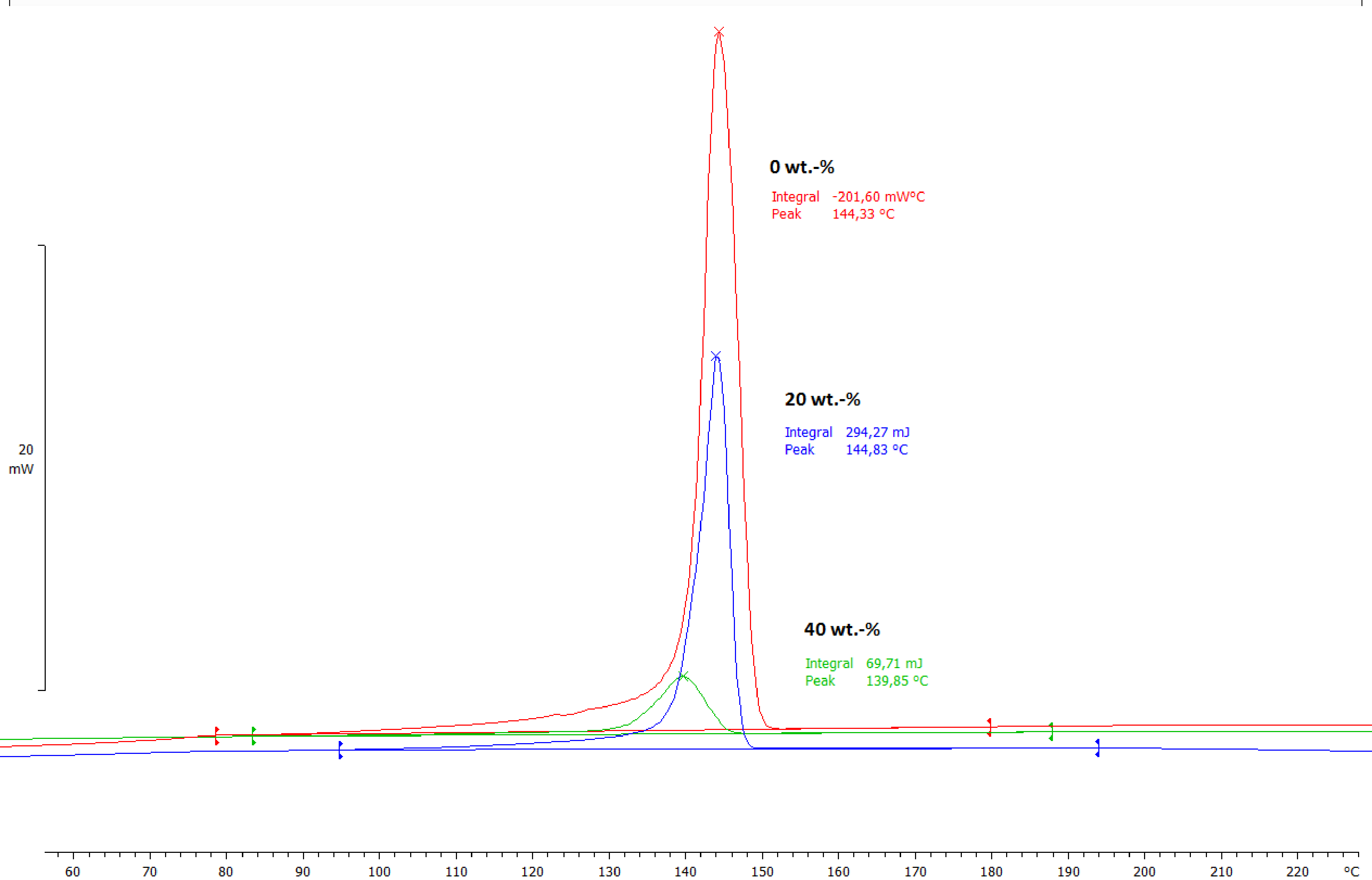
DSC



DSC tests were performed at Poznan University of Technology - Faculty of Chemical Technology using MettlerToledo DSC with computer software for test analysis. Measurements were made on the samples obtained from a central part of the injcection moulded standart dumbbell-shape specimens in the temperature range between -85 and 290 °C under argon atmosphere.

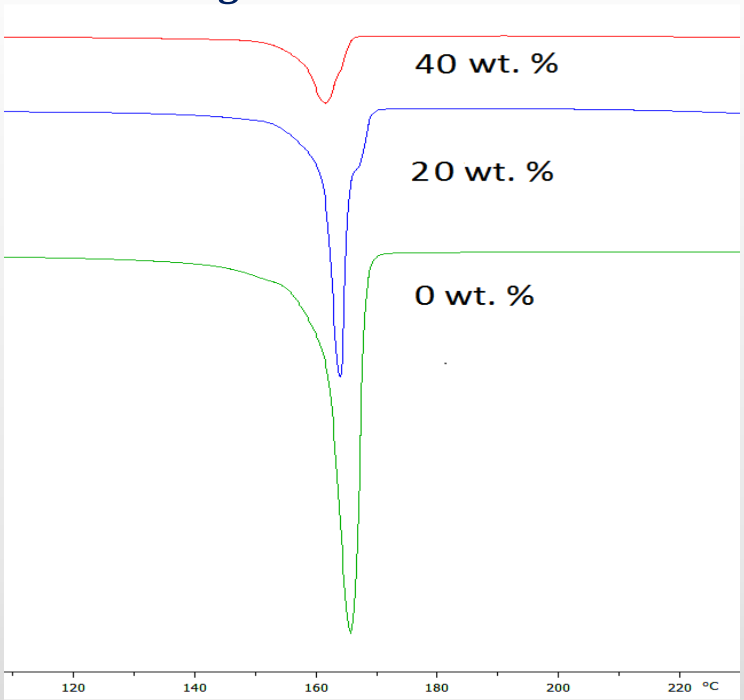
All measurements were taken according to the following program heating between -85 and 290°C at a scanning rate of 10°C/min and cooling at a scanning rate of 5°C/min. The whole process was carried out twice to analyze processing memory/history of the materials (the first heating-cooling cycle) and the thermal properties of the composites (the second heating-cooling cycle). An empty pan was used as a reference.

Differential Scanning Calorimetry (DSC) - Mettler Toledo

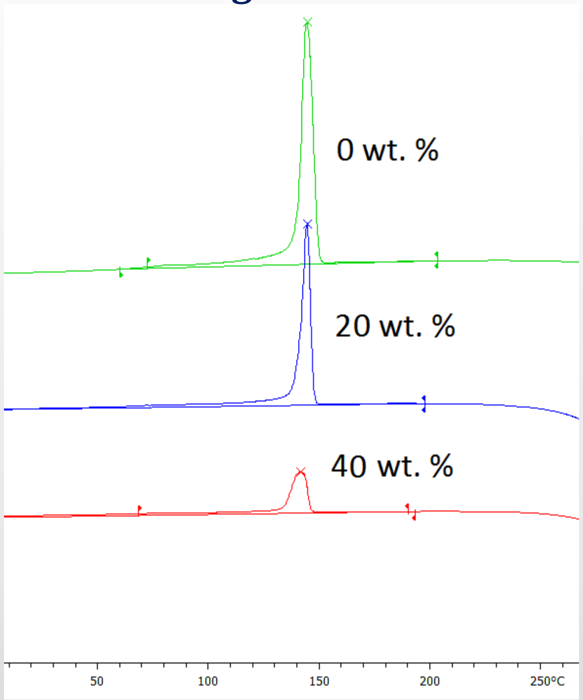


0 wt.-%
Integral -201,60 mW°C
Peak 144,33 °C
20 wt.-%
Integral 294,27 mJ
Peak 144,83 °C
40 wt.-%
Integral 69,71 mJ
Peak 139,85 °C
20
mW
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
°C

DSC heating curves



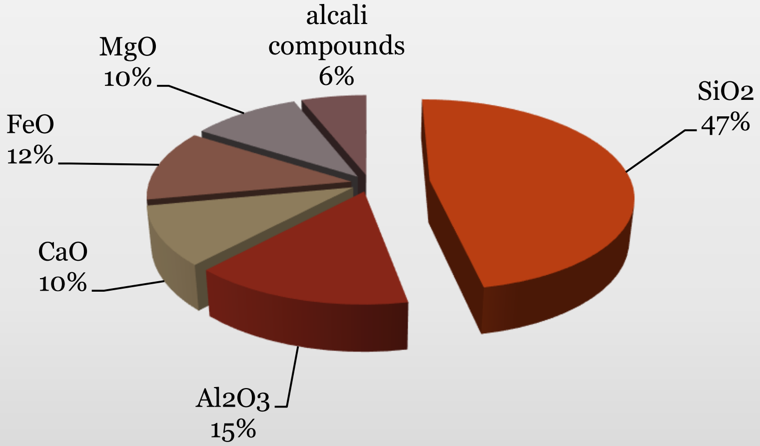
and cooling curves

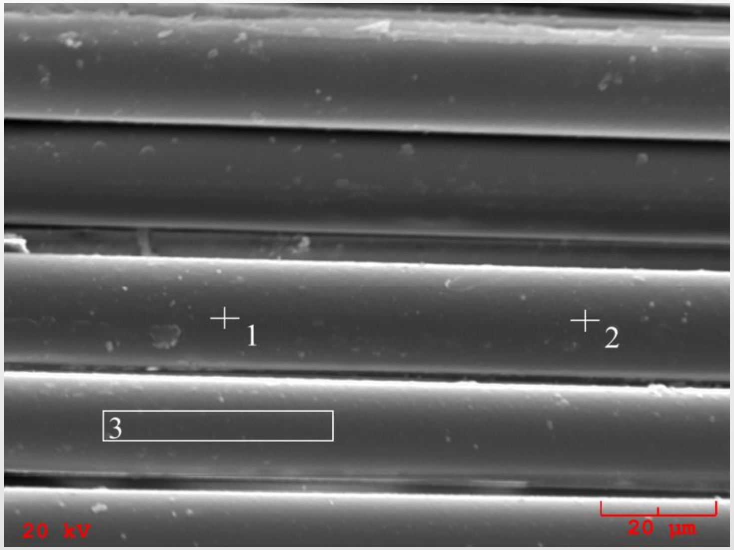


The picture shows DSC curves for POM and its composites with basalt fibers(20 and 30%wt.). In the temperature range close to the glass transition temperature POM and its composites are hard and brittle. In this range thermal energy is too low to overcome potential barrier for displacement and rotational motion of macromolecules. The system is in the non-equilibrium state. For POM and its composites, glass transition point was found to be at the temperature of about - 75°C.

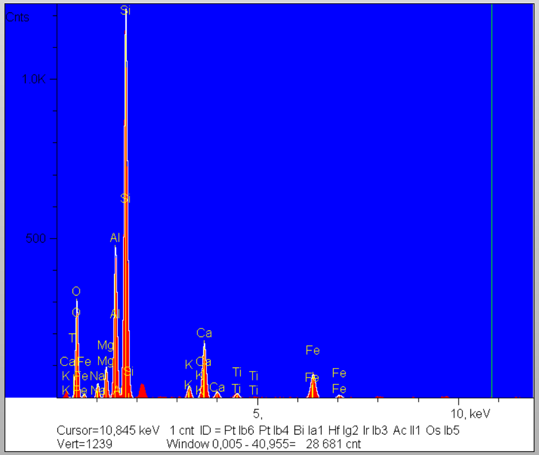
Polymer crystallization, due to the length of the macromolecules which hinders their movement, starts upon significant undercooling of the melt in the range of 10 - 100 °C (comparing to the melting temperature). In the case of POM, addition of basalt fiber causes small increase in crystallization temperature of the composites (up to 140°C) which may suggest that the size of crystals is smaller because of fiber surface induced heterogeneous nucleation.

SEM/EDS : Scanning Electron Microscopy with X-ray microanalysis





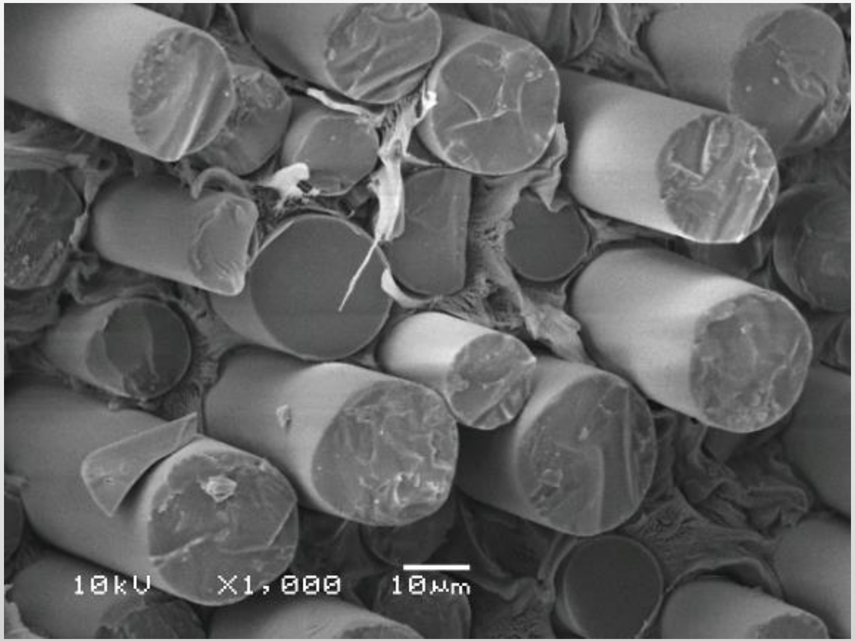
Analysis Report: Image2-2



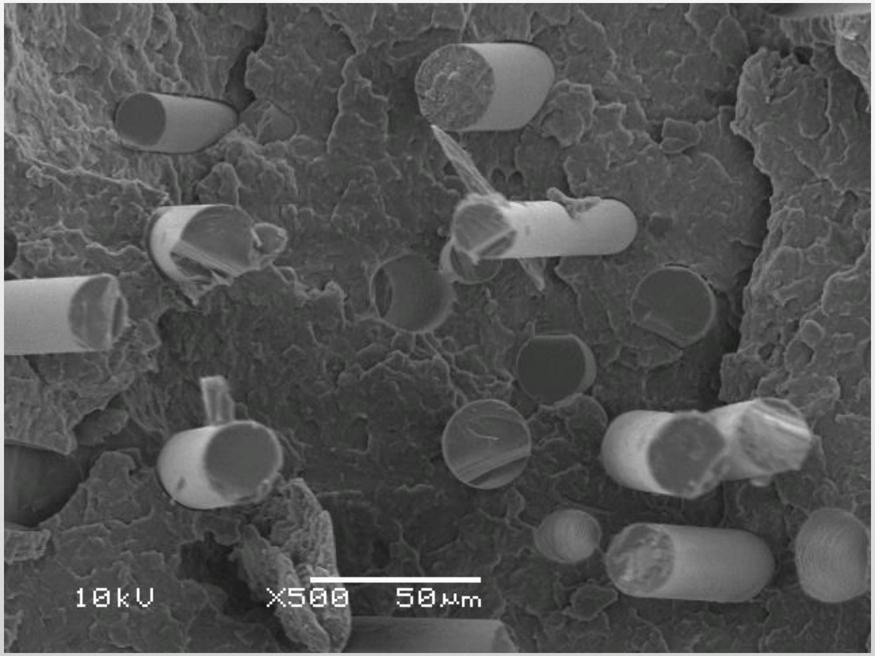
Elt.	Line	Intensity (c/s)	Error 2-sig	Atomic %	Conc	Units	
O	Ka	84,47	1,790	56,911	**41,678**	wt.%	
Na	Ka	14,34	0,952	1,954	**2,056**	wt.%	
Mg	Ka	30,33	1,274	2,585	**2,876**	wt.%	
Al	Ka	150,97	2,413	9,291	**11,474**	wt.%	
Si	Ka	412,76	3,778	23,895	**30,718**	wt.%	
K	Ka	14,84	0,912	0,607	**1,086**	wt.%	
Ca	Ka	68,90	1,603	2,701	**4,954**	wt.%	
Ti	Ka	7,36	0,684	0,279	**0,612**	wt.%	
Fe	Ka	39,18	1,192	1,778	**4,545**	wt.%	
				100,000	100,000	wt.%	Total

SEM images:

A



B

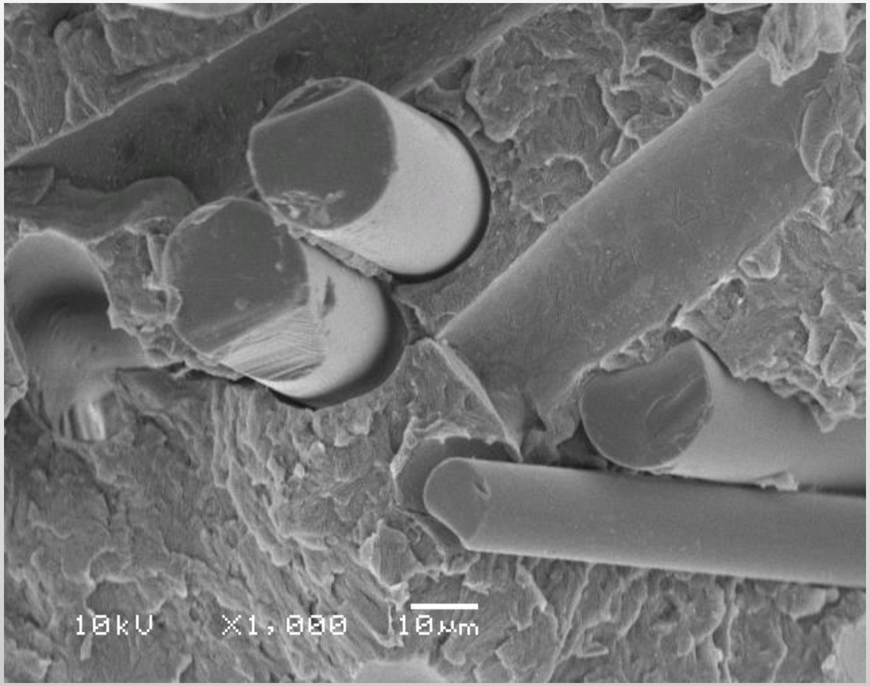


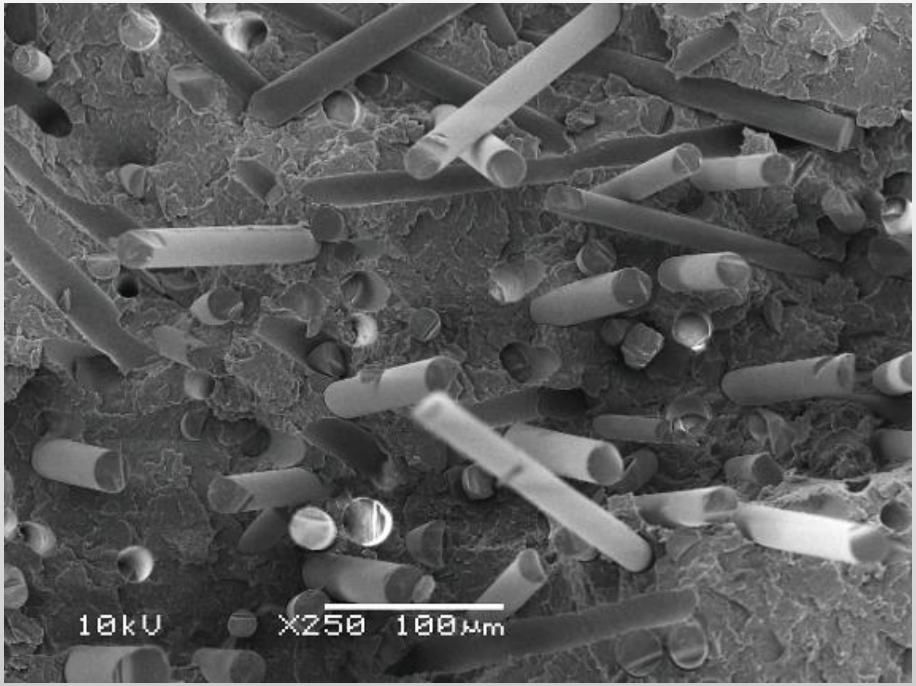
SEM images of tensile fracture surfaces of basalt fiber composites (POM2B):
A – group of basalt fibers of varying diameter in a polymer matrix
B - basalt fibers in polymer matrix without – pulling out effect

SEM images:

A

B





SEM images of tensile fracture surfaces: of basalt fiber filled composites in a polymer matrix (POM4B)

A – single basalt fiber in POM matrix –diameter approx. 12-14 µm

B – broken and firmly seated fiber in polymer matrix

Summary:

The results of the research indicate a possibilities a many new application to use basalt fiber composites on the base on of poly(oxymethylene) POM

- **High increase in stiffness and bending modulus improved resistance to deformation on heat and thermal properties stabilization within the temperatures of usage were the main advantages of the composites**
- **very good impact strenght for composites with 40% basalt fibers**
- **low water absorption and good stability of mechanical properties**
- **fine much better surface compare to glass fiber composites**

IT PREDESTINES THE COMPOSITES WITH FIBERS OF BASALT FOR THE USAGE ON ELEMENTS STRONGLY BURDENED AND TRANSFERRING THE VIBRATION - DUE TO THE PRESERVED POSSIBILITY OF DISSIPATION OF MECHANICAL ENERGY IN HIGH TEMPERATURES

GOAL OF THE WORK

Composites of biobased HDPE with wood flour, kenaf fibers, cellulose powder and tuff powder added in amount of 25%wt. to the matrix were previously tested by the authors and the results encouraged them to continue the research and to add higher amounts of selected fillers (40%wt.) into the same matrix in order to obtain materials for injection molding of high-stiffness products. **Biocomposites with high amount of fillers, especially natural fibers, are rarely tested because of difficulties connected with their processing.**

MATERIALS AND SPECIMENTS

MATRIX:

- **PE - GREEN PE** SHC7260 a High Density Biopolyethylene (**HDBPE**) produced from sugarcane-based ethanol was supplied by Braskem from Brazil. The biopolyethylene received the **highest certification** for renewable products from Vinçotte Belgium certification association and it is authorized to use the 'Ok Biobased' seal.

FILLERS – 40%:

- (**PEB**) BASALT FIBERS, DIAMETER10-16 MM AND 150-200 MM, FIBERBET
- (**PEL**) UNTREATMENT FLAX FIBER APPROX. 100-150 MM, SAFILIN
- (**PEO**) NUT SHELL FLOUR UFC 100 IN FORM OF POWDER (APPROX. 20-40 MM), RETTENMAIER
- (**PEMD**) WOOD FLOUR LIGNOCEL BK 40/90 FROM SOFT WOOD (SPRUCE) WITH PARTICLE SIZE 200-300 MM, RETTENMAIER

BASALT FIBER

BASALT FIBER IS MADE FROM A SINGLE MATERIAL, CRUSHED BASALT. THE MANUFACTURE OF BASALT FIBER REQUIRES THE MELTING OF THE QUARRIED BASALT ROCK AT ABOUT 1,400 °C (2,550 °F). THE MOLTEN ROCK IS THEN EXTRUDED THROUGH SMALL NOZZLES TO PRODUCE CONTINUOUS FILAMENTS OF BASALT FIBER. THE FIBERS TYPICALLY HAVE A FILAMENT DIAMETER OF BETWEEN 9 AND 13 MM. THEY HAVE A HIGH ELASTIC MODULUS, RESULTING IN EXCELLENT SPECIFIC TENACITY—THREE TIMES THAT OF STEEL.

Properties	Basalt fiber	Glass fiber	Carbon fiber
Tensile strenght [GPa]	4,84	4,5	3,6-6,0
Elastic moduls [GPa]	89	85,5	400
Elongation at break [%]	3,2	5,6	1,5
Maximum operating temperature[°C]	650	300	500
Density [g/cm^3]	2,7	2,49	1,5
Lenght fibers [µm]	7-22	5-20	6-9
Melting point[°C]	1050 do 1460	850 do 1000	3500
Indicator of thermal insulation[W/m^2K]	0,031-0,038	0,034-0,4	0,20
Short term operating temperature[°C]	750	600	1650

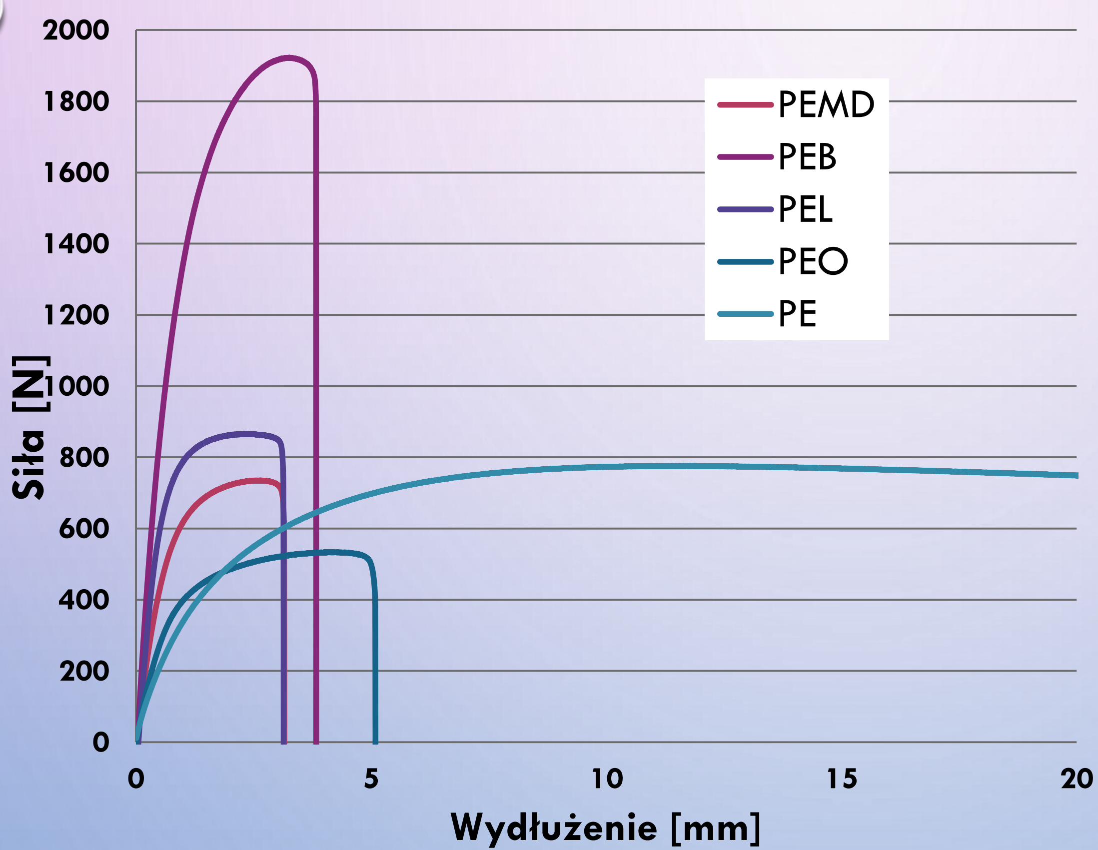
Standard dumbbell type specimens (10 x 4 x 150 mm) were produced in Grupa Azoty in Tarnow, Poland, in a two step process. First, composite pellets were obtained by compounding extrusion using two-screw extruder MARIS TM 30VI with a gravimetric twin screw feeder (cylinder temperature: 100°C (zone 1), 130°C (zones 2-10), screw rotation: 60 rpm) and then injection molded using Engel ES 200/40 HSL.

Material	Temperature [°C]			Time [s]					Pressure [bar]		
	cylinder	die	mould	break	holding	cooling	injection	cycle	injection	holding	plastification
PE	160	160	40	1	30	20	0,83	48	110	110	6
PEMD	160-170	175	40	1	30	20	1,87	60	100	100	6
PEO	160-170	175	40	1	30	20	1,55	60	100	100	6
PEL	160-175	180	40	1	30	20	1,95	60	100	100	6
PEB	160-180	180	60	1	30	20	1,30	60	100	100	6

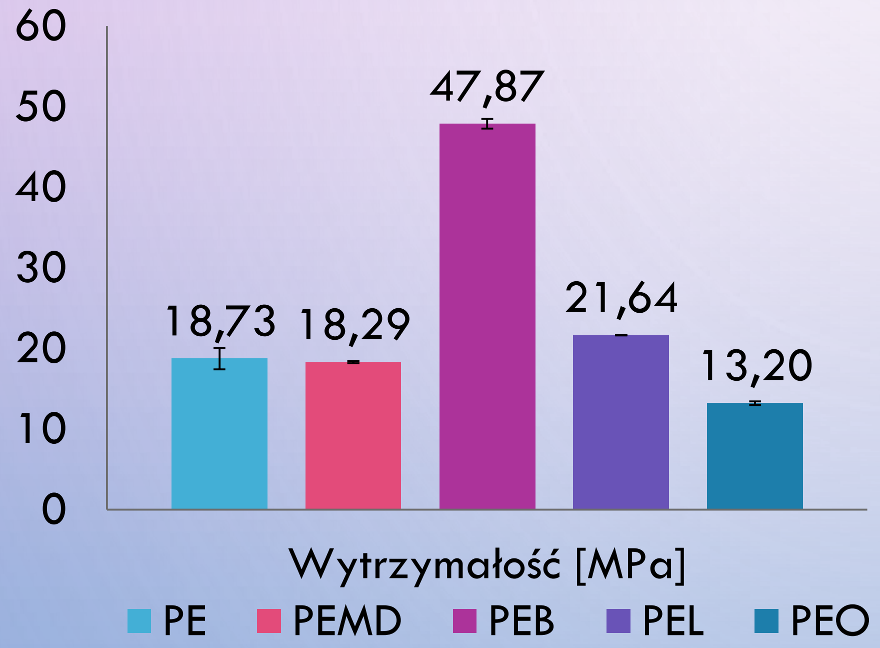
TESTS METHODS

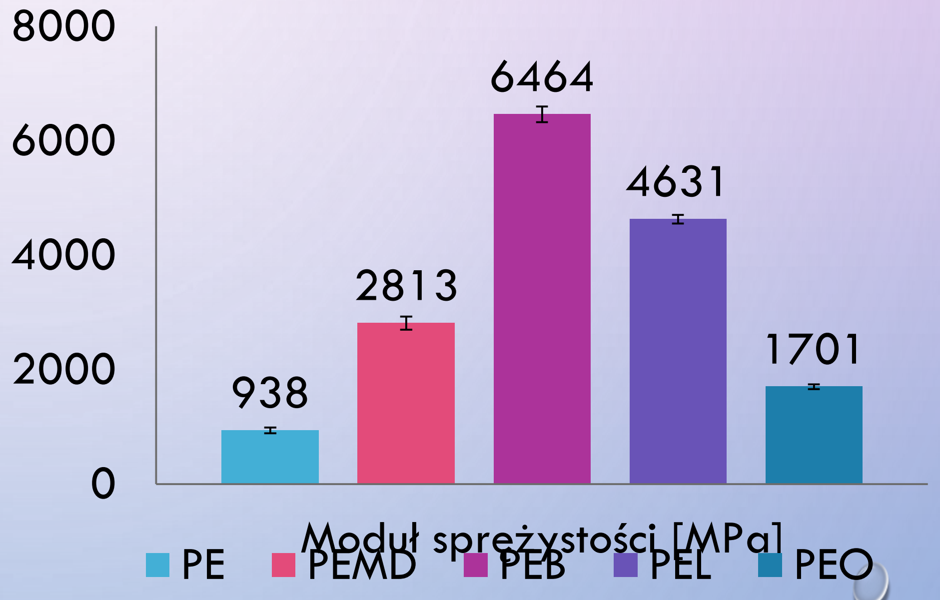
- TENSILE TESTS ACC. PN-EN ISO 527
  (CRITERION 30 MTS WITH MTS AXIAL EXTENSOMETER)
- CHARPY IMPACT TESTS (ZWICK HIT5.5P)
- SORPTION OF WATER (20°C) DETERMINATION AFTER 1, 7, 30, 240 DAYS OF SOAKING, ACC. PN-EN ISO 62:2000.
- **VICAT SOFTENING TEMPERATURE (VST)** WAS MEASURED ACCORDING TO ISO 306 UNDER 50 N LOADING AND WITH 50ºC/H HEATING RATE USING CEAST MACHINE
- WETTABILITY MEASUREMENT
  (KRÜSS DSA 10 DROP SHAPE ANALYSIS INSTRUMENT)
- THE SURFACE ROUGHNESS AVERAGE (R_A) MEASUREMENT
  (MITUTOYO SJ-301)
- NETZSCH MODEL DSC-200
  WITH COMPUTER SOFTWARE FOR TEST ANALYSIS
- SEM OBSERVATIONS (JEOL JSN5510LV)

Tensile tests and density

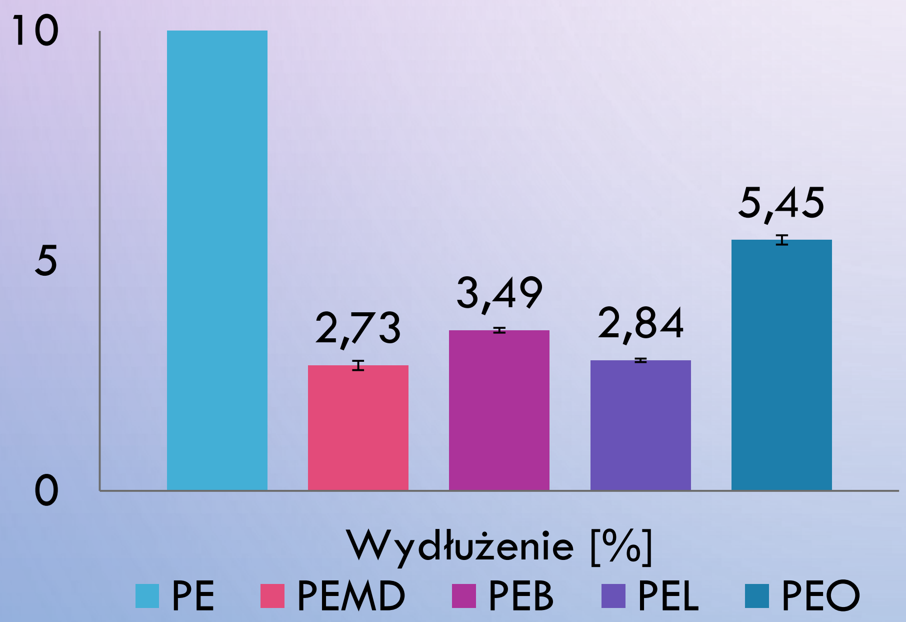


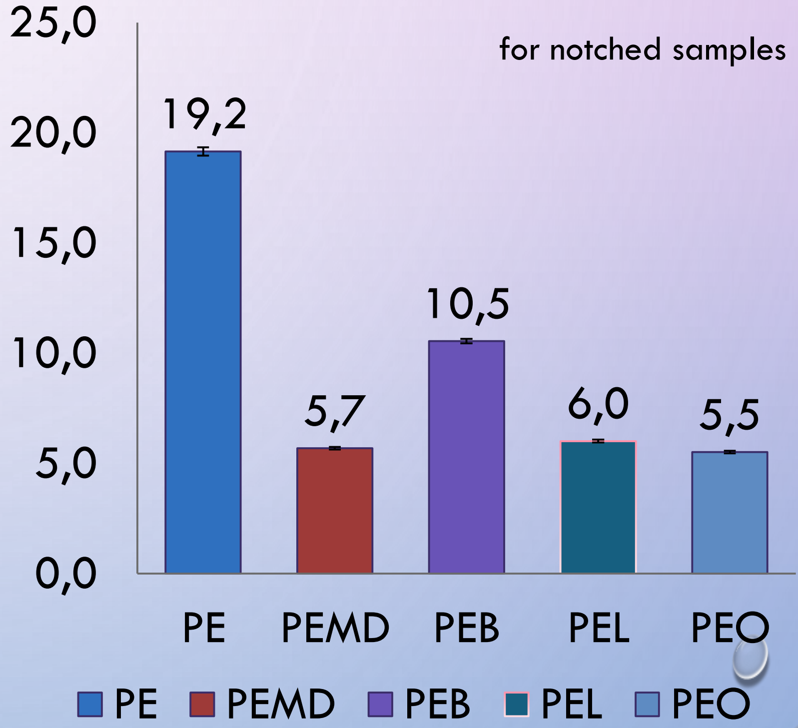
RESULTS OF TEST – STATIC TENSILE TEST



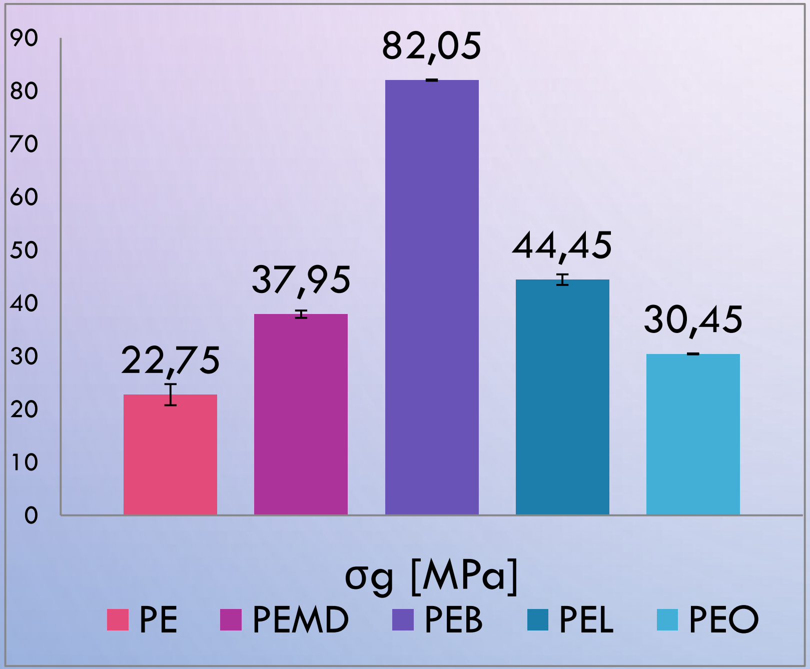


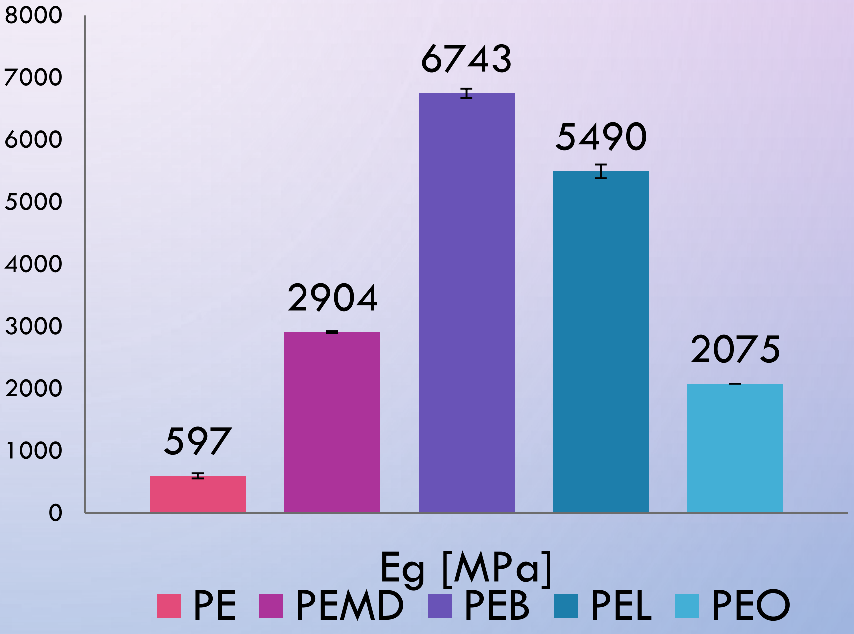
ELONGATION AT BREAK AND CHARPY IMPACT TEST



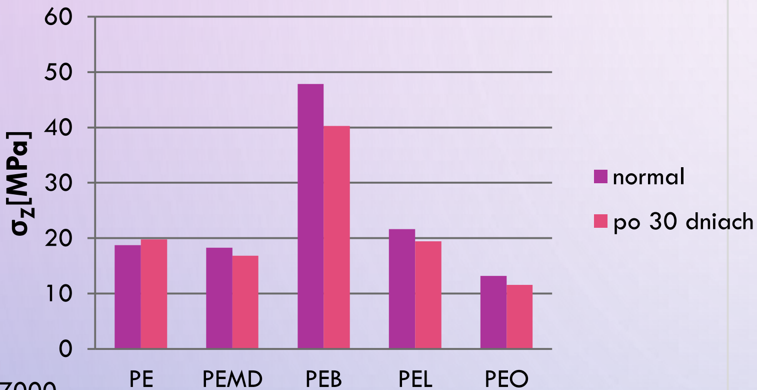


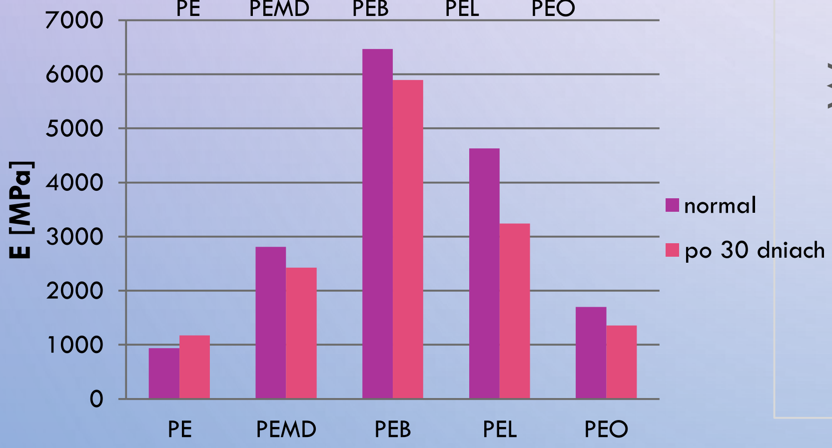
BENDING TEST

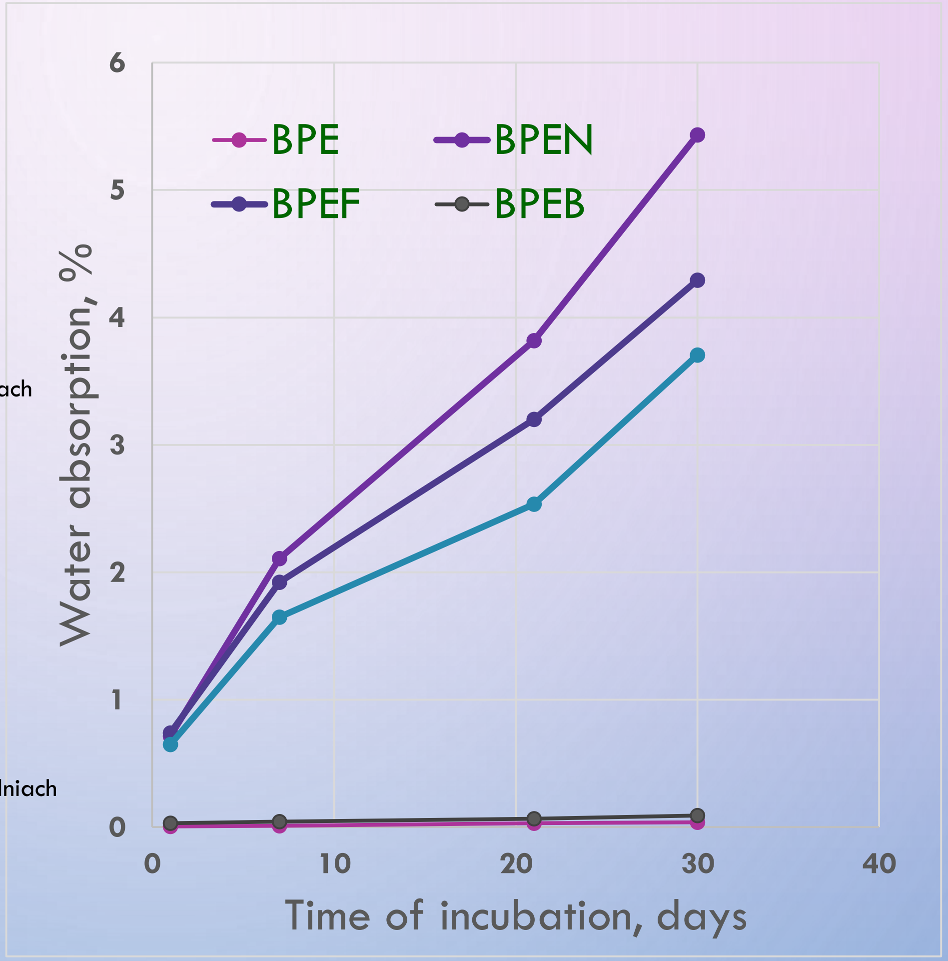




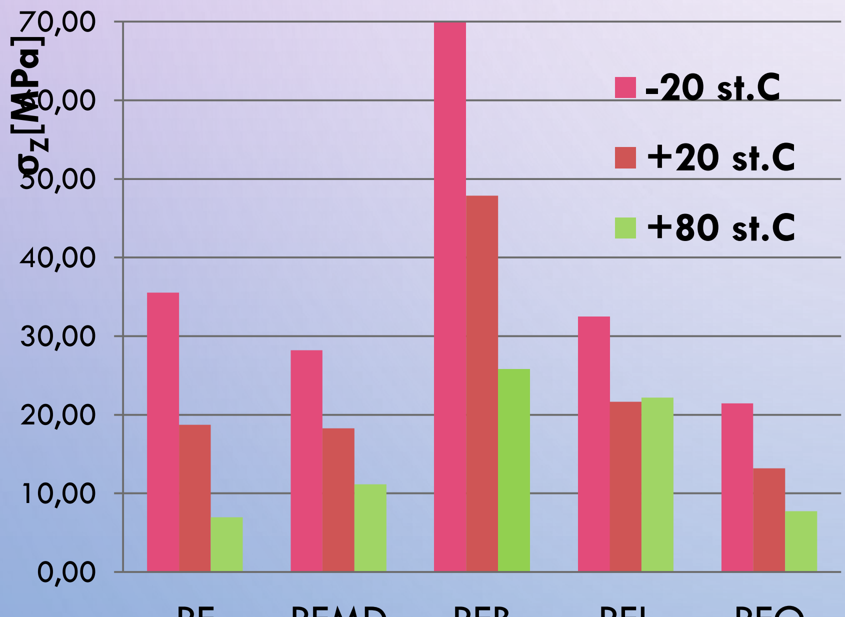
WATER ABSORPTION

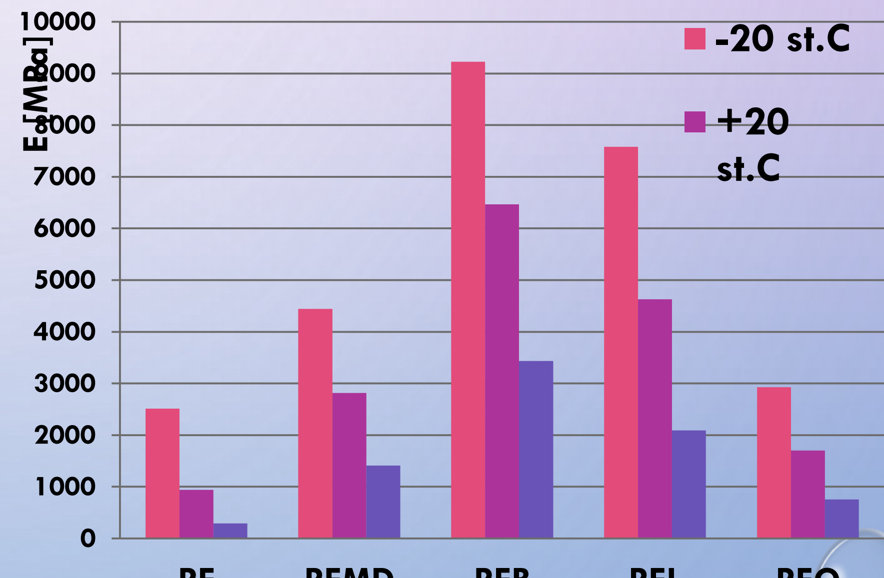




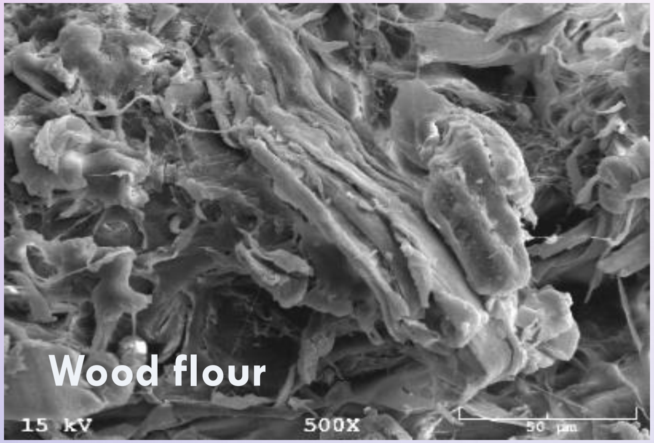


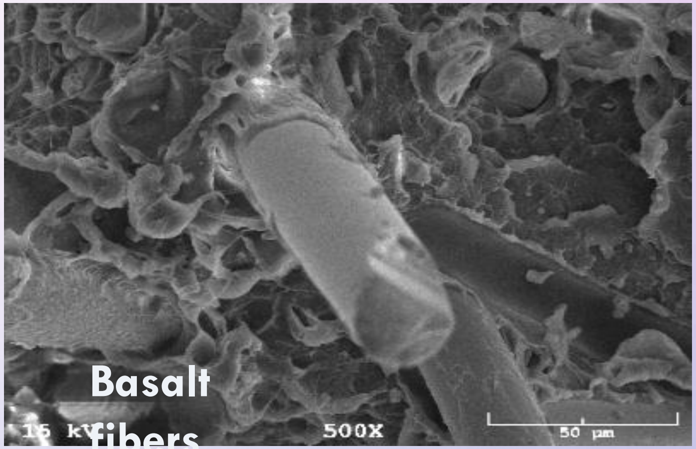
RESULTS - STATIC TENSILE TEST AT TEMPERATURES:

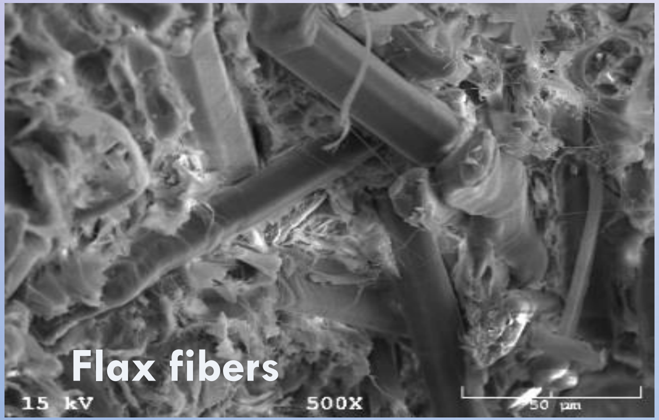




SEM images


Wood flour
15 kV
500X
50 µm


Basalt fibers
500X
50 µm


Flax fibers
15 kV
500X
50 µm


nut shell flour
15 kV
1kX
20 µm

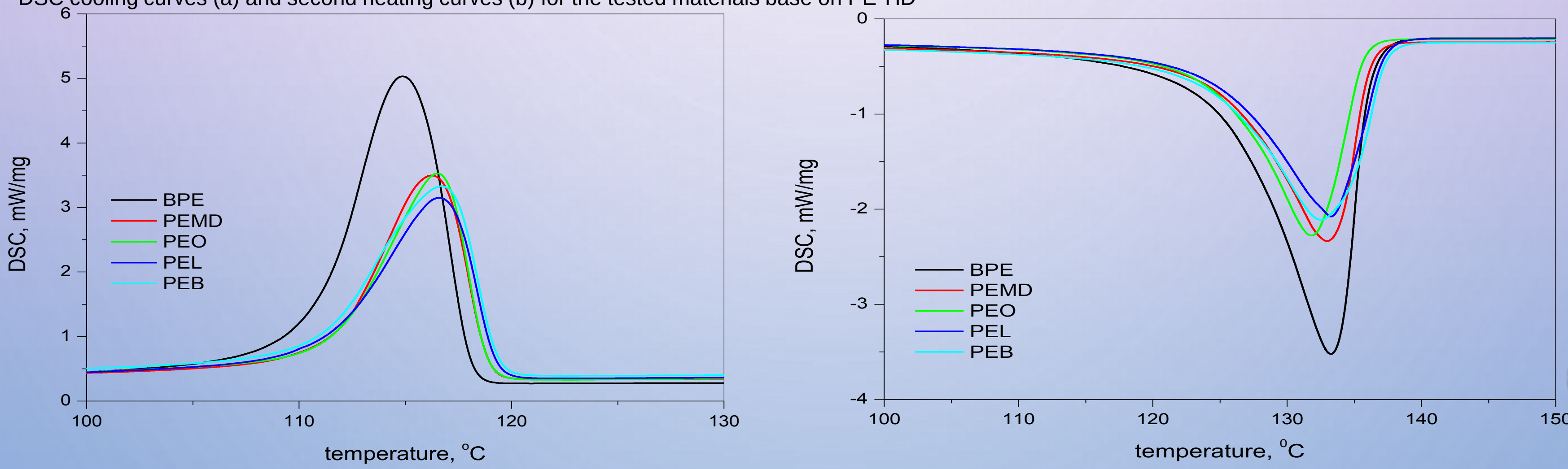
DSC results

fillers made slightly alter the melting point of the composite and increase the crystallization temperature

Temperatures of melting (T_m) and crystallization (T_c), melting enthalpy (ΔH_m), degree of crystallinity (X_c) and values of ΔT for tested materials (1 – first heating cycle, 2 – second heating cycle)

Material	T_{m1} (ºC)	ΔH_{m1}	Xc_1 (%)	T_c (ºC)	T_{m2} (ºC)	ΔH_{m2}	Xc_2 (%)	ΔT
BPE	133,9	154,8	52,82	114,9	133,3	170,6	57,87	18,4
PEMD	134,0	95,8	32,70	116,3	133,0	110,9	37,86	16,7
PEO	132,1	95,8	32,70	116,5	131,8	107,8	36,78	15,3
PEL	132,5	96,5	32,95	116,6	133,3	106,3	36,28	16,7
PEB	132,1	102,1	34,83	116,7	132,6	115,9	39,56	15,9

DSC cooling curves (a) and second heating curves (b) for the tested materials base on PE-HD



REMARKS

- Manufacturing of biocomposites containing high amount of filler is a difficult task especially for plant fibers prone to degradation.
- It is however feasible and may result in substantial increase in modulus of elasticity. Increase in tensile strength was not significant and the authors would recommend the tested composites for light weight stiffness critical applications.
- Applying plant fillers one must remember of considerable water absorption, which, in the case of high amount of the filler leads to dimensional changes, deterioration in surface quality and increase in weight.
- Basalt fiber is a new and promising filler for thermoplastic composites, providing high reinforcement efficiency, stability of the properties and profits for the environment while being used instead of glass fibers.
- Material recykling or cumbusting with recovery of energy can be used for utylisation of composite products

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