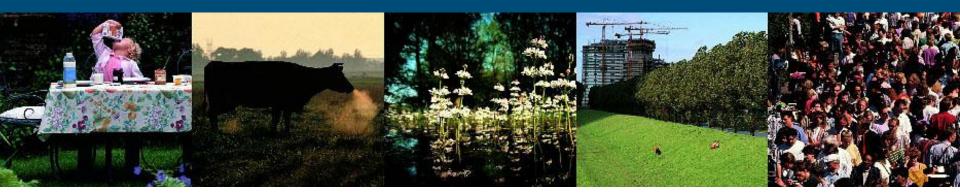
Biobased plastics for packaging

Christiaan Bolck (christiaan.bolck@wur.nl)

Schiphol, October 2010





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- Introduction FBR-Biobased Products
- Market

Related issues

- Food vs fuel
- Biobased vs Biodegradable
- Technical
 - Performance
 - Types
 - Application
- Latest developments



Wageningen UR (University & Research centre)

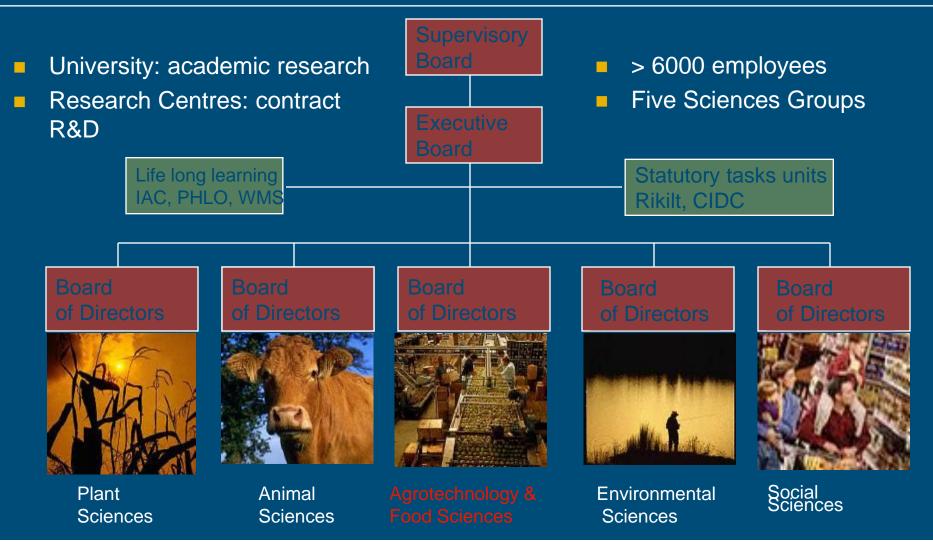
- Three pillars:
 - Wageningen University
 - Van Hall Larenstein Univ. of Appl. Sci
 - DLO Applied Research Institutes
- Annual budget about 650 m euros
- About 6500 employees
- 9000 BSc/MSc; 1200 PhD (>100 countr.)
- Extensive international network
- Active partner in Food Valley

...to explore the potential of nature to improve the quality of life...





Wageningen University & Research Centre





Agrotechnology & Food Sciences Group

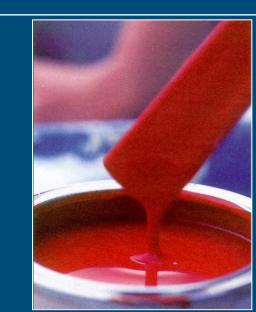
AFSG: ~ 1000 employees

- University: ~ 700
- Research Centre Food and Biobased Research: ~ 300
- Food and Biobased Research (formally ATO)
 - : two business units
 - Fresh, Food & Chains
 - Biobased Products
- BU Biobased Products
 - Biomass conversion technologies
 - Renewable chemicals and materials development



Biobased Products

- Development of novel technologies, materials and products (mainly) based on renewable raw materials
- Focus on Materials, Chemicals and Biofuels following a biorefinery approach



 Cooperation with industry to find innovative, sustainable solutions (towards a biobased economy)



FBR-Biobased Products

Technologies

- Biotechnology (enzyme catalysis, fermentation, etc)
- (Bio)polymer processing (extrusion, injection moulding,)
- Organic chemistry and catalysis on carbohydrates and fatty acids

Markets

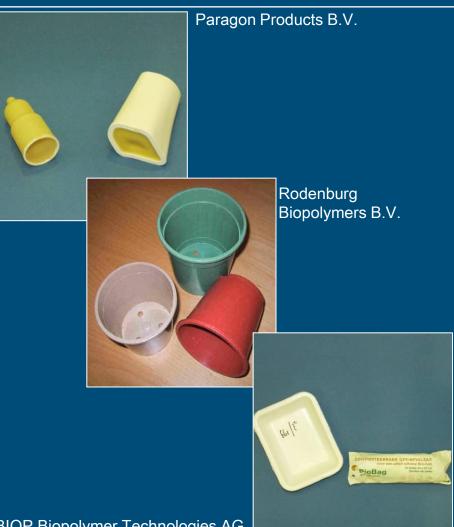
- Plastics and additives
- Coatings, inks and adhesives
- Bio fuels
- Chemicals
- Paper





Bioplastics research at FBR-BBP

- Since 1990 important research topic at FBR-BBP
- Various multi-partner EUprojects
- Many bilateral contracts
 - With raw material producers
 - With plastic converters
 - With additive manufacturers



BIOP Biopolymer Technologies AG

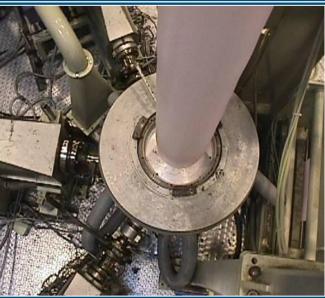


Research facilities at FBR-BBP

Processing

- Extrusion (single/double screw)
- Co-extrusion; 1-5 layers sheet/blown film
- Injection moulding
- Compression moulding
- Thermo forming
- Analysis
 - Thermal (DSC, TGA, HDT)
 - Mechanical (tension, bending, compression, DMTA, impact, falling dart)
 - Rheological (capillary, dynamic)
 - Structural (SAXS, FTIR, SEM)
 - Chemical (ss-NMR, HPSEC-MALLS, GPC tri-sec, GC-MS)
 - Biodegradation (controlled composting, pilot-scale composting, aquatic tests)





Contents

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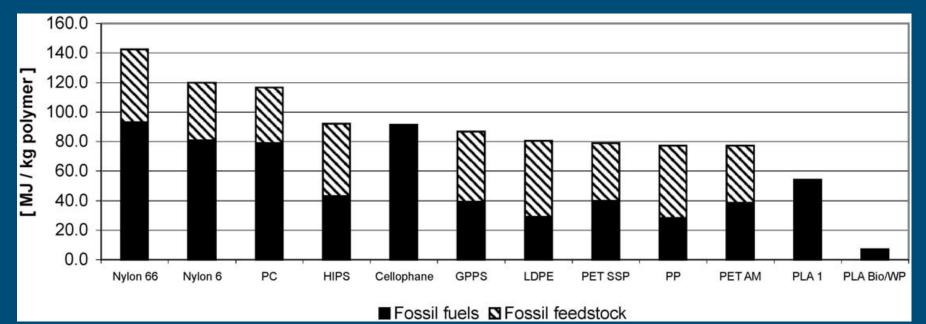






Greenhouse effect

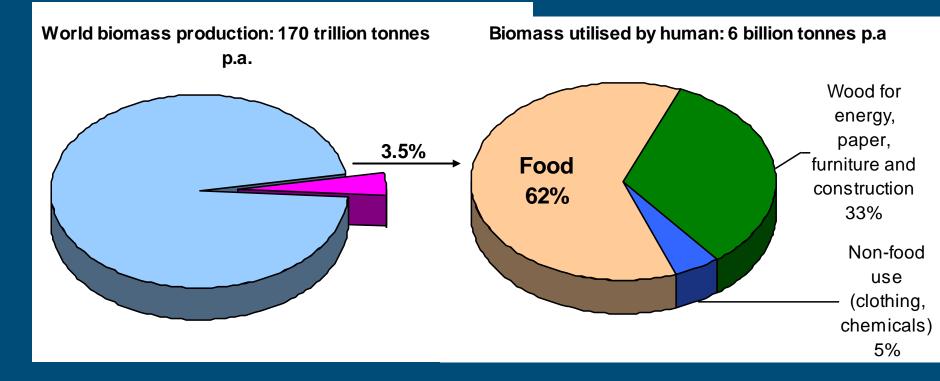
Energy in productEnergy for production



PLA & Energy



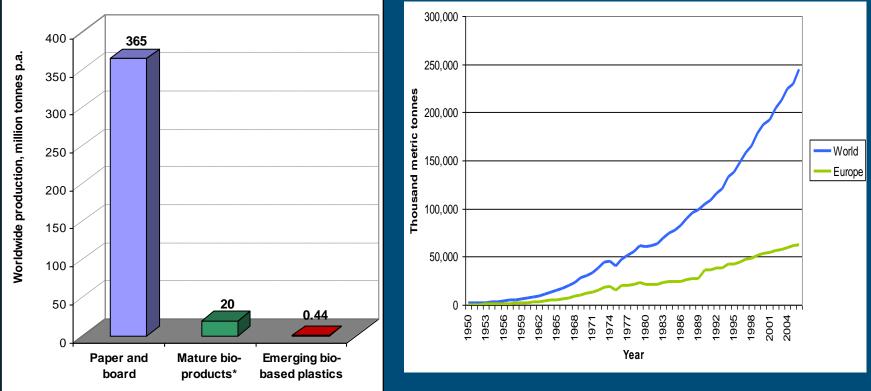
Food vs Fuel



World biomass production (left) and biomass utilised by human (right)



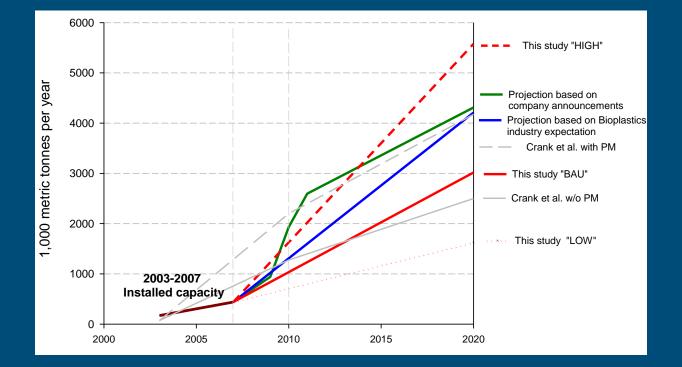
Food vs Fuel



Production of plastics



Market

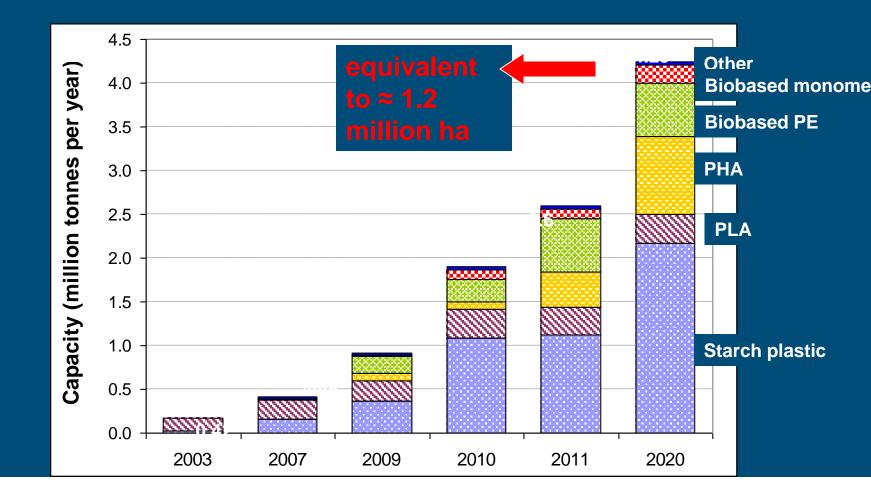


Projection of the worldwide production capacity of bio-based plastics until 2020 (Probip 2009)



Production capacity (in kt)

(historie 2003-2007; aankondigingen voor >2007)





Production capacity

(2007)

PI	A materials			ton/year	
		Natureworks polymer	USA	70.000	(140.000 in 2009)
		Hisun	China	4.000	(expanding)
		1 Hour	Europe/Asia	4.000	(starting up)
	arch based materials				
		Mater-bi	Italy	60.000	
		Solanyl	The Netherlands	40.000	
		Bioplast	Germany	10.000	
		Biopar	Germany	4.000	
		Plantic	Australia		
		Biograde	Australia		
			USA		
				>>	
	ellulose based materials			10.000	
•		Natureflex	England	10.000	
•		Clarifoil	England		
		Biograde	Germany	4.000	
PF	1B				
•	Tianan	Enmat	China	4.000	
•	Biomer	Biomer	Germany	1.000	
•	PHB Industrial SA	Biocycle	Brazil		(starting up)
•	Telles	Mirel	USA		(starting up)
Bio	odegradable polyesters				
•		Ecoflex	Germany	8.000	(expanding in 2010)
•		Bionolle	Japan	3.000	
•		CAPA	England		
•		GS Pla	Japan	3.000	
Ot	hers				
		Biolice	France		
		Hydrolene (PVA)	Italy		
	านางคุณระ	Hydrolene (PVA)	naly)



WAGENINGEN UR



Types

		etc. Fully fossil-based	-Alkyd resin Partially Biobased	Fully Biobased
Biodegr	Non- Biodegradable	-PE -PP -PET -PBT -PA6, 66 -PVC -PUR -ABS -Epoxy resin -Synthetic rubber	-Starch blends (with polyolefins) -PA 610 -PTT from biobased 1,3-PDO -PBT from biobased succinic acid -PET from biobased ethylene -PEIT from sorbitol and bio ethylene -PVC from biobased ethylene -PUR from biobased polyol -Epoxy resin from biobased glycerol -ABS from biobased succinic acid -SBR from biobased succinic acid	-Biobased PE -PA 11 -Biobased PB
Biodegradability	Fully Biodegradable	-PBS -PBSL -PBSA -PCL -PBST -PBSAT -PTMAT -PCBS	-Starch blends (with biodegradable fossil-based coplymers) -PLA blends (with biodegradable fossil-based copolymers)	-TPS -Starch blends (with biobased and biodegradable copolymers) -Starch acetate -PLA -PHA -PLA/PHA blends -Regenerated cellulose -Cellulose acetate -PO3G

Current and emerging (partially) bio-based plastics and their biodegradability



Biodegradable vs. biobased materials

Finished productNon-biodegradableBiodegradable

Raw m	Non renewable	Traditional PE PET	Ecof Bionolle	starch	
aterials	Renewable	Eco – LDPE (Braskem Rilsan (Arkema) Sorona (Dupont)	⁾ PLA (PHB	based blends	ks))



Renewable or biobased polymers are polymers from which the raw materials originate directly or indirectly from nature

Classification of biobased polymers:

- (Modified) natural polymers
- Directly from micro-organisms or gene-modified crops
- From biobased feed stock (eg via fermentation)

Biobased plastics ≠ biodegradable plastics



Biodegradable plastics

- Biodegradation: degradation catalyzed by biological activity leading to mineralization and/or biomass
- Biodegradability: degree to which biodegradation leads to mineralization and/or biomass
- Mineralization: the conversion of (organic) constituents in naturally occurring gasses, water and inorganic constituents

Composteerbaar

 Standardisation and certification is very important!
 Demands for biodegradable products are described in EN13432



EN 13432: Test scheme for compostable products

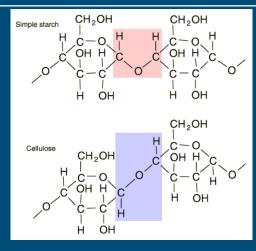
Characterisation of materials and individual components Assessment of **biodegradability** of materials or components in laboratory tests

Evaluation of results

Assessment of disintegration of product (components) in pilot-scale plants

Assessment of effect on composting process in pilot-scale plants Assessment of effect on compost quality in pilot-scale plants

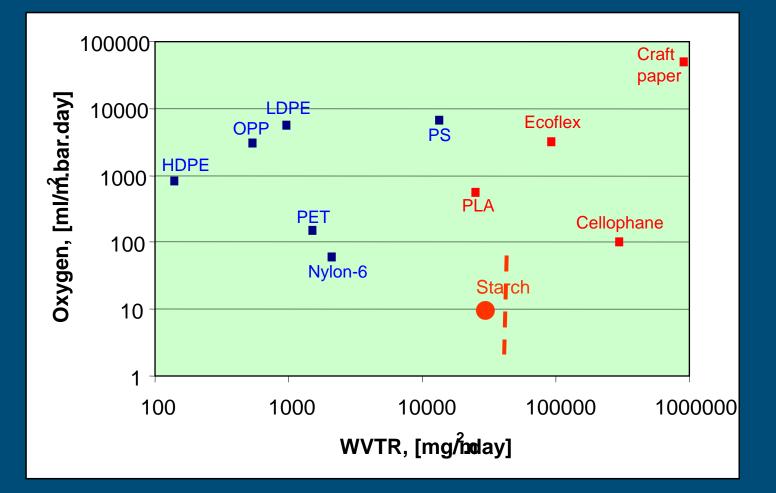




Technical



Permeability of plastics





Available biodegradable plastics

Most important groups of biodegradable plastics

- Cellulose and cellulose derivatives
- Starch based plastics (thermoplastic starch)
- Polyesters
 - Poly lactic acid (PLA)
 - Poly caprolactone (PCL)
 - Polyhydroxy alkanoates (PHA, PHBV)
 - Several (co-)polyesters
- Materials based on industrial proteins
- Blends of various bioplastics (eg thermoplastic starch & polyesters)



Cellulose derivatives (cellulose diacetate)

Advantages

- Good mechanical properties (like PS)
- Good thermal resistance
- Glossy transparent appearance
- Renewable



- Disadvantages
 - Price (>4€/kg)
 - Use plasticiser
- Processing
 - It is advised to dry the material
 - Suitable for:
 - Injection moulding
 - Sheet extrusion (thermo forming
 - Fibre extrusion
 - Processing temperature 190-240°C
 - Thermal degradation possible



Polylactic acid (PLA)

Advantages

- Good mechanical properties (like PET)
- Transparent
- Price (1.8-2.0 €/kg)
- Renewable



Disadvantages

- Only compostable in industrial composting facilities
- Water sensitivity during processing

Ο

+ O - C - CH + n

CH₃

Processing

- Material needs to be dried
- Suitable for:
 - Film extrusion (and thermo forming)
 - Blow molding
 - Injection moulding
 - Fibre extrusion
- Processing temperature 170-210°C



Starch based plastics

Advantages

- Good mechanical properties (LDPE to PS)
- Excellent gas barrier properties
- Anti-static
- Fast biodegradable



Disadvantages

- Humidity dependent
- Not completely transparent
- Processing
 - Processed as delivered (no drying)
 - Suitable for:
 - Film blowing (incl multilayer)
 - Injection moulding
 - Sheet extrusion (and thermo forming)
 - Foam extrusion
 - Processing temperature 120-180°C



Poly hydroxy alkanoates (PHA's)

 $\begin{bmatrix} \mathbf{R} & \mathbf{O} \\ \mathbf{0} & \mathbf{H} \\ -\mathbf{O} - \mathbf{C} \mathbf{H} - \mathbf{C} \mathbf{H}_2 \\ -\mathbf{C} & \mathbf{H}_2 \end{bmatrix}_{\mathbf{X}}$

Advantages

- Mechanical properties can be varied
- Hydrophobic (low water vapour permeability)
- Rather high HDT (>100°C)
- Renewable

Disadvantages

- Expensive (for now > 4€/kg)
- Harvested from micro organisms
- Low melt strength



Processing

- Suitable for:
 - Injection moulding
 - Sheet extrusion (and thermo forming)
 - Film blowing, Film casting



Synthetic (co)polyesters and polyester amides

- Not renewable (not yet)
- Mechanical properties possible from PE to PP
- Compostable
- Suitable for films and extrusion (in most cases not for injection moulding)





Biodegradable (packaging) products



Towards biodegradable products

Biodegradable products are preferably applied:

- Where biodegradation is a functional advantage or a requirement: green waste bag
- Where biodegradability is imposed by law
- When recycling is impossible or too costly or impractical (various agricultural applications)
- In case of better price-performance (PLA fibres for clothes)





Examples of (existing) packaging applications





Examples of (existing) agricultural applications



New developments: Recourses Polymers from nature Biobased building blocs Application of available polymers









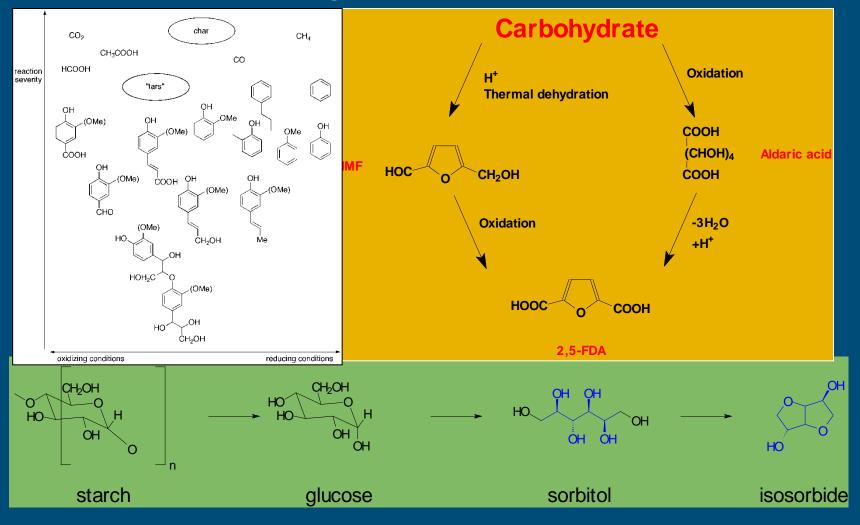


Polymeren from nature





Biobased building blocs







Application of available polymers5 examples





Example 1: processing aspects PLA



Without reology modifier

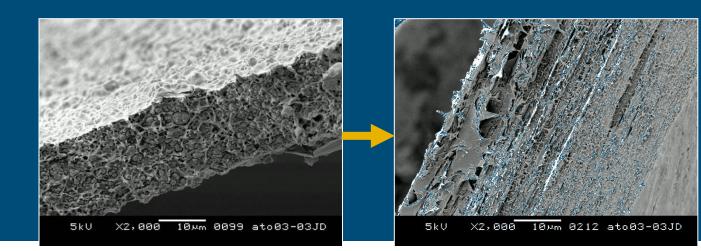


With reology modifier



Example 2: Compatibilisers in blends

- Example of a compatibilised starch/polyester blend with improved properties
 - Cost reduction: increase starch content
 - Improved properties: co-continuous system
 - Toughness
 - Barrier properties
 - Clarity





Example 3: Improving heat stability

Material	HDT-B value (°C)	
Biograde 300A (cellulose derivative)	> 100	
Enmat 1000 (PHBV)	> 100	
Natureworks 4042D (PLA)	50-60	
Starch based materials	< 80	

Hot coffee in PLA cup for cold drinks





Example 4 : Thermoformed products

High HDT

- PLA type
- Nucleation
- Processing







Example 5 : 3D-foamed structures

Expandable bead technique

- Good cell structure
- Density <30 g/l





Thank you for your attention

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www.fbr.wur.nl/UK/

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