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DOI
10.1002/macp.202300186

Publication date
2023

Document Version
Final published version

Published in
Macromolecular Chemistry and Physics

Citation (APA)
Dyer, W. E., & Kumru, B. (2023). Polymers as Aerospace Structural Components: How to Reach Sustainability? *Macromolecular Chemistry and Physics*, *224*(24), Article 2300186. https://doi.org/10.1002/macp.202300186

REVIEW

Macromolecular Chemistry and Physics
www.mcp-journal.de

Polymers as Aerospace Structural Components: How to Reach Sustainability?

*William E. Dyer and Baris Kumru**

The aerospace industry has been benefiting from the utilization of polymer materials since fiber-reinforced polymer composites (FRPC) offer high performances at low densities compared to metals. FRPC facilitated the design of lightweight materials, which is extensively used in aviation today. Since their first integration into structural parts, FRPC has experienced exponential growth over the years and has received a special interest from manufacturing engineering. While FRPC today is a major focus in engineering, the design of polymer matrix relies on polymer chemistry. However, aircraft materials are facing a pressing issue related to sustainability, since their environmental footprint is at an alarming level. In this review, commercial thermosetting polymer composites employed in aircraft structures are exhibited from a chemistry perspective by depicting starting products and curing reactions. The potential of chemistry to help design next-generation sustainable FRPC for structural parts by means of utilization of sustainable feedstock, energy-efficient processing, and recycling, is disseminated.

1. Introduction

Macromolecules have existed on Earth for as long as natural polymers, however, massive progress in synthetic polymers in the last 100 years led to a large library of polymer materials which are employed almost everywhere in daily life.[1,2] When the performance of a polymer is not satisfactory, blends and composites can be structured in order to introduce/enhance many physical values such as mechanics,[3] electrical conductivity,[4] photoactivity,[5,6] thermal resistance,[7] and so on. Polymer composites can have varying architectures including particles,[8] whiskers,[9] sheets,[10] short fibers,[11] continuous fibers,[12] and laminates[13] from nano- to macroscale using organic/inorganic materials. Fiber reinforcement has been popular in structural applications since anisotropic or isotropic mechanical properties can be obtained. Fibers possess low densities and high mechanical strengths, yet lack structural integrity. Polymer matrices, which can commercially be thermoset or thermoplastic, offer good shear values to form a composite.[14] Despite the variety of fibers that are available (glass, aramid, flax, etc.), carbon fibers (CF) are superior when structural applications are desired.[15] Once viable matrix chemistries are identified, manufacturing engineering has a big role to play since many defects can be introduced during the manufacturing step which can hinder the potential of a composite material even though the matrix possesses good characteristics.[16]

The aviation industry was born thanks to developments in aerospace engineering. Understanding flight physics and safe material design resulted in modern aviation concepts, which have reached their current shape after evolving for many years. We will not go into the physics and engineering of aircraft in this review, but it is clear that thermal and mechanical requirements for aerospace applications from a material science perspective are quite demanding.[17] Despite carbon fibre reinforced polymer composite (CFRP) being employed in automotive, train, and wind turbine structures, requirements for aerospace applications demand stringent matrix recipes. Lightweight structures save fuel and therefore are economically beneficial (and thankfully more sustainable) – while is it hard to quantify this, one estimation puts the Boeing 787–9 (around 40% composite material by weight) as using 10% less fuel than the Airbus A330 (around 10% composite material by weight).[18,19] High strength is needed due to extreme forces such as wind shear, especially with turbulence considerations. Fatigue performance is also required as these structures are heavily loaded and unloaded on a daily basis. Better fatigue resistance also prolongs component life span, making for a more sustainable life cycle analysis (LCA). High fracture toughness prevents quick crack propagation, which can result in catastrophic failure. High-impact resistance is also essential when considering impact with foreign objects. Electromagnetic waves must be somewhat shielded in order to protect electrical components, especially in the case of radomes where sensitive electronic sensors are present hence the use of a large temperature service window must be present.[20] Structural health monitoring (SHM) is a field of growing importance and impact – the ability to accurately monitor large structures' health and carry out timely maintenance can increase economic and sustainability credentials.[21]

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The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/macp.202300186

DOI: 10.1002/macp.202300186

For more details on each requirement in aerospace, we direct the reader to this book by Rana and Fangueiro[22] or the review by Zhang, Chen, and Hu.[23] All of these requirements are fulfilled through the use of high-performance composite materials, and this inherently requires a polymer chemistry perspective to understand how such high performance can be achieved by thermosetting FRP composites.[24] It is very difficult to quantify composite material requirements for aerospace as the performance of these materials in bulk structures determines their suitability, and testing is done behind commercial doors. For the interested reader general requirements for aerospace structures and materials according to the European Union Aviation Safety Agency (EASA) can be found on website and the cited documents.[25,26] On top of this the American Society for Testing Materials (ASTM) Aerospace Material Standards showcases the benchmark tests to evaluate materials and components for the aerospace industry.

Safety has always been the prime consideration since any mistake and misunderstanding in material choice can result in fatal accidents (e.g., the Challenger disaster, 1986). In the 1960s, aviation was exclusively accessible for wealthy families – aircraft were designed using metals and alloys as structural components (i.e., DH Comet, Concorde).[27] This results in an enormous overall weight of aircraft which leads to high fuel consumption and costly ticket prices. Carbon fiber-reinforced polymer (CFRP) composites offered similar mechanical performances compared to metals whilst being lightweight.[28] Epoxy/phenolic resins are used as matrix and CFRP manufacturing has received significant attention since the 1960s. Since their first introduction into aircraft in small percentages, their potential for large-scale implementation was obvious. After successful safety procedures (certification in the aviation industry takes around 11 years on average) regarding CFRP, today a modern aircraft contains more than 50% (by weight) CFRP in structural parts.[29] It is important to highlight that polymers are applied much more abundantly in aircraft structures known as secondaries including floors, cabin doors, food trays, cable insulators, and so on.[30] CFRP composites led to aviation becoming a public transport method, and now the continents are connected better than ever. Additionally, modern drones and potential electric vertical takeoff and landing (eVTOL) devices rely on polymer composites.[31] Space shuttles are more complicated by design, nevertheless, polymer composites constitute high importance for such applications as well.

In this review, we will depict the chemistry of CFRP matrices and introduce their manufacturing in order to be applied as aerospace structural components. Following that, the sustainability of current technology will be discussed and potential approaches to introduce sustainability via macromolecular chemistry will be presented.

2. Polymer Composites as Aerospace Structural Components: How It is Made?

Aerospace structural components are dominated by the use of CFRP composites. Carbon fiber displays superior properties to other types of fiber.[23] Fiber surfaces are coated (called "sizing") in order to bring compatibility and wettability with employed resin systems. A variety of layup techniques exist to produce CFRP composite components for aerospace, each having particular advantages and disadvantages. Layup techniques include: pick and place, automated tape layup (ATL), automated fiber placement (AFP), and out-of autoclave methods that apply vacuum, pressure, and heat.[32] The choice of resin will heavily affect the layup techniques that are appropriate for part production.

Following fiber layup, the next process is curing which involves either heat, pressure, vacuum, or a combination of these parameters (sometimes a forming step is used to achieve specific geometries and ensure a good part-mold match).[33] Again, different resins require different curing techniques.[34] Curing techniques include vacuum bagging, autoclave curing, co-curing, and hot-press curing.[35] A somewhat unique technique is resin transfer molding (RTM), which utilizes dry-fiber layup followed by resin injection under pressure to achieve impregnated fibers. Heat and/or pressure are then applied to cure the resin and produce the desired part. RTM is capable of producing high-quality components with complex geometries, dimensional accuracy, and consistent mechanical properties on a large scale.[36] Resin properties such as viscosity, melting point (in case of solid products), curing kinetics, boiling point, environmental stability, solubility (in case accelerators or reactive diluents are employed), and fiber wetting have prime importance while manufacturing composite structures.

The below sections outline the current state of a variety of thermosetting resin groups used in aerospace composites, their applications, and composite production techniques are briefly mentioned. Since high thermal and mechanical properties are demanded, it is no surprise that this industry is dominated by the use of aromatic molecules. We will not cover phthalonitrile and polyimide resins in this section due to their non-structural applications. It is important to mention that there is a great interest in employing high-performance thermoplastics (mainly PEEK, PAEK, and LM-PAEK) as matrix material for CFRP composites, however, these will not be covered since no current structural application in aviation is present.

2.1. Epoxies

The most widely employed matrix system for CFRP composites in aerospace structural components is the epoxy system.[37] Epoxies exhibit excellent properties such as good thermomechanical performance (especially when aromatic monomers are used), chemical resistance due to ether linkages, electrical insulation, adhesion through the -OH groups formed upon curing, and processability due to the liquid nature of the starting materials.[38] Additionally, carbon fibers can be easily sized with epoxies to promote fiber-matrix adhesion. Epoxies can be cured via a polyaddition mechanism using functional groups such as amines, thiols, and anhydrides. Primary and secondary curing reactions determine crosslinking density. Prior to curing, epoxy equivalent ratios must be calculated.

Epoxy composites are often manufactured from prepreg systems in which an initial cure is sometimes performed to obtain optimum processing properties of the prepreg. Final curing typically occurs using economical temperatures (100–180 °C) and times, whilst still achieving good performance.[39] These dual curing systems often rely on different curing agents with differing curing kinetics. The chemical structure of the hardener dictates the curing kinetics so that fast curing (i.e., linear amines) and

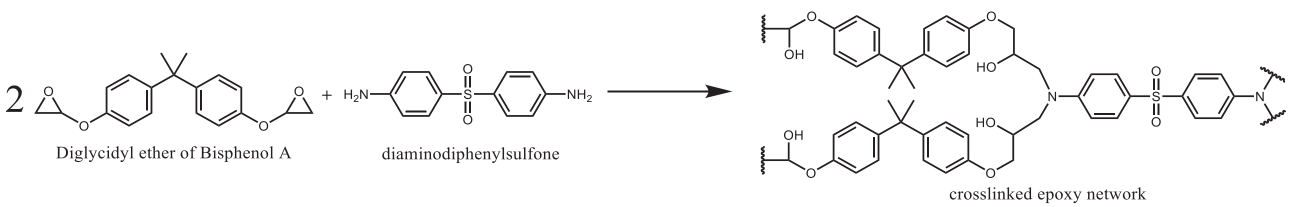

Figure 1. General depiction of the ring opening crosslinking reaction between DGEBA and DDS to form a crosslinked network in which each amine ideally reacts with two epoxy groups.

slow curing (i.e., aromatic amines) formulations are available.[40] The liquid nature of epoxies also makes them suitable for RTM, as the two parts can be mixed and injected into the mold under high pressure.[41]

The most widely employed system uses the difunctional epoxy bisphenol A diglycidyl ether (DGEBA) or diglycidyl ether of bisphenol F (DGEBF). A commonly employed trifunctional epoxy is N,N-triglycidyl-meta-aminophenol (TGMAP). The most common hardener employed in these systems is diaminodiphenylsulfone (DDS).[42] **Figure 1** shows the chemical structures of the aforementioned monomers. These monomers are all highly aromatic, which helps endow structural rigidity to composite materials. Epoxy matrix systems are commonly employed in structural composite components, including fuselage and wing components. Cycloaliphatic epoxies are systems that display increased UV stability due to fully saturated aliphatic backbones.[43] They are employed in applications that may experience greater exposure to environmental conditions.

Epoxy systems have been utilized and refined for over six decades to become the bedrock on which the modern aerospace industry is founded. Whilst current epoxy systems offer a good balance between cost, performance, and processability, the fact remains that they are derived from petroleum-based and toxic chemistries. For practical reasons, there is a drive to move away from petroleum-based chemistries. Therefore, sustainable epoxy systems are being explored by a variety of researchers and fall within the clean aviation goals.

2.2. Phenolic Resins

Phenolic resins find widespread use in aerospace due to their inherently high char yield, which results from their highly aromatic nature (being synthesized from phenol) and ability to readily convert to vitreous carbon above decomposition temperatures (300–600 °C).[44] This makes them ideal resins for use in secondary, internal structural components (an application with more stringent fire smoke and toxicity (FST) regulations) and are often employed as fiberglass honeycomb composite materials.[45] The current industry standard for these semi-structural interior parts utilizes resole- and novolac-type phenolic resins.[46] Resoles are synthesized using an excess of formaldehyde, a basic catalyst, and are self-curing when heated. Novolacs are synthesized using excess phenol, acid, or metal salt catalysts, and require the addition of a curing agent (**Figure 2**).[47]

The majority of aerospace phenolic composites are produced from prepreg systems with curing temperatures between 100–180 °C.[48] Traditional resole- and novolac-type phenolics produce water as a condensation product. This requires a curing process with outgassing steps to minimize void formation.[49] Phenolic systems all have similar starting materials, with the majority utilizing phenols or methylphenols and formaldehyde. Differentiation in thermomechanical properties comes through varying levels of crosslinking and the use of additives.

A third type of phenolic resin is being explored as a potential alternative to traditional phenolics with which the condensation products of the crosslinking reaction limit their uses. Benzoxazines are currently employed in applications including coatings, adhesives, and fire-retardant composites (Figure 2).[50] However, it is only in recent decades that polybenzoxazines have been rediscovered and researched as potential high-performance thermosetting matrices for aerospace structural applications.[51] Polybenzoxazines display many attractive properties, including low volumetric change during curing, and good dimensional stability, T_g can be higher than cure temperature, high char yield (inherently flame-retardant), catalyst-free curing, and no curing by-products.[52] Benzoxazines are being considered as an alternative to current standards due to toxicological and sustainability issues with traditional phenolic resins (amongst others).[50] The range and tunability of benzoxazine structure also allow for the incorporation of a wide range of starting materials potentially increasing functionality, properties, and green credentials.[53] Their chemical structure presents compatibility with commercial epoxy-based fiber sizing yet their massive brittleness must be handled for a potential large-scale industrial use.

2.3. Bismaleimides/Polyimides

Bismaleimide (BMI) resins are typically employed in aerospace applications that require particularly high service temperature and toughness – in or around aero-engine components and airframe components.[54] BMI resins can provide a higher service temperature than epoxies, whilst still being as easily processed.[55] Typical properties of BMI resins include high T_g (230–380 °C), low flammability, good hot-wet performance, competitive pricing, and constant electric properties – all of which make this resin class an excellent candidate for high-performance aerospace composite matrix material.[56]

BMI monomers are synthesized from diamines and maleic anhydride with acetic anhydride and sodium acetate catalysts, leading to the formation of BMI monomers, which are generally liquid. Various diamines can be used to tailor the final thermoset characteristics. BMI curing results in a crosslinked thermoset structure, and the curing reaction does not produce volatile

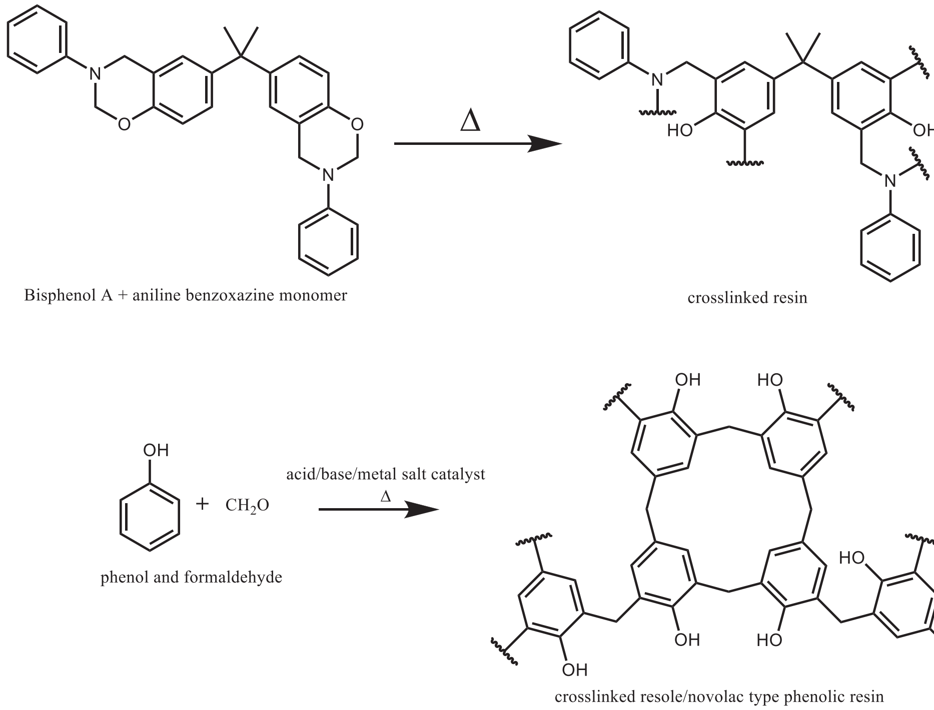

Figure 2. Depiction of BPA/aniline benzoxazine monomer crosslinking reaction (top) and generic schematic of phenolic resin crosslinking reaction (bottom).

side products.[57] As with most polymers, BMIs went through a series of changes before reaching their current commercial level. First-generation BMIs had low fracture toughness due to their high degree of crosslinking. In addition, polar carbonyl groups cause chain stacking, making energy dissipation difficult and the thermosets prone to fracture.[58] Matrimid 5292 is the current benchmark BMI/polyimide system and represents the second-generation class of "toughened" BMIs with superior physical properties. Produced by Ciba Geigy and Huntsman, it consists of a combination of 4,4′-bismaleimidodiphenyl methane (BDM) and diallylbisphenol A (DABA) (**Figure 3**).[59] The uniqueness of its system is in the fact that these materials copolymerize in a near-alternating fashion – the reaction pathway for these molecules has a lower activation energy than that of the homopolymerization of either molecule.[60] This repeating, alternating structure is thought to reduce brittleness by disrupting the previously mentioned chain stacking, allowing for better energy dissipation.[57]

The introduction of comonomers not only improves mechanical properties but also processability, as BMI monomers typically polymerize above their T_m (155 °C for BDM). Comonomers, such as DABA, decrease the system's viscosity and allow for the use of a variety of processing techniques such as vacuum bagging, autoclave curing, co-curing, hot-press curing, and RTM.[61,62] Phenolic units provide good adhesion to fiber reinforcers.

Whilst these systems provide excellent thermomechanical properties, the chemistries in question are all petroleum-derived and present health hazards during handling and production. The potential for reuse of these materials is also incredibly low, as crosslinks are formed by the reaction of alkene bonds forming uninterrupted carbon chains with no heteroatoms.

2.4. Cyanate Ester

Cyanate esters (CE) are used in aerospace industries for some high-temperature applications due to their high T_g, excellent dielectric properties, high thermal stability (between epoxies and BMIs), low water absorption, and low thermal coefficient of expansion.[63,64] The low dielectric constant, in particular, makes CE composites particularly applicable for aerospace radomes and other sensitive components when employed with quartz fibers.[65]

To produce cyanate ester resins, diphenolic compounds are used to produce multicyanate monomers using cyanogen halides

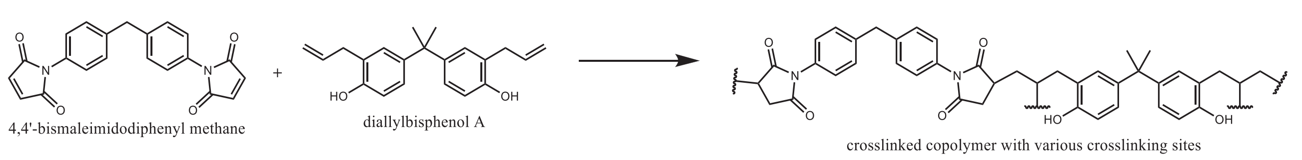

Figure 3. Crosslinking reaction between BDM and DABA, the benchmark commercial BMI system.

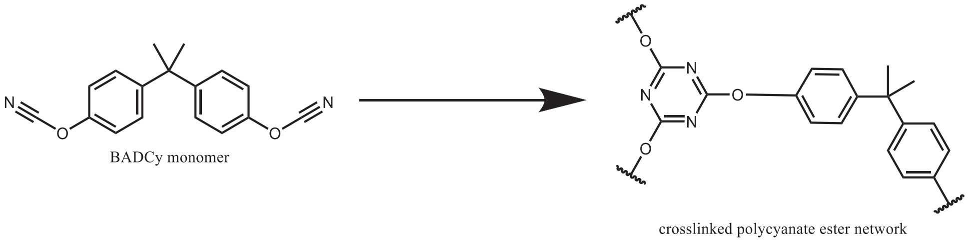

Figure 4. Polymerization reaction of BADCy monomer, producing triazine ring formations between three monomer units.

and a basic catalyst.[66] A classic cyanate ester monomer is 2,2-bis-(4-cyanatophenyl)propane (the BPA-derived cyanate ester monomer known commonly at BADCy).[67] These incredibly reactive cyanate esters can be homopolymerized through heat to produce cyanurate linkages (**Figure 4**).[68] This system requires elaborate transition metal catalysts that are dissolved in monomers.[69] However, due to high reactivity, all cyanate ester resins are transported in frozen form which is a great disadvantage on a large scale. Cyanate ester composites are generally manufactured via prepreg systems followed by OOA/autoclave curing procedures, or using RTM systems for lower viscosity systems. Curing temperatures are above 200 °C to achieve good mechanical properties, and at commercial levels always use metal ion catalysts.[70] The curing reaction produces no volatiles, so only low outgassing is required.

Cyanate resins fill an important role in aerospace where very low dielectric properties and high heat resistance are required.[71] Starting materials are petroleum-derived, and cyanogen halides, in particular, are reactive, volatile, and toxic chemicals. Due to the high mechanical performance, highly crosslinked nature, and stability of the cyanate bonds, the potential for recyclability is low.

3. Sustainability in Aerospace Polymer Materials: How to Get There?

The aerospace engineering community is focused on changing propulsion systems such as using sustainable aviation fuels (SAF) obtained from renewable resources and employing cryogenic hydrogen as fuel. Particularly for cryogenic hydrogen, polymer composites will play a pivotal role in storing liquid hydrogen under cryogenic conditions.[72] Batteries are prime candidates for powering electric vertical takeoff and landing (eVTOL) structures.[73] In addition to fuel systems, one must start to question the sustainability of polymer materials employed in aerospace applications since they possess massive CO_2 footprints that are often not considered as they are not obvious. There are serious developments in AI-assisted digital manufacturing methods[74] and structural health monitoring of polymer composites.[75] However, it is imperative that the macromolecular materials be upgraded to meet sustainability criteria in the aviation industry.

As highlighted above, the current state of polymer composites employed in aerospace applications is far from being sustainable, both from a materials and manufacturing perspective. Resin recipes are composed of toxic and hazardous starting products obtained from petro refineries, the environmental footprint of CF production is immense, and composite manufacturing is associated with massive energy consumption. Since there is no recyclability option, aircraft (as well as wind turbines) are accumulated at aircraft graveyards in remote deserts at their end-of-life.

There are many developments in the fields of material science and engineering to assist sustainable components and processes for aerospace materials. For example, finding renewable starting materials for CF manufacturing[76] and energy-efficient welding technologies for joining thermoplastic composites[77] are being developed, however, these concepts will not be discussed in this review. We will exhibit macromolecular chemistry-based emerging technologies under three pillars to help sculpt a sustainable aviation industry.

3.1. Utilization of Sustainable Feedstock

Current matrix technology relies on decades-old chemistry research, most commonly employing an epoxy system based on the BADGE monomer. Even when epoxy chemistry is not used, the bisphenol A starting material is employed across a huge range of resins including all of the above-mentioned. Whilst this system has proved very useful and adaptable within aerospace, the fact remains that this system is not sustainable for long term. These systems also present health and safety concerns due to their toxic nature.[78] BPA in particular has faced negative attention for decades due to its oestrogen-mimicking properties.[79] Restrictions are being imposed on the use of BPA and similar toxic precursors such as in polycarbonate formulations, paving the way for more biobased and biocompatible starting materials.[80]

Thermoset resins from biobased starting materials present a wealth of opportunity for new research, and in the coming decades will infiltrate the aerospace market either as primary or secondary structure materials.[81] It is useful to be able to use one feedstock chemical to produce a large variety of materials but, as shall be elucidated in the following sections, a compromise is made. There are undoubtedly better-starting materials and formulations that can produce not only more sustainable materials but higher-performance materials too, depending on the specific application. This is an important consideration when assessing biobased materials – the array of chemical functionalities and formulations that are present in nature can pave the way for next-generation aerospace composite materials that are also biobased. This is an important point to highlight as impressions of biobased materials are that they are inferior, but as we will see having multiple functionalities alongside each other often increases performance. Biobased starting materials are generally less toxic than petroleum-based starting materials too. These synthetically useful bio-molecules are present in large quantities

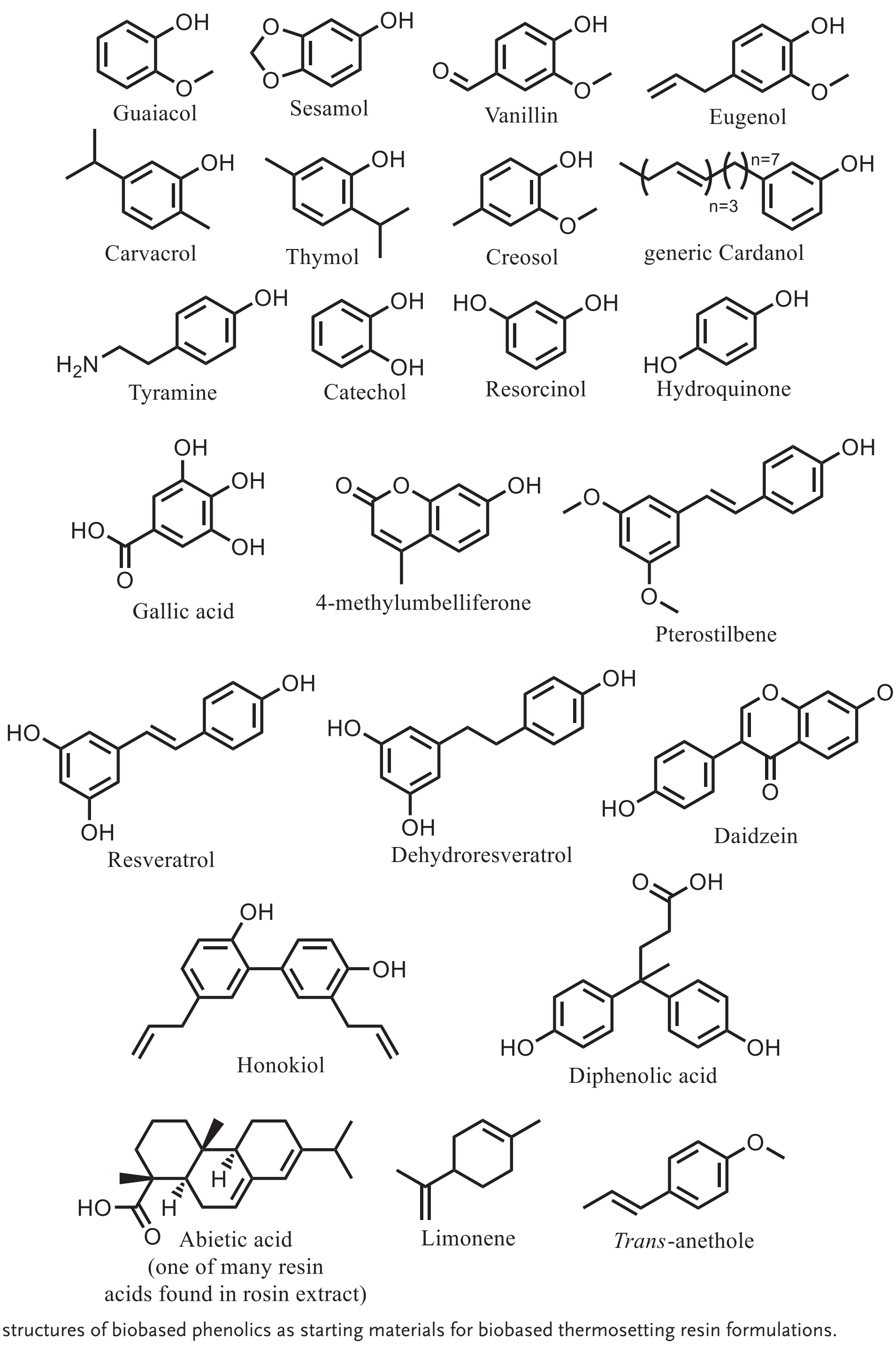

Figure 5. Chemical structures of biobased phenolics as starting materials for biobased thermosetting resin formulations.

in lignin, and in much smaller quantities they can be found throughout the plant and animal kingdom.[82]

One of the biggest sources of sustainable resins lies in lignin – present in all plants and at 20–30 weight % in the dry biomass of trees.[83] Lignin is a phenolic crosslinked polymer biosynthesized via complex oxidative polymerization of guaiacol, sinapyl alcohol, and coniferyl alcohol in the presence of enzymes.[84] Upon depolymerization, lignin produces phenolic starting materials. This cracking process can be optimized to produce synthetically useful chemicals in large quantities, such as vanillin.[83] Lignin plays a large role in many biorefinery concepts. Phenolic structures are particularly useful starting materials when considering high-performance thermosets due to the so-called functional handle of the alcohol group for chemical modification, and the aromatic nature imparts high-performance characteristics. Biobased starting compounds discussed in this review are shown in **Figure 5**.

The current research landscape into high-performance bio-based thermosets focuses mostly on synthetic methods

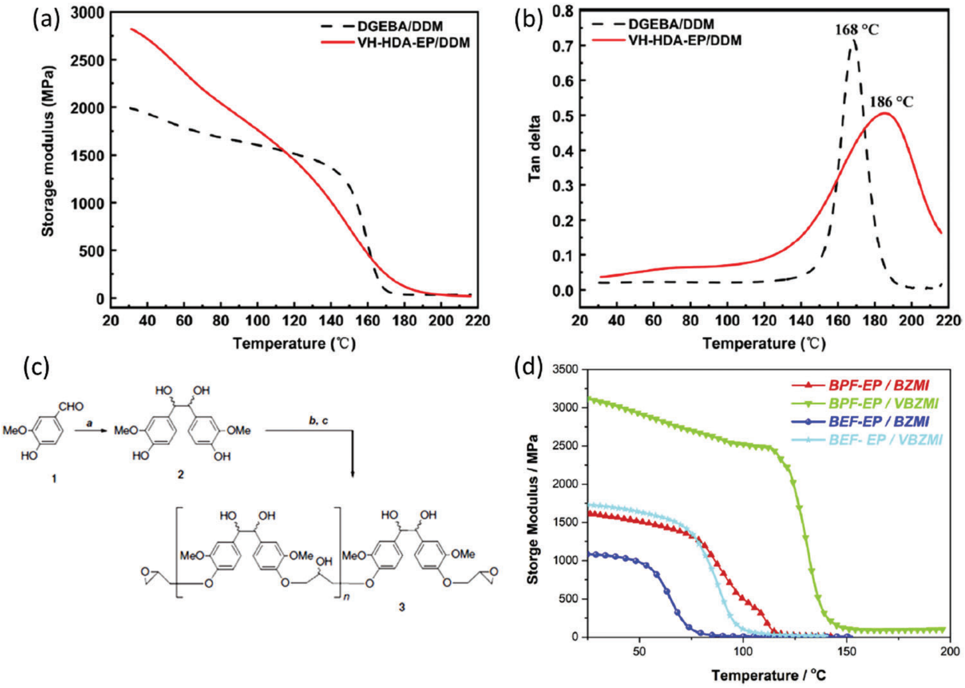

Figure 6. a,b) Storage modulus and DMA results for vanillin+HAD+DDM epoxy resin are shown. Adapted with permission.[87] Copyright 2023, American Chemical Society. c) Synthesis of hydrovanilloin and resulting thermoset structure. Adapted with permission.[88] Copyright 2018, John Wiley and Sons. d) Storage modulus of various epoxy resins using eugenol-based epoxy, BPF-based epoxy, vanillin-based benzimidazole hardener, and benzimidazole hardener. Adapted with permission.[89] Copyright 2019, Elsevier.

employed, thermal characteristics of monomers and resins, and dynamic mechanical analysis (DMA)/Rheology behavior of resins. There is a large gap in research that links chemistry-focused research to composite manufacturing and engineering. Since resin properties dictate manufacturing methodology, it is essential to generate data translatable to manufacturing and engineering. In addition, it is advisable that the best candidates are screened with regard to mechanical performance, shifting this material-science-focused field to engineering.

3.1.1. Sustainable Epoxies

Epoxy systems utilizing renewable and biobased molecules are plentiful. Reviews by Baroncini et al.[85] (discussing biobased epoxy resins and curing agents in a general context) and Kumar et al.[38] (discussing current epoxy technology and potential renewable systems) are very in-depth and provide a good overall picture of sustainable epoxy research. The following section expands upon these reviews by covering biobased epoxy systems in the context of aerospace structural applications.

A well-respected route to generate renewable epichlorohydrin has been developed and commercialized. Epichlorohydrin is the main reagent used to epoxidize phenolic starting materials. So, the focus for renewable aerospace epoxies is mainly on renewable phenols as these impart good mechanical properties to the final composite. Yet, there is some research on epoxidizing unsaturated alkene units through oxidation reactions for epoxy formation, such as biobased oils.

A vanillin-based epoxy system was synthesized with both aldehyde and epoxy groups. The aldehyde groups led to the formation of imine bonds, imparting vitrimeric-like behavior in the final resin. The T_g, as calculated by DMA, was 9°C higher than the equivalent DGEBA system, and the vanillin-based resin displayed a higher crosslinking density due to Schiff base reactions. A significantly higher storage modulus than the DGEBA counterpart, 35.2 versus 16.9 MPa respectively, was observed Upon reprocessing, the vanillin-based epoxy showed a decrease in performance and crosslinking density to 82% of the original, due to epoxy crosslinks being permanently broken upon recycling.[86] Other researchers synthesized a vanillin-based epoxy monomer which displayed a char yield nearly twice as high as the analogous DGEBA system (30.8% vs 17.9%). Storage modulus and T_g were also significantly higher for the vanillin-based system (2821 vs 1990 MPa and 186 vs 168 °C respectively) (**Figure 6**a,b).[87] Vanillin has also been dimerized via the aldehyde group. The reaction of this dimer with epichlorohydrin in varying ratios yields highly insoluble phenoxy resins of T_gs of 135 and 146 °C with a high hardness of around 80 (out of 100, Shore Durometer type D setup) according to ASTM 2240 standard) (Figure 6c).[88]

The chemical versatility of biobased starting materials allows for the multifunctional use of biobased molecules. For example, vanillin can also be modified and used as the hardener component in an epoxy system. For example, eugenol-based epoxy monomer was attained and co-cured with a vanillin-based hardener. Significantly, the team assessed the oestrogen-mimicking behavior of the eugenol-based epoxy (as we may recall BPA and other petroleum-based starting materials are hormone mimicking and therefore detrimental to human health) and found it presented a lower estrogenic activity than BPA and other commercial bisphenols. Whilst this result is encouraging, the thermomechanical behavior of the eugenol-based resin was poorer than the petroleum-based counterparts, including a storage modulus of roughly half and T_g around 50 °C lower. However, the use of vanillin-based imidazole hardener compared to the petroleum-based hardener almost doubled the storage modulus (3250 to 1730 MPa) in the bisphenol F epoxy system due to the aromatic structure of vanillin increasing stiffness in the material through π–π interactions (Figure 6d).[89] Vanillin's structure lends itself to the production of a wide range of epoxy precursors, and recent advances in its synthesis by metal-catalyzed air oxidation of lignin are promising for its future use as an epoxy precursor.[90]

Eugenol is a biobased aromatic phenol with a relatively low cost and multiple functional groups. A trifunctional eugenol-based monomer was prepared using cyanuric chloride followed by epoxidation of the allyl group of each eugenol moiety. The eugenol molecules are connected by a triazine moiety, which enhances mechanical, thermal, and electrical properties. The monomer was cured using DDS, a standard petroleum-based diamine hardener. The eugenol-based system displayed a T_g of 241 °C, 25 °C higher than the DGEBA system. Even at 170 °C, the eugenol system displays a storage modulus of 2033 MPa compared to 420 MPa for the DGEBA system. The final epoxy has a biobased content of 61% by mass-balance approach.[83] Whilst this is something to be celebrated, the fact remains that the synthesis of this trifunctional monomer requires the use of toxic cyanate halogens. Another article exploits the phenol functionality of eugenol to form a trifunctional phosphate monomer, the synthesis of which used no CMR compounds. Following this allyl groups were epoxidized in a standard green way, using *m*-CPBA. Curing with an aromatic diamine (MXDA) yielded a thermoset with properties such as T_g of 84 °C (30 °C lower than DGEBA) and storage modulus of 1210 MPa (equal to DGEBA). The lower T_g may be unexpected given the higher functionality of the eugenol-based monomer, however, the presence of methoxy groups is known to decrease the T_g of thermosetting materials.[91] Char yields at 600 °C were significantly higher for the eugenol-based systems when compared to the DGEBA systems (between 3 and 4.7 times higher) suggesting this monomer could find use in secondary structural applications.[92] Eugenol has also been coupled via esterification reaction to a variety of other biobased molecules followed by epoxidation to yield self-curing epoxy monomers using a 4-dimethylpyridine (DMAP) catalyst. The ester functionality provides the route for self-curing. Curing with MDA (a standard aromatic diamine curing agent) was also investigated. Self-cured thermosets had a maximum T_g of 147 °C, compared to 169 °C for MDA-cured samples. The resin with T_g of 147 °C is derived from eugenol and 2,5-furandicarbonyl chloride, two aromatic moieties imparting structural rigidity to the final thermoset material. Storage modulus during the rubbery state was reported and was significantly higher for most self-cured resins compared to the MDA-cured resins. However, the 2,5-furan-containing resin had a similar rubbery storage modulus in the self-cured and MDA-cured samples of 3 and 36 MPa respectively.[93]

Epoxidized cardanol, a terpene extracted from cashew nut shell liquid (CNSL), contains both aromatic and aliphatic moieties theoretically leading to resins with a mixture of tough and rigid properties. The cardanol is first coupled through alkene bonds on the aliphatic chains to yield bi- or tri-functional epoxy monomers upon epoxidation. Cardanol-based epoxy resins were synthesized using isophorone diamine as the hardener. The long alkyl chains present in cardanol led to a resin with a T_g of 50 °C. Thermal degradation results were comparable to DGEBA. Room-temperature storage modulus was 1218 MPa, comparable to the DGEBA system result of 1480 °C.[94] Cardanol-based epoxies could be viable for the production of lower-performance aerospace composites, however, the low char yield puts this formulation behind other inherently flame-retardant biobased formulations. An important consideration that will be routinely highlighted is the availability of biobased starting materials, and CNSL is one of the more abundant sources of chemical feedstocks.

Daidzein is a diphenolic compound that can be obtained from soybeans. It exhibits a structure comparable to BPA, and indeed the mechanical properties of tensile and flexural strength exceed that of the analogous DGEBA resin. The thermal properties of the daidzein-based resin were equally impressive, with T_g of 205 °C, $T_{d5\%}$ of 335 °C, and exceptional char yield of 42.9% at 800 °C. These excellent thermal and mechanical properties are attributed to enhanced crosslinking through the double bond on the benzopyrone ring, which was confirmed by FTIR and NMR.[95]

Itaconic acid can be derived from biomass sugars and, in a two-step process, was used to produce a trifunctional epoxy monomer with a lower viscosity than DGEBA, which is advantageous from a processing and fiber-matrix mixing point of view. T_g of the itaconic acid-based system cured with MMHPA (an anhydride) was 135 °C, 25 °C higher than that of the analogous DGEBA system. Itaconic acid contains no aromatic moieties, however, the presence of two ester groups in each monomer unit leads to strong chain interactions. The flexural modulus and strain at break for the itaconic acid system were higher than those of the analogous DGEBA system (3600 vs 2950 MPa and 20.9% vs 12.8%) for the systems cured with a linear diamine containing ether functionality.[96]

Limonene is a monocyclic terpene produced as a by-product of the citrus industry. It has two alkene functionalities that can be epoxidized. Formulations with glutaric anhydride hardener (biobased) yielded a resin with T_g of 98 °C, compared to 143 °C for the analogous DGEBA system. The room-temperature storage modulus was 1.65 GPa for the limonene-based system, compared to 1.6 GPa for the DGEBA system.[97]

Papers exploring the use of resveratrol consistently produce resins with high-performance characteristics. One team synthesized from resveratrol a biobased trifunctional epoxy monomer with an allyl bond yielding a resin with T_g of over 320 °C and mechanical properties comparable to the analogous DGEBA resin. On top of this, the melting point of the trifunctional resveratrol-based epoxy monomer is low (52 °C) allowing for a good processing window.[98] This resveratrol monomer was also studied for its flame-retardant behavior in a system using an anhydride hardener, and revealed a char yield at 800 °C of 19%, compared to 9.5% for the analogous DGEBA system. Dielectric permittivity analysis also showed better results for the biobased resin. Finally,

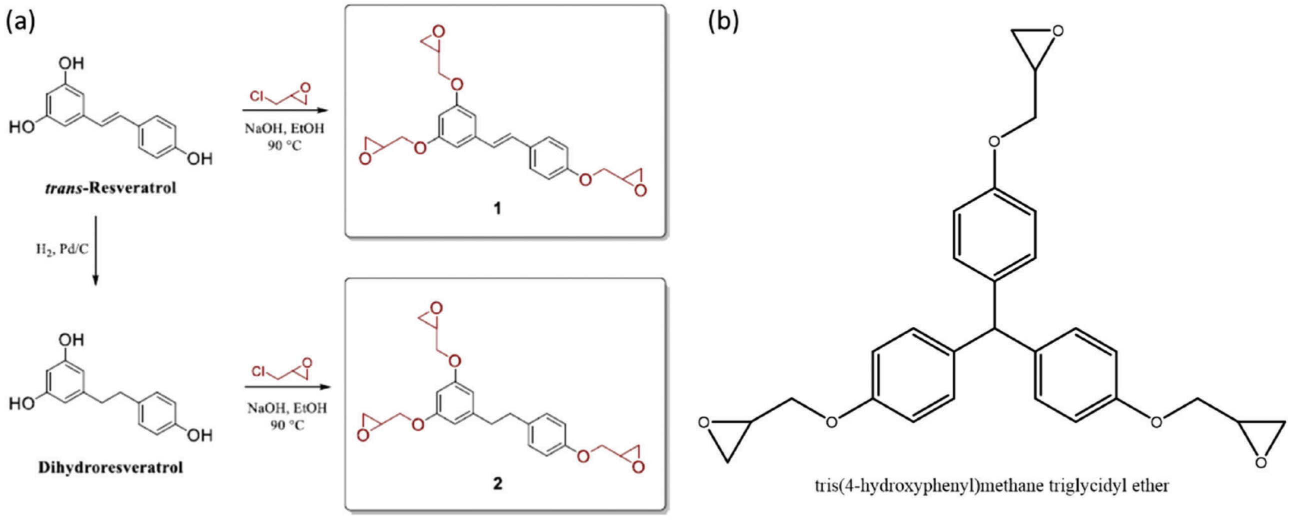

Figure 7. a) Synthesis of renewable epoxy monomers from resveratrol and b) chemical structure of petroleum-based trifunctional epoxy monomer tris(4-hydroxyphenyl)methane triglycidyl ether (industry-leading in aerospace). Adapted with permission.[100] Copyright 2020, American Chemical Society.

tensile strength tests for this resveratrol-anhydride system revealed better performance from the resveratrol system (73.5 MPa compared to 59.1 MPa from the DGEBA system).[99] Another group invested in the effect of removing the alkene group from resveratrol by hydrogenation (**Figure 7**a). They also converted resveratrol to a trifunctional amine which exhibited a lower overall toxicity than MDA, a common hardener employed in epoxy systems. The alkene-based resin displayed a T_g over 100 °C higher than the saturated resin, due to the rigidity of the alkene bond leading to less mobility. The saturated resin has a T_g of 178 °C, comparable to the analogous DGEBA resin.[100] Resveratrol is commercially available and can be produced from lignin and by fermentation of biomass sugars, and is naturally occurring in grape seeds.[101]

Some research focuses on the epoxidation of naturally occurring oils such as karanja[102] and soybean.[103] The resulting resins consist of largely linear aliphatic chains, and whilst biobased content is high, performance is inadequate for aerospace structural applications. Nevertheless, linear epoxy monomers find use as plasticizers in aromatic systems, increasing toughness and therefore performance.[42] Oleic acid derived from pumpkin, grape, avocado, and mango seed oil, has been coupled using diols and diamines, followed by epoxidation of double bonds to yield difunctional aliphatic epoxy monomers with ester or amide linkages. The monomers were then cured with aromatic diamine (PPD). No thermal nor mechanical properties of resulting resins were reported in this paper.[104] A similar paper reported very low T_gs (−14 °C) for oleic acid-derived resins cured with an anhydride, which is not surprising given the aliphatic nature of oleic acid.[105] Epoxidized oleic acid could be used as a toughening agent, and indeed finds uses in epoxy-based coating.[106]

Not all epoxies are derived from epichlorohydrin. Naturally occurring acids can be epoxidized to produce epoxy monomers. Gallic acid was epoxidized in a two-step process to produce a tetrafunctional aromatic epoxy monomer.[107] A two-step conversion from alcohol to allyl to epoxy functionality was required, as direct epoxidation from the aromatic alcohol groups led to incomplete epoxidation. Epoxidized gallic acid was cured with isophorone diamine and yielded a resin with higher T_g and very similar storage and loss modulus values to an analogous DGEBA system.

Another example of naturally occurring acids being directly epoxidized is in the use of rosin. Rosin can be prepared from liquid tree sap, mainly from conifers, and consists of various resin acids, many of which are aromatic.[108] Rosin in the form of polygral – a by-product of the paper and forestry industry – has been epoxidized and cured with amines to yield biobased epoxy systems. Cured in varying ratios with DGEBA and isophorone diamine, the epoxies displayed similar properties to the pure DGEBA system, with a T_g of 114 °C observed for a 60/40 wt% Rosin/DGEBA system, compared to 140 °C for pure DGEBA. T_g for the pure rosin/isophorone diamine thermoset was 93 °C, and storage modulus was reported as up to 1.2 GPa, compared to 1 GPa for the pure DGEBA system using DMA measurement.[109] Whilst the T_g is a significant decrease this resin could find applications in secondary structures in aerospace.

Diphenolic acid (DPA) is a renewable alternative to BPA, synthesized from phenol and levulinic acid.[110] Researchers amidated the carboxylic acid group and epoxidized the alcohol groups before curing the monomer with an anhydride. The diphenolic amide monomers showed lower cytotoxicity than BPA. Autocatalytic behavior from the amide groups was observed when cured with an anhydride, with exothermic DSC peaks being observed at 178 °C and T_{onset} at 125 °C, compared to 297 and 220 °C, respectively for the analogous DGEBA system. Mechanical properties were comparable to the DGEBA system, and in some cases, the biobased system displayed better mechanical properties in relation to aerospace applications. For example, T_g of 114 versus 85 °C, E′ of 2773 versus 2522 MPa, and tensile strength of 60.2 versus 51.2 MPa for the diphenolic ethylamide-based system versus DGEBA system respectively.[111]

Catechol refers to a phenol with two alcohol groups next to each other. These chemical functionalities are responsible for the adhesion of muscles to rocks in the sea and are of intense interest for adhesive applications, including aerospace thermosetting adhesives. A catechol-modified epoxy adhesive displayed almost twice as strong lap shear strength compared to the epoxy adhesives, due to the combination of epoxy groups crosslinking and catechol-anchoring effect.[112] Whilst the catechol group was not biobased in this instance they are available from the modification of lignin cracking products and other biobased phenolic starting materials.

As previously mentioned lignin is a versatile and abundant feedstock for useful biobased thermoset monomers. Less refining leads to a more renewable product, as energy is saved in processing and less material is wasted. The oily product of lignin hydrogenolysis was epoxidized and cured with amines to produce resin blends with superior flexural properties when compared to analogous DGEBA systems.[113] A similar study used the products of the depolymerization of various lignin fractions to produce epoxy resins using a commercial tall oil fatty acid-based curing agent. These resins displayed mechanical properties comparable to DGEBA systems. The process of starting material production is also one that leads to little waste, as the solvents can theoretically be recycled, and different fractions can find different applications depending on the required resin properties.[114]

The field of biobased epoxies is large and contains many potential starting materials for use in aerospace composite materials. Biobased epoxies are the largest biobased thermosetting area of research, and as a result, have a large influence on the research of other biobased thermosetting systems. However, their integration into a composite is mostly unknown.

3.1.2. Sustainable Benzoxazines

Benzoxazine resins were first synthesized in the 1910s but were not researched extensively until the 1990s when a solvent-free synthesis method was reported. They are an attractive class of thermosetting resins due to properties including catalyst-free curing mechanism, limited shrinkage during curing, high T_g, high char yield, low thermal expansion, low dielectric constant, and the wide variety of thermoset structures (and therefore properties) accessible due to the versatility in starting reagents of the Mannich condensation reaction often used to synthesize benzoxazine monomers.[115]

Over the last three decades, there has been a great increase in research on bio-based benzoxazines. The starting reagents of phenol, amine, and aldehyde, can be replaced with bio-derived renewable resources. Furthermore, phenolic starting materials are abundant in both quantity and variety when extracted from renewable sources such as lignin, terpenoids, rosin, and biosynthesis using enzyme catalysis.[116] As such, there is a huge interest in determining which combinations of starting materials, reaction conditions, purification processes, and curing conditions yield appropriate resins for different applications. Here we discuss these parameters in the context of aerospace materials.

Many amines have been utilized for benzoxazine synthesis including stearylamine,[117] 1,10-diaminodecane,[118] aniline,[119] and so on. However, only a few fully biobased amines have been explored for use in benzoxazine synthesis. Furfurylamine is the most commonly employed amine for bio-based benzoxazine synthesis in research articles. It is synthesized via the reductive amination of furfural (an aldehyde derived from the dehydration of sugars) and ammonia and is therefore 100% biobased.[120] The structure of furfurylamine also lends itself to producing high-performance thermosetting resins due to the aromatic nature of the furan moiety, and its ability to crosslink alongside the benzoxazine moieties.[121] The use of pterostilbene, a naturally occurring phenol abundant in antioxidant-rich foods, with furfurylamine led to a benzoxazine resin with a T_g of 253 °C and char yield of 56% at 800 °C in N_2.[122] The use of biobased phenols with alkyl substituents such as carvacrol and thymol (terpene derivatives), alongside furfurylamine, has led to polybenzoxazines with T_g of 86 and 88 °C, respectively.[123] The authors attempted to reveal the effects of alkyl substituents on polymer properties, noting that the thymol-based polymer has a slightly higher T_g due to more hydrogen bonding as the isopropyl group is less shielded in the thymol derivative. The melting point of these two monomers was 72 and 55 °C for the carvacrol and thymol monomers respectively – a significant difference considering the similar structures of these molecules. This observation is an important step in moving towards more easily processable bio-based benzoxazine monomers (**Figure 8**a). In a separate study, thymol-based benzoxazines were synthesized using a variety of petroleum-based amines. The authors state that an investigation of mechanical properties was attempted, however, the highly brittle nature of these resins makes the production of a uniform specimen difficult.[124] A catechol-furfurylamine-based bisbenzoxazine has been synthesized using a PEG400 solvent and IR irradiation methods to yield a monomer with a melting point of 198 °C and an onset of curing temperature of 213 °C.[125] This small processing window is a common theme for bisbenzoxazines which is a hurdle for composite manufacturing. One study utilizes the enzymatic synthesis of diphenols from biobased dialcohols and *p*-coumaric acid to produce bisbenzoxazine resins alongside furfurylamine. Resulting resins displayed T_gs above 200 °C and char yields around 50% at 800 °C – very promising results. Storage modulus at 20 °C was between 2.4–3 GPa. The monomeric materials were solid and did not exhibit a melting temperature, only T_g below 0 °C, again highlighting the process challenges associated with benzoxazine curing.[126]

Catechol-containing biobased benzoxazines have been investigated for their adhesive strength, with results showing up to five times greater shear strength compared to a commercial benzoxazine resin (bisphenol A + aniline). In this study, the catechol units were functional groups on the benzoxazine monomer and did not partake in the Mannich condensation reaction to produce the benzoxazine ring due to protection from TBS moieties. One resin in particular, derived from tyramine, aniline, and catecholic acid, had flexural modulus and stress at failure comparable to the BPA resin. However, T_m was 181 °C and the curing maximum endotherm was 196 °C, giving little to no processing window for degassing, yielding samples with many voids.[127]

Vanillin has been used to synthesize bisbenzoxazine monomers. One study produced phosphorus-containing vanillin-based diamine, and via Mannich condensation with vanillin produced a bisfunctional benzoxazine monomer. A melting point of 119 °C was observed, with curing between 164–293 °C giving an adequate processing window. Char yield at 600 °C was 53% for the pure benzoxazine resin, and when the polybenzoxazine powder is blended with epoxy, the epoxy char yield slightly increases. Significantly, the authors observed

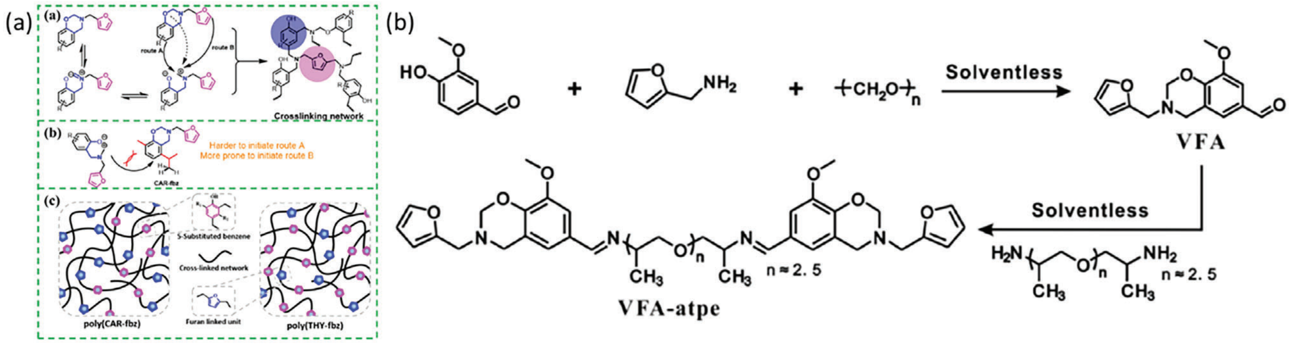

Figure 8. a) Carvacrol and thymol benzoxazine comparison. Adapted with permission.[123] Copyright 2021, Elsevier. b) Synthesis of shape-memory benzoxazines via Schiff base chemistry. Adapted with permission.[131] Copyright 2020, Elsevier.

a low gel content value of 76.6% for the polybenzoxazine. This low crosslink density is due to the lack of an available ortho position on the benzoxazine monomer, which is the preferred crosslinking site. This is an important consideration when designing biobased benzoxazine monomers. No mechanical test results were reported due to the brittle nature of the benzoxazine resins.[128]

Resorcinol and hydroquinone were combined with furfurylamine in a solventless process to produce two bisbenzoxazine monomers. Charring at 60% was observed at 1000 °C from TGA analysis. T_g was mechanically determined and is above 250 °C for both resins – in the case of the resorcinol-based resin it overlaps with resin degradation.[115] The authors significantly highlight monomer degradation which is an important consideration during benzoxazine curing – studies show two species can be formed at high temperatures, one of which leads to polymerization and the other to degradation of the monomer and evolution of a volatile imine compound.[129] As the reader will know, the evolution of volatile compounds during curing will lead to defect-rich composites with poor mechanical properties.

A highly biobased bisbenzoxazine with three furan moieties was synthesized in a two-step procedure, using guaiacol, furfural, and furfurylamine. A T_g of 287 °C was observed through TMA analysis. Storage modulus was in the magnitude of 10^3 MPa which is comparable to commercial thermosetting epoxy systems. Thermal stability was excellent, with a char yield of 62% at 800 °C in N_2. Two melting points at 126 and 153 °C were observed, with curing onset at 204 °C, giving a fair processing window. The high density of furan groups endows good flame-retardant properties and slow thermal degradation behavior in the resin.[130]

Monobenzoxazine resins tend to have very poor mechanical properties due to difficulties in reaching high crosslinking densities, leading to oligomeric structures.[130] One of the earlier examples synthesized benzoxazines from guaiacol, using stearylamine and furfurylamine as the amine components. Blends of the two monomers were investigated, with a max T_g of 153 °C being observed for a blend with 90% furfurylamine-based benzoxazine. The pure furfurylamine-based resin displayed a char yield of 56% at 800 °C in N_2. However no mechanical properties were reported, which suggested the resins were very brittle in nature with low crosslink density.[117] Pterostilbene was utilized alongside furfurylamine (PTE-fa) and stearylamine (PTE-sa) to produce biobased monobenzoxazine monomers. PTE-fa exhibited a T_m of 123 °C and a T_{onset} of around 215 °C, giving a wide processing window. T_g were observed at 252 and 179 °C for the fast resins respectively – considerable T_gs that are due to additional crosslinking from the pterostilbene double bond, and the furan moiety in the PTE-fa sample, setting this monomer aside from its other monofunctional counterparts. Water contact angles were reported at 109° and 129° respectively. Alongside OPC-time curves and Tafel plots, this suggests the resins have good potential as corrosion-resistant coatings.[122]

One study used vanillin and furfurylamine to produce a monobenzoxazine monomer which was then grafted to amine-terminated short polyether chains (Figure 8b). The authors present a benzoxazine resin with shape memory. The resin shows a storage modulus of 4.20 GPa and tensile strength of 90.4 MPa at room temperature, significantly higher than other reported biobased benzoxazines. This is due to the tough polyether chains coupled with the crosslinked benzoxazine units, endowing rigidity, and toughness. The Schiff base structures allow for shape memory.[131] One study utilized guaiacol and isoeugenol, alongside 1,10-diaminodecane, in a solvent-free process to produce biobased benzoxazines that also displayed shape memory behavior. Additionally, these resins displayed a high storage modulus of around 2.5 GPa, and tensile strength between 65–85 MPa, the highest reported for fully biobased shape memory polymers (SMPs). Additionally, T_gs were 138 and 216 °C for the isoeugenol- and guaiacol-based polymers respectively, which are within some aerospace requirements.[132] SMP composites are significant in the aerospace context due to properties such as large recoverable deformation capability and biocompatibility, and are generally lightweight.[133]

One team investigated the use of a biobased alternative to formaldehyde employed in benzoxazine synthesis, using the bioderived benzaldehyde alongside sesamol and furfurylamine in a solvent-free procedure. The resulting monomer has a melting point of 191 °C and onset of polymerization at 208 °C, bringing into question its processability. The resulting resin had a T_g of 165 °C and a high char yield of 46% as measured at 800 °C in nitrogen. Unfortunately, mechanical properties are not reported for this resin, which represents the 1st potentially fully biobased benzoxazine thermosetting system.[134]

One study investigates the use of modified rosin extracts to produce monobenzoxazine monomers and resins for coating applications, using guaiacol and 4-methylumbelliferone as phenol and dehydroabietylamine as amine. The resulting monomers showed high T_{onset} temperatures of 180 and 198 °C, compared to T_{m}s of 104 and 133 °C. This gives an adequate processing window. The resins displayed good anticorrosion resistance. T_{g}s varied significantly at 124 and 207 °C for the guaiacol and 4-methylumbelliferone resin respectively, attributed to the rigid structure of the α-pyrone in the latter.[135]

Daidzein has been used alongside furfurylamine and polyetheramine to synthesize so-called main-chain benzoxazine polymer (MCBP) monomers. In a similar fashion as the above study, incorporating some flexible chains in benzoxazine resin compositions is important in reducing brittle nature and increasing toughness. The ratio of benzoxazine moieties to polyetheramine chains was modulated by using differing levels of furfurylamine, which in essence terminated the Mannich condensation polymerization of MCPSs. Resins with fewer polyetheramine chains had higher tensile strength, Young's modulus, flexural strength, and lower tensile strain and strain at break. T_{g}s varied significantly, from 93 to 269 °C in accordance with increasing benzoxazine and furan ratios. Similarly, char yield at 800 °C in N_2 increased from 35% to 54%. This paper presents a good comparison between ratios of benzoxazine and linear polyether segments and the resulting effects on thermal and mechanical properties.[136]

As the above section highlights, much research has been done into the synthesis and curing behavior of biobased benzoxazine resins. However there is a distinct lack of thermomechanical properties reported – and in terms of composite research relevant to aerospace, there is no reported data for bio-based benzoxazine composite materials. Composite research is the next step in commodifying biobased benzoxazine technology. For this, viscoelastic properties of resin and curing kinetics must be well analyzed to ensure defect-free resin integration onto fibers. Problems regarding resin brittleness must be answered – through the use of linear chain additives, copolymers, and the use of MCBPs we are surely on track to realizing high-performance biobased benzoxazine resins for use in aerospace within the decade.

3.1.3. Sustainable Bismaleimides

Research concerning biobased BMI resins concentrates mainly on replacing the diallyl comonomer (essential to reduce brittleness and endow toughness) DABA with a biobased alternative. Only a few articles explore replacing BPA in the maleimide-containing monomer.

Shibata and co-workers have been combining bi-based alkenes with the aforementioned BDM system to investigate the properties and increased sustainability credentials of BMI systems. Small aromatic molecules, such as terpene and eugenol variants, have been shown to maintain good temperature performance.[137] As of 2017, properties such as impact resistance and water absorption have not yet been investigated. As expected, biobased additives with long alkyl chains decrease the T_{g} considerably but can offer toughening properties to BMI resins.[138,139]

Eugenol has been used to produce biobased alternatives to DABA (aromatic monomers/oligomers with free allyl groups) and copolymerized with BDM to produce partially biobased BMI thermosets (**Figure 9**a). Resins displayed behavior comparable to DABA/BMI resins at slightly higher ratios of BDM. Resins synthesized using eugenol/BDM ratios of 1:2 and 1:3 showed high T_{g}s of 346 and 377 °C, respectively. Storage modulus decline did not occur until 320 °C showcasing the superior heat resistance of these partially biobased BMI resins.[140] A trifunctional eugenol-derived monomer with phosphorus functionality was copolymerized with BDM and DABA in differing ratios. The resin wherein 100% of DABA was replaced showed a T_{g} of 70 °C higher than the original BDM/DABA resin at over 380 °C as determined by DMA results. The authors highlight the large increase in T_{g} alongside the increase in biobased content as standing out compared to other eugenol-based BMI resins.[141] Succinic acid and eugenol have been coupled to produce a diallyl comonomer for BMI synthesis. Significantly, they also explored a partially biobased alternative to the BDM monomer, using succinic chloride (which can be synthesized by fermentation) to couple two HPM units (containing BMI moiety). The copolymer of these two biobased molecules showed a T_{g} of 280 °C when ratios of 1:3 allyl:BMI monomer were used. Compared to the analogous petroleum-based resin, the T_{g} was 75 °C higher. Tensile strength and modulus were higher for the petroleum-based BMI resin (Figure 9b).[142]

In a similar fashion, cardanyl linolenate and allyl cardanyl ether (synthesized from CNSL extract) were copolymerized with BDM. The resulting resins showed that the allyl cardanyl ether has a higher reactivity for the BDM monomer – BDM was observed to homopolymerize when cured with the linolenate. T_{g}s were determined through DMA to be around 270–300 °C, however, authors report highly brittle behavior from the samples. Additionally, the allyl ether maintained storage modulus until T_{g}, whereas a consistent drop in storage modulus was observed for the linolenate resins.[138] Cardanol novolacs (of a similar structure to the above-discussed cardanyl linolenates) have been copolymerized with BDM. Increasing the BDM component led to increases in T_{g} and brittleness, whilst increasing cardanol novolac components increased flexural properties, with the best balance being found at a ratio of 1:4 cardanol novolac:BDM giving flexural strength of 60–80 MPa and modulus of 2.0–2.5 GPa.[143] Dehydrated castor oil has been copolymerized with BDM monomer to yield a thermoset with an unsurprisingly low glass transition temperature, given the linear aliphatic nature of castor oil constituents.[139]

A biobased lignin derivative referred to as ABE was used to produce BMI resins displaying a longer processing window and higher T_{g} than the commercial BMI resin. Creosol was coupled, and allyl groups were attached to form a suitable copolymer with BMI. The biobased BMI had a higher impact strength and K_{IC} (facture toughness parameter) than the analogous DABA resin at a ratio of 1:0.86 BDM:allyl monomer. The authors theorize that the structure of the creosol-derived comonomer allows for both toughness and rigidity. Ether bonds and low crosslinking density endow toughness, and allyl groups on ortho- and meta-positions are rigid, and methoxy and hydroxy groups produced through Claisen rearrangement lead to hydrogen bonding, endowing rigidity.[144]

Renewably sourced furfural and cinnamaldehyde were reacted with cyclopentanone to produce two allyl-containing monomers suitable for copolymerization with BDM. T_{g} values for varying

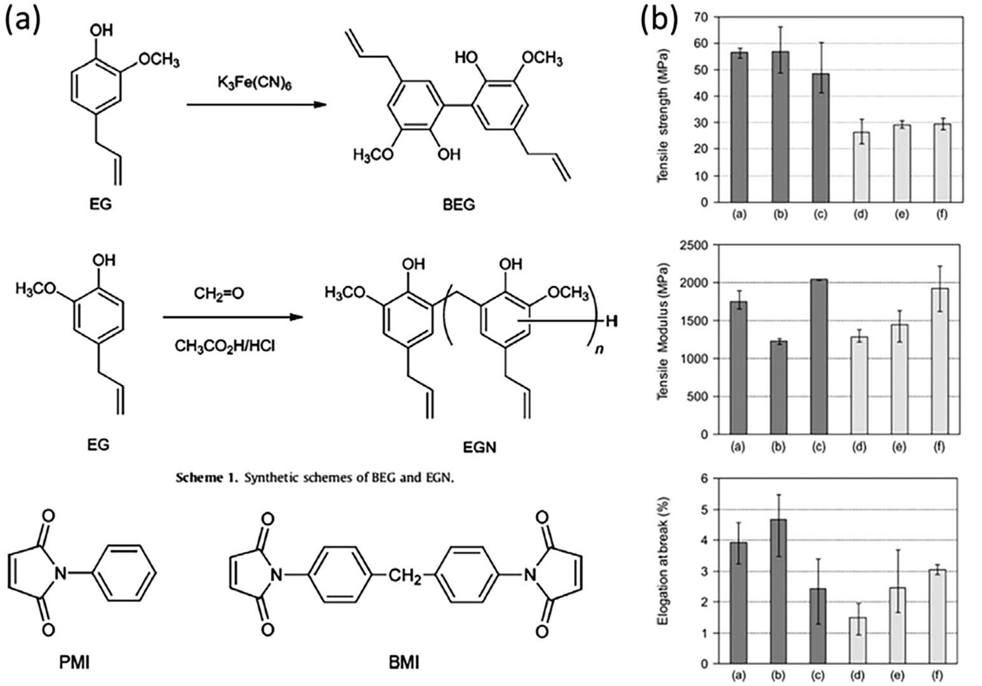

Figure 9. a) Synthesis of eugenol-based diallyl/oligomeric comonomers. Adapted with permission.[140] Copyright 2013, Elsevier. b) Tensile properties of biseugenyl succinate (BEUS)/bis(4-maleimidephenyl) succinate (BMIS)s: a) 1/1, b) 1/2, and c) 1/3 and 2,2′-diallyl bisphenol A (DABA)/4,4′-bismaleimidediphenylmethane (BMIM)s: d) 1/1, e) 1/2, and f) 1/3. Adapted with permission.[142] Copyright 2011, Springer Nature.

ratios were all above 370 °C, much higher than the 295 °C of the DABA/BDM petroleum resin. Storage modulus changed very little up to 330 °C suggesting good high-temperature performance. Flexural strength and modulus were however lower than the values of the petroleum-based counterpart.[145] Recently honokiol, a diphenol extracted from magnolia tree bark, was used to produce BMI copolymers from BDM with T_g (> 440 °C) and storage modulus (> 1.3 GPa at 400 °C) higher than any previously reported biobased BMI. The authors suggest this is due to additional crosslinking from aryl propargyl ether groups.[146]

As summarised above, many studies have investigated biobased allyl comonomers for the production of BMI resins, as well as some studies investigating alternative bismaleimide monomers. Resins studied by Ge[146] and Miao[141] in particular appear to show properties that can compete with commercial standards, however more thorough investigation of thermal and mechanical characteristics, as well as composite material formation and properties studies, must be performed. The question of starting material availability and cost is of course of prime importance.

3.1.4. Sustainable Cyanate Esters

As outlined in the previous section, cyanate ester resins rely on toxic chemistries for the synthesis of the cyanate ester monomers, employing cyanurate halogens and basic catalysts. This process seems to be very difficult to replicate using greener or less toxic chemistries – the nature of cyanate bonds is such. So, research focuses on replacing petroleum-based phenolic compounds with biobased phenolics to increase sustainability credentials. An extensive review conducted by Ramdani et al. was published in 2021 and provides a good overview of current work on biobased cyanate esters with high-temperature performance characteristics. Researchers in this specific field are encouraged to read their review for an in-depth understanding of biobased cyanate esters.[147]

Trans-anethole (extracted from star anise essential oil) was used to produce di- and tri-functional cyanate ester monomers. Curing studies suggest high-temperature curing led to degradation of the crosslinking network, shown by a substantial decrease in T_g when cured at 250 °C. Melting points were similar to commercial monomers, and a max T_g of 290 °C was produced from these difunctional biobased resins, which is comparable to commercial resins.[148] The other study synthesized trifunctional monomers, which had T_ms ranging from 97–165 °C depending on the phenolic ring substituents, compared to 82 °C for the BADCy monomer. Cure onset was > 40 °C lower for the biobased systems. Char yields were significantly improved, standing at 70% and 75% for biobased tricyanurate esters compared to 25% for the BADCy system, tested in air at 600 °C. Water uptake was also low (1–3%). Authors suggest this tricyanurate monomer could be used as a substitute for the BADCy monomer in cyanate ester formulations.[149]

Eugenol is a popular choice for the preparation of biobased thermosets and was utilized to produce a difunctional cyanate ester monomer. T_g was low for cyanate esters due to the four carbon chains between each phenol moiety.[150] In other work the same researchers further investigated a eugenol-derived cyanate ester monomer, leading to a resin with T_g of 186 °C (**Figure 10**a). Char yield was low for cyanate esters, 31% at 600 °C in N_2, which is not surprising given the thermally labile methoxy and aliphatic

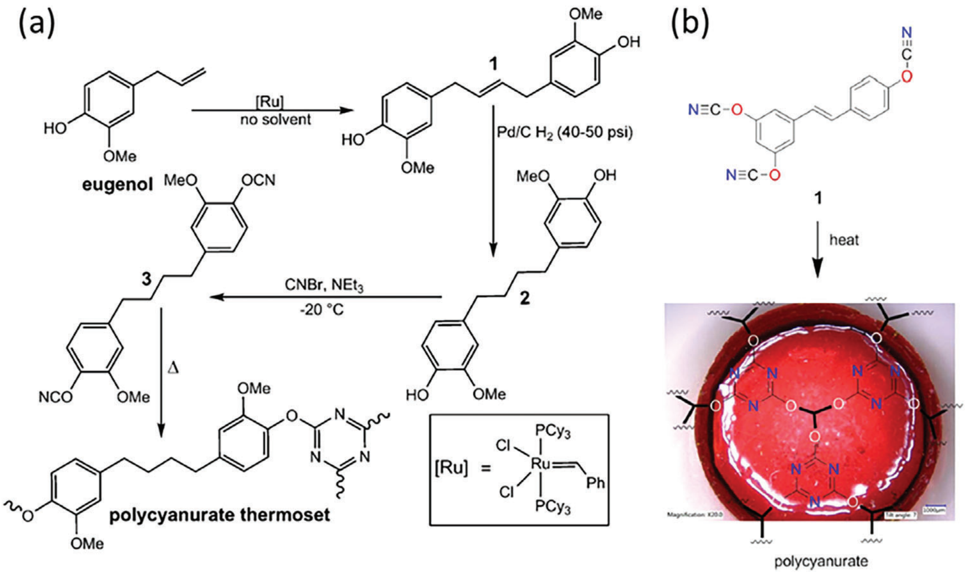

Figure 10. a) Synthesis of eugenol-based cyanate ester monomer and resin. Adapted with permission.[152] Copyright 2014, John Wiley and Sons. b) Resveratrol tricyanurate and digital image of cured resin. Adapted with permission.[154] Copyright 2017, John Wiley and Sons.

portions of the monomer units. Significantly, the resin showed water uptake of only 1.8% compared to 3% for the BADCy resin. Wet T_g for the eugenol-based resin was only 19 °C lower than dry T_g, which is comparable to dry T_g of aerospace-grade epoxy resins.[151] The authors suggest that whilst this resin has inferior properties to other cyanate esters, it could be used to replace some petroleum-based epoxy resins in suitable wet applications. More studies are needed to investigate the mechanical properties of this resin and its composites.

Creosol was used to produce a variety of difunctional cyanate ester monomers with methoxy functionalities. Melting points were high, with the lowest of 88 °C and highest of 146 °C for the creosol-based cyanate ester monomers which present some processing challenges. Compound 3 had a processing window of 120°C which is relatively feasible. T_g of this resin was 257 °C, lower than petroleum alternatives. Char yields at 600 °C in N_2 were disappointing, with a max of 35%.[152]

Trans-resveratrol and dehydroresveratrol were chemically modified to yield monomers with high T_ms of 165 and 123 °C respectively. The onset of curing was 60 °C+ lower than the BADCy system, however, this left a small processing window for the monomers. Indeed, the unsaturated monomer was polymerizing and melting within the same window, possibly leading to sample inhomogeneity. Char yields, similarly to the *cis* monomer, were high at 66% and 71% in air for the unsaturated and saturated resins respectively. Wet T_g for the dihydroresveratrol resin was comparable to the BADCy system, indicating it could be substituted in applications where wet T_g is important.[153] Building on this study, *trans*-resveratrol was isomerized to *cis*-resveratrol using UV light, producing a monomer that melts at 80 °C thereby increasing its processability. Polymerized trifunctional monomers yielded a resin with $T_g > 350$ °C and a char yield of 73% at 600 °C in air indicating the potential for high-performance applications (Figure 10b).[154] Blends of *cis*-resveratrol cyanate ester monomers with petroleum-based commercial formulations were later explored and successfully improved processability by decreasing formulation T_m. Authors suggest *cis*-ResCy could find use as an additive to commercial cyanate ester resins, due to its ability to enhance properties including T_g and char yield. Of note is that increasing levels of biobased monomer led to higher water uptakes and significantly lower wet T_gs.[155]

Many biobased phenols are available for the synthesis of more sustainable cyanate ester resins. Techniques range from direct synthesis of cyanate ester monomers to coupling of molecules to increase functionality followed by cyanate ester synthesis and polymerization. Many resins display initial characteristics comparable to current commercial resins. Further studies are needed into the mechanical properties of such resins and specifically their composite materials.

3.1.5. Sustainable Phthalonitrile

Phthalonitrile resins are produced from monomers containing phthalonitrile groups and possess better retention of mechanical properties at elevated temperatures compared to other high-performance thermosetting resins. However, they require high curing temperatures (300–350 °C) and long cure times.[156] Nevertheless, they are of great interest to the aerospace industry.

A study investigates the use of green solvent in the synthesis of biobased phthalonitrile monomers via nucleophilic substitution. Dimethyl carbonate (DMC) was used to convert a biobased bisphenol (derived from vanillin and tyramine) into a phthalonitrile monomer. The Schiff base moiety was shown to promote crosslinking, achieving high performance under moderate curing conditions. T_m of the monomer was around 180 °C, and a low viscosity of under 1 Pa s was maintained up to 260 °C, giving an 80 °C processing window. Char yield was around 48% at 800 °C indicating potential for use as a flame retardant material.

Figure 11. Synthesis of honokiol-based phthalonitrile monomer. Adapted with permission.[159] Copyright 2021, Elsevier.

Storage modulus at 400 °C was between 800–1000 MPa showing good high-temperature performance capabilities.[157]

Another study utilized catechin-derived monomers to produce a phthalonitrile resin. Authors directly compared this resin with a BPA-based counterpart, a method that is highly encouraged as it allows for direct comparison of biobased versus petroleum-based resins. Properties of the resin include a lower T_m and T_{onset} than the BPA resin. Additionally, the catechin-derived monomers required no curing agent to cure, whereas the BPA resin was cured with 5w% of DDS. Char yield was also comparable between the resins at above 70%.[158]

An honokiol-derived resin showed a T_m of below 70 °C and a T_{onset} of around 230 °C, giving a good processing window and low onset of curing, again without the need for an additional curing agent (**Figure 11**). The melt viscosity of this resin and the magnolol resin studied were below that of an analogous petroleum resin, suggesting better resin infiltration characteristics. Char yields were exceptional, standing at above 70% at 1000 °C in N_2. Storage modulus for the honokiol resin was 4.6 GPa at 30 °C indicating good mechanical properties. Water absorption was lower than the petroleum-based resin, peaking at around 2% compared to 3% for the petroleum-based resin.[159]

As has been suggested numerous times, more studies are needed on the thermomechanical properties of both pure biobased phthalonitrile resins and their composite materials to enable utilization in commercial aerospace settings.

Further Considerations for Sustainable Thermoset Design and Development: Many research in the literature reports on the utilization of renewable feedstocks to forge thermoset resins. The chemistry of upgrading phenolic starting products into a resin monomer is straightforward and can be integrated into today's industrial processes (i.e., epoxidation). Even though one can encounter mechanical properties of so-formed resins such as tensile modulus and strength, many tests are not performed according to ASTM standards. Unfortunately, this eliminates a chance to conduct a fair comparison amongst them. Our humble suggestion regarding future studies would be to report mechanical tests according to ASTM standards, which would help scientists generate a library.

To our surprise, despite the vast number of articles on sustainable thermoset resins; their translation into composite structures is almost unknown. Careful investigation of mechanical performances reported for renewable resins hints towards suitability for thermomechanically less demanding applications (adhesion, water protection layers, etc.) for the majority of articles. Few industrial renewable epoxy systems employing vegetable oils prove that situation. Very few reports investigate the properties and potential manufacturing of resin (such as viscosity, cure kinetics, crosslink density, activation energy, cure shrinkage, pot life, etc.) for the formation of composite structures. Research at this stage must consider potential manufacturing options when high-performance composite applications are pursued. Hence, detailed documentation on renewable resin characteristics is required for manufacturing steps. Generating additives based on renewable starting products can be exploited, which would require smaller volumes of production.

Exploring the potential of renewable molecules as starting products for resin development is a great initiative and is a must. As far as an impact on the aviation industry is concerned, scalability must be a prime consideration. Unfortunately, most of the renewable molecules discussed above are either not available on a large scale and/or are extremely expensive (honokiol is reported with outstanding mechanical properties, however 125 mg costs more than 100 euros). Even for lab-scale composite studies including manufacturing and ASTM tests, more than a kilo of resin is required. Additionally, obtaining such molecules must be realistically contemplated. Employing edible crops as starting products is out of discussion as it would create competition with the food chain. Focus must be placed on the valorization of waste streams, however major risk in obtaining renewable phenolics via extraction is the purity and scalability issues. Reliable life cycle assessment of renewable molecules must be studied not only by means of resources but also on water consumption, required land, CO_2 footprint, impact on local economy and social dynamics, manufacturing, and availability of supply chain.

3.2. Composite Manufacturing via Frontal Polymerization

Utilization of renewable starting products to form FRPC would be a giant leap toward the generation of sustainable aviation materials, however, large-scale manufacturing operations will continue to increase global CO_2 pollution due to high energy requirements. Prepregs must be cured in large autoclaves (i.e., larger than the size of a fuselage) for very long times (tens of hours) under pressure and applied temperatures. Besides the economic burden of such setups (estimated to cost around 100 million dollars) for manufacturing companies, real attention must be paid to CO_2 generation during autoclave curing, which is projected to be around 80 tonnes for Boeing 787 fuselage curing.[160]

Frontal polymerization is an energy-efficient polymerization technique based on an autocatalytic self-propagating polymerization front in the form of thermal waves.[161] Since the 1970s, and especially within the last 10 years, it has been an attractive

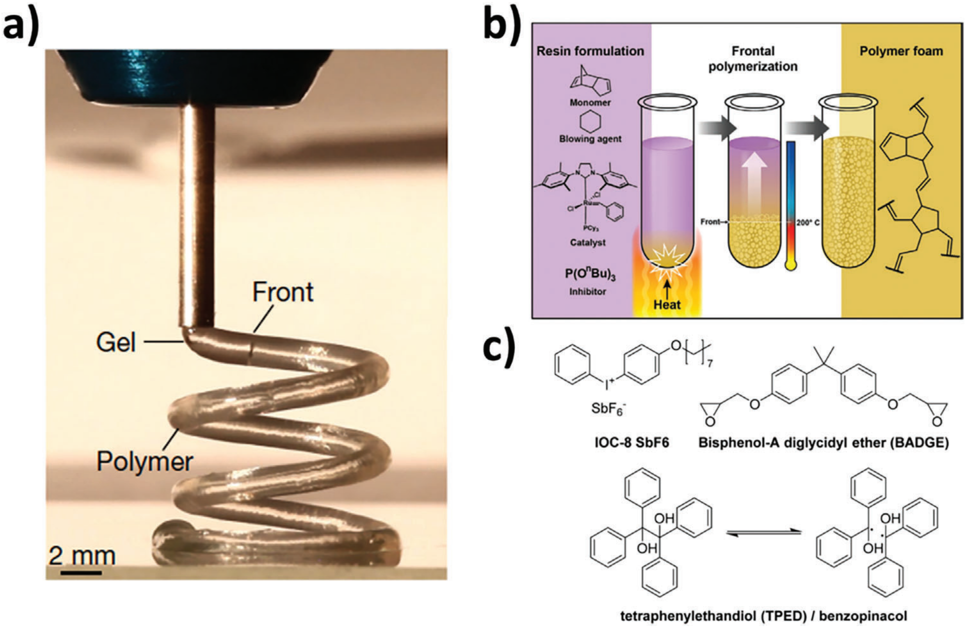

Figure 12. a) Visual demonstration of polymerizing front in DCPD resin system during the extrusion process. Adapted with permission.[152] Copyright 2018, Springer Nature. b) Schematic depiction of frontal polymerization-induced DCPD foam generation by tailoring resin composition. Adapted with permission.[155] Copyright 2022, Wiley. c) Resin formulation for radical-induced cationic frontal polymerization of epoxy. Adapted with permission.[166] Copyright 2016, Wiley.

area of research that requires a multidisciplinary understanding of polymer chemistry (to design efficient initiating systems) and polymer physics (understanding polymerization dynamics). It is reported to work effectively for acrylate-methacrylate monomers in bulk forms via radical initiators[162] however alternative monomers as well as their composites have been explored recently. Dicyclopentadiene (DCPD) is a structural part of commercially available unsaturated polyester resin (Synolite) with diverse surface applications. Efficient frontal polymerization technology has been introduced for pure DCPD using Grubbs second-generation catalysts and alkyl phosphite inhibitors to conduct ring-opening metathesis polymerization, which can be activated thermally (**Figure 12**a)[163] or via light irradiation.[164] Since then, DCPD-based frontal polymerization technology has been employed as a powerful tool to generate advanced materials thanks to engineering approaches. Such engineering tools for example include a detailed investigation of the frontal polymerization of thin DCDP layers on an insulating substrate.[165] The authors studied heat loss events and propagation rate by means of monomer layer thickness on insulating surfaces which revealed an interplay of monomer-surface interaction as a function of thickness and its influence on stable propagating wave formation. Anisotropic DCPD foams can be synthesized via frontal polymerization employing cyclohexane as a blowing agent (Figure 12b).[166] Anisotropy is influenced by blowing agent concentration, gelation time, and resin curing kinetics, yet authors observed interconnected porous structures that can transport liquids. Two frontal polymerization methods (ring-opening metathesis for DCPD and radical for acrylates) can be merged in a tube to architect welded thermoset structures.[167] Two immiscible resins undergo gelation which can be tuned via initiation location, initiation type, and resin composition. DCPD can be a matrix for carbon fiber-reinforced composites manufacturing, and in these cases, authors reported the role of carbon fibers in polymerization front propagation.[168,169] This is in relation to heat conductivity and the presence of fibers that can affect the shape of propagating growth, hence causing disparity in cured samples. Therefore, engineering-based investigations such as modeling[170] and heat-conducting metal wire-based setups[171] have been presented for the frontal polymerization of DCPD-based composites. For a comprehensive explanation of existing chemistries and engineering approaches, we guide reviewers to a recent review by Suslick et al.[172] Epoxy resins are vital for aerospace materials, and can be tailored for frontal polymerization mainly by employing iodonium salts to assist cationic ring-opening polymerization initiated thermally or via light irradiation.[173] It is important to note that these systems are mostly hardener-free and focus on bulk polymerization of epoxy monomers. Initiators must be well dissolved in epoxy resin and solvent must be removed under vacuum if present. Generally, multiple initiating species are required to ensure successful propagation front formation. Superacids that can protonate and trigger ring opening of oxiranes are the main initiating species, hence the acidity of so-formed intermediates determines frontal photopolymerization conditions.[174] Iodonium salt decomposition can be triggered by radical initiators as well, mainly by so-called C–C labile compounds such as tetraphenylethanediol.[175] From a materials perspective; epoxy monomers can be merged with acrylate monomers for orthogonal initiation (Figure 12c)[176,177] and composite structures[178,179] can be obtained using frontal polymerization of epoxy monomers.

In order to be employed for aerospace/wind turbine component production, chemical knowledge of thermosetting resin systems obtained at the lab scale must be translated to manufacturing engineering. Frontal polymerization would remove the necessity for autoclaves, meaning that the curing of large prepregs can be conducted by applying localized stimuli to initiate curing reactions. However, from a manufacturing perspective, many aspects must be considered. First, as in all aerospace components, creating defect-free structures is the priority. During frontal polymerization of prepregs, one must ensure the homogeneous growth of a curing phase especially at the edges and curves since major heat losses take place which form partially uncured and defect-containing composites. Considering the area and thickness of prepregs required for aerospace and wind turbine applications, the propagating front can terminate easily. Thickness also hinders the potential of using light-induced frontal polymerization since light penetration in carbon fiber prepregs is limited. Modeling to estimate propagating front and in situ imaging methods must be developed to ensure uniform curing via frontal polymerization. Furthermore, since the thermal conductivity of fibers differs, suitable formulations and molding setups must be designed accordingly. As aerospace structural components require high fiber volume content (more than 60%), delicate initiating systems with tailored molds must be created. From the matrix perspective, resins must be stable against vaporizing since defects can be formed, and some inherent parameters such as viscosity, monomer infusion, cure shrinkage, and cure kinetics must be well understood.[180] Nevertheless, frontal polymerization will enable a big step towards energy-efficient manufacturing of aerospace components.

3.3. Composite Recycling

Thermoset matrices are identified via their robustness and high thermal, mechanical, and chemical stabilities due to crosslinked structures. While it is a fantastic property to possess during performance, it becomes problematic at end-of-life since recyclability options are scarce. Readers desiring a more extensive overview on this particular topic are directed to the review by Post et al., detailing the advantages and limitations of recyclable thermosets for structural applications.[181]

Supercritical methanol can be employed to dissolve thermosetting epoxy matrices for matrix-fiber separation.[182] In this system, epoxy was cured with anhydrides and catalyzed with trimethylamine to form the matrix of CFRP composites. Supercritical methanol at 270 °C at 8 MPa can dissolve the matrix within 90 min, and fibers were noted to retain their mechanical properties after treatment. Water[183] and some other alcohols[184] under supercritical conditions exhibit similar recycling potential as shown in the literature. Recently it has been shown that hot acetic acid (at 160–220 °C) possesses catalytic properties, enabling delamination of CFRP composites into soft layers, alongside slight degradation of the epoxy matrix.[185] Aerospace grade CFRP epoxy composite can be degraded using zinc chloride/ethanol mixture at 200 °C for 5 h in a pressurized reactor, and the resulting decomposed matrix polymer powder contains reactive end groups that can be merged with new epoxy formulations.[186]

Labile bonds such as imine, disulfide, acetal, alkoxyamine, acylhydrazone, secondary/tertiary ester, aminal, carbonate, and Diels–Alder addition structures introduce a recyclability mechanism once embedded in thermosets.[187] Methods in organic chemistry allow modification of starting products to introduce labile bonds, which can promote composite recyclability. Curing epoxy with anhydrides and carboxylic acids endows transesterification reaction possibilities. For example, the epoxy monomer can be cured with methylhexahydrophthalic anhydride at 180 °C for 2 h to form a thermoset (**Figure 13**a).[188] For composite preparation, the authors used dip coating of T300 CF fabrics with epoxy monomer and curing agent, followed by hot pressing. For both cases, thermosets can be degraded by treating with ethylene glycol at 180 °C in the presence of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) catalyst. In this way, fibers can be recycled from composites with high efficiencies. Similarly, it was reported that anhydride-cured epoxy resin undergoes degradation in ethylene glycol/*N*-methyl 2-pyrrolidone (NMP) solvent mixture in the presence of TBD catalyst, where NMP swells resin and increases contact with the catalyst.[189] Composites can be recycled by network dissolution, and the authors elucidated the collection of active oligomeric units that can be employed further in epoxy formulations. A thermoset recipe including epoxy monomers cured by fatty acids in the presence of zinc acetylacetonate affords a dynamic network that can be dissolved via a transesterification reaction with ethylene glycol.[190] The authors showed recyclable CFRP composite structures where a full recycling of CF takes place due to thermoset dissolution and recovered polymer powder can be hot-pressed to repair composites. Chemical methods to introduce imine,[191] cyclic acetal,[192] and hexahydro-s-triazine[193] groups into epoxy monomers endow dynamic thermosetting matrices for recyclable composite formation.

Similar functionalities can be introduced for thermosetting benzoxazine resins as well.[194] For the curing of multifunctional benzoxazines, chain flexibility has prime importance in generating matrix-type thermosetting structures. Melting point and curing degrees must be well studied for composite manufacturing. BMI-CF composite recycling was investigated using basic catalysts at 190 °C around 10 h to selectively degrade imide bonds for matrix dissolution as well as CF separation.[195] Authors reported the gain of valuable polymer powders from their reaction mixture. Without a doubt, other thermosetting resins can benefit from chemical degradation for composite recycling options.[196–198]

4-Aminophenyl disulfide can harden epoxy monomers, and the labile disulfide can be exploited for composite recycling. Commercial epoxy resins can be mixed with 4-aminophenyl disulfide solid crystals first to dissolve it at 80 °C, followed by infusion and curing to synthesize a composite. Due to dynamic S-S linkage resulting vitrimeric composites can be repaired, recycled, and thermoformed.[199] A similar recipe was examined for pultrusion-based manufacturing, which requires higher temperatures and lower pulling rates compared to commercial epoxy but pultruded profiles elucidate vitrimer properties.[200] Resin dissolution takes place in a 2-mercaptoethanol/DMF mixture at room temperature (Figure 13b).[201] In such dynamic systems, identifying creep and stress relaxation behaviors for high-performance applications is a must. The authors highlight that their technology has the potential to be employed in aerospace applications.

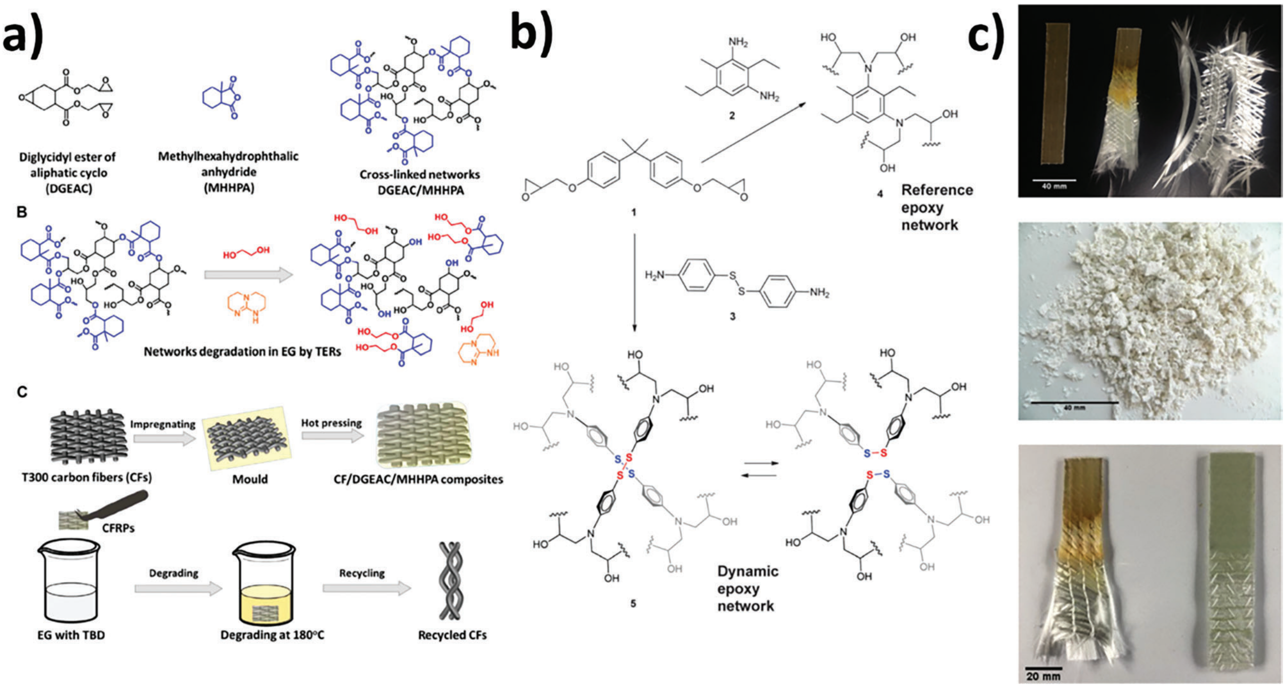

Figure 13. a) Resin formulation and glycolysis-based resin/composite degradation in the presence of a basic catalyst. Adapted with permission.[188] Copyright 2022, Frontiers. b) Chemical structures of resin formulation which contains dynamic disulfide crosslinks. Adapted with permission.[201] Copyright 2016, Royal Society of Chemistry. c) Digital images of glass fiber-epoxy composite made with recyclable hardener elucidating recycled fibers (top), recycled resin (middle), and comparative study (bottom). Adapted with permission.[202] Copyright 2019, Taylor & Francis.

In industry, a few curing agents containing labile bonds serve as recycling composite formulation ingredients. Such curing agents are available at large scale and their properties such as viscosity are well characterized. Cleaveamine hardener possesses a degradable acetal core, and composites based on Cleaveamine can be degraded in glacial acetic acid-hydrogen peroxide mixture at 110 °C liberating glass fibers as shown in a research study (Figure 13c).[202] The Recyclamine curing agent family contains degradable ketal/acetal groups which have been investigated in the literature.[203] Flax-epoxy composites (40% fiber volume) using Recyclamine hardener can be degraded in concentrated acetic acid at 80 °C within a few hours.[204] In this system the polymer matrix dissolves and can be used as a thermoplastic and flax fibers can be filtered, however, their initial fabric state is converted into individual fibers. Additionally, Recyclamine is now being explored to form recyclable blades for wind turbines in collaboration with Siemens Gamesa.

When high-performance thermoplastics are utilized as a matrix, they can offer recyclability options too. Due to the absence of chemical crosslinks, matrix-fiber separation is theoretically more straightforward compared to thermosets.[205] Mechanical recycling leads to efficient matrix and fiber separation, however, fibers are shredded and lose their initial value for structural composite formation due to reduced fiber sizes.[206] However, recycled parts can be processed using methods such as injection molding and hot pressing to (re)form composite structures. Chemical recycling of thermoplastic composites is challenging since polymers such as PPS and PEEK show almost no solubility in common solvents. Efforts for chemical recycling that target depolymerization of the matrix involve many strong chemical species (strong acids, bases, oxidants) or supercritical conditions – currently research is at very low TRL, and these methods are questionable from the sustainability perspective.[207] Thermal recycling is performed at high temperatures in order to thermally degrade the polymer matrix to smaller gaseous fragments.[208] In this case, the polymer matrix is removed to recycle the fibers. However, at degradation temperatures sizing and fiber surface can be damaged,[209] which requires additional steps to reform fibers before composite formation. High energy input and loss of polymer matrix (which is composed of hazardous starting materials) hinder circularity and sustainability. Thermoforming and consolidation of fiber-reinforced thermoplastic composites seem plausible and require manufacturing input to generate functional composites from recycled components. Vitrimer matrices can assist with recycling, repairing, and reprocessing composites;[210] however vitrimer research for aerospace applications is in its infancy.

In summary, composite recycling will determine the circularity of the industry. Using thermosets with degradable bonds allows for chemical recycling with fiber-matrix separation. However, it must be conducted at low temperatures using benign solvents and must be feasible for larger-scale treatments so that the original fiber length can be retained. The recycled polymer should have a practical use or it should reform a thermoset to retain its original properties. Potentially scalable chemical reaction systems to create dynamic bonds within thermosets must be stressed. For thermoplastic composites, mechanical recycling and thermoforming are popular recycling methods, however, components are downgraded by means of performance and

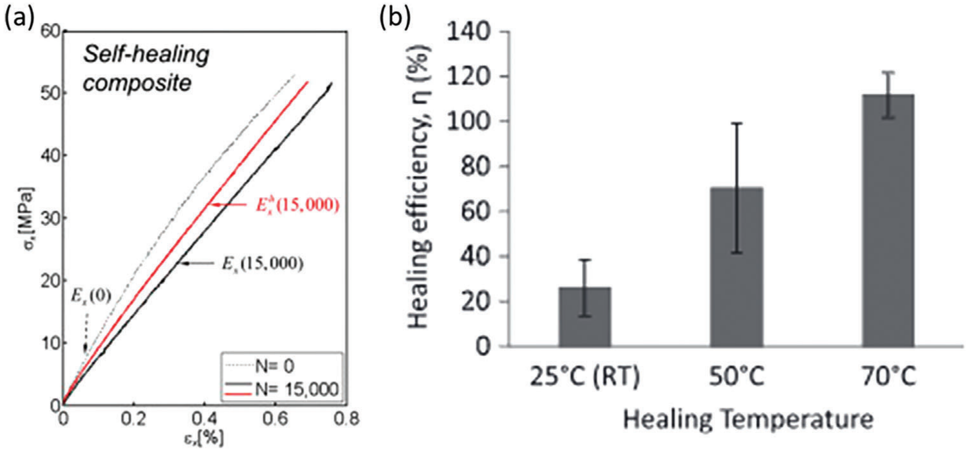

Figure 14. a) Stress–strain curve of original ($N = 0$), unmodified ($N = 15\,000$ black), and modified ($N = 15\,000$ red) showing 54% recovery from self-healing material. Adapted with permission.[215] Copyright 2019, Elsevier. b) Healing efficiency at different temperatures for the epoxy-mercaptan dual-capsule system. Adapted with permission.[217] Copyright 2021, SAGE journals.

application. Merging chemistry with manufacturing will realize viable composite recycling routes, enabling a shift towards a more circular economy within aerospace.

3.4. Self-Healing Composite Matrices

Self-healing materials can extend the lifetime of products and components, thus contributing to the sustainability of these products.[211] In the context of aerospace thermosetting composites, continuous thermomechanical loading and energy absorption via damage creation can lead to composite failure via matrix fracture, fiber fracture, delamination, and fiber-matrix debonding. These damages can be hard to detect and require expensive maintenance. Reducing these damages through the use of self-healing matrix materials can in theory extend the lifespan of aerospace composite materials and reduce maintenance costs. The following section will briefly summarize self-healing systems of particular relevance to aerospace thermosetting composites. Readers who wish to learn more about this developing and potentially highly impactful area of research are directed to reviews by Hillewaere et al[212] and Paolillo et al.[213]

Mechanisms for self-healing come in two broad forms: extrinsic and intrinsic. Extrinsic self-healing mechanisms (including capsule/vascular-based healing systems) require an external healing species. Upon damage, the healing species enters the damaged area and reacts to fill the damage and regain some strength. Intrinsic systems self-heal due to the properties of the bulk material, for example through bond re-formation.[214] Many considerations inform an appropriate choice of self-healing technology for industrial-scale applications including healing stimuli, healing time, healing conditions, healing efficiency (η), and of course the thermal and mechanical properties of the virgin and healed composite.

For example, the self-healing of a GFRP epoxy prepreg was investigated using microcapsules of DGEBA in a solvent. Following tension fatigue testing and a 24-h rest period at RT, 52% of the initial Young's modulus was recovered due to self-healing (**Figure 14**a).[215] DGEBA and mercaptan-filled capsules are suitable dual-capsule systems for structural composite self-healing.[216] One study highlights the effect of healing temperature on healing efficiency, due to a decrease in healing agent viscosity with temperature allowing for better penetration into the damaged region.

10 wt % loading led to healing efficiencies of 70% and 111% at 50 and 70 °C respectively when held for 24 h, as measured by fracture toughness (Figure 14b).[217] Whilst these results are encouraging, the reality of applying heat to a large aerospace structure is arduous. On top of this, extrinsic systems can only withstand one damage event at any given site. Intrinsic healing systems, as we will now explore, can offer repetitive healing.[218]

Intrinsic healing systems rely on a change in the chemistry of the thermosetting system and therefore may take longer to penetrate aerospace structural applications due to the extensive certification process. However, these systems can theoretically repair damages to a greater extent than extrinsic systems due to the reformation of the original chemical structure and physical properties in some systems. Intrinsic self-healing can occur through two broad systems: Reversible covalent bonds and reversible supramolecular interactions (i.e., ionic interactions, H-bonding, metal coordination, π–π stacking).[218] In the context of aerospace structural applications, the weaker supramolecular self-healing systems show poor thermal and mechanical properties.[213,219,220]

The most promising chemistries to enable intrinsic self-healing in aerospace materials are those that a) do not compromise bulk properties, b) self-heal under ambient/mild conditions, and c) are economically feasible. Diels–Alder dissociative covalent chemistry is reversible (and therefore self-healable) at temperatures approaching 150 °C, which is difficult to achieve on a bulk scale.[221] Alkoxyamine and imine exchange chemistry presents a catalyst-free system that will not experience a sudden drop in mechanical properties at degradation temperatures, however, the reaction is prone to oxidation and is therefore difficult to implement at industry levels. Nevertheless, Zhang et al. synthesized an imine-based epoxy elastomer that exhibited

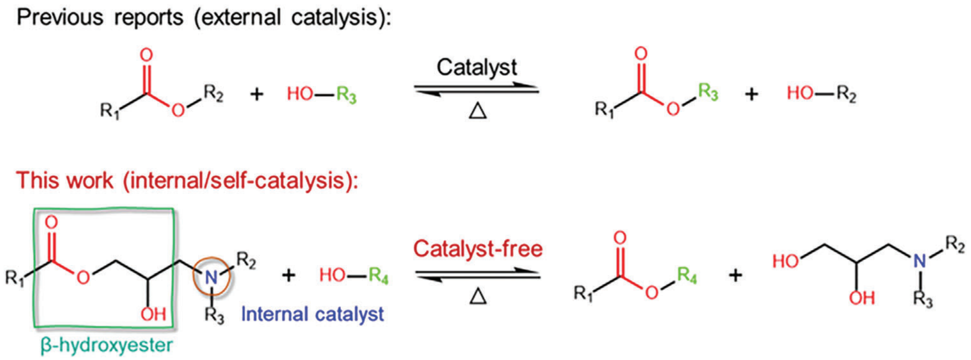

Figure 15. Self-catalyzed transesterification reaction that can be exploited to low E_a and temperature of transesterification reaction. Adapted with permission.[228] Copyright 2021, American Chemical Society.

healing efficiency of 60% when healed at RT. More research should be done to investigate the potential of this system to operate at much higher T_g.[222] Many studies with benzoxazines indicate their potential for self-healing, including through the use of dynamic imine bonds introduced through the biobased and economically attractive vanillin moiety.[118,194] Sulfur chemistry is appealing for intrinsic self-healing due to the weaker disulfide bonds being broken more easily than carbon–carbon bonds. In theory, small damage leads to the breaking of these bonds, which can then be reformed when contact is made. Post et al. presented a disulfide-containing epoxy glass-fiber composite system that could be healed at mild temperatures with a moderate stiffness of 80–1200 MPa, which could be acceptable for some secondary structural applications.[223] Aromatic disulfides reportedly can be exchanged at room temperature, which is more attractive from an industrial perspective. Significant research is currently being undertaken to allow for the tailoring of these systems to specific applications, paving the way for commercial formulations.[224,225] The transesterification reaction can also be exploited for self-healing characteristics – recently a simple system employing adipic acid with a primary amine in an epoxy system achieved up to 77% recovery, however under conditions of 190 °C for 2 h in a hot press, which are not feasible for aerospace structures.[226] Nevertheless, mild crosslinking of low M_w polyethyleneimine with ester bond containing epoxy monomer was shown to display healing efficiencies of 84% due to hydrogen bond formation, and self-catalyzed transesterification also occurred above T_g, which was low (max 45 °C) (**Figure 15**). This work highlights the link between self-healing and recyclability, both of which can be achieved through the use of covalent adaptable networks (CANs).[227]

As outlined above, self-healing of thermosetting matrices for aerospace applications is a rich research field with many potential avenues. We would like to highlight aromatic sulfide chemistry in particular, as the theory of weaker bonds breaking upon damage and reforming upon contact at room temperature is elegant, and indeed research is proving this to be a feasible route to self-healing of composite matrices (from a mechanical and economic point of view). Other chemistries mentioned can also endow self-healing capabilities, but due to higher temperature requirements are better suited to recycling applications. A combination of systems is likely to be required to achieve both industrially feasible self-healing and recyclability. Readers are encouraged to view recent reviews on the topic of CANs to gain more insight into the thermodynamics of dynamic bonds.[228]

4. Conclusion and Outlook

CFRP as structural components enabled commercial aviation by being lightweight while performing well under high mechanical requirements. Today constituting more than 50% by weight of structural parts, the need for CFRP in the aviation industry is clear, especially considering expected aircraft deliveries in the upcoming years. In their current form, aerospace materials contribute massively to global CO_2 level increases. This is mainly due to the utilization of petrol refinery-based starting products which are finite and do not sequester any carbon in their production. They also possess toxicity and hazard risks (especially monomers for high-performance engineering thermoplastics). CF production at very high temperatures is a very energy-intensive process. Curing composites (in the case of thermosets) require enormous autoclaves which are very energy-intensive. Thermoplastic composites do not possess such drawbacks, however, their manufacturing is currently far from being optimized and high melting points also present significant energy demands. Once aircraft reach end-of-life, they add to landfill waste since there are no recyclability options (thermosets), meaning all of the components must be reproduced from scratch in order to manufacture new aircraft. For thermoplastic composites, even though recyclability options by means of CF-matrix separation are possible in theory, in reality, it is quite complicated and not as feasible as suggested.

For such a big market, it is vital to consider serious steps towards sustainability. Initiatives should start from chemistry, where innovations in chemistry must be translated by engineering and manufacturing to realize next-generation sustainable aircraft components. Here we covered a few examples from the chemistry perspective that can bring pioneering solutions on a large scale. Employing renewable starting products, developing frontal polymerization for energy-saving manufacturing options, and exploring composite recycling activities will have a major influence on sustainable aerospace materials design. It is important to remember that everything discovered on a lab scale must be scalable in order to translate innovations into industry. Hence, interdisciplinary communications and collaborations must exist in academia with significant support from industry. Additionally, a transparent life cycle assessment (LCA) for each component must be presented, and such LCA studies must consider chemical synthetic pathways.

As material scientists we can do our best to summarize the most feasible starting materials for the production of high-performance thermosetting matrices with greater sustainability credentials. For example, Borregaard is producing biovanillin from Norway spruce lignin on an industrial scale, proving that advancements in biorefinery technology and catalysis can allow for biobased plastics on a larger scale. Many of the bio-compounds researched are at the moment simply a novelty – for example, natural honokiol is present in such small quantities it is completely unfeasible to use on even a medium scale. This is also the case for resveratrol, catechol, pterostilbene, and daidzein. Of note is the development of enzymatic synthesis via genetically modified bacteria, which has the potential to produce unique small molecules on a larger scale.[229,230] Whilst it is of scientific curiosity to push for high-performance thermosets by investigating the use of these unique compounds, the reality is that we need practical solutions as fast as possible – this means economically feasible and mechanically sound thermosetting matrices from biorefinery sources and the inclusion of self-healing and cleavable crosslinks that will allow for fiber and matrix recovery. Once again, we highlight the high sustainability credentials and feasible economics of using vanillin, alongside its ability to form labile imine bonds, as a very promising foundation for the next generation of biobased, recyclable, and self-healing high-performance thermosetting resins. Furfurylamine is also a noteworthy molecule that has been employed extensively in biobenzoxazine synthesis. It also possesses the ability to form DA-adducts, and it can be derived from furfural which is a by-product of the sugar extraction process. With this being said, materials scientists across disciplines must welcome the input from LCA assessments of feedstocks encompassing economic and environmental credentials of starting materials to better inform applied research focus. It is also important to realize there will be no monoculture feedstock that can solve the issues of biobased composites, as feedstocks have to be grown in an ecologically sound manner, which itself mandates ecological variety.[231]

As previously mentioned the certification demands for aerospace are very high. For this reason, the question of whether recycled carbon fibers and matrix materials could ever be reused in virgin aerospace structures looms large. Nevertheless, recycled carbon fiber was valued at $50 per pound in 2012, and its recovery and reuse in other applications is economically feasible.[232]

In the near future, chemists should be researching in close collaboration with manufacturing engineers to monitor the products being optimized for aerospace-grade requirements. Despite the chemical solutions seeming accessible, their translation into defect-free composite formation is highly challenging as we also observe in our labs. Yet, we firmly believe that the future is full of opportunities and macromolecular materials will be spotted everywhere in aerospace-related fields: Aircraft on Earth, satellites orbiting Earth, and space shuttles performing planetary discoveries. It is not futuristic to dream of the role of polymers in space: self-healing CFRP space shuttles for long-range missions, CFRP-based structural batteries, photocatalytic structural composites, composites polymers synthesized in space, and polymers for the colonization of Mars?

Acknowledgements

The authors greatly acknowledge Delft University of Technology – Faculty of Aerospace Engineering and Department of Aerospace Structures and Materials for their continuous support.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

aircraft polymers, composite manufacturing, composite recycling, frontal polymerization, polymer composites, sustainable resins

Received: June 13, 2023
Revised: August 17, 2023
Published online:

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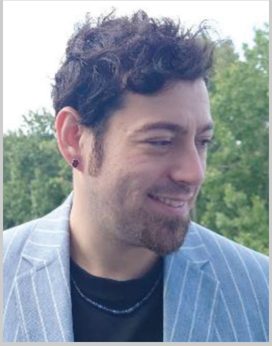

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