Recyclable Thermoset Polymer Composites Based on Degradable and Dynamic Covalent Chemistry

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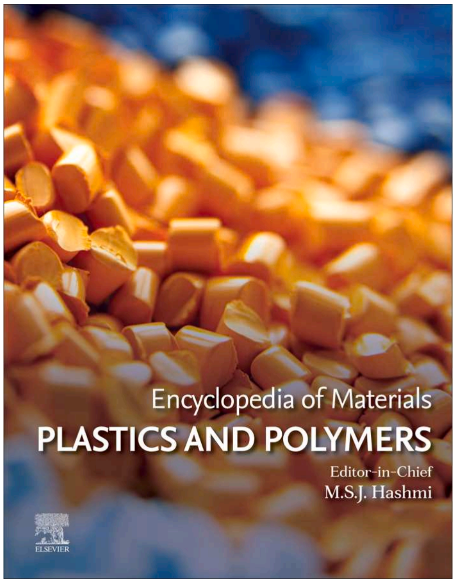

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Recyclable Thermoset Polymer Composites Based on Degradable and Dynamic Covalent Chemistry

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Key Terms

Degradable linkage which is a built-in labile bond that will degrade upon the introduction of a specific stimulus. The location and amount of these labile bonds determines the extent of (possible) degradation leading to either total, partial or selective degradation.

Dynamic covalent linkage which is a molecular bond that is capable of temporary stimuli-triggered mobility of the polymer chains. Dynamic covalent bonds have either an associative or a dissociative debonding mechanism.

Introduction

Polymer composites typically consist of a polymer matrix and a particulate or fiber phase. The particles or fibers can improve the mechanical performance, introduce specific functionalities (e.g., thermal or electric conductivity) or simply lower the costs of the material. The polymer phase acts as the binder between the individual particles or fibers and reduces the overall density. This leads to materials with specific moduli and strengths that are difficult to be matched by monolytical structural materials such as aluminum and steel. Thermosets, which are classified by their irreversibly cross-linked polymer chains, are often selected as the polymer phase for polymer composites. They are typically synthesized by two or more reactive liquid monomers that can easily be infused or mixed with the second phase. This poses great advantages during composite processing. In addition, their covalently crosslinked network leads to higher strengths and a significant reduction in creep compared to their thermoplastic counterparts. These features also lead to a lower susceptibility to damage by thermal and chemical impulses from the nearby environment. The unique combination of the aforementioned properties makes that thermoset polymer composites are materials that are often used in structural and protective applications (Post *et al.*, 2020).

However, besides a unique set of structural and functional properties, the presence of covalent intermolecular chemical cross-links also leads to an inherent difficulty to recycle thermoset based composites. As a result, the main end-of-life scenario of thermoset composite products is landfilling, which is considered to be the least preferred waste management approach from a circular point of view. Other industrial practices to process disposed thermoset composites are limited to grinding or combustion (Yang *et al.*, 2012; Oliveux *et al.*, 2015). The recyclates from these methods mainly consist of ground particles or segments of recovered fiber that are used in lower-end applications, while the thermoset polymer is typically completely degraded during the process (Pickering, 2006). As governments and society strive for a transition from a linear to a circular economy it is crucial that new methods to more effectively recycle this unique class of materials will be developed.

In order to regain and recycle more material from waste products, many technological advancements have been made in the field of recycling processes. Some of these newly developed techniques also pose advantages for the recycling of thermoset based composites such as the anaerobic breakdown of thermoset polymers via pyrolysis at temperatures within the range of 300–800°C. The anaerobic process conditions prevent oxidization of the reinforcing fibers or functional particulates and therefore allow for a more qualitative recycling of these materials compared to incineration. Furthermore, the thermoset matrix is processed into lower molecular weight organic fractions that can be used as feedstock for further chemical processing (Yang *et al.*, 2012; Al-Salem *et al.*, 2017; Cunliffe *et al.*, 2003). Another recently emerging recycling route that shows added value for treating polymer composites is solvolysis. This recycling technique uses a liquid medium to degrade and dissolve the thermoset polymer which enables the fibers or particles to be filtered out. Different types of solvolysis processes exist, such as hydrolysis and glycolysis, based on the liquid medium in which the treatment is performed (Kuang *et al.*, 2018a; Oliveux *et al.*, 2013). The remaining liquid substance can be post-processed to regain the organic fractions originating from the thermoset matrix. These organic compounds can be used as molecular building blocks for new chemicals and polymers. Solvolysis treatments were successfully reported for a wide range of polymer networks including those with amine-epoxy (Ma *et al.*, 2017; Ma and Nutt, 2018), anhydride-epoxy, polyester (Kuang *et al.*, 2018a,b; Vallee *et al.*, 2004) and polyurethane (Simón *et al.*, 2018) linkages. While these recycling strategies are an improvement compared to the industrially applied grinding, incineration, and landfill end-of-life routes, the high energy levels, low yields and complex downstream processing required for pyrolysis and solvolysis remain significant challenges that need to be addressed. Furthermore, both pyrolysis and solvolysis will break down the covalently bonded interconnected network structure which has to be chemically restored in order to make new thermoset materials. As this is often not technically feasible, the thermoset polymers end up being downcycled rather than truly recycled.

In order to prevent the chemical decomposition of thermoset polymer composites, much research was performed in the last decades to either repair or recycle composites, while preserving the thermoset network or even the whole composite material

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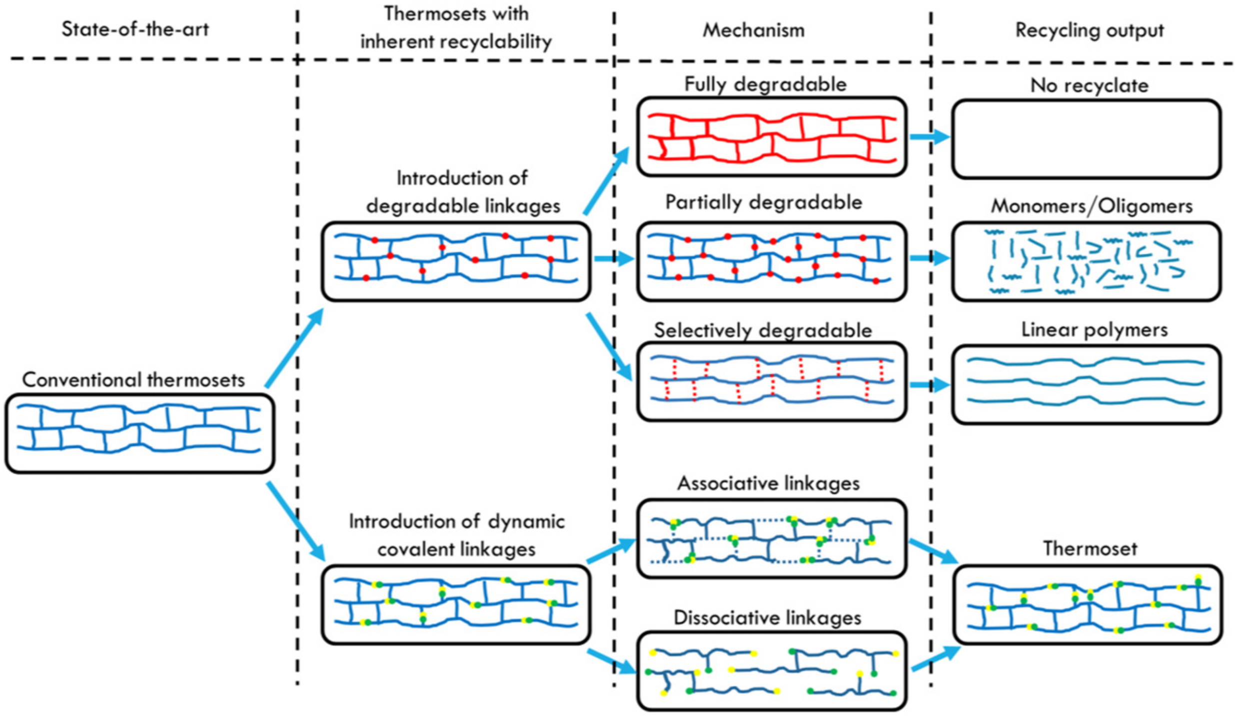


Fig. 1 Schematic overview of the different molecular linkages that facilitate the recycling of thermoset polymers. Reprinted with permission from Post, W., Susa, A., Blaauw, R., Molenveld, K., Knoop, R.J.I., 2020. A review on the potential and limitations of recyclable thermosets for structural applications. Polymer Reviews 359–388, Copyright 2020 Taylor & Francis.

(Zhong and Post, 2015). Autonomous repair of epoxy based composites was pioneered by the Beckman institute who developed capsule-based additives that would excrete a liquid repair agent upon fracture of the composite (White *et al.*, 2001, 2014). These concepts were translated to liquid containing fibrous structures that provided a more even distribution of repair agent, thereby enabling multiple repair events (Pang and Bond, 2005; Toohey *et al.*, 2007; Post *et al.*, 2019). A similar approach using dispersed thermoplastic particles that fill cavities upon a mild temperature stimulus has been demonstrated on an industrial level. It shows great potential for the life extension of a wide variety of thermoset products (Cohades *et al.*, 2018; Cohades and Michaud, 2017). However, ultimately also these polymer thermoset composites will suffer from unrepairable fiber or matrix damage due to a depletion of repair agents and they will have to be handled by one of the earlier addressed end-of-life scenarios.

A more circular thermoset recycling route that is able to maintain the original polymer network structure with a theoretically infinite material lifetime is the introduction of degradable or dynamic covalent bonds within the molecular structure. The dynamic response of these bonds is triggered by an external stimulus which can be of thermal, chemical or optical nature (Zhong and Post, 2015; García and Smulders, 2016). This class of thermosets has received substantial attention in academic literature in recent years. Still, many of the reported materials are industrially irrelevant due to complex expensive chemistry or irrelevant mechanical properties. Nevertheless, this new class of thermosets is slowly moving out of the academic spectrum, and the first examples of recyclable thermosets are approaching the market (Pastine, 2013a; La Rosa *et al.*, 2018; Kissounko *et al.*, 2018).

Recyclable thermosets reported in literature can be subdivided based on the type of molecular linkages that facilitate the stimuli-triggered recycling processes being (1) degradable, (2) associative or (3) dissociative in nature. A schematic overview of these linkages and their general mechanism is shown in **Fig. 1**. Thermosets with degradable linkages are typically based on conventional thermoset resins with built-in labile bonds that will degrade upon the introduction of a specific stimulus. The location and amount of these labile bonds determines the extent of (possible) degradation leading to either total, partial or selective degradation. This yields no recyclates, low molecular weight organic components (monomers/oligomers) or linear (potentially thermoplastic) polymers respectively, as is illustrated in **Fig. 1**. Although the inclusion of stimuli-triggered degradable linkages can result in an improved recyclability of thermoset matrix material, the original polymer architecture is irreversibly destroyed which implies that the resulting recyclate either requires to be resynthesized or will be down-cycled into less demanding applications. Contrary to degradable linkages, dynamic covalent bonds are capable of temporary stimuli-triggered mobility of polymer chains. This results in a recycling process that yields recyclates that are physically identical to the original thermoset polymer. Dynamic covalent bonds have either an associative or a dissociative debonding mechanism. In both cases the properties of the recycled product are unaffected, but the physical behavior of the materials during the recycling process is different.

Upon the application of a triggering stimulus, thermosets with associative linkages will show a simultaneous exchange of one reaction partner for another, in which the original linkage is broken only when a new covalent bond to another position is formed.

As a result, the cross-link density and thereby the viscosity will remain constant during application of the stimulus. Dissociative covalently bonded linkages on the other hand, will actually break and will only establish a new covalent bond when the stimulus is removed. This leads to a net decrease in cross-link density during recycling, that is typically accompanied by a temporary viscosity drop of the polymer. These mechanisms are schematically depicted in **Fig. 1**.

The impact and potential of degradable and dynamic covalent thermoset composites in realizing a circular materials economy is illustrated in **Fig. 2**. In this figure, the conventional, mostly linear, thermoset composite waste treatment process (A) is compared with the anticipated circular recycling routes (B) that are created upon the introduction of degradable and dynamic covalent linkages in thermoset composite materials. The remainder of this article will highlight the most illustrative and advanced examples of recyclable thermoset composites that have been developed in the past decades. In order to contribute to the development of truly circular composite materials it is important that the thermoset resins are developed from renewable resources. Therefore special attention is given to composite matrices that are (partially) biobased and the chemical pathways that are required in order to synthesize them.

Degradable Acetal Linkages

Fig. 1 schematically shows the different options that exist for the inclusion of degradable linkages in thermoset matrices. There are many types of covalent bonds that are known to degrade after the application of a certain stimulus. Most of them are already used for decades in traditional organic chemistry. The chemistry of many of these degradable linkages has been reviewed by multiple groups (Ma and Webster, 2018; Bednarek and Kubisa, 2019; Wang *et al.*, 2019a). This article focusses on the chemistry and application potential of degradable thermosets using acetal linkages, as this linkage is the main driver in the development and commercialization of degradable thermoset composites.

Acetals are characterized by the general chemical structure $R_2C(OR')_2$, and are formed by the nucleophilic addition of an alcohol to a ketone, an aldehyde, or (para)formaldehyde (**Scheme 1**). It has to be noted that the nomenclature "acetal" is sometimes used for both the family of bonds as well as the specific bond derived from an aldehyde. Due to the reversible nature, acetals can be hydrolyzed in the presence of an acid, while neutral and alkaline environments leave the bond unaffected. The hydrolytic stability and rate of disassembly can be tuned by the structure of the acetal. The hydrolysis rate decreases in the order ketal $>$ acetal $>$ formal.

Bisphenolic diepoxy functionalized monomers that are crosslinked with amine hardener monomers are amongst the most conventional thermoset resin utilized for structural polymer composites. Degradable acetal linkages can be incorporated in either of these monomers. Both strategies result mainly in partially degradable networks, i.e., networks which yield monomers and oligomers after recycling.

Diepoxy Acetals

The first diepoxy acetals, and corresponding degradable thermosets, are reported by researchers from IBM (Afzali-Ardakani *et al.*, 1996; Batzer and Erwin, 1962; Buchwalter *et al.*, 1993; Buchwalter *et al.*, 2001; Buchwalter and Kosbar, 1996). The researchers used a two-step approach to obtain cycloaliphatic acetal diepoxides. First, an acetal diolefin is prepared, which is subsequently oxidized to its corresponding acetal diepoxide. The conditions of this oxidation step have to be carefully chosen, since acidic conditions will result in prematurely hydrolysis of the acetal linkage. Thermosets of these acetal diepoxides could be formed by crosslinking with cyclic anhydride in a fashion very similar to conventional diepoxides. All thermosets were readily degradable in acidic conditions, with the rate of hydrolysis in the expected order. Even though the thermosets of the IBM team were amongst the first reported degradable acetal-based polymers, their mechanical properties already showed their high potential as matrices in structural composite materials. Young's moduli in the range of 4–8 GPa and tensile strengths between 30 and 60 MPa were reported for these thermosets (Buchwalter and Kosbar, 1996).

An alternative method of obtaining acetal diepoxides is based on the reaction of a vinyl ether with an alcohol (**Scheme 2**) (Mangold *et al.*, 2011; Hashimoto *et al.*, 2012). Although this mechanism avoids the oxidation under alkaline conditions, it is relying on potentially carcinogenic epichlorohydrin. Hashimoto *et al.* (2012) reported on degradable thermosets based on four different aromatic acetal diepoxides by using phenols. The networks had T_gs comparable to conventional thermosets, but lower decomposition temperatures (225–273°C versus 332°C) due to degradation of the acetal linkage. After acidic degradation in THF/water the phenols could be retrieved. Furthermore, the authors showed that the carbon fibers could be effectively regained from a composite prepared with this resin.

In order to further direct the mechanical properties of acetal linkages towards those required for competitive composite materials, cyclic and spiro acetal linkages were developed. As acetal linkages are typically aliphatic and therefore flexible, they often tend to possess relatively poor thermal, mechanical, and chemical stability. Cyclic and spiro acetal linkages introduce more rigid bonds in the polymer backbone. This results in competitive moduli around 3 GPa, high tensile strengths of 80 MPa and an increased strain at break compared to their linear analogs (Ma *et al.*, 2019; Yuan *et al.*, 2019).

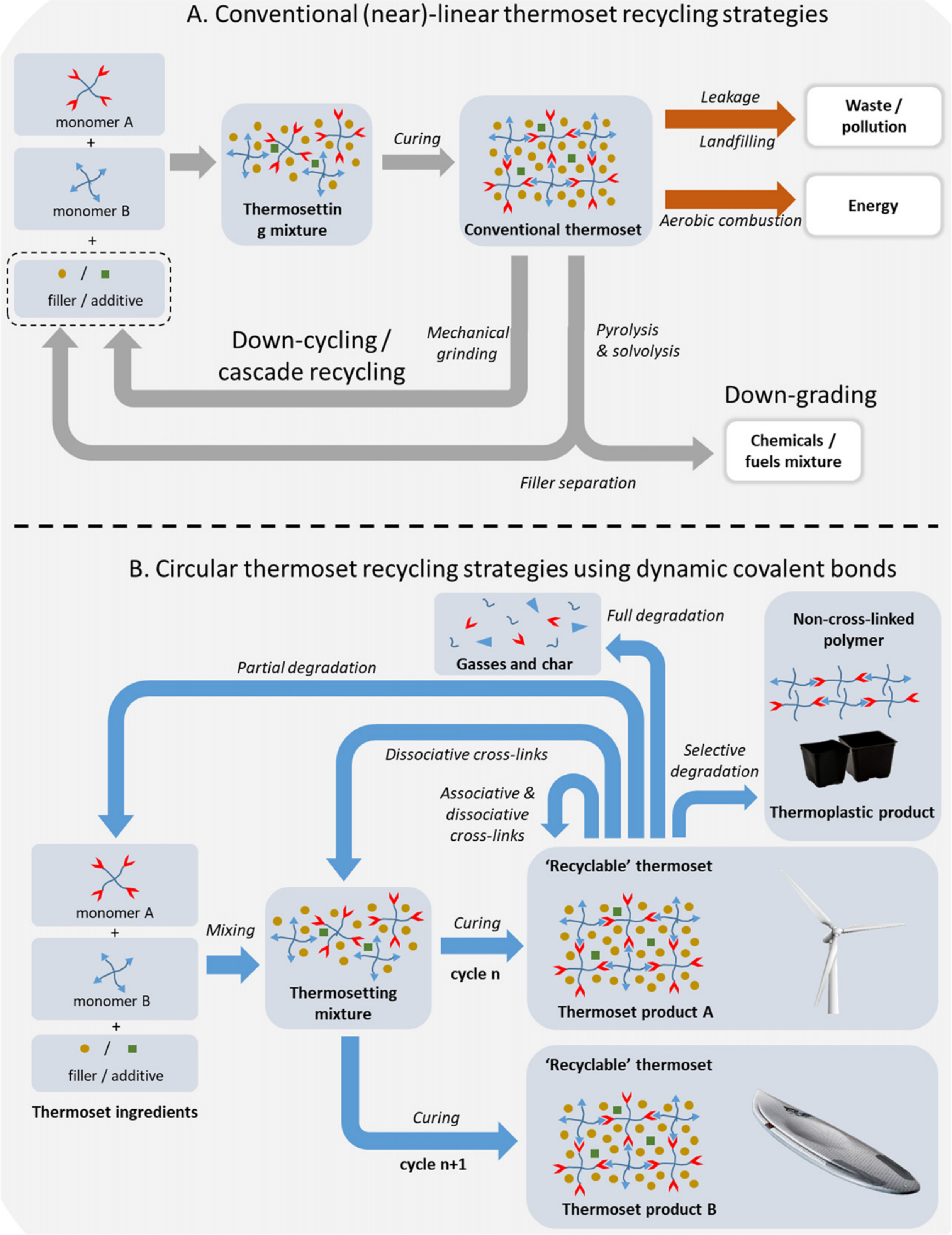
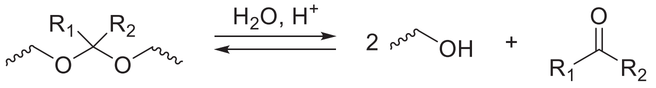
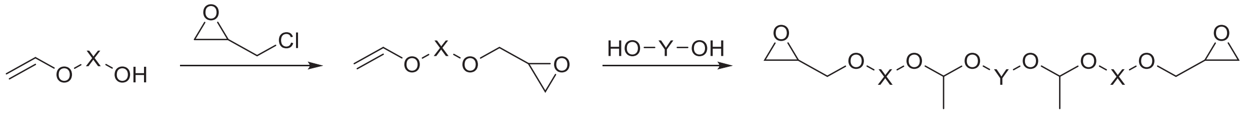


Fig. 2 Schematic representation of (A) conventional linear thermoset composite waste processing and recycling routes and (B) the circular composite recycling routes that are facilitated by the introduction of degradable and dynamic covalent chemistries. Reprinted with permission from Post, W., Susa, A., Blaauw, R., Molenveld, K., Knoop, R.J.I., 2020. A review on the potential and limitations of recyclable thermosets for structural applications. Polymer Reviews 359–388, Copyright 2020 Taylor & Francis.

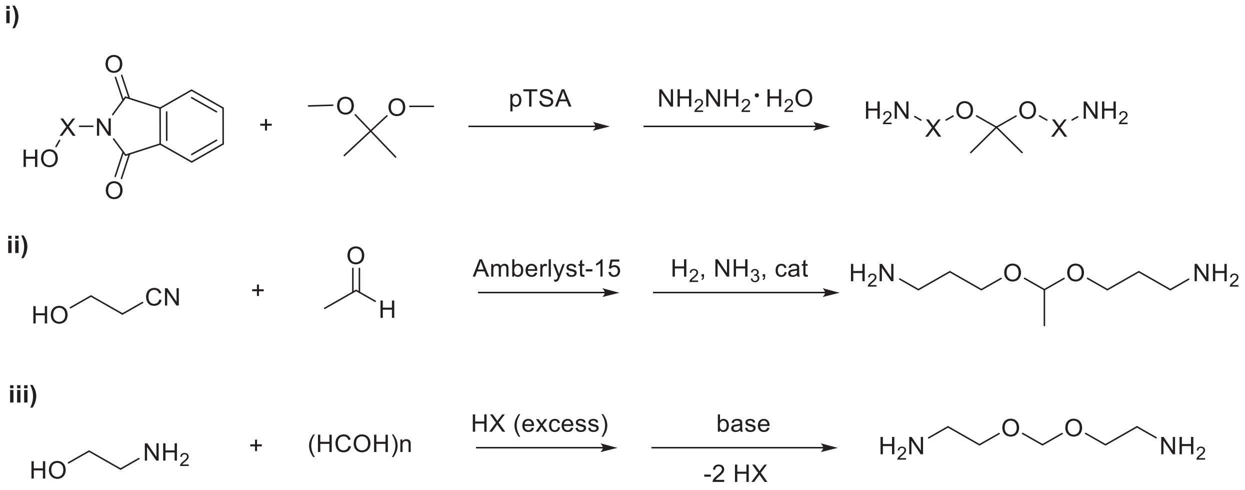


R_1, R_2 = H: formal
R_1 = H, R_2 = CH_3: acetal
R_1, R_2 = CH_3: ketal

Scheme 1. The degradation of an acetal in an acidic environment yields an alcohol and a ketone, an aldehyde, or formaldehyde.



Scheme 2. Alternative method of obtaining acetal diepoxides via vinyl ethers.

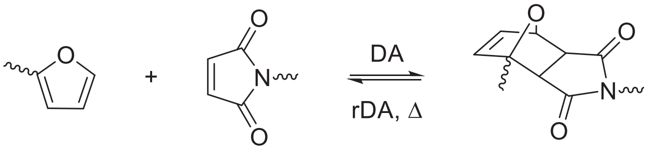


Scheme 3. Three examples of synthetic routes to obtain acetal diamines. (i) Acetal synthesis using 2,2-dimethoxypropane while protecting the amine moiety with a functional group (ii) ketal synthesis using acetaldehyde and an amine precursor that can be reduced to a primary amine after acetal formation (iii) formal synthesis using paraformaldehyde and a strong acid to prepare the ammonium salt. Reproduced from (i) Pastine, S.J., Liang, B., Qin, B., 2017. Agents for Reworkable Epoxy Resins. US patent 9631049. (ii) and (iii) Pastine, S.J., 2013b. Synthesis of and Compositions Containing Diaminoacetals and Diaminoketals. WO patent 184827.

Diamine Acetals

A broad range of amine acetals containing different functionalities have been reported over the past decades (Pastine, 2013b; Pastine *et al.*, 2017; Qin *et al.*, 2014; Cicala *et al.*, 2018). Nucleophilic addition of hydroxy amines to ketones or aldehydes does not result in acetal formation due to competition of the higher reactivity of the amino group compared to the hydroxyl group. **Scheme 3** shows three examples of strategies that avoid the use of hydroxyl amines in the synthesis of diamine acetals. The amine functionality can be shielded by a protecting group that can be removed after acetal formation (route i), or a non-reactive amine precursor such as -CN, -NO_2, or -Cl can be used (route ii), or the primary amine can be converted into the less reactive ammonium salt (route iii). Like in epoxy acetals, cyclic amine acetals have been reported as well. Examples of cyclic amine acetals can be found in references (Hufendiek *et al.*, 2019; Qin *et al.*, 2014).

The development towards structural composites containing degradable acetal linkages was largely progressed by the work of Pastine and co-workers (La Rosa *et al.*, 2018; Pastine, 2013a; Cicala *et al.*, 2016). They developed multiple acetal containing amine hardeners for cross-linking of commercially available epoxy resins. These resins can be used to impregnate glass and carbon fiber fabrics resulting in structural polymer composites that show mechanical performances comparable to their non-recyclable commercially available counterparts. The unique feature of the developed resins is that upon acid catalysed degradation of the acetal linkages the resulting recyclate consists of linear thermoplastic polymers. Based on this technology Cicala *et al.* reported the



Scheme 4. Formation of an Diels-Alder adduct from a furan and maleimide functionalized polymer.

production of high performance recyclable carbon fiber-reinforced polymer (FRP) composites with Young's moduli over 40 GPa and tensile strengths over 400 MPa. However, this work also showed that the reclaimed thermoplastic polymer after recycling has rather poor mechanical properties with a tensile strength below 10 MPa and a strain at break below 1%. This clearly limits the current applicability of these recyclates (Cicala *et al.*, 2018). Nevertheless, the concept is anticipated to be further improved in the upcoming years. Currently, amine acetal thermosets are amongst the most commercially developed recyclable thermosets which is reflected by the exploitation by companies such as Connora Technologies and Adesso Materials (Liang *et al.*, 2017; Pastine *et al.*, 2017, 2013b).

Dynamic Dissociative Diels-Alder Linkages

As depicted in **Fig. 1** dissociative linkages will break upon the application of a stimulus and will reform as soon as the stimulus is withdrawn thereby restoring the thermoset network. The most investigated dissociative linkage in reversible thermosets is the Diels-Alder adduct formed by the (4 + 2) cycloaddition of a diene and dienophile. When heat is applied, the dynamic equilibrium shifts towards the retro-Diels-Alder reaction, yielding back the diene and dienophile. The viscosity drop that is accompanied with this dissociative process allows for reshaping or reprocessing of the thermoset.

Many diene-dienophile pairs that can undergo the Diels-Alder reaction have been described in literature. For reversible thermosets, the most investigated and developed pair is furan-maleimide, which will therefore be the focus of this section. Other pairs that have been used in reversible thermosets are, amongst others, furan-itaconimide (Lejeail and Fischer, 2021), cyclopentadiene-cyclopentadiene (Toncelli *et al.*, 2016; Salamone *et al.*, 1988), cyclopentadiene-benzoquinone (Shi *et al.*, 2020), and anthracene-maleimide (Omurtag *et al.*, 2013).

Scheme 4 shows the Diels-Alder/retro-Diels-Alder equilibrium between a furan an a maleimide moiety. At room temperature this equilibrium shifts towards the Diels-Alder adduct whereas at increasing temperatures the equilibrium shifts towards the reactants. The retro-Diels-Alder reaction occurs already at relatively low temperatures (above 100°C) and does not require a catalyst (Ikezaki *et al.*, 2014; Ishida and Yoshie, 2008; Liu and Chuo, 2013).

Although there are many possibilities to create polymeric networks containing furan-maleimide linkages, the synthesis approach can be roughly divided into two strategies: (1) the reaction of small bi- or multifunctional molecules containing either furan or maleimide moieties, or (2) the reaction of furan-functionalized polymers with either small bi- or tri-functional maleimide cross-linkers or other maleimide-functional polymers.

Small Bi- or Multi-Functional Molecules

A mixture of small bi- or multi-functional molecules containing furan and maleimide moieties can form a reversible polymeric network without the need for a solvent or catalyst (Fortunato *et al.*, 2019; Chen *et al.*, 2003; Mayo and Adronov, 2013). Typically, highly cross-linked networks are formed. With respect to composite production, care must be taken that the melting point of the individual components is not too high, or alternatively that one component will dissolve the other. When this is taken into account, a liquid reaction mixture is obtained that can be mixed with or infused into the particulate or fiber phase. The use of a co-solvent can help to dissolve one of the reactants, but results in difficulties when processing the material due to unremovable solvent residues. The work by Chen *et al.* was a milestone in the development of dynamic DA furan-maleimide based thermosets for applications in polymer composites. The reported thermosets possessed competitive Young's moduli of around 4 GPa and high tensile strengths of over 200 MPa which were also experimentally demonstrated as matrices in polymer composites (Chen *et al.*, 2003, 2002; Park *et al.*, 2008b).

Furan-Functionalized Polymers and Small Maleimide Cross-Linkers

Bednarek and Kubisa (2019) reported an extensive overview of polymers with different geometries bearing furan units used in Diels-Alder reactions. These polymers are cross-linked with small bi- or multifunctional maleimides or maleimide-functionalized polymers to obtain a reversible cross-linked polymer network. Polymers can be functionalized with furan moieties in several ways; **Fig. 3** gives a schematic overview of three different possible geometries: (1) telechelic polymers, (2) polymers with pendant groups, or (3) polymers with functional groups in the backbone.

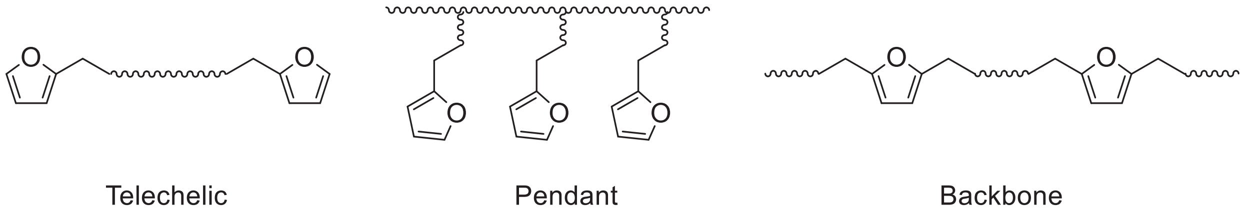


Fig. 3 Different geometries of polymers containing the furan diene that can undergo the Diels-Alder reaction with an dienophile. Wavy lines represent the polymer chains, note that the length is not to scale.

The type of polymer can be, but is not limited to, a polyester (Ikezaki *et al.*, 2014; Ishida and Yoshie, 2008; Zeng *et al.*, 2013), polyurethane (Gu and Wu, 2018), polycarbonate (Durand *et al.*, 2019), polyketone (Zhang *et al.*, 2009), polyamide (Luo *et al.*, 2018; Kossmehl *et al.*, 1995), or an inorganic polymer such as polydimethylsiloxane or polyphosphazene (Wang *et al.*, 2018; Cheng *et al.*, 2013). Linear polymers can be end-capped yielding telechelic polymers (Tsukahara and Adachi, 2015). Also star-shaped polymers (having three or more arms) can be end-capped with furan moieties. Especially with increasing molecular weight of the polymer, full conversion of the end-groups can be difficult to achieve due to a low concentration of end-groups and inaccessibility of them (Goethals, 1989). The concentration of furanic groups can be significantly increased by introducing pendant furan moieties. These can be distributed regularly or randomly along the polymer chain with good control over the concentration, i.e., the amount of furanic moieties in the polymer chain can be tuned. Alternatively, the furan moieties can be incorporated in the polymer backbone, in both a random or regular distribution. Again the concentration of these units can be controlled to a great extent. Polymers having furanic moieties in the backbone are often polyesters made by the condensation of 2,5-bis(hydroxymethyl furan) (BHMF) with a diacid and an optional co-diol (Ikezaki *et al.*, 2014; Zeng *et al.*, 2013; Gu and Wu, 2018). Although condensation of BHMF is an effective way of introducing dienes in the polymeric backbone, BMHF and its corresponding polymers are suffering from low (thermal) stability due to the lability of methylene hydrogens connected to the furan ring (Gandini, 1977; Gandini and Belgacem, 1997; Moore and Kelly, 1974).

The diverse chemical toolbox for furan-maleimide based thermosets has led to a wide variety in mechanical properties for this class of polymers, ranging from elastomers to rigid thermosets suitable for polymer composite materials (Gu and Wu, 2018; Chen *et al.*, 2003). This wide variety was illustrated in reports by Zeng *et al.* and Ikezaki *et al.* Both groups developed multiple biobased polyesters with DA functionality (Ikezaki *et al.*, 2014; Zeng *et al.*, 2013). While the methods of Ikezaki *et al.* did not seem to render matrix materials suitable for structural polymer composites, Zeng *et al.* showed that by varying the ratio between the monomer and the crosslinking agent both flexible and rigid thermosets could be obtained. The flexible systems were capable of truly autonomous repair; they could be rewelded at room temperature. The more rigid polymers with interesting properties for composite materials (Young's modulus > 1 GPa, tensile strength of 20 MPa and strain at break > 100%) did no show this effect. However, the recycling potential at elevated temperatures was not tested. This indicates that the recycling potential of these systems has not yet been fully explored. Luo *et al.* did demonstrate recycling at elevated temperature of DA moiety-containing polyetherketones. Young's moduli above 2 GPa and strengths up to 80 MPa were obtained for these materials. It was shown that multiple recycling treatments led to a 20% reduction of mechanical properties. The potential to prepare composites was not investigated (Luo *et al.*, 2018).

Initial reports on the actual utilization of the DA reversible functionality in composites were made by researchers who grafted both furan and maleimides onto glass and carbon reinforcing fibers. By introducing the reactive counterpart of the grafted fibers in the matrix, composites were created with reversible interfaces (Fei *et al.*, 2018; Zhang *et al.*, 2014; Peterson *et al.*, 2011). However, as only the composite interface is functionalized this approach does typically not result in sufficient mobility for the polymer matrix to be recycled. FRP composites in which the matrix itself possesses mobility for thermally triggered repair were prepared by various researchers using different processing methods such as compression-, injection- and vacuum assisted autoclave molding (Turkenburg and Fischer, 2015; Coope *et al.*, 2016; Ghezzo *et al.*, 2010; Park *et al.*, 2008a; Park *et al.*, 2010). As these composites were mainly developed for healable and easy repair composites, the recycling by separating the matrix from the fibers was not investigated. Complete separation of a DA moiety containing matrix and glass and aramid reinforcing fiber was reported in a number of recent publications (Lejeail and Fischer, 2021; Zhou *et al.*, 2020; Lejeail and Fischer, 2021). Interestingly, in all cases the assistance of solvents is required. Apparently, the DA reversibility alone is insufficient to yield complete separation of matrix and fibers. This is exemplified by the work of Fortunato el al. who developed a carbon FRP composites with DA resin as matrix. These composites have mechanical properties in the range of commercial epoxy resins as is illustrated in **Fig. 4**. After solvent-assisted recycling the carbon fibers retained sufficient mechanical integrity for re-use in structural composites while the matrix could be re-used in coating applications (Fortunato *et al.*, 2019). Another example of solvent-assisted recycling of DA matrices is shown by the work of Lejeail *et al.* They show the production of glass FRP composites with moduli in the range 4–6 GPa and a fracture strength around 50 MPa. They report a decrease in mechanical behavior (30% strength reduction) and a color change of the composite after recycling which could indicate partial degradation. (Lejeail and Fischer, 2021). Furthermore, they showed the option of increasing biobased content of epoxy based DA composites by substituting bismalemide components by bis-itaconimide groups (Lejeail and Fischer, 2021).

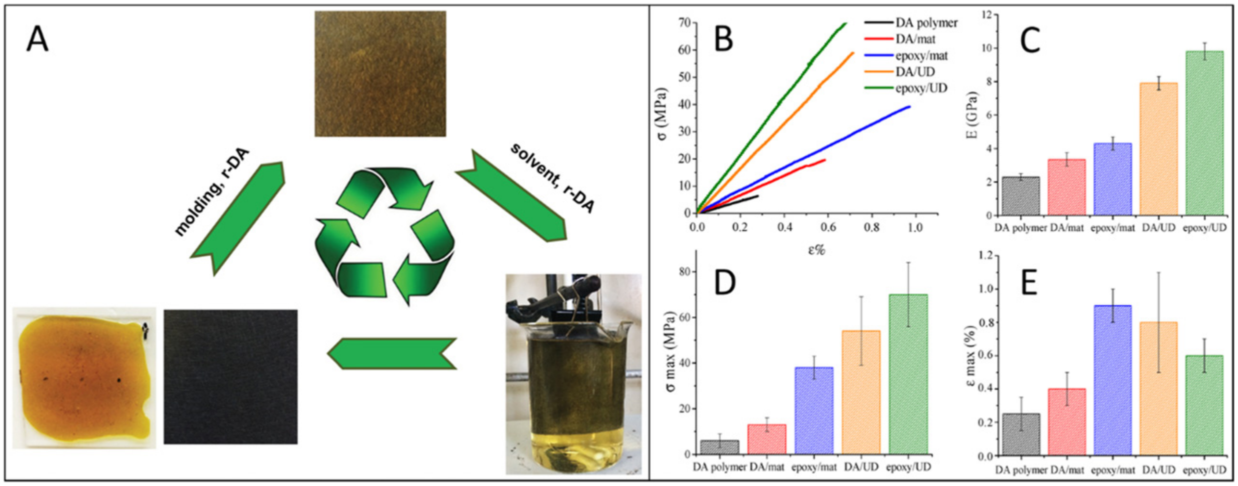
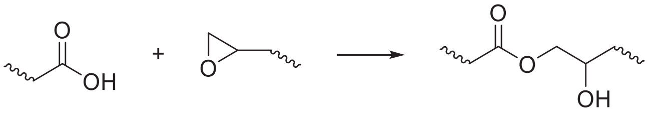
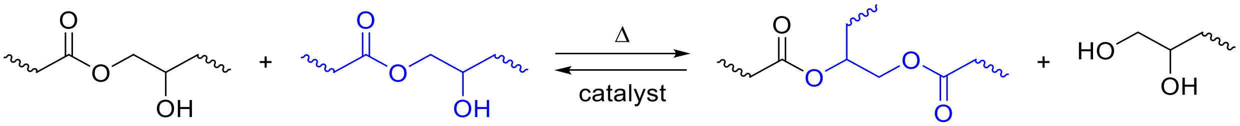


Fig. 4 Illustrative example of the solvent-assisted recycling of a FRP with a DA linkage containing matrix (A). The developed composites show strength, moduli and elongation in the range of commerical epoxy composites composed of unidirectional (UD) and woven fiber fabrics (mat) (B-E). Reprinted with permission from Fortunato, G., Anghileri, L., Griffini, G., Turri, S., 2019. Simultaneous recovery of matrix and fiber in carbon reinforced composites through a diels-alder solvolysis process. Polymers 11, Copyright 2020 MDPI.



Scheme 5. Formation of a carboxylate bond from the reaction of a carboxylic acid with an epoxide. Note that an anhydride can be used as well instead of an carboxylic acid to obtain a vitrimeric network.



Scheme 6. The carboxylate transesterification reaction at elevated temperatures in the pressure of a transesterification catalyst.

Vitrimers; Reversible Networks Containing Associative Linkages

As is graphically described in **Fig. 1**, associative dynamic covalent bonds are characterized by dynamic linkages that are only broken when new chemical linkages are formed. Compared to the dissociative mechanism, materials with associative linkages only show a gradual viscosity decrease upon the application of a stimulus. A more detailed description of the characteristics of these associative dynamic covalent bonds is given by Denissen *et al.* (2016) and Krishnakumar *et al.* (2020). One of the first and most prominent examples of associative dynamic covalent bonds, was reported in 2011 by Leibler and co-workers. Their thermoset showed a gradual decrease in viscosity upon heating. This phenomenon had so far not occurred, and the authors named their material a vitrimer after vitreous silica; a material that is known for its viscosity decrease upon heating (Montarnal *et al.*, 2011). In the past decade many researchers reported on the development of vitrimers with different types of associative linkages. The most relevant examples will be summarized in this section.

Carboxylate Transesterification

The first vitrimers developed by Leibler and co-workers consist of an epoxy/acid or epoxy/anhydride network (see **Scheme 5**) containing a transesterification catalyst. The use of an epoxide monomer results in a free hydroxyl group that is able to undergo a transesterification reaction as depicted in **Scheme 6**. The rate of this catalysed transesterification is insignificant at room temperature, whereas upon heating the transesterification reaction proceeds smoothly resulting in a deformable material. Since then many examples have been published of these epoxy-based vitrimers (Capelot *et al.*, 2012a; Yu *et al.*, 2014; Capelot *et al.*, 2012b; Liu *et al.*, 2018; Zhang *et al.*, 2018; Altuna *et al.*, 2013; Yang *et al.*, 2020; Zhang *et al.*, 2019).

Vitrimer thermosets show a wide range of mechanical properties, ranging from elastomeric materials to rigid thermoset matrices with Young's moduli ranging from 1 to 2000 MPa as described by the recent review of Krishnakumar *et al.* (2020). This variation in mechanical properties was already displayed by the breakthrough publications of Capelot, Monternal and Leibler who showed both elastomeric (modulus of 4 MPa) materials (Capelot *et al.*, 2012a) and more rigid thermoset matrices with a modulus of 1.8 GPa and strength at break of 55 MPa (Montarnal *et al.*, 2011). More recently Zhang *et al*. published an approach to tune the mechanical properties of a vitrimer system by blending a soft and a hard thermoset. Based on the ratio, the properties can be tuned from elastomeric to rigid thermoset materials (Zhang *et al.*, 2019).

Asides from being recyclable, the transition towards a circular material economy will also require vitrimers to be biobased. In this respect, a partially biobased, lignin containing, vitrimer with limited mechanical properties (Young's modulus below 300 MPa and a maximum elongation of 10%) were reported by Zhang *et al.* (2018). Vitrimers based on epoxidized soybean oil were reported by both Altuna *et al.* (2013) and Yang *et al.* (2020). Although these vitrimers do not possess mechanical properties of structural composite materials, they do show potential as adhesive materials. Nevertheless, the reported mechanical properties of these biobased vitrimers are not yet in the range of earlier developed fossil based counterparts. This indicates that more development is required towards recyclable biobased thermoset materials.

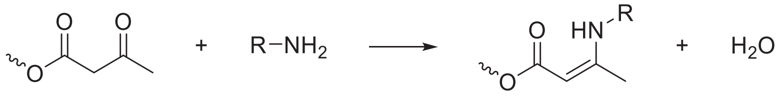
Epoxy-based transesterification vitrimers have the great advantage that they are made from easily accessible building blocks, and can be prepared by simple synthesis procedures. However, the requirement of a catalyst has several drawbacks. The preferred catalysts are not always completely soluble in the vitrimer network, and even if the catalyst could be homogeneously dispersed in the network it could leach out over time (Denissen *et al.*, 2016). In addition, ester linkages in hydrophilic thermoset networks can hydrolyze in the presence of water. Another disadvantage is that the associative nature of the dynamic ester linkages severely limits the mobility of the polymer upon stimulus application. This is exemplified by Liu *et al*. who prepared high T_g (180°C) epoxy based vitrimers that can be reprocessed at 220°C. The mechanical properties are relevant for composite matrices (strength above 60 MPa and Young's modulus above 2 GPa), but broken specimens lacked mobility during the recycling treatment and were unable to be rewelded. Recycling of an epoxy based matrix with a strength of more than 40 MPa via transesterification was reported by Lu *et al.* (2017). Here it was shown that ground thermoset particles can be fully recycled via compression molding. This concept was later translated to the production of carbon FRP composites, but recycling of either the fibers or matrix was not discussed (Yu *et al.*, 2019). In another study, glass FRP composites capable of transesterification were reported. Via resin transfer molding of an anhydride containing epoxy resin, composites were developed with a Young's Modulus above 20 GPa and a tensile strength above 500 MPa. These composites showed good repair characteristics, but separation of fiber and matrix was not shown (Chabert *et al.*, 2016). The full recycling of this type of vitrimer matrix and reinforcing fibers was shown in recent years by several authors that used a solvent-assisted transesterification approach (Kuang *et al.*, 2018b; Yu *et al.*, 2016).

Vinylogous Urethanes

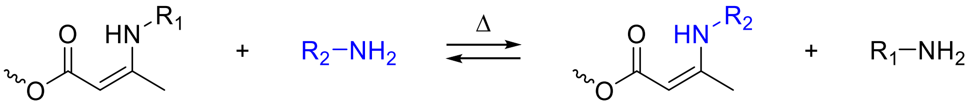
More recently, du Prez and co-workers reported on a catalyst-free vinylogous urethane linkage as an alternative to the carboxylate transesterification vitrimers thereby avoiding solubility issues or leaching of the catalyst out of the network over time (Denissen *et al.*, 2017, 2015). This associative dynamic covalent bond is prepared by the reaction of acetoacetate and amine functionalized monomers (**Scheme 7**). The reaction runs at room temperature and can even be performed in the presence of water (Stefani *et al.*, 2000).

By tuning the reaction stoichiometry a slight excess of amine groups in the network can be obtained. Upon heating to moderate temperatures (>100°C), the weak carbon-carbon double bond can undergo nucleophilic attack by the excess amine (a Michael addition) resulting in the exchange of vinylogous urethanes and amines (**Scheme 8**).

The resulting vitrimers show mechanical properties that are suitable for composite fabrication with moduli around 2 GPa and a strength at break around 100 MPa (99,100). Resin optimization and proof of concept composite production was shown by the same authors following the hand lay-up approach depicted in **Fig. 5**. The resulting composites possess mechanical properties (Young's modulus above 40 GPa and strength at break above 700 MPa) in the range of commercial epoxy based composites.



Scheme 7. Formation of a vinylogous urethane bond by the reaction of an acetoacetate with an amine.



Scheme 8. The vinylogous urethane-amine exchange reaction upon heating to temperatures above 100°C without the need for a catalyst.

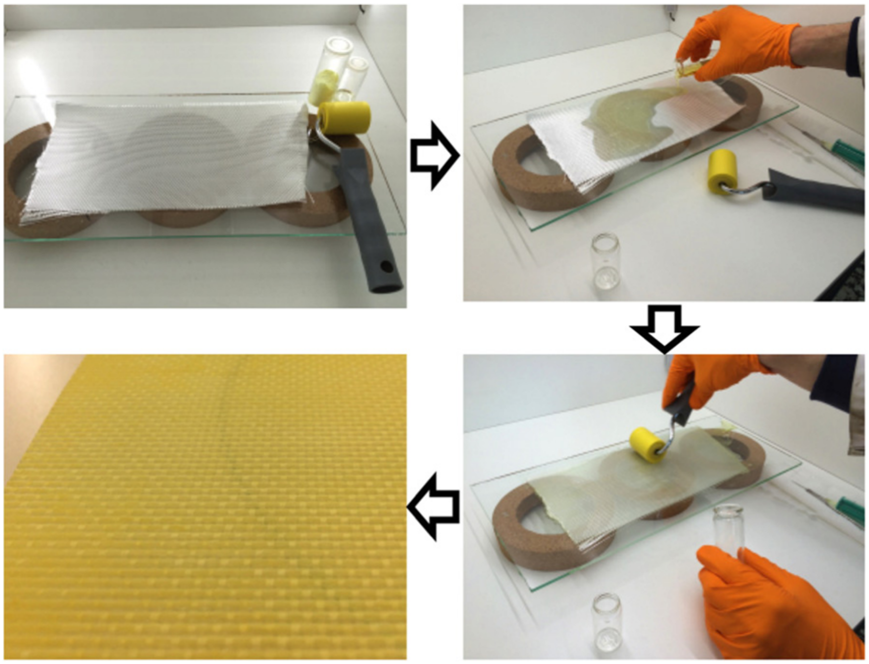


Fig. 5 Hand lay-up composite preparation of Vurea, glass fiber reinforced vinylogous vitrimer, composites. Reprinted with permission from Denissen, W., De Baere, I., Van Paepegem, W., *et al.*, 2018. Vinylogous urea vitrimers and their application in fiber reinforced composites. Macromolecules 51, 2054–2064, Copyright 2020 John Wiley and Sons.

Lastly, they showed organic solvent-assisted recycling of the developed composites by depolymerizing the vitrimer matrix in an amine doped N-methylpyrrolidon (NMP) solution.

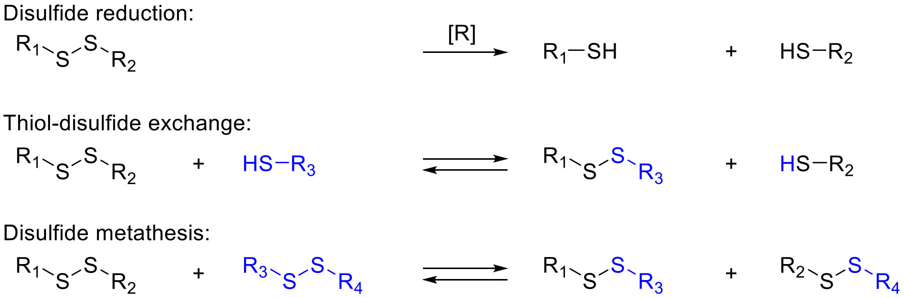
Even though the vinylogous urethanes are amongst the most promising recyclable thermoset matrices, a significant disadvantage is that the reversibility is dependent on the presence of a slight excess of amine. These amines are prone to oxidation over time, making them inactive in the exchange reaction and hence reducing the reversibility of the network over time. This drawback needs to be accounted for in order to make commercialization of these materials feasible.

Dynamic Covalent Linkages With Ambiguous Bond Exchange Mechanisms

The bond exchange mechanism that facilitates the composite recycling process is clearly identified for the described acetal (degradable), Diels Alder (dissociative) and vitrimer (associative) linkages. However, the nature of the debonding mechanism is often more ambiguous which makes that a dynamic linkage cannot be characterized by a single exchange reaction. These linkages can be, for example, hydrolyzed (degradable or dissociative), or can exchange bonds in an associative pathway. For some thermosetting networks containing these types of linkages, the exact mechanism of reversibility is still under debate. Disulfide and imine linkages are two of the most prominent examples of these ambiguous bond exchange mechanisms that are regularly incorporated into composite matrices. They are therefore described in more detail in this section.

Disulfide Linkages

Disulfide linkages (-S-S-) can be included in thermoset resins either by using monomers containing disulfide linkages, or by using monomers having pendant thiol groups that are subsequently oxidized to disulfide bonds (Bednarek and Kubisa, 2019). Often these disulfide linkages are included in gels or nanoparticles for, for example, drug delivery. In these systems, reduction of the disulfide linkage into two thiols is the most important mechanism, see **Scheme 9**. The formed thiols can be oxidized back into disulfides. Therefore, this reduction-oxidation cycle can be considered as a dissociative mechanism that has been applied in thermosets (Tsarevsky and Matyjaszewski, 2002; Sastri and Tesoro, 1990; Tesoro and Sastri, 1990). Disulfides can also undergo exchange reactions with free thiols (thiol-disulfide exchange) or with other disulfides (disulfide metathesis) yielding an associative mechanism (**Scheme 9**) (Otsuka *et al.*, 2010; Johnson *et al.*, 2015; Zhou *et al.*, 2017; Arulkashmir *et al.*, 2013). Disulfide metathesis is already occurring at room temperature; it is the main mechanism responsible for creep in natural rubbers (Jin *et al.*, 2019). It has been reported that the reversibility of the disulfide bonds decreases over time due to oxidation of the thiol moieties (Pepels *et al.*, 2013). In general, it can be concluded that the reversibility mechanism of dynamic disulfide linkages is rather complex. It involves several mechanisms that depend on the applied conditions/stimuli and on the chemistry of the thermoset.



Scheme 9. Possible reversible reactions that a disulfide linkage can undergo; disulfide cleavage by reducing agents, thiol-disulfide exchange reaction, and disulfide metathesis.

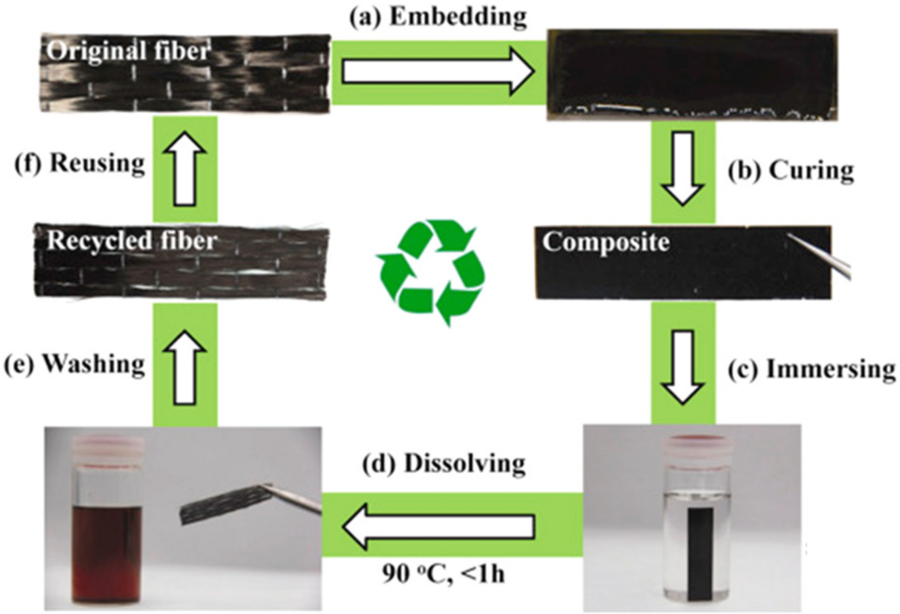
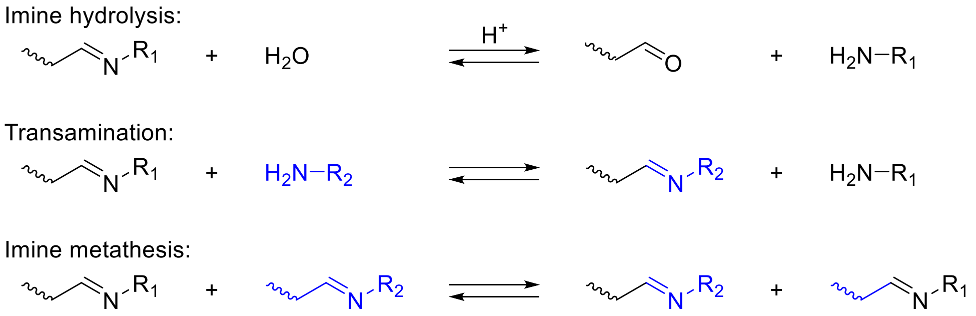


Fig. 6 The recycling process of a carbon FRP composites based on a disulfide containing thermoset: (a) embedding the carbon fibers in a disulfide linkage containing epoxy matrix; (b) obtaining FRP composites by curing; (c) immersing the CFRP composites in a suitable solvent; (d) dissolving the epoxy matrix at 90°C; (e) washing and drying the recovered carbon fibers; (f) reusing the recycled carbon fibers to form new composites. Reproduced from Si, H., Zhou, L., Wu, Y., *et al.*, 2020. Rapidly reprocessable, degradable epoxy vitrimer and recyclable carbon fiber reinforced thermoset composites relied on high contents of exchangeable aromatic disulfide crosslinks. Composites Part B Engineering 199, 108278 Copyright 2020 Elsevier.

The development of composites that can be repaired or recycled using an epoxy based resin modified with dynamic disulfide linkages was reported by several authors (Post *et al.*, 2017; Ruiz De Luzuriaga *et al.*, 2016; Si *et al.*, 2020). These FRP composites could be prepared by standard composite infusion processing and yielded Young's moduli higher than 10 GPa. The repair conditions ranged from low temperature (70 °C) restoration of delaminations and microcracks (Post *et al.*, 2017) to full reprocessing and reshaping of the composites at temperatures around 200°C (Ruiz De Luzuriaga *et al.*, 2016). As was shown for the vast majority of other recyclable composites, separation of fibers and matrix seems only effective using thiol-assisted solvolysis of which the process is illustrated in **Fig. 6** (Si *et al.*, 2020).

Imine Linkages

Imines, and related Schiff bases and azomethines, are classes of compounds that contain a carbon-nitrogen double bond. They are synthesized by the condensation of an aldehyde (or ketone) and a primary amine. Water is formed as by-product that has to be removed to shift the equilibrium towards the imine. In the presence of water and acid, imines can hydrolyze via a dissociative mechanism (**Scheme 10**). In addition, imines can undergo two different associative reactions: transamination and imine metathesis (Ciaccia and Di Stefano, 2015). When an imine bond undergoes an exchange reaction with a primary amine, it is



Scheme 10. Possible reversible reactions that an imine linkage can undergo; hydrolysis by water, transamination between an imine and amine, and imine metathesis.

referred to as transamination. Exchange with another imine, is called imine metathesis (**Scheme 10**). It is very likely that a very small amount of unreacted primary amines is always present in these polyimine thermosets. This allows for very fast transamination reactions even at room temperature (Denissen *et al.*, 2016). However, polyimines are prone to hydrolysis in the presence of water or moisture, limiting the applications for these materials. Cross-linking the polyimine matrix (Wang *et al.*, 2019a) or the use of hydrophobic monomers (Jin *et al.*, 2019) could help to increase the hydrolytic stability. The mechanical properties of polyimine thermosets can be directed towards those of high performance resins by using hybrid thermosets which combine dynamic imine linkages with for example more rigid imide bonds without comprising the repairability.

Polyimine linkages have successfully been incorporated into thermoset resins for FRP composite processing. The most illustrative example is given by Taynton *et al*. They reported on the wet lay-up development of carbon FRP composites with a Young's modulus higher than 10 GPa that can be recycled by dissolving the matrix in a mixture of diethylenetriamine (DETA) and ethanol (Taynton *et al.*, 2016). An interesting step towards biobased recyclable composites was made by Wang *et al*. They developed a carbon FRP composite with a partially biobased Schiff base containing matrix with relevant mechanical properties (Young's modulus above 2 GPa and tensile strength above 80 MPa). The resulting composites yielded moduli above 35 GPa and tensile strengths above 700 MPa which is well in the range of high performance composite materials. The composites were capable of rewelding and could be fully degraded upon a mild acid treatment in order to reclaim the fibers. However, the polymer resin could not be recycled in this concept (Wang *et al.*, 2019b).

Concluding Remarks

Structural polymer composites for high-performance applications are still amongst the most difficult materials to recycle effectively. However, as it is foreseen that the end-of-life scenario of materials and products will have an increasingly prominent role in material selection, it is crucial that circular recycling solutions are developed for both the resin and the fibrous/particulate phase of these materials. Thermosets with dynamic covalent bonds can fulfill an important role in achieving this goal, as they allow for a certain mobility of the matrix phase that could theoretically enable effective separation of the different composite phases. However, the mobility obtained during a recycling treatment will greatly depend on the nature of the selected dynamic covalent bond.

Thermosets with degradable linkages will undergo a significant drop in viscosity upon the first recycling treatment as a result of the permanently broken chemical bonds. The resulting monomers or polymers can be re-used for different applications, but the original integrity of the thermoset will not return when the recycling stimulus is withdrawn. This is different for both associative and dissociative linkages; their viscosity is reduced upon the application of the (often thermal) recycling stimulus. This allows for easy-repair, reshaping and potentially better recycling. Upon release of the stimulus, the viscosity returns to its original level as the net amount of covalent linkages present is fully restored. The main difference between the dissociative and associative mechanism is the extent of the viscosity drop that is expected to occur. Since the dissociative linkages actually break during the stimulus, the overall thermoset viscosity can be reduced significantly further than those containing associative bonds. The latter will only fully break while simultaneously forming other bonds. It can be theorized that this difference will cause the ultimate recycling potential of dissociative linkages to be favored over associative ones. After all, the large viscosity drop during simple recycling treatments (e.g., moderate temperature or hydrolysis) will enable a more facile separation of the individual composite phases. To date, matrix-to-matrix recycling of composites without the use of organic solvents has not been reported, and it is not a given that this will become practically possible in the upcoming decades. In this respect, achieving the right balance between matrix-fiber affinity during composite use and reversing this affinity upon recycling is anticipated to become one of the largest challenges ahead. To conclude, it is clear that there is no universal strategy for structural composite recycling as each application will require an individual evaluation on the most suitable end-of-life scenario.

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