THERMOPLASTICS FROM LIGNOCELLULOSE - BAGASSE ESTERS AND ETHERS

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GEFÖRDERT VOM
Bundesministerium für Bildung und Forschung
Projektträger Jülich
Forschungszentrum Jülich
Funding initiative „Bioeconomy international“

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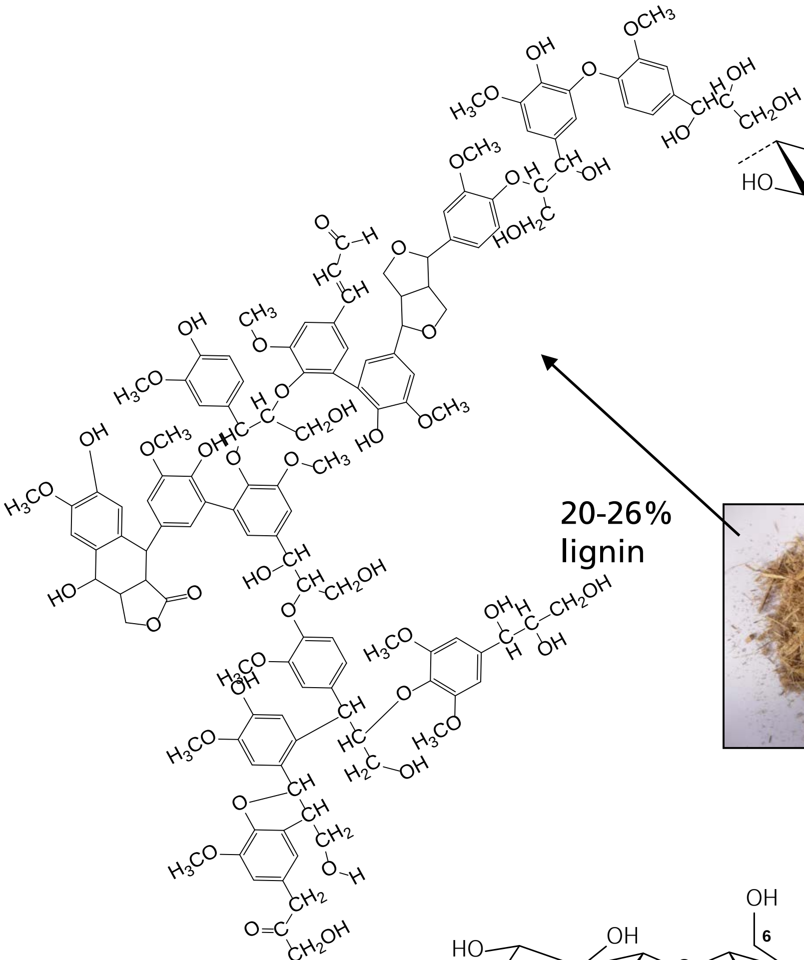
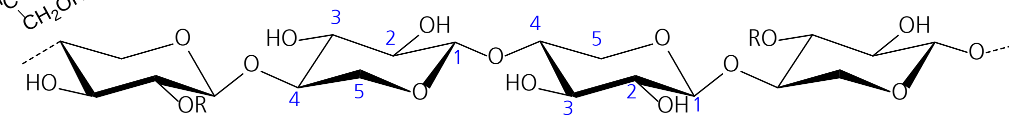
AGENDA

- Status quo / project overview
- Project results
  - Chemical modification/plastification of bagasse
  - Mechanical Properties
  - Bagasse as a fiber reinforcing material
- Conclusion

Sources and composition of bagasse in Brazil

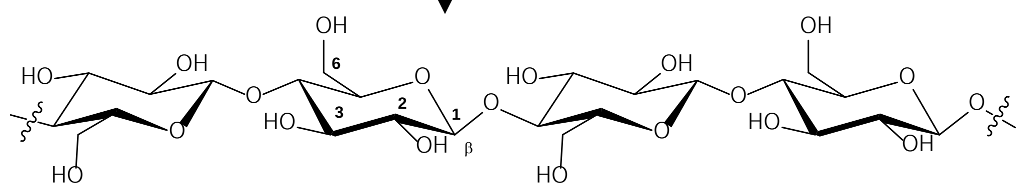


20-26% lignin



20-26% hemicellulose

40-46% cellulose



- 650 million tons of sugarcane were produced in ethanol plants (2013/14)
- 200 million tons of bagasse were generated
  - 10 % of the bagasse was destined to animal feed
  - 90 % were discarded as waste, returned to the soil or generated energy

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Aim of the project

- Usage of **biomass** as a basis for the development of **new materials** in order to **replace fossil resources** by bio-based raw materials
  - Sugar cane **bagasse** resulting as a by-product from the bio-ethanol production shall be transformed into a **thermoplastic material** by chemical modification (esterification) in order to obtain a **value-added bio-based product** suitable for extrusion and injection molding
  - Usage of **bagasse fractions** like cellulose, lignin and hemicelluloses as fillers and **reinforcing materials** in bio-based matrix systems (e. g. bio-PE, PLA, etc. and the novel bagasse esters)

⇨ Concept of bioeconomy:
Minimizing wastes and making efficient use of all resources - e.g. via conversion of bio-based waste streams into fuels and bio-based materials

Project partners

- Project duration: 01.09.2014 bis 30.08.2017
- Funding initiative „Bioeconomy international“

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Bagasse supplier

raízen

Fractionation, milling, surface modification

CNPEM
Centro Nacional de Pesquisa
em Energia e Materiais

LNNano

CTBE

Chemical modification/plastification, compounding

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Material development, scale-up

TECNARO
GESELLSCHAFT ZUR INDUSTRIELLEN ANWENDUNG
NACHWACHSENDER ROHSTOFFE mbH

Eco-efficiency assessment

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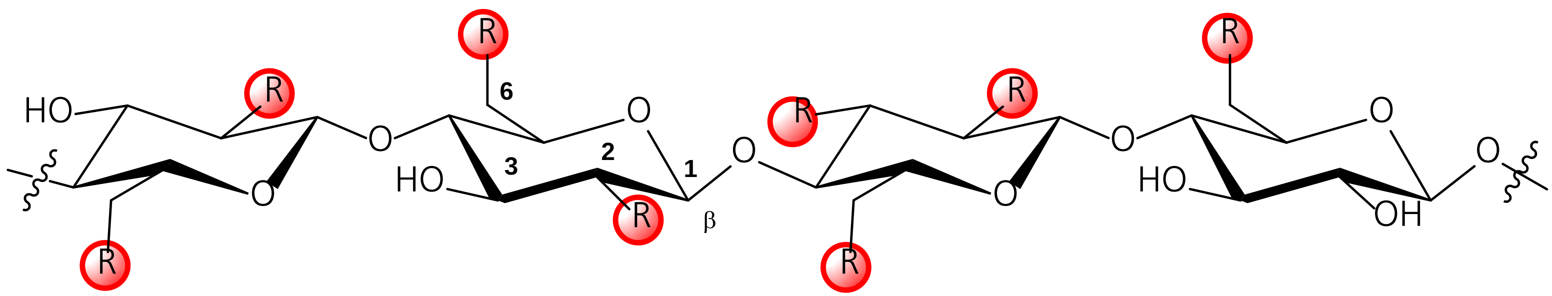
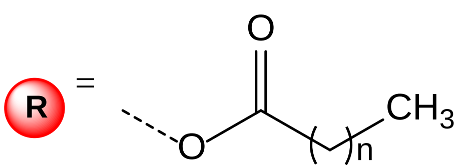
ISI

Properties of thermoplastic cellulose esters

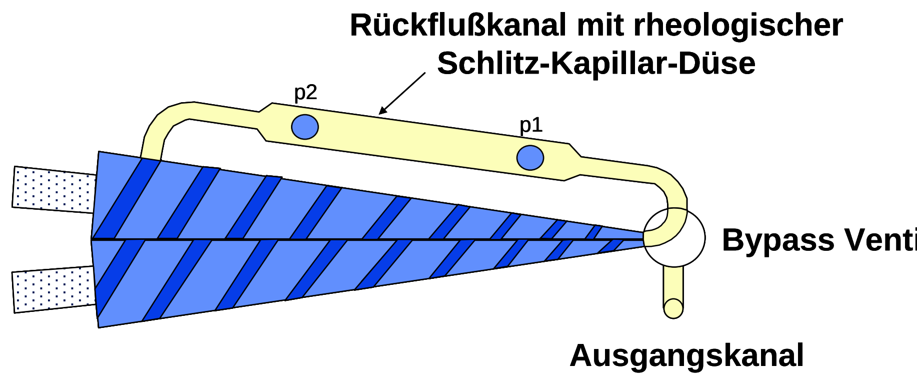




n	0	1	2	...	10
	Acetate	Propionate	Butyrate		Laurate
Strength					
E-Modul					
Elongation					

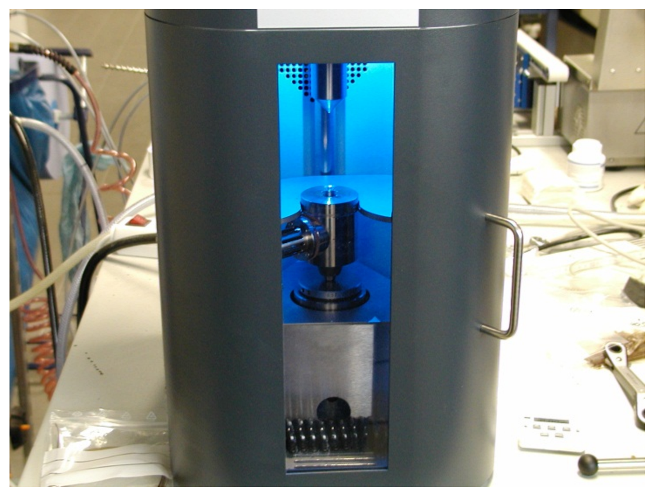
Melt processing

MiniLab-Extruder



Generell design of the extrusion unit

- Mixing with 30 % triacetin as plasticizer
- Processing at 240 °C in the extruder
- Injection molding at 230 °C
- Mechanical characterization (stress-strain curve)



Injection-molding MiniJet

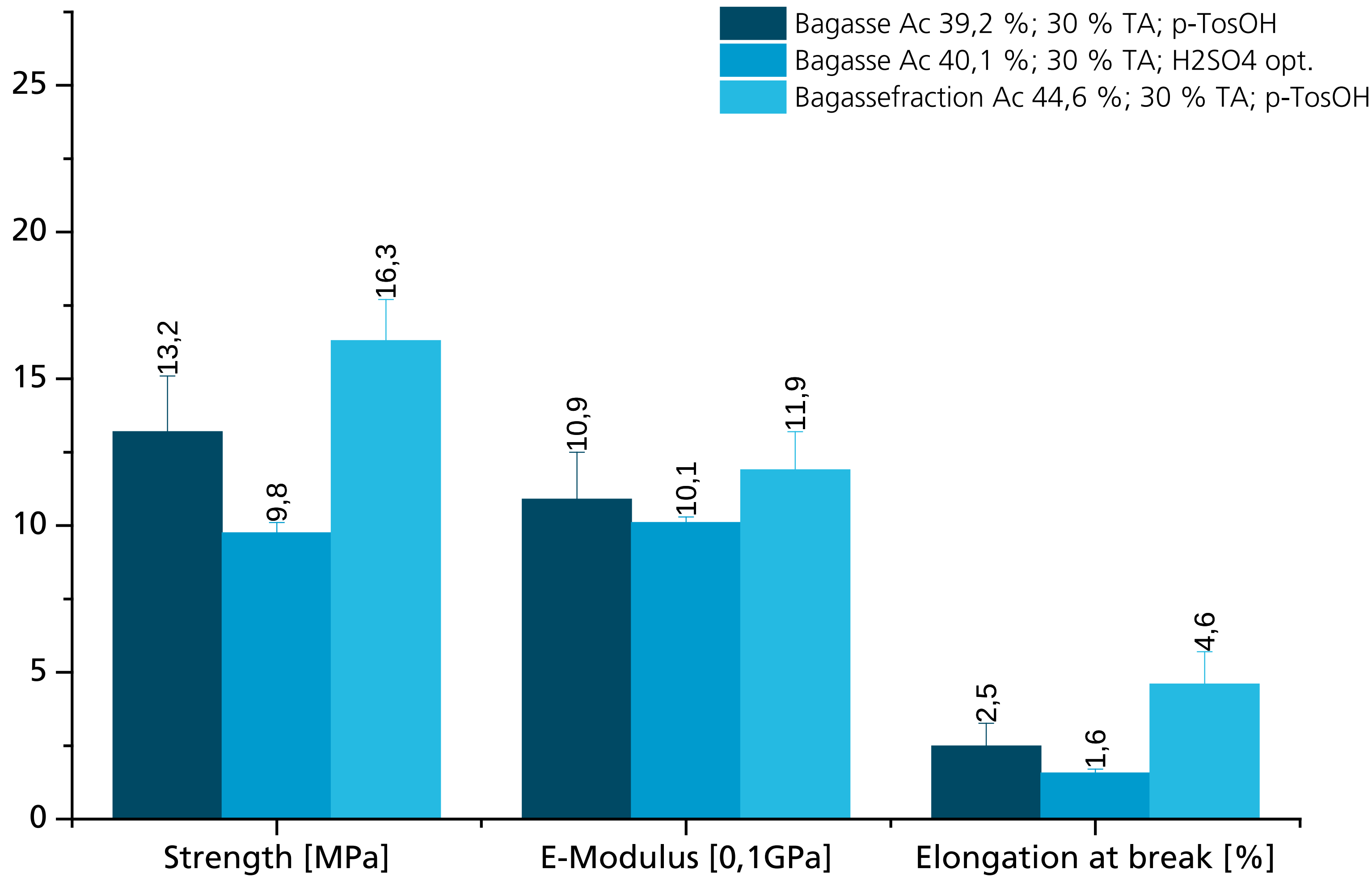
Acetylation – variation of reaction conditions

- Bagasse (milled 0,25 mm)
- Reagent $AcOH/Ac_2O$
- Different catalysts:
  - H_2SO_4 (different amounts)
  - $ZnCl_2$
  - p-TosOH
  - $HClO_4$ in toluene
  - Methylimidazol
  - NaOH
  - H_2SO_4 in CH_2Cl_2
  - p-TosOH in CH_2Cl_2

Best results:

Using p-TosOH
as catalyst yields
- high acetyl contents
- processible products

Mechanical properties of bagasse acetates (selected samples)



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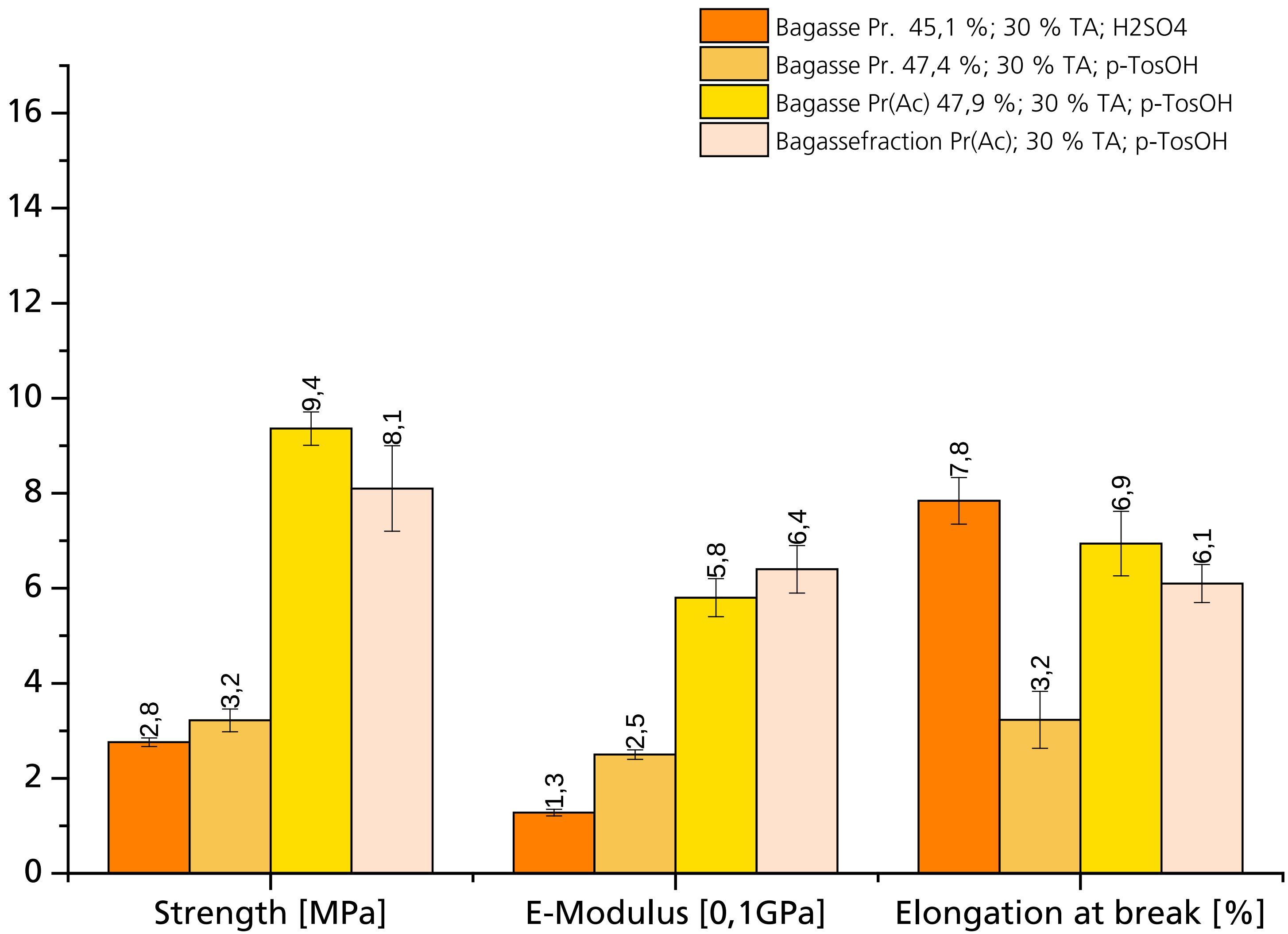
Propionylation – variation of reaction conditions

- Bagasse (milled 0,25 mm)
- Reagent a) $AcOH/Pro_2O$
  b) $ProOH/Pro_2O$
- Different catalysts:
  - H_2SO_4 (different amounts)
  - p-TosOH
  - H_2SO_4 in CH_2Cl_2

Best results: → Using p-TosOH as catalyst yields
- high propionyl contents
- processible products

Mechanical properties of bagasse propionates



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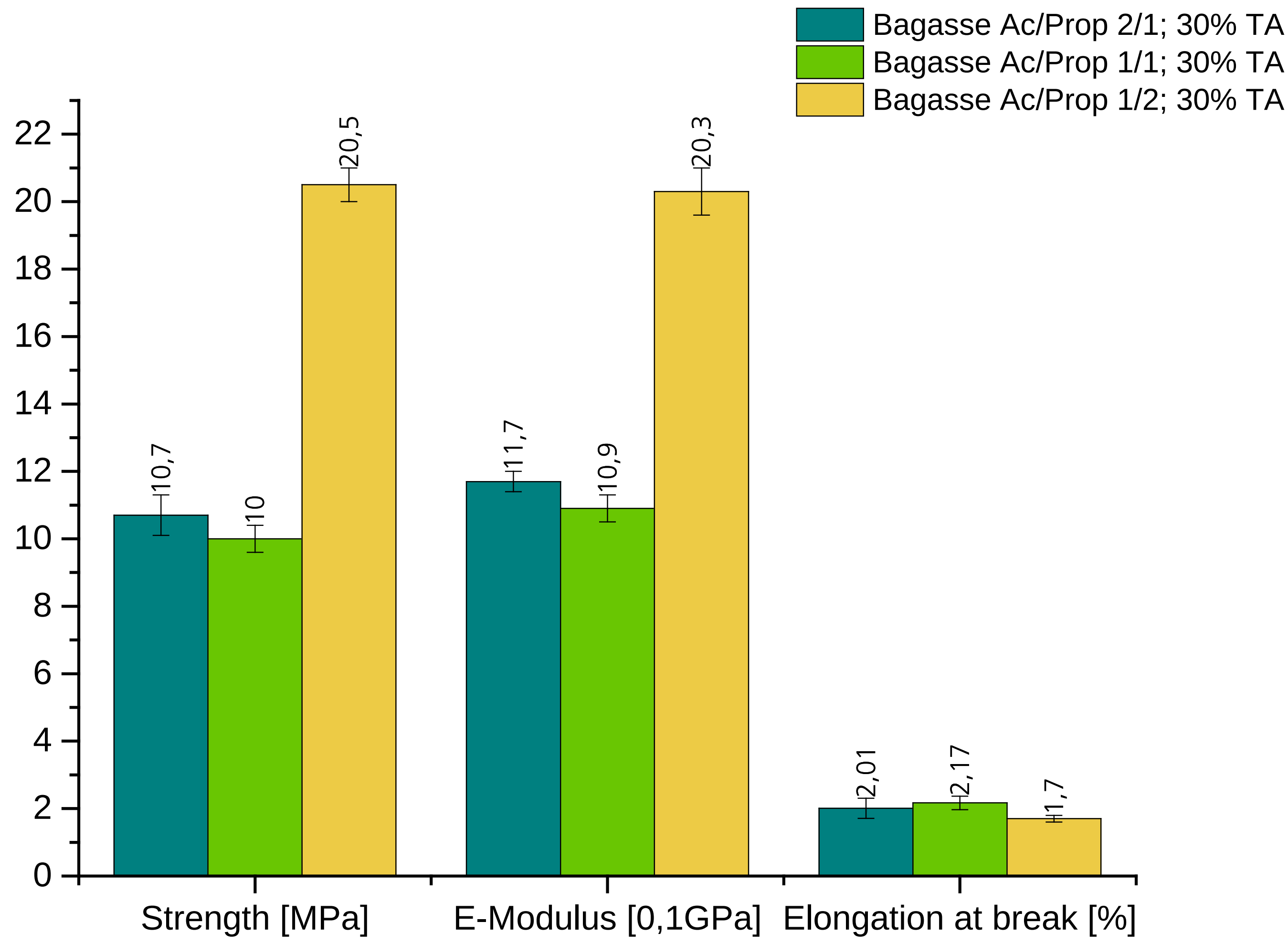
Bagasse mixed esters

- Bagasse BA1

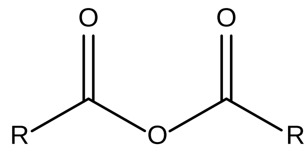
Sample	Reagents	Catalyst	Temp [°C]	Time [h]	Ester cont. [%]	Remarks
BP15-058	AcOH + Ac_2O/Pro_2O 2:1	p-TosOH	60	3	32-42	
BP15-059	AcOH + Ac_2O/Pro_2O 1:1	p-TosOH	60	3	30-40	
BP15-060	AcOH + Ac_2O/Pro_2O 1:2	p-TosOH	60	3	30-40	

Mechanical properties of bagasse mixed esters



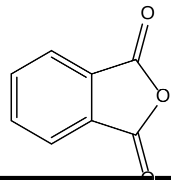
Longer chain bagasse esters

- Bagasse BA1
- Reagents:



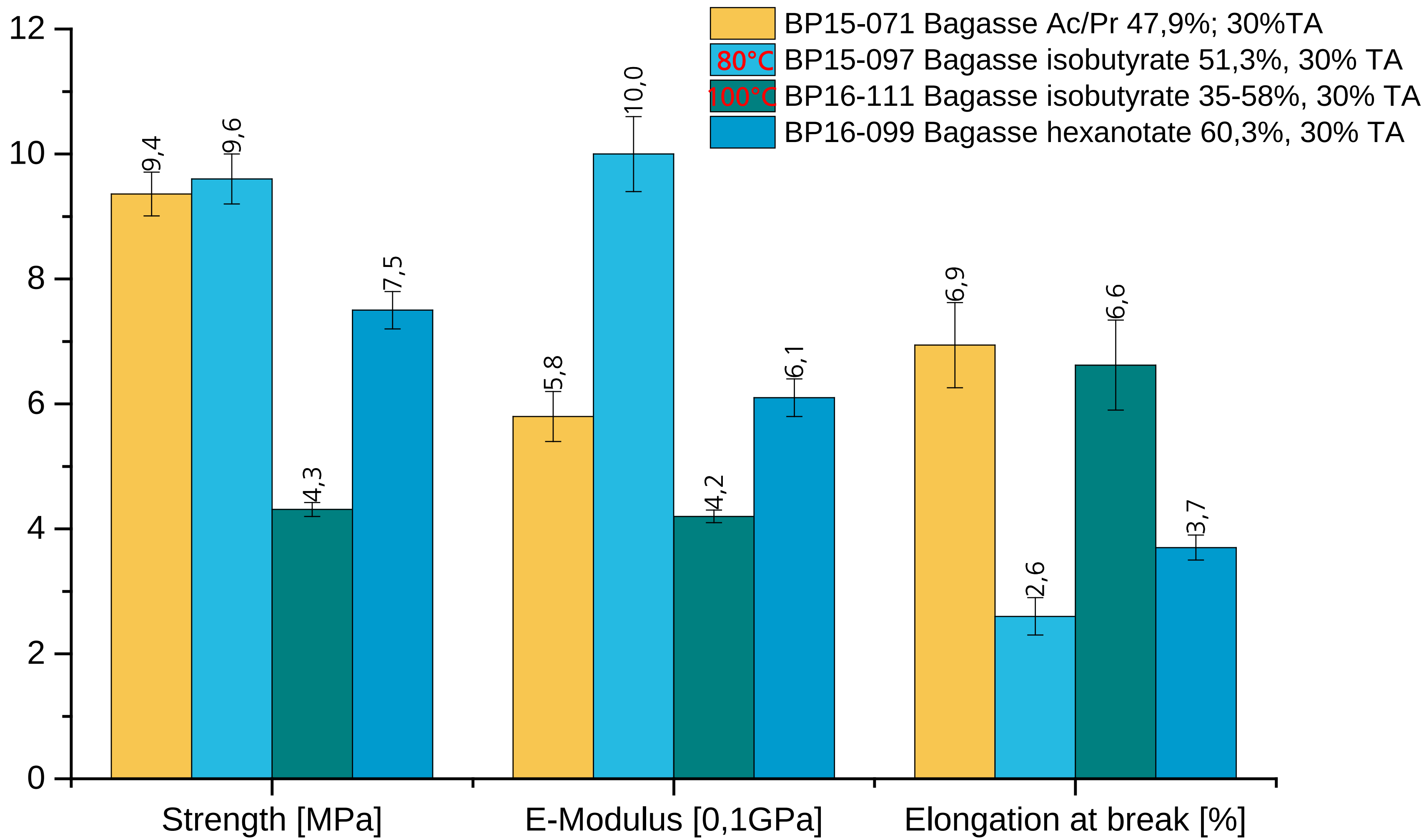
	-R
iBu	$-CH_2-CH(CH_3)_2$
Hex	$-CH_2-CH_2-CH_2-CH_2-CH_3$
Bz	-Ph

Pht_2O



Sample	Reagents	Catalyst	Temp [°C]	Time [h]	Ester cont. [%]	Remarks
BP15-057	AcOH/iBu_2O	p-TosOH	60	4.75	27-46	Not processible
BP15-063	AcOH/Hex_2O	p-TosOH	60	5	21-48	Not processible
BP15-064	AcOH/Pht_2O	p-TosOH	60	5	-	
BP15-065	AcOH/Bz_2O	p-TosOH	60	5	-	
BP16-097	AcOH/iBu_2O	p-TosOH	80	5	30-51	
BP16-098	AcOH/Bz_2O	p-TosOH	80	5	4-11	Not processible
BP16-099	AcOH/Hex_2O	p-TosOH	80	5	26-60	
BP16-111	AcOH/iBu_2O	p-TosOH	110	3	35-58	

Mechanical properties of longer chained bagasse esters



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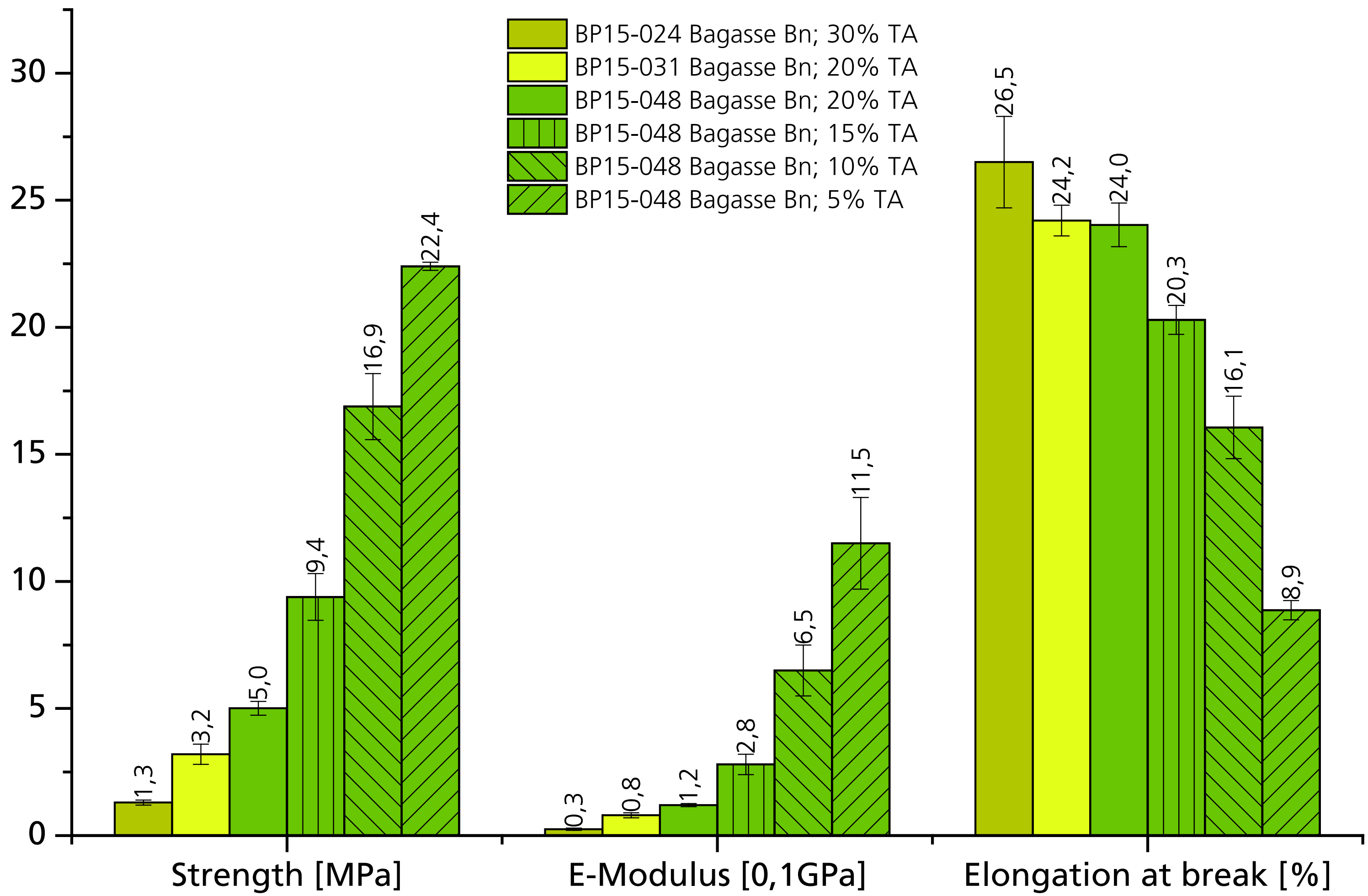
Etherification

- Benzylation of SM019 (*BA1) with benzyl chloride (BnCl)
- $NaOH_{aq}$
- 110 °C, 4 h

Sample	Reagents/ mol ratio	Catalyst	Temp [°C]	Time [h]	Remarks
BP15-024	BnCl/4.33	$NaOH_{aq}$	110	4	20 g scale
BP15-031	BnCl/4.33	$NaOH_{aq}$	110	4	50 g scale
BP15-048*	BnCl/4.33	$NaOH_{aq}$	110	4	50 g scale
BP17-117*	BnCl/3.9	$NaOH_{aq}$	110	4	5 kg scale
BP17-118*	BnCl/3.9	$NaOH_{aq}$	110	4	5 kg scale

Mechanical properties of benzylbagasse



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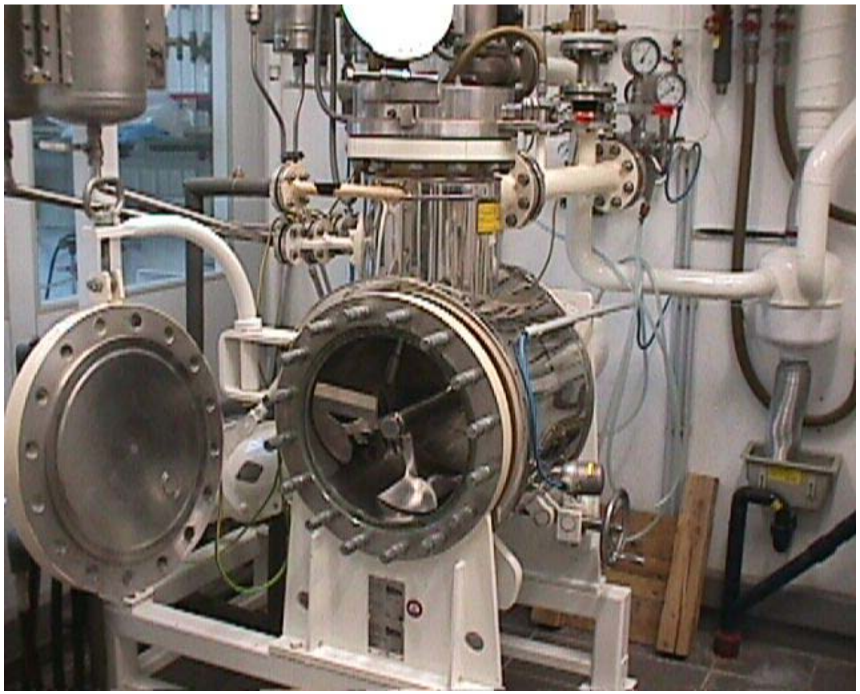
Synthesis of bagasse esters and ethers in the kg-scale



- 50 l Loedige ploughshare mixer
- 5 kg bagasse for one trial
- Synthesis of
  - 10 kg bagasse acetate
  - 10 kg bagasse acetate/propionate
  - 10 kg benzyl bagasse

=> material testing at TECNARO

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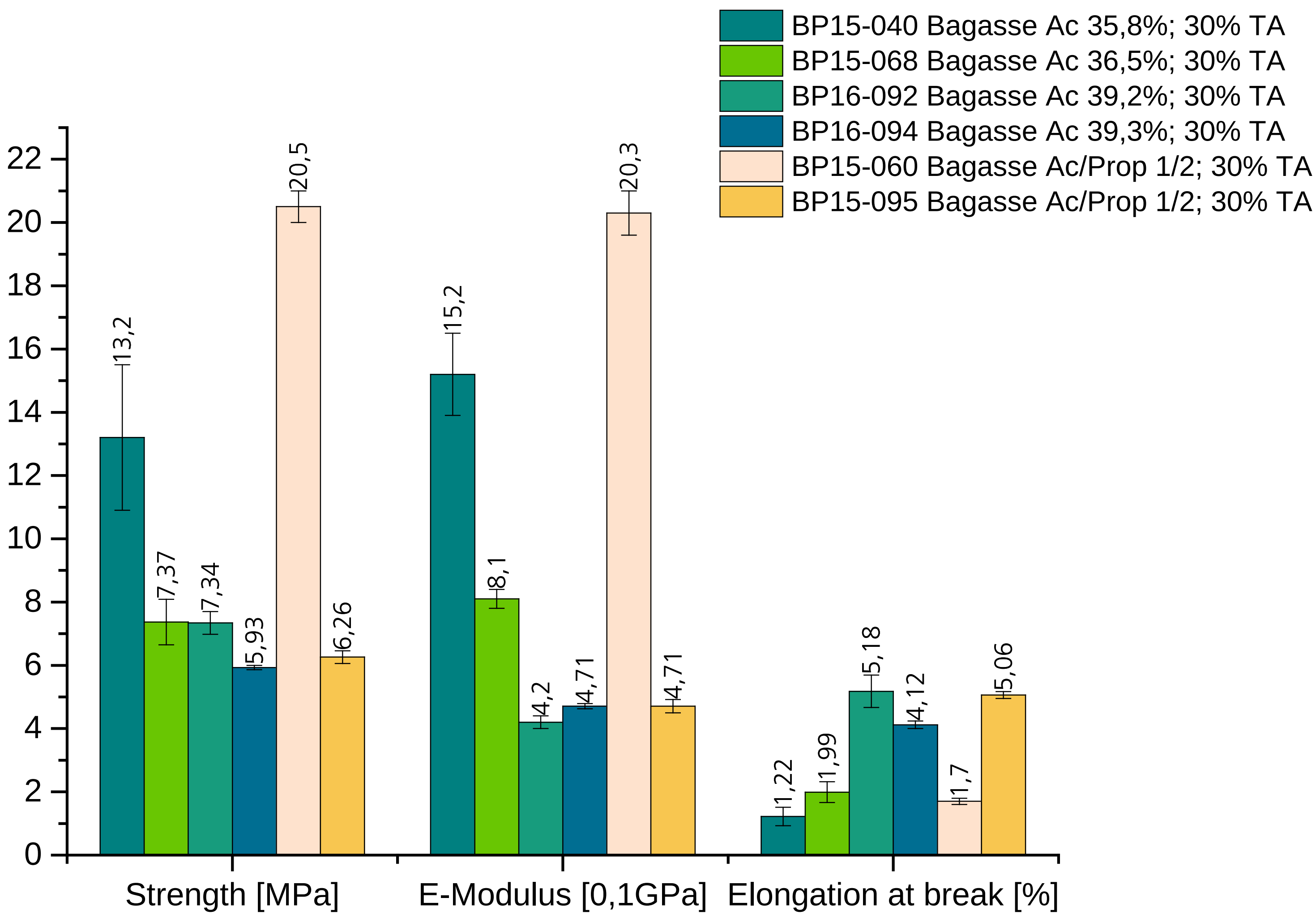
Mechanical properties of upscaled bagasse esters



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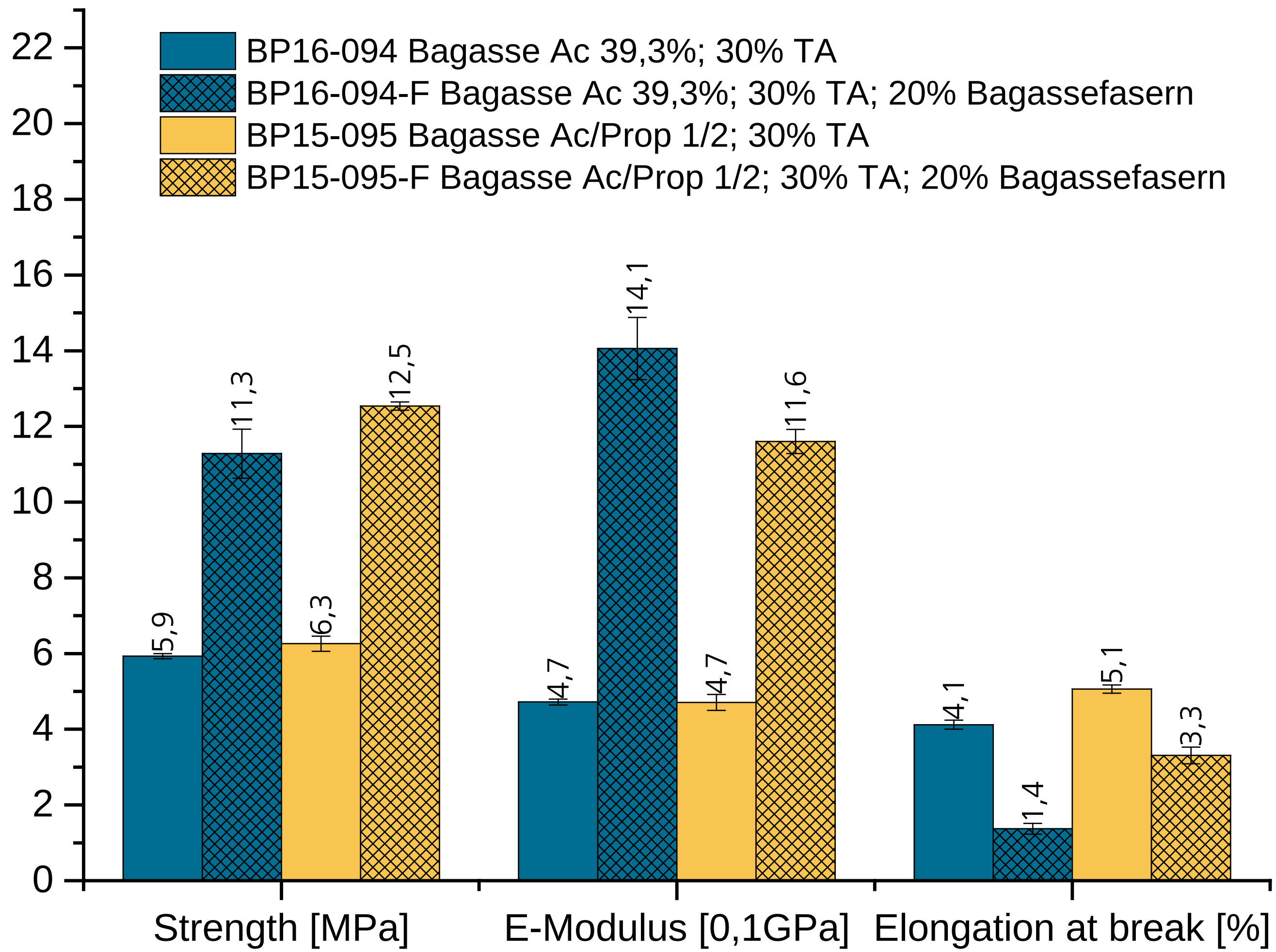
Fiber reinforced bagasse ester



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Sugarcane bagasse as a fiber reinforcing material

- Milling of bagasse in a cutting mill Retsch SM 200 and sieving with different sieves [0,75mm; 2mm, 6mm]

- Adding of the fibers to polyethylene (LDPE) in different concentrations together with a coupling agent (maleic acid anhydrid-PE)

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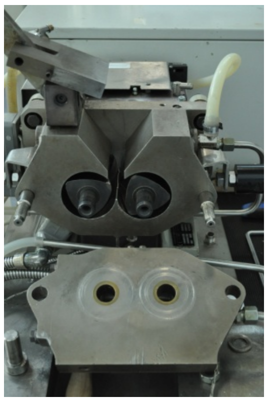
Compounding

Batch-process (Scale ca 200 g)

Mixinig



„*Brabender*“ Kneader

Bagasse-
polymer compound

→

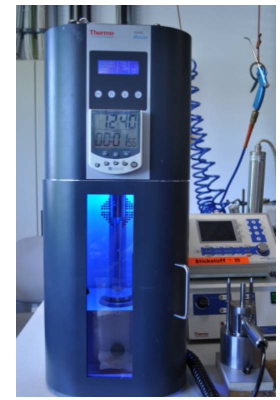
Pelletizing

mill

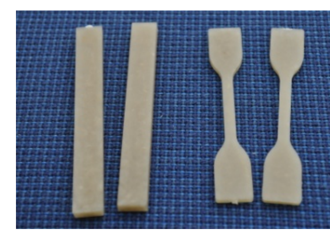
Free flowing granulate

→

Injection-molding

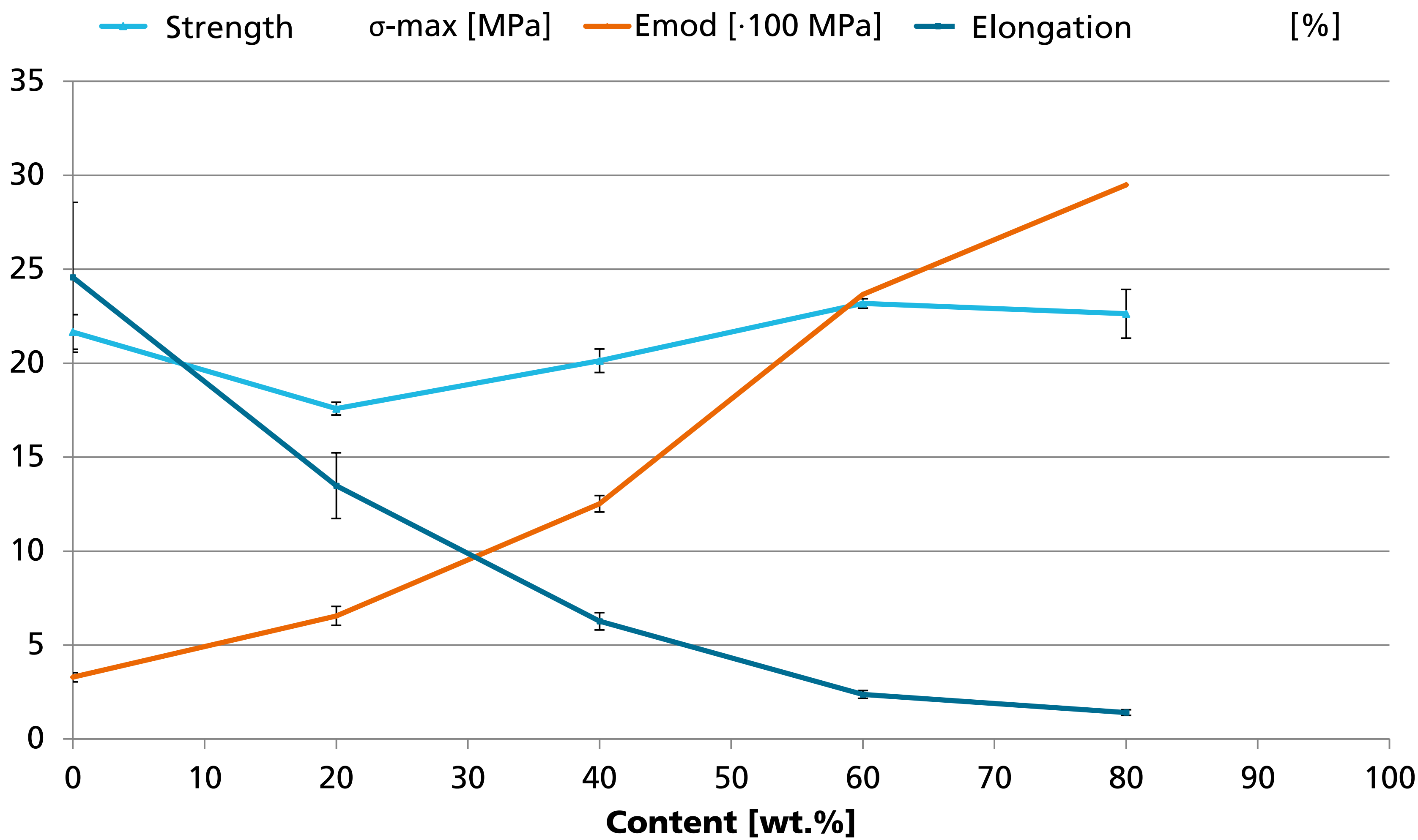


Haake Mini-Jet



Standardized specimen
(ISO 3167 und 179)

Variation of the bagasse content – mechanical properties



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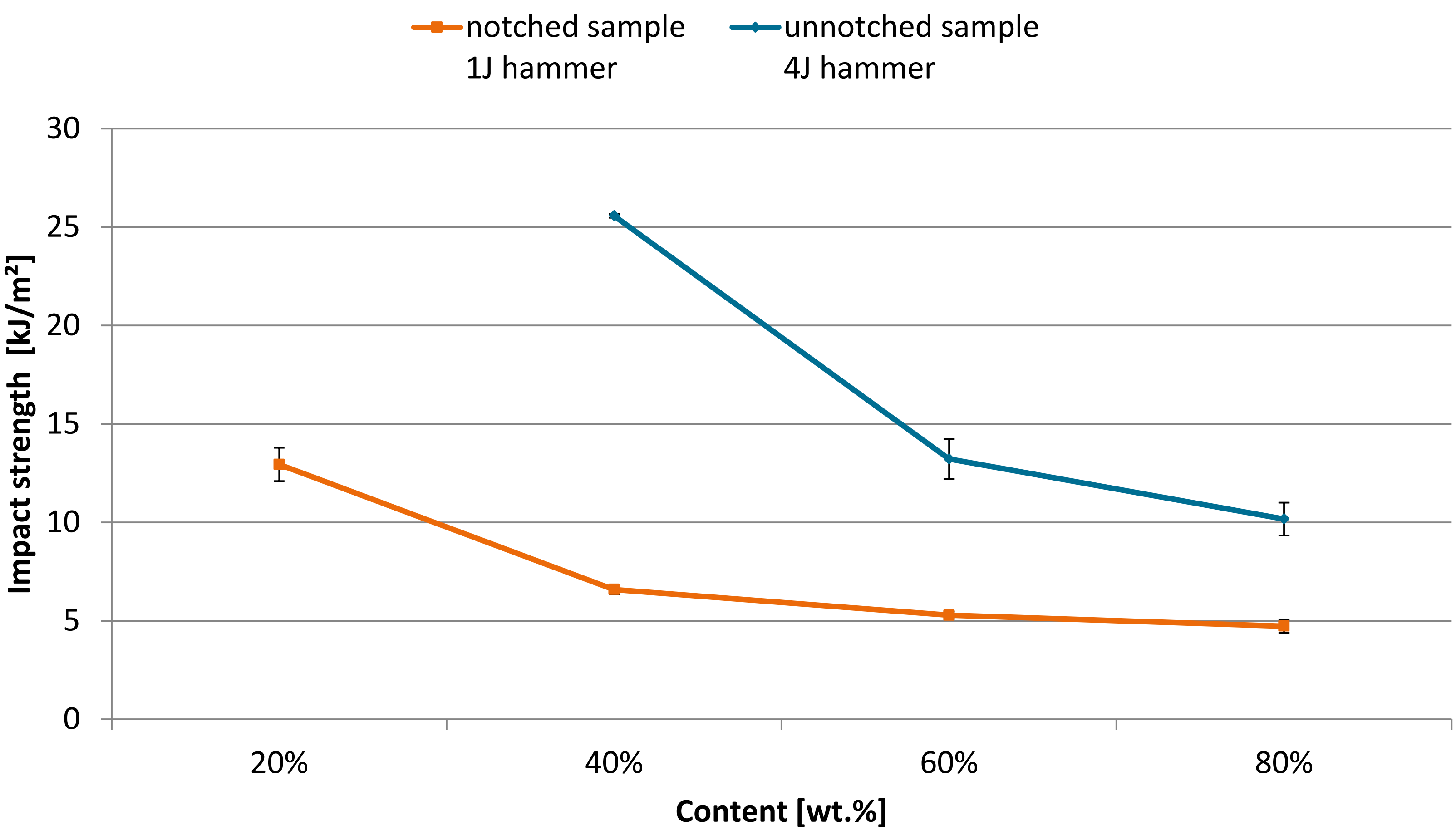
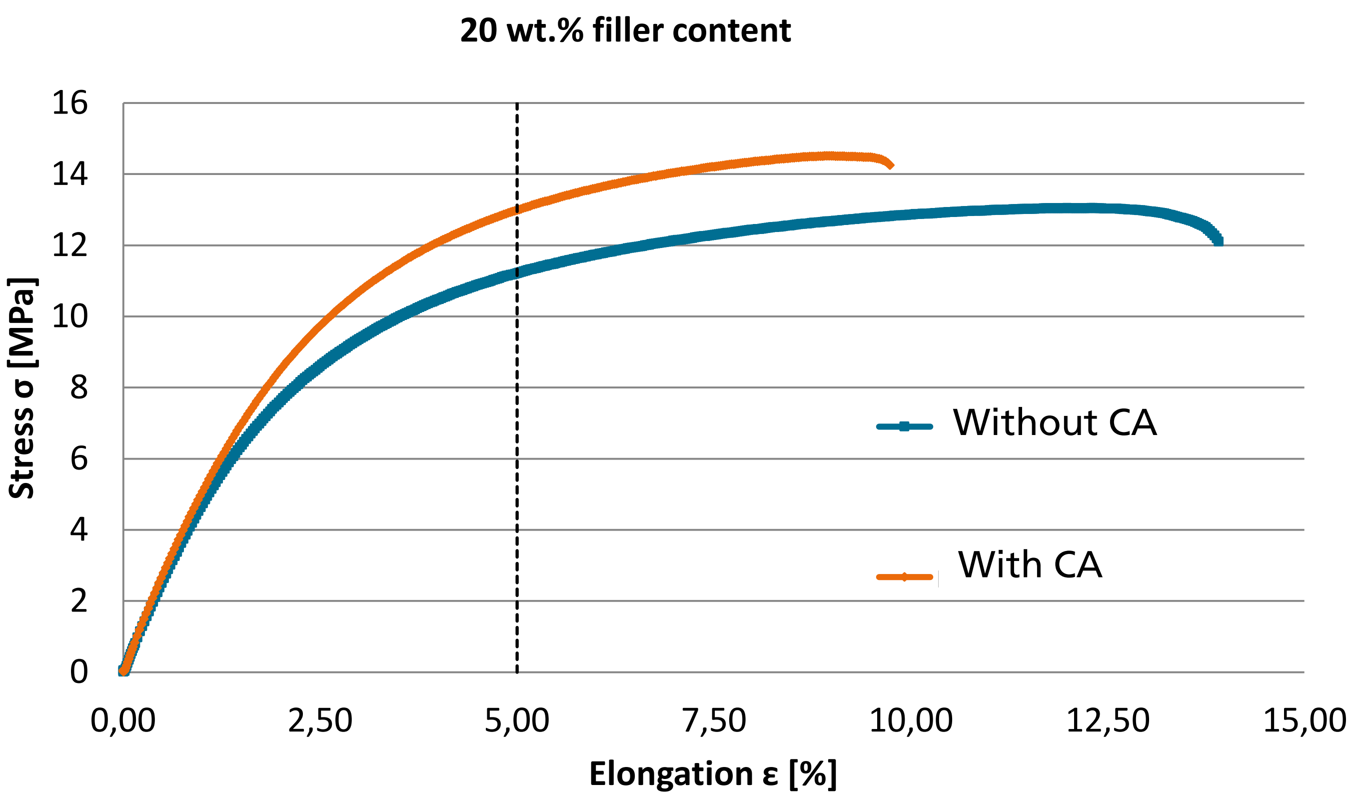
Variation of the bagasse content – Impact strength



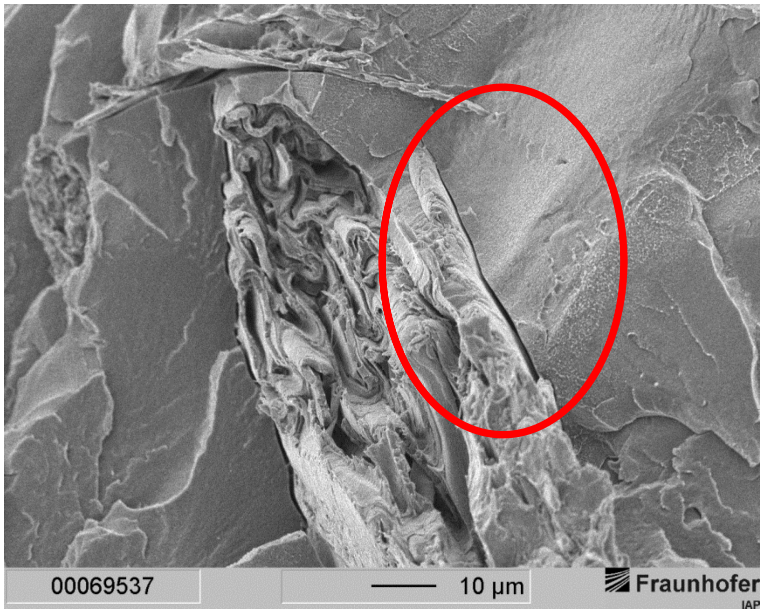
Influence of the Coupling Agent (CA)

Averaged stress-strain curve

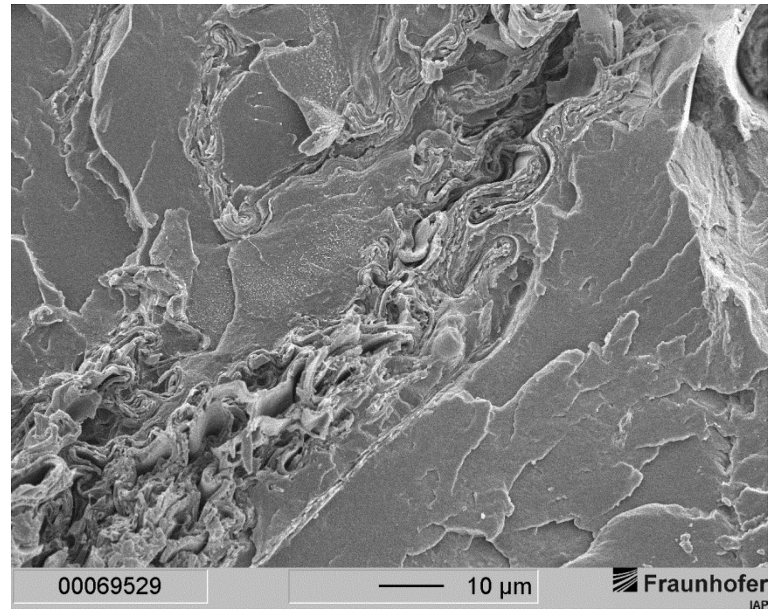


Influence of the coupling agent

SEM images of bagasse compound with 20 wt.% filler content



Without CA



With CA

- Gap between bagasse and polymer
- Bad fiber-matrix-cohesion

- Good wettability of the fibers
- Good fiber-matrix-cohesion

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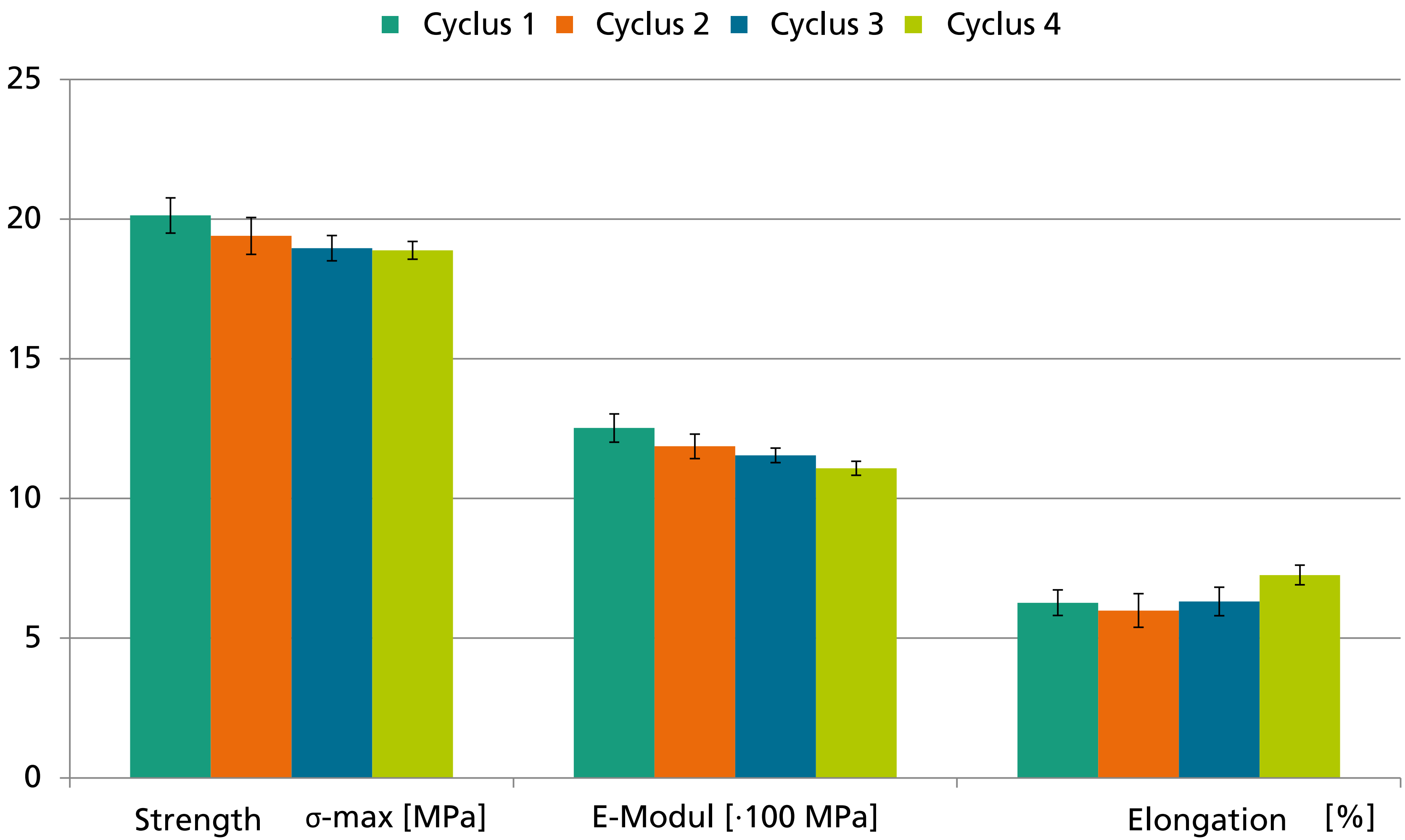
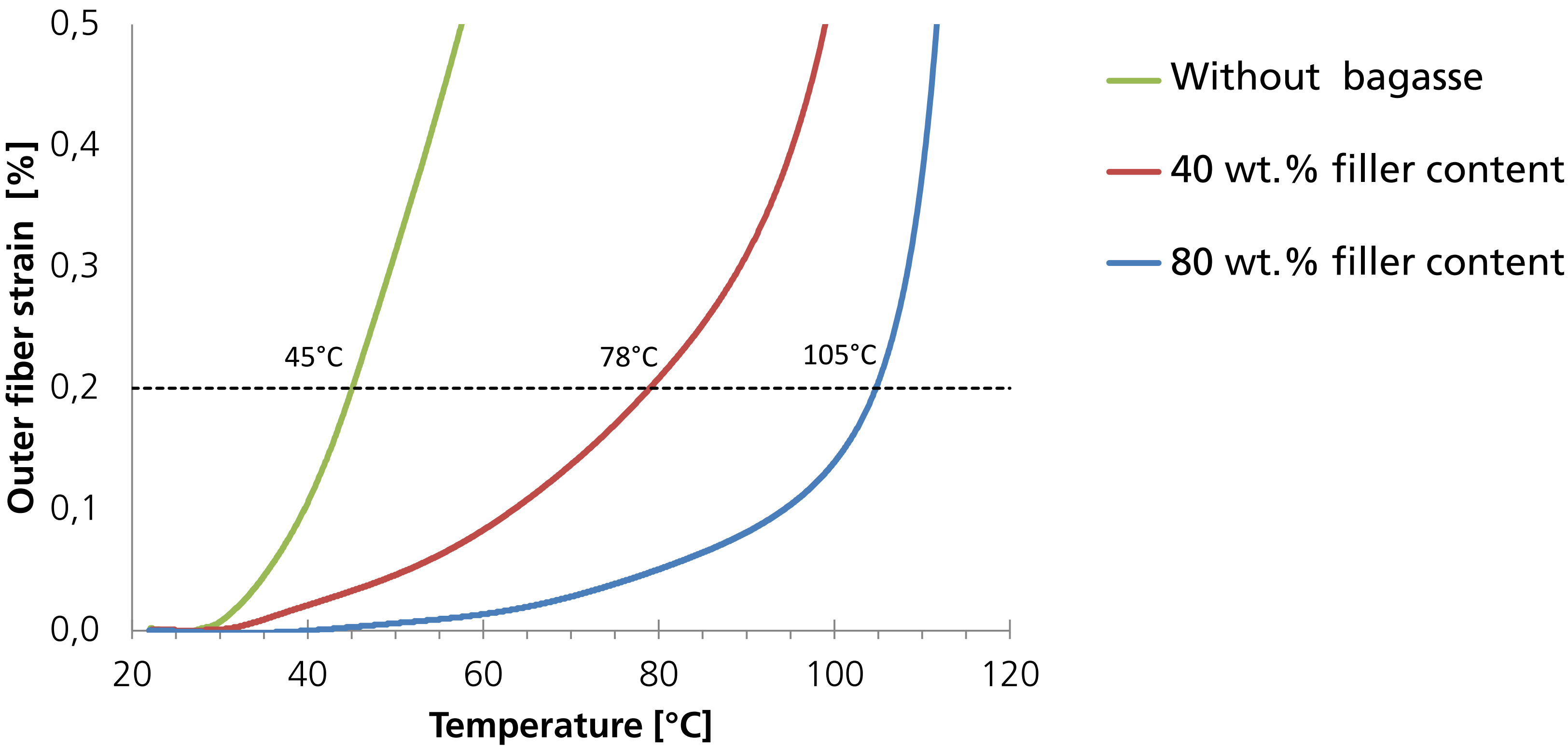
Recycling



Cyclus 1
Cyclus 2
Cyclus 3
Cyclus 4
25
20
15
10
5
0
Strength σ-max [MPa]
E-Modul [·100 MPa]
Elongation [%]

Heat Deflection Temperature of LDPE



By using bagasse as a filler the heat deflection temperature increases significantly

Conclusion

- Bagasse can be plastizised by chemical modification (esters and ether)
- Strength and stiffness are nearly in the range of PE und PP

- Bagasse can be used as a filler in (bio-)PE and in bagasse esters
- By using a coupling agent no activation step is necessary
- Bagasse can be added up to 80 wt.%
- Bagasse-polymer compound is recyclable, with only slight changes of the mechanical properties
- By using bagasse as a filler in LDPE the heat deflection temperature increases significantly

=> Development of a natural fiber composite (analog WPC)

Acknowledgement

- Gabriele Paul,
  Kristin Schade – Syntheses of bagasse esters and ethers
- Markus Koch – Melt processing
- Dino Mujkic – Fiber reinforcement

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