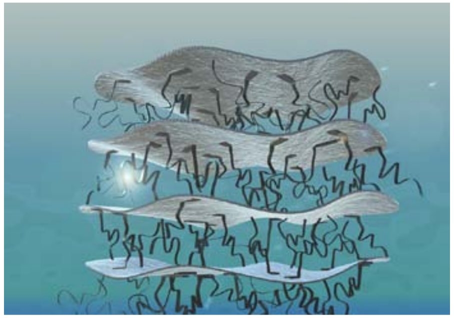
ECOMATERIALS PLATFORMS

Developing new biobased materials and polymers for high value application



Professor Pete Halley

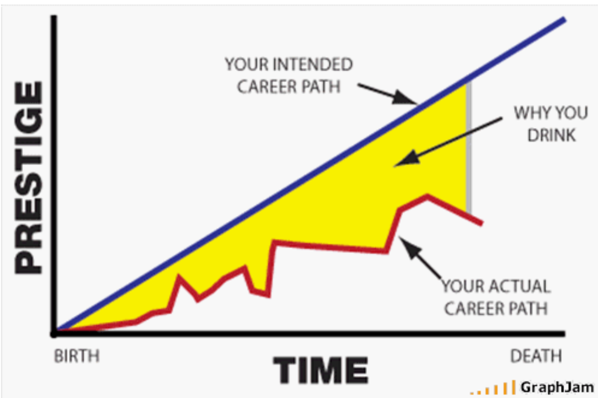
Centre for High Performance Polymers,
School of Chemical Engineering and
Australian Institute for Bioengineering and Nanotechnology
The University of Queensland QLD 4072

Web: www.chemeng.uq.edu.au/chpp or www.aibn.uq.edu.au
Email: p.halley@uq.edu.au

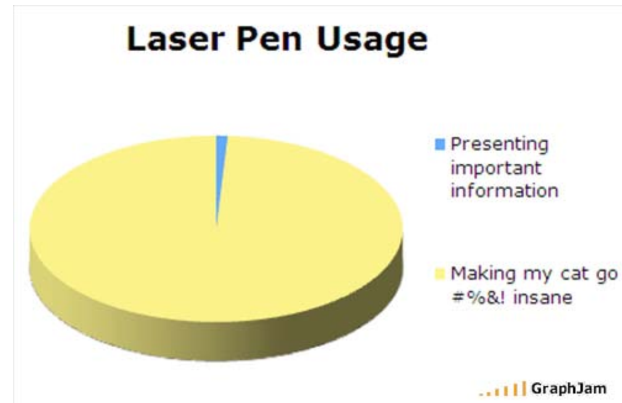
SCION, 20 Oct 2011
(t minus 3 days before world cup final)

Sabbatical learnings... so far

LONG TERM CAREER DEVELOPMENT



IMPROVE PRESENTATION SKILLS



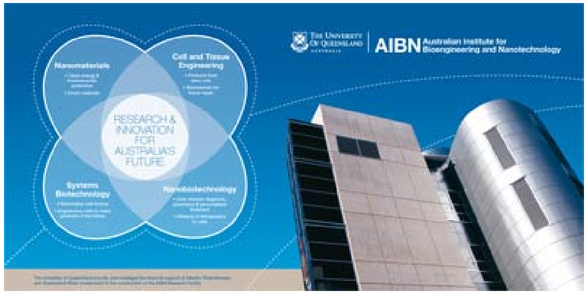
LEARN NEW CULTURES
(But be culturally sensitive)

NETWORK

Sabbatical learnings... This week

20 – 6 scoreline

Australian Institute for Bioengineering and Nanotechnology AIBN



Links to 15 other groups in chemistry, biology, engineering

Polymer science / Discovery

Chemical Engineering

Fluids, materials, polymers, food

Polymer rheology and processing

Advanced Materials Processing and Manufacturing Centre -AMPAM

Centre for High Performance Polymers (CHPP)

Links to 4 other materials CRCs/ARC COE

Manufacturing / Scale-up

CHPP centre – key people

Prof Andrew Whittaker;	Centre for Magnetic Resonance / AIBN
Dr David Hill	AIBN
Dr Michael Montiero	School Molecular and Microbial Sciences / AIBN
Dr Firas Rasoul	Centre for Magnetic Resonance / AIBN
Dr Katia Strounina	Centre for Magnetic Resonance
Dr Idriss Blakey	Centre for Magnetic Resonance / AIBN
Dr Heping Liu	Centre for Magnetic Resonance / AIBN
Dr Wael Ghafor	AIBN
Dr Tim Dargaville	AIBN/ QUT
Dr Lan Chen	AIBN
Dr Bronwin Dargaville	AIBN
Dr Imelda Keen	AIBN
Dr Zul Merican	AIBN
Dr Rulin Wang	AIBN
Dr Hui Peng	AIBN / QUT
Prof Peter Halley;	School of Chemical Engineering /AIBN
Dr Tim Nicholson;	School of Chemical Engineering;
Dr Bronwyn Laycock	School of Chemical Engineering / AIBN
Dr Greg Cash	School of Chemical Engineering
Dr Emilie Gauthier	School of Chemical Engineering;
Dr Celine Chaleat	AIBN
Dr Ashok Shrestha	CNAFS
Dr Bernadine Flannagan	CNAFS
Dr Polly Burey	AIBN
Dr Fengwei Xie	AIBN
Dr Melissa Russo	CRCPolymers
Dr Babak Radi	CRCPolymers
Prof. Justin Cooper-White	School of Engineering / AIBN
A/Prof. Rowan Truss;	School of Chemical Engineering;
A/Prof Darren Martin;	School of Chemical Engineering / AIBN
A/Prof Martin Veidt	School of Mechanical&Mining Engineering
Dr Lisbeth Grondahl	School of Molecular and Microbial Sciences
A/Prof. Anne Symons	Dentistry;
Prof. Traian Chirila	Queensland Eye Institute;
Prof. Julie Campbell	Anatomical Sciences;
Prof. Craig Hawker	UCSB (USA);
Dr Stewart McGlashan	Adjunct
Dr Geoff Covey	Adjunct

Synthesis

↕

Chararcterisation

↕

Processing

↕

Performance

↕

Practioners

CHPP Infrastructure Capabilities

Chemical Characterisation & Synthesis		Small scale processing and formulation	
Vibrational	Nicolet 5700 ATR-FTIR	Granulator	Drum Granulator
	Nicolet 5700 FTIR-NIR	Miniprocessing	Haake Mini- extruder
	FT-Raman		Axon single screw extruder
	Dispersive Raman Microscope		Prism twin screw extruder (16 mm diameter)
	FT-SPR module		Haake Polylab twin screw extruder system (19mm) x 2
	Grazing angle accessory		DSM mini injection molder
	Grazing Angle ATR	Mixing	Ultrasonic mixer
	High Pressure ATR cell		Brabender batch mixer [Partec]
	Diamond ATR accessory	Sample preparation	Compression molders x2
NMR	Solid State	Grinding	Particle Grinder
	Microimaging		
	Solution Chemistry	**Rheology**	
	Solution CMR	Rheometers	Rheometrics Low shear RDSII and ARES rheometers (x2)
HPLC	Waters HPLC		Rheometrics DMTA
Thermal	MT DSC		Slit die rheometers
	MT TGA		Capillary rheometer
	MT DMA		Elongation rheometer
	PE DSC		Haake Rheoscope
Lasers	157 nm F2		Multipass Rheometer
	193 nm ArF	Viscometers	Brookfield viscometer
Centrifuge	Hermule Z323		Low Viscosity Ubelodhe viscometers
GC-MS	Trace GCMS		Rapid Visco Analyser
Ellipsometers	JA Woolam VUV Vase		
	Gaertner	**Properties**	
GPC	GPC x 2	PVT	Pressure-Volume-Temperature
	Waters GPC with inline Wyatt MAL	Tensile	Instron tensile testers (x3)
LCMS/MS	Waters LCMS/MS	Microscopy	Optical Microscope
UV-VIS	Cary 4000	Moisture	KF Moisture analyser
	UV/Vis Plate Reader (Tecan)	Barrier	*MOCON O2 and H2O barrier property testers*
Fluorescence	Horiba Fluoromax-4		*Custom made specialty gas barrier cells*
	Fluorescence Scanner (Tecan)		
UV exposure	Runray 600	**Processing**	
	Sematech Exposure Tool	Extruders	Entek twinscrew extruder (27mm)
Spin Coaters	POLOS Coater		Haake coextruder setup (19mm)
	Chemat Coater		*Supercritical CO2 extruder*
Glove Box Station	M-Braun Station	Film blowing	Axon Film blowing tower
Parallel Synthesis	MT Multimax	Injection molding	Demag 80t injection moulder
Flash Chromatography	Buchi Sepacore	Rotomolding	Uniaxial rotational moulder
Plasma	Low poser plasma deposition		
XPS	Kratos	**Simulation**	
AFM	Various - CMM + BnDF	Software	Flowsolve flow simluation software
SEM	CMM		Atomistic modelling software
TEM	CMM		
XRD	WAXS and SAXS		
Weatherometer	QUV Weatherometer		

CHPP-P research areas

Key core skills

- Characterisation, rheology, processing, simulation and product development

Key project streams [application areas]

ECOMATERIALS AND BIOMEDICAL POLYMERS

- Renewable polymer processing and product design
- Biofluids rheology - Swallowing fluids, CF sputum
- Nanostructured polymers [DM]
- Biomedical polymer processing [JCW]

BIOFLUIDS/PROCESSING

- TM foods, food extrusion and processing [TN, PB]
- Rheology and processing and simultation [TN]
- Polymer Properties and failure [RT]
- Online rheology [TN]
- Predicting coating lifetimes for aircraft [DMTC]

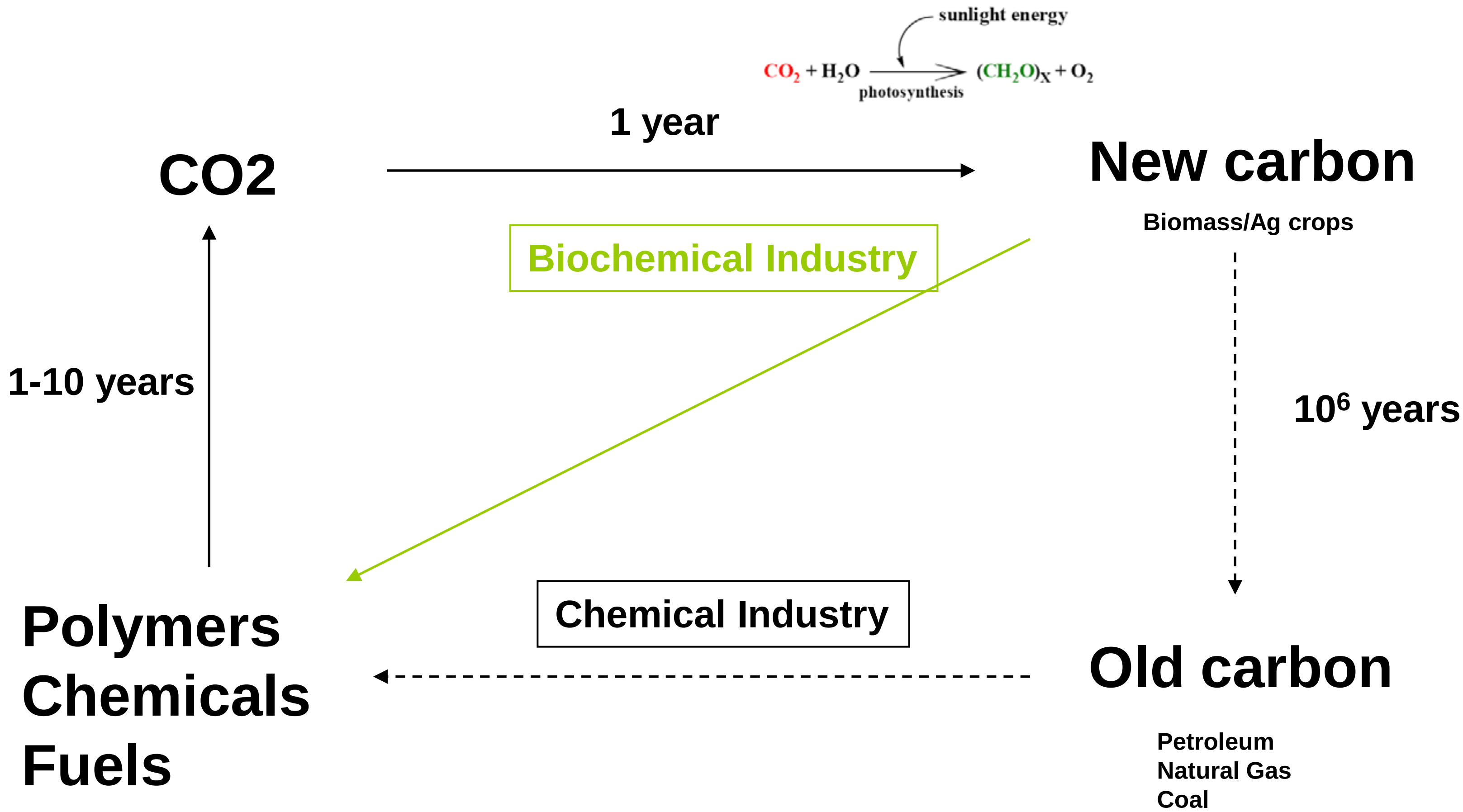
Ecomaterials - current projects

- **Water resistant thermoplastic starch polymers** Celine Chaleat, Rowan Truss Plantic, National Starch, CRC Polymers
- **Model starch systems** Fengwei Xie, Mike Gidley, Bob Gilbert, Rowan Truss, Tim Nicholson
- **Lignin coatings** SRI CRC Sugar
- **Photodegradable PE films for sustainable agriculture** Vito Ferro, Mel Russo, Greg Cash, Emilie Gauthier, Sherri Hsu, Integrated Packaging, CRC Polymers
- **PHB from mixed solid waste** Paul Lant, Steve Pratt, Bronwyn Laycock, Anox, Veola
- ***Novel proteins from sorghum*** *Esther Lau, KS, SJ, RS*
- ***Novel monomers from sugar*** *[AIBN]*
- ***Supercritical CO2 processing for starch polymers*** *Johnny Fu, KT*
- ***Novel starch/ionic liquid plasticisers*** *Sainimili Mateyawa*
- ***Degradation of aircraft coatings*** *[DMTC], Donna Capararo, GG, SP*

Thanks

- CRCPolymers, CRCFoodPack, CRC Sugar, ARC and Plantic Technologies funding
- CSIRO Plant Industry: Dr Matthew Morell
- Penford Australia
- UQ Chemical Engineering Super Scholarship, UQIPRS, AIBN funding.
- 55 Researchers involved in this work from 1995-now

Global Carbon Cycle - feedstock



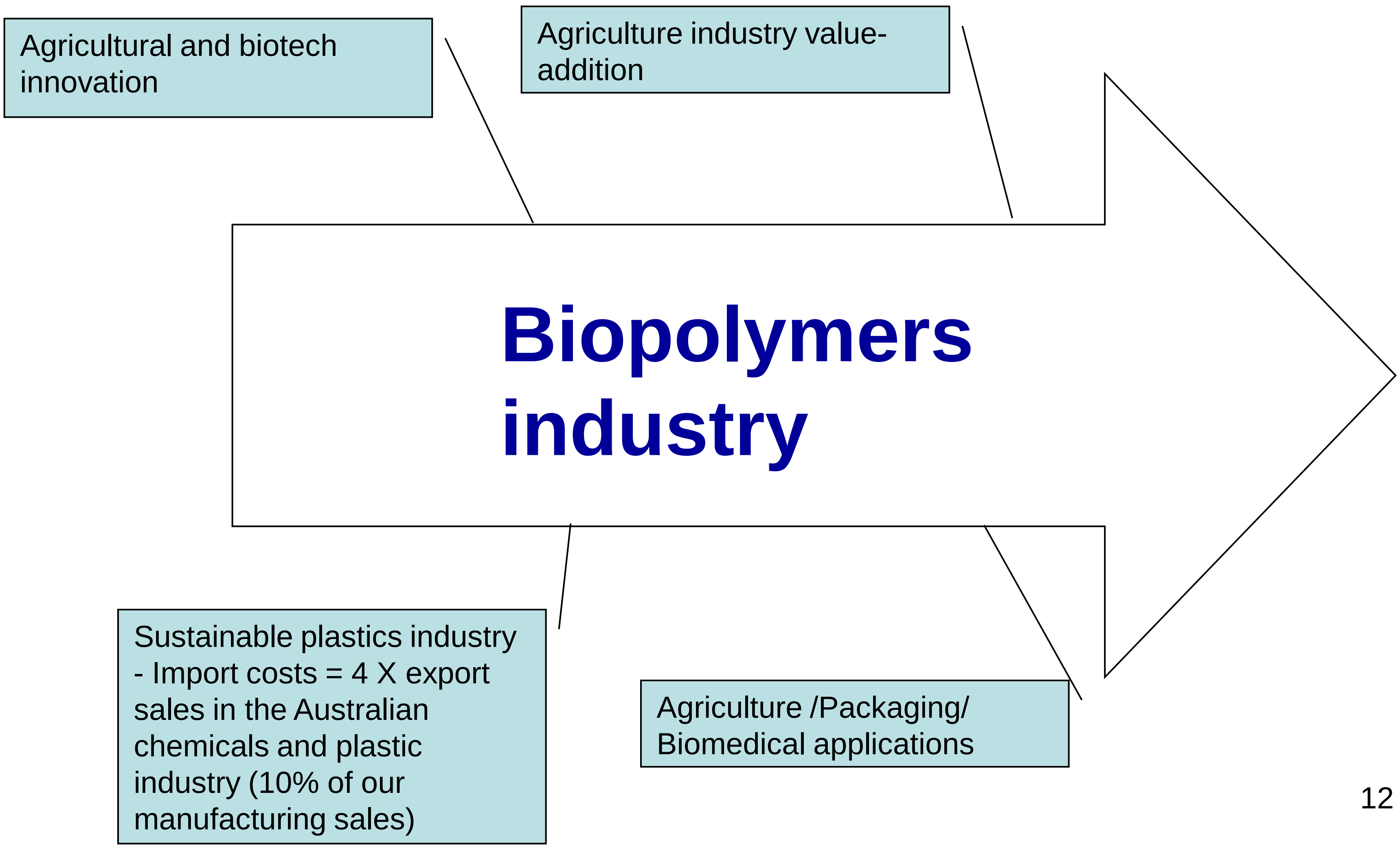
New carbon feedstock >> Zero carbon footprint

R.Narayan-UMichigan http://www.farmfoundation.org/news/articlefiles/371-NARAYAN.pdf

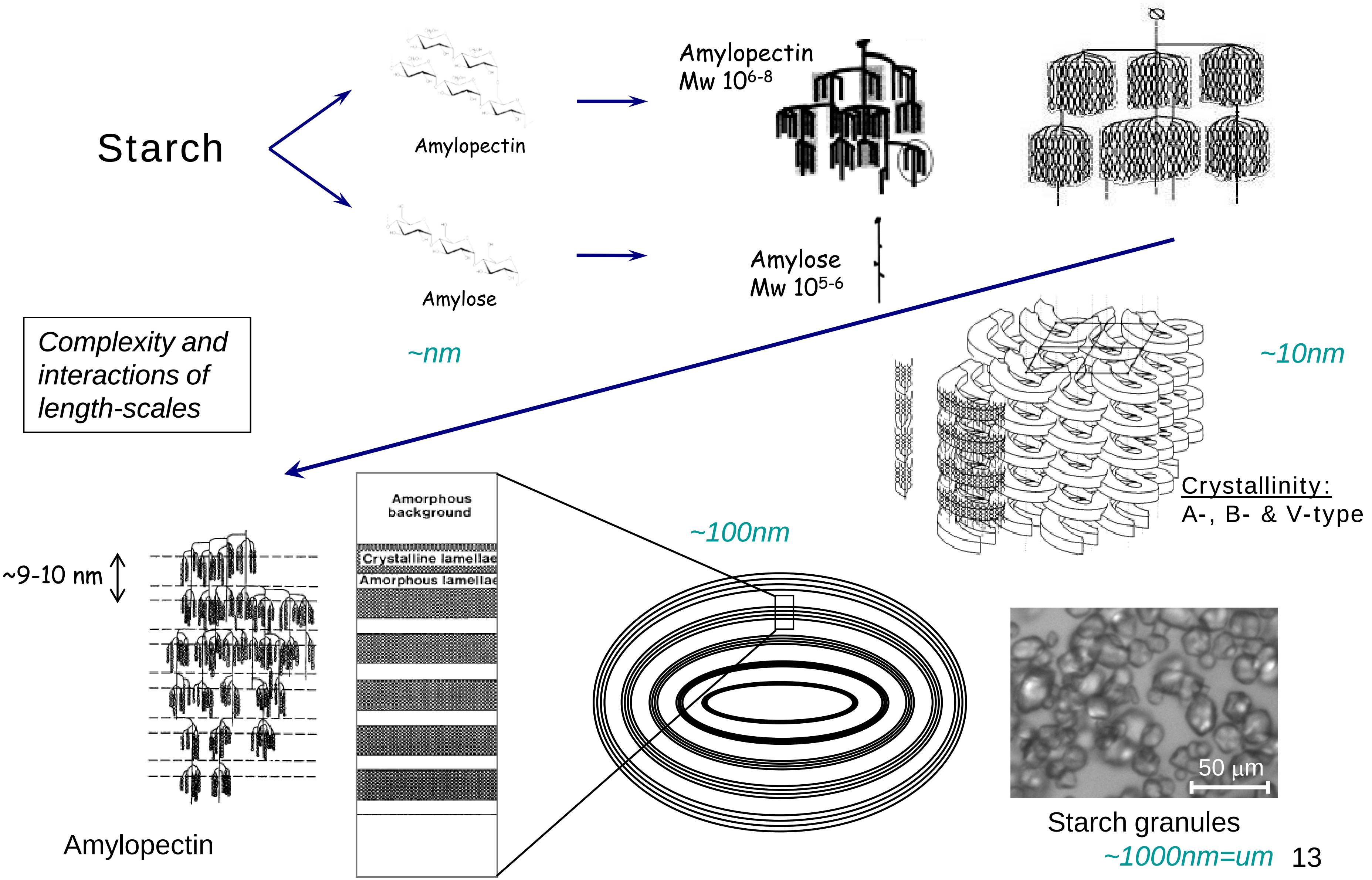
Part of the solution

- Plastic waste minimisation and reuse
- Plastics recycling
- Plastic incineration / energy recovery
- Sustainable polymers
  - **Bio-based polymers**
  - **Biodegradable polymers**
  - **Degradable polymers**

Sustainable polymer industry drivers



Starch: multi-scale



History

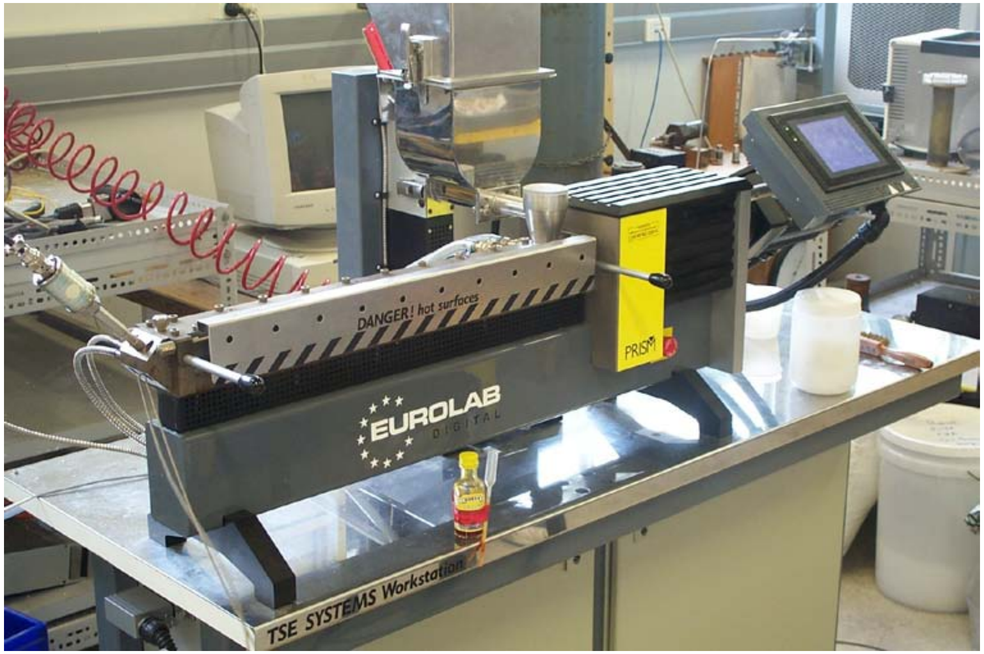
- CRC International Food Manufacture and Packaging Science (1995-2002)
- IP protected and transferred to spin off company Plantic Technologies in 2002
- Plantic Technologies commercialised technology
- Plantic collaborated with UQ via ARC/CRC funded projects for further innovation

Cost focused

- ✓ **Aim: Cost competitive biodegradable plastic via;**
  - **Use on <u>standard processing</u> equipment**
  - **Determine mechanical/physical properties <u>required</u> for application; <u>not over-engineered properties</u>**
    - **e.g. ASTM 3891-95: Standard Specification for Polyethylene Films Made Medium-Density Polyethylene for General Use and Packaging Applications.)**
  - **Use of <u>nanocomposite technology [mulch films]</u> to reduce need for polyester component and/or improve processing rates**

Pellet Compounding

- Optimize mixing and melting of starch-based pellets



Processing - Film blowing

- Lab Processing using film blowing.
  - Determine film blowing ability
  - Optimise blowing conditions

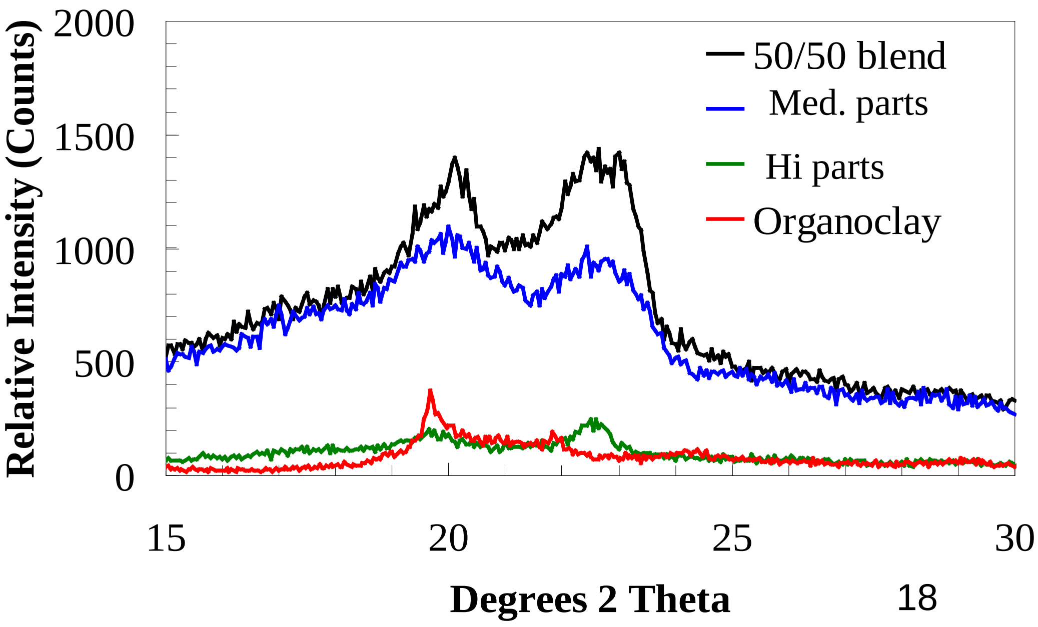
25mm, L/D=20, Dfilm=40mm, Gap=1mm

Ex. Different Clarity

med parts organoclay 50/50 blend hi parts organoclay

Clay content inc>>
Crystallinity dec>>
Clarity inc

? Disrupt crystallinity
? Nucleation site for smaller crystalls



Pilot Scale – Film blowing

Polyester	SBP/Polyester	SBP/Polyester/Nanocomposite
		
~LDPE shape "stable"	~HDPE shape "unstable"	~LDPE/HDPE shape "stable" *

* about 80% of LDPE production rate

Properties

Material / Standard	Tensile Strength (MPa)		Elongation @ Break (%)	
	MD	CD	MD	CD
SBP/Polyester/Nanocomposite film (laboratory)	25.3	19.5	251	279
SBP/Polyester/Nanocomposite film (industrial)	26.3	19.1	252	134
ASTM D 3981	14.1	10.5	100	300
ASTM D 4397	11.7	8.3	225	350
ASTM D 4635	11.7	8.3	225	350

- TS & elongation acceptable cf ASTM film requirements
- Tear strengths were also improved by nanocomposite addition

Compounding scale-up

- Maximise gelatinisation
- Minimise fragmentation
- Maximise distribution and exfoliation of nanoclay
- Maximise throughput
- Maintaining mechanical properties/quality control

Production at 20-800kg/hour on D=83mm

Film blowing scale-up

Correct layflat (1200mm) and thickness (35µm) achieved

Starch Mulch Film

•Low cost starch resin film blown on lab scale to required thickness (30 microns) [world first]
•Scale up production of CRC mulch film on CSIRO extruder
•Production able to run without assistance after start-up time.

✓Large scale field trial successful with starch/synthetic blends (14 weeks) with

- ✓No weed growth and good soil condition rentention
- ✓Good film quality and coverage during trial
- ✓Good crop yields

Injection molded products

- 5 commercial grades of injection molded resins developed [GP to WR grades]
- Application focus of project on Biodegradable Mosquito Ovitrap for Dengue Fever outbreak control

BENEFITS
- Reduce costs and health risks in collection
- Reduce litter

Trays

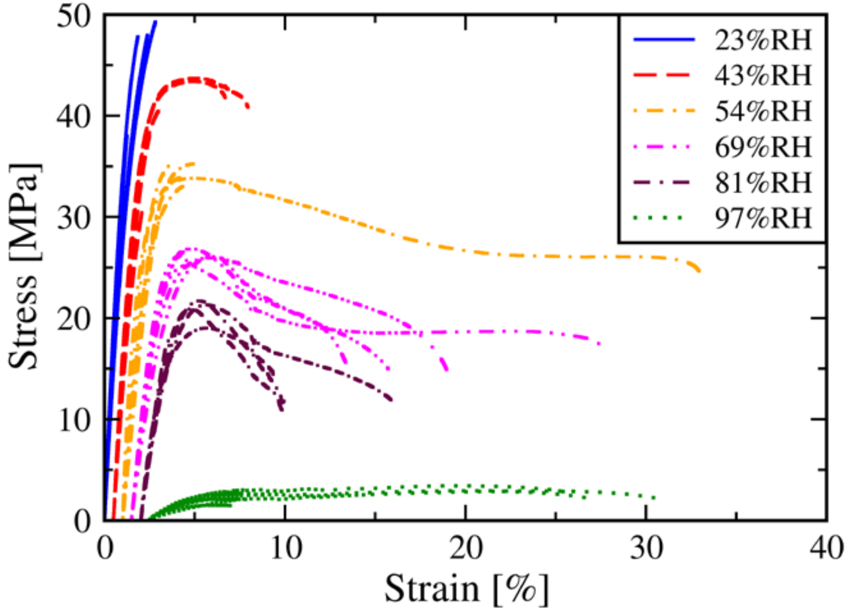
- Plantic™ thermoformable trays

- 2002 CRC Association Tech Transfer Award
- 2004 Eureka Prize for Industry
- $VCapital ($20M), AIM listing ($50M);
- Continued research grants -ARC, BIF, START, CRC ($8M)

Trays

Plantic® biodegradable insert launched in Cadbury Milk Tray box October 2003 in Australia

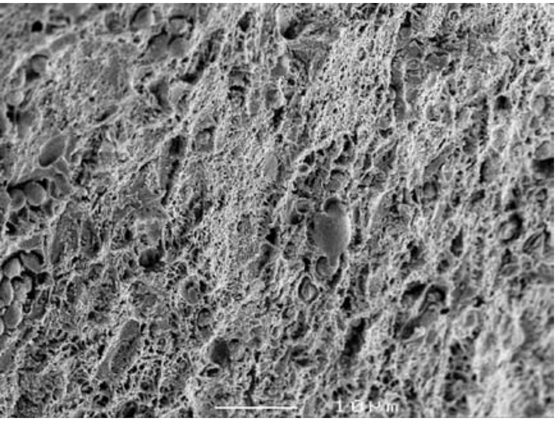
Fundamentals
Structure – property relations



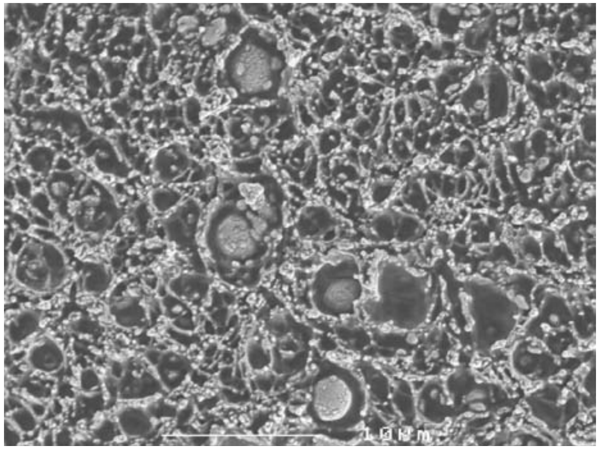
- Stress –strain plots of specimens stored at various RH for 14 days
- Extremely wide range of behaviour is seen!

Structure - SEM

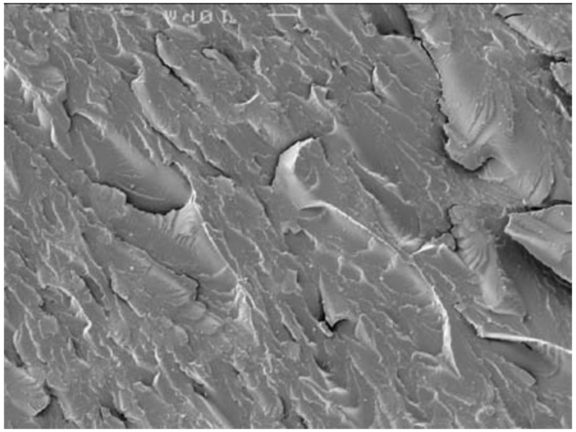
- SEM of fracture surfaces as a function of RH storage



69%RH – 5mm.min^{-1}



54%RH – 5mm.min^{-1}



25%RH – 5mm.min^{-1}

Ductile → Brittle

Water Diffusion

- Faster diffusion:
  - Higher temp
  - Higher RH
  - Increased plasticisation
  - Increased free volume
- n=0.5 concentration dependant Fickian diffusion
- **Now examining relationship between formulation and water diffusion/biodegradation**

25 ^{0}C

Condition	D_0 x 10^{-7} (cm²/s)	A	n
vac dried	0.53	2.30	0.50
23%	1.56	2.30	0.53
43%	1.57	2.13	0.51
54%	2.13	2.00	0.50
81%	3.80	2.40	0.47

37 ^{0}C

Condition	D_0 x 10^{-7} (cm²/s)	A	n
vac dried	1.00	2.30	0.50
23%	2.00	2.00	0.57
43%	2.00	2.16	0.52
54%	2.66	2.37	0.51
81%	4.07	2.26	0.50

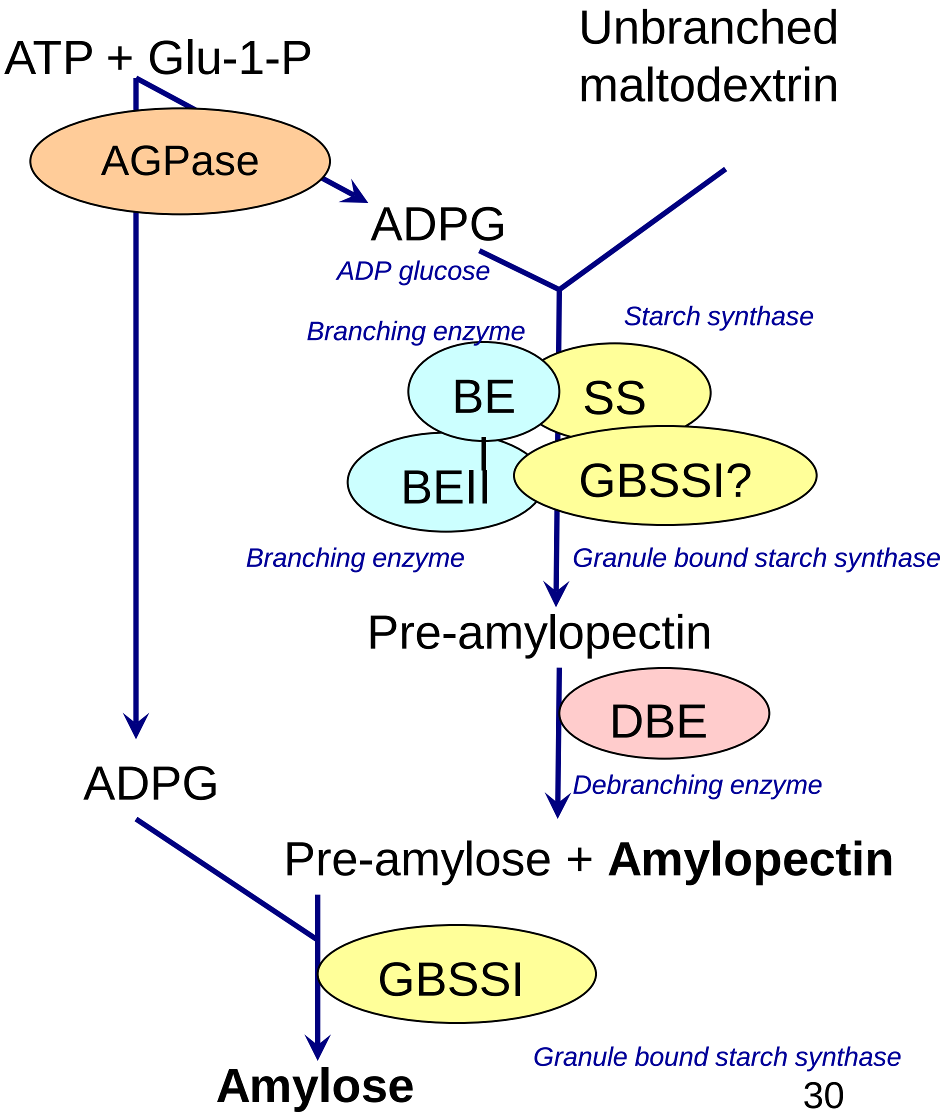
45 ^{0}C

Condition	D_0 x 10^{-7} (cm²/s)	A	n
vac dried	2.56	2.07	0.53
23%	2.85	1.85	0.50
43%	3.63	2.13	0.50
54%	3.00	1.50	0.52
81%	4.20	2.10	0.50

M. Russo, E. Strounina, M.Waret, T.Nicholson, R.Truss, P.J.Halley,.A Study of Water Diffusion into a High-Amylose Starch Blend: The Effect of Moisture Content and Temperature Biomacromolecules;; 2007; 8(1); 296-301.

Model starches

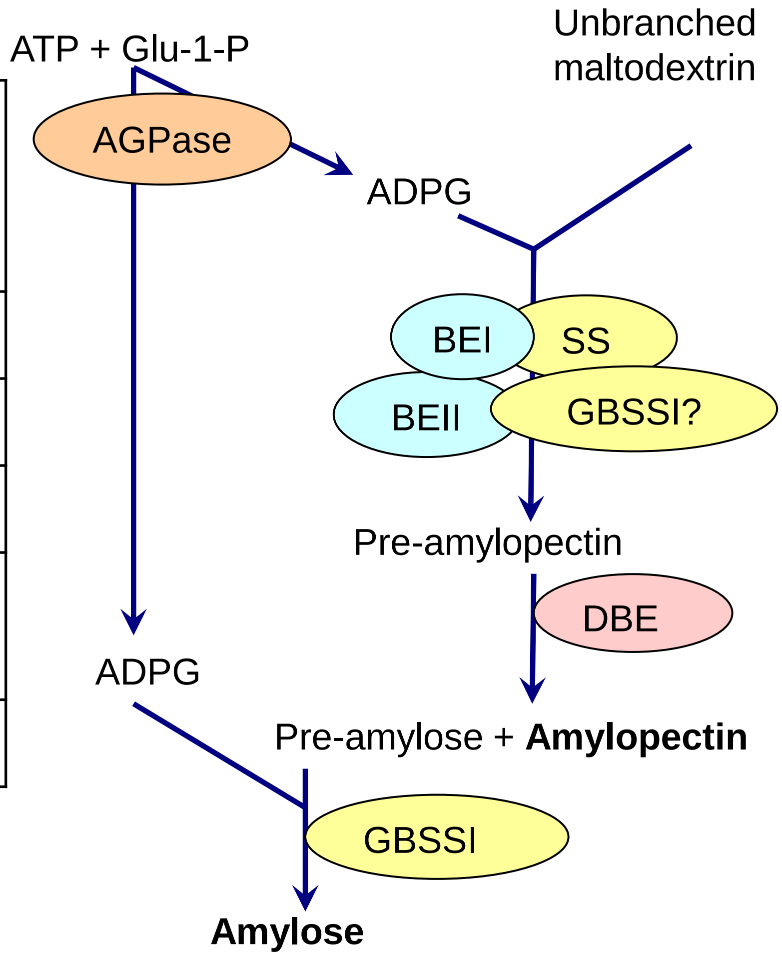
- Advances in starch biosynthesis → novel starches
- Starches from different species:
  - Spatial and temporal regulation of genes encoding various enzymes
  - Activities of participating enzymes (and their isoforms)
  - Modulation of the extent of enzymes activities
- The availability of novel starch varieties → increase the versatility of starch as raw material



Maize starches

Starch	Deficient in Starch Biosynthesis Enzyme	Amylose Content* (%)
W64A	-	13.6
Wx1	GBSSI	0.4
Du1R	SSIII	25.4
Su1R	DBE (isoamylase type)	49.9
HAM	BEIIb	75.3

* The maximum standard error for amylose content was 7.2%



Model starches - summary

- The extent of structural order (double helix and crystallinity) decreases with increasing amylose content
- Increasing amylose content → increase in % V-type polymorph
- The transition of the polymorph structure of double helices can be attributed to the alteration in amylopectin CLD
- The variation in granules size distribution is independent of the variation in macromolecular properties

Ex. Product development

- Other products
- Basic science behind current products

Fund./basic research

- Basic science
- Thermoplastic starch polymer development
- Processing development

$A 7M

1995

PLANTIC™
Plantic from plants

Strategic CRC research

$A 3M

Further research

2002

Valuable IP

Time and money

2003

- Scale up proven
- Production quality assured
- Product quality assured

Product Sales/profits

$A xM

2002

Start-up company

$A 6M

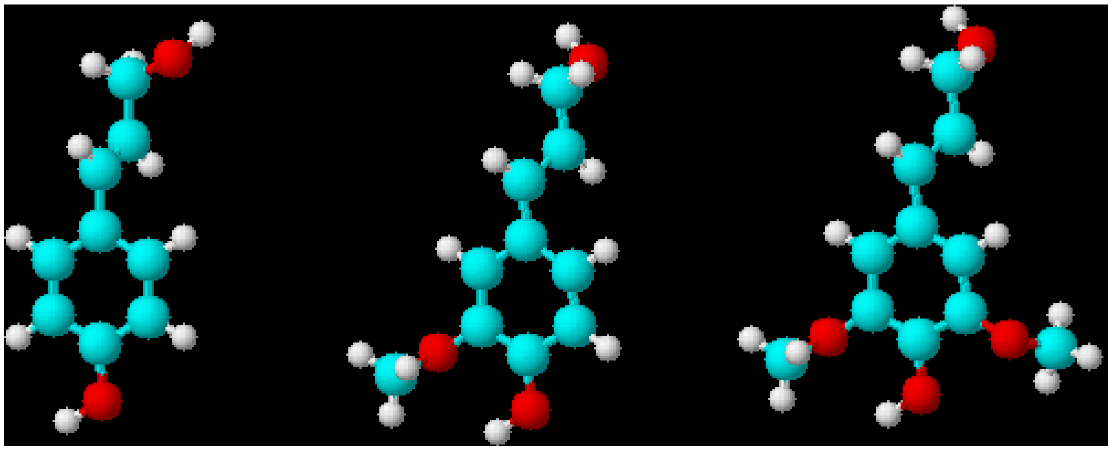
Oxo degradable PE films

To develop photo- and thermally degradable ultra-thin polyethylene films for increasing the benefits [yields/quality/early germination] for a range of crops/environments

Oxo-PE project conclusions

- Degradation depends on : prodegradant, pretreatment & environmental conditions such as site/soil specific variables.
- We can correlate laboratory aging with outdoor aging and predict breakdown time.
- Above the ground we can "control" time to embrittlement.
- Below the ground we have found a way to initiate rapid degradation.
- License agreement signed and technology in commercial transfer (native trees and potatoes)
- CRC-P Chairman Award Winners 2011

Ex. Renewable lignin coatings/ composites

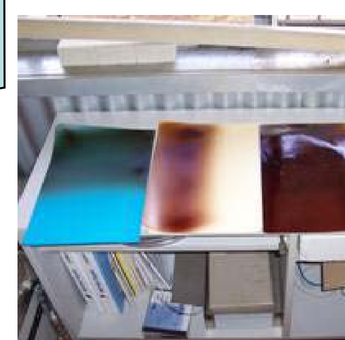


p - Coumaryl alcohol (H)	Coniferyl alcohol (G)	Sinapyl alcohol (S)
$C_9H_{10}O_2$	$C_9H_9O_2(OCH_3)_1$	$C_9H_8O_2(OCH_3)_2$
4-[(1E)-3-hydroxyprop-1-enyl]phenol	4-[(1E)-3-hydroxyprop-1-enyl]-2-methoxyphenol	4-[(1E)-3-hydroxyprop-1-enyl]-2,6-dimethoxyphenol

Treating paper product by providing mixture containing lignin in aqueous solution at concentration and pH, treating paper product with cationic polymer, and treating paper product with lignin mixture
Patent Number(s): EP2014829-A1 ; WO2009009821-A1
Inventor(s): EDYE L A, HALLEY P O E, CRONIN D, DOHERTY W O S, HALLEY P
Patent Assignee(s) and Codes(s):SUGAR IND INNOVATION PTY LTD

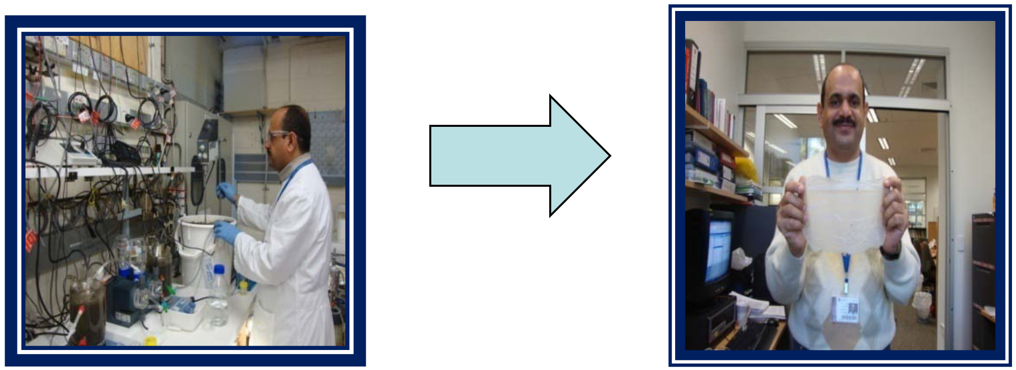
- Extraction/modification of lignin
- Thermoset lignin polymers
- Lignin polymer blends/composites

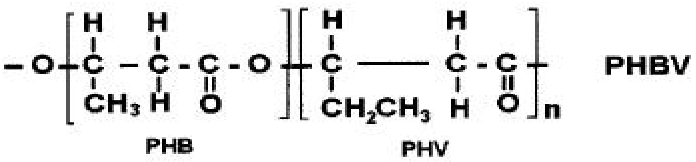
SIIB
CRC Sugar Industry Innovation through Biotechnology



Ex. PHA from waste streams

Objective: To develop low cost PHA polymers from mixed solids waste streams





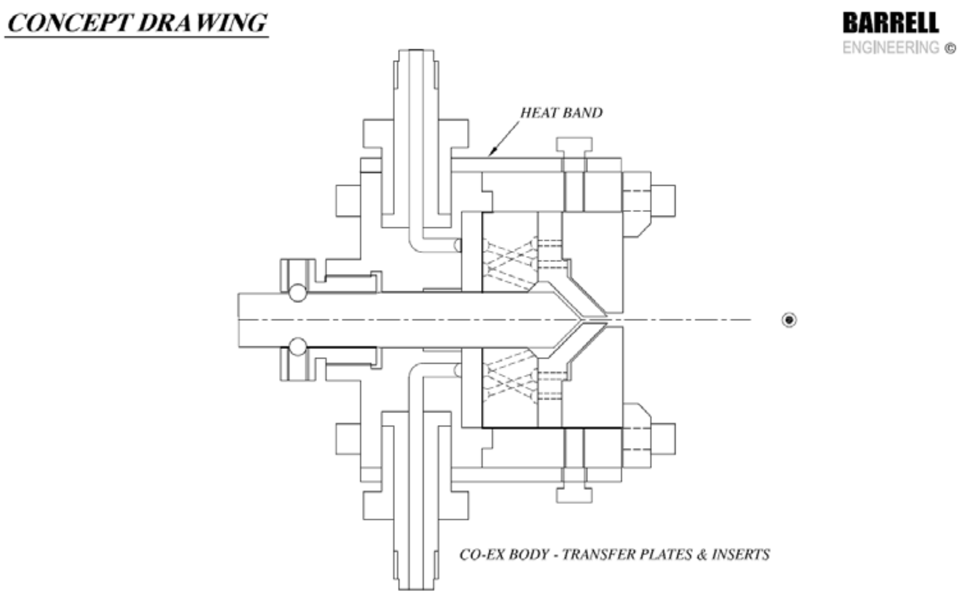
ANOXKALDNES

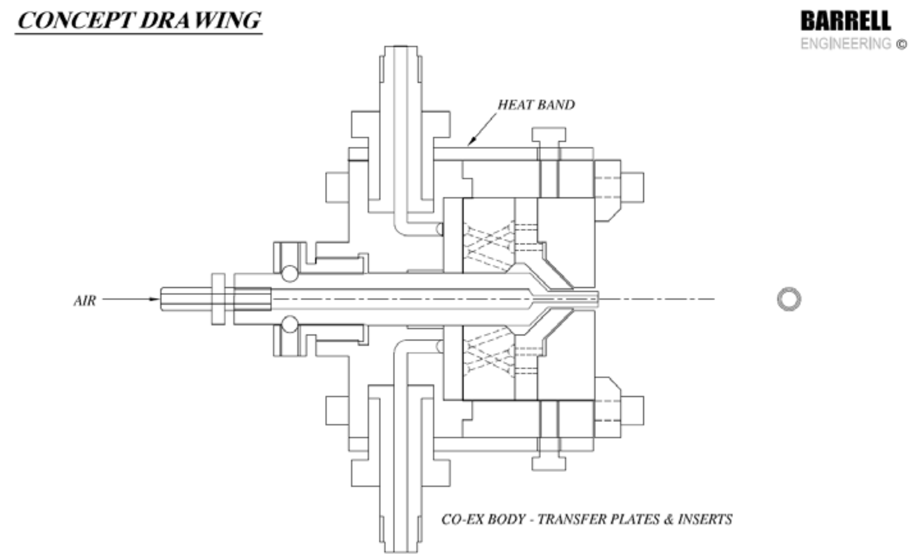
VEOLIA ENVIRONMENTAL SERVICES

FUTURE: Sustainable polymer platforms

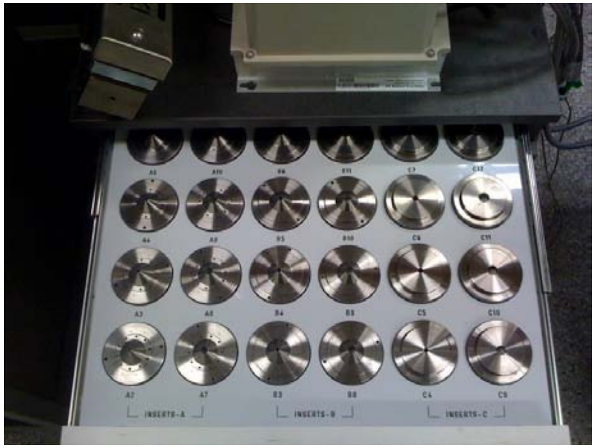
- Low cost PHA polymers from waste streams (Anox, Veolia)
- Nove coextrusion of biobased materials (ARCLP, Plantic)
- Oxodegradable PE for agricultural and industrial films (CRC Polymers extension, Integrated Packaging, GA, BCG)
  - Greenhouse, mulch and solarisation agricultural films
  - Newspaper wrap
- Kafirin protein tablets (PACE, UQ)
- Wider bio-based monomers/plasticisers

Future : Co-extrusion





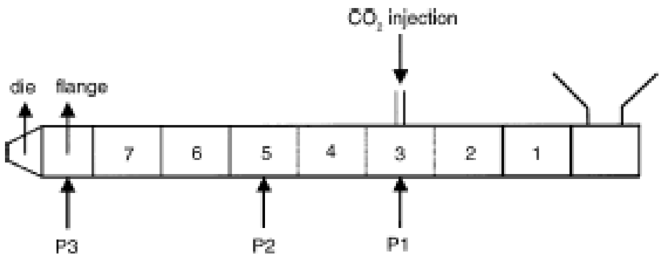
ARCLP 2012-2015 Plantic Technologies
Halley, Gidley, Truss, Roberts



FUTURE: Green sCO2 biopolymer processing

- Green sCO2 processing of biopolymers
  - Lower viscosity (power requirements)
  - Better mixing (nanocomposites)
  - Better gelatinisation (starch)

- Links with QUB (Hornsby) sCO2 processing and AIBN (Thurecht, Whittaker) sCO2 characterisation
  - sCO2 NMR and Raman



GVerreck , ADecorte , H Li , D Tomasko A Arien, JPeeters, PRombautc, GVan den Mooter, ME Brewster The effect of pressurized carbon dioxide as a plasticizer and foaming agent on the hot melt extrusion process and extrudate properties of pharmaceutical polymers **J. of Supercritical Fluids** 38 (2006) 383–391

FUTURE: Biomedical biopolymers

- "Hot melt" co-extrusion for drug delivery
  - New melt co-extrusion process for biopolymer co-extrudates
  - Partnership with QUB
    - MOU UQ-QUB Research, PG and UG exchange
  - Polymer processing (structure development), nanocomposite and co-extrusion technology to control drug release

TABLE 4
Drug Substances Processed by Hot-melt Extrusion Techniques

Drug	T_m (°C)	Reference(s)
Nifedipine	175	(Forster et al., 2001a, 2001c; Nakamichi et al., 2002)
Indomethacin	162.7	(Forster et al., 2001a, 2001b; Forster et al., 2001c)
Piroxicam	204.9	(Forster et al., 2001b)
Tolbutamide	128.4	(Forster et al., 2001a, 2001b)
Lacidipine	184.8	(Forster et al., 2001a, 2001b, 2001c)
Chlorpheniramine Maleate	135	(Crowley et al., 2002; Fukuda et al., 2006a; Repka et al., 1999a, 2001c; Zhang, 1999; Zhu et al., 2002)
Theophylline	255	(Henrist, D. et al., 1999, 1999a 1999b; Sprockel et al., 1997; Young Cr, 2005; Young et al., 2002; Zhang et al., 2000)
17β-estradiol hemihydrate	–	(Hulsmann, S. et al., 2000; Hulsmann et al., 2001)
Oxprenolol hydrochloride	108	(Follonier, N. et al., 1994)
Fenoprofen calcium	–	(Cuff et al., 1998)
Lidocaine	68.5	(Aitken-Nichol et al., 1996; Repka et al., 2005)
Hydrocortisone	220	(Repka et al., 1999a)
Phenylpropanolamine Hydrochloride	192	(Liu et al., 2001)
Hydrochlorothiazide	274	(Keleb et al., 2001; Ndindayino et al., 2002b, 2002c)
Carbamazepine	192	(Perissutti et al., 2002)
Ibuprofen	76	(De Brabander et al., 2002, 2000; Kidokoro et al., 2001)
Melanotan-1	–	(Bhardwaj et al., 1997, 1998)
Diclofenac Sodium	284	(Lyons. J.G., 2006; Sato et al., 1997)
Acetaminophen	170	(Ndindayino et al., 2002a)
Nicardipine Hydrochloride	180	(Nakamichi et al., 2001)
Etonogestrel	200	(Van Laarhoven, J. A. H. et al., 2002; Van Laarhoven, J.A.H. et al., 2002)
Ethinyl estradiol	144	(Van Laarhoven, J.A.H. et al., 2002)
Acetylsalicylic Acid	135	(Stepto, 1997; Stepto, 2000)
Diltiazem Hydrochloride	210	(Follonier, N. et al., 1994; Zhu Y, 2006)
5-Aminosalicylic acid	280	(L. Diane Bruce, 2005)
Itraconazole	166	(Miller. D.A, 2006)
Ketoconazole	148–152	(Mididoddi et al., 2006)
Guaifenesin	78.5	(Crowley et al., 2004a)
Ketoprofen	94	(Crowley et al., 2004a)

Ruixiang Zhao, Peter Torley, Pete Halley, Emerging biodegradable materials: starch- and protein-based bio-nanocomposites, **J Mater Sci (2008) 43:3058–3071**

FUTURE: Biorefinery optimisation

- Process optmisation for biorefineries
  - What is best mix of products/coproducts for given input stream
  - What are state of art technologies for separations and polymerisation
    - Biofuel
      - Biojetfuel
      - Bioethanol
      - biobutanol
    - Biomonomers
    - Biopolymers
  - Local vs large scale

Ruixiang Zhao, Peter Torley, Pete Halley, Emerging biodegradable materials: starch- and protein-based bio-nanocomposites, **J Mater Sci (2008) 43:3058–3071**

FUTURE: World trends

- Interesting perspective on the future of plastics from Ramani Narayan (MSU, USA) at BIOPOL 29-31 Aug, Strasbourg
  - Very large opportunites for Bio-PE and Bio-PET as drop in sustainable technologies
  - defined “green washing” new term for people claiming green credentials but don’t have them
  - Standards drive change (policy and research funding) – so he wants to get the c-accounting standards done properly
  - He would love to see coke go to bio-PET; then the coke vs pepsi “bio-war” will increase biobased polymer interest

FUTURE: World trends

- Ramani Narayan (MSU, USA) (cont.)
  - He thinks the future will be driven by <u>low carbon foot prints </u>(less empahsis on LCA – because they can be manipulated); but C-footprint is harder to cheat – it is what it is
  - Once companies take on the <u>'low carbon footprint value proposition' </u>to make money – it will move very fast and he thinks petroleum based plastics will become a minor player
  - Eventually he thinks 'plastics' will be the name that biobased polymers will be shortened to

FUTURE: World trends

Other comments from BIOPOL 29-31 Aug, Strasbourg and visits to UK, Fr, USA labs and USDA

- Polymers from waste streams very big in research
  - Biorefinery ‘co products’ being set up
  - Refinery optimisation?
- Lots of interest in international exchanges (frozen US govt hiring, UK exchange programs, UQ new 5 yr engineering degree)

FUTURE: World trends

- Compare and contrast
  - UK biotech scientist view of future innovation http://www.timeshighereducation.co.uk/story.asp?sectioncode=26&storycode=417611&c=2
  - Adapt – T.Harford
    - Ex NIH vs HHMR funding outcomes
  - AIC conference/industry workshop view on future of innovation http://www.ausicom.com/news-535-next-generation-networked-research-and-development

Uni-Ind interface R&D

LEARNINGS

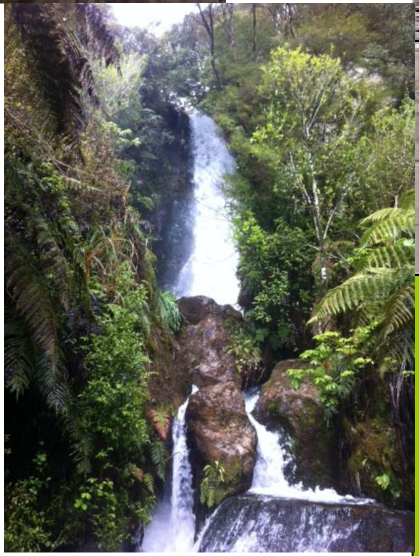
- Commercialisation of research is very rewarding
- Know what you and your partner want
  - IP, shares, licence, further research opportunities
- Critical mass of good research/researchers will attract more funding
- There are funding mechanisms across all research areas
  - Fundamental to scale-up
  - Leverage (university and industry)

Uni-Ind interface R&D (cont…)

- LEARNINGS
- Know when to continue/increase resource/kill projects
  - Use KPRs -Key property requirements – all way through research (including material, processing, product, cost properties)
  - Project management team from all stakeholder areas
- People don't die with projects
  - Opportunities
- Explore traditional and non-traditional funding
  - Build programs from projects and 'failed' grants

Conclusions

- Think of the impact of your entire process [ex carbon footprint]
- Biobased polymers can be processed and have properties like conventional polymers
- Future work needs to work with [not against] inherent properties of sustainable polymers to their advantage in applications that make a difference

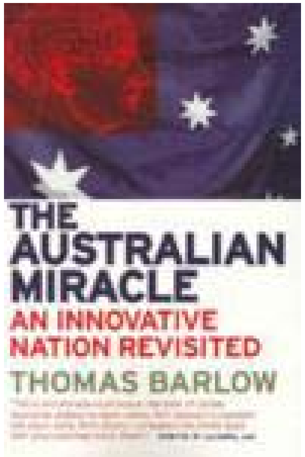
Questions?




Future trends

Thomas Barlow: 'The Australian Miracle: An Innovative Nation Revisited' (2006)

- 1. Blurring of (so-called) low and high technologies
  - *Innovations in mining, agriculture, biotechnology to blend*
- 2. Outsourcing of innovation
- 3. International research partnerships
- 4. Australia's history of innovation AND quickly adapting new technologies



Product life cycle

Life Cycle Assessment (LCA) is a very important tool

Raw material extraction/supply	Plastic manufacture	Use and disposal

LCA
- Scope
- Material and energy flows
- Impact of flows on environment
- Mitigation measures for impact

•CO2
•Energy
•Acid Rain potential
•Other emissions

Plastics carbon footprint

CARBON FOOTPRINT: The total amount of CO_2 produced to directly and indirectly support an activity, usually expressed in (kg CO_2)

Each of the following activities add 1 kg of CO_2 to your carbon footprint:

- **Travel by public transportation (train or bus) 10km**
- **Drive your car 6 km**
- **Fly with a plane a distance of 2.2 km**
- **Use your computer for 32 hours**
- **Production of 5 plastic bags**
- **Production of 2 plastic bottles**
- **Production of 1/3 of a cheeseburger**

Low plastic footprint solution?

VALUE PROPOSITION: need feedstock that

- **<u>Reduces our carbon footprint</u> and moves us to zero carbon or carbon neutral footprint**
- **Provides or potential to provide a <u>positive environmental footprint/profile</u> using LCA tools**

- **>> Biopolymers [plastics from biological sources]**

R.Narayan-UMichigan http://www.farmfoundation.org/news/articlefiles/371-NARAYAN.pdf

Important calculations

(1) Calculate **Biobased carbon content** determination

- Narayan - Rationale, Drivers, Standards and Technology for Biobased Materials; Ch1 in **Renewable Resources and Renewable Energy**, Ed Mauro Graziani & Paolo Fornasiero; CRC Press, 2006
- Codified in **ASTM D6866** to determine biocarbon content (C14 measure) or “Modern” carbon

(2) Report **Total environmental footprint** (the carbon footprint is part of that) using **LCA** tools

Life cycle

MATERIALS DESIGN PRINCIPLES FOR THE ENVIRONMENT

FEEDSTOCK ← **BIOBASED "Intrinsic value proposition" vs PETROCHEMICAL**

↓

PRODUCT MANUFACTURE ← **Energy efficiency**
Reduce environmental impacts

↓

ULTIMATE DISPOSABILITY
Transform into Useful Product ← **BIODEGRADABILITY**
Waste to Energy
Recycling

Carbon & environmental footprint/profile for conversion, use and disposal should be comparable to or has the potential to be comparable to existing petro feedstock conversion!!

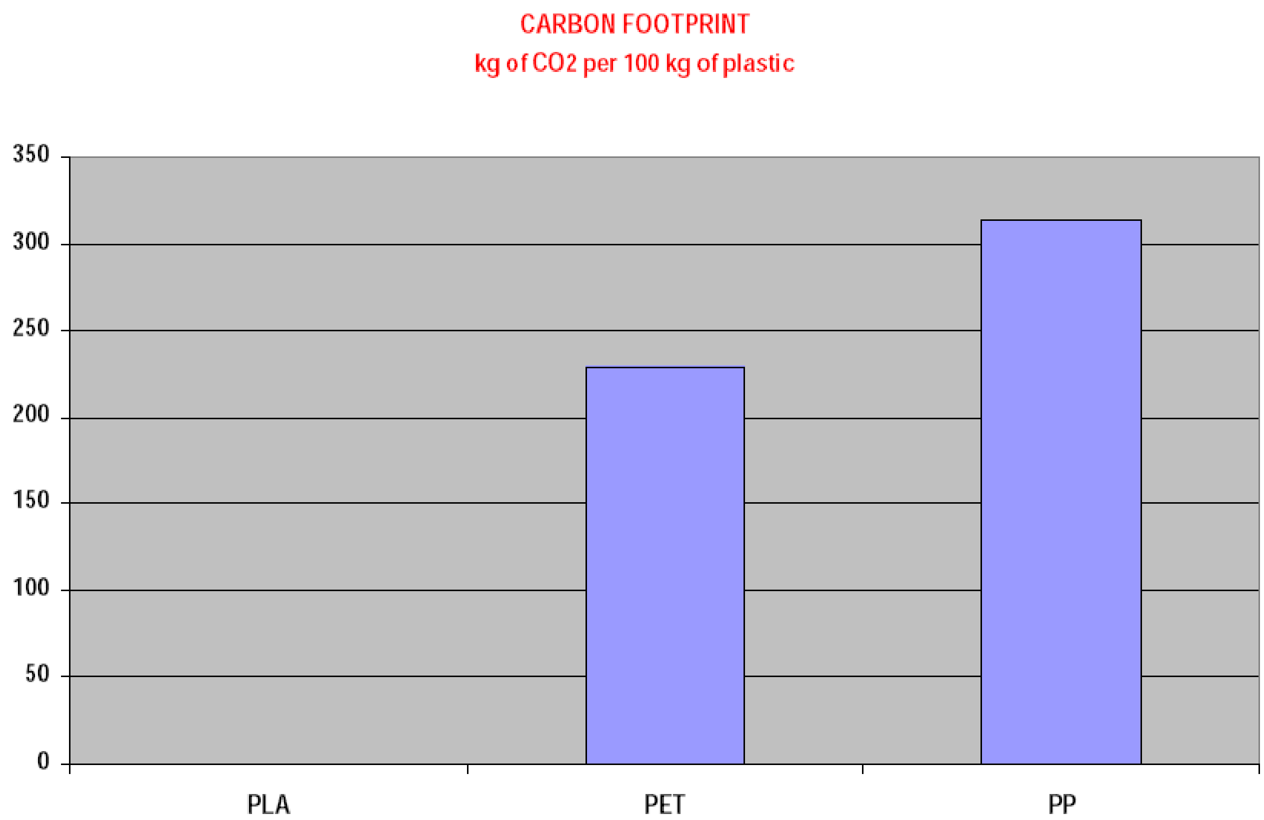
Develop a carbon and environmental footprint/profile using Life Cycle Assessment (LCA) tools" -- ASTM D7075

R.Narayan-UMichigan http://www.farmfoundation.org/news/articlefiles/371-NARAYAN.pdf

Ex PLA

Vink et al
www.natureworksllc.com/our-values-and-views/life-cycle-assessment.aspx

Intrinsic Value Proposition for "Bio" feedstock



R.Narayan-UMichigan http://www.farmfoundation.org/news/articlefiles/371-NARAYAN.pdf

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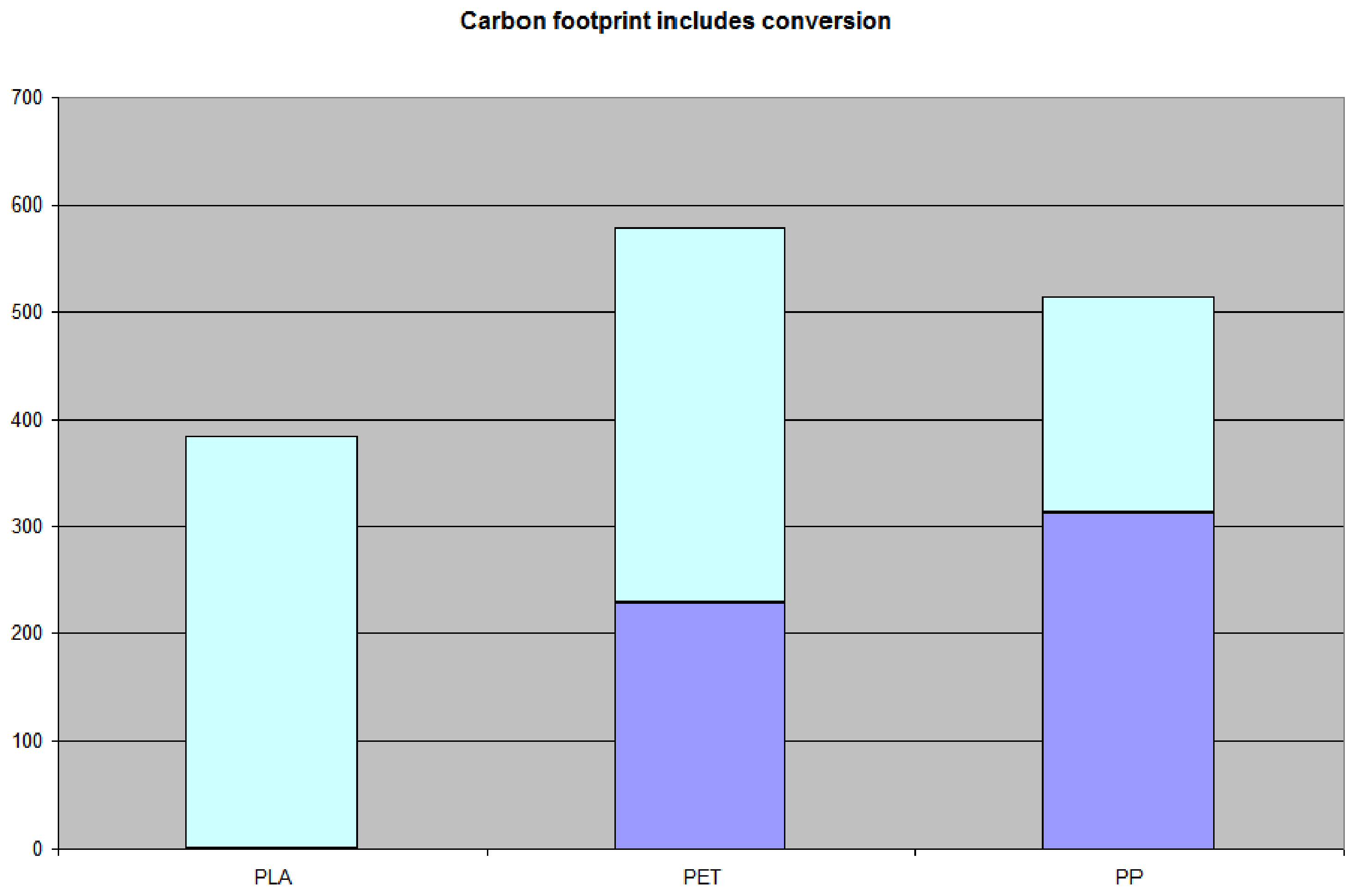

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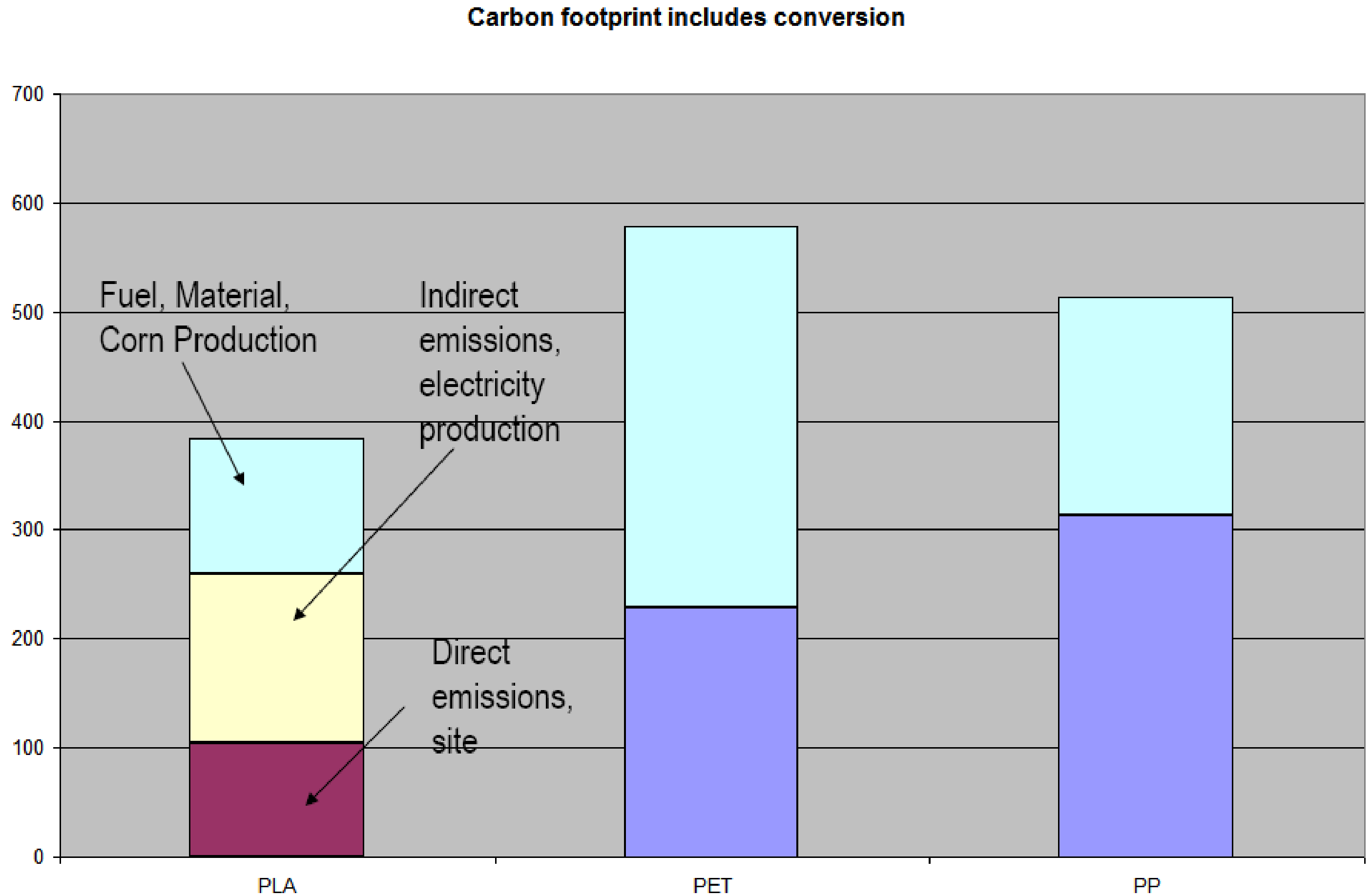

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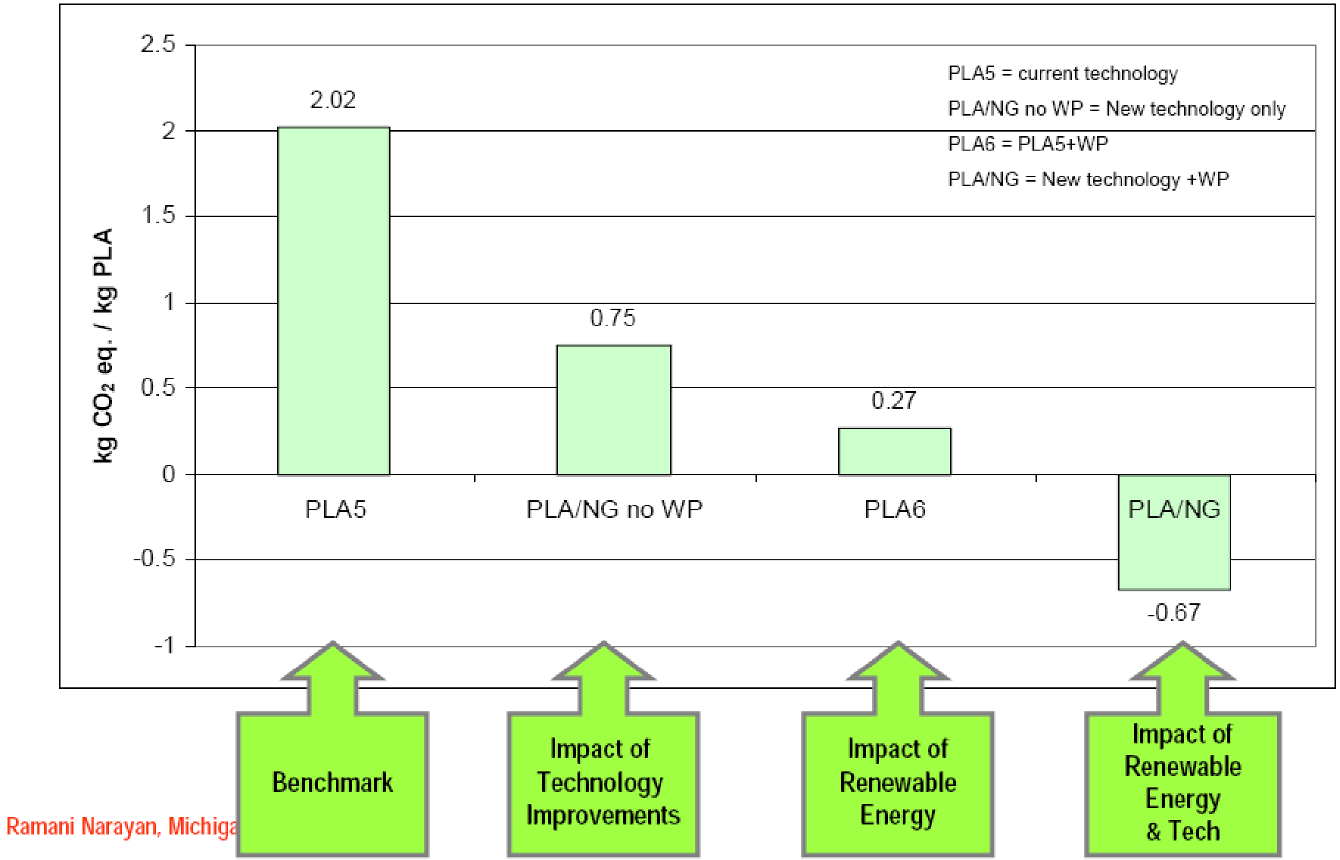
Ex PLA

Results of the utilization of renewable energy and new technology on GHG



R.Narayan-UMichigan http://www.farmfoundation.org/news/articlefiles/371-NARAYAN.pdf

Food vs plastics land use debate?

<u>3300 MHa Available cropland</u>

1500 MHa Cropland used today
330 MHa Protected area [10%]
800 MHa potential forest
100 MHa residential [3%]
570 MHa "free" unused agricultural area

Cultivated land use

92% for food/animal feed
6% for industrial materials
2% for biofuels
0.1% for biopolymers

<u>By 2020</u>

160 MHa Increased food
32 MHa residential
<u>18MHa biofuel/biopolymer</u>
210MHa total

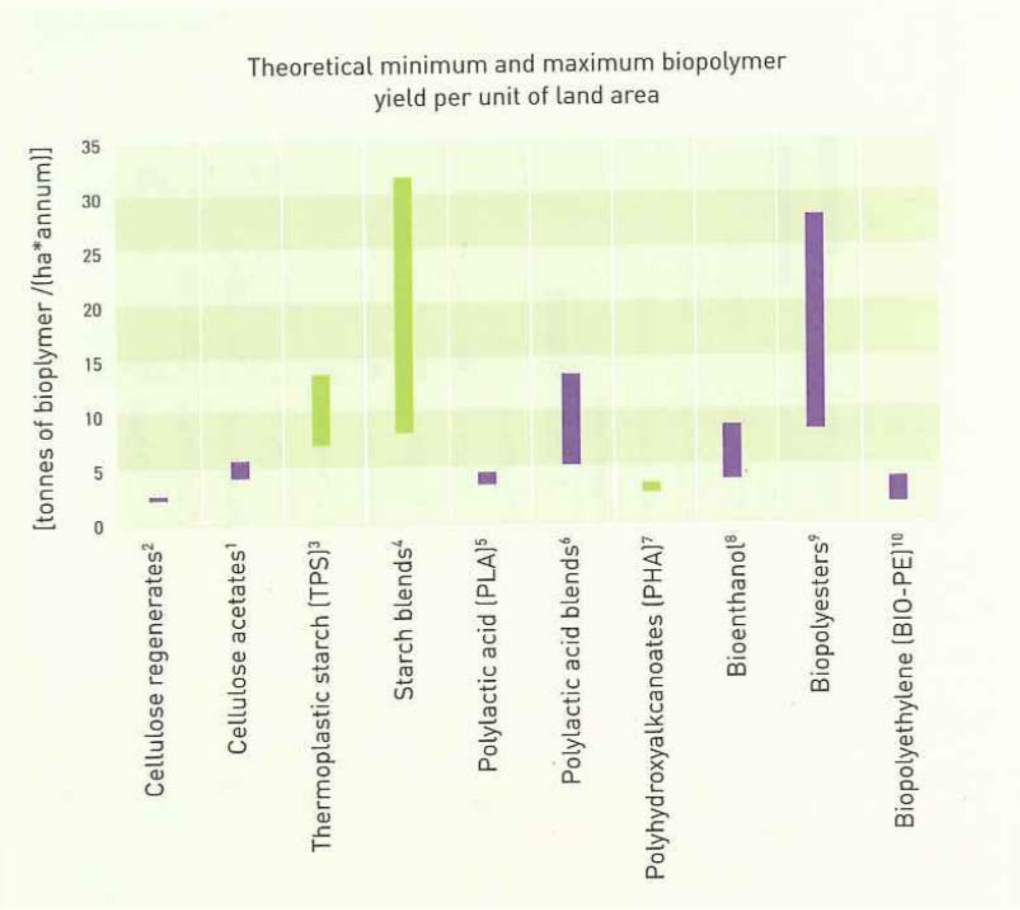
360 MHa "free" unused agricultural area

Bioplastic magazine, v6 2009

- There is more than enough space to provide food for everyone on the planet.
- The problem is not unavailable land, but distribution/logistics/political problems

Land use depends on biopolymer

T / Ha / yr

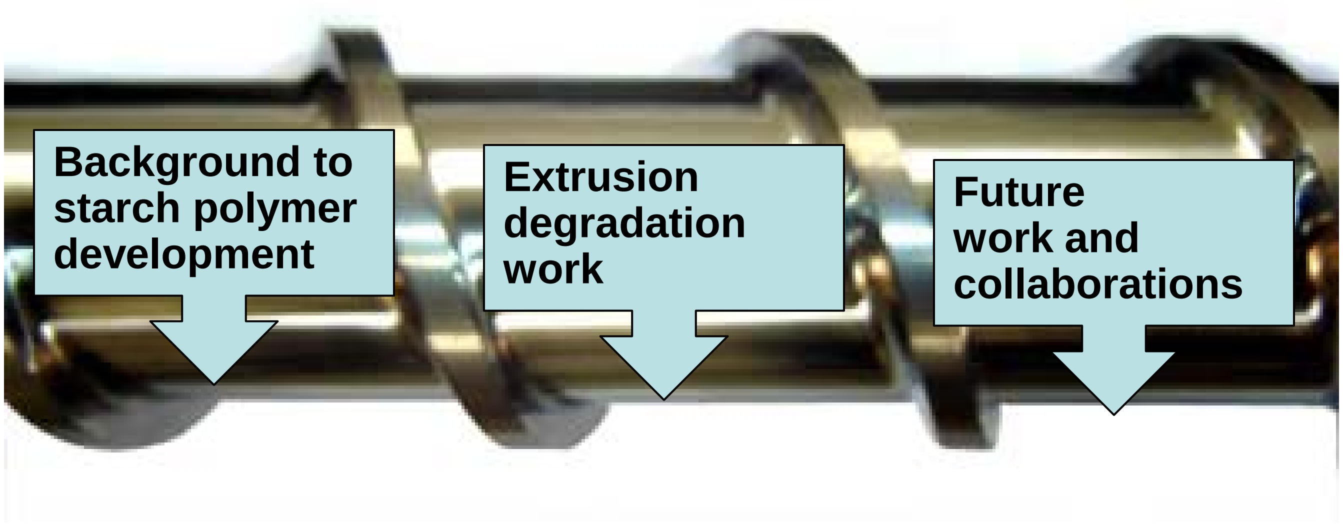


- Tonnes/Ha depends on type of biopolymer
- Crop yields will increase due to advances in agricultural science and farming practices

Sustainable polymer research at UQ

- Thermoplastic Starch Polymers (CRCFoodPack/Plantic/CRCPolymers)
- Photodegradable PE films for sustainable agriculture (CRC Polymers)
- Lignin coatings (CRC Sugar)

Le tour du sujet




Sketch of Cadel Evans (#1 le tour de France 2011)

Thermoplastic starch extrusion

Starch processing is difficult to master due to this complexity and interactions of length-scales

*“Starch is a *&*$-ing plant not a plastic!”*

Quote from early postdoc after a frustrating day of extrusion

Want

- Maximise gelatinisation (cook)
- Maximise plasticisation
- Minimise degradation (fragmentation)

Structure changes during extrusion

“Structural Extrusion”

to develop thermoplastic starch (TPS)

Mw characterisation

GPC (Agilent 1100 series SEC system (Agilent Technologies, Santa Clara, USA) equipped with a Shimadzu RID-10A differential refractive index detector)

+ Novel solvent -99.5 wt % DMSO and 0.5 wt % LiBr(as a hydrogen-bond disrupter and prevents retrogradation (crystallization followed by spontaneous precipitation), enhances the solubility of high-amylose starch)

- **Properly dissolve starch**
- **Reduce fragmentation**
- **Measure high Mw**

Mw characterisation

Debranching

The samples were **enzymatically debranched** using isoamylase
-cleaves α-1,6 branch point.

Lead to the **complete debranching** of starch[1]

Lead to a dual population of two chain lengths:

1. branches of degree of polymerization 6–100 (typically averaging 20–24) for the short branches comprising the **amylopectin** fraction

2. branches that are more than an order of magnitude longer for the longer branches that comprise the **amylose** fraction (e.g.[1,2]).

- *Extruded thermoplastic starch (20 mg) was mixed with water/NaOH solution and then completely solubilized in a thermomixer*
- *The solution was cooled to room temperature acetic acid/ sodium acetate solution were added/mixed*
- *Then Isoamylase.water were added and incubated for 24h/37˚C.*
- *Then heated to 95 ˚C to denature the enzyme, and freeze dried.*

- **Examine chain degradation**

1 Ward, R. M.; Gao, Q.; de Bruyn, H.; Gilbert, R. G.; Fitzgerald, M. A. *Biomacromolecules* 2006, *7*, 866-876.
2 Castro, J. V.; Dumas, C.; Chiou, H.; Fitzgerald, M. A.; Gilbert, R. G. *Biomacromolecules* 2005, *6*, 2248-2259.

Materials

Three varieties of commercially available, genetically modified corn starches (**Mazaca, Gelose 50 and Gelose 80**) were supplied by Penford Australia Ltd.

All starches were chemically unmodified and the amylose contents for these three types of starches were **0%, 55% and 85%**, respectively.

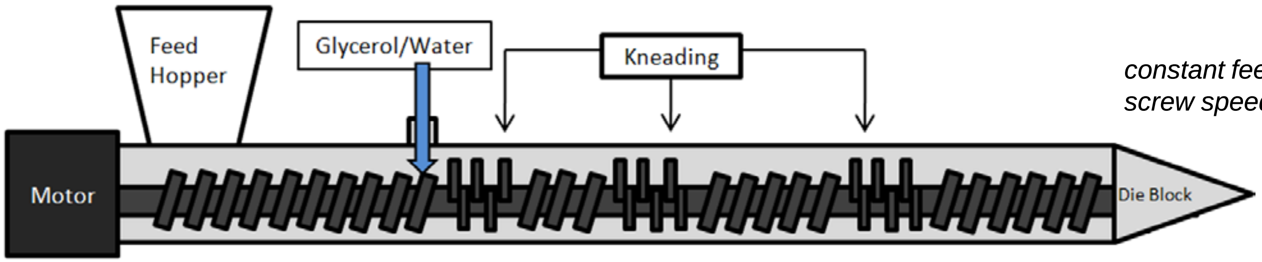
Total starch and plasticizer contents were adjusted to **60% starch, 28% glycerol, and 12% water**.

Extruder setup

2. Different extruder configurations and operating conditions

1. Extrude different TPS formulations

60% [different] starch
28% glycerol
12% water



constant feed rate = 0.312 kg/hr
screw speed = 180 rpm

Interval	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Temperature (°C)	50		80		140		140		140		140		140		140		140		Not heated	

3. Sample extrudate at various points along extruder >> Mw and MWD

Prism Eurolab 16XL co-rotating twin–screw extruder (Thermo Electron Corporation, Karlsruhe, Germany)
D=16mm, L=640mm, Ddie= 3 mm

The screw contains forward conveying elements and kneading elements.

The barrel was divided into 20 intervals for sample collection purpose [interval length= 30 mm]

Liu W-C, et al. "Mechanism of Degradation of Starch, a Highly Branched Polymer, during Extrusion", Macromolecules, **43** (6), 2855–2864 (2010)

Extrusion effects on Mw

Further comments

- **Significant shear degradation of the amylopectin component, and the changes in size distribution.** Due to;
  - Large size
  - Shorter branched structure
  - Hyperbranched connectivity of amylopectin gives it a relatively inflexible structure

Extrusion effects on Mw

Further comments

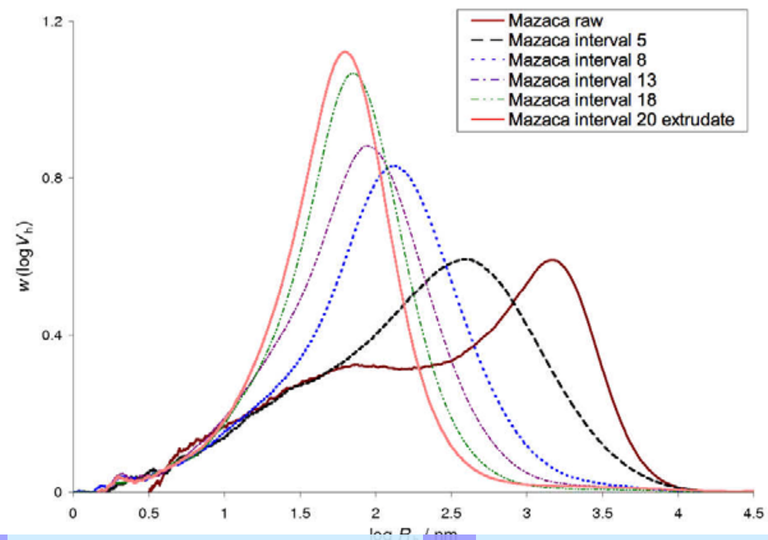
•It was also found that the concept of **maximum stable size**, similar to droplet breakup in an emulsion system, is applicable

•below the maximum stable size, little shear degradation occurs for given extrusion conditions.

•Size distribution of amylopectin molecules **narrowed and converged toward this maximum stable size** as extrusion proceeded, due to

•selective scission

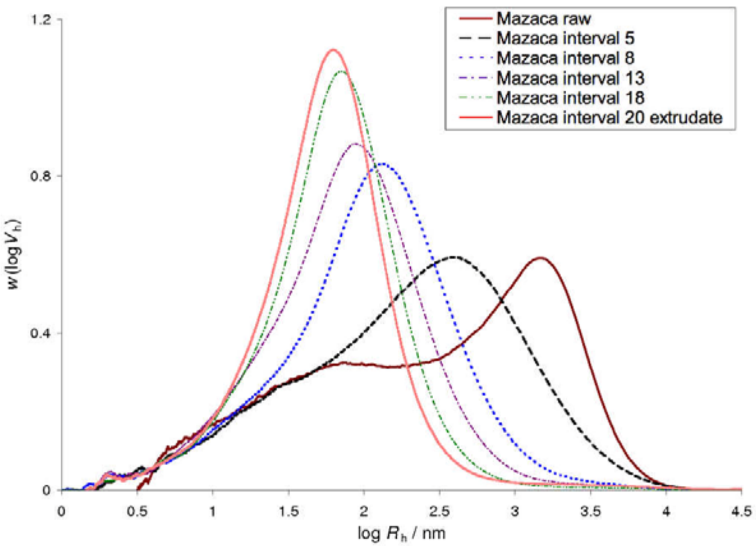
•maximum stable size concept.



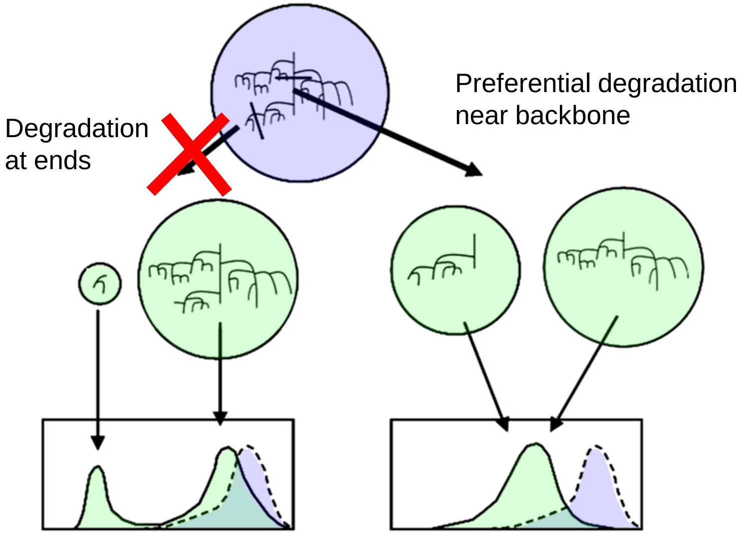
Extrusion effects on Mw

Further comments

- The mechanism for scission of the polymer chains is believed to preferentially take place **close to the centre of the molecule**, as suggested in the literature for other polymer systems
  - This is inferred from the absence of a bimodal distribution after extrusion.



Mechanisms



Future: Mw characterisation

Mn

Starch can be labelled with a fluorophore and then be subjected to flow cytometry with fluorescence detection[1]

Mw

MALLS (multiple-angle laser light scattering) will be used to measure the overall weight-average molecular weight

Branching structure

Enzymatic debranching of starch, then characterizing the resulting linear ‘starch’ by FACE (fluorophoreassisted capillary electrophoresis[2] (Amylopectin) or use SEC (Amylose)

•RGG labs

(1) Gilbert RG et al *Journal of Chromatography A 2008, 1205, 60-70.*
(2) O'Shea, M.G et al *Carbohydrate Research 1998, 307, 1-12.*

Conclusions

- Extrusion effects on TPS Mw and MWD
  - Extrusion degradation involved **preferential cleaving of larger molecules**, while causing the size distribution to **narrow and converge** towards **a maximum stable size**.
  - Susceptibility of polymer molecules to shear degradation is not only dependent on the **size** of the molecule but also extensively influenced by the **branching structure**.
    - High branching density and short branch length were associated with higher susceptibility to shear degradation.
  - The degradation process is not significantly selective towards the length of individual branches
- Need symbiotic development in
  - Novel characterisation tools
  - Novel processing
  - Optimisation of processing

FUTURE: Green platforms

- Sustainable materials/polymers industry is developing
  - "**Green collar industry**" paper in 2009, AustConservCouncil/ACTU
  - Alignment with agriculture and biotech industries and innovation
- Thomas Barlow: 'The Australian Miracle: An Innovative Nation Revisited' (2006)
  - Build on innovation in mining, biotech and agriculture industries
- EU FR **biorefinery** call
- Interest is wider than bio-based polymers
  - Biorefineries and Bio-based monomers and materials
  - Sustainable processes
  - Green Industries
    - Process Economy: prevent waste generation
    - Atom economy: consider reagents in products
    - Process safety : green solvents
    - Process Efficiency : r/c
    - Bio-based materials

The opportunity for Australia is tremendous – strong action on climate and industry policy could trigger the creation of an additional 500,000 jobs in these six sectors alone by 2030.

FUTURE: Green platforms

>> But make sure the focus is on…

1. Target applications that **make a difference** [water, health, energy]
2. Applications that use polymers **inherent ability** [ie biodegradation >> drug release; degradation >> soil enrichment/protection) in the application
   – Build on the **inherent strengths** (not weaknesses) of the polymers
3. And use the right vehicle
   – R.Batterham 2007 talk at AIBN, UQ…

   a) Team should have : Clustering + Focus + Excellence = Impact
   b) Individuals should have :
   - Gumption
   - Planning
   - Thinking and doing [do, review, re-do cycle]
   - Networking

Funding history

1995-2002

- funding: CRC Food Packaging funding, Program C
- partners: CSIRO, UQ, SUT, ACI packaging, Goodman Fielder Ingredients
- areas: fundamental/applied research into Rigid packaging and Flexible packaging/agricultural films; technology transfer
- additional funding: HAL mulch film funding (x2)
- comments: projects incorporated formulation development, small scale processing; property testing; scaleup trials; product testing and qualification and biodegradation protocols for a range of possible product types (foamed trays, solid trays, bread bags, mulch films)

2002

- funding: VC funding (6M) for Plantic setup; DM- plantic setup and finalisation of technology transfer

Funding history

2002-2005

- funding: Direct research contract UQ-Plantic
- partners: Plantic/UQ
- areas: to transfer trays and films technology
-comments: projects product qualification and processing validation/scaleup on confectionery/biscuit trays and mulch film; in 2003 trays work brought into plantic and films work halted (know when to kill projects)

2005-2008

- funding: ARCLP
- partners: UQ/Plantic/SUT
- areas: develop injection molded products and associated biodegradation protocols
- additional funding: BIF funding (with JCU/Qld Health on dengue ovitraps). Applied for AusIndustry COMET funding but unsuccessful.
- comments: projects on product qualification and processing validation/scaleup on injection molded products

Funding history

2007
- Plantic float on London Stock Exchange AIM (DM)

2009-2012
- funding: CRCPolymers
- partners: UQ/Plantic
- areas: develop formulations for water resistant/enhanced barrier properties
-comments: project on development of new formulations/extrusion processing;

2011
-Plantic sold to private owner

2012
-applied for ARCLP funding on coextruded paroducts

My Learnings

- Commercialisation of research is very rewarding
- Know what you and your partner want
  - IP, shares, licence, further research opportunities
- Critical mass of good research/researchers will attract more funding
- There are funding mechanisms across all research areas
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