Perspective

Perspective on the Development of Monomer Recovery Technologies from Plastics Designed to Last

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ABSTRACT: In order to prevent the current unsustainable waste handling of the enormous volumes of end-of-use organic polymer material sent to landfilling or incineration, extensive research efforts have been devoted toward the development of appropriate solutions for the recycling of commercial thermoset polymers. The inability of such cross-linked polymers to be remelted once cured implies that mechanical recycling processes used for thermoplastic materials do not translate to the recycling of thermoset polymers. Moreover, the structural diversity within the materials from the use of different monomers as well as the use of such polymers for the fabrication of fiber-reinforced polymer composites make recycling of these materials highly challenging. In this Perspective, depolymerization strategies for thermoset polymers are discussed with an emphasis on

recent advancements within our group on recovering polymer building blocks from polyurethane (PU) and epoxy-based materials. While these two represent the largest thermoset polymer groups with respect to the production volumes, the recycling landscapes for these classes of materials are vastly different. For PU, increased collaboration between academia and industry has resulted in major advancements within solvolysis, acidolysis, aminolysis, and split-phase glycolysis for polyol recovery, where several processes are being evaluated for further scaling studies. For epoxy-based materials, the molecular skeleton has no obvious target for chemical scission. Nevertheless, we have recently demonstrated the possibility of the disassembly of the epoxy polymer in fiber-reinforced composites for bisphenol A (BPA) recovery through catalytic C−O bond cleavage. Furthermore, a base promoted cleavage developed by us and others shows tremendous potential for the recovery of BPA from epoxy polymers. Further efforts are still required for evaluating the suitability of such monomer recovery strategies for epoxy materials at an industrial scale. Nonetheless, recent advancements as illustrated with the presented chemistry suggest that the future of thermoset polymer recycling could include processes that emphasize monomer recovery in an energy efficient manner for closed-loop recycling.

KEYWORDS: polyurethane, epoxy resins, chemical depolymerization, closed-loop recycling, catalysis
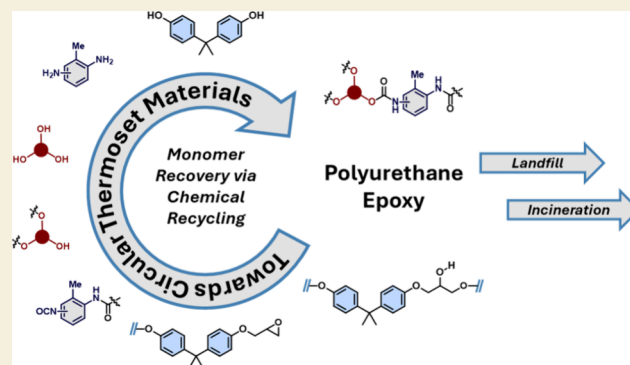
INTRODUCTION

In this Perspective, we will focus on recent advances toward selective depolymerization methods that allow for the recovery of polymer building blocks from commodity polyurethane and epoxy resin based thermoset materials. Moreover, it will present an account of our own efforts to facilitate the development of cost-efficient and industrially viable solutions to recycle such indispensable thermoset polymers, on which our society has grown so dependent on for a multitude of purposes. In addition, based on insights obtained from key stakeholders throughout the value-chains of both PU and epoxy, an outlook for monomer recovery for these highly engineered materials will be given.

In meeting the climate goals of the 2015 Paris Agreement, fossil fuel-based polymers are often put under scrutiny due to the environmental impact of their production and lack of sustainable recycling solutions. Plastic and plastic-based

materials are ubiquitous due to their beneficial properties, enabling favorable logistics, food and water preservation, hygienic healthcare, insulation, and much more. Nonetheless, the current end-of-life management remains unsustainable.[1] The annual production of synthetic polymers exceeds 390 million tons and accounts for 6% of global oil consumption. The latter is expected to increase to 20% as of 2050 due to both increasing dependency and growing human population.[2,3] Structurally, polymers can be separated into thermoplastics and thermoset plastics depending on the polymeric macro-
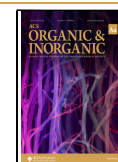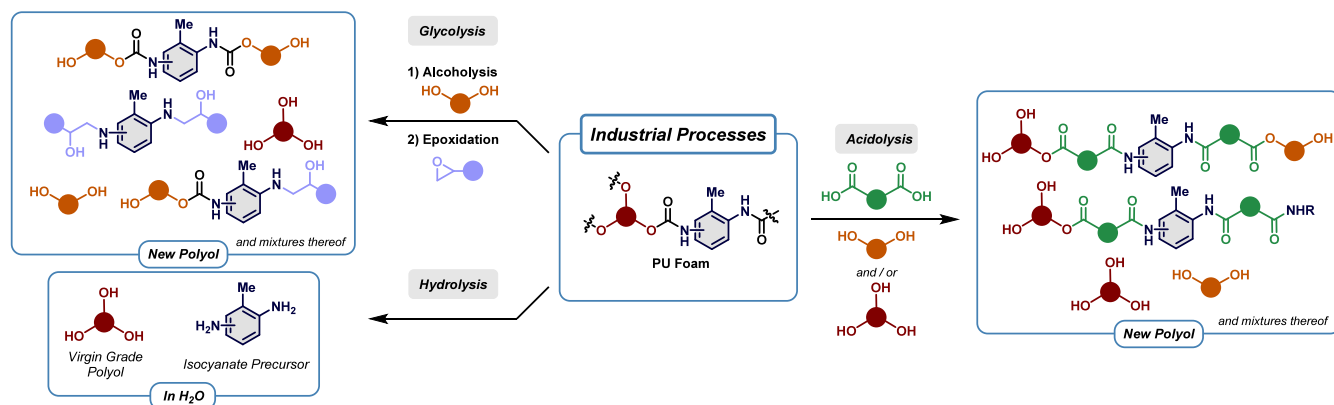
Scheme 1. Industrially Used Chemical Recycling Technologies for Deconstruction of PU Materials

structure. Thermoplastics, such as polyethylene (PE), polypropylene (PP), polycarbonates (PC), and polyesters (e.g., PET), consist of predominantly linear polymer chains, allowing them to be processable by dissolution or melting processes. Thermoset plastics, such as polyurethanes (PU), epoxy resins, vulcanized rubber, melamine, and more, on the other hand, consist of cross-linked polymer networks, which are no longer formable once cured.

Ultimately, nonrenewable resources for polymer production need to be replaced entirely by sustainable chemical feedstocks. While using biomass as feedstock and end-of-use materials as a carbon sink have been proposed, studies by Bardow and co-workers concluded that such a scenario would be unsustainable as well.[4] Instead, CO_2 must be included as a feedstock. Even then, plastics produced entirely from renewables require efficient recycling rates in order to minimize their environmental impact,[4] while residual waste and emissions from production must be taking into account.[5] Due to processability but also because of their large production volumes, several methods for thermoplastic recycling have been developed. Besides the dominating mechanical recycling processes, different chemical recycling strategies, including depolymerizations for monomer recovery, have been explored.[6−12] Life-cycle assessment (LCA) and techno-economic analysis (TEA) represent important tools to assess and compare the ecological and economical viability of these processes as high investment costs, low product quality, and costs of recycled products can make it challenging to compete with virgin grade polymers.[13−17]

Approximately 44 million tons of thermoset polymers are produced annually, accounting for about 12% of the global plastic production.[18] It is estimated that around two kg of crude oil is used for the production of one kg of synthetic polymers. However, this number is extensively higher for molecularly more advanced polymers as those found in thermosets.[19−21] Cross-linked polymer networks defining thermosets result in highly durable materials. Another layer of complexity is added for fiber-reinforced polymer composites. Here, glass or carbon fibers are embedded in a polymer matrix, resulting in high performance structures. These are often utilized for components that are required to last for years or decades, exemplified by wind turbine blades, the fuselage of airplanes, and much more.[22] The flipside of their physical and chemical durability lies in the challenge of processing thermoset-based materials at their end-of-use. The inapplicability of mechanical recycling on thermosets due to their

cross-linkages results in unsustainable practices such as landfilling, downgrading to fillers, or incineration for energy recovery.[18,23−25]

With an increasing focus on the identification of more sustainable thermoset plastics, advancements have mainly been focused on the use of biobased monomers[26−29] and designing recyclable polymers containing dynamic covalent bonds that deconstruct upon external stimuli.[30−33] A transition to new materials tailored for disassembly will likely be an important part of reaching a more sustainable future. Nonetheless, the introduction of new polymers as a substitute for current thermoset materials does not provide a solution to the lack of recycling technologies for existing materials.

The recycling of commercial thermoset polymers remains in its infancy. Here, chemical recycling strategies may enable breaking down polymers into carbon feedstocks via pyrolysis or recovering monomers via selective bond disconnections. While pyrolysis oils and gases could supply chemical production chains upstream, depolymerizations could feed monomers back into polymer production. In either case, there is the potential for producing virgin grade polymers from end-of-use plastic waste.

Eventually, implementing recycling technologies requires access to end-of-use materials. For thermoset plastics used in highly engineered products, waste streams are often well-defined. Slabstock cut-offs, decommissioned wind turbine blades and airplanes, or insulation from dismembered buildings could be directed toward appropriate recycling facilities as uniform waste-fractions. This would avoid costly waste separation processes and turn waste streams into value-streams. As recycling technologies for thermoset polymers mature, materials could re-enter the product life cycle. Once legislative demand for recycled content in plastics will be in place, the price of polymers could be partially decoupled from that of oil.[34]

POLYURETHANE AND ITS INDUSTRIAL HANDLING

PU is the sixth most produced synthetic polymer with an annual production volume above 24 million tons.[35] While examples of PU as thermoplastic materials exist, used for elastomers within coatings, wheels, sports equipment, and textiles,[36] it is predominantly utilized as a thermoset polymer as flexible- and rigid foams, accounting for over 60% of the global market.[37] The increasing reliance on PU-materials is often attributed to the vast amounts of materials that can be

Scheme 2. Transition Metal Catalyzed Hydrogenation of PU Materials and the Formation of Soluble Carbamate Fragments
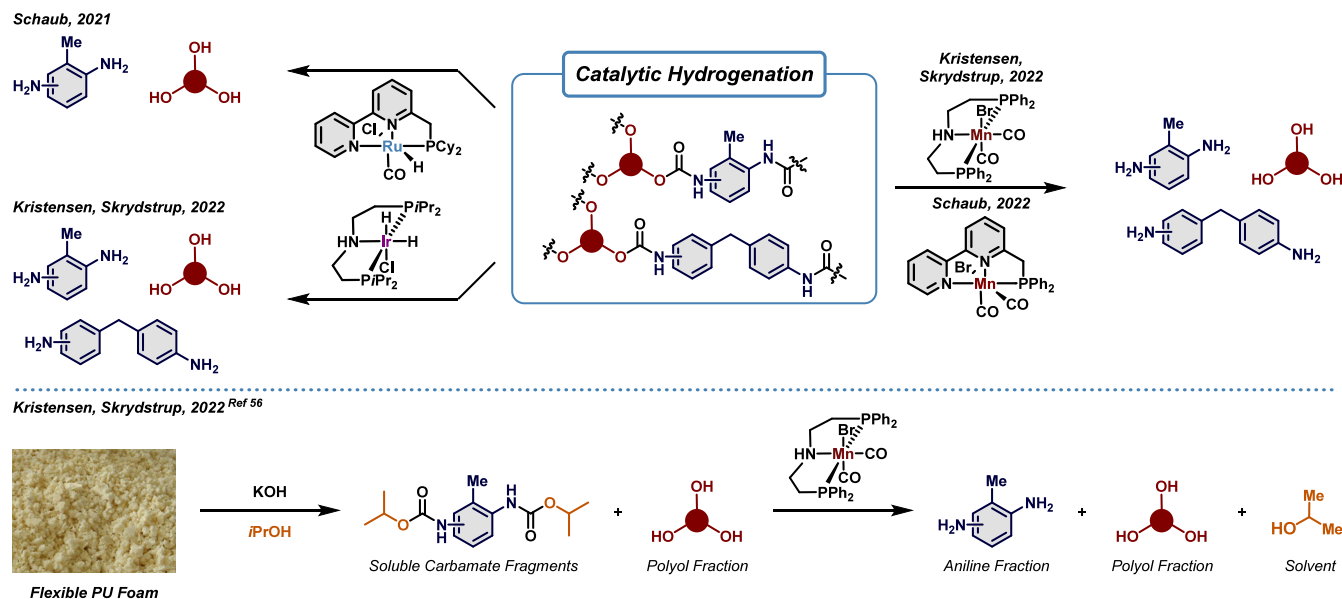
formed from a judicious choice of isocyanates, alcohols, and additives.[38] However, the lack of recycling processes means that PU-waste, if it is not landfilled or incinerated, becomes downcycled to secondary materials through mechanical or chemical processes. In the former, cut-offs are glued together using a polyisocyanate binder often under compression. This process only has a limited demand as material integrity is lost after finite recycling rounds, meaning that mechanical recycling of PU only delays landfilling or incineration.[6,39]

Most industrial efforts are concentrated on handling flexible PU foam waste streams, of which the aromatic component arises mainly from toluene diisocyanate (TDI). This selection is made partially due to the increased molecular complexity of other PU materials, such as insulation- or viscoelastic foam being comprised of mixtures of TDI, methylene diphenyl diisocyanate (MDI), polymeric MDI (polyMDI), and a plethora of short diols, triols, sugars, and polymeric alcohols as the polyol.[38] Historically, glycolysis has been the main chemical recycling methodology for PU-waste (Scheme 1). By heating PU in the presence of a diol, such as ethylene glycol, diethylene glycol, or glycol, and a catalyst, a polyol feed composed of residual diol, polyol, dianiline, and (amino)-carbamate derivatives is obtained. As anilines are unwanted due to safety- and foaming issues, they are capped with epoxides or cyclic carbonates thus creating a plethora of different alcohols, which altogether are used as a new polyol.[40] As this polyol is often of a low quality, it is diluted with virgin polyol to meet required specifications of the desired PU-materials.[41–43]

More recently, attention has been drawn toward the chemical recycling of PU applying acidolysis for polyol recovery or hydrolysis for polyol and aniline recovery (Scheme 1). In the former, a dicarboxylic acid is used to sequester the aromatics originating from isocyanates, allowing for easy purification of the polyol.[44–46] This methodology finds great value around slabstock waste, as normal incineration or landfilling processes can be omitted for on-site recycling of PU polyols. Nonetheless, the relative amount of acid must be finely adjusted to the functional groups present in the PU-waste (carbamates and ureas) to attain a certain quality of the

polyol. Different variations on this recycling methodology are currently being implemented by several industries, among which H&S Anlagentechnik, DOW, and IKEA can be mentioned. Nonetheless, due to the low quality of the polyol, virgin polyol input is needed to reach the required specifications of the ensuing products.[42,47,48]

Hydrolysis has often been discredited as being uneconomical due to the high temperature and pressure needed to afford an aqueous mixture of polyols and anilines. However, building on discoveries described in the early 1990s,[49] Evonik has recently made some interesting advancements within the hydrolysis of PU using a combination of a base and a phase-transfer catalyst, allowing the hydrolysis process to operate under relatively mild reaction temperatures (approximately 150 °C) for the deconstruction of flexible PU foam for virgin grade polyols (Scheme 1).[50,51] The Vita Group and REMONDIS are planning to utilize this technology to handle flexible foam waste.

ADVANCEMENTS WITHIN CHEMICAL RECYCLING OF POLYURETHANE

Recent academic efforts have shown new methodologies and improvements for existing PU recycling methods. Nonetheless, most of these processes provide a costly prospect for closed-loop recycling or afford a secondary feed, which raises the question if these processes are making any clear advancements within PU recycling beyond the academic novelty. Transition metal catalyzed hydrogenation of polyurethane represents one of these new chemical technologies, whereby a catalyst is exploited to deconstruct the carbamate moiety into an alcohol, amine, and methanol applying excess hydrogen in autoclaves (Scheme 2, top). Here, Milstein and co-workers revealed the first hydrogenative disassembly of a model PU-elastomer based on H_{12}MDI with a ruthenium catalyst in the presence of 70 bar H_2 at 150 °C for 2 days.[52] Shortly after this seminal result, Schaub and co-workers moved into a real-life PU sample by hydrogenating a TDI-based PU sponge promoted by Ru-PNN catalysts with 100 bar of H_2 at 200 °C for 2 days.[53] Likewise, we demonstrated the use of a commercially available Ir-^{iPr}MACHO complex for promoting the catalytic decon-

Scheme 3. Recent Advancements within Chemical Recycling of PU Materials
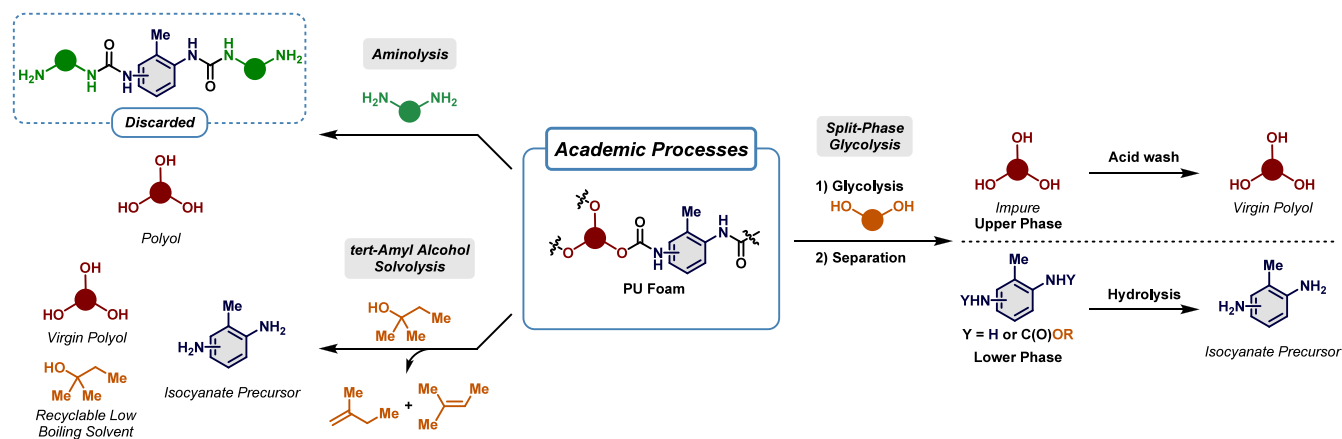
struction of a wide range of different commercial- and end-of-life PU-samples in the presence of 30 bar H_2 with reaction temperatures between 150−180 °C for 21 h.[54] While these processes are intriguing and in essence can rely on the use of green hydrogen, the combination of expensive metals and ligands for generating a catalyst with low turnover numbers (TON), along with the use of industrially unviable solvents, speak against their implementation in an industrial setting. To partially resolve one of these issues, Schaub and co-workers simultaneous with our group reported on the catalytic deconstruction of commercial- and end-of-life flexible PU-samples with two different manganese catalysts.[55,56] Here, the group of Schaub successfully depolymerized a range of flexible PU materials using a Mn-PNN ligand in THF in the presence of KO*t*Bu and 60 bar H_2 at 200 °C for 24 h demonstrating TONs up to 78. Meanwhile, we reported a maximum TON of 905 on the disassembly of a flexible PU foam with a Mn-[Ph]MACHO complex in *i*PrOH in the presence of KOH and 50 bar of H_2 at 180 °C for 21 h. Whereas, the use of such catalysts based on an earth abundant metal shows promise, as an atom efficient process, the cost of ligands and scaling homogeneous transition metal catalyzed processes beyond gram-scale, along with the inevitable safety aspects of dealing with hydrogenation reactions on large scale would remain obstacles for this approach. As such, unless a process is devised whereby a highly efficient hydrogenation catalyst can be reisolated and reused without compromising reactivity, scaling hydrogenation processes will not transcend from academia into industry as a viable solution for PU recycling.

During our work on the transition metal catalyzed deconstruction of PU in isopropyl alcohol, a background transcarbamoylation reaction was observed to take place between the solvent and the carbamate groups of polyurethane, creating small soluble polymeric fragments. This pathway could explain the increased turnover numbers noted in our Mn-catalyzed hydrogenation of PU performed in this alcoholic solvent compared to that of the Schaub group using THF or THF/toluene mixtures.[55,56] The transcarbamoylation with the solvent promoted by the base solubilizes the PU, thus easing the accessibility of the catalyst to the otherwise heterogeneous plastic material (Scheme 2, bottom).

As the adducts formed in the homogeneous plastic feed obtained from the reaction of *i*PrOH with the flexible PU-material resemble the *tert*-butyloxycarbonyl (Boc) amine protecting groups, we envisioned that conditions could be devised, whereby the thermal decomposition of this intermediate could be achieved in analogy to the removal of Boc-protecting groups under high temperature conditions.[57,58] After screening different alcohol-based solvents, we were able to show that heating flexible PU foam in *tert*-amyl alcohol to 200 °C for 18 h resulted in the depolymerization of the thermoset material with 88% isolated yield of toluenediamine (TDA), based on the original input of TDI. Upon optimizing the reaction conditions, we discovered that by increasing the reaction temperature to 225 °C and adding a catalytic amount of KOH, full depolymerization could be achieved affording >95% yield of TDA (Scheme 3).[59]

The applicability of the methodology was showcased through the depolymerization of 20 different PU materials ranging from rigid foams, rigid solids, and flexible solids to flexible foams, where the latter was successfully depolymerized on a 50 g scale without comprising the quality of the ensuing polyol. As *tert*-amyl alcohol can easily be removed, this newly devised methodology for PU-recycling can be seen as an advancement to the well-established glycolysis processes based on high-boiling alcohols, as the virgin grade polyol is obtained as opposed to a complex nonvirgin polyol (see Scheme 1).[43] The solvolysis process using *tert*-amyl alcohol directly provides polyols and diamines as opposed to recent split-phase glycolysis processes. Here, the original polyol is recovered through a careful choice of solvent, allowing for phase-separation, whereby the aromatic rich lower phase is either discarded or valorized through a combined glycolysis-hydrolysis process (Scheme 3).[60−64] Recent academic efforts have also been focused on improving chemical recycling of PU through aminolysis processes which either provide a complex mixture of depolymerized PU or a polyol, which is based on ~50% recycled polyol, as virgin polyol is used as the solvent for the aminolysis process (Scheme 3).[65,66]

■ EVALUATION AND PURIFICATION OF RECYCLED CONTENT

Holistically, advancements and refinement within chemical recycling of PU should be evaluated based on their resource pressure through LCA and their economic viability through TEA. Nonetheless, for the depolymerization of PU, the quality of the ensuing monomers is also a good measure of the potential value of the process. However, as the market for PU materials is immensely diverse, manufacturers often produce commodities based on unique formulations. This means that

Scheme 4. Closed-Loop Recycling of Polyols from Flexible PU Foams
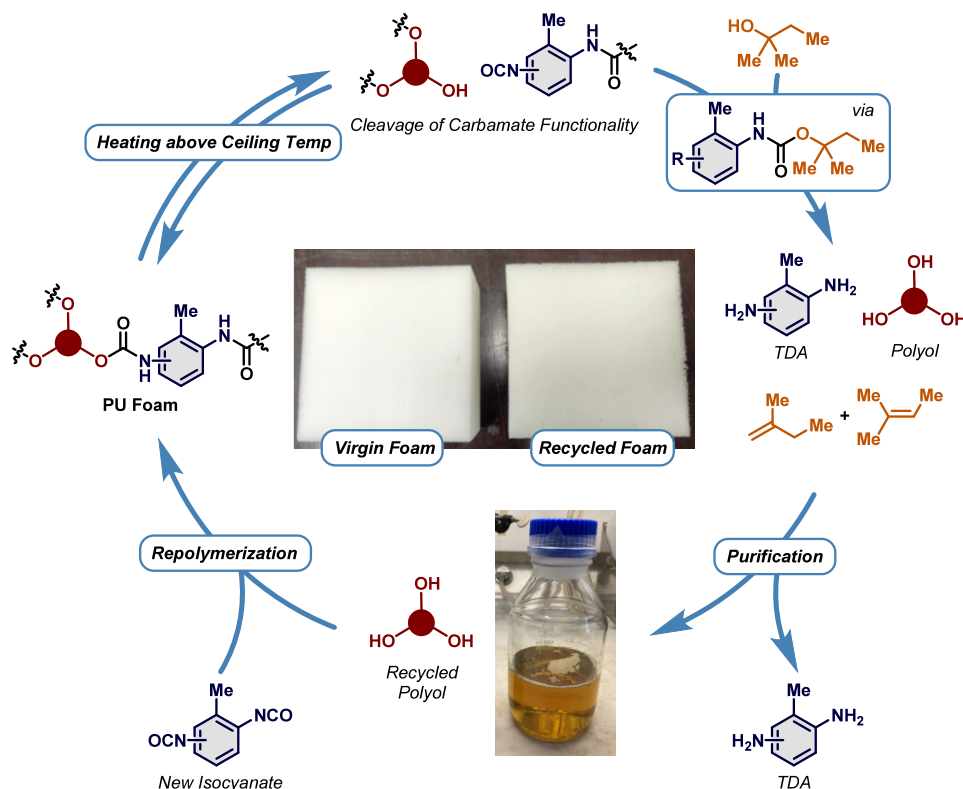
for each product type (i.e., rigid foam, flexible foam, and elastomers), different companies often formulate PU based on their own recipes. As such, the preliminary waste sorting of PU becomes a crucial aspect of the recycling process, as it simplifies the ensuing purification of monomers. It is therefore not surprising that industry-academia collaborations are paving the way for advancements within PU recycling. This is exemplified by the PUREsmart,[63] the PolynSPIRE,[48,65] and the RePURpose consortium,[54,56,59,67] where industry partners are providing PU materials with known composition to academic partners, thereby easing the quality assessment of the process and the ensuing purification after depolymerization.

For the recycled polyol, its quality is often verified using the OH-value (titration), water content (Karl Fischer titration), NMR and MALDI analysis. To further evaluate the quality of polyol, some studies include examples of foam formulation using their recycled polyols, to showcase how much virgin fossil fuel-based polyol can be exchanged for recycled content before mechanical properties like density, cross-link density value (CLD), ball rebound, air permeability, tensile strength, and elongation to break start to deteriorate. With the above thoughts in mind, the *tert*-amyl alcohol solvolysis process was scaled up in order to obtain enough recycled polyol to verify its direct substitution for virgin polyol thereby enabling the first closed-loop recycling of flexible foam polyols (Scheme 4).[67] Here, it is worth to mention that in the aminolysis- and acidolysis process, the amine adducts are either filtered off or embedded in the polyol,[48,65] while in the split-phase glycolysis, the amines are separated through phase separation followed by the washing of the polyol with aqueous acid.[63] On the other hand, in the solvolysis process using *tert*-amyl alcohol, anilines can be separated either through acid-base wash, precipitation of the HCl-aniline salts, or through the use of an anti-solvent

to precipitate free anilines. More specifically, in the scale-up process using *tert*-amyl alcohol, the TDA was removed from the recycled polyol by initially using an anti-solvent to precipitate most of the TDA. The remaining TDA in the polyol was removed by precipitation as 2HCl·TDA thereby avoiding formation of aqueous waste. Initially, the deconstruction of the flexible PU foam was performed under ambient air. However, decolorization of the polyol was observed due to oxidation of TDA into azo dyes, resulting in the isolation of an inferior polyol. This led to flexible foams with visual and mechanical flaws.[68]
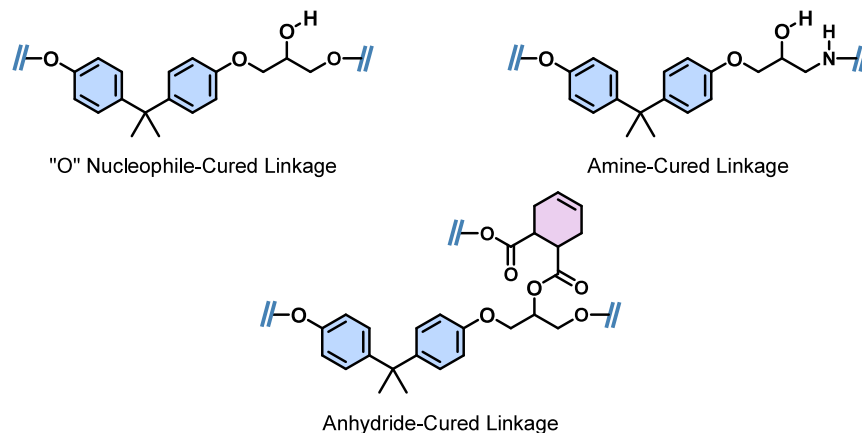
Once, the depolymerization was performed under an atmosphere of nitrogen and with sufficient amounts of acid to remove all the TDA from the polyol, a recycled polyol was prepared, which was indistinguishable from virgin polyol with respect to OH-value, water content, and MALDI analysis. As such, the *tert*-amyl alcohol solvolysis process provides a recycled polyol capable of substituting 100% virgin polyol in new formulations. Within recent advances on acidolysis of flexible PU foam, 30%,[46] 40%,[47] and 50%[48] of the virgin polyol can be substituted depending on the process conditions, whereas recycled polyol from the split-phase glycolysis can substitute 50% of the virgin polyol before the mechanical properties of the ensuing materials start to deteriorate.[63] More recently, the deconstruction of flexible PU foam has been reported through a microwave assisted aminolysis process. Here, the recycled polyol content is close to 50%.[65]
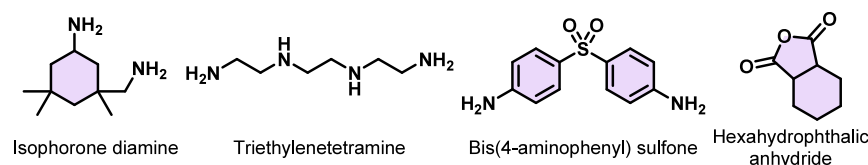
■ OUTLOOK FOR MONOMER RECOVERY FROM PU

The immense diversity of PU polymers and the extensively cross-linked nature of the different materials mean that while certain advances within the recycling of flexible PU foams show promise, these technologies are not necessarily fully

Scheme 5. Common Linear Linkage Motives in Amine-Cured and Anhydride-Cured Epoxy Resins and a Selection of Nucleophiles Used in Curing Agents

A Common linkage motifs in amine-cured or anhydride-cured epoxy resins

"O" Nucleophile-Cured Linkage　　　　　　　　　　　　Amine-Cured Linkage

Anhydride-Cured Linkage

B Selected examples of nucleophiles used in curing agents

Isophorone diamine　　　Triethylenetetramine　　　Bis(4-aminophenyl) sulfone　　Hexahydrophthalic anhydride

transferable to rigid PU foams or other PU materials. Advances have been made dealing with enzymatic hydrolysis of PU, but access of the carbamate functionality of the polymer to the active site of the enzymes can be challenging. As such, an initial chemical treatment is required to create suitable substrates for the enzymatic process. This raises the question if enzymatic processes are viable for PU recycling.[69,70] Therefore, we argue that the future of closed-loop PU recycling will rely on several chemical processes. Nevertheless, in all cases, careful presorting is mandatory, as full control of input feed will ease separation and purification of the ensuing monomers. Recent years have seen collaborations between industry and academia, facilitating advances in current PU recycling strategies. Here, acidolysis, aminolysis, and split-phase glycolysis provide a straightforward way to chemically recycle PU while simultaneously separating aromatic compounds from the polyol. Unfortunately, none of these processes provide a recycled polyol that can fully substitute for the virgin polyol. On the contrary, transition metal catalyzed hydrogenation, hydrolysis, and *tert*-amyl alcohol solvolysis lead to a polyol in a mixture with the aromatic compounds, meaning that an ensuing separation is needed to valorize both fractions. Nonetheless, the recycled polyol obtained from both the *tert*-amyl alcohol solvolysis and the hydrolysis processes have proven to be adaptable as substitutes for virgin polyol, leading to indistinguishable flexible PU foams.

Following PU degradation into its monomeric constituents and reformulation of the polyol, one is left with the diamines. Conversion of these recycled diamines into isocyanates and incorporation into new PU have not been disclosed to the best of our knowledge. Diamines, isocyanates, and especially phosgene are toxic. In our laboratories, the handling of phosgene, or even the safer alternative triphosgene, on a

sufficient scale for reformulation has held us back from moving in this direction. We believe collaboration with industrial partners who can provide specifications for diamines is the way forward. Numerous challenges are apparent when looking into the composition and purity of the diamines, such as regioisomeric ratios for both TDA, MDA, and MDA/polyMDA, and monoalkylation byproducts formed in the presence of alcohols. Generally, the handling of diamines poses an obstacle to the recycling processes where free amines are formed due to toxicity, oxidation, and transportation issues. However, this currently appears to be the best route toward full circularity.

The increased reliance on PU-materials, exemplified by a 2029 production forecast of over 29 million tons of PU,[35] has created a lock-in effect, whereby PU produced from biobased monomers or with dynamic covalent linkages can only be expected to cover a niche aspect of future markets. Even if current PU materials would be phased out in the strive to replace fossil fuel-based polymers, the legacy burden of PU-materials means that materials from future disassembly of buildings, wind-turbine blades etc. still need to be recycled to avoid the current end-of-life handling through landfilling or incineration. If the use of established PU monomers continues, advancement within PU recycling could partially substitute for current fossil-fuel input.

With the different recycling processes furnishing different feeds of different quality, the future of PU recycling must be assessed not only on atom economy and environmental impact factors (total weight of input material to total weight of output products),[71] but also on the quality of the ensuing monomers. This differentiation is crucial as the chemical recycling can fit into a closed-loop recycling scheme, where recycled polyols are direct substitutes for virgin input. Alternatively, if a lower grade

of the original polyol is obtained, then dilution with virgin polyol is required before it can be applied for the same purpose. A third option is the creation of an entirely new polyol used for different applications. Moreover, advances within PU recycling should be measured by LCA and TEA to establish the environmental impact and economic aspects of recycling a complex polymeric material. As PU is so diverse, depolymerization becomes a small part of an overall recycling scheme that includes initial separation of materials, PU dosage, reactor setup, potential separation of monomers, purification, batch control, and much more. As such, for complex waste fractions, glycolysis/acidolysis to afford a generic low-quality polyol with higher OH-number that can be used "as is", might be the best recycling solution. For slabstock waste or end-of-life flexible foam, acidolysis might be an optimal recycling solution as it can provide a polyol without tedious purification and separation of unwanted amines. With current recycling solutions, LCA, TEA, and the quality of the recycled feed might show that aiming for a lower quality polyol while simultaneously separating the toxic amine from the mixture is the right solution. However, once technologies and purification methods mature, it is our hope that the future of PU recycling becomes fully circular, where both monomers can be obtained and reused without tedious purification and separations using excessive amounts of organic solvents, water, or energy.

■ EPOXY RESINS AND THEIR COMPOSITES

Epoxy resins are chemically and physically highly durable polymeric materials. Considerable degrees of cross-linking and complex formulations relying on several different compounds result in molecularly complex 3D networks.[72,73] As with other thermosets, epoxy resins are not processable once cured. Therefore, epoxy resins are often shipped out as two components with the final polymerization step being carried out on-site of production depending on the application.

The first and name-giving component is based on rigid aromatic components difunctionalized with electrophilic epoxide moieties. The most common backbone motif is bisphenol A (BPA), the use of which has been called into question due to its adverse health effects (Scheme 5A).[74,75] However, the second most common bisphenol (bisphenol S, BPS), which has been used to replace BPA in certain products, has been found to have similar detrimental pharmacological activities.[76] Biomass based alternatives have been studied,[77] but not commercialized on large scale yet. The second component is a corresponding curing agent, the most common being multifunctional alkyl amines and anilines, which attack the epoxides, forming C−N bonds adjacent to the alcohol moiety. Another common curing agent is represented by anhydride systems, which act both as electrophiles and nucleophiles, forming tightly knitted ester networks (Scheme 5B). Other mostly nucleophilic curing agents have been used as well.[72]

Because epoxy resins possess high chemical and physical resistance properties, they are highly relevant for specific applications, aiming at long-lasting products and structures. Coatings, laminations, and adhesives together are the largest markets for epoxy systems.[72,73] However, when considering the potential for recovering and recycling such types of resins used in, e.g., laminations, there are significant challenges in separating and collecting this polymer from waste streams. Carbon and glass fiber-reinforced composite materials represent another large application field for epoxy polymers.

Around 70% of such composites rely on thermoset matrices, while 95% are glass fiber based.[78] These materials are crucial to aeronautical engineering, wind energy, (electric) automotives, and sporting goods.[73] Here, end-of-life materials are more accessible to collect in defined waste streams.

The production volumes of epoxy composites are expected to grow each year. Driving factors for such growth include shifts in sustainability driven technologies, including the expansion of CO_2 neutral wind energy, as well as the implementation of lightweight car chassis advantageous for electromobility. However, epoxy composite waste remains notoriously difficult to handle.[73,78] While BPA or other chemicals are not known to leach from discarded epoxy resin-based structures, landfilling remains undesirable due to the large land areas necessary for burying such voluminous structures. Therefore, European policy is moving toward banning landfilling of decommissioned wind turbine blades.[79] As an alternative to landfilling and incineration, shredding of the structures has been implemented for commercial use as filler materials in constructions.[78,80,81] Here, it has to be considered that composites are high performance materials containing molecular complex polymers and valuable fibers, each with considerable CO_2 footprints. As such, mechanical downcycling of the epoxy composites can be considered a loss of value while also being noncircular in nature. Refitting end-of-life wind turbine blades for use as bike sheds, playgrounds or other infrastructure has been advertised as end-of-life solutions.[80] However, these secondary constructs built from decommissioned wind turbine blades will eventually end up in waste streams again. This time, however, it will no longer be in a defined waste fraction. Furthermore, with 43 million metric tons of decommissioned wind turbine blade to be expected by 2050,[82] which does not account for airplanes, boats or other composite waste sources, the volume of end-of-life materials will likely massively exceed the demand for secondary composite constructs. Therefore, re-entering end-of-life materials into a circular economy would be desirable.

Chemical recycling processes have been investigated to recover fibers from composite materials. While glass fibers dominate the composite market, the focus has mostly been on the recovery of carbon fibers due to their significantly higher value. Pyrolysis has been utilized to strip the polymer matrix off of embedded fibers. However, such processes are energy intense and may deteriorate the mechanical properties of the recovered fibers.[73,78,80] Solvolysis methods tend to be more suitable for protecting the quality of the fiber mesh. A range of solvents, reagents, and cleavage modes has been explored. Nonetheless, efficient polymer removal commonly requires undesirable reagents, such as concentrated nitric acid, molten potassium hydroxide, or peroxides.[73] These studies, however, do not aim at monomer recovery and are thus out of the scope of this perspective. This approach has been comprehensively reviewed[73,83,84] and will not be discussed further in this perspective. Recent studies by Ballout et al. are of note, as they demonstrate a mild formic acid-based solvolysis of aerospace grade epoxy composites.[85] While some reuse potential for the fibers was demonstrated, the recovered carbon fibers could not be entirely separated from the polymer. This will undoubtedly affect the reuse potential for the recovered materials.[78,86]

While the issue of legacy materials in circulation and production is not addressed as of now, developing new formulations of resins designed for disassembly at their end-of-life is a promising approach to ease future waste handling.

Scheme 6. PCET-Based Deconstruction of a Thiol-Cured Epoxy Resin
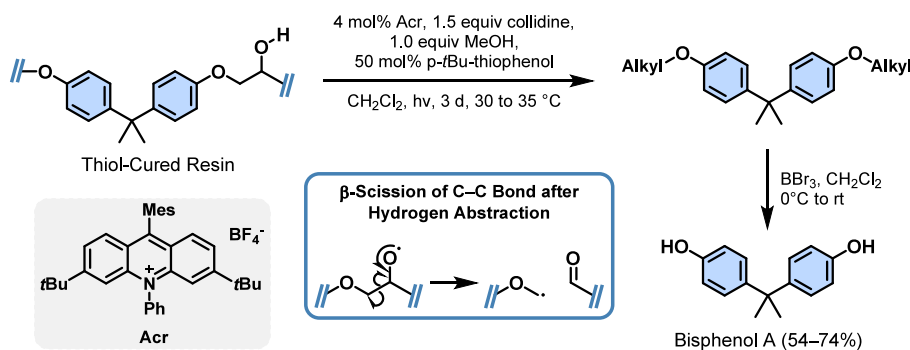
Scheme 7. Deconstruction of an Amine-Cured Epoxy Resin Using Nickel-Catalyzed Hydrogenolysis
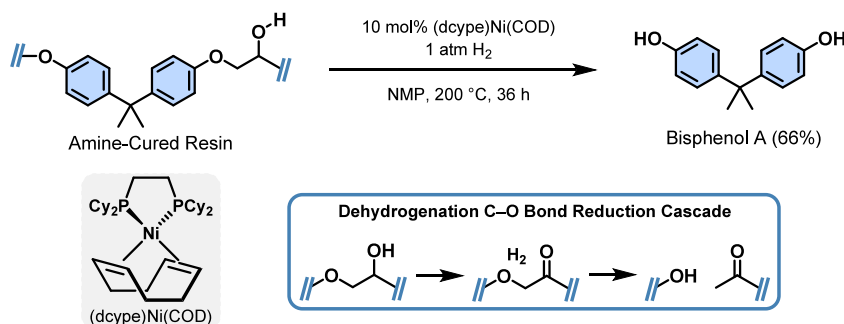
Introducing certain molecular functionalities that will disconnect under specific trigger conditions, will allow tailored resins to be easily removed from fibers while maintaining favorable properties.[30,31,87] In 2012, US-based company Connora Technologies launched a thermoset epoxy resin system tailored for disassembly. By incorporating an acid-sensitive ketal group into the backbone of alkyl amines within the curing agent, referred to as recyclamine, fibers could cleanly be recovered from composite materials using mild acidic conditions.[88,89] In 2019, Connora Technologies, together with its recyclamine process, was acquired by the Indian chemical company Aditya Birla.[90] Using this tailored resin system, the German-Spanish wind turbine producer Siemens Gamesa commercialized RecyclableBlade in 2021. These wind turbine blades are thus suitable for stripping the resin off the fiber textiles under mild conditions using aqueous acetic acid.[91] Although this certainly is a major advancement in the field of wind turbine waste handling, prospects for circularity regarding the end-of-life polymer fraction remain unaddressed. While the organic recyclates of certain solvolysis processes were characterized,[83] they have diminished potential regarding reuse, as these processes unselectively break the polymer into a diverse set of organic fragments.[92−97]

## ■ DEPOLYMERIZATION OF EPOXY POLYMERS

The selective chemical deconstruction (i.e., depolymerization)[98] of thermoset epoxy resins into monomers or related building blocks is challenging. When compared with carbonyl-based polymers such as polyurethanes, the molecular skeleton of epoxy polymers possesses no obvious attack points for chemical scission. Only recently, the first methodologies enabling the depolymerization of epoxy polymers were demonstrated.

Knowles and co-workers reported a proton-coupled electron transfer (PCET), which allows β-scission of C−C bonds of secondary alcohols after the light-driven generation of an alkoxy radical.[99] This bond scission approach could then be applied to the deconstruction of soluble thermoplastic[100] and powdered thiol-cured thermoset epoxy resins (Scheme 6).[101] The protocol relies on a transition metal or organic photocatalyst, which, once excited, transforms the alcohol moiety into the alkoxy radical in the presence of an amine acting as a base. The alkoxy radical then rearranges under C−C bond scission, forming a carbonyl moiety and a carbon centered radical. A thiol acting as a hydrogen atom transfer reagent (HAT) quenches the carbon radical. When applied to epoxy polymers, this enabled efficient recovery of alkylated BPA in dichloromethane at 30 to 35 °C after 2 days. Reacting the recovered compounds with excess BBr₃ in turn released the polymer building block BPA. Composite materials or other resin formulation systems were not tested. However, Fors, Knowles, and co-workers demonstrated that the presence of carbon fibers, coloring agents or triphenyl phosphate did not hinder the depolymerization.[101]

A recent report in 2023 by Takahashi, Nozaki, and Liao discloses a nickel-catalyzed C−O bond hydrogenolysis approach developed on 1-aryloxy-3-amino-2-propanols as models for amine-cured epoxy resins. Mechanistic studies revealed that similar to our ruthenium-catalyzed hydrogenolysis (see below), the central alcohol motif is dehydrogenated initially. Thereafter, the Ni(0) species inserts into the targeted C−O bond via a remote concerted oxidative addition.[102] The chemoselectivity of this insertion is interesting, as nickel generally favors insertion into $C_{(aryl)}$−O bonds over $C_{(alkyl)}$−O bonds.[103] Under 1 atm of H₂ at 200 °C in N-methyl-2-pyrrolidone (NMP) using 10 mol % of a nickel(0) precursor with the bidentate 1,2-bis-(dicyclohexylphosphino)ethane (dcype) as ligand, this methodology allowed for the recovery of BPA in good yields from a

Scheme 8. Ruthenium-Catalyzed and NaOH-Based Deconstruction Approaches to Epoxy Composites
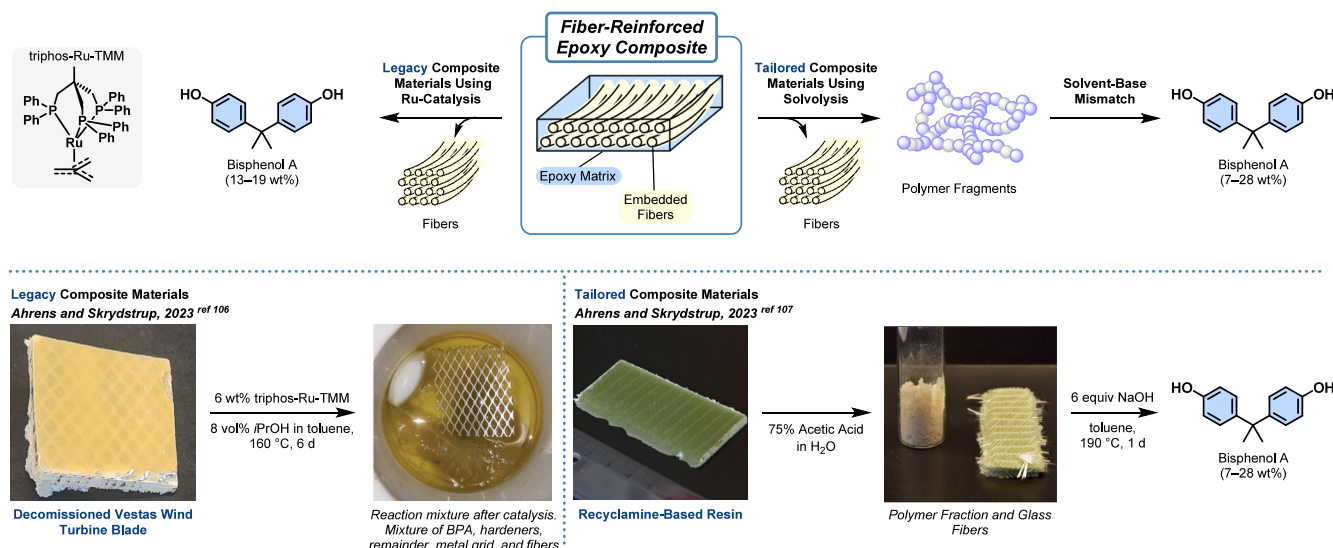
powdered amine-cured thermoset resin over the course of 36 h (Scheme 7).[102]

In 2020, our group set out to recover BPA from thermoset epoxy resins. Our interests were focused on developing a C−O bond scission strategy for the direct liberation of BPA from the polymeric resin. Furthermore, we aimed to identify a protocol that could be applicable with fiber-reinforced composites, as used commercially. Ideally, such a chemical transformation would not only release BPA, but also depolymerize the matrix and in turn release the embedded fibers in good quality, thereby enabling closed-loop recycling for both the monomer and the fiber fractions. Initial efforts in this direction were inspired by ruthenium catalyzed protocols developed for the cleavage of lignin models.[104,105] Interestingly, these methodologies could not be directly transferred to simple epoxy model compounds. Nonetheless, suitable conditions were developed using triphos-Ru-TMM in toluene and isopropanol at 160 °C.[106] The catalysis proved competent for the deconstruction of powdered state-of-the art amine-cured resins used in wind energy, maritime engineering, and as adhesive. However, anhydride-cured resins were inert under the optimized conditions. The reason lies in the mechanism of the catalysis. Initially, the central alcohol moiety is dehydrogenated to a ketone, thereby weakening the adjacent C−O bond. Although not understood in detail, it is then proposed that an electron rich ruthenium species inserts into the aforementioned bond. For anhydride-cured resins, the alcohol motif is protected as an ester and evidently inert against the dehydrogenation (Scheme 5). Lastly, the methodology could be applied to legacy composite materials, including a piece of a decommissioned wind turbine blade (Scheme 8). BPA and the fibers were efficiently liberated from the untreated sample. Analytics of the recovered glass fibers confirmed their high quality. However, as the chemical transformation is limited to the surface area of the solid sample, reaction times of several days and high catalyst loadings were required to achieve full disassembly.

In an alternative approach for enabling the closed-loop recycling of composite materials, we considered resins tailored for separating fibers from the epoxy matrix. We envisioned a two-step approach starting with a reported solvolysis process, followed by the depolymerization of the separated epoxy

fraction. As such, recycling of both the polymer and the fibers could be achieved. Many of the disassembly processes, including the one commercialized by Siemens-Gamesa and Aditya Birla, rely on aqueous acidic conditions to trigger the fragmentation of the polymer matrix.[30,31,87,89] Therefore, we aimed at developing a robust reaction system that would tolerate residues of water and acid within the resin fraction. While originally envisioning a catalytic dehydrogenation in tandem with a nucleophilic substitution on the resulting ketone in basic media, serendipity led us to a much simpler protocol.[107] By combining an alkali (NaOH) with an apolar aromatic solvent at high temperature, a fragmentation through epoxide intermediates results in the efficient liberation of BPA from amine-cured and anhydride-cured thermoset epoxy resins. The mismatch in the polarity of the base and solvent was found to be the key for achieving this simple deconstruction protocol. While not suitable for direct application to legacy composite materials, the protocol proved competent for the recovery of BPA from a sample of Aditya Birla's Recyclamine-based composite (Scheme 8). Nevertheless, if suitable and efficient separation techniques for acquiring both the epoxy resins and fibers of the more common composite materials can be identified, the base-mediated process developed by our group could prove to be a simple and broad chemical technology for BPA recovery from epoxy resins. Independently and at the same time, Beckham and co-workers published a base-induced epoxy deconstruction using potassium *tert*-butoxide.[108]

◼ OUTLOOK FOR THE DEPOLYMERIZATION OF EPOXY POLYMERS

Developing economically and ecologically viable technologies for recovering base chemicals together with fiber textiles from state-of-the-art epoxy composites on a large scale remains a herculean challenge. Nonetheless, these recent first reports on the depolymerization of epoxy resins show that polymer building blocks can be extracted from thermoset epoxy resins. Further investigation and improvement of the chemistries developed, as well as exploration of alternative methodologies, will be key to scrutinizing the potential for the chemical recycling of epoxy polymers. While potentially also applicable

to laminations, coatings, and adhesives, focusing on composite materials as accessible waste streams from decommissioned wind turbine blades, airplanes, boats, and cars is sensible.

Implementing tailored resins as the Recyclableblade/ Recyclamine technology is a major steppingstone for waste management of composite structures. For these materials, using the simple base-solvent mismatch protocol could potentially already be a way to commercially recover monomers from end-of-life epoxy resins if upscaling trials are favorable. Nonetheless, the ruthenium-catalyzed C−O bond scission serves as a proof-of-principle that catalytic depolymerizations can be applied directly to state-of-the-art epoxy composite materials. Economically, competing with established production chains that yield BPA from fossil fuels at more than 10 million metric tons per year represents a major hindrance to implement such new technologies. However, pushed by legislation, consumers favoring the use of sustainable products may nonetheless pave the way for commercializing future composite materials containing recycled monomers and fibers. Beyond the isolation of BPA, the recovery of the amine-based hardeners is an uncharted waters of considerable interest. Components as multifunctional alkyl amines are produced over a range of synthetic steps, including more complex chemical transformations such as reductive amination and hydrocyanation. Ideally, an epoxy composite could be broken down into its aromatic building block, its curing agent, as well as its fibers. This would maximize the total value recovered and thus increase the attractiveness of such a recycling approach.

THE FUTURE OF POLYURETHANE AND EPOXY-BASED THERMOSETS

The sheer complexity of thermosets owing to material specific formulation makes chemical recycling for monomer recovery challenging. Both for PU and epoxy resins, it is intangible that a single chemical recycling technology will fit the diverse portfolio of materials on the market.

For PU, several chemical recycling solutions are being developed at the scale. It is unlikely that one process will take on all types and purity grades of PU materials. As such, unless legislation calls for phasing out certain PU monomers, the future will be based on applying the right chemical recycling method for the right PU materials. Here, issues like sorting, separation, purification, monomer quality etc. makes it difficult to directly compare different recycling processes by LCA and/ or TEA. Nonetheless, these analyses are necessary to assess relative environmental and economic impacts of each process. This will help identify so-called hotspots where further development is necessary to mature a certain technology prior to its potential industrial implementation.

For epoxy polymers and their composites, chemical recycling strategies are less advanced, with the first depolymerization methods having only been reported recently. As the research is still on a fundamental proof-of-principle level, there remains a long way to go before industrial implementation could be considered. As opposed to PU materials, introducing novel resin formulations designed for disassembly and thus recovering fibers may be part of the solution. As the unit size and documentation for wind turbine blades, aviation, and automotive parts far exceed those of PU-based pillows and mattresses, traceability within epoxy-based materials should be easier. Nonetheless, new recycling solutions are still needed to address current epoxy-based materials in commission and those that are already landfilled as well as recovering

monomers from novel resin formulations targeting fiber recovery.

As the chemical recycling scheme of thermoset materials continuously advances, it is our hope that processes will be implemented, which will focus on enhancing material recovery and quality while simultaneously lowering energy consumption and waste generation in doing so. This could potentially lower the current unsustainable make−use−dispose mentality that governs the use of thermoset polymers.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article.

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Notes

The authors declare the following competing financial interest(s): S.K.K., B.S.D., and T.S. are inventors of patent PCT/EP2023/058993 on the *tert*-amyl alcohol solvolysis process for deconstruction of polyurethane, submitted by Aarhus University. A.A. and T.S. are inventors on patent PCT/ EP2022/156129 on the catalytic disconnection of C-O bonds in epoxy resins and composites and PCT/2022/200007 on solvent-base mismatch for the disassembly of epoxy polymers, both submitted by Aarhus University.

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■ ABBREVIATIONS

Boc, *tert*-butyloxycarbonyl; BPA, bisphenol A; CLD, cross-link density value; COD, cycloocta-1,5-diene; dcype, 1,2-bis-(dicyclohexylphosphino)ethane; GHG, greenhouse gas; HAT, hydrogen atom transfer; LCA, life-cycle assessment; MALDI, matrix-assisted laser desorption-ionization; MDI, methylene diphenyl diisocyanate; NMR, nuclear magnetic resonance; NMP, *N*-methyl-2-pyrrolidone; PCET, proton-coupled electron transfer; polyMDI, polymeric MDI; PU, polyurethane; TDI, toluene diisocyanate; TEA, techno-economic analysis; THF, tetrahydrofuran; TMM, trimethylenemethane; TON, turnover number

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