OUTLOOK

Biobased polymers can frame the future of plastics, provided that scientists continue to develop efficient, often catalytic, conversion of biomass to useful polymer ingredients; generate new and established monomers from biomass in high yields and purities; and discover new polymers with outstanding properties that are comparable or superior to their petrochemical analogs. An exciting contemporary example of this future is the substitution of terephthalic acid with the bioderived 2,5-furandicarboxylic acid to produce a high-performing fully biobased PET replacement (15). Support for this type of research should come not only from government. University-industry partnerships can be very effective at producing basic research that is couched in the economic realities of the polymer marketplace.

For polymers from renewable resources to penetrate the marketplace, they must outcompete traditional materials in both price and performance. But as the fundamental research in the conversion of biomass to polymer precursors continues to evolve, the resultant technologies will become more and more practical. Similarly, as the basic research on converting these compounds into polymers with exceptional property, processing, and performance profiles continues to be established, the resultant materials will be increasingly competitive. If the economic and environmental costs of extracting fossil resources and converting them into plastics continue to rise, there will likely be an inversion point where biobased polymers become the less expensive alternative, akin to what is starting to happen in the renewable energy sector. Societal pressures and policies that are conducive to environmental stewardship will only help the cause. We are not there yet, but there is good reason to stay the course and continue to push the frontiers of biobased polymers for the sake of sustainability. ■

REFERENCES AND NOTES


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POLYMER CHEMISTRY

The future of plastics recycling

Chemical advances are increasing the proportion of polymer waste that can be recycled

By Jeannette M. Garcia† and Megan L. Robertson

The environmental consequences of plastic solid waste are visible in the ever-increasing levels of global plastic pollution both on land and in the oceans. But although there are important economic and environmental incentives for plastics recycling, end-of-life treatment options for plastic solid waste are in practice quite limited. Presorting of plastics before recycling is costly and time-intensive, recycling requires large amounts of energy and often leads to low-quality polymers, and current technologies cannot be applied to many polymeric materials. Recent research points the way toward chemical recycling methods with lower energy requirements, compatibilization of mixed plastic wastes to avoid the need for sorting, and expanding recycling technologies to traditionally nonrecyclable polymers.

Roughly half of the annual global production of solid plastics, or 150 million tons, is thrown away worldwide each year. The United States generates ~20% of the global amount of plastic solid waste generated (1). Not only is plastic waste residing in landfills harmful to the environment, but it also represents missed economic opportunities. For example, the commodity market value of the total landfilled packaging material waste in the United States has been estimated to be $11.4 billion dollars; $8.3 billion of this is attributed to plastic waste (2). Furthermore, recycling plastic for reuse saves energy compared with producing virgin materials; 1 ton of recycled plastic can save up to ~130 million kJ of energy. The potential annual energy savings that could be achieved from recycling all global plastic solid waste is

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equivalent to 3.5 billion barrels of oil, worth approximately $176 billion dollars (3).

CURRENT RECYCLING APPROACHES
Mechanical recycling is the only widely adopted technology for large-scale treatment of plastic solid waste. The main steps are the removal of organic residue through washing, followed by shredding, melting, and remodeling of the polymer, which is often blended with virgin plastic of the same type to produce a material with suitable properties for manufacturing.

There are limitations to mechanical recycling technologies because each type of plastic responds differently to the process depending on its chemical makeup, mechanical behavior, and thermal properties. Temperature-sensitive plastics, composites, and plastics that do not flow at elevated temperatures (as in the case of thermosets) cannot be processed mechanically. Consequently, only two types of plastic are recovered and recycled with mechanical processes: poly(ethylene terephthalate) (PET) and polystyrenes, which represent 9% and 37% of the annual plastic produced, respectively. All other plastic solid waste is either not recovered or in amounts representing less than 1% of production (4). According to the most recent U.S. Environmental Protection Agency report, a mere 8.8% of all plastic produced in the U.S. annually is recovered from municipal solid waste and then incinerated, recycled, or industrially composted (1). The recycling rate is slightly higher in Europe, at ~30% for plastic waste (3).

Current technologies that move beyond mechanical recycling include pyrolysis (thermolysis) to selectively produce gases, fuels, or waxes through the use of catalysts (4); this is referred to as chemical recycling. Chemical recycling is not a widespread recycling practice, mainly because of energy costs. A further option is the incineration of materials and collection of energy in the form of heat. Incineration is convenient for the treatment of mixed waste because it avoids the need for sorting, but it does not allow for the recovery and reuse of the starting components once burned. It also does not save as much energy as recycling (3).

ADVANCING PLASTICS RECYCLING
Three ongoing research directions have great potential to advance plastic recycling practices: improving chemical recycling efficiency and selectivity through catalyst development, minimizing the need for sorting through compatibilizer design, and expanding recycling beyond thermoplastics.

Chemical recycling with thermolysis offers a recycling strategy through decomposition of a polymer to lower-molecular-weight products. However, depolymerization to monomers will require the development of catalysts that are selective and efficient yet preserve the functional groups in monomers while meeting requisite cost and energy metrics. Jia et al. recently reported the low-temperature (∼150°C) depolymerization of polystyrene through cascade reactions with a cocatalyst system (5). Although they did not achieve complete depolymerization to monomer, the work represents a promising proof of concept that can be further developed.

Researchers are also working on approaches that allow direct processing of commingled plastic waste. Current technologies for recycling plastics mainly rely on access to pure waste polymer feedstocks, which require costly and time-intensive sorting of municipal solid waste. The greatest challenge in recycling commingled plastic waste is that most plastics are immiscible with one another, producing phase-separated mixtures with diminished properties. Even small amounts of contamination of one plastic type with another may change the properties and potentially hinder use of the recycled material. This problem can be overcome through the development of compatibilizers that control the phase behavior of polymer mixtures (6).

Polymer compatibilizers are generally multicomponent polymers of various architectures—such as block copolymers, graft copolymers, and random copolymers—that are designed to have tailored thermodynamic interactions with the immiscible polymers in the mixture. They are analogous to surfactants developed for stabilizing immiscible oil/water mixtures. Applying polymer compatibilizer design principles to plastic solid waste would allow for more widespread recycling without presorting. For example, Eagan et al. recently developed a highly effective copolymer for blending polyethylene and polypropylene (7, 8). Ongoing areas of research include developing effective, and likely customized, compatibilizers for diverse plastic mixtures of varied compositions, accounting for polymer degradation during processing before recycling (9), and applying highly effective reactive compatibilization approaches to plastic solid waste (10).

All current recycling technologies focus on thermoplastics and take advantage of their processability in the high-temperature melt state. Cross-linked polymers, found in thermosets and elastomers, are not suited to these traditional mechanical recycling processes (although they can be ground into particulates or powders for limited applications). New developments that overcome these limitations include polymers with cross-links that reverse (11) or exchange (12) at elevated temperatures, which allow for reworking of the materials before reuse. Alternatively, polymers that can undergo chemical (13, 14), thermal, photo-, or biodegradation (15) may be recast into a new product or—in the case of complete depolymerization—repolymerized. An ongoing challenge is ensuring that material performance during its useful lifetime is not hindered while allowing for end-of-life degradation and/or reprocessing.

OUTLOOK
Enhancing plastics recycling beyond the current level (see the figure) has many potential societal advantages, such as reducing greenhouse gas emissions, avoiding waste buildup in the environment, decreasing the dependence on finite petroleum resources for its production, and recovering the economic value of plastic solid waste. Expanding recycling to a diverse array of polymeric materials will, however, require sustained research efforts.

To increase the recycling rate of plastics, new low-energy catalysts for chemical recycling must be designed that target polymers by type. In addition, decontamination techniques for the rapid cleaning of spent plastic and more efficient sorting in recycling plants...
to access higher-purity polymer feedstocks will be required to minimize the dependence on consumer separation of materials manually during disposal for collection.

Strategies for recycling mixed or contaminated feedstocks are also needed. Current compatibilizers must be customized for a given waste composition, which is not going to be practical on the large scale. More versatile methods are needed for controlling the physical behavior of plastic waste mixtures, which are diverse and variable in composition. Of similar importance is the ability to recycle composites containing more than one type of material (typically polymers, metals, or ceramics). Low-energy separations of mixed materials such as composites and multilayer packaging will require further development; there is currently no effective way to achieve such separation mechanically.

Successful adoption of new recycling approaches will require cooperation among researchers, industry, and government. New practices are already beginning to find their way into cities. For example, startup companies are scaling up chemical recycling methods for polystyrene waste and developing sorting processes for separation of materials into pure feedstocks. Such efforts are enhanced by programs to educate the public on the benefits of recycling. Furthermore, advanced computational modeling and data analytics for new catalyst, compatibilizer, and polymer discovery (with the ultimate goal of developing predictive capabilities) will aid in the optimization of recycling processes. Such efforts raise hope that before long, recycling rates for plastics will be much higher than today.

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POLYMER CHEMISTRY

Designed to degrade
Suitably designed degradable polymers can play a role in reducing plastic waste

By Ann Christine Albertsson and Minna Hakkarainen

Around 50 years ago, interest arose in making plastics that can degrade in the environment (1). Since then, a stream of research efforts has chased the dream of environmentally friendly materials that disappear without leaving behind fragments or harmful products. Such environmentally degradable plastics are, however, difficult to produce in practice. Durability is one of the requirements for plastic in most technical applications, whereas degradability is necessary for recycling in nature. Although advances are being made in developing degradable materials with suitable properties for particular applications, it is crucial that they are seen as part of a range of approaches and that degradation will always require particular conditions that depend on the specific material and its chemical and physical structure and composition.

CHALLENGING CONDITIONS

In biomedical applications, degradable polymers, including polyglycolide, polylactide, polycaprolactone, and polylactidemethylene carbonate, have been used successfully for decades. The materials can be kept under safe conditions such as low temperature and nitrogen until used, after which they start to hydrolyze. Through designing the polymer’s molecular architecture, it is possible to tuned the degradation rate and even degradation products (2). The human body is a relatively controlled environment with known temperature and degradation conditions, making it possible to create these materials with optimum degradation properties.

“Even plastics...that rapidly degrade in compost might not readily degrade in seawater or even soil...”

By comparison, natural environments have much wider diversity in variables such as humidity, microorganisms, oxygen, sunlight, and temperature, making it extremely difficult if not impossible to control and ensure the complete degradability of even potentially degradable plastic materials. Controlled conditions can be created in commercial composting plants, allowing plastics classified as compostable to be successfully degraded through the combined action of heat, moisture, and microorganisms. In a compost, degradation of a material to acceptable degradation products can be sufficient; this is, however, different from complete mineralization. One of the major problems connected to the development, use, and disposal of degradable materials is that none are degraded in all natural environments; a specific environment is needed, and the conditions required depend on the type of plastic. Claims of degradability or environmental degradability should thus always be connected to a specific environment. This is of course quite difficult, if we consider environmentally degradable plastics as an answer to the problem of plastic litter.

For example, plastic debris in marine environments is now widely recognized as an enormous environmental problem, requiring critical improvements in plastic handling and waste management (3). However, degradable plastics might not be the solution, because the conditions in seawater are not ideal for rapid degradation. Even plastics such as starch-based plastic carrier bags that rapidly degrade in compost might not readily degrade in seawater or even soil, because the favorable degradation process achieved in compost is not always achieved in the sea and in other natural environments (4). The degradation rate and the degradation products are also highly dependent on local characteristics such as the presence of light, oxygen, bacteria, and the temperature. This can cause serious problems; both conventional and degradable bags can rapidly alter marine assemblages and the ecosystem services they provide (4). A further complication arises from the fact that although we want the material to rapidly degrade in natural environments, it should not degrade during its shelf and service life.
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