



Poster Abstracts

Closing the Loop on the Plastics Dilemma: A Chemical Sciences Roundtable Workshop

1. Title: Catalytic Upcycling of Single-Use Polyethylene

Presenter: Massimiliano Delferro, Argonne National Laboratory

Abstract: Synthetic polymers are ubiquitous and critical to the function of modern life. However, the ubiquity of polymers has resulted in an enormous and growing amount of polymer waste, which has a long lifetime in the environment and is inefficient to recycle. Polymer waste is both a threat to the environment and economy, and an untapped resource of energy-rich hydrocarbons. If the large macromolecules that make polymers could be chemically transformed or "upcycled" into value-added chemicals, rather than disposed of as waste or downcycled into lower grade plastics, the energy and value put into the polymers could be reclaimed and turned into new applications. Here, we focus on developing efficient and innovative catalytic materials for converting waste polymers into more valuable products in a selective manner – catalytic upcycling. Novel approaches are being explored where the selective catalytic conversion of waste polymers is achieved by designing supported metal catalysts with spatially organized sites. These sites cleave hydrocarbon polymers into relatively uniform fragments through interactions of the polymer macromolecules with the spatially organized metal catalysts. The production of uniform fragments, rather than a random distribution, is the first step to efficiently converting waste polymers into new high-value hydrocarbon feedstocks.

2. Title: Deinking of Plastics for Recycling

Presenter: Brian Grady, University of Oklahoma

Abstract: If used polymer items are sorted into single component streams, one of the most, if not the most significant factor that reduces the quality of the product is the inclusion of non-polymeric materials into the recycled materials. One of the most common non-polymeric materials, especially on flexible film, is ink. I will present our efforts on using surfactants to deink both flexible and rigid polyethylene-based materials. Our work has shown that high pH and cationic surfactants are most effective for deinking as measured by colorimetric measurements. The proposed mechanism involves both solubilization of the likely negatively charged polymer binder as well as wetting of the negatively charged particles. Other types of surfactant are effective at deinking as well. The tensile strength and elongation at break after deinking are significantly better than the material recycled without deinking, but still are slightly lower than the material with no printed ink.

3. Title: Edible Biological Materials

Presenter: Challa Vijaya Kumar, University of Connecticut

Abstract: Plastics pollution is an ever-growing problem and one way to combat it is by establishing materials that naturally degrade, under predictable conditions when discarded after use. Our group is developing functional materials that also degrade when exposed to bacteria/fungi/plants or digestible by animals without deleterious effects. Based on these materials, we have already developed protein-based supercapacitors that outperform commercial super capacitors, bioPhosphors that can compete with commercial phosphors, and luminescent nanoparticles that can outcompete traditional quantum dots. Working along these lines, we hope to replace high-end plastic materials with biologics, as a first step toward solving the above problem of environmental pollution by persistent plastics and polymers.

4. Title: Systems Analysis for Polymers in a Global Circular Economy

Presenter: Robert Handler, Michigan Technological University

Abstract: Landfilling and leakage to the environment (as opposed to recycling or re-use) are the largest end-of-life fates for plastics that are used in packaging, which is the most common use of plastics. Plastic packaging exhibits the shortest lifetime between its production and it appearing at end-of-life as waste in need of management. A circular economy for these polymeric materials rather than a linear economy is proposed by many as an ideal solution to the responsible management of waste plastics. However, large-scale implementation of a circular economy for plastics is not well-understood with respect to economic costs and benefits, environmental impacts, and societal effects relative to business-as-usual linear management. The circular economy of plastics can be understood and improved through systems analysis (SA) with a view on

- > materials flow analysis (MFA),
- > techno-economic analyses (TEA),
- > environmental life cycle assessments (LCA),
- > regional economic modeling to reveal societal benefits and costs, and
- > policies to encourage greater commercial adoption.

A systems analysis (SA) for a circular economy of plastics has not been conducted because of several factors;

- i. a conceptual modeling framework designed to answer specific research questions has yet to be developed,
- ii. knowledge gaps on current and future recycling processes,
- iii. a multidisciplinary approach is needed

This poster will highlight the main features of a new funded DOE Advanced Manufacturing Institute project supported by the REMADE Institute. This exploratory project features a proposed framework for conducting a SA for a global circular economy of plastics.

5. Title: Functionalized Self-Immolative Polymers

Presenter: Edmund F. Palermo, Rensselaer Polytechnic Institute

Abstract: Self-immolative polymers are metastable plastics that are specifically triggered to undergo end-to-end depolymerization upon chemical removal of an end-capping agent. Based on kinetic trapping of low ceiling temperature polymers, these materials will rapidly revert to N small molecules upon reaction with a single equivalent of the triggering agent. Thus, chemically amplified downcycling of plastics is a key target in the field although several challenges remain. In particular, there are currently no proven strategies to tune the mechanical and thermal properties of these materials and their robustness in applications remains entirely unexplored. We will present recent process on post-polymerization functionalization of poly(benzyl ether)s, derived from abundant and inexpensive bisphenol feedstocks, to obtain materials with controlled properties. Since the ceiling temperature is ~0 degrees C, these materials degrade easily at room temperature, even in the solid state, but only when the triggering chemistry is introduced.

6. Title: Beyond Sustainability: Post-Consumer Recycled Plastics as Performance Enhancing Additives

Presenter: Greg Curtzwiler, Iowa State University

Abstract: As global demand for consumer goods expands, the production of virgin/first pass plastic feedstocks increases pressure on the global environment from natural resource consumption and environmental accumulation. Post-consumer recycled (PCR) plastics are often characterized as having poor physical properties from reduced polymer molecular weight and defects in the polymer backbone

due to chain degradation. However, some degradation events lead to improved performance properties of post-consumer/virgin blends which is proven to be beneficial in a variety of applications. PCR feedstocks were melt-blended with their corresponding virgin/first pass plastic and the chemical and physical properties characterized. Our data supports measurable and repeatable increases in tensile modulus, gas barrier properties, and light blocking characteristics for virgin poly(ethylene terephthalate), polyethylene, and polypropylene plastic when blended with PCR materials. As many of the properties followed the Rule of Mixtures, we further demonstrated the ability to predict physical properties from in-process measurements. These data can be utilized as inputs into a decision-making platform and property database coupled to a neural network enabling brand owners and manufacturers to monitor safety and quality of parts during manufacturing. An in-process decision making platform will increase potential for using additional post-consumer feedstocks for manufacturers with targeted markets and applications while opening new markets and economies for refuse plastics previously unfeasible with current technologies. The performance gains in PCR/virgin blends demonstrate increased economic value of post-consumer plastic beyond sustainability due to their potential use as performance additives in virgin plastic.

7. Title: Challenges and Opportunities in Measurement of Ocean Plastics

Presenter: Sara Orski, National Institute of Standards and Technology

Abstract: To further advances in chemical and biological recycling, the extent, mechanisms, and kinetics of plastic degradation under abiotic and biotic conditions must be better quantified. The variability in degradation conditions among materials of different sizes, surfaces areas, differing commercial compositions and formulations must be understood to incorporate appropriate catalysts and biological systems to degrade and depolymerize plastics into useful and greener feedstocks. Herein, we report systematic measurements of polymer fragments recovered from sea turtles and beaches near Oahu, Hawaii to determine changes in chemical composition, molar mass, molar mass distribution, intrinsic viscosity, and short and long chain branching content within each fragment. A subset of polypropylene samples were each sectioned for depth profiling and characterized by x-ray photoelectron spectroscopy (XPS), high-temperature size exclusion chromatography (HT-SEC) with tetra-detection, and differential scanning calorimetry (DSC). Polypropylene sections within the same parent fragment all demonstrated a clear decrease in the number and weight average molar masses, a broader molar mass distribution, a high degree of oxidation, and greater incidence of foreign chemical elements relative to materials sampled from the internal material core. Among all polypropylene fragments measured, molar mass decreases were predominately due to chain scission, as very little long chain branched content was observed by differential viscosity measurements. This research can be used to aid materials scientists, ecologists, chemists, and recycling experts by providing them with alternate techniques of identification, quantitative degradation measurements, and (ultimately) information to develop predictive quantitative models of chemical and biological degradation pathways and kinetics.

8. Title: Why a Public Private Partnership is Necessary for the Discovery of New Food Packaging Materials

Presenter: Jack Copper, Animal Digestible Food Packaging Initiative

Abstract: Single use plastic, including plastic food packaging, is being challenged by local, state and national governments and consumers due to its presence in the marine environment and because plastic degrades into "forever" micro plastic and nano plastic particles – It is currently unknown the extent to which these particles cause adverse environmental and health effects, but several research organizations are conducting research to find out. While, some plastic food packaging can be recycled or composted, segregation, transportation, and special facilities are required, which are not readily available today in most urban areas of the United States. Increasingly, consumers are demanding social responsibility from

companies they do business with. Consumers want to reward companies that take bold stands on important issues, such as reduction of food waste and single-use plastic. This poster will address how a food industry supported public private partnership could address the single use plastic waste issue by funding research for the discovery of new food packaging materials that would be digestible by animals, that if found and widely used, would turn food waste that is accompanied by packaging into a resource by making animal feed out of it, keeping it out of landfills and the environment. The poster will also address the necessity for food packaging to meet food safety, quality and integrity requirements.

9. Title: Controlling Polymer Folding with Porous Materials

Presenter: Frederic Perras, US Department of Energy, Ames Laboratory

Abstract: One of the principal challenges associated with the catalytic upcycling of polymers is that useful, high-value, products tend to have a high degree of structural uniformity. While this can easily be achieved from a bottom-up approach through polymerization, for instance, the reverse, is far more challenging. In order to obtain a narrow product distribution from a polymer feedstock it is necessary to tame its flexible structure. We have sought to determine whether this structural control may be achieved with the use of porous materials having a high degree of uniformity. Using solid-state NMR we studied the conformation of polyethylene that was adsorbed onto a number of silica materials. We found that we were indeed able to extend the polymer by threading it through narrow pores and maintain it in a rigid conformation that is prone for controlled chemical modifications aimed at polymer upcycling.

10. Title: Carbonylative Polymerizations for Sustainable Polymers

Presenter: Li Jia, The University of Akron

Abstract: The pollution of the earth surface by plastic wastes is a problem of massive scale. The key challenge in replacing current nondegradable plastics with plastics degradable in the environments is that the raw materials of the degradable plastics must be readily available at costs comparable to the raw materials used to make the current nondegradable plastics. A low-carbon footprint of these raw materials is highly desirable in order to achieve the overall environmental sustainability. To meet the practical challenges, fundamental breakthroughs are necessary. In this presentation, carbonylative polymerizations (i.e., copolymerization involving carbon monoxide as a comonomer) of ethylene and cyclic ethers are developed to produce plastics that are photolytically and hydrolytically degradable. These plastics are therefore expected to break down in various environments on the surface of the Earth. The raw materials for making these plastics are inexpensive and have low carbon footprints. The catalysts are based on the earth-abundant metal, nickel, adding another sustainable feature to the technology.

11. Title: BASF Technologies for the Sustainable Management of Plastics

Presenter: Kat Knauer, BASF Corporation

Abstract: BASF recently joined a global alliance of nearly 30 companies to advance solutions that reduce and eliminate plastic waste in the environment, especially in the ocean. The Alliance to End Plastic Waste (AEPW) has committed over \$1.0 billion with the goal of investing \$1.5 billion over the next five years to help end plastic waste in the environment. New solutions will be developed and brought to scale that will minimize and manage plastic waste. This also includes the promotion of solutions for used plastics by helping to enable a circular economy. At BASF we are developing technologies for the sustainable management of plastics via plastic additives for durability and recyclability, 100% compostable plastics, and our new pilot chemcycling plant. This poster will provide an overview of the key BASF chemistries that can enable a circular economy for plastics.

12. Title: Responsible Innovation for Plastics Performance Plus: Designing for Environmental Compatibility

Presenter: Cristina Negri, Argonne National Laboratory

Abstract: While benefiting society in countless ways, plastics have also created an enormous environmental challenge. Because the same properties that make them useful also make them persist in the environment after they are discarded, plastics have become the newest member of the "unintended consequences" family. Like previous chemical innovations (from gasoline additives to fire retardants), the design of plastics has emphasized functional use rather than post-use performance. To begin to address the exponential growth of discarded plastics in the environment, it is imperative that we change how these materials are designed. We describe a novel paradigm that brings environmental considerations up front to the design phase. This approach expands conventional design factors to account for environmental performance beyond the product's useful life. The criteria combine physical, chemical, and biological factors that influence the fate of plastics in the environment (including degradation, transformation, partitioning, and dispersion) across multiple media (marine and fresh water, soil, sediment, air, and biota) and geographic settings, as well as evolving climate conditions. Applying a "plastics performance plus" approach that explicitly accounts for environmental performance can strengthen computational modeling for new plastics, including enabling practical comparisons of different feedstocks (bio- vs. petroleum-based) and tradeoffs between functional performance and environmental performance. Future plastics can realize a distinct performance advantage by accounting for environmental compatibility at the outset, toward achieving a biofriendly life after use.