Multifunctionality in Epoxy Resins

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ABSTRACT: Epoxy resin will continue to be in the forefront of many thermoset applications due to its versatile properties. However, with advancement in manufacturing, changing societal outlook for the chemical industries and emerging technologies that disrupt conventional approaches to thermoset fabrication, there is a need for a multifunctional epoxy resin that is able to adapt to newer and robust requirements. Epoxy resins that behave both like a thermoplastic and a thermoset resin with better properties are now the norm in research and development. In this paper, we viewed multifunctionality in epoxy resins in terms of other desirable properties such as its toughness and flexibility, rapid curing potential, self-healing ability, reprocessability and recyclability, high temperature stability and conductivity, which other authors failed to recognize. These aspects, when considered in the synthesis and formulation of epoxy resins will be a radical advance for thermosetting polymers, with a lot of applications. Therefore, we present an overview of the recent finding as to pave the way for varied approaches towards multifunctional epoxy resins.

Keywords: Epoxy resin, conductivity, self-healing, reversibility and rapid curing.

Subject classification codes:

1. Introduction

Due to its versatility from chemical and processing perspectives, the utility of epoxy resins is ubiquitous in industries that require high performing materials. In the aviation and renewable energy sectors, epoxy resins are widely employed in fiber reinforced composites for the manufacture of structural parts of airplanes and wind turbines.[1–6] Epoxy resins are, to a large extent, utilized in more conventional applications such as engineering adhesives, coatings and paints as well as matrix for fabrication of electronic

parts in consideration of the resins' excellent adhesion strength and processability. Since its discovery, the use of epoxy resins had become prevalent in composite research and development. Its robustness is attributed to the ability to form three dimensional cross-linked networks upon reaction with suitable curatives, and it is this highly cross-linked structures that determines the thermal and mechanical properties of epoxy thermosets.[7, 8] Properties such as high modulus, high strength, good adhesion and high chemical resistance among others are desirable in many high-performance applications.

Ironically, a higher crosslinking density can also be a "downside" for epoxy thermosets which could lead to lower fracture toughness, loss of flexibility and difficulty in the recycling of processed materials.[9, 10] Moreover, the epoxy polymerization reaction is slow at ambient conditions and requires high polymerization enthalpies. Although epoxy resins can be stable in high temperature applications, new processes and application technologies necessitate pushing the benchmark further. In addition, the rapid automation and digitization in manufacturing especially of transformative composite material or smart structures requires epoxy resins to exhibit hybrid properties.[11] Highly desirable in aviation, automotive and rail vehicles, and shipbuilding industries, is an epoxy resin of higher toughness yet is flexible and mouldable; and in some of the automated processes rapid curing is essential.[12, 13] Fabrication of structural parts that are nearly or intended to be exposed in extreme physical and chemical conditions such as in automotive engines and rockets mandates an epoxy matrix of high temperature and chemical stability. In some niche markets where megastructures are manufactured in pieces, composite parts need to exhibit toughness and flexibility to withstand wear and tear during stages of manufacture. At some point during parts assembly, a thermoset composite maybe required to behave like

thermoplastics on demand, able to rapidly cure and re-cure in the automated settings. Evidently, in the era of smart materials and structures, epoxies still refuse to join the bandwagon, being already content with extrinsic modifications to suit for the purpose. This had limited its applicability in otherwise developing sensor- interfaced polymer products that require high sensitivity and provide real-time monitoring.[14, 15] Furthermore, epoxy based composite product, at the current age, is yet to promote a circular economy. As one of those robust polymers in the market, end-of-life epoxy composite products mostly show up in landfills where they are slow to degrade and, in the process, gradually wreaking havoc to both life and the environment. With its base monomers and other ingredients mostly derived from limited fossil reserves, it is now expedient that they be recovered and recycled.

Desirable as they are now, innovative approaches towards a multifunctional epoxy resin will need to be addressed by the scientific community in order to satisfy the requirements of our evolving manufacturing environment, to further its uptake on emerging technologies and surpass the current demands of our changing society. These among others, therefore, entails research work on multifunctional epoxy resins for advanced materials. The aim of this paper is to provide an overview on the scientific efforts carried out to identify suitable materials and processes that will satisfy the demanding properties of a multifunctional epoxy resin for varied applications.

2. Epoxy resins

In organic chemistry oxiranes are also referred to as epoxides. They are organic compounds in which an oxygen atom is bonded to two adjacent carbon atoms, forming a 3-membered ring. This three-membered ring in oxiranes is highly strained and readily opens even under mild conditions. Widely used in organic synthesis are 1,2-disubstituted products formed via ring opening from the addition of nucleophiles to

oxiranes. Ring opening is observed in neutral, basic and acidic media; however, the reaction is significantly accelerated in the presence of an acid.[16] Examples of nucleophiles include hydroxides, alkoxides, ammonia, primary and secondary amines, etc. Consequently, diepoxides are compounds containing two oxirane groups in a molecule, as in the case of diglycidyl ether of bisphenol-A, DGEBA **(Scheme 1a-3)**; and in chemical nomenclature the prefix epoxy indicates the epoxide as a substituent. The extra functional center in diepoxides gives rise to the formation of a networked structure during epoxy polymerization. Multi-epoxides, those containing more than two epoxy moieties also exist. The type of crosslinker used during polymerization will determine the final physical and mechanical property of the epoxy thermoset.

There is a plethora of epoxy compounds used in different applications; with the epoxy substituents attached to either aliphatic, cyclic or aromatic hydrocarbons. *DGEBA type resins*, the most common of which are synthesized from polyhydric compounds like bisphenol-A **(Scheme 1a-1)** and epichlorohydrin **(Scheme 1a-2)**. A miscellaneous collection of this well-known glycidyl ether resins which includes Bisphenol-F and Bisphenol-H are extensively used especially for processes that require low viscosity epoxy resins.
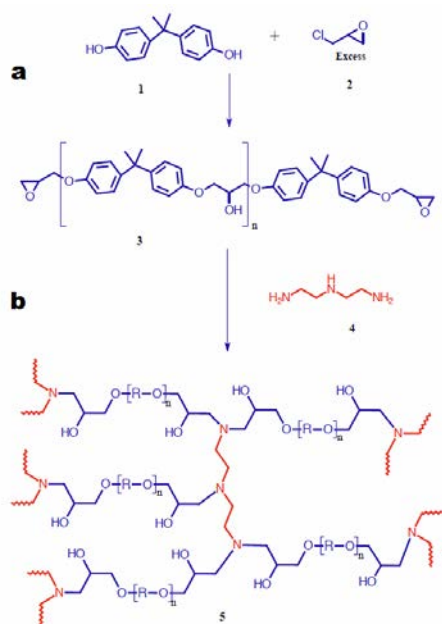
Scheme 1. Formation of a crosslinked epoxy network. (a) Synthesis of DGEBA from bisphenol-A and epichlorohydrin. (b) Polymerization using an amine as a crosslinker.

Phenoxy resins, classified as polyols or polyhydric ethers, have the same repeating units as advanced epoxy resins. They are thermoplastic polymers derived from bisphenols and epichlorohydrin.[17, 18] Epoxidized phenol novolac resins (EPN) came from the reaction product of epichlorohydrin and phenol/cresol-formaldehyde condensates while glycidylamine resins are from aliphatic/aromatic primary or secondary amines precursors that underwent glycidylation reactions.[19–21] Glycidylamines are reportedly stable products, especially if the substituent amine is aromatic or when highly substituted alkyl groups are used as precursors. Also, in existence are a class of non-glycidyl ether epoxides such as epoxidized diene polymers, epoxidized oils and polyglycol diepoxides; collectively termed as acyclic aliphatic non-glycidyl ether epoxides.[22–24] Cyclic aliphatic non-glycidyl ether epoxides ethers are typically based from vinyl cyclohexene dioxide or dicyclopentadiene dioxide.[25, 26]

We will encounter these epoxy compounds and their derivatives in the later sections of this paper.

The epoxy polymeric architecture brought about by the mechanism of its polymerization influences the mechanical properties of the bulk thermosets. Epoxy resins are typically cured in the presence of amines or anhydride in a step growth manner, and in some cases Lewis bases such as tertiary amine and imidazoles are also employed. Amine hardeners, for example in (Scheme 1b- 4), will react with epoxy groups forming a cross-linked network with pendant hydroxyl groups (Scheme 1b-5). At elevated temperature these hydroxyl groups can also react with epoxy rings especially at low amine concentrations. On the other hand, when acid anhydrides are used as curing agents, temperatures of as high as >200 °C are required for crosslinking and the mechanism is rather complex. It is proposed that the epoxy-acid anhydride crosslinking occurs via condensation of the anhydride with secondary alcohol of the epoxy monomer; with the resulting carboxylic acid further propagating the reaction by opening more epoxide rings forming new secondary alcohol moieties. Lewis bases are used either alone where they act as catalytic nucleophiles for epoxy homopolymerization, as catalysts for anhydrides or as co-curatives with primary amines and polyamides. In the absence of a proton, a tertiary amine, for instance will act as a nucleophile initiating the ring opening of the epoxide to form a zwitterion with the positive charge on the amine nitrogen stabilized by a hydroxyl anion. This hydroxyl anion can then open another epoxide ring to form a new anion that will propagate the polymerization. If weak proton donors such as alcohols are present, chain transfer will occur from the zwitterion. In cases where a stronger proton donor such as phenols and thiols are present, a proton is donated to the amine and the phenyl or thiyl anion serves as the nucleophile for the ring opening of epoxy groups. The choice of curing agents for

an epoxy resin rests on its intended application and taking into considerations its pot life, curing and ultimate physical and mechanical properties.

Since the 1940s, epoxy resins have been and continue to be among the most prevailing materials for applications such as in paints and coatings, adhesives, electronic parts, composites and structural components. Recent literature on epoxy structure, synthesis, including its synthetic modification, the use of bio-epoxy resin precursors, and its applications had been published extensively with some delved-on advances in natural fiber-based epoxy composites and nanocomposites research, and others include discussions on manufacturing techniques and their industrial applications.[27–32] With the expansion of knowledge on polymeric behavior, new synthetic methodologies and novel application techniques, the employment of epoxy resins in industry and exploration in research will consequently progress further.

3. Recent development in multifunctional epoxy resins

The quest for a multifunctional epoxy resin is an emerging field of research, brought about by the rapid automation and digitization of the manufacturing processes, the need for more robust and smart materials in high performance engineering, and the emergence of unprecedented technological breakthroughs in all sectors of the polymer industry. As epoxy resins are increasingly adopted by composite manufacturers, encumbrances in their uptake in non-traditional composite fabrication may be addressed by making conventional epoxy resins multifunctional either through chemical modification or manipulation of thermoset formulations to tailored properties. As all other polymers, epoxy resins even in some niche application still suffer from issues of brittleness, slow cure, non-recyclability, and temperature stability amongst others. Those skilled in the art have employed intrinsically tuning the epoxy polymer in such a

way where various groups within the polymer network reactively associate to induce toughness and flexibility. Some utilized rapid bond exchange reactions (BER) which enable the material to reform and deform so as to reshape, rework, repair fractures and at some stages recover valuable starting materials.[33–36] In some other approaches, intermolecular interactions that permits lower activation energies for the epoxy polymerization were explored for such purpose. Some researchers even go to extreme lengths of synthesizing new epoxy monomers and oligomers with tailored multifunctional properties.[37–39] The succeeding pages present some of these advances towards creating multifunctional epoxy resins.

## 3.1 Toughness enhanced resins

It has been accepted for some time that a thermally cured epoxy resin is inherently brittle, and this has actively engaged researchers in advancing the case for a multifunctional epoxy resin possessing the desirable properties of both thermosets and thermoplastic polymers. In the recent past, toughness enhanced epoxy resins had been largely accomplished by using extrinsic modifiers made of nanoparticles of organic and inorganic origins. A review on improving the fracture toughness and the strength of epoxy using nanomaterials have been published by Domun et.al.[40] They have elucidated the toughening effect of using nanoparticles such as carbon nanotubes (CNT), graphene, nanoclay and nanosilica as reinforcement to the epoxy matrix. Other materials such as titanium dioxide, nanosilica-rubber core-shell particles, phase separating rubber particles, silica and/or polysiloxane-rubber core-shell particles in a reactive diluent were also found to have a toughening effect in reinforced epoxy nanocomposites.[41–47] Other tougheners such as hyperbranched polymers which do not form non-phase separated networks and can still improve the glass transition temperature (T_g), toughness and mechanical properties were also reported.[48]

Toughness and stiffness enhancement resulting from the synergistic effect of the rigid aromatic rings and the flexible ether linkages in the epoxy backbone were also reported and found to have not compromised the thermal and mechanical properties of thermosets; paving the way for synthesis of monomers containing such modifications.[49, 50] The effect of crystalline domains in the polymer chains as well as the effect of liquid crystal mesogens in the backbone of polymers also showed improvements in toughness and on other mechanical properties in epoxy resins.[51, 52] In categorizing different ways of toughening epoxy resins, the succeeding approaches can fall in any of the following categories: (1) in sub-atomic level (modifying the molecules and using additives or micelles), (2) atomic level (crystalline structures and short-range vs. long-range order), and (3) microscopic level (introducing fibers to make isotropic vs. anisotropic composites).

Studies on the efficacy of reactive block copolymers are progressing. Both non-reactive and reactive copolymer modifiers can be employed as toughening agents for epoxy resins. It was reported that the advantage of non-reactive copolymers rest on its morphology adoption. Perez et.al observed that when a non-reactive polymer adopts a vesicular morphology, significant improvement in toughness is attained than when it underwent a micellar conformation. For both reactive and non-reactive copolymers, adoption of a wormlike micelles' morphology affords better toughness. Their review which examined the comparative studies between non-reactive and reactive inclusions suggested that reactive vesicles whereby the blocks are chemically bonded to the matrix provide better toughness than non-reactive ones.[53]

To improve the toughness of epoxy thermosets, He et.al, incorporated a tailored reactive tetrablock copolymer, poly[styrene-*alt*-(maleic anhydride)]-*block*-polystyrene-*block*-poly(*n*-butyl acrylate)-*block*-polystyrene in the DGEBA based epoxy

formulation.[54] They found out that a 10 wt% addition of this block copolymer improved the toughness of the thermoset, imparting close to a 70% increase in critical stress field intensity factor (K_{IC}). In another study the same researchers showed that addition of reactive core-shell nanoparticles, poly[styrene-*alt*-(maleic acid)]-*block*-polystyrene-*block*-poly(*n*-butyl acrylate), led to 142% increase in K_{IC}. They first prepared emulsified styrene maleic anhydride polymer by way of reversible addition fragmentation chain transfer (RAFT) polymerization mediated by macro RAFT agent as in shown in **(Scheme 2)**. The obtained emulsion was then reacted with n-butyl acrylate, resulting to a diblock copolymer with a dual layer core shell particle. This was then further modified by reacting with ethylene glycol dimethacrylate (EGDMA), forming a triblock copolymer with a three-layer core shell particle. When mixed with a DGEBA based epoxy resin and diaminodiphenylmethane in stoichiometric amounts, this reactive core shell triblock assembles by itself into micelles similar to the core-shell particles of latex, and the aggregates remain stable until the formation of crosslinks.[55]
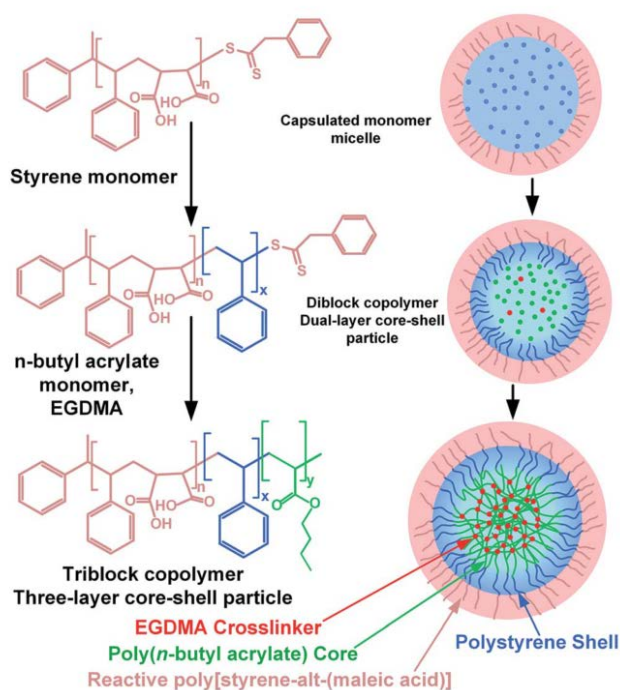
Scheme 2. An illustration of the synthesis of core-shell nanoparticles and the micellar self-assembly of reactive block copolymers. Adapted from Reference[55] with permission from the Royal Society of Chemistry.

The innovative reactive blending work of He and his group provides an insight on developing toughened epoxy thermosets utilized for both high and low fracture rates.[56] With the introduction of a new family of reactive block copolymer, poly[styrene-*alt*-(maleic anhydride)]-*block*-polystyrene-*block*-poly(*n*-butyl acrylate)-*block*-polystyrene, with different reactivity in epoxy blends, they were able to control the inclusion size of reactive block copolymer in cured blends from nanometer to micrometer by simply adjusting the fraction of the reactive block in reactive block copolymer. The systematic study on the structure-property relationship revealed that the thermal and mechanical properties of modified blends strongly depend on inclusion size.

Francis and Baby, on the other hand, synthesized a novel polystyrene-*block*-polyisoprene star polymer via photochemical reversible addition fragmentation chain transfer (RAFT) polymerization which was subsequently epoxidized using *m*-chloroperbenzoic acid.[57] This was then used as a reactive toughening agent with epoxy thermoset. Addition of this reactive block copolymer formed sphere-like nanostructures before crosslinking. This led to an increase in the tensile strength and toughness of the thermoset. Garate et.al, also used a derivatized poly(styrene-*b*-isoprene) block copolymers (eSIS-AEP) containing an epoxy miscible block as a toughening agent in epoxy thermosets.[58] Derivatization was accomplished through a controlled epoxidation of the olefinic bonds followed by partial ring opening of the oxirane ring using *1*-(*2*-aminoethyl) piperazine as the amine reactive group[59]. This derivatized block copolymer can crosslink together with a DGEBA based epoxy resin,

Epikote 828, and Ancamine 2500; with the mixture forming nanostructured materials with spherelike nanodomains before curing as is illustrated in **(Scheme 3)**. This ability to control the nanodomain morphology, using reactive diblock copolymers, is important in modulating the mechanical properties of the crosslinked matrix.
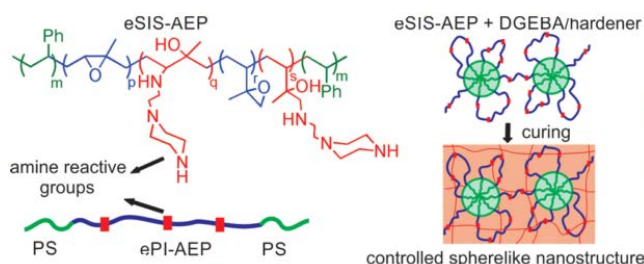
Scheme 3. An illustration of the formation of sphere-like nanostructures using reactive block copolymers. Adapted with permission from Reference[58] Copyright (2014) American Chemical Society.

Belmonte et.al used hyperstar polymers with poly-methylmethacrylate and poly-hydroxyethylmethacrylate block copolymers of different degrees of polymerization on the arms and studied its effects on the anionic curing process of cycloaliphatic epoxy anhydride thermosets.[60] These hyperstar polymers consist of hyperbranched aromatic polyester core from the polycondensation of *4,4-bis*[*4′*-hydroxyphenyl] valeric acid. This core was further functionalized with methylmethacrylate initially, and then with protected hydroxyethylmethacrylate, which is then deprotected for subsequent reaction. They found out that when mixed with a cycloaliphatic diepoxide, UVR-6105 from Dow, hydrophthalic anhydride and catalytic amount of 1-methylimidazole, the hyperstar polymers participate in the curing reaction without compromising the thermal-mechanical properties of thermosets obtained. The potential of this hyperstar polymers as a toughening agent for epoxy thermosets is due to the formation of nanograined morphology. Morell and co-workers also used multi-arm star copolymers to toughen

DGEBA based epoxy thermosets.[61] The star copolymers were prepared from a hyperbranched poly(glycidol-b-poly(ε-caprolactone) of different arm lengths, synthesized via cationic ring-opening polymerization. The addition of this block copolymer to an epoxy thermoset formulation had a slight retardation on curing, a decrease in the overall shrinkage and an increase of conversion at gelation. A 5 wt% addition of the block copolymer led to viscosity reduction when compared to the neat formulation, suggesting that it is a good rheological agent during processing. Although the Tg was found to be lower than neat formulation, the values obtained are still higher for practical applications. The materials obtained from this star copolymers could also be considered as thermally reworkable thermosets.

In the past, other authors have utilized the toughening effect of reactive diblock or triblock copolymers with epoxy thermosets. Yi and co-workers used poly(*2,2,2,*-trifluoroethyl acrylate)-*block*-poly(glycidyl methacrylate) copolymer, obtained by sequential RAFT polymerization with 2-phenyl-propyldithiobenzoate as a chain transfer reagent.[62] A highly ordered poly(dimethyl siloxane)-poly(glycidylmethacrylate) reactive diblock was also utilized by our research group.[63] Xu and co-workers synthesized a polystyrene-*b*-poly(glycidyl methacrylate) via atom transfer radical polymerization (ATRP).[64] Guo et.al, prepared epoxy thermoset blends with polyisoprene-*b*-poly(4-vinylpyridine) for the same purpose.[65]

The use of ionic liquids (IL) including polymeric ionic liquids as a toughening agent is a recent undertaking. Ionic liquids are molten salts with a bulky organic cation stabilized by an organic or inorganic anion and its use in synthetic organic, polymer and electrochemistry are well known.[66, 67] They are known to possess excellent thermal stability, good ionic conductivity, low saturated vapor pressure, and inflammability. It is

for these reasons that ionic liquids find great utility as a component in many composite products.

A work by Chen and his team demonstrated the toughening effect of hyperbranched polymeric ionic liquid **(Fig. 1a-6)** in benzoxazine-epoxy thermoset systems.[68] Benzoxazine can polymerize through a ring opening reaction to form condensed phenolic structures and the addition of an epoxy component improves its fracture toughness. The benzoxazine component was obtained from a bisphenol-F benzoxazine and the epoxy component was derived from *3,4*-epoxycyclohexylmethyl-*3,4*-epoxycyclohexanecarboxylate. The hyperbranched polymeric ionic liquids were synthesized employing click chemistry reaction between thiol-ended hyperbranched polyesters. When these polymeric ionic liquids were mixed with the benzoxazine-epoxy system, they found out that the polymeric liquids had a toughening effect on the resulting composites attributed to in-situ toughening mechanisms. The main improvements of toughness hinge on the increased free volumes resulting from the intramolecular cavities of hyperbranched polymers, enabling more impact energy to be absorbed. Apart from the improvement of strength and thermal properties, it was observed to have decreased the overall curing temperature of the composites with the polymeric ionic liquids acting as catalyst for both ring opening reaction of benzoxazine and the consequential crosslinking of the epoxide moieties. The study showed that the optimal composition sits around 3 wt. % of the hyperbranched polymeric ionic liquids mixed with equal amounts of benzoxazine-epoxy components when compared with neat resins.

While on a search for a bio-based replacement for a DGEBA based epoxy system, Nguyen's team synthesized epoxy networks using hydrophobic phosphonium-based ionic liquids combined with dicyanamide and phosphinate counteranions as

initiators of epoxy prepolymerization.[69] Initially, they studied the catalytic effect of ionic liquids by homogeneously mixing stoichiometric amounts of Cardolite NC5014, a biobased epoxy prepolymer derived from Cardanol, with ionic liquid [HDP] [DCA] **(Fig. 1b-7)** or [HDP] [TMP] **(Fig. 1b-8)** at 10 parts per hundred resin or with Jeffamine D230. Results showed that these ionic liquids displayed high reactivity toward cardanol-based epoxy prepolymers, with the biobased epoxy/IL networks highlighting a glass transition temperature of around 30 °C, an excellent thermal stability higher than 450 °C and higher hydrophobic behavior when compared to biobased epoxy−amine networks. The second part of their work deals with the study of the effect of Cardolite incorporation in the properties of epoxy networks. They prepared Cardolite-modified epoxy systems by adding 10 phr of Cardolite in the mixture of DGEBA and curing agent (Jeffamine D230 or ionic liquids) at room temperature. They found out that the use of Cardolite as a modifier of epoxy/ phosphonium ionic liquids networks led to a very low surface energy as well as increased fracture toughness (+180%). Previously, similar authors have also used phosphonium based ionic liquids combined with phosphinate, carboxylate, and phosphate counter anions to synthesize epoxy networks. They investigated the influence of the chemical nature of the anions on the polymerization kinetics of epoxy systems as well as the thermal and mechanical properties of epoxy-ionic liquid networks. They observed that in all cases the ionic liquids displayed a high reactivity toward epoxy pre-polymer which led to poly-epoxy networks with up to 90% epoxy group conversion.[70] The work of Leclere shows almost similar results, when they used ionic liquids [HDP] [TMP] and [HDP] [DCA] as reactive additives within epoxy/amine networks.[71]
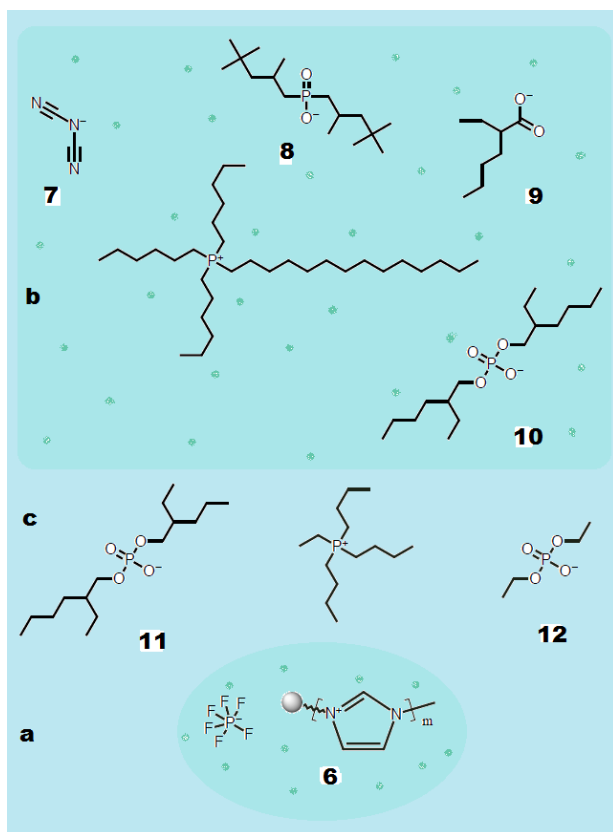
Figure. 1. Structures of common ionic liquids used with epoxy resin. (a) A polymeric ionic liquid. (b,c) Phosphonium based ionic liquids.

In a different study Nguyen et.al, achieved full distribution of commercial core-shell rubber particles (CSR) such as Genioperl P52 into epoxy/ionic liquid networks, leading to an increase in fracture toughness compared to modified epoxy/amine networks. The phosphonium based ionic liquids they used were [HDP] [TMP] and [BEP] [DEP] **(Fig. 1c-11)**. Results showed that a 54% improvement in K_{IC} was obtained for DGEBA/[BEP] [DEP] system as compared to 27% higher for a DGEBA/MCDEA, with both systems modified by 20 phr of CSR particles. Nevertheless, the toughening mechanism can also be influenced by the interaction between cured epoxy matrix and CSR particles.[72]

3.2 Flexible and formable resins

Epoxy polymers often praised for its superior mechanical properties and chemical resistance; however, these materials do not behave like thermoplastics polymers as they cannot be easily reshaped once crosslinking has been initiated. Developing novel methods for a multifunctional epoxy resin to make crosslinked networks reversible on demand permits a composite material to be reshaped, reworked or recycled at all stages of its manufacture, service and end of life. To achieve this, the concept of *covalent adaptable network (CAN)* had been employed by researchers in the modification of epoxy resins with tailored properties such as reworkability and recyclability of its otherwise highly crosslinked morphology. The presence of covalent adaptable bonds in an epoxy resin will enable it to exhibit dynamic behavior after failure. Triggered by stimuli such as light, irradiation or changes in temperatures, bond breakage and reformation can occur in some fractions of covalent bonds in the epoxy network with disulphide linkages, siloxane and radical moieties, and those forming Diels-Alder (DA) adducts. As illustrated in **Figure 2**, network integrity and mechanical property are maintained in covalent adaptable network during BER.[73] Since the introduction of a third class of polymers by Liebler and co-workers, known as vitrimers, more research have surfaced to advance the reworkability and self-healing behavior of epoxy thermosets. Vitrimers are cross-linked polymer networks containing linkages that undergo thermally activated, associative exchange reactions, such that the cross-link density and overall network connectivity are preserved. In a kinetic and viscoelastic study of fatty acid cured epoxy vitrimers, double relaxation behavior was also observed. However, it was not confirmed whether this double behavior is a universal fingerprint for vitrimers.[74] Recently, vitrimers have also been successful employed in the development of non-epoxy polymers such as hydroxyl-functionalized polycarbonate

networks, liquid crystalline elastomers (LCE), multi-responsive oligo-aniline smart polymers and some polyurethane based thermosets.[75–78]
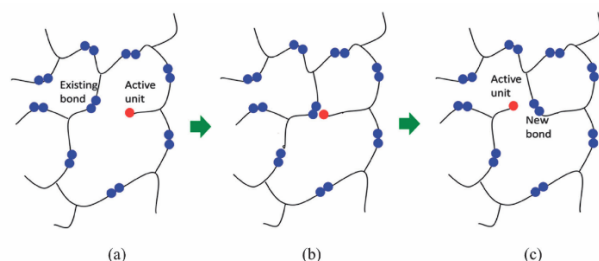

Figure 2. An illustration of network rearrangement with covalent adaptable networks. (a) Prior to bond exchange reactions, where an active unit attaches to an existing bond. **(b)** Formation of a metastable tertiary structure, leading to one unit being kicked off. **(c)** Post bond exchange, where a new bond and active unit is formed. Adapted from Reference[73] with permission from the Royal Society of Chemistry.

In a work by Montarnal et.al, they produced epoxy resin formulation by reacting a 1:1 ratio of a DGEBA with a mixture of dicarboxylic and tricarboxylic acids using zinc acetate as catalyst.[33] The cross-linked product exhibited elastomeric behavior at room temperature with a modulus of about 4 MPa, elongation of 180% and stress at break of 9 MPa. The product is insoluble in tricholorobenzene even when heated for a long time. It can also be reprocessed by injection moulding after curing as the polymer is flexible and malleable enough to make recycled materials having the same mechanical and solubility properties as the original resin system at these processing temperatures. They showcased this viscoelastic behavior and suitability for reprocessing via injection moulding using 1:1 formulation of DGEBA and glutaric anhydride catalyzed with zinc acetylacetonate. The work of Altuna et.al achieved a 63% stress relaxation in less than 1 hour at 160 °C with their vitrimeric formulations out of DGEBA and carboxylic acids such as citric acid (CA), sebacic acid (SA) and glutaric acid (GA), with imidazole as catalyst.[34] An epoxy formulation mixture of CA with

SA, used in **(Fig. 3)**, was noted for reducing excess epoxy while maintaining a high *Tg* value and faster stress relaxation. Formulations that exhibited good shape fixity and shape recovery ratios can be used to create different permanent and temporary shapes on thermosets.
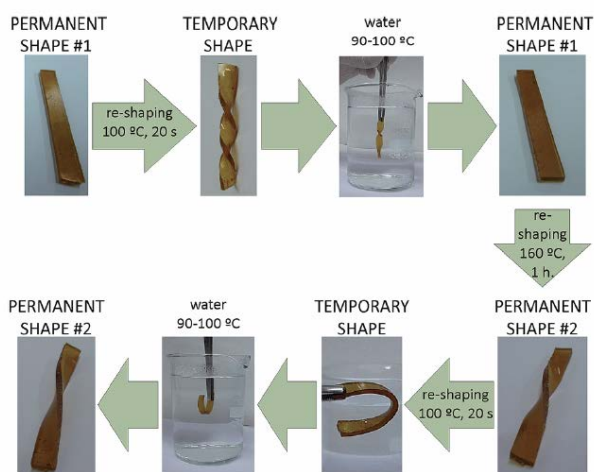

Figure 3. A qualitative assessment of shape memory and permanent shape changing for epoxy vitrimer cross-linked with (CA) + (SA). Adapted from Reference[34] with permission from the Royal Society of Chemistry.

One of the most trailblazing application of ionic liquids, apart as a toughening agent, is the inducement of flexibility in inherently stiff, highly cross-linked epoxy networks. Our team had for the first-time prepared graphene-based nanocomposite with epoxy thermosets that is flexible at room temperature.[79] We used an ionic liquid, *1-butyl-3*-methylimidazolium chloride ([BMIM] [Cl]), to induce flexibility in the thermoset structure. Functional groups on the cross-linked epoxy forms charge transfer complexes with the ionic liquid ions that can break and reform when external forces are applied, resulting to the observed flexibility of the material at room temperature. Based on results of our previous work, crosslinkable epoxy systems that behave like a hard and brittle thermoset, perfectly ductile thermoplastic and an elastomer can be achieved

through controllable network compositions facilitated by ionic liquids.[80] Illustrated in

Figure 4, this work may pave the way for manufactures of high-performance

nanocomposite materials based on graphene and epoxy thermosets. In another first, we

demonstrated the use of the same ionic liquid as solvent for two non-compatible

polymers, epoxy resin and cellulose.[81] It is known that due to the preferential intra-

molecular bonds within epoxy and within cellulose molecules, neither polymer will mix

together. The ionic liquid disrupts these intramolecular bonds and facilitates

intermolecular bonding between these otherwise incompatible polymers resulting to

dissolution. During cure, the ionic liquid is incorporated within the thermoset and these

bridging bonds of the ionic liquid gives flexibility to the polymer network. We found

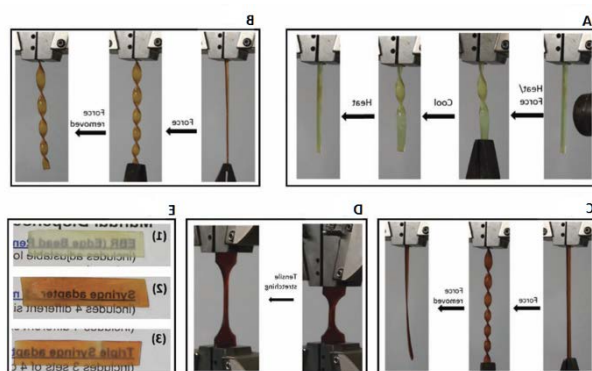out that cellulose addition improves the tensile mechanical properties of epoxy.

Figure 4. Inducement of flexibility in epoxy thermoset using ionic liquids. Adapted
from Reference[80] with permission from The Royal Society of Chemistry. (a)
Reversible bending and twisting on application of heat and force with retention of the
original shape on cooling. (b) Bending and twisting at room temperature after
application of small force with retention of new shape even after removal of force. (c)
Bending and twisting after application of small force with retention of original shape
after removal of force. (d) Elastomeric thermoset before and after 280% elongation. (e)
Thermoset transparency (1) hard thermoset at 10% IL (2) plastic thermoset at 30% IL
(3) elastomeric thermoset at 50% IL.

The work of Soares and Alves showed that both CNT and ionic liquids can accelerate the curing process of an epoxy matrix treated with a polyetheramine, Jeffamine D230.[82] Nanostructuration is due to the covalent interaction between the functionalized rubber and the epoxy resin, resulting in material with outstanding thermo-mechanical and adhesion properties as compared to neat resins. In this work, isocyanate-modified polybutadiene (PBNCO) was first functionalised by reacting the hydroxyl terminated polybutadiene with toluene diisocyanate, in an NCO/OH molar ratio of 2.82 under the catalytic action of dibutyltin dioctoate for 2 hours at 70 °C in nitrogen atmosphere. An epoxy resin is then pre-reacted with this PBNCO in 100:10 w/w for 4 hours at 70 °C under nitrogen, to form a triblock copolymer. To achieve different amounts of CNT in the nanocomposite, an epoxy-based masterbatch, containing 6 wt % of CNT was diluted with the triblock copolymer in acetone (triblock copolymer/acetone= 51:2 w/w). After sonicating the mixture at room temperature for 30 min and 135 W, an ionic liquid, *1*-butyl-*3*-methylimidazolium tetrafluoroborate ([BMIM] [BF_4]) was added only to samples studying the effect of this ionic liquid. The acetone and bubbles were removed at 80 °C, under vacuum for 24 hours. These were then cured with Jeffamine D230. Results indicate that prior processing of CNT in the form of masterbatch disperses the nanofiller well within the rubber-modified epoxy matrix, resulting to nanocomposites with higher modulus and outstanding adhesion properties. Addition of this ionic liquid improved the electrical properties, consequently decreasing the *Tg*, modulus and adhesion properties as the ionic liquid acts as a plasticizer as well as effecting a decrease on the degree of crosslinking of the network. The use of ionic liquid provides a way to the development of conducting adhesive for antistatic purpose, with further work need to counter the effect of impaired adhesion due to its known lubricating effect.

Saurin and Bermudez also demonstrated that a conventional epoxy resin can be modified with ionic liquids yielding softer, more ductile materials with self-healing ability for surface abrasion damage.[83] They studied the abrasion resistance of Ampreg 22, a conventional epoxy resin from SP Systems, containing a 9 wt % of *1*-octyl-*3*-methylimidazolium tetrafluoroborate ([OMIM] [BF$_4$]) as the ionic liquid. Soares et.al confirmed the plasticizing effect of ionic liquids when he studied different ionic liquids based on tetraalkylphosphonium cations such as [HDP] [DCA], [HDP] [FSI], and [BDP] [DBS] with epoxy resin (EPON 828) cured with poly(propyleneglycol)-*bis*(*2*-aminopropyl ether).[84]

3.3 Rapid cure resins

Normally, the epoxy polymerization is a slow process and takes a long time to full cure. In many cases, heating to higher temperatures is needed. In their continued search for a rapid curing system, researches started with initially using catalyst to hasten curing at ambient to elevated temperatures, which oftentimes led to poor shelf life. A faster than normal curing at an elevated temperature were accomplished with the use of latent curing catalysts. Latent curing agents are a compromise between highly reactive curatives at room temperature such as imidazoles or thiols, and those that require high temperatures such as anhydrides or phenols. Zhang and co-workers have explored the application of polybenzoxazines as thermal latent curing agent for epoxy resins.[85] They proved that in polybenzoxazines, the reactive hydroxyl group is locked in deep intramolecular hydrogen bonding, which is disrupted only at elevated temperature, releasing the active hydroxyl group for reaction with epoxides. After cure, the afforded copolymers of epoxy and polybenzoxazines results to enhanced properties. Kudo et.al exploited derivatives of *2*-(*2*-hydroxyphenyl) imidazoles with restrained nucleophilicity towards epoxy groups by locking the phenolic hydroxyl group and the nitrogen atom of

the imidazole ring in hydrogen bonding.[86] This H-bonding is broken thermally around 150 °C where the active imidazole initiates the curing reaction. The epoxy resin composition with these latent thermal catalysts exhibited long term storage stability at room temperature. The base catalyzed cure reaction of epoxy-thiol is rapid at room temperature. Hence Konuray et.al employed a triazabicyclodecene tetraphenylborate (TBD·HBPh$_4$) as a photobase (PB) generator during curing of Epikote 828 with pentaerythrithol-*tetrakis*(*3*-mercaptopropionate).[87] The PB is activated either thermally or by UV light whereby it releases the reactive *1,5,7*-triazabicyclo[4.4.0]dec-5-ene (TBD) to form thiolate anions responsible for the ring opening of epoxides. Depending on the catalytic system, they observed that the rate of the thiol-epoxy reaction was in the following order: Neat base > UV activated PB > thermally activated PB > uncatalyzed system. The predictions of their kinetic study fit well with actual storage behavior at room temperature of systems under study. Whilst the main objective of the research work of Nikafshar and co-workers is to find a suitable bio-based substitute for DGEBA in epoxy formulations that can compete comparatively with DGEBA system, they were also able to speed up the reaction of their vanillin derived epoxy resin by using an accelerator.[88] The accelerator was obtained from the reaction of calcium carbonate and nitric acid to form a green solution of calcium nitrate. The vanillin derived epoxy resin, however, was obtained via Dakin oxidation, converting all the ketone and aldehyde groups of vanillin to methoxyhydroquinone which was subsequently epoxidated. Results showed that mechanical properties of the bio-based vanillin derived epoxy resin were enhanced, and the curing reaction was accelerated with the use of the calcium nitrate accelerator. Using the inorganic accelerator at 2 wt% loadings, the tensile strength increased to about 3% and about 8% for the Izod impact strength. These were higher than those for a DGEBA system. In previous sections, ionic

liquids were also shown to catalyze the polymerization of epoxy resins. Silva and co-workers were the first to use an ionic liquid, [HDP] [TMP], commercially known as CYPHOS® IL104, as catalytic curative for DGEBA based epoxy formulations.[89] They found out that [HDP] [TMP] is able to cure the epoxy prepolymer EPON 828 even at low amounts of 2.5 phr of ionic liquids. With the novel single step room temperature ionic liquid preparation strategy of the group of Throckmorton, they have demonstrated that [EMIM] [DCA] can be used both as dispersing agent and curative for EPON 828 reinforced with silica nanoparticles, SWCNT and graphite nanoplatelets.[90] Similar findings were observed by Maka and co-workers when they used [HDP] [TMP] in their work. Apart from its dispersion capacity and catalytic activity, [HDP] [TMP] was also found to exhibit flame retarding capacity.[91] To initiate cure of epoxy composites modified with hemp fibers, Xu and co-workers also took advantage of the heat release during the exothermic reaction between *4,4'*-diaminodiphenylmethane (DDM) and acrylic acid (AA) to produce acrylamide, which in turn further reacted with DDM via Michael addition reaction.[92] Although complete curing occurred after 3 hours, hence, may not be considered as a rapid cure system, this novel approach made it feasible for a shorter than normal epoxy curing time at ambient condition. Results of composite blends reinforced with alkaline treated short natural hemp fibers fabricated using this approach showed that the tensile strength of the composites increases with an increase of the fiber content, and the elongation at break decreases. An increase of about 233% in impact strength, 52% in flexural modulus, and 213% in Young's modulus were recorded for the cured composite having 7.5 wt. % fiber content as compared to a neat cured epoxy resin.

Rapid curing epoxy resins, until now, are still uncommon, although they are called for in industries that produce high-volume composite structures to shorten the

required production time. Manufacturers are currently focused on improving their processes to effect this rapid cure systems rather than on modifying epoxy resins to having lower polymerization enthalpies. For instance, the research group of Odom knew that carbon nanotubes can heat up rapidly under the influence of microwave radiation. They took advantage of this property to effect rapid curing in epoxy thermosets modified with 5 wt% of multi-walled carbon nanotubes (MWCNT's). They have demonstrated that it is possible to use a scanning microwave technique in the rapid curing of carbon modified epoxy thermosets.[93] This approach provides not only an increase in cure rate but also uniform cure with respect to conductivity and composition when compared with a conventional oven and an oven under a forced thermal gradient. They also developed a novel deposition-and-scan technique for additive manufacturing of *3D* print aerospace and other industrial parts. This technique could also be employed to thermoset processing that have previously been difficult to manufacture using conventional methods. Yang and co-workers dispersed MWCNTs into an epoxy vitrimer and achieved welding epoxy materials by light with remote and spatial control within seconds or minutes depending on the CNT loadings.[94] The vitrimer was synthesized by reacting DGEBA with adipic acid in the presence of triazobicyclodecene as catalyst for transesterification and used PIM 1, a polymer of intrinsic microporosity, as dispersing agent. The photothermal effect of dispersed CNTs easily increased the local temperature to above 230 °C enabling welding. In the absence of CNT, the sample could not be welded at all even after 5 minutes. An illustration of these findings is given in **Figure 5**. They also found out that CNT vitrimers can be photo welded with common epoxy or even thermoplastics. Such an approach showcases a multifunctional epoxy that can rapidly cure while exhibiting flexibility and toughness as in Sections 3.1

and 3.2 and can also be used for in situ joining or repair of epoxy network as in Section 3.5
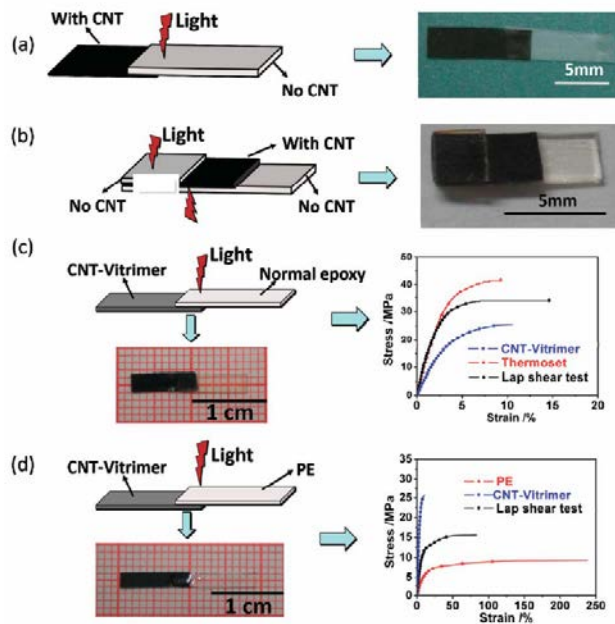

Figure 5. An illustration of the photo welding approach by Yang et.al. Adopted from Reference[94] with permission from The Royal Society of Chemistry. **(a)** Joining non-CNT vitrimer with CNT-vitrimer. **(b)** Joining two pieces of non-CNT vitrimer using CNT vitrimer as an adhesive. **(c)** Joining normal epoxy with CNT-vitrimer. **(d)** Joining thermoplastic PE with CNT-vitrimer.

Method of blending of epoxy resin with other resins that can cure rapidly was also employed. The rapid UV-assisted *3D* printing work of Griffini's group utilized a photo-curable acrylic resin with a thermo-curable epoxy as matrix for the fabrication of carbon-fiber reinforced (CFR) composite structures.[95] The photo-curable acrylic resin is a stock solution of bisphenol-A ethoxylate diacrylate (SR349), doped with 3 wt% of photo initiator *2,4,6*-trimethylbenzoylphenyl phosphinate (Irgacure TPO-L) while the thermo-curable epoxy was a premix of bisphenol-A diglycidylether, *1,1*-dimethyl, *3-(3', 4'*-dichlorophenyl)urea or Diuron™ as an accelerator and dicyandiamide (DICY) as the hardener. The formulation was blended in a 1:1 weight ratio with fumed silica as

rheology modifier and reinforced with carbon fibers, then *3D* printed in a thermal cycle of 220 °C for 20 minutes in a ventilated oven. This new dual cure system further advances the technology of additive manufacturing. The work of Shi et.al, [36] on recyclable *3D* printing of vitrimer epoxy, discussed in detail in Section 3.4, is similarly a rapid curing process.

Joosten et.al, who investigated and characterized interlaminar fatigue caused by residual stresses on epoxy composites, utilized the rapid reaction between epoxy and anhydride moieties.[96] They employed a system comprising of a cyclohexylmethyl-*3,4*-epoxy-cyclohexane carboxylate, bi-functional cycloaliphatic epoxy infusion resin with an anhydride hardener and imidazole catalyst in their laminate manufacture. Initial cure for each composite laminate was carried out using the Resin Transfer Moulding (RTM) process. A recent development in high-throughput automotive composite parts fabrication was made possible by the work of Wang et.al where they employed a one component, fast curing epoxy formulation using *1*-(*2*-cyanoethyl)-*2*-ethyl-*4*-methylimidazole as hardener.[97] CFRP's were prepared using this formulation via vacuum-assisted resin infusion process and cured for 30 minutes at 120 °C. The latency of the hardener, resulting to a longer pot life at lower temperatures was attributed to the electron withdrawing effects and perhaps from the steric hindrance of the bulky cyano group. The mechanical properties of CFRP composites out of this system were tested to be superior to that of current commercial product.

Kinetic studies on epoxy polymerization have been reported,[98–100] and other researchers deemed microwave curing to be advantageous.[35, 101, 102]. Johnston et. al. observed higher curing rates with no change in glass transition temperature (*Tg*) using microwave energy as compared to conventional thermal process. At any given temperature under *Tg*, they found that microwave cured samples have similar ageing

properties as conventionally cured samples.[35] Photo-curing affords ambient temperature cure and control over where and when the polymer cures. The applications of photo-curing are limited by a complete understanding of the photo-polymerization process, with the main drawback being inhibition by oxygen. The kinetics of a photo-curable epoxy polymer used in stereolithography was studied by Martin et.al, where the kinetics model includes the dependency of the rate of cure on the light intensity and cure state.[103] Although, kinetic studies and models exist for many simple epoxy systems, the methodology presented above will still require full kinetic evaluation, as they begin to show complexity in their approach and use more complex additives that can affect curing behaviour. One such complexity, as for example, is a rapid curing system that involved BER, where in the interfacial kinetics must also be considered. Characterization of BER kinetics using temperature dependent stress relaxation tests were already reported.[104, 105] Furthermore, research on the kinetics of materials applicable to additive manufacturing requires attention.

3.4 Recyclable resins

Tuning a dynamic epoxy polymer backbone, which is currently a progressing field of study, transcends simple thermoset processing as it also has ramification on its infinite recyclability and re-use. As regulations become ever more stringent and with the cost of synthetic materials skyrocketing because of dependence on limited fossil fuels, the development of recyclable resins is now expedient. The various chemistries and approaches of producing degradable, self-healing polymers have been reviewed by many authors with some of the methodologies also pertain to epoxy thermosets.[106–109]

The utility of vitrimers in making recyclable polymers hinge on their behavior as conventional thermosets below the T_g and the ability to initiate flow at the transition

temperature for topology rearrangement, *Tv*, via BER especially when *Tv* > *Tg*. In the case of epoxy vitrimers, trans-esterification reactions are responsible for this behavior that enables not only recycling but also flow, thermoforming, stress relaxation and self-healing. With epoxy systems, this bond exchange is presented in **Figure 6**. However, these transesterification rates are still inadequate for many practical applications as they occur at rather high temperatures. The effect of trans-esterification reactions on the evolution of the cross-linked epoxy network has been elucidated in detail by Altuna et.al.[110] Their statistical analyses can be used as a model on how polyfunctional monomers behave in trans-esterification reactions so as to affect network structure during BER. Zhang and Xu were able to considerably drop the *Tv* of their epoxy vitrimer, hence lowering the transesterification temperature through doping with a conductive polymer wrapped carbon nanotubes. The polypyrrole/CNT dopant had also increased the conductivity of the epoxy vitrimer.[111]
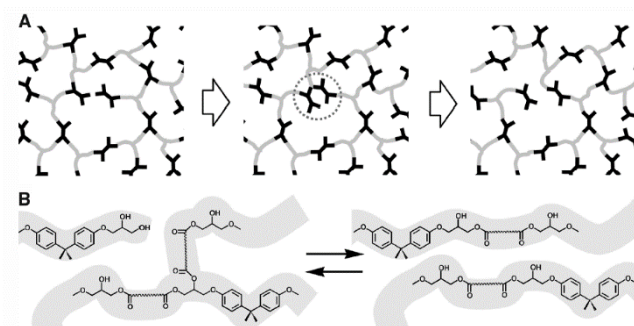

Figure 6. An illustration of bond breaking and reforming during trans-esterification reaction. Adapted with permission form Reference[33] Copyright (2011), American Association for the Advancement of Science. **(a)** Schematic view of a network during bond exchange process preserving network integrity. **(b)** Exchange processes via transesterification in hydroxyl-ester networks.

The work of Shi and others not only showed the formability of an epoxy vitrimer, used as an ink in 3D printing, but also on how it can be recycled.[36] The

epoxy resin ink system is made out of the reaction of DGEBA with fatty acids Pripol 1040 and catalyzed by zinc acetate. Nanoclay Nanomer 1.28E at 18 wt% was added as a rheology modifier. After mixing the component homogeneously together, it was heated at 130 °C for 30 minutes under vacuum. The pre-cured ink was used in the first printing cycle using an in-house built *3D* printer. Thereafter the *3D* printed structure was cured in an oven, initially at 60 °C for 20 hours, then finally for 6 hours at 130 °C with vacuum. The integrity of the *3D* printed structure remained intact after these two stages of curing. The recyclability of the epoxy ink system was demonstrated by dissolving the printout in ethylene glycol at 180 °C for 6 hours. When fully dissolved, ethylene glycol was evaporated at 180 °C for 8 hours. The viscous residue is re-used as an ink suitable for another *3D* printing work without need of further material preparation.

The work of Liu et.al, also employed trans-esterification reaction to demonstrate the re-processability and recyclability of a bio-based epoxy vitrimer.[112] An excess amount of eugenol was reacted with *1,4*-dibromobutane following the Williamson ether synthesis route. The resulting product is then epoxidized using MCPBA. This eugenol derived diepoxide is then reacted with succinic anhydride at different mole ratios (1:0.5, 1:0.75, and 1:1) using zinc acetylacetonate hydrate as the catalyst. They showed that although all epoxy formulations of different mole ratios are mendable, only the formulation with 1:0.5 is recyclable via hot pressing the sample at 200 °C to produce new desired structures. This is because the 1:0.5 mole ratio is where the fastest trans-esterification reaction took place. They however demonstrated partial recycling of other formulations by depolymerization in ethanol at 160 °C for 6 hours or until dissolved. The broken-down polymers can be repolymerized to make new epoxy vitrimers by simply heating to 190 °C without need of extra catalyst for 3 hours even on non-inert atmospheres.

Ma and Webster addressed sustainability and recyclability of raw materials by developing epoxy thermosets from epoxidized sucrose soyate (ESS) and crosslinked with organic acids found in nature using water as catalyst.[113] They exploited the use of citric acid, DL-malic acid, L-tartaric acid, oxalic acid and glutaric acid as curatives for epoxy. They achieved excellent thermal and mechanical properties with these thermosets for coatings application. Moreover, the thermosets were thermally degradable and can rapidly dissolved in sodium hydroxide solutions. An additional advantage is the VOC-free manufacture of these thermosets.

Luzuriaga and co-workers presented a unique kind of epoxy vitrimer based on the reversible exchange of aromatic disulfides.[114] The uniqueness of the approach as compared to previously mentioned other systems hinges on factors such as (1) easy synthesis with readily available starting materials, (2) rapid vitrimeric behavior at high temperatures sans catalysts and (3) simple application for (re)processing, repairing, and recycling fiber reinforced plastics composites. Of particular interest is in the two ways where recycling can be accomplished, either via chemical or mechanical recycling. In the chemical method, a fragment of the enduring prepregs, prepared out of the epoxy vitrimer, was immersed in a solution of *2*-mercaptothiol in DMF until the matrix is dissolved. Dissolution is facilitated by thiol-disulphide exchange reaction. The glass fiber or multilayer carbon fiber reinforcement was recovered without damage by oven drying at 100 °C under vacuum. The mechanical recycling, on the other hand, involved a two-step process. Firstly, the FRPC scraps are transformed into a ground powder and finally compress and moulded as "second generation" parts for non-structural composite applications.
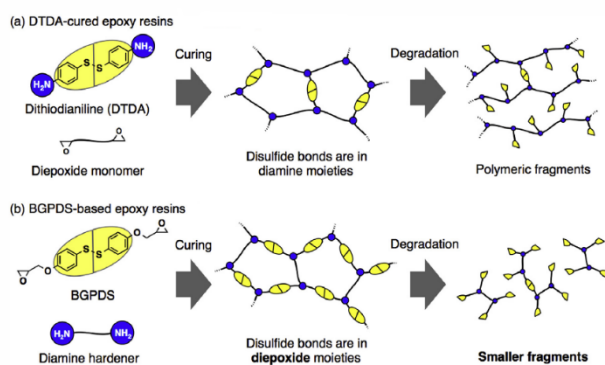
Figure 7. Bond-forming and breaking with disulphide bridges. Adapted with permission from Reference[115], Copyright 2015, Elsevier Ltd. **(a)** Employed by Luzuriaga et.al in polymer recycling. **(b)** Employed by Takahashi et.al in polymer recycling.

In a slightly opposite design from Luzuriaga's group (**Fig.7b**), Takahashi et.al, synthesized the epoxy resin, *bis*(*4*-glycidyloxyphenyl)disulphide, with the disulphide linkages attached to the main epoxy chains and not on the amine crosslinker chains.[115] The resin showed comparable tensile strength to DGEBA based resins without disulphide bonds. They evinced that facile degradation via disulphide exchange reactions is faster in the catalytic presence of DBU, with the efficacy of degradation resting on the ability of the disulphide bridges to fragment and detach from the main epoxy chains.

The above methods of recycling especially those that involve depolymerizing networks by breaking ester links through hydrolysis or alcoholysis, although feasible will still require high temperature and pressure and can still be logistically cumbersome in an industrial scale. While disulphide exchange reactions which offer more advantages but uses even nastier chemicals, will first require chemical safety and hazard assessment before adoption in the workplace.

3.5 Self-healing resins

Polymeric composites used in building, microelectronics, aviation, transportation, and as biomedical implements, during their lifetime will suffer from breaks and cracks; and if left unattended, could result to catastrophic failures. There is therefore a demand for self-healing materials in composites with intact mechanical properties as to suppress these failures and abate future recurrence. The use of extrinsic and intrinsic self-healing approaches has been listed in the literature. Extrinsic self-healing systems contains polymers with embedded distinct self-healing agents which are activated after flexural, fracture or impact damages. Polymers with intrinsic self-healing capacity are most preferred as they can undergo repeated healing events if damage to the reinforcement is not severe or highly localized. **Figure 8** shows the relationship of elastic modulus versus healing temperature of intrinsically self-healing polymeric matrices developed within the past decades. This illustrates that only a handful chemistries that satisfy self-healing behavior at lower temperatures are currently available.
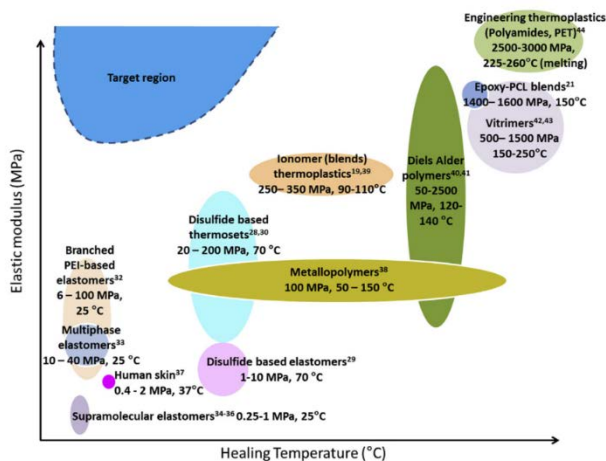

Figure 8. Overview of elastic modulus vs healing temperature of intrinsically self-healing polymeric matrices. Adapted with permission from Reference[116], Copyright 2017, Elsevier Ltd.

The incorporation of small amount of ionic liquids aside from efficiently improving the thermo-mechanical properties and ionic conductivity of conventional epoxy networks was also reported to have desirable impacts on its wear and scratch resistance. In some instances, it was observed to have triggered self-healing on the surface of the epoxy-amine system after multiple scratch tests. Novel research on the use of ionic liquids as a component in autonomous self-healing epoxy polymers is gaining ground. For instance, protic ionic liquid, tri-[*bis*(*2*-hydroxyethyl)ammonium)] citrate was used in the manufacture of a wear resistant epoxy material, where this protic ionic liquid acts not only as curing agent but also as a plasticizer for the polymer. Self-lubrication is accomplished when the ionic liquid trapped as microspheres within the polymer network, is released under load.[117] Figure 9 illustrates self-healing in an epoxy ionic liquid network by tracking the continuous reduction of formed groves with time.
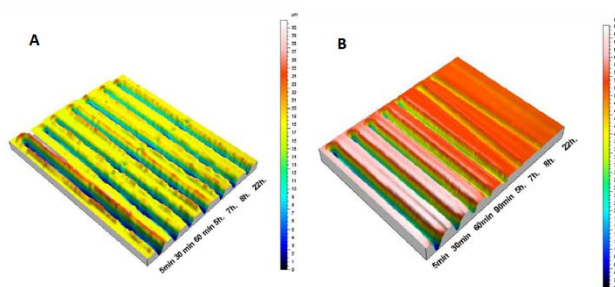
Figure 9. An illustration of self-healing studied under profilometry surface topography. (**a**) For a neat epoxy. (**b**) Epoxy with ionic liquid [OMIM] [BF$_4$], showing continuous reduction on wear groves with time. Adapted by permission from Springer Nature: Tribol. Lett., Reference[83].

The concept of *covalent adaptable network* in tailoring self-healing ability in epoxies came into play early on previous sections. Liu et.al have reviewed the utility of

thermally reversible Diels-Alder chemistry in the fabrication of stimuli responsive self-healing polymeric materials.[118] In Diels-Alder reaction, the presence of a diene and a dienophile facilitates bond exchange reactions when the necessary thermal/light stimulus is triggered. The research group of Iacono utilized Diels-Alder chemistry in the synthesis of mendable epoxy vitrimers with self-healing properties.[119] In their work, DA epoxy adduct was obtained from the reaction of *1,1′-(methylene-di-4,1-phenylene)bismaleimide* and glycidyl furfuryl ether. This epoxy adduct was mixed with EC01, a commercial DGEBA and then subsequently cured with an aromatic amine DDM or a commercial alkylamine called Jeff 500. Self-healing is thermally triggered by heating the sample at 120 °C for 20 minutes which facilitates the reverse Diels-Alder reaction. At this point the polymer is mendable. Subsequently heating the polymer at 90 °C for 24 hours proceeds with the forward reaction, reforming the polymer. This bond forming and bond breaking reactions occur within the temperature range of 100-150 °C for this system.

A better and recent approach to obtain both sufficient mechanical properties and low-temperature healing is to integrate covalently bonded disulphide groups with the epoxy-based network while processing by conventional vacuum infusion process. Post et.al reported intrinsic healing in glass fiber reinforced composite based on disulphide containing organic-inorganic thermoset matrix using such an approach.[116] Young's modulus values of 800-1200 MPa were reported for the epoxy matrix as well as multiple healing ability when delamination was thermally induced between 70 °C to 85 °C. Small sized damage in the range of square-centimeters could be partially healed multiple times with minimal healing pressure, ensuring good alignment of the damaged interfaces. Enhanced healing level for large surface damage located within the matrix phase was achieved by increasing the healing pressure.

Huang and co-workers also took advantage of disulphide chemistry in the manufacture of epoxy vitrimers.[120] They reacted DGEBA with *4-aminophenyldisulfide* (AFD) to make an epoxy resin system and mixed it with nanoparticles of silica, the surface of which, is either pre-modified by an epoxy resin or by thiol compounds such as *3*-mercaptopropyltrimethoxysilane (MPTMS) and *3*-glycidoxypropyltrimethoxysilane (GPTMS). The pre-modified silica nanoparticles were used as fillers. They found out that both pre-modified silica nanoparticles fillers offered better matrix reinforcement effect than unmodified silica nanoparticles. Composites out of epoxy modified silica possessed slightly higher *Tg* and mechanical properties than those out of thiol modified silica of similar loadings. Although silica reinforcement in these composites showed negative effects on the stress relaxation and topological arrangement, it was determined that the stress relaxation rate, at similar loadings, of thiol modified silica composite was much faster than epoxy modified silica composite. This was attributed to a decrease in cross-linking density in thiol modified silica composites as well as to faster exchange rates of thiol-disulphide reactions; hence, more efficient self-healing. This self-healing behavior was corroborated by time dependent healing experiments. This study showed further that an increase in loadings of thiol modified silica fillers yield a positive impact in the mechanical properties but with a consequent reduced effect in the stress relaxation. This study showed the potential advantages of thiol functionalization of fillers in disulphide-based composites with tuneable adaptive and mechanical properties.

A major issue in composite fabrication is matrix micro-cracking due to low-velocity impact damage. The research group of Cohades evinced the feasibility of a combined autonomous crack closure followed by crack healing in fiber reinforced plastics application.[121] Glass fiber reinforced epoxy-polycarbonate (EP-PCL)

composites were manufactured via Vacuum Assisted Resin Infusion Moulding (VARIM) in which shape memory alloy (SMA) wires stitched transversally to the stacked preform before resin impregnation. These stitched NiTiCu SMA wires were responsible for closing longitudinal cracks in woven plates while the EP-PCL matrix performs crack healing. Results showed that with heat treatment at 150 °C after a low-velocity impact at up to 17 J, almost complete healing was observed in 85% of the damaged area. This is a 55% improvement in the degree of healing for EP-PCL composites without SMA, and the highest reported value for this range of impact energies and this type of system. Shape memory systems such as SMA could also pave the way for multifunctional epoxy systems as they have added functionality apart from self-healing which include, among others, sensing, actuation, porosity control, as well as recycling. These had been underlined in a review by Kocsis and Keki.[122]

Other researchers have already paved for the synthesis of epoxy monomers and precursor which need further exploration for tailored multifunctional properties. Such as the biobased epoxy resins presented by Ng et.al.[123] Of particular interest is **(Fig. 10-13)** of which had been synthesized, yet no epoxy polymeric material has been made. Properties of the monofuran analogue of (Fig. 10-13) has already been studied in detail by Hu et.al and was deemed as promising epoxy precursor for composites.[124] The chemistry of this monomer apart from being bio-based, can form Diels-Alder adduct which may exhibit self-healing or switch chemistry. Moazzen and his group successfully demonstrated the repeatable thermal self-healing of poly(furfuryl alcohol) bioresin (PFA) crosslinked by a bismaleimide (BMI) via a Diels-Alder reaction. When they used PFA as a toughening agent in DETA cured epoxy-novolac resin, improvement in tensile properties and toughness was observed, only with a consequent slight deterioration in flexural properties and maximum decrease of 22 °C in Tg.[125] A

recent study suggests that more efficient self-healing was observed when the furan group is substituted with electron rich moieties.[126] Correspondingly, other monomers of similar chemical make-up should be investigated.

With covalent adaptable network, it would be beneficial to determine the shelf life of materials under cyclic loading or dynamic loading which can create heat and as a result break chemical bond. It is clear that high temperature can trigger these networks for self-healing and recyclability, but how long they would last in certain conditions such as high temperature or under load remain unexplored. The work of He et.al., provides some insights when they investigated the cyclic welding behavior of thermal-sensitive CAN epoxy polymers. They found out after uniaxial tension and stress relaxation tests, that the network modulus and BER activation energy increases after long-time heating at temperatures highly above the Tg, which results in a lower mobility of polymer chains and BER rate at equivalent temperature. They were able to model the interfacial fracture energy and found the cyclic interfacial fracture energy of CANs depends on the competition of the decreasing surface roughness and increasing BER activation energy.[105] On the other hand, Yu et.al, observed the dependence of BER rate with temperature by adjusting the stoichiometry of monomers. Consequently, increasing the ratio of hard segments in the epoxy thermoset network increases the material's Tg. This increased in Tg increases the temperature required to achieve a given stress relaxation rate.[127] These insights provide additional tunable parameters in the design of self-healing and recyclable materials.

3.6 High temperature resins

The use of polymeric composites today is not only meant for making light weight structures. They are now starting to replace metallic parts in automobiles and airplanes which demands them to perform in more extreme conditions than before. There is

therefore a case for high temperature resins, so as to make the polymeric matrix more stable when exposed to temperatures 300 °C or above. This field is just emerging, and a small amount of related work exists in the literature.

A thermoplastic toughened epoxy was shown to exhibit heat resistance property and excellent processability by Ying's team.[128] They investigated and synthesized two new polysulfone-type thermoplastic resins poly[*1,4-bis*(azidomethyl)benzene-*co-4,4'*-sulfonyl-*bis*-(propynyloxy)benzene] or [poly(*p*-BAB/SPB)] and poly[*1,3-bis*(azido-methyl)benzene-*co*-4,4'-sulfonyl-*bis*-(propynyloxy)benzene] or [poly(*m*-BAB/SPB)], formed in-situ via azide–alkyne polymerization during the curing of TGAP and DDS. The toughened epoxy has a *Tg* of ~ 230 °C, higher than epoxies toughened with a commercial polyethersulfone. They also proved the toughening mechanism, although indirectly, is a result of the formation of semi-interpenetrating polymer networks comprising the epoxy network and the linear polysulfone-type polymers.

A novel triazine-bridge eugenol-based epoxy resin cured by *3,3'*-DDS exhibited high glass transition temperature (*Tg*) of 207 °C as compared to a DGEBA/*3,3'*-DDS systems.[129] This 33 °C enhancement in *Tg*, is by far the highest reported value for a bio-based epoxy resin derived from as high as 61 wt% renewable precursors, suitable for high temperature processing. The epoxy system also gave a 39% enhancement of Young's modulus and 55% improvement in hardness. It was also characterized to have better creep resistance and dimensional stability, higher softening temperature, and lower permittivity and dielectric loss factor, including higher residual yield during pyrolysis and lowered flammability. Apart from being sustainable, the epoxy system was envisaged to have high utility in EE industries. Electrical insulating epoxy thermosets, and at the same time having high thermal conductivity, high thermal stability, high glass transition temperatures and excellent dielectric properties were

successfully prepared by Mo et.al.[130] This was accomplished by forming ordered nanostructure in epoxy resin via introducing *4,4'*-dihydroxydiphenyl (DHDP) when cured with methyl tetrahydrophthalic anhydride (MTHPA). It is believed that the ordered nanostructure and the enhanced chain rigidity are the key factors for the property's enhancement of DHDP modified epoxy thermosets. The introduction of aromatic DHDP in this system improved the thermal degradation.

To improve performance and lifetime of epoxy thermosets, some researchers turn to filler reinforcements to enhance the thermal conductivity of epoxy matrices, resulting to improved thermal dissipation.[131, 132] Although some improvements in thermal stability may be achieved with fillers, the long-term heat stability of these thermosets are still dependent on the epoxy matrix. With equilibrium molecular dynamics simulations, Li et.al, investigated the thermal conductivities of cross-linked, parallel-linked and single chain epoxy resins.[133] Their study revealed that more than two-fold enhancement (0.80 $Wm^{-1}K^{-1}$) of the along-chain thermal conductivity of bulk epoxies are achieved when a bottom-up parallel linked epoxy resin chains are configured. Further enhancement, reaching 6.45 $Wm^{-1}K^{-1}$ was obtained when a uniaxial tensile strain along the intra-chain direction was applied. Moreover, the thermal conductivity of the parallel-linked single chain is about three-fold higher than that of the cross-linked network (0.32-0.35 $Wm^{-1}K^{-1}$) and this value can reach as high as ~33.82 $Wm^{-1}K^{-1}$ when the strain reaches 0.80. X-ray diffraction pattern showed that the deformed parallel-linked epoxy resin has a perfect crystalline structure, hence, the high thermal conductivity. This study provides new insights when designing and fabricating epoxy resins of high thermal conductivity.

Future electric vehicles out of composite materials, apart from being light weight, will need to be robust to protect the electric battery from mechanical and

thermal damage. Research work on the relationship of mechanical or thermal damage which may lead to thermal runaway has already been published.[134–136] With enhanced safety in mind, such works could further the adoption of *e*-vehicles in public transport.
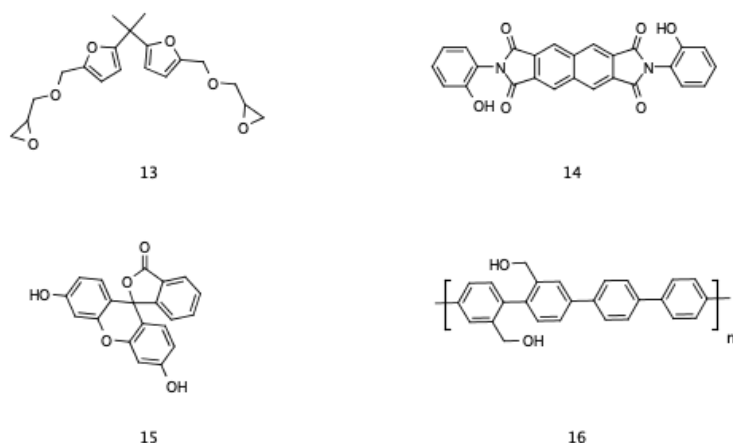

Figure 10. Possible sources of epoxy monomers possessing thermal stability and conductivity.

To date, no epoxy resin that is heat stable at temperatures greater than 300 – 400 °C has been developed. However, a recent molecular modelling work by Radue and others on a more complex cross-linking mechanism of bismaleimide resin paves a predictive way of finding one.[137] Applying the same approach coupled with quantum mechanical calculations, researchers should be able to develop high temperature epoxy resins for such purpose as the epoxy-amine reaction involves a single cure mechanism. Moreover, monomer from highly condensed molecules such as benzoxazines may pave the way for a high temperature resin. No one has attempted the controlled epoxidation of benzoxazine compounds, although studies showed that reactive hydroxyl group is partly responsible for its highly cross-linked nature. Also, when mixed with conventional epoxy group, it is the hydroxyl group that take part in the reaction.

Biomonomer sources of highly condensed structures such as cardanol, lignin and tannins that could impart thermal robustness for epoxy composites had also been reviewed by Raquez et.al.[138] The Mannich like condensation of cardanol with formaldehyde and ammonia is similar to the formation of polybenzoxazines. On the same fashion, the hydroxyphenyl group of lignin, or any of the hydroxyphenyl from both the A and B rings of tannin may be precursors for polybenzoxazines. On a slightly different approach from that reported by Ghost et.al, on the synthesis of *1,3*-oxazine ring from *2*-hydroxybenzylamine, epoxidation of the triazine structure produced with only one mole of formaldehyde would lead to the formation of triepoxides with hemiaminal dynamic covalent network (HDCN).[139] HDCN's were found to be strong thermosets with (re)processable and recyclable potential by Garcia et.al.[140] Other molecules that may be used for this purpose may include **(Fig. 10-14)** that had been previously used in a slightly different application.[141] The amino analogue of **(Fig. 10-15)** was used as a curative in the past but not directly with its epoxy analogue. It is interesting to see how two similar make up can influence the thermal and mechanical properties of the resulting polymer.

3.7 Electrically conductive resins

Traditional epoxies have typically low or no electrical conductivity. Normally, to increase the electrical conductivity of epoxy resin systems, researchers used nanoscale reinforcements, such as nanofibers, carbon nanotubes and graphene nanoplatelets.[142–145] Metallic powder fillers such as copper and nickel were also used in the past for a similar purpose.[146] On previous sections, ionic liquids were also reported to have enhanced the electrical conductivity of epoxy thermosets. Zhang et.al prepared an epoxy-anhydride type electrically conductive adhesive (ECA) catalyzed by ionic liquid [BMIM] [I], where they reported a decreased in its electrical resistivity by almost two

magnitudes in comparison with ECA's catalyzed by other common imidazole compounds.[147] The ionic liquid catalyzed epoxy resin gelled at a low degree of cure, favoring the formation of a conductive network. To illustrate the discrepancies in percolation dynamics, an interphase layer model was proposed according to these findings. A conductive composite is a consequence of the formation of an infinite conductive cluster (I_C) when the volume filler fraction, φ, reaches a critical value, φ_c, so called as the percolation threshold.[148, 149] Some class of ionic liquids such as [APBIM] [NTf$_2$] and [N$_{4444}$] [Leu], considered as "green chemicals" substrates have conductive base ions. It was for these reasons that some authors used them both as substrate and catalyst for epoxy polymerization. They found out that the catalytic activity of this ionic liquids follows a different mechanism as compared to ordinary amine-based hardeners. Although the polymers out of these ionic liquid-epoxy systems have relatively high conductivities, still, more work is needed for their industrial use as solid state electrolytes.[150]
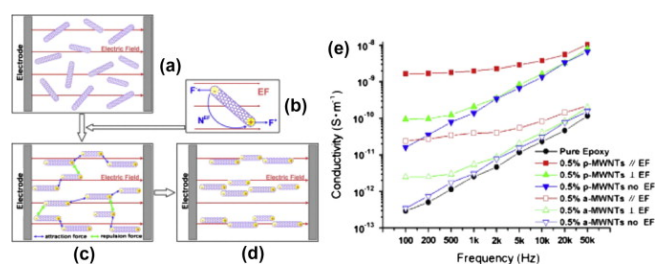

Figure 11. Schematic of the CNT network forming process. (**a**) Involving a randomly aligned CNT. (**b**) With electrical polarization and alignment. (**c**) interaction between aligned CNT and (**d**) CNT move closer and form network of aligned bundles. (**e**) Electrical conductivities of pure epoxy and the nanocomposite with aligned MWCNTs in parallel (//) and perpendicular ($\perp$) direction with the applied electric field. Adapted with permission from Reference[151], Copyright 2014, Elsevier Ltd.

Nanoparticle alignment in an electric field (**Fig. 11**) was observed to influence material conductivity. Ladani et.al., studied how the concentration, shape and orientation of carbon nano-reinforcement affect the electrical conductivity and fracture toughness in multi epoxy nanocomposites.[152] They initially achieved alignment of CNF's and GNP's parallel to the external field using an AC current. The electrical conductivity of these aligned CNF's or GNP's increased by about ten and seven orders of magnitude as compared to the unmodified epoxy. Moreover, with the aligned nano-reinforcements, the percolation threshold was found to be about 50% lower than that of randomly oriented counterparts. Nano-composites containing 0.5 wt% of randomly oriented one-dimensional CNF's or two-dimensional GNP's exhibited about 200% improvement in the values of the fracture energy, G_{IC}, compared to unmodified epoxy. An additional 40% improvement in G_{IC} was obtained by aligning the nano-reinforcements transverse to the crack growth direction. However, at higher concentration of the nano-reinforcements, improvements in electrical conductivity and G_{IC} becomes ineffective. Their mechanistic model revealed that apart from nano-reinforcement alignment, both intrinsic (e.g. interfacial debonding and void growth) and extrinsic (e.g. pull out and bridging) mechanisms result to toughness (**Fig. 12**). Furthermore, the model glossed that one-dimensional CNF's are better than GNP's at increasing the toughness of epoxy via void growth. On the other hand, two-dimensional GNP's are more effective in improving the extrinsic toughness than CNF's. Khan et.al, also accomplished alignment of MWCNT's in an epoxy matrix with the application of a DC current.[153] Similarly, The CNT alignment yielded improvements in both electrical conductivity and mechanical properties measured in the direction of CNT orientation compared to composites containing randomly-oriented CNTs. They also obtained a low percolation threshold of about 0.0031 vol% in the direction of CNT

alignment as compared to 0.034 vol% for the randomly-oriented CNT composites or that measured in the transverse direction of the aligned composites. They measured a 40% maximum improvement in elastic modulus and 50% in fracture toughness of the CNT aligned composites, at levels of 0.3 wt% CNT. Above this level, less improvement in the mechanical properties were observed due to a reduction in the efficiency of CNT alignment. They also identified crack tip deflection and bifurcation, as well as bridging and pullout of single and bundle CNTs as the major toughening mechanisms of the composites containing aligned CNTs. Other approaches in the directional alignment of CNT's in polymer matrices, apart from using AC and DC current, had been presented in a review by Goh et.al.[151]
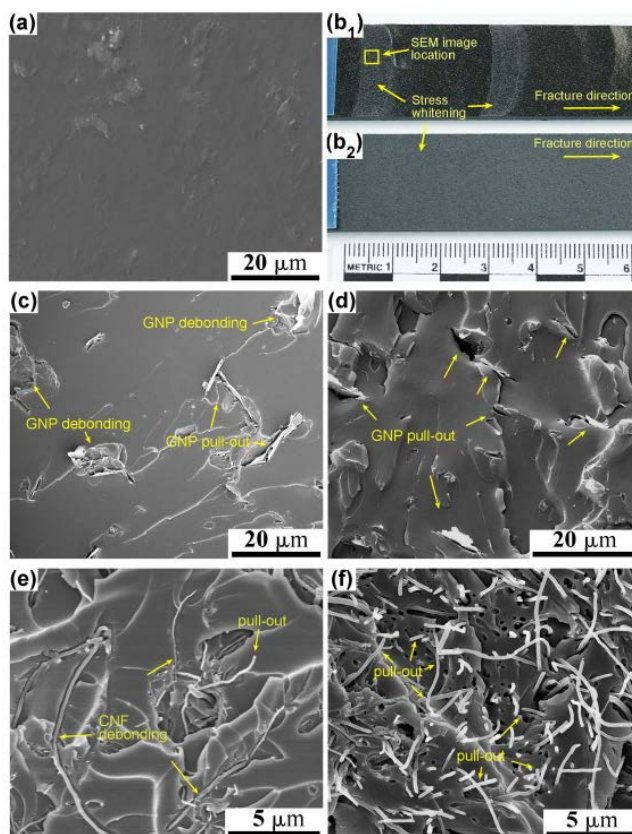

Figure 12. An illustration of the intrinsic and extrinsic toughening mechanisms in epoxy-carbon reinforced composites. Adapted with permission from Reference[152]. (a) SEM image of the fracture surface of unmodified epoxy polymer; photograph of the fracture surface of epoxy nanocomposites with (b1) 1.5 wt% aligned CNFs and (b2) 1.5

wt% aligned GNPs; SEM images of the fracture surface of epoxy nanocomposites containing (c) 1.5 wt% randomly-orientated GNPs; (d) 1.5 wt% aligned GNPs; (e) 1.5 wt% randomly-orientated CNFs; and (f) 1.5 wt% aligned CNFs.

Currently the nonconductive nature of epoxy resins has wide applications, an intrinsically electrically conductive epoxy polymer, to the best of our knowledge has not been reported, although conductive polymers from mono-epoxides containing persistent organic radical compound tethered to the polymeric backbone has already been developed.[154] Similar methodologies can be adopted for the development of conductive multi-epoxides that may be useful for epoxy composites. Approaches such as controlled epoxidation of already conductive polymers **(Fig.10-16)** and similar analogues will need further exploration.[155] In aviation, conductive epoxies could improve aircraft safety by improving the response of the outside sensing environment of airplanes and shield important navigational devices from EMI.[156] It may also aid aircraft manufactures to detect early structural failures.[14, 157] In the automotive industry conductive epoxy can further the case of the *e*-vehicle. Future "smart roads" built from conductive epoxy modified asphalt can act as a wireless charger for electric vehicles even when on the move.[158] Apart from this, a conductive epoxy matrix had potential applications on materials that possess smart features such as sensing, strain monitoring and actuation capabilities. Areas of applications apart from aviation and transport sectors can include health and life monitoring devices.

4. Summary and future challenges

Epoxy resin and its concomitant manufacturing technologies have been in existence for decades. Although epoxy resin chemistry and its multitudinous applications have been in the past reviewed and studied in detail, none has so far delved

on its potential application as a thermoset resin for the inevitable unfolding of the fourth industrial revolution in this age. The digitisation of manufacturing with its interrelatedness on the industrial internet-of-things will disrupt traditional thermoset and composite fabrication processes on the areas of automotive, aerospace, energy generation, and healthcare amongst others. Moreover, a grand linchpin for the development of smart materials and structures in anticipation of these disruptive technologies exists for many polymers except on the decades old epoxy thermosets. Epoxy resins being the prevalent precursor of composite materials, though acknowledged to have the required desirable properties on this field will need to possess multifunctional attributes as to further its uptake in the future of manufacturing. This review attempts to showcase recent studies on overcoming the current limitations of epoxy resin in composite applications. The methods and synthetic modifications of epoxy resins discussed in this review may provide sundry approaches towards the development of multifunctional epoxy resins for varied composite applications. Approaches in toughening, flexibility inducement, recycling, and capacity for repair, already exist in the literature, with some needing further improvement and detailed studies while others are close for adoption by composite manufacturers.

The efficacy of intrinsic toughening mechanisms is down sided by the tedious and complex synthesis procedure necessary to affect the final polymer property. The same impediment including the cost of raw materials exist for inducement of flexibility. Approaches such as introduction of substituent groups that are affected by external electric or magnetic fields that can force the system to adopt desired sizeable inclusion morphologies should be explored. This will somehow require the presence of a conductive pathway or magnetic sites in the matrix.

Whereas epoxy polymerization requires high enthalpies, modicum works were found that focused on rapid cure epoxy resins or resins that cure even at near ambient conditions. These were circumvented mostly with improvements in manufacturing rather than the resin per se. Approaches beyond the use of hindered catalyst as to effect latency is now exigent. Further exploration of the effects of residual stresses, shrinkage during rapid curing and control of the extreme heat generated during cure must continue as this largely depend on the epoxy system being employed. Conductive epoxies with dense radical sites of unpaired electrons as in persistent organic radicals has not been explored as rapid curing systems, although in theory, unpaired electrons are sensitive to microwave irradiation that could easily facilitate an increase in the local temperature. Furthermore, the unpaired electrons are available to a wide array of chemistries enabling in situ generation of other catalytic systems, or sites for polymeric ionic liquids transformation, as for examples.

It is still a long way to making epoxy resins infinitely recyclable and ultimately degradable. Combining similar approaches of recycling in one system as discussed in the above sections is required to at least re-use the starting materials. A system whereby covalent adaptable networks are available to both the parent backbone and the crosslinker can be an optimal way of recovering valuable starting raw materials. Such a system may include but are not limited to HDCN's in the epoxy backbone with disulphide bridging on the crosslinker. Moreover, results from oxidative induction studies for epoxides tethered with persistent organic radicals may yield insights to the eventual environmental degradation of end of life epoxy-based composites.

Successes in the stability assessment of the self-healing mechanism after so many loads, large deformation and higher surface fractures, as well as the reduction in Tg due to plasticization comes with many caveats, especially with composite materials.

One of which is that the damage must at least be localized within the polymer matrix for efficiency. Therefore, self-healing system must not compromise the mechanical property contribution of the epoxy matrix.

High temperature epoxy resin that is heat stable at temperatures higher than 300 °C will still need to be developed. Molecular simulations with correlative experimental studies are a way forward. On the chemistry side, condensed chemical structure should serve as basis.

An increasing demand for ionic liquids is foreseen towards the development of multifunctional epoxy resins. The use of ionic liquids is one way forward for a tougher, more flexible, self-healing, even conductive composites, and to some extent to a faster than normal cure resin. Therefore, more and more ionic liquids suited to the application at hand will need to be synthesized and their interaction with epoxy networks explored further.

Methods and approaches beyond nanoscale reinforcement to induce conductivity of epoxy matrix should be given focus. Consequently, this will require the matrix to also possess better structural performances in terms of toughness and flexibility and if possible, with self-repair and recycling mechanisms. Getting these desirable attributes will pose a big challenge for researchers. Conducting epoxy matrices, similarly with CNT reinforced matrices or in combination thereof, can be utilized as highly sensitive sensor for detecting the onset, the source and propagation of damage in advanced polymer-based composites. In tandem with CNT's or conductive fillers, a conductive matrix is envisaged to facilitate directional alignment by creating a conductivity pathway throughout the sample. Alignment under the influence of a magnetic field is also possible with paramagnetic electrons as in organic radicals tethered in the epoxy backbone. All these aside, ways of combining the sundry approaches together to suit

tailored properties for a multifunctional epoxy resin, although not an easy task, yet is still feasible. Nevertheless, there is a huge need and application of epoxy resins with conductive potential or magnetic susceptibility.

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ABBREVIATIONS

[APBIM] [NTf$_2$], *1*-(*3*-aminopropyl)-*3*-butylimidazolium-*bis*(trifluoromethylsulfonyl) imide; BADGE/DGEBA, bisphenol-A diglycidylether; [BDP] [DBS], tributyl(tetradecyl)phosphonium dodecylbenzenesulfonate; [BEP] [DEP], tributyl(ethylphosphonium)-diethylphosphate; BER, bond exchange reactions; [BMIM] [BF$_4$], *1*-butyl-*3*-methylimidazolium tetrafluoroborate; [BMIM] [Cl], *1*-butyl-*3*-methylimidazolium chloride; [BMIM] [I], *1*-butyl-*3*-methylimidazolium iodide; CAN, covalent adaptable network; [EMIM] [DCN], *1*-ethyl-*3*-methylimidazolium dicyanamide; CNT, carbon nanotubes; CNF, carbon nanofibers; DBU, *1,8*-diazabicyclo[*5.4.0.*]undec-*7*-ene; DDM, *4,4'*-diaminodiphenylmethane; DDS, *4,4'*-diaminodiphenylsulfone; FRPC, fiber reinforced plastics composite; GNP, graphene nanoplatelets; K_{IC}, critical stress field intensity factor; [N$_{4444}$] [Leu], tetrabutylammonium leucine; RAFT, reversible addition fragmentation chain transfer; TETA, triethylenetetramine; TGAP, Triglycidyl *p*-aminophenol; [HDP] [DCA], trihexyl(tetradecyl)phosphonium dicyanamide; [HDP] [EHP], trihexyl(tetradecyl)phosphonium *bis*(*2*-ethylhexylhexanoate); [HDP] [TMP],

trihexyl(tetradecyl)phosphonium *bis-2,4,4*-(trimethyl pentyl) phosphinate; [HDP] [FSI], trihexyl(tetradecyl) phosphonium-*bis*(trifluoromethanesulfonyl) imide); MCDEA, *4,4'-*methylene-*bis*(*3*-chloro-*2,6*-diethylaniline); MCPBA, *m*-chloroperoxybenzoic acid; MDA, *4, 4'-* methylenedianiline; VARIM, Vacuum Assisted Resin Infusion Moulding.

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