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Review

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Sustainability in polyurethanes: old hat or new strategy for future developments?

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Polyurethanes are facing health and environmental problems related to their chemistry, processing and end-of-life management. This review summarizes the most recent strategies within the framework of sustainability and circularity related to the use of polyurethanes with low environmental impact, focusing on the possibility of performing their synthesis by replacing fossil-based building blocks with renewable ones, designing vitrimeric polyurethanes, and managing their end-of-life through enzymatic degradation or biodegradation processes.

Polyurethanes (PUs) undoubtedly represent an important part of the overall polymer market[1]. Their utilization involves different advanced sectors, ranging from elastomers, adhesives and sealants, coatings, and biomedical materials to civil engineering and even furniture[2–4]. It must be noted that almost all PUs undergo a foaming process, with typical density values ranging from 40 to 960 kg/m^3, depending on the identified application[5]. From their discovery dating back to the 1940s with the first patent filed by Otto Bayer and co-workers[6], the world of polyurethanes has expanded progressively and remarkably, achieving a global market size value of about 78 billion dollars, with a revenue forecast of around 105 billion dollars in 2030, and envisaging a compound annual growth rate of 4.5% (3.9% for the USA market only) from 2024 to 2030[7].

The current broad use of polyurethanes and their increasing economic/market success are thoroughly justified not only by their interesting physico-chemical and thermo-mechanical features but also by the availability of a large variety of PU building blocks that allow for tuning the overall behavior envisaged for the final polymers, promoting a wide, customized, and tailored range of properties. In particular, it is possible to easily change such parameters as stiffness, foam density, thermal resistance, and mechanical behavior by simply selecting different structures of the PU precursors. Another important characteristic of PUs is the fast polymerization/curing kinetics that does not require high reaction temperatures (indeed, the reaction can take place at room temperature in the presence of a suitable catalyst), hence leading to high productivity even at the industrial level.

However, these peculiar advantages are somehow limited by health and environmental problems specifically related to the chemistry, processing, and end-of-life management of polyurethanes. In fact, unlike diols and polyols, which do not show toxicity or hazard, some isocyanates and catalysts (such as dibutyltin dilaurate) employed for the synthesis of PUs are toxic and even mutagenic or carcinogenic[8–12]. Furthermore, incineration or landfill confinement (Fig. 1) may account for CO_2 emissions (and, therefore, global warming) or soil/ecosystem pollution, respectively[13–15].

As a consequence, in the last five to ten years, important efforts from academia and industry have been addressed toward: (i) the design of new polyurethane systems, made of renewable building blocks[16] and/or (ii) the setup of efficient recycling processes, aiming to limit the carbon-footprint of PU industry and, at the same time, using low environmental impact chemistry and cleaner processes, thus leading to a significant increase in the sustainability of these materials and well matching the current circular economy strategy[17–20].

For this latter, apart from the quite well-established mechanical and chemical recycling of PUs[13,17,21–29], the most recent strategies have been focused on the design and development of effective enzymatic degradation and bio-degradation processes[30–34]; further, on one side, non-isocyanate polyurethanes (NIPUs) have been developed and implemented[35–38]. On the other side, the synthesis of organic catalysts showing lower toxicity and environmental impact has been carried out[39–42], achieving promising results. Further, the exploitation of renewable building blocks (mainly concerning diols and polyols, despite the presence of some examples about the use of renewable isocyanates[43–46]) is currently significantly growing and it is expected that will take over a large share of the future polyurethane market.

In parallel, a few years ago, the design of vitrimeric PUs, i.e., polyurethane systems consisting of dynamic covalent adaptive networks (CANs), started to be investigated, as these modified polyurethanes behave like thermosetting 3D networks until a certain temperature, at which the crosslinking density dramatically drops down (as a consequence of the breakage of the dynamic bonds linking the macromolecular chains), hence accounting for the possibility of processing and even recycling these polymers as they were thermoplastic materials[47–53].

The huge research work that has been performed in the last years toward sustainability in polyurethane chemistry, processing, and end-of-life is considerably witnessed by the increasing trend of the publications (articles, reviews, book chapters) on this research topic (Fig. 2).

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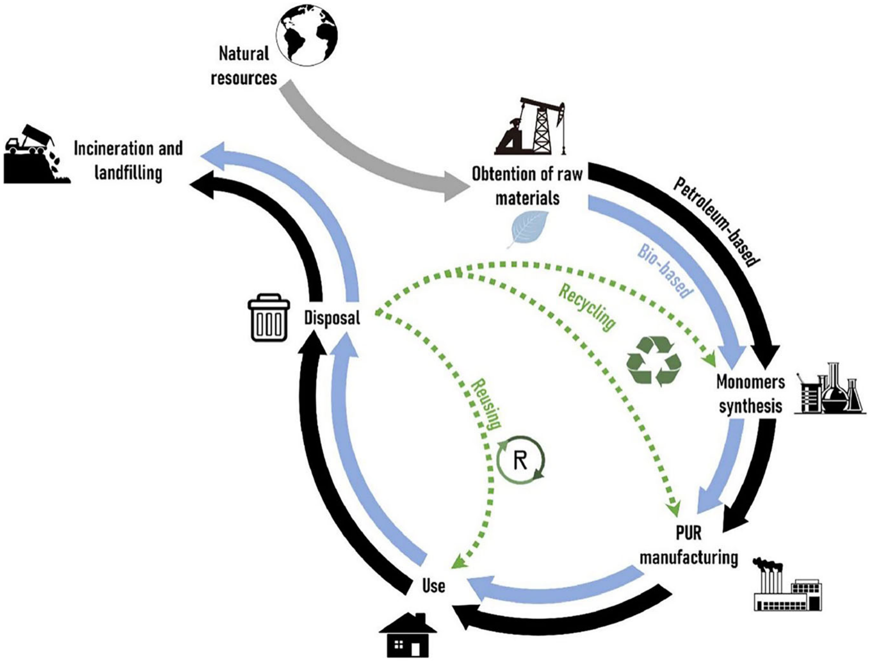


Fig. 1 | Polyurethane life cycle: a general scheme. Reprinted from[39] under CC-BY-NC License.

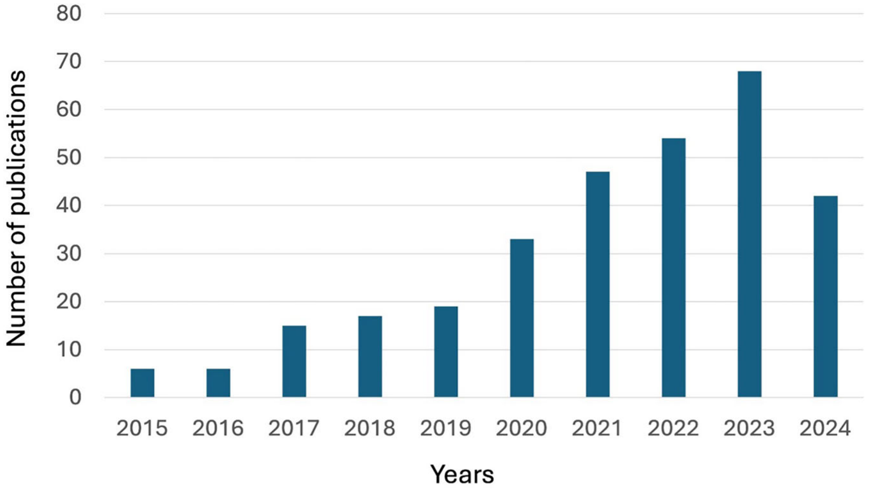


Fig. 2 | Number of publications (from 2015 to 2024) in peer-reviewed journals dealing with "sustainability AND polyurethanes" (AND is the Boolean operator; the data were collected from the Web of Science™ database, accessed on June 17, 2024).

Therefore, this work is aimed at summarizing the most recent outcomes achieved in the synthesis, processing, and end-of-life strategies for the design of sustainable PUs (in the light of the circular economy approach), highlighting the research efforts carried out so far, and suggesting some possible perspectives for the forthcoming years. A particular attention will be devoted to the design and development of renewable building blocks, the design of vitrimeric PUs, and the enzymatic degradation and biodegradation of the polyurethanes, which represent the "hottest" research topics in this field. Finally, as it is progressively emerging as a very useful tool for the assessment of the sustainability of polyurethanes, the current state-of-the-art of life cycle analysis (LCA) applied to these polymer systems will be summarized, providing the reader with some nice and up-to-date examples.

Biosourced polyols and isocyanates

As said before, the use of biobased monomers, i.e., polyols and isocyanates, to produce polyurethanes, represents a step to increase their sustainability. While the use of polyols obtained from vegetable oils has been reported for a long time[54], the production of isocyanates from renewable resources is a more recent topic.

Biobased polyols

Generally speaking, there are two classes of polyols for rigid and flexible applications. The first class has OH values between 300 and 600 mgKOH/g and functionalities between 3 and 8; the second possesses an OH value of 30–50 mgKOH/g and functionality 2–3. Both classes can be obtained starting from biobased raw materials.

In chronological order, the first example of the use of bio-based components was the synthesis of polyether polyols by employing biobased starters (i.e., chain initiators) like sorbitol, sucrose, and xylitol in the polymerization of alkylene oxides (e.g., ethylene, propylene, and butylene oxides). However, the biobased content in this case was not beyond 30% in the polyol, which means a content not exceeding 8% in the final polyurethane foams. Another way to use sugars to obtain short-chain diols is through fermentation of sugars[45]. For example, propylene glycol and butanediol can be obtained by employing different sources of glucose and different genetically modified microorganisms. These polyols are used in polymers other than polyurethanes (e.g., polyesters)[55] or are employed in the polyurethane chemistry as chain extenders or to manufacture polyether polyols for elastomer applications, such as poly(trimethylene ether) glycol and

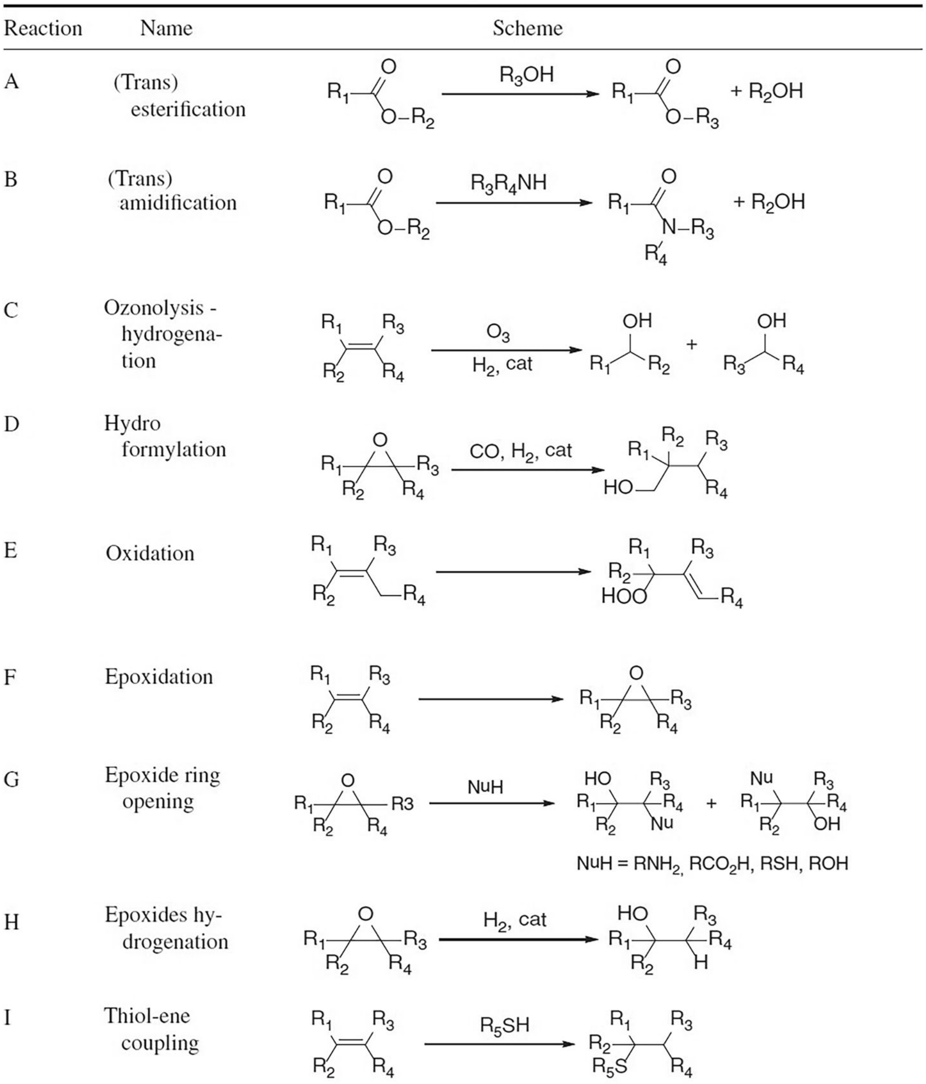


Fig. 3 | Main reactions employed for functionalising vegetable oils to obtain Natural Oil Polyols. Adapted from[63], copyright 2012, Taylor & Francis.

polytetrahydrofuran. Examples of commercially available polyols of this nature are provided elsewhere[39,56].

The most common approach proposed to obtain biobased polyols is using vegetable oils as raw materials; these polyols are very often referred to as Natural Oil Polyols (NOPs).

There are some oils, namely castor and lesquerella oils[57,58], which can be used directly as polyol substitutes because they already possess hydroxyl groups. It shall be mentioned that in terms of commercial availability, castor oil has advantages over lesquerella one[57] because the cultivation of this latter is characterized by a low crop yield[59] and a small quantity of oil that can be extracted from the plant (no more than 25 wt.%), which hinder its industrial applications[60]. However, castor oil is sometimes subjected to transesterification to solve problems related to its low hydroxyl number, low reactivity because the hydroxyl groups are secondary only, and low functionality.

Most of the vegetable oils do not contain hydroxyl groups; therefore, to be used as polyols, hydroxyl groups must be introduced in their chemical structure[61]. In general, the functionalization of vegetable oils to obtain suitable polyols involves the ester groups of the oils or the double bonds of the fatty acid hydrocarbon chains (Fig. 3). Transesterification of vegetable oils (e.g., soybean, palm, linseed, sunflower and rapeseed oils) with multifunctional alcohols (e.g., glycerol, pentaerythritol, neopentyl glycol, trimethylolpropane) to prepare biobased polyols has extensively been reported[54,61,62]. This reaction involves the ester groups of the oil. Similarly to transesterification, amidation of vegetable oils with amines (e.g., diethanolamine) can be employed to obtain fatty acid diethanol amides for producing polyurethanes. These compounds improve the polyols compatibility, thus leading to polyurethanes with enhanced physico-mechanical properties[62]. The synthesis of NOPs can also be carried out through the oxidation of double bonds. Different kinds of oxidation reactions are reported as, for example, ozonolysis or hydroformylation, which lead to the formation of an aldehyde that is further hydrogenated to a primary hydroxyl group, or oxidation of double bonds into peroxides and reduction into alcohols[63].

For example, Renuva™ polyols, produced by Dow Chemical, are obtained by hydroformylation[62]. Besides, the epoxidation reaction is the most common synthetic method proposed to introduce hydroxyl groups at the double bonds position of the aliphatic chain of the vegetable oils. With respect to the direct oxidation of vegetable oils, epoxidation allows for better control and thus it is a well-established and industrially relevant process. Indeed, one of the first commercial bio-polyols available on a large scale (BiOH® produced by Cargill) for the flexible polyurethane foam market was obtained by epoxidation of the C-C double bonds of oil, followed by methanolysis carried out at ambient pressure and mild temperature[62].

More recently, the thiol–ene reaction, although known since 1905, has been proposed as a new and promising alternative for producing biobased polyols, as this method is based on simple procedures, without any solvents, does not require high temperatures and gives high yields. For these reasons,

Table 1 | Main properties and remarks for polyols obtained from diverse biomass using several functionalization processes

Modification	Feedstock	Polyol properties	Remarks	Ref
None	Castor oil	nOH = 153 mgKOH/g Secondary OH	Low hydroxyl number, low reactivity, low functionality	57,223
	Lesquerella oil	nOH = 105 mgKOH/g Secondary OH		58
Transesterification	Soybean, palm, linseed, sunflower, rapeseed, castor, and neem oils	nOH = 300–500 mgKOH/g Both primary and secondary OH Double bonds in the chain	Good reactivity Limited thermal stability	39,55,61,62,67,116
Transamidation	Linseed, soybean, rapeseed, sunflower oils	high functionality (3.6–5.8) possible nOH = 380–635 mgKOH/g	Improved polyol compatibility	62,67,224
Ozonolysis	Soybean, canola, castor, and rapeseed oils Used cooking oils	nOH =220-300mgKOH/g Primary OH groups functionality below 3 Higher free fatty acid content than virgin oil	Fast curing rates Polyols without dangling chains for PU with high Tg	39,61,63,80,116,225
	Algae oil	High content of impurities with respect vegetable oils. nOH = 123mgKOH/g Low functionality (1.5)		79
Hydroformylation	Soybean, linseed, sunflower, and safflower oil	Primary OH groups nOH = 160–240 mgKOH/g	High curing ability and low gel time	39,46,61,79,116
	Algae oil	High content of impurities nOH = 147 mgKOH/g	High reactivity and the very fast reaction	79
Epoxidation	Jatropha, rapeseed, olive, sunflower, linseed, soybean, and cottonseed oils. Used cooking oils	nOH = 50–400 mgKOH/g (most common 100–200) Secondary OH Saturated aliphatic chain Higher free fatty acid content than virgin oil	Presence of dangling chains, not suitable for rigid applications Double bonds can promote UV curing for coatings	39,46,61,63,67,80,81,116
	Algae oil	High impurities content nOH up to 300mgKOH/g		45,73,79
	Cashew nut shell liquid	Reaction with epoxy of the Mannich base nOH =331 mgKOH/g	Polyols for spray and rigid foams	45,102
Thiol-ene	corn, soybean, sunflower and castor oils	Primary OH groups nOH = 165–500 mgKOH/g Functionality up to 5	Green, low-cost, high yield reaction. Double bond conversion beyond 90%	39,57,65,66,116,226
	Cashew nutshell liquid	nOH = 340–440 mgKOH/g	Polyols for coatings and rigid foams	100,103,104
Oxypropylation	Lignocellulosic biomass	nOH = 100–780 mgKOH/g	The reactivity of the OH groups of lignin was identical to that of propylene oxide homopolymer Used for rigid foams	94,96
	Cashew nut shell liquid (CNSL)	Propoxylation of the Mannich base obtained by using CNSL nOH = 410–530 mgKOH/g Functionality = 3–5	Polyols for spray and rigid foams	45
Liquefaction	Lignocellulosic biomass	nOH = 300–810 mgKOH/g; lower nOH (190 mgKOH/g) are possible by using high molar mass solvent. Recondensation of lignin is an issue	Generally used for rigid foams	45,46
Hydroxymethylation, esterification and demethylation	Lignin	Increase in the content of OH reactive groups (e.g., hydroxymethyl) or aromatic OH	Used for adhesives	46,227

it is a green and low-cost synthetic procedure and is becoming one of the most effective methods[60,63,64]. The synthesis of NOPs starting from corn, soybean, and castor oils by thiol-ene chemistry was proposed recently[57,60,65,66]: in this way, by functionalizing the double bonds of the oils with mercapto compounds, the resulting polyols contain a primary hydroxyl group at the end of the chain.

Obviously, the final characteristics of the NOPs developed vary depending on the functionalization process employed. The main properties and remarks for polyols obtained from diverse biomass using several functionalization processes are reported in Table 1.

For example, Prociak et al. [67] obtained polyols from rapeseed oil by epoxidation, transamidation, and transesterification methods. They showed that these NOPs have different reactivity during polyurethane foam production: the polyols obtained by transamidation and transesterification are much more catalytically active than those obtained by epoxidation, owing to the presence of amines that have catalytic action during the polyurethane production. These more reactive polyols can be used for polyurethane systems requiring fast reactivity (e.g., in spray foams); the use of these polyols leads to the enhancement of the thermal properties of the PU foams produced. On the contrary, less reactive polyols obtained by epoxidation can be used in the preparation of PU foams for thermal insulation because of their more regular cellular structure that enhances also the mechanical properties. An interesting comparison among different functionalization processes and the related polyol properties was reported also by Amri et al. [68], who showed that the NOPs obtained by ozonolysis followed by reduction are more reactive than those prepared by epoxidation and ring opening because the former have primary hydroxyl groups while the latter have secondary groups. However, while the functionality of the first polyols is limited to three hydroxyl groups per triglyceride, in the case of epoxidized polyols the functionality can be finely tuned, depending on the epoxy content that is influenced by the vegetable oil employed, and the amount of ring opening agent used. In the case of hydroformylation, polyols with primary hydroxyl groups and tunable functionality are obtained. Thiol-ene chemistry shows the same advantages as hydroformylation, although, in the presence of polyunsaturated fatty compounds, the oligomerization is favored with respect to the functionalization, so the choice of the vegetable oil becomes crucial[69] Many other examples of commercial bio-polyols obtained starting from vegetable oils using the functionalization processes reported above are described in several reviews[63,70–72].

Although there are several advantages to using polyols from vegetable oils (e.g., they are obtained from renewable resources), there are also some disadvantages. For instance, some of the synthetic procedures to prepare them require expensive catalysts, and this makes bio-polyols more expensive than traditional ones. Moreover, high viscosity, impurities and residual fatty acid content can limit their application in place of petrochemical-based polyols[73]. For these reasons, although there are already many oil-based polyols on the market, they are generally used in mixture with petrochemical polyols. It is also noteworthy to consider that the use of vegetable oils for producing biobased polyols is not always optimal and sustainable since they can be edible, and this creates a feed-food competition[74].

For this reason, more recently, several second-generation biomass feedstocks (i.e., sources that are not suitable for human consumption) have been reported for the production of biobased polyols.

Non-edible vegetable oils (NEVOs) represent an example of second-generation feedstocks. NEVOs can be used as industrial raw materials for chemical synthesis because they are low cost and can be produced worldwide, also in arid conditions and on marginal lands[75]. In general, the synthesis of polyols from NEVOs is almost similar to that from edible VOs, employing the methods reported before. Important examples of NEVOs are tung, jatropha, jojoba, linseed and castor oils; algae oils belong to NEVOs category too. For example, jatropha oil has a high content of double bonds, because it contains mainly oleic (43%) and linoleic (34%) acids, which is beneficial in terms of possible chemical modification to prepare chemicals and polymers[76].

Algae oil represents another source of sustainable raw materials for producing polyols; it can be obtained in good yield, because it grows fast and without the need for arable lands[77]. Currently, the main problem related to the exploitation of this kind of oil is its high cost, which is roughly twice with respect to other VOs, due to its limited oil fraction[73]. For this reason, new technological processes are being developed to make this oil cheaper and comparable to that of common plant-based oils[73] Another drawback of algae oil is the presence of organic contaminants (e.g., hydrophobic co-factors and pigments), which can interfere during the synthesis of polyols[78]. Compared to standard VOs, algae oil takes advantage of the higher content of unsaturated fatty acids, although this feature depends on the species[79]. The most common functionalization method used for algae oil is epoxidation followed by ring opening. In this way, polyols with hydroxyl values up to 300 mg KOH/g or over can be obtained, making them suitable for the substitution of the conventional fossil-based counterparts in the PU synthesis[45,73]. However, Petrovic et al.[79]. showed that the conversion of the epoxidation of algae oil was lower than for vegetable oils and required a higher catalyst concentration. In the same work, they also used ozonolysis, showing that low functionality (1.5) of the polyol obtained hinders its suitability for PU formulation. Conversely, if ozonolysis is combined with oxidation using sodium chlorite, azelaic acid can be prepared using palmitoleic acid extracted from algae oil; azelaic acid can then be reacted with ethylene glycol by polycondensation catalyzed with acid, thus obtaining a polyester polyol. Such polyol can then be used to prepare shape-memory flexible PU foams[78].

Another possible solution to overcome the competition with food sources is to employ used cooking oils (UCOs), also known as waste cooking oils (WCOs). Globally, very huge amount of UCOs are produced every year (more than 27 Mtons), so they are largely available. Moreover, since they are waste, their cost is significantly lower (i.e., 2–3 times) than that of virgin oils[80]. The use of UCOs to synthesize biocompounds (and in particular bio-polyols) is beneficial not only from the economic point of view but also from the environmental one because the need for virging raw materials is avoided and the closing of material loops is favored[81].

Three primary chemical reactions occurred in UCO after it has been used at high temperatures: hydrolysis, which rises the concentration of total polar molecules (i.e., glycerol and free fatty acids) and causes color darkening; oxidation, which changes the concentration of conjugated diene and triene; polymerization of the double bonds of the fatty acid chains, leading to the formation of dimers and oligomers of triglycerides[82]. Thus, in general, heating of UCO changes the molecular chains of the oil that undergo breaking, oxidation, and oligomerization; however, it has been shown that their main functional groups are kept so the chemical structure of UCO is suitable to be exploited in polyols synthesis[83]. A measure of the extent of degradation during frying can be obtained by quantification of iodine and acid values of UCOs[82]. It has been shown that the iodine index, that is a measure of the unsaturation degree, is similar between used and virgin castor oil, showing that used oil still possesses double bonds, which can be further exploited for the synthesis of polyols, through epoxidation or ozonolysis[80]. On the contrary, the acid value of the used oil, linked to the free fatty acids content, is higher than that of virgin oil[80,84]. Thus, in the case of transesterification, it is necessary to decrease the acid value of waste oil before carrying out the reaction, because the unwanted esterification of free fatty acids during the process leads to the hydrolysis of the oil and decreases the reaction yield[85]. This pre-treatment can be done by using activated carbon from bagasse or coconut husk or by chemical bleaching[86,87]. The transesterification of UCO is carried out by using the same reactants employed with virgin oils, like for example glycerin, ethylene, propylene and diethylene glycols; triethanolamine can also be used.

The most reactive agent is the amine[19], while the reactivity of the alcohols depends on the type of hydroxyl group. Alcohols with two primary hydroxyl groups are more reactive than alcohols with at least one secondary group, although the latter can also be used[88]. Indeed, different biopolyols can be produced by transesterification of UCO with glycerin and reacting this product with depolymerized polycarbonate, polyurethane, or polyethylene terephthalate waste. By blending these polyols with commercial ones at different ratio (namely, 20, 40, and 60%), PU foams can be produced and their properties are shown to be comparable to those of commercial materials. Similar results were obtained in another work[84] where refined, unrefined, and frying palm oils were used as raw materials to obtain three biobased polyols, which then were used to replace 20 wt.% of polyol in open-cell polyurethane foams. The properties of the resulting foams were almost the same regardless of the raw material used for polyol production. No difference between the polyol obtained from virgin and used oils is reported also for corn and soybean oils[83,89]; the only difference refers to the epoxidation yield that is slightly lower for the used oil.

Another sustainable raw material that can be exploited for the bio-polyols synthesis is lignocellulosic biomass (LCB), like agroindustrial waste (e.g., lignin from the pulp and paper mills process or wood residues) and the non-edibile part of crops[90]. Unfortunately, although the large availability and the low price of LCB, its industrial relevance for the chemical industries is very limited because of the complex chemical nature of this feedstock and the need for expensive transformation processes to obtain chemicals of interest, which makes the use of LCB not economically beneficial[57]. Indeed, while cellulose and hemicellulose contained in the LCB are already used in the synthesis of several chemicals, the exploitation of lignin, which is the only aromatic compound in the LCB, is particularly challenging because of its refractory nature[91]. Since lignin contains a lot of alcoholic and phenolic hydroxyl groups, it represents a potential source for preparing bio-polyols; however, since it is solid, first it must be transformed into a liquid compound. Currently, the two most common methods available for producing polyols from LCB are oxypropylation and liquefaction[57]. Although oxypropylation of lignin was first described in 1984[92], liquefaction of biomass is more convenient and safer, so it is more extensively reported in the literature[93]. Oxypropylation, that is generally carried out with propylene oxide, changes the reactivity of the OH groups of the lignin, since they are "shifted" to the end of the chains of the polyether part, while the OH content is not modified[94]. To try to make oxypropylation safer, some authors proposed the use of propylene carbonate instead of propylene oxide[95]. The results showed that, using such an agent, the oxypropylation of not only the phenolic OH groups (which are more reactive), but also of the aliphatic ones is almost complete in 24 h. In the oxypropylation, the nature of the lignin (from softwood, hardwood or non-wood) and the process, from which it is obtained (organosolv, kraft, soda) influences the reactivity of the lignin itself as well as the properties of the polyurethanes prepared by using these polyols. For example, lignin obtained from soda or organosolv process is more reactive in the oxypropylation than kraft lignin, because of the different molecular weight of the starting lignins and the position of the hydroxyl groups; however, polyurethanes obtained from kraft lignin have better properties than those obtained from soda lignin, but similar to those from organosolv lignin[45,96].

Lignin liquefaction is a process involving the degradation of lignin at high temperatures and pressures, with a catalyst, in presence of a solvent. In general, although the exact reaction mechanism is quite complicated because of the heterogeneous structure of the lignin itself[46], the depolymerization of the lignin takes place, generating oligomers and small molecular weight compounds. However, if the process is carried out for a very long time and/or at too high temperature, the recondensation of those fragments prevails on the depolymerization, thus increasing the molecular weight again. Hardwood lignin is more difficult to depolymerize than softwood type, though the latter undergoes recondensation reactions more easily than the former[97]. To prepare polyols, the solvents most commonly used are polyhydric alcohols, and, usually, a mixture of glycerin and polyethylene glycol. Obviously, the selection of the solvent and the biomass type used in the process affect the hydroxyl value of the final polyols, which, in turn, influences the kind of polyurethane that can be produced by using it. Polyols with hydroxyl values between 200 and 600 mgKOH/g with a molecular weight in the range 200–7000 Da, viscosity is up to 40 Pa*s, and acidity index less than 40 mg KOH/g are most commonly reported in lignin liquefaction synthesis[57,97]. Similar liquefaction processes have also been reported recently for other kinds of lignocellulosic biomasses like bark and wheat straw[98,99]. Bark has a lower viscosity than NOPs while wheat straw shows some biodegradability (16% after 1 year under soil conditions).

To increase the reactivity of lignin with isocyanates in the PU synthesis, several methods are proposed in the literature: hydroxymethylation, esterification and demethylation[46,91]. In hydroxymethylation, lignin is reacted with formaldehyde, in acidic or alkaline environment, to create hydroxymethyl groups that are more reactive than pristine hydroxyl groups. Also demethylation increases the content of aromatic OH groups, through the demethylation of a methoxyl group, which yields a catechol moiety. Esterification of the lignin hydroxyl groups is likewise useful because it increases the solubility in non-polar organic solvents, thus favoring the mixing with the other components of the PU formulation; besides, esterified lignin polyols show lower melting point and increased thermal stability.

Cashew nutshell liquid (CNSL) is another aromatic waste material that can be used to synthesize polyols. It is a waste obtained from the cashew nut tree, containing several phenolic compounds derivatives with both saturated and unsaturated hydrocarbon chains. One of the main component of CNSL is cardanol, obtained by high vacuum distillation of CNSL, which can be used to prepare polyols, in particular Mannich polyols[100,101]. These polyols are aromatic polyether polyols bearing amino groups in their structure, thus showing a high reactivity toward isocyanates, since it is well know that amines catalyse the reaction between isocyanate and polyol. Because of their high reactivity, Mannich polyols are generally suitable for spray foaming; however, if their reactivity is too high, they must be used in formulation with less reactive polyols, like biobased polyols[45]. Although Mannich polyols are commonly produced by the oxazolidine route[102], to synthesize them in a more sustainable way, Wang et al. [103] reported a new sulfur-based click reaction. They proposed the thiol-epoxy click reaction to overcome the limitation shown by the thiol-ene reaction in terms of number of hydroxyl groups in the final polyol, limited by the amount of C-C double bonds present: they obtained a polyol with an hydroxyl value of 440 mgKOH/g with respect to 340 mgKOH/g that can be obtained by the thiol-ene reaction of cardanol. However, the thiol-ene reaction can be exploited to prepare polyols less reactive than Mannich polyols, through the reaction of the double bond of the cardanol chains with 2-mercaptoethanol[104].

Finally, it is noteworthy to mention that aliphatic polyester polyols can represent another class of biobased polyols. Although they are already available on the market[39], their commercial exploitation is limited by the current high cost of bio-based carboxylic acids: their commercial development will only be possible if these costs are reduced[105]. Indeed, aliphatic polyester polyols are commonly obtained by reacting a dicarboxylic acid, like adipic, succinic, or sebacic acid (or such derivatives as esters or anhydrides) and diols (or polyols), like ethylene glycol, 1,4 butandiol or glycerin. Biobased succinic acid is obtained from fermentation and its cost compared to the petrochemical equivalent (obtained hydrogenation of maleic acid) was recognized as a big issue already in the past[106]. However, more recently, bio-based succinic acid (Biosuccinium™) has been commercialized by Roquette and DSM and its cost is expected to decrease; a similar trend is forecast for bio-based sebacic acid (Oleris®) and adipic acid, which are supplied on a commercial scale by Arkema and Genomatica, respectively[39]. It is worth mentioning that the polyesters used for elastomer manufacturing are adipic acid-based. For this reason, bio-adipic acid would be a drop-in product for the PU industry.

On the contrary, azelaic acid is already available in quite large amounts and used on an industrial scale to prepare commercial polyester polyols. They are produced by Croda Sipo, Emery, and, more recently, P2 science by ozonolysis of oleic acid or Matrica by using hydrogen peroxide as an oxidant[107]. Azelaic acid can also be sourced from second-generation feedstock, like algae oil[78]. The use of polyester polyol obtained from azelaic acid has been reported for thermoplastic polyurethane[105,108], polyurethane foams[109], and coatings[110].

Biobased isocyanates

As reported so far, a very large variety of biobased polyols can be used to synthesize very different polyurethanes (rigid or flexible foams, coatings, elastomers, etc.). Although the present review is focused on the development in the last years, the synthesis of biobased polyols has been known for a very long time. On the contrary, the synthesis of biobased isocyanates, the second essential component to prepare polyurethane, is a more recent topic. The most prominently used starting materials to obtain biobased isocyanates are fatty acids and dimer fatty acids, derived from vegetable oils. Other kinds of renewable isocyanates are based on algae oil, sugars, amino acids, furan, lignin, and cashew nutshell liquid[73,111–113].

In general, diisocyanates based on fatty acids were prepared through Curtius rearrangement[114,115], converting the fatty acid to a diacid and then to acyl azides that can be thermally decomposed to isocyanates[116] (Fig. 4). This synthetic procedure avoids the hazards of synthesizing conventional isocyanates, and involves amine (not only aliphatic and cycloaliphatic but also carcinogenic aromatic ones) and gaseous phosgene which is highly toxic. However, it should be underlined that the Curtius process uses highly toxic and explosive azides. Other methods to synthesize biobased isocyanates are Hoffman or Lossen rearrangement, which, however, lead only to aliphatic isocyanates[43]. Another synthetic pathway for fatty acids-based isocyanates involves the bromination at the allylic positions of the triglycerides and reaction with AgNCO[61]. A similar method involves the synthesis of iodine

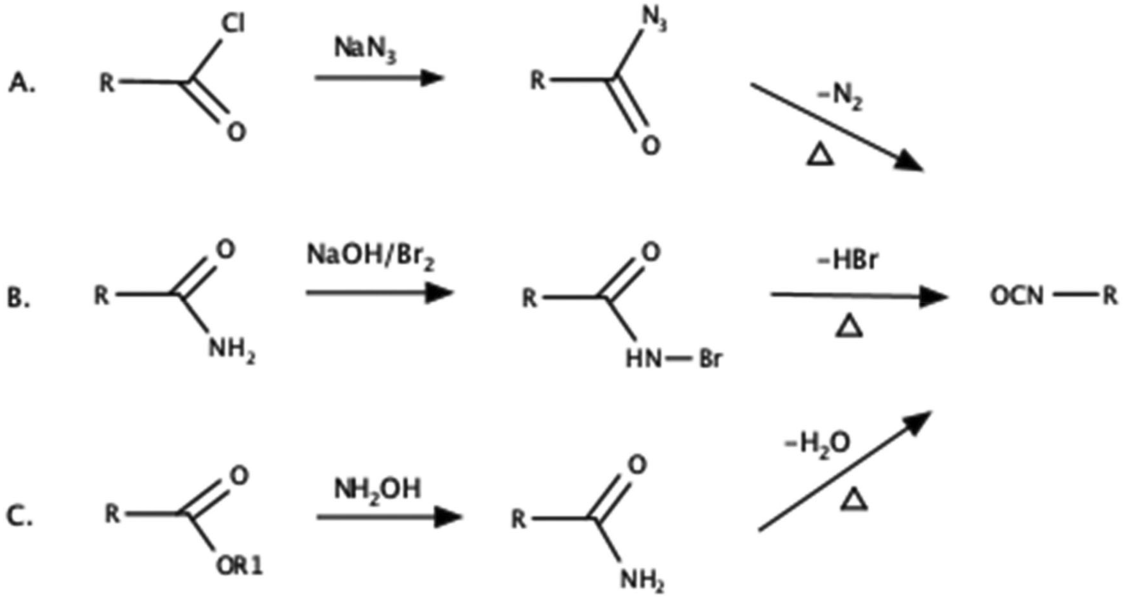


Fig. 4 | Synthesis of isocyanates by rearrangement. Synthesis of isocyanates by rearrangement: Curtius (**A**), Hoffman (**B**), Lossen (**C**). Reprinted from ref. 43, copyright 2023, Royal Society of Chemistry.

isocyanate adduct of soybean oil through the reaction of iodine isocyanate and soybean oil at room temperature. This strategy is simpler than the previous one, based on bromination, because it occurs in a single step; moreover, the isocyanate obtained is completely saturated, so it has a better oxidative stability[61]. The synthesis of algae-derived bio-isocyanates is quite similar to that used for fatty acids coming from oils: the main difference refers to the source of fatty acids only[113].

Sugars-based isocyanates are obtained starting from isosorbide, isomannide, and isoidide, using a two-step Curtius rearrangement of their diacid chloride derivatives, giving yields around 55%[117].

One amino acid used to prepare isocyanates is lysine; L-Lysine diisocyanates (LDIs) were synthesized by phosgenation of amine-terminated lysine ester by using a quite old method[118]. Some examples are lysine methyl ester diisocyanate (EELDI) and lysine triisocyanate[56]. Since LDIs are aliphatic in nature[43], their reactivity toward polyols is similar to that of hexamethylene diisocyanate (HDI)[119] but higher than that of isophorone diisocyanate (IPDI); obviously, they are less reactive than aromatic isocyanates, such as diphenylmethane diisocyanate (MDI) and toluene diisocyanate (TDI).

For this reason, and, in general, biobased diisocyanates are not reactive enough for application in foams (which are based on aromatic isocyanates), but they could be used for coatings and other urethane applications[54]. It is worth mentioning that recently Covestro developed the first bio-based process for producing aromatic aniline. The process produces bio-based aniline via two-stages: first, sugar is fermented by *Corynebacterium Glutamicum* to aminobenzoic acid, which is then catalytically decarboxylated to aniline[120]. By using this biobased aniline, aromatic isocyanates, such as MDI, can be produced in the future.

Alternatively, to produce PU foams by using biobased aliphatic isocyanates, specific formulations, with fast reaction rates, must be developed. In this context, very recently, Quienne et al. [121] reported specific formulation for PU foams, with a renewable carbon content ranging from 41 to 93%, based on a diol obtained via the dimerization of fatty acids, diglycerol as a cross-linker and biobased isocyanates (namely, fatty acid based Tolonate X FLO 100 and LDI). Water was used as the blowing agent. It is important to mention that one of the PU formulations based on LDI fully foamed at room temperature, achieving a final density of 78 kg/m^3, while the use of Tolonate X FLO 100 led to a limited expansion, achieving a final density of at least 147 kg/m^3 and the cellular structure is only partly formed. Similarly, Das et al. [122] showed that the complete conversion of Tolonate isocyanate, reacted with a polyol obtained by transesterification of castor oil with pentaerythritol, occurred after 12 h at 90 °C. In another work[123], flexible PU foams were obtained by reacting a prepolymer based on Tolonate X FLO 100 and polypropylene glycol (NCO content of about 30%) with and epoxidized soybean-based polyol. Quite fast reaction rates were obtained: cream time was almost similar, while the free rise time was slightly longer compared to petrochemical flexible foams; however, the free rise time was always below 2 min. These fast reaction rates can partly be due to the presence of triethylamine, deriving from the synthesis of biobased polyol, since it is also a well-known catalyst in the synthesis of PU foams. Also in the case of pentamethylene diisocyanate, which is a sugar-based isocyanate, the synthesis of the foams required the heating to 80 °C of the biobased polyol mixture[124].

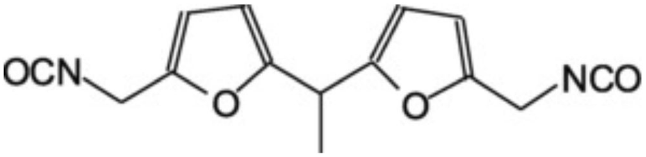
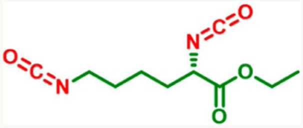
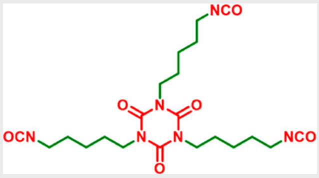
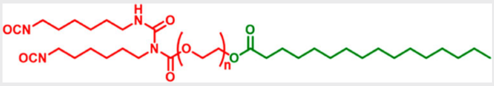


Fig. 5 | Structural formula of difurfuryl diisocyanate. Reprinted from[127] under CC-BY-NC License.

Finally, also furan-based isocyanates must be mentioned. It has been shown that furan-based chemicals, such as 2,5-furandicarboxylic acid (FDCA), can be utilized as a biobased replacement of fossil-based aromatic compounds, due to their similar aromatic nature. For example, biobased FDCA can be used in place of like terephthalic acid in polyethylene terephthalate (PET) production, thus leading to poly(2,5-furan dicarboxylic acid)[125], having similar properties. In another work, it has been shown that the furan ring can be converted into diisocyanate, serving as the hard segment of a thermoplastic polyurethane[126]. It has been reported that ethylidene bis (2,5-furandiylmethylene) diisocyanate (EDFI) (Fig. 5), or difurfuryl diisocyanates in general are structurally similar to diphenylmethane diisocyanate (MDI), hence they can be good substitutes for it[127].

Recently, green synthetic pathways to synthesize furan-based isocyanates have been proposed in the literature[125]. Although furan 2,5-diisocyanate is a promising monomer as a renewable diisocyanate since it is quite reactive toward polyols, its industrial use seems to be difficult because of its low storage stability owing to its quite high reactivity with moisture and oxygen[128]. To overcome this limitation, the use of the blocked-isocyanate

Table 2 | Chemical structures, tradenames and properties of the commercial partially bio-based isocyanates

Structure	Chemical/commercial name	Biomass %	NCO %
	L-lysine ethyl ester diisocyanate (LDI)	75	34
	Pentamethylene diisocyanate (PDI) isocyanurate DESMODUR eco N 7300	70	21.5
	Pentamethylene diisocyanate (PDI) STABiO D-370N D-376N	70 67	25 24
	Dimer acid diisocyanate (DDI) Tolonate X FLO 100 DDI 1410	25 N.A.	11-13 13-14

Green-colored moieties come from bio-based molecules, and red-colored moiety atoms come from petro-sourced molecules. N.A. = data not available. Adapted from[119], under CC-BY-NC-ND License.

strategy could be implemented (like in coatings and adhesives applications), though this requires the use of high temperature or a special catalyst during the PU synthesis, to remove the blocking group[128].

Although the scientific literature on biobased isocyanate is quite recent, several aliphatic diisocyanates from dimerized fatty acids have been commercially available for several years (Table 2). These isocyanates are dimer acid diisocyanate (DDI) and are commercially supplied by Henkel Corporation and General Mills Co[56,61,116,119]. Other commercial examples of DDI are the Tolonate X FLO 100 (produced by Perstorp, Sweden, in different grades) with a 25% of biobased content, palm oil-based isocyanate by Vencorex (subsidiary of PTT Global Chemical, Thailand) or 2-heptyl-3,4-bis(9-isocyanatononyl)-1-pentylcyclohexane, sold as DDI 1410, produced by Cognis-BASF (Germany)[56,116,119]. Pentamethylene diisocyanate (PDI), a sugar-based diisocyanate, synthesized by reaction of glucose with ammonia, and then further reacted with phosgene and oligomerized[119], is marketed, in its isocyanurate form, by Covestro Company, under trade name of Desmodur eco N7300 (2-ethyl-1-hexanol-blocked 1,5-Pentamethylene-diisocyanate homopolymer) with 68% biobased content[56,119]. Mitsui Chemicals produces similar compounds, namely STABiO™ D-370N and D-376N, which are still based on PDI, with a biomass content beyond 60% and a high NCO content (up to 25%)[43,56]. Although also L-lysine ethyl ester diisocyanate (LDI) is reported to be commercially available[56,119] with 75% biobased content[56], no tradename has been found.

Although several bio-based isocyanates are commercially available, their cost is generally quite high, making them more suitable for PUs dedicated to e.g., biomedical purposes, like drug delivery systems, hydrogels, and implant materials, among others[39,44]. Indeed, the replacement of fossil-based isocyanates with biobased ones is not so trivial, although it can be feasible by using different strategies[43]. The use of bio-based isocyanates only is rarely applied while the use of a mixture of bio- and fossil-isocyanates is more commonly proposed[129]. The first solution has obviously an advantage in terms of environmental performance, while the use of the mixture allows for decreasing the cost.

In addition to bio-based isocyanates, a more recent strategy for synthesizing more sustainable PUs that avoid the hazards associated with the production and use of fossil-based isocyanates is the production of non-isocyanate PUs (NIPUs). For example, polyhydroxyurethanes are gathering more and more attractiveness, as they can be produced from carbon dioxide and bio-based chemical products. There are many, recent, and interesting reviews on NIPUs[29,35–39,45,62,116,130] Although the several synthetic pathways used to obtain NIPUs are promising, their utilization is still limited, because of the unfavorable conditions required for their synthesis (i.e., high temperatures and very long reaction times), which significantly limit their industrial exploitation. It is for this reason, and because the subject is so vast, that the present review will not focus on NIPUs.

Life cycle assessment of bio-sourced polyols and isocyanates

Papers related to biobased monomers (polyols or isocyanates) often claim that “these materials are eco-friendlier and more sustainable than petroleum-based alternatives” without giving any evidence. In a scientific context, Life Cycle Assessment (LCA) shall be used to provide a quantification in terms of environmental impacts and benefits when fossil-based monomers (in particular polyols and isocyanates) are substituted with their biobased counterparts. A very comprehensive review on this subject was recently published by Silva et al. [131]. The main characteristics of the LCA studies of the publications analyzed in this review are reported in Table 3.

One of the first works related to this topic studied the environmental benefits of polyols obtained from vegetable oils (castor and soybean oils) for the synthesis of PU flexible foams by considering a cradle-to-gate approach[132]; the polyols are made using Dow’s RENUVA™ Renewable Resource Technology. This work showed that soy or castor oil-based polyols would use 33–64% less fossil resources when they are used in place of the fossil-based polyols and generate up to 46% less greenhouse gas (GHG) emissions. However, the impact on gas emissions and water use is highly dependent on the farming model chosen. Conversely, in another work dealing with sugar-based polyols, obtained by copolymerization of succinic acid, 2,5-furandicarboxylic acid, 1,3-propanediol, and glycerin, no significant effect of the farming model on the environmental performance was revealed by a sensitivity analysis. Also for these sugar-based polyols, great enhancement of the environmental performance was reported when they are used in place of fossil-based counterpart: GHG emissions were decreased between 70 and 80% and Not Renewable Energy Use (NREU) between 36 and 60%[133]. Similar results were obtained through the life cycle analysis by using a cradle-to-gate approach, of sugar-derived diol prepared by bio-based hydroxymethylfurfural and pentaerythritol: its production is characterized by greatly smaller GHG emissions, compared not only to the petro-based equivalent but also to the biobased 1,3-propanediol[134]. In another study[109], a PU formulation obtained by using biopolyols based on azelaic acid and lignin showed reductions in all the impact categories when compared to

Table 3 | Main characteristics of the LCA studies of the reviewed publications

Type of feedstock	PU type	System boundary	Functional unit	Main results	Ref.
castor and soybean oils	Flexible Foam	cradle-to-gate	1 kg of unblown polymer solution	33% to 64% reduction of the fossil resources; 13% (i.e., sequestration) to 46% reduction of GHG	132
2,5-furandicarboxylic acid (FDCA) from sugar beet	Coating	cradle-to-gate	1 kg of 100% biobased polyester binder	GHG emissions were decreased between 70 and 80%; NREU between 36 and 60%.	133
5-hydroxymethylfurfural (HMF) from sugar beet	Coating	cradle-to-gate	1 kg of HMF-based diol	GHG emission reduced (up to 76%) than biobased and fossil based 1,3-propanediol, respectively.	134
Lignin, azelaic acid	Rigid foam	cradle-to-gate	amount of foam needed to achieve 1 $m^2 \cdot K/W$ of thermal resistance	PU formulation containing azelaic-acid or lignin derived polyol show reductions of impacts in all the of the impact categories (GHG emission, eutrophication, ODP, ADP) when compared to their fossil counterpart	109
Rapeseed oil	Rigid foam Spray coating	cradle-to-gate	1 kg of rapeseed oil-based polyol	GHG emissions is reduced up to 75%, NREU is reduced up to 70% with respect to fossil-based polyols. In certain categories (land use, marine eutrophication, and ecotoxicity), the biobased polyols show higher impacts than the fossil-based ones	135
Soybean oil	No PU synthesis	cradle-to-gate	1 kg of biobased polyol	GWP is lower for reusable catalysts, working at lower synthesis temperature	136
Crude glycerol (CG), by-products of biodiesel production, from rapeseed, soybean, palm and used cooking oil (UCO)	Rigid foam	cradle-to-grave (End of life: landfill and/or polyol recovery)	1 kg of rigid foam	Soybean-derived CG has higher GWP. High impacts are generally observed for rapeseed-derived CG. UCO-derived CG has -20% GWP than crude-oil derived glycerol. Marine eutrophication is lower than crude-oil derived glycerol only for UCO-derived CG	137
Soybean oil	No PU synthesis	cradle-to-gate	1 kg of poly(propylene/ethylene oxides) glycol	Soybean-based polyol has higher impact in GWP (+ 144%), primary energy demand (+ 46%) and photochemical oxidation (+ 160%) than fossil counterpart	138

their petrochemical counterpart. Overall results also demonstrated that the introduction of lignin is not always preferable to the use of only azelaic acid-derived polyols.

By comparing different synthetic pathways for producing the same rapeseed-based polyols, e.g., by transesterification with triethanolamine or by amidization with diethanolamine, it has been shown that both biobased polyols have similar total environmental impacts, while there is a clear decrease of GHG emissions, water consumption and NREU with respect to the fossil-based polyols[135]. However, in certain midpoint categories (land use, marine eutrophication, and ecotoxicity), the biobased polyols show higher impacts than the fossil-based counterparts[135]. The results of comparing the same synthetic pathway for polyol production (i.e., epoxide ring opening of soybean oil) but using 4 different catalysts (namely, coated Fe/Fe_3O_4 nanoparticles, H_2SO_4, Nafion SAC13, and Amberlyst-15) demonstrated that the global warming potential is lower for catalytic systems that work at lower synthesis temperature and utilize low solvent amounts; however, the differences among the four different catalysts were not so relevant[136].

Nevertheless, there are some scenarios where the biobased polyols have worse performance than the fossil-based counterparts. For example, when the land use is changed from forest plantation to areas for cultivation, the higher CO_2 emissions associated with this new scenario are responsible for the higher global warming potential (GWP) related to soybean based polyols with respect to the petrochemical one[137]; in some scenarios, also a worsening of the photochemical oxidation index is reported[138]. Similar results were obtained also by Fridrihsone et al. [139] for polyols obtained by epoxidation and ring opening of tall oil: the main environmental impacts are related to the production of the oil, but also the alcohols used in the ring opening reaction must be considered in environmental terms. They also showed that the catalyst and the energy used in the synthesis are not relevant for this analysis. Using an alcohol obtained as by-product, e.g., crude glycerol which is a by-product of biodiesel production, is not always better from the environmental point of view than using the equivalent based on crude oil since it depends on the vegetable oil employed to produce biodiesel[137].

Therefore, to enhance the environmental profile of biobased polyols, in particular the carbon capture (CC) impact, the most important point to consider is the production of the vegetable oils; this feature is relevant for all kind of crops, but it is extremely important for soybean one[131]. While this is true for virgin oils, when UCO is used as an oil source, the most significant parameter to consider is the transport from the production to processing site[140]. In general, polyols derived from UCOs have a better environmental profile than virgin oils for all impact categories, although some impacts are not so different (e.g. fossil resource scarcity impact differs less than 1%)[137].

Dealing with the isocyanate component, several studies showed that diphenylmethane diisocyanate (MDI) is the main hotspot for all impact categories considered (e.g., GWP, ozone formation, mineral and fossil resource scarcity, acidification) except marine eutrophication[137]. Similarly, Manzardo et al. [109], Silva et al. [131] and Cardarelli et al. [141] identified the MDI as one of the major sources of impacts in the climate change for rigid PU foams. This is related to the production of aniline or nitric acid and toluene, which are the intermediates to produce MDI and TDI, respectively. Therefore, to improve the environmental performance of rigid PU foams production, alternatives to TDI or MDI must be used. There are some commercial products that can meet this requirement. Indeed, it has been reported that Desmodur® eco N 7300 (biobased aliphatic polyisocyanate, PDI-trimer) has a reduced carbon footprint (by 30%) compared to fossil-based products[43]. A TDI based on renewable raw materials is supplied by Covestro[142], which claims a significant decrease of the carbon dioxide emissions associated with it, although there are no public data available to demonstrate this statement[131]. BASF sells Lupranat ZERO, a polymeric MDI obtained from renewable raw materials, which is stated to be GHG neutral[56]. In any case, further research on sustainable bio-based isocyanates is strictly needed.

Vitrimeric polyurethanes

Chemical resistance, thermal stability, and mechanical strength are among the most important characteristics of thermosetting PUs: these features can be ascribed to both the static chemical crosslinking structure and the quite high crosslinking density of the resulting network. At variance, these latter are responsible for the difficulties in reprocessing, degrading (under controlled conditions), and recycling PUs, leading to important waste generation and possible severe environmental pollution at their end-of-life. One of the strategies that have recently been proposed to fix these issues is the use of vitrimerization reactions during the synthesis of polyurethanes[143–145]: indeed, the vitrimer chemistry approach is capable of ensuring reprocessability and recyclability to PUs, maintaining, at the same time, an overall thermal, mechanical and chemical behavior similar to that of conventional thermosetting PUs. Besides, as vitrimer chemistry is based on the design of polymer structures bearing dynamic exchangeable bonds (and, therefore, based on covalent adaptable networks), vitrimerized polyurethanes may possess weldability characteristics, self-healing and shape memory features, as well as adhesion and tunable degradability. In other words, below a certain temperature (responsible for the activation/breakage of the dynamic exchangeable covalent bonds), they behave as thermosetting materials, though they can be reprocessed and recycled beyond this temperature.

Thanks to these peculiarities, the vitrimerization concept has successfully been applied to different polymer matrices, such as polyesters, epoxy resins, polyimines, and polylactides, among others[146–152] Further, the world of PUs has experienced several types of vitrimerization reactions, comprising boronic ester exchange, carboxylate transesterification, disulfide exchange, imine exchange, and urea bond exchange: all these reactions will be described in the following, summarizing the most recent outcomes.

Vitrimeric PUs based on boronic ester (B-O) exchange reactions

The condensation of boronic acid with hydroxyl groups allows for obtaining reversible boronic ester covalent bonds. In fact, these latter can be (i) hydrolyzed with H_2O and subsequently re-esterified, (ii) reacted with a diol, or (iii) subjected to metathesis reactions involving two boronic ester groups (Fig. 6). The high energy of B-O bonds provides the so-vitrimerized polymer with higher thermal stability; at the same time, thanks to the dynamic reversibility of boronic ester bonds under not severe conditions, the material can be easily reprocessed/recycled and may also exhibit self-mending features[153–155].

Looking at the recent literature on this topic, Zhang and co-workers[156] assessed the feasibility of the use of reversible B-O bonds for the design of vitrimerized PUs with enhanced hydrolytic resistance and thermal stability as compared to those obtained through conventional boronic esters, thanks to the existence of N → B internal coordination. Besides, the proposed materials turned out to be recyclable through a simple hot pressing carried out in mild conditions (i.e., applying a pressure of 1 MPa, for 30 min at 150°C), without affecting both Tg and the overall mechanical behavior. Finally, it was possible to perform a recycling process in the liquid phase, by treating the vitrimerized PUs with an excess of either 4-(hydroxymethyl) phenylboronic acid or triethanolamine.

Zhao and co-workers[157] exploited the B-N coordination for synthesizing a six-membered B-O structure showing a changeable ring strain, enhanced thermal and hydrolytic stability, and recyclability. All these findings were ascribed to the peculiar characteristics of the obtained boronic ester molecule, i.e., its low strain at ambient conditions and high strain (of the ten-membered ring, to which the six-membered shifts upon heating during the dissociation of the heat-responsive coordination bonds) at high temperature. This molecule was employed for designing highly mechanically performing, stable, and recyclable (below 130 °C) vitrimeric polyurethane adhesives through its reaction with hexamethylene diisocyanate trimer.

Recently, Ren and co-workers[158] succeeded in synthesizing a series of castor oil-derived vitrimeric PUs containing different amounts of dynamic covalent B-O crosslinks (using 2,2′-(1,4-phenylene)-bis[4-(4-

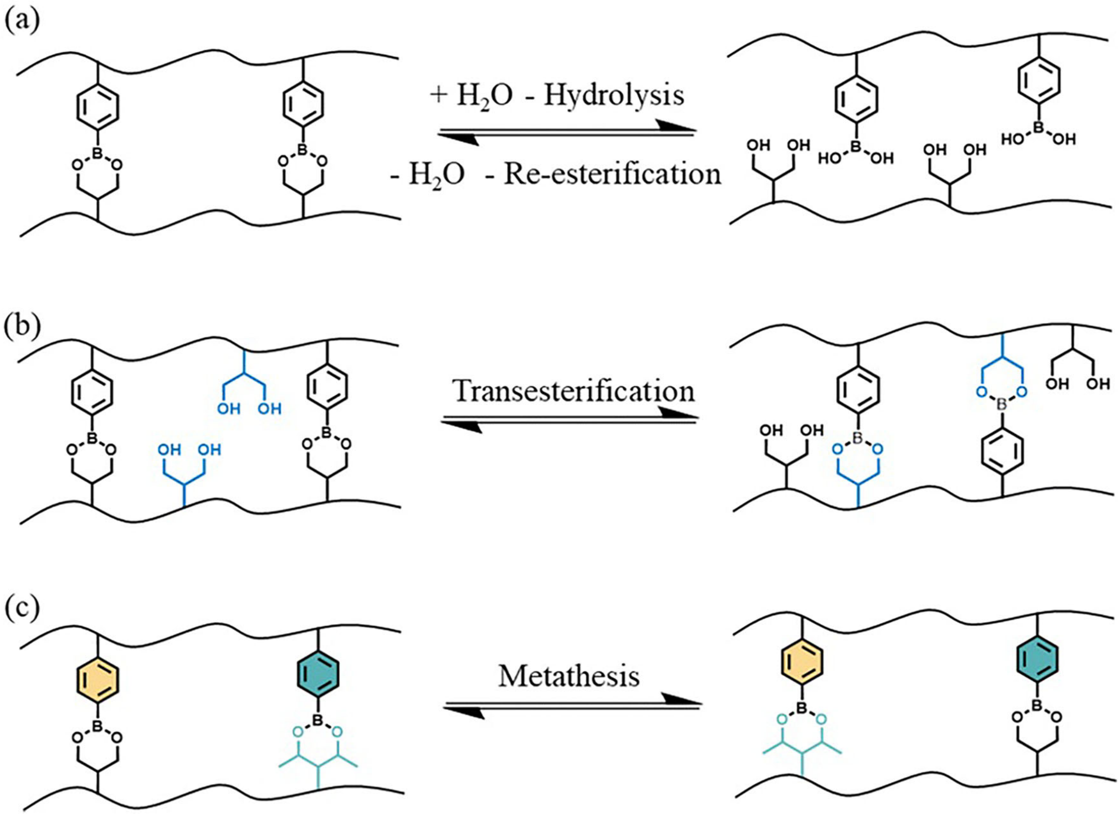


Fig. 6 | Three possible exchange mechanisms of boronic esters. Three possible exchange mechanisms of boronic esters: **a** hydrolysis/re-esterification, **b** transesterification, and **c** metathesis. Black lines represent polymer chains of the crosslinked network. Reprinted from ref. 253 under CC-BY License.

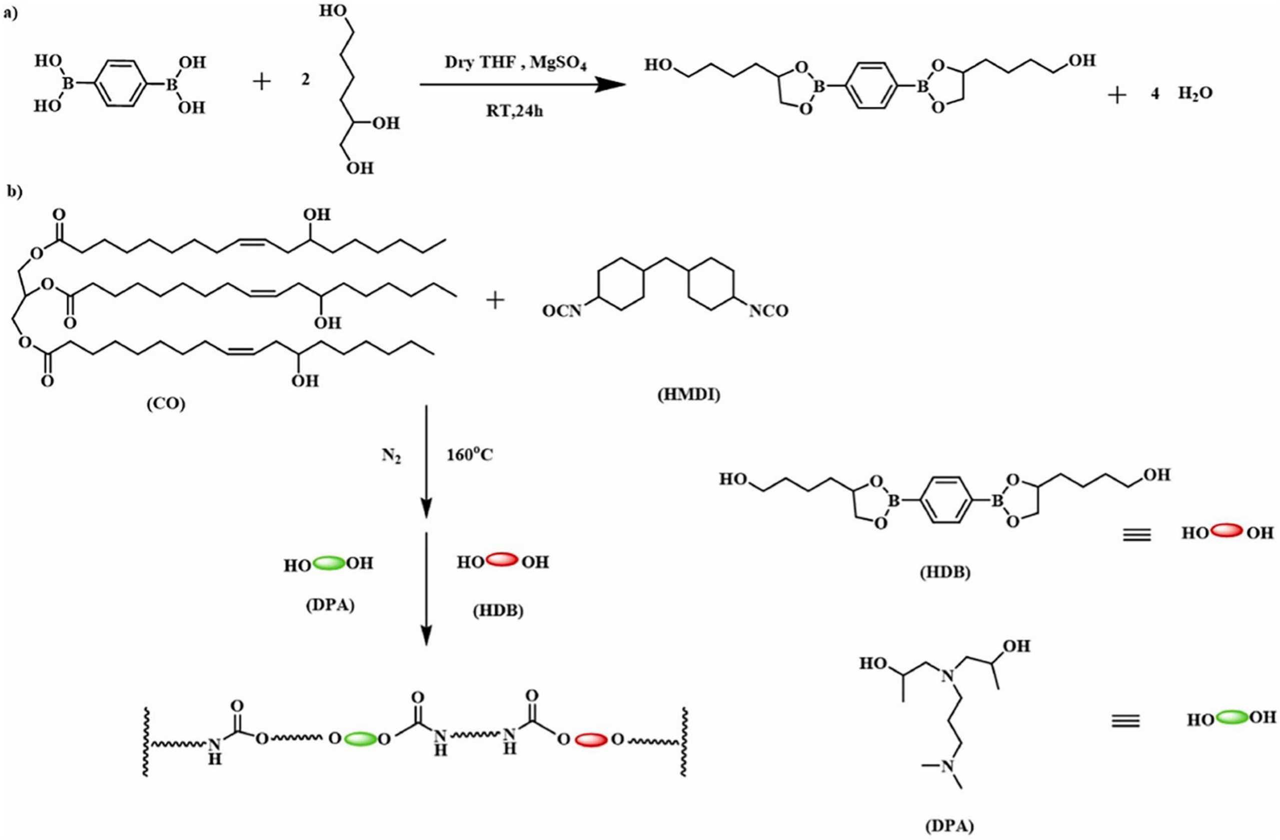


Fig. 7 | Castor oil-derived vitrimeric PUs. a Synthesis of 2,2′-(1,4-phenylene)-bis[4-(4-hydroxybutyl)-1,3,2-dioxaborolane] (HDB); **b** preparation of castor oil (CO)-derived vitrimeric PUs using HDB and N-(3-dimethylaminopropyl)-N,N-diisopropanolamine (DPA) as chain extenders. THF tetrahydrofurane, HMDI hexamethylene diisocyanate, RT room temperature. Reprinted with permission from ref. 158, copyright 2023, Elsevier.

hydroxybutyl)-1,3,2-dioxaborolane] as chain extender to establish reversible B-O groups) and B-N coordination (promoted by the introduction of nitrogen donors provided by N-(3-dimethylaminopropyl)-N,N-diisopropanolamine, employed as chain extender), using a catalyst- and solvent-free approach (Fig. 7). Thanks to the occurred reversible supramolecular interactions of B-N coordination bonds and hydrogen bonds, the so-obtained polymers exhibited enhanced mechanical behavior (with increased tensile strength and Young's modulus by about 89 and 99%, respectively, compared to the non-vitrimeric control polymer), self-healing capability, and easy reprocessability (through compression molding carried out at 120 °C, applying 10 MPa pressure for 10 min).

Pursuing this research, Pan et al. [159] synthesized vitrimeric castor oil-based poly(thiourethane-urethane)s taking advantage of the reaction of castor oil with 2,2′-(1,4-phenylene)-bis[4-mercaptan-1,3,2-dioxaborolane] and with 4,4′-diphenylmethane diisocyanate. The resulting vitrimers exhibited very high thermal stability (with initial degradation temperatures beyond 312 °C), thanks to the aromatic rings present in the polyurethane structure. Besides, the synthesized networks showed interesting self-healing (with healing efficiencies up to 100%, depending on the selected healing temperature and time), welding, and shape memory features; in addition, the dynamic B-O bonds accounted for an easy reprocessability in mild conditions (i.e., at 140° C, under 6 MPa for 1 h).

Zeng and co-workers[160] exploited a one-pot condensation process for preparing hydroxy-terminated polybutadiene-based vitrimeric polyurethanes bearing dual reversible covalent bonds (i.e., boronic ester and disulfide bonds). More specifically, hydroxy-terminated polybutadiene/bis(4-hydroxyphenyl) disulfide was condensed with diphenylmethane diisocyanate. Meanwhile, the unsaturations present in the polybutadiene chain were reacted with 2,2'-(1,4-phenylene)-bis[4-mercaptan-1,3,2-dioxaborolane], leading to the formation of the final covalent adaptive network. The high tensile strength and elongation at break exhibited by the latter were ascribed to the interactions taking place between the hard segments of the vitrimeric network (provided by 2,2′-(1,4-phenylene)-bis [4-methyl-1,3,2-dioxaborolane], diphenylmethane diisocyanate, and bis(4-hydroxyphenyl) disulfide groups) and the soft polybutadiene counterparts. In particular, at the highest crosslinking density (equal to 16.4×10^{-4} mol/cm^3), corresponding to 20 wt.% of 2,2′-(1,4-phenylene)-bis[4-methyl-1,3,2-dioxaborolane], a tensile strength of about 7 MPa was attained. Further, the vitrimeric PUs showed self-healing and reprocessing capabilities.

Vitrimeric PUs based on transesterification reactions

Transesterification reactions, proposed by Montarnal and co-workers in 2011[161], were the first to be employed (and the most often used) for the synthesis of epoxy-carboxylic acid and epoxy-anhydride vitrimeric networks, exploiting the dynamic exchange reactions occurring between ester and alcohol moieties at temperatures as high as 200 °C, in the presence of zinc acetate as catalyst. The transesterification method was also applied to design vitrimeric PUs, as demonstrated by Lian and co-workers[162], who synthesized a polyurethane-modified epoxy vitrimer through a two-step process involving: (i) the synthesis of a polyurethane prepolymer (employing the reaction of poly(ethylene glycol) with isophorone diisocyanate) and (ii) its incorporation into the Bisphenol A epoxy resin-based vitrimer and subsequent curing with tetrahydrophthalic anhydride. The presence of amino ester groups accounted for an easy transesterification reaction to occur (its activation energy was as low as about 34 kJ/mol, vs. 88 kJ/mol for the pristine epoxy vitrimer, i.e., not incorporating PU), for the possibility of reprocessing the material up to five times, and for its self-healing characteristics, hence significantly prolonging the material's service life. Finally, the toughness of the vitrimer was enhanced without any detrimental effect on its mechanical strength.

Transcarbamoylation (TC), i.e., the interchange reaction between carbamate/urethane functions and hydroxyls (similar to transesterification), can be exploited to obtain vitrimeric PUs. However, despite strong similarities with transesterification, TC is more difficult to perform than transesterification since it generally requires higher temperatures (typically above 120 °C) even in a catalyzed process (it is catalyzed by the same type of molecules used for transesterification), and thus it has been less studied despite strong potential in PUs chemistry. Vitrimers based on TC exchange reactions have been recently reviewed[163].

Denissen et al. [164] proposed transamidation reactions as an alternative to the use of the transesterification exchange reactions in vitrimers, because the amide group is thermodynamically more favored as compared to the ester group. To overcome the need for air- and moisture-sensitive catalysts, which are also incompatible with many other functional groups, they explored vinylogous amides. Vinylogous amides and the corresponding vinylogous urethanes can undertake associative transamination reactions at high temperatures (beyond 100–120 °C), even in the absence of a catalyst. Since many of the catalysts proposed for transesterification are tin-based and because of the known toxicity of tin compounds, the absence of a catalyst can be a great advantage. They obtained PUs that are insoluble, exhibit a T_g above 80 °C, show very short relaxation times at high temperatures, and have excellent mechanical properties. They also demonstrate that these poly(vinylogous urethane) networks can tolerate repeated recycling processes (through grinding and subsequent remolding), with a limited impact on the overall mechanical behavior.

Vitrimeric PUs based on imine bond exchange reactions

Reacting primary imine with aldehyde moieties allows for the formation of imine groups, which can be considered weak reversible covalent bonds. Indeed, imine groups are easily hydrolyzable in the presence of H_2O[165,166], and can undergo transamination reactions with another amine group, exploiting an associative pathway[167]. In addition, this latter can be employed for making the reaction between two imine groups, hence promoting reversible exchange reactions[168,169].

Specifically referring to the synthesis of vitrimeric PUs bearing imine bonds, there exists a boundary condition that must be fulfilled: in fact, the reactants should contain aldehyde, primary amine, and hydroxyl functionalities. This is the reason that justifies the use of vanillin and castor oil as respectively main and renewable feedstock for imine-based vitrimers.

Hu et al. [170] exploited the presence of imine bonds for designing a vitrimeric PU exhibiting interesting self-mending features. In particular, an NCO-terminated polyurethane prepolymer was obtained by reacting poly(tetramethylene ether glycol) with diphenylmethane diisocyanate in the presence of dibutyltin dilaurate as a catalyst; then, an imine-diol (synthesized on purpose) was added dropwise to the prepolymer solution heating the system at 60 °C for 4 h. This way it was possible to prepare vitrimeric PUs with different contents of hard segments (between 42 and 68%) and of imine bonds (from 1.05 to 2.40 mmol/g). The resulting PUs showed high tensile strength (up to 40 MPa), toughness (up to 166.1 MJ/m^3), and ductility (the elongation at the break achieved 880%). Besides, the reversible dynamic character of the imine bonds accounted for interesting self-healing properties, with a full recovery of the mechanical behavior after a thermal treatment performed at 2 h at 80 °C. This finding was attributed to the continuous relaxation phenomena occurring in the hard domains of the vitrimeric PUs, triggered by the applied thermal treatments, during the activation of the imine bond exchange reactions.

Sun and co-workers[52] reacted *m*-xylylenediamine with vanillin, hence obtaining a vanillin diol bearing imine groups. The latter was then reacted with castor oil and isocyanates, to prepare a bio-based vitrimeric PU (Fig. 8). It is worth noticing that the so-obtained vitrimeric PUs maintained a high ductility even after three compression molding cycles (their initial elongation at break was as high as 86% and slightly decreased to 78% after the thermal cycles). Besides, 60% of their initial mechanical strength was preserved after a healing treatment performed at 160 °C for 30 min. However, the vitrimeric materials exhibited an overall poor mechanical behavior, due to the high flexibility provided by the castor oil segments.

This issue was fixed by Xie and co-workers[171], who proposed the use of a vanillin-derived Schiff base bearing multiple aromatic rings, hence allowing for the proper tuning of the stiffness of castor oil-derived vitrimeric PUs (Fig. 9). Compared to the non-vitrimeric counterpart, raising the vanillin-derived Schiff base loading in the PU formulation accounted for a significant increase in tensile strength and Young's modulus (respectively by about 347 and 72%, in the presence of 55 wt.% of vanillin-derived Schiff base). Further, the Tg value shifted from −26.7 to +82.7 °C. Finally, the

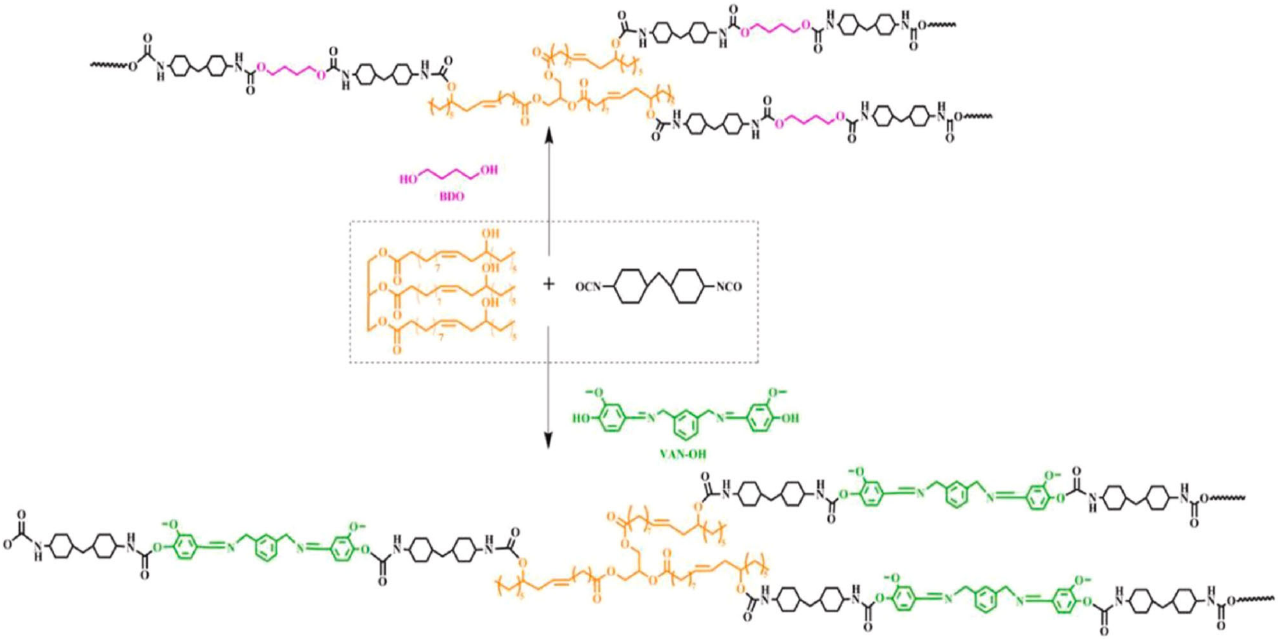


Fig. 8 | Scheme of the synthetic route for the obtainment of bio-based vitrimeric PUs based on imine bond exchange reactions. Reprinted with permission from[52], copyright 2021, Elsevier.

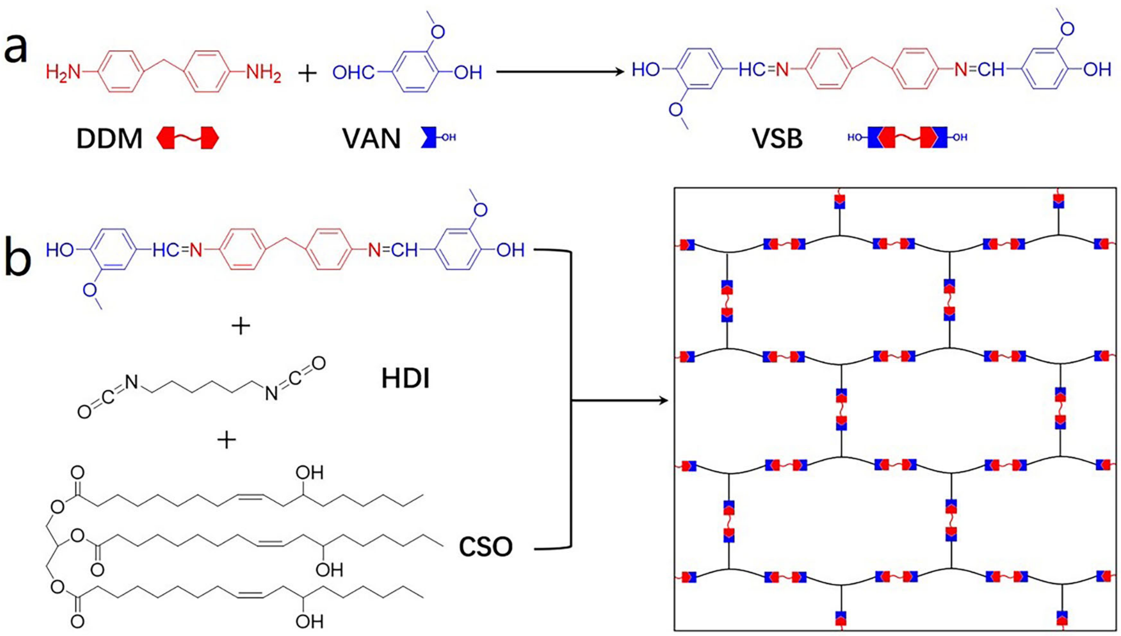


Fig. 9 | Castor oil-derived vitrimeric PUs. Preparation of vanillin-derived Schiff base (**a**) and of the castor oil-based vitrimeric polyurethane (**b**). DDM= 4,4′-diaminodiphenylmethane; VAN vanillin, VSB vanillin-derived Schiff base, CSO castor oil, HDI hexamethylene diisocyanate. Reprinted with permission from ref. 171, copyright 2021, Elsevier.

synthesized vitrimers exhibited interesting reprocessability, malleability, and recyclability features.

Vitrimeric PUs based on urea bond exchange

The main limitation concerning the use of reversible exchange reactions involving covalent adaptive networks in vitrimeric PUs relies on the need to perform these reactions at quite elevated temperatures and usually in the presence of a suitable catalyst. This issue can be fixed by exploiting a different vitrimeric chemical approach that takes advantage of the utilization of urea bond exchange. This strategy was first demonstrated by Ying and Chen[172], who designed hydrolyzable polyureas bearing dynamic hindered 1-tert-butyl-1-ethylurea bonds that are capable of reversibly dissociating, giving rise to the formation of bulky amines and isocyanates. Further, the possibility of hydrolyzing the formed isocyanates with water can promote an easy degradation of the polyureas. These findings can be attributed specifically to the presence of alkyl groups linked to N atoms, which can reversibly dissociate into bulky amine and isocyanate groups.

Zhang and co-workers[173] succeeded in synthesizing vitrimeric polyurethane-urea elastomers embedding N,N′-diaryl urea with an electron-donating effect. To this aim, poly(oxytetramethylene) glycol was first reacted with 4,4′-diphenylmethane diisocyanate, leading to the formation of a prepolymer that, in turn, was reacted with 3,5-dimethylthio-2,4-toluenediamine. The resulting vitrimeric products exhibited remarkable mechanical features, with tensile strength and elongation-at-break values beyond 20.0 MPa and 529%, respectively. In addition, thanks to the urea bond exchange reactions (occurring at about 120 °C), the vitrimeric PUs were reprocessable and reshapeable in mild conditions.

Erice et al. [174] designed vitrimeric poly(urethane-urea) elastomers through the reaction of 3-isocyanatemethyl-3,5,5-trimethylcyclohexyl isocyanate with a tris-isocyanate-terminated poly(propylene glycol) (employing dibutyltin dilaurate as a catalyst) and the successive polyaddition with 4, 4’-methylenedianiline. The obtained elastomers exhibited reprocessability (through compression molding under 100 bar pressure, 150 °C for 1 h) and recyclability, thanks to the dynamic exchange between aromatic amine and aromatic urea moieties, controlled by an associative crosslink exchange mechanism.

Very recently, Engelen and coworkers[175] demonstrated the possibility of exploiting hydrogen bonds for catalyzing covalent exchange and reinforcing vinylogous urea-urethane vitrimeric networks through the exploitation of non-covalent interactions. This way, it was possible to obtain highly reactive room-temperature dynamic covalent bonds that can be employed for designing soft materials with high creep resistance, through the establishment of supramolecular constraints.

Vitrimeric PUs based on disulfide bond exchange

Disulfide (S-S) bonds can be exploited for designing vitrimeric polymers: the disulfide bond exchange may take place according to two different mechanisms, namely the disulfide metathesis and the thiol-disulfide exchange[176–180]. The reactions that involve aliphatic disulfide bonds usually require an external trigger to occur, namely a thermal treatment or exposure to UV radiation; conversely, aromatic disulfide bonds do not need the use of a catalyst, and their kinetics is usually high at room temperature.

One of the pioneering works on the use of aromatic S-S bond exchange for the synthesis of vitrimeric poly(urethane-urea) elastomers dates to 2014[181]. For this purpose, the authors employed bis(4-aminophenyl)disulfide as a dynamic crosslinker. The resulting vitrimeric elastomers showed remarkable self-mending properties (with a quantitative self-healing efficiency at room temperature), without needing an external stimulus (i.e., UV radiation or heat).

Fortman and co-workers[182] demonstrated the possibility of using cystamine, an aliphatic disulfide derived from cysteine, as the comonomer with bis(cyclic carbonate and tris(2-aminoethyl)amine, Fig. 10) for the design of vitrimeric polyhydroxyurethanes exhibiting self-healing and reprocessability features. In particular, the incorporation of S-S bonds into the polymer backbone remarkably sped up stress relaxation phenomena (with relaxation times as low as 30 s at 150 °C), enabling reprocessing through compression molding with a quantitative recovery of the crosslinking degree of the polymer network.

Hu and co-workers[183] prepared a series of glycidyl azide polymer-based vitrimeric PUs, employing 2-hydroxyethyl disulfide as chain extender, and trimethylolpropane as crosslinker. The presence of dynamic S-S bonds improved the resulting PUs’ mechanical behavior, accounting for healing capability (triggered by mild heating) and reprocessability. Besides, using

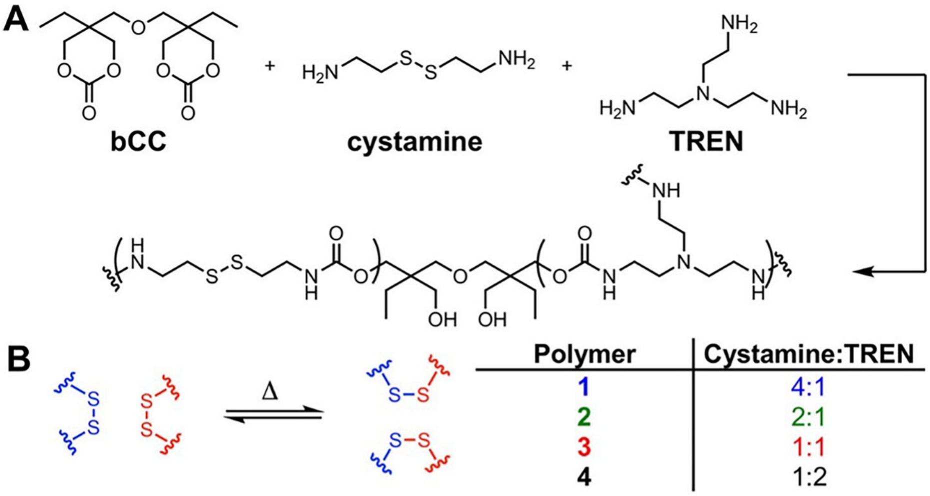


Fig. 10 | Design of vitrimeric polyhydroxyurethanes. **A** Crosslinked polymers obtained from the polyaddition of bis(cyclic carbonate) (bCC) with various ratios (from 4:1 to 1:2) of cystamine and tris(2-aminoethylamine) (TREN). **B** The presence of disulfide bonds in the polymer backbone enables reprocessing. Reprinted with permission from ref. 182, copyright 2018, American Chemical Society.

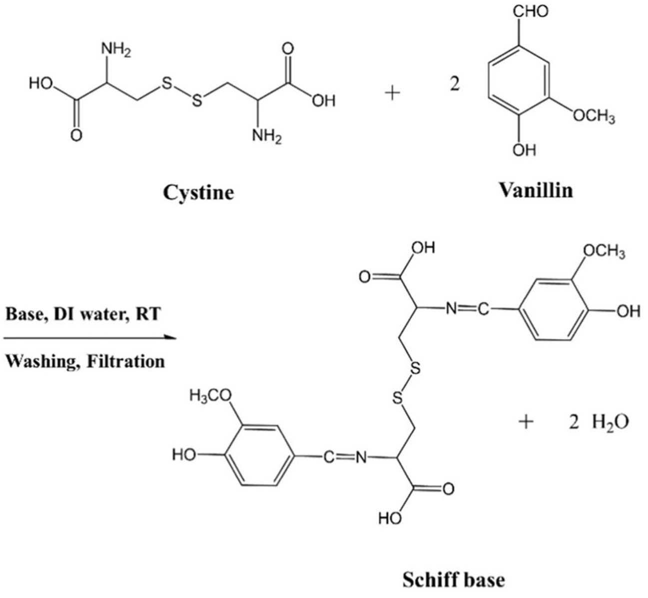


Fig. 11 | Synthesis of Schiff base from cystine and vanillin. Reprinted from[185] under CC-BY-NC-ND license.

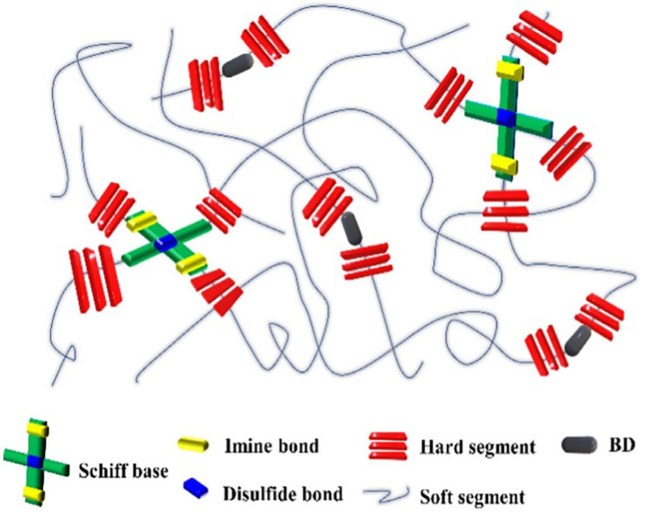


Fig. 12 | Schematic of synthesized vitrimeric polyurethane crosslinked with Schiff base. Reprinted from[185] under CC-BY-NC-ND license.

these systems as polymer matrices of composites containing Al powders allowed for the fabrication of healable materials showing a high healing efficiency (higher than 95%).

A similar approach was recently proposed by Liu and co-workers[49], who modified a flexible polyether-based polyurethane foam through a disulfide diol (namely, 2-hydroxyethyl disulfide), employed as a co-chain extender and reacted with diphenylmethane diisocyanate. The incorporation of the disulfide diol into the hard segments of the network, together with the increase in carbamate content (thanks to the reaction between diol and isocyanate), provided the PU foams with thermal reprocessability at relatively mild conditions (i.e., 150 °C and 30–60 min). The reprocessed PUs exhibited acceptable mechanical features, with relatively high Young's moduli (up to 120 MPa) and tensile strength (up to 14 MPa).

Vitrimeric PUs based on multitype dynamic exchange bonds

It is possible to exploit the concurrent presence of more than a single dynamic exchange bond to significantly enhance the overall characteristics of vitrimers (namely, processability, ease of welding, recyclability, and self-healing[184]).

Specifically referring to vitrimeric PUs, to the best of the authors' knowledge, the scientific literature reports only one paper by Lee and co-workers[185], who synthesized a Schiff base containing dual-dynamic imine and disulfide bonds by reacting cystine with vanillin (Fig. 11). This Schiff base, mixed with 1,4-butanediol (at 0.06:1.38 molar ratio), was utilized as a chain extender for designing self-healing and reprocessable vitrimeric PUs (a schematic structure of the obtained polymers is presented in Fig. 12). The activation energies of the relaxation processes (about 77 kJ/mol) were significantly lower compared to those involving just one type of dynamic exchange bond, hence demonstrating the development of synergistic effects between imine and disulfide bonds. Finally, the vitrimeric PUs exhibited a dual-responsive self-mending ability, triggered by either UV exposure or thermal heating.

Mechanical recycling of polyurethanes

The mechanical recycling of PUs is the most general and standard way to revalorize these materials at the end-of-life. Besides, it is a cost-effective approach that can be performed on all the types of polyurethanes, particularly referring to polyurethane matrices in composites and rigid foams. Though in polymer science and technology mechanical recycling generally requires the use of thermoplastic materials, it is possible to carry it out also on thermosetting polyurethanes, even foamed. However, it is necessary to reduce the average size of the collected PUs: for this purpose, several

Table 4 | Main feedstock recycling reactions

Type of reaction	Main reactants	Experimental conditions	Main products obtained
Hydrolysis[228–233]	Liquid water, Steam, Binary mixtures (H_2O and glycerol), Ternary mixtures (H_2O, sorbitol and glycerol)	Usually carried out at high temperatures (200-400°C) and pressures (15-50 atm), in the presence of acid or basic (preferable) catalysts	Polyols, Amine intermediates, CO_2
Glycolysis[234–245]	Diethylene glycol, Ethylene glycol, Propylene glycol, Dipropyleneglycol, Poly(ethylene glycol), 1,4-butanediol, 1,6-hexanediol	Usually performed at temperatures beyond 200°C and atmospheric pressure, in the presence of catalysts (acetate inorganic salts, hydroxides of alkaline metals, amines, metal-organic compounds)	Polyols, Glycolyzates
Aminolysis (transesterification)[246–248]	Tetraethylenepentamine, Triethylenetetramine, Diethylenetriamine, Alkanolamines	Using highly reactive amines allows for performing the reaction at low temperatures	Polyether polyols, Curing agents for epoxy systems
Ammonolysis[249,250]	Ammonia (even in supercritical conditions), Ammonium hydroxide	Temperatures can vary from 25 to 100°C, depending on the concentration of the ammonolytic reactant	Polyols, Amines, Urea
Acidolysis[23,251]	Organic (dicarboxylic) acids (saturated or unsaturated), Inorganic acids (HCl)	Mild conditions (i.e., low temperatures – around 60°C – and short times) are needed when saturated acids (e.g., adipic acid) are used	Polyols, CO_2, and amine salts (when inorganic acids are used), amide groups (when organic acids are employed)
Phosphorolysis[252]	Esters of phosphoric or phosphonic acid (dimethyl phosphonate, diethyl phosphonate, triethyl phosphate, tris (1-methyl-2-chloroethyl) phosphate)	Processing temperatures range from 140 to 190°C	Glycolyzates

techniques, like grinding, shredding, cutting, and tearing can be successfully exploited. Each of these methods can produce various types of processed materials, from flakes to granules and even powders, i.e., with a different average dimension and shape, depending on both the particular kind of polyurethane waste that undergoes the recycling process and the specific apparatus employed (e.g., pellet mills, knife cutting machines, two-roll mills,…). The so-obtained products can directly be employed as fillers for pillows, toys, and other objects (through a primary mechanical recycling strategy) or as possible substrates in subsequent secondary mechanical recycling or in feedstock recycling.

Further, the processing of the polyurethane products with reduced size can exploit three main pathways, namely: rebonding, hot compression molding, and injection molding.

Rebonding is a sort of mechanical reprocessing that exploits an adhesive like diphenylmethane diisocyanate or poly(phenylenemethylene isocyanate) at a low concentration (i.e., beyond 10 wt.%) to coat the polyurethane pellets or flakes. These latter then undergo a treatment with hot water or steam and a subsequent compression (up to 200 bar of pressure): the final material can be employed for the manufacturing of contoured components (carpet underlays, cover for tires, car lining, and building panels, among a few to mention)[186].

Hot compression molding is the typical mechanical recycling process that does not require the use of adhesives and is suitable for thermoplastic PUs. In particular, after a grinding step, the so-obtained fine particles are compressed at high pressure (about 350 bar) and temperature (around 180°C) and give rise to such stiff parts as pump and motor covers. Further, the incorporation of glass fibers at about 15 wt.% loading into the polyurethane fine particles allows for obtaining strengthened components for dashboard and door panels[187]. Also, these particles can be exploited as fillers in other resin systems (e.g., polyester resins), taking benefit from the toughening effect exerted by the incorporated polyurethane particles. It is noteworthy that two are the main issues referring to the use of hot compression molding for the recycling of PUs, namely: the presence of pigments and dyes in the polymer wastes and scraps and the difficulty in achieving fine particles through grinding[188,189]. To solve this latter, a possible strategy relies on the use of Structure Reaction Injection Molding (SRIM) technique that allows for the creation of a layered structure consisting of two glass fiber layers sandwiching coarsely ground polyurethane waste (not exceeding 30 wt.%) and coated with a two-component polyurethane resin.

Finally, the recycling of relatively crosslinked PUs can be performed through injection molding: the process was successfully applied to polyurethane pellets (dimensions ranging from 250 to 1000 micron), working at about 180 °C and using high shear compression values (exceeding 350 bar)[190]. Besides, this technique (as a dual injection method) was successfully applied for the manufacturing of skin-core components with enhanced surface finish[191]: the core is made of recycled polyurethane (even pigmented). In contrast, virgin polyurethane is employed for the skin.

Chemical (feedstock) recycling of polyurethanes

The possibility of making the polymerization of PUs reversible allows for the design of feasible and reliable processes of chemical recycling. From an overall point of view, the triggering of depolymerization involves the reaction of organic species that contain active hydrogen atoms with the polar segments of the polyurethane skeleton. In this context, depolymerization is strongly affected by several parameters: the type of organic species, the possible presence of catalysts, the pH of the medium, in which the reaction is carried out, and, finally, the adopted pressures and temperatures. The so-obtained depolymerization products usually undergo distillation and purification steps, hence allowing for the recovery of polyols and amines. These latter can be successfully exploited for the synthesis of different polymers, also comprising new PUs.

Table 4 collects the main feedstock recycling processes, highlighting the employed organic compounds and the main reaction conditions.

Biodegradation of polyurethanes: recent advances

One of the most interesting and up-to-date trends refers to the design, development, and implementation of new biodegradation approaches exploiting the availability of specific enzymes and living microorganisms (e.g., fungi and bacteria)[17,192–198]. A general scheme of biodegradation is presented in Fig. 13.

As reported in the scientific literature, despite the availability of some biodegradable polyurethanes commercially available, the biodegradation of PUs is typically investigated in laboratories, employing stable and favorable temperature conditions, conferring supplementary nutrients to the selected/isolated microorganisms, and utilizing enzymes at quite high concentrations[199,200].

From a general point of view, it is worth noticing that the biodegradation of PUs is strictly dependent on the degradation site (compost, soil, seawater, and fresh water, …), as the type and composition of the living environment

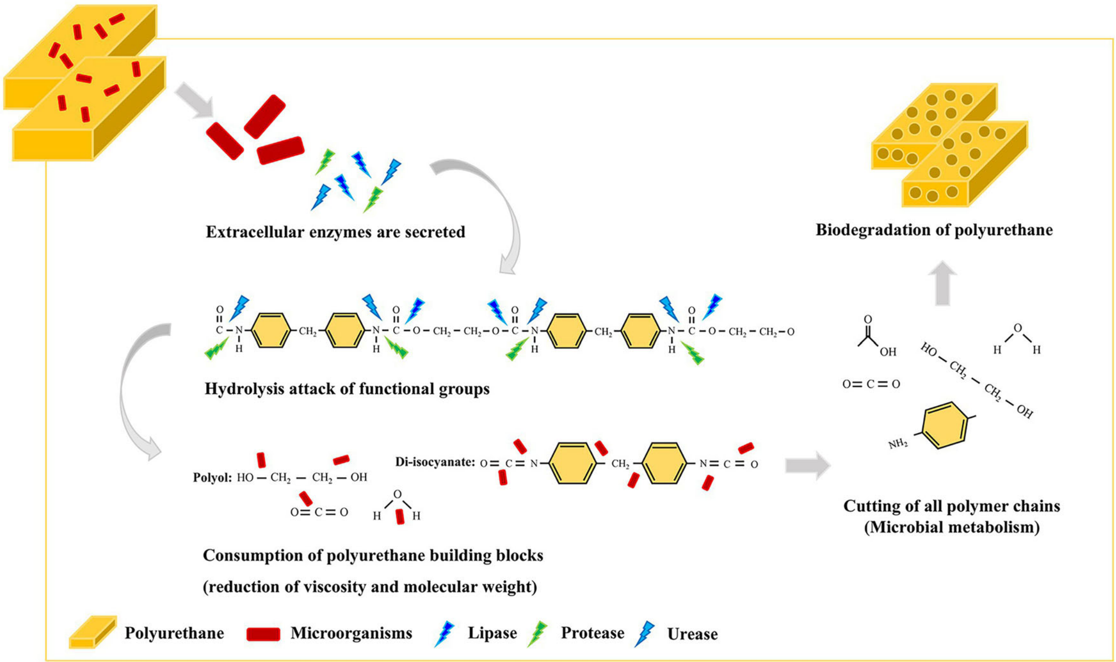


Fig. 13 | General scheme of the biodegradation process of PUs. Reprinted from[254] under CC-BY License.

(i.e., type of microorganisms responsible for the biodegradation, pH, temperature, relative humidity, among others) can be widely variable.

Regardless of its type (i.e., using isolated/screened microorganisms, expressing and purifying enzymes or in a real environment), the degradation proceeds according to three consecutive steps that may occur in aerobic or anaerobic conditions. First, macromolecular chains are broken, hence originating oligomeric fragments; these latter are further degraded to low MW products, which, in turn, convert into water and carbon dioxide (when biodegradation takes place in aerobic conditions) or methane (anaerobic biodegradation). Unlike the traditional thermo-chemical degradation, the overall biodegradation process does not require the utilization of chemicals impacting the environment and usually occurs under mild conditions (at ambient temperature, without the need for heating the systems that are undergoing the degradation process). In general, the biodegradation process of polyurethanes is affected by several parameters, comprising molecular orientation[201,202], degree of crystallinity, and degree of crosslinking of the PU system; in addition, as they are more accessible, the amorphous moieties of the PUs are usually more suitable for being degraded as compared with the crystalline counterparts[199].

Also, it is noteworthy that most of the academic research has been focused on investigating the biodegradation of polyester-polyurethane (PS-PU) systems, rather than that of polyether-polyurethane (PE-PU) counterparts. In fact, compared with PS-PU, these latter show more hydrogen bond interactions taking place among their soft/hard segments, hence increasing the phase separation level and consequently making biodegradation more difficult to occur. Conversely, PS-PU systems exhibit a weak biostability, due to the ease of hydrolytic degradation undergone by the ester groups present in the soft segments[203], and result vulnerable to the attack of microorganisms[204].

Regarding enzymatic degradation, several enzymes belonging to the class of hydrolases (like urease, protease, and esterase, among others) can successfully be employed for degrading both thermoplastic bulk PUs and polyurethane coatings. In particular, esterase are the preferred enzymes for hydrolyzing the ester bonds (aliphatic or aromatic) in PS-PU systems, with the release of degradation products bearing terminal alcoholic or carboxylic acid groups[205]. These reactions can be performed in acidic or basic conditions. Ureases can catalyze the breakdown of urea bonds in specific forms of PS-PU, generating amines and CO_2. Nevertheless, the degradation of urethane through urease is rather ineffective, as urea bonds are harder to break in comparison to ester bonds. In addition, protease represents another category of enzymes that can be utilized in the degradation of PUs. It possesses the ability to inherently hydrolyze peptide linkages and has demonstrated its capacity to hydrolyze urethane bonds[32].

Contrary to PS-PU, PE-PU systems show a high resistance to hydrolysis, which makes difficult their biodegradation. Therefore, biodegradation proceeds according to an oxidation process that involves the abstraction of methylene hydrogen atoms adjacent to oxygen in the polyether soft segments[203]. Then, a hemiacetal, formed through the addition of a hydroxyl group to a carbon radical, is oxidized to ester. A similar oxidation pathway is observed as far as the degradation of PE-PU hard segments is considered, with the abstraction of methylene hydrogen atoms from carbamate chain extender by oxygen free radicals[206].

The recent research outcomes related to the biodegradation of polyurethanes are detailed in the next paragraphs and summarized in Table 5.

Cladosporium halotolerans, a fungal strain isolated from the deep sea, was exploited for biodegrading a PU Impranil DLN foam (namely, a poly(1,4-butylene adipate)-based polyurethane, produced by Covestro as waterborne dispersion, and here employed as the only carbon source)[207]: the break of C = O and C-N-H bonds accounted for quite fast biodegradation of the polymer, achieving about 80% of degradation within three days of incubation at 28 °C. Besides, as revealed by gas chromatography-mass spectroscopy analyses, the main intermediate products originating from biodegradation were polyols and alkanes.

The construction of a metagenome library from the soil allowed for demonstrating the appropriateness of urethanases for the chemo-enzymatic recycling of polyether-polyurethane foams[208]. More specifically, apart from its suitability for hydrolyzing low molecular weight dicarbamates originating from the glycolysis of the PU foams, urethanases was very effective in recovering the polyether-polyol products obtained from the chemocatalytic glycolysis of the polymers.

The modification of toluene diisocyanate-derived polyurethane foams through the incorporation of a sugar (namely, sucrose, at 15 wt.%) in the polymer backbone allowed for a remarkable enzymatic (invertase) degradation; besides, the presence of propolis at 20 wt.% in the foam formulation accounted for remarkable antibacterial properties (with about 94% bacteria activity reduction)[209].

Table 5 | Biodegradation of polyurethanes: current research outcomes

Type of PU	Microorganism/Enzyme	Source	Culture conditions	Main outcomes	ref
PS-PU	*Cladosporium hatolerance* (fungal strain)	Deep sea	Incubation at 28 °C in liquid minimal medium; pH=7	Around 80% of degradation reached within 3 days; polyols and alkanes as main intermediate degradation products	207
PE-PU	Urethanases	Soil	N.D.	Construction of a metagenome library; demonstration of the suitability of urethanases for the chemo-enzymatic recycling of the foam	208
Different thermoplastic PUs	N.D.	Compost	Controlled industrial composting conditions according to ISO 14855	72% maximum biodegradation rate; PU fragmentation was slowed down by incorporating hydrolysis stabilizers	34
Thermoplastic PUs	N.D.	Compost	Incubation and burial in compost at 45 °C, with 75–85% R.H.	57% decrease in molecular weight after 9 weeks in compost; 97% biodegraded PU in 120 days	210
PS-PU	*Cladosporium sp. P7* (fungal strain)	Soil	Incubation at 28 °C	After 28 days, around 32 (PU employed as the only carbon source) or 44% (PU combined with other co-carbon sources) of degradation achieved	211
PS-PU	Lipase from *Candida rugosa* and *Aspergillus niger*		Incubation at 37 °C	Around 10 and 35% weight loss after 1 month for PUs fully or partially crosslinked	212
PS-PU	Microbial consortia	Landfill soil and leachate	Incubation in minimal essential medium at 30 °C	Degradation of PU achieved in one week of incubation; adipic acid and butanediol as main degradation products	213
Aliphatic PU foams	Microbial consortia	Soil	Soil burial test according to ASTM D5988 standard	Up to 53% mineralization achieved in soil without nutrient addition; absence of negative ecotoxicological effects in soils during biodegradation	214
PS-PU foams and films	Amidase GatA250	N.D.	Incubation at 30°C	Biodegradation efficiency of amidase enhanced by introducing cutinase LCC; the combined system showed degradation efficiencies of 13.94 and 42.2% for the PU foam and PU film	215
PS-PU foams and films	*Bacillus sp. YXP1*	Plastic landfill	Incubation at 30 °C	The films fully biodegraded in one week; the foams showed 41.2% weight loss in one month; five degradation intermediates comprising adipic acid, 1,4-butanediol, and 4,4'-methylenedianiline	216

N.D. not defined.

Pfohl and co-workers[34] selected different thermoplastic polyurethanes showing either aromatic or aliphatic backbone, various ratios between soft and hard segments, the possible presence of hydrolysis stabilizers, and even crosslinking degree to some extent. As assessed in compost (by evaluating the CO_2 evolution), 72% was the maximum biodegradation rate achieved: this latter decreased with decreasing the soft-to-hard segments ratio and increasing the crosslinking degree. Finally, incorporating a hydrolysis stabilizer into the PU formulation slowed down the PU fragmentation, with very limited impact on the conversion of carbon into CO_2.

Rajput and co-workers[210] synthesized biodegradable (in compost) thermoplastic PUs starting from polyether-polyols derived from bio-based 1,3 propanediol, sebacic acid, and azelaic acid. 9 weeks of biodegradation in compost accounted for 57% decrease in the PU molecular weight; besides, 97% of the thermoplastic PUs underwent biodegradation in 120 days, as revealed by respirometric tests.

Liu and co-workers[211] assessed the effectiveness of nine fungi- and eleven bacteria-isolated strains for the biodegradation of a poly(1,4-butylene adipate)-based polyurethane. The most effective strain was *Cladosporium sp. P7*, which was able to attack both urethane and ester bonds, giving rise to six different metabolites including 1,4-butanediol, adipic acid, and 4,4′-methylenedianiline. In addition, 28 days of cultivation were enough to convert about 32% (when employed as the only carbon source) or around 44% (when combined with other co-carbon sources) of the PU into soluble low molecular weight products.

Recently, Kasmi and co-workers[212] exploited melt polycondensation for preparing six fully biobased branched polyester-polyols obtained through the reaction of hemicellulosic sugars and dicarboxylic acids; then, the polyester-polyols were employed for synthesizing 12 transparent thermosetting PUs, using a solvent-free step growth polymerization under very mild reaction conditions (namely, operating at 40–65 °C for 2–5 min). Lipases from *Candida rugosa* and *Aspergillus niger* was selected for evaluating the enzymatic hydrolysis behavior of the polyurethanes. Irrespective of the structure and chemical composition, all the PUs were prone to biodegrade, with a maximum weight loss of around 35% after 1 month when partially crosslinked; this value dropped to about 10% when the polyurethanes were fully crosslinked. Finally, it is worth noticing that the enzymatic degradation rate strictly depended not only on the crosslinking degree but also on the molecular weight of the diacid unit embedded in the polyol backbone.

Su and co-workers[213] isolated three microbial consortia from the landfill leachate and enriched them using a polyester-polyurethane powder as the only carbon source. The identified consortia accounted for efficient biodegradation of the polymer films, promoting the biomass accumulation during 1 week of incubation.

Skleničková and co-workers[214] assessed the aerobic biodegradation of fully aliphatic PU foams possibly embedding hydrolyzable amide linkages, employing a six-month soil burial test and evaluating CO_2 release, and the enzymatic activities of ureases, esterases, and proteases. The mineralization rate achieved for the polyurethane foams highlighted not only their important level of biodegradation but also the possibility of using the foams as an effective source of energy and nutrients for the soil microorganisms. Further, no toxic effects associated with the biodegradation products of the foams were observed. Finally, from a chemical point of view, soil microorganisms were effective in biodegrading only the ester bonds present in the PU foams, whereas amide linkages were not enzymatically cleavable. These findings were attributed to some changes occurring in the supramolecular network arrangement because of the increased quantity of hard segments, which, in turn, accounted for decreased biodegradability.

Xin et al. [215] expressed the amidase GatA250 and assessed the enzymatic degradation of poly(1,4-butylene adipate)-polyurethane, both in the form of film and post-consumption foam. The biodegradation efficiency of amidase GatA250 was significantly enhanced by introducing the cutinase LCC: the concurrent utilization of the two enzymes accounted for biodegradation efficiencies as high as 42.2 and 13.94%, for the polyurethane film and foam respectively. In addition, during the biodegradation, the film released 4,4′-methylenedianiline only (neither 1,4-butanediol nor adipic acid were released).

Ji and co-workers[216] isolated *Bacillus sp. YXP1* strain from a plastic landfill and exploited the bacterium for biodegrading three polyurethane substrates (namely, a poly(1,4-butylene adipate)-based polyurethane, Impranil DLN, and a polyester-polyurethane foam). 0.5% Impranil DLN was fully biodegraded over 1 week, while the polyester-polyurethane foam exhibited 41.2% weight loss after 1 month. Finally, the effectiveness of the bacterium strain in promoting the hydrolysis of ester and urethane linkages of the polyester-polyurethane was proven through the identification of five degradation intermediates comprising 4,4′-methylenedianiline, adipic acid, and 1,4-butanediol.

Finally, the current research on the biodegradation of polyurethanes is involving molecular dynamics simulations as a reliable, predictive and feasible tool. In this context, Świderek and co-workers[217] investigated the molecular mechanism of polyurethane esterase A, which accounted for the biodegradation of a polyester-urethane system in *Pseudomonas chlororaphis*. First, the known genome of the protein allowed for the identification of its unsolved 3D structure. Then, the enzymatic hydrolysis of the polyester-urethane system was studied using a hybrid quantum mechanics/molecular mechanics approach, preliminarily analyzing the 3D structure of the apo-enzyme, labeling its active site, and, finally, picking out the ideal site for binding the protein to the substrate. The obtained results in terms of free energy landscape confirmed the suitability of polyurethane esterase A for biodegrading polyurethanes, despite a low biodegradation activity.

Conclusions and perspectives

Origin, toxicity, sustainability, recyclability, and end-of-life surely represent the main up-to-date key issues associated with the world of polyurethanes and are currently driving both the academic and the industrial research efforts toward the design, development, and implementation of new systems well fulfilling the present concept of circular economy that is widely spreading in the polymeric materials sector[218–220].

The origin of PUs plays a fundamental role in paving the way toward a smart use of greener materials: in this context, the identification and selection of bio-based monomers (i.e., polyols, chain extenders, and di- and poly-functional isocyanates) has allowed to significantly move from the fossil-based chemistry to a more environmentally friendly approach. The biobased polyurethanes have shown an overall thermo-mechanical behavior that is similar to (or, in a few cases, even better) that of fossil-based counterparts, hence demonstrating the feasibility of this strategy. In this context, the use of vitrimeric polyurethanes, which combine the characteristics of thermosets with the easy processability of thermoplastic polymers, thanks to the structure of covalent adaptive networks, fits well. Although the bio-based strategy is worthy to explore and assess, some questions are still open: in particular, it is questionable to employ feedstocks and cultural land (which are theoretically intended for the food chain) for chemical industry purposes, thereby diverting resources initially earmarked for other purposes. Moreover, life cycle assessment showed that there are some scenarios where the biobased polyols have better performance than fossil-based counterparts while, in other scenarios, the environmental impacts can be worse. Since many studies showed that diphenylmethane diisocyanate (MDI) is the main hotspot for all impact categories considered, alternatives to the most used TDI or MDI must be found.

Apart from origin and environmental impact, the attention to end-of-life and potential recyclability of PUs has remarkably grown in the last decade. Taking into account that, at the end-of-life, only about 5% of PUs are recycled, while around 45 and 50% are respectively landfill-confined and incinerated [39], proper PU waste management is a very demanding issue. In this context, it is nonsense to try to adopt green and sustainable approaches in the synthesis of these polymers, when they will turn into wastes (and, therefore, accumulate) at the end-of-life. Recycling standard PU waste streams is not easy at all because of the inherent physicochemical complexity of PU waste streams: indeed, they exhibit differences in crosslinking degree, chemical structure, crystallinity, and ratio of soft to hard segments. While an ideal recycling pathway can be designed, developed, and implemented for most plastic materials, the structural variety of PUs makes it difficult to develop a universal recycling process, requiring, at the same time, specific research efforts[17]. As pointed out in the present review, mechanical and chemical recycling of PU wastes are quite well-consolidated approaches, even at the industrial scale, which do not foresee important implementations in the forthcoming years, despite a continuous and progressive use[22,29,221]. Conversely, the exploitation of selected enzymes and living microorganisms (i.e., fungi and bacteria) seems a very promising strategy with a high potential also considering the possibility of scalability of the biodegradation processes, the use of molecular dynamics simulations as a reliable, predictive, and feasible tool, and the development and implementation of metagenomic analyses of the microbial population that promotes the biodegradation of PUs. In fact, metagenomic analyses may help clarify the structure of this population, picking out the enzymes involved in PU degradation and envisaging their performance during the biodegradation process[31,222].

Further, the integration of covalent adaptive networks in PUs is at present gathering significant attention mainly from academia, as the structure of these polymeric systems ensures reprocessability and recyclability, maintaining an overall thermal, mechanical and chemical behavior similar to that of conventional thermosetting PUs, and providing, at the same time, such multifunctional features as weldability characteristics, self-healing and shape memory properties, as well as adhesion and tunable degradability. Conversely, the industrial interest for the vitrimeric approach is still very limited: indeed, this strategy is in its infancy stage, and the industry might be interested in exploiting this approach once the scaling-up is defined, developed, and implemented: this is very challenging, as it should rely on the design of overall cost-effective processes, with acceptable/affordable investment and management costs.

In conclusion, further progress is likely to be made in exploiting the concepts of sustainability and circularity applied to polyurethanes, thereby contributing to the management of the end-of-life of these polymer systems, providing them with interesting added value and opening new technical prospects for valuable reuses.

Data availability

No datasets were generated or analysed during the current study.

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A.L. and G.M. wrote the main manuscript text and G.M. prepared all the figures. All authors reviewed the manuscript.

Competing interests

The authors declare no competing interests.

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