Roundtable on Chemical Upcycling of Polymers

Briefing to BESAC

Phillip Britt
Oak Ridge National Laboratory
March 8, 2018
BES Roundtable on Chemical Upcycling of Polymers

Workshop Chair: Phillip Britt (ORNL)
Co-Chairs: Geoff Coates (Cornell Univ.)
           Karen Winey (Univ. of Penn.)
SC Technical Lead: Bruce Garrett

Charge:

• Assess the fundamental challenges that would enable transformation of discarded plastics to higher value fuels, chemicals, or materials

• Identify fundamental research opportunities in chemical, materials, and biological sciences that will provide foundational knowledge leading to efficient, low-temperature conversion of discarded plastics to high-value chemicals, fuels, or materials

• Identify research opportunities for the design of new polymeric materials for efficient conversion, after end of life, to high-value chemicals or materials
Globally Plastics are Growing

- If plastic production continues its current growth rate, then the plastics industry may account for 20% of the world’s total oil consumption
- In 2015, global plastic waste disposal:
  - Discard: 55%; Recycle: 19.5%; Incineration: 25.5%
• Packaging is the largest use for plastics but single use:
  – Plastics used in packaging include: LDPE (30%), PET (23%), HDPE (21%), PP (18%), PS (5%), and PVC (2%)

• If current trends continue, by 2050, the ocean will contain more plastic than fish, by weight

Global Flow of Packaging Waste
40% Landfill
32% Leakage
14% Incinerated
14% Recycled

### Majority of Plastics (87%) Fall into Categories 1-6

Recovery Rates for Plastic Recycling in US are Low

<table>
<thead>
<tr>
<th>Category</th>
<th>Common Products</th>
<th>Recycled Products</th>
<th>Recovery Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>PETE</td>
<td>Polyethylene</td>
<td>Clothing, carpet, clamshells, soda &amp; water bottles</td>
<td>19.5%</td>
</tr>
<tr>
<td>HDPE</td>
<td>High-Density Polyethylene</td>
<td>Detergent bottles, flower pots, crates, pipe, decking</td>
<td>10%</td>
</tr>
<tr>
<td>PVC</td>
<td>Polyvinyl Chloride</td>
<td>Pipe, wall siding, binders, carpet backing, flooring</td>
<td>0%</td>
</tr>
<tr>
<td>LDPE</td>
<td>Low-Density Polyethylene</td>
<td>Trash bags, plastic lumber, furniture, shipping envelopes, compost bins</td>
<td>5%</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene</td>
<td>Paint cans, speed bumps, auto parts, food containers, hangers, plant pots, razor handles</td>
<td>1%</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
<td>Picture frames, crown molding, rulers, flower pots, hangers, toys, tape dispensers</td>
<td>1%</td>
</tr>
<tr>
<td>OTHER</td>
<td>Other</td>
<td>Common types &amp; products: polycarbonate, nylon, ABS, acrylic, PLA; bottles, safety glasses, CDs, headlight lenses</td>
<td>varies</td>
</tr>
</tbody>
</table>

Motivation for Chemical Upcycling of Polymers

**Upcycling**: the process of selectively converting waste materials into products with greater value as opposed to traditional recycling which typically converts waste into materials for reuse but with reduced properties (downcycling)

- In the US, plastic materials contribute 13% (34.5M tons) to municipal solid wastes in 2015 with less than 10% recycled, approximately 15% combusted for energy recovery, and the remained sent to the landfill (75%)\(^1\)
- Most recycling of plastic wastes typically involves mechanical processes (primary or secondary recycling: sort, grind, wash, extrude) and is only applied to limited plastic types but the products are cheaper than new materials
- More energy is saved by recycling than recovered by burning plastic (heating value of plastics 36 MJ kg\(^{-1}\) while mechanical recycling conserves 60 – 90 MJ kg\(^{-1}\))
- On average, each tonne of plastic recycled saves the energy equivalent in the combustion of 22 barrels of oil\(^2\)
- Increased plastic recycling is an important pathway to reduce plastic waste and has clear energy, economic, and environmental impacts
- Opportunity exists for fundamental research to provide the foundational knowledge needed to design chemical reactions, processes, and materials that enable efficient, low-temperature conversion of discarded plastics to high-value chemicals or materials

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\(^2\) Rahimi, A.; Garcia, J. M. Nat. Rev. Chem. **2017**, 1, Article Number 0046
Challenges for Chemical Upcycling of Polymers

- Difficult to sorting plastics to get a clean stream (density, electrostatics, wettability, spectral signature)
- Plastics are not pure and contain additives, food residues, dirt, degradation products, etc. that could impact upcycling
- Polyolefins are often combined with other materials in multi-layer packaging which can not be recycled
- High chemical, thermal, and mechanical stability of polymers provide challenges to deconstruction (and thus, new chemistry is needed)
- Thermosets are crosslinked polymers that can not currently be recycled by mechanical, thermal, or solvent processing methods

<table>
<thead>
<tr>
<th>Additives in Polymers</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasticizers</td>
<td>34%</td>
</tr>
<tr>
<td>Flame retardants</td>
<td>13%</td>
</tr>
<tr>
<td>Heat stabilizers</td>
<td>5%</td>
</tr>
<tr>
<td>Fillers</td>
<td>28%</td>
</tr>
<tr>
<td>Impact modifiers</td>
<td>5%</td>
</tr>
<tr>
<td>Antioxidants</td>
<td>6%</td>
</tr>
<tr>
<td>Colorants</td>
<td>2%</td>
</tr>
<tr>
<td>Lubricants</td>
<td>2%</td>
</tr>
<tr>
<td>Light stabilizers</td>
<td>1%</td>
</tr>
<tr>
<td>Other</td>
<td>4%</td>
</tr>
</tbody>
</table>

In 2016, two reports published by World Economic Forum, the Ellen MacArthur Foundation and McKinsey & Company which makes the case for rethinking the current plastics economy and identifies a number of significant knowledge gaps and open questions:

- *The New Plastics Economy – Rethinking the future of plastics*
- *The New Plastics Economy – Catalyzing Action*

In the second report, three distinct strategies were proposed to accelerate the shift towards the new plastics economy.
Energy Efficient Chemical Upcycling of Polymers Aligns with DOE BES Mission

- Fundamental chemical and materials sciences required to enable upcycling of polymers fall directly within BES’s and DOE’s energy mission.
- BES research has contributed significantly to the scientific foundations in catalysis, thermochemical kinetics, control of chemical transformations, materials synthesis (control of structure and properties) and characterization, biosciences (bio-inspired catalysts), and computational modeling required to advance a fundamental research agenda in polymer construction, deconstruction and reassembly.
- Strength in understanding the link between atomic and molecular scale organization and bulk properties.
- Unique strength in combining research in chemical and natural systems.
- Unique tools (neutrons, x-rays, nanoscience, and computation) to support atomic scale and mesoscale research in upcycling.

Opportunities in Chemical Upcycling of Polymers

• This Roundtable will focus on four challenges and research opportunities for chemical upcycling of polymers that build off the strengths in BES portfolio
  – Design chemical mechanisms to deconstruct polymers and create targeted molecular intermediates that provide building blocks for new products
  – Create integrated depolymerization-reassembly processes that target high-value end products from starting polymers
  – Design next-generation polymeric materials that enable efficient depolymerization-reassembly
  – Investigate crosscut opportunities for advancing experimental, computational and data science driven approaches for upcycling of polymers
Design chemical mechanisms to deconstruct polymers and create targeted molecular intermediates that provide building blocks for new products

For example, IBM has developed a process that separates contaminants (e.g., food residue, glue, dirt, dyes, and pigments) from PET and produces pure monomer in an energy-efficient cycle.

Challenge 2: Create Integrated Deconstruction-Reassembly Processes

- Create integrated depolymerization-reassembly processes that target high-value end products from starting polymers
  - For example, most processes today take polymers back to monomers and then repolymerize to products with similar performance
  - Another approach is to process immiscible polymers, such as polyethylene and isotactic polypropylene, by stitching together with a block copolymer
Challenge 3:
Design Next Generation Recyclable Polymers

• Design next-generation polymeric materials that enable efficient depolymerization-reassembly
  • Significant interest in recycling thermosets (cross-linked polymers) which are 15-20% of the market but currently are not recyclable or reprocessable
  • Examples of approaches to depolymerization and reprocessing thermosets include:
    • Dynamic covalent networks and covalent adaptive networks (CAN)
    • Vitrimers – a strategy for direct mechanical reprocessing where polymers rearrange their topology by exchange reactions without depolymerization

Klooxin, C. J. et al., Chem. Soc. Rev. 2013, 42, 7161

Fortman, D. J. et al. ACS Sustainable Chem. Eng. 2018, 6, 11145
Goal: Chemical Upcycling of Polymers Roundtable

• Convene a small group (ca. 20) of experts from industry, academia, and national labs to address fundamental challenges to enable transformation of discarded plastics to high-value fuels, chemicals, and materials

• Prepare a factual document to provide the workshop participants with a high-level assessment of the current status of polymer upcycling

• Identify priority research opportunities in which fundamental research over the next 5-10 years could result in a significant impact on chemical upcycling of polymers

• Prepare a report which captures these possible priority research opportunities for chemical upcycling of polymers

• Status:
  – Chairs confirmed; Panel Leads selected/contacting; Participants almost final
  – Date, Location selected: April 30 – May 1; Bethesda North Marriott
  – Factual Document being written (completed draft delivered mid-April)
  – Webinar in advance of the workshop (tentatively mid-late April)
Polymer Upcycling Roundtable - Format

- Introductory remarks by DOE-SC leadership
- Goals and logistics
- Presentations: Three short presentations on polymer upcycling
- Panel discussion on each focus area (with cross-cut integrated):
  - Each participant will come prepared to discuss roadblocks, knowledge gaps, research needs, and research opportunities
    - Mechanisms for deconstructing to molecular intermediates
    - Create integrated deconstruction-reassembly processes
    - Design next generation recyclable polymers
- Report out
- Refine Priority Research Opportunities (PRO)
- Final report out of Priority Research Opportunities
- Report writing - writers and panel leads stay extra half day to capture input and pull together a rough draft
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