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Innovations Toward the Valorization of Plastics Waste

Zachary R. Hinton,[1] Michael R. Talley,[1,2]
Pavel A. Kots,[1] Anne V. Le,[1,3] Tan Zhang,[1]
Michael E. Mackay,[1,4,5] Aditya M. Kunjapur,[1,5]
Peng Bai,[1,3] Dionisios G. Vlachos,[1,5] Mary P. Watson,[1,2]
Michael C. Berg,[1] Thomas H. Epps, III,[1,4,5]
and LaShanda T.J. Korley[1,4,5]

[1] Center for Plastics Innovation, University of Delaware, Newark, Delaware, USA;
email: zhinton@udel.edu, thepps@udel.edu, lkorley@udel.edu

[2] Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware, USA

[3] Department of Chemical Engineering, University of Massachusetts, Amherst, Massachusetts, USA

[4] Department of Materials Science and Engineering, University of Delaware, Newark, Delaware, USA

[5] Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, Delaware, USA

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Abstract

Plastics are an extremely important class of materials that are prevalent in all facets of society; however, their widespread use over time, combined with limited end-of-life strategies, has led to increasing levels of waste accumulation. Although currently considered a burden, plastics waste is potentially an untapped feedstock for numerous chemical and manufacturing processes. In this review, we discuss the state of the art of approaches for valorization of plastics waste from a materials research perspective, including previous efforts to utilize plastics waste and recent innovations that have opportunities to add significant value. Although additional progress is necessary, we present several diverse capabilities and strategies for valorization that, when brought together, address end-of-life challenges for plastics at every stage of design and product consumption. In short, a materials research–based framework offers a unique perspective to address the urgent issues posed by plastics, unlocking the potential of polymers and plastics waste.

1. INTRODUCTION

Plastic: polymer-based material that can be molded or extruded into defined structures

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Plastics are one of the most important innovations in materials science; however, the impact of these macromolecular materials on the planet is complex. Polymers have contributed immensely to global society, improving human quality of life and reducing the energy consumption and environmental harm associated with other materials (1). In the United States, plastics production began in earnest in the late 1950s and immediately overtook the production of copper and aluminum, increasing at a rate unparalleled by other key commodity materials (see **Supplemental Figure 1**) (2, 3). Yet plastics consumption is particularly problematic for several reasons. The major uses of plastics, packaging (40.8% by weight in 2012) and consumer/institutional goods (24.0% by weight in 2012) (4), direct more production toward shorter-lifetime applications than other commodity materials such as aluminum and steel (for which packaging and consumer/institutional goods combined accounted for <30% by weight of each material in 2012) (3). The demand for high-turnover products has pushed plastics production in the United States to reach levels comparable to wood/paper, steel, and cement, and production is likely to continue growing (see **Supplemental Figure 1*a***) (2, 3). Unfortunately, the difficulty of managing plastics waste has resulted in more than 75% (by weight in 2018) of discarded plastics being directed to landfills (5), in which they persist for longer than many other commodities, sometimes by orders of magnitude (see **Supplemental Figure 2**) (6, 7). Reliance on hydrocarbon feedstocks, widespread pollution by plastics in the environment, and the energy demands of manufacturing also contribute to the challenges posed by plastics (1, 8). Increased public awareness of these issues and others has spurred greater research activity to address the plastics problem (9), shifting the focus of plastics materials investigation from the development of novel polymers toward innovations that optimize end-of-life opportunities.

The recycling of materials is a longstanding concept for end-of-life management with significant economic and environmental benefits (10, 11). For commodity materials such as aluminum and copper, processes for continuous reuse greatly reduce greenhouse gas (GHG) emissions and energy demands compared with primary production (see **Supplemental Figure 2*b***) (10). Recycled metals frequently retain a large percentage of their original value; for example, recycled aluminum typically sells for 75% of the price per metric ton of its pristine counterpart (12) (see **Supplemental Figure 2*c***). Some recycled materials, such as paper and glass, have a broad range of applications that somewhat preserve value by directing waste to appropriate, lower-cost products, such as newspapers or bottles (12). Plastics, however, are often difficult to recycle while maintaining their value because of their wide-ranging physical forms and high degree of macromolecular complexity.

The increasing presence of plastics in consumer, medical, industrial, defense, and infrastructural areas has led to growing consumption of a variety of plastic types (13). Plastics in general offer a high strength-to-weight ratio, relatively low manufacturing cost, and high selectivity of material properties, making them beneficial in many applications compared with metal, glass, and paper (see **Supplemental Figure 1*b***) (1). In general, the properties of polymers and plastics are highly controllable through the manipulation of multiple chemical and structural handles. Specifically, the individual type of polymer used largely controls the properties of plastics. Over half (by weight) of the plastics produced globally consist of polyolefins, including polyethylene (PE) and polypropylene (PP). These polymers are unique due to their many possible molecular architectures (e.g., branching, stereochemistry), which contribute to a range of thermomechanical properties (e.g., modulus, crystallinity, density, dielectric quality, melt rheology, adhesion). Polymers containing heteroatoms or pendant functional groups include poly(vinyl chloride) (PVC), polystyrene (PS), and poly(ethylene terephthalate) (PET), which together account for approximately a third (by weight) of plastics produced globally (13). The functional groups contained in these polymers enable the tunability of macromolecular interactions and microstructures to yield properties such as chemical resistance, transparency, or flexibility. The remaining plastics are largely comprised of polyurethanes (PUs), polyamides (PAs), and acrylics [e.g., poly(acrylonitrile-co-butadiene-co-styrene) (ABS), poly(methyl methacrylate) (PMMA)] (13). These polymers utilize a library of monomeric chemistries, leading to high degrees of molecular tunability and properties such as flexibility, adhesion, foamability, and toughness, which facilitates their adoption for highly varied applications. In general, changing the molecular weight of any polymer is one of the simplest means of altering macromolecular behavior, impacting both processability and performance. Processing history, including molding method, thermal annealing, and mechanical drawing, can also modify properties such as appearance, strength, and toughness. Plastics also often contain an assortment of functional additives, processing aids, and fillers that serve to enhance material properties such as shelf stability, color, and strength (14). In short, the global scale of plastics was built on the diversity of material options; yet, these functional features now present significant challenges in the cost-effective treatment of plastics waste.

Mechanical recycling: the processing of waste to yield a secondary raw material (e.g., a reusable plastic)

Valorization: the controlling or increasing of a commodity's value through economic or production means

Circularity: the ability to retain a commodity in the production and consumption cycle

Approaches to valorizing plastics waste are incredibly diverse, utilizing numerous processes to obtain wide-ranging products; representative state-of-the-art routes are summarized in **Figure 1**. Although the practice of mechanical recycling is most widespread, challenges posed by the collection, separation, purity, and stability of polymers have historically limited valorization via this route (15, 16). The incorporation of chemical and biological processing methods can transform plastics waste into a variety of potential products including fuels, lubricants, monomers, new polymers, and carbonaceous materials (15, 17–22). Innovations in processing approaches rely on materials research to design efficient practices that tackle a broad spectrum of plastics waste. For example, the development of catalysts with unique geometries, chemical compositions, or hierarchical structures enables targeting of desired products using minimal energy (23, 24). Furthermore, the fate of expended plastics is increasingly being considered in manufacturing techniques and the design of polymers. Significant growth in minimizing the complexity of multicomponent plastics (e.g., via single-polymer multilayers enabled by advanced processing) and designing novel polymers with inherent circularity illustrate a pathway for instituting the potential for valorization as a performance characteristic (25–30). A variety of important innovations in developing complementary approaches toward scientific progress and stakeholder involvement are also advancing the field; for instance, computational calculations can accelerate the exploration of new valorization routes (31, 32), systems analyses can aid in the design of the most effective processes for leveraging the value of plastics waste (33–35), and educational outreach or political action can maximize the efficacy of upgrading tactics (36, 37). Moving from indiscriminate material development to addressing circularity using new strategies represents a critical leap forward in materials science and engineering.

In this review, we first address the historical aspects of discarded plastics, highlighting the need for innovation in this field. We then examine the most expansive development that has become commonplace: the chemical and biological conversion and transformation of plastics waste. We discuss the materials-focused aspects of these valorization routes and the challenges that restrict further advancement. We next survey the current state of the art of plastic materials designed for more controllable fates. Finally, we address key complementary approaches that streamline and enhance the impact of scientific research on tackling plastics waste on a larger scale. Throughout, we connect the various processing strategies and identify areas of focus for future innovation. This review highlights the progress achieved toward harnessing the power of plastics waste and raises awareness about the materials research needed for solving this persistent, global challenge.

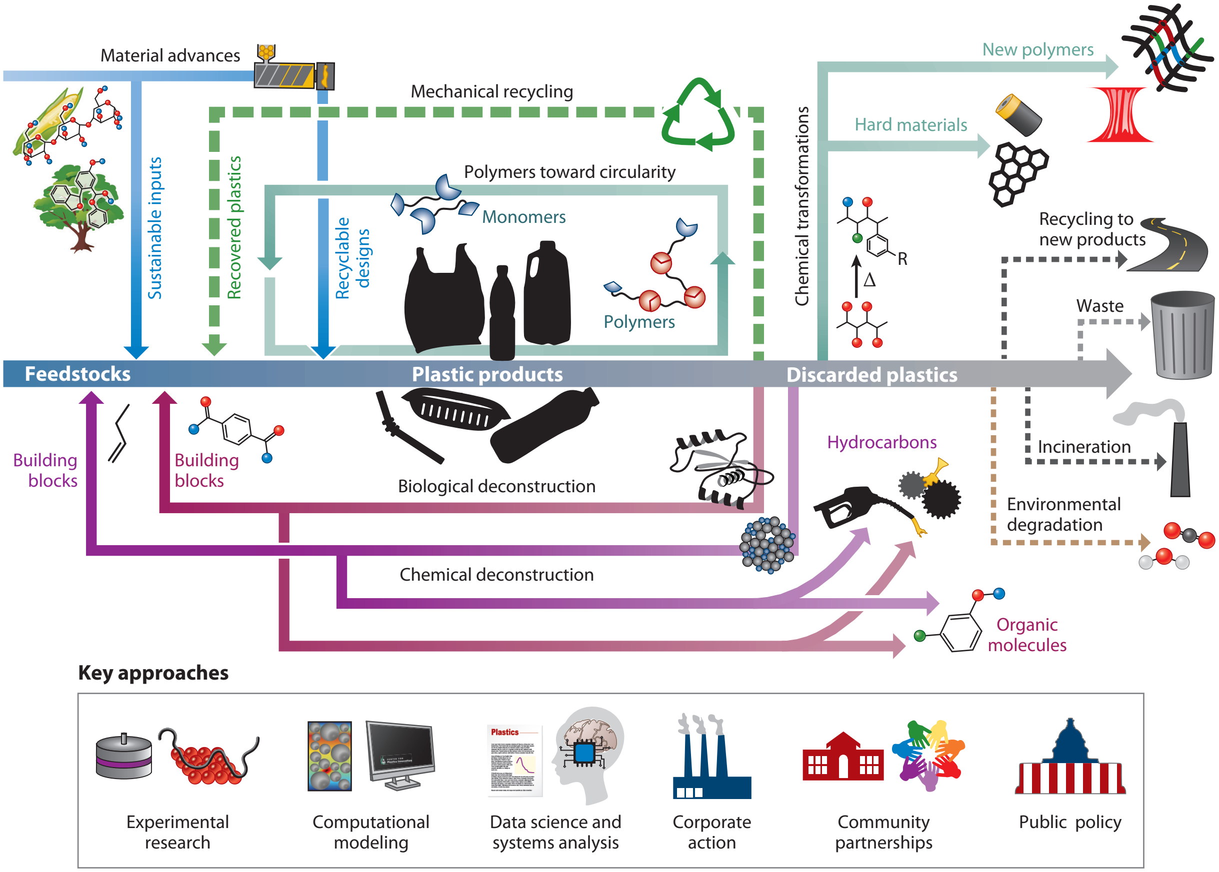

Figure 1

A summary of the key technologies and complementary approaches comprising innovations in plastics waste valorization. The traditional production cycle (*center*) proceeds from left to right, with feedstocks transformed into plastics that are eventually discarded. Approaches to upgrading waste into common products are illustrated, with arrows leading to the right representing products that lead to final use and arrows returning to the production cycle representing streams reentering plastics production.

2. CURRENT MANAGEMENT APPROACHES FOR PLASTICS WASTE

Management strategies for plastics waste have traditionally directed discarded materials to end-of-life options with negative environmental impacts and no (e.g., landfilling) or marginal (e.g., incineration) economic benefits or to circular options (e.g., mechanical recycling) with minimal value recovery. Plastics, as with most commodity materials, were almost exclusively discarded in landfills until the 1980s, and more than 70% (by weight) of plastics waste is currently subjected to this fate in the United States (5). The majority of commodity polymers do not degrade in landfills or in the environment on appreciable timescales (6, 38) and accumulate with detrimental ecological impacts (16). The oldest alternative to landfilling is the incineration of plastics waste, with or without recovery of energy (i.e., heat, electricity) (5). Although plastics have inherently high heating values and burning addresses accumulation, mitigation of considerable GHG emissions and the availability of lower-cost alternative fuel sources often result in poor economic value with this approach (16). Routes that maintain plastics in some economic cycle (i.e., recycling) offer an opportunity to extend the value of waste and potentially minimize the detriments of landfilling and incineration.

Recycling approaches that have been widely successful for other commodity materials (i.e., mechanical recycling) are often inadequate for plastics waste streams due to the difficulty in maintaining processing and performance properties in the recycled product. Since the 1980s, the percentage (by weight) of discarded plastics that has been mechanically recycled has been consistently less than half that of other materials (see **Supplemental Figure 2**) (5) due to the unique challenges of reprocessing plastics, as discussed below. These obstacles are further complicated by a shift to single-stream recycling (i.e., the comingled collection of plastics and paper) and the complexity of plastic products (39). Mechanical recycling involves the application of temperature to plastics waste to enable polymer flow through reforming operations (e.g., extrusion) to generate secondary raw, polymeric materials for manufacturing processes; however, heterogeneous plastics waste streams do not flow consistently at the same temperatures, and nonplastic contaminants (e.g., paper, metals, food residues) interrupt machinery and affect recyclate quality (40, 41).

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Efficient separation methods are needed for successful secondary (i.e., open loop, postconsumer) recycling by traditional means (42), whereas primary (i.e., closed loop, preconsumer) recycling keeps plastics waste within a single processing cycle. The wide range of consumed polymers cannot be treated as a single stream because of intrinsic thermodynamic incompatibilities and mixed properties (e.g., color, form factor, viscosity) that necessitate separation of waste by polymer type (40, 43). Polymer blends from comingled waste streams are extremely difficult to process because of phase separation–induced changes to rheological behavior and the high dependence of mechanical properties on composition and morphology (40). For example, blends of PE and PP phase separate to yield unpredictable melt viscosities, poor impact resistance, and low elongation at break (40, 43). Although compatibilization of mixed waste can be achieved with copolymers, nanoparticles, grafting, cross-linking, or significant dilution, the success of this approach is highly dependent on polymer types and increases demands on polymer production and, eventually, waste management (40). Complex industrial separation schemes already are in place (43), yet appreciable volumes of waste (e.g., multilayer films) cannot easily be separated into component parts due to strong adhesion between constituents (42, 44). Mechanical or solvent-based delamination of layers (e.g., erosion of adhesives) or dissolution and precipitation of component polymers alleviates separation challenges for some multilayer films (e.g., PET–PE); however, these methods rely on the identification of appropriate solvents and temperatures for specific waste streams and lead to added processing costs without necessarily achieving high degrees of separation on a large scale (16, 45, 46).

Notwithstanding advances to separation schemes, valorization by mechanical recycling hinges on the ability to obtain inputs for plastic manufacturing that are of an equivalent nature to virgin materials. Recycled polymers undergo thermal and mechanical degradation of macromolecular properties, either during original use (e.g., photooxidation-generated molecular fragments and oxygenated polymers) or during reprocessing (e.g., thermally induced chain scission, branching, or cross-linking) (41, 43). These fundamental changes to the polymer can pose threats to reprocessing equipment (e.g., corrosion) and to processability and performance (e.g., degassing) (43). For example, repeated extrusion of PP and PET leads to decreased elongation at break and impact strength, respectively, because of increased melt flow index, added dispersity, and lowered molecular weight (43). The addition of new additives, fillers, or fiber reinforcements may improve performance of recycled polymers; however, these components add cost and difficulty to subsequent recycling loops (40).

Even in the case of sorted plastics waste, the streams still contain diverse polymer and additive compositions that reduce the quality of recycled plastics (14, 47). Polyolefins are widely employed in a variety of products because of their easily tailored macromolecular architectures (e.g., branching) and corresponding properties (e.g., density, crystallinity); however, a stream of a single type of recycled plastic may be comprised of products that were manufactured using different techniques, yielding recyclates that require distinct processing characteristics (41). For example, waste milk jugs and margarine tubs are both classified as high-density PE (HDPE) but contain different molecular weights and degrees of branching that enable blow molding and injection molding, respectively; however, when mixed, the combined polymers yield a viscosity and crystallinity that are not suitable for reprocessing via either molding technique or for reuse in either product (41). Mixed contaminants and additives also challenge mechanical recycling because of their effects on melting behavior or viscosity and their potential as pollutants, which reduces recyclate value and acceptance because of undesirable characteristics (e.g., mixed colors, thermal instability) or potential risks to consumers (e.g., migration into food) (14, 41). For instance, flame retardants found in electronic waste have the potential to degrade into acids at elevated temperatures and are potentially toxic when recycled into household or packaging plastics (14).

Chemical recycling: the processing of waste to yield a primary feedstock (e.g., organic molecules)

Circular economy: economic system founded upon the retention of end-of-life goods in the production and consumption cycle

Deconstruction: the breaking down of macromolecules into smaller constituents by chemical, thermal, biological, or mechanical means

Another strategy for mechanical recycling reduces the need for a direct equivalent of virgin polymers by employing plastics waste as fillers or binders in other materials. As fillers, ground solid plastic can occupy a considerable volume fraction within another (typically nonplastic) material, which may reduce cost and divert considerable amounts of waste away from landfills without requiring traditional extrusion; however, utilization of plastics waste in this capacity remains difficult (48). For example, waste-filled cement can benefit structurally (e.g., high modulus, low density) from added plastic particles, but the effects of particle morphology and poor interfacial adhesion between the cement and plastic often limit the fraction of waste that can be incorporated and may negatively impact other mechanical properties (e.g., compressive strength) (48). Although plastics waste may act as a strong binder (e.g., in tiles or bricks) when melted to adhere solid particles (e.g., sand, wood), this approach also is limited by technological challenges (48). For instance, the thermodynamic incompatibility between mixed polymers and between polymers and solid particles leads to premature crack development and low porosity (48). Systems models show plastics waste directed toward new markets (i.e., not as plastic products) has limited impact on long-term waste generation (49); however, this route may be valuable to displace harmful materials, replace scarce feedstocks, or alleviate waste accumulation.

3. CONVERSION OF PLASTICS WASTE TOWARD VALUE, CIRCULARITY, AND BEYOND

Current state-of-the-art approaches to the valorization of plastics waste focus on means that utilize polymers as feedstock materials for a wide variety of products via chemical recycling. For each method, there are key material considerations and significant promise for increasing the value of plastics waste, establishing circular economies, and introducing new opportunities for discarded polymers (15–19, 22, 43, 50–57).

3.1. From Polymers to Molecules

Valorization of plastics waste often occurs via the deconstruction of polymers into smaller molecules; however, myriad polymeric feedstocks and sought-after products necessitate diverse strategies to optimize value. Deconstruction generally refers to any means of converting polymers into smaller constituents, ranging from chemicals and monomers to oligomers (58), and is typically achieved by either chemical processes (15–18, 22, 43, 50–57) or biological processes that employ living organisms or enzymes (19, 47, 59, 60). For either strategy, a major factor that influences process efficacy and potential products generated is the energy associated with the disassembly of a given polymeric feedstock. Heteroatoms in polymer (e.g., PET, PU, PA) backbones allow energetically favorable deconstruction at uniformly spaced bonds to yield homogeneous products (e.g., monomers, chemical building blocks), whereas carbon–carbon bonds, found in other polymers (e.g., PE, PP, PS), require more energy to break and can lead to a wider assortment of products from a single feedstock (15, 16, 51, 57). Furthermore, the variety of polymer types, macromolecular architectures, and processing histories found in plastics waste necessitates the development of new approaches to effectively target high-value products and minimize energy and environmental costs. Although deconstructive methods for the valorization of plastics waste currently treat less plastic (by weight) than mechanical recycling by an order of magnitude (15), research in this field continues to grow rapidly (9) and industrial-scale adoption is emerging (57, 60).

Depolymerization: the breaking down of macromolecules into their monomeric precursors

3.1.1. Chemical deconstruction.

Diverse options for chemical deconstruction processes exist wherein unique mechanisms lead to desirable products given a particular input of plastics waste. Thermochemical deconstruction, including gasification (61) and pyrolysis (62), operates at high temperatures to induce chain scission, indiscriminately converting polymers to gaseous (e.g., syngas, methane) or liquid (e.g., short aliphatic and aromatic hydrocarbons) chemicals. Solvolysis employs solvent to break bonds between backbone heteroatoms, obtaining building blocks or oligomers from the input polymers (46). Often gasification, pyrolysis, or solvolysis is restricted by high energy demands, poor product selectivity and value, or inadequate applicability to certain polymer types (16); however, catalysts have enhanced efficiency and control in these processes. Additional catalytic strategies (e.g., hydrogenolysis, hydrocracking) provide unique deconstruction mechanisms to convert plastics waste to a variety of high-value chemicals (e.g., fuels, waxes, lubricants) and monomers with moderate energy consumption and improved product selectivity (15, 21, 54). The range of chemical processes combined with the complexity of plastics waste has led to numerous possibilities for valorization.

The primary material criterion considered for the selection of a chemical deconstruction approach is polymer chemistry, and heteroatoms in polymer backbones facilitate valorization by production of polymer building blocks. Solvolytic techniques, typically involving alcohols, glycols, water, or amines that break labile bonds, have long been used for the depolymerization of PET and PUs (15). These techniques are widely applied, including industrially (57); however, material challenges limit broader implementation. For example, high crystallinity or low surface area can increase the time and energy needed to dissolve polymers (16). The various monomers comprising individual PUs, PAs, or polyesters can lead to complex product mixtures upon deconstruction; therefore, more advanced separations are necessary downstream. For some polymers, particularly PUs, the original polymer chemistry cannot always be reconstructed from the products of solvolysis, and processes that target the highest-value monomers require more attention (16). Furthermore, dilute polymer solutions are vital for facilitating processing (i.e., lower viscosity and temperature), increasing the scale of process equipment and the amount of solvent required (i.e., increased cost) and lowering kinetic rates despite the presence of catalysts (16).

Advanced catalytic approaches can provide additional options for processing conditions and potential products for heteroatom-containing polymers (63). For example, melt-phase pyrolysis, hydrogenolysis, or depolymerization can facilitate deconstruction of PET into monomers, fuel, and aromatic chemicals with minimal need for solvents (15, 57). The development of catalysts from earth-abundant materials (e.g., activated carbon) has made the hydrogenolysis of PET an even more attractive option because of the high conversion achievable at moderate pressures and temperatures (64). When molecules other than monomers are desired, tandem mechanisms (e.g., hydrolysis-hydrogenolysis) can also be employed to derive a larger slate of products from PET feedstocks (65). Less abundant polymer types (e.g., polyethers, PAs, polycarbonates) may also be valorizable using the approaches developed for PET (50); however, additional investigation is required to expand these technologies to address a wider variety of plastics and direct more complex waste streams toward high-value products and efficient processes.

Polymers containing only carbon–carbon bonds in their backbones (e.g., PE, PP, PS, PVC) require greater energy for deconstruction, and their lack of labile bonds leads to a wide number of possible products, depending upon the chosen catalyst (47). The introduction of heterogeneous and homogenous catalysts for pyrolysis processes has lowered energy requirements and increased product selectivity for the deconstruction of these polymers (15, 16); however, the deconstruction products are not always of high value. For example, many common catalysts (e.g., zeolites, amorphous silica-alumina, mesoporous acids such as MCM-41) produce only light alkanes of marginal value and still require substantial energy input (66–68). Researchers have sought to address these challenges by borrowing hydrocracking and hydrogenolysis technology from the refining industry for the deconstruction of polymers, with a wide variety of material chemistries, surface morphologies, and geometric structures employed in catalytic technology (15, 16, 51, 56, 57, 63, 69–71). By selecting appropriate catalyst support materials, product molecular weight or chemical structure (e.g., branching) can more easily be targeted, which expands the potential to generate high-value products (15, 35, 69, 72). For example, hydrocracking of PE and PP to lubricants and heavy waxes can occur at mild temperatures with high selectivity of products on the basis of catalyst properties (e.g., site types, site balance, geometry), leading to products that do not require additional chemical modification (e.g., chemical conversion, polymerization) to obtain high value (70, 73). In the case of PS, manipulation of the identity of the catalyst support material and the coordination number of Brønsted acid sites to limit hydrogen adsorption assists selectivity toward valuable aromatic products (see **Figure 2*a***), making deconstruction robust for additional markets (e.g., as solvents or chemical precursors) (23). These deconstruction methods will benefit from further refinement toward industrial relevance by improving scalability, selectivity, and profitability.

The unique material properties of bulk plastics waste can challenge the efficacy of many chemical deconstruction processes. Factors such as thermal behavior (glass transition temperature, crystallinity, melting temperature, etc.) are important to deconstruction pathways in the absence of solvent, which suggests that understanding the material properties of plastics waste is needed to guide process development (47). Separation by polymer type is required by many chemical deconstruction routes because many of the strategies that have been developed consider only one chemistry type; however, limited advances have been made toward adaptable processes that accept heterogeneous inputs with potential for valorization (15). For example, pyrolysis of mixed plastics waste and biomass has been demonstrated to yield valuable fuels (74). It should be noted that deconstruction could possibly enable better separation because molecular separation techniques (e.g., filtration, distillation) that are impractical for polymers (because of high viscosity or degradation without boiling) are simpler for small molecules. There is an opportunity for materials research that takes advantage of separation technology to convert mixed plastics waste to diverse product molecules.

Macromolecular characteristics, such as chain architecture and molecular weight, often lead to high variability of deconstruction products for a given process due to polymer dynamics (e.g., rheology, transport, adsorption, kinetics). These factors are seldom explored systematically (47); however, examples in the literature of multiple plastics of the same type being deconstructed at equivalent conditions (e.g., temperature, pressure, catalyst) illustrate the potential challenges (63, 73). For instance, hydrocracking of various HDPE and low-density PE (LDPE) pellets, bottles, and bags can yield different product distributions and selectivity for higher-value products (see **Figure 2*b***) (73). Catalyst design may improve processes despite unfavorable macromolecular phenomena by introducing novel structures to orchestrate desired deconstruction activity. For example, platinum (Pt) nanoparticle–decorated nanocuboids (shown in **Figure 2*c***) direct polyolefin adsorption to scission-active sites of the catalyst, improving yields of higher-value lubricants (24). Therefore, chemical approaches that are tolerant of mixed feedstocks of multiple plastic types and macromolecular structures and that drive controlled pathways for catalyst–macromolecule

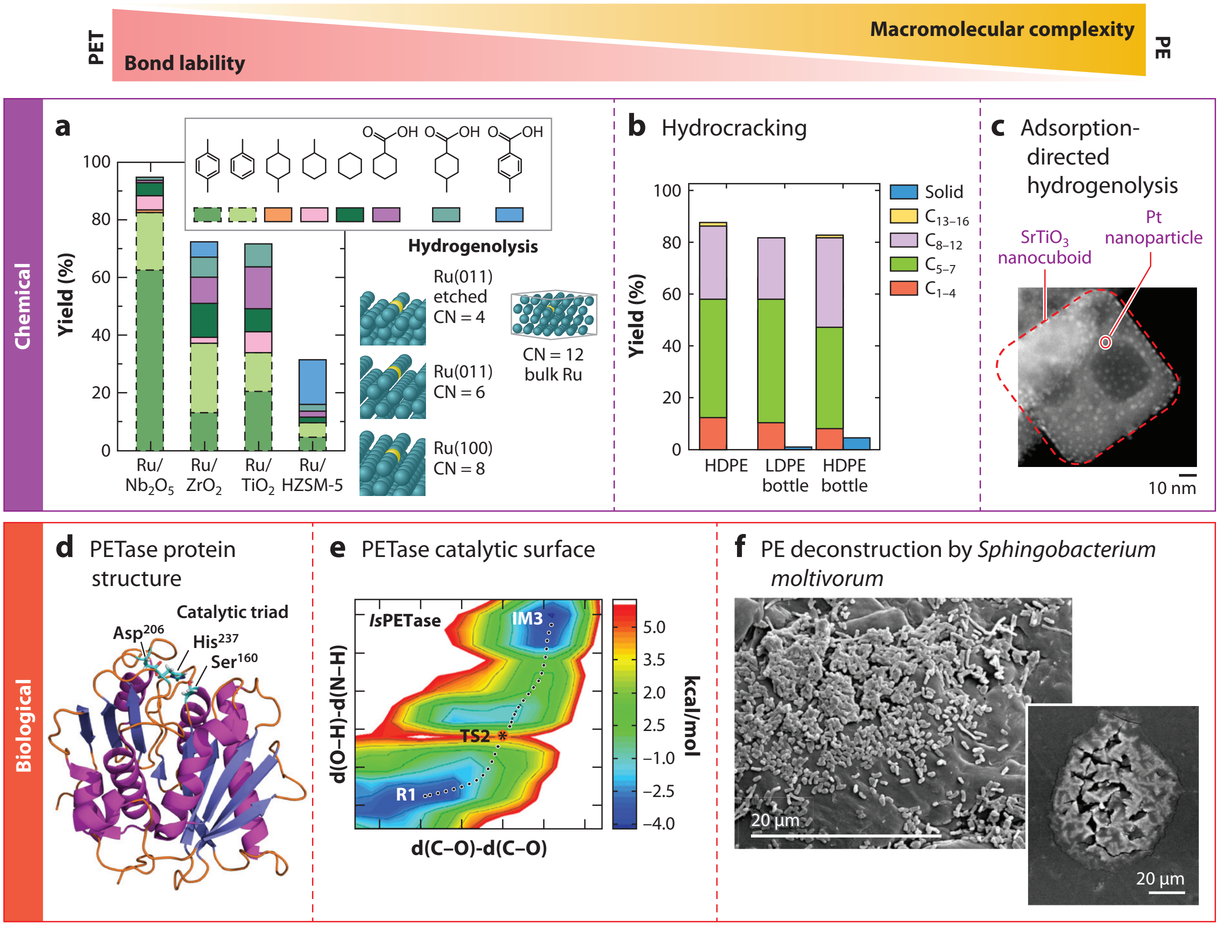

Figure 2

Example aspects of plastics waste deconstruction organized by methodology and feedstock characteristics, specifically bond lability and macromolecular complexity (e.g., branching). (*a*) Ruthenium catalyst support chemistry controls arene selectivity (*left*) of PET hydrogenolysis (*right*) via changing Brønsted acid site surfaces (*yellow*) of different CNs. Panel adapted with permission from Reference 23; copyright 2020 Wiley-VCH GmbH. (*b*) Specific types of single waste plastic (e.g., PE) impact the hydrocracking yield of products and selectivity of different carbon number ranges, likely due to macromolecular phenomena. Panel adapted from Reference 73 (CC BY-NC 4.0). (*c*) Pt nanoparticle–decorated $SrTiO_3$ nanocuboid hydrogenolysis catalysts direct adsorption of PE to scission-active sites. Panel adapted with permission from Reference 24; copyright 2021 Wiley-VCH GmbH. (*d*) The protein crystal structure design of PETase is critical for maintaining activity of the catalytic triad. Panel adapted with permission from Reference 75; copyright 2020 American Chemical Society. (*e*) Quantum mechanical calculations can identify transition structures and energetic pathways of PET deconstruction catalyzed by *Ideonella sakaiensis*–derived PETase (*Is*PETase). Panel adapted with permission from Reference 76; copyright 2021 American Chemical Society. (*f*) Scanning electron microscopy reveals the differences between PE particle (*left*) and film (*right*) erosion resulting from microbial colonization and decomposition by *Sphingobacterium moltivorum*. Panel adapted from Reference 77 (CC BY 4.0). Abbreviations: CN, coordination number; HDPE, high-density PE; IM3, charged tetrahedron intermediate; LDPE, low-density PE; PE, polyethylene; PET, poly(ethylene terephthalate); R1, PET reactant; TS2, transition structure.

interaction are highly desirable for improving the value of products and lowering the cost of processes.

3.1.2. Biological deconstruction.

In contrast to chemical routes, biological deconstruction occurs via organisms or components of living things. Although most synthetic plastics do not degrade

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Bioderived: sourced primarily from biological and biobased feedstocks

in natural environments within relevant timescales (see **Supplemental Figure 2**) (6, 38), enzymes and microorganisms can be engineered to valorize plastics waste in controlled systems. Recent advances in metabolic engineering and synthetic biology have enabled rapid modification of a variety of microbes to perform well-controlled chemistries, including those that are uncommon or are not known to exist in nature (78). During the past decade, much effort has been invested into identifying or conceiving of microbes that deconstruct other recalcitrant materials, such as lignocellulose (79), sometimes within biphasic or highly organic systems. In these cases, cells, organisms, and ecosystems act as catalysts via their component enzymatic activity. Although enzymes are sometimes perceived as expensive or fragile, they are not limited to service in high-value applications (e.g., pharmaceutical production) (78). For instance, enzymes typically function under mild conditions (e.g., near ambient temperature, atmospheric pressure, neutral pH), but subsets of enzymes can function under process conditions required for polymer dissolution or monomer stabilization (e.g., in organic solvents, with detergents, at 50–100°C) (60). With the correct choice of input material and target product, enzymatic biocatalysis using cells or in cell-free systems can also be an attractive option for the deconstruction of plastics waste, both in natural environments and in synthetic processes, with low energy requirements and high selectivity toward valuable products.

As with chemical methods, biological approaches are dependent upon substrate chemistry, and polymers with heteroatoms in their backbones (e.g., PET, PA) possess energetically favorable bonds for facile biological deconstruction. Natural hydrolase enzymes are most successful when applied to polymers with structures that resemble the natural macromolecules that organisms utilize for nutrient storage [e.g., poly(hydroxyalkanoates) (PHAs)] (80–82). The identification and engineering of hydrolases, such as cutinases and PETases, have made the enzymatic degradation of PET industrially competitive (75, 76, 83–85). Microbes have been designed to perform multiple process stages (e.g., deconstruction, bioconversion) to yield new aromatic hydrocarbons from waste PET that are useful as cosmetic, pharmaceutical, and agricultural feedstocks (82), increasing the value of deconstruction products. Enhanced efficiency can be gained by combining biological functionalization with thermochemical deconstruction, for example, by using solvolysis as a pretreatment for bioconversion to more valuable molecules than monomers (86). Thus, biocatalysis offers an opportunity for biological deconstruction to serve as an alternative and as a complement to chemical routes; however, strategic engineering of effective microbial processes to generate the desired products is ongoing.

The sharp contrast between the chemistries of carbon-only polymer backbones (e.g., PE, PP, PS, PVC) and those of natural molecules presents greater difficulty in engineering biocatalytic strategies for valorization. Nature has provided selective and evolutionary pressure for microbes to break down hydrocarbons in natural environments (e.g., near geologic leakage, after oil spills), but while cells containing these enzymes (e.g., alkane hydroxylases) tolerate natural alkanes (i.e., petroleum), they are unlikely to accept polymer substrates because of the difficulty of transporting synthetic macromolecules across cell membranes (87). The introduction of synthetic plastics into the environment for over 50 years provides a driving force for microbes to learn to handle these carbon-rich sources for growth (88). For example, the larvae of some insects have demonstrated an ability to breakdown LDPE via synergistic contributions of the digestive system mediated by gut microbes, host enzymes, and digestive fluid (89). This example, and other examples of bacteria, fungi, and enzymes developed from environmental sources, highlights the potential of natural organisms to accelerate the degradation of many synthetic plastics (19, 59, 90). Although biologically mediated deconstruction often cannot compete with the timescales of a typical chemical process, opportunities exist to utilize bioderived agents to valorize plastics waste in scenarios in which separations are challenging or chemical resources are scarce.

Material properties of plastics waste are often of greater significance to biological valorization processes than chemical ones because some enzymes and many microbes are thus far viable only at conditions for which polymers are solid (i.e., below softening/melting temperatures, in the absence of solvent). Careful design of cellular components (e.g., surface enzyme structure) can enhance biocatalytic activity for as-received plastics waste with great success (91, 92), and optimization of biological strategies that match substrate to organism can be facilitated by computationally driven design or mechanistic studies (as illustrated in **Figure 2*d*,*e*** for PETase) (75, 76). For most commodity plastics, biological deconstruction must be capable of targeting semicrystalline, high-modulus substrates, and process outcomes are highly dependent on properties such as polymer chain mobility, elasticity, and density (93), as well as form factor. For example, eroding bacteria colonize PE particle surfaces differently than they colonize films found in many experimental measurements (see **Figure 2*f***) (77). Additional pretreatment stages (e.g., mechanical grinding, amorphization) may make substrate characteristics more favorable for microbes (16, 60); however, these processes could contribute to higher costs or energy demands. Further progress is needed to harness the power of bioengineering to address the complexity and prevalence of plastics waste and desire for more valuable outputs from deconstruction.

Upgrade: increase the worth or utility of a material by transforming it into a more valuable product

3.1.3. Deconstruction for the circular economy. Both chemical and biological deconstruction of plastics waste can be employed to produce hydrocarbons and other organic molecules for use as fuels and fine chemicals; however, a prime target for these processes is the facile production of feedstocks for virgin polymers. Theoretically, these deconstruction routes to new plastics can supersede mechanical recycling because chemical structure, molecular weight, and architecture is obtainable in ways that reflect conventional polymerization, leading to upgraded plastics with the exact properties, and therefore value, of the original materials (50). For polymers that are easily depolymerized or deconstructed to monomeric or small molecules, the circular economy is conceptually straightforward. For example, in the presence of appropriate solvents, solid catalysts, or PETase enzymes, waste PET can be exploited to produce the majority of chemicals needed for PET production (15), and similar results have also been reported for PS and PMMA (94, 95). In some cases, deconstruction does not lead to monomers that are identical to the starting materials of the input polymer; however, opportunities exist to develop new polymers from mixtures of monomers or oligomers without the need for costly separations (57). For processes that yield nonmonomeric products (e.g., from PE, PP, PVC), circularity requires more complex strategies due to the inherent difference between the deconstruction products and their typical building blocks. Using the appropriate catalyst and process parameters, monomers may be more targetable than other products; for example, pyrolysis of PE to ethylene and hydrogenolysis to small alkenes could provide the raw materials for many types of PE (20, 96). Technological advances must overcome the economic challenges that currently hinder the competitiveness of circular efforts within conventional polymer manufacturing (35). Further emphasis on cost-effective and environmentally sound processes that enable a circular economy for plastics should be a priority for all types of plastics (9) with additional attention to the quality and value of polymers derived from waste.

3.2. Chemical Transformation: From Plastics Waste to Virgin Materials

Transformation of plastics waste to directly produce new virgin materials is an often-overlooked alternative to deconstruction that takes advantage of the macromolecular nature of discarded polymers as a foundation for new products. Chemical transformations modify polymer chemistry (i.e., by adding or changing functional groups) to facilitate the synthesis of novel polymers or hard materials (e.g., carbon nanotubes, salts) (22, 47, 97) or to enhance aspects of other valorization strategies (e.g., sorting, deconstruction, compatibilization) (15, 40).

3.2.1. Transformation of waste polymer chemistry toward new polymers. The use of polymer feedstocks of a specific chemistry to produce polymers with different functional groups offers opportunities for plastics waste valorization along with advantages for the production of performance materials. Post-polymerization functionalization is a well-established technique whereby even small numbers of added or converted pendant chemical groups can induce fundamental changes to macromolecular behavior. This approach has often aided in the tailoring of polymer functionality for specialized applications such as therapeutics delivery (98). Transformation of existing macromolecules may facilitate efficient polymerization approaches to achieve a suitable backbone structure (e.g., molecular weight, branching) with subsequent functionalization to provide other desirable macromolecular properties (e.g., self-assembly, phase behavior) without copolymerization or blending. For cases in which functional monomers may be difficult to polymerize directly, chemical transformation represents an alternative approach for the fabrication of specialized materials for many applications (e.g., medicine, textiles, water treatment, packaging) (99). For instance, difficulties in step-growth polymerization of monomers with dissimilar electronegativity (e.g., highly fluorinated versus hydrogenated aromatics) or molecular size [e.g., poly(ethylene glycol) acrylate versus methyl acrylate] can be alleviated by chemical modification of PET or PS (100). Therefore, chemical transformation of plastics waste should be considered an important route for valorization that may have unique benefits over conventional manufacturing.

While deconstruction is often facilitated by heteroatoms in the backbone, transformation is enabled by pendant functional groups that are chemically addressable (e.g., those found in PVC, PMMA). Transformations of this type have potential in a variety of valorization schemes, depending on the targeted application and appropriate chemical reaction. For example, chemical grafting of bulky molecules (e.g., natural compounds) onto PVC can introduce new, self-plasticizing architecture (101) (see **Figure 3*a***) that improves melt processability and holds promise for compatibilization (40). Other chemical schemes often involve click reactions (e.g., cycloadditions to azides, thiol-ene/yne processes, nucleophilic additions) and substitution (e.g., azidation, thiolation), which can be used to graft any corresponding molecule onto already well-defined polymer backbones, provided optimized conditions (102, 103). Thus, given a desired product specification, plastics waste could be substituted as a feedstock; however, new markets for the products are yet to be fully defined (9).

Polymers (e.g., PE, PP, PS, PET) without reactive pendant groups to enable chemical reactions must have entirely new functional groups introduced to achieve significant chemical transformation. One common approach to functionalize all-carbon polymer backbones is C–H activation (102). Oxidation of various PEs has been demonstrated to produce both adhesives and functional materials using a homogeneous catalyst (104) (see **Figure 3*b***). Other pathways, such as esterification, borylation, and dehydrogenation, have been reported for polyolefins, with the addition of a variety of functional groups (e.g., maleimides, anhydrides, carboxylic acids) achievable (102). These modifications can also be applied to polymers containing heteroatoms, leaving the backbone intact when adding new chemical groups. For example, arene substitution of both PS and PET can be achieved catalytically to add tunability to modulus, viscosity, and wettability (108). Thermoplastics can also be transformed into novel thermosets (see **Figure 3*c***) (105), and cross-linked polymers that are typically nonrecyclable [e.g., poly(sodium acrylate) absorbents in diapers] can be transformed into thermoplastics (109). Modest changes to the chemistry of a polymer, particularly by adding dissimilar chemical groups, often lead to marked changes in rheology, thermodynamics, and mechanical properties; therefore, transformations may require lower conversions of input polymers than deconstruction to achieve higher value (47).

Chemical transformation also can be a route for the enhancement of other valorization strategies. Selective surface functionalization of ABS can improve separation of mixed plastics via

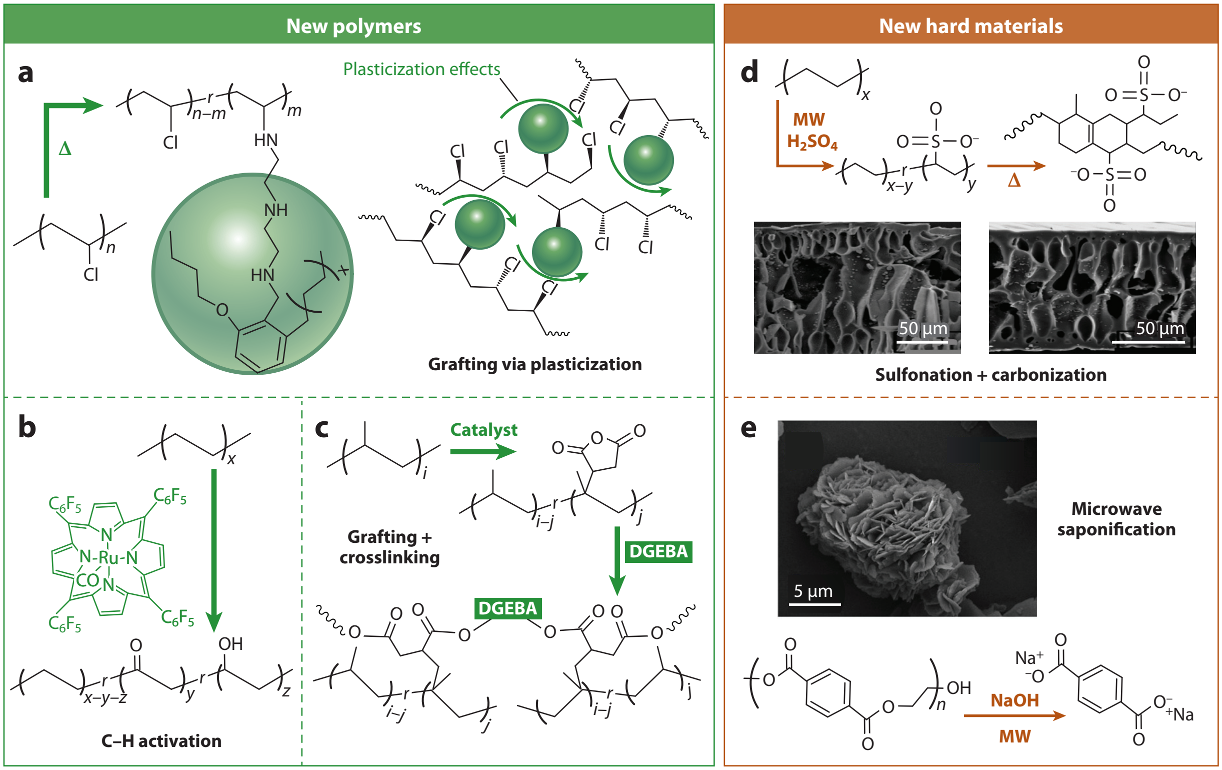

Figure 3

Examples of chemical transformation strategies for plastics waste organized by end product. (*a*) Self-plasticization of PVC by chemical grafting of biobased molecules reduces interchain friction to improve processability. Panel adapted with permission from Reference 101; copyright 2017 American Chemical Society. (*b*) C–H activation of PE using a polyfluorinated ruthenium porphyrin catalyst creates adhesives (104). (*c*) Maleic anhydride grafting of waste PP enables cross-linking with DGEBA (105). (*d*) Microwave sulfonation of LDPE film (*left*) facilitates carbonization to structured carbon scaffolds (*right*) for lithium–sulfur battery interlayers. Micrograph images adapted with permission from Reference 106; copyright 2018 American Chemical Society. (*e*) Microwave-assisted saponification of PET flakes yields disodium terephthalate flowers. Micrograph image adapted with permission from Reference 107; copyright 2020 American Chemical Society. Abbreviations: DGEBA, bisphenol A diglycidyl ether; LDPE, low-density PE; MW, microwaves; PE, polyethylene; PET, poly(ethylene terephthalate); PP, polypropylene; PVC, poly(vinyl chloride).

flotation (110). The reduction of phase separation and control of the microstructure of mechanically recycled mixed plastics waste can be enabled by reactive compatibilization or cross-linking, improving the mechanical performance of recycled plastics (40) and potentially reducing reliance on separations. Transformations may also enhance chemical or biological recycling. For example, challenges due to the evolution of corrosives during the chemical deconstruction of chlorinated plastics (e.g., catalyst poisoning, fouled process equipment) may be alleviated by catalytic dechlorination (15). Additionally, the introduction of functional groups to expand chemical vulnerability or microbial growth can augment catalytic and enzymatic action to accelerate deconstruction (88). These novel chemical strategies highlight the potential of chemically transformed plastics waste, but widespread adoption will require assessment of the entire plastics value chain.

3.2.2. From old plastics to new hard materials. Chemical transformations also can target nonpolymeric products, valorizing plastics waste for entirely new material applications. The high carbon content of most commodity polymers restricts many valorization outputs to hydrocarbon or organic polymer products. This feature also makes plastics waste a useful feedstock for a range of carbonaceous materials, for which there is an increasing demand for various applications (22). Thermochemical methods for pyrolysis, liquefaction, and gasification to synthesize carbon nanomaterials from waste polymers represent the most widespread examples of this route (22). These processes can be streamlined using a variety of catalysts that can be tuned to produce unique carbon structures, such as nanotubes, graphene, hollow carbon spheres, fullerenes, and magnetic carbon, all of which have applications in commodities and advanced materials (15). Carbonization of plastics waste offers a potential replacement for petroleum-based processes, often with enhanced design capabilities and added value.

Plastics waste can also be transformed to functional, carbon-based materials, which often take advantage of form factors to enhance the resultant properties. The simple formation of plastics into desired geometries (e.g., films) adds value both to the original plastic product and to potential hard materials made from waste. For example, thin HDPE and LDPE bags can enhance solvothermal sulfonation to produce carbon interlayers for lithium–sulfur batteries, in which advanced structures (see **Figure 3*d***) provide high capacity and cycle retention (106, 111). HDPE films are conducive to flash heating to quickly convert to graphene due to their already planar morphology (112). Other hard materials can also be derived from lower-carbon-containing polymers (e.g., PET, PVC). Combined depolymerization and saponification of PET takes advantage of backbone regularity to generate small-molecule-based hard materials such as disodium terephthalate 'flowers' for electrodes (see **Figure 3*e***) (107). Dechlorination and carbonization of PVC have led to capacitive materials comparable to the state of the art (113), and other hard materials (e.g., coke, calcium salts) have been derived from PVC waste (114). Although the range of options for hard materials from plastics waste appears relatively limited, the development of thermochemical and transformational strategies means that hard materials of many types are likely possible given careful selection of process flow. Notwithstanding this fact, the shift from petroleum to plastics waste for production illustrates the great opportunity for valorization in many unconventional markets.

3.3. Potential Widespread Challenges to Upgrading

Although chemical and biological routes to valorizing plastics waste hold vast opportunities for end-of-life management, several widespread challenges remain. Drawbacks to chemical approaches include their significant energy demands and potential for negative environmental impacts (115); however, the utilization of plastics waste as an alternative feedstock likely means savings in costs and increases in benefits over landfilling (16). Because of the technological limitations of many processes, chemical and biological routes may strongly depend on the ability to sort plastics waste, which is similar to mechanical recycling in its correlation between effective separations and higher potential value. In 2020, the average sorting process in the northeast United States cost $106/metric ton, and collection and sorting efforts across the United States contributed an additional GHG emission of 93–98 kg CO_2 equivalents per metric ton and consumed 552–604 MJ/metric ton in energy (116). These figures highlight the need for approaches that reduce the burden on sorting waste without sacrificing ultimate value. Another challenge to the adoption of chemical recycling is capital cost, leading to only limited commercial instances (57). For example, typical deconstruction facilities have capital requirements of $0.98–$1.41/kg, which is higher than the market prices of fuel products and virgin plastics derived from petroleum (34, 116, 117). Separation of deconstruction products is responsible for around half of the GHG emissions and capital cost of chemical recycling, suggesting the need for carefully planned strategies that maximize value from every product and reduce ecological harm in comparison with traditional routes (34, 116). These factors demonstrate the need for industrially relevant process design that integrates with existing chemical processes, supply chains, and environmental mitigations. It is critical that future technological innovations, particularly those approaching circularity, focus on designing processes that lead to a competitive economy with virgin polymer, chemical, or material production.

4. MATERIALS ADVANCES TOWARD INHERENT CIRCULARITY

Beyond deconstruction and upgrading approaches, there are opportunities to reimagine the landscape of plastics production, especially in view of the burgeoning demand for increasingly complex, multifunctional materials (25, 45, 118). In this section, we outline selected advances in manufacturing technology and material design and synthesis to reduce plastics waste and balance product performance, cost effectiveness, ecological impact, and recycling infrastructure.

4.1. Manufacturing for Valorization Potential

The valorization of plastics waste can be facilitated by manufacturing advances that address the complexity of product formulation (e.g., additives, polymer types) and composition (e.g., multilayer, multicomponent) in product design. These approaches can yield materials that are more tolerant to mechanical and chemical recycling approaches and maintain product performance. Single objects (e.g., plastic bottles for beverages or detergents) comprised of several distinct polymeric components in various forms (e.g., PET bottle, HDPE cap, PU adhesive, PVC label) represent complex plastics that require separation toward individual valorization pathways to address the material diversity inherent in and critical to their intended use. By simplifying product design and manufacturing (i.e., reducing plastics composition across individual components), there is potential to reduce reliance on advanced sorting techniques and to enhance the quality of recycled feedstocks (119). For example, plastics manufacturers have begun implementing shrink labels in place of adhered labels to reduce unnecessary contaminants (e.g., paper, adhesives) in plastics waste (119). Furthermore, application of polymers (e.g., metallocene linear LDPE) with specific macromolecular characteristics, such as short-chain branches and low dispersities, specialty coatings (e.g., heat-resistant varnishes), and forming techniques (e.g., mechanical drawing) have led to advanced multilayer structures that maintain functionality (e.g., barrier properties, stiffness) and require fewer types of polymer (e.g., all-PE pouches) (120). Additional investigations are necessary to optimize factors such as mechanical robustness, printability, and adhesion, as well as to balance cost and promote consumer adoption of new products designed to minimize component variability (121).

Similar challenges exist in materials, such as multilayer packaging, that contain multiple, difficult-to-separate components (e.g., chemical additives, fillers, polymers) that are often utilized in applications requiring specific performance qualities (e.g., barrier properties, tear resistance, toughness, shelf stability) (45, 118). There are new opportunities to reshape manufacturing and design strategies to enable valorization by imparting unique chemical or structural features. Multilayer packaging designs that incorporate stimuli-responsive polymers, nanoparticles, or surface-modified macromolecules to replace numerous components have the potential to enable rapid separation by imparting triggerable surface activity that facilitates the decoupling of layers for reprocessing (25). These strategies may also assist in the reduction of additives (e.g., compatibilizers, plasticizers, colorants) (121) that limit the value of mechanical recyclates (122) and potentially impede deconstruction and upgrading pathways (16). It is critical that new product design and manufacturing strategies address reducing material complexity, while also maintaining functionality (121).

4.2. New Polymers: Waste Mitigation to Circularity

Upcycling: repurposing of waste material as new products not originally part of the production cycle

Biodegradable: able to be broken down by the action of living organisms (e.g., via bacteria)

A complementary approach to improving the recycling and upcycling of plastics waste is the conception of new polymers with unique chemistries that enable circularity or reduce environmental impact by reconsidering the molecular-level stability of commodity plastics (123). We highlight the design of new polymers with chemical functionality that promotes degradation or depolymerization and the development of polymers derivable from sustainable building blocks with the potential to mitigate pollution and health concerns.

4.2.1. (Bio)degradable and bioderived polymers.

Many of the most common plastics, such as PE and PP, are relatively inert under natural conditions due to the stability of the C–C backbone (38); however, degradable polymers that contain labile groups (e.g., esters) to enable cleavage under specific conditions (e.g., exposure to light, water, or oxygen) lead to lower-energy routes for targeted plastics waste deconstruction (124). A few examples of popular degradable polymers include poly(lactic acid) (PLA), PHAs, and poly(caprolactone) (PCL). For instance, PLA is commonly lauded as a potential biodegradable replacement for PS and PET in single-use plastics; however, degradation in natural environments is prohibitively slow and highly dependent upon stereoisomer content (124). Although composting in controlled temperature environments speeds degradation, industrial composting is currently lacking large-scale implementation, and degradation products typically are not capturable or valuable (125). These challenges may be alleviated by further development of potential circular economies. For example, environmentally degradable polymers discarded in a dedicated landfill could support agricultural feedstocks for biological production of new polymers (126); however, this approach would necessitate significant infrastructure investments. Without mitigating technologies such as those addressed above, these polymers are suited to impact only waste accumulation and not valorization.

It is also possible to employ engineered microorganisms and enzymes to promote plastics degradation (124, 127, 128). Biodegradable polymers utilize these living organisms to accelerate breakdown of plastics waste via targeted pathways to yield degradation products with the potential for several upgrading routes (e.g., toward compost) (126). Advancing the implementation of biodegradable polymers as replacements for plastics production is challenging due to the difficulty of defining the criteria for biodegradation and the lack of waste-management infrastructure (e.g., sorting, landfill/compost) for ensuring the appropriate conditions for breakdown are met (127). For example, PCL degradation depends strongly on soil type and does not typically occur in wet or anaerobic environments; however, it is commonly labeled as biodegradable without consideration of the disposal conditions (124, 127). Although burgeoning biocatalytic methods for deconstruction have the potential to address degradable and commodity polymers together, valorization will require additional efforts to direct degradable waste to appropriate management facilities.

Material properties are a critical consideration for biodegradable polymers, but qualities that impart desired performance often reduce the efficacy of degradation. For example, highly crystalline PCL and PLA have limited degradability because microorganisms preferentially attach to the amorphous regions (124). Furthermore, degradable polymers typically perform poorly (e.g., low moisture resistance, short shelf stability) in common plastics products or present difficulties in processing (e.g., uncontrollable viscosity, tendency to foam, thermal instability) (124, 125). Although additives often improve the properties of degradable polymers, they also hinder degradation. For instance, plasticized PHA is more easily processed, yet when its additives leach in degradation environments, they often poison microorganisms and slow decomposition (126).

Another avenue often considered for mitigating plastics waste is the use of bioderived polymers, which may be potential replacements for traditional petrochemical-based polymers.

Depending upon the biomass source and resulting building blocks, these bioderived polymers may have reduced energy reliance and potentially lower environmental concerns related to plastics manufacturing and consumption; however, bioderived polymers are not inherently degradable (26, 124, 129). New plastics derived from biomass offer a unique framework for the replacement of current high-performance materials. There must be careful consideration of the ways in which these materials not only reduce reliance on fossil fuels but also alleviate plastics waste pollution via synthetic and manufacturing innovations that enable efficient and selective recycling and upgrading (9). For example, enhanced biodegradability can be achieved by blending biomass-derived thermoplastic starch with PLA (26) or by grafting biodegradable polymers onto lignin fillers (129). Expansion of monomer syntheses that utilize lignin feedstocks, as one example, offers promise for the development of new routes to many high-performance polymers, but it is also important to balance these bioderived material design strategies with consideration of the renewable nature of the feedstocks utilized and the potential impact of bioderived plastics on the end-of-life treatment of already complex plastics waste streams (9, 39).

4.2.2. Polymer chemistries toward circularity. Polymers containing chemical linkages that, at moderate temperatures or other conditions (e.g., pH), facilitate depolymerization are an example of materials designed for continuous valorization to monomers within a circular economy. For commodity polymers, polymerizations have energetic barriers such that deconstruction requires high energy input with modest selectivity for monomers; however, polymers whose threshold for depolymerization is sufficiently minimized at reasonable temperatures (near ambient) offer routes toward continuous monomer–polymer cycles (50, 97). Examples of polymers containing ether, carbonate, ester, amide, or disulfide linkages have been demonstrated in the literature, with favorable deconstruction energies achieved using heat (30, 130), pH (131), catalyst (27), or solvent (29) toward high monomer yields (132, 133). Although these materials address the thermodynamic limitations of a circular economy, challenges to wide-scale adoption, like waste collection and polymer performance, remain (50).

Energetic advantages that facilitate the recycling of polymers into monomers may be accompanied by processing constraints, which must be overcome to develop replacements for commodity plastics. Low energy barriers to depolymerization near ambient temperatures carry the potential risk of poor polymer integrity in common applications; however, chemical modification strategies can alleviate these challenges (50). For example, poly(γ-butyrolactone) endcapping (134) and catalysts for reversible deactivation of poly(acetal)s (133) modulate depolymerization to be more controllable at desired temperatures. For large-scale growth of circularity to take place, direct replacement of commodity polymers must be achievable, meaning similar chemical structures, macromolecular architectures, processability, and performance are required (50). Newly developed polyesters [e.g., polyester-18,18] and polycarbonates [e.g., polycarbonate-18] have been constructed with large alkyl sections within the monomer, imparting similar crystalline structures and tensile properties to HDPE (see **Figure 4**) with an enhanced ability to obtain monomers from waste (29). Using multifunctional monomers offers the ability to tune mechanical properties (e.g., melt flow, density, strength) (28) and could have significant potential for designer monomers that yield mimics for existing, desirable architectures (e.g., branches). Polymers that contain both breakable intra- and interchain bonds yield tunable performance qualities, rheological characteristics, adhesion strengths, and more with a single base monomer (131). These macromolecular structures can promote a more sustainable product design. For instance, multilayer films could be composed of polymers with different interchain bonds but the same backbone chemistry, imparting desired properties to individual layers while also enabling the entire film to be recycled simultaneously without delamination (28, 29, 131).

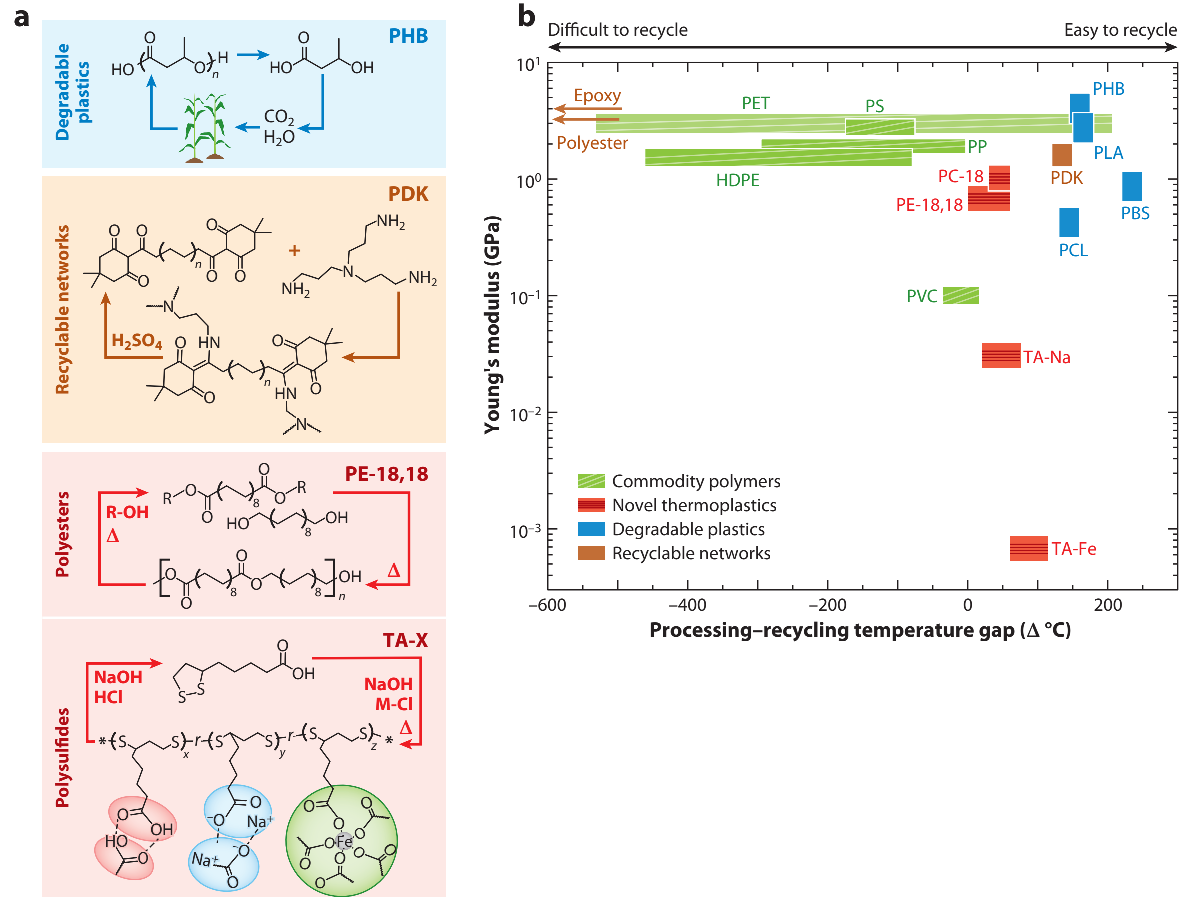

Figure 4

(*a*) Examples of chemical schemes for polymers exhibiting circularity. PHB environmentally degrades to agriculturally derived feedstocks (126). Recyclable PDK covalent networks undergo acid catalyzed depolymerization to monomers (28). Novel aliphatic polyesters with polyethylene-like properties, such as PE-18,18 (where 18 refers to the number of carbons in both monomers and, hence, the number of carbons between ester linkages), are deconstructed to monomers by alcohols (29). Tunable TA monomers yield new thermoplastic dynamic networks via various association mechanisms (e.g., ionic interactions and metal–ligand coordination, as highlighted in the *colored circles*) between X atoms (e.g., sodium, iron) (131). (*b*) Pseudo-Ashby plot of modulus versus the difference between processing and recycling temperature (i.e., the relative energy requirement needed to recycle or upgrade). Details of this analysis are provided in the **Supplemental Material**. Abbreviations: HDPE, high-density polyethylene; PBS, poly(butylene succinate); PC-18, polycarbonate-18; PCL, polycaprolactone; PDK, poly(diketoenamine); PE-18,18, polyester-18,18; PET, poly(ethylene terephthalate); PHB, poly(hydroxybutyrate); PLA, poly(lactic acid); PP, polypropylene; PS, polystyrene; PVC, poly(vinyl chloride); TA, thioctic acid; TA-Fe: poly(iron thioctic acid); TA-Na: poly(sodium thioctic acid).

Supplemental Material >

A balance between energetically favorable depolymerization and suitable processing and performance may be achieved with dynamic polymer networks that perform well in demanding applications and can be reprocessed to new products. Covalent adaptable networks (CANs) combine the properties of thermoplastics and thermosets by inclusion of stimuli-reversible (e.g., by heat, light), covalent cross-links that impart rigidity or elasticity for performance and plasticity for processability (30, 130, 135). Other malleable thermosets contain physical interactions (e.g., H-bonds, metal–ligand coordination, ionic interactions) that impart cross-links with controllable energies and tangible relaxation times (136). In both cases, the polymer networks can be processed using conventional means (e.g., extrusion, injection molding) due to their comparable rheological behavior to thermoplastics and typically possess attractive performance properties (e.g., toughness, resistance to chemicals, elasticity) resulting from their highly cross-linked architecture. For example, cross-linked poly(hydroxyurethane) can undergo exchange reactions that relax stress upon application of a mechanical stimulus (30). These materials represent a new opportunity to impart greater value to discarded thermosets, which are typically considered unrecyclable and appear to be good candidates for replacement of thermoplastics (30, 97, 130). Valorization of discarded recyclable thermosets may be possible with careful design of monomer chemistry. In the case of permanently or dynamically cross-linked networks with enhanced malleability, mechanical recycling may be enabled by established (e.g., thermal) or newer (e.g., photochemical) methods because these systems exhibit significant network relaxation in comparison with traditional thermosets (30). For monomers that form networks with reversible cross-links, valorization to small molecules is possible through similar chemical mechanisms to novel, recyclable thermoplastics (28, 30), offering opportunities to design thermosets with high performance and circularity in mind.

Lessons learned from current plastics manufacturing and recycling must be applied directly to new polymer advances. Without marked improvements in collection and sorting schemes, theoretically simple-to-depolymerize materials may increase the burden of valorization by the introduction of countless new polymers that require different strategies for recycling (50). Although initial estimates of cost and environmental impacts are favorable (132), many conclusions are based on the hypothetical establishment of a circular economy with related commercial pipelines, which is only possible with significant adoption. Further attention to the incorporation of new product designs and polymer chemistries into current plastics markets and recycling infrastructure is needed to exploit the advantages of inherent circularity.

5. COMPLEMENTARY APPROACHES TO TACKLING PLASTICS WASTE

Rapid development of pathways for the valorization of plastics waste requires cross-cutting methods (58), described below, to address fundamental material aspects (e.g., form factor, polymer architecture, formulation) and fundamental physics (e.g., adsorption, transport, kinetics) that impact the development and comparison of targeted approaches. We highlight opportunities to harness established methods and to develop new strategies, including experimental (e.g., standardized methodology), computational (e.g., rapid simulations), systems-level (e.g., life-cycle assessment), and stakeholder (e.g., corporate and government policy) considerations, which are necessary to enable innovation across the value chain.

5.1. Experimental Research

The development of approaches that are translatable across the plastics field requires accessible, traceable, accurate, and reliable experimental data. Composition and variability of valorization feedstocks are a key consideration, including the effects of these factors on robust and diverse technological methods (e.g., deconstruction or transformation). Material characterization of industrially relevant plastics waste (or surrogates for the same) must rely upon well-vetted techniques (e.g., calorimetry, chromatography, thermogravimetry, spectroscopy) to link macromolecular characteristics (e.g., glass transition temperature, molecular weight, thermal stability) to valorization outputs by means that are highly accessible and easily translatable (47).

Fundamental studies hold potential for relating the results of deconstruction or upgrading to relevant thermodynamic, interfacial, rheological, and transport parameters (47, 137, 138). In addition to commonly quantified kinetic parameters (e.g., rate constants) (139, 140), other factors further enable physical understanding and translatability. For example, diffusion-reaction models of pyrolysis have identified gas diffusion through products as a rate-limiting step (141), suggesting directions for the improvement of efficiency and relating process parameters (e.g., temperature, flow rate) to outcomes across multiple studies of the same system (63). Identification and characterization of polymeric and additive components, along with assessment of physical forms and regional variation in composition, provide insight into prospective feedstocks for novel chemical recycling processes with the potential to enhance industrial-scale adoption (42, 142). These approaches will be enabled by input from computational and machine learning strategies.

For innovations in all aspects of plastics waste identification, valorization, and reduction, full disclosure of well-understood experimental parameters (e.g., process temperature, catalyst loading, reaction time, analytical procedure) and standardization of feedstocks, methodology, and analysis are key to synergy within the field. For instance, assessment and clear definition of performance metrics (e.g., permeability, strength, shelf life) of novel degradable polymers, combined with measurements of circularity (e.g., cost, degradation rate, monomer recovery) should be considered when reporting new materials to facilitate large-scale implementation (121, 127). For deconstruction experiments, complete descriptions of catalytic strategy (e.g., catalyst, organism, experimental conditions), investigation of a wide selection of relevant process variables (e.g., temperature, pressure), and quantification of classical thermodynamic and kinetic parameters (e.g., activation energy, enthalpy of reaction) support experimental reproducibility and enhance adoption (47). Overall, fundamental studies that address the complexity and diversity of plastics waste via tactics that promote data reliability and accessibility are essential to the advancement of valorization technologies.

5.2. Theoretical, Computational, and Systems Approaches

Theoretical and computational modeling of valorization strategies aid in the identification and optimization of processes, including catalysts, reactions, and organisms, often with higher throughputs than are feasible experimentally. For example, simulations that combinatorially screen materials can aid in the fast identification of potential catalytic candidates for improving deconstruction efficiency. Density-functional theory (DFT) calculations can be used to search for effective propane dehydrogenation catalysts with high-throughput identification of suitable materials enabled by the correlation of results to a small number of the most valuable parameters (32). The results establish a landscape of catalyst activity and selectivity (see **Figure 5*a***), identifying high-performing, nonprecious alloys (e.g., NiMo) and confirming experimental findings that platinum is the optimal pure metal (32). In another instance, a simulation of more than 330,000 nanoporous hydroisomerization catalysts identified the suitability (i.e., high activity and yield) of most already patented materials and predicted important factors (e.g., pore diameter) that have the potential to improve newly developed zeolites (143). DFT, molecular dynamics (MD), and semiempirical calculations offer advancement for biological catalysts as well. Studies that match protein structure and conformation can enable coordination between deconstruction activity (e.g., protein melting) and substrate characteristics (e.g., crystallinity) (75, 85). For example, improvement of a PETase from *Ideonella sakaiensis* is guided by an optimization algorithm that predicts beneficial mutations to enhance biological deconstruction (see **Figure 5*b***) (31). Computational and theoretical approaches, in collaboration with experiments, offer promise for accelerating process development; however, further utilization of these methods to examine plastics waste valorization specifically is needed.

In addition to the identification of suitable process components, computational models also enable faster investigations of fundamental physics and empower forecasts of crucial parameters and

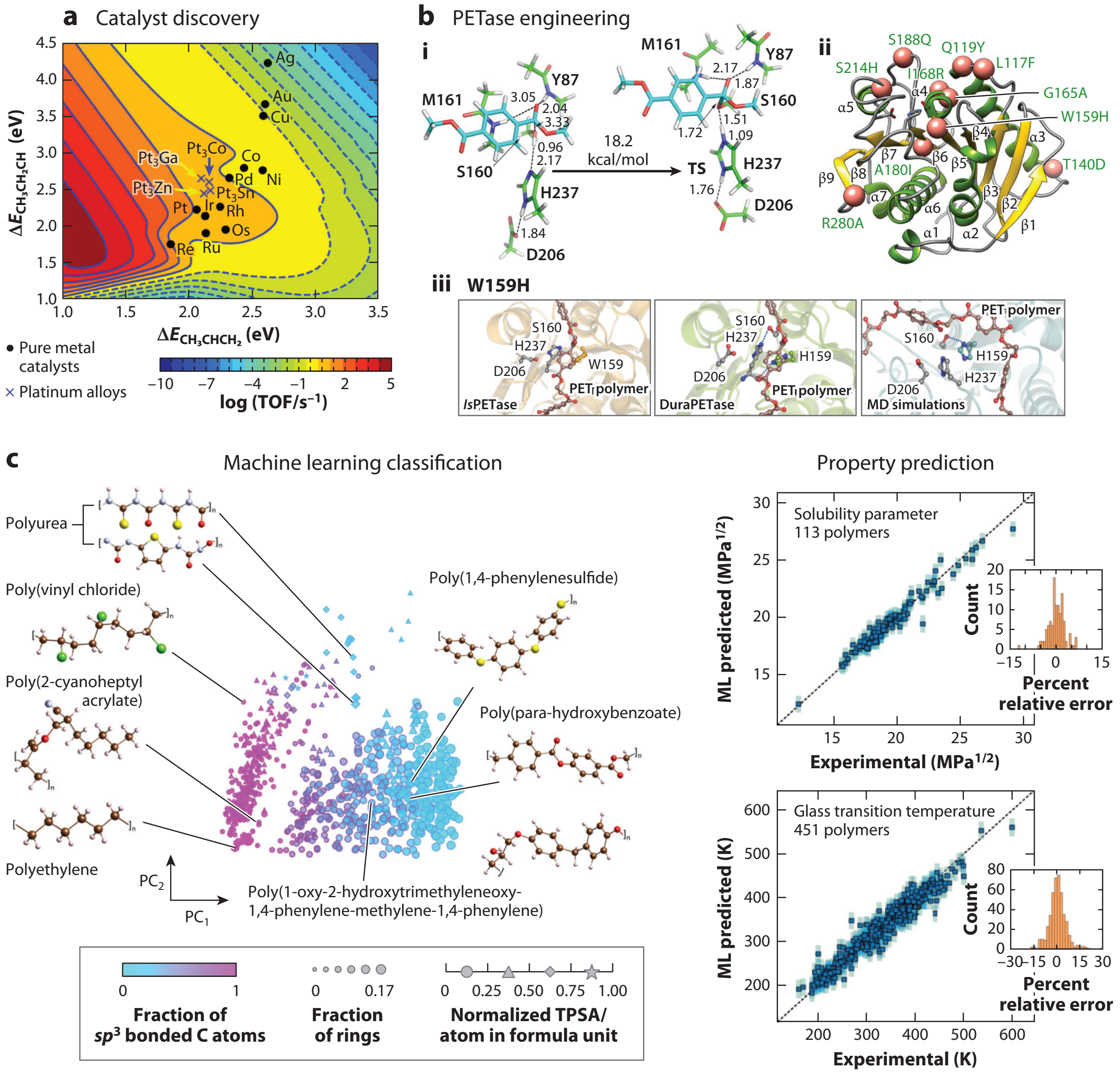

Figure 5

Examples of computational approaches for end-of-life plastics. (*a*) Map of propane dehydrogenation catalyst activity (adsorption energies) generated using DFT calculations of reaction pathways. Panel adapted with permission from Reference 32; copyright 2021 American Chemical Society. (*b*) Computational strategy for redesigned PETase (DuraPETase) from the original *Ideonella sakaiensis*–derived PETase (*Is*PETase) showing (*i*) DFT-simulated hydrolysis activation barriers with distances reported in Å, (*ii*) a schematic of DuraPETase structure highlighting stabilizing mutations, and (*iii*) molecular docking and MD-simulated effects of W159H mutation on the structure of PETase-PET interactions. Panel adapted with permission from Reference 31; copyright 2021 American Chemical Society. (*c*) Polymer classification by an ML method of structure prediction (*left*) and comparison between DFT-predicted and experimentally measured properties for a variety of polymer chemistries, wherein shaded regions represent error bounds of the ML values and insets display distributions of relative percent error between experimental and ML-predicted values (*right*). Panel adapted with permission from Reference 151; copyright 2018 American Chemical Society. Abbreviations: DFT, density-functional theory; MD, molecular dynamics; ML, machine learning; PC, principal component; PET, poly(ethylene terephthalate); TOF, turnover frequency; TPSA, topological polar surface area; TS, transition state.

Artificial intelligence: ability of a machine to simulate intelligent behavior, i.e., perceive its environment and take appropriate action

properties. Due to the complexity of plastics waste feedstocks and the evolution of composition during deconstruction/transformation, robust models for the quantification of coupled physical phenomena involving dynamic, many-component systems are required to assist optimization. For example, kinetic events are commonly predicted using MD and Monte Carlo (MC) simulations to improve insight toward a generalized picture of catalytic selectivity for higher-value products (144). Thermodynamic and transport parameters (e.g., Henry's law constants, adsorption isotherms, diffusion coefficients) for the myriad of feedstock–process–product combinations are more easily obtained by computational methods than by experiments (144, 145). These parameters enable application of experimental findings to larger numbers of relevant systems by nondimensionalization of the problem. Clear identification of systems of interest and the associated phenomena is iterative, and interaction between experimentalists and theoreticians is crucial.

The value of computational methods is clear; however, further refinement of approaches to address the unique challenges (e.g., long length and time scales of polymer simulations) of plastics waste valorization is needed. The multitiered nature of solutions that exploit plastics waste as a feedstock requires models that unite local physical phenomena (e.g., kinetics, adsorption), process-scale behaviors (e.g., diffusion, phase equilibrium), and polymer properties (e.g., persistence length, reptation times) to ensure accuracy. For example, broader computational schemes have been designed to connect reaction energy barriers, intermediate species, and adsorption energies for alkanes on zeolitic Brønsted sites to optimize processes given models of individual steps (146). There also is an opportunity to translate phenomenological simulations of small molecules to macromolecules with preserved accuracy such that their findings are directly applicable to plastics waste. Field-theoretical treatments or particle-based simulations (147) can be used to assess macromolecular interactions with catalyst surfaces to apply previously simulated results to new studies involving polymeric, rather than small-molecule, components. Techniques that are capable of exploring larger, more complex energy landscapes than are MC or MD methods, like umbrella sampling, which quantifies rare but important system configurations, or metadynamics, which directs simulations to explore new configurations, will likely be needed to connect the polymer dynamics and molecular phenomena related to valorization (148). Comprehensive computational approaches represent opportunities to expedite deconstruction pathways for plastics waste and offer promise for innovations in upgrading strategies; however, enhanced utilization and refinement of these methods, along with stronger connections to real plastics waste characteristics, are required.

Computational methods increase capacity for addressing plastics waste challenges, and the extent of plastics in society and the scope of valorization approaches benefits from methods that operate on a greater scale. Data mining offers a wide-reaching vantage point for the assessment of several aspects of the life cycles of plastics. Information concerning the production and consumption of particular plastic products is often dispersed among manufacturers; however, studies that collect these data direct researchers to materials in need of attention (13) and allow evaluation of various waste mitigation strategies (149). Neural-network-based artificial intelligence aids in predictions of geographic and seasonal variation of discarded plastic types (150). Valorization of multicomponent plastics waste is often focused on important systems by application of real-world data; for example, the characteristics of the proprietary combinations of plastics found in packaging films can be characterized best by using sales statistics to direct experimental analysis (42). The establishment of systematic data mining and classification can connect commercial, academic, and government stakeholders to identify commonly used and hazardous additives, which may be a challenge for chemical and mechanical recycling (142), and to address variations in plastics waste streams.

Large-scale, data-driven techniques can directly inform recycling processes. The combination of blockchain management (i.e., a system of recording and validating transaction data) and artificial intelligence presents an opportunity to connect plastics production and disposal in a single tracking scheme to reduce the burden of waste separation and encourage industrial utilization of discarded plastics (152). Machine learning enables the discovery of new catalysts for deconstruction by enhancing other computational approaches when used to extract large amounts of literature data. For example, automated curation of zeolite synthesis details has aided the identification of important topological descriptors that signal high yields from chemical processes (153). Similar approaches can be employed to uncover catalysts for plastics waste. Informatics also can accelerate physical property and thermodynamic parameter prediction, relying on established data sets to hasten calculations. Macromolecular descriptors enable prediction of properties critical to valorization processes (e.g., solubility, glass transition temperature) for an array of polymer chemistries (see **Figure 5*c***) (151). Further work should address the incorporation of recycling concepts (e.g., degradability, deconstruction routes, appropriate solvents for solvolysis) into materials data sets [e.g., the Materials Genome Initiative (154)] and incorporate direct machine learning technology (155, 156) toward supporting valorization of plastics waste.

Data science at the systems level is a growing field that has contextualized technological innovations to tackle real waste streams (157). Life-cycle assessment (LCA) offers objective guidance related to the feasibility of valorization approaches from energy and environmental perspectives. LCA uses quantifiable metrics (e.g., global warming potential, ecotoxicity, human toxicity) to interrelate recycling technologies either by comparing them with traditional end-of-life management techniques (i.e., to determine improved outcomes) or by treating them as connected chemical processes (i.e., to reduce harm by combining approaches) (157). LCA often informs more efficient industrial conditions for implementing successful valorization processes. For example, heat integration and geographical variation in energy sources were found to be instrumental in lowering GHG emissions in the production of small molecules via the pyrolysis of PE (34). LCA, in tandem with experimental studies, holds promise for the design of strategies that address both valorization and the reduction of environmental impacts of plastics waste.

Beyond environmental impacts, technoeconomic analysis (TEA) incorporates indicators of whether potential processes are truly improving the value of plastics waste. By objectively considering the worth of plastics waste by including costs related to separation, deconstruction, and virgin material production, the selection of processes that result in scalable economic benefits can be led toward tangible implementation (33, 115). For example, TEA has identified the contrasting economic impacts of waste separation on mechanical versus chemical recycling (33). TEA comparisons between different PP deconstruction strategies and sensitivity analysis of key parameters (e.g., waste price, plant capacity, energy costs) have suggested that fast pyrolysis is a candidate deconstruction process with the potential for reducing environmental impacts and maximizing profitability with respect to several other deconstruction technologies (115). The combination of LCA and TEA to examine a single process guides experimentalists to address aspects that currently limit wide-scale adoption and hamper valorization (34, 35). However, consistent methodologies and reliable data sets/parameters are needed to achieve dependable application of LCA and TEA with greater agreement between different studies (157, 158). Implementation of these methodologies to assess rapidly developing technology across the value chain is vital to continued success (9).

5.3. Corporate Action, Public Policy, and Community Partnerships

The global plastics waste problem impacts all communities, and meaningful action toward improvement must connect scientific advancement to industry, government, and individuals. Corporations that either manufacture polymers and plastic products or are potential customers for plastics waste are uniquely poised for engagement and may directly benefit from successful valorization (159). Documented examples of collaborations between large companies and entrepreneurs illustrate a variety of corporate actions that help to promote a circular economy by adjusting sales models and supply chains and providing incentives to employees, businesses, and consumers (160). Large-volume customers of plastics already profit from reduction and recycling strategies that reduce material costs (159); however, a stronger commitment to waste reduction and reuse requires corporate attention to actions such as product and material redesign, scale-up of valorization strategies, and consistent messaging and transparency of sustainability efforts (39, 161).

Wide-scale valorization of plastics waste is often difficult to achieve without effective public policies that offer key restrictions, guidelines, and incentives to improve outcomes for plastics at all stages of the life cycle. National, regional, and local governments have increasingly enacted legislation to address plastics waste with particular emphasis on certain product bans (e.g., on plastic bags, drinking straws, microbeads), financial incentives or disincentives (e.g., payments for returned waste, taxes on plastics), and product labeling (e.g., unified identifiers of recyclability, accurate reporting of sustainable content) (37). Policy items that promote increased application of waste are key to adoption, although concerns over the disproportionate production and means of waste management are important at the global level (8). Additional work is required to connect technological understanding with political bodies to direct resources to aspects of plastics life cycles with the greatest potential impact.

Effective action from stakeholders requires the engagement of all concerned parties, including consumers and developers. Although the general public is often aware of plastics as an environmental concern, widespread knowledge of responsible consumption and disposal, mitigation strategies, and context of environmental impacts is often lacking, leading to confusion about areas that need involvement (162). Education on sustainable practices and appropriate community guidance (e.g., outreach campaigns) may influence consumer habits, including more purchases of products in sustainable packaging, or evoke increased, effective residential waste separation (36, 37). Incorporation of end-of-life fate and inherently sustainable design strategies into both curricula and guidelines for practicing scientists and engineers holds potential for shifting paradigms in plastics production and promoting the development of a circular economy. The ubiquity of plastics in society and the growing challenges of end-of-life management require action from all stages of the supply chain to shift the balance of plastics waste from burden to benefit.

6. PLASTICS ON THE HORIZON: MOVING FORWARD

Plastics are among the most vital materials to society and have contributed long-lasting improvements to daily life; however, their persistence in the environment and dependence on nonrenewable feedstocks present a significant need for consideration in materials research. Although there is some debate regarding the detriments of prioritizing the plastics waste problem over other environmental issues (1), an assessment of plastics consumption and accumulation demonstrates that unless a fundamental change to the production, use, and waste management of plastics occurs, the threat posed by these materials will continue to grow uncontrollably (149).

Consideration of plastics waste as a burden has been slowly replaced in favor of its valorization as valuable feedstocks. Mechanical recycling and incineration have historically represented the predominant options to for diverting discarded plastics from landfills and the environment; however, hindrance by energy or separation requirements and challenges related to the performance of recycled materials are driving innovation into new avenues for valorization of plastics waste. Deconstruction via chemical and biological routes to molecules, including fuels, reagents, and monomers, offers value-added pathways for the replacement of petrochemicals with plastics waste. With changes to the chemical recycling paradigm, chemical transformations afford alternative means to synthesize new polymers and hard materials using plastics waste. These valorization strategies have enabled new areas of materials research to develop catalysts with enhanced selectivity and performance, to target material products with desired features, and to connect the fundamental material quantities of plastics waste to process optimization. The field is at a critical point for development, and further focus is required to ensure that novel technologies are robust and address aspects of real plastics waste. Furthermore, materials research plays a vital part in balancing product value and minimizing environmental impact in the quest to develop new processes and target products.

An emerging pathway to address value throughout the life cycle of plastics is to introduce end-of-life value as a material selection criterion toward a circular economy. New manufacturing approaches for complex and multifunctional plastics are being explored that contribute to lower waste generation via synthetic and processing innovations that yield comparable performance and minimize plastics complexity (i.e., fewer components). Understanding of synthetic and microbial pathways that enable plastics waste degradation under natural and controlled conditions is expanding options for disposal and valorization. It is important that the materials field continues to broaden the landscape of macromolecular design and production for circularity by embracing strategies that promote inherent recyclability.

Plastics waste valorization also demands integration beyond the materials world to connect consumer demand characteristics, economic considerations, and societal needs at a global scale. It is the coupling of experimental, theoretical and computational, and systems analysis frameworks that will create strategic approaches that enable revolutionary action to reduce the negative impacts of plastics waste worldwide. Further attention toward reducing collaborative boundaries across academic, national laboratory, government, and industrial sectors; standardizing methods; disseminating data; and wielding extant techniques to facilitate advancement is required. Real-world solutions to the plastics waste problem are within reach, and partnerships and innovations across the materials value chain are the key to implementing solutions with global benefits.

SUMMARY POINTS

1. Plastics waste can lead to significant environmental harm across the globe but can also be an extremely valuable feedstock.
2. Mechanical recycling alone can neither fully address nor valorize plastics waste.
3. Chemical and biological methods for the deconstruction and transformation of plastics waste offer promising routes to valorization and circularity. Consideration of the effects of material characteristics, in addition to the continued development of catalysts and organisms, is crucial for further advances and widespread adoption.
4. Architectural or chemical features that impart recyclability as an inherent material property facilitate valorization of plastic products.
5. Synergies across experimental, theoretical/computational, and systems approaches are necessary to develop technologies with realistic benchmarks and maximal positive impacts.
6. Plastics waste cannot be addressed using a single approach or within a single field. Stakeholders across plastics value chains must be cognizant of the challenges of plastics waste and promote policy and action that ensure successful valorization.

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