

Diels-Alder Macromolecular Networks in Recyclable, Repairable and Reprocessable Polymer Composites for the Circular Economy – A Review

Gianmarco Griffini,* Benedetta Rigatelli, and Stefano Turri

In the expanding field of high-performance materials, polymer-based thermoset composites play an important role due to their favorably-high strength/weight ratio and their mechanical performance, thermal stability, and chemical resistance. However, their chemically-crosslinked nature hampers their re-processability and efficient recyclability, thus making them not compliant with the principles of the circular economy and of end-of-life valorization. Dynamic covalent polymers able to modify their network topology upon thermal stimulus can be considered valid alternatives to commonly used thermosets as they offer advantages in terms of recyclability and reusability, normally not achievable with conventional cross-linked systems. Within the broad field of dynamic polymers, thermally-triggered Diels-Alder based materials represent reliable platforms with enormous technological and industrial potential as repairable, reusable and recyclable matrices in composites given their chemical versatility, suitable mechanical performance and ease of production and processing. In this review, a comprehensive discussion of the most recent demonstrations of the reversibility, reprocessability and recyclability of such systems is provided, in the context of their use as polymer matrices in composites. It is hoped that this work will stimulate further discussion and research in the area of reversible polymer composites with increased functionality and extended lifetime, in view of their application in future circular economy scenarios.

applications in which the combination of multiple characteristics is simultaneously required due to specific performance needs. Composite materials are conventionally based on the synergistic interplay of two or more distinct, phase-separated constituents, where one or more reinforcing or functional materials are dispersed in a continuous-phase matrix that bonds them together, distributes the load among them and ultimately provides structural integrity to the part. Their multiphasic nature allows to attain structural and/or functional properties not achievable by the use of the individual components alone.^[1] This characteristic and the possibility to tailor the final properties of the composite material by appropriate selection of the nature of its constituents, their proportions and their physical-chemical and morphological features have made this class of materials the winning choice for a great variety of industrial fields, from electronics^[2] to aerospace,^[3] from automotive^[4] to sport and leisure,^[5] from biomedicine^[6–8] to human safety and protection,^[9] from energy to construction.^[10]

As the peculiar behavior of composites is largely affected by the nature of the dispersed phase, its choice is typically driven by the target application. To this end, a distinction can be made between structural and functional elements, where the former are usually devoted to mechanical reinforcement (e.g., carbon fibers – CFs, or glass fibers – GFs),^[11,12] while the latter provide the composite material with specific functions such as for example thermal or electrical conductivity,^[13,14] sensing or actuating characteristics,^[2] energy generation capability.^[15] In both cases, their geometrical and morphological structure (e.g., whether they are in the form of particles, flakes, platelets or fibers) deeply influences their effective contribution to the final properties of the composite. Similarly, the size and the dimensionality of the dispersed phase play a crucial role in defining the fundamental characteristics of the material, with macroscopic reinforcements such as CFs and GFs used in more conventional structural composites going along with 1D (e.g., carbon nanotubes, silver nanowires)^[16,17] 2D (e.g., layered nanoclays, graphene nanoplatelets, graphite)^[18,19] or 3D (e.g., silica nanoparticles)^[20] nanostructured fillers in nanocomposite systems.

1. Introduction

Composite materials are ubiquitous in our everyday life, and their enormous versatility has given access to several advanced

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In terms of continuous phase, among the currently available classes of matrix materials, polymers have gained increasing significance in the past few decades, given their intrinsic corrosion resistance, easy processability and favorably high strength/weight ratio, which have positioned them ahead of metals when lightweight (mobile) applications are targeted. Although thermoplastic polymers find use as composite matrices in different fields where ductility, toughness and moldability are required,^[21] in structural composites (e.g., CF- and GF-reinforced composites, CFRCs and GFRCS respectively) or for highly demanding applications thermosets usually represent the materials of choice, as they can offer superior mechanical response, higher thermal stability and excellent chemical resistance thanks to the covalent nature of their highly cross-linked macromolecular structure.^[22] In this respect, polymers such as epoxies, vinyl esters, unsaturated polyesters, polyurethanes and phenol-formaldehyde resins have found extensive use as matrices in the field of composite materials as bulk components or as coatings.^[23]

Despite their excellent characteristics when compared with thermoplastics, the presence of a 3D network of intermolecular chemical cross-links makes conventional thermosets virtually impossible to be reprocessed after curing and shape forming, mended after failure, and reused or recycled at the end of their life cycle. These negative features of thermosets clearly contrast with the basic circular economy principles of reduce, repair, reuse, refurbish and recycle. This misalignment is even more compelling in the light of the Waste Framework Directive released by the European Commission already more than a decade ago (Directive 2008/98/EC), that clearly defines a hierarchical structure for waste management from the least (landfill disposal and incineration) to the most favorable (reuse and prevention) solution.^[24] Considering structural components based on thermoset CFRCS and GFRCS, these issues factually prevent the efficient recovery of the reinforcing fibers and/or the matrix material from end-of-life parts, while also limiting potential pathways for second-life applications of these materials due to difficulties in repairing and remolding. Similarly, the functionality of thermoset-based composites may be affected during prolonged operation because of structural damages potentially occurring in their service cycle, thus reducing their useful lifetime. Based on these considerations, the implementation of new approaches to incorporate intrinsic remanufacturing functionalities in thermoset-based composites at the material design stage represents a viable strategy to enable virtuous circular-economy scenarios in the field of thermosets.

To this end, recent progresses in organic and polymer chemistry offer innovative pathways that may help to improve the life cycle, end-of-life and waste management of thermosets by predictive material design. In particular, the incorporation of dynamic, reversible cross-linking bonds in the macromolecular network of thermosetting materials has been introduced as a powerful chemical tool to equip them with new thermally-triggered functionalities potentially enabling their repairing, welding, reprocessing and reuse.^[25] The development of novel classes of polymer-based covalent adaptable networks (CANs)^[26] has allowed to obtain new smart polymeric systems to be used as matrix components in composite and nanocomposite materials exhibiting multiple capabilities when heated at specific processing tem-

peratures, without affecting their usability and functionality. Several examples of such dynamic systems have been demonstrated based on different types of associative and dissociative bond chemistries^[27–31] and several excellent reviews have recently discussed the synthetic,^[32–37] mechanistic^[38,39] and functional^[40–42] aspects of such approaches to obtain thermosetting polymeric materials with enhanced characteristics. Given the tremendous interest and opportunity for the use of CAN-based polymers in the field of composite materials, it seems now appropriate to focus on their practical potential as repairable, reusable and recyclable multifunctional composite matrices.

In this review we aim to discuss the most recent examples of dynamic thermosets used as matrices in the field of composites, providing a comprehensive account of recent investigations focused on the demonstration of the reversibility, reprocessability and/or recyclability of the proposed dynamic systems. In particular, we concentrate on reversible polymer networks based on the thermally-triggered Diels-Alder (DA) reaction between dienes and dienophiles,^[37,43] given the potential of this chemical system as viable material production tool for real industrial use.^[44,45] Applications of polymer matrices based on such systems for both structural and functional composites are discussed, to highlight the added-value the use of these systems can provide in practical contexts. An outlook on the significance and potential role of these reversible materials in the framework of the circular economy of reinforced composites is also provided, with associated benefits and potential advantages with respect to conventional thermoset systems.

We hope this work will serve as a useful account of recent findings in the field of advanced composite materials based on DA bonds, while stimulating further discussion and research in the area of repairable, reprocessable and fully recyclable polymer matrices with increased functionality, extended lifetime and enhanced sustainability.

2. Dynamic Bonds in Thermoset-Based Composites: Self-Healing and Beyond Through the Diels-Alder Reaction

Traditionally, one of the most common applications of thermally reversible thermosetting polymers is their use as self-healing materials, where the external heat trigger is exploited to repair surface scratches or mend macroscopic damages via a chemical rearrangement of the bond structure within the macromolecular network.^[40,46,47] Different literature works have already extensively reviewed the synthetic efforts devoted to the development of self-healing polymer matrices based on DA systems^[41,48–54] or other reversible material platforms like vitrimers,^[55] and their functional response has been thoroughly characterized for applications in the fields of both structural^[40] and functional^[51] composites.

While self-healing behavior allows the thermosetting matrix to be repaired thus extending its potential service life with respect to conventional covalently cross-linked systems, this characteristic cannot be considered sufficient for the effective and complete reusability and reprocessability of the component. Indeed, the possibility to gain control of the repairing process, to perform multiple healing cycles without significant loss of functionality

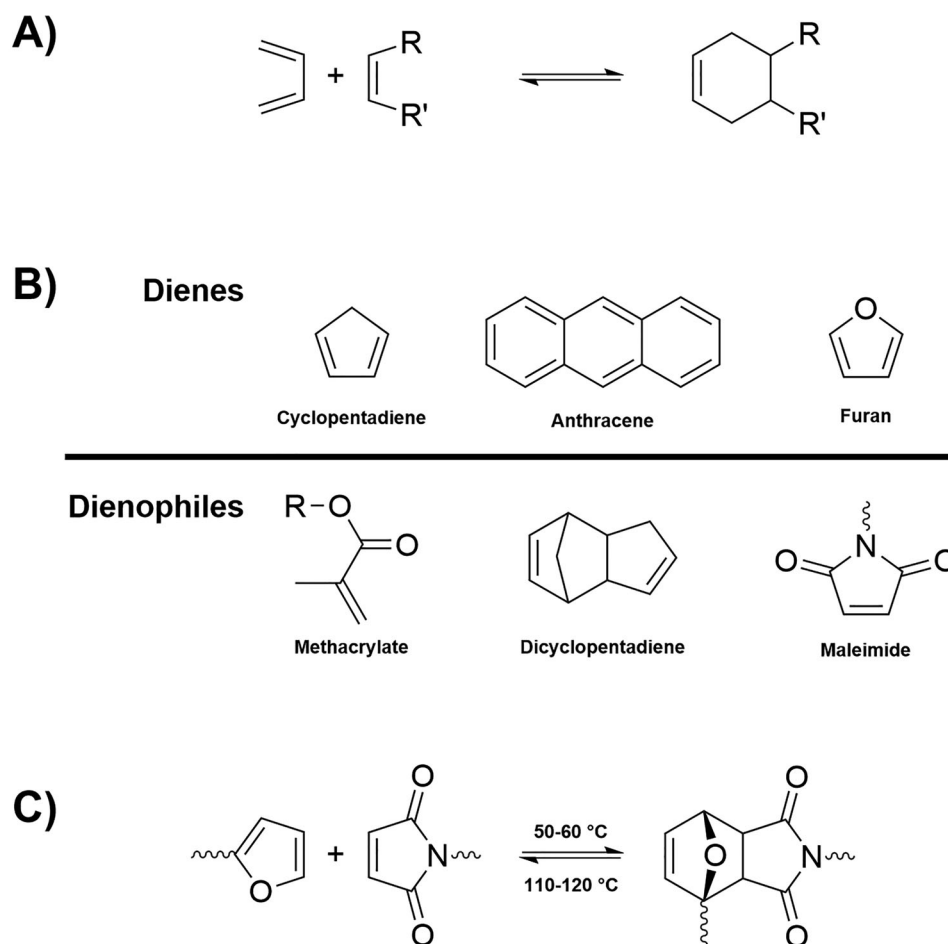


Figure 1. A) General DA mechanism, B) some examples of dienes and dienophiles and C) DA and retro-DA mechanism of the furan-maleimide adduct.

and to acquire a deeper understanding on how the reinforcing or functional element may react during the thermally-induced dynamic process on the matrix have become topics of growing interest and exceptional practical utility in the last few decades. Moreover, the ability to fully recover all the constituents of the end-of-life composite part (separately or as a mixture) without damaging their original structural or functional properties represents a key turning point for the adoption of truly circular approaches in this field. Therefore, the development of thermally-responsive matrices based on CANs emerges as a powerful tool to incorporate into the composite thermoset multiple functionalities beyond self-healing, ultimately yielding fully remoldable, reprocessable and recyclable materials.

One of the most well-known thermally reversible reaction currently applied in the field of self-healable and mendable composites is the DA reaction. From a chemical point of view, this is a cycloaddition reaction between a diene and a dienophile species,^[35] in which the electrons of the reactants recombine to form a six-membered system with considerable regiochemical and stereochemical control. In the vast array of different functional groups amenable to form a reversible DA adduct, the most commonly found are maleimides, as the dienophile species, and furans, as the diene counterpart (**Figure 1**).^[56–58] The reasons for their

widespread use as DA precursors are manifold. Among them, the most important is associated to the relatively low temperature ($\approx 110\text{ }^{\circ}\text{C}$) needed for the retro-DA reaction to occur, leading to the dissociation of the DA chemical bond and to the recovery of the original furan and maleimide precursors. Since this temperature is much lower than the degradation temperatures typically observed on polymeric systems, the DA click/unclick mechanism between these two chemical functionalities may be exploited as controlled chemical trigger for recyclable macromolecular networks and self-healing materials.^[59]

In the following sections, an overview of the most recent examples of the use of the DA reaction based on the furan/maleimide couple in the field of composites will be presented. In particular, both structural and functional applications will be targeted, with a discussion on the chemical routes to achieve thermal reversibility as well as on the ultimate properties enabled by the incorporation of the DA functionality.

3. Carbon-Fiber-Reinforced Diels-Alder Composites

The field of structural polymer-based composites is largely dominated using CFs as reinforcing element, because of their excellent mechanical response combined with their ease of

incorporation into different types of polymeric matrices. The addition of reversible DA bonds into these systems can improve their lifecycle and end-of-life (EoL) fate in view of a circular economy of CFRC materials.

3.1. Matrix Reversibility for CFRC Repair and Reuse

In one of the first studies dealing with the application of the DA chemistry for CFRCs,^[60] differential scanning calorimetry (DSC) was used to investigate and model the reversibility of the DA reaction and the mendability of a polymer matrix made of Mendomer, a highly cross-linked multi-diene (multi-furan) multi-dienophile (multi-maleimide) macromolecular network with thermally-reversible linkages resulting from multiple DA-connections originally developed by Wudl and co-workers in their pioneering works on self-healing thermoset materials.^[61,62] By means of a detailed study on the kinetic of the DA/retro-DA reaction process in this material, excellent self-healing properties were demonstrated on the polymer matrix, which was able to recover micrometric indents upon a suitable electrically-induced thermal treatment (<1 min at a current of 0.5 A, leading to a localized increase in temperature up to 150 °C). In particular, the structural response of the healed CFRC material was evaluated using the same three-point bending test employed for inducing the micrometric crack, and multiple healing ability was demonstrated with strain energy recovery >90% compared with the pristine sample. In a subsequent work by the same group,^[63] the effect of multiple electrically-induced healing cycles on the structural integrity of a similar DA-based CFRCs obtained by vacuum-assisted resin transfer molding was evaluated by means of dynamic thermal mechanical analysis (DTMA). Similar to their previous work, it was shown that matrix damages (e.g., delamination) could be successfully healed using electrical resistive heating via CFs. However, since the healing process was restricted to the thermally remendable polymer, the strength of the healed CFRC material was found to be affected by the integrity of the reinforcing CFs, as upon successive mechanical damage/healing cycles a slight decline of strain energy was observed as a result of partial CF rupture.

In a more recent work, an original approach to CFRC repairing was proposed based on the localized incorporation of the same type of thermally triggered monomers in composite laminates.^[64] In particular, inkjet printing was used to deposit a modified ink formulation containing a monomeric system analogous to Mendomer 400/401 based on DA functionalities (5% solutions in the inkjet formulation) onto commercial aerospace grade toughened unidirectional epoxy-carbon prepregs. The thermally-triggerable polymers were co-cured with the prepreg into composite laminates and the effect on the interlaminar properties of the resulting system was investigated. The incorporation of such modified DA-based ink into single and multiple ply prepreg specimens was shown to yield an improvement in the interlaminar fracture toughness and in the apparent interlaminar shear strength with respect to the control non-modified samples. A significant retention of interlaminar properties was found in inkjet modified mended samples versus control systems after a suitable thermal treatment (180 °C, 6 h), ascribed to the repair of the laminate material, thus demonstrating the effectiveness of

this approach. However, a deeper analysis of the healing behavior (e.g., through fatigue testing) would be required to effectively assess the repairing ability of the composite.

In order to ensure prolonged structural robustness in CFRC parts, the toughness of the composite component need to be preserved throughout the service life of the material. Focusing on this aspect, Kostopoulos and co-workers conducted a series of investigations on the incorporation of DA precursors in composites reinforced with continuous CFs and on its effect on material toughness.^[65–67] In particular, they enveloped unidirectional (UD) CF prepregs impregnated with a bismaleimide-based polymer (a glycidylether-based trifuran monomer reacted with a commercially available imide-extended bismaleimide (BMI) oligomer, **Figure 2A**) into the mid-plane of a UD CF-reinforced epoxy matrix.^[65] The so obtained modified composites displayed a great improvement in mode I interlaminar fracture toughness, exhibiting an increase of ≈ 1.5 times in the maximum load and of almost 3.5 times in mode I fracture energy when compared to the reference composites. On the other hand, the self-healing capabilities resulting from the introduction of the DA moieties within the matrix were found to be relatively modest, as a maximum of 30% recovery of interlaminar properties was demonstrated. In a subsequent more recent study, the same team tested a novel CFRC in which the repairing behavior was provided by the incorporation of the so-called self-healing agent (SHA) based on the same precursors used in the previous work in powder form in the mid-plane of a high-performance CF-reinforced prepreg, to create an internal layer with healing functionality.^[66] Interesting results were found by varying different process parameters, including time of curing and SHA concentration (in grams per square meter, gsm). An increase in the SHA loading level led to a general decrease in the flexural strength together with an enhancement of the fracture toughness of the final composite up to a SHA concentration of 120 gsm. In addition, the sample containing 120 gsm of SHA displayed high healing efficiencies while still retaining satisfactory mechanical properties (**Figure 2B,C**).

The incorporation of thermally triggered functionalities can not only provide increased fracture toughness. Indeed, it was shown that the possibility to thermally heal some small damage in the CFRC material could lead to a further improvement in the fatigue life.^[67] To address this aspect, a series of fatigue life tests (continuous loading; alternated loading with load release; alternated loading with load release and application of the thermal healing cycle during load release) were conducted on high performance aerospace UD CF/epoxy prepregs containing the previously described DA-based prepolymer resin in powder form (80–120 μm particle size distribution). As shown in **Figure 2D,E**, the composite system incorporating the DA-based polymer (BMI pp, in the plots) was found to exhibit superior performance compared to the reference sample, with the fatigue life of BMI-modified CFRCs extended by 75% as a result of the damage restoration provided by the SHA component. An analogous effect was observed on the modulus (E/E_0) of the modified CFRCs during fatigue cycling, which was shown to exhibit an improved response with respect to the reference systems.

Together with epoxy resins, polyurethanes (PUs) represent another important class of polymeric materials of great industrial interest and widespread use in the field of composites.^[68] One of the first demonstrations of DA-based PUs for use as matrices

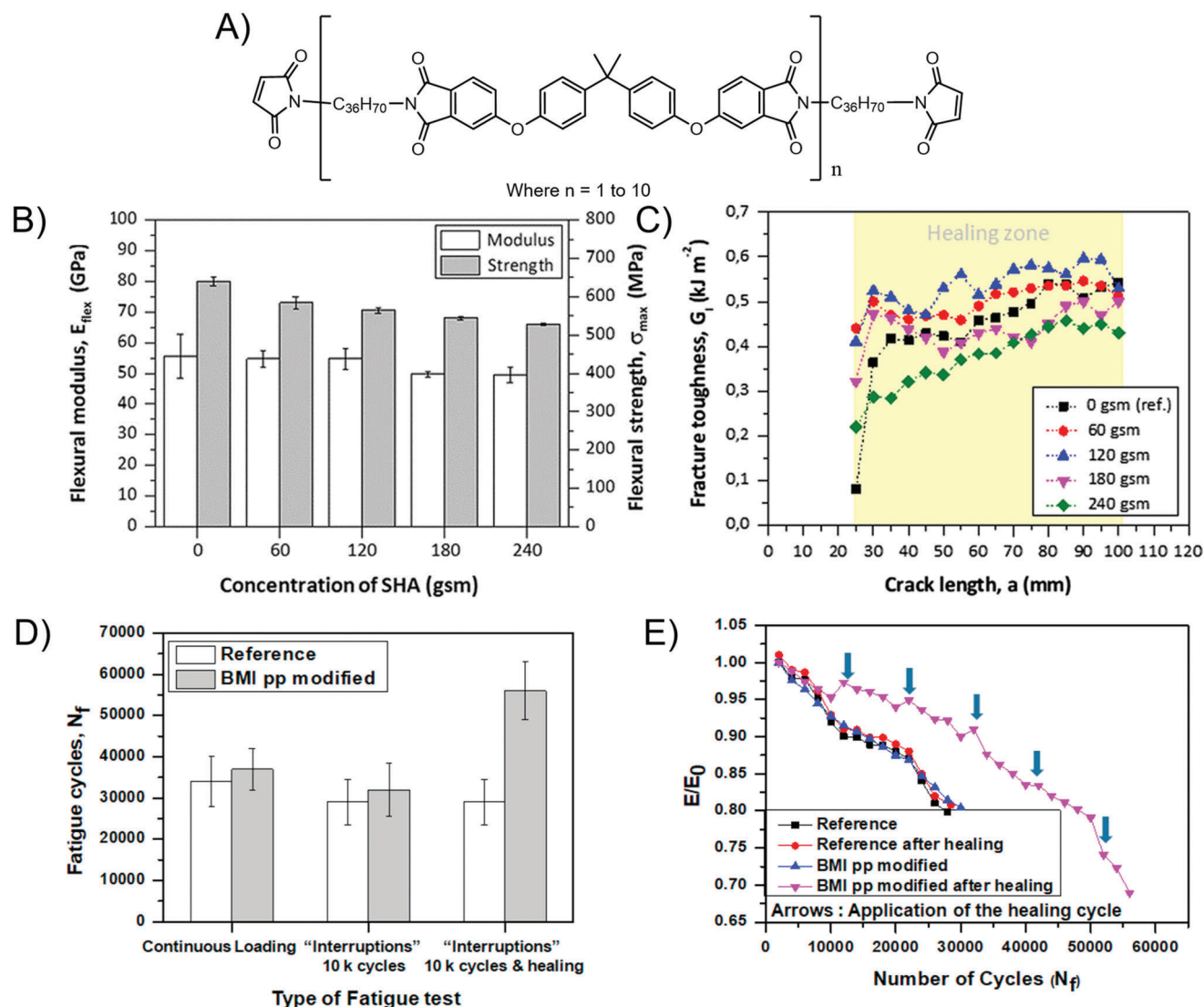


Figure 2. A) Chemical structure of commercially available imide-extended BMI oligomer. B) Knock down effect of the various concentrations of self-healing agent (SHA) (0 (reference), 60, 120, 180, and 240 gsm) on the flexural modulus (E_{flex}) and flexural strength (σ_{max}) of the CFRCs, after curing cycle 1. C) Typical mode I crack opening resistance curves for the reference (0 gsm) CFRC and for the modified CFRCs with 60, 120, 180, or 240 gsm SHA. Reproduced with permission.^[66] Copyright 2019, Wiley Periodicals. D) Depiction of the fatigue life of both CFRCs, for all fatigue test types; at continuous loading conditions, with “interruption” and with “interruption” together with the application of the healing activations. E) Modulus ratio evolution for reference and BMI pp modified CFRCs (with and without the application of the healing cycles) as a function of the number of fatigue cycles (N_f). Reproduced with permission.^[67] Copyright 2018, Elsevier Ltd.

in CFRCs was recently reported by the Sodano's group.^[69] They developed thermally-reversible PU materials using different proportions of a pre-crosslinked DA diol consisting of the adduct formed by N-(2-hydroxyethyl)-maleimide (HEM) and furfuryl alcohol, the polyols tri-ethanol amine (TEA) and N,N,N',N'-tetrakis(hydroxypropyl)ethylenediamine, and hexamethylene diisocyanate (HDI) as the cross-linker (**Figure 3A**). These PU systems were then used in conjunction with UD carbon fabrics to obtain CFRCs by vacuum-assisted resin transfer molding. The mechanical properties of the obtained systems were measured by means of tensile tests, and were found to be comparable with standard epoxy resins. As evidenced by optical microscopy images, by subjecting the damaged CFRC materials to a suitable

healing treatment (in a hot press: 135 °C for 2 h, 90 °C for 2 h, 70 °C for 2 h) it was possible to practically eliminate delamination effects due to fiber-matrix debonding, as a result of the effective action of the DA/retro-DA process.

One of the main limitations of using the furan/maleimide couple to form reversible DA adducts is its relatively low application temperature window, due to the retro-DA cleavage reaction occurring at ≈ 120 °C. This represents a critical aspect when high-temperature applications are targeted, because the polymer matrix may lose its mechanical integrity above the cleavage temperature as a result of de-crosslinking or decrease in molecular weight. To address this issue, anthracene moieties were introduced in the polymer network as diene species to replace the

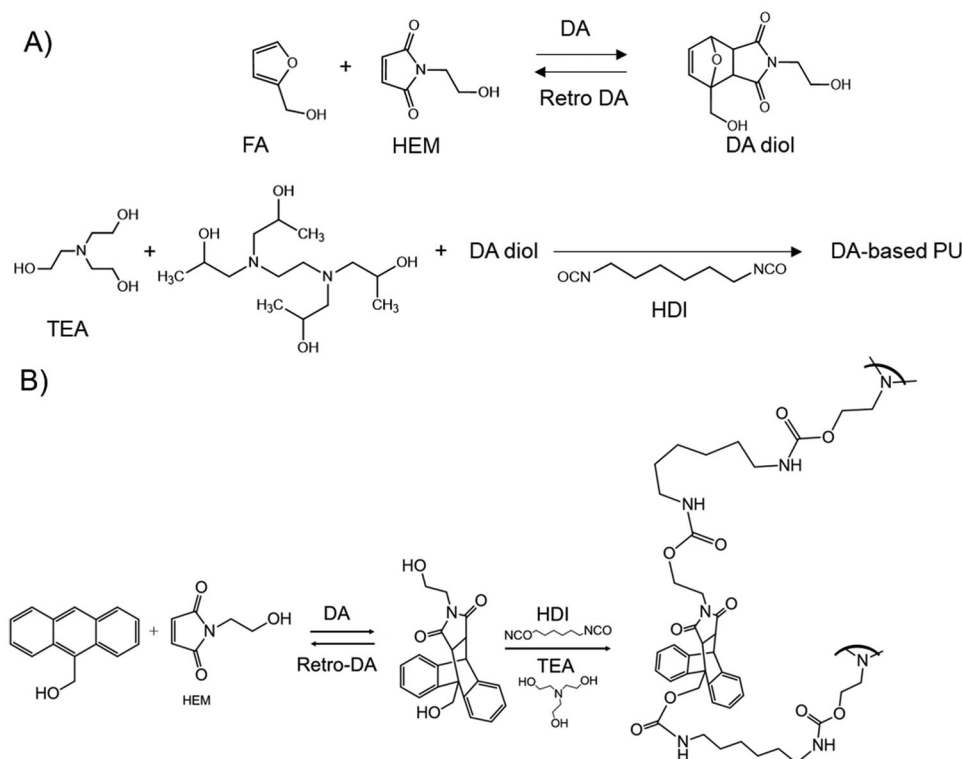


Figure 3. A) A schematic of monomer and DA-based PU synthesis procedures. Adapted with permission.^[69] Copyright 2015, Elsevier Ltd. B) A schematic of the methodology used to synthesize the healable monomer and its polymerization process through triethanolamine (TEA) and HDI. Adapted with permission.^[70] Copyright 2016, The Royal Society of Chemistry.

more commonly used furan, as a result of the higher temperature stability of the anthracene/maleimide adduct.^[70] In particular, a viscous resin incorporating HDI to precross-linked adducts of 9-anthracenemethanol and HEM was developed, suitable for impregnating UD CF fabrics by means of vacuum-assisted resin transfer molding (Figure 3B). The so obtained CFRCs exhibited excellent thermal stability, as evidenced by TGA measurements (the onset of the mass loss was found to be at temperatures higher than 240 °C), while the glass transition temperature (T_g) was found to lie in the 60–70 °C range. Their mechanical response (strength, stiffness, toughness) was evaluated in terms of tensile and compact tension fracture testing and was found to be comparable to that of structural grade commercial epoxy-based CFRCs. Average healing efficiencies (based on the short beam shear strength) of ≈69% and ≈52% were measured on such composite systems after the first and the second healing cycle, respectively. These values are noticeably lower than those observed on the pure matrix (up to ≈94%), likely due to the irreversible failure of the primary load-bearing components in the composite, namely the CFs. It was also mentioned by the authors that the healing behavior of the proposed material could be ascribed to the re-formation of mechanically cleaved DA adducts rather than thermally reversible DA reactions. Indeed, the healing cycle was conducted in a hot press for several hours and the applied compression for closing the crack required additional human intervention to heal the cracked specimens. This fact was mentioned as an evident limitation for the practical application of this polymer system.

3.2. Matrix Reversibility for CFRC Recycling and Reprocessing

In the past few years, the increasing need to implement circular economy models at industrial scale has pushed the research in the field of fiber-reinforced materials toward the use of sustainable routes to produce composites as well as to the development of recyclable and/or re-usable systems. In this context, one of the most recent works on DA-based CFRCs demonstrated the possibility of simultaneous recovery of both matrix material and CFs through an optimized solvolysis process.^[12] To this end, a DA polymer network was developed from the cross-linking of bi-functional and trifunctional furan-modified epoxides with an aromatic BMI in order to obtain a moldable polymer (Figure 4A).^[71] The resulting polymer was able to be reprocessed multiple times still retaining similar properties (T_g, thermal stability, mechanical response) to the virgin material. When CFs were introduced in the form of a nonwoven mat via compression molding, both Young's modulus and tensile strength resulted to be comparable with epoxy composites loaded with the same type of reinforcement. Interestingly, the optimization of a dedicated solvolysis process conducted at 120 °C allowed to recover the clean reinforcing mat with no visible damages thanks to the temperature-activated retro-DA reaction that led to the formation of the soluble monomeric precursors. Because of the relatively high recovery efficiency (residual matrix mass on recovered CFs < 5%), the liberated CFs could be directly re-used in second-generation CFRCs, which were able to fully retain (≈97%) their mechanical response (Young's modulus) while exhibiting a slight decrease (≈35%) in

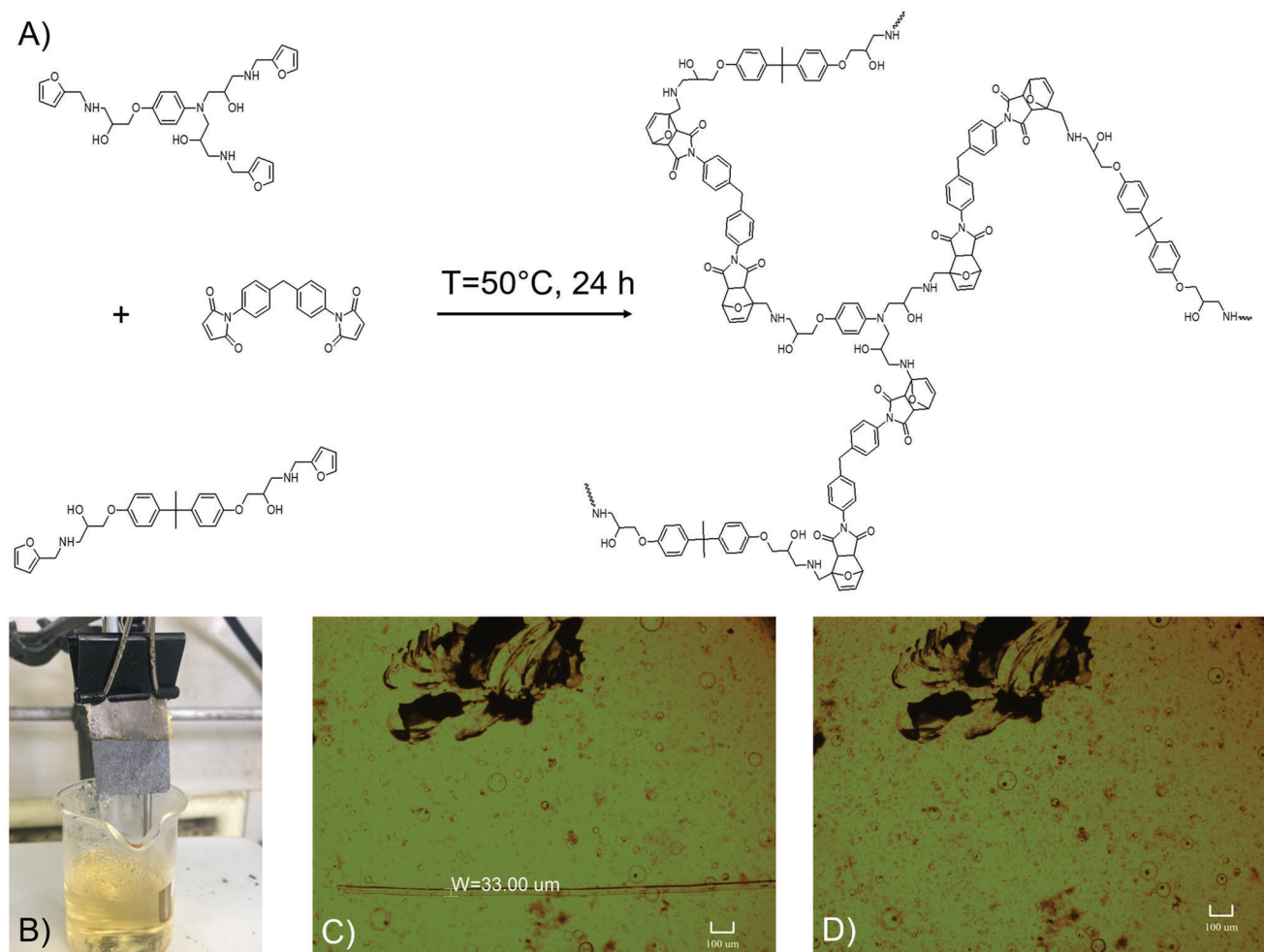


Figure 4. A) Schematic representation of cross-linking and decross-linking of bifunctional and trifunctional furan-modified epoxies with an aromatic BMI via DA and retro-DA. B) Composite sample partially immersed in solvent and removed after washing at 120 °C. C, D) Optical microscope images of coating obtained from recovered DA polymer: (C) Damaged by scalpel scratching and (D) after thermal treatment at 120 °C and slow cooling to room temperature. Reproduced with permission.^[12] Copyright 2019, Multidisciplinary Digital Publishing Institute.

strength compared with the virgin first-generation material. Such decline was attributed to the loss of sizing on the recovered CFs that inevitably reduces the fiber/matrix adhesion, thus suggesting the need for reprocessing the fibers prior to their further use in second generation composites. Finally, the DA-precursor solution obtained from the solvolysis process was also re-used to produce smart protective coatings capable to be repaired upon thermal treatment as a result of the DA/retro-DA mechanism, thus providing one of the first demonstrations of a holistic approach to full CFRC recovery and reuse (Figure 4B,C,D). An analogous strategy was demonstrated by Zhou and co-workers,^[72] who developed tri- and tetra-functional furan-containing precursors to be reacted with tri-maleimides cross-linkers, leading to DA resin systems employed as matrix material for solvent-assisted impregnation of aramidic fiber mats. After three cycles of solvolytic recycling (130 °C, 30 min) in N-methyl-2-pyrrolidone (NMP) and subsequent re-cross-linking at 60 °C for three days, mechanical testing on the final composites revealed good retention of Young's modulus and yield strength (>85%), as well as elongation at break (up to 97%). In addition, the final composite was

shown to be fully thermally re-shapable and solvolysis-assisted undamaged fiber liberation was also demonstrated.

3.3. Surface and Interfacial Reversibility for Increased CFRC Service Life

As suggested from the previously discussed reports, in addition to equipping the matrix material with thermally-triggerable self-healing functionalities, excellent interfacial bonding between fibers and matrix material also needs to be preserved in order to ensure that the mechanical response of damaged CFRCs is fully recovered after the healing process. Within this context, a crucial role is played by the development of suitable interface engineering strategies to optimize the interaction and the adhesion between the reinforcing fibers and the polymer matrix, to allow efficient transfer of the loads even after the CFRC is damaged.^[73] An interesting approach to address this issue consists in the surface functionalization of the reinforcing phase by means of thermally-triggerable moieties prior to the incorporation of

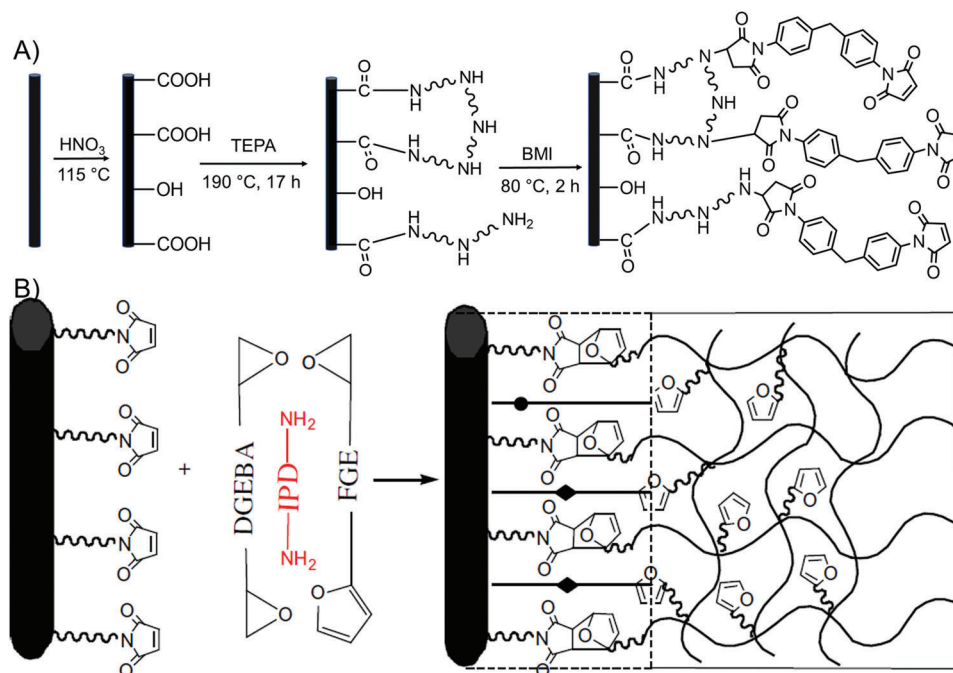


Figure 5. A) Protocol for grafting maleimide groups on carbon fiber surface by means of tetraethylenepentamine (TEPA) and BMI. B) Formation of a thermo-reversible interface with isophorone diamine (IPDA): DA thermal reversible bonds, ● irreversible covalent bonds and ◆ Van der Waals force. Adapted with permission.^[74] Copyright 2014, Elsevier Inc.

the CFs into the composite.^[74,75] In particular, a first surface treatment based on oxidation reactions was performed on the CFs to generate reactive polar (carboxylic or carbonyl) groups on their surface. After oxidation, the modified CFs were allowed to react with a polyamine precursor (tetraethylenepentamine) to graft amino groups on their surface, followed by functionalization via Michael addition with an aromatic BMI (Figure 5A). The obtained maleimide-grafted CFs could then be incorporated as reinforcing phase into a furan functionalized epoxy resin based on bisphenol-A diglycidyl ether (DGEBA), furfuryl glycidyl ether (FGE) and isophorone diamine (IPDA) (Figure 5B).^[74] The occurrence of the DA/retro-DA reaction provides the fiber/matrix interface with thermally activated self-healing ability.

Using micro-droplet debonding tests, it was shown that this approach allowed to achieve a relatively high healing efficiency (82%, measured as debonding recovery) after damage and suitable thermal cycles, which was found to be repeatable thanks to the reversibility of the click reaction. Given that the surface abundance of initial reactive groups on the CF was reported to be a key parameter for optimal interface interaction and self-healing, additional work will be needed to improve the efficiency and the yield of surface grafting as well as to extend the approach to the whole CFRC bulk material by appropriately optimizing the matrix formulation.^[75]

In a similar attempt to improve the interfacial mendability of CF-reinforced epoxy/amine composites, a thermally-reversible surface treatment for CFs based on a two-component DA system was developed.^[76] The reversible sizing formulation was obtained by functionalization of a diepoxy resin with furfurylamine, which was subsequently mixed with a trifunctional maleimide-modified jeffamine. This treatment was applied to oxidized un-

sized individual CFs (from a CF tow) by dip coating from a 3% dichloromethane solution, followed by drying at 70°C for 30 min. This allowed the formation of a smooth, homogenous DA coating (thickness $\approx 0.1\ \mu\text{m}$), whose structural, morphological, and surface characteristics were gauged by X-rays photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), FTIR and contact angle measurements. The effective interfacial healing ability of the system was assessed by conducting interfacial shear strength (IFSS) measurements through a micro-bond testing apparatus on such DA-coated CFs using micro-droplets of standard amine-cure epoxy resin to mimic the thermoset matrix. Measurements were repeated after debonding and subsequent heating (130°C for 5 min)/cooling (80°C for 2 h) cycles to reform the DA adduct at the interface. The healing efficiency, defined as the ratio between IFSS of healed and pristine interface, was found to be as high as 93.8% after the first debonding cycle. This value was however shown to drop to 73.3% after the second cycle and to 16.5% after the fourth cycle, likely because of the progressive occurrence of mechanical defects at the matrix/fiber interface upon repeated micro-bond tests and the formation of irreversible bonds due to thermal fatigue induced by the DA heating/cooling cycle.

An alternative approach to bath coating for sizing CFs with a reversible surface treatment was proposed by Kostopoulos and colleagues,^[77] who investigated the use of unreacted BMI and a trifuran (TF) precursor as SHA. In particular, a solution-based electrospinning process was used to directly deposit these compounds onto the surface of aerospace grade commercial CF prepreps, to obtain surface-modified DA-enabled CF prepreps. After fabrication of the laminated composite by autoclave processing, the effect of such surface treatment on mechanical properties was studied by low velocity impact tests and compression

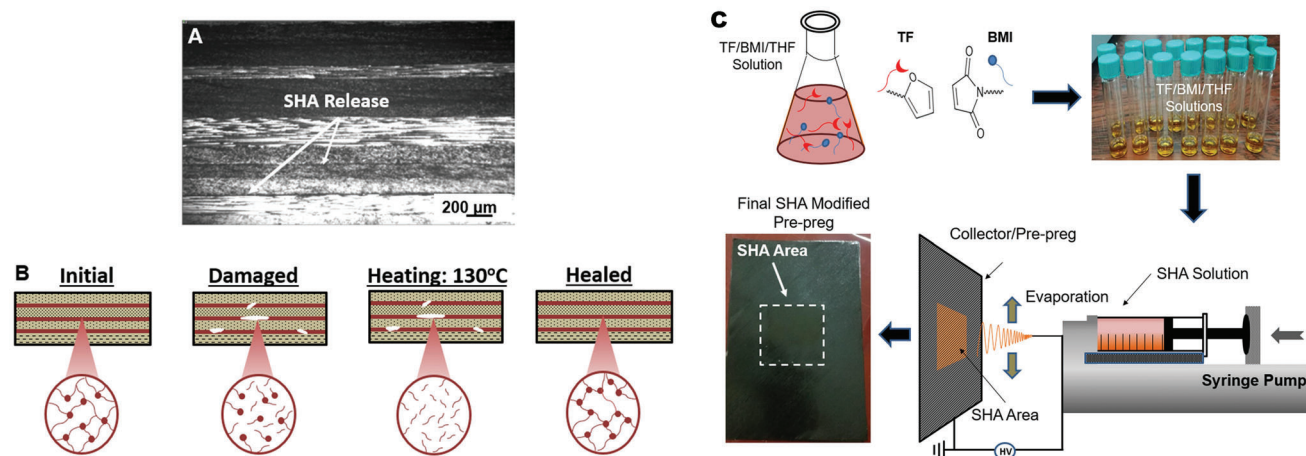


Figure 6. A) Optical microscopy (OM) image of a BMI modified CFRP after the application of the healing process. B) Description of the healing mechanism based on the DA reaction mechanism inside a damaged CFRC material with healing capability. C) Illustration of the experimental approach followed for prepreg surface modification by solution electrospinning. Adapted with permission.^[77] Copyright 2020, Elsevier Inc.

tests after impact. While the introduction of the SHA did not appear to influence thickness, delamination behavior and low velocity impact force/energy of the resulting SHA-containing composite, its compressive healing activation (130 °C, 30 min, 0.67 bar) was able to fully restore the damaged area with significant improvement of compression strength, as schematically shown in Figure 6.

The resistive character of CFs could also be exploited to enable electrothermal activation at the interface of epoxy-based CF-reinforced reversible composites.^[78] To do that, the reinforcing fibers were first functionalized through co-deposition of polyethyleneimine/dopamine. This allowed the surface enrichment with $-OH$ and $-NH_2$ groups, avoiding the degradative fiber oxidation. The following steps were furan grafting by reaction with furanoyl chloride (room temperature, 6 h) followed by treatment with 1,4-bis (maleimido)butane. IFSS was again measured through micro-bond tests, using an undisclosed commercial epoxy-amine system incorporating up to 20% of 2-furanmethanamine as micro-droplet resin. The DA/retro-DA cycloaddition reactions were allowed via the application of microcurrents of the order of 3–5 mA. Interfacial self-healing was assessed by multiple debonding and healing cycles of micro-droplet/functionalized-CF specimens, demonstrating healing efficiencies of 71.7% and 44.1% after one and two cycles, respectively. Similar to previous studies,^[76] such performance decrease with increasing bonding times was associated to the reduction of furan and maleimide groups in the interphase region after successive loadings, coupled with the progressive formation of micro-gaps between resin micro-droplets and CF surface during testing, ultimately preventing the furan-maleimide reaction responsible for the interfacial healing ability.

4. Glass-Fiber-Reinforced Diels-Alder Composites

Together with CFs, GFs also occupy a prominent role in the field of structural composite materials. Indeed, GFRCs are widely employed in the construction, automotive and energy sectors,

among others.^[79] The incorporation of reversible DA functionalities in such materials may open new scenarios for the EoL of GFRCs in line with the circular economy principles.

4.1. Matrix and Interfacial Reversibility for GFRC Repair and Reuse

In one of the first examples of self-healing functionality in GFRCs, a polymeric network with tunable T_g based on the functionalization of an epoxy-amine thermoset with furfuryl glycidyl ether was used as matrix material for the preparation of composites reinforced with woven glass fibers via resin transfer molding.^[80] In order to enable crack recovery, a BMI solution in *N,N'*-dimethylformamide was injected at room temperature into the induced crack under minimal pressure. Healing of the furan-functionalized epoxy-amine thermoset was investigated under different stress conditions (three-point bending, short beam shear, and double cantilever beam) and was reported to occur multiple times in a given location with average healing efficiencies of ~70%, as a result of both physical and covalent bonding. While solvent-induced swelling and softening of the crack surfaces allows for mechanical interlocking, compatible functionalization of the polymer network and healing agent causes covalent bonding through the DA reaction between furan and maleimide groups. As expected, the concentration of BMI in the healing solution as well as the amount of solvent used were found to affect the healing ability of the system, suggesting that additional process optimization is required in this respect to enable a faster and more efficient damage recovery.

In the attempt to further enhance the mechanical properties of the GFRC component after healing, functionalization approaches were proposed to modify the surface chemistry of the reinforcing GFs, similarly to what previously discussed for CFRCs. Within this framework, an interesting and scalable strategy was reported to not only covalently cross-link GFs to the polymeric matrix but also to thermally repair the fiber/matrix

interface upon a suitable thermal stimulus.^[81] GF functionalization was performed in a two-step process starting from a 1 wt.% solution of 3-aminopropyltrimethoxysilane (APTMS) in ethanol/water to provide amine groups on the glass surface (93 °C, 1 h), followed by the Michael addition reaction (80 °C, 2 h) between maleimide moieties in BMI and amine groups previously grafted on the GF surface. The healing ability of the maleimide-functionalized fiber/resin interface was investigated with single fiber microdroplet pull-out testing employing a DGEBA/FGE/4,4'-methylene bis(cyclohexylamine) (PACM) resin as furan-based matrix material. Thanks to the maleimide-based grafting on GFs, reversible covalent link with such furan-functionalized polymer matrix was possible. Since the bonding at the glass–polymer interface is reversible, interfacial debonding of the GFs from the matrix can be healed and mechanical properties can be recovered. It was demonstrated that multiple healing cycles (90 °C for 1 h and 12 h at 22 °C) were possible with an overall average healing efficiency of 41%. Interestingly, healing efficiency was found to be independent of furan loading at the concentrations investigated. A subsequent investigation by the same group on the kinetic aspects of these systems revealed the importance of the mobility of the macromolecular chain for the efficiency of the DA reaction.^[82] As expected, decreasing the T_g of the polymer matrix led to increased chain mobility of the matrix system, ultimately resulting in improved self-healing ability. As a matter of fact, a DA based polymer with T_g below room temperature (T_g = 6.1 °C) could achieve complete recovery of the interfacial shear strength when heated at the retro-DA temperature.^[82] This model system is however not of immediate interest for practical applications where outdoor structural use is sought.

In a more recent work on thermally-reversible GFRC systems, DGEBA-based epoxy resins were functionalized with furfuryl amine to allow the formation of DA-based cross-links in the presence of BMI, thus enabling the fabrication of composites capable of multiple self-healing/repair processes.^[83] With the aim of achieving a high conversion in the formation of the reversibly crosslinked polymer network while avoiding major side-reactions, a two-step synthetic process was developed consisting of a bulk prepolymerization reaction of the functionalized epoxy resin followed by a network formation step with the introduction of the bismaleimide cross-linker. The second step was performed in a twin-screw extruder to realize a good mixing at high temperatures, while keeping the residence time at that temperature short enough to avoid maleimide side reactions. By tuning the process conditions (BMI concentration and average functionality of the system), fully cross-linked polymeric networks could be demonstrated, characterized by the ability to regain fluid behavior above the retro-DA temperature for at least five subsequent heating cycles. GFRC films could be obtained by sandwiching a layer of self-healing material dispensed in powder form between two layers of woven GF fabric and hot pressing at 150 °C for a few minutes. After a suitable thermal treatment, full repair of severely cracked and delaminated GFRC specimens was demonstrated, thus providing a direct strategy for thermo-reversible composite systems with potential industrial scalability. Interestingly, a similar DA-based composition was found to provide excellent thermally-induced healing ability on GFRCs, as inferred from tapered double-cantilever beam tests.^[84] In particular, self-healing efficiencies exceeding 100% after two thermally-induced mend-

ing cycles could be achieved in both mode-II interlaminar fracture toughness (G_{IIC}) and interlaminar shear strength (ILSS), making this formulation particularly promising for the production of GFRCs of mechanical response close to that of traditional structural composites, while ensuring the required thermally-induced reversibility.

The use of reversible DA resins in GFRCs was reported to be effective not only for healing mechanical damages, but also for the restoration of other functional properties. Within this context, thermally conductive GFRCs for circuit boards were obtained by introduction of functionalized hexagonal boron nitride in the DA-based epoxy resin used as matrix material, leading to high in-plane ($6.22 \text{ W m}^{-1} \text{ K}^{-1}$) and through-plane ($1.53 \text{ W m}^{-1} \text{ K}^{-1}$) thermal conductivities.^[85] The composite was realized using a standard furfuryl amine-modified DGEBA and bis(3-ethyl-5-methyl-4-maleimidophenyl) methane as cross-linker. The reversibility of the DA reaction enabled interlaminar crack healing with recovery of both mechanical strength (70%–85%) and thermal conductivity (62%–89%) upon suitable thermal treatment (130 °C for 30 min and 80 °C for 24 h, under a 2 MPa pressure).

4.2. Matrix Reversibility for GFRC Recycling and Reprocessing

In addition to the crack-healing ability, the thermally induced DA/retro-DA reaction system was exploited to provide GFRCs with recycling functions. In analogy to some previous studies on CFRCs,^[12] it was shown that suitable thermal treatments allowed a fast and efficient solvolysis of GFRCs based on a DA resin made of DGEBA chain-extended with furfuryl amine and cured with BMI.^[86] The composites were obtained by dispersing milled grains of pre-polymerized DA resin on GF fabrics, followed by compression molding at 120 °C for 3 min under a 15-bar pressure. Solvolysis with fiber liberation occurred in a few minutes at $T > 100 \text{ °C}$ in a variety of solvents like isopropyl acetate, toluene, butanol and acetic acid. Reprocessing of both organic and fiber components into new composites with comparable physical properties was also reported, providing an interesting example of material recovery in line with the principles of the circular economy.

5. Multifunctional Diels-Alder Composites

In the steadily growing field of high-performance computing and information technology, functional composite materials with thermal conductivity behavior have started to play an increasingly important role as light-weight heat dissipation elements for thermal management and device reliability. Currently, so-called thermal interface materials (TIMs) are commonly used to adhere the hardware component to a heat sink in high-performance computing devices. One major issue encountered with currently used adhesive solutions is associated with their limited versatility when it comes to localized device failure, because in these cases the strong adhesion of the TIM to the operating device prevents pointwise substitution without mechanical failure. Thus, reworkability of these thermally conductive, high-adhesion materials is a highly desirable feature to ensure localized repairability of the IT component. To address this issue, a blend of two different polydimethylsiloxane copolymers functionalized with either

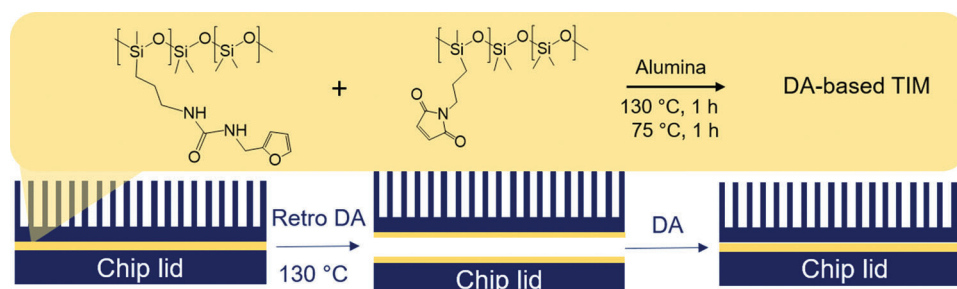


Figure 7. Set up of the DA-based TIM applied on a heat sink with a sketch of the last step of chemical synthesis shown above. Adapted with permission.^[87] Copyright 2016, American Chemical Society.

furan or maleimide was loaded with thermally-conductive aluminium oxide and employed as thermally-reversible DA-based TIM (**Figure 7**).^[87] A good adhesion was demonstrated for the functional silicone material within the typical operating range for TIMs (<130 °C), while exhibiting straightforward reworkability when heated above 130 °C. By means of adhesive peel tests, the mechanical strength was found to decrease linearly with temperature, indicating the easy reworkability of the material. Moreover, the addition of alumina allowed to achieve thermal conductivities ($0.4 \text{ W m}^{-1} \text{ K}^{-1}$) on-par with control samples, suggesting the potential of these materials as replacement of conventional TIMs. In a similar study, a silicone-based PU with pendant furan groups was developed and cross-linked by means of BMI molecules, to obtain a self-healing, reworkable matrix material.^[13] In order to impart thermal conductivity to the system, alumina powder (60 wt.%) was added to the matrix yielding a thermally-reversible functional composite exhibiting a thermal resistance of 0.48 K/W. Thanks to the presence of DA-adducts, thermally-induced decrosslinking of the obtained material could be shown without any major deterioration of the thermal performance of the component during the DA/retro-DA process, thus providing a first example of fully recyclable thermal pad. More recently, Al_2O_3 -loaded bifuran telechelic polycaprolactone (PCL) oligomers were prepared for crosslinking with BMI via DA bonds in the presence of tetrafunctional polyetheramine.^[88] The low viscosity exhibited by this PCL-based DA matrix at temperatures higher than the retro-DA temperature ($\approx 120^\circ \text{C}$) allowed the homogeneous incorporation of high concentrations (up to 60%) of maleimide-functionalized alumina particles by melt blending. The resulting composites were found to exhibit through-plane thermal conductivities ($0.2\text{--}1 \text{ W m}^{-1} \text{ K}^{-1}$) on-par or superior to conventional injection molded or compression molded Al_2O_3 -loaded composites, while providing straightforward thermally-induced self-healing ability and enhanced recyclability.

Similar DA/retro-DA architectures based on the furan/maleimide couple were adopted in the past few years also in the broad field of multifunctional composites. This approach has led to the development of reversible systems able to undergo thermally-assisted mendability and recyclability, while providing additional properties such as controlled gas permeability, triboelectric response, thermal energy storage, sensing ability, electrical conductivity, magnetic or microwave sensitivity, as a result of the incorporation of functional organic or inorganic fillers like MoS_2 ,^[89] SiO_2 ,^[90] polydopamine,^[91] polyaniline,^[92] liquid metal particles,^[93] Fe_3O_4 ^[94] or carbonyl

iron,^[95] respectively. The implementation of this strategy has proven particularly valuable in this field to obtain complex functional composite systems with intrinsic recyclable-by-design characteristics for prospective application in high-added-value scenarios.

6. Biobased Precursors for Diels-Alder Composites

In the context of materials sustainability, one of the clear benefits of the furan/maleimide couple used in most reversible DA composite systems is the biogenic origin of the diene component, as it can be obtained industrially via decarbonylation of furfural, a biobased aldehyde distilled from agricultural biomass.^[43] Similarly, some of the most commonly employed furan derivatives for incorporation into polymeric systems (viz., furfuryl alcohol, furoic acid, furfuryl amine and furfuryl methacrylate) can also be obtained through suitable multistep processing and functionalization starting from polymeric carbohydrates like cellulose and hemicellulose.^[96] Along these lines, the use of furanic compounds for the preparation of reversible DA polymeric systems can be regarded as an intrinsically effective strategy to enhance materials sustainability in the frame of the circular economy.

In addition to the direct use of furan derivatives,^[97] functionalization with furanic moieties of compounds derived from lignocellulosic biomass has also been an explored strategy. In this respect, lignin^[98,99] as well as smaller-molecular-weight lignin derivatives such as magnolol,^[100] rosin^[101] and tannins^[102] have also been investigated as biosourced platforms to increase the renewable carbon content in furan/maleimide reversible DA systems.

As to the dienophile counterpart, while the vast majority of furan/maleimide reversible DA polymers employ oil-based aromatic bis-maleimides^[103] with a few cases of lab-scale aliphatic ones,^[56,104,105] recent efforts have also focused on the development of biosourced bismaleimides obtained from vegetable oils and fatty acids,^[57b,106] and commercial examples of those have also started to appear.^[107]

Despite this growing interest in biobased furan/maleimide precursors, the field of reversible matrices for fiber-reinforced composite materials has remained surprisingly unpopulated of examples of this type. Only recently, attempts were made to replace the commonly used oil-based aromatic BMIs with biobased bisitaconamides, readily obtained from itaconic anhydride and an aromatic diamine (**Figure 8A,B**).^[108]

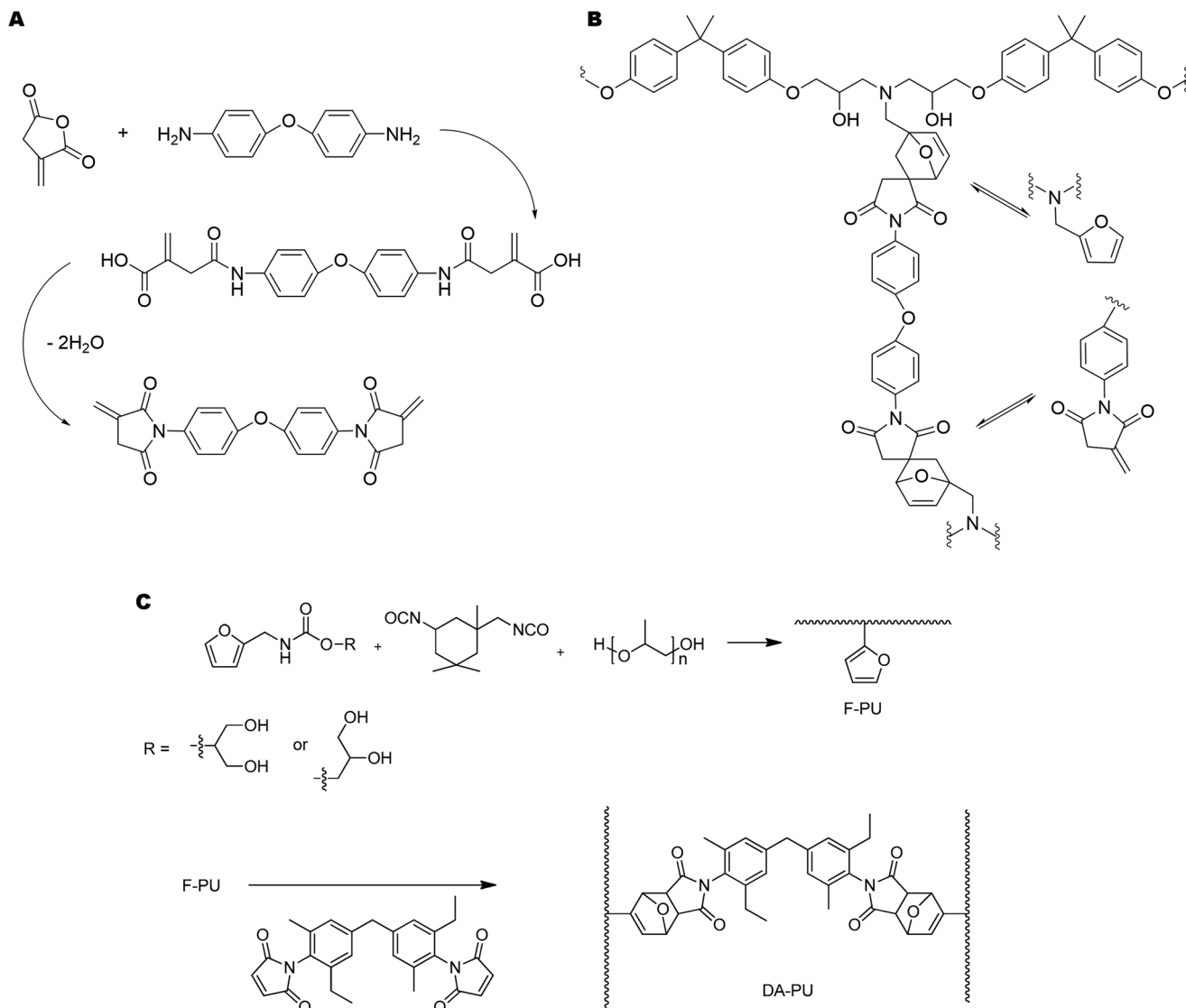


Figure 8. A) Bisitaconimide synthesis reaction from itaconic anhydride and 4,4'-Oxydianiline. B) Resin based on epoxy amine polymers connected with thermo-reversible crosslinks based on furfuryl-itaconimide DA chemistry. Adapted with permission.^[108] Copyright 2020, Elsevier Inc. C) Synthesis of PU-based cross-linked network. Reproduced with permission.^[113] Copyright 2019, Multidisciplinary Digital Publishing Institute.

This biobased dienophile was successfully used as crosslinker for DGEBA-furfuryl amine prepolymers. The new composition displayed lower T_g ($\approx 45^\circ\text{C}$) and lower retro-DA temperature ($\approx 85^\circ\text{C}$) with respect to the fully-oil-based counterpart, allowing a faster solvolysis at 80°C . As a result, the obtained composite was characterized by an easier recyclability, but also by poorer thermochemical stability, which might pose issues if high-temperature applications are sought.

While the use of biobased precursors for the reversible DA matrix formulation certainly contributes to lowering the carbon footprint of the composite material and increase its prospective circularity potential, a parallel approach to be pursued to increase the renewable carbon content of reversible composites is the use of bioderived reinforcements. To that end, bioderived fibers have gained increasing attention in recent years as sus-

tainable and renewable sources of high-performance composite materials.^[109–111] In this respect, cellulose fibers represent one of the most promising reinforcing platforms for composites because of their natural abundance, low cost, and favorable mechanical properties.^[112] The use of cellulose fibers in the context of thermally-reversible polymer-based composite materials was recently addressed through their incorporation into a new furan-functionalized PU matrix crosslinked by means of an aromatic bismaleimide (Figure 8C).^[113] In order to ensure homogeneous dispersion into the DA-based PU matrix, a suitable surface pretreatment to impart hydrophobicity was carried out on the natural reinforcing fibers with different quaternary alkyl ammonium salts. Composite materials incorporating the surface-functionalized cellulose fibers at different loadings were then produced by solution casting. It was shown that the addition of

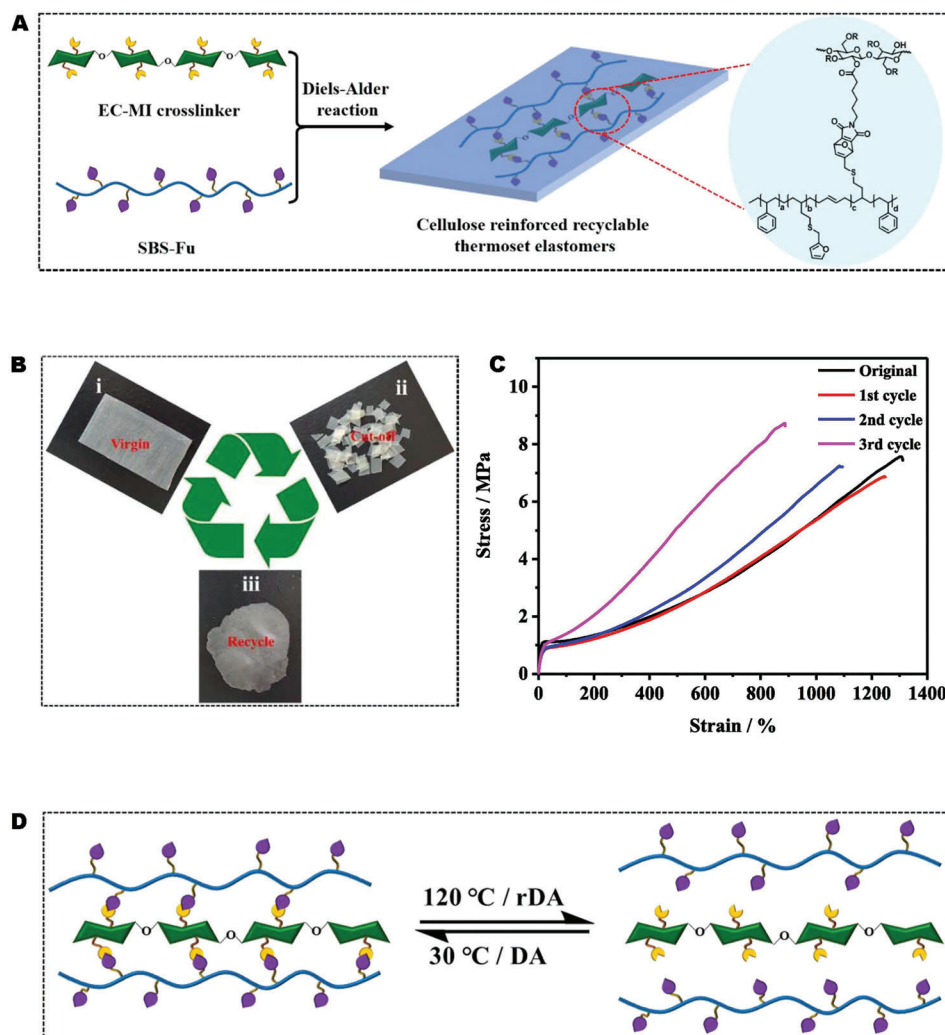


Figure 9. A) Synthetic approach for the preparation of cellulose-reinforced thermoset elastomers. B) Recycling process of the thermoset elastomer. C) Stress–strain curves of the recyclable thermoset elastomer. D) Schematic representation of the DA mechanism for the recycling process. Reproduced with permission.^[114] Copyright 2022, Elsevier Ltd.

cellulose in the cross-linked polymeric network leads to a noticeable improvement of mechanical (tensile) properties up to a certain concentration (5 wt.%) above which a sharp decline was observed. Furthermore, self-healing abilities were demonstrated and exploited in terms of recyclability of the composite system. Finally, by means of a solvolysis process conducted at the retro-DA temperature (120 °C, in propylene glycol monomethyl ether acetate), material recycling was demonstrated leading to second-generation composites exhibiting a slight decrease in tensile strength and modulus with respect to the virgin system, but a marked increase in the elongation at break. This behavior was ascribed to a reduced cross-linking density after recycling because of the reversible conversion of DA adducts to their diene and dienophile moieties at high temperature. On the other hand, the increased elongation was explained in terms of a plasticization effect provided by the cellulose fibers, which led to preservation of the composite toughness after reprocessing.

More recently, a thermally-reversible cellulose-reinforced thermoset elastomer was prepared based on the reaction between a cellulose macro-crosslinker bearing maleimide groups and a furan-modified poly(styrene-*block*-butadiene-*block*-styrene) (SBS).^[114] It was shown that the formation of the DA-based cross-linked network allowed the reinforced thermoset elastomer to be readily recycled via mechanical shredding followed by hot-press compression molding at 120 °C for 10 min under a 10 MPa pressure (Figure 9). The recycling efficiency was measured in terms of retention of the mechanical performance (fracture toughness) after the recycling process, which was found to be as high as 88.1%. To provide additional functionalities to this cellulose-based reversible composite system, carbon nanotubes were incorporated in the formulation yielding photothermal conversion response and Joule heating characteristics, thus prospecting potential applications in the fields of photoelectric generators and de-icing coatings.

7. The Circular Economy of Diels-Alder Composites

While fiber-reinforced composites are important materials for a diverse variety of manufacturing sectors, their EoL management is still very challenging when the principles of the circular economy are to be addressed. Considering the two most widely employed fiber materials (namely, GFs and CFs), in 2021 alone the production volume of GFRCS was $\approx 2'910'000$ ton, while that of CFRCS was $\approx 52'000$ ton, with a steady increase versus the past couple of years by 18.3%.^[115] In addition, the cumulative volume of decommissioned products based on such fiber reinforced composites is also expected to become critical in the next coming years. According to these numbers and taking into account that GFRCS and CFRCS have very different EoL scenarios, this situation poses serious environmental concerns while at the same time offering interesting opportunities.

The raw cost of GFs is $\approx 2-3$ €/Kg and therefore comparable to that of a standard polymer matrix.^[115] Recovery of both the reinforcing fibers and the polymeric matrix is therefore essential for this kind of composite products to allow some profitability margin and economic viability. In the case of GFRCS, mature recycling technologies are mechanical grinding and pyrolysis. However, the former method is not able to produce completely liberated fibers and strongly reduces their length, thus negatively affecting their impact on the mechanical properties of the resulting composite. Pyrolysis is hardly applicable to EoL GFRCS in real industrial contexts because a drop of $\approx 50\%$ of the mechanical properties of GFs (typically, their Young modulus and their ultimate strength) is generally observed upon this treatment, and the recovery of the organic fraction results technically difficult. For GFRCS, the adoption and development of reuse and repair options is therefore very advisable, since recycling alternatives are currently not economically viable.

CFs show higher mechanical properties and superior lightness versus GFs, but their costs are much higher (4 to 40 times as much, compared with the price of glass).^[115] Given their favorable characteristics, there is a potentially high market demand for competitive-cost, recycled CFs, for example in the automotive sector. At present, pyrolysis is the recycling technology of choice for CFRCS because CFs are minimally damaged by such non-oxidative thermal treatment. Solvolysis may also be an alternative, but it is very often impossible to carry out on current generation CFRCS due to the permanent network structure of the polymer matrices used for these systems, which are in most cases epoxies.

Based on these considerations, the current lifecycle of fiber-reinforced composites appears largely linear, consisting in a nearly 100% input of virgin materials (both resins and fibers) and ending in incineration or landfilling. Within this context, the adoption of DA-based resins as impregnating matrices may help to significantly increase the circularity potential of the composite sector.

One of the most widely recognized figures of merit that can be adopted to measure the circularity of a product, or of a technology, is the *Material Circularity Indicator (MCI)*, proposed a few years ago by the Ellen McArthur Foundation.^[116] This is expressed as:

$$MCI = 1 - (LFI \cdot (0.9/X)) \quad (1)$$

where *LFI* is the *Linear Flow Index* and *X* is the *utility* of the material.

X is defined as:

$$X = (L/L_{av}) \cdot (U/U_{av}) \quad (2)$$

where *L* is the average lifetime of the product and *U* is its intensity of use (number of functional units achieved during its use phase), compared to industry-average standard values (*L_{av}* and *U_{av}*, respectively).

LFI gives a measure of the proportion of product flowing linearly (i.e., coming from virgin materials and ending up as unrecoverable waste) and it is instead defined as:

$$LFI = (V + W) / (2M + (W_F - W_C) / 2) \quad (3)$$

being *V* the mass of virgin input material, *W* the total amount of unrecoverable waste associated with the product, *M* the mass of the product, *W_F* and *W_C* the mass of unrecoverable waste associated with the production of the secondary material feedstock for the product and the mass of unrecoverable waste generated in the process of recycling parts of the product, respectively. Accordingly, 0 (completely restorative flow) $\leq LFI \leq 1$ (completely linear flow).

It is worth noting that *V* is related to *M* through the following expression:

$$V = M \cdot (1 - F_R - F_U - F_S) \quad (4)$$

where the fraction of biological, renewable material *F_S* is included, together with the fraction of material from recycled feedstock *F_R* and the fraction of material from reused feedstock *F_U*.

In the case of a fully linear production model for the current fiber-reinforced composite sector, *W_F* = 0 (no secondary material used), *W_C* = 0 (no recycling considered), both *V* and *W* correspond to the mass of the product *M* (only virgin material employed, so *V* = *M*; the entire product mass is considered a waste at the product EoL, so *W* = *M*). Accordingly, *LFI* = 1. Based on these assumptions and considering *X* = 1 (i.e., product in line with industry standard in terms of both lifetime and intensity of use), the application of (1) yields *MCI* = 0.1, which can be considered as the baseline value for the current composite sector.

The use of reversible DA resins as matrix materials for the design of the next generation of polymer-based composites may significantly contribute to increase the *MCI* of the composite technology according to different scenarios, as briefly outlined in the following.

In the presence of such dynamic matrices, a certain number of thermal repair cycles could be foreseen with the effect of extending the overall utility *X* of the fiber-reinforced composite product, through the independent increase of parameters *L* (lifetime of the product), *U* (intensity of use) or a combination of both, with respect to the current industry-reference standard *L_{av}* and *U_{av}*. After such multiple repair cycles, the EoL composite products could be eventually subjected to chemical recycling for an efficient separation and recovery of both fibers and resin material. Due to the dissociative nature of the DA polymer network, recycling should be preferentially carried out by solvolysis in mild process conditions (atmospheric pressure and temperature

approaching or slightly above the retro-DA temperature, typically in the 110–120 °C range), preserving the physical properties of the fibers and the chemical structure of the resin, thus making them suitable secondary materials for reprocessing and reuse.

However, some limitations of the DA technology for the composite sectors exist. First, although the temperature threshold for the retro-DA reaction is somewhat depending on the chemical structure of the polymer (on the chain stiffness, on its T_g), it is always ≈ 110 –120 °C. This makes thermoreversible DA resins not suitable for applications where continuous-use service-temperatures above 100 °C are foreseen, due to the significant softening of the materials. Second, the DA and retro-DA cycloaddition reactions are not fully reversible in practical conditions, especially when heating is carried out in the higher temperature range (120 °C and above). As recently reported,^[54,117] this is due to the occurrence of some irreversible side-reactions, namely self-polymerization of maleimide moieties and Michael addition of residual, unreacted amine groups (such as those coming from furfurylamine) to maleimide. While the latter side-reaction can be avoided by a careful control of the stoichiometry of the DA formulation, self-polymerization of maleimides is a free-radical chain process that cannot be completely suppressed. In particular, although some possible strategies to mitigate the occurrence of maleimide self-polymerization exist (formulation with free-radical inhibitors like hydroquinone; unbalanced stoichiometry in favor of the diene species; replacement of conventional bis-maleimides with less mobile and reactive tris-maleimides), the persistence of such side-reaction entails practical limitations to the real long-term recyclability of DA resins.

Based on all the considerations above, a futuristic scenario can be envisaged in order to quantify the potential effect of the DA technology on the circularity of the composite sector, taking as reference case the production of 1 kg of fiber-reinforced composite material.

In particular, a realistically limited number of thermally-induced repairing cycles can be foreseen, in line with the experimental evidences discussed in the previous sections of this work. This would lead to an extension of the useful average lifetime L of the product for a given intensity of use U , with respect to the corresponding industry-average standards. In turn, the product utility X will increase by a factor larger than 1. If a 10% increase in L is considered ($L = 1.1 L_{av}$), $X \approx 1.1$.

The chemical recycling process by mild solvolysis could be eventually carried out on the EoL part, allowing the recovery of clean and undamaged fibers, reusable as 100% secondary feedstock for a new composite manufacturing cycle. The recovered DA liquid resin would be instead more difficult to be directly reused as matrix material for composite remanufacturing, due to the presence of the solvent used in the solvolysis process. However, it could be still exploited in the coating sector,^[12] the latter still representing an open-loop recycling pathway compliant with the principles of the circular economy.

Even neglecting the circular contribution of the recovered DA resin ($V = W$) and considering an average composite composition consisting of a fiber content $\geq 60\%$ by weight and all reinforcing fibers obtained from secondary feedstock, out of 1 kg of composite taken as reference, a reduction of at least 0.6 kg is achieved for the computation of both V and W in the expression of LFI . From (4) it follows that $V = 1 \cdot (1 - 0.6) = 0.4 = W$ (as

the entire product mass is considered unrecoverable waste at the EoL).

The estimation of W_C and W_F is more difficult at this stage of knowledge, given the still limited readiness level of this technology. For the purpose of simplified calculations, a default value of $(W_F - W_C)/2 = 0$ could be used in (3), considering a closed-loop recycling where $W_F = W_C$. Therefore, the numerical results for DA-based composites can be estimated as follows:

$$LFI = (0.4 + 0.4) / (2 \cdot 1 + 0) = 0.40 \quad (5)$$

and

$$MCI = 1 - (0.40 \cdot 0.9/1.1) = 0.67 \quad (6)$$

showing a strong potential improvement of the circularity performance for such reversible systems over the baseline reference value estimated for the current composite sector ($MCI = 0.1$).

These results could be further improved considering the potential biobased content of the DA resin or the incorporation of bio-sourced reinforcing fibers, as discussed in the previous sections.

With an introduction in the virgin matrix material of a 20% biobased fraction ($F_S = 0.2$) and in the presence of a fiber content of 60% by weight all coming from secondary feedstock ($F_R = 0.6$), $V = 1 \cdot (1 - 0.2 - 0.6) = 0.2$. If all matrix material (both oil-based and biobased) is considered non-recyclable, $W = 0.4$. Based on the same arguments as before, this would in turn yield:

$$LFI = (0.2 + 0.4) / (2 \cdot 1 + 0) = 0.30 \quad (7)$$

and

$$MCI = 1 - (0.30 \cdot 0.9/1.1) = 0.75 \quad (8)$$

with additional positive enhancements in the circularity of DA composite materials.

8. Conclusions and Outlook

In the last few decades, composite materials have found widespread use in many application areas, from industrial fields such as aerospace, automotive and biomedicine to sport and leisure. In this framework, polymer composites have been extensively employed as matrix materials especially because of their favourable high strength/weight ratio that allows for light and stiff components. In particular, thermosets can provide the material with pronounced mechanical performance, high thermal stability and resistance to chemicals, which are essential features for structural composites or for highly demanding applications. However, their superior stability associated with the presence of a continuous intermolecular cross-linked network within the matrix constitutes a disadvantage in terms of re-processability and recyclability, thus making these systems not fully compatible with the compelling needs of emerging life cycle scenarios based on the principles of the circular economy and of end-of-life material valorization. In this respect, thermo-responsive dynamic polymers are considered to be valid alternatives to commonly used thermosets as matrix materials, as they provide straightforward

advantages in terms of recyclability and reusability, normally not achievable with conventional cross-linked systems. Within the broad area of dynamic bond chemistry, DA-based polymers represent up-and-coming material platforms with enormous valorization potential due to their broad chemical versatility, suitable mechanical performance and ease of processing. In particular, their role in the field of composite systems have proven useful to simultaneously achieve increased functionality and easy reprocessability.

In this account, it was shown that glass and carbon fiber reinforcements could be successfully incorporated in such dynamic materials, providing increased mechanical response while offering additional interesting technological perspectives toward self-healing of delaminated components, reprocessing, and ultimately complete recovery of reinforcing fibers by means of dedicated solvolysis approaches. Indeed, DA-based matrices were shown to be successfully dissolved in high-temperature solvents due to the dissociative nature of their covalent network. Matrix reclamation was demonstrated after solvent evaporation or similar processes. In contrast, mechanical recycling was found to be a rarely exploited technique, as cutting and consequently shortening of long fibers would cause a significant decrease in structural performance in second generation composites.

A preliminary analysis of the circularity potential of DA composites was also proposed, highlighting the benefits of employing reversible materials as matrix component in fiber-reinforced composites with respect to conventional systems. In particular, it was shown that noticeable improvements in some key circularity metrics could be attained due to the possibility of extending the lifetime of the composite product through repetitive repair and reuse cycles, as a result of the thermo-reversibility of the DA materials. In addition, resorting to biobased precursors could also yield further positive effects on the circularity of future composite systems.

Possible avenues for future research in the field will need to target the development of dynamic composites with broader temperature-application windows, in order to expand the potential use of these materials in areas such as aerospace and automotive where thermal constraints are usually highly demanding. Additional research efforts should also focus on obtaining thermally-triggerable polymer composites starting from biobased precursors, in order to meet the increasingly more stringent requirements imposed by the global environmental legislation. In a broader context, the development of waterborne systems is certainly an interesting and viable approach, to be more deeply investigated in the future.

To conclude, although further work is essential to achieve effective repair, reuse, recycling and reprocessing of composites and to enable their factual and profitable implementation in large-scale production scenarios, thermo-responsive systems based on reversible bonds represent promising platforms that could open interesting avenues toward new circular economy models in the field of advanced materials. Based on these considerations, we hope this work will provide a useful outline of the most interesting findings in the broad area of composite systems based on DA polymers, and will serve as a key reference for further research in the field of high-performance polymer-based materials with increased functionality, extended lifetime and enhanced circularity potential.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

circular economy, composites, Diels-Alder, polymers, recycling, reversible bonds, self-healing

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- [1] D. D. L. Chung, *Composite Materials – Science and Applications*, 2nd ed., Springer-Verlag, London **2010**.
- [2] J. Li, Q. Liu, D. Ho, S. Zhao, S. Wu, L. Ling, F. Han, X. Wu, G. Zhang, R. Sun, C.-P. Wong, *ACS Appl. Mater. Interfaces* **2018**, 10, 9727.
- [3] T. S. Coope, D. H. Turkenburg, H. R. Fischer, R. Luterbacher, H. van Bracht, I. P. Bond, *Smart. Mater. Struct.* **2016**, 25, 084010.
- [4] G. V. Mahajan, P. V. S. Aher, *Int. J. Sci. Res. Publ.* **2012**, 2, 463.
- [5] O. E. Ismail, R. Paul, in *High-Performance Apparel – Materials, Development, and Applications* (Eds: J. McLoughlin, S. Tasneem), Woodhead Publishing, Kidlington, United Kingdom **2018**, Ch. 17.
- [6] W. Zhao, L. Liu, F. Zhang, J. Leng, Y. Liu, *Mater. Sci. Eng., C* **2019**, 97, 864.
- [7] P. Pesce, A. Lagazzo, F. Barberis, L. Repetto, F. Pera, D. Baldi, M. Menini, *Mater. Sci. Eng., C* **2019**, 102, 186.
- [8] H. H. Warder, J. K. Fairley, J. Coutts, R. R. Glisson, K. Gall, *Prosthet Orthot Int* **2018**, 42, 644.
- [9] Y. P. Shettigar, R. Obed D'souza, A. Jose, A. Gopinath, D. Prakashan, V. Rajeev, *IOP Conf. Ser.: Mater. Sci. Eng.* **2018**, 376, 012066.
- [10] M. Lachheb, M. Karkri, S. B. Nasrallah, *Energy Build.* **2015**, 107, 93.
- [11] A. Ruiz De Luzuriaga, R. Martin, N. Markaide, A. Rekondo, G. Cabañero, J. Rodríguez, I. Odriozola, *Mater. Horiz.* **2016**, 3, 241.
- [12] G. Fortunato, L. Anghileri, G. Griffini, S. Turri, *Polymers (Basel)* **2019**, 11, 1007.
- [13] J.-W. Kim, D. H. Lee, H.-J. Jeon, S. I. Jang, H. M. Cho, Y. Kim, *Appl. Surf. Sci.* **2018**, 429, 128.
- [14] C.-M. Chang, Y.-L. Liu, *ACS Appl. Mater. Interfaces* **2011**, 3, 2204.
- [15] C. K. Jeong, J. Lee, S. Han, J. Ryu, G.-T. Hwang, D. Y. Park, J. H. Park, S. S. Lee, M. Byun, S. H. Ko, K. J. Lee, *Adv. Mater.* **2015**, 27, 2866.
- [16] P. Kasemsiri, N. Lorwanishpaisarn, U. Pongsa, S. Ando, *Polymers (Basel)* **2018**, 10, 482.
- [17] K.-H. Pyo, D. H. Lee, Y. Kim, J.-W. Kim, *J. Mater. Chem. C* **2016**, 4, 972.
- [18] X. He, Z. Lei, W. Zhang, K. Yu, *3D Print. Addit. Manuf.* **2019**, 6, 31.
- [19] N. Islam, S. Halder, J. Wang, *Polym. Test.* **2019**, 74, 138.
- [20] S. Schäfer, G. Kickelbick, *Polymer (Guildf)* **2015**, 69, 357.
- [21] M. Biron, *Thermoplastics and Thermoplastic Composites*, 3rd ed., William Andrew, Oxford, United Kingdom **2018**.
- [22] Q. Guo, *Thermosets – Structure, Properties and Applications*, 2nd ed., Elsevier, Amsterdam, Netherlands **2018**.
- [23] M. Biron, *Thermosets and Composites – Material Selection, Applications, Manufacturing, and Cost Analysis*, 2nd ed., William Andrew, Oxford, United Kingdom **2014**.

- [24] European Parliament and Council, Directive 2008/98/EC of the European Parliament and of the Council of **19 November 2008** on waste and repealing certain directives. *LexUriServ Do* **2008**:3–30.
- [25] T. Maeda, H. Otsuka, A. Takahara, *Prog. Polym. Sci.* **2009**, *34*, 581.
- [26] Y. Jin, C. Yu, R. J. Denman, W. Zhang, *Chem. Soc. Rev.* **2013**, *42*, 6634.
- [27] R. J. Wojtecki, M. A. Meador, S. J. Rowan, *Nat. Mater.* **2011**, *10*, 14.
- [28] N. Zhong, W. Post, *Compos Part A Appl Sci Manuf* **2015**, *69*, 226.
- [29] F. García, M. M. J. Smulders, *J. Polym. Sci., Part A: Polym. Chem.* **2016**, *54*, 3551.
- [30] D. J. Fortman, J. P. Brutman, G. X. De Hoe, R. L. Snyder, W. R. Dichtel, M. A. Hillmyer, *ACS Sustainable Chem. Eng.* **2018**, *6*, 11145.
- [31] W. Denissen, J. M. Winne, F. E. Du Prez, *Chem. Sci.* **2015**, *7*, 30.
- [32] H. Otsuka, *Polym J* **2013**, *45*, 879.
- [33] W. Zou, J. Dong, Y. Luo, Q. Zhao, T. Xie, *Adv. Mater.* **2017**, *29*, 1606100.
- [34] P. Chakma, D. Konkolewicz, *Angew. Chem., Int. Ed.* **2019**, *58*, 9682.
- [35] A. Sanyal, *Macromol. Chem. Phys.* **2010**, *211*, 1417.
- [36] A. Gandini, A. J. F. Carvalho, E. Trovatti, R. K. Kramer, T. M. Lacerda, *Eur. J. Lipid Sci. Technol.* **2018**, *120*, 1700091.
- [37] A. Gandini, *Prog. Polym. Sci.* **2013**, *38*, 1.
- [38] J. M. Winne, L. Leibler, F. E. Du Prez, *Polym. Chem.* **2019**, *10*, 6091.
- [39] V. Zhang, B. Kang, J. V. Accardo, J. A. Kalow, *J. Am. Chem. Soc.* **2022**, *144*, 22358.
- [40] Y.-L. Liu, T.-W. Chuo, *Polym. Chem.* **2013**, *4*, 2194.
- [41] N. I. Khan, S. Halder, S. B. Gunjan, T. Prasad, *IOP Conf. Ser.: Mater. Sci. Eng.* **2018**, *377*, 012007.
- [42] W. Post, A. Susa, R. Blaauw, K. Molenveld, R. J. I. Knoop, *Polym. Rev.* **2020**, *60*, 359.
- [43] B. Briou, B. Améduri, B. Boutevin, *Chem. Soc. Rev.* **2021**, *50*, 11055.
- [44] Evonik, leading beyond chemistry. <https://corporate.evonik.com/en/media/press-releases/corporate/evonik-wants-to-facilitate-bulk-production-of-composites-101325.html> [accessed March 2023].
- [45] J.-A. Funel, S. Abele, *Angew. Chem., Int. Ed.* **2013**, *52*, 3822.
- [46] C. J. Kloxin, C. N. Bowman, *Chem. Soc. Rev.* **2013**, *42*, 7161.
- [47] N. K. Guimard, K. K. Oehlenschlaeger, J. Zhou, S. Hilf, F. G. Schmidt, C. Barner-Kowollik, *Macromol. Chem. Phys.* **2012**, *213*, 131.
- [48] I. L. Hia, V. Vahedi, P. Pasbakhsh, *Polym. Rev.* **2016**, *56*, 225.
- [49] J. R. Kim, A. N. Netravali, in *Advanced Green Composites* (Eds: A. Netravali), Scrivener Publishing, Beverly, MA **2018**, Ch. 7.
- [50] N. Ali, M. Bilal, A. Khan, T. A. Nguyen, R. Gupta, *Smart Polymer Nanocomposites – Design, Synthesis, Functionalization, Properties, and Applications*, Elsevier, Amsterdam, Netherlands **2023**.
- [51] M. Arslan, M. Tasdelen, *Polymers (Basel)* **2017**, *9*, 499.
- [52] K. C. Nicolaou, S. A. Snyder, T. Montagnon, G. Vassilikogiannakis, *Angew. Chem., Int. Ed.* **2002**, *41*, 1668.
- [53] C. R. Ratwani, A. R. Kamali, A. M. Abdelkader, *Prog. Mater. Sci.* **2023**, *131*, 101001.
- [54] P. Van Den Tempel, F. Picchioni, R. K. Bose, *Macromol. Rapid Commun.* **2022**, *43*, 2200023.
- [55] M. K. McBride, B. T. Worrell, T. Brown, L. M. Cox, N. Sowan, C. Wang, M. Podgorski, A. M. Martinez, C. N. Bowman, *Annu. Rev. Chem. Biomol. Eng.* **2019**, *10*, 175.
- [56] a) G. Fortunato, E. Tatsi, B. Rigatelli, S. Turri, G. Griffini, *Macromol. Mater. Eng.* **2020**, *305*, 1900652; b) E. Tatsi, G. Fortunato, B. Rigatelli, G. Lyu, S. Turri, R. C. Evans, G. Griffini, *ACS Appl. Energy Mater.* **2020**, *3*, 1152; c) G. Fortunato, V. Marroccoli, F. Corsini, S. Turri, G. Griffini, *Prog. Org. Coat.* **2020**, *147*, 105840.
- [57] a) C. Vilela, L. Cruciani, A. J. D. Silvestre, A. Gandini, *RSC Adv.* **2012**, *2*, 2966; b) C. Vilela, A. J. D. Silvestre, A. Gandini, *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*, 2260.
- [58] J. Xu, Z. Li, B. Wang, F. Liu, Y. Liu, F. Liu, *J. Appl. Polym. Sci.* **2019**, *136*, 47352.
- [59] K. Luo, J. Li, G. Duan, Y. Wang, J. Yu, J. Zhu, Z. Hu, *Polymer (Guildf)* **2018**, *142*, 33.
- [60] J. S. Park, H. S. Kim, H. Thomas Hahn, *Compos. Sci. Technol.* **2009**, *69*, 1082.
- [61] X. Chen, M. A. Dam, K. Ono, A. Mal, H. Shen, S. R. Nutt, K. Sheran, F. Wudl, *Science* **2002**, *295*, 1698.
- [62] E. B. Murphy, E. Bolanos, C. Schaffner-Hamann, F. Wudl, S. R. Nutt, M. L. Auad, *Macromolecules* **2008**, *41*, 5203.
- [63] J. S. Park, T. Darlington, A. F. Starr, K. Takahashi, J. Riendeau, H. Thomas Hahn, *Compos. Sci. Technol.* **2010**, *70*, 2154.
- [64] E. J. Fleet, Y. Zhang, S. A. Hayes, P. J. Smith, *J. Mater. Chem. A* **2015**, *3*, 2283.
- [65] T. Loutas, A. C. Christopoulos, V. Kostopoulos, A. Kotrotsos, P. Tsokanas, S. Tsantalis, *Smart Mater. Struct.* **2016**, *25*, 084011.
- [66] A. Kotrotsos, P. Tsokanas, S. Tsantalis, V. Kostopoulos, *J. Appl. Polym. Sci.* **2019**, *136*, 47478.
- [67] V. Kostopoulos, A. Kotrotsos, A. Sousanis, G. Sotiriadis, *Compos. Sci. Technol.* **2019**, *171*, 86.
- [68] H.-W. Engels, H.-G. Pirkel, R. Albers, R. W. Albach, J. Krause, A. Hoffmann, H. Casselmann, J. Dormish, *Angew. Chem., Int. Ed.* **2013**, *52*, 9422.
- [69] Y. Heo, H. A. Sodano, *Compos. Sci. Technol.* **2015**, *118*, 244.
- [70] Y. Heo, M. H. Malakooti, H. A. Sodano, *J. Mater. Chem. A* **2016**, *4*, 17403.
- [71] G. Postiglione, S. Turri, M. Levi, *Prog. Org. Coat.* **2015**, *78*, 526.
- [72] D. Zhou, H. Huang, Y. Wang, J. Yu, Z. Hu, *Comp. Sci. Technol.* **2020**, *197*, 108280.
- [73] J. Karger-Kocsis, H. Mahmood, A. Pegoretti, *Prog. Mater. Sci.* **2015**, *73*, 1.
- [74] W. Zhang, J. Duchet, J. F. Gérard, *J. Colloid Interface Sci.* **2014**, *430*, 61.
- [75] W. Zhang, J. Duchet, J. F. Gérard, *RSC Adv.* **2016**, *6*, 114235.
- [76] X. Zhang, S. Liu, Z. He, C. Lei, *Mod. Polym. Mater. Environ. Appl., Int. Semin., 6th* **2021**, *42*, 4289.
- [77] V. Kostopoulos, A. Kotrotsos, A. Geitona, S. Tsantalis, *Compos Part A Appl Sci Manuf* **2021**, *140*, 106151.
- [78] C. Yang, D. Zhu, C. Sun, B. Chen, Y. Li, I. N. Pulidindi, Z. Zheng, X. Wang, *Compos. Sci. Technol.* **2021**, *208*, 108767.
- [79] T.p Sathishkumar, S. Satheeshkumar, J. Naveen, *J. Reinf. Plast. Compos.* **2014**, *33*, 1258.
- [80] A. M. Peterson, R. E. Jensen, G. R. Palmese, *ACS Appl. Mater. Interfaces* **2010**, *2*, 1141.
- [81] A. M. Peterson, R. E. Jensen, G. R. Palmese, *Compos. Sci. Technol.* **2011**, *71*, 586.
- [82] A. M. Peterson, R. E. Jensen, G. R. Palmese, *ACS Appl. Mater. Interfaces* **2013**, *5*, 815.
- [83] D. H. Turkenburg, H. R. Fischer, *Polymer (Guildf)* **2015**, *79*, 187.
- [84] P. Wu, L. Liu, Z. Wu, *Macromol. Mater. Eng.* **2020**, *305*, 2000359.
- [85] F. Chen, H. Xiao, Z. Q. Peng, Z. P. Zhang, M. Z. Rong, M. Q. Zhang, *Adv. Compos. Hybrid Mater.* **2021**, *4*, 1048.
- [86] M. Lejeail, H. R. Fischer, *J. Appl. Polym. Sci.* **2021**, *138*, 49690.
- [87] J. T. Wertz, J. P. Kuczynski, D. J. Boday, *ACS Appl. Mater. Interfaces* **2016**, *8*, 13669.
- [88] Y. Cao, M. Z. Rong, M. Q. Zhang, *Compos Part A Appl Sci Manuf* **2021**, *151*, 106647.
- [89] Y. Huo, C. Lin, H. Ge, P. Ying, M. Huang, P. Zhang, T. Yang, T. Wang, J. Wu, Y. Yan, V. Levchenko, *J. Polym. Res.* **2023**, *30*, 38.
- [90] X. Xu, Y. Ouyang, S. Lu, H. Ruan, Y. Li, *Comp. Sci. Technol.* **2021**, *216*, 109068.
- [91] S. Yang, X. Du, S. Deng, J. Qiu, Z. Du, X. Cheng, H. Wang, *Chem. Eng. J.* **2021**, *398*, 125654.
- [92] Y. Fang, J. Xu, F. Gao, X. Du, Z. Du, X. Cheng, H. Wang, *Composites, Part B* **2021**, *219*, 108965.

- [93] G. Chen, X. Deng, L. Zhu, S. Handschuh-Wang, T. Gan, B. Wang, Q. Wu, H. Fang, N. Ren, X. Zhou, *J. Mater. Chem. A* **2021**, 9, 10953.
- [94] K. Cerdan, G. Van Assche, P. Van Puyvelde, J. Brancart, *Polymer* **2020**, 204, 122819.
- [95] C. Ouyang, C. Zhao, W. Li, X. Wu, X. Le, T. Chen, W. Huang, Q. Gao, X. Shan, R. Zhg, W. Zhang, *Macromol. Mater. Eng.* **2020**, 305, 2000089.
- [96] J. K. Cho, J.-S. Lee, J. Jeong, B. Kim, B. Kim, S. Kim, S. Shin, H.-J. Kim, S.-H. Lee, *J. Adhesion Sci. Technol.* **2013**, 27, 2127.
- [97] M. A. Lucherelli, A. Duval, L. Averous, *ACS Sustainable Chem. Eng.* **2023**, 11, 2334.
- [98] M. Thys, J. Brancart, G. Van Assche, R. Vendamme, N. Van Den Brande, *Macromolecules* **2021**, 54, 9750.
- [99] P. Buono, A. Duval, L. Averous, Y. Habibi, *Polymer* **2017**, 133, 78.
- [100] Z. Liu, X. Zhu, Y. Tian, K. Zhou, J. Cheng, J. Zhang, *Chem. Eng. J.* **2022**, 448, 137749.
- [101] S. Parihar, B. Gaur, *Prog. Org. Coat.* **2022**, 168, 106889.
- [102] A. Duval, G. Couture, S. Caillol, L. Averous, *ACS Sustainable Chem. Eng.* **2017**, 5, 1199.
- [103] E. Dolci, V. Froidevaux, C. Joly-Duhamel, R. Auvergne, B. Boutevin, S. Caillol, *Polym. Rev.* **2016**, 56, 512.
- [104] V. Froidevaux, C. Negrell, E. Laborbe, R. Auvergne, B. Boutevin, *Eur. Polym. J.* **2015**, 69, 510.
- [105] A. Tortelli, E. Manarin, F. Corsini, G. Griffini, S. Turri, *Prog. Org. Coat.* **2022**, 171, 107012.
- [106] A. Costa Cornellà, S. K. Tabrizian, P. Ferrentino, E. Roels, S. Terryn, B. Vanderborght, G. Van Assche, J. Brancart, *ACS Sustainable Chem. Eng.* **2023**, 11, 3437.
- [107] *Designer Molecules Inc.* <https://www.designermoleculesinc.com/products.cfm>. [accessed June 2023].
- [108] M. Lejeail, H. R. Fischer, *Eur. Polym. J.* **2020**, 131, 109699.
- [109] Y. G. Thyavihalli Girijappa, S. Mavinkere Rangappa, J. Parameswaranpillai, S. Siengchin, *Front. Mater.* **2019**, 6, 226.
- [110] S. M. Rangappa, S. Siengchin, J. Parameswaranpillai, M. Jawaid, T. Ozbakkaloglu, *Polym. Compos.* **2022**, 43, 645.
- [111] O. Faruk, A. K. Bledzki, H.-P. Fink, M. Sain, *Macromol. Mater. Eng.* **2014**, 299, 9.
- [112] K.-Y. Lee, Y. Aitomäki, L. A. Berglund, K. Oksman, A. Bismarck, *Compos. Sci. Technol.* **2014**, 105, 15.
- [113] K. Park, C. Shin, Y.-S. Song, H.-J. Lee, C. Shin, Y. Kim, *Polymers (Basel)* **2019**, 11, 117.
- [114] C. Lu, Y. Liu, X. Wang, J. Yu, Y. Xu, C. Wang, J. Wang, Q. Yong, F. Chu, *Eur. Polym. J.* **2022**, 181, 111710.
- [115] M. Colledani, S. Turri, *Systemic Circular Economy Solutions for Fiber Reinforced Composites*, Springer, Cham, Switzerland **2022**.
- [116] Material Circularity Indicator, The Ellen MacArthur Foundation. <https://ellenmacarthurfoundation.org/material-circularity-indicator>. [accessed June 2023].
- [117] B. T. McCreynolds, K. D. Mojtabai, N. Penners, G. Kim, S. Lindholm, Y. Lee, J. D. McCoy, S. Chowdhury, *Polymers (Basel)* **2023**, 15, 1106.



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