Roundtable on Chemical Upcycling of Polymers

Briefing to BESAC

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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


UNEP (2018). Single Use Plastic: A Road Map for Sustainability
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>Type</th>
<th>Common Products</th>
<th>Recycled Products</th>
<th>Recovery Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PETE</td>
<td>Polyethylene Terephthalate</td>
<td>soda &amp; water bottles; cups, jars, trays, clamshells</td>
<td>19.5%</td>
</tr>
<tr>
<td>2</td>
<td>HDPE</td>
<td>High-Density Polyethylene</td>
<td>milk jugs, detergent &amp; shampoo bottles, flower pots, grocery bags</td>
<td>10%</td>
</tr>
<tr>
<td>3</td>
<td>PVC</td>
<td>Polyvinyl Chloride</td>
<td>cleaning supply jugs, pool liners, twine, sheeting, automotive product bottles, sheeting</td>
<td>0%</td>
</tr>
<tr>
<td>4</td>
<td>LDPE</td>
<td>Low-Density Polyethylene</td>
<td>bread bags, paper towels &amp; tissue overwrap, squeeze bottles, trash bags, six-pack rings</td>
<td>5%</td>
</tr>
<tr>
<td>5</td>
<td>PP</td>
<td>Polypropylene</td>
<td>yogurt tubs, cups, juice bottles, straws, hangers, sand &amp; shipping bags</td>
<td>1%</td>
</tr>
<tr>
<td>6</td>
<td>PS</td>
<td>Polystyrene</td>
<td>to-go containers &amp; flatware, hot cups, razors, CD cases, shipping cushion, cartons, trays</td>
<td>1%</td>
</tr>
<tr>
<td>7</td>
<td>OTHER</td>
<td></td>
<td></td>
<td>varies</td>
</tr>
</tbody>
</table>

https://www.bluelinelabels.com/glossary-of-resins-containers-decorating/
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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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
Challenge 1: Design Chemical Mechanisms for Deconstruction

- 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

Fortman, D. J. et al. ACS Sustainable Chem. Eng. 2018, 6, 11145
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
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
Charge and focus areas:

- Assess the fundamental challenges and identify the research opportunities that would enable transformation of discarded plastics to higher value fuels, chemicals, or materials
  - 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 approaches for chemical upcycling of polymers