BIOBASED THERMOPLASTIC RESINS FROM STARCH AND LIGNOCELLULOSE

Sino-German Symposium on Biomaterials from Lignocelluloses

March 6-11, 2016 Beijing, China

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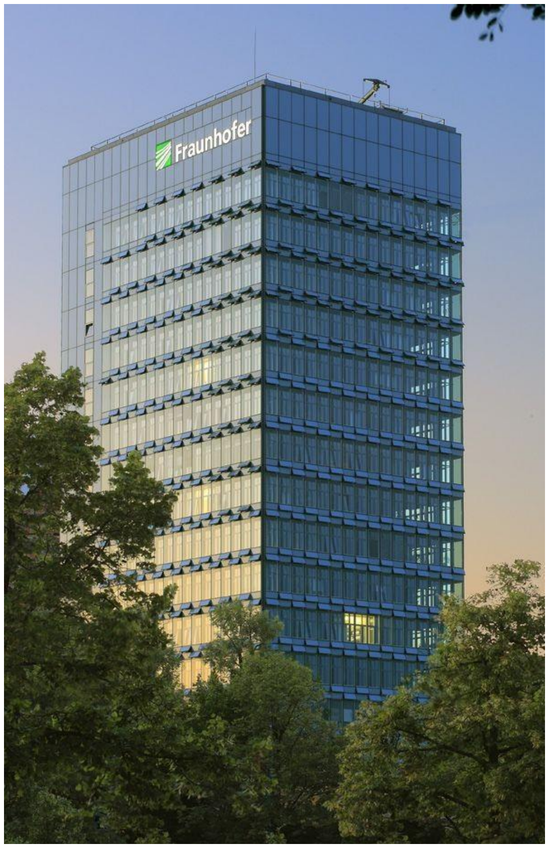
AGENDA

- Short introduction to the Fraunhofer-Gesellschaft and Fraunhofer-Institute for Applied Polymer Research IAP

- Thermoplastics from lignocellulosic feedstock in ionic liquids
- Thermoplastics from bagasse without ionic liquids
- Thermoplastic starch derivatives

- Conclusion

The Fraunhofer-Gesellschaft

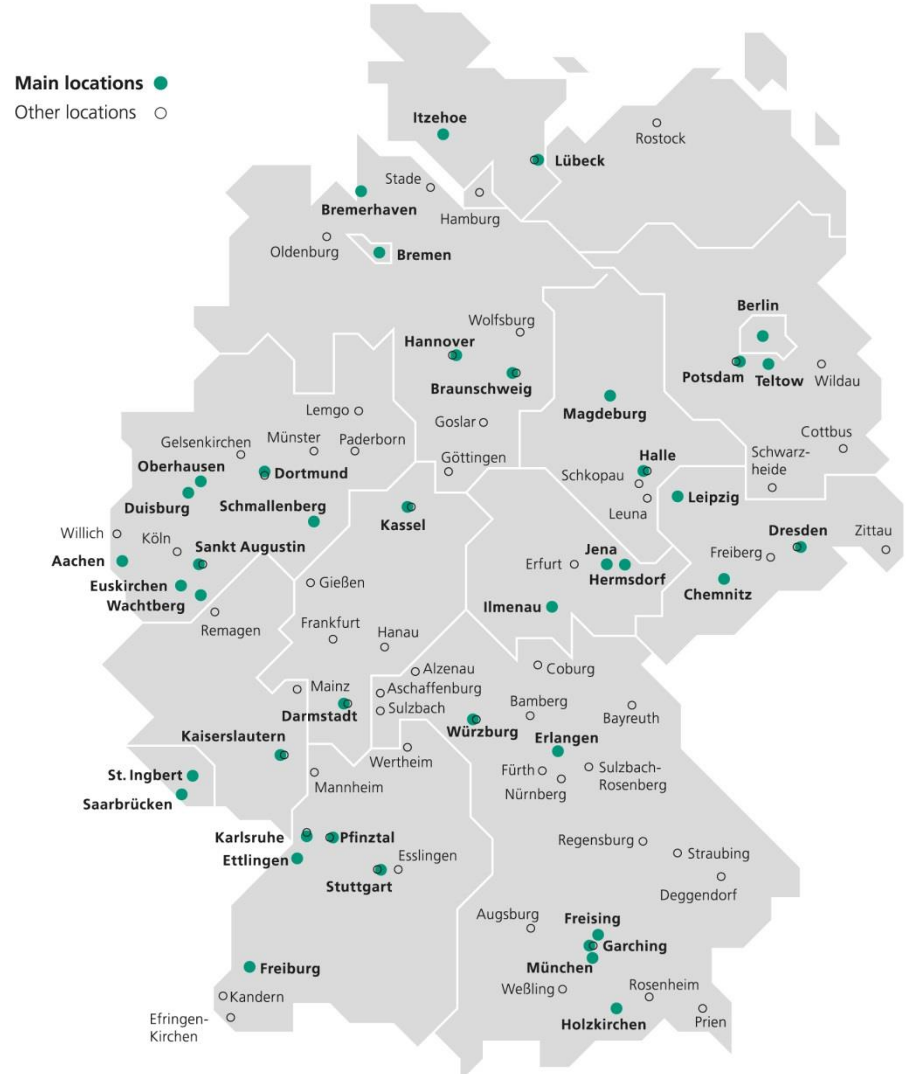


- the largest organization for applied research in Europe
- undertakes applied research of direct utility to private and public enterprise and of wide benefit to society

Our Customers:

- Industry
- Service sector
- Public administration

The Fraunhofer-Gesellschaft
Locations in Germany



- 66 institutes and research units
- Nearly 24,000 staff

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FRAUNHOFER INSTITUTE
FOR APPLIED POLYMER RESEARCH IAP

Director: Prof. Dr. Alexander Böker

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Fraunhofer IAP at a glance

- 210 employees, incl. PhD students, apprentices, etc.

- ca. €16.8 million institute‘s budget
  ca. €12.0 million external revenues

- Research sites: Potsdam-Golm
  Adlershof
  Schkopau
  Schwarzheide

Status: 12 | 2014

Fraunhofer IAP

Research divisions

Biopolymers

Dr. Johannes Ganster

Biopolymers (cellulose, starch, lignin)
Biobased plastics (PLA, PHA, PA)
Blends and composites

Functional Polymer Systems

Dr. Armin Wedel

Polymeric OLEDs,
Polymer electronic components

Synthesis and Polymer Technology

Dr. Thorsten Pretsch

Polymer synthesis and process development, Microencapsulation/ particle applications, Membrane development and application

Specialty Polymers

Prof. Dr. André Laschewsky

Water-soluble polymers, Hydrogels, Polymer dispersions, “Smart materials”

Pilot Plant Center Schkopau

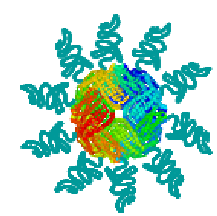
Prof. Dr. Michael Bartke

Polymer synthesis and processing,
Upscaling to ton scale

Functional Protein Systems/ Biotechnology

Prof. Dr. Alexander Böker

Keratin fibers
Biotechnological processes
Protein conjugates
Self-assembly techniques



THERMOPLASTICS FROM LIGNOCELLULOSIC FEEDSTOCK IN IONIC LIQUIDS

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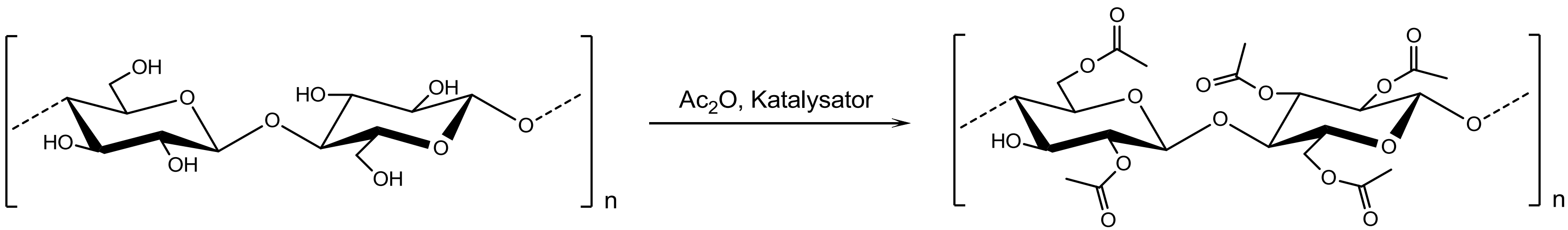
Acetylation of cellulose in ionic liquids



- Barthel & Heinze, Green Chem., 2006, 301-306
  Acetylation of cellulose in ionic liquid
- J. Zhang et al., Carbohydr. Polym., 2007, 69, 665-672
  Synthesis of cellulose-2,5-acetate in AmimCl
- Argyropoulos et al., 2007, 8, 3740-3748
  Acetylation of spruce wood in AmimCl und BmimCl
- Lehmann & Volkert, 2009, 114, 369-376
  amongst others: acetylation of spruce cellulose in BmimCl bis DS = 2,8
- …

Acetylation of spruce wood in a stirring reactor

- 5 % spruce-TMP in IL, 3 h dissolving time
- + 2,7-times mass excess Ac_2O, 110 °C

Sample.	IL	Reaction time [h]	Acetyl content [%]
PLC10-2	EmimAc	0,5	20,0
PLC10-4	EmimAc	1,5	19,8
PLC10-5	EmimAc	2	21,4
PLC10-6	EmimAc	4	21,2
PLC10-19	EmimCl	1	35,1
PLC10-20	EmimCl	3	37,2

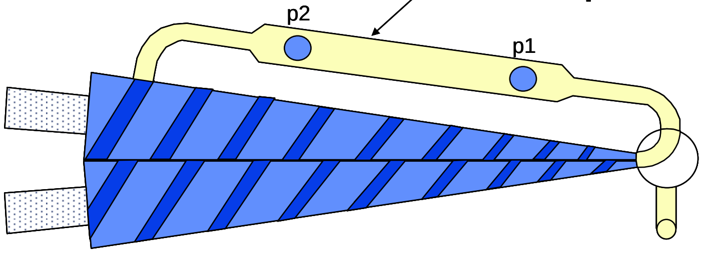
Esterification in a kneader

- 15 % lignocellulose (LC) in IL
- „Dissolution" of LC in IL (125 °C, 3 h), then addition of anhydride

Sample	IL	Temp. [°C]	Time [h]	Starting material	Ac/Prop content [%]
PLC11-062	EmimAc	125	2	poplar-TMP <1mm	35,1
PLC11-069	EmimAc	125	2	poplar-TMP wet, 1%AcOH	35,0
PLC11-063	EmimAc	125	2	beech-TMP <1mm	34,7
PLC11-068	EmimAc	125	2	spruce-TMP	36,2
PLC11-074	EmimAc	125	2	wheat-TMP	34,6
PLC11-071	EmimAc	125	2	spruce-TMP-H_2O_2	48,6
PLC11-072	EmimAc	125	2	beech-TMP	49,2
PLC11-073	EmimAc	125	2	wheat-TMP	48,0

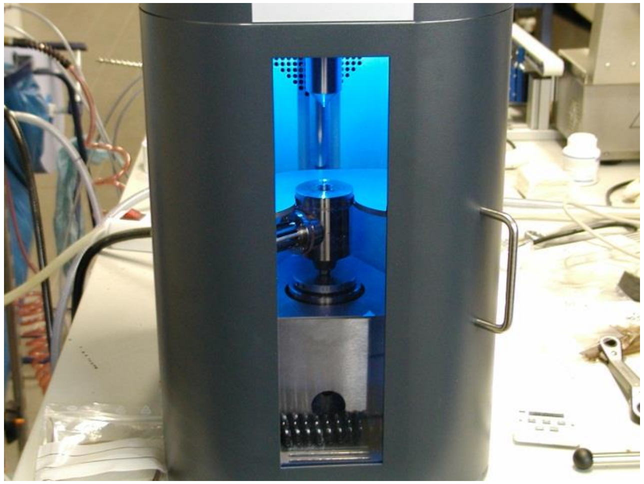
Melt processing

MiniLab-Extruder



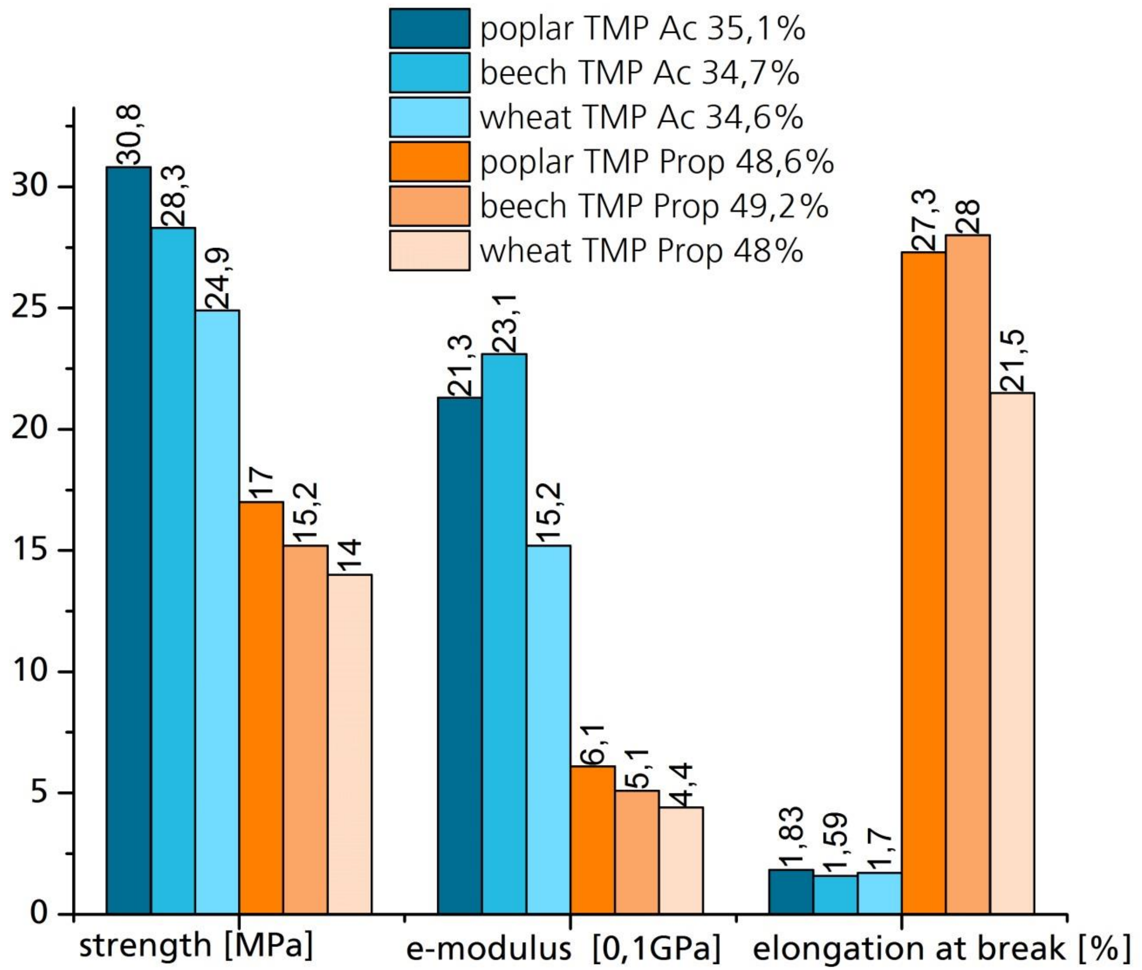
Generell design of the extrusion unit

- Mixing with 30 % triacetin as plasticizer
- Processing at 240 °C in the extruder
- Injection molding at 170 °C
- Mechanical characterization (stress-strain curve)



Injection molding MiniJet

Mechanical properties – comparison acetate/propionate



Scale-up: Acetylation of wheat-TMP in a kneader/ ploughshare mixer

- 15 % LC in EmimAc, „dissolution“ LC in IL (125 °C, 3 h), then add. of Ac_2O

Sample	Mass LC [g]	Temp. [°C]	Time [h]	Reactor	Ac content [%]
PLC11-074	20	125	2	0,25l-IKA-kneader[1]	34,6
PLC11-083	50	125	2	0,75l-defibrator[1]	34,0
PLC11-100	428	125 (150)	2	5l-kneader[1]	34,9
PLC12-110	428	130 (150)	2	5l-kneader[2]	36,3
PLC12-111	428	130 (150)	2	5l-ploughshare mixer[2]	34,1
PLC12-118	4280	125 (145)	2	50l-ploughshare mixer[2]	40,4

[1] Precipitation and washing with ethanol

[2] Precipitionn and washing with water

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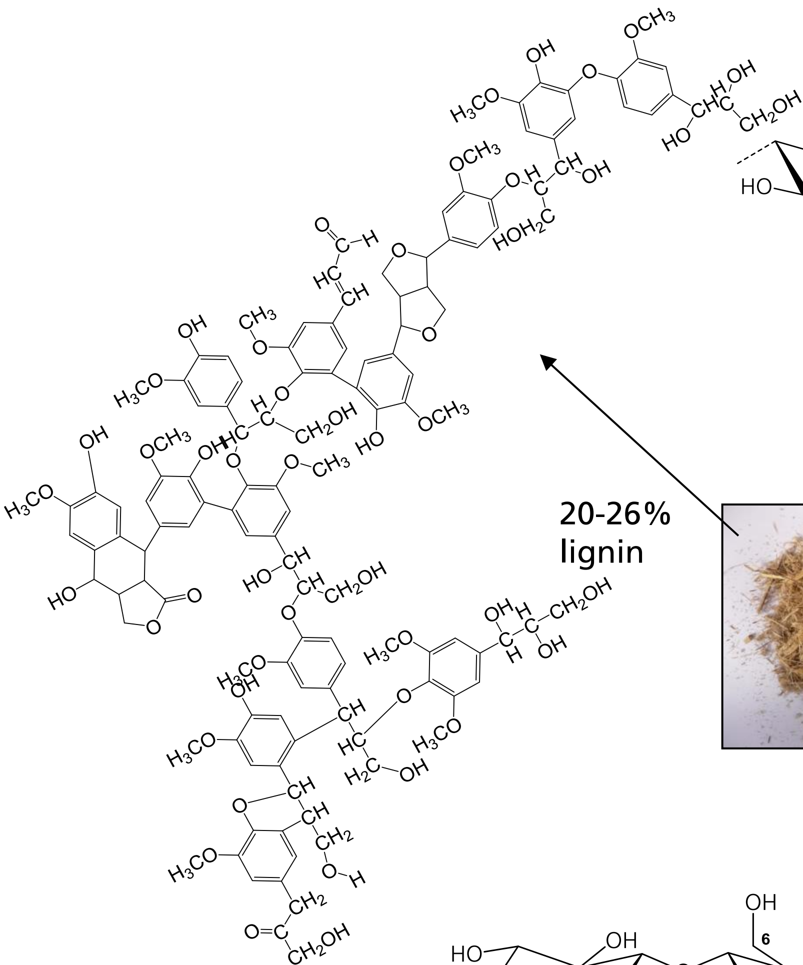
Acetylation with recycled IL (EmimAc)

- 15 % wheat-TMP in a kneader

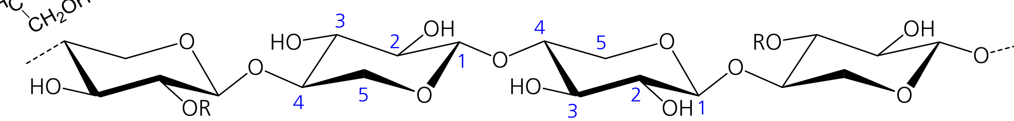
Sample	Recycling	Ac content [%]	Strength [MPa]	E-Modulus [GPa]	Elongation at break [%]
PLC12-132	Evaporation, MTBE extraction	34,6	25,0	1,50	4,20
PLC12-133	evaporation	35,0	23,4	1,52	3,05
PLC12-135	evaporation	34,8	20,8	1,41	3,13
Two times recycling:					
PLC13-140	Evaporation, extraction	27,9	Injection molding was not possible		
PLC13-142	evaporation	33,0	Injection molding was not possible		

THERMOPLASTICS FROM BAGASSE WITHOUT IONIC LIQUIDS

Sources and composition of bagasse in Brazil

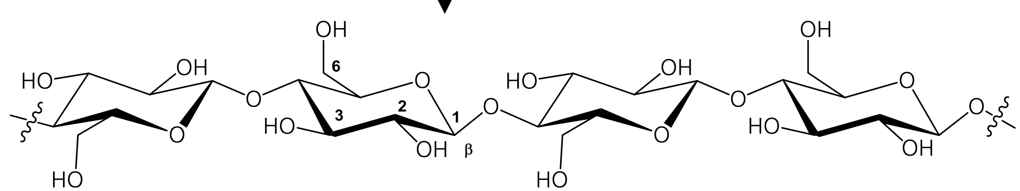


20-26% lignin



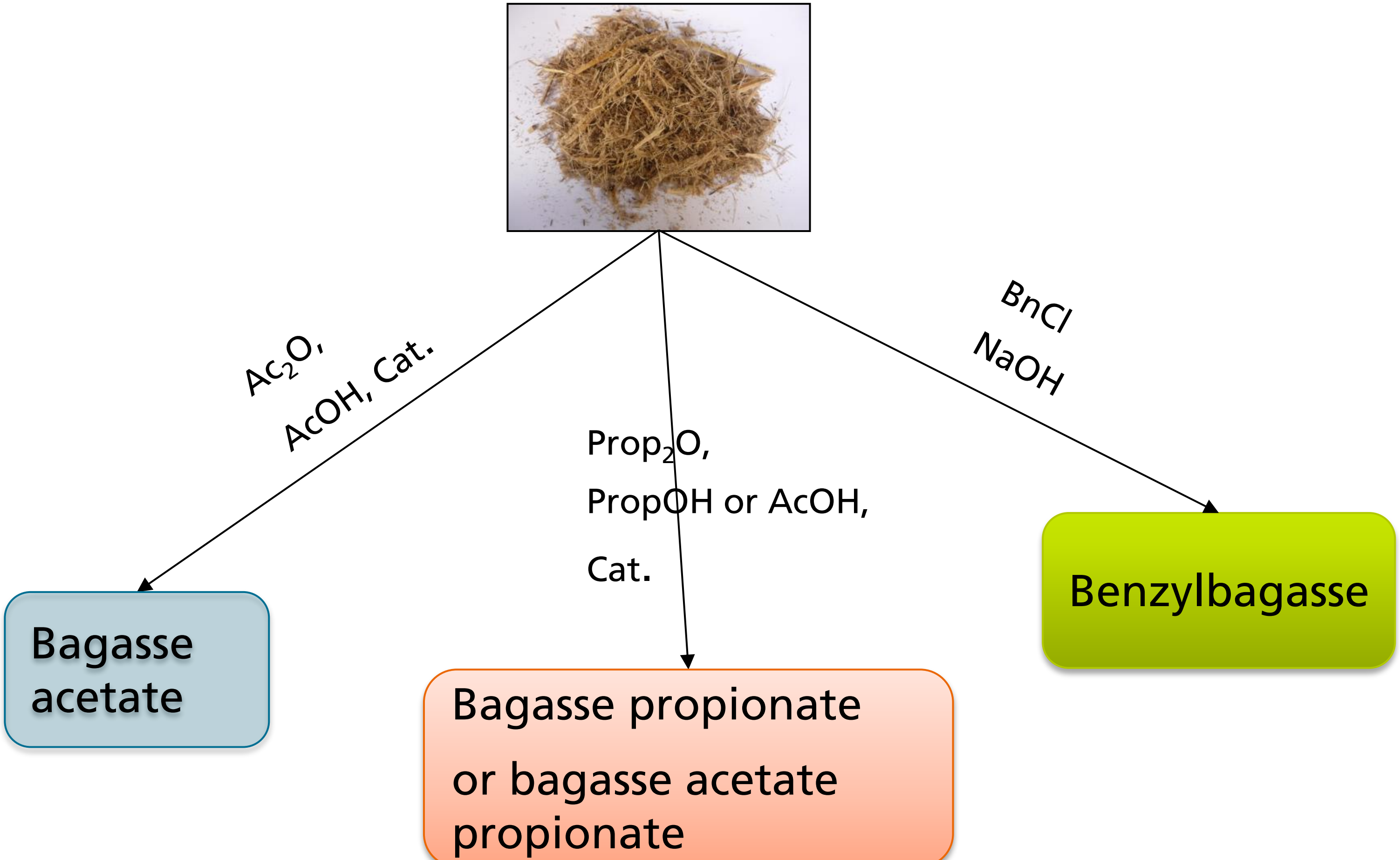
20-26% hemicellulose

40-46% cellulose



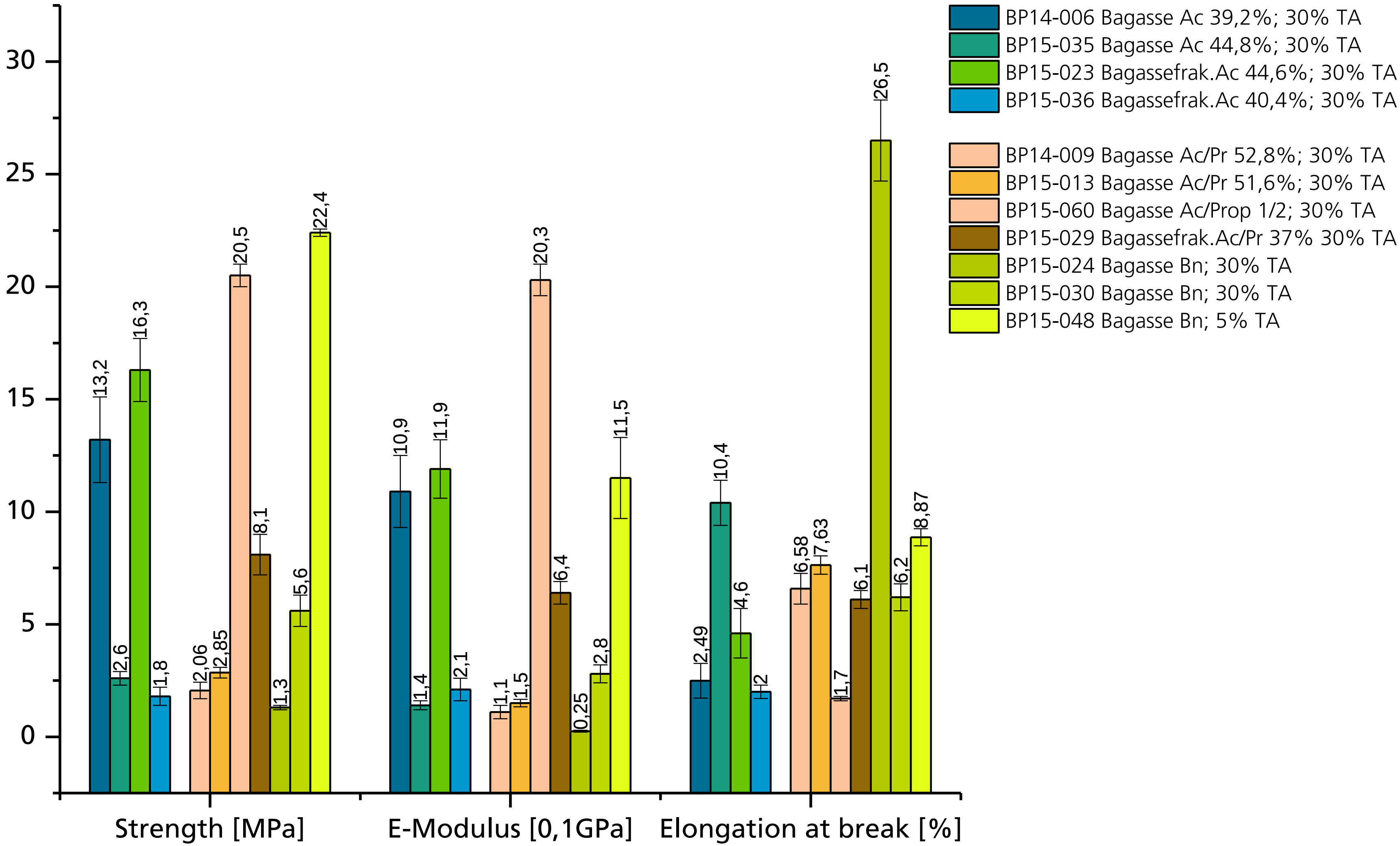
- 650 million tons of sugarcane were produced in ethanol plants (2013/14)
- 200 million tons of bagasse were generated
  - 10 % of the bagasse was destined to animal feed
  - 90 % were discarded as waste, returned to the soil or generated energy

Chemical modification of bagasse



Prop: CH_3CH_2CO

Comparison of mechanical properties of bagasse derivatives



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THERMOPLASTIC STARCH DERIVATIVES

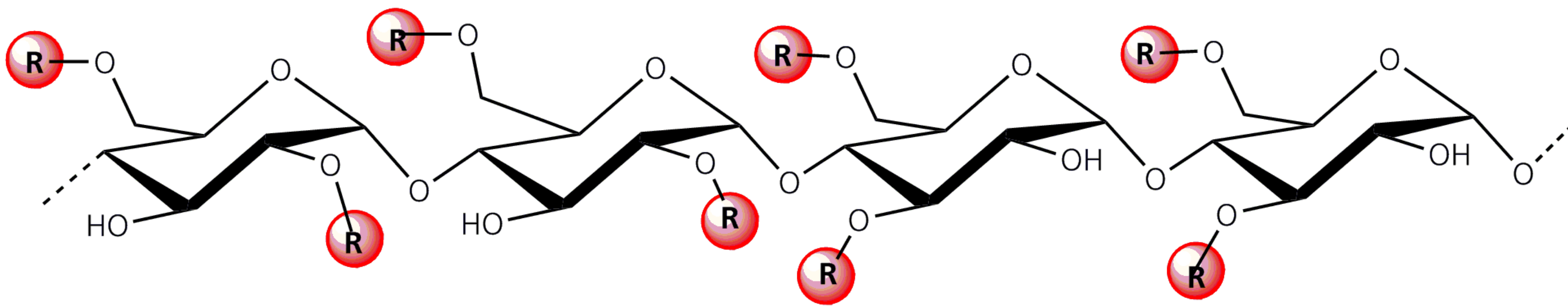
Starch as a Thermoplastic Material

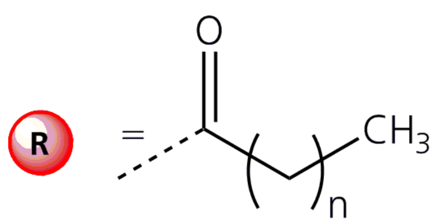
- Starch can be processed by extrusion and injection moulding by adding plasticizers

  - Advantages:
    - Cheap starting material
    - Abundant raw material
    - Biodegradability

  - Disadvantages:
    - Brittleness
    - Needs plasticizer (water, glycerol)
    - Lack of moisture resistance

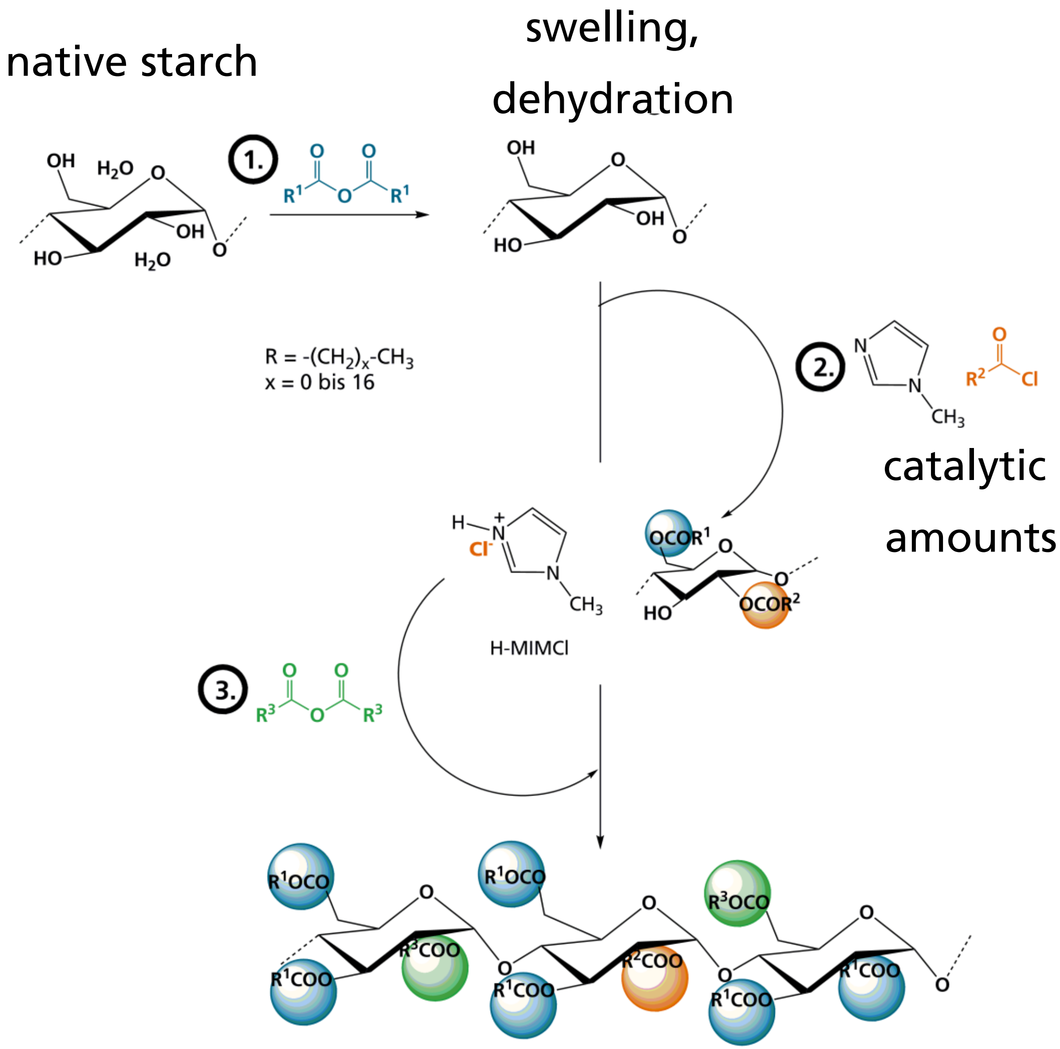
Mechanical Properties of Starch Esters





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

Synthesis of Starch Mixed Esters



- in-situ generation of ionic liquid
- derivatization of starch catalyzed by IL

A. Lehmann, B. Volkert et al.:

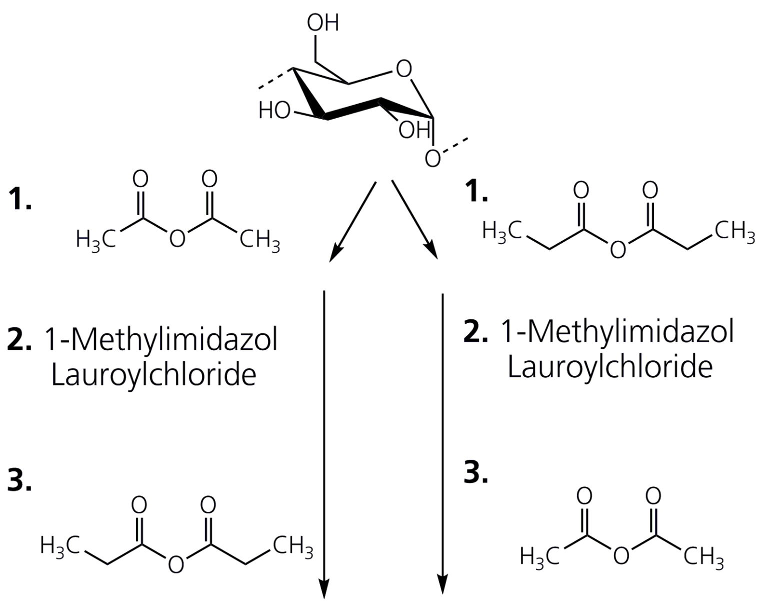
•J Appl Polym Sci (2009) 114, 369

•Green Chem (2010) 12, 2164

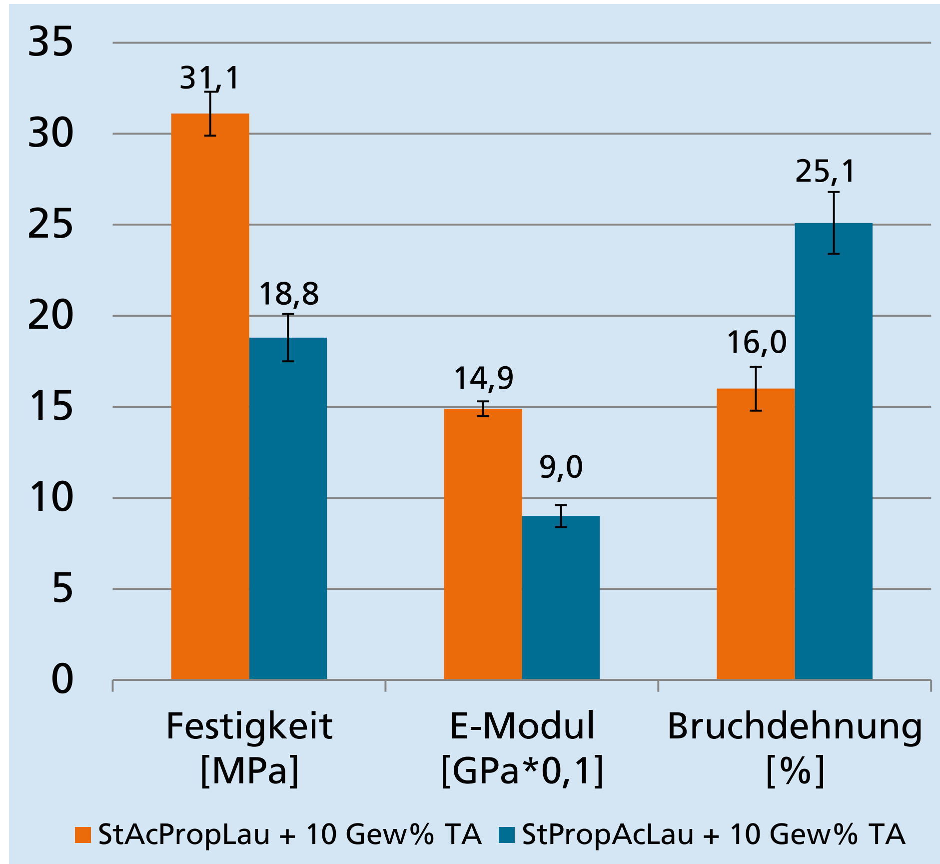
•Carbohydr Polym (2011) 83, 1529

Patent appl. DE 102009022805 A1

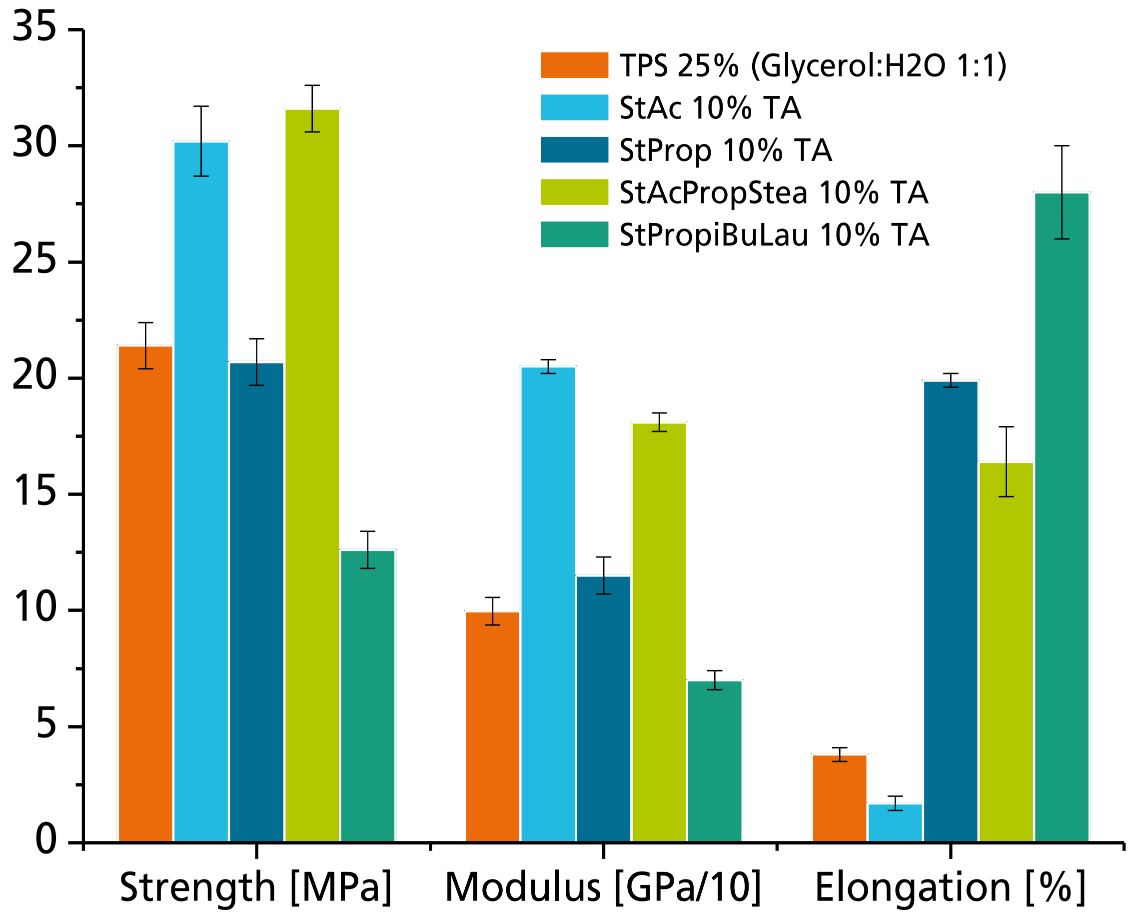
Properties of Starch Mixed Esters



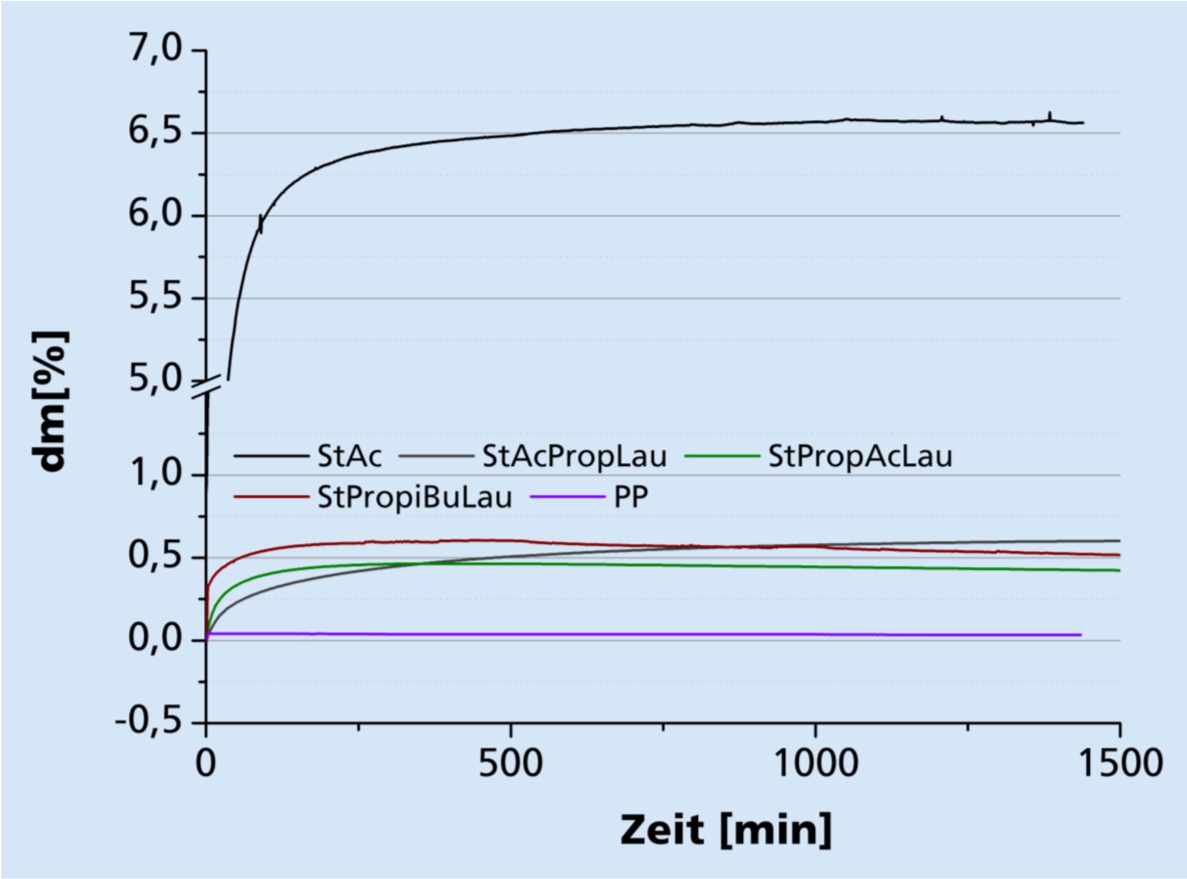
StAcPropLau	**StPropAcLau**
DS_{Ac} = 2,28	DS_{Ac} = 0,55
DS_{Prop} = 0,62	DS_{Prop} = 2,32
DS_{Lau} = 0,10	DS_{Lau} = 0,13
T_g = 125,7 °C	T_g = 99,5 °C



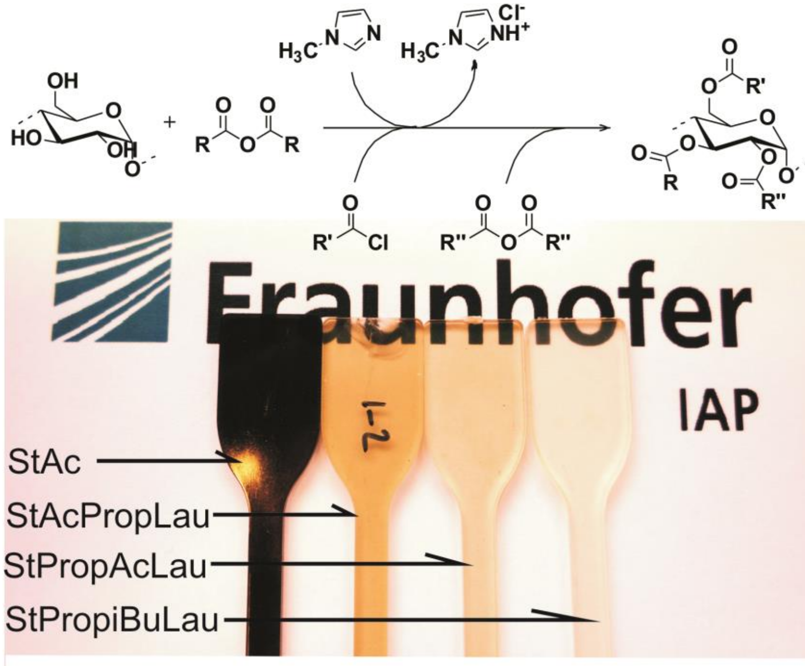
Mechanical properties of starch mixed esters



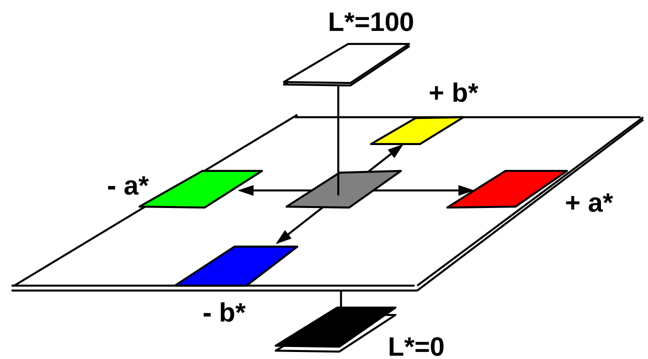
Humidity absorption – Dynamic Vapour Sorption



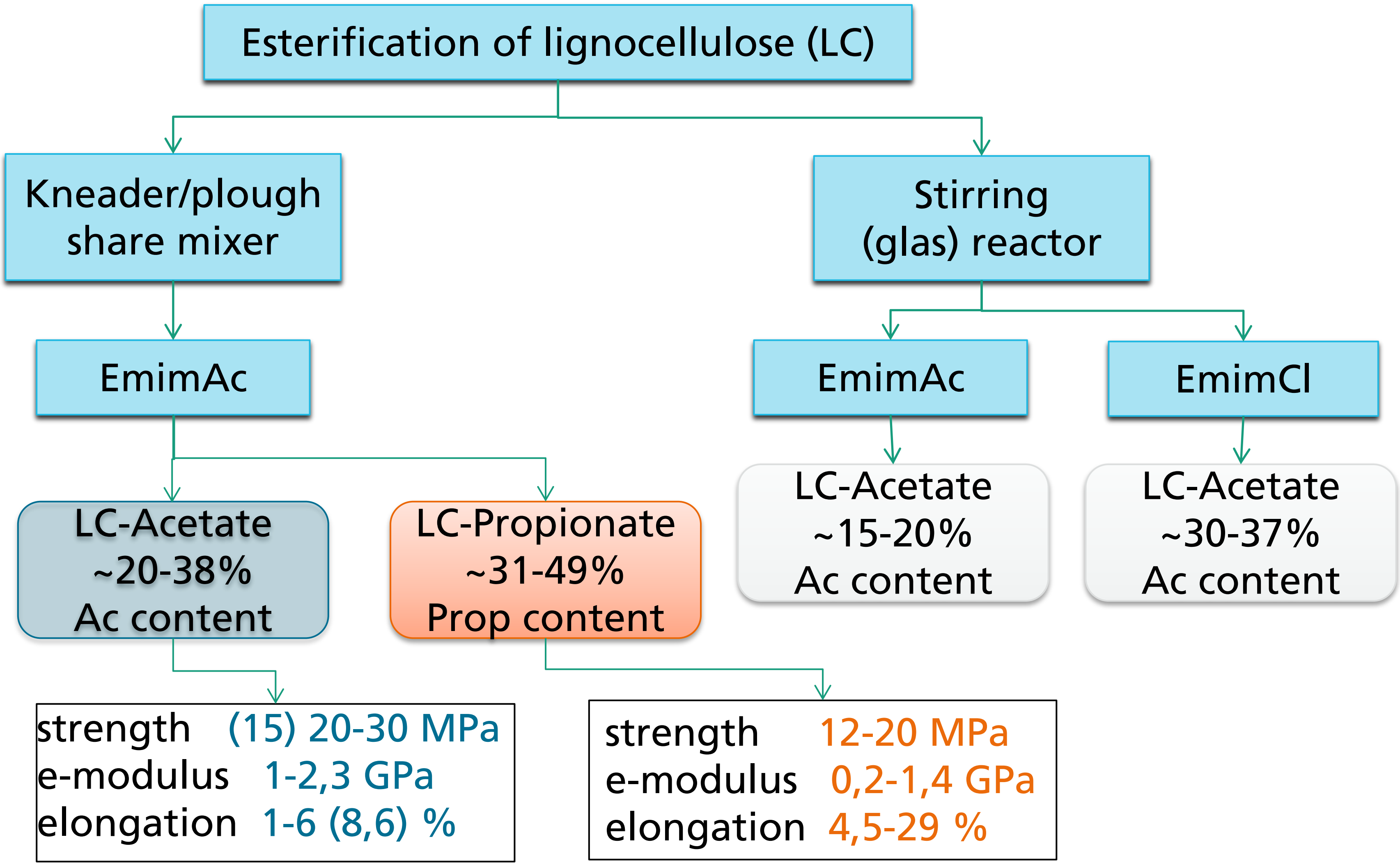
Investigations regarding the coloration



Test specimen	L	a*	b*
Teflon	93,4	-0,8	-2,0
StAc	26,7	8,1	5,6
StAcPropLau	69,9	3,1	25,5
StPropAcLau	77,3	0,8	19,4
StPropiBuLau	81,4	-1,0	9,3

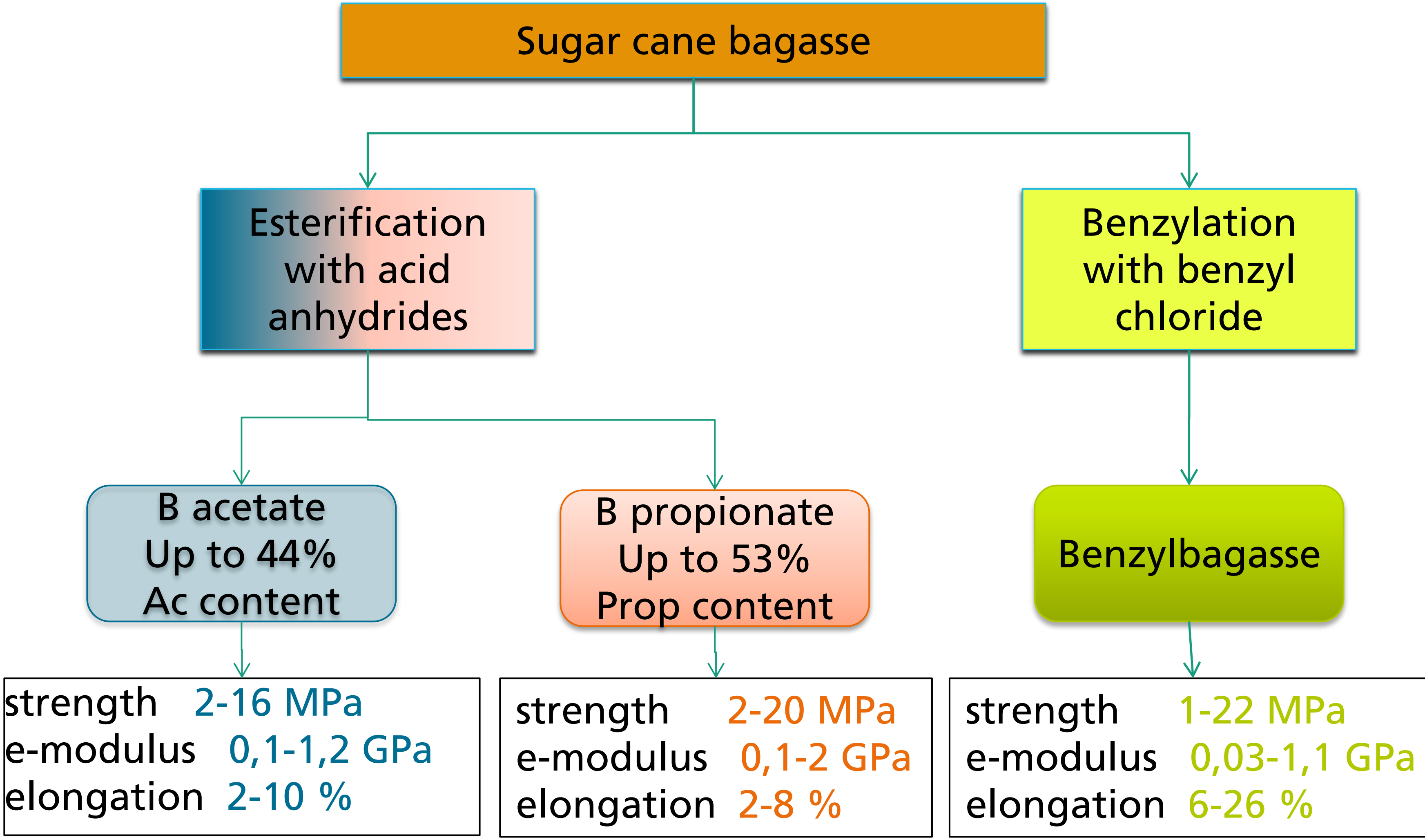


Conclusion/Summary 1 – LC esterified in ionic liquid



- ➢ Reaction and processing with single recycled IL is possible

Conclusion/Summary 2 – Bagasse ether and ester



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Conlusion 3 – Starch mixed esters

- By in-situ generation of IL´s novel starch mixed ester can be realized
- After thermoplastic processing these starch mixed esters show high stiffness without any brittleness
- The water uptake could be lowered
- The coloration and transparency could be significant improved

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