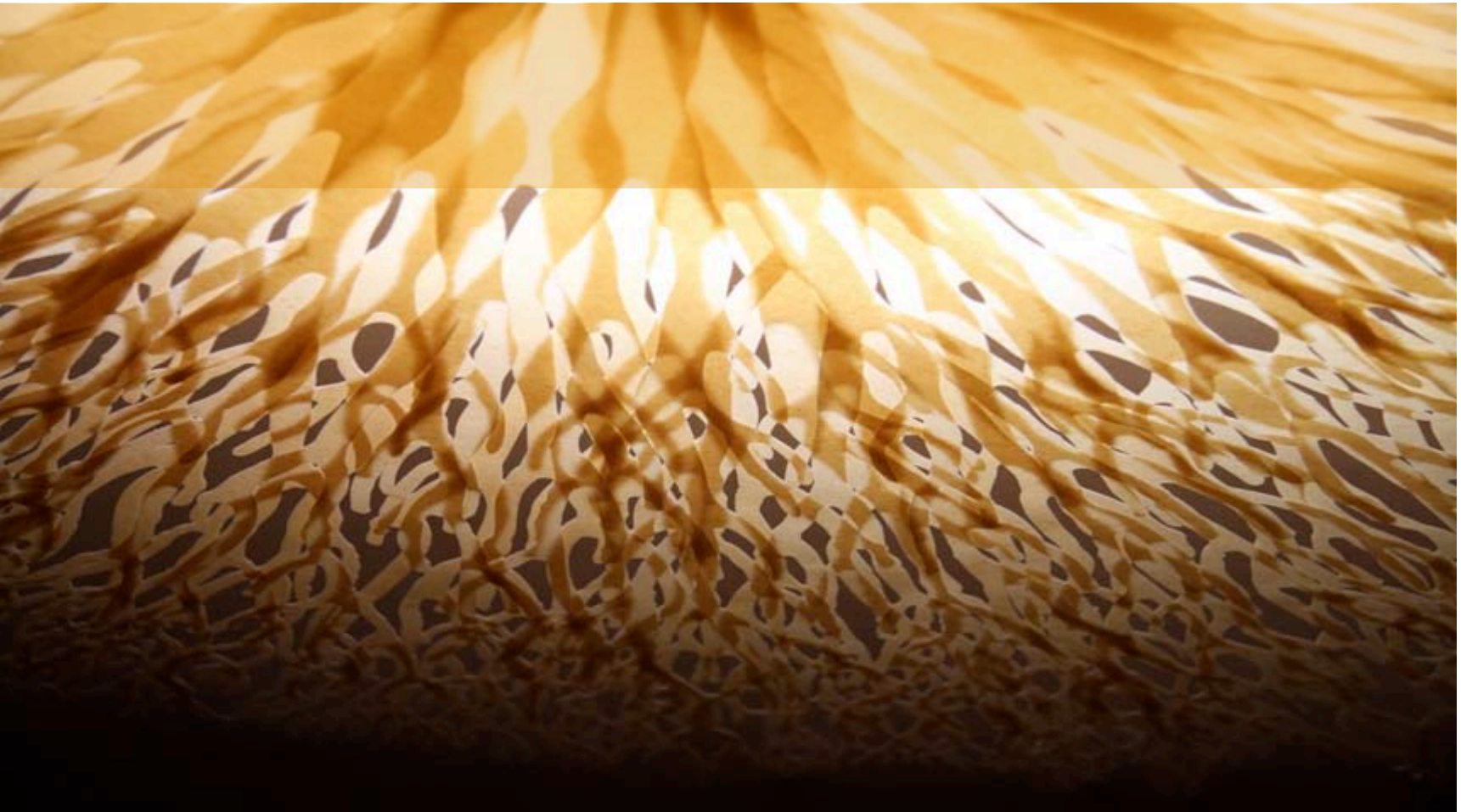


Other Emerging Bioplastics

Dawn A. Smith, Scion



Emerging bioplastics

- Bio-refinery concept
- Recent advances in renewable resourced traditional plastics
 - Bio-polyethylene (bio-PP & bio-PVC proposed)
 - Hybrids
 - Bio-PET
 - Bio-polyamides and polyurethanes
 - Bio-blends
- Latest advances in additive technologies for bioplastics

Moving to renewably resourced plastics



Heat, pressure
→
Millions of years



→
Plastics
PE, PP
PET, ...



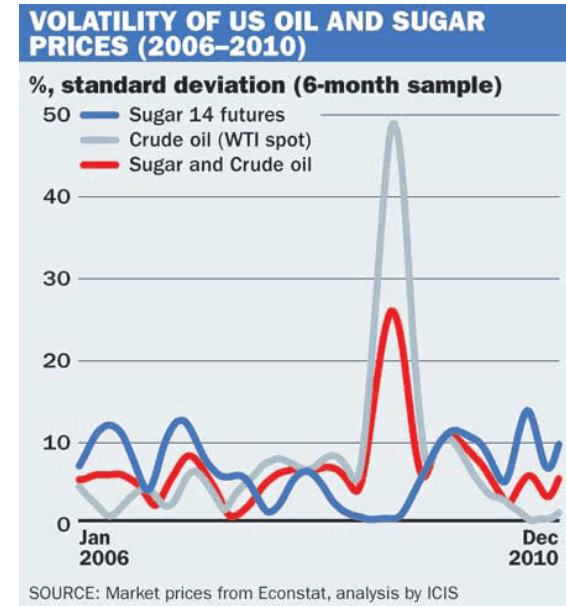
Modern chemical
→
processes



→
bio-Plastics
bio-PE, bio-PP
bio-PET, ...

Supplementing Supply Chain

- Price of crude oil fluctuates, so price of intermediates and polymers fluctuates.
- Industrial biotechnology
 - True drop-in materials (origin only difference)
 - Supplement the existing supply chain
 - Lower price volatility
- Agriculture can also be volatile.
- Future feedstock: biomass / municipal waste
- “story” or not, it’s good business



Oil-Refineries and Bio-Refineries



- Oil-refinery:
 - Crude oil (finite) as feedstock
 - Established technology
 - Very efficient use of feedstock



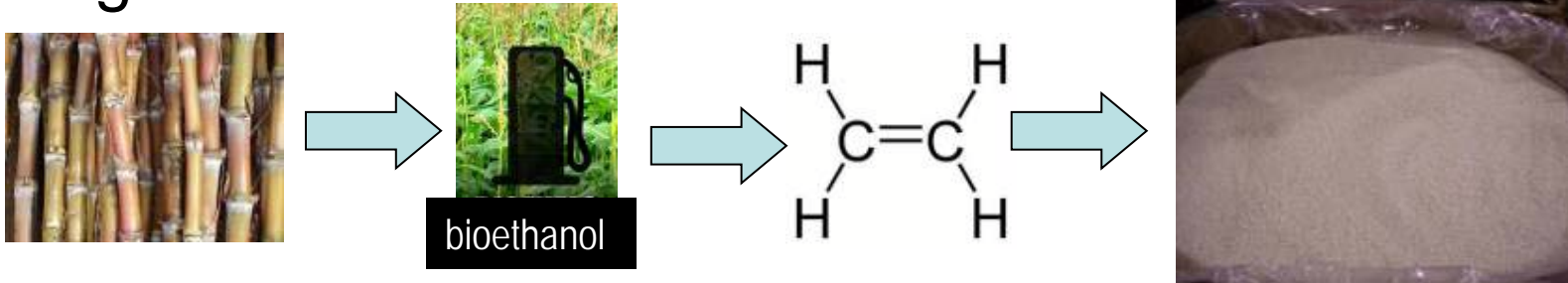
- Bio-refinery (1st generation)
 - Starch/sugar (renewable) as feedstock
 - Technology established
 - Efficient use of feedstock



- Bio-refinery (2nd generation)
 - Non-food biomass (renewable) as feedstock
 - Logistics?
 - Technology under development

Bio-ethylene

- No technical hurdles for producing ethylene from sugars/starch



- **Braskem (Brazil)**

- Q4 2010: 250,000 tpa
- Planned by Q4 2012: 1 million tpa

- **Dow/Mitsui (Brazil)**

- Planned by 2015: 350,000 tpa bioethanol

- **Solvay (Brazil)**

- Planned PVC and PVA from bioethylene
- expected capacity of 60,000 tpa of bioethylene for conversion into PVC.

PE: polyethylene

renewable;
not compostable

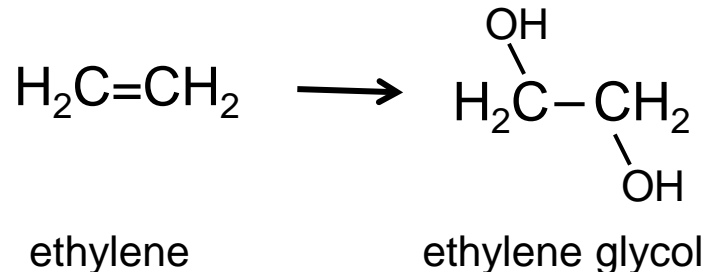
Brazil - Braskem

- 80% of the plant's production already sold
 - Toyota, Tetrapak, P&G
 - blown packaging (food & hygiene products)
 - household appliances, toy & automobile industries
- Bio-HDPE potential for lower cost than petrochemical technology
 - initial pricing ~ 25-50% higher
- Bio-based butene → bio-derived LLDPE
- Bio-polypropylene - under development



Bio-ethylene glycol from bio-ethanol

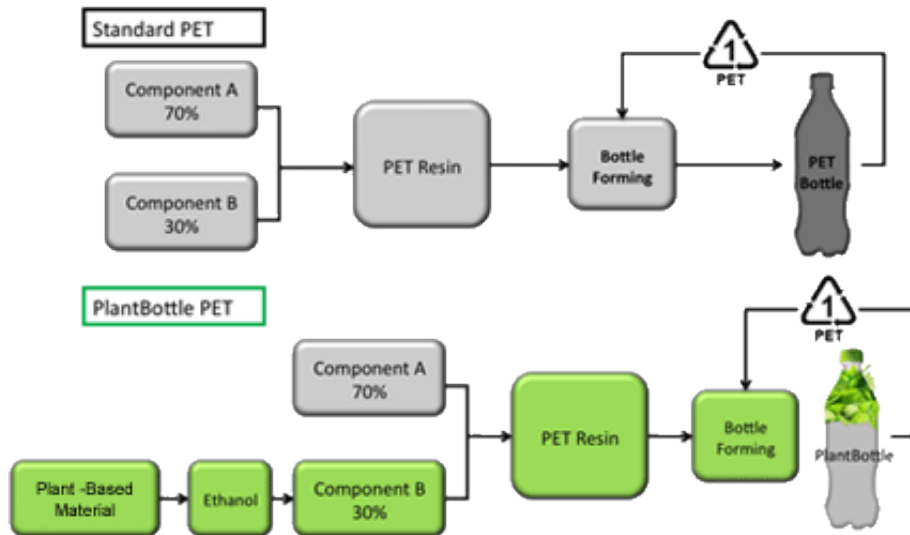
- Bio-ethylene glycol (bio-EG)
 - India Glycols - from bio-ethanol since 1989
 - Novepha in China
 - GTC (Greencol Taiwan Corp), a 50/50 JV (China Man-Made Fiber & Toyota Tsusho), is building a 100,000 metric ton biobased ethylene facility in Taiwan and will produce bio-EG



Hybrid Polyester - PET

- **“Partial Bio-PET” The PlantBottle™**
 - bio-EG (the “E” in PET) → ~30% renewable
 - sugar cane / molasses (Brazil) to bioethanol to bio-EG
 - future feedstocks: corn stover, switchgrass, wood chips
 - Terephthalic acid = non-renewable content
 - processes in existing manufacturing/recycling facilities

How is plantbottle™ PET Manufactured?




plantbottle™
up to 30% plant-based
100% recyclable bottle
redesigned plastic,
recyclable as ever.



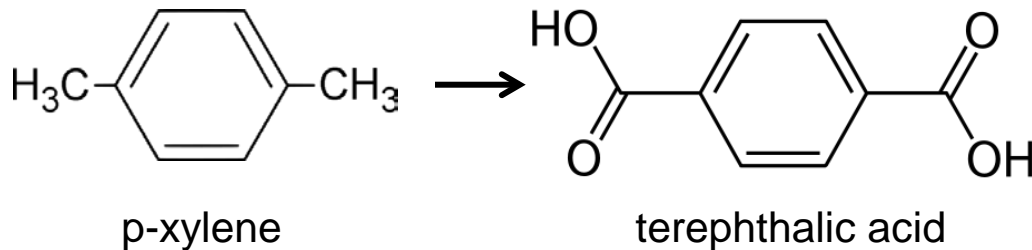
Bottle-Wars !

- **Pepsi unveils 100% plant based PET bottle (2011)**
- PepsiCo. has developed its own bio-PET bottle – 100% bio-based raw materials
- The bio-PET is manufactured using the company's agricultural by-products from its food business, including switch grass, pine bark and corn husks.
- Processes in existing manufacturing/recycling facilities
- Pilot production phase of bottle in 2012



Bio-paraxylene (PX)

- US-based Virent to produce bio-PX in a commercial biorefinery via catalytic chemical reactions (not fermentation) from plant sugars
- PX is a precursor for terephthalic acid, PET
- In 2011 - 38,000 L PX / year



More bio-intermediates

- Bio-succinic acid
 - BioAmber, DSM/Roquette, BASF/Purac, Mitsubishi and Myriant
- Bio-butanediol (also THF and γ -butyrolactone)
 - Tate & Lyle, M & G and Mitsubishi Chemical
- Bio-isobutene and isobutanol
 - Gevo/Cargill and LANXESS
- Bio-acrylic acid
 - Dow, Arkema, BASF and Nippon Shokubai
- Bio-methyl methacrylate
 - Arkema and Evonik

Bio-polyamides (Nylons) based castor oil

Nylon11 (100% castor oil)

- Arkema/Atofina: Rilsan
- Rhodia: Technyl



Nylon4,10; Nylon6,10 (~60 – 70%)

- BASF: Ultramid Balance
- DSM: EcoPaXX
- DuPont: Zytel
- Evonik: Vestamid Terra HS



Nylon10,10 (100%)

- DuPont: Zytel
- Evonik: Vestamid Terra DS



bio-based TPE from Nylon11 / polyether blocks

- Arkema Pebax® Rnew

“The big reason for the surge in castor oil nylons is reduction of the material's carbon footprint “

Bio-polyurethanes

- **Bio-polyurethanes / bio-polyols (soy or castor oil)**
 - Bayer, Huntsman, Urethane Soy Systems Co. (USSC)
 - Dow RENUVA™ Technology (soy)
 - Agrol® polyols (soy)
 - Vertellus (castor)
- **Mouldings & Foams**
 - Lupranol Balance 50 foams (BASF)



Bio-polyols

Produce less emissions, use less total energy

- **Note:** isocyanate component still petrochemical based

Ford Motor Company – now (and then)

- As of 2011, all Ford North American-built vehicles use bio-based foam in seat cushions and backs.



media.ford.com



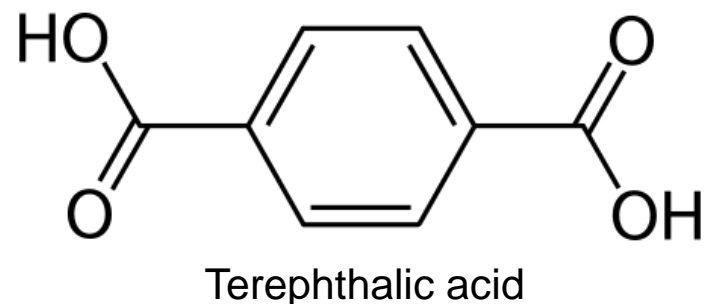
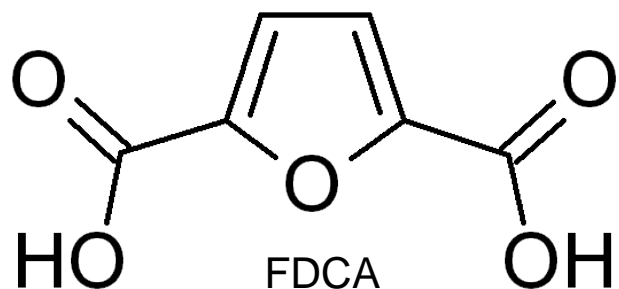
- Henry Ford unveiled the now-legendary "soybean car," with soy-based plastic body panels, in 1941.

NEW intermediates

- Industrial biotechnology is a way to supplement existing supply chains
- Not seen as a source of novel green intermediates YET!
- Current materials don't meet all needs.

New monomers – FDCA by Avantium

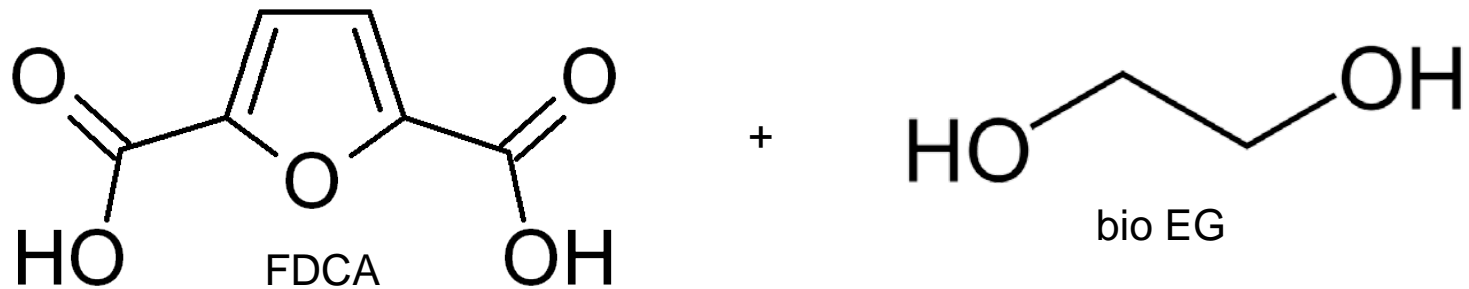
- FDCA from fructose, similar to terephthalate (PET)



- Pilot plant - 40 tpa of FDCA monomer in 2H 2011
- Polymerise with EG to for PEF
- Solvay and Avantium to jointly develop green engineering plastics - polyamides from FDCA

New polymers – PEF “yxy” by Avantium

- PEF “yxy” – a PET alternative

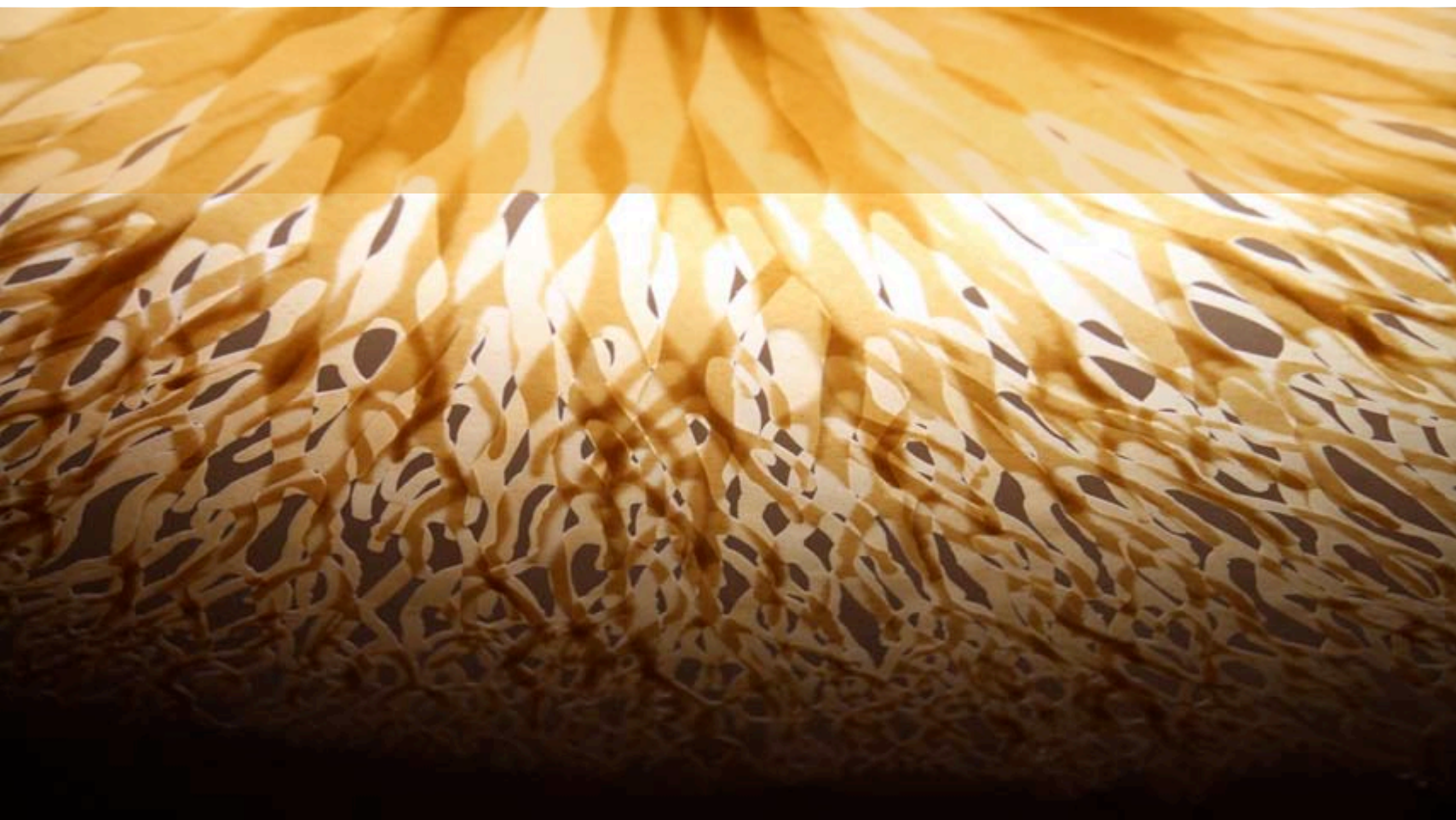


- 6 x O₂ barrier than PET
- 2 x CO₂ & H₂O barrier than PET
- Higher T_g and lower processing temp than PET

renewable;
not compostable



Bioplastic Blends



Hybrid Blends

- Biopolymers
 - relatively costly
 - less than desired properties or processability
- Blends (PVC-PLA, PC-PLA, PET-PLA ...)
 - Can claim x% renewable content
 - retain properties and reduce cost
- *Natureworks* PLA 3801X: 80% biobased (PLA)
 - thermal stability to 120°C & high impact strength
- *PolyOne* - reSound Biopolymer: ≥ 30% PLA, PHB, or PHBV
- *RTP Company*
 - PLA - Bio-PA blends: 32-80% bio-content
 - PLA with PC, PMMA, or ABS
- Starch blends
 - Starch-PE; Starch-PP etc (Cereplast & others.....)
 - *Caution “biopropylene”*



PLA Blends: “Bio-Polycarbonate”

- *Bayer Material Science*
 - two bio-content PC/PLA blends
 - *Unitika* : hybrid PLA,PC, compatibiliser
 - increased HDT, reduced brittleness and rapid crystallisation
 - suitable for electronics applications
 - *Mitsubishi Plastics*
-
- PLA/PC blends don't readily decompose like PLA
 - Uses include mobile/smart phones, portable electronics, furniture, sporting goods and automotive interiors
 - In some examples, PLA improves the properties
 - Samsung Reclaim uses PLA/PC for cell phone housing
 - PC/PLA showed better fatigue resistance than PC/ABS



www.samsung.com

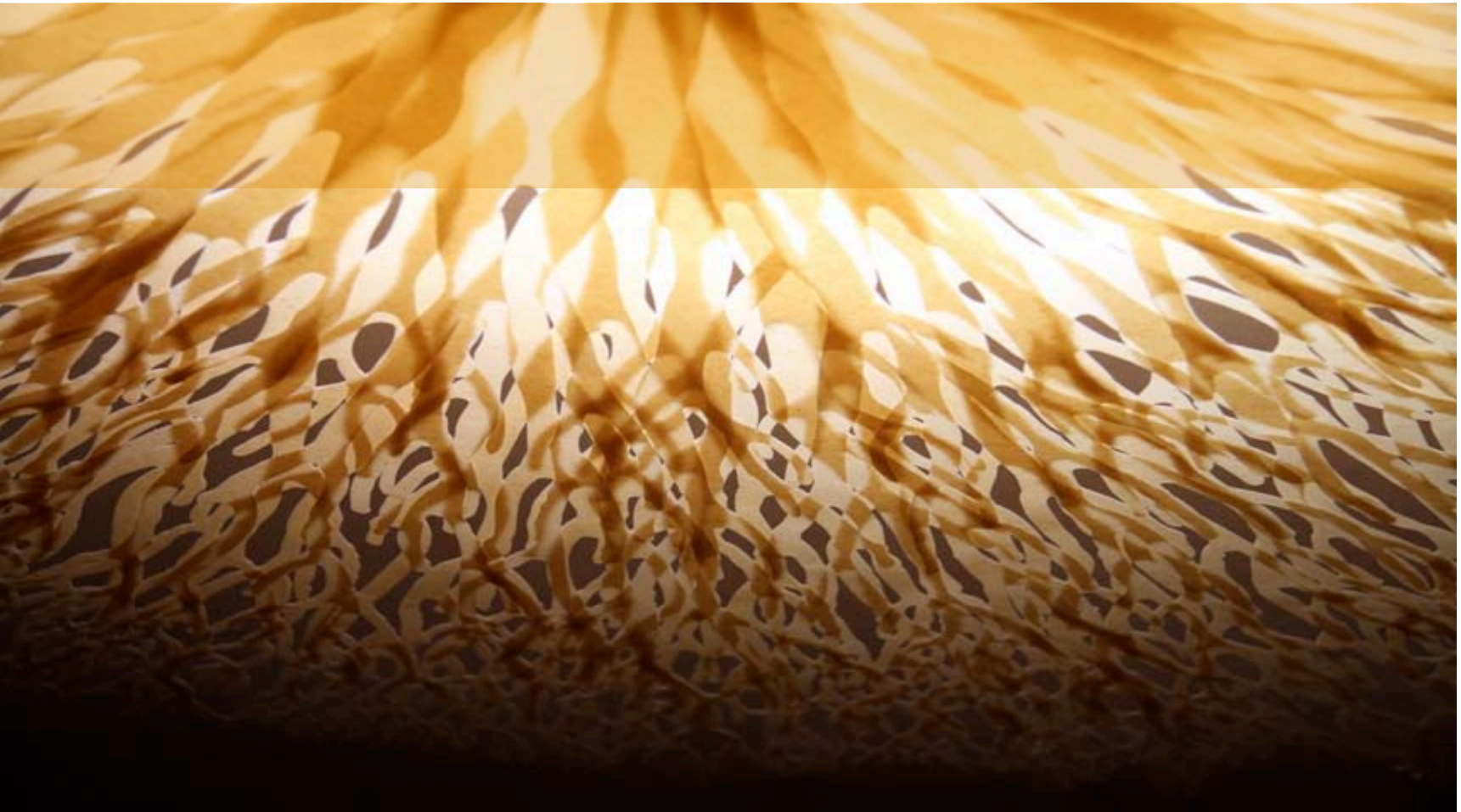
PLA - Blends

- ABS with PLA, a 2-phase blend that is opaque with reduced brittleness
- Blending PLA with PE or copolyesters also reduces brittleness
 - e.g. FKUR Bio-flex – PLA with copolyesters
- Unitika
 - PLA/PMMA blends (clear): PMMA raises T_g
 - developing PLA alloys with PP and PC
- Polymaterial Technology Co. (Thailand)
 - Four commercial EcoHybrid grades are alloys of bio- and petro-based plastics: PLA/PHA with either PP, TPU, PETG or ABS
 - Heat-resistant PLA/PHA and PLA/PHBV compounds with T_g up to 80 C for injection moulded durables - dishes and housewares
- PLA/Nylon 6 compounds for durable applications



Fully degradable toothpaste tube for Swedish company, FKUR Bioresin

Trends in Additive Technologies



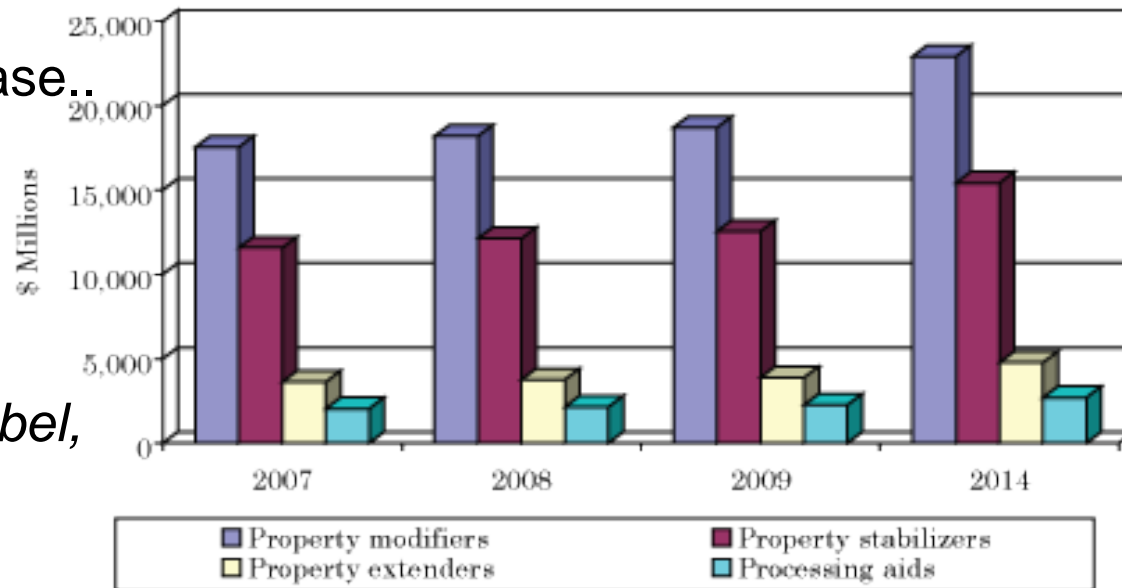
Additive Technologies

- Plastics Additives industry
- Additives for bioplastics to improve/change properties
- Bio-fillers for all plastics

Plastic Additives

- **>US\$30B**
- plasticisers, colourants
- impact modifiers, flame retardants
- heat/light stabilisers,
- antioxidants, antimicrobials
- conductive: heat/thermal
- anti-fogging; lubricants/release..
- Major producers
 - Chemtura, Exxon Mobil
 - BASF-Ciba, Eastman,
 - Rohm & Haas (Dow),
 - Ferro, Arkema, Akzo Nobel,
 - Clariant, Albermarle
- PVC major market

SUMMARY FIGURE
GLOBAL MARKET FOR PLASTICS ADDITIVES, 2007-2014
(\$ MILLIONS)



Source: BCC Research

Additives for Bioplastics

Various companies are investing in additives and compounds for bioplastics:

- *Sukano*
- *Danimer*
- *DuPont*
- *Rohm & Haas (Dow)*
- *Arkema*
- *Polyone*
- *Clariant*
- *Ampacet*
- *Teknor*
- *Cereplast*
- *BASF*

Additives for Bioplastics

- **Not all options are bio-based**
- ***“Traditional” additives***
 - no adverse effects (health, environment; compostability stds)
- ***“Renewable” additives*** derived from natural sources
 - not necessarily biodegradable: renewable story/benefits
- ***“Renewable” and “biodegradable”***
 - single-use/short-lived products or end-of-life compostability
- **Tianan Biologic (PHBV)**
 - *“not bound by renewably sourced additives, as long as no adverse effects”*
- **Metabolix, and Meredian (PHAs)**
 - *“only biobased additives”*



Impact/Strength Modifiers for PLA



Biostrength® 280 Impact Modifier for PLA clear

Biostrength® 150 Impact Modifier for PLA opaque

Teknor Apex will supply masterbatches based on these additives under its **Terraloy™** bioplastics brand name.



Paraloid™ BPM-500 and 515 Acrylic Impact Modifiers for PLA clear

Paraloid™ BPM-520 Impact Modifier for PLA opaque



Biomax® Strong additives for impact strength, flexibility and melt stability for PLA clear



Sukano im S555 – impact modifier for PLA clear



Danimer Impact Modifier



Heat Deflection Temperature (HDT) enhancers



HDT additive – raises HDT from ~57 °C for neat PLA to as high as 100 °C



Danimer HDT modifier to 88 °C



Biomax Thermal 300 modifier to 95 °C



Terraloy BP-39070 series to 100 °C (high heat & impact resistant - microwaveable, thermoformed trays)

Mould release agents



Biostrength® 900 Metal Release for PLA



Sukano mr S533 – mold release



Melt strength modifiers



Biostrength® 700 Melt Strength Enhancer



Joncryl® ADR Chain Extender for PLA



Exactly your chemistry.

Clariant's CESA-extend chain extender



Colour/Opacity/Clarity modifiers



translucent & opaque masterbatches



Exactly your chemistry.

Renol-natur color masterbatches -“all-natural” pigments derived from plants.



Sukano na S516 and na S516-IceClear – transparent and opaque nucleating agents

Sukano ob S515-N or ob S515-BL – optical brightener and white, black, and colour masterbatches



PolyOne Bio-Color (partly sustainable raw materials)



Teknor Color for PLA resins and blends.



UV resistance / antioxidants

PolyOne[™]

 Clariant

Exactly your chemistry.

CESA-natur antioxidants, which use natural antioxidants like vitamin E

Others

**KA
SUONO**

 Clariant

Exactly your chemistry.

Sukano dc S511 – anti-blocking
Sukano as S546 – antistatic
CESA-natur antistatic masterbatches



Plasticisers – natural alternatives

- Alternates to phthalate plasticisers for PVC
 - Polyone and ADM – soybean-based
 - Segetis – ketal monomers from corn cobs
 - Roquette - Polysorb ID37 from isosorbides
 - Dow ECOLIBRIUM™ Bio-Based Plasticizers
 - Specifically for wire and cable applications
- General Bio-based Plasticisers
 - Glycerols/polyglycerol/glycerides
 - Sorbitols, lactates, citrates

“open source” strategy - Ingeo™ 3801X

- Ingeo 3801X – semi-durable, not certified as compostable, high-heat, high-impact bioresin
- Spurring innovation, NatureWorks LLC provides open source access to both formulation and compounding procedure.
- The full details of Ingeo 3801X recipe including impact modifier, crystallisation accelerant, and agents for reinforcement and nucleation are openly available to Ingeo customers.

Bio-fillers for all plastics – “weight savers”

- LignoMAXX – steam-exploded DDGs (Lignotech)
- Agriplast – wheat straw reinforced compounds
- Scion WPP – recently licensed to Sonae Industria
- Kareline® composites - fibre reinforced thermoplastic composites in PP, ABS, PS, acetal and PLA
- Fibrolon (FKuR) – injection mouldable
 - Fibrolon P = PP with ~40% wood fibre
 - Fibrolon F = PLA with wood fibre
- Neroplast – xylite from lignite coal
 - Hydrophobic filler that can be processed with Nylon – up to 280C

The Future For Bio-Additives

- **More & More “Bio-based”**
 - Gas barrier enhancements
 - Tough (& transparent)
 - Heat & fire resistance
 - Durability
 - Anti-microbial
 - Anti-oxidant / stabilisers

Scion has technologies and current programmes in all of thesemost using NZ resources or residues
www.scionresearch.com

