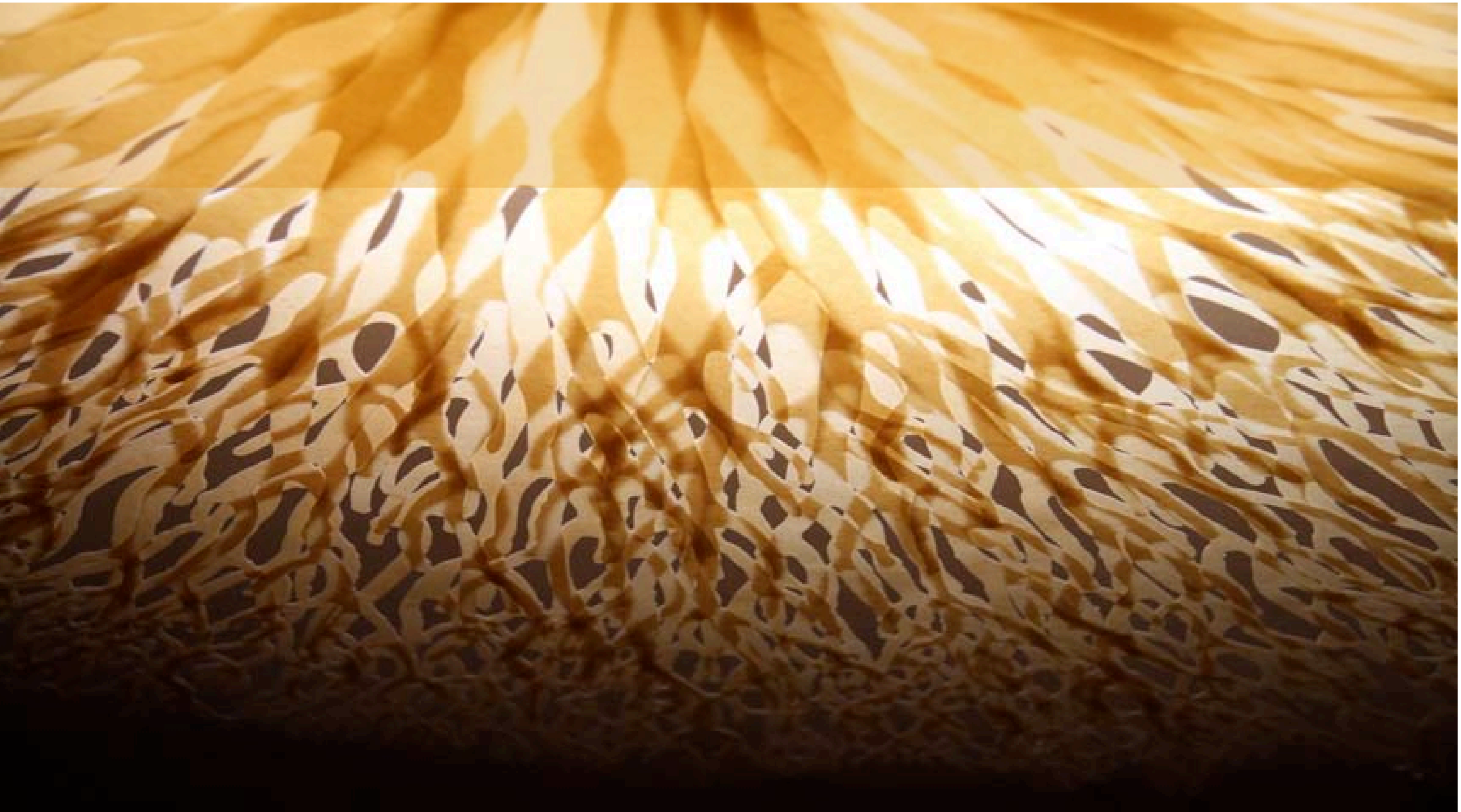
Introduction to Bioplastics

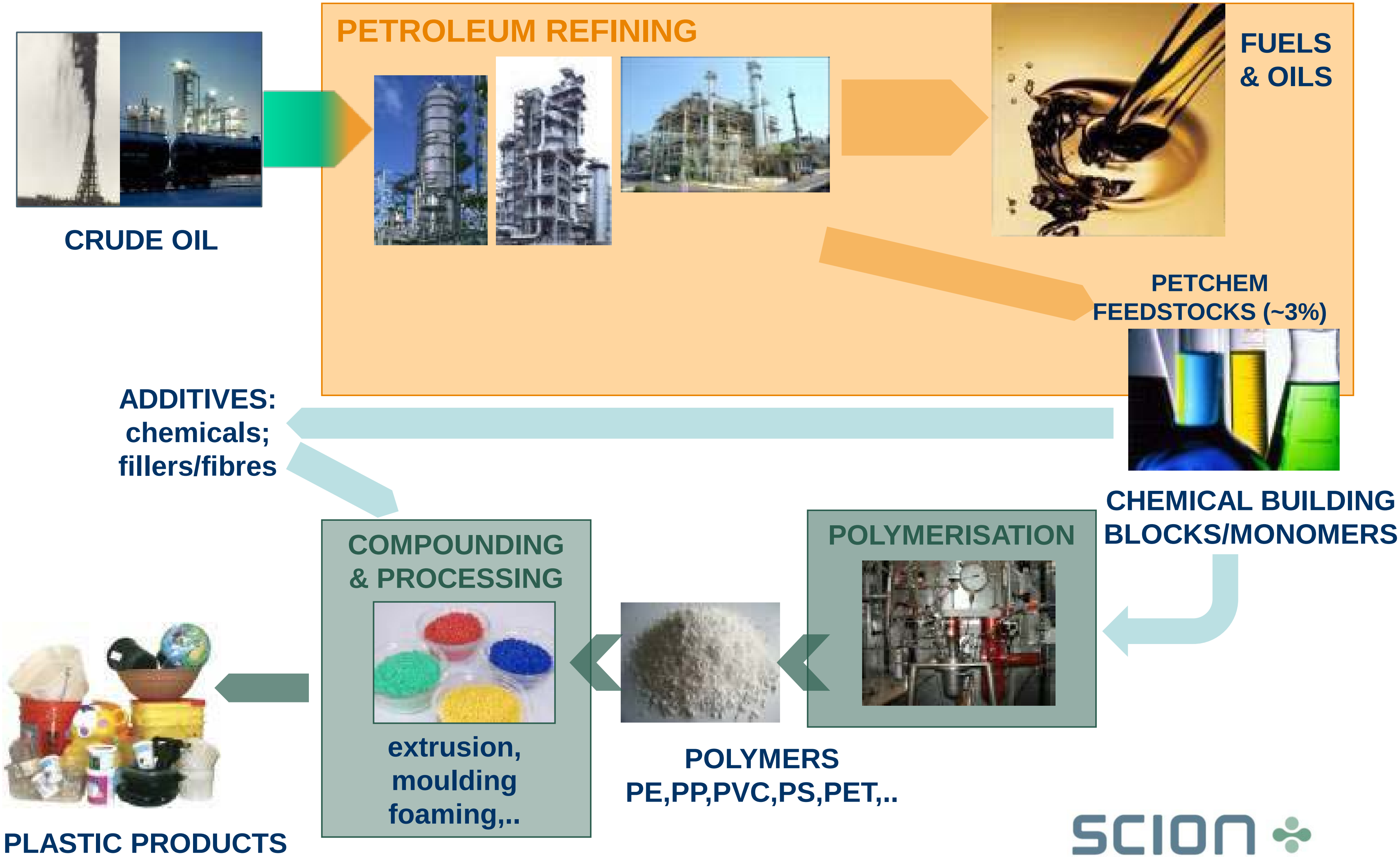
Alan Fernyhough, October 20th 2011



Outline: Introduction to Bioplastics

- Petrochemical plastics background
- What are bioplastics?
- Bioplastic market growth and drivers
- The three leading **compostable** bioplastics
  - Starches
  - Celluloses
  - Compostable Polyesters

Petroleum → Fuels, Chemicals & Plastics



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Example Monomers & Derived Polymers (Petroleum Refining)

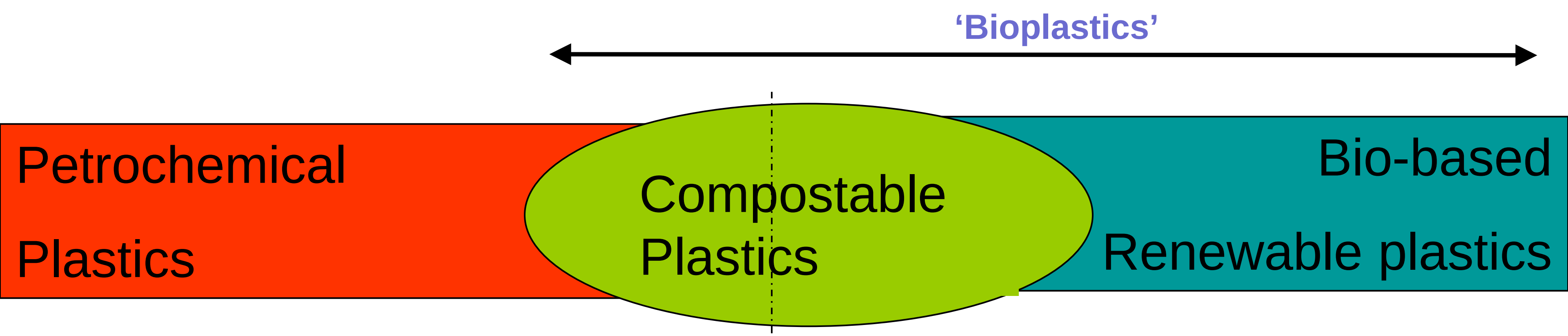
Petrochemical / Monomer/intermediate	Further Derived Monomer/intermediate	Example Polymers
Ethylene, propylene	→	PE, PP, ..
↘	Vinyl chloride	PVC,..
	Vinyl acetate	PVac; EVA, PVAlc.,.
	Acrylic acid	EAA,...
	Acrylonitrile	SAN, ABS,...
	Ethylene glycol →	**PET,..**
	Methyl methacrylate	PMMA,...
Lower alkenes	→	LLDPE
Butadiene	→	ABS, PBD,...
→ Xylenes / alkylated benzenes **(PX)** →	**Terephthalic acid** →	**PET**, PBT, PBAT
	Styrene	PS/EPS, SAN, ABS
	Adipic Acid	Nylon 6,6 ; PBAT
	Butanediol	PBS, PBAT

What are bioplastics?

Two concepts*:

1. **Biodegradable/Compostable** – end of life functionality

2. Derived from **Renewable Resources** – start of life : renewable carbon



PE, PP, PET, PVC,..

PCL, PBS

Starch, Cellulosics, PLA, PHB,

Bio-PE, Bio-PET,...

** European Bioplastics www.european-bioplastics.org*

Bioplastics

Can be polymers that are:

- *biobased (renewable resource) and ‘biodegradable’(compostable)*
- *biobased and durable* (‘traditional polymers’)
- based on *fossil resources* and ‘*biodegradable*‘ *(compostable)*

- **‘Biodegradability’** is directly linked to the chemical structure and not to the origin of the raw materials.

- Hybrids (mixed bio-content - fossil content) exist :
  - Hybrid polymers / copolymers
  - Hybrid blends / compounds

Types of Bioplastics (Renewable)

Biomass

Others: eg algae

Biopolymers ***directly* extracted** from **plant biomass** & variously processed/formulated

Biopolymers made by ***bacteria*** – using biomass/waste/sugars ... extracted......

Biopolymers made **from *biobased precursors*** (intermediates / monomers extracted/derived from biomass – then *polymerised*)

Polysaccharides:
Starches; Celluloses
Proteins;
Natural rubber (polyisoprene) ;
Oils (lipids),..
Modified lignins,..

Biopolyesters:
Polyhydroxyalkanoates (PHAs; PHB)
Xanthans / Polysaccharides,..

Biopolyesters:
Polylactic acid (PLA)
Polysuccinate esters (PBS), other polyesters

Other polymers:
from monomers derived from bio-ethanol/butanol, fermented sugars,.
Bio-polyamides,
Bio-polyurethanes...
Bio-polyethylene,
Bio-PET,..
Bio-acrylics,….

Bioplastics Growth

GLOBAL PLASTICS : >250Mtpa

MARKET PROJECTIONS: BIOPLASTICS

- **2011 - 2015**
  - **~1 % of plastics market (1-2.5 Mtpa)**
- **2020**
  - **10 - 30% of plastics market (>20 Mtpa)**

VALUE FORECAST :

- **$6 billion by 2015**
- **> $10 billion by 2020**

"Demand for biopolymers is expected to show double-digit growth every year to 2020"
"Annualised growth for bioplastics for the next 5 years is estimated at 32% pa"

Sources: European Bioplastics; Freedonia; PIRA; Frost & Sullivan; Plastics Europe;

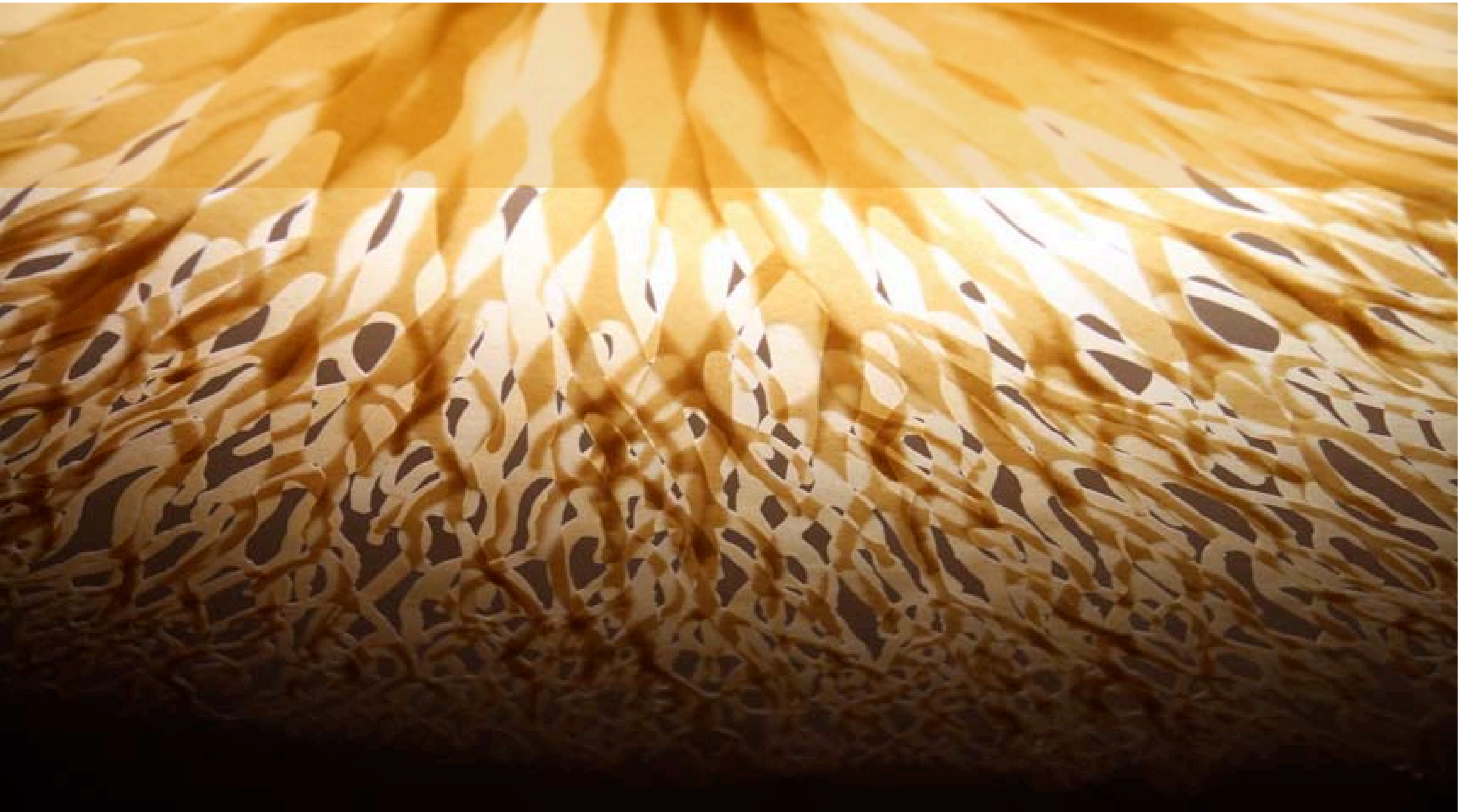
Drivers for Growth

- Oil independence / price of oil

- Price and availability of bioplastics
  - Integration: biofuels/biorefineries
- Environmental/Social Impacts/Responsibility
  - Carbon foot-print / sustainability,..
  - Pollution/end of life
  - Health concerns

- Branding/product differentiation
  - Marketing
  - Company values
- Legislation

Leading Compostable Bioplastics

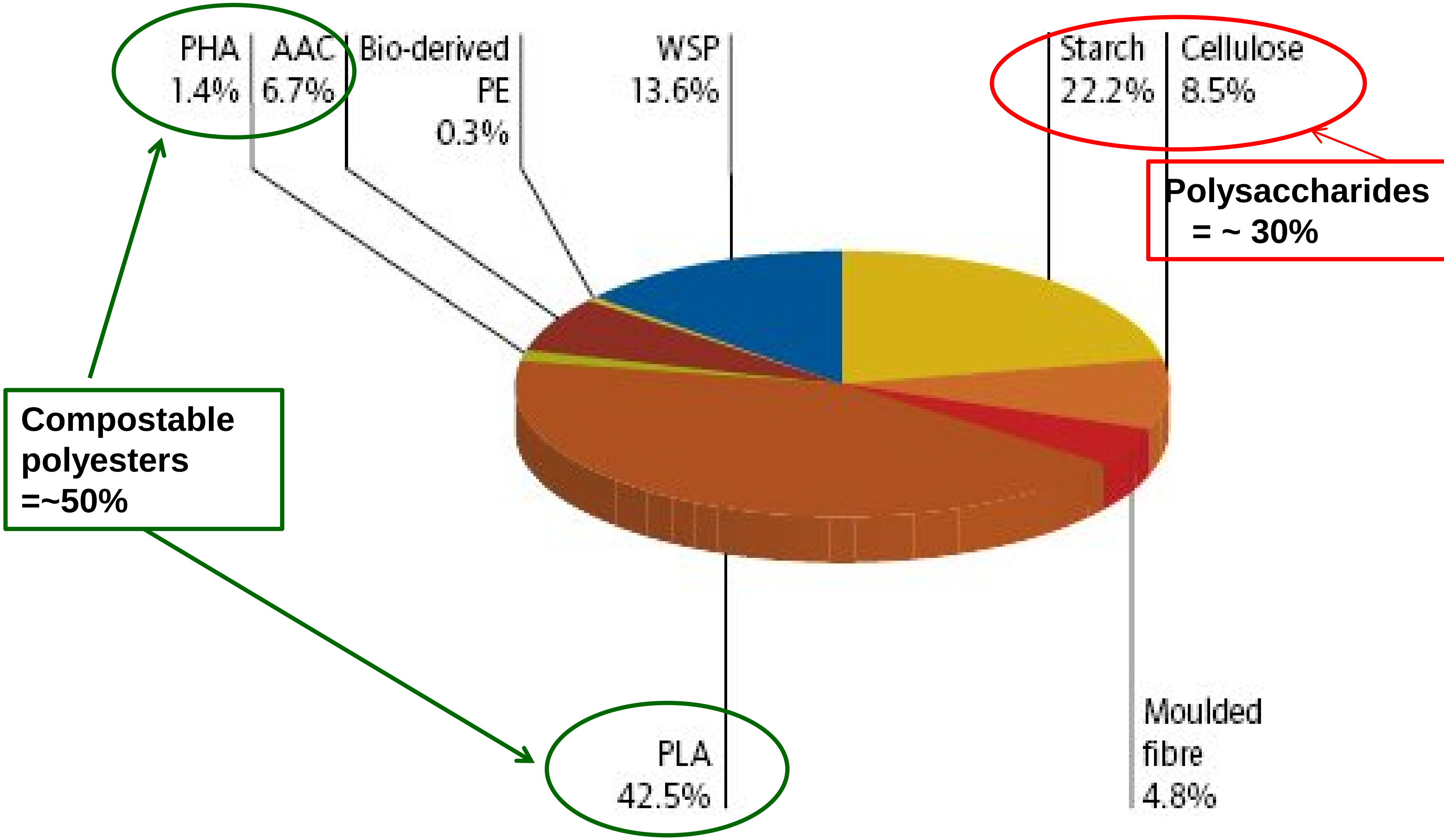


Leading Compostable Bioplastics

- **Polysaccharides**
  - Starches
  - Cellulosics

- **Polyesters**
  - Polylactic acid (PLA)
  - Polyhydroxyalkanoates (PHAs)
  - Polysuccinate esters (PBS, PBAT,...)
    (aliphatic/aromatic co-polyesters (AAC))
  - Others
    - Polycaprolactone (PCL)

FIGURE E.1 Global bioplastic packaging market by product type, 2010 (%)



Note: AAC, aliphatic and aromatic co-polyesters; PLA, polylactic acid; PHA, polyhydroxyalkanoate; WSP, water-soluble polymers Source: Pira International Ltd

Starch Bioplastics

What is the feedstock?

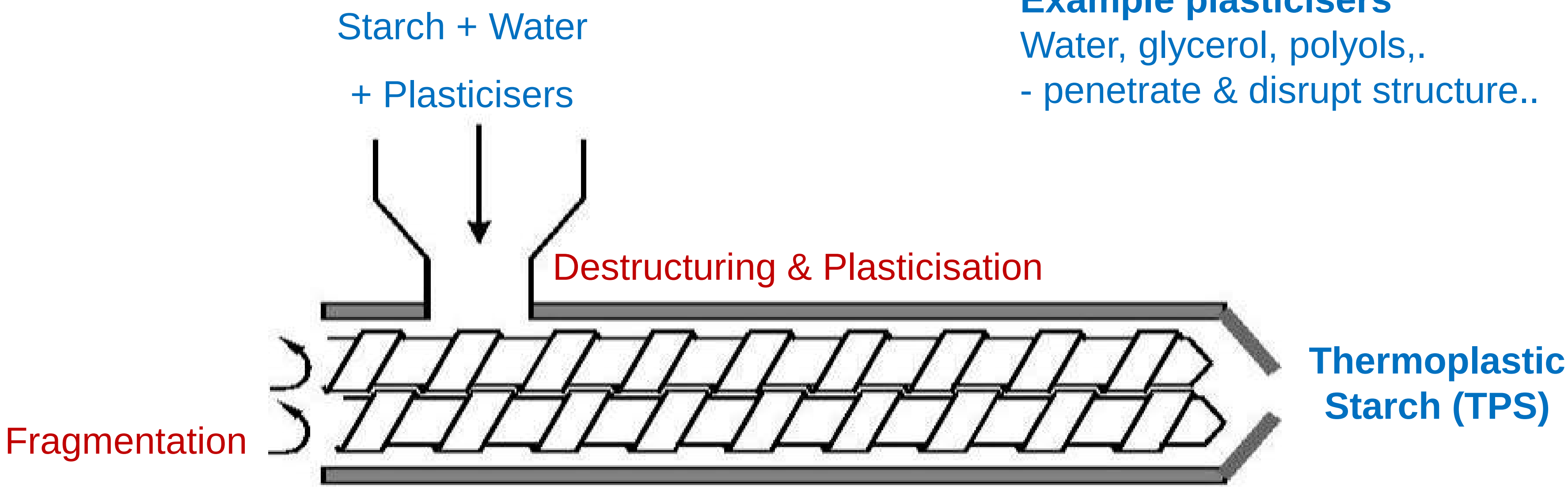
- Extracted cereals, legumes, tubers:
  - wheat, potato, maize, rice, cassava, pea,.
- Widely available, low cost & renewable
- Not inherently plastically processable
- Compostable

How are the plastics made?

- Use as a filler
  - In bioplastics & plastics (hybrids)
- Plasticisation
- Reactive modification
- Blending / reactive blending

Thermoplastic Starch (TPS) / Plasticised Starch

- Starch can be gelatinised with heat and water
- Plastically processable material



Example plasticisers
Water, glycerol, polyols,.
- penetrate & disrupt structure..

TPS - Performance

- Moisture sensitivity
- Basic TPS: low mechanical properties
- Can release water during processing
- Modification / blending improves processing/properties

- Wide range of blends with other polymers/reinforcements
  - can improve/tailor properties : “PE-like”
  - can increase cost
  - PVAC/PVOH, .. polyesters....
  - Cellulose fibres/fillers
  - Oils, waxes, other additives

Comparative Properties – Mater-Bi / Polyethylene

	Mater-Bi Film	PE Film (typical)
Tensile Strength at Break (MPa)	25-45	8-18
Elongation (%)	250-800	150-700
Modulus (MPa)	100-450	100-200
MFI (dg/min)	2-6	0.1-22

Example Producers (Starch Bioplastics)

Company	Tradename	Capacity tpa	
Novamont	Mater-Bi	60 - 80,000	Starch-PCL/PVOH blends; others (polyesters; oils)
Rodenberg	Solanyl	40,000	Partially fermented starch
Biotec	Bioplast	20,000	Starch polyester blends TPS
Cereplast		20 - 100,000 ?	Starch – PE / PP Starch polyester blends
Limagran	Biolice	10,000	Starch polyester blends
Livan		10,000	Starch blends
BIOP	Biopar Bioparen	3,500	Starch polyester blend Starch acetate blends
Cardia			
Plantic		5,000	

Example Uses

www.plantic.com.au

www.novamont.com

Cellulose Plastics

What is the feedstock?

- Extracted from plants (wood, grasses, crops, ..)
- Widely available, low cost (feedstock) & renewable
- Not inherently plastically processable
- Compostable

How are the plastics made?

- Use as a filler (powders/fibres) in plastics/bioplastics
- Dissolution &/or in-situ processing/modification
  - Regenerated cellulose (pulp) process
    - Cellophane™ / Natureflex™ : **cast films (Innovia)**
  - Cellulose Esters/Ethers
    - o Acetate (CA), Butyrate (CAB), Propionate (CAP)….
    - o *Tenite-Eastman; Rotuba Naturacell*

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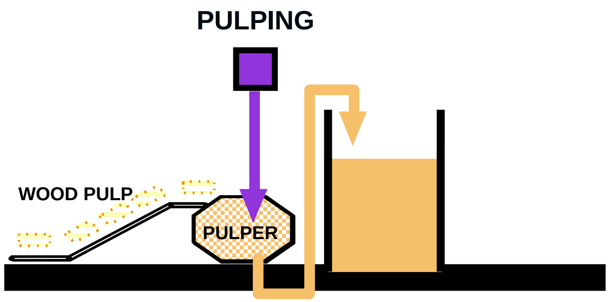
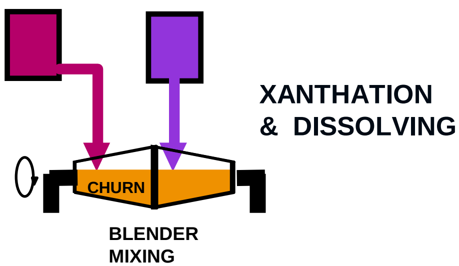
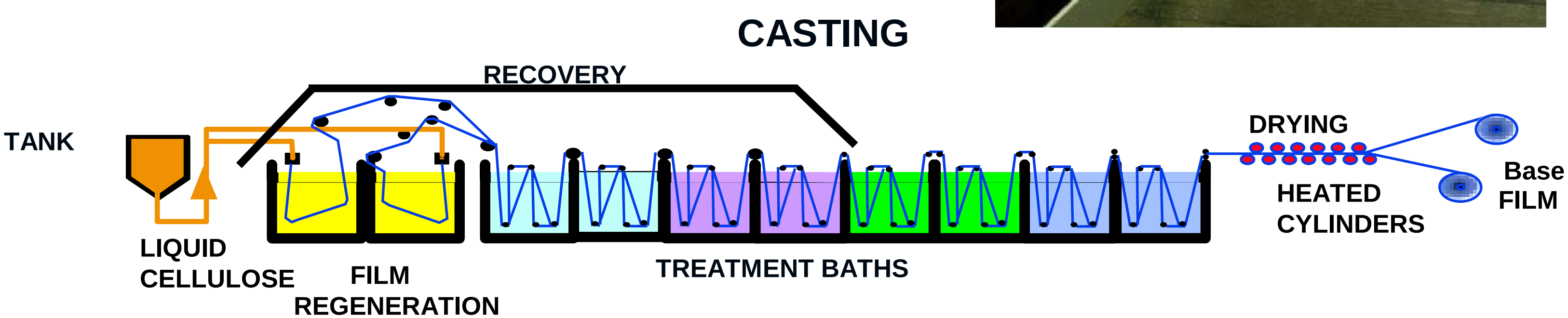
The Regenerated Cellulose process



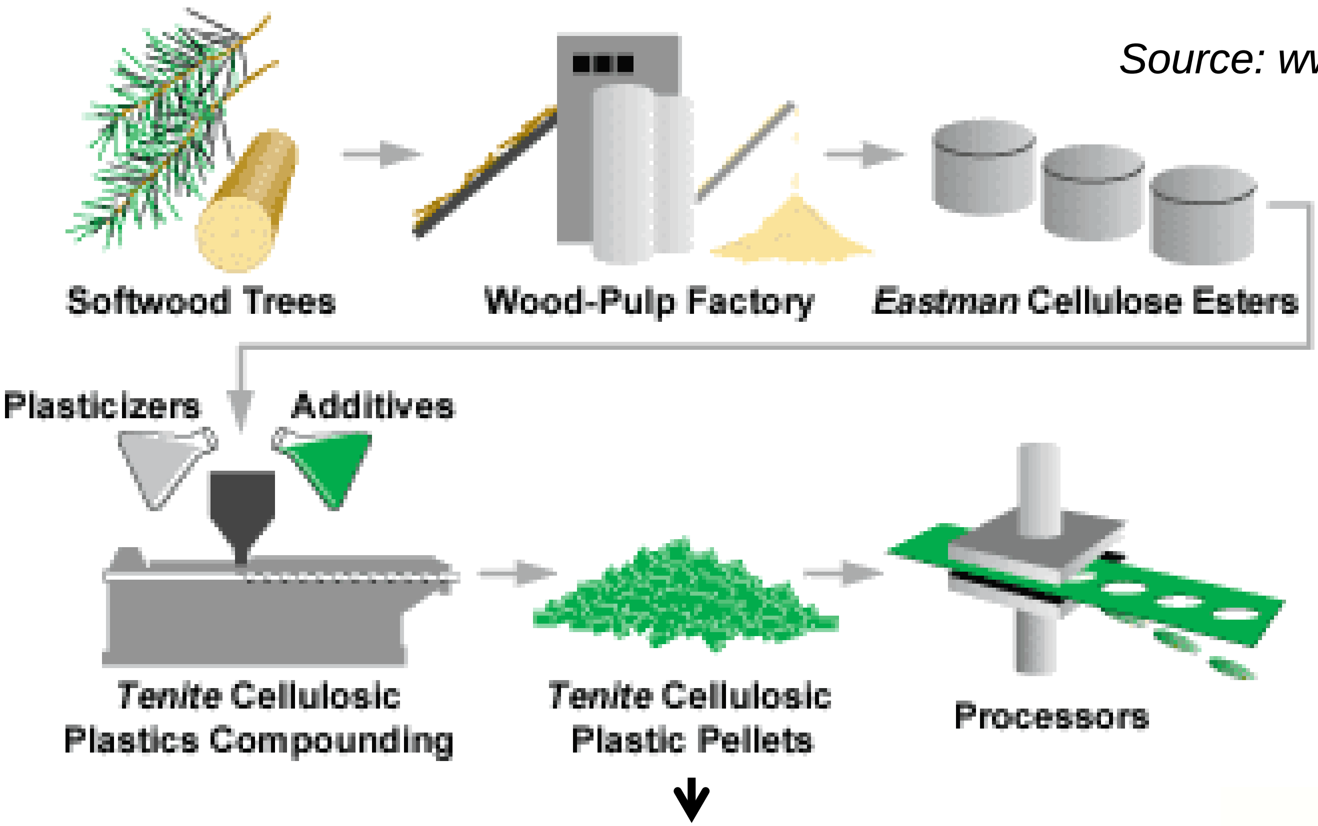




Source: Innovia Films

Cellulose Ester (Tenite – Eastman)

Source: www.eastman.com

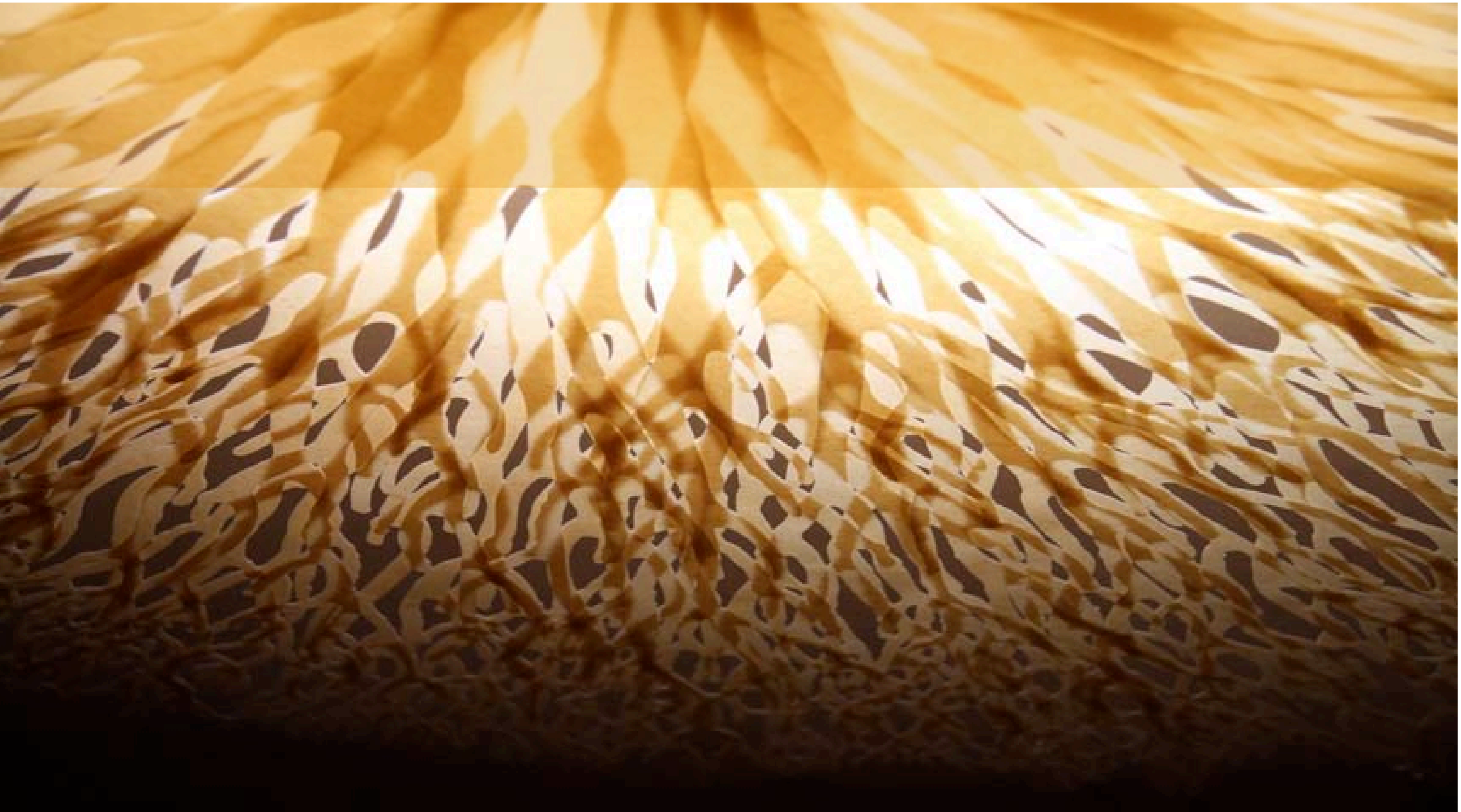


CA - cellulose acetate
CAB - cellulose acetate butyrate
CAP - cellulose acetate propionate

Cellulosic Esters: Example Performance

	CA Cellulose acetate (+ plasticisers)	CAB Cellulose acetate butyrate	CAP Cellulose acetate propionate
Tensile Strength at Break (MPa)	30-50	40-50	33
Elongation (%)	20-80	~ 50	45
Modulus (MPa)	1260	880	940
	Lowest cost	Lowest water absorption	
	excellent gloss & colours/transparency; good chemical resistance,....		

Leading Compostable Polyesters



Compostable Polyesters

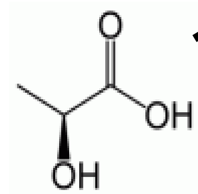
Renewable & Compostable	Not yet fully renewable- but compostable	Precursors & Processes
PLA		Lactic acid/lactide *fermentation + chemical polymerisation*
PHAs		Biomass/waste + microbes *fermentation to polymer (+ extraction)*
	PBS	**B**utanediol + **S**uccinic acid *(chemical polymerisation)*
	PBSA	**B**utanediol + **S**uccinic & **A**dipic acids
	PBAT	**B**utanediol + **A**dipic & **T**erephthalic acids
	PCL	Caprolactone

Reference : PET (not compostable) : **E**thylene Glycol + **T**erephthalic Acid
PBT (not compostable) : **B**utanediol + **T**erephthalic Acid

PLA – Polylactide/Polylactic acid

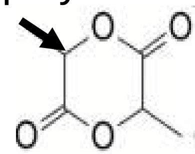
Starch/sugar source

Fermentation



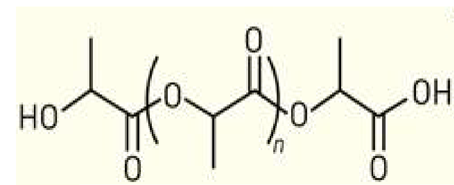
Lactic acid
(LA)

Prepolymer



Lactide
(acid dimer)

Polymerisation



Polylactic acid

Chemical Processes

Products

Future trends:

- Current sugar sources : corn, sugar beets/cane,..
- PLA (LA) from **cellulosic** raw materials, agri-wastes, non-food plants
- Copolymers (eg M700 lactide) & higher performance

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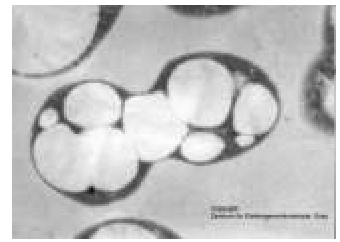
PHA(s) - PolyHydroxy*Alkanoates*

Starch/sugar
Source

→

Fermentation
(bacteria make the polymer)

→



Bacteria with PHA

↓

Downstream extraction to polymer & processing / products

Future trends:

- PHA from bacteria & wider range of feedstocks
  - municipal waste water, palm oil,.....
- Copolymers, co-products & advanced gene technologies
- Lower cost downstream processing/compounding
- PHA grown IN plants (GMO)

PBS/PBSA/PBAT: Compostable Aliphatic Polyesters

Butanediol (B)
+
Succinic Acid (S)
etc

www.petnology.com

Chemical Processes
Esterification & Polycondensation
(*similar to PET production*)

Polymer
PBS *etc*

processing/products

Future trends:

- Scale up & lower cost production
- New bio-monomers → polymers / copolymers
  - Bio-succinate (Bioamber ; DSM/Roquette)
  - Bio-butanediol *from* bio-succinate ;
  - Bio-adipate

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Example PLA & PHA Producers

Company	Tradename	tpa capacity	
Natureworks (USA)	Ingeo	140,000 -	PLA
Teijin (JP)	BIOFRONT	10,000	PLA
Mitsui, Shimadzu, Dai Nippon, Unitika (JP)	Lacty, Lacea, ..Terramac	each <5,000	PLA
Purac (NL) + Futerro/Galactic; Synbra		5,000 / 5,000	PLA
Pyramid (D)		5,000 -	PLA
Hisun ; Henan Jindan (China)			PLA
Mitr Phol (Thailand)			PLA
Mirel (Metabolix-ADM)	Telles	50,000	PHB/PHBV
Biomer (D)		3,000	PHB/PHBV
Tianan Biologic(China)	ENMAT	5,000- 50,000	PHB/PHBV
Meredian (USA)	Nodax	5,000	PHB/PHBV
Tianjin/DSM (China)			PHB
Kaneka (JP)			PHB

Example PBS, PBSA, PCL Producers

Company	Tradename	tpa capacity	
Showa Highpolymer (JP)	Bionolle		PBS/PBSA
IRe (K)	Enpol		
SK Polymers (K)	SkyGreen BDP		
PTT/Mitsubishi (Th)		20,000 ?	PBS
BASF (EU)	Ecoflex	14,000-60,000	PBAT
IRe (K)	Enpol G8060	~ 10,000	
Novamont (EU)	Eastar Bio	~ 10,000	
SK Polymers (K)	SkyGreen BDP	5,000	
Union Carbide (USA)	Tone		PCL
Perstorp (ex Solvay) (EU)	CAPA		
Daicel Chemical (JP)	Placeel		
BASF (EU)	Capromer		

Reference: Global PET Production ~ 30Mtpa (30,000,0000 tpa)

PLA – Properties

- Compostable (industrially), and recyclable
- Plastically processable
- **Limitations**
  - brittle; poor heat stability & melt strength ; poor gas barrier

Property	**PLA relative to PS**	**PLA relative to PET**
Optical properties	Similar	Similar
Mechanical properties	Similar or Better	Worse or Similar
Heat Distortion (HDT)	Lower	Lower
Heat sealing	Better	Better
O_2 and CO_2 barrier	Better	Worse (~ 1/10)
Water permeability	Higher	Higher
Aroma barrier	Better	Similar

PLA – Example Uses

PLA Modifications & Related Developments

- **Compounding / Reactive Compounding**
  - Other biopolymers (PLA/starch; PLA/PBS; PLA/PBAT,...)
  - Other polymers (PLA/PC; PLA/ABS; PLA/PET; PLA/PVC)
  - Additives
    - Fillers / Fibres / Chemicals / Polymers

- **Copolymers/Related New Polymers**
  - Developmental
  - **Polyglycolic acid (PGA: Kureha: 4000tpa (~$100M))**
    - High gas barrier coating
  - **Stereo-isomers & co-crystallisation**
    - High heat resistance

PHB (Polyhydroxybutyrate) – Properties

- Industrial and **home** compostable & recyclable
- High humidity barrier
- Better O_2 & CO_2 barrier than PLA ; worse than PET
- **Limitations:** opacity; cost / availability, processing window

Barrier Properties	**WVTR**	**O_2**	**CO_2**
NatureWorks PLA	18 - 22	38 - 42	170 - 200
PET	1 - 2	3 - 6	15 - 25
PHB	7 - 15	~ 25	~125

units: g-mil/100 in2 day for WVTR and
cc-mil/100 in2 day atm @ 20 C and 0% RH for O2 and CO2

PHAs are a family: PHB, PHV, ... PHBV

- PH**B** : polyhydroxy**b**utyrate
- PH**V:** polyhydroxy**v**alerate, ... and
- Copolymers (eg PH**BV** : polyhydroxy**b**utyrate-**v**alerate):
  more "V" content : more processable; greater ductility

Property	**PHB**	**PHBV (10 mol% V)**	**PHBV (20 mol% V)**
Tm, C	177	140	130
Crystallinity, %	80	60	35
Tensile strength, MPa	40	25	20
Flexural modulus, GPa	3.5	1.2	0.8
Extension to break, %	8	20	50
Notched izod impact strength, J/m	60	110	350

PHA – Uses

- Slow uptake (Mirel)
  - Production-extraction ?
  - Pricing ?
  - Client product developments/sampling

- BioTuf® (by Heritage - US) compostable bags
- Shampoo bottles - US, Germany, and Japan
- Injection moulded: cutlery, closures,....
- Thermoformed: hot cups, lids, food trays

- *www.ecogenlife.com*

mirel
Bioplastics by Telles

PBS/PBSA - Properties, Uses, Limitations

Properties

- Degrade: compost, wet soil, fresh/sea water & activated sludge
- Good processability
  - films, sheets, filaments, laminates, moulded products

Uses/Developments

- Blended with starch
  - improves moisture resistance & processing of starches
- Blended with PLA to toughen

Limitations

- Cost and availability
- Not yet renewable

PBAT - Properties, Uses, Limitations

- Ecoflex (PBAT) - designed to process like LDPE
- Blended with PLA = Ecovio® by BASF
  - First application - flexible films for shopping bags
  - Degrades faster than PLA alone
  - Good adhesion of thin layers to paper for coatings
- Blended with starches to improve processing & water resistance/other properties
- Blended with PHA for BioTuf® (by Heritage - US) compostable bags
- Low strength/modulus

Property Comparisons

	PLA	PBS	PBSA	PBAT	PCL
HDT (C) (0.45MPa)	**55**	**97**	**69**		
Modulus (GPa)	**2 - 3.3**	**0.6-0.7**	**0.3-0.35**	**0.35-0.5**	**0.4**
Tensile Strength (MPa)	**50-60**	**30-40**	**~20**	**25-45**	**15-30**
Elongation (%)	**<10**	**50-700**	**400-900**	**560-700**	**>500**

Many blend possibilities

Bioplastics Summary

- HIgh market growth
- Biobased (renewable) and ‘biodegradable’
- Biobased / partly biobased and durable
- Based on fossil resources and ‘biodegradable‘

- **‘Biodegradability’** and other behaviours are directly linked to the chemical structure and not to the origin of the raw materials

- Three leading types of **compostable bioplastics** are:
  - Starches
  - Cellulosic
  - Polyesters (some)

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Thank You