Basic definitions, classifications and drivers for bioplastics

Feedstocks and concept of platform chemicals

Commercial and potential future biobased polymers for flexible packaging

Biodegradable plastics and barrier layer materials for flexible packaging

Some current markets and applications, bioplastics growth projections and market trends

“Green issues”, consumer and environmental concerns
Portmanteau term for plastics which are biobased, biodegradable or both. These include:

- Biobased plastics that are not necessarily biodegradable (including conventional polymers, e.g. PE, made from biobased monomers)
- Plastics containing both petro-based and bio-based components, e.g. PET, not necessarily biodegradable
- Biodegradable or compostable plastics derived from biobased materials, such as starch, cellulose, polylactides or polyhydroxyalkanoates
- Biodegradable petroleum-based plastics, e.g. PBAT
CLASSIFICATIONS OF BIOPLASTICS (I)

BIOBASED OR RENEWABLE PLASTICS:

- USDA Definition: Organic plastics composed wholly or significantly of recently fixed (new) carbon from biological sources such as renewable plant, forestry, animal, algal or marine materials (based on C\textsuperscript{14} content measurement as defined by ASTM D6866)

- Renewable within 1-2 years (vs. millions of years for petro-) via plant-biomass photosynthesis from CO\textsubscript{2} (biological carbon cycle)

- Focus is only on origin of carbon constituents

- May be fully biobased or partially biobased

- May be biodegradable or non-biodegradable. For non-biodegradables, end-of-life process is mechanical or chemical recycling or conversion to energy or downstream chemicals
CLASSIFICATIONS OF BIOPLASTICS (II)

BIODEGRADABLE AND COMPOSTABLE PLASTICS:

- Focus is only on disposal or “end-of-life” processes, independent of carbon sources
- Biodegradability is determined by polymer structure, not carbon source
- May be bio-based (renewable) or petro-(fossil-)based

THESE TWO CLASSIFICATIONS, BIOBASED AND BIODEGRADABLE, ARE NOT MUTUALLY EXCLUSIVE

BIOBASED DOES NOT NECESSARILY MEAN BIODEGRADABLE AND BIODEGRADABLE DOES NOT NECESSARILY MEAN BIOBASED

Over the past two decades, emphasis has moved from biodegradability to biobased origin.
Key factor is now whether the material has the performance properties for the specific application, including biodegradability where appropriate, and “biobased” being an expectation
INDUSTRY DRIVERS FOR BIOPLASTICS

- Increasing legislation & regulations globally restricting uses and disposal of petrochemical plastics and promoting bioplastics

- Growing regulatory, NGO and consumer concerns over carbon footprint, climate change, environmental & ocean pollution, health, “single use” plastics; Paris Agreement (COP21); circular economy

- Government & consumer demands worldwide to reduce dependence on fossil fuels and feedstocks and convert to materials made from sustainable and biobased resources which are recyclable, carbon neutral and have low environmental and health impacts

- Reduced production costs from agricultural/biomass feedstocks due to advances in thermal, catalytic, gasification, pyrolytic, supercritical fluid, microbiological and other processes to make cheaper, novel, improved-function materials
USDA “CERTIFIED BIOBASED PRODUCT LABELING PROGRAM”

- SETS MINIMUM THRESHOLD OF 25% NEW CARBON FOR PRODUCTS TO BE CONSIDERED BIOBASED

- FIRST “CERTIFIED BIOBASED PRODUCT” LABELS AWARDED MARCH 2011. NOW OVER 2700 CERTIFIED PRODUCTS
EUROPEAN COMMISSION LEAD MARKET INITIATIVE AND NEW BIOECONOMY STRATEGY

Improvement and scale-up of sustainable use of renewable resources and development of new sustainable bio-refineries across EU

Financing and research funding - €100M circular investment platform

Standards, labeling and certifications

Legislation promoting market development/green public procurement

EU Circular Economy package
EUROPEAN BIOBASED CERTIFICATION PROGRAMS

- **VINCOTTE “OK BIOBASED”** (Now TUV Austria)
  Certification marks for biobased content levels of:
  20-40%  40-60%  60-80%  >80%

- **DIN CERTCO**
  Requires minimum organic material proportion of 50% and minimum biobased proportion of 20%
  Certification marks for biobased content levels of:
  20-50%  50-85%  >85%
Bio-based plastics are made from a wide range of renewable BIO-BASED feedstocks.

- Agro-based feedstocks – plants that are rich in carbohydrate, such as corn or sugar cane.
- Ligno-cellulosic feedstocks – plants that are not eligible for food or feed production.
- Organic waste feedstocks
CONCEPT OF PLATFORM CHEMICALS

To make a renewably sourced material, only the FIRST chemical or monomer in the synthesis chain needs to be made from a renewably sourced feedstock. All later synthetic steps can be performed using standard chemical processes already developed for petrochemicals.

BIOETHYLENE CHEMICAL PLATFORM

Source: NNFCC
SOME POTENTIAL BIOBASED PLASTICS FOR FLEXPACK

Commercial:

- **POLYOLEFINS** - PE from bioethanol (totally biobased)
- **POLYESTERS** - PET (PlantBottle®) – partially biobased
  PLA (polylactide) & PBS (polybutylene succinate), 100% biobased/biodegradable
- **POLYAMIDES** - PA 5,10 (totally biobased)
  PA 4,10; 5,6; 6,10; 6,12; 10,10; 10,12 (partial bio)

Developmental:

- **POLYOLEFINS**: Polypropylene, PVC
- **POLYESTERS**: PET (totally biobased)
  PEF – polyethylene furanoate
  PTF – polytrimethylene furanoate
- **POLYAMIDES**: PA 6,6

Many are “conventional” rather than “new polymers”
SOME PRESENT AND POTENTIAL MANUFACTURERS OF BIOBASED NON-BIODEGRADABLE PACKAGING POLYMERS

- Braskem, DSM, Solvay, Arkema, Sabic, Neste  PE, PP, PVC

- DuPont, Teijin, DSM, SK Chemicals, Toray, Indorama  Aromatic Polyesters

- Synvina, DuPont/ADM, Origin  Furanoate Polyesters

- BASF, DSM, Arkema, DuPont, Toray, Cathay  Polyamides
GREEN POLYETHYLENE

- Braskem production in Brazil started 2010 using ethylene from sugar cane ethanol, capacity 200 ktpa
- HDPE, LDPE and LLDPE grades available, identical to petro-PE made by same polymerization process
- “Green PE” recyclable in same way as petro-PE
- Higher cost than PE from shale ethylene given 40% mass loss when ethanol is converted to ethylene
- Advantageous carbon-negative footprint and global warming potential over petro-based ethylene (-3.09 kg CO2 eq vs + 1.86) provides green marketing credentials
- Early packaging users included Coca-Cola (Odwalla), P&G, Danone, J&J, Tetra Pak, Avery Dennison, Seventh Generation, Ecover, Bramhults, Rosport, Plastic Omnium, Trudi, Printpack, Peel Plastics & Nestlé
“Only Natural Pet” dry dog food

Packaging incorporates 30% bioPE

Source: Braskem
PARTIALLY BIOBASED PET
Coca-Cola PlantBottle®

- Made with commercially available biobased ethylene glycol component up to 30% by weight
- This is up to 20% of renewable carbon
- Active development to produce biobased terephthalic acid to make commercial 100% biobased PET a commercial reality
BIOBASED ROUTES TO TEREPTHALIC ACID

Via p-Xylene

- Gevo: Fermentation of plant sugars (from lignocellulosic biomass) to isobutanol, then chemical route to isobutene and p-xylene
- Virent (Tesoro)/Renmatix: Chemical catalytic BioForming® Platform from plant sugars or cellulosic biomass to p-xylene. 10,000 gallon/yr pilot plant. 100% biobased PET bottles demonstrated with Coca-Cola
- Anellotech/Suntory/Toyota Tsusho: Catalytic Fast Pyrolysis (BioT-Cat) route to convert biomass to aromatics (BTX)
- Origin: Fermentation process from cellulosics to furanic intermediates to p-xylene
- BioBTX bv (Holland): Catalytic pyrolysis from glycerol or fatty acids. Pilot plant started up September, 2018
- Competitiveness with petro-TPA depends on oil prices
Catalytic Fast Pyrolysis (BioT-Cat) route converts non-food biomass (wood and wood wastes, sugar-cane bagasse etc.) to aromatics (BTX). BTX produced is a mixture of benzene, toluene and xylenes chemically identical to petroleum-based counterparts.

Pilot plant in Silsbee, TX. Over 2000 hours of cumulative onstream time achieved with continuous catalyst circulation. Plant scale-up design underway based on pilot plant data.

Cost competitive with petrochemical production together with large reduction in GHG emissions. Converting 100 KTA PET to 100% biobased PET is equivalent to removing 34 Mkm/year of car usage.

First shipment from pilot plant being converted by IFPEN (France) to p-xylene for production of bio-terephthalic acid.

BTX aromatics also used to make polystyrene, polycarbonates,nylons and urethanes and as biofuels blendstock for gasoline.
POLYETHYLENE FURANOATE (PEF)

- Synvina (Avantium/BASF; thermocatalytic); Corbion (microbiological); Dupont/ADM; Origin; AVA Biochem; routes from C6 plant sugars (fructose) or cellulosics to furan-2,5-dicarboxylic acid (FDCA) or methyl esters:

![Furan-2,5-dicarboxylic acid (FDCA) or methyl esters]

as alternative monomer to terephthalic acid (TPA)

- Potentially more favorable economics from plant sugars than TPA. No added hydrogen needed. Requires less than half the mass of sugar to produce a kg of FDCA compared to purified TPA
- Generates PEF as alternative to PET with improved properties
POLYETHYLENE FURANOATE (PEF) PROPERTIES VERSUS PET

- Property improvements over PET:
  THERMAL, PHYSICAL, PROCESSABILITY
  - Higher Tg; Heat distortion temperature increased by 12°C to 87°C
  - Lower Tm (213-235°C): easier processability at lower temperature
  - 60% higher modulus and tensile strength
  - Permits greater lightweighting and better thermal stability without heat setting – hot fillable at 85-90°C

BARRIER PROPERTIES

- Oxygen barrier: 6-10 times higher than PET
- Carbon dioxide barrier: 6-10 times higher than PET
- Water vapor barrier: 2-3 times higher than PET

- Can be biaxially oriented to improve properties
- 100% Biobased
- Recyclable with PET at least up to 7% level with no adverse effect on PET performance, or separable by NIR scanning and recyclable
FURANOATE POLYESTERS

SYNVINA (BASF/AVANTIUM) – POLYETHYLENE FURANOATE (PEF):
■ 40 tpa pilot plant in operation in Geleen, Holland.
■ Development with Coca Cola for beverage bottles, Danone for food packaging, and ALPLA Werke
■ Strategic partnerships with Mitsui and Toyobo for film, sheet and fiber products in Asia
■ 50ktpa “reference” plant in Antwerp, BE planned to be onstream 2023-2024 although parent companies are in dispute about investment timing. Technology then to be licensed to accelerate global industrial scale adoption

DuPont/ADM - POLYTRIMETHYLENE FURANOATE (PTF)
■ Furane dicarboxylic acid methyl ester (FDME) 60tpa pilot plant started operation 2018 in Decatur, IL.
**BIODEGRADABILITY**

- Biodegradable - undergoes enzymatic fragmentation and degradation by microorganisms to form water, CO2 (aerobic) and methane (anaerobic)
- Very imprecise term – no defined criteria, environments, products or time limits. Biodegradability under one set of conditions does not necessarily imply biodegradability under other conditions
- Biodegradability is NOT a license to litter

**COMPOSTABILITY**

- Meets specific requirements of industrial compostability (eg ASTM D6400, EN13432 or JIS K6950 ) or home compostability standards (TUV-Vincotte OK Home Compost) – aerobic processes
- Certification covers a product, not just a material, and includes determining the maximum thickness of material which can be degraded within one composting cycle

**NOT ALL BIODEGRADABLE MATERIALS ARE BIOBASED**

**NOT ALL BIOBASED MATERIALS ARE BIODEGRADABLE**
MAJOR COMPOSTABLE CERTIFICATION PROGRAMS

• TUV-VINCOTTE “OK Compost” and “OK Compost HOME”
• DIN CERTCO
  ▪ EN 13432

Japan Green Pla
▪ JIS K 6950

Biodegradable Product Institute (US)
▪ ASTM D-6400
BIODEGRADABLE AND COMPOSTABLE PLASTICS

Major current commercial types are:

- Polylactic acid (PLA) – biosourced lactic acid monomer from starches or biomethane, then ring-opening chemical polymerization
- Polyhydroxyalkanoates (PHAs; PHB, PHBV, PHBH, PHBO etc.) - direct fermentation of starch, plant-based fatty acids, oils or bioCH₄

Note: The above are new polymers, not drop-ins, and are both biodegradable and biobased

- Aliphatic and aliphatic/aromatic copolyesters (PBS, PBSA, PBAT, PCL) – mostly petro-based but becoming biobased. Generally used for incorporating in PLA- and starch-blend formulations
- Starch blends and derivatized starch blends
- Cellulose and some derivatives and blends
- Polyvinyl alcohol

Under development:

- Protein-based materials, e.g. keratin-, zein-, casein-, whey and soy-based (e.g. whey-based barrier layers)
- Bacterial-, algal- and fungal-based materials
SOME CURRENT LEADERS IN BIODEGRADABLE PLASTICS

Primary Polymer Producers

- **PLA**
  - NatureWorks-PTT, Total-Corbion, Hisun
- **PHAs**
  - From starches: - Kaneka, CJ CheilJedang, Ecomann, Tianjin BioGreen/DSM, Tianan
  - From sucrose: Biomer, Bio-On
  - From plant oils: Danimer, Nafigate Hydald
  - From organic waste: Full Cycle Bioplastics
  - From biomethane: Newlight, Mango Materials
- **Aliphatic/Aromatic Polyesters (PBAT)**
  - BASF, Jinhui Zhaolong, Xinfu
- **Aliphatic Polyesters (PBS, PBSA etc)**
  - Kingfa, Xinfu, Reverdia, PTT-Mitsubishi, Hexing, Novamont
- **Polycaprolactone**
  - Perstorp, Daicel, BASF
- **Polyglycolic acid (PGA)**
  - Kureha, Solvay
- **Polyvinyl alcohol**
  - Kuraray, Nippon Gohsei, Sekisui
PLA APPLICATIONS

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ingenious materials from plants not oil
TRANSPARENT DEGRADABLE O$_2$-BARRIER LAYERS (1)

Aim to replace non-biodegradable petro-based barriers such as EVOH & PA which complicate recyclability and to avoid metallization

Approach to recyclable or compostable multilayer flexible packaging

- **CELLULOSICS:**
  - High oxygen and oil barrier but low water barrier (improved by PVdC coating). Recyclable and compostable
  - Cellulose films – can be laminated with PLA or starch blend films for moisture-breathable food packaging or lidding films
  - Nano-fibrillated and nanocrystalline cellulose and cellulose/chitin coatings

- **WHEY PROTEINS:**
  - High oxygen barrier, applied as aqueous coating. Recyclable and compostable

- **ALGINATES (Polysaccharides):**
  - Oxygen and fat barriers, applied as aqueous coating
Futamura NatureFlex cellulosic laminated to a Novamont Mater-Bi starch blend film.
POLYVINYL ALCOHOL COPOLYMERS:

- G-polymer – extrudable amorphous PVOH copolymer barrier which can replace Al foil in many applications
- Multilayer transparent biobased blown film for dry food packaging:
  - EVAP Environmentals Ltd (UK):
  - NatureWorks, Eurotech, Nippon Gohsei, Sukano:
    Structure types: PLA/tie/G-Polymer/tie/PLA
- Industrially compostable and recyclable
- Oxygen barrier better than PP/EVOH/PP
- Excellent aroma barrier and highly transparent
HIGH BARRIER POLYESTER (POLYGLYCOLIC ACID)

- Previously only available for specialized biomedical and fracking ball uses at high price
- Expected to become commercially available early 2019 from Solvay for barrier packaging applications. Plant in Augusta GA
- Final FDA food contact approval expected by end 2018
- Oxygen and moisture barriers better than EVOH and PA-MXD6
- Expected to be price/performance competitive with non-biodegradable EVOH and polyamides
- Initial application with Husky for blow-molded PET bottles
- Biodegradable and compostable
- Hydrolyzes and dissolves in alkaline wash stage of recycling process and biodegrades in waste stream
PROJECTED GLOBAL BIOPLASTIC CAPACITY

Global production capacities of bioplastics

GLOBAL BIOPLASTICS CAPACITY BY MARKET

**Global production capacities of bioplastics 2017 (by market segment)**

**Global production capacities of bioplastics 2022 (by market segment)**

MAJOR CONCERNS WITH BIOPLASTICS

- Use of foodstuff feedstocks. Major work on routes from non-food biomass to avoid competition with food
- Land and water availability and competition for these with foodstuffs and other uses
- Whether bioplastics really have lower carbon footprints than petroleum-based materials, given agricultural and fuel inputs to grow the crop feedstocks

- Not all chemical and polymer production will become bio-based.

BIOPLASTICS WILL ONLY BE SUCCESSFUL IF:
1. Equal product functionality is delivered at lower cost
2. New functionality is provided at the right price
3. The carbon footprint in the value chain is improved
FUTURE GROWTH OF BIOPLASTICS IN PACKAGING

This will depend on:

- Future trends in oil prices and impact of shale gas

- Continuing transition from petro- to bio-based feedstocks and improvements in pricing, carbon footprint and performance

- Development of economic production routes from non-food feedstocks for biobased monomers and polymers identical to existing petrochemical counterparts which are drop-ins for existing processes, manufacturing facilities and recycling infrastructure

- Increasing deployment of recycling, recovery and disposal (composting, anaerobic digestion) infrastructure to aid sustainability

- Continuing increases in legislation enforcing use of renewable packaging materials and restricting petrochemical polymers

- How well the use of bioplastics addresses future environmental, societal, political and economic issues
THANK YOU FOR YOUR INTEREST

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