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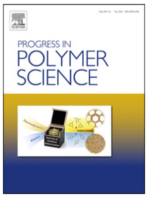

Sustainability of self-healing polymers: A holistic perspective towards circularity in polymer networks

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ABSTRACT

Permanent polymer networks present an important sustainability challenge. Irreversible covalent crosslinks impart these materials excellent mechanical properties, thermal and chemical resistance, yet also render them difficult to repair and to recycle. Self-healing mechanisms can extend the lifetime of thermosets and elastomers, improving their durability and making their lifecycle more sustainable. In addition to the lifetime extension, this paper reviews the sustainability of self-healing polymers from a holistic point of view. The entire lifecycle of self-healing polymers is critically assessed with reference to the green chemistry principles and sustainable development. The relation between the self-healing chemistries and the sustainability aspects of each of the phases of the lifecycle are discussed, starting from the feedstocks, monomer functionalisation and polymer synthesis, to processing and manufacturing as well as end-of-life considerations, *i.e.* recycling or (bio)degradation. The review provides a toolbox for the development of more sustainable thermosets, elastomers and their composites. It is of utmost importance to consider the entire lifecycle of self-healing materials, derived products and – by extension – any material or product. The self-healing ability and often related recyclability should primarily reduce the amount of new materials that are necessary to fulfill societal needs, by extending the lifetime of products and maximizing reprocessing into new products. Increasing healing efficiency and the number of healing cycles improves the overall environmental impact relative to the extended service lifetime. Renewable resources derived from biomass, recycling processes or waste streams should be the first choice to create new self-healing polymers. Finally, biodegradability can be considered as a complementary end-of-life scenario upon accidental loss of self-healing polymer to the environment, provided that the biodegradation does not start under the prospected use conditions of the self-healing polymers and products, but can be postponed until contact with stimuli present in the environment.

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Abbreviations: ACAT, Amino-capped aniline trimer; CA, citric acid; CAD, Computational aided design; CNC, Computerized numerical control; DCM, dichloromethane; DCPD, Dicyclopentadiene; DIW, Direct ink writing; DMI, 1,2-dimethylimidazole; ENR, Epoxidized natural rubber; FA, Furfuryl amine; FDC, 2,5-furandicarboxaldehyde; FDCA, 2,5-furandicaboxylic acid; FFF, Fused filament fabrication; FGF, Fused granule fabrication; HBE, hyperbranched epoxy; IPN, Interpenetrated network; KDV, Catalytic pressure-less depolymerization; LCA, Life cycle analysis; Mw, Molecular weight; NGP, neighbouring group participation; PDMS, Polydimethylsiloxane; PEDOT, 3,4-ethylenedioxythiophene; PET, Polyethylene terephthalate; PHAs, Polyhydroxyalkanoates; PLA, Polylactic acid; PVA, Polyvinyl alcohol; PVP, Polyvinylpyrrolidone; ROMP, Ring opening metathesis polymerization; SLA, Stereolithography; SLS, Selective laser sintering; SH, Self-healing; Tgel, gel transition temperature; THF, Tetrahydrofuran; TPS, thermoplastic starch; TsOH, p-toluenesulfonic acid; Tv, Topology freezing transition temperature; UPy, 2-uredio-4-pyrimidone; VOC, Volatile organic compounds.

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1. Introduction

Already in the 1840′s, natural rubbers were being vulcanized and other natural polymers such as cellulose were processed to make the first man-made polymers. Just before the 20th century, the first artificial polymers were created from milk casein and formaldehyde, followed by the conception of the first thermoset by Leo Baekeland, Bakelite. Over the course of more than a century, natural and artificial polymers have contributed considerably to the improvement of our everyday lives. However, it has also been shown that the deficient resource management and end-of-life waste build-up of these polymers pose tremendous risks for the health of humankind and its environment. The risks that their synthetic chemistries entail (high energy demand, use of organic solvents…), as well as physicochemical stability and high-volume output of the final polymer products, have become a threat to life on Earth, menacing wildlife and human health as a consequence of the massive amount of waste formation. Plastic waste can be found throughout oceans, rivers, soils, and even in freshwater streams used for human consumption in the shape of microplastics. It is estimated that, following the current trends, about 12,000 Mt of plastic waste will be discarded in landfills or the natural environment by 2025, while nowadays only an estimated amount of 9 % of the total manufactured plastics are being recycled [1]. The proportion diminishes markedly to less than 1 % for plastic recycled more than once. While thermoplastics may be recycled by way of (thermo)mechanical methods, thermosets and elastomers that are crosslinked by irreversible bonds cannot be reprocessed. Permanent covalent bonds impart superior mechanical properties, thermal and chemical stability to crosslinked polymers, compared to their linear or physically crosslinked analogues, while rendering them challenging to recycle.

The ubiquitous societal demand towards a sustainable economy belongs to some of present-day government agendas. To face this challenge, it is required to devise and set the ground rules that must be integrated in future business mindset. The most representative and accepted sustainability assessment benchmark corresponds the 12 principles of Green Chemistry introduced by Anastas and Eghbali in 2010 [2]. These principles serve as the basis to establish the main prerequisites to design sustainable products and operations. The depletion of petroleum resources must be accompanied by the implementation of these guidelines. The first principle pertains the *prevention of waste formation*. In the scope of this review, this involves every step of the material's life cycle. The second principle is to *promote atom efficiency* in synthetic methods, which contributes to waste prevention by minimizing side products and emissions. The third principle is to *avoid the use of hazardous or toxic substances* and methodologies. *Preservation of the efficacy of the employed chemicals* while improving their safety and to *avoid the use of auxiliary substances* such as solvents or additives are the next principles, while *maximizing the energy efficiency of the process*. If auxiliary substances would be necessary, they should be innocuous. The *use of renewable resources* should be enhanced, the *use of derivatives should be minimized* and *catalysts should be employed as selective as possible* to perform chemical reactions. *Promoting the degradability* of the prepared products marks the tenth principle. The final two principles are the design of *analytical methods to in-situ monitor the formation of pollutants* and *to minimize accident risks* (explosions, fires, leakages) by using safer chemicals.

Anastas and Eghbali placed waste prevention at the top of the list. Firstly, waste prevention leads to an improved atom economy throughout the entire lifecycle of the material and no matter is lost to the environment. Secondly, the energy stored in the material can be recovered and reused if waste is collected and recycled. No new resources need to be extracted, as the material remains in the loop. Inspired by Nature, scientists came up with the idea that an effective route towards waste prevention can be realized through self-healing of damage in synthetic materials, mimicking natural organisms. Many natural materials can regenerate when injured, restoring their functionality to that previous to damage. Wound sealing, bone healing or even DNA repair are some examples of the outstanding healing performance of biological systems [3]. The application of this concept to synthetic materials was adopted for the first time during the 80′s by means of intermolecular diffusion of polymer chains when heated above T_g [4]. This finding has prompted the conceptualization of novel advanced engineered materials, so-called self-healing materials, that can repair their structure upon external damage, avoiding catastrophic failure. It is evidenced that the concept of self-healing materials has the potential to contribute greatly towards the sustainability of all classes of materials by limiting waste formation and avoiding the need to produce new products. However, not all that glitters is gold. Despite the promising outcomes, the sometimes devaluated “green” or “eco-friendly” terms have blindsided the critical perspective of whether a material or procedure is truly sustainable or not, disregarding other fundamental criteria such as energy efficiency, carbon footprint or employment of toxic reactants. This also applies to self-healing polymers, as their chemical composition, production or healing triggers might result in environmentally more pernicious solutions than their classic plastic counterparts. Therefore, this review will also consider other aspects from the Green Chemistry principles of Anastas and Eghbali, such as the use of environmentally taxing chemicals and auxiliary substances, the feedstocks and their derivatives, the energy consumption during synthesis, the processing and manufacturing and end-of-life considerations such as the recyclability and degradability.

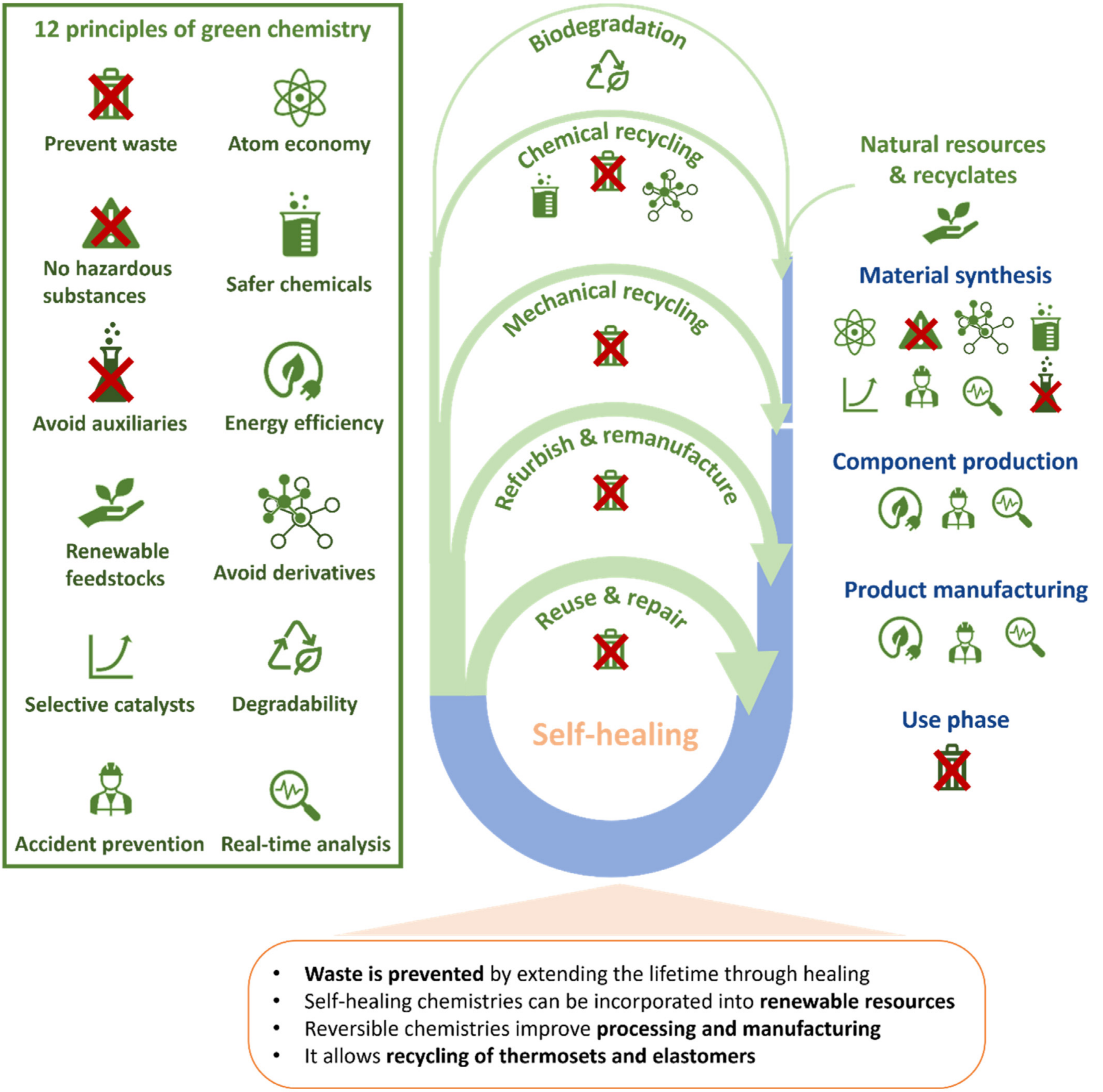
Complementary to the Green Chemistry principles and more from an engineering perspective, circular economy models have been developed that involve an increasing number of R-words. Already several decades ago, we learned about Reduce, Reuse and Recycle. As the efforts of consumers and producers to limit waste production were and are still severely lacking, these models have been expanded with more R-words [5]. However, these merely provide examples and ultimately boil down to the original three. Refuse is the customer's strongest signal to Reduce the consumption and, ultimately, the production of obsolete products. Redesign and Rethink are methods to Reduce waste formation and to improve Reusability and Recyclability. Remanufacture is a subsection of Recycling that also focuses on the Reuse of components into new products, without needing to completely Recycle the materials. Renew and Repair are practical examples how to extend the lifecycle of certain products and to enhance Reusability. Finally, it is possible to Recover (part of) the energy invested in the materials through incineration. This is the least desirable form of Recycling. Ultimately, the chances for success of any of these R-words, however many are proposed, depend on the willingness of consumers, producers and policy makers to put these R-words into general practice. The lack of waste management resources and policies demands a hasty remedy to both academia and industry to find potential solutions that might mitigate this sharply rising problem. The formulation and manufacturing of novel polymeric materials that are recyclable, biodegradable or bio-sourced are some of the proposed alternatives, despite still not generally practiced due to financial and scale constraints.

Self-healing materials have repair mechanisms built into their material structure that enable them to “heal” after damage and recover their functional properties, similar to biological systems. They primarily target lifetime extension and hence reuse of the product or component. For over three decades, a broad range of different healing strategies and related self-healing formulations have been proposed in scientific literature. Two major classifications have been adopted based on their healing mechanism. Extrinsic self-healing materials are based on the incorporation of capsules, hollow fibres or vascular networks to store a healing agent within a polymer matrix. Upon mechanical damage, the healing agent leaks out of the reservoir to fill the damage volume and cure to recover the mechanical properties of the material. Intrinsic self-healing materials owe their properties to the presence of physicochemical interactions or dynamic chemical bonds in the polymer structure. Upon damage, these bonds are broken in a reversible fashion and can be reformed at the damage surfaces to reconnect the damaged parts. The mechanism resembles the classic intermolecular diffusion approach, with the added value of providing bond exchange upon randomization at the crack location. In general, extrinsic self-healing systems can autonomously repair damage as the mechanical force itself triggers the healing action upon rupture of the reservoir containing the liquid healing agent, while intrinsic healing mechanisms often need to be submitted to an external stimulus, such as heat or light, to activate the healing mechanism. In certain instances, the physicochemical interactions or dynamic covalent bonds can be reversibly broken by the damaging force and possess sufficient mobility and reactivity to autonomously reform and heal the damage, without the need for external intervention, but often at the expense of the mechanical properties.

Self-healing materials are a direct solution to the first Green Chemistry principle, since waste is prevented by extending the lifetime through damage healing and reuse, and thus avoiding the need for disposal of damaged products and the production of replacement products (Fig. 1). However, current self-healing materials and their synthetic methods do not necessarily follow the other Green Chemistry principles. For example, some self-healing polymers might be based on biomass-derived resources, but the healing step required to restore the material properties can be highly energy demanding. Hence, there exists room for the development of more sustainable alternative routes towards novel self-healing materials formulations, or to appraise how much can non-sustainable methods be elongated to compensate other limitations associated to the actual greener approaches. The aim of this review is to provide scientists from both industry and academy with a toolbox for a sustainable development of future self-healing materials, and to do an in-depth analysis of how self-healing relates to sustainability and how it can be improved. In the framework of this study, extra attention will be paid to intrinsic systems since these are considered the group with a larger optimization window to obtain durable and efficient healable polymeric systems, focusing on the different dynamic chemistries in charge of their stimuli-responsiveness.

Many types of self-healing materials that possess the ability to repair damage, autonomously or under the application of an external or internal stimulus, have been developed in the past decades in view of improving many aspects of the sustainability of these material types. In current literature, the service lifetime extension by healing incurred damage has been the major aspect considered in the sustainability assessment of this recent class of smart materials. In this literature review, the authors thoroughly assess the efforts performed to improve the sustainability of all phases from the cradle to the grave of self-healing polymers. Different classes and types of self-healing polymers are compared to their traditional, non-recyclable and non-self-healing alternatives. Haines-Gadd et al. raised the discussion whether self-healing materials would lead to “immortal” products or would pose a risk to a circular economy [6]. They found that despite the intensity of research efforts in the materials science community in the development of self-healing materials, there was a lack of debate regarding the implications of product lifetime extension on the implementation of self-healing products in a circular economy. So far, there have been no life cycle assessments (LCA) on self-healing polymers, while this is already much more mature for cementitious self-healing materials. Bernardo et al. compared the life cycles of concretes based on a self-healing geopolymer with ordinary Portland cement (OPC) [7]. The self-healing geopolymer concrete was much more prone to microcrack formation, yet able to extend the lifetime by healing these microcracks using microcapsules filled with a healing agent. The performance in global warming potential was found to be better for the self-healing geopolymer concrete, but worse in other environmental impact categories than OPC concrete. The boundaries of the LCA were limited from cradle to gate, not considering the effect of the self-healing properties of the useful lifetime of the concrete in their application. Another cradle-to-gate LCA was performed on self-healing concrete by the De Belie group, comparing different superabsorbent polymers [8]. They estimated that considering 100 % healing efficiency and accounting for the required replacements over a course of 100 years, the CML-IA impacts of the self-healing concretes remain lower than traditional concrete.

Most life cycle assessments (LCA), life cycle costings (LCC) and techno-economical assessments (TEA) limit the boundaries of the assessment from gate to gate, from cradle to gate or at most from cradle to grave, yet even in the latter not accounting for the use phase and potential implications of lifetime extension. Ramesh et al. came to these conclusions after reviewing LCA and TEA on polymers, often comparing fossil fuel-based polymers with bio-based alternatives [9]. Bernardo et al. concluded that many of the LCA on polymers and polymer composites were consistent and found that global warming potential (GWP) and total energy use (TEU) are good indicators for the comparison of different materials for the studied applications [7]. They further criticize that in most cases, and especially in governmental bodies and firms, the LCC are still often limited to conventional LCC that do not consider external costs such as GWP and TEU, confirming the conclusions of Ramesh et al. The overarching conclusion of their literature review was that polymers and polymer composites often economically and ecologically outperform conventional materials such as metals, wood, cardboard. Hence, it is important to consider the sustainability of newly developed materials from a holistic perspective. Cseke et al. are the first to propose a framework accounting for the lifetime extension by self-healing [10]. They estimate the probability of failure, the probability of healing and restoring the function and the probability of user acceptance to avoid the need to produce a new product. They also relate what they call the healing capability maturity index (HCMI) with the level of autonomy of the healing mechanism, where the highest level of autonomy results in the highest HCMI score, which in a very simplistic manner is related to the difference in resources needed to effectuate the healing action. Cseke et al. describe a user acceptance level that is in a 1-to-1 relation with the product function and define 50 % as the acceptance limit. They compare two materials with different healing efficiencies, where one loses most of its product function already after a few cycles, while the other maintains a high product function upon consecutive healing cycles. They state that the two materials have the same life extension, as they reach 0 product function after the same number of cycles and, hence, could be considered equivalent. From an engineering point of view, successful healing is defined based on the ability to recover the product's function to the level that is adequate for the application. Economically and ecologically, the user acceptance limit should also be much higher than 50 %. For the example of a self-healing coating on the propellor blade of a drone, a tipping point was found where the self-healing product scores better than the conventional product, accounting for additional impact during fabrication of the self-healing product and accounting for the input and output during the healing action *versus* the considerable lifetime extension, avoiding the production of 4 new products. In a second example,



- **Waste is prevented** by extending the lifetime through healing
- Self-healing chemistries can be incorporated into **renewable resources**
- Reversible chemistries improve **processing and manufacturing**
- It allows **recycling of thermosets and elastomers**

Fig. 1. The circularity of self-healing polymers: The 12 green chemistry principles (left) are linked to each of the phases of the life cycle (right) and to the circularity principles (middle). The highlights (bottom) summarize the contributions of the self-healing chemistries and mechanisms to their overall sustainability.

Cseke et al. apply the framework to printed products, comparing self-healing polyurethanes with the 3D printing standard polylactic acid [11]. Here, the authors argue again that the lifetime extension due to self-healing mainly impacts the avoided production of new products, with a major impact of the electricity consumption during manufacturing. The environmental impact improvement due to self-healing thus depends strongly on the energy consumption and origin of the energy. These initial studies showcase the potential of self-healing materials through the useful service lifetime extension of related products by avoiding the production of new products to replace the damaged ones.

The aim of this review is not to perform a quantitative life cycle assessment of the different types of self-healing polymer classes or even within the different classes. This literature review qualitatively compares the best practices and serves as a toolbox for the further improvement of the sustainability of self-healing polymers. A critical assessment is performed that can be used by materials scientists, process engineers and application developers to make the proper choices for their desired products: (1) Different sources are compared for the 'extraction' of raw materials for the production of materials; (2) Various types of processing techniques are compared for the manufacturing into products and for the recycling of collectable waste streams back into useful materials and products; (3) The impact of the self-healing ability on the service lifetime extension is assessed for different self-healing mechanisms; (4) The service lifetime extension will also have an impact on transport logistics and also collection, sorting and recycling will have an effect thereon; (5) End-of-life considerations are made in case self-healing is no longer possible.

2. Sustainability of intrinsic self-healing mechanisms

Intrinsic self-healing polymers rely on the reversible breaking and (re)formation of dynamic bonds incorporated into their chemical structure. Two main types of dynamic bonds can be differentiated. *Physicochemical interactions*, such as hydrogen bonds [12] or electrostatic interactions [13], are used to assemble monomers, oligomers or macromolecules into *supramolecular networks*. Physicochemical interactions are weak interactions that are easily broken and reformed. They are often used to impart self-healing properties to (hydro)gels and soft elastomers. Generally, supramolecular networks have limited mechanical properties, while recovering their properties rapidly and efficiently, usually without the need for additional stimulation. *Dynamic covalent chemistries* are the result of chemical reactions that can either be reversed or where bonding partners can be exchanged upon activation by a certain stimulus, such as heat [14], light irradiation [15] or mechanical force [16]. *Dissociative dynamic covalent bonds* break (dissociate) upon the application of an adequate stimulus, while *associative dynamic covalent chemistries* exchange existing dynamic bonds without a net change in reaction conversion or crosslink density. In this section, supramolecular, dissociative and associative chemistries are discussed for their use in self-healing materials. A detailed understanding of the self-healing mechanisms forms the basis to assess the impact of the resulting dynamic polymer networks on the sustainability in the different phases of their lifecycle. Intrinsic self-healing chemistries are theoretically infinitely reversible. They provide the perspective of infinite self-healing capability and reprocessability, showing potential to drastically improve the sustainability of derived polymer networks.

2.1. Supramolecular dynamic interactions

Supramolecular chemistry studies the interactions between two or more chemical species joined by physicochemical interactions characterized by low bonding energies in comparison to covalent bonds. Nevertheless, high concentrations of these physicochemical interactions can lead to the formation of mechanically strong supramolecular networks. Physicochemical interactions are inherently dynamic, which makes them suitable for designing self-healing materials with high healing efficiencies and rates, even at room temperature [12,17]. Due to this dynamic nature, supramolecular materials can rapidly respond to multiple external stimuli, such as temperature, pH, humidity, light, electrical or magnetic fields [17]. However, the fast dynamic character of the interactions can potentially jeopardize their use for applications where robustness and structural integrity are needed.

Most biological systems base their structure and functionality on these non-covalent interactions. For example, proteins fold into their native conformation thanks to hydrogen bonding. The double helix structure of DNA is assembled through a combination of hydrogen bonds and π-π stacking interactions. Physicochemical interactions are also used in the animal kingdom to promote adhesion to the environment, reversibly, like geckos, or irreversibly, like mussels and other types of molluscs. This section covers the different non-covalent interactions that are used to create self-healing supramolecular networks: hydrogen bonding [18,19], metal-ligand coordination [20,21], ionic [22,23], host-guest [24], and π-π interactions [25,26], highlighting their potential advantages and drawbacks in the development of sustainable self-healing materials. A summary of these potential advantages and drawbacks can be found in Fig. 2.

Hydrogen bonding is among the strongest physicochemical interactions (4–50 KJ/mol) [27] . This strength and its directionality enable to form materials with decent mechanical properties and high reversibility that can be used to synthesize self-healing materials. The first example using this strategy to make self-healing elastomers was proposed by Leibler et al. [28], who used di- and tri- carboxylic acids derived from fatty acids to create a material with abundant hydrogen bonds. Thanks to their capability to form hydrogen bonds, its abundancy in nature, its versatility, and low price, strategies using fatty acids are commonly used in literature [29,30]. Following a similar strategy, polymeric materials with thermoplastic properties that can self-heal autonomously in just 30 s have been synthesized by melt polycondensation of the biomass-derived monomers citric acid and succinic acid [31].

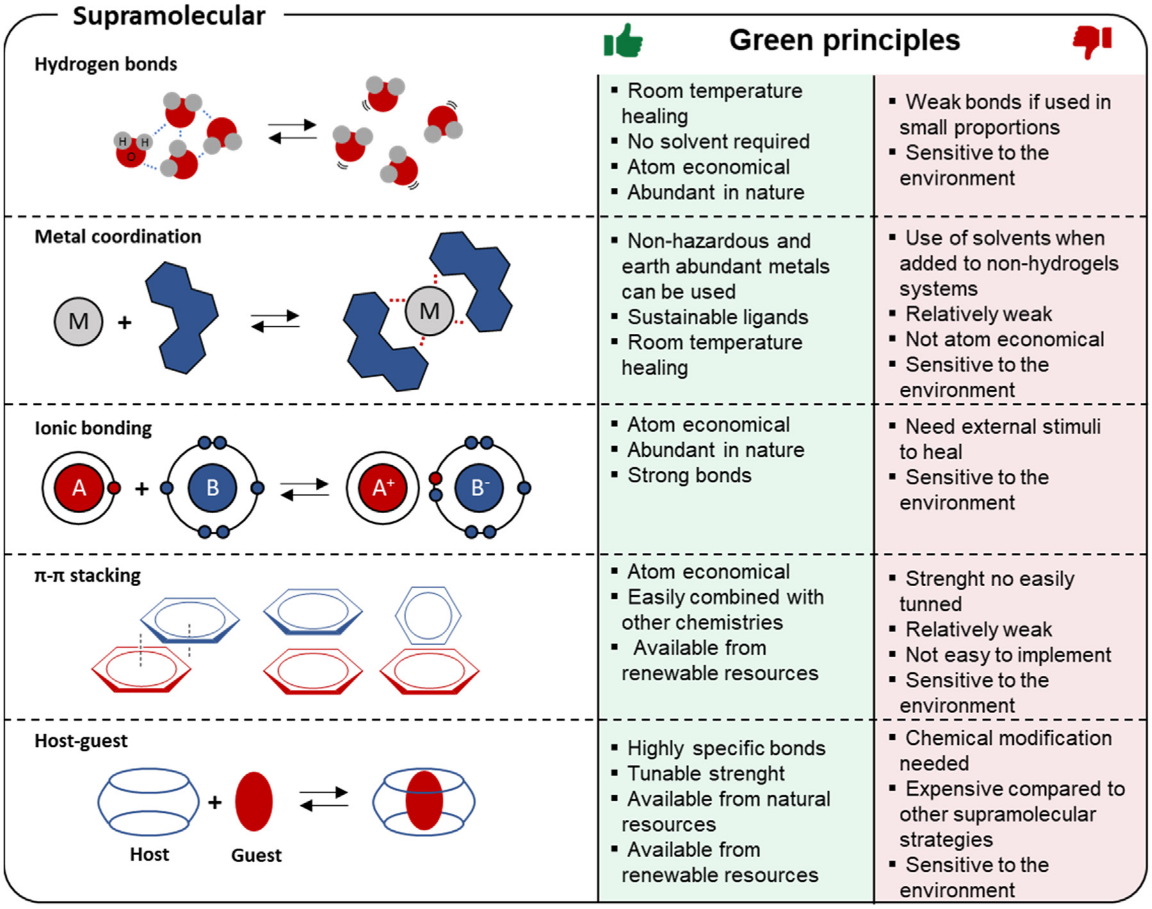
The strength of the hydrogen-binding crosslinks depends on the nature of the hydrogen bonding donor and acceptor pairs [32] and the multivalency of the interactions in the crosslinking moiety [33]. An example of this multiple hydrogen bonding is 2-uredio-4-pyrimidone (UPy) units [19], being able to create four hydrogen bonds per UPy moiety. UPy units are a promising choice in the field of self-healing polymers due to the potential high mechanical properties of the polymer, versatility and fast self-healing [34]. However, to become the leading technology for sustainable self-healing polymers, the synthesis needs to become greener, since toxic chemicals such as isocyanates or N, N-dimethylformamide are still commonly used during the synthesis [35].

Another common use of hydrogen bonding is to improve the filler-matrix compatibility in polymer composites. A good interaction between the filler particles and the host matrix is key for controlling the viscoelastic properties of the composite and to achieve a high reinforcement [36]. This strategy presents a simple but effective way to improve the sustainability of a given system as there exist a great variety of renewable fillers, such as nanochitin [37], nanocellulose [38,39], or lignin [40,41].

Hydrogen bonds are also often used in combination with other chemistries as a support to increase the healing performance and the mechanical strength, or as sacrificial bond to increase the toughness of the material [42,43].

Metal-ligand coordination is a type of non-covalent interaction between a metal ion (coordination centre) and one or more organic molecules (ligands) [44]. The strength of the metal-ligand coordination depends on the coordination pair, which influences the strength (5–400 KJ/mol) [27] and the number of the electrostatic interactions [44]. Additionally, metal-ligand coordination interactions can provide other functionalities such as luminescence, magnetism or catalytic properties [44]. A well-known example of such structures is present in mussels, where catechol clusters play a major role in the adhesion of these molluscs to rocks [45]. Inspired by this, Filippidi et al. synthesized hydrogels whose mechanical properties could be tuned by varying the pH thanks to the pH-sensitive metal-catechol links [46]. Carboxylate ligands are ideal for the preparation of self-healing materials thanks to their capacity to bind with metal atoms through monodentate, bidentate or polydentate coordination bonds [44]. They are widely available in bio-based materials such as carboxymethyl cellulose [47], lignin [48], cellulose-derived materials such as cellulose nanocrystals [49], hydroxymethyl cellulose [50,51], or even gelatine [52]. On top of that, they interact with the three most common metal centres: Zn^{2+} [48], Fe^{3+} [53], and Al^{3+} [47].

The highlights on sustainability of these type of materials are the great selection of benign and sustainable ligands, non-hazardous and earth-abundant metals, like Fe^{3+} and Zn^{2+}, and their compatibility with water-based systems [54]. On the downside, hazardous solvents like dichloromethane (DCM) or chloroform are still commonly used [21,55,56].



Supramolecular	Green principles 👍	👎
Hydrogen bonds	▪ Room temperature healing ▪ No solvent required ▪ Atom economical ▪ Abundant in nature	▪ Weak bonds if used in small proportions ▪ Sensitive to the environment
Metal coordination	▪ Non-hazardous and earth abundant metals can be used ▪ Sustainable ligands ▪ Room temperature healing	▪ Use of solvents when added to non-hydrogels systems ▪ Relatively weak ▪ Not atom economical ▪ Sensitive to the environment
Ionic bonding	▪ Atom economical ▪ Abundant in nature ▪ Strong bonds	▪ Need external stimuli to heal ▪ Sensitive to the environment
π-π stacking	▪ Atom economical ▪ Easily combined with other chemisties ▪ Available from renewable resources	▪ Strenght no easily tunned ▪ Relatively weak ▪ Not easy to implement ▪ Sensitive to the environment
Host-guest	▪ Highly specific bonds ▪ Tunable strenght ▪ Available from natural resources ▪ Available from renewable resources	▪ Chemical modification needed ▪ Expensive compared to other supramolecular strategies ▪ Sensitive to the environment

Fig. 2. Advantages and disadvantages of the main supramolecular chemistry types from a green chemistry perspective.

Ionic interactions can be used to form supramolecular networks called ionomers. Ion-Ion interactions are the strongest among the non-covalent interactions (200–300 KJ/mol) [27]. Ionomers contain as much as 20 % of ionic species, which tend to cluster forming physical crosslinks. The ionic bond strength benefits the mechanical properties of the network, while the self-healing properties are generally lower than the previously shown supramolecular networks. Consequently, ionomers often require external stimuli to rearrange and heal damage. The most common example of ionic interaction to form crosslinks in Nature is a salt bridge, which is partially ionic and partially hydrogen bonding [57]. This type of bond has also been largely used to synthesize self-healing materials derived from renewable resources by using the naturally abundant carboxylate and amine groups [58–60].

***π-π* stacking** refers to the interaction between aromatic rings by means of π orbital. They are relatively week, with a strength between 5 and 50 KJ/mol [27]. Such π-π interactions are highly important in many biological systems, especially in proteins or DNA whose structure is determined by such interactions. Despite its importance in biological systems, in synthetic self-healing polymers, these interactions have been solely used in combination with other supramolecular chemistries, such as hydrogen bonding and metal coordination, most likely due to a more difficult implementation in comparison to other supramolecular chemistries such as hydrogen bonding or metal-coordination bonds. Both types of bonds contribute to the mechanical properties and dynamic behaviour required for self-healing. An example of this synergetic effect is shown when combining Pt(II)…=Pt(II) and π-π interactions to make self-healing polymers [61].

Host-guest supramolecular networks are assembled by the non-covalent interactions between a host molecule and a guest molecule or ion that create a bond with high specificity. The most used strategy to achieve these types of interactions is by taking advantage of the hydrophilicity of the guest and the host molecules. For this reason, host-guest interactions are commonly used to synthesize hydrogels. One example is the hydrophobic cavity of β-cyclodextrin reported by Highley et al. [62,63] to prepare self-healing hydrogels. Hyaluronic acid was modified with β-Cyclodextrin (host) and adamantane (guest) to make a network that can be directly 3D-printed. Ren et al. developed a sensor used to monitor tissue deformations, using poly β-cyclodextrin (host), carboxymethyl- chitosan, Polyvinyl alcohol (PVA) and diamantane (guest) [62]. The material can adhere to wet tissue and can completely self-heal in just 15 s.

Remarks on the sustainability character of Supramolecular dynamic chemistry

Using supramolecular dynamic chemistries for designing self-healing polymer networks is favorable to develop polymeric materials with improved sustainability thanks to their readily availability in nature and their low toxicity. Most systems do not require any solvent or are water-based. Additionally, most of them self-heal autonomously or require only mild activation conditions, which makes them more energy efficient, being also reprocessable under similarly mild conditions. However, these sustainability advantages come at a price. In general, self-healing materials based on non-covalent interactions, present poor mechanical properties that are sensitive to external stimuli, such as temperature, humidity and pH, thus to the environment in general. Recent work has been undertaken for addressing or mitigating this environmental sensitivity [64–66].

In summary, supramolecular interactions are a very promising platform for improving the sustainability of self-healing polymeric materials, but their use is limited to applications that do not require high mechanical strength and thermal/chemical stability. Their main uses are thus far as hydrogels and to improve the compatibility of fillers. The most popular strategy is using hydrogen bonds, owing to their directionality, sensitivity and strength. The most used bio-based feedstock are polysaccharides, especially derivates of chitosan and cellulose. Finally, most common applications are in the biomedical field [67]

2.2. Dissociative dynamic covalent chemistries

In contrast to the physicochemical interactions used to create supramolecular networks, dynamic covalent bonds are much stronger, yet require a stimulus to break. Many chemical reactions can be reversed upon the application of heat, resulting in *thermoreversible* covalent polymer networks. The most popular example is the Diels-Alder cycloaddition reaction for which the equilibrium depends on temperature. Raising the temperature speeds up both forward and reverse reactions, while shifting the reaction equilibrium towards gradual breaking of the thermoreversible covalent bonds. *Photoreversible* covalent polymer networks are constructed using chemical bonds that can be formed at a certain wavelength and dissociated at a different one, such as anthracene photodimerization. Bond formation or dissociation only happens upon irradiation with light of the right wavelength. In view of self-healing properties, it is important that the covalent bonds can be broken in a reversible fashion upon the application of the mechanical force of the damaging action. Such *mechanoreversible* covalent bonds can reform upon removal of the mechanical force.

The application of the adequate stimulus results in reversible bond dissociation. At the location of stimulation, bonds dissociate depending on the intensity of the applied stimulus. Subsequently, the crosslink density changes, and mobility is created due to the abundant breaking of covalent crosslinks. This increase in mobility allows to fill damaged areas. In turn, when the adequate stimulus is removed, the dynamic crosslinks will recombine and “heal” the damaged area. Notably, the intensity and/or duration of the applied stimulus had an immense impact on the kinetics of this reversible interaction.

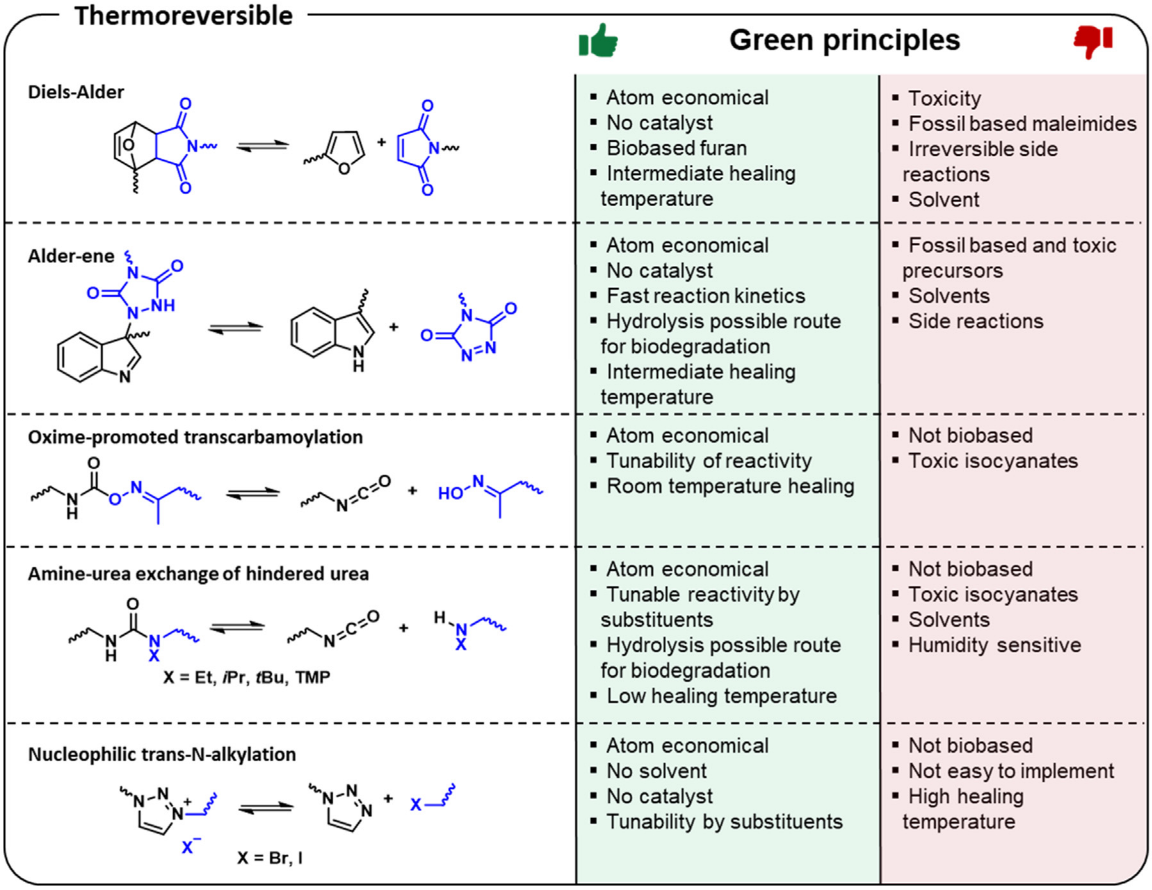
2.2.1. Thermoreversible covalent chemistries

Thermoreversible covalent polymer networks are characterized by the dynamic dependence of the reaction conversion, and hence crosslink density of the polymer network, on temperature and the time spent at that temperature. These reactions are dynamically reversible at every temperature, but the reaction rates and their equilibrium depend on temperature. Raising the temperature results in a shift of the dynamic reaction equilibrium between the forward and reverse reaction. This shift further results in a net change in reaction conversion, thus in a net lowering of the crosslink density. At a certain point, the connectivity of the polymer networks drops below the critical gel conversion and the polymer network transitions from predominantly solid to liquid-like behaviour. This is referred to as the reversible gel transition and is characterized by the gel transition temperature T_{gel}. Damage healing is typically performed at conditions where the material remains in a solid state, where structural stability is warranted (below T_{gel}), yet chain segmental mobility and chemical reactivity can be raised considerably at elevated temperatures to substantially increase the healing efficiency and rate. Above T_{gel}, the material becomes malleable and can be reprocessed using common thermal methods. Thermo-dissociative chemistries, their advantages and disadvantages, are summarized in Fig. 3.

Diels-Alder (DA) cycloaddition reactions between an electron-rich, conjugated diene and an electron-deficient dienophile to yield the corresponding [4 + 2]-cycloadducts are the most popular thermoreversible covalent chemistries. The most comprehensively studied DA combination is furan (diene) and maleimide (dienophile), which has been extensively reviewed by Gandini et al. [68,69]. The furan-maleimide combination is thermoreversible with the largest change in the reaction equilibrium between 60 °C and 110 °C [70]. Moreover, the reaction proceeds atom-economically without the need for a catalyst. Furthermore, bio-based furan derivatives such as furfuryl alcohol and furoic acid can be easily synthesized from furfural, which is a bio-based aldehyde obtained from the distillation of cereals [71]. This biosynthesis of furan derivatives significantly contributes towards a higher sustainability of the DA reaction. In contrast, finding bio-based and environmentally friendly procedures to synthesize maleimides is still extremely challenging. Maleimides are mainly synthesized from maleic anhydride, an important monomer in polymer chemistry that is produced from the oxidation of butane [72]. Although many studies on the biosynthesis of maleic anhydride have been recently performed, further improvement on the catalysis of the reactions is required to make the processes more efficient and sustainable [73]. Nevertheless, reacting maleic anhydride with bio-based backbone structures can greatly contribute to their sustainability by already substantially increasing the bio-based content in many applications.

Besides the challenges regarding the biosynthesis of maleimides, other characteristic properties of the furan-maleimide reaction have a negative contribution towards sustainability. First, maleimides and some furan derivatives are toxic and/or carcinogenic, even though sometimes made from bio-based resources. In addition, in most cases, organic solvents (often chlorinated) are required for the DA network development, especially when crystalline bismaleimides are used. Amorphous, liquid bismaleimides can overcome the latter disadvantage. Finally, the maleimide groups are sensitive towards irreversible side reactions at elevated temperatures [74]. Since the pioneering work of Chen et al. [75] in 2002 on the incorporation of reversible furan-maleimide DA bonds in crosslinked networks [76], many attempts have been made in optimizing the sustainability of DA-containing polymers. These attempts include the optimization of the furan-maleimide pair to improve the reaction kinetics and equilibrium conditions of the materials [70], the increase of the bio-based content [77–84], solvent-free network synthesis [85,86], and even room-temperature healing to avoid the need for a thermal stimulus [16,87]. This latter aspect of room-temperature healing was also investigated for Diels-Alder-based thermosetting materials, wherein the healing mechanism was controlled by diffusion [88]. Unfortunately, the time required for proper healing took several days at ambient conditions, which is not very beneficial regarding its sustainability. Nevertheless, further research on the efficient healing of high-modulus networks described by Van den Brande et al., revealed that a synergy between Diels-Alder chemistry and supramolecular hydrogen bonds could drastically influence the healing times at ambient temperatures. This synergy of different healing mechanisms may prove to be an essential strategy in the development of healable thermosetting materials [89].

Alder-ene reactions occur between an alkene with an allylic hydrogen and a compound containing a double bond (the enophile). The ene reaction can be a reversible click and transclick reaction, as is the case between a triazolinedione (TAD) and an indole. TAD reagents are known to be highly reactive towards delocalized π-systems such as alkenes. As a result, the TAD-indole forward reaction proceeds under extremely fast reaction kinetics resulting in



Thermoreversible	👍 Green principles	👎
Diels-Alder	▪ Atom economical ▪ No catalyst ▪ Biobased furan ▪ Intermediate healing temperature	▪ Toxicity ▪ Fossil based maleimides ▪ Irreversible side reactions ▪ Solvent
Alder-ene	▪ Atom economical ▪ No catalyst ▪ Fast reaction kinetics ▪ Hydrolysis possible route for biodegradation ▪ Intermediate healing temperature	▪ Fossil based and toxic precursors ▪ Solvents ▪ Side reactions
Oxime-promoted transcarbamoylation	▪ Atom economical ▪ Tunability of reactivity ▪ Room temperature healing	▪ Not biobased ▪ Toxic isocyanates
Amine-urea exchange of hindered urea X = Et, *i*Pr, *t*Bu, TMP	▪ Atom economical ▪ Tunable reactivity by substituents ▪ Hydrolysis possible route for biodegradation ▪ Low healing temperature	▪ Not biobased ▪ Toxic isocyanates ▪ Solvents ▪ Humidity sensitive
Nucleophilic trans-N-alkylation X = Br, I	▪ Atom economical ▪ No solvent ▪ No catalyst ▪ Tunability by substituents	▪ Not biobased ▪ Not easy to implement ▪ High healing temperature

Fig. 3. Overview of thermoreversible dissociative interactions with their corresponding advantages and disadvantages on the green chemistry principles.

room-temperature coupling in the order of minutes. This fast reaction kinetics are in sharp contrast with the Diels-Alder cycloaddition which proceeds in the order of hours. However, TAD-indole reaction has many similarities with the DA reaction. They both proceed atom-economically without a catalyst. Initially, the reversible character was described as a method to protect and deprotect indoles [90]. The group of Du Prez further discovered the effectiveness of this dynamic chemistry in crosslinked networks for recycling and processing properties [91]. They developed remouldable networks by reversibly crosslinking either an indole-functionalized polyurethane or methylmethacrylate with a bifunctional TAD compound. Both TAD-indole reactions proceeded within minutes at room temperature and the final networks were remoldable when heated above 110 °C for 30 min.

TAD reagents can be synthesized on large scale from readily available isocyanates with a high yield and without purification requirements [92]. In addition, indoles can be easily prepared from aromatic hydrazines and ketones via straightforward routes and inexpensive starting materials. However, although inexpensive, most of these starting materials are toxic or harmful for the environment and derived from fossil-based resources. In this regard, bio-based alternatives could improve the sustainability aspect in these networks significantly but are not yet investigated. Du Prez et al. investigated coupling commercially available plant oils such as olive oil with a TAD reagent via a TAD-ene reaction [93]. However, this type of TAD-ene reaction was not reversible.

TAD reagents are suspectable to side-reactions when certain conditions are applied as indicated in an extensive review on triazolides by De Bruycker et al. [92]. Most of these side reactions proceed at slower rates compared to the TAD-ene reaction but are still relevant to be considered as they slowly decrease the reversibility of the system. In addition, TAD molecules can slowly hydrolyse when exposed to water, which could be accelerated by the presence of acids or bases. Although hydrolysis can be seen as an unwanted side reaction, it offers opportunities regarding biodegradability [95].

Isocyanate reactions result in a multitude of dynamic covalent bonds, of which the oxime-promoted transcarbamoylation and hindered ureas are the most interesting to discuss. Traditional polyurethanes and polyureas are an important class of polymers due to their versatility, utility and performance. However, the poor recyclability and the usage of toxic isocyanates remain the two main limitations. As a result, finding new strategies to enhance the sustainability of these polymers is extremely important and therefore discussed in this review.

Oxime-promoted transcarbamoylation

Oxime-promoted transcarbamoylation is a dynamic interaction between an isocyanate group and an oxime resulting in poly(oxime-polyurethane). In contrast to transcarbamoylation in traditional polyurethanes [94,95], this mechanism is dissociative and occurs at lower temperatures without the need for a catalyst. The incorporation of this dynamic bond into reversible polymer networks was first reported by Liu et al. in 2017 [96]. They developed reversible crosslinked networks of synthesized multifunctional oximes with hexamethylene diisocyanate (HDI). The final networks showed outstanding mechanical properties reaching strain at breaks higher than 600 % combined with stresses at break around 50 MPa. When the networks were remoulded, a recovery between 82 and 90 % was obtained. Compared to traditional transcarbamoylation [94], these recoveries were more effective and obtained under milder conditions which shows the improvement in sustainability. Further work simplified the poly(oxime-polyurethane) synthesis by using commercially available oximes [97]. Moreover, these networks showed promising healing and moulding recoveries of almost 100 % at temperatures around 110 °C. Both oxime-promoted transcarbamoylations require higher temperatures to promote the dissociation of the poly(oxime-polyurethane) to heal or reprocess the networks. However, You et al. developed a room-temperature healable oxime-transcarbamoylation network which after only 6 h of healing, reached a recovery up to 96 % [98]. However, it must be noted that the overall mechanical properties were weak and did not allow the use in structural applications. As a result, the same group developed a new method of obtaining room-temperature healable networks with improved mechanical properties [99]. This new formulation involves the addition of metal complexes in the polymer structure . The promising mechanical properties of these networks combined with the efficient healing and moulding properties resulted in much research towards application possibilities [100]. In this way, the incorporation of the oxime-transcarbamoylation was already investigated as protective materials [101], flexible electronics [102,103], adhesives [104], soft robotics [105], 3D printing [106] and even for biomedicine [109].

Oximes are easily accessible and can be reacted with a variety of isocyanates which allows the development of different dynamic poly(oxime-polyurethane) displaying diverse viscoelastic and responsive properties. Choosing the oxime and isocyanate carefully, the transcarbamoylation temperature can be adjusted towards the desired conditions for application and processing purposes [107].

Hindered urea

The hindered urea is the result of the chemical reaction between an isocyanate and an amine containing bulky substituents. It was discovered that attaching bulky substituents onto the amide nitrogen atom weakens the amide bond and favours amidolysis under mild conditions without the need for a catalyst [108]. Cheng et al. first introduced the concept of hindered urea in polymer networks, as they synthesized a series of hindered urea bonds and related the bulkiness of the substituent to the forward and reverse reaction progression [109]. They discovered that the substituents have a crucial role in the reaction equilibrium and polymerization process, two processes that are extremely important in dynamic chemistry. They found that 1-(tert–butyl)−1-ethyl urea showed a promising balance between urea bond formation and dynamic character and showed healing efficiencies of 87 % (recovery of strain) when exposed to 37 °C for 12 h. The same group also developed recyclable poly(urea-urethane) thermosets which showed higher tensile strength compared to their previous work and could be processed and healed when exposed for only 20 min to 100 °C [110].

Analogous to oxime-promoted transcarbamoylation, bulky amines can be readily reacted with various isocyanates to adjust the final mechanical properties of the polymer. In addition, by changing the bulkiness of the substituents, one can easily manipulate both the equilibrium reaction and the polymerization process. These properties allow to finetune the polymer structure and reversibility towards desired application properties. In addition, amines and isocyanates are also readily available at low prices which makes it industrially viable. However, as this reversible chemistry is rather new, not many publications focused on the sustainability aspects. Solvents are still required in the initial synthesis, and bio-derived monomeric compounds have not yet been incorporated in these dynamic polymers. However, a study regarding the hydrolysis of hindered urea might be promising for the biodegradability of these networks [111].

Nucleophilic trans-N-alkylation reactions. Reversible trans-N-alkylation reactions involve the exchange of an alkyl group between a quaternary nitrogen compound and a halide counterion (often bromide or iodide). The incorporation of trans-N-alkylation dynamic chemistry in processable networks was first reported in 2015 by Drockenmuller et al. who developed reprocessable and recyclable ion-conducting networks based on the transalkylation of 1,2,3-triazoliumsalts [112]. A one-pot thermally induced cycloaddition of an α-azide-ω-alkyne monomer and 1,6-dibromohexane crosslinker resulted in reprocessable ion-conducting networks. Compared to previously reported crosslinked polyionic liquids [113], their network development did not require the use of a solvent or catalyst which shows the improvement of the sustainability for these types of materials, finding application in *e.g.* gas separation membranes [114] and adhesives [115]. Reprocessing of the networks was achieved at 160 °C for 60 min, though accompanied by a decrease in Young's modulus and stress at break during each repeated cycle, related to side reactions. Other reported networks based on 1,2,3-triazolium salts and perfluoropolyether show relatively high processing temperatures close to the degradation temperature range [116]. Nevertheless, further investigation of 1,2,3-triazolium reversible chemistry in network formulations showed that the rheological properties such as the viscosity and relaxation dynamics strongly depend on the chemical composition of the triazolium [117,118]. Especially the N-substituents on the 1,2,3-triazolium crosslinks have a significant impact on the reaction dynamics. Recent developments in trans-N-alkylation reactions resulted in transalkylation networks based on anilinium [119,120] and pyridinium [121–124]. However, the usage of solvents and the minimized versatility in structural variety compared to the trans-1,2,3-triazolium based networks reduce the sustainability aspect of these networks. A recent development in triazolium based networks is the incorporation of the difunctional 1,4-diazabicyclo[2.2.2]octane (DABCO) [125]. Although a solvent is required to develop these networks, they showed faster relaxation times compared to previously reported triazolium based systems [112,118]. Other attempts to improve the sustainability of these dynamic networks, such as the incorporation of bio-based alternatives, were up till the author's knowledge not accomplished yet.

Sustainability character of thermoreversible mechanisms

Although most of these dynamic chemistries have been known for many decades in organic chemistry, their integration into reversible polymeric networks is a much more recent concept. As a result, only a few studies regarding the improvement of the sustainability aspects have been performed. In almost all cases, solvents are required in the polymer development, and the usage of toxic chemicals, catalysts or high temperatures often limits the overall sustainability aspects. In addition, it must be noted that each specific attempt to improve the sustainability might be accompanied by negative contribution in other areas. As an example, the incorporation of bio-based derivatives might result in higher healing temperatures or higher solvent requirements.

When focusing specifically on the healing performance and energy requirements needed for successful self-healing and recycling, the Diels-Alder, Alder-ene and isocyanate-based reversible chemistries are currently the most promising. These chemistries result in successful healing at relatively low temperatures (around and below 100 °C) for short periods of time (< 30 min) with a decent recovery of the initial mechanical properties. In contrast, the trans-N-alkylation and other reversible mechanisms, such as the thiol-ene/yne, are often accompanied with high healing temperatures for longer periods of time. This of course contributes tremendously to the overall sustainability of the self-healing material and can therefore not be ignored.

Besides the dynamic chemistries described above, other dissociative mechanisms led to the development of promising healable or processable polymers in, for example, radical dissociations of alkoxyamines [126], S-S [127], and C–C [128], ring-opening/closing metathesis [129] or aminal transaminations [15]. However, only limited research regarding these dynamic chemistries has been performed whereas studies focusing on the optimization of sustainability were not yet performed.

2.2.2. Photoreversible covalent chemistries

Self-healing systems based on direct photoreversible chemistries involve no heating of any sort, instead, upon illuminating the polymer network with light of the appropriate wavelength, photoreversible dynamic covalent bonds can be reversibly formed or broken.

Photoreversible covalent chemistries can be used to render network polymerization reversible upon the application of a photostimulus, which enables damage healing via local UV-light exposure of the damaged surface [15,130]. Upon damage, photoreversible bonds are mechanically broken. After bringing the damage surfaces back into contact, the material is irradiated using light at relatively high wavelengths ($\lambda > 300$ nm, depending on the chemistry used), leading the reformation of the broken bonds and healing the damage [131]. The material may also first be irradiated using light at a lower wavelength ($\lambda < 300$ nm) to further break the photoreversible bonds to increase the local chain segmental mobility that may be necessary to achieve fast and efficient healing. Photochemical reactions are generally faster than the thermal curing and the photoreversible bonds can be activated locally and temporarily, as light irradiation offers efficient spatial and temporal control, which enables efficient, local damage healing triggered by light [132].

The major disadvantage of using light irradiation as a stimulus is the limited penetration depth of light waves into the material due to continued absorption by the cured material. Another disadvantage is the requirement of long irradiation of high energy UV light which inevitably results in undesirable irreversible side reactions especially during repetitive self-healing cycles. Therefore, photoreversible covalent bonds are mostly used in thin layer applications.

Up to now, most common photochemical self-healing polymers are based on the [2 + 2] cycloaddition of coumarin [133–135], cinnamate [136–138], thymine [139], and [4 + 4] cycloaddition of anthracene [140–144] as illustrated in Fig. 4.

Coumarin, a plant-derived natural product [145], has potential for increasing sustainability when incorporated into polymers. The [2 + 2] cycloaddition of coumarin is considered sustainable because the forward and backward reactions only require light, rather than chemicals or heat [146]. Coumarin derivatives can undergo cycloaddition with UV light higher than 300 nm to generate cyclobutene derivatives, which can form networks without the need for additional monomers or photo initiators. The double bonds can be regenerated using light below 250 nm, allowing for a reversible process. This feature provides networks with various properties, including self-healing [147,148]. For example; coumarin derivatives were embedded into bio-based polyurethane and synthesized polymer exhibits self-healing by low energy UV-light [149].

Another photoreversible dynamic covalent reaction example for self-healing purpose is based on [2 + 2] cycloaddition of cinnamate. Upon the damage of the elastomeric sample, the cleavage of the corresponding cyclobutane rings at the fracture interface were self-healed using UV irradiation at 280 nm within 10 min [137]. In another recent example; a bio-based, environmentally friendly material group based on tri-functional cinnamate-like monomers derived from lignin and glycerol were photopolymerized to form a photoreversible crosslinked polymer with photoresponsive self-healing properties [138].

Similarly, the reversible [4 + 4] cycloaddition of anthracene and dissociation of its photodimers offers opportunities to render polymer networks reprocessable and self-healing [144]. Anthracene dimerizes upon exposure to light of around 365 nm and the dimers dissociate either upon exposure to UV light at wavelengths around 250 nm or thermally [150]. The wavelength at which the photodimerization takes place depends strongly on the electronic effects of the substituents, ranging from 359 nm for unsubstituted anthracene to 372 nm when substituted with an ether group in the 9-position [151]. Brancart et al. studied the thermal dissociation kinetics of the photodimers of 9-substituted anthracene rings with different substituent chemistries [152]. It was found that the dissociation rates increase with increasing mesomeric electron-donating and -withdrawing substituent effects compared to the unsubstituted anthracene reference. More importantly, it was found that the decrease of the thermal stability of the photodimers could be related to the red shift of the maximum absorption wavelength, imposing a practical limit to the shift in photodimerization wavelength of the 9-substituted anthracene derivatives. To further push the dimerization wavelength to the visible light region, Van Damme et al. synthesized a 2,6-substituted donor-acceptor anthracene derivative with a maximum absorption wavelength as high as 380 nm [143]. Thermal dissociation of anthracene photodimers enables recycling and reprocessing using heat. The dissociated monomers can then be cured again using light irradiation of the right wavelength. Similarly, the thermal dissociation allows spatially and temporally well-controlled healing procedures by thermal dissociation to generate the necessary chain mobility and subsequent bond reformation using light irradiation heating [144]. UV light initiated radical reshufflings of sulphur based dynamic covalent bonds for self-healing purposes also widely studied. First disulfide metathesis [153], then thiuram disulfide [154] and later dithiocarbamate [155] and trithiocarbame [156] chemistries were demonstrated for self-healing purposes. Diselenide bonds on the other hand were designed to be activated with lights of longer wavelength such as visible light [157].

Remarks of sustainability character of photoreversible mechanisms

The photoactive process of reversible cleavage and formation of bonds can be considered as green and sustainable, since the forward and backward reactions require only light rather than the use of chemicals [133]. Essentially photopolymerization in general enables solvent-free conditions, avoiding the release of volatile organic compounds [158] in addition to the advantages lower electrical power input and energy requirements and low temperature operation. The use of low-energy UV-light sources for the regeneration step reduces the energy requirements for the process, leading to a more sustainable approach.

The photopolymerization of renewable monomers and oligomers and generation of bio-based polymers contributes toward the circular economy [158]. Avoiding the use of Hg-based lamps or more energetic UV wavelengths but instead the use of high intensity LED or laser diodes operating at definite near UV/visible wavelengths or moving the system towards a UV-free zone can be proposed for greener technologies with photinitiated chemistries [158]. Likewise, using sunlight, which is a cheap and sustainable energy source, attracts attention, especially in outdoor applications and curing large-surface products, without the need for any irradiation device. Another unfold can be reached with the invention of new photoinitiators that can absorb visible light that often is lost while using conventional mercury lamps.

2.2.3. Mechanoreversible covalent chemistries

Mechanochemistry is a very prolific field of chemistry that is becoming more widespread and has recently been named by IUPAC as one of the top ten chemical innovations that will make our world more sustainable [159]. Due to the solvent-free nature of most mechanochemical protocols, mechanochemistry is often introduced as a sustainable alternative for chemical synthesis. A re-

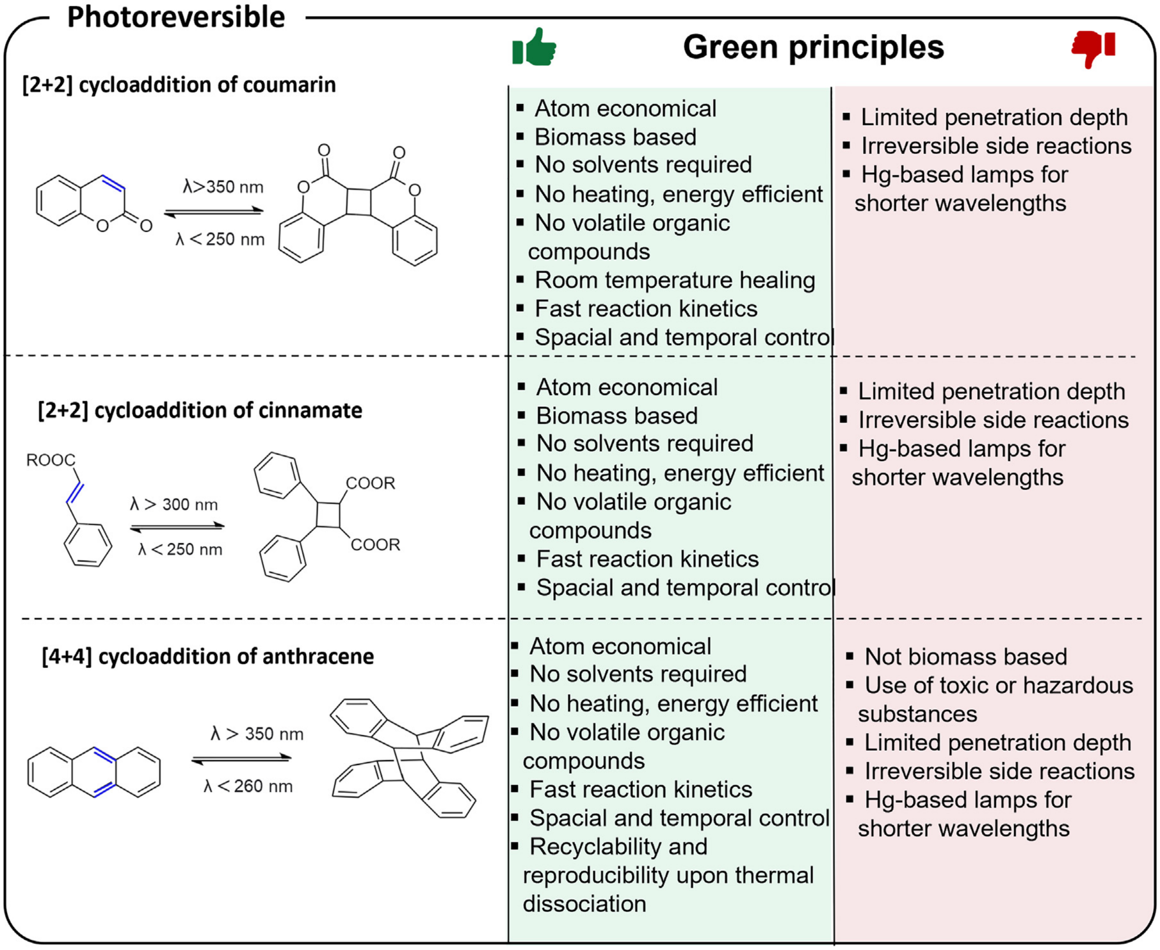


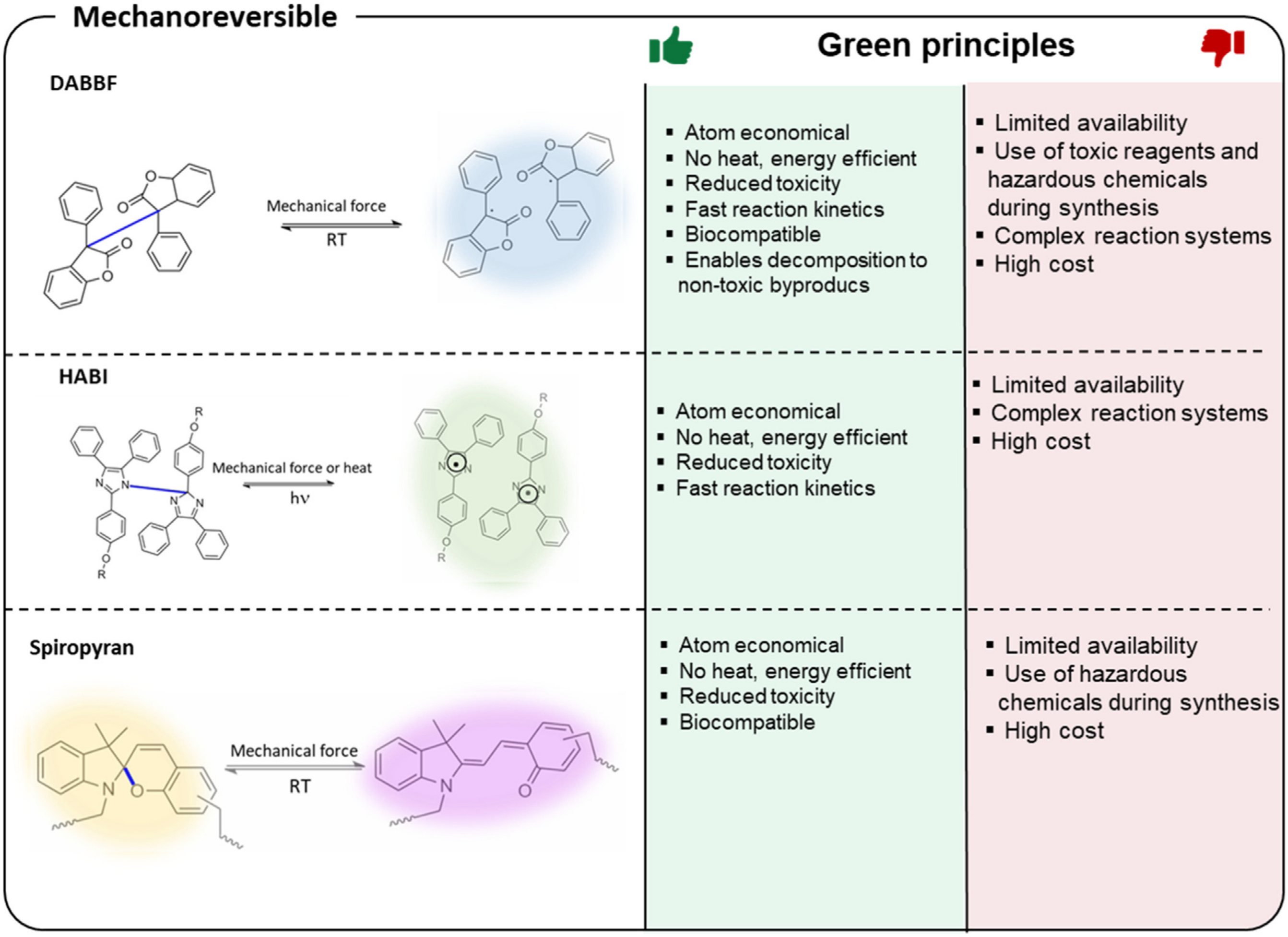
Fig. 4. Overview of the most common photoreversible dissociative interactions with their corresponding advantages and disadvantages on the green chemistry principles.

cent review [160] has clearly illustrated with a series of examples how mechanochemistry contributes to the fulfilment of twelve principles of Green Chemistry [2]. In terms of autonomous control of polymers' life cycle, waste reduction has the key importance for sustainability, and it requires life extension and recycling of polymeric material [161]. The idea of using mechanophores to extend the lifetimes of widely used polymeric materials by incorporating mechanically triggered damage sensing/reporting and healing functionalities was proposed as a functional analytical tool. Upon damage, mechanophores locally activate to report damage or initiate healing.

Mechanoreversibility is at the very basis of intrinsic self-healing. It is a prerequisite for damage healing that the covalent bonds are broken in a reversible fashion by a mechanical force to allow reformation of the broken bonds. In other words, mechanochemical reactions are induced by the direct absorption of mechanical energy. The force required for a reaction can be provided by macroscopic deformation of material through shearing, stretching, compression, extension, grinding or even sonication. Ideally, an autonomous mechanoreversible self-healing polymer should display a complete and repeatable self-repair directly and exclusively by way of the mechanical stimulus, without the need for additional (external) stimulation. Examples have been reported of the mechanical activation of thermoreversible covalent chemistries that could be healed autonomously, without the application of a thermal stimulus [16,87]. It should be argued that similarly, many thermally and photochemically reversible covalent chemistries could be mechanically activated, reversibly breaking the covalent bonds, allowing reformation under the appropriate stimulus. This section will focus on the various types of mechanoreversible covalent bonds that have been reported for self-healing polymers [160,162,163].

The reactive sites that undergo mechanochemical reactions are usually radicals in polymer chains. Mechanical force induced covalent bond activation is mainly maintained by mechanically sensitive functional groups, so called mechanophores that can quantify and locate force on the molecular scale [164]. Although not intentionally designed for self-healing features, several mechanophores offer materials new potential self-healing abilities due to basic chemistry to form new dynamic reversible bonds [165]. Mechanophores promote self-healing either via the production of reactive species, via activation of catalytic species or via disruption of equilibrium [165]. In fact, in most of the self-healing reports that includes mechanical force induced covalent bond activation, the mechanophores are mainly used for damage detection and self-reporting (via color change) instead of a direct healing stimulus. The healing stimuli in most cases is heating, but the healing mechanism happens via the mechanochemically active species, more specifically via dynamic C–C linkages.

Reversible dissociation of diarylbibenzofuranones (DABBF, Fig. 5) results into radicals upon applied mechanical force. Otsuka et al. used DABBF as a reversible linkage in self-healing polymeric materials, in gels at room temperature [166] and at various elevated temperatures [167], in bulk [168] and in nanocomposites [169]. The group used the strategy of utilizing DABBF in which the central C–C bond is in an equilibrium state between homolytic



Mechanoreversible	Green principles 👍	👎
DABBF	▪ Atom economical ▪ No heat, energy efficient ▪ Reduced toxicity ▪ Fast reaction kinetics ▪ Biocompatible ▪ Enables decomposition to non-toxic byprodcus	▪ Limited availability ▪ Use of toxic reagents and hazardous chemicals during synthesis ▪ Complex reaction systems ▪ High cost
HABI	▪ Atom economical ▪ No heat, energy efficient ▪ Reduced toxicity ▪ Fast reaction kinetics	▪ Limited availability ▪ Complex reaction systems ▪ High cost
Spiropyran	▪ Atom economical ▪ No heat, energy efficient ▪ Reduced toxicity ▪ Biocompatible	▪ Limited availability ▪ Use of hazardous chemicals during synthesis ▪ High cost

Fig. 5. Overview of the most common mechanoreversible dissociative interactions with their corresponding advantages and disadvantages on the green chemistry principles.

bond cleavage and recombination at room temperature. The radical species formed by the cleavage of DABBF enable electron paramagnetic resonance (EPR) spectroscopic assessment of the equilibrium in the polymer chains via the in-situ detection of the radicals [168]. It was reported that due to the dynamic nature of DABBF, the polymer showed self-healing at mild temperatures and good recyclability due to the bond exchange of the linkages and subsequent network rearrangement and re-casted samples show similar mechanical properties as the original ones [168]. Later, the same group reported damage self-reporting and self-healing in bulk and composite materials using dynamic covalent mechanophore [169].

Instead of a C–C bond, the cleavable C–N bond in the hexaarylbiimidazole (HABI) motif was also targeted by researchers [170]. Under the influence of heat, light or mechanical stress, two identical delocalized triphenylimidazoyl radicals were generated and the material turns from yellow to green [171]. Modification on the phenyl groups result in further colour variations [172]. Nevertheless, no further mechanochemical stimuli-triggered self-healing material has been reported for HABI-containing materials to date.

Another mechanoresponsive molecular switch that is used for self-healing polymers is spiropyran (Fig. 5). After many previous examples involving the spiropyran and self-healing relationship [169–171], the synthesis of another self-healable polymer with the incorporation of spiropyran mechanophore into the polymer main chain was reported [173]. Mechanically induced colour changes and thermally induced self-healing on the dynamic hydrogen bonding were demonstrated.

Besides only producing mechanoradicals in response to a mechanical stimulus, the radicals can further initiate the polymerization of monomers at the damaged location and thus, enable the self-reinforcement [171,174]. For instance, Matsuda et al. published a pioneering work (inspired by muscle training) on the mechanochemically initiated free-radical polymerization for regenerative self-strengthening [170]. Their strategy was applied on covalently crosslinked double-network (DN) hydrogels (one brittle and the other stretchable), by using the mechanoradical generation at the broken ends of the brittle network strands that result from repetitive mechanical stress. Generated mechanoradicals trigger the polymerization of a sustained monomer supply within the network and new polymer network is spontaneously formed, resulting in self-recovery, self-growth and thus self-strengthening of the compound. Their strategy is promising with some practical drawbacks, including the requirement for external monomer supply to the network and challenges related to mass diffusion that restrict the formation of gels.

Self-reinforcement of polymers is an additional feature of the self-healing strategy that can increase the sustainability and lifetime of the material. Recent studies have explored the use of mechanical force as a triggering stimulus for self-reinforcement. For example, Liu et al. engineered a self-healable PU elastomer with both thermo-responsive self-healing and mechano-responsive self-reinforcing properties. [101]. They created a reinforcing phase using stress-induced crystallization domains as physical crosslinking junctions, resulting in synchronous strengthening and toughening akin to natural rubber's strain-hardening phenomenon. Similarly, Eom et al. designed a thermoplastic polyurethane that operates in dual mode, responding to external stress through a reversible structural disorder to order transition via its H-bonding [175]. In static mode, the amorphous matrix promotes reversible self-healing bond exchange, while in dynamic mode, the amorphous phase transforms into a rigid metastable crystal, toughening and reinforcing the material. This material shows promise for biocompatibility.

In general, the development of mechanochemically activated self-healing systems among other various applications is found to be under development. The major limitation of a mechanochemical self-healing system is the activation of the material in the solid state, which is directly related to T_g of the material. A still unmet challenge is the development of an autonomic SH system in which the mechanical energy should be the main and only trigger, leading to the chemical bond formation without external intervention [165].

Remarks on sustainability character of mechanoreversible mechanisms

Mechanoreversible mechanisms for covalent chemistries will increasingly continue to be reported in the future, not only because mechanochemistry enables chemical reactivity under solvent free conditions, but also because of the significant contribution of mechanochemistry to more than one of the 12 green chemistry principles in a holistic manner. In addition, robustness of mechanoreversible chemistries as a sustainable alternative for synthesis will also enable discovery of chemical reactivity under mild conditions. Overall, the sustainability character of these chemistries is promising, as they reduce waste, energy consumption, and the use of harsh chemical reagents, making them an attractive option for developing sustainable materials. It is important to underline that the mechanochemical process itself does not necessarily render sufficient sustainability, environmentally friendly reagents and reactants should also be ensured. Furthermore, scaling up of mechanochemical reactions for possible applications and requirement of simpler monitoring techniques are still a challenge for practical reasons.

2.3. Associative dynamic covalent chemistries

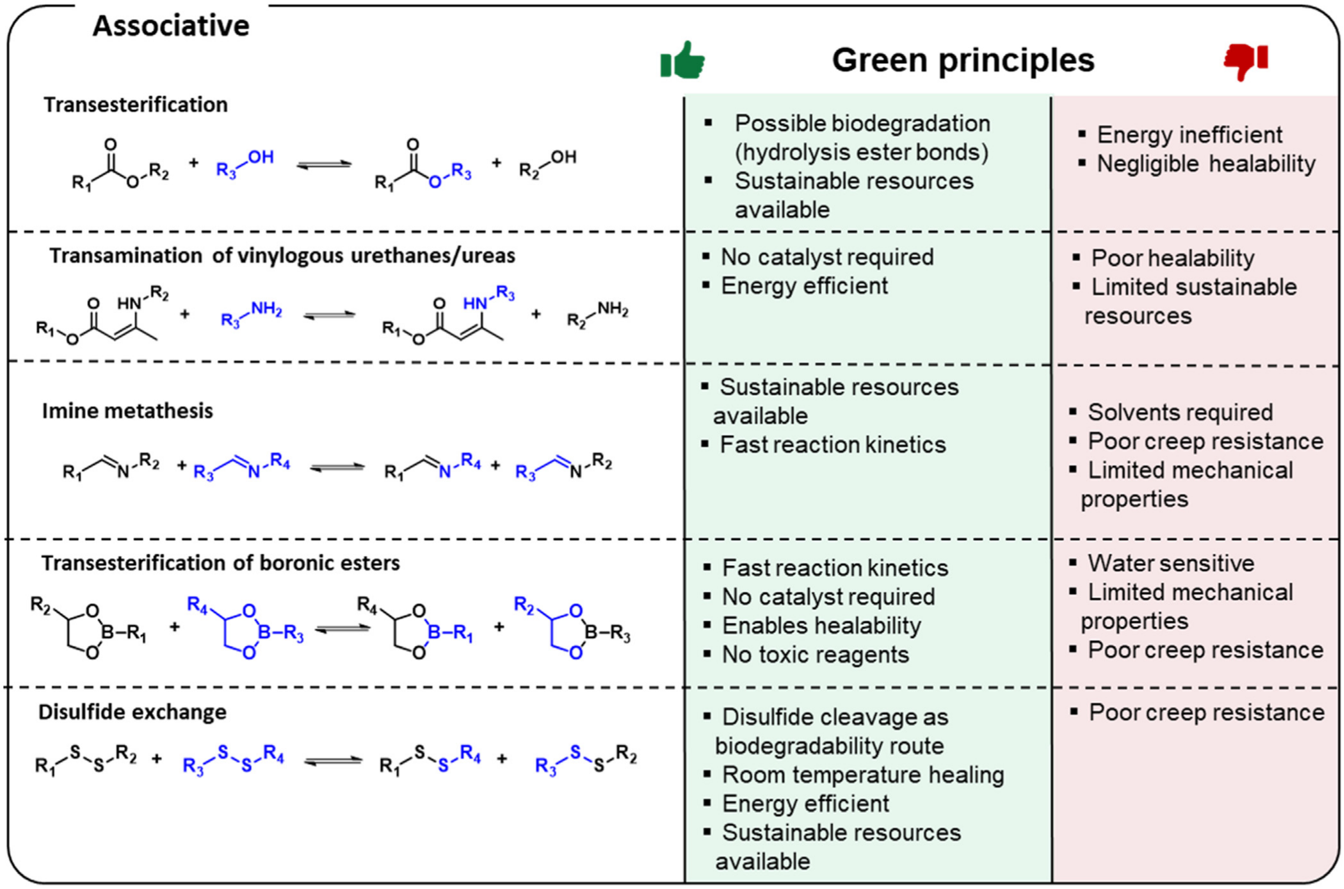
In contrast to dissociative dynamic covalent chemistries, where bonds first break upon the application of an adequate stimulus, associative dynamic covalent chemistries exchange bonds while keeping the crosslink density constant. A detailed analysis of both mechanisms, which strongly impact the material behaviour, may be found in a review from Winne, Leibler and Du Prez [176].

Dissociative exchange reactions follow a stepwise elimination/addition pathway, analogous to the S_N1 reaction. The first elimination step is endothermic. Rising temperature causes depolymerization and liberates free reactive moieties. The equilibrium constant between associated and dissociated crosslinks, and thus the crosslinking density, depends on the temperature. Increasing temperature decreases connectivity causing a loss of network integrity, whereas crosslinks reform upon cooling, restoring mechanical properties of the network [177].

Conversely, associative exchange reactions correspond to an equilibrium where the chemical entities are thermodynamically identical on both sides. In other words, the equilibrium constant is independent of temperature and equal to 1. These exchange reactions follow a stepwise addition/elimination pathway analogous to the S_N2 reaction [178]. A new crosslink is produced from the breakdown of an intermediate species formed after a reactive moiety has encountered an existing crosslink. The intermediate species, which possesses a higher degree of connectivity, exhibits a lifetime negligible in practice [176]. Hence, the network exhibits an essentially constant number of crosslinks at all temperatures, while the rate at which crosslinks are exchanged increases with temperature. This results in a gradual decrease of the viscosity due to topological changes that follow an Arrhenius relationship, while the connectivity remains constant. This thermal behaviour, which is unusual for polymers, was previously found in materials known as strong glass formers, like vitreous silica. Because of this resemblance, Leibler et al., who first described such materials in 2011, coined the term vitrimers [179].

As a result of their permanently crosslinked architecture, vitrimers remain insoluble in non-reactive solvents at all temperatures. These materials thus combine the advantages of both thermosets and thermoplastics, displaying dimensional stability at service temperature, good mechanical properties and chemical resistance, while at elevated temperatures they behave as malleable and repairable. This permanent structure is a prominent characteristic of vitrimers, contrarily to the distinction between dissociative *vs* associative dynamic networks, as several examples of dissociative dynamic networks demonstrated an Arrhenius behaviour over their reprocessing temperatures [176,180]. Like other polymer networks, vitrimers possess a glass transition temperature, depending on the crosslink density of the polymer network. While the exchange reaction takes place at all temperatures and speeds up gradually, researchers in the field of vitrimers deem it important to be able to describe the dynamic nature with a characteristic temperature. This characteristic temperature is called the topology freezing temperature T_v, above which the exchange reactions take place fast enough to perceive a viscosity lower than 10^{12} Pa.s [181]. Note that this is not a solid-liquid transition, but a threshold at which the material is deemed malleable. Above T_v, as the viscous flow shows an Arrhenius type dependence on temperature, rheological measurements can be used to determine the chemical activation energy. Since all net molecular motion leading to network rearrangements is controlled by a single chemical exchange reaction, the fixed crosslink density results in a flow behaviour controlled solely by a chemical reaction rate [182]. Stress relaxation measurements are the most common methods to determine the exchange rates of the dynamic associative reactions. Relaxation times can be determined by modelling the stress relaxation at different temperatures or estimated as the time required to relax 63 % of the applied stress. An Arrhenius plot gives access to an activation energy, found to be on average around 80–100 $kJ.mol^{-1}$ [180]. To overcome such energy barrier, high temperatures are required to obtain the desired mobility required for damage healing and reprocessing, and a catalyst is often unavoidable. This undesirable component is a limitation for the sustainability of such systems. Increasing the catalyst concentration increases the rate of exchange between the dynamic linkages, *i.e.* decreases the T_v. The catalyst nature and loading are also critical parameters defining the temperature windows for both usage and (re)processability [178].

First, vitrimers designed by Leibler et al. were based on transesterification in epoxy-based resins [179,183]. After this seminal work, numerous alternative chemistries have been explored [184], such as transamination of vinylogous urethanes [185,186] or ureas [187], olefin metathesis [188], imine metathesis [189–191], transesterification of boronic esters [192–194], exchange between hydroxyl and siloxanes in silyl ethers [195], or between thiols and thioesters [196], disulfide exchange [197,198], trialkylsulfonium salts exchange [199,200], diketoenamines exchange [201] or hemiacetal ester exchange [202]. A summary of the most common associative dynamic chemistries can be found in Fig. 6. Moreover, many efforts have been made to further enhance the overall sustainability of these associative networks. This section focuses on how associative covalent chemistries may be used to achieve intrinsic healing and how this relates to the overall sustainability assessment. The choice of (renewable) feedstocks and a more thor-



Associative	👍 Green principles	👎
Transesterification	▪ Possible biodegradation (hydrolysis ester bonds) ▪ Sustainable resources available	▪ Energy inefficient ▪ Negligible healability
Transamination of vinylogous urethanes/ureas	▪ No catalyst required ▪ Energy efficient	▪ Poor healability ▪ Limited sustainable resources
Imine metathesis	▪ Sustainable resources available ▪ Fast reaction kinetics	▪ Solvents required ▪ Poor creep resistance ▪ Limited mechanical properties
Transesterification of boronic esters	▪ Fast reaction kinetics ▪ No catalyst required ▪ Enables healability ▪ No toxic reagents	▪ Water sensitive ▪ Limited mechanical properties ▪ Poor creep resistance
Disulfide exchange	▪ Disulfide cleavage as biodegradability route ▪ Room temperature healing ▪ Energy efficient ▪ Sustainable resources available	▪ Poor creep resistance

Fig. 6. Overview of dynamic associative chemistries with their corresponding advantages and disadvantages on the green chemistry principles.

ough discussion of the processability and recyclability are the topics of later sections.

To go from the laboratory to industry, vitrimers must be suitable for recycling processes existing for thermoplastics [203] Moreover, the high temperatures often necessary to overcome the activation barrier for bond exchange reactions may degrade the vitrimer on repeated recycling [204]. To activate the cross-link exchange on relevant time scales, to speed stress relaxation up and tune the topology freezing transition broadness, catalysts are often necessary. Many vitrimer processes, especially transesterification, rely on the presence of an exogenous catalyst [205]. This is the case for epoxy vitrimers in general, polycarbonate vitrimers [206], and polylactide vitrimers [207]. Vitrimer chemistry based on transesterification has primarily utilized a limited number of catalysts including Zn-based [179], Sn derivatives such as $Sn(Oct)_2$ [207], tertiary amines [208,209], guanidines or phosphines [181]. Such organic or organometallic compounds are suspected of toxicity and ensure limited number of reprocessing cycles in case of premature degradation or leaching of the catalyst, undermining the recyclability of the material.

Design of vitrimers that do not rely on catalysis appears as a way to improve their sustainability. To achieve this goal, vitrimer systems based on fast exchange have been developed, that do not require any catalyst to afford short reprocessing times. The first catalyst-free vitrimer was based on vinylogous urethanes exchange [186]. Other examples of catalyst-free vitrimers based on fast exchange reactions were proposed since then. Catalyst-free transcarbamoylation has been reported in hydroxyurethanes, which would be activated by the mechanical stress attributed to the twisting of N lone pairs out of conjugation with the carbonyl π orbitals [94]. The polyhydroxyurethane networks synthesis from cyclic carbonates and amines provides one hydroxyl group per carbamate linkage, avoiding toxic isocyanates. Other examples of catalyst-free vitrimers based on fast exchange reactions were proposed, such as imines [191], trialkylsulfonium salts [199], oxime-esters [204], hemiacetal esters [202]. For example, a bio-based catalyst-free polyimine vitrimer content was prepared by combining in THF the 2,5-furandicarboxaldehyde (FDC) obtained from fructose with a diamine and triamine mixture prepared from fatty acids [191]. Due to the dynamic nature of the imine reversible bonds, the obtained films exhibited fast stress relaxation around room temperature. The furan dialdehyde is obtained from fructose through reactions involving catalysts, but the green synthesis of FDC from fructose is an active research area in particular studies using recyclable catalysts [191]. The low temperature needed for synthesis, the stability of the vitrimer in different aqueous environments, the reprocessability comparable to most vitrimers afford to this system a potential towards sustainable vitrimers. Still, a greener alternative to THF remains desirable. The same is true for most of the preparation methods for polyimine vitrimers that use questionable organic solvents, such as chloroform, dichloromethane, dimethyformamide, alcohols. Exploration of greener solvent-free synthesis routes for the polyimine vitrimers is needed [210].

A sustainable approach to disulfide bond exchange in aryl disulfides under effects of pressure has been recently demonstrated [211]. The catalyst-free exchange of aryl disulfides has been systematically studied under pressures in between 100-400 MPa, accessible in large-scale technological installations. Reactions were conducted in isopropanol, methanol and acetonitrile, all solvents that remain liquid within the range of the high-pressure experiments. The application of a high pressure allows high-entropy effects leading to non-catalytic disulfide exchanges. Besides sustainability, the one-pot approach is economically relevant.

Even transesterification vitrimers have been produced without an embedded catalyst, by obviating conventional ester bonds in favour of hetero-ester, as oxime-esters, [204] or phosphate esters [212,213].

As oximes have a lower pKa than aliphatic alcohols, it was hypothesized that the transesterification reactions in poly(oxime–ester) vitrimers would be possible without using an embedded catalyst [204]. Indeed, catalyst-free poly(oxime–ester) vitrimers affording high stretchability and malleability were synthesized using photochemical thiol–ene click chemistry [204]. The UV-polymerization of vitrimers opens a facile and efficient route for vitrimer manufacturing, which from the environmental point of view could compete with standard long processes in solution.

Carboxylic diacid may be in turn replaced by phosphoric acids. The bond energy of P–O is lower than the carboxylate C–O one, resulting in easier bond rupture generating phosphoric acid and hydroxy compounds upon heating, giving rise to catalyst-free transesterification in phosphate esters as a new dynamic covalent chemistry in polymeric networks [214]. Epoxidized natural rubber (ENR) also was crosslinked with biomass derived D-fructose-1,6-bisphosphoric acid to get a catalyst-free vitrimer elastomer crosslinked by β–hydroxy phosphate ester bonds [212]. The crosslinker benefits from the abundant hydroxy groups of fructose, forming numerous hydrogen bonds that dissipate energy, improving the mechanical properties of the material while maintaining the dynamic performance. In another study, as phosphorus is known as an effective element for use in flame retardants [215], phosphaphenanthrene derivatives presenting low toxicity have been used to synthesize intrinsically flame-retardant catalyst-free vitrimers reinforced by carbon fibres [213]. The material possessed reprocessability and repairability in 10 min at 200 °C. The epoxy matrix could be completely degraded in ethylene glycol, owing to abundant hydroxyl groups of the low mass diol and dynamic hetero-ester bonds, affording recycled carbon fibres retaining the chemical structure and mechanical properties at the same level as the original ones.

Increasing the number of exchangeable moieties was another way to enhance the reshaping abilities of catalyst-free systems. Using a large excess of exchangeable hydroxyl groups, Guo and Zhang reported a catalyst-free epoxy vitrimer based on a hyperbranched epoxy (HBE) synthesized via a solvent-free one step reaction and then cured with succinic anhydride [216]. Because of the abundant hydroxyl groups in the HBE which serve as both reacting moiety in curing and catalyst in the transesterification process, the curing reaction could proceed without an external catalyst. The high concentration of hydroxyl functions can provide a more polar reaction environment in which exchanges with ionic intermediates may be promoted [217]. The catalyst-free vitrimer used as a coating for metal plate exhibited good adhesion properties and can be healed by heating at 150 °C for 1 h after being scratched. In another study, a catalyst-free vitrimer was prepared by curing of a bio-based dimer acid and a tetrafunctional glycidylamine epoxy [218]. The network contains abundant tertiary amines which may serve the transesterification. In addition, the elastomer is degradable in water at above 170 °C without using any catalyst, again because of the tertiary amines that may catalyse the hydrolysis of the ester bonds. The degraded product is repolymerizable to give new crosslinked elastomers. It is likely that the influence of the amines in this system may be associated to the neighbouring group participation (NGP) effect which is described just below.

Indeed, another strategy relies on chemical functions near the exchangeable bond to enhance the reaction rate. This strategy is inspired by organic chemistry in solutions, where this effect is called either NGP when the accelerating substituents are covalently bonded to the reaction centre during the exchange, or internal catalysis for effects at longer distance such as electrostatic interactions, steric effects, or weak bonds [219]. Vitrimers with internal catalysts are becoming increasingly relevant for environmental and performance reasons [220]. Altuna et al. already reported in 2013 a catalyst-free dynamic polymer network relying on an additional carboxylic acid present on the citric acid (CA) used to crosslink epoxidized soybean oil (ESO). They assigned this effect to the proton derived from the CA dissociation in water that would catalyse the epoxy–acid reaction [221]. Alternatively, it has been suggested that the presence of an unreacted free carboxyl acid near ester bonds could be an early example of internal catalysis [217]. Similarly, the first vitrimers reported by the Leibler group also incorporate internal catalysis, as the beta–hydroxy ester links catalyse the transesterification reaction, due to the hydroxyl–ester proximity [222]. Later, Altuna et al. introduced in epoxy vitrimers a tertiary amine which catalysed transesterification reactions through general base catalysis [209]. The tertiary amine is generated *in situ* and becomes covalently bonded to the epoxy precursor by adding secondary or primary amines to a large excess of the epoxy monomer. This neighbouring tertiary amines strategy was already used to enhance the transesterification rate in boronic ester networks [194]. A novel activating agent as the alpha-difluoromethylene group was reported recently [223]. The strong fluorine electronegativity enables CF_2 groups to activate the epoxy–acid polymerization, and more interestingly also the transesterification reaction on adjacent esters. This catalyst-free green vitrimer was reprocessable and underwent 10 consecutive cycles without loss of mechanical properties.

Remarks on the sustainability character of associative dynamic covalent bonds

In terms of dynamicity and relaxation dynamics, associative dynamic covalent bonds, in general, fall in the slower range. This characteristic has a clear advantage in comparison with other chemistries, which is a higher mechanical stability, especially at higher temperatures. However, this comes as a disadvantage when talking about self-healing, as the great majority of associative system do not allow self-healing. It is also a disadvantage when it comes to reprocessability and recyclability as higher temperatures, times and pressures are needed. In order to speed up these exchange reactions, catalysts are needed in most cases, which doesn't help to the overall sustainability of the system. Thanks to its higher mechanical stability, systems based on associative dynamic covalent bond will have a major impact on the polymer network industry, but not for its self-healing capabilities, but its reprocessing and recyclability. Currently, numerous efforts and resources are being used to speed up these systems, by developing new chemistries or even combining different chemistries in one system, which would ease this trade-off and make associative dynamic chemistries competitive also in the self-healing polymers landscape.

3. Sustainability of extrinsic self-healing mechanisms

Extrinsic self-healing (SH) polymeric systems rely on the incorporation of an external healing agent within a non-self-healing polymer matrix as a method to repair damage incurred. The healing agent is stored in reservoirs that are dispersed in the polymer matrix. When damage occurs, the shells of the reservoirs break and release the liquid healing agent, which flows into the damage volume and reacts to restore the material properties. The healing agents are stored in discrete hollow fibres [224], microcapsules [225], vascular networks [226]. This approach was introduced by White et al. and further optimized during the past two decades [227]. One of the greatest advantages of extrinsic self-healing systems is their healing autonomy when damage is incurred. This is

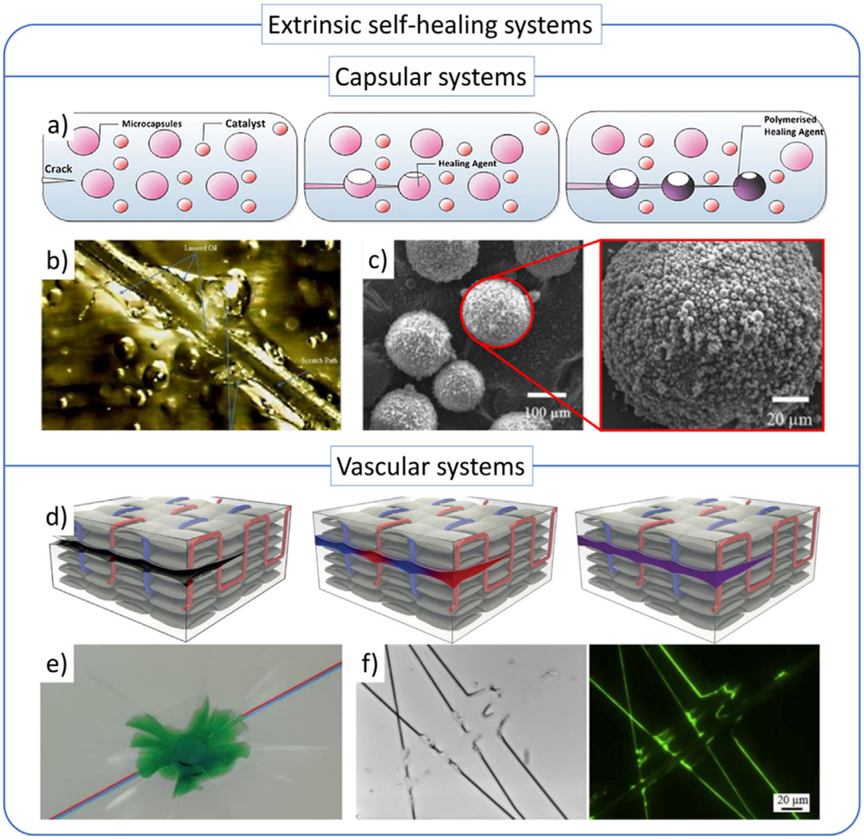


Fig. 7. a) Self-healing mechanism of capsule-based self-healing materials (Copyright 2016. Reproduced with permission from Informa UK Limited [[279]). b) Damage healing of a capsule-based self-healing epoxy coating using linseed oil as healing agent (Copyright 2018. Reproduced with permission from Elsevier [243]). c) Hierarchical microcapsule for repeatable release of healing active agents (Copyright 2020. Reproduced with permission from Elsevier [275]). d) Self-healing mechanism of vascular self-healing materials (Copyright 2014. Reproduced with permission from John Wiley & Sons, Inc. [[280]). e) Healing of large volume radiating cracks in a vascularized specimen able to efficiently repair damage diameters up to 8 mm (Copyright 2014. Reproduced with permission from Science AAAS [281]). f) Fluorescence image of damaged pullulan nanofibers releasing the healing liquid agent (Copyright 2018. Reproduced with permission from Elsevier [[282]).

due to the incorporation of efficient catalytic systems, leading to fast and high reaction conversions under moderate temperature conditions, hence resulting in a high healing performance without the need for external intervention. This process is illustrated in Fig. 7a.

3.1. Capsule-based self-healing systems

The variety of extrinsic SH materials, their processing, and healing performance have been sufficiently developed to become industrially attractive, especially in the corrosion-protective coatings, building materials, and dentistry [228]. A detailed description of the fundamentals of these capsule-based systems, formulation, healing pathways, and applications have been extensively reviewed during the last years but are outside the scope of this review [161,229,230]. Several healing chemistries have been successfully applied to perform the healing action. The most popular healing pathway is based on the ring-opening metathesis polymerization (ROMP). This process relies on the reaction of dicyclopentadiene (DCPD) or other norbornene derivatives in the presence of a catalyst, typically a Grubbs' ruthenium catalyst, which has been previously homogeneously dispersed within a suitable host matrix, normally an epoxy crosslinked network. However, other reaction mechanisms have been also explored, including polymerizations based on polycondensation, addition, cationic, anionic or free-radical reactions. A schematic illustration of this healing process can be observed in Fig. 7a. For a more detailed explanation of the proposed routes, the readers are suggested to consult the review of Zhu *et al.* [230].

From a sustainability perspective, extrinsic self-healing materials exhibit the great advantage of being highly selective, fast, and efficient under mild conditions because of the presence of a catalyst. However, the main disadvantage resides in the irreversibility of the healing process. After the healing agent is consumed, the healing potential diminishes or becomes entirely depleted at the original damage location, limiting the healing ability to a finite number of cycles. This is a considerable limitation in terms of waste prevention, as reprocessing or recycling of severely damaged extrinsic SH material is limited. Extrinsic self-healing polymers are almost always based on irreversibly crosslinked networks. This is of great importance since the covalent crosslinks of the matrix must transfer the damaging forces to the capsule walls to leach the healing agent. Otherwise, the crack would just propagate through the host matrix, following the capsule-matrix interface along the crack propagation path, while leaving the microcapsules intact. Thus, strong covalent bonds forming the matrix, as well as enough compatibility between the matrix and the capsule shell (with matching moduli) are needed to accomplish the release of the healing agent. Note that most of these systems rely on glassy thermoset matrices. This aspect adds significant value to the sustainability of these materials, as glassy thermosets are often nonreprocessable or difficult to heal when using dynamic chemistries. However, the existence of such bonds jeopardizes other aspects of the life cycle of extrinsic self-healing systems such as their recyclability or (bio)degradability. One promising route towards the reprocessing of these materials is the use of thermoplastics as thermally processable matrix instead of irreversibly crosslinked networks. This allowed, for example, the exploitation of capsule-filled thermoplastics such as high-impact polystyrene for additive manufacturing [231]. There are several opportunities to improve the sustainability of conventional extrinsic SH compositions. Firstly, most of the feedstock employed as healing agents arise from non-biobased sources. To the best of our knowledge, there are only a few attempts reported in literature showing the use of bio-based healing agents that can proceed using the mentioned healing mechanisms. Alkyd, starch or plant-based protein resins resulting from the polycondensation reaction of a polyhydric alcohol, a polybasic acid or their anhydrides, and fatty acids [232] or triglyceride oils [233,234] have been found to be promising candidates for healing agents. Similarly, plant-based soy proteins [235–237] or starch-based [238,239] can undergo similar nucleophilic reactions when connected with suitable crosslinkers (regularly carboxylic acids or aldehydes) to produce rigid resins. Additional functionalities such as UV aging resistance have been achieved by dispersing sodium lignosulfonate as emulsifier to prepare lignin-based rigid capsule shells [240].

In addition, vegetable oils are exhibiting promising features to undergo healing reactions via an auto-oxidative drying mechanism in the presence of air. The uptake of oxygen free radicals by the unsaturated double bonds of plant oils allows the creation of crosslink centres or other degradation products that can polymerize and repair cracks. Thus, highly unsaturated vegetable oils such as almond oil [241], chia oil [242], linseed oil [243–246], soybean oil [247,248], tung oil [249] or clove oil [250] have been successfully employed as healing agents following this procedure. An example of vegetable oils as healing agent is shown in Fig. 7b, proving the efficacy of linseed oil to seal damage. A strong limitation of this strategy is the oxygen requirement to perform the healing oxidation reaction, hence the application of these materials in other environments such as underwater (especially interesting for corrosion-protective coatings) remains an unsolved issue. A more detailed description of these aspects can be found in the recent review authored by Ataei et al. [251]. A similar approach can be followed for the composition of the capsule shells found in literature. Less exhaustively, some authors have explored the use of renewable resources such as cellulose or cardanol for the formulation of microcapsules suitable for self-healing purposes. Finally, the combination of the previous approaches with a compatible sustainable polymer host, such as lignocellulosic feedstocks, green epoxy resins, or natural rubber, could lead to composites prepared from fully renewable resources.

The use of hazardous or toxic compounds is an important green aspect to be considered, especially for extrinsic SH systems applied as biomaterials for health-related applications such as dentistry or orthopaedics [252]. The most popular approach to prepare microcapsule-based SH systems is by the ring-opening metathesis polymerization (ROMP) reaction of dicyclopentadiene (DCPD) in the presence of a Grubb's catalyst. However, there are some concerns about the use of these compounds due to their toxicity. Seeking safer alternatives is a must when considering their application in biomedical fields. Strategies such as the free-radical polymerization of tri(ethylene glycol) dimethacrylate and *N*,*N*-dihydroxyethyl-*p*-toluidine in the presence of benzoyl peroxide as initiator have been proposed as potential biocompatible solutions. A different but efficient approach consists of the encapsulation of an aqueous polyacrylic acid solution which reacts with a strontium fluoroaluminosilicate powder previously dispersed in the matrix. When the capsules break and both components physically interact at the damaged crack, the reaction triggers the formation of a glass ionomer cement with great robustness and healing efficiency in water medium [253]. The current progress in the fields of extrinsic SH biomaterials has been recently reviewed by other authors [228,252]. Despite the recent encouraging progress in the field of biomaterials, toxicity remains a concern for scaling up many extrinsic SH applications and exploring new potential applications. Thus, finding outperforming combinations of green and efficient catalysts that can replace Grubb's catalysts (or other investigated toxic alternatives such as [254] or di-n-butyltin di-laurate [255] biocompatible healing agents and cleaner synthetic protocols is envisioned as a potential sustainable improvement.

Methods used for the microcapsules processing can also jeopardize the sustainability of extrinsic self-healing systems. Typical synthetic processes are in-situ and interfacial polymerizations. These polymerizations are performed via oil-in-water emulsion methods. Zhu et al. highlighted in more detail the most common encapsulation processes for the preparation of extrinsic SH systems [230]. These emulsion polymerizations are well-known to be sustainable mechanisms as water (recognized as the preferred solvent for green processes) is the major synthesis medium phase. Water utilization is encouraged from a chemical perspective and acts as an excellent heat dissipator. An appropriate heat dissipation route is of great importance for highly exothermic polymerization reactions, thus enhancing the energy efficiency of the process. Emulsion polymerization strategies under non-isothermal conditions are recognized to improve even further the energy efficiency of the process [256]. Other greener protocols to maximize the energy efficiency of the polymerization processes consist of the use of alternative energy sources such as UV–Vis exposure [158], ultrasound pulses [257,258], or microwave irradiation [259]. UV–Vis light irradiation is growing as a popular choice for the preparation of novel extrinsic SH systems. This trigger allows not only the encapsulation of the SH agent via photopolymerization, focusing mostly on thiol-ene [260,261]) or polyacrylate [262,263] shells, but also as a temperature-substitute efficient healing trigger [264–266]. Ultrasound has been reported to be an interesting source for the preparation of highly dispersed and nanosized capsules with great SH performance [267]. To the best of our knowledge, microwave-responsive extrinsic SH systems have been reported only for asphalt materials, hence polymer-derived systems are not yet examined. Similarly, alternating magnetic fields on microcapsules filled with magnetic nanoparticles are proven to show an efficient capsule content release but remains unexplored for SH polymer applications [268].

Emulsion polymerizations under batch conditions generate waste containing residual unreacted monomer, solvents, and surfactants, among other additives. These not only endanger waste prevention but might also be troublesome owing to their hazardous nature. Waste treatment methods such as physical (evaporation, solvent extraction, ion-exchange resins, or supercritical CO_2 extraction) or chemical (posterior reaction of residual monomer to enhance the process yield or make it removable) extraction methods are potential alternatives to promote waste reduction of batch emulsion encapsulation methods [269,270]. In addition, other droplet-based or encapsulation techniques based on miniaturization and/or solvent removal during the polymerization step are promising candidates to be used as a way for waste minimization and overall process simplification [271]. In this regard, more recent approaches such as continuous-flow microfluidics [272,273] or (electro-)spraying emulsion [232,247,274] arise as excellent alternatives to conventional batch techniques for highly efficient and more environmentally friendly encapsulation processes. Shifting towards an industrial-scale polymerization can be troublesome for the previously mentioned alternative encapsulation methods due to their low throughput. In addition, Pickering emulsions allow the preparation of hierarchical multi-storage microcapsules that can undergo repeatable healing cycles [275] as illustrated in Fig. 7c. Besides, it is well-known that production scalability leads to reactor fouling under batch conditions because of particulates and aggregated polymers deposited onto the reactor wall, limiting the reaction output yield [276,277]. Fouling is more pronounced on heated surfaces, required to keep the bulk batch reactor temperature constant when considering large-scale emulsion production [278].

3.2. Vascular self-healing systems

Despite the clear advantages that the extrinsic SH systems offer, their main shortcoming resides in the irreversible healing agent consumption when the damage is healed. To overcome this issue, inspired by biological systems, researchers attempted to encapsulate the healing agents within hollow fibers or vascular networks. In such manner, the healing agent can be continuously supplied from other material locations (Fig. 7d). This concept was initially adopted by White *et al.* and further expanded, showing materials that can be successfully healed over 30 times when the damage is incurred at the same location [227,283]. Thus, vascular networks can be considered as a successful improvement in the extrinsic SH materials sustainability by considerably upgrading their healing efficiency and operable lifespan. In addition, the interconnection between the vascular channels allows the material to leach larger volumes of healing agent throughout the damage as compared to the microcapsules' counterpart, where the healing agent volume is restricted to the capsules' diameter [284]. As shown in Fig. 7e, this is translated into the capability to heal large damage volumes using vascular networks, finding reported systems able to successfully repair damage larger than 3 cm [280,281]. Also, more complex damages such as delamination in laminar composites can be healed using a three-dimensional vascular network approach [280].

Considering the assessment of the sustainability concepts of this review, similar conclusions can be withdrawn out of these materials when compared to the capsule-based systems. There exist three main routes towards the fabrication of vascular constructs for extrinsic SH systems: Glass tube integration, subtractive manufacturing, and spinning techniques. Shields et al. reviewed these techniques for self-healing applications [226]. Glass tube integration makes use of hollow glass fibres as hollow channels. Despite the low price and chemically inert properties, significant drawbacks such as too high brittleness for processing or the possibility to create only one-dimensional configurations make them not the best choice in terms of performance. Thus, the two most popular choices for the preparation of vascular networks for SH applications are subtractive and spinning techniques. In subtractive manufacturing t2D or 3D fibre networks are first deposited, being then removed in a post-treatment step, generally by melting/vaporization or flushing with a suitable solution, leaving hollow structures within the host matrix. From a sustainable perspective, this technique deals with waste formation as a remarkable issue to eliminate the fibres but can be partially compensated using biobased or biodegradable feedstocks such as gelatin [285] or polylactic acid [280,286]. To date, this approach is mostly evaluated on non-polymeric matrixes such as concrete or ceramics, hence more research needs to be conducted to expand this method to SH polymers. Thus, the most exploited method to manufacture SH polymers with embedded vascular networks are spinning techniques, with electrospinning being the most popular [287]. More precisely, coaxial electrospinning arises as a cost-effective and scalable technique to produce core-shell or sacrificial fibres to encapsulate the self-healing agents (Fig. 7f). This is a promising technique from a sustainability perspective since there are no residues generated and uses mild synthesis conditions. Energy savings are proven to be feasibly optimized, for example, substituting conventional metallic spinnerets by Teflon-based ones to convey more efficiently the electrostatic energy to the working fluid [288].

Healing agents and matrices compositions are analogous to those reported for classic microcapsules extrinsic SH systems. To date, the most popular choice as healing agent for hollow fibre or vascularized systems is the ROMP reaction using DCPD with Grubbs' catalyst, owing to its efficient healing performance [289,290]. Other alternatives, such as bisphenol A, are available in literature to heal epoxy resin matrices, yet exhibiting similar sustainability concerns [291]. Less hazardous alternatives such as polydimethylsiloxane exist, but they often have much longer curing periods [292]. Thus, the evident lack of sustainable and efficient solutions extends to channel-based systems as well. To the best of our knowledge, the use of vegetable oils as healing agent in vascular SH systems remains unexplored. Regarding fibre synthesis resources, pullulan [282,293,294] or PLA [295] sacrificial fibers have been successfully manufactured via co-axial electrospinning. Despite these notable advancements in the development of more sustainable solutions, significant opportunities for further enhancement remain unexplored, particularly through the utilization of other established renewable feedstocks. An overview of the different classes of extrinsic self-healing systems, together with their corresponding advantages and disadvantages related to sustainability, are summarized in Fig. 8.

Remarks on the sustainability character of extrinsic self-healing systems

It has been extensively proven that imparting resins with extrinsic self-healing features can significantly prolong their effective usage time. Their rapid, autonomous healing mechanism, capable of repairing even large damage, provides an efficient pathway to restore the mechanical integrity of these systems. Additionally, the synthetic simplicity of capsular systems enables their cost-effective production at industrial scales. Nevertheless, there are certain boundaries to be addressed to ensure the sustainability of these systems, spanning from their production to their end-life.

Capsular systems exhibit limited healing cyclability due to the consumption of the healing agent. This limits not only the operational lifespan of the material but also hinders certain aspects of its life cycle, such as reprocessability, recyclability, or (bio-)degradability. Vascular networks offer a partial solution to this issue, as interconnected channels can effectively exhaust the healing agent from different regions of the matrix to the damage location. This approach has demonstrated complete recoveries for up to 20 healing cycles at the same spot. Furthermore, investigating pathways for reprocessing these systems, such as the use of thermoplastic polymer matrixes, offers a promising avenue for advancing in the field of extrinsic self-healing materials in a manner that aligns with both environmental and functional considerations.

Another route to enhance the sustainability of these systems involves exploring novel bio-based alternatives to replace conventional synthetic feedstocks. This applies to the healing agent, the reservoir shell and, most significantly, the host matrix, given its high volume. While many bio-based options have been proposed in the past decade, finding innovative formulations and production routes is still required to ensure the cost-efficient feasibility of extrinsic self-healing systems. This consideration extends to the biocompatibility of the healing agents and catalysts. For instance, the widely used Grubb's catalyst, employed to expedite the healing process, raises concerns about their toxicity that limits their suitability for biomedical applications. To the authors' knowledge, enzymatic catalysis remains unexplored for microencapsulated extrinsic self-healing systems, presenting a promising and sustainable alternative to conventional catalysts, potentially leading to higher yields and selectivity.

Finally, exploring alternative energy inputs, such as UV–Vis or microwave irradiation, and ultrasound pulses, can enhance the energy efficiency of production processes for these systems. Additionally, the application of miniaturizing modern methods like electro-

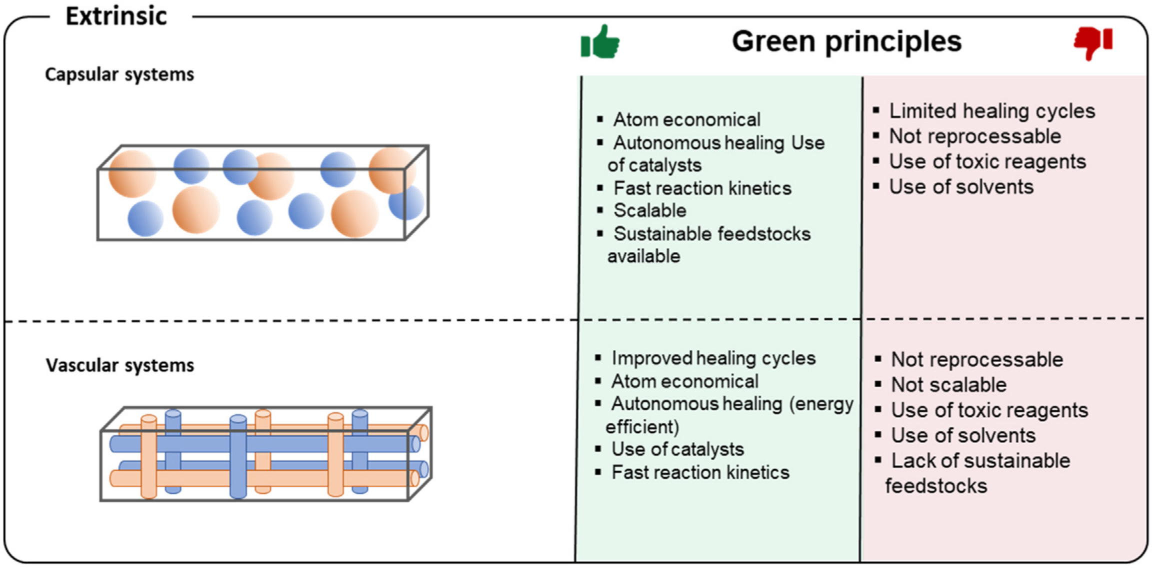


Fig. 8. Overview of the most common extrinsic self-healing systems with their corresponding advantages and disadvantages on the green chemistry principles.

spraying or microfluidics can contribute to achieving more precise manufacturing routes and minimizing waste formation. All these considerations serve as general guidelines to envision future, more sustainable extrinsic self-healing systems and manufacturing methods.

4. Sustainable resources

The incorporation of renewable feedstocks in polymers, blends or composites can significantly improve the sustainability of the final material. In addition, they often enhance mechanical properties, thermal stability, and provide additional functionalities. Currently, many different renewable feedstocks are available including natural resources, waste streams, or CO_2 capturing (Fig. 9). However, the choice of feedstock strongly depends on the desired properties for a specific application.

Self-healing materials can be used for a variety of applications in very different environments, which will require synthetizing them with a tailored set of properties. The objective of these section is to offer an overview of the different sustainable resources and to give the tools to select the most suitable resource, or a combination of, to synthesize a self-healing material that fulfils the application requirements in a sustainable fashion. When designing a self-healing material, the most important parameters to consider are the mechanical properties, the self-healing mechanism, the exposure environment, the end of life, and additional functionalities of the material. The latter includes electrical or ionic conductivity, shape memory, magnetic response or luminescence, amongst others. The exploitation of renewable natural resources instead of their fossil-derived counterparts carries several advantages. Biological feedstocks are generally better distributed around the globe than fossil feedstocks and they are not finite. Moreover, natural raw materials intrinsically possess more different functionalities than oil hydrocarbons, which allows finding alternative synthetic routes that might be more benign towards the environment. Sustainable feedstocks are available across a wide range of forms and volumes. In the following, these feedstocks have been sorted according to their origin and their main characteristics and opportunities were identified and compared for their use in the synthesis of self-healing materials.

Most of the natural resources such as cellulose, hemicellulose, and lignin are high molecular weight polymers with a unique structure that allows them to fulfil specific functions in the plant's cell wall. After these polymers are isolated by different extraction methods, further depolymerization and fractionation can be performed to obtain more defined fractions. Each fraction, from polymer to monomer, has its own advantages and disadvantages and the choice of fraction strongly depends on the final application. As an example: technical lignin is a heterogenous polymer with a broad dispersity having many issues regarding their compatibility and solubility. Still, technical lignin as such can be used as filler in bitumen or rubbers. In this case, no additional depolymerization processes are required. However, by depolymerization and fractionation, oligomeric fractions and even monomeric fractions can be obtained which can be used in higher value applications such as resins or for specialty chemicals. The higher the fractionation, the higher the value of the final application needs to be to compensate for the energy costs. In-depth LCA studies are required to analyse the full process from resource to application and a proper comparison with fossil-based materials is necessary [296].

4.1. Renewable resources from biomass

Biomass has proved to be a fertile feedstock to produce permanently cross-linked polymers. Despite being derived from biomass, these permanently cross-linked polymers they are still impossible to recycle. Adding dynamic covalent bonds to these biomass derived polymers has a synergistic effect that multiplies the sustainability of the networks [297]. Biomass resources have a great advantage for producing dynamic covalent bonds as they are produced at very large scales, and with a great variety of functional groups, which allows them to be used in all the types of dynamic chemistries. Using this criteria, large scale production, great variety of functional groups, and not toxicity, there are four resources from biomass that stand out: polysaccharides, lignin, vegetable oils and terpenes [298].

4.1.1. Biomass polymers

Polysaccharides

Polysaccharides are the most abundant component of biomass. It is estimated that more than 90 % of the carbohydrate mass in nature exists in the form of polysaccharides [299]. Structurally, they are monosaccharide units bonded by glycosidic bonds with a degree of polymerization that can be as high as tenths of thou-

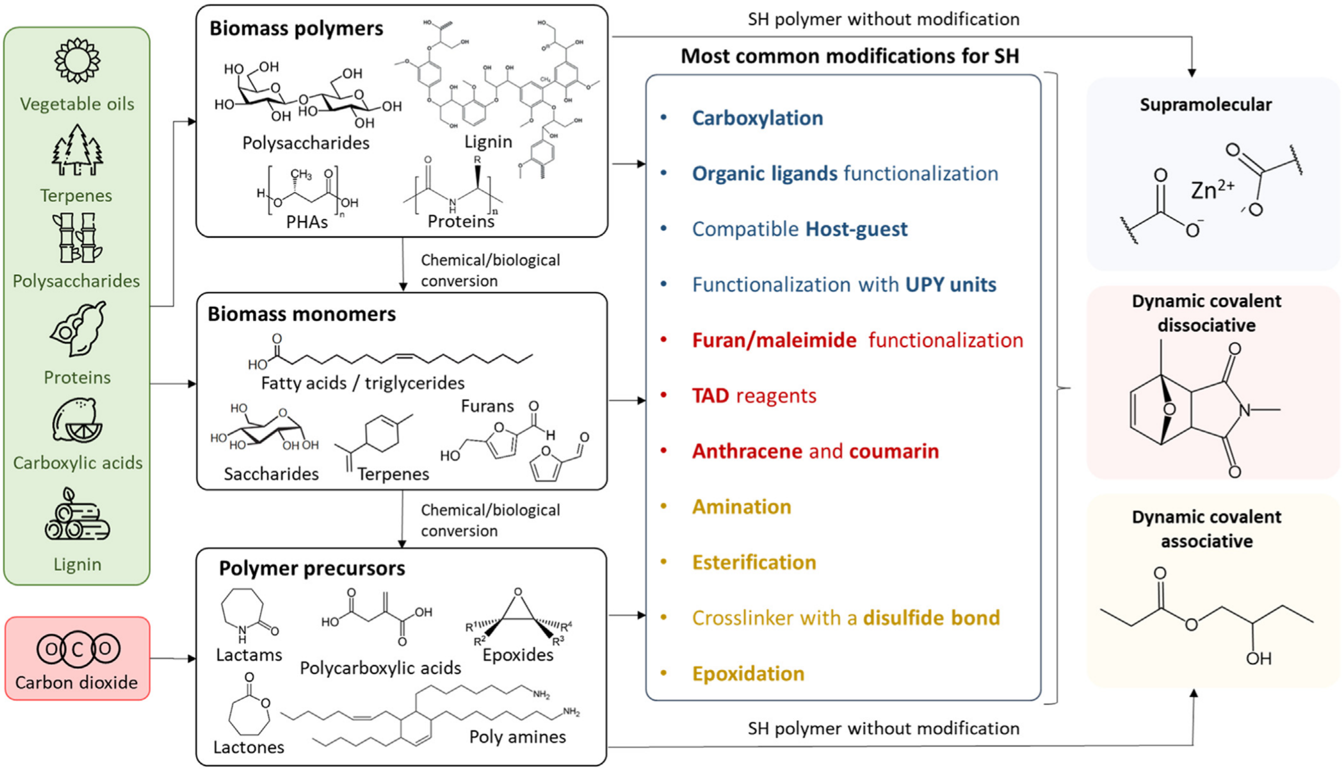


Fig. 9. Self-healing polymers from renewable resources. Renewable resources are used to produce biomass polymers, monomers or polymer precursors. By chemical or biological transformation, biomass polymers can be transformed into monomers and biomass.

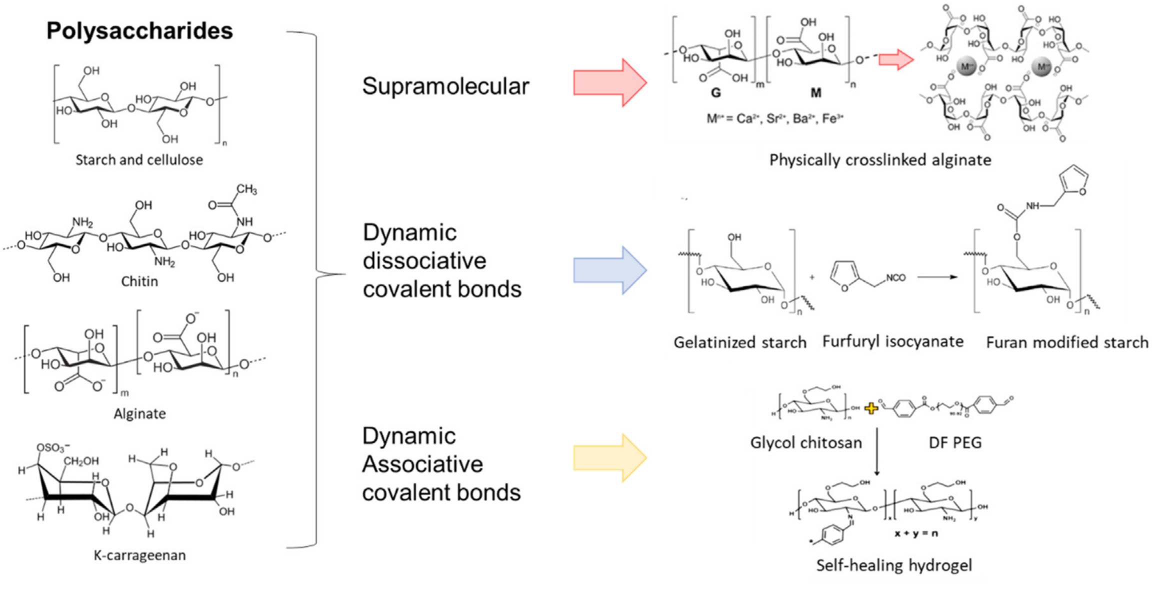


Fig. 10. Self-healing materials made with polysaccharides based on supramolecular interactions (Copyright 2012. Adapted with permission [332]), dissociative covalent chemistries (Copyright 2018. Adapted with permission from Elsevier Science Ltd [321]) and associative covalent chemistries (Copyright 2015. Adapted with permission from John Wiley & Sons Inc [329]).

sands. The simplest polysaccharide possesses hydroxyl groups as the only functional groups, such as cellulose or starch, whereas some polysaccharides, such as chitin or alginate, present other additional functional groups (amide or carboxylic acid groups, respectively). Besides their functional groups, the properties of polysaccharides are also determined by their molecular structure, ranging from linear structures to highly branched ones, and their molecular weight. Their abundancy and variety make them highly desirable to design self-healing materials (Fig. 10). However, they tend to form highly crystalline structures difficult to process, and are susceptible to moisture absorption, which is detrimental for most applications. For this reason, polysaccharides are mostly used in hydrogels or as (nano)fillers.

Cellulose is the most abundant polysaccharide. It consists of a linear chain of $\beta(1\rightarrow4)$linked d-glucose units. Its linear structure promotes a high cohesive energy and crystalline structure. Nanocrystals are the most used form of cellulose for the preparation of self-healing materials [300,301]. These nanocrystals can be carboxylated to enhance their compatibilization with the host matrix [302,303], or to make them conductive by coating them with Polyvinylpyrrolidone (PVP) and 3,4-ethylenedioxythiophene (PEDOT) [304]. Cellulose nanocrystals can also form liquid crystalline structures, which can be used to make self-healing elastomers with strain-induced dynamic structural colours [305].

Native cellulose can also be used as the network matrix in the form of hydrogel as water can disrupt the highly dense hydrogen bonds structures to create soft and stretchable materials. This allows the synthesis of industrially relevant hydrogels from natural polymers that are otherwise impossible to reprocess. Using plasticizers to improve its processability can be applied to the rest of polysaccharides discussed in this section. However, due to its high crystallinity, cellulose is almost impossible to dissolve without any chemical modification to its structure. Native cellulose can be modified with carboxylic groups [306,307] and used to synthesize SH hydrogels based on metal coordination [47,51]. It can also be functionalized with disulfide bonds [308] or with amines [309] to obtain polymer networks with associative dynamic covalent bonds. Cellulose can be functionalized with many other groups, like with fatty acids [310], double bonds [311] or ionic moieties to bring SH and ionic conductivity to hydrogels [312]. This variety of functionalization opens a wide range of SH materials with tailored properties.

Starch is composed of two basic macromolecular architectures, amylose poly($\alpha-1$,4,D-glucopyranose), which is linear, and amylopectin $\alpha-1$,6,D-glucopyranose, which is highly branched. Like cellulose, it possesses only hydroxyl functional groups. Despite the chemical similarities with cellulose, it forms granules instead of fibers due to its high branching. The proportion between these two structures determines the properties of the native starch. The difference in branching also makes starch more easily biodegradable, being even digestible by humans [313]. Native starch can be used in combination with plasticizers to form thermoplastic starch (TPS), or alone as a filler. Thermoplastic starch results from the thermo-mechanical fragmentation of starch in the presence of water and a plasticizer, normally glycerol. This process is called gelatinization and increases the amount of amorphous phase, improving its processability and tuning its mechanical properties [314–316]. As cellulose, thermoplastic starch can be further modified with other functionalities, [317] such as hydroxypropyl [318], carboxymethyl [319] or furan groups to obtain self-healing materials via Diels-Alder reaction [320,321]. Thermoplastic starch can form abundant hydrogen bonds that can be used to interact with other polymers such as PVA [322,323], or alginate [318], to form self-healing double networks. Native starch can also be used to improve the biodegradability, and overall sustainability of other polymers, such as natural rubber [324,325] or PDMS [325], by blending them together during the processing. Finally, gelatinized starch can also be used as the capsule filler for extrinsic SH [239].

Chitosan is the deacylated variant of chitin, which is the main component of the exoskeleton of insects and crustaceans. This modification is done to improve its solubility in water. This natural polymer is linear and characterized by the presence of amino groups attached to the molecular backbone. Analogous to starch, chitosan can be used as a matrix by using an acidic aqueous solution and/or other plasticizers [326], or as nanofiller [37]. Apart from the modifications that can be done to cellulose and starch, the presence of amino groups allows other functionalization routes that can be used to produce self-healing materials, such as aldehydes to make reversible Schiff base groups [327–329]. They can also be functionalized with catechol to form metal-ligand based hydrogels [330]. Self-healing properties can be also obtained thanks to the hydrogen bonds formed between the amine groups of chitosan and other hydrogen bond acceptors like the carbonyl groups of citric acid [331].

Alginate is a linear anionic polysaccharide with -COOH groups mainly found in brown algae [333]. Divalent metallic cations such as Ca^{2+}, or Zn^{2+} can crosslink alginate forming an egg box structure [334]. Oxidized sodium alginate has been used in combination with chitosan to make a self-healing hydrogel based on dynamic imine bonds [318]. Except from this example, alginate has not been extensively used to formulate self-healing polymers. Nonetheless, the carboxylate groups present in their structure and their possibility to crosslink via metallic cations opens the door to make self-healing polymers based on ionic interactions.

Other polysaccharides such as K-carrageenan, pectin or hyaluronic acid possess characteristic functional groups or structures that can be exploited to prepare self-healing polymers. Fan et al. functionalized hyaluronic acid with furan and maleimide moieties to obtain self-healing hydrogels via the Diels-Alder reaction [335].

Proteins/peptides

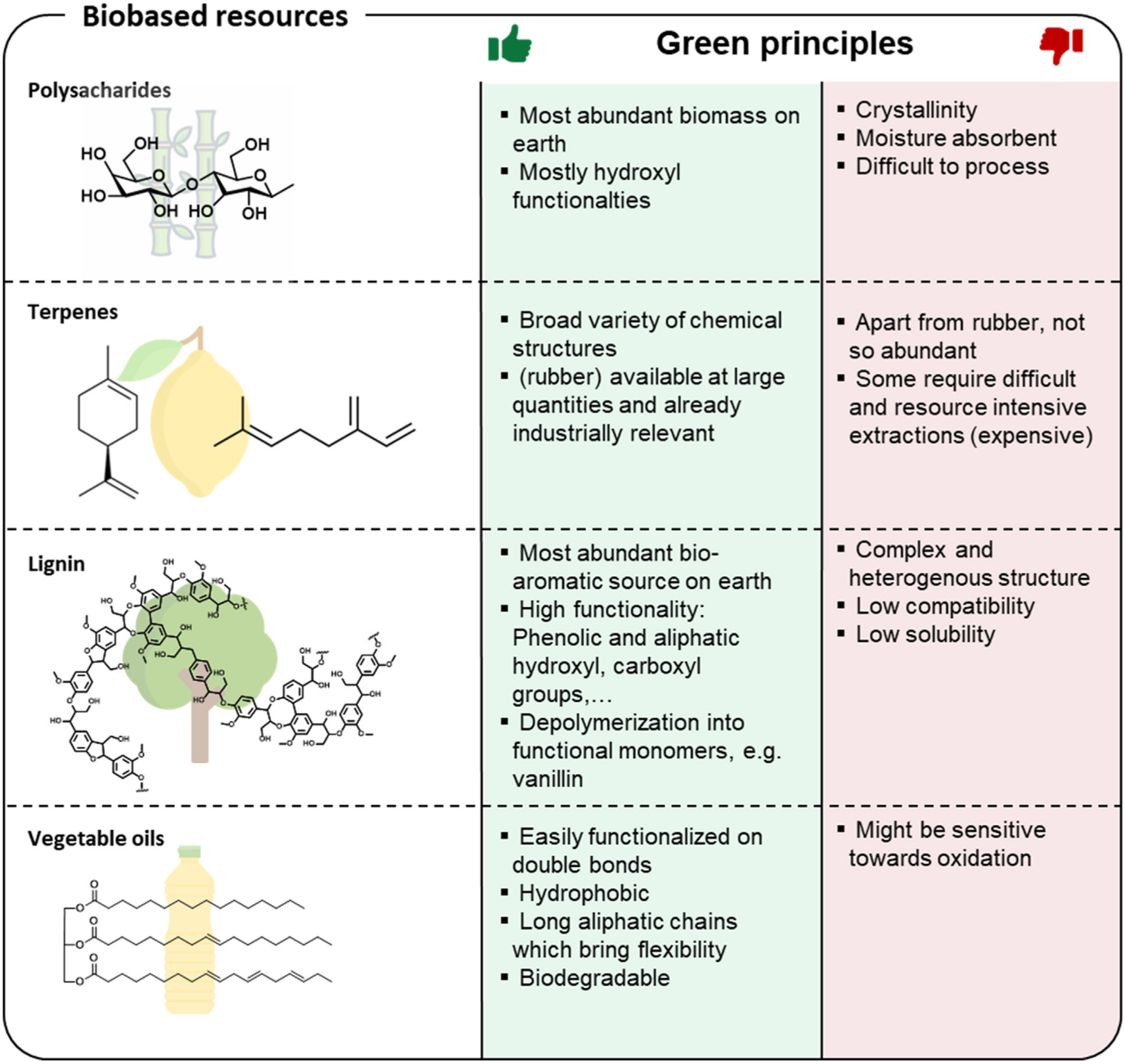
Proteins are biomacromolecules made of amino acids linked by peptide bonds. Proteins can exhibit a broad diversity of shapes and functions, ranging from accelerating chemical reactions to providing structural support for cells [336]. Proteins can form complex supramolecular structures, which have been recently used in the development of self-healing materials. These proteins can be sourced from animals, such as gelatine [337,338] or silk fibroin [339], vegetables [340], or made artificially [341]. Pena-Francesch et al. synthesized protein-based self-healing polymers inspired by squid teeth that can heal in seconds [341]. While using proteins to synthesize self-healing polymers is still a recent approach, the wide variety of functions and structures that proteins can have shows great potential for the development of novel self-healing polymers.

Lignin

Lignin is an aromatic heterogenous polymer and is, besides cellulose, the most abundant biomass-derived resource available in nature. As a byproduct of the paper and pulp industry and lignocellulosic biorefineries, more than 50 million tons of lignin are anually produced but are mainly incinerated for internal energy demands [342]. The remaining lignin, which is roughly 2 %, is sold externally to be used for higher-value applications [343]. However, the high molecular weight, non-uniform structure, high dispersity and presence of impurities in the technical lignin fractions limit their incorporation in polymers or composites due to low compatibility and solubility issues. As a result, fractionation and depolymerization techniques are often performed to normalize the obtained lignin fractions and broaden their application window.

Besides the aromatic core structure of lignin, several functional groups such as phenolic and aliphatic hydroxyl groups and carboxylic acid groups are available to be modified towards desired functionalities. Especially for the development of self-healing networks, the specific modification of these groups is readily performed to compatibilize lignin with the healing system. Zhang et al. and Hao et al. both increased the carboxylic acid groups on the lignin core by an ozonation reaction and a reaction between the OH-groups of lignin and a cyclic anhydride, respectively [344,345]. Subsequently, lignin was integrated within a vitrimer polymer matrix where the lignin could reversibly exchange due transesterification. Other examples of lignin-based vitrimers were based on transcarbamoylation [346] and disulfide exchange [347]. In case of dissociative mechanisms, furan and maleimide modifications of the lignin were performed to incorporate lignin in reversible Diels-Alder networks [81,82]. Examples of lignin-based reversible networks are depicted in Fig. 11.

Further depolymerization of lignin leads to monomeric aromatic fractions such as vanillin, guaiacol and catechol. The former possesses an aldehyde functionality which favours other types



Biobased resources	👍 Green principles	👎
Polysacharides	▪ Most abundant biomass on earth ▪ Mostly hydroxyl functionalties	▪ Crystallinity ▪ Moisture absorbent ▪ Difficult to process
Terpenes	▪ Broad variety of chemical structures ▪ (rubber) available at large quantities and already industrially relevant	▪ Apart from rubber, not so abundant ▪ Some require difficult and resource intensive extractions (expensive)
Lignin	▪ Most abundant bio-aromatic source on earth ▪ High functionality: Phenolic and aliphatic hydroxyl, carboxyl groups,… ▪ Depolymerization into functional monomers, e.g. vanillin	▪ Complex and heterogenous structure ▪ Low compatibility ▪ Low solubility
Vegetable oils	▪ Easily functionalized on double bonds ▪ Hydrophobic ▪ Long aliphatic chains which bring flexibility ▪ Biodegradable	▪ Might be sensitive towards oxidation

Fig. 11. Overview of the most common biobased resources with their corresponding advantages and disadvantages on the green chemistry principles.

of modifications for self-healing chemistries, *i.e.* imine-based vitrimers [348,349].

Tannins

The second most abundant source of aromatics on earth are tannins, with an average annual production of 160 kt [350]. Unlike lignin, tannins are mainly found in the soft tissues of plants, such as leaves. Although all tannins are high molecular weight polyphenolics, their exact structure strongly depends on the source. As a result, three different types of tannins can be classified: condensed, hydrolysable, and complex tannins [351]. The development of self-healing polymers using tannins is pioneered by Duval et al. [352]. In their work, a furan-modification of the tannins phenolic groups was performed and crosslinked with a maleimide to obtain a thermo-reversible network. Other reversible networks including tannins have been developed by Handique et al. and Liu et al. who both used tannic acid (a specific type of tannin) to develop dynamic networks based on Diels-Alder chemistry and dynamic phenol-carbamate bonds, respectively [353,354].

Polyhydroxyalkanoates

Polyhydroxyalkanoates (PHAs) are a family of polyesters derived from various microorganisms including bacteria. More than 150 different monomers exist that give rise to PHAs, resulting in a wide variety of polymers (homopolymers, random copolymers, and block copolymers) and properties [355,356]. PHAs are also biodegradable, making PHAs interesting from a sustainability perspective. Nevertheless, the industrialization of PHA is challenging due to inconveniences owing to their biosynthesis, such as production costs. In addition, PHA production has still a rather low efficiency and the obtained polymerized structures do not possess consistent structures and properties [355].

The incorporation of PHAs in self-healing polymers is, to the authors' knowledge, not yet investigated. However, an innovative healing mechanism for self-healing concrete was recently discov-

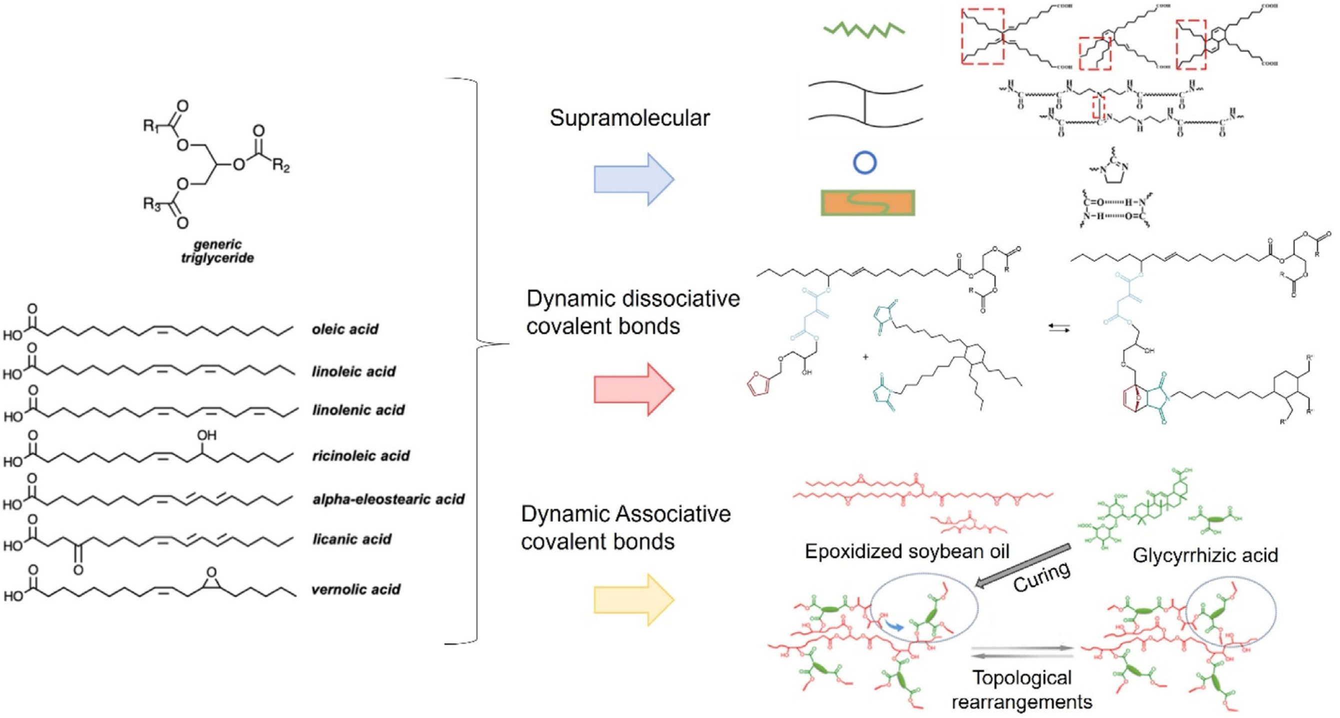


Fig. 12. Self-healing materials made from vegetable oils. By taking advantage of the different functionalities and unsaturation of the different types of vegetables oils (Copyright 2020. Adapted with permission from MDPI [368] it is possible to prepare self-healing materials based on supramolecular (Copyright 2020. Adapted with permission from Elsevier Science Ltd [30]), and dynamic dissociative (Copyright 2023. Adapted with permission from American Chemical Society publications [83]) and associative covalent bonds (Copyright 2020. Adapted with permission from American Chemical Society publications [365].

ered where PHA was used as a bacterial substrate for bacteria-based healing of concrete [357].

4.1.2. Biomass monomers

Vegetable oils

Vegetable oils are extracted from the seed of certain plants, like soybean, oil palm, oilseed rape, sunflower, or castor at very large scale [358]. The structure of a generic triglyceride consists of three fatty acid moieties bound together by a glycerol unit (Fig. 12). They vary in length of the alkyl chain, number of C=C bonds and in the possible presence of other functional groups such as hydroxy or epoxy groups. Vegetable oils can be used to produce materials using its triglyceride form or by separating the three chains in fatty esters or fatty acids. Moreover, they can be easily functionalized, with epoxidation the most used modification route [359]. This broad number of potential modifications allows to synthesize materials with a very wide range of properties, from soft elastomers to stiff thermosets [360]. Added to this structural versatility, they are hydrophobic, which allows them to be used in a wider range of environments compared to the hydrophilic polysaccharides, and they are biodegradable. It is no surprise then, that they have been largely used to produce self-healing materials.

Fatty diacids and triacids have been used since the beginning of the self-healing polymer field as they were used in the first reported example of intrinsic self-healing, which was based on hydrogen bonds [28]. Vegetable oils have been also functionalized with furan groups and crosslinked with maleimides to form dissociative dynamic covalent networks based on Diels-Alder bonds [83,361–364]. Also, vegetable oils have been extensively used to synthesize associative dynamic covalent networks. Those based on transesterification are the most popular choice [221,365] due to the widespread use and ease of epoxidizing vegetable oils, but also other types of vitrimers, for example, based on disulfide bond metathesis [366], or Schiff base bonds [367].

Terpenes

Terpenes and terpenoids are components of essential oils derived from plants and have an isoprene unit in common in their chemical structure (Fig. 13) [369]. The best-know example of a polyterpene is natural rubber. Some other examples, which are produced in much more modest scales, are α and β-pinene, limonene, myrcene, or menthol. Several examples of polymers produced from these terpenes already exist [370].

Crosslinked natural rubber is one of the most used polymers nowadays, however, its irreversible crosslinks cause severe environmental issues that are currently still unresolved [371–373]. Combining it with a reversible chemistry can help to deal with this issue and drastically increase the sustainability of rubber products. Epoxidized natural rubber (ENR) has recently been used as a bio-sourced feedstock in numerous vitrimer systems. The epoxy functions of ENR allow for reversible crosslinking with various reactive species, in addition to the double bonds already present in parent natural rubber. It was shown that ENR could be efficiently cross linked using aliphatic diacids, via an esterification reaction highly accelerated in presence of 1,2-dimethylimidazole (DMI) [374–376]. Moreover, crosslinking may be carried out in bulk, without use of solvent, nor production of any by-products.

A rubber reprocessable above 150 °C was obtained using dithiodibutyric acid as a carboxylic diacid crosslinker, bearing exchangeable disulfide links [377]. ENR was crosslinked in the presence of DMI and $Zn(OAc)_2$ with various diacids like hydrolysed maleic anhydride [378], dimer fatty acids [379] and dodecanedioic acid in the presence of aniline trimer [380].

Guo et al. developed dual networks combining transesterification and hydrogen bonding using sebacic acid and N-acetylglycine [381]. The hydrogen bonds arising from amide functionalities act as a sacrificial network, breaking and reforming to dissipate mechanical energy under external load, thus improving the mechanical performance of rubber while accelerating the stress relaxation.

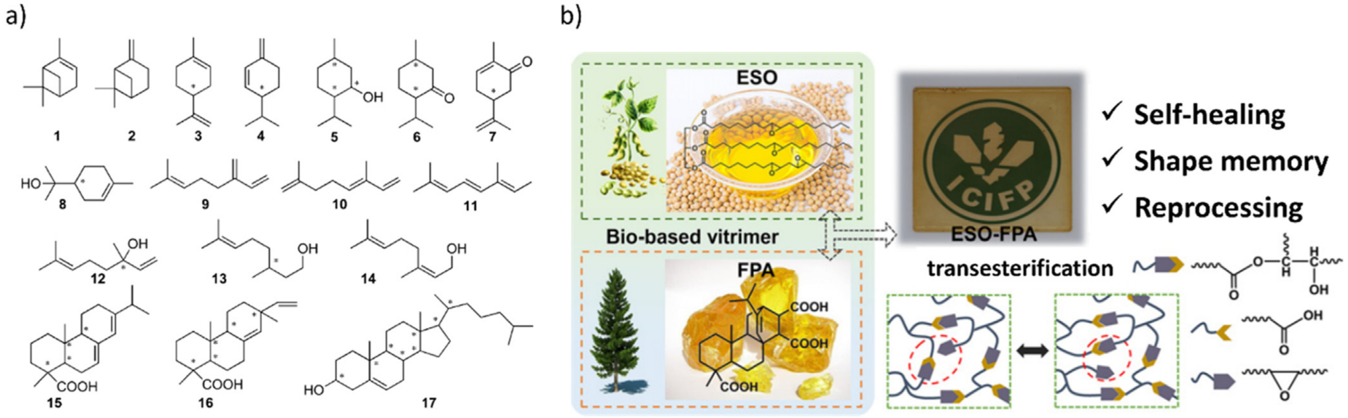


Fig. 13. a) Different terpene structures with functionalities that can be exploited to make self-healing materials (Copyright 2015. Reproduced with permission from John Wiley & Sons, Inc [369]. b) Vitrimer made with epoxidized soybean oil and fumaropimaric acid terpene (Copyright 2020. Adapted with permission from Elsevier Science Ltd. [387].

A multiple network prepared by combining dithiodibenzoic acid, dithiodianiline, and sulphur vulcanization was also reported. [382]

In a different approach, ENR was transformed into a thermoreversible elastomer after grafting of furfuryl amine (FA) via a catalysed ring opening [383]. Using a simple one-pot blending with bismaleimide, a thermoreversible ENR with good thermoreversibility and self-healable behaviour was successfully prepared, with cross-linking temperatures at 130 °C and decrosslinking temperature of 150 °C. This one-pot melt processing is environmentally friendly, compared to usual thermos-reversible elastomer syntheses operating for long times in solution. However, as the oxirane groups of ENR have low reactivity, a non-negligible quantity of catalyst, ytterbium(III) trifluoromethanesulfonate ($Yb(OTf)_3$) should be introduced in the mixture to activate the ring opening and synthesize ENR-FA, which impedes the sustainable character of the whole process.

Apart from natural rubber, which has been largely studied in self-healing materials [380,384], the impact of the other terpenes is still relatively modest. Limonene has been used, in combination with castor oil, to make vinylogous urethane vitrimers by introducing two amine functionalities to the limonene via thiol-ene reaction [385]. 1,8-Menthane diamine can be derived from turpentine and reacted with carbonate functional soybean oil to prepare a fully bio-based polyhydroxyurethane dynamic network, showing modest healing properties [386]. Fumaropimaric acid, a derivate of pine rosin, was reacted with epoxidized soybean oil to make vitrimers based on transesterification [387]. Terpenes have also been used to make materials with self-healing properties based on the Diels-Alder reaction by reacting β-myrcene with furfuryl methacrylate and crosslink it with a bismaleimide [388]. Despite these initial efforts, apart from rubber and rubber derivates, terpenes are still relatively expensive, and they do not offer major advantages in the synthesis of self-healing materials in comparison with other more abundant resources.

Furans

Furan and its derivatives are reactive 5-membered ring dienophiles that find multiple commercial applications in, for example, the textile, paint, and coating industry. The furan-maleimide chemistry is also the most popular dynamic covalent chemistry for self-healing polymers due to their unique combination of decent covalent bond strength and excellent mechanical and thermal reversibility, leading to fast and efficient damage healing, even under ambient conditions. A variety of furan-containing molecules can be derived from lignocellulosic biomass, more specifically from cellulose and hemicellulose. Depolymerization and catalytic dehydration of these polymeric carbohydrates results in furfural intermediates which can be further chemically modified towards desired furan derivatives such as furfuryl amine or 2,5-furandicaboxylic acid (FDCA) [71]. Especially regarding the latter one some studies regarding LCA and FDCA-based self-healing materials were recently published [389,390]. Due to this versatility of furan chemistry, furan-based or end-capped polymers are easily developed and result in a wide variety of different polymers.

Incorporation of biobased furans in self-healing polymers leads unambiguously to Diels-Alder based networks (see Section 2.1.1). Here the furan functionality itself plays a key role in the thermoreversibility of the network. Nevertheless, examples of incorporated furans in associative networks based on transesterification [389], transamination [191], and transimination [391] were also studied and showed effective healing behaviour.

4.1.3. Polymer precursors

Polycarboxylic acids - Anhydrides

Bio-based carboxylic acids and anhydrides are key precursors in the development of a variety of commodity plastics. Polylactic acid derived from lactic acid is probably the best-known example of this. Other known bio-based acids are sebacic acid, citric acid, and itaconic acid. As carboxylic acids are desired functionalities for transesterification reactions, most of the studies are performed in this area. Transesterification networks based on sebacic acid [209,392] and itaconic acid [393] showed already promising healing properties.

Further chemical processes can transform carboxylic acids into anhydrides or even lactones or lactams, which will not be further discussed in this review.

4.2. Waste streams

4.2.1. Recycled resins

For certain plastic waste streams, mechanical recycling is not always economically or even ecologically viable. Highly mixed waste streams need to be divided into concentrated and purified streams of the constituting fractions by identifying, sorting and separating these constituents. Moreover, traditional permanent network polymers cannot be recycled mechanically into materials that can be used in the same production processes and applications (closed loop recycling), while they can be broken down mechanically into granulates that can be used as reinforcing fillers for the preparation of other materials or they can be thermally or chemically converted into smaller fractions. In such cases, chemical recycling may provide the answer. Fast pyrolysis is a thermochemical process that converts biomass, waste streams and others into oils that can be

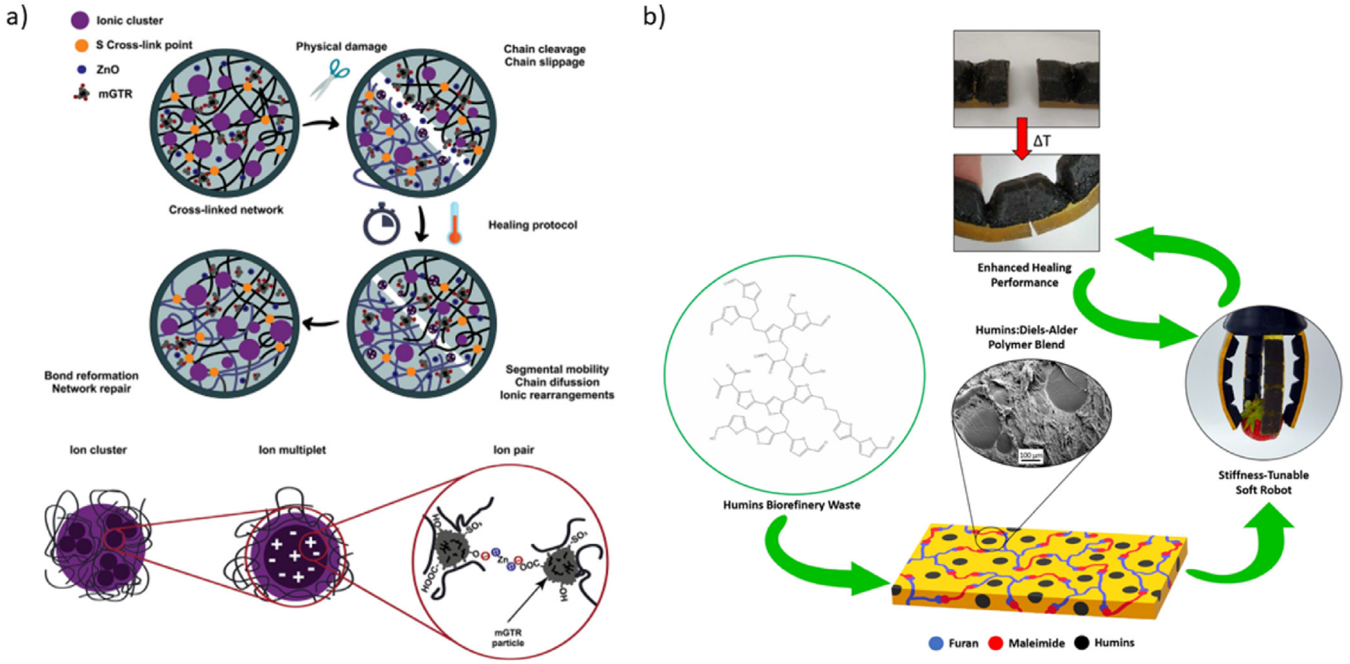


Fig. 14. a) Scheme of the self-healing mechanism of a styrene-butadiene rubber bearing dynamic ionic clusters (Copyright 2022. Reproduced with permission from Wiley & Sons, Inc) [399], b) humins-derived Diels-Alder polymer blends with enhanced healing performance for multi-material soft robotics (Copyright 2022. Reproduced with permission from MDPI) [404].

used as fuel or as monomers for further functionalisation or direct polymerization [394]. Devulcanization of ground waste tyre rubber is a thermomechanical process that results in the breaking of the sulphur bonds originally formed during the vulcanization process. During the process, also C–C bonds are broken, and polymers and oligomers are obtained that resemble the original unvulcanised rubber. The polymers and oligomers can be entered into new network polymerization processes. Alonso Pastor et al. investigated the effect of the structure of the devulcanized ground tire rubber (dGTR) on the self-healing properties of the resulting rubber composites [395]. GTR from different mechanical processes (cryogenic milling and water jetting) and dGTR from thermomechanical (devulcanization) and thermochemical (microwave) were characterized and their effect on the mechanical and self-healing properties compared. It was found that both the mechanical properties and self-healing efficiency improved with higher specific surface area of the GTR particles and with the percentage of free surface polymeric chains. Healing efficiencies up to 80 % were obtained at GTR loadings of 30 phr. In other cases, GTR is used as a filler, reducing the need for the extraction of raw resources or fillers [396]. Several alternatives to recycle rubbers with healable features have been developed by Utrera-Barrios et al., including epoxidized natural rubber [397], nitrile rubber [398] and reinforced styrene-butadiene rubber [399] by introducing reversible ionic clusters within their structure (Fig. 14a).

4.2.2. Humins

The dehydration of feedstocks such as glucose, fructose or xylose leads to the unavoidable formation of side-products commonly known as humins. Humins are black, viscous, highly disperse, poorly soluble and recalcitrant liquids composed by polycondensed furanic molecules under acidic conditions. Despite that some progress has been made towards the understanding of humins' formation pathways to hinder their formation, their presence in the synthetic route of novel bio-based platform molecules make this side-product to partially hinder the economic viability of some biorefinery processes [400].

In this regard, the valorization of humins, either towards the obtaining of humins-derived platform molecules or their intrinsic valorization as a raw bioresource, are appealing to both academia and industry. The latter includes the formulation of humins-based polymer materials such as glassy thermosets [401], elastomers [402] or foams [403]. Recently, Cerdan et al. explored the incorporation of humins within the self-healing field [404]. In this research, as shown in Fig. 14b, an immiscible polymer blend based on a thermoreversible Diels-Alder network and humins showed how humins can both enhance the healing material performance while having a higher stiffness than the pristine Diels-Alder. This blend was used to manufacture a multi-material robotic gripper that mimics the biological growth of calluses. This is accomplished owing to the thermal gelation mechanism of humins, being able to form a transient network that experiences an abrupt decrease in viscoelasticity when heated to mild temperatures [405]. Zhang et al. synthesized humins under the photocatalytic oligomerization of 5-hydroxymethylfurfural and subsequently leveraged the presence of furan rings within humins to create healable Diels-Alder soft polymer networks [406].

The use of humins as a waste stream feedstock is a scarcely approached field that still has plenty of opportunities to offer, not only in the self-healing polymers field but for the preparation of more generic polymeric materials. Since the production of bio-based platform molecules is expected to continue growing during the coming years, the increased formation of humins emerges as a potential issue that can be tackled at different levels. Their use for the formulation of self-healing materials cannot only valorise this waste but also lower the costs of conventional self-healing materials, promoting their scalability. The wide variety of functionalities (hydroxyls, carbonyl, carboxylic acids…), as well as their furanic units, make humins a very interesting choice for polymer chemists to better understand and their structure and perform the required modifications to formulate novel humins-based materials. In addition, humins have proven to not to present any immediate ecotoxicological concerns with the current production pathways, thus engaging with the proposed green chemistry sustainability principles [407].

4.3. Carbon utilization

A different method to incorporate renewable feedstock in polymer formulations is the usage of CO_2. As the extreme emission of CO_2 in the environment is the main reason for global warming, there is an urgent need for rethinking our global energy consumption, mobility and industrial processes [408]. Evidently, prevention is the best cure, however when prevention is not possible, an alternative must be found. In this case, the alternative is carbon capture and subsequently using CO_2 in polymer matrices.

Specifically for self-healing networks, a few recent examples were studied in carbon-based reversible polymers. As a first examples, Yang et al. developed a CO_2-based healable polycarbonate with incorporated amide functionalities which could reversibly dissociate due to the presence of hydrogen bonds [409]. Further work of the same group incorporated reversible boronic esters in a CO_2-based thermoplastic network [410]. In both cases, autonomous self-healing at room temperature was achieved. Similarly, Zhao et al. developed a reversible hydrogen bonding CO_2-based polyurea. In this work, CO_2 was reacted with organic and inorganic diamines to create room temperature healable networks [411]. As a last example, Diels-Alder-based polyurethanes were incorporated with CO_2 and furfuryl amine by Wu et al. [412]. The usage of both these renewable feedstocks makes the overall polymer quite sustainable. Moreover, the high healing efficiency of 94% was established both by reversible Diels-Alder chemistry and hydrogen bond forming units which also contributed to promising mechanical properties.

5. Processing and manufacturing

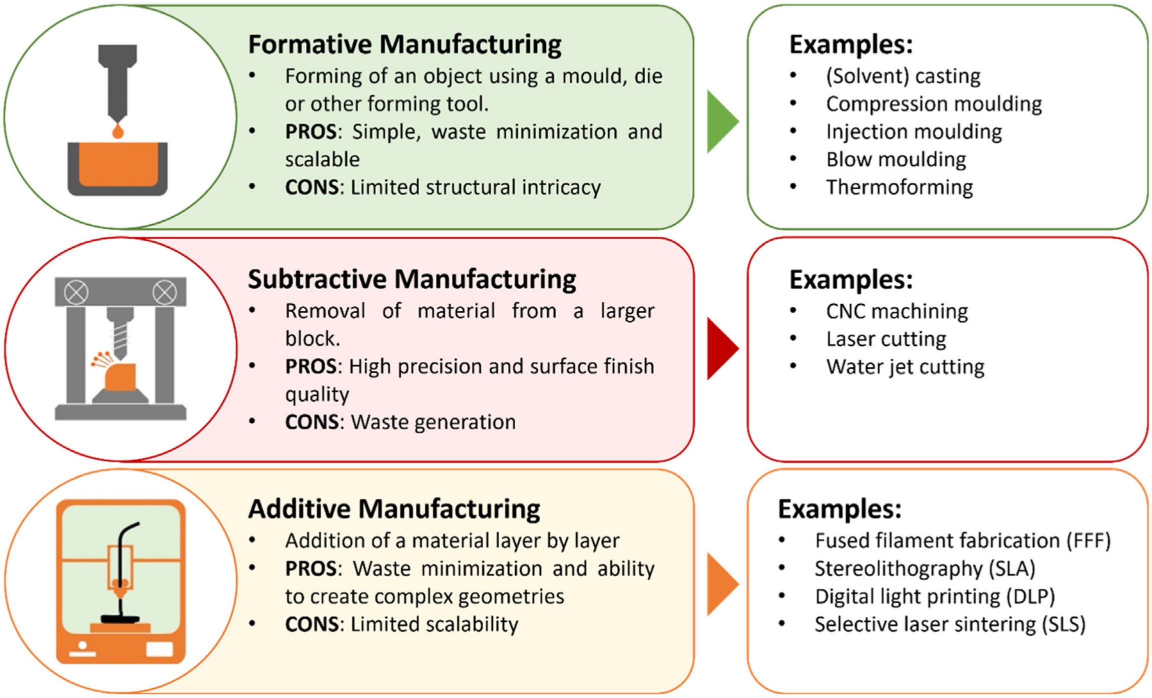
Traditionally, polymers have attracted considerable attention due to their manufacturing versatility, even enabling recycling multiple times. This section deals with the many methods that can be used to process self-healing materials and manufacture them into self-healing products. Focus will be drawn to the limits and new opportunities self-healing material pose on typical processing methods and how they impact the sustainability of these processes.

The methods used to process polymers depend on the chemical nature of the polymer and related viscoelastic behaviour and thermal properties. Thermoplastics are the most attractive type of polymer for large volume production due to their thermal (re)processability as a polymer melt and low cost. Precise control of the environmental and processing conditions enables tuning their rheological behaviour during processing. This enables us to manufacture structures with broadly different morphologies, ranging from thick pipes to thin films or foams. Commonly used processing techniques for thermoplastics include extrusion, injection moulding, film blowing and additive manufacturing [407,413,414]. A great advantage of these methods is that a large amount of the heat generated to melt the polymer arises from viscous dissipation of the sheared polymer thin film between the screw and the barrel wall [415]. This makes this approach environmentally attractive since it allows for low energy consumption to process large amounts of plastics.

Thermosetting polymers are characterized by their irreversibly crosslinked chemical structure. This crosslinked network is built via a gelation process, in which monomers with multiple functionalities react (or “cure”) to form a single macromolecule with theoretically infinite molecular weight, which yields superior mechanical properties, thermal stability and chemical resistance. Thermosets are processed by reactive methods, forming a three-dimensional polymer network when exposed to heat or light during shaping. Reactive methods encompass all the processes that involve chemical modifications during the manufacturing period. This englobes a very wide range of mechanisms and techniques, including classic well-known methods such as in-situ bulk polymerization and subsequent mould casting (solvent or solventless), stereolithography (SLA), injection moulding of polymer composites, or more recent approaches such as frontal [416,417] or combinatorial polymerizations [418]. Tuning the monomer composition influences the final network structure and resulting crosslink density, enabling a wide tailoring of the glass transition and mechanical properties. Following this approach, polymer networks ranging from soft, flexible elastomers to hard, brittle thermoset resins can be prepared [419]. Despite the advantages of their crosslinked nature, it also acts in detriment of the reprocessability of polymer networks. Since thermal processing is not possible, reactive processing methods are used to shape the thermosets during network polymerization.

Extrinsic self-healing materials are prepared using reactive methods, analogous to those of thermosets, as the reservoirs filled with the healing agents are commonly embedded in polymer networks. Conversely, intrinsic self-healing materials rely on their reversible nature to be further processed. Dynamic covalent networks and supramolecular networks blur the line between thermal and reactive processing due to the reversible nature of the dynamic crosslinks that can result into reprocessability if enough crosslinks are broken. Owing to their reversible nature, these polymers address both the issues of thermoset recyclability and the thermal and chemical vulnerability of thermoplastics. Thermosets that would be suitable for usual shaping techniques such as injection moulding or extrusion, reserved so far for thermoplastics, would have a decisive impact for their industrial development. Besides, thermoset recyclability would answer the soaring demand for green materials. Dissociative covalent networks and supramolecular networks experience a pronounced change in the rheological properties by fine-tuning their crosslink density. For example, thermoreversible covalent networks can change their viscoelastic moduli several orders of magnitude within a narrow temperature window spanning the gel transition [420]. Similar behaviours are observed for photoreversible or mechanoreversible covalent networks exposed to light or external forces, respectively. The resulting tuning of the dynamic networks causes a profound effect in processing parameters analogue to those of thermosets and thermoplastics such as melt strength, extensional rheology or crystallization/curing kinetics.

Regrettably, several features limit the true sustainability of vitrimers, as well as their industrial applicability and thus the potential development of sustainable materials. The materials may present too long relaxation times and high viscosity during reprocessing, incompatible with common industrial recycling processes of thermoplastics. Thus, developing a vitrimer having a low viscosity at high temperature for reprocessing, and high viscosity at service temperature for creep resistance, is still a challenge. Most vitrimers based on transesterification are not reprocessable fast enough for the industrial manufacturing standards. The viscous flow of the polymer network is hindered by the rate of the exchange reaction, hence the use of continuous processing techniques such as injection moulding is limited. Thus, the relatively slow stress relaxation only permits compression moulding. In this regard, transamination of vinylogous urethanes or ureas has shown to be a competitive alternative to transesterification. Vinylogous urethanes might relax in 85 s at 170 °C, and vinylogous ureas in 57 s at 170 °C. Adding p-toluenesulfonic acid (TsOH) as a proton donor catalyst resulted in a further decrease of the relaxation times to 2.4 s at 170 °C. This corresponds to viscosities on the order



Formative Manufacturing
- Forming of an object using a mould, die or other forming tool.
- **PROS**: Simple, waste minimization and scalable
- **CONS**: Limited structural intricacy

Examples:
- (Solvent) casting
- Compression moulding
- Injection moulding
- Blow moulding
- Thermoforming

Subtractive Manufacturing
- Removal of material from a larger block.
- **PROS**: High precision and surface finish quality
- **CONS**: Waste generation

Examples:
- CNC machining
- Laser cutting
- Water jet cutting

Additive Manufacturing
- Addition of a material layer by layer
- **PROS**: Waste minimization and ability to create complex geometries
- **CONS**: Limited scalability

Examples:
- Fused filament fabrication (FFF)
- Stereolithography (SLA)
- Digital light printing (DLP)
- Selective laser sintering (SLS)

Fig. 15. Polymer processing technologies applicable to self-healing polymers, namely formative, subtractive and additive manufacturing techniques.

of 10^6 Pa.s, suitable for processing as thermoplastic materials. Another study shows a vinylogous urethane system that might be extruded, relaxing the stress of a 1 % deformation in 0.9 s at 160 °C. Future sustainable vitrimers should be designed to fulfil this demand of materials malleable enough to be processed industrially.

There are numerous processing techniques for polymers that can be used to manufacture final objects. These techniques can be classified into three categories: formative, additive and subtractive manufacturing, with possible combinations of these basic methods (Fig. 15).

Formative manufacturing involves shaping a certain amount of material using moulds or dies and external forces such as gravity, pressure, shear, extension, or a combination of these methods. These processes occur when the polymer is in a liquid or soft malleable state, allowing it to fill the voids of the mould via liquid flow or plastic deformation. The polymer is then solidified through curing or cooling. For low-viscosity monomer mixtures, casting is possible without external intervention by using low M_w monomers, elevated temperatures or a solvent that will eventually evaporate. For more viscous materials, such as polymer melts, high M_w reactive monomer mixtures, or highly filled composites, compression moulding or, for high-volume manufacturing, injection moulding, are preferred to achieve an adequate filling of the mould cavity. In terms of sustainability, polymers that can cure without any energy input or solvent presence are desirable.

Researchers commonly use casting techniques to prepare self-healing materials due to their simplicity and availability of low M_w or soluble monomers. However, formative manufacturing offers limited design freedom, which makes making small modifications time-consuming and costly, especially in fields like rapid prototyping where creating an entirely new mould is necessary for this purpose. To overcome this issue and expand the applicability of self-healing polymers in formative manufacturing, researchers have found that forming strong interfacial contact between two or more dynamic covalent networks to build reconfigurable 3D geometries is easily accessible without the need for adhesives. This is possible by bringing together two parts bearing the same dynamic motifs and, upon physical contact, enabling a sufficiently high chain diffusion at the interface under controlled stimuli [404,421–423]. This approach, schematized in Fig. 16, is fast and energetically mild for soft networks, where diffusion of dynamic groups along the interface is possible. However, a higher energetic input is required for more robust and stiffer materials, an energetic input is required. This can be overcome by casting and crosslinking one of the phases on top of another already crosslinked to form bonds also at the interface. Despite its promising outcomes, conventional casting or compression moulding methods are not scalable, thus new high-throughput manufacturing methods must be developed to make self-healing polymers competitive in the market.

Injection moulding is one of the most widely used formative manufacturing methods in industry, where a liquid polymer such as molten thermoplastic, unreacted monomers or prepolymers, is injected into a mould. The liquid mixture is driven by a rotating screw towards an extruder barrel and accumulated at the end zone (metering section). Then, the material is injected into the mould and solidified upon cooling or curing before demoulding. The choice of polymer, type of machining, and processing conditions are important factors that can significantly affect environmental aspects such as electricity consumption [425–427]. Although injection moulding has obvious advantages, self-healing materials have not been processed using this technology yet. Vitrimers are a promising option for this method due to their high viscosity, which enables them to withstand the high pressures characteristic of this process [428]. The same approach appears to be valid for highly filled dynamic covalent networks based on dissociative mechanisms, since a high filler fraction can strongly contribute to maintaining the rheological properties required for this process [399,429]. In addition, mixing throughout the extruder barrel can enhance the dispersion of these fillers before injection, constituting an additional benefit of this technique compared to other formative methods. However, more research is needed to prove the

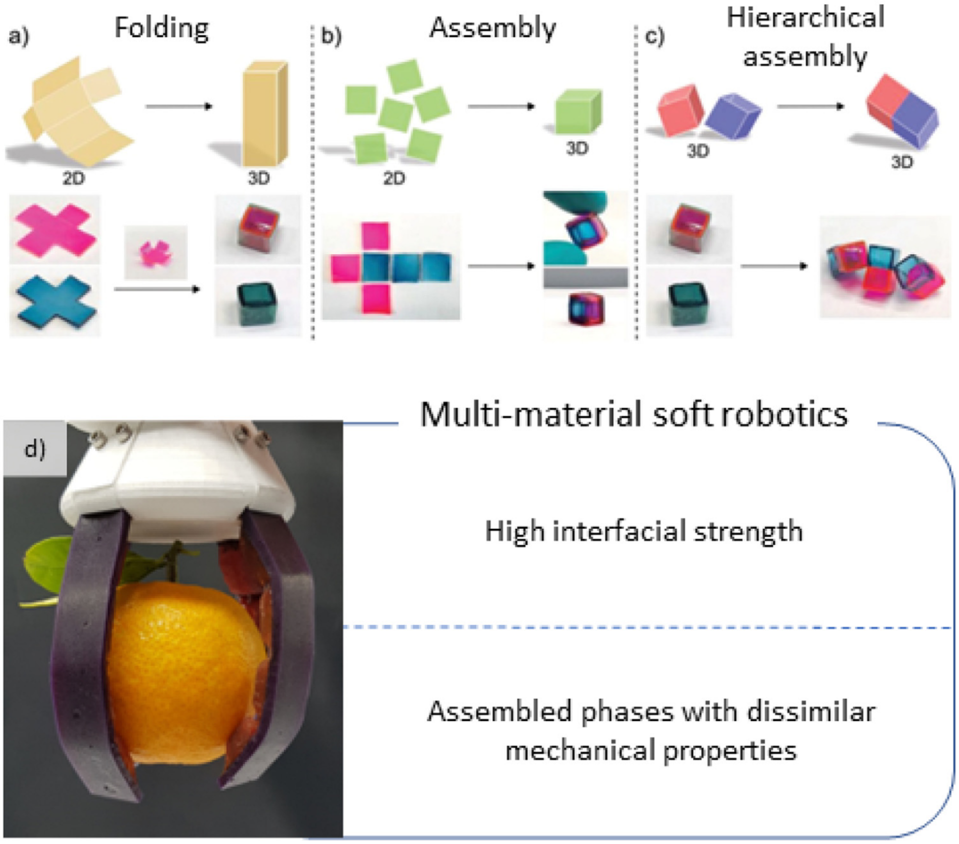


Fig. 16. Capability of dynamic covalent chemistry for the assembly of multi-material structures via a) folding, b) rational assembly and c) hierarchical assembly (Copyright 2022, Reproduced with permission from Wiley & Sons, Inc) [421]. The resulting assembled structures, as stated in d) exhibit high interfacial strength due to the formation of covalent bonds upon interdiffusion and enables the assembly of phases with dissimilar mechanical behaviour (Copyright 2019. Reproduced with permission from Institute of Electrical and Electronics Engineers (IEEE)) [424].

feasibility and sustainability of this technique for the manufacturing of self-healing materials, including a detailed LCA of the process.

Subtractive manufacturing involves removing material from a pristine block to obtain the desired shape through cutting, milling or hollowing. This method is commonly used in industries working with metals, stiff plastics or wood, and employs techniques such as Computerized Numerical Control (CNC) machining, laser cutting, or water jet cutting. Subtractive manufacturing allows for the creation of more complex geometries at a faster rate than formative manufacturing techniques. However, it has significant environmental limitations, including waste generation and high energy consumption. While recycling waste materials can help to mitigate these issues, it involves additional manufacturing steps that reduce the energy efficiency and profitability of the process. Moreover, cutting soft materials can cause surface wear, leading to poor surface finishing.

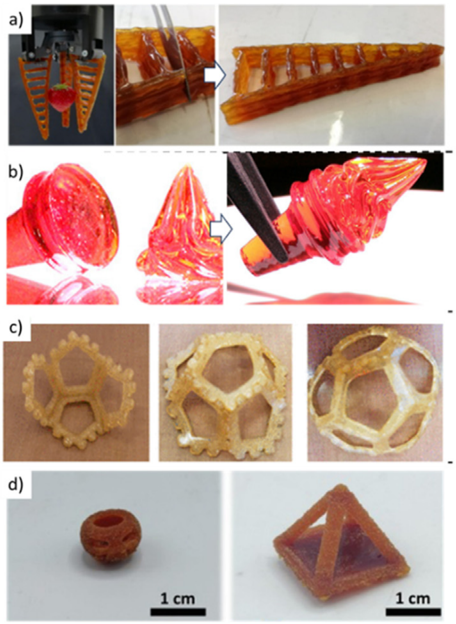
To our best knowledge, subtractive manufacturing has yet to be explored in self-healing materials. Due to their inherent softness, these materials hold promise for improved healing performance but may not be well-suited to withstand high shear forces during manufacturing. Excessive shear forces can cause thermoreversible materials to soften and reach T_{gel} due to strong viscous dissipation. The same reasoning applies to mechanoreversible systems when submitted to external forces. However, thermoreversible and photoreversible thermosets, both dissociative and associative, may be suitable for CNC machining. Degelation needs to be avoided for dissociative covalent networks while enduring aggressive mechanical treatments.

Laser cutting has not been used in the manufacturing of self-healing polymer networks. Instead, it has been employed as an alternative heating source to join different parts together in a formative approach [430,431]. This method is restricted to thin sheets due to the low laser depth penetration, making it suitable only for certain applications such as pneumatic soft robots or coatings [432].

Additive manufacturing, commonly referred to as 3D-printing, has been garnering interest in both academia and industry due to its ability for free-forming complex geometries and potential customization. The process involves the layer-by-layer deposition of material that is predefined in a Computational-Aided Design (CAD) model pattern to obtain a desired shape for further manufacturing. This presents a promising path towards greener, automated, and cost-effective processing of polymers and metals with low waste generation.

The main sustainability concern associated with additive manufacturing is its energy consumption. Despite its advantages for small-scale production, 3D-printing consumes more energy than conventional manufacturing processes. However, the development of lightweight complex geometries with improved performance in the final product can partially compensate for this [433]. Another environmental benefit of additive manufacturing is its distributed manufacturing, which avoids issues related to energy consumption and greenhouse gas emissions related to shipping, which is common in local large-scale production [434].

Despite its many advantages, this technology is still limited to small-scale production, primarily due to the long printing times. Moreover, when considering desktop 3D-printers for small produc-



	👍	👎	🌱
FFF	▪ Low-cost ▪ Easily accesible ▪ Wide range of materials available	▪ Limited resolution and surface quality ▪ Weak interlayer bonding ▪ Restricted freedom of design	▪ Mechanical isotropy in the z-axis ▪ Enables healability
VAT	▪ High resolution and smooth surfaces ▪ Complex geometries	▪ High cost ▪ Limited materials options ▪ Resins are brittle and sensitive to UV light ▪ Requires post-processing	▪ Soft options available ▪ Enables healability ▪ Enables reprocessability (photo-curable vitrimers)
DIW	▪ High resolution and smooth surfaces ▪ Complex geometries ▪ Easily accessible ▪ Requires almost no pre-processing	▪ Limited printing speed and volume ▪ Requires post-processing ▪ Demands specific rheological requirements	▪ Mechanical isotropy in the z-axis ▪ Enables healability ▪ Enables reprocessability
SLS	▪ Complex geometries ▪ High printing speed and volume ▪ Minimal waste (powder can be reused)	▪ High cost ▪ High energy consumption ▪ Limited resolution and surface quality ▪ Requires post-processing	▪ Enables healability ▪ Lower energy consumption ▪ Improved surface smoothness

Fig. 17. Self-healing polymers processed using different additive manufacturing techniques. a) Soft robotic gripper printed using FFF out of a Diels-Alder elastomer (Copyright 2020. Reproduced with permission from Mary Ann Liebert, Inc.) [420]. b) Healable vitrimer processed using vat photopolymerization and healed after 16 h at 65 °C by the dynamic exchange of boronate crosslinks (Copyright 2021. Reproduced with permission from American Chemical Society publications) [452]. C) 3D printing of an elastomeric imidazolium polyamide-ionene which exhibits intrinsic shape-memory and self-healing (Copyright 2020. Reproduced with permission from American Chemical Society publications) [455]. d) SLS printed of thermoreversible Diels-Alder healable thermosets (Copyright 2022. Reproduced with permission from Elsevier) [460].

ers, researchers have identified concerns related to the emission of volatile organic compounds (VOCs). VOC formation can pose health hazards and air contamination issues, which are particularly troublesome for indoor operations [435–437]. Therefore, more safety-related adaptations and policies are of utmost importance prior advocating the use of these techniques.

A wide range of materials, including self-healing polymers and composites, have been proven to be suitable for additive manufacturing in different material states such as powders, granules, filaments or liquid resins. A summary of the different additive manufacturing used for self-healing polymers, together with their advantages, disadvantages and sustainability remarks, are represented in Fig. 17. To process these materials, various additive manufacturing technologies are available and classified as follows:

Fused Filament Fabrication (FFF) and Fused Granule Fabrication (FGF) are 3D-printing techniques where a material, in the form of filament or granules, respectively, is extruded through a heated nozzle and deposited layer by layer onto a printing bed. Thermoplastics are the most used materials for these extrusion printing techniques due to their thermal processability. As the material is deposited layer by layer, it solidifies, eventually building the final object. For more complex geometries, a support is usually manufactured, and the printed material is selectively deposited on it. Once the final piece is fabricated, the support is removed, either by manual peeling or dissolution if the support is water-soluble (*i.e.*, PLA). In addition, by assembling various nozzles, FFF and FGF are suitable techniques for multi-material printing.

Thermoreversible self-healing elastomers can be heated above T_{gel}, making them extrudable through the nozzle as a viscous liquid that reversibly gels upon cooling. The main difference between traditional printable thermoplastics and thermoreversible self-healing polymers lies in the evolution of the viscosity profiles of the latter, abruptly changing as a function of the crosslink density. Precise control of the printing temperature is necessary to assess the rheological properties and reaction kinetics of the polymer during printing. Recent simulations have shown a rapid decay of viscosity when T_{gel} is reached during printing, which does not follow any of the previously reported well-established models for thermoplastic filaments [420,438]. This also implies that thermoreversible networks cannot benefit energetically from viscous dissipation. However, this disadvantage can be compensated for by the lower temperatures required to bring the thermoreversible networks to an extrudable state. A more detailed energy consumption study of these processes is needed to further evaluate this trade-off.

Dynamic covalent networks must be printed with a sufficiently high crosslink density to avoid dripping and spreading upon deposition. This can be achieved by using a printing temperature close to T_{gel}, so the polymer is printed as a percolated critical gel that can immediately develop a yield stress. Accurately monitoring the rheological properties at the sol-gel transition is essential for building parts with high resolution [439]. In addition, dynamic covalent bonds yield robust interlayer adhesion, as these bonds are also active at the interface between printed layers, leading to highly isotropic mechanical properties [440]. In the case of thermoplastics printing, interlayer thermal diffusion is inefficient, which is a significant limitation for bearing the force load applied in the printed height direction [441–443]. This makes self-healing materials an interesting alternative for waste prevention not only caused by their healability and recyclability, but also due to the more reliable mechanical properties, bolstering durability.

Vat photopolymerization, including stereolithography (SLA) and digital light printing (DLP), utilizes liquid photo-curable resins as feedstock to fabricate 3D objects. A light source, typically a laser, is used to irradiate a specific area of a liquid resin bath according to a pre-programmed pattern. Upon light irradiation, the liquid resin undergoes polymerization and solidifies to create a layer. The printing platform then moves to allow for the creation of subsequent layers until the object is complete. SLA can produce objects with high resolution and isotropy and with low energy consumption. However, incomplete crosslinking is a common issue that often requires a post-curing step.

Most of the photo-curable resins available for SLA are based on petroleum-derived monomers, such as epoxy or acrylates. This contributes to the accumulation of plastic waste, and therefore, the selection of biobased monomers that can be photopolymerized, such as (meth)acrylate groups derived from lignocellulosic-derived phenolic compounds, polycaprolactone, terpenes, lactic acid, isosorbide, glycerol or vegetable oils, can help to improve the sustainability of SLA [444]. In addition, the reprocessability or degradability of these materials can alleviate the sustainability concerns of 3D printing. When considering reprocessing, the SLA prints cannot be used again for SLA purposes. However, other routes such as thermal remoulding [445], the incorporation of dynamic covalent bonds in the network [446,447] or combined with interpenetrated networks (IPN) or double networks [448–450] have shown excellent reprocessability of healable parts manufactured using SLA. Despite the encouraging progress, the use of biobased and reprocessable photo-cured resins suitable for SLA is still in its initial stage. In addition, another advantage of biobased feedstocks, such as vegetable oils, is the presence of biodegradable linkages. This can limit their accumulation in the environment when improperly disposed. The combination of (dynamic) photo-curable, thermally reversible and degradable linkages within a single self-healing system seems to be an excellent candidate to fulfil the lifecycle requirements for a sustainable development of SLA. Finally, some progress has been recently devoted to 3D-print extrinsic self-healing materials using this additive manufacturing technique too [451]. A remarkable achievement in this field was accomplished by Robinson et al., developing a dynamic covalent network based on boronate esters with reactive sites for post-printing functionalization, enabling additional functionalities such as fluorescence or swelling capability to the printed parts [452].

Direct ink writing (DIW) involves the extrusion of liquid monomers or pre-polymers through a nozzle or syringe, followed by subsequent solidification on a substrate via polymerization or solvent removal. Unlike other extrusion techniques that rely on temperature for solidification, the solidification mechanism in DIW depends on the rheological properties of the ink during the polymerization process [453,454]. Achieving suitable printability of objects with high quality requires the ink to yield low viscosity and shear thinning properties. This technique, as for FFF and FGF, also allows for multi-material printing by using multiple nozzles or by sequentially depositing different inks.

When using thermoreversible dissociative networks, as in FFF and FGF, the ink consists of the heated network above T_{gel}. Moreover, some printing advantages such as enhanced interlayer diffusion apply to this additive manufacturing technique [455,456]. Some researchers have used rheology modifiers to improve the printing performance of thermoreversible inks [457,458]. Keeping the ink above T_{gel} and the bed temperature high to accelerate the reaction kinetics requires a considerable energy input, comparable to that of FFF and FGF. However, DIW requires almost no material pre-processing compared to FFF or powder-based 3D printing, which involves additional energy-consuming processes such as filament or powder fabrication, respectively.

To ensure high-quality printing, it is important to monitor and control the rheological properties of the ink during the printing process. This involves optimizing ink viscosity, shear-thinning behaviour, and gelation kinetics to achieve the desired printability and structural integrity of the printed object. In addition, the rheology and printing parameters can be tuned to control the microstructure of the printed object, including its porosity, surface roughness, and mechanical properties. Moreover, the use of novel materials and composites with tuneable rheological properties is an exciting avenue for future research in DIW.

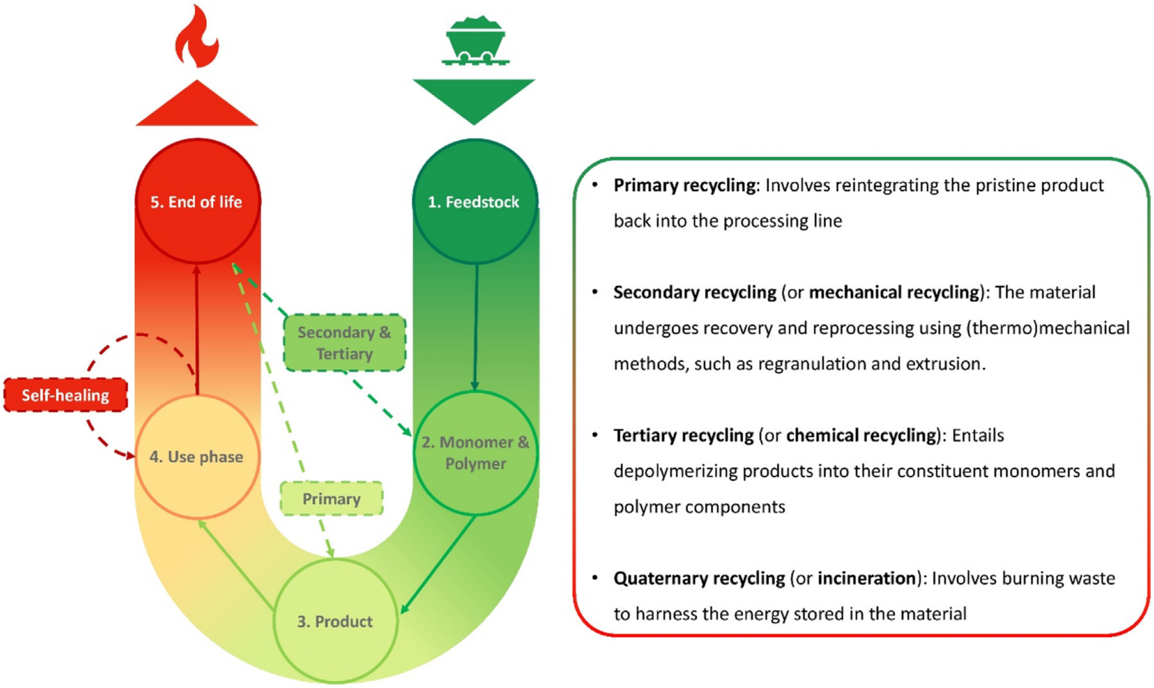
Selective Laser Sintering (SLS) uses polymers, typically polyamide-12, shaped as fine powders to manufacture 3D objects by heating the particles upon laser irradiation. The heated polymer particles melt and coalesce (sinter) together, forming a smooth printed layer. Subsequently, a roller or blade deposits another layer of powder, and the process is repeated until the final object is formed. SLS is popular due to its ability to print highly complex geometries without the need to use any support structure since the powder bed acts as the support itself. However, it has some sustainability issues, such as the need for extensive processing to achieve a suitable powder size and morphology, highly energy-consuming heat treatment and limited polymer palette suitable for SLS makes.

The electricity consumption required to maintain the powder bed at a suitable temperature during printing is the dominant environmental burden of SLS [459]. This is caused by the narrow and heat-consuming thermal window required for suitable printing to avoid thermal shrinkage of the printed part and to keep the laser power low enough to extend the printer service time. To address this issue, as proven by Cerdan et al., thermoreversible covalent networks such as a Diels-Alder thermoset can be efficiently printed via SLS at room temperature [460]. This allows not only to print a reprocessable and recyclable glassy thermosets via SLS but also to greatly alleviate the environmental burden of this process diminishing the energy consumption to the minimum extent. Other more flexible healable polymer networks have been printed using this technique [461,462]. A significant limitation on the laser sintering of thermoreversible networks relies on the residual heating generated by the laser, hence inevitably heating the bed chamber during the printing process. When the powders are heated above, the formation of rubbery particles would strongly reduce the flow properties by partially sintering them together, leading to clogging the powder. This makes it challenging to print softer thermoreversible materials, such as elastomers, with the current technology. Further research is needed to understand how heated thermoreversible polymer powders can withstand the elevated temperatures generated during the printing process. This is of great importance to speed up the printing process and reuse the unsintered powder.

6. Waste prevention and management

Waste production needs to be reduced as much as possible, ideally avoided. The best way to limit waste formation is to increase the useful service lifetime of products, by making products more robust or by way of reuse. The ability to heal damage and recover functional properties is a clear way to increase the useful lifetime of materials and derived objects and structures. This extends the use and reuse phase of such materials and postpones the production of waste. In previous sections, the synthesis, production and manufacturing of self-healing polymers have been critically reviewed. In each process, waste stream production, such as side products, accidental loss of material or suboptimal processing conditions, must be avoided or at least limited.

The current linear plastic economy entails solid waste landfilling coupled to micro- and nanoplastic pollution, which has a direct impact on human and environmental wellbeing. Thus, suitable waste management strategies are of utmost importance to promote polymers circularity. Although there are important incentives for recycling strategies, their implementation is still challenging to say the least. This includes the insufficient consumer compliance, low recovery rate of plastic waste and complex waste collection and logistics, difficult pre-sorting and elevated expenditures, polymer degradation during use and during the recycling process and the



- **Primary recycling**: Involves reintegrating the pristine product back into the processing line
- **Secondary recycling** (or **mechanical recycling**): The material undergoes recovery and reprocessing using (thermo)mechanical methods, such as regranulation and extrusion.
- **Tertiary recycling** (or **chemical recycling**): Entails depolymerizing products into their constituent monomers and polymer components
- **Quaternary recycling** (or **incineration**): Involves burning waste to harness the energy stored in the material

Fig. 18. Types of currently existing methods for polymer recycling. The scheme portrays the lifecycle of a self-healing material, spanning from its initial state as raw feedstock, through production and use, to its end-of-life phase. By adopting suitable recycling pathways, non-functional products can be reintegrated into the manufacturing process, contributing to the production of additional pre-polymer or polymeric materials. Self-healing polymers offer a unique ability to restore their functionality without necessitating a complete recycling procedure, at least for a finite amount of healing cycles.

low cost of raw materials. These limitations lead to an inefficient polymer recovering and reuse [463,464].

6.1. Recycling

Circularity relies on effective reuse and recycling strategies that keep materials and products in the loop. Postconsumer products can be used as feedstocks for new materials, which has been a topic of significant research interest over the past two decades [465]. Recycling helps to limit the piling up of plastic waste in landfills, saves energy compared to producing virgin materials, and avoids the need to extract new resources [466]. Modern recycling methods are mostly focused on thermoplastics that can undergo flow at high temperatures and large shear forces. However, thermosets and elastomers cannot be recycled due to their inherent irreversibly crosslinked nature. Self-healing polymers offer several advantages and disadvantages in terms of recyclability depending on the dynamic chemistries used. Polymer networks crosslinked by dynamic chemistry have the potential to be recycled in several ways by the application of the adequate stimulus [467]. To date, there exists four main material recycling approaches, namely primary, secondary, tertiary and quaternary recycling. A summary of the recycling routes suitable for self-healing materials throughout their lifetime are schematized in Fig. 18 and these methods are discussed in more detail, with the focus on the potential contribution of certain self-healing systems to that recycling.

Primary recycling or ***closed-loop recycling*** utilizes clean, non-degraded and homogeneous plastic waste, and incorporates this source back into processing of materials and manufacturing of products. This is the most efficient recycling method, but can only be applied to clean waste streams, *e.g.,* at production plants. As soon as the product/material leaves the plant, the entropy starts increasing due to contamination, variations in the composition of plastics on the market and their degradation during their different lifespans. Hence, such a recycling process is mostly applicable to process scrap at the production plant or post-consumer materials of known origin with short lifespans and low degree of contamination.

Secondary recycling or ***mechanical recycling*** is the most widely adopted recycling technology forsolid plastic waste. The polymer is physically recovered and reprocessed by (thermo)mechanical methods. This includes collection and sorting of polymer waste streams, washing and drying, size reduction by grinding and subsequent compounding and pelletizing (regranulation). These processes are widely applied in thermoplastics. However, sometimes unavoidable events such as the presence of impurities, moisture, oxygen, temperature inhomogeneities and high shear forces lead to chain scissions or branching, which affects the average molecular weight and polymer architecture of the recycled thermoplastics. Such variations lead to an important change of their macroscopic properties, such as their mechanical and rheological properties [468,469]. Degradation is considered as the main constraint of mechanical recycling of plastics, although it can be partially mitigated by using additives (stabilizers and compatibilizers) or by better controlling the processing conditions. To compensate for the degradation of the recycled material, some industrial plants operate under open-loop or semi-closed-loop methods by feeding virgin polymer during the recycling process. Irreversibly crosslinked thermosets, rubbers and their composites cannot be recycled using thermomechanical methods. An open-loop approach for irreversible covalent polymer networks consists in mechanical grinding into smaller chunks or even fine powders for their use as reinforcing fillers for thermoplastic composites or new thermoset or rubber composites [470].

Intrinsic self-healing polymers depend on dynamically reversible crosslinks in their polymer network structure. These reversible networks can be (re)processed by activating dynamic chemistries using the adequate stimulus. Most intrinsic self-healing polymers are thermally triggered, resulting in either the dissociation of the polymer network or accelerating the exchange of dynamic bonds upon raising the temperature. Hence, these intrinsic SHP can be reprocessed and recycled using similar methods used for other thermoplastics. Replacing irreversible covalent crosslinks by dynamic covalent bonds opens mechanical recycling opportunities of factory and post-consumer waste from thermosets and rubber products. This is particularly interesting for thermoreversible covalent networks due to the well-developed processes already existing for thermal (re)processing. Dynamic bonds can be dissociated in a much less energetic way (temperature and pressure) than the conventional irreversible covalent bonds. This is a step towards the sustainability of chemical recycling by greatly reducing energy input. However, special attention needs to be paid to the monomer degradation since they might become unstable under the recycling conditions. An example of this inconvenience is the homopolymerization of bismaleimides that can take place at temperatures above 140 °C in Diels-Alder systems [471]. This can be partially prevented using additives such as radical inhibitors during the synthesis or recycling steps. This makes the formulation of novel bio-based additives (*i.e.*, antioxidants) an interesting route to improve further both the stability and the renewability of self-healing polymers upon recycling [472].

It has been reported in literature that dynamic covalent networks can be submitted to repeated thermal and thermomechanical manufacturing processes, such as milling [460], extrusion (FFF) [420], pelletizing (FGF) and subsequent additive manufacturing using SLS, FFF and FGF, respectively, hence proving their recyclability. Dissociative and supramolecular dynamic networks experience a drastic reduction in viscosity when heated above T_{gel}. This offers opportunities for waste separation and purification via different methods. Low viscous liquids allow a much easier filtration and recovery of solid fillers or contaminants, improving mechanical and optical properties of the recyclate. Other parameters such as the solid concentration or cake resistance upon filtration also determine the efficiency of the filtration/centrifugation process, but generally a low viscous medium allows suitable pressure drops under milder conditions than a higher viscous medium [473]. In addition, it has been demonstrated that high solid filler concentrations in self-healing polymers lower substantially the healing performance, hence this issue is not a desirable scenario [429].

Tertiary recycling or ***chemical recycling*** refers to processes where polymers are chemically depolymerized for their conversion into monomers or oligomers that can be used to manufacture new value-added products. This includes the production of new polymers, or their use in other applications such as fuels or other chemicals. The advantage of chemical processes compared to mechanical recycling is the widening of life cycle boundaries. While mechanical recycling is restricted to a certain number of reprocessing cycles due to thermomechanical degradation, chemically depolymerized products can always be used as raw chemicals if properly purified. Examples of chemical recycling processes are chemolysis, pyrolysis, fluid catalytic cracking, catalytic pressureless depolymerization (KDV) process, hydrogen-based technologies or gasification [469]. Some other chemical degradation routes, such as enzymolysis [474] or the use of supercritical fluids [475,476] are showing promising performances at their early research stage. Chemical recycling performs better to those polymers with low mechanical resistance, such as polyethylene terephthalate (PET), since solvents can attack and break these bonds under milder conditions than other covalent bonds such as C–C bonds in polyolefins [477]. Permanent polymer networks can undergo some chemical recycling methods such as devulcanization of rubbers or chemolysis of irreversible crosslinks [478]. Despite the promising features of chemical recycling, there are still some limitations to be scalable and profitable such as the required high feed volumes, purification complexity, high temperatures and pressures needed for chains splicing, catalysts deactivation or instabilities in presence of impurities [478]. Moreover, depolymerization requires much higher energy inputs compared to (thermo)mechanical recycling processes.

Intrinsic self-healing polymers that are either crosslinked by physicochemical interactions (supramolecular networks) or by reversible chemical reactions (dynamic covalent networks), can be depolymerized using the adequate stimulus to reverse the reaction. The same principle also forms the basis for the processability and mechanical recyclability of these two new classes of polymer networks. In view of tertiary or chemical recycling, these reactions would need to be reversed to the extent that the monomers can be recovered. Whether this is practically or even theoretically possible depends on several factors. First and foremost, this depends on the reversible reaction mechanism. Physicochemical interactions are often easily broken by the application of a thermal stimulus or by changes of the pH or redox potential. Upon cooling, the interactions and, in turn, the supramolecular network reforms. This method is suitable for secondary (thermomechanical) recycling, while it is not straightforward to separate monomers again. Keeping the pH or redox potential constant in conditions where the physicochemical interactions are broken is practically more easily performed.

Reversible chemical reactions that follow a dissociative mechanism can be dissociated back into the monomers upon the application of the right stimulus. In the case of thermoreversible reactions, a reaction equilibrium needs to be overcome and the equilibrium needs to be pushed towards the further dissociation of the reaction products back into the reactants, theoretically at infinitely high temperatures. Alternatively, this could be achieved by removing one or more of the reactants from the reactive medium to continue to drive the equilibrium towards further dissociation, following Le Chatelier's principle. In the example of the furan-maleimide Diels-Alder reaction, this would entail the removal of either furan, maleimide or both from the reactive medium to drive the equilibrium towards further thermal dissociation of the adducts. Photoreversible reactions can be directed to the dissociation of the photodimers by the application of light at the right wavelength or by thermal dissociation. In the absence of the stimulus for bond formation, the reaction products can be completely dissociated back into the monomers. In the case of anthracene dimerization, the photo-dimers could be dissociated using UV light at a wavelength of 250 nm. Similarly, it has been shown that anthracene photodimers could also be dissociated by thermal stimulation, following a first order decay [152,479].

An important consideration for the recyclability of dynamic covalent networks is the monomer architecture and functionality. Separating and storing the monomer reactants is only possible if the bond formation reaction can be avoided. If a one-component reaction is considered, where a monomer bears two types of functional groups that can spontaneously react with each other under practical storage conditions, it is not possible to prevent repolymerization, unless special measures are taken. Willocq et al. described a one-component strategy for Diels-Alder-based self-healing polyurethanes by copolymerization of both furan and maleimide moieties into the same oligomeric backbones [480]. Hence, it is not possible to separate the reactive functional groups and to recover the monomeric reactants.

Associative networks do not show a net change in connectivity upon increase of the adequate stimulus, *e.g.* heat or light. Hence, they cannot be chemically recycled as described by dissociative chemistries. However, the polymer networks can be broken down in a reactive (monofunctional) solvent that can exchange with the formed crosslinks. Ogden et al. demonstrated that an associative network based on boroxines could be easily recycled upon boiling in water, recovering the diboronic acid starting monomer as a white precipitate upon cooling [481]. In a similar way, the polyols used to create dynamic networks based on exchangeable acetal crosslinks were recovered at yields above 90 % within 1 h at 100 °C in water, methanol or ethanol, and could be re-crosslinked with a divinyl ether to re-obtain the dynamic network [482,483]. The divinyl ether partner could not be recovered, but the diol and acetaldehyde resulting from the degradation could be readily recycled. Degradation and recycling of epoxy-amine thermosets has been shown by hydrolysis and reformation of imine bonds [484]. Imine exchange (associative mechanism) enables reshaping and welding at relevant temperature, the dissociative mechanism of imine bonds results in bond breaking and lowering of the crosslink density. Ultimately, the polymer network can be solubilized in organic or aqueous solutions under mild conditions and recycled from the solution with the virgin mechanical properties restored.

Alternatively, it is also possible to shift the equilibrium of some exchange reaction in the presence of bases or acids. Qin et al. reported recycling of networks based on transamidation between maleic anhydrides and secondary amines, which can be completely depolymerized in an acidic aqueous solution at ambient temperature [485]. A mild two-phase separation allows to regenerate the amine and anhydride monomers with $>$ 94 % separation yields. The recovered monomers can be used to remanufacture crosslinked materials without losing their virgin mechanical performance. In another study, acid hydrolysis was used to break down vanillin-based vitrimers [348]. The dialdehyde monomers could be fully recovered from the acid solution at 50 °C and used to regenerate the poly-Schiff vitrimers. Other vanillin-based vitrimers integrating Schiff base hardeners were reported to degrade in the presence of an amine in ethanol solution at 60 °C [486]. The original precursors were not isolated again, but the degradation products were used to prepare new epoxy resins. It should be noted that these chemical recycling pathways, breaking down the networks into the monomers and the reformation of the associative networks, often require harsh organic solvents and high catalyst loadings.

Chemical recycling of associative networks based on the most popular epoxy-acid transesterification remains a challenge. Epoxy vitrimers that were produced from ferulic acid, citric acid and epoxy resins were decomposed in 30 wt% NaOH solution at 80 °C in 30 min [487]. A small portion of ferulic acid-based hyperbranched epoxy resin was added to facilitate the (catalyst-free) transesterification thanks to the large excess of hydroxyl groups of the hyperbranched structure. Upon addition of 10 phr FEHBP, the activation energy and relaxation time decreased from 98 kJ mol^{-1} and 164 s to 58 kJ mol^{-1} and 45 s at 140 °C. After acidic neutralization, ferulic acid was filtered obtained by filtration. The filtrate was distilled to obtain a recycled citric acid-derived polyester (CAP). Both could be re-used to prepare epoxy vitrimers with properties approximately resembling the ones of the original vitrimers.

Weng and Zhang developed another strategy embedding an enzyme-sensitive crosslinker that can destroy the epoxy-acid vitrimer network [488]. Oxidized starch was synthesized with adjustable carboxyl content and used to crosslink epoxidized natural rubber (ENR). The vitrimer may be decomposed into saccharide oligomers upon immersion in a solution containing the thermostable enzyme alpha-amylase. The recovered ENR lost the epoxy functions but retains the carbon—carbon double bonds, and thus may be re-crosslinked with standard vulcanization agents like peroxides. The recycled material presents the same mechanical performance as pristine when 0.5 phr dicumylperoxide was adopted for crosslinking. Regrettably, such process appears as a one-shot recycling as peroxide-crosslinked rubbers are not reprocessable anymore.

There is a great interest in the use of dynamic covalent networks not only to extend the product's lifespan but also to enable its recyclability in an easier fashion than for irreversible systems. This perspective is at its initial stage, and there are challenges to overcome strongly related to the self-healing applications market. This includes, for example, issues such as the recycling of robotic multi-material assemblies, coatings recovery or the combination of different networks (double networks or IPN) in a single system. Thus, there is a strong need to design methods that can accurately promote suitable chemical reversion and purification while keeping the high performance. Recycling by triggering reversible networks depolymerization under the right conditions is a challenge that is expected to grow as self-healing materials find the market demands across the potential applications board. The development of specific applications for self-healing materials must be accompanied by specific tools and technologies for an efficient recycling of the material to maintain their circularity.

Finally, ***quaternary recycling*** applies to the ***incineration*** of polymer waste. This waste-to-energy approach is not a recycling process from a material reusability point of view but enables to partially recover the energy stored in the material during synthesis. It is the least sustainable end-of-life process, even considering collection of the degradation products, *a.o.* CO, CO_2 and water, which enables the utilization of these waste products for other processes. Despite its simplicity and widespread use, the energy recovered is much lower compared to the original feedstock processing, synthesis, processing and manufacturing into useful products. This route should only be considered if none of the other end-of-life options presents a feasible and more sustainable alternative. With dynamic covalent bonds opening recycling opportunities for even chemically crosslinked polymer networks, the need for such a quaternary recycling method may be entirely omitted.

Extrinsic self-healing polymers are based on the incorporation of a liquid healing agent inside a permanent polymer network. Once the healing potential that is stored inside these extrinsic self-healing polymers is depleted, these systems need to be recycled in a similar manner as traditional permanent polymer networks, while taking into account the presence of remnants of liquid healing agent, the presence of catalysts inside the polymer matrix and the overall higher entropy of the system due to the presence of the shells of the containers, which typically have a different chemistry than the polymer matrix they are embedded in. To the authors' knowledge, no studies have been conducted so far on the potential recycling opportunities and challenges for extrinsic self-healing polymers. Previously mentioned systems using thermoplastics instead of thermosets as a host matrix show potential opportunities in the recycling field.

6.2. Bio-degradation

Accidental or purposeful release of polymeric materials into the environment is inevitable. Hence, it is very important to consider degradation pathways that can avoid accumulation of plastic waste in the environment. All plastics undergo a certain degree of degradation under atmospheric and weathering conditions, either physicochemical or biological. The primary cause of microplastics is physicochemical degradation caused by exposure to atmospheric oxygen (oxidation), sunlight (UV degradation), humidity (hydrolysis), eroding and abrading conditions, such as wind, and especially any combinations thereof. Biodegradation of plastics, on the other hand, is caused by microorganisms such as bacterial and fungal species and depends on the temperature and humidity. In general, plastic polymers can degrade to form CO_2, methane, water and edible biomass/compost. The compost of the compostable plastics (organic matter not harmful to animal or plants) can either form at room temperature with the help of food waste or more commonly in industrial plants at controlled temperatures (mostly at 58 °C) and requires appropriate collection and sorting of the waste [489].

A variety of analytical techniques are used to determine the biodegradability of polymers in general but combinations of a series of them could give better estimations of the biodegradation. Simply, polymer powders less than 250 µm or 5 × 5 mm film were placed in closed dark vessels either in air (aerobic) or inert (anaerobic) at a certain temperature of 20–25 °C for mesophilic or 58 °C for thermophilic microbes. Then evolved CO_2, mass loss, O_2 demand, change in molecular weight, change in chemical structure or bonds and are tracked over time using FTIR, UV spectroscopy, NMR, GPC and Maldi TOF [489].

The biodegradability of a new material is appealing since it can provide solutions to littering, waste management and microplastics pollution conflicts. Today, bio-based or biodegradable plastics are used mainly in the food packaging industry.

While the ability to heal incurred damage and the improved recyclability of most intrinsic self-healing polymers have been assessed to greatly impact the sustainability of polymeric materials such as elastomers, thermosets and their composites, there may still be loss of material to the environment. This may be due to loss of material during the use phase, poor material management, poor waste management. This may be an important consideration for self-healing polymers that are not straightforwardly recyclable. Therefore, this section looks at recent developments to improve the end-of-life of polymers in general and more specifically applied to self-healing polymers.

A series of copolyesters synthesized from 2,5-furandicarboxylic acid [389], epoxidized natural rubber [490], boronic ester vitrimers from epoxidized soybean oil acrylate [491] are recent examples of biodegradable self-healing polymers. Evaluation of the biodegradability of these polymers were assessed by means of enzymatic degradation [389], mass loss [490] biochemical oxygen demand (monitoring the oxygen consumption at the certain environment) [491]. Some others are a completely biodegradable polymer blend, constituted by a CNT modified carboxyl methyl cellulose (CMC) masterbatch and a commercial biodegradable highly amorphous vinyl alcohol polymer (HVA) using Murexide salt and a vinyl alcohol copolymer (HVA) [492,493].

In most literature reports, self-healing materials are not biodegradable and only in a few cases the biodegradability is the result of the incorporation of a dynamic chemistry into the polymer network. (Bio)degradability can be considered as a contradictory aspect for SH materials, as it seemingly stands directly in contrast to the intended maximization of their useful service lifetime. While self-healing can indeed extend the service lifetime of products and structures, their useful lifetime still depends on the user. End-of-life considerations such as recyclability and degradability are thus important aspects to lift the sustainability of the SH material farther than just the product lifetime. To the authors' knowledge, there have been no reports of approaches combining extrinsic SH systems with degradation mechanisms. Some approaches such as the formulation of matrixes using biodegradable polymers such as polylactic acid (PLA), polybutylene adipate terephthalate (PBAT), polybutylene succinate (PBS), polyhydroxyalkanoates (PHA) or the encapsulation of degradation agents that can be selectively released under certain conditions (*i.e.* light irradiation, water contact…) are interesting options to close the sustainability loop of extrinsic SH materials. The undesired release of these materials to the environment can be mitigated by wisely tuning their composition, limiting mismanaged waste buildup, which are particularly hard to be reprocessed hence more prone to be eventually released to the environment.

In the context of self-healing polymers, the relationship between biodegradability and material composition is a crucial aspect to consider. Biodegradability can arise from both the matrix used, such as starch-based components, as well as from the specific self-healing mechanisms embedded within the material. For instance, certain self-healing polymers, like transesterification vitrimers, contain ester bonds that have the potential to be degradable under suitable conditions. While many self-healing materials are not inherently biodegradable, some recent advancements in polymer chemistry have explored the incorporation of dynamic chemistries into the polymer network, which could introduce biodegradability as an inherent property. It's important to recognize that the biodegradability of self-healing materials represents a complex interplay between their chemical composition, the self-healing mechanism, and the environmental conditions to which they are exposed. As we strive to extend the useful service lifetime of self-healing materials, it becomes increasingly vital to also address their end-of-life considerations, including recyclability and degradability, to enhance their overall sustainability and minimize environmental impact.

A recent topic of discussion is on the negative contribution of the bio-degradable polymers suggests that they could potentially produce a higher quantity of microplastics than conventional polymers during degradation processes. These microplastics, despite being derived from biodegradable sources, possess a large surface area with high adsorptive potential, which allow them to interact with other organic molecules and heavy metals [494], antibiotics and pesticides [495] which can further contaminate the soil [496], oceans and freshwater [497]. This accumulation of pollutants within biodegradable materials presents a challenge in achieving a truly sustainable and closed-loop material cycle, highlighting the need for comprehensive strategies to mitigate these negative impacts while maximizing the environmental benefits of biodegradable polymers within the circular economy framework.

7. Future perspectives

The chemistries used to develop self-healing polymers have the potential to significantly improve the sustainability of polymer networks. First, the ability to heal damage, avoid catastrophic failure and recover the functional performance of the materials and products upon damage healing offers an extension of the useful lifetime of the self-healing materials and products beyond those of conventional alternatives. Multiple prospective lifecycle assessments confirmed the assumption that one of the major reductions in environmental impact is the service lifetime extension by damage healing and the resulting reduced need to produce new replacement products, provided a sufficient level of recovery of the product performance is achieved and depending on the user acceptance thereof. Less new feedstocks need to be extracted for the synthesis of new materials and less energy is required to manufacture replacement products. Provided that the energy and other input that are required to achieve damage healing are limited compared to the energy that is required to create the materials and products, a reduction of the environmental impact regarding energy use can be obtained relative to its lifetime (extension). Self-healing supports extended use and reuse of products and components. This is the shortest loop in a circular material economy, where the same material and product is continued to be (re)used thanks to the damage healing ability. Lifecycle assessments of materials have long been limited from the cradle to the gate. This is still very common in industrial practices. Recently, the end of life has been considered in cradle-to-the-grave approaches and cradle-to-cradle for lifecycle assessments that include recycling activities. More extensive lifecycle assessments will be necessary in the future to consider the full lifecycle of the materials from the cradle to the grave, while accounting for the (re)use phase and recycling to postpone materials ending up in their graves.

The ability to heal damage is the most unique feature of self-healing polymers, that enables primarily to extend the service lifetime of the materials and products. In addition, intrinsic self-healing polymers that are reversibly crosslinked by way of physicochemical interactions (supramolecular networks) or dynamic covalent chemistries (dynamic covalent networks) further enhance their sustainability by way of the reversible network polymerization. Supramolecular networks and dynamic covalent networks have the potential to change the paradigm of polymer (network) recycling, by opening (thermo)mechanical and chemical recycling methods for thermosets, elastomers and their composites. Thanks to the reversible (de)polymerization, these intrinsic self-healing polymers can be (re)processed into different shapes and objects and potentially even reformulated into new (self-healing) polymers with different properties by blending or by repolymerization with alter monomer composition after chemical recycling. It has been demonstrated how thermoreversible networks could be (re)processed by traditional thermal processing methods, originally developed for traditional thermoplastics, such as extrusion, moulding and additive manufacturing, and reactive methods such as casting, reaction injection moulding and direct writing methods. Furthermore, it was shown how the use of these reversible chemical reactions poses certain advantages over physical methods such as crystallization and melting. Generally, a higher property isotropy can be obtained with improved interfacial covalent bonding between different layers or materials with dissimilar properties. The reversibility of the bond formation reaction also opens opportunities that were not otherwise available for conventional thermosets and rubbers, such as fusion and welding techniques. Finally, the formulation of dynamic covalent networks based on photoreversible or mechanoreversible crosslinks raises the opportunity to design new reprocessing routes that do not rely on thermal methods, but instead use other suitable energy input, *i.e.*, light or mechanical forces, respectively, that have the potential of further reducing the environmental impact.

The volume of polymers produced increases every year. This is in part due to the increased human population, due to the replacement of other materials by polymers and their composites, and in part also due to the ever-increasing consumption. Renewable feedstocks avoid the need to extract fossil-based and other less renewable feedstocks. However, this needs to be performed consciously. While some single-use products are gradually being banned, this does not seem to be the case for compostable and biodegradable single-use products, as their often bio-based and biodegradable nature serves as an excuse to continue producing and consuming single-use products. The bio-based and biodegradable alternatives often require more energy to be produced. Even considering increasing recycling efforts and considering the lifetime extension by damage healing, the growing demand requires large volumes of resources for the creation of new products. Therefore, renewable feedstocks will play an important role. In the past three decades, research into bio-based polymers has been booming. In the past decade, this trend has been strongly adopted for self-healing polymers, thanks to the maturity of both fields growing side by side. The wide availability and variety of self-healing chemistries has opened the doors widely for matching with increasing renewable resources.

The potential for thermoset and rubber recycling is prospected to have an even greater impact on sustainability than the service lifetime extension by damage healing. While the circle is larger and a higher energy input is required for recycling compared to healing, the volume of materials produced today that will benefit from recycling is much greater than the number of applications that strongly benefit from lifetime extension through self-healing, especially in the current capitalistic economical models, where the tendency is to continue to increase consumption. A major change of consumer mentality and governmental directives is required to demand the production of more sustainable products. The notion of ‘right to repair’ and selling services and functionalities, rather than maximizing consumption materials and products, will be a key enabler to further lift self-healing and other smart repair technologies to the markets to extend product lifetimes and reduce environmental impacts.

Few self-healing polymers have so far made it into industrial applications. A handful of companies has made the leap to cross the so-called ‘valley of death’ with this emerging technology. Some companies commercialize capsules containing blends of healing agents, corrosion inhibitors and adhesion promoters to create self-healing coatings for the corrosion protection of the underlying substrates. Other companies develop self-healing prepregs and composites based on intrinsic self-healing polymers, usually thermally activated. The applications focus mainly on buildings and construction, transportation industry and infrastructure and energy. In these markets, the incentive to adopt self-healing technologies grows, as a reduction in the frequency of inspections, maintenance and repairs substantially saves labour and costs, while potentially increasing reliability and safety. While market analyses annually report exponential growth of the self-healing materials market, the segment of polymers remains rather small. A main hurdle for any technology to overcome is raising the maturity and scale of the technology. Many intrinsic healing chemistries have reached the point where efforts are being made to assess their viability at scale. Life cycle assessments are one example of this increasing maturity, while the increasing investment of funding agencies in such valorization projects and the emergence of startup companies confirm this landmark.

Commercialization can only be achieved in the case of an economically viable business model. In addition, there are some important show-stopper, or conversely requirements for practical application, that need to be mentioned. For extrinsic self-healing mechanisms, the major restraining factors are the limited healing potential, *i.e.* the volume of healing agent that can be stored inside the materials and the depletion thereof at the healed damage site. Intrinsic healing systems suffer the inherent trade-off between the mechanical properties that can be achieved and the healing rate, efficiency and autonomy. Fast, efficient and autonomous healing generally require a high degree of mobility under damaged healing conditions, thus leading to soft and flexible materials. Higher mechanical properties can be achieved with stiffer materials, which generally require the application of an external stimulus to activate the healing action. In many applications, the need for external activation is not easily accepted. Therefore, researchers have been effortlessly trying to overcome these drawbacks by developing more complex polymer architectures and the continuous quest for alternative dynamic chemistries. Damage is often local, and it is not ecologically, nor economically efficient to heat up entire objects and structures to heal local damage. Therefore, many ways have been evaluated to provide heat stimuli, including hot air blowing, light and laser irradiation and point welding. These methods may provide more local heating, without globally altering the material properties, but provide varying levels of control of the local temperature that is generated. Material-oriented solutions are based on the addition of filler particles into the self-healing polymer matrices. Electrically conductive particles enable resistive heating through the Joule effect upon application of an electric potential [498], while magnetic particles enable heating up the resulting composite by magnetic induction upon the application of an alternating magnetic field [499]. Many types of filler particles, such as carbon-based fillers, absorb a much larger fraction of the light spectrum, making radiative heating more effective. The addition of fillers has an adverse impact on the polymer chain segmental mobility and, hence, on the self-healing properties. On the other hand, the fillers help improve the mechanical properties of the resulting self-healing composite.

In the case that (accidental) loss to the environment cannot be avoided, biodegradability plays a vital role in limiting or avoiding polymer waste accumulation in the environment. In most cases, biodegradation is unrelated to the dynamic chemistry used to incorporate the self-healing ability into the polymer network. While only few literature reports consider biodegradation for self-healing materials, and the two mechanisms are seemingly contradictory, biodegradable bonds can be incorporated into the polymer backbone, complementary to the self-healing chemistries that are most often used for reversible crosslinking. This contradiction originates from the notion that biodegradation during the lifecycle should be avoided when aiming for lifetime extension. These seemingly contradictory material properties could be combined, provided that the biodegradation is only triggered upon loss to the environment and that the conditions required for degradation are not met during the use phase of the self-healing polymer.

Declaration of competing interest

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

CRediT authorship contribution statement

Kenneth Cerdan: Conceptualization, Writing – original draft. **Marlies Thys:** Writing – original draft. **Aleix Costa Cornellà:** Writing – original draft. **Fatma Demir:** Writing – original draft. **Sophie Norvez:** Writing – original draft, Writing – review & editing. **Richard Vendamme:** Writing – review & editing, Funding acquisition. **Niko Van den Brande:** Writing – review & editing, Funding acquisition. **Peter Van Puyvelde:** Writing – review & editing, Funding acquisition. **Joost Brancart:** Conceptualization, Writing – original draft, Writing – review & editing, Funding acquisition.

Data availability

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