



# Reducing the carbon footprint of polyurethanes by chemical and biological depolymerization: Fact or fiction?

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## Abstract

Polyurethanes (PUs) are one of the most widely employed classes of polymers, with a continuously increasing production demand that is expected to reach around 21 million tons in 2022. Due to the simple polymerization process by which they are produced, the versatility in PU chemistry, and the strong inter/intramolecular interactions present between urethane moieties, these robust materials can be used in diverse applications ranging from elastomers to foams. However, this high versatility, combined with the high stability of the urethane bond and the chemically cross-linked nature of most commercial PUs, leads to long-lasting, potentially contaminating, PU waste in landfill sites. While many strategies are under investigation to improve the end-of-life options for polyurethanes, in this review we focus primarily on the latest advances in the chemical and biological routes for PU recycling. These two routes can potentially allow for monomer recovery and reuse for further synthesis of PUs, achieving materials with identical properties to the virgin materials. Aside from reviewing the latest advances in the field, we will highlight the importance of using life cycle assessment (LCA) to find a truly sustainable solution to land-filling and to incentivize the implementation of chemical and biological recycling approaches at the industrial scale.

## Addresses

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## Keywords

Polyurethane, Depolymerization, Recycling, Life-cycle analysis, Enzymatic.

## Introduction

Polyurethanes (PUs) are one of the most important classes of polymers [1], with a production demand expected to reach 21.3 million tons in 2022 [2]. Indeed, it is thought that despite the current economic crisis the PU market will grow from \$67.27 billion in 2021 to \$78.01 billion in 2022 [3]. The commercial success of this polymer family is the result of i) the simplicity and fast reaction rates of the polymerization process, which occurs by the nucleophilic addition of poly(isocyanates) and polyols [4]; ii) the wide diversity of available polyols, which allows for the adaptation of PUs to a huge range of applications ranging from coatings and/or adhesives to sealants and/or elastomers [5]; iii) the self-blowing ability of isocyanates in the presence of water, which permits the production of foams and iv) the strong intra- and intermolecular hydrogen bonding between urethane groups, which promotes toughness and resilience [1,4]. Thus, polyurethanes are versatile materials that are available in a wide range of forms depending on the specific application. For example, in 2018, flexible and rigid PUs foams made up 36% and 32% of the market share, respectively, while coatings represented 14%, elastomers 8%, adhesives and sealants 6%, and binders had the lowest market share of 4% [6]. Additionally, while the whole PU market size in 2021 was evaluated at around 71.7 billion US\$ in 2021 [7], the market of thermoplastic PU consists of only 2.4 billion US\$ [8], being the vast majority of PU production related to thermosets, which cannot undergo thermomechanical recycling. Therefore, this review will emphasize PU recycling approaches that can be used for both PU thermosets and thermoplastic recycling, such as chemical and biological depolymerization.

As with most polymeric materials, PUs are primarily produced from non-renewable resources, which is problematic considering the large production volumes. A trending strategy to increase the sustainability of PUs and to reduce our reliance on fossil resources is the

replacement of oil-based precursors with new precursors derived from renewable resources, such as bio-based isocyanates [9,10], and polyols [11–13], as well as polyols based on CO<sub>2</sub> [14–18]. While we believe that this is an important trend to increase the sustainability of the polyurethane production, it has been extensively covered by previous reviews and will not be discussed below [18–21].

Another way to increase the sustainability of PU production is to move from our current linear PU production model to a more circular one. Nowadays, most polyurethanes are discarded and placed into landfill after use. In principle, polymers that contain backbones linked by C–O and C–N bonds exhibit relatively low reaction barriers and near-neutral reaction-free energies, which is ideal for the chemical deconstruction of plastics. Even so, the recycling of PUs is not as developed as the deconstruction of polyethylene terephthalate (PET). Most of the issues associated with PU recycling derive from the chemically cross-linked nature of most commercialized PUs (thermosets), and the high variety of PU compositions that are mixed during waste disposal. This makes it difficult to develop a universal method for recycling different PU families [22–32].

Different options are available for treating PU-based plastic waste including 1) mechanical recycling through reuse in the polymer form, 2) thermo-chemical recycling including energy recovery, and 3) chemical and biological recycling to recover different building blocks. While mechanical recycling could be of great interest in the case of thermoplastic PUs and research in this direction should continue, most polyurethanes are commercialized as thermosets, which reduces considerably the potential for mechanical recycling. While some groups have taken advantage of the dynamic character of urethane bonds for reshaping polyurethane thermosets by a thermomechanical process [6,23,33], [–] [39] achieving PU melts with viscosities low enough to allow extrusion is still highly challenging. For such reasons, thermo-mechanical recycling approaches will not be addressed deeply in this review.

To recycle PU thermosets by a “universal” method, one can focus on thermo-chemical recycling. Thermo-chemical recycling of PU waste is motivated by avoiding environmental pollution while producing a valuable product, that can be either energy, an energy carrier (such as syngas or hydrocarbon fuels), or valuable chemicals [40]. Moreover, the cross-linked nature of the polymer does not have any impact on the recycling process and the impact of the chemical nature of the PU is limited in comparison to mechanical, chemical, and biological recycling. However, the composition of the waste stream as well as the scale of the plant should be carefully considered to design an economically and environmentally sustainable process [40].

Another alternative to minimize the negative impact of PUs on the environment, and to address the end-of-life issues, is to develop a circular economy approach based on chemical and biological depolymerization of polyurethanes [6,31,41–47]. The idea behind chemical and biological recycling is to obtain virgin-like materials by energy-efficient and environmentally benign processes that can be implemented in the synthesis of polyurethanes or other polymers. From this perspective, we will cover the most recent and relevant advances related to the chemical and biological depolymerization of PUs, [Figure 1](#). Moreover, we will highlight the importance of life cycle assessment (LCA) for the proper implementation of chemical and biological recycling approaches.

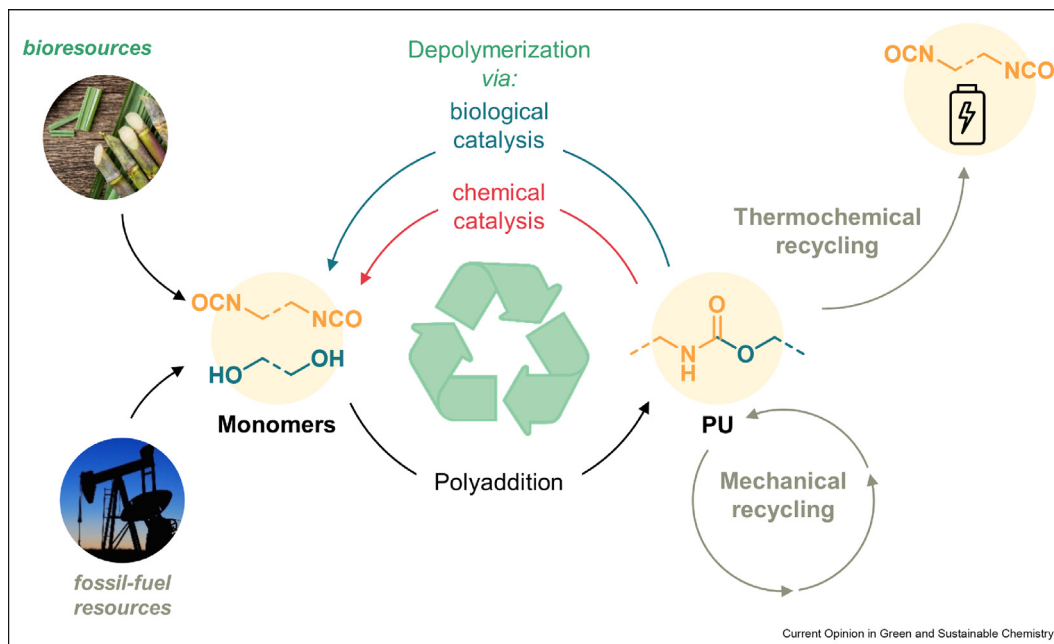
### PU depolymerization *via* chemical catalysis

Commercially available PUs generally contain different functionalities besides the urethane bond, such as esters, ethers, carbonates, and amides, derived from the precursors used for PU production [4]. Therefore, chemical depolymerization of polyurethanes can be divided into two main approaches: Depolymerization based on the cleavage/exchange of urethane bonds [6,41,42,45,47–51] or depolymerization based on the cleavage/exchange of chemical bonds of the precursors used for PU production, such as esters [52–54]. Introducing labile functionalities into the PU backbone, such as hindered ureas [26,55,56], disulfides [33,39,57–60], thiourethanes [22,27,30,61,62], acetals [63–65], and so on, can also facilitate the effective depolymerization of a given PU. However, when dealing with complex waste streams, containing different types of PUs, the depolymerization approaches based on non-urethane chemistry are highly dependent on the employed reagents and difficult to implement industrially. Therefore, this review will primarily focus on depolymerization reactions based on deconstructing urethane bonds.

Regarding depolymerizations based on urethane chemistry, the most studied reactions are based on transcarbamoylation of the urethane group, with hydrolysis, acidolysis, aminolysis, and alcoholysis (or “glycolysis”) the most common types of transcarbamoylation reactions. Nevertheless, in the last decade process for PUs depolymerization *via* catalytic hydrogenation reactions have also been developed ([Figure 2](#)) [41,51].

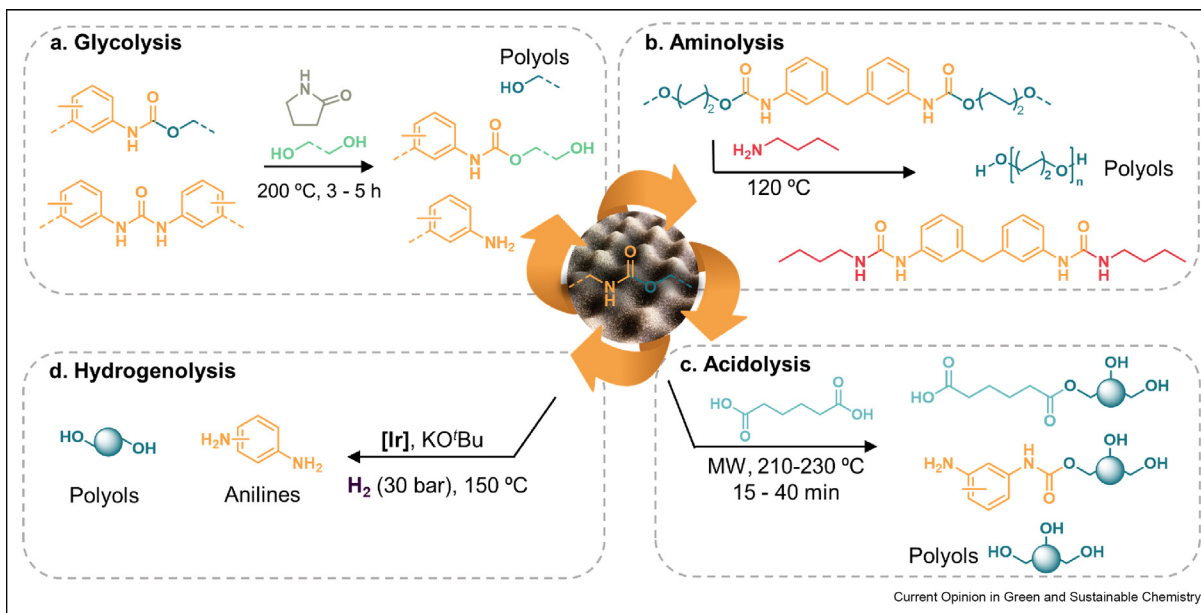
The depolymerization of PUs *via* transcarbamoylation consists of nucleophilic substitution reactions between low molar mass diols, diamines, or water, and the electrophilic carbon center of the urethane group ([Figure 2a–c](#)). As the reaction is highly energy-demanding, catalysts and/or temperature are required to enable effective depolymerization of PU *via* transcarbamoylation. Among the PU depolymerization

Figure 1



PU circular economy.

Figure 2



Examples of PU depolymerization *via* chemical catalysis (a) glycolysis [66], (b) aminolysis [67], (c) acidolysis [68], and (d) hydrogenolysis [69].

approaches *via* transcarbamoylation, glycolysis is the most widely investigated and is the only one currently applied on an industrial scale [5,6,34,41,47,66]. The reaction is carried out by mixing an excess of low molar

mass diols (i.e. ethylene glycol) to ground PUs in the presence of catalysts and heating at  $T \geq 170$  °C. The products of the reaction are the recovered polyols (the desired product), and lower molar mass hydroxyl-

terminated polycarbamates as byproducts [5,6,34,47]. Those are highly immiscible and tend to phase-separate into two distinct phases: one phase is rich in polyol, and the other is rich in excess diols and lower molar mass polycarbamates. Therefore, this process is generally referred to as split-phase glycolysis [5,6].

The polyol phase is recovered and used for PU production, while secondary procedures are currently being studied towards recovering valuable monomers such as diamines from the polycarbamate-rich byproducts. Although split-phase glycolysis is a well-established PU chemical recycling process, it requires high temperatures ( $T \geq 170$  °C) and the contamination of the recovered polyols with lower molar mass glycols means that further purification procedures, such as distillation, are required [66]. Those features, coupled with the large excess of glycols needed to recycle PU thermosets (typically 1.5 kg of glycol per kg of PU), increase the process carbon footprint and have hindered the spread of glycolysis as a widely employed method for recycling PUs [66].

To reduce the energy requirements in depolymerization of PUs *via* glycolysis, organic base-catalyzed methanolysis has been proposed as an alternative. This method allows for the recovery of the polyol and methanolic carbamates with 85% yield, while employing reaction temperatures below 65 °C [41]. Methanolic carbamates can then be used for further PU production [49]. For example, Beran et al. [49] reported the use of the polycarbamate byproducts of glycolysis for production of adhesives, which reduces the waste and carbon footprint associated with PU glycolysis. As an alternative to reduce the amount of glycol needed in PU glycolysis, the use of lactam as a co-reactant of glycols was proposed by De Vos et al. (Figure 2a) [66]. It was found by adding only 6 wt% of lactam to the reaction mixture the amount of glycol required was reduced from 60 wt% to 33 wt% without decreasing the purity or yield of the recycled polyol [66].

Besides the use of diols, other reagents can also be used to trigger the depolymerization of PUs. For instance, aminolysis, which yields polyols and amine-terminated polycarbamates, has been investigated to target PU depolymerization under milder conditions [67,70,71]. For example, a urethane depolymerization conversion of 100% was achieved by the aminolysis of a segmented PU with butylamine at 120 °C in a DMF/toluene solution (Figure 2b) [67]. As amines are stronger nucleophiles this process seems interesting in comparison to alcoholysis [72], although research on aminolysis of PU has been less investigated due to problems associated with potential side reactions occurring in the aminolysis process [73].

On the other hand, hydrolysis together with acidolysis also showed promising results in the literature. Nevertheless, one should consider that in both processes unstable carbamic acid is formed, which promotes the

formation of undesired CO<sub>2</sub> as a byproduct [41,42]. Zahedifar et al. [47] recently reported that the time to depolymerize PUs could be reduced from 2 h to 90 min with water addition. In the same direction, acidolysis may be the fastest PU depolymerization approach and does not require solvents [68]. Grdadolnik et al. [68] reported the acidolysis of PU foams with adipic acid in bulk with temperatures ranging from 210 to 230 °C and reaction times of 15–40 min, assisted by microwave irradiation (Figure 2c). The polyols were fully recovered together with carbamate-rich dicarboxylic acid byproducts [47].

Over the past few years, PU depolymerization driven by catalytic hydrogenation has been investigated as a promising approach for the upcycling of PUs, due to its ability to depolymerize PU into valuable polyols and diamines [6,51,69,74,75]. In contrast to traditional carboxylic reduction processes and transcarbamoylation, catalytic hydrogenation is particularly attractive as it does not produce stoichiometric byproducts (waste) [74].

Schaub et al. [74] reported the depolymerization of PUs *via* ruthenium-catalyzed hydrogenation. Several catalysts were screened, with and without basic conditions, using THF or toluene as solvent, with temperatures ranging from 120 to 200 °C, and H<sub>2</sub> pressure of 50 bar. For PUs based on toluene diisocyanate or methylene diphenyl diisocyanate and 1,6-hexanediol, the recovery of hexanediol was as high as 85%, while recovery of the diamines (toluene-diamine and methylene diphenyl-diamine) was 76%. Nevertheless, for commercial PUs the yield of polyol and diamine recovery was significantly lower, reaching a maximum of around 50% for an additive-free PU foam, and around 24% for a PU sponge at extreme conditions (H<sub>2</sub> pressure of 100 bar,  $T = 200$  °C). When using manganese-based catalysts combined with H<sub>2</sub> pressure of 60 bar,  $T = 200$  °C, THF/toluene mixture, and KO<sup>t</sup>Bu as co-catalyst, the depolymerization yield for a commercial PU was increased up to 90% [51].

Skrydstrup et al. [69] reported the catalytic hydrogenation of an end-of-life-cycle PU with commercial iridium catalysts under milder conditions ( $T = 150$  °C, isopropanol, 30 bar of H<sub>2</sub>), Figure 2d. For flexible commercial PU foams, up to 90% recovery of polyols and diamines was achieved, while for rigid PU foams the yield was lower, recovering only 24% of diamine [69]. On the other hand, Baráth et al. [75] recently reported the depolymerization of silicon-based polyureas *via* Ru- or Mn-catalyzed hydrogenation. Yields of up to 84% of aliphatic diamine and silicon-containing diamine were obtained using a commercially available PNP-Ru catalyst, H<sub>2</sub> pressure of 50 bar, and a temperature of 165 °C. Thus, catalytic hydrogenation of PUs has emerged as a promising depolymerization approach for PUs, especially considering its capacity to recover not only the



polyol but also diamines that can be reused for diisocyanate production.

Although significant advancement has been made with chemical recycling strategies, significant improvement is still required for proper PU waste management. For instance, alcoholysis/glycolysis should target lower energy requirements and reduction of the stoichiometric excess of glycols needed for high polyol recovery efficiency [51,69,74,75]. The use of optimized catalysts, and of additives that favor the interaction of the nucleophile and the PUs should reduce both the energy demand and the excess glycols needed for depolymerization [41,42,47,66,68]. On the other hand, in the case of hydrogenation, the organometallic catalysts required for hydrogenation tend to be expensive or are synthesized by complex procedures [76], offering room for further improvement. Besides, we believe that future research on the catalytic hydrogenation of PU must target the use of green solvents and the reduction of the energy requirement *via* higher catalytic efficiency [69].

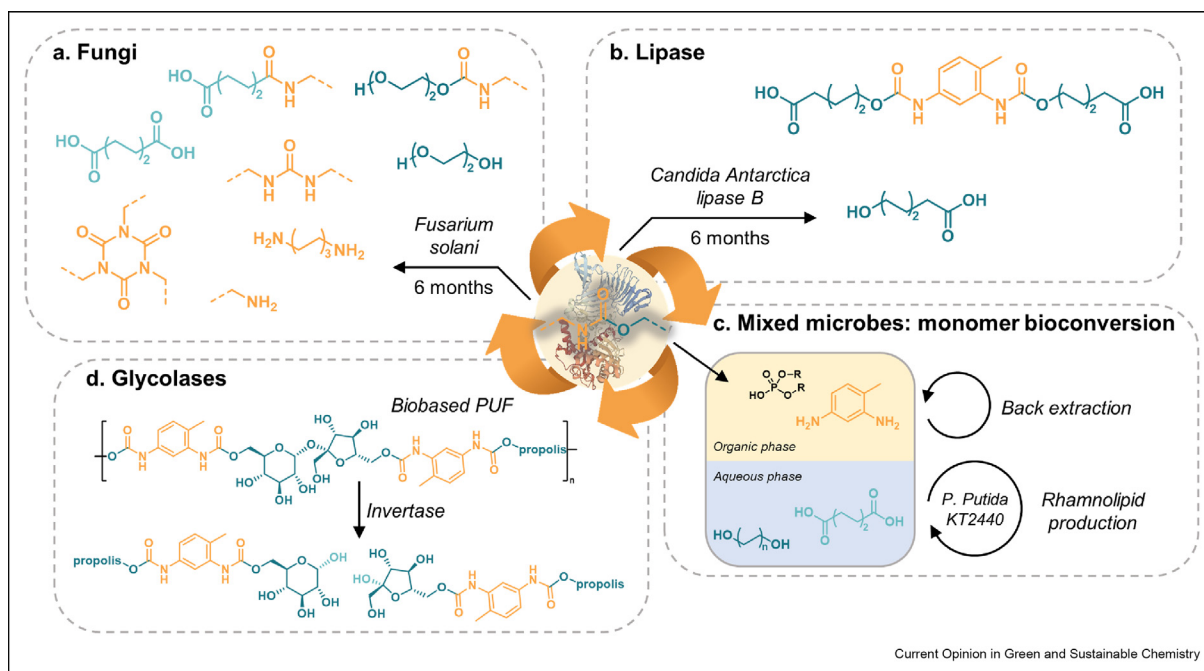
### Depolymerization of PUs *via* biological catalysis

Biotic degradation of PUs, performed either by microorganisms or by isolated enzymes, is the basis of the so-called “bio-recycling” of PUs [77]. Microorganisms secrete a set of enzymes that can catalyze PU

depolymerization [43,77]. Filamentous fungi usually perform better than bacteria in depolymerization of PU foams (Figure 3a) [78] because their filaments can penetrate inside the pores providing stress, thus combining biotic and abiotic degradation [44,77]. Recent developments have seen the identification of new fungi, such as *Embarria clematidis* [79,80] or the marine fungus *Cladosporium haloterans* [81,82], that are able to degrade polyester-PUs. The released monomers can be assimilated by the microorganisms which use them as carbon sources to grow, leading to their mineralization with the release of H<sub>2</sub>O and CO<sub>2</sub> in aerobic environments [44,77]. This is aligned with great interest to treat solid PU waste and avoid disposal or landfilling, although does not allow for the recovery and valorization of products of major importance from a circular economy point of view [44,83].

Microorganisms can be present as single strains in cultures, or as consortia, for example in soil or compost [84]. Microbial communities isolated from PU waste recovered in landfills have been used to biodegrade commercial PU coatings or dispersions [85–87]. Interestingly, growth of isolated members was much lower than growth of the complete community, suggesting synergistic effects between the different microbes [86]. Among the consortia, several bacteria such as *Paracoccus* and *Acinetobacter* were identified as potential PU degraders.

Figure 3



Examples of PUs *via* biological catalysis (a) fungi filament-assisted [78], (b) lipase catalyzed [102], (c) mixed microbe-assisted [103], and (d) invertase assisted [104].

The ability of some insect larvae to ingest and biodegrade different kinds of plastics, including PU, has also received much attention lately. Larvae from *Tenebrio molitor* and *Zophobas atratus*, colloquially called mealworms and superworms, respectively, have been used to treat different kinds of PU wastes, including polyether- and polyester-PU foams [88–93]. Larvae were able to survive on a sole PU diet during the experiment time (33–58 days), but lost weight, indicating that the PU diet did not meet their nutrient requirements. Mass loss of PU samples reach up to 67% [88], but the amount of frass (*i.e.*, the larvae excrements) is never quantified, although it contains 40%–45% of PU that is not (fully) degraded [91], thus precluding a true mass balance calculation. The PU diet causes important changes in the gut microbiome of the worms, with higher abundance of some bacteria, such as *Enterococcus* and *Mangrovibacter* [89,90], *Lactococcus* [93] or unclassified Enterobacteriaceae [88,89,92], suggesting that they can play a specific role in PU degradation.

Enzymes capable of degrading specific bonds in PU materials can be produced and isolated after cloning and overexpressing the relevant genes, as recently performed with esterases from *Pseudomonas* [94,95] and from the Antarctic bacterium *Morexalla* [96,97]. Although in the ideal case depolymerization of PUs should focus on the urethane group, most of the investigated enzymes reported to date are only able to hydrolyze ester bonds. Thus, hydrolases (EC 3), and the less frequently used oxidoreductases (EC 1), used to degrade PUs have only been able to degrade polyester-based urethanes. The enzymatic cleavage of urethane bonds is more difficult to achieve. Esterases and proteases or amidases have been reported to potentially cleave urethane bonds. Different mechanisms are involved since esterases cleave C–O bonds whereas proteases cleave C–N bonds, but both can lead to the formation of amines and OH groups with the release of CO<sub>2</sub> *via* an unstable carbamic or carbonic acid intermediate. However, as pointed out by several authors [43,77,98–100], most of the reported enzymes in the literature able to break PUs were actually esterases, and therefore are only able to hydrolyze the ester bonds in polyester-PUs and do not lead to cleavage of the stronger urethane bonds. Apart from hydrolases, oxidoreductases such as laccases, have occasionally been used in PU degradation. Activity on polyester- and polyether-PU foams have recently been reported [101], but without further insights into the molecular mechanisms. Metagenomic analyses of microbial communities able to biodegrade PU also revealed the presence of genes coding for various dehydrogenase, mono- and dioxygenase. Analysis of degradation products confirmed the probable occurrence of PU degradation by oxidative mechanisms [85], thus opening new perspectives for PU enzymatic degradation beyond the classical use of hydrolases.

Analytical efforts are important to understand biocatalytic mechanisms [105]. The degradation of low molar mass models containing ester or urethane linkages is a good way to evaluate enzyme activity but does not ensure that these enzymes will actually be able to degrade the same bonds in PUs. Overall, the detection of amines in the degradation products of PUs seems to be the main quantitative way to confirm the hydrolysis of the urethane linkage [77]. This has recently been shown in the degradation of a polyester-PU by a cutinase [106].

In absence of true “urethanases,” the enzymatic degradation of PUs remains mainly limited to polyester-PUs. Unlike chemical depolymerization, which allows for the recovery of polyols that can be reused in a closed-loop recycling approach, biotic depolymerization leads to the recovery of low molar mass diols [e.g., ethylene glycol (EG), 1,4-butanediol (BDO)], diacids [e.g., succinic acid, adipic acid (AA)] or ω-hydroxy acids [e.g., 6-hydroxycaproic acid (6-HCA)], depending on the nature of the polyester polyol used. The recovered building blocks can then be used for the synthesis of new polymers, or for the bioproduction of other synthons of interest in an open-loop upcycling strategy [43,46,98,107].

Thus, some building blocks obtained from the degradation of PU foams based on a polycaprolactone (PCL) diol by lipases from *Candida antarctica* [108] have been used to build second-generation polymers. Recovered 6-HCA was successfully polymerized either by organometallic or enzymatic catalysis and showed the potential to be used with other recovered building blocks containing urethane bonds (Figure 3b) [102]. This successful example, however, points to the need for purification of the recovered building blocks after PU enzymatic depolymerization, as their incorporation resulted in a net decrease of both the yields and molar mass of the polymers.

The second upcycling approach is to find microbial communities able to grow on the released monomers. However, it is complex in the case of PUs because of the toxicity of the released monomers, especially in the case of aromatic amines produced by the cleavage of PUs made with aromatic isocyanates [e.g., MDI, 2,4-toluene diisocyanate (TDI)]. Recently, a strain of *Pseudomonas* has for the first time been identified as able to grow on 2,4-toluene diamine (TDA), the diamine released from PUs based on TDI, as the sole carbon and nitrogen source [32,109]. However, when included in a mixed microbial culture with other bacterial strains of the *Pseudomonas* genus, the growth was inhibited by the presence of TDA (Figure 3c) [103]. After selective removal of TDA, the mixed culture was able to assimilate simultaneously the other PU monomers (EG, BDO, and AA) for the production of rhamnolipids, which can be used as biobased surfactants (Figure 3c) [103].

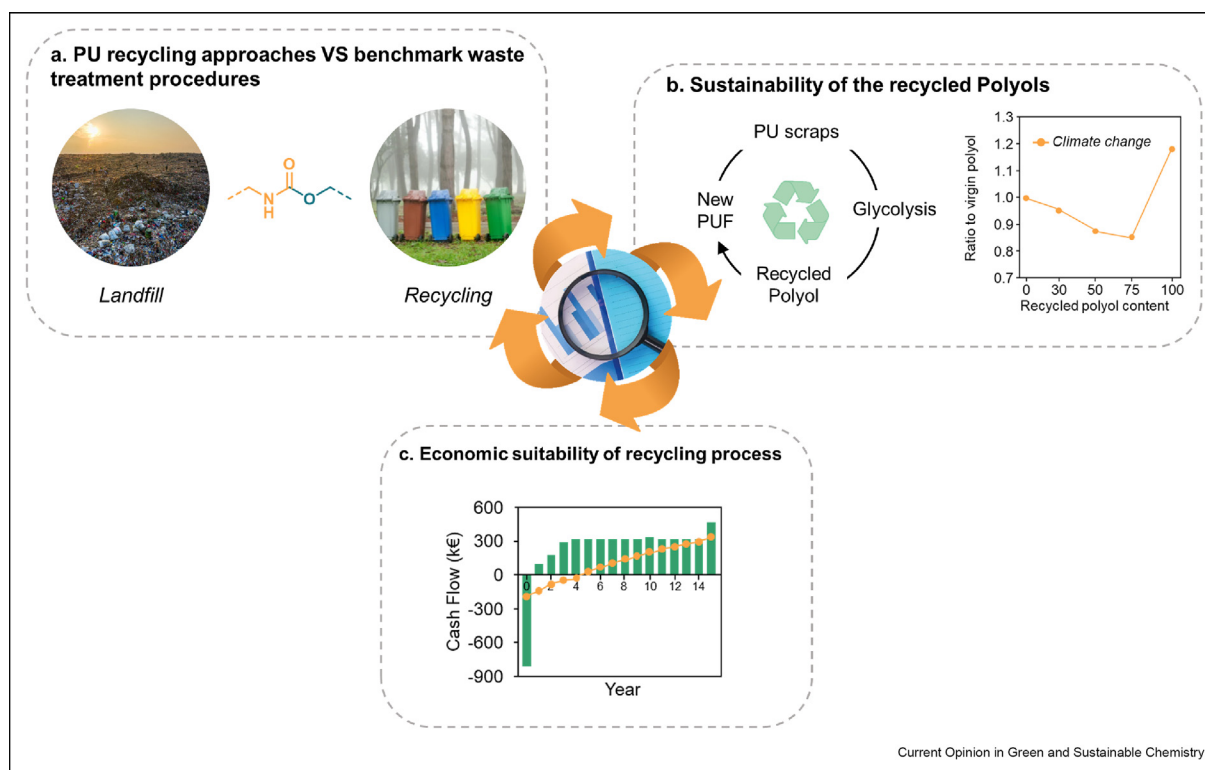
The potential of microorganisms or enzymes to degrade PUs is high and with the continuous development of biocatalysis in the recycling of plastics, it is clear that sooner or later scientists will identify or achieve new microorganisms or enzymes able to degrade PUs. However, current enzymes seem much more appropriate to recycle PUs containing ester bonds. Therefore, one potential strategy to facilitate biotic degradation may be related to the incorporation of more appropriate monomers for biotic assimilation. Thus, sugars have recently been introduced as monomers in PU foams, allowing their degradation by glycolytic enzymes (Figure 3d) [104]. The introduction of an unsaturated chain extender has also been shown to enhance the fungal degradation of PU, because of possible oxidative attack on the double bond by microorganisms [110]. Nevertheless, in order to implement bio-recycling strategies in PU materials it is imperative to consider the large heterogeneity in PU formulations such as the chemical structure, hydrophobicity, crystallinity, and  $T_g$  of the PU [43,44,77]. Moreover, this bio-recycling should be much more selective than it is at present, because yielding multiple building blocks only further complicates the already complex downstream processing of commercial PU samples [43].

## Life-cycle assessment

The LCA methodology has been implemented in the past to evaluate the environmental performance of different mechanical recycling strategies to treat PU waste against other end-of-life treatments such as incineration and landfilling. [3]–[6] These studies reported a reduction of greenhouse gas emissions besides lower scores in other impact categories due to a decrease in the demand for both non-renewable energy and raw materials. It also emphasized the fatigue and loss in properties of the recycled polyurethanes upon reprocessing cycles. This highlights the need for chemical or biological recycling approaches for PU waste, aiming to achieve upcycling and a truly circular PU plastic economy.

Therefore, despite the increasing amount of research into different approaches to depolymerizing PUs, there is still a lack of sustainability assessment to prove the superiority of chemical recycling against the benchmark end-of-life treatments of PU waste Figure 4a [111–116]. This is probably a consequence of the early stage of maturity of PU depolymerization technologies. As such, there is no framework to support a process-oriented Life Cycle Assessment (LCA) in its design phase [114,117–119]. Furthermore, in the few reports

Figure 4



Examples of benefits of LCA methodologies (a) critical comparison between waste treatment procedures, (b) sustainability assessment of the recycled polyols [116], and (c) economic suitability of the recycling process [119].

in which product-oriented LCAs were implemented to compare the environmental impact of recycled polyol-based PUs against the crude oil-based one, the sample containing 100% recycled polyol had even higher environmental burdens than its virgin counterpart (Figure 4b) [116,120]. This lower sustainability performance of recycled polyol-based PU can be attributed to several factors. For instance, higher amounts of isocyanates and additives are added to compensate for the effect of the lower quality of the recycled polyol in the physical properties of the material, leading to higher use of fossil fuels and higher energy consumption [120–126]. Moreover, the energy consumption and emissions derived from different stages of the product life-cycle contribute to the higher environmental impact of polyurethanes based solely on recycled polyols. This includes additional energy-consuming stages such as PU waste collection, transport, treatment of the PU scrap to convert it into high-quality recycled feedstock (e.g., sorting, grinding), and the depolymerization process itself [116]. However, LCA results also proved that when using 50 and 75 wt% of recycled polyol content, a better environmental performance was achieved in most of the environmental impact categories, as compared to the PU richer in virgin polyols (Figure 4b) [116].

Looking at these results, it is clear that research in chemical and biological recycling should go hand in hand with LCA methodology when defining the best depolymerization technologies in terms of sustainability and competitiveness (Figure 4c) [119]. However, assessing circular economy developments by holistic methods is complex. As some of us recently reviewed [126], large-scale recycling of PUs can induce market changes that are not always considered properly in LCA methods. Moreover, the quality of the recycled product may play a pivotal role, as due to their lower performance in some cases a one-to-one substitution is not possible. Thus, the LCA should include some correction factors to introduce the variants which in many of the LCAs remain somewhat unexplored.

## Conclusions

The complexity of PUs waste streams in terms of chemical structure, crystallinity, cross-linking density, and soft-to-hard segment ratio is daunting in comparison to other plastics. Thus, while for most plastics there is an ideal recycling pathway, the structural diversity of PUs makes it difficult to develop a universal recycling process. In this perspective, we have elaborated on the chemical and biological recycling of PU which could potentially deliver virgin-like materials economically and in an energy efficient manner. Taking into account the relatively low reaction barriers and near-neutral Gibbs free energy of reaction for C–O and C–N bond-cleavage, different approaches have been

investigated to deconstruct PUs. However, it is important to point out that the urethane group is not as accessible as other carbonyls such as esters or carbonates for chemical and biological recycling.

Indeed, in the field of chemical depolymerization relatively harsh conditions are used to trigger depolymerization reactors. In depolymerization *via* transcarbamoylation great efforts have been devoted in the literature to reduce the energy demands of the depolymerization process by implementing specific catalysts or by using specific compounds to enhance the polyurethane–nucleophile interaction. While it seems that these approaches may reduce the carbon footprint of the PU, a proper life cycle analysis has not been performed to assess the sustainability of such approaches. Besides transcarbamoylation, in the last few years, catalytic hydrogenation of polyurethanes has emerged as an interesting alternative for the chemical recycling of PUs. Catalytic hydrogenation is particularly attractive as it allows for the recovery of diamines and polyols, reduces the number of byproducts, and does not require a stoichiometric excess of chemical reagents. However, research should be directed to develop less energy-demanding, and solvent-free or green solvent-based approaches for large-scale applications.

Analogously, the enzymatic degradation of PUs is also a very promising strategy, as it is carried out under mild conditions with substantially lower energy requirements and allows for the recovery of valuable polyamines/polyhydroxylated compounds. Still, research must be carried to optimize enzymatic depolymerization procedures for commercial PU formulations. In particular, future work should be directed towards targeting the cleavage of urethane bonds. One potential strategy to facilitate both the chemical and biological recycling of polyurethanes could be related to development of circular-by-design PUs that contain chemical bonds that favor depolymerization. However, care must be taken not to increase even more the complexity of the already complex recycling of PU waste streams.

The input of specifications, such as material performance and sustainability metrics (LCA and TEA), in the material flow analysis (MFA) at early stages is crucial to develop approaches that could have a long term effect. Nevertheless, this should not limit fundamental research, which will remain critical to re-imagine what is possible and identify the boundary conditions for future development of the recycling of PUs. Therefore, the high interest and investment in academic/industrial research into PU recycling points towards a bright future in which PUs are produced and used as part of a circular economy, which can be achieved by turning “fake” recycling processes into genuinely sustainable procedures.



## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

No data was used for the research described in the article.

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## References

Papers of particular interest, published within the period of review, have been highlighted as:

\* of special interest

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