the truth about plastics
an educational forum

saturday
april 27, 2019
Whatcom Community College, Syre Auditorium
8:45 am-3:30 pm
Plastics 101: What’s, How’s and Where’s

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WWU Plastics and Composites Engineering

April, 2019
Outline

• What are plastics?
• Where do they come from?
• How are they used?
• Quantities and trends
• How are they made into products
• Meaning of “Natural”, “Bioplastics”, “Biobased”, etc
• Concept of biodegradability
• End of life & sustainability options
• Plasticulture – example
• Next generation plastics
• Reasons for optimism
Types of macromolecules

**Cellulosics**
- Abundant in nature
- Extensive hydrogen-bonding prevents “melt processing”
- Degrades upon heating

**Thermosets**
- Covalent chemical-bonded 3D network molecule
- Crosslinks prevent “melt processing”
- Degrades upon heating

**Thermoplastics**
- Weak secondary bonding
- “Melt processable”
- Degrades above processing temperatures
How are plastics formed and what is unique?

Polypropylene

- Very long chains produced
- Homopolymers are common
- Ethylene co-polymers are “tougher”
- Low density: 0.90 g/cm³
- Injection molding grade: “low” viscosity
- Extrusion grade: “high” viscosity
- Recyclability is good
- Poor UV resistance

General Features of Plastics

- Long chain molecules
- Chemically modifiable to alter properties
- Low density relative to mechanical performance
- Melt processable for any shape product
- Environmentally stable/persistent
- Recyclability is good for some, poor for others
- Thermal performance is good for some, poor for others
- Generally quite hydrophobic.
What plastics are the most common?

Produced in 2015 (million of tons)

- LDPE: polyethylene
- PP&A fibers: polypropylene, polyamide, acrylic
- HDPE: polyethylene
- PVC: polyvinyl chloride
- PET: polyethylene terephthalate
- PU: polyurethane
- Additives
- PS: polystyrenes
- Other
- All bioplastics

PP&A = polyester, polyamide & acrylic

Sources: plasticinsights.com
Science Advances July 19, 2017
What is the source of the monomers?

Fractional Distillation & Absorption

Crude oil/Petroleum

Naphtha/Natural Gas

Percent Usage of Oil Feedstocks

Transportation

Heating & energy

Industrial chemicals

Plastics

Other

Source: British Plastics Federation
What are the largest usage categories?

2017 market share by application

Source: grandviewresearch.com

Product lifetime distributions

Other plastic market trends

2016 textile market share (% by mass)

- Polyester: 55%
- Cotton: 27%
- Cellulosics: 6%
- Other materials: 8%

Source: www.plasticsinsight.com

U.S. plastics market size, by product, 2014 - 2025 (USD Billion)

Source: www.grandviewresearch.com
Why two types of polyethylene (PE)?

**LDPE**

Low Density Polyethylene

0.90 – 0.93 g/cm³

**HDPE**

High Density Polyethylene

0.94 – 0.97 g/cm³  More crystalline

Source: essentialchemicalindustry.org
How are plastics processed into products?

**Injection Molding**

![Injection Molding Diagram]

- Press
- Hopper
- Heaters
- Mold
- Nozzle

Source: Bacalhau et al., 2017. DOI: 10.26678/ABCM.COBEM2017.COB17-1174

**Extrusion**

![Extrusion Diagram]

- Feed hopper
- Plastic pellets
- Heaters
- Shaping die
- Turning screw
- Barrel
- Molten plastic
- Extrudate
- Tubing and pipes
- Sheet and film
- Structural parts

Source: Bacalhau et al., 2017. DOI: 10.26678/ABCM.COBEM2017.COB17-1174
Questions to scratch your chin over and consider . . .

1) Are bioplastics more biodegradable than synthetic plastics?

2) Can a plastic be degradable, but not biodegradable?

3) Are bioplastics greener materials than synthetic materials?
What is the definition of a “bio-based” plastic?

1) Biobased products have a defined minimum
   Established by agricultural standards.

2) Common sources (often starches)
   • Starches: corn, potato, tapioca, rice wheat
   • Oils: palm, linseed, soy bean
   • Fermentation products (microbial production)

3) Biobased ≠ biodegradable

“In a survey of 800 of its business customers in 2011, DuPont found that nearly 90% said delivering products with environmental benefits is a long-term market opportunity.”

Plastics Today

USDA BioPreferred Program

Economic impact
What are bioplastics?

**Starches**
- Abundant plant sources
- Must be chemically modified to be melt processable
- Poor mechanical properties, but can be blended

**PHAs**
- Naturally occurring class of polymers
- Bacteria use PHAs for energy storage
- Can be > 50% of bacterium’s mass

**PLA**
- poly(lactide)
- Fermented from corn starch
- Synthetically polymerized
- < $1/lb

**PHB**
- poly(3-hydroxybutyrate)

**PHV**
- poly(3-hydroxyvalerate)

**PETE**
- poly(ethylene-terephthalate)

**PE**
- poly(ethylene)

**World bioplastics demand**
- Overall 19%↑/yr

- Graph showing demand in millions of lb from 2005 to 2015 for different regions:
  - N. America
  - W. Europe
  - Asia Pacific
  - Other
Composting
Biodegradability is NOT a material property

30,000 LOGS UNDER THE SEA
Washington Post 1996

"This is a red oak," he says, grinning. "Probably 250 years old when it was cut. It's been on the bottom for another hundred years or more."

A log like this was cut from the original, old-growth North American forest that was virtually leveled as the country was being build.

It's in perfect condition. The low oxygen content and frigid temperatures of Superior have preserved it for a century.

Peat is 20 – 60% cellulose
Agricultural film market

2012 – 2019: 7.9% annual growth

2012 global demand: 8.8 billion lb/yr

2012 – 2019: 5.7% annual growth

“High Tunnels”
• fastest growing segment
• LDPE is 55% of market

“Mulch Films”
• 40% of market

Sources:
Freedonia Group Forecast, 2013.
Plastics News.
Why are plasticulture films used?

- Moisture retention
- Weed suppression
- Pest management
- Improved productivity
- Increased soil temperature extends growing season

But, the actual lifetime of the films generally exceeds the requirement of the application (i.e., one growing cycle)

Potential problems arise after the seasonal use of ag films
China’s present and everyone’s future?

**MORE FOR LESS**

Using farm designs informed by modelling, Chinese agricultural researchers are increasing yields in experimental plots and in farm studies while reducing the amount of resources used and nutrients lost.

<table>
<thead>
<tr>
<th>Maize produced</th>
<th>Maize per kilogram of fertilizer</th>
<th>Maize per millimetre of water consumed</th>
<th>Excess nitrogen applied</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tonne per hectare</td>
<td>Kilogram</td>
<td>Kilogram per hectare</td>
<td>Kilogram per hectare</td>
</tr>
<tr>
<td>15</td>
<td>60</td>
<td>30</td>
<td>150</td>
</tr>
<tr>
<td>10</td>
<td>40</td>
<td>20</td>
<td>100</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

- **Everyday practice** (n = 4,548)
- **Experimental approach** (n = 66)


China: > 60% market
End of life options for ag films

**Desirability**

**Polyethylene**
- tilled in
- landfill

**“Biodegradable” film**
- recycled
- incinerated for energy recovery
- composted ASTM/ISO standards
- tilled in

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Greg Scullin, *The Weekly Times*
How do plastic films break down?

Soil or compost conditions
- Temperature
- $O_2$, $H_2O$, pH, nutrients

Microbial populations

Enzymes (hydrolytic & oxidative)

Mineralization ($CO_2$, $H_2O$, $CH_4$)

Assimilation into microbial biomass & humic environment

Persistent plastic components (aromatic-block regions & hydrophobic regions)

Polymer film components

Polyolefin
- Hydrophobic
- Little hydrolysis; slow degrading

Polyester
- Hydrolysis via enzymes or at low or high pH
- Moderate rate of hydrolysis/degradation

Polysaccharide
- Hydrophilic
- Readily hydrolyzed via enzymes and chemical mechanisms (low pH)

Abiotic agents
- UV (oxidation)
- Weathering (oxidation, fragmentation)
- pH and water content
What happens to a plastic as it degrades?

At the molecular level, below some critical chain length, short molecules can dissolve into the aqueous environment.

- Measurement of the complete mass balance vs time has not been measured under realistic conditions.
- Thus the fate and distribution of the plastic components in soil & water is not well understood.
# Biodegradable certification conditions differ from natural soils

<table>
<thead>
<tr>
<th>Test conditions</th>
<th>Standard for plastic biodegradation in compost (ASTM 6400 / ISO 17088)</th>
<th>Standard for plastic biodegradation in soil (ASTM WK 29802)</th>
</tr>
</thead>
<tbody>
<tr>
<td>• temperature</td>
<td>56 – 62 °C</td>
<td>20 – 23 °C</td>
</tr>
<tr>
<td>• pH</td>
<td>7.0 – 8.2</td>
<td>6.0 – 8.0</td>
</tr>
<tr>
<td>• C:N ratio</td>
<td>10:1 – 40:1</td>
<td>10:1 and 20:1</td>
</tr>
<tr>
<td>• oxygen</td>
<td>aerated to &gt; 6%</td>
<td>not specified; not aerated</td>
</tr>
<tr>
<td>• moisture (% MHC)</td>
<td>optimal</td>
<td>80 – 100 %</td>
</tr>
</tbody>
</table>

### What can remain?

- 1) 10% of organic carbon from plastic film after 180 days
- 2) fragments smaller than 2.0 mm after 84 days

### How is extent of biodegradation estimated?

- CO₂ generation
- CO₂ generation
Properties of polymers used in ag films

**Polyolefins**
- Poly(ethylene) (PE)
- Poly(ethylene-terephthalate) (PET)

**Aromatic polyesters**
- Poly(butylene-adipate-co-terephthalate) (PBAT)

**Aliphatic polyesters**
- Poly(lactic acid) (PLA)
- Poly(butylene succinate) (PBS)

**Polysaccharides**
- Cellulose
- Starches (Amylose, amylopectin & chemically-modified starch)

**PHAs (polyhydroxyalkanoates)**
- Poly(3-hydroxybutyrate) (PHB)
- Poly(3-hydroxyvalerate) (PHV)
Experience with some compostable materials

TaterWare utensils commercially composted in San Francisco (minimum 60-90 days):

Univ. Vermont's experience

"after one year, the cutlery shows no sign of composting"

"the only thing disappearing here are the company's customers"

"hundreds of thousands of these forks, knives, and spoons had to be hand-picked out of the compost"

"no longer accepting composting cutlery and hasn't tested other brands"

https://myplasticfreelife.com/2010/03/are-compostable-utensils-really-compostable/
How can we assess the potential biodegradability of materials?

**MUST Define**

1) Relevant context for degradation
2) Sample sizes and conditions
3) Acceptable rate of degradation
Recycling
**Recycling rates: metals (90%) vs plastics (9%)**

- **Density (g/cm³)**: Metals like aluminum, tin, cast iron, steel, brass, and copper have densities ranging from 2 to 8. Plastics such as PP, LDPE, HDPE, PS, PU, ABS, Nylon, Acrylic, PLA, PVC, and PET have lower densities, with values ranging from 0.5 to 5.

**Metals** are almost infinitely recyclable as they are "atomic" materials with metal chemical bonds.

**Plastics** are molecular materials; properties depend on chain length. They are degraded by heating, mechanical shearing, UV/oxidative degradation, etc.

Mixed plastic wastes require complex systems of sorting and economically are favorable only for the highest value products.
Cradle to Cradle Recycling

Accumulation of clean plastic at large scale “plastics mine”

Size reduction & washing

Repeated cycles of:

- Sorting based on chemical sensors
- Air flotation & centrifugation
- Contaminant removal
- Size reduction
- Color sorting

Baling product for shipment to customer
What can communities do?

- 1989: Community recycling efforts and League of Women Voters Task Force led to citywide curbside pickup.
- 1991: first county in the State to offer curbside pickup.
- City has always had segregated recycling (mixed paper, newspaper, and cans/glass/plastic).
- Non-segregated waste has 15-30% contamination.
- Bellingham’s segregated plastic waste has only 1% contamination.
- Paper, glass and newsprint also are clean resources.
Reasons for optimism

Europe has made dramatic progress using harmonized rules and clear requirements for consumers and producers.

Source: Plastics Europe 2017
Reasons for optimism

Water refill stations at WWU have prevented the use of 2 million disposable water bottles
### End of Product Life Options for Plastics

#### Plastic waste to liquid fuel (Purdue)

<table>
<thead>
<tr>
<th>Material</th>
<th>Btu/lb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel oil</td>
<td>20,900</td>
</tr>
<tr>
<td>Polyethylene (PE)</td>
<td>19,900</td>
</tr>
<tr>
<td>Polypropylene (PP)</td>
<td>19,850</td>
</tr>
<tr>
<td>Gasoline</td>
<td>19,200</td>
</tr>
<tr>
<td>Polystyrene (PS)</td>
<td>17,800</td>
</tr>
<tr>
<td>Coal</td>
<td>12,000</td>
</tr>
<tr>
<td>Wood</td>
<td>6,700</td>
</tr>
</tbody>
</table>

#### Plasticulture waste to solid fuel (Penn St)

- Plastofuel™ fuel nugget extruded from waste agriculture plastic
- Tolerant of dirt and debris
- Only outer portion melted, so requires only about 1/10 the energy compared to producing plastic pellets.

Source: extension.psu.edu/waste-plastics-as-fuel
Next generation plastics . . .

Vitrimer chemistry: Weak bonds engineered into then, and the material can be de-polymerized into monomers ... then reused.

Source: C&E News, June 2018
Questions?

More information on C2C Recycling
TED Talk: Mike Biddle
mbapolymers.com

More information on Plasticulture
WSU: Carol Miles & Debra Inglis
plasticulture.wsu.edu
Major components of ocean plastic

Ocean plastics of most concern

- **PE** poly(ethylene)
- **PP** poly(propylene)
- **PS** poly(styrene)
- **PVC** poly(vinyl chloride)
- **SBR** styrene butadiene rubber
- **PET** poly(ethylene-terephthalate)

**Common features**

- Commodity plastics
- Hydrophobic
- Abiotic degradation is most significant
- Biological degradation is very limited
Chemical Recycling of Plastic

Chemical Degradation (*specific*)
- Glycolysis [PET to bis(2-hydroxyethyl) terephthalate (BHET) monomer]
- Methanolysis [PET to dimethyl terephthalate (DMT) monomer]

Degradative Processing
- Destructive distillation
- Degradative extrusion
  \[ \text{polymer} \rightarrow \text{monomer} \]

High Temperature Degradation (*non-specific*)
- Pyrolysis
- BASF thermal cracking
- Catalytic cracking
  \[ \text{polymer} \rightarrow \text{chemical sub-units} \rightarrow \text{re-processing} \rightarrow \text{monomers} \]
- Cracking by hydrogenation
- Polymer cracking in fluidized bed

Gasification Processes
- Steam gasification
  \[ \text{polymer} \rightarrow \text{chemical sub-units} \rightarrow \text{re-processing} \rightarrow \text{monomers} \]
- Gasification (Texaco process)
- High temperature gasification (Battelle process)
Pyrolysis Process

P2F Pyrolysis of Plastic to Oil
(SIMPLIFIED PROCESS FLOW)

Plasticulture: Questions to be answered

<table>
<thead>
<tr>
<th>Time after incorporation (d)</th>
<th>42</th>
<th>132</th>
<th>223</th>
<th>299</th>
<th>397</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crown 1</td>
<td>![Image](Crown 1)</td>
<td>![Image](Crown 1)</td>
<td>![Image](Crown 1)</td>
<td>![Image](Crown 1)</td>
<td>![Image](Crown 1)</td>
</tr>
<tr>
<td>BioAgri</td>
<td><img src="BioAgri" alt="Image" /></td>
<td><img src="BioAgri" alt="Image" /></td>
<td><img src="BioAgri" alt="Image" /></td>
<td><img src="BioAgri" alt="Image" /></td>
<td><img src="BioAgri" alt="Image" /></td>
</tr>
<tr>
<td>SB-PLA-11</td>
<td><img src="SB-PLA-11" alt="Image" /></td>
<td><img src="SB-PLA-11" alt="Image" /></td>
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</tbody>
</table>

Fig. 3. Representative samples of Crown 1 (Crown Films, Burlington, WA), BioAgri (BIOgroupUSA, Palm Harbor, FL), and SB-PLA-11 (fabricated by Saxony Textiles, Chemnitz, Germany) mulch recovered from soil [226.2 inch\(^3\) (3706.75 cm\(^3\))] 42, 132, 223, 299, and 397 d after mulch was incorporated by tillage. The white boxes represent the theoretical maximum mulch area [37.5 inch\(^2\) (241.7 cm\(^2\))] for each sample. 1 cm\(^2\) = 0.1550 inch\(^2\).

Jeremy Cowan, Debra Inglis, Carol Miles