



Festus Ifeanyi Anagwu

Synthesis and manufacturing of fibre-reinforced vitrimeric
composites based on epoxy and benzoxazine matrices

School of Aerospace, Transport and Manufacturing
PhD in Manufacturing

PhD

Academic Year: 2020 - 2024

Supervisor: Dr Alexandros A. Skordos

Associate Supervisor: Prof. Vijay Kumar Thakur

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ABSTRACT

Epoxy and polybenzoxazine vitrimers have been synthesised in this study and used as composites matrices to assess their self-healability. A disulphide bond-endowed reference epoxy vitrimer was formulated based on the established chemistry of diglycidyl ether of bisphenol A and 4-aminophenyl disulphide. Also, a new high-temperature benzoxazine vitrimer (coded BH-A) was synthesised through solventless one-pot method, featuring disulphide bond. The thermal, rheological, cure kinetics and relaxation behaviour of the vitrimers was studied as well as the mode I delamination response of their carbon fibre composites before and after healing. Both the epoxy and benzoxazine systems are high-temperature systems with a glass transition temperature of 163°C and 155°C, respectively and topology freezing transition temperatures of 149.5°C and 78°C, respectively. The cure kinetics of both resins are autocatalytic and were modelled with an average reaction rate error of 5.2% and 14.1% for the epoxy and benzoxazine systems, respectively. The rheological behaviour of the epoxy vitrimer allows manufacturing of composites by liquid moulding, whereas the rheological behaviour of benzoxazine vitrimer is appropriate for manufacturing of composites through resin film infusion. The epoxy system undergoes full stress relaxation in 16 seconds at 220°C and can be healed at this temperature under a pressure of 50 bar in 90 minutes, whereas the benzoxazine system relaxes fully within 5 seconds at 190°C and can be healed at this temperature with a pressure of 4 bar in 30 minutes. Fracture toughness recovery in both composites depends on the historical crack opening prior to healing and follows an exponential decay from a value of 100% at the previous crack tip to about 13 – 20 % at the position of maximum previous crack opening. The self-healing of the benzoxazine composite is superior to that of the epoxy system, as it is achieved within the practically realistic composite manufacturing conditions.

Keywords: Vitrimer, epoxy, benzoxazine, cure kinetics, chemorheology, self-healing composite, delamination

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LIST OF ABBREVIATIONS

T_g	Glass transition temperature
T_v	Topology freezing transition temperature
4-APDS	4-Aminophenyl Disulphide
AIE	Aggregation-Induced-Emissions
APB	Aldehyde-terminated Polybutadiene rubber
APU	Auxiliary power unit
ASTM	ASTM International
BH-A	Bis-4 (Hydroxyphenyl) Disulphide-Aniline benzoxazine
BS ISO	British Standards: International Organisation for Standardisation
CANs	Covalent Adaptable Networks
CF	Carbon Fibre
CFRCs	Carbon Fibre-Reinforced Composites
DCB	Dual Cantilever Beam
DGEBA	Diglycidyl Ether of Bisphenol A
DI	Deionised
DMA	Dynamic Mechanical Analysis
DMF	N,N-Dimethylformamide
DMSO	Dimethyl Sulfoxide
DSC	Differential Scanning Calorimetry
EPS	Epoxy Polysulphide

FTIR	Fourier Transform Infrared
FWO	Flynn-Wall-Ozawa
G _{1C}	Mode I critical strain energy release rate
HMD	Hexamethylenediamine
ILSS	Interlaminar Shear Strength
IS-EPO	Isosorbide-derived Epoxy
KAS	Kissinger-Akahira-Sunose
KWW	Kohlrausch-Williams-Watts
LOI	Limiting Oxygen Index
MDA	4,4-Diaminodiphenylmethane
MDS	4,4'-Disulphanedioldianiline
PACM	4,4-Diaminodicyclohexylmethane
PolyBH-A	Polymerised BH-A
PolyDGEBA/4-APDS	Polymerised DGEBA and 4-APDS
POSS	Polyhedral Oligomeric Silsesquioxane
RFI	Resin Film Infusion
RTM	Resin Transfer Moulding
TDCB	Tapered Dual Cantilever Beam
TGA	Thermogravimetric Analysis
TTT	Temperature-Time-Transformation
VARTM	Vacuum-Assisted Resin Transfer Moulding

Chapter One

1 Introduction

1.1 Background and motivation

Thermoset composites are widely used in manufacturing structural components in industries ranging from aerospace to automotive, due to their remarkable high strength-to-weight ratio, desirably high stiffness-to-weight ratio, excellent fatigue resistance and structural design flexibility [1,2]. Due to these advantages, the airframes of Boeing's 787 Dreamliner and Airbus A350 XWB aircrafts are made of about 50 weight % of carbon fibre-reinforced composites (CFRCs), permitting an average weight saving of 20 % when compared to conventional metal alloy-based structures [3]. Similarly, the automotive industry uses thermoset composites extensively for exterior body panels such as fenders and bumpers, interior components such as dashboards and door panels, structural components such as chassis parts and suspension components, electrical and battery enclosures.

However, thermoset composite waste generated either during manufacturing or due to products reaching their the-end-of-service constitute serious disposal implications, as they cannot be recycled due to the irreversibility of the matrix crosslinks. They are often collected for disposal either by landfilling or incineration, posing serious environmental problems, or downcycled, downgraded or converted to energy [4] (**Figure 1.1**). Although thermoset composites may be recycled chemically or broken down into valuable chemicals such as fuels via pyrolysis, these options are not attractive due to the high-cost and overall environmental impact of the solvents involved.

Apart from the environmental challenge posed by nonrecyclability of thermoset composites, they are susceptible to failure processes such as interlaminar fracture or delamination, intralaminar fracture or matrix cracking, matrix-to-fibre debonding, fibre pullout and fibre breaking [5]. The susceptibility of composites

to damage, particularly delamination, remains an unresolved challenge to the industry. Delamination is responsible for 60% of all damage modes during aircraft assembly [6,7] and significantly reduced the material stiffness, resulting in structural failure during service [8–10].

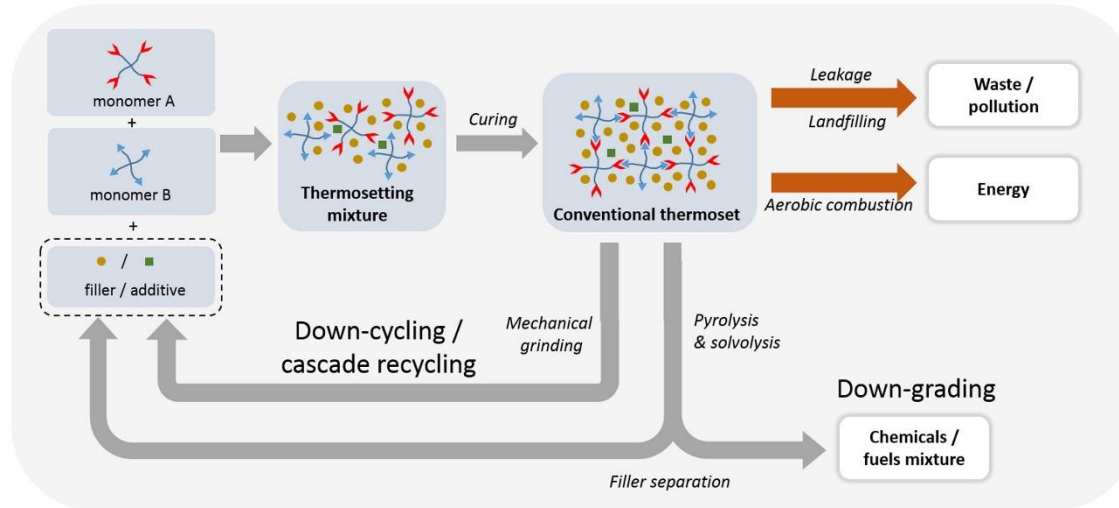


Figure 1.1. Schematic overview of conventional thermoset composite waste processing and recycling routes. Reprinted from with permission from [4].
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In the last decade, vitrimers – a family of polymers capable of inherent stimuli-induced self-repair of damage – emerged as a promising option for multicycle thermal recycling of thermosets with a retention of material mechanical properties [11], potentially addressing the problem of in-service damage accumulation in composite structures, due to their unique ability to repair microcracks and delamination. This can extend the service life and reliability of composite structures as well as postpone structural fatigue failure indefinitely in vitrimer composites [12], thus contributing towards the attainment of a circular economy [13]. Since the emergence of vitrimers, most of the relevant research focuses on the development and characterisation of new formulations [14–21] and has sufficiently addressed the formulation and characterisation of vitrimer functionality based on different thermosetting chemistries such as epoxies [22–25], polybutadienes [26–29], polyurethanes [30,31], polybenzoxazines [16,17], polyimides [32], and polyesters [33–35]. The composites industry, whose future

ultimately depends on polymer chemistry, is the major target for these developments. For vitrimers to gain widespread acceptability as the recipe for thermoset recycling and in-service damage accumulation prevention, three key issues need to be resolved: first, understanding material behaviour of vitrimers during processing and development of appropriate manufacturing implementation; second, developing methods for achieving healing of vitrimeric composites using setups and conditions that are compatible with current manufacturing practices; and third developing an understanding of how matrix healing translates to recovery of composite mechanical properties.

Since the self-healability and recyclability of thermosets constitute the central focus of vitrimer research, most formulations have centred on epoxy resins which currently dominate the composites matrix market. For certain industrial applications such as the aerospace, more functionalities are also needed in addition to self-healing and recyclability. These include fire retardancy, hydrophobicity and high thermal stability. These attractive features are inherent characteristics of benzoxazines, which are versatile compounds easily synthesised through a condensation reaction involving a formaldehyde, a primary amine and a phenolic compound, illustrated in **Figure 1.2**. The oxazine ring in benzoxazine – which exists as a bicycle with benzene ring – opens at elevated temperature, leading to an autocatalytic homopolymerisation. High temperature polybenzoxazine vitrimers are recognised and envisioned as promising options to achieve these multiple functionalities in an efficient manner. Polybenzoxazines have been applied as adhesives in aerospace tooling assemblies, as composite matrix for the fabrication of the auxiliary power unit (APU) housing for Airbus A380 (**Figure 1.3**), and as a tooling system for the manufacture of wing flaps of the Airbus A350 aircraft [36]. Currently, there is no known high temperature polybenzoxazine vitrimer produced through the traditional cost-effective solventless one-pot method, nor a high fire-retardant polybenzoxazine vitrimer. The few reported polybenzoxazine vitrimers are synthesised through complex routes that involve intermediate purification steps prior to final synthesis of

benzoxazine monomers [17,37–39], making the processes unattractive, just as they are not established matrices for composites manufacturing.

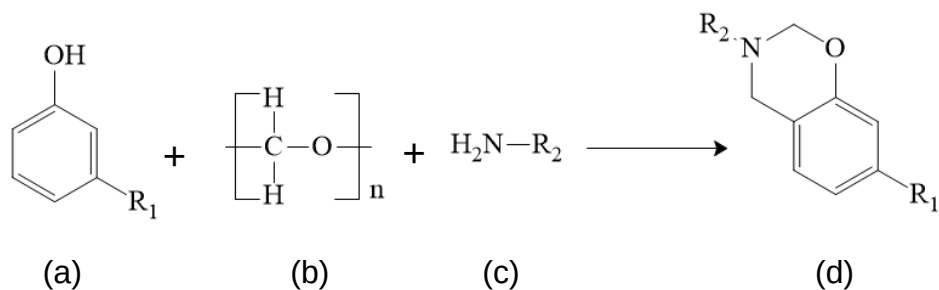


Figure 1.2. Synthesis of benzoxazine (d) from phenolic compound (a), formaldehyde (b) and primary amine (c).

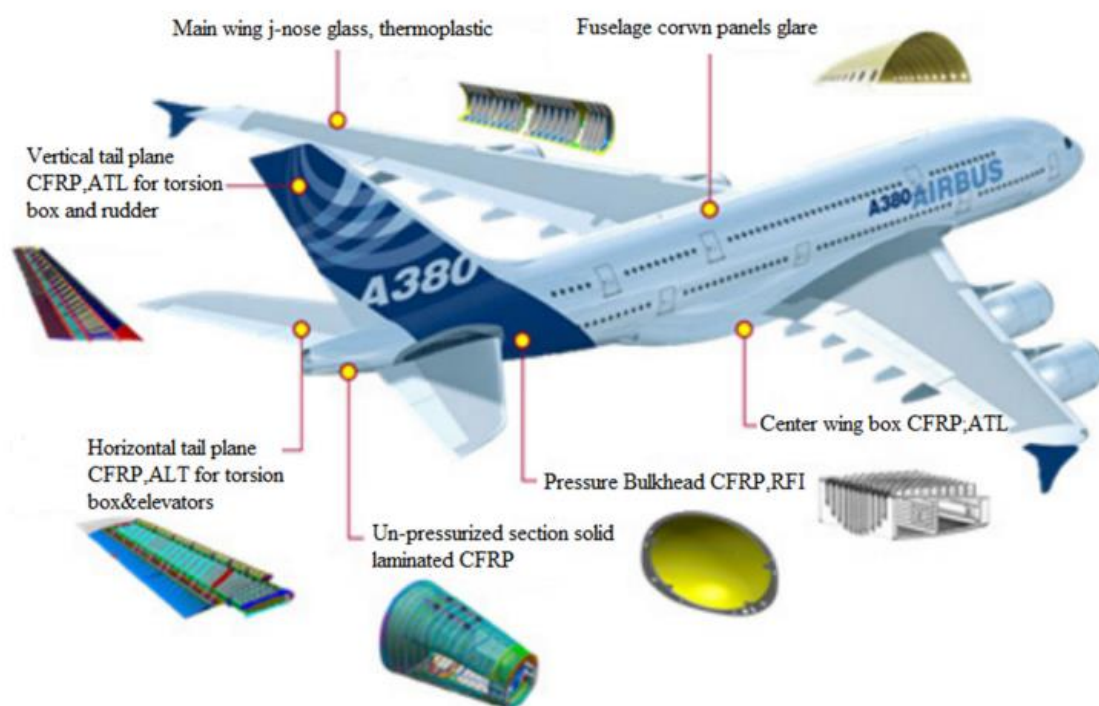


Figure 1.3. Airbus A380 Long-range jetliner showing carbon fibre-reinforced polymer parts including APU housing made of polybenzoxazine (unpressurised section). Reprinted from [40]

The current study is driven by three key motivations: the need to provide an understanding of the cure kinetics, glass transition advancement and chemoviscosity of typical aerospace-grade vitrimers to ensure their optimal manufacturing by predicting and controlling the curing process as well as guiding the specification of process parameters in order to ensure manufacturing process efficiency, desired product quality and performance; the need to understand the capability of vitrimeric composites to self-heal structural damage such as delamination; and the need to design, synthesise and manufacture a high-temperature polybenzoxazine vitrimer that exhibits high fire retardancy as well as very low water absorption capacity for wet environment operations through a cost-effective solventless one-pot method. For simplicity and cost-effectiveness of synthesising the benzoxazine vitrimer, the strategy targeted is solventless one-pot method, similar to that of a low-temperature benzoxazine vitrimer synthesised from cardanol, paraformaldehyde and a disulphide bond-containing diamine, taking advantage of the disulphide bond in, at least, one of the precursors to achieve a vitrimer [16]. This is illustrated in **Figure 1.4**.

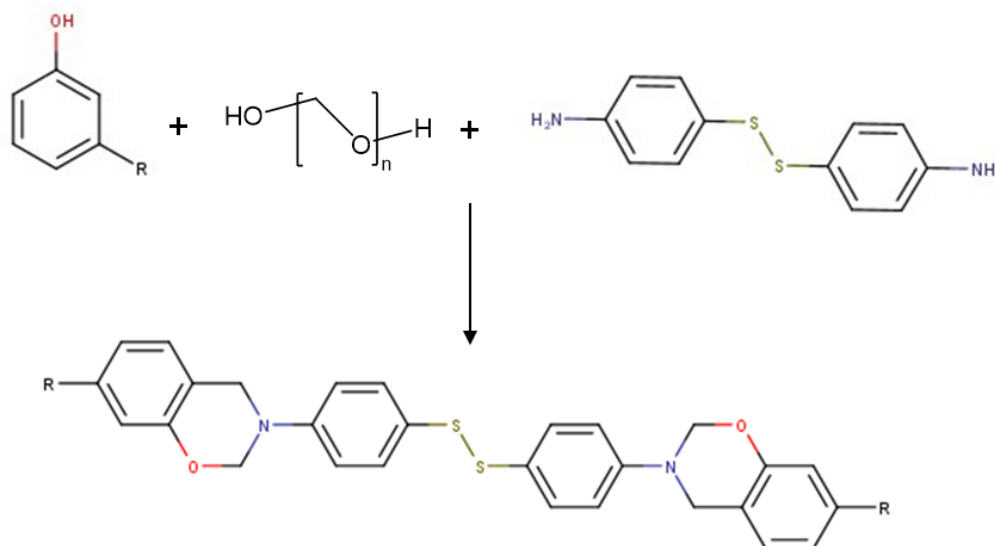


Figure 1.4. Synthesis of low-temperature benzoxazine vitrimer incorporating disulphide bond.

1.2 Aim and objectives

The aim of this study is to develop self-healing high-performance fibre-reinforced vitrimer composites based on epoxy and benzoxazine matrix systems for aerospace, automotive, energy, marine and other industrial applications. The objectives of the study include:

- i. Synthesis and characterisation of a high-temperature reference epoxy vitrimer based on established chemistry as a baseline material solution.
- ii. Development and validation of analytical/numerical models for simulation of the cure kinetics glass transition evolution and chemoviscosity of the epoxy vitrimer for optimal manufacturing.
- iii. Design and synthesis of sustainable/cost-effective high-performance novel benzoxazine vitrimer.
- iv. Characterisation of novel high-performance benzoxazine vitrimer.
- v. Development and validation of models for simulation of the cure kinetics, glass transition advancement and chemoviscosity of the benzoxazine vitrimer for optimal manufacturing.
- vi. Manufacturing of sustainable and functional fibre-reinforced vitrimeric composites.
- vii. Validation of delamination healing functionality of vitrimeric composites.

1.3 Roadmap of the thesis

The thesis is organised in 10 chapters. Chapter 1 introduces the study background and contextualising the study. Chapter 2 reviews the existing literature, showcasing the advances in the field as well as the state of the art prior to this study. In chapter 3, the methodology of the study is presented. Chapter 4 presents the results of the cure kinetics, glass transition advancement and chemorheological modelling of the epoxy vitrimer. Chapter 5 deals with the results of the synthesis and characterisation of the new benzoxazine vitrimer.

Chapter 6 presents the results of the cure kinetics, glass transition advancement and chemorheological modelling of the benzoxazine vitrimer. The results of the delamination and self-healing of the epoxy vitrimer are presented in chapter 7, whilst chapter 8 deals with the results of the delamination and self-healing of the benzoxazine vitrimer. Chapter 9 presents the overall discussion of the results, whilst the main conclusions of the research and recommendation for future work are summarised in chapter 10.

1.4 List of publications

1. **Anagwu FI**, Skordos AA. Cure kinetics, glass transition advancement and chemo-rheological modelling of an epoxy vitrimer based on disulphide metathesis. *Polymer* 288 (2023) 126427.
<https://doi.org/10.1016/j.polymer.2023.126427>.
2. **Anagwu FI**, Thakur VK, Skordos AA. High-performance vitrimeric benzoxazines for sustainable advanced materials: design, synthesis, and applications. *Macromol Mater Eng* 308 (2023) 2200534.
<https://doi.org/10.1002/MAME.202200534>.
3. **Anagwu FI**, Skordos AA. High glass transition catalyst-free fire-retardant polybenzoxazine vitrimer through solventless one-pot method. *Macromol* (under review)
Preprint: ChemRxiv (2023).
<https://doi.org/10.26434/chemrxiv-2023-c4dgb>
4. **Anagwu FI**, Skordos AA. Vitrimer carbon fibre composites based on a novel polybenzoxazine matrix, ECCM21 (abstract accepted for oral presentation)
5. **Anagwu FI**, Skordos AA. Fracture toughness recovery in a damaged vitrimer composite through multicycle delamination and healing of DCB specimens (in preparation).
6. **Anagwu FI**, Skordos AA. High-performance polybenzoxazine vitrimer composite: Cure kinetics, glass transition evolution, chemorheological

modelling and multicycle toughness recovery using DCB specimens (in preparation).

Chapter Two

2 Literature Review

2.1 Introduction

This chapter provides an overview of the current state of research in the field of vitrimers. The review starts with the concept of topology rearrangement in vitrimers – a phenomenon driven by dynamic covalent bond exchanges occurring at elevated temperatures – focusing on the topology freezing temperature, a characteristic temperature controlling network rearrangement in vitrimers. Subsequently, diverse bond exchange chemistries utilised in transforming thermosetting polymers into vitrimers are reviewed. The chapter proceeds to provide an in-depth analysis of polybenzoxazine vitrimers, elucidating the latest advancements and breakthroughs in the design of vitrimeric polybenzoxazines as well as identifying the research gap in the synthesis of benzoxazine-based vitrimers. This is then followed by the processing characterisation of vitrimers, which deals with the cure kinetics and chemoviscosity studies on vitrimers, an aspect that is vital for optimal manufacturing of vitrimeric composites. The chapter identifies that there is lack of work regarding cure and viscosity modelling of vitrimers and finishes with a review of the techniques used to manufacture vitrimer composites, studies on self-healing vitrimers and mechanical resilience tests and results for vitrimeric composites conducted to date.

2.2 Vitrimers and topology freezing temperature

The topology freezing temperature (topology freezing transition temperature), T_v , of a vitrimer which has become a subject of research interest due to its significance to vitrimer reprocessing. It relates to the chemical phenomenon of bond exchange rather than a physical phenomenon. Molecular mobility induces dynamic bond exchange, driving macroscopic flow in vitrimers. T_v represents the critical temperature for topological rearrangement. For a vitrimer to be considered a viable material solution for self-healable and reprocessable composites

application, its T_v must fall within the resin practical processing temperature, allowing reprocessing within a sufficient temperature window below the vitrimer degradation point. Unlike phenomena such as glass transition and melting which are measurable by differential scanning calorimetry (DSC), T_v does not appear on the DSC thermogram. Four methods are applied in literature to probe T_v , the most prominent of which is the stress relaxation method (**Figure 2.1**), in which viscosity-dependent relaxation time is studied as a function of temperature, using the time at which the initial modulus decreases to $1/e$ (i.e., 37 %) of the initial values, the viscosity of 10^{12} Pas, and Maxwell's relation:

$$\eta = G\tau^* \quad (2.1)$$

where η is viscosity, G is the plateau complex modulus in the rubbery region (typically measured using dynamic mechanical analysis), and τ^* is the relaxation time [16,22,25,41–48]. The stress relaxation of vitrimers can also be analysed using the Kohlrausch-Williams-Watts (KWW) function to estimate the average relaxation time [49,50]. Other established methods of measuring vitrimer T_v include aggregation-induced-emissions (AIE) luminogens (**Figure 2.2**) [51], dilatometry (**Figure 2.3**) [11,52–63], sometimes called nonisothermal elongational creep measurement [62,63], and multifrequency oscillatory scan rheometry (**Figure 2.4**) [64–66].

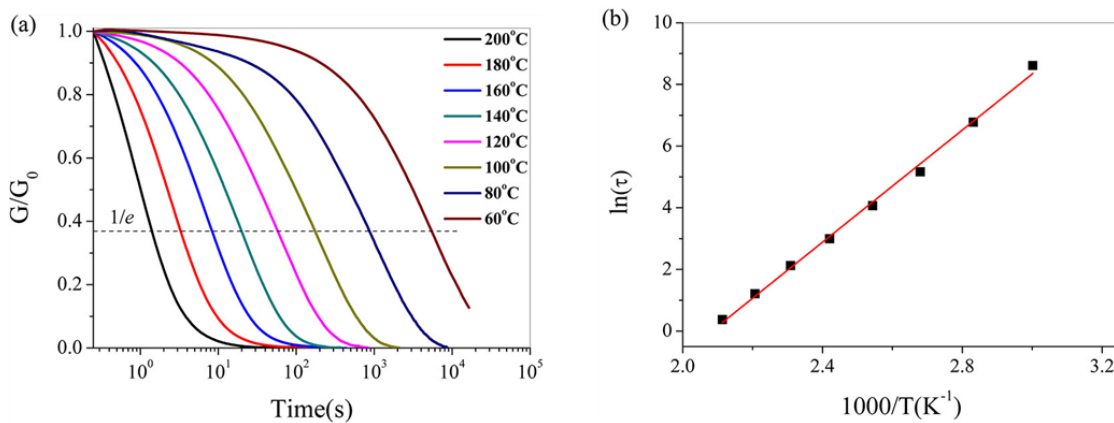


Figure 2.1. T_v detection using relaxation (a) Normalized stress relaxation as a function of temperature (b) Arrhenius dependence of relaxation. Reprinted with permission from [67]. Copyright (2019) American Chemical Society.

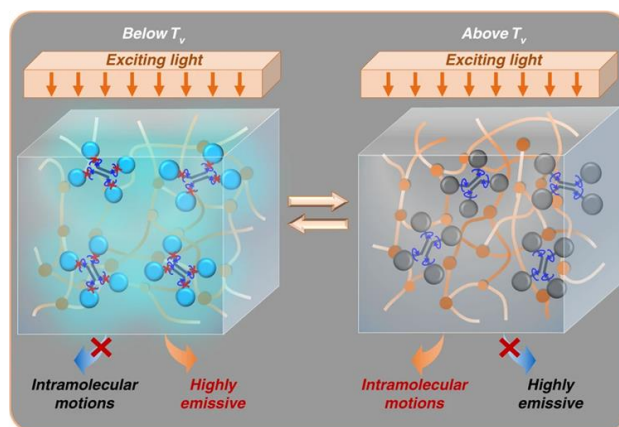


Figure 2.2. Florescence emission of AIE molecules as a function of temperature. Below T_v , emissivity is high. Above T_v , emissivity is weak. Reprinted with permission from [51]. Copyright (2019) Springer Nature.

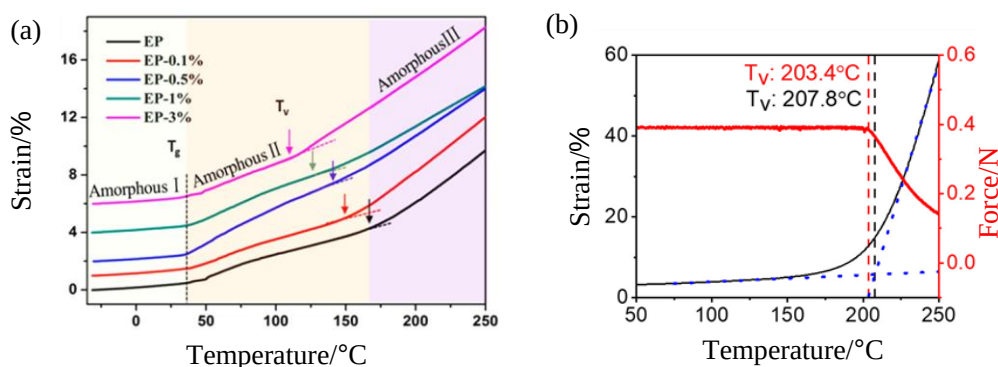


Figure 2.3. T_v detection by dilatometry (a) T_v as a point of initial deviation from approximately linear strain curve. Reprinted with permission from [53]. Copyright (2016) American Chemical Society. (b) Both strain and force curves as indicators of T_v , which is taken as the onset of plastic flow rather than an initial deviation from an approximately linear strain curve. Reprinted with permission from [62]. Copyright (2021) American Chemical Society.

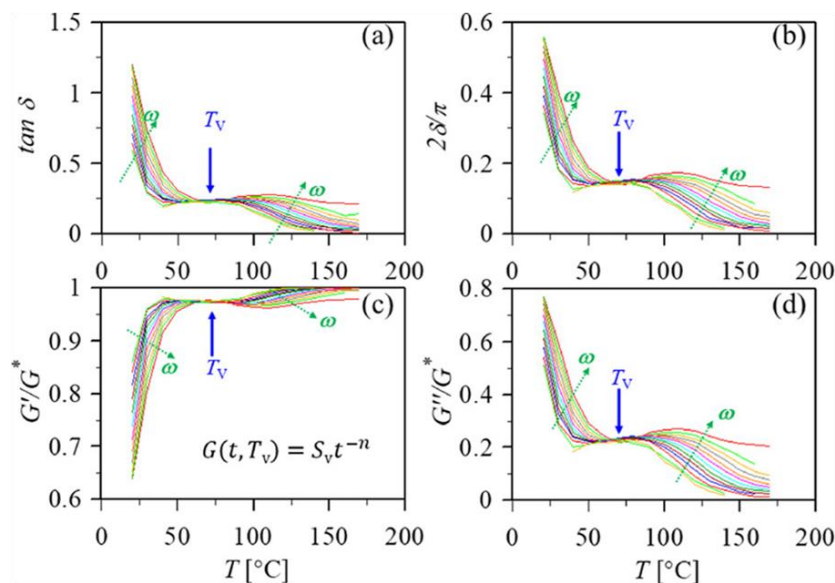


Figure 2.4. T_v as an expression of a power-law relaxation modulus where the point of coalescence of lines of constant frequency: $\tan \delta$, $2\delta/\pi$, G'/G^* , and G''/G^* at an intermediate temperature indicates T_v , temperature being the independent variable. Reprinted with permission from [64]. Copyright (2020) American Chemical Society.

Two classes of vitrimers are distinguishable, depending on the position of the vitrimer T_v relative to its T_g which determines the thermomechanical and rheological properties of the vitrimer [68,69]: vitrimers having T_v greater than T_g and vitrimers having T_v lower than T_g . The rheological behaviour of these two classes of vitrimers are shown in **Figure 2.5**. The type of behaviour can be tuned to an extent, as T_v can be controlled by the catalyst type and concentration, whilst T_g is controlled by polymer composition [61]. To design a new vitrimer, these tailorable properties of vitrimers is taken into account to formulate a system that suits the desired industrial application.

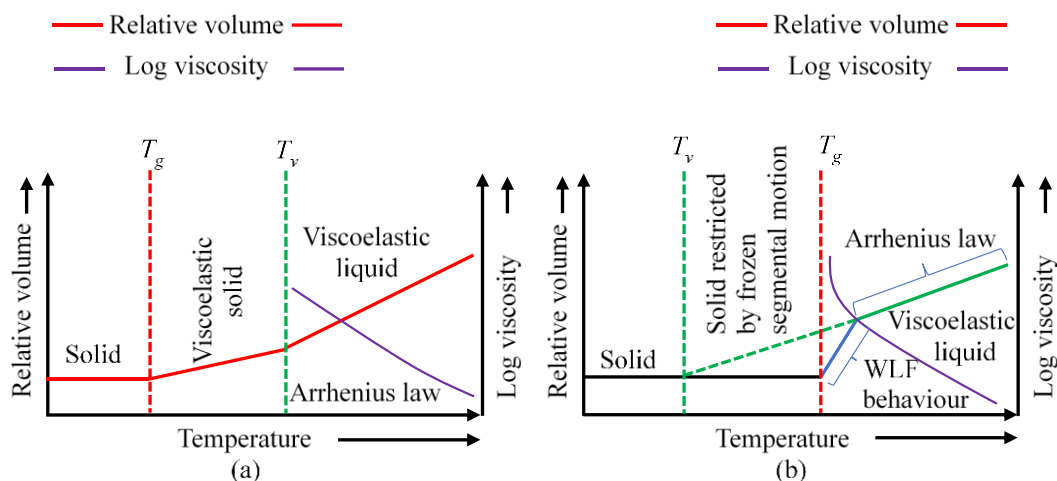


Figure 2.5. Plots of vitrimer's relative volume and Log viscosity versus temperature: (a) $T_v > T_g$. (b) $T_v < T_g$.

2.3 Dynamic covalent bond chemistry in vitrimer systems

Various chemistries can produce associative covalent adaptable networks (CANs), including transesterification, imine bond, disulphide exchange, transamination of vinylogous urethanes, diketoenamine transamination, transcarbamylation, transalkylation of sulfonium salts, siloxane-silanol exchange, olefin metathesis, transcarbonation, and silyl ether exchange. Each of these bond transfer mechanisms is reviewed in the following sections with examples of their applications to the vitrimerisation of resin systems. This aims at uncovering potential reactions relevant to benzoxazines, with an established mechanism leading to dynamic topological transitions. These can serve as the basis for future research on benzoxazine-based vitrimeric systems. An associative CAN is one for which dynamic bond exchange occurs by a simultaneous bond breaking and reforming such that the network integrity is maintained constant at all times. This is in contrast to a dissociative CAN in which dynamic bond exchange occurs by initial bond breaking which is followed by bond reformation in series. In dissociative CANs, network integrity is compromised.

2.3.1 Transesterification exchange chemistry

Transesterification is an equilibrium isodesmic exchange reaction in which an ester and alcohol are transformed into another ester and another alcohol via an alkoxy chain interchange. Various catalysts – such as organic bases, inorganic salts, acid catalysts, amine catalysts, Lewis acids, alkoxide catalysts, titanium tetraalkoxide catalysts, and organotin catalysts – are used to control transesterification reactions [61,70]. The transesterification exchange is shown in **Figure 2.6**.

Transesterification was employed to synthesise the first known vitrimer, utilising a Lewis acid catalyst - zinc acetate - in an epoxy system involving diglycidyl ether of bisphenol A (DGEBA) and a mixture of fatty dicarboxylic and tricarboxylic acids [11]. It is widely applied in various resin systems for matrix vitrimerisation [11,17,24,52,53,57,60,61,67,71–81]. Since benzoxazine polymerisation is autocatalysed, a dynamic bond exchange chemistry not requiring catalysis would be appropriate for its vitrimerisation. In this regard, catalyst-free transesterification-enabled polybenzoxazine vitrimers with moderate T_g (79 – 125°C), depending on the ratio of the precursors, are developed, incorporating tertiary amines and hydroxyl groups in the polymer chain, since tertiary amines can catalyse transesterification reactions.[17]

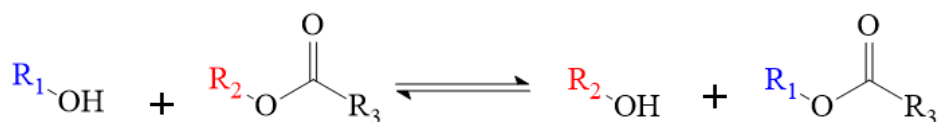


Figure 2.6. Transesterification exchange mechanism.

2.3.2 Imine bond exchange chemistry

Imines contain a nitrogen-carbon double bond in which the nitrogen has a lone pair of electrons and is bonded to either an organic group, in which case the molecule is a Schiff base, or to a hydrogen atom resulting in a non-Schiff base imine. Imine bonds – usually formed from the condensation reaction of aldehydes and amines – participate in dynamic exchange reactions in one of three

equilibrium processes: dissociative imine hydrolysis/condensation (reaction with water), associative imine-amine transamination, and associative imine-imine exchange (imine metathesis or transamination) [41,82–86]. The three equilibrium processes are represented in **Figure 2.7**.

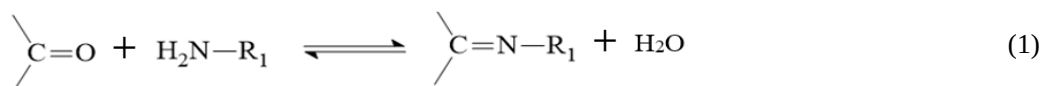
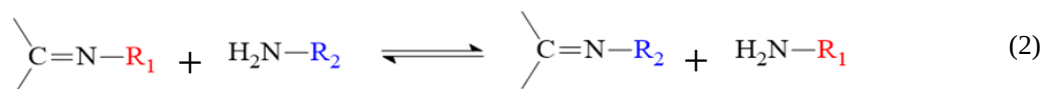
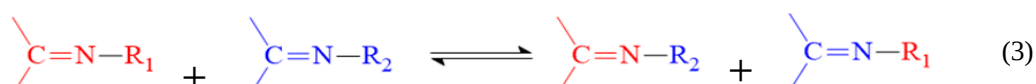


Figure 2.7. Equilibrium processes of imine bond chemistry.

Imine dynamic chemistry is mainly exploited using dissociative imine hydrolysis [85]. This is the case with a chemically degradable vitrimer-like polyurethane network with good antibacterial ability, attributed to imine bond which was exploited for its reprocessability [87]. However, for true vitrimers involving imine bonds, imine-amine transamination or imine-imine exchange dominate, since vitrimers undergo associative network topology rearrangement. The application of imine chemistry in vitrimeric systems is attractive, partly due to the versatility of potential imine-containing CANs made possible by the diversity of commercially available aldehydes and amines, [44] and partly because, unlike transesterification reactions, imine bonds do not require the use of catalysts to undergo intermolecular exchange, as they are weak covalent bonds [44,46,68,82,83,88–100]. The mechanism of transamination is illustrated in **Figure 2.8**. The associative dynamic imine chemistry – through one or both of imine-amine transamination and imine metathesis – is applied to develop a broad range of vitrimeric systems for industrial application.

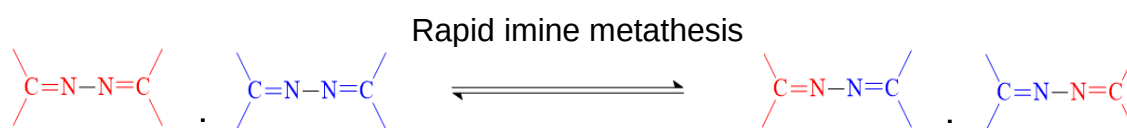


Figure 2.8. Mechanism of transimination (imine metathesis) using 1,2-di(propan-2-ylidene) hydrazine moiety of a polyimine network.

A Schiff base precursor, tris(4-formyl-2-methoxyphenyl) phosphate, is synthesised through a typical condensation reaction between lignin-derived vanillin and phosphorus oxychloride and cured with 4,4-diaminodiphenylmethane (MDA), 4,4-diaminodicyclohexylmethane (PACM), or hexamethylenediamine (HMD) to produce malleable thermosets (Schiff base CANs) as shown in **Figure 2.9**. The thermosetting material exhibits rapid processibility, and high monomer recovery upon treatment with a solution of tetrahydrofuran, hydrochloric acid, and deionized water. The material also exhibits permanent shape changeability and outstanding fire retardance [86]. Other material properties include activation energy of bond exchange ranging from 49 to 81 kJ/mol, high T_g of about 180°C, tensile strength of about 70 MPa, and tensile modulus close to 1.9 GPa. Stress relaxation for this material is completed within 2–10 minutes at 180°C.

Dynamic self-healing imine bond vitrimers exhibit recovery of tensile strength up to 71–73%, through imine metathesis after three hot-pressing cycles [95] with elongation at break ranging from 21 to 24%, Young's modulus, ranging from 4.4 to 5.1 MPa, and strength from 0.69 to 0.73 MPa) after successive recycling [46]. A high T_g imine vitrimer (172°C) with a tensile strength of 81 MPa, modulus of 2.1 GPa, high thermal stability ($T_{d5\%} = 323^\circ\text{C}$) and elongation at break of 15% shows retention of these mechanical properties after successive reprocessing cycles [101]. Other imine-endowed vitrimers – one having T_g exceeding 120°C, tensile strength and Young's modulus above 60 MPa and 250 MPa, respectively [23], and another with T_g of 56°C and fast bond exchange at 80°C [91] – exhibit full retention of mechanical properties after successive recycling. Other vitrimers based on imine bond exchange include biobased polyimine elastomeric systems

exploiting the reaction between di- and trifunctional polyether amines and a furan-based dialdehyde [84], and an aldehyde group-terminated polybutadiene rubber (APB) with different molecular weights crosslinked with tris(2-aminoethyl) amine via imine bond linkages [100].

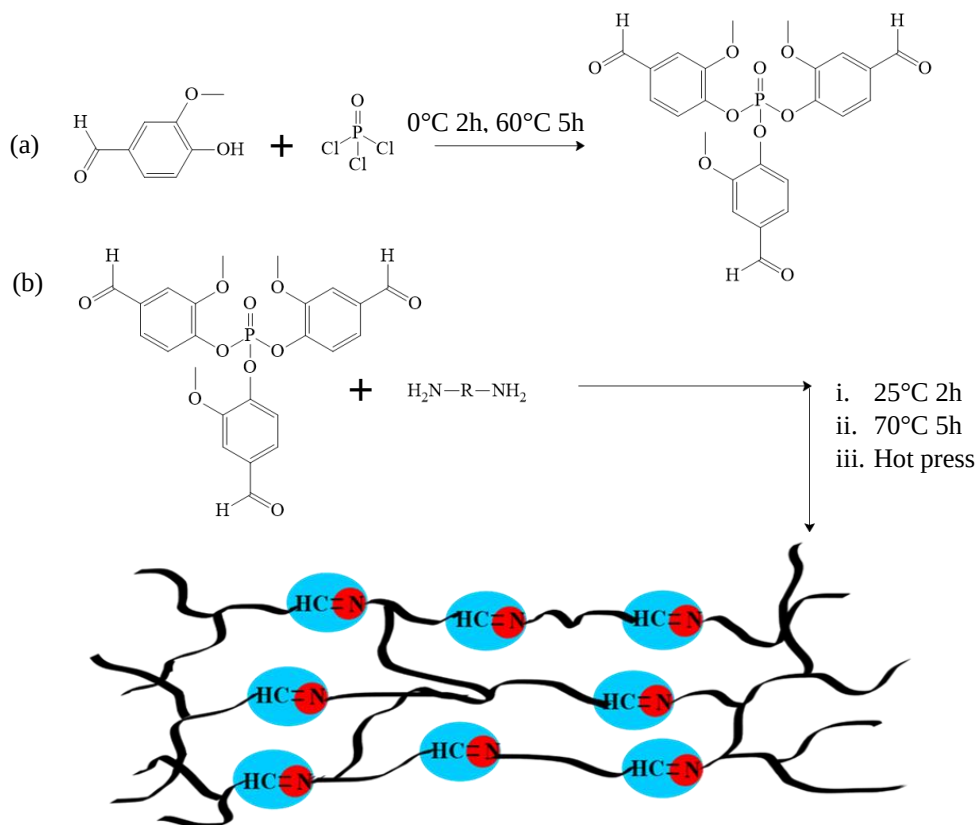


Figure 2.9. Schematic for the synthesis of a renewable Schiff base CAN. (a) Synthesis of tris(4-formyl-2-methoxyphenyl) phosphate. (b) Preparation of Schiff base CAN [86].

2.3.3 Disulphide metathesis

Polymer networks endowed with disulphide bonds normally undergo catalyst-free reversible disulphide metathesis when exposed to an appropriate stimulus such as heat, or light [14,102–110], due to the low energy barrier needed to achieve reversible simultaneous breaking and formation of S-S bonds [111]. The process may involve either of, or both, dissociative and associative pathways, depending on the prevailing conditions and patterns of substitution involved [85]. The

network is a vitrimer only when the bond exchange is solely associative; i.e. the dynamic bonds are formed simultaneously as they are broken such that average number and functionality of crosslink remains constant. Disulphide bond is suitable for the design of materials exhibiting good shape-memory [45] and self-healing at moderate temperatures [109], as well as recyclability with the retention of mechanical properties [112,113].

The effects of network crosslinking density and chain rigidity, and mobility on the self-healing characteristics of an adhesive epoxy polysulphide thermoset material (EPS25 and EPS70) were demonstrated [114], indicating that apart from being deployable for self-healing applications, disulphides do not significantly affect the thermal stability of resins [108], neither do they have a deleterious effect on mechanical properties [115], as the material exhibits full recovery of mechanical integrity by re-establishing cohesive as well as adhesive properties after 10 cycles of healing involving thermal treatment at 100°C.

An isosorbide-derived epoxy (IS-EPO) reacts with 4,4'-disulphanedieldianiline (MDS) to yield MDS-EPO vitrimer, which shows fast stress relaxation, good recycling, reprocessing, and controllable shape memory, unlike another IS-EPO cured with 4,4'-methylenedianiline (MDA), a traditional curing agent for epoxy [116]. The glass transition temperature of the MDS-EPO vitrimer is 41.4°C, and its tensile strength is 11 MPa. The vitrimer (**Figure 2.10**) exhibits thermal stability with an onset degradation temperature of 270°C, which is far above the reprocessing temperature of 100°C.

The dynamic character of the disulphide bond has been further demonstrated by comparing two similar monomers of polyurethane networks consisting of castor oil, isosorbide, and hexamethylene diisocyanate with a poly(urethane urea) composed of castor oil, isosorbide, hexamethylene diisocyanate, and 4-aminophenyl disulphide prepared under the same experimental conditions [117]. The difference between the two prepolymers is that the latter contains 4-aminophenyl disulphide whilst the former does not. The permanently crosslinked polyurethane cannot be reprocessed, whilst poly(urethane urea) can be

reprocessed with full recovery of mechanical properties due to the network topology rearrangement resulting from associative dynamic disulphide exchange. In a related study, it has been demonstrated that upon the withdrawal of isosorbide from the reaction system, the mechanical properties of the poly(urethane urea) can be controlled by varying the 4-aminophenyl disulphide content and by manipulating molar ratios of relevant functional groups [118].

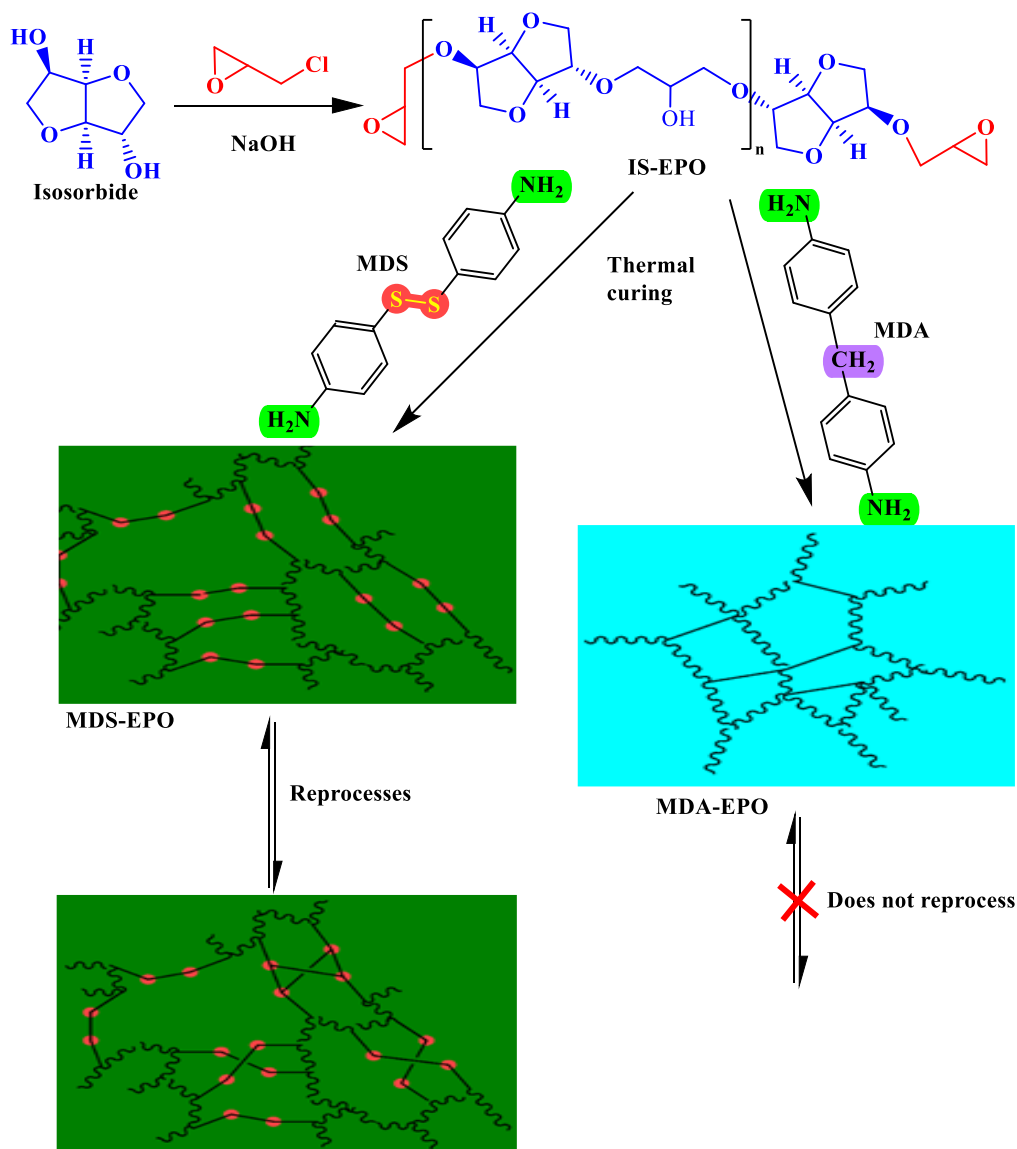


Figure 2.10. Synthetic route of isosorbide-derived epoxy (IS-EPO).[116]

A self-healing bis-disulphide bond-enabled vitrimeric epoxy resin ($T_g = 133^\circ\text{C}$) is successfully synthesised by the reaction of a difunctional epoxy monomer

containing disulphide bonds and 4-aminophenyl disulphide [47]. The self-healing matrix (**Figure 2.11**) can be doped with recoverable conductive carbon nanotube-polypyrrole fillers to enhance the mechanical properties of the epoxy vitrimer resin, giving rise to a nanocomposite material reprocessable at 180°C [47]. The stress relaxation time decreases from 3 hr at 130°C to 9 s at 200°C without a catalyst, following an Arrhenius temperature dependence of viscosity with low activation energy. The stress relaxation time is lowered by increasing the density of disulphide bonds in the epoxy resin, whilst the thermomechanical properties of the dynamic epoxy network remain unaffected. The dynamic bond results in unique self-healing and processing properties of the epoxy. Thiols can degrade the dynamic epoxy network by reducing disulphide bonds. This reaction is exploited in recovering the nanofillers. The composite material can be dissolved in dimethylformamide solution of dithiothreitol at 50°C for 24 hours to recover the filler. The material has thermal stability with a degradation temperature of 275°C, which is 95°C above the reprocessing temperature. A similar study that employed disulphide bond-enabled epoxy vitrimer to develop a graphene oxide epoxy vitrimer nanocomposite reported a catalyst-free strategy where the nanofillers enhance self-healing properties, including the shape memory and flexural strength of the materials [45]. From these results, it is envisioned that potential high-performance disulphide-enabled polybenzoxazine vitrimers would feature highly attractive characteristics.

Added to the advantage of operating catalyst-free, dynamic disulphide exchange is preferred over transesterification for faster stress relaxation, as evidenced by a self-healing recyclable dual dynamic exchange epoxy vitrimer exploiting the synergistic effect of disulphide metathesis and carboxylate transesterification exchange to achieve rapid stress relaxation and moderate malleability [67]. Vitrimeric systems governed solely by dynamic disulphide metathesis exhibit topology transitions below their glass transition [14,16,45,67,104,116,119]. This allows fast stress relaxation and ease of reprocessability of thermosets, thus underscoring dynamic disulphide metathesis as a simple and efficient catalyst-free bond transfer mechanism for vitrimers [120]. The application of dynamic

disulphide exchange reaction in benzoxazine vitrimerisation is very attractive due to the disulphide bond catalyst-free fast exchange reaction on one side and its self-healing and shape memory properties on the other side.

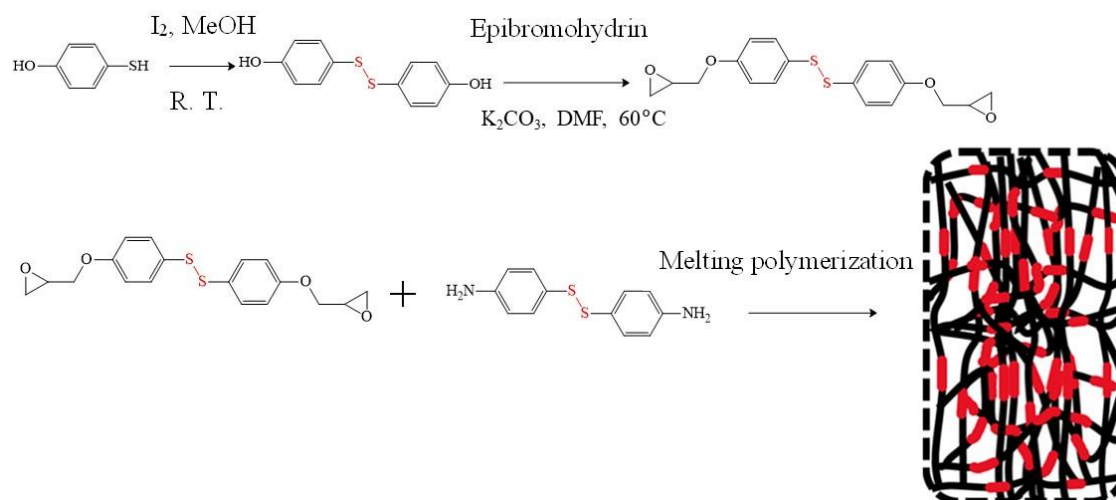


Figure 2.11. Schemes for the synthesis of bis-disulphide bond dynamic epoxy resin.[47]

2.3.4 Transamination

Amine-amine bond exchange reactions are applied in vitrimeric systems. One such formulation, the first catalyst-free vitrimer, exploits the condensation reaction between acetoacetates and amines to yield poly(vinylogous urethanes) capable of reshuffling their network topology via an associative transamination [121]. The transamination reaction is shown in **Figure 2.12**. The group labelled X represents either a vinylogous urethane ($X = O$) or a vinylogous amide ($X = CH_2$). Both vinylogous urethanes and vinylogous amides can undergo catalyst-free associative dynamic transamination at elevated temperatures [121]. Other vitrimers based on transamination of vinylogous urethanes can be synthesised [27,122]. Transamination has also been applied to diketoenamine bonds, yielding closed-loop recycling of processable thermosets, adaptable for high-performance dynamic covalent polymers involving both aliphatic and aromatic amine monomers [123]. This is illustrated in **Figure 2.13**. Apart from the amine-amine

dynamic bond exchange and diketoenamine bond transfer, transamination also manifests as one of the three equilibrium processes of imine bond exchange known as imine-amine transamination. In general, transamination is an appropriate exchange chemistry for the vitrimerisation of benzoxazines due to the amine functional group derivable from amine and phenolic precursors of potential benzoxazines.

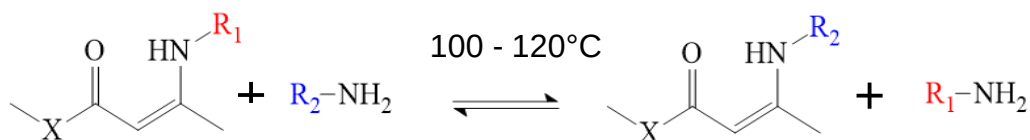


Figure 2.12. Transamination exchange of vinylogous urethanes and amides [121].

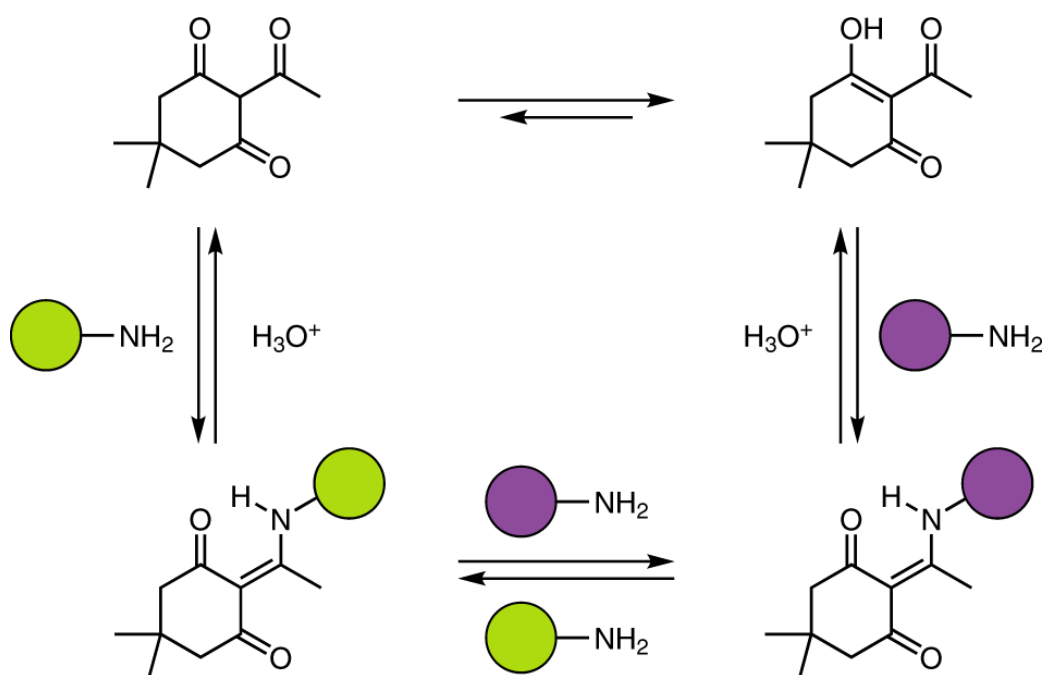


Figure 2.13. Transamination involving reversible dynamic covalent diketoenamine bonds Reprinted with permission from [123]. Copyright (2019)

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2.3.5 Transcarbamoylation exchange

Transcarbamoylation is the transfer of the carbamoyl moiety from one molecule to another, arising from carbamate-only bond exchange which is generally applicable to polyurethanes [124]. The mechanism for carbamate bond exchange depends on the nature of polymer network [125] and the presence of a catalyst [126]. Some transcarbamoylation reactions occurring in polyurethane CANs operate via dissociative mechanism [127–130], due to the dissociative reaction of urethane bonds which normally requires a catalyst [126], whilst others operate via associative mechanism [126,131,132] often requiring no catalyst. Concurrent associative and dissociative dynamic chemistry due to the synergistic effect of associative transcarbamoylation and dissociative reversible cyclic carbonate aminolysis (**Figure 2.14**) has been reported for polyhydroxyurethane networks [133]. Such network is not a true vitrimer due to the dissociative component of the dynamic chemistry.

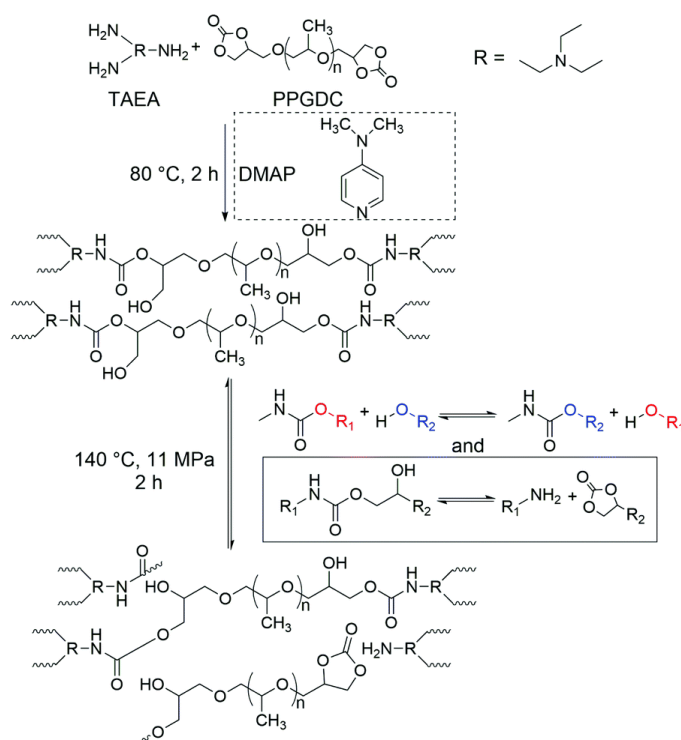


Figure 2.14 Synthesis of polyhydroxyurethane network and topological rearrangement involving transcarbamoylation and reversible cyclic carbonate aminolysis. Reprinted with permission from [133]. Copyright 2017. Royal Society of chemistry.

A recently reported polybenzoxazine-polyurethane vitrimer featuring transcarbamoylation undergoes catalyst-free associative bond exchange [31]. For a polybenzoxazine incorporating carbamate chemistry to be categorized as a vitrimer, the dynamic bond exchange must strictly follow the associative mechanism. The potential of transcarbamoylation for the design of new functional polymers has not been fully exploited. The excellent properties and molecular design flexibility of benzoxazines, already highlighted, place them at the forefront of all candidates in this regard. Transcarbamoylation exchange is shown in **Figure 2.15**.

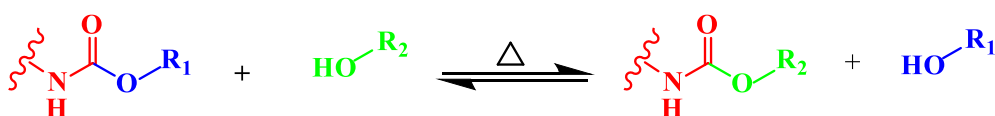


Figure 2.15. Transcarbamoylation in polyhydroxyurethanes [125,133].

2.3.6 Transalkylation exchange chemistry

Transalkylation exchange chemistry is applied to polymer science for the design of vitrimers and dissociative CANs. Of the four reported transalkylation types [134], only catalyst-free S_N2-type transalkylation between trialkyl sulfonium salts and thioethers (sulphides) proceed through the associative pathway. Such transalkylation is sub-grouped as transalkylation of sulfonium salts and is implemented for poly(thioether) networks [135] with appreciably higher bond exchange activation energy (108 – 113 kJ/mol) compared to catalyst-free transamination of vinylogous acyl compounds (59 kJ/mol) [121]. Transalkylation of sulfonium salts is proposed as a useful strategy for the recycling of industrial scrap rubber cured with sulfur [136]. Other subgroups of transalkylation, namely trans-N-alkylation of pyridiniums [56,137], trans-N-alkylation of anilinium salts, and trans-N-alkylation of 1,2,3-triazolium salts [138], all proceed via the dissociative pathway. Therefore, materials incorporating these types of transalkylation are not vitrimers. In fact 1,2,3-triazolium-based poly(ionic liquid) is viewed as the link between vitrimers and dissociative CANs due to their versatility which enables their tunability between completely depolymerisable dissociative

CANs and CANs whose rheological characteristics are indistinguishable from vitrimers [138].

Transalkylation can be extended to a variety of thermosets, including benzoxazines to achieve functional vitrimers. To achieve a benzoxazine vitrimer design through transalkylation, systems capable of yielding dissociative CANs as detailed herein should be avoided. The mechanisms for the transalkylation of sulfonium salts and trans-N-alkylation of 1,2,3-triazolium salts are shown in **Figure 2.16** and **2.17**, respectively.

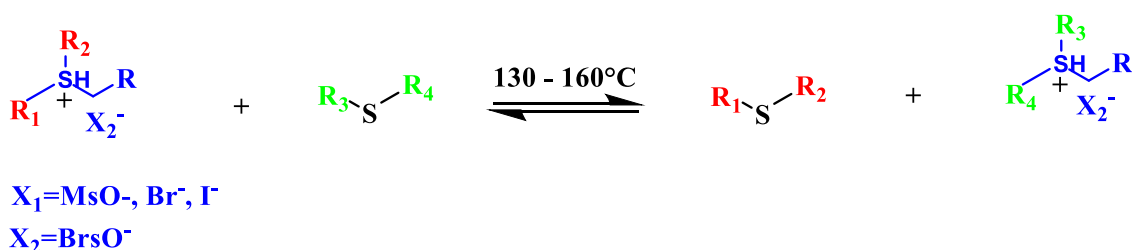


Figure 2.16. S_N2 transalkylation between trialkyl sulfonium salts and thioethers used for the design of poly(thioether) vitrimer networks [135].

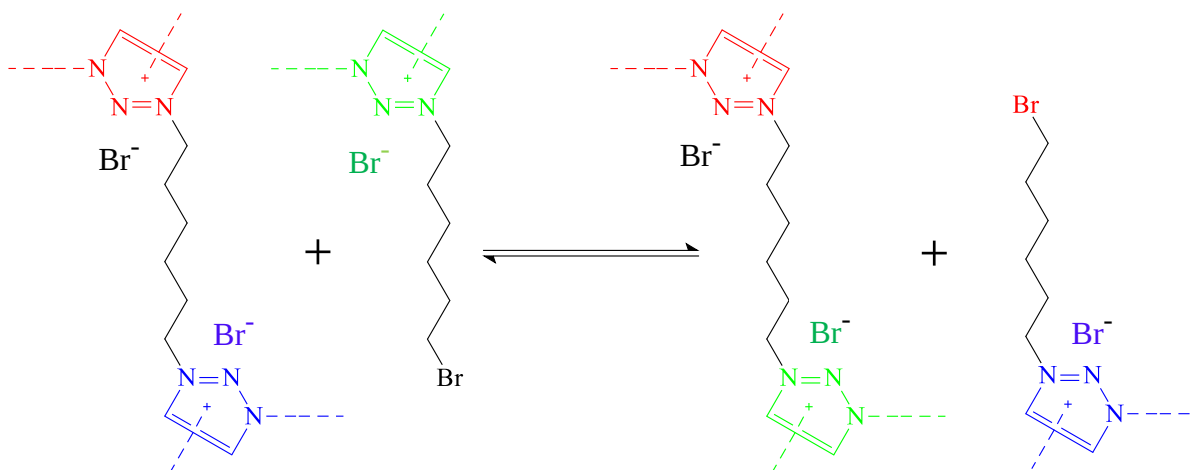


Figure 2.17. Transalkylation reaction mechanism of triazolium bond [138].

2.3.7 Olefin metathesis

Olefin metathesis is widely used in ring-opening metathesis polymerisation due to the ease with which it forms carbon-carbon bonds [139–142]. It is an attractive

method for thermoset vitrimerisation [85], as demonstrated using cross-linked polybutadiene networks incorporating second-generation Grubbs catalyst [143,144]. The selection of Grubbs catalysts in preference to the more common metathesis catalysts is supported by the fact that they exhibit superior air and moisture stability and are generally functional group-compatible [145]. The ambient temperature exchange reaction of olefin bonds can be exploited for possible self-healing applications.

Furthermore, olefin bonds can be used to increase the crosslinking density of polybenzoxazines, as they participate in co-reaction with the benzoxazine functionality shown in **Figure 1.2** [146]. However, compared to more straightforward imine, amine, or disulphide chemistry, applying olefin metathesis towards benzoxazine vitrimerisation may be hindered by cost, dependence on catalyst, and creep associated with olefin-enabled networks [85]. These facts are summarised in **Table 2.1**.

Table 2.1. Advantages and disadvantage of olefin metathesis [85,146]

Advantages	Disadvantages
Ambient temperature bond exchange	Expensive
Self-healing application	Catalytic, risk of catalyst toxicity
Compatible with benzoxazine chemistry	Network prone to creep

2.3.8 Transcarbonation exchange

Polycarbonates, which are organic compounds containing the carbonate functional group, generally undergo catalytic transcarbonation exchange reactions with free hydroxyl groups at elevated temperatures, similar to transesterification exchange [147–151]. This concept is extended to polycarbonate vitrimers exhibiting hydroxyl or titanium (IV) alkoxide-catalysed stress relaxation at elevated temperatures with activation energy in the range of 80 – 120 kJ/mol, depending on catalyst loading [152]. The associated chemically recyclable and acid-degradable vitrimer show full reprocessability without

compromising chemical and mechanical integrity of the material, confirming the occurrence of topology rearrangement without depolymerisation. The topology of the crosslinked polymer and the transcarbonation exchange is shown in **Figure 2.18**. This exchange chemistry may not be optimal for benzoxazine vitrimerisation since it relies on catalysis to achieve stress relaxation in the vitrimer.

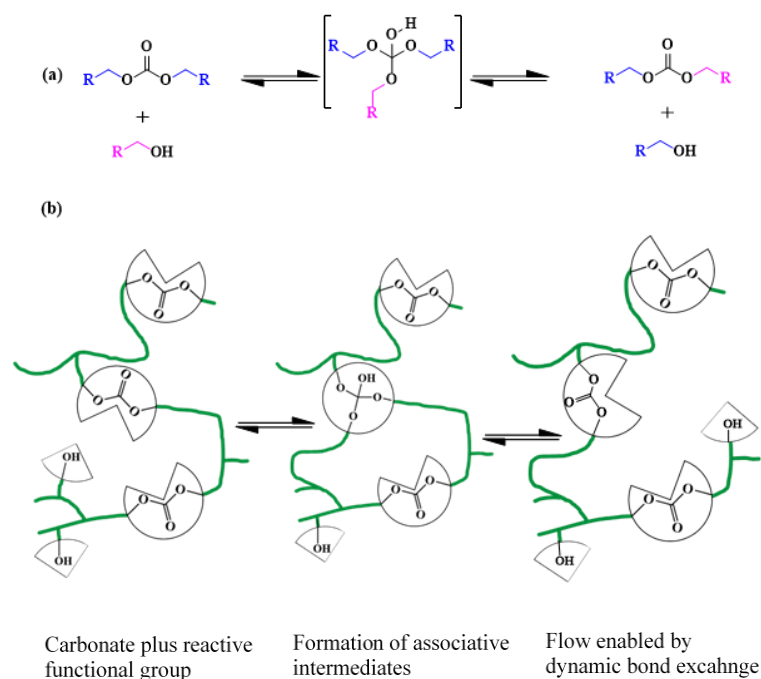


Figure 2.18. (a) Transcarbonation exchange reaction between a hydroxyl nucleophile and a carbonate by the formation of an associative intermediate and the release of the exchanged carbonate and hydroxyl group. (b) The topology of a cross-linked polymer network containing carbonates and hydroxyls is adjustable via transcarbonation exchange reactions [152].

2.3.9 Siloxane-silanol exchange

Polydimethylsiloxanes are capable of dynamic siloxane rearrangement via acid or base-catalysed stress relaxation [153]. Siloxane-silanol bond exchange has been demonstrated in a material formulated by ring-opening copolymerisation of octamethylcyclotetrasiloxane and bis(heptamethyl cyclotetrasiloxanyl)ethane initiated by tetramethylammonium silanolate, which yields cross-linked polydimethylsiloxane (PDMS) networks with ethylene bridges and highly reactive

anionic species of silanolate end groups (**Figure 2.19**) [154]. The material heals by siloxane equilibration, and the original mechanical strength of the silicone sample is fully restored. Polydimethylsiloxane-based vitrimers incorporating excellent performance can be synthesised [42,155–157]. The general siloxane-silanol exchange reaction is illustrated in **Figure 2.20**. Siloxane-silanol exchange can be incorporated in benzoxazine synthesis with obvious cost implications since it involves catalysis for the polymer to relax stress. Although known silanolate anion systems are susceptible to thermal degradation at 150°C [85], incorporating siloxane-silanol exchange into thermostable benzoxazine systems needs to be explored as this may provide a good compromise between the high temperature needed for high-performance benzoxazine malleability on the one side and thermal degradation of the silanol system on the other side.

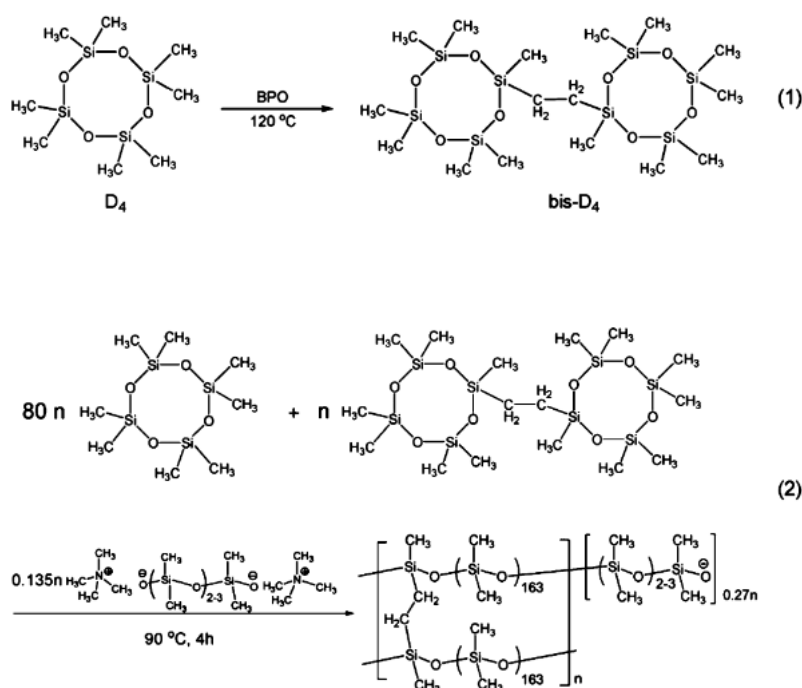


Figure 2.19. Ring-opening copolymerisation of octamethylcyclotetrasiloxane (D4) and bis(heptamethylcyclotetrasiloxanyl)ethane (bis-D4) initiated by tetramethylammonium silanolate, healable by siloxane equilibration. Reprinted with permission from [154]. Copyright (2012) American Chemical Society.

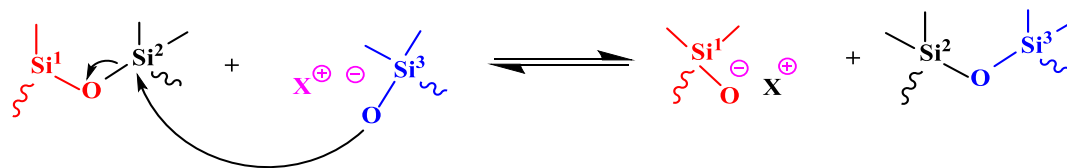


Figure 2.20. Siloxane-silanol exchange through addition and elimination of silanolate anion [85].

2.3.10 Silyl ether exchange

Bis-silyl ethers are identified as appropriate crosslinkers in vitrimer chemistry. They are used for crosslinking pendant hydroxyl group-functionalised polystyrene vitrimers, thermally stable up to 350°C [158], and for the development of thermostable polyethylene-co-vinyl alcohol vitrimers based on silyl ether metathesis, with degradation temperature of 427°C and increased creep resistance[159] (**Figure 2.21**). Silyl ethers have also been used in the synthesis of crosslinked vinylogous urethane polyethylene in reactive extrusion, yielding thermosets that exhibit stress relaxation by a heat-induced topological transition which enhances their reprocessability, recyclability, and hydrolytic stability [43,48]. An extension of silyl ether metathesis to the vitrimerisation of benzoxazines, is possible and would potentially yield a thermally and mechanically robust polybenzoxazine for high-temperature applications.

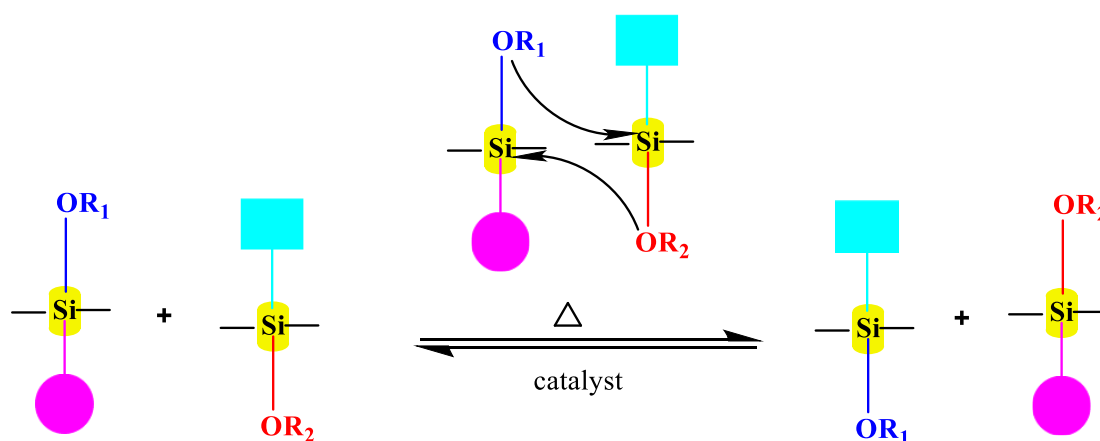


Figure 2.21. Schematic representation of silyl ether metathesis [159].

2.3.11 Dioxaborolane metathesis

Reversible interchange of moieties connected by the strong boron-oxygen (B-O) bonds of boronic ester groups (**Figure 2.22**) is exploited to formulate vitrimers from polymers containing carbon-carbon single bonds in their backbone [160]. The vitrimer can undergo catalyst-free dioxaborolane metathesis at low temperature (60°C). This is employed in polydioxaborolane vitrimer networks [161] with topology freezing transition estimated below the glass transition, enabling fast dioxaborolane metathesis immediately above the glass transition.

In an earlier study to synthesise some dioxaborolane-enabled polybutadiene vitrimers, topology transitions have also been found to occur below the glass transitions [26]. Such chemistry yields vitrimers that exhibit improved creep resistance at service temperatures and desirable flow properties at processing temperatures [26] as well as outstanding thermomechanical and chemical resistance, and can be applied to poly(methyl methacrylate), polystyrene [160], and high-density polyethylene [160,162].

Dioxaborolane bond exchange finds application in vitrimerisation of many thermosetting systems and has been shown to be compatible with benzoxazine chemistry in various ways. It has been demonstrated that treating a thiol-functionalised cardanol-based benzoxazine monomer with 1,4-phenylenebisboronic acid, water and tetrahydrofuran at room temperature in the presence of magnesium sulphate produces a benzoxazine vitrimer with fast catalyst-free bond exchange activation energy of the order of 50 – 63 kJ/mol [163]. This is illustrated in **Figure 2.23**.

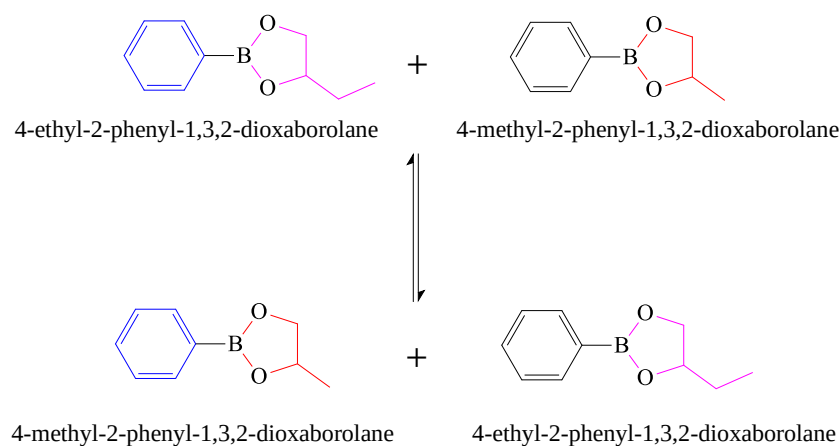


Figure 2.22. Schematic representation of dioxaborolane metathesis.

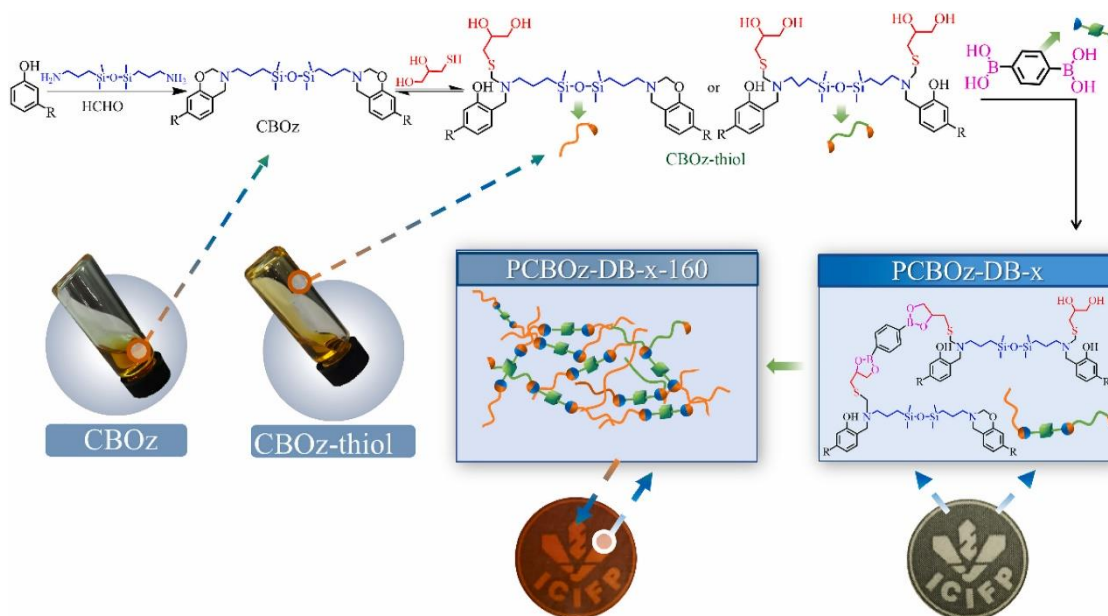


Figure 2.23. Synthesis and curing of dioxaborolane-functionalised benzoxazine vitrimer. Reprinted with permission from [163]. Copyright (2022) Elsevier.

2.4 Benzoxazine vitrimers

There is currently significant research focus on the design of polybenzoxazine vitrimers as alternatives to epoxies, motivated by the superiority of polybenzoxazines to both epoxies and phenolics in terms of char yield, hygrothermal performance, and cure shrinkage. Like epoxies, benzoxazines

equally feature excellent molecular design flexibility, dimensional stability, and compatibility with sustainable precursors.

Of the few established reprocessable polybenzoxazines, the materials incorporating boronic ester bond [39], and transesterification [37,38], exhibit high thermomechanical properties. Whilst synthesis of polybenzoxazine crosslinked with boronic ester bond involves the use of toluene as solvent in a time-consuming three-pot strategy that involves a purification step, the synthesis of benzoxazine vitrimers based on transesterification involves two distinct steps: esterification of a phenolic precursor using an acid, followed by the synthesis of benzoxazine using the esterified phenolic, paraformaldehyde and an amine [17,37,38]. This strategy yields moderate-to-high glass transition (T_g) systems, with transesterification bond exchange being internally catalysed by the benzoxazine tertiary amine. It is not a direct synthesis route and involves purification of the esterified precursor prior to use for benzoxazine synthesis. Other reprocessable polybenzoxazines featuring dynamic covalent bond exchange do so via fast dioxaborolane metathesis (**Figure 2.23**) [163] and transcarbamoylation (**Figure 2.24**) [31], with low glass transition of 29°C and 55°C, respectively, whilst each formulation involves more than one-pot method, just as the self-healing of main-chain polybenzoxazine synthesised from poly(propylene/ethylene oxide) bisamine is achieved by mixing with phenyl boronic acid in chloroform prior to curing, producing a low T_g system, illustrated in **Figure 2.25** [164]. In this study, the strategy for synthesising high-performance benzoxazine vitrimer is to incorporate covalent adaptable bonds in the benzoxazine backbone to functionalise the main-chain benzoxazine into a vitrimer.

Disulphide metathesis is an excellent bond exchange for catalyst-free vitrimers. A recent review documented the relaxation times of the established polybenzoxazine vitrimers, revealing that a system incorporating disulphide bond features the fastest evolution of stress relaxation modulus at moderate temperature, whilst its synthesis involves the simple implementation of one-pot

Mannich condensation reaction [16]. However, this polybenzoxazine vitrimer performs quite low in terms of its thermomechanical behaviour, as it has a T_g of 40°C and degradation temperature of 252°C. The current study is motivated by the need to develop moderate-to-high-performance benzoxazine vitrimer following the established solventless one-pot Mannich condensation method [165], incorporating very fast catalyst-free bond exchange. No success has yet been reported in this regard. This is possible to achieve if the precursors exhibit the needed solubility for one another at the temperature of the reaction without solidifying prior to the end of the reaction.

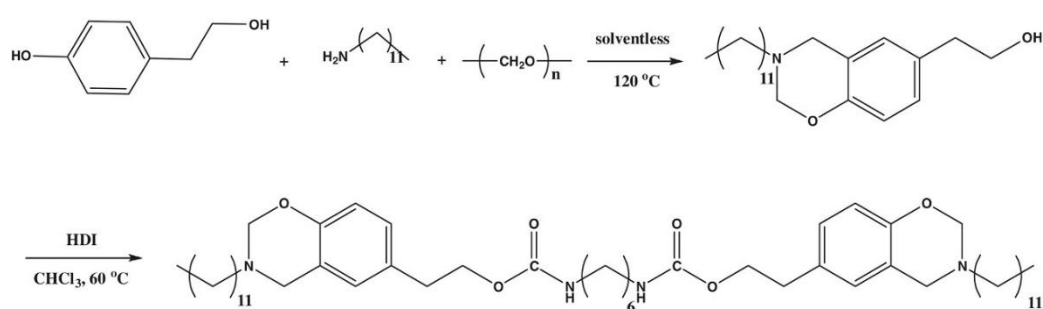


Figure 2.24. Synthesis of polyurethane-based benzoxazine incorporating carbamate chemistry to enable transcarbamoylation bond exchange within the network. Reprinted with permission from [31]. Copyright (2022) Wiley online library.

Amongst established vitrimers, chemistries based on disulphide bonds feature prominently [16,18,25,166], satisfying aerospace requirements, such as high T_g and thermomechanical performance [18,167,168]. Disulphide bonds are known to express fast catalyst-free topology reconfiguration under mild stimuli such as heat or light, enabling self-repair without compromising network integrity. If the characteristics of polybenzoxazines that render them an excellent platform for aerospace applications [169] are combined with disulphide bond chemistry, this would hold a promising potential to produce a class of polybenzoxazine vitrimers with a multiplicity of smart functionalities whilst still meeting aero-grade requirements, including solvent resistance, high glass transition, self-healability, fire retardancy, and excellent hydrophobic behaviour for wet environment

operation. This is possible, given the molecular design flexibility of benzoxazines, and can be achieved through the simple cost-effective solventless one-pot method of benzoxazine synthesis. This remains a research gap in this field. The current study seeks to close this gap and apply the outcomes in the area of reprocessable smart thermosetting composite matrices.

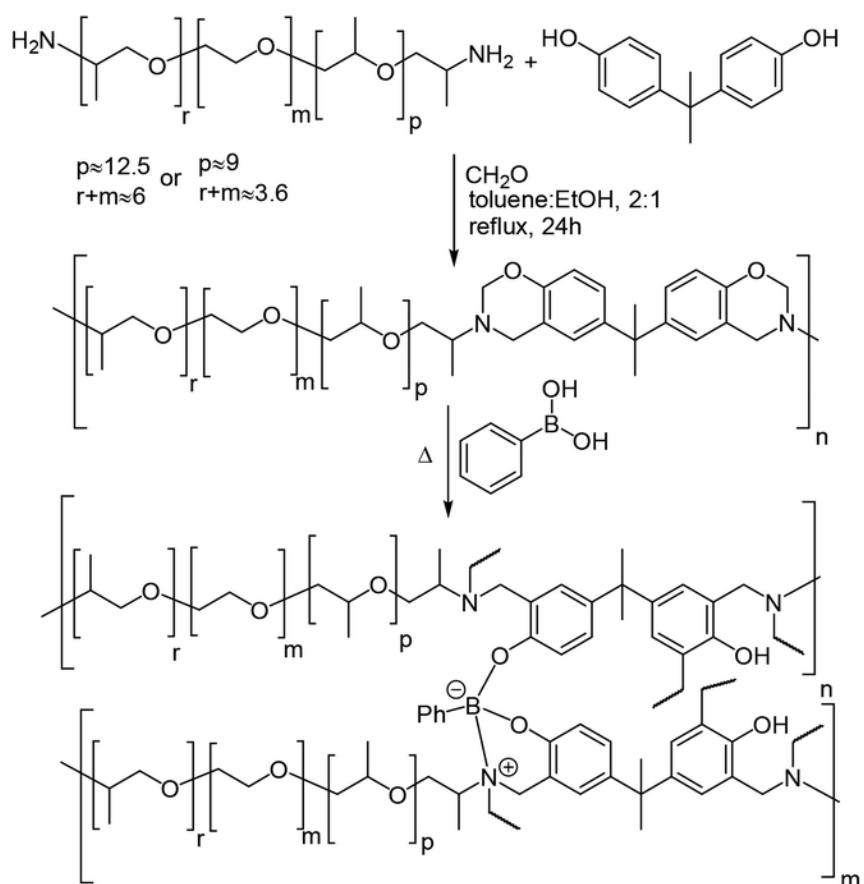


Figure 2.25. Synthesis of benzoxazine vitrimers based on two types of poly(propylene/ethylene oxide) bisamine and their simultaneous curing. Reprinted with permission from [164]. Copyright (2022) Royal Society of Chemistry.

2.5 Processing characterisation of vitrimers

2.5.1 Cure kinetics

Since most of the research on the topic of vitrimers focuses mainly on the formulation and characterisation of novel vitrimers from various thermosetting

systems, literature is lacking in the cure kinetics and rheological modelling of vitrimers for optimised composite manufacturing. However, a few attempts have been made to date towards quantifying cure kinetics of vitrimeric systems, particularly epoxy/acid vitrimers with zinc catalyst, following the techniques used in conventional thermosets [170,171].

A cure kinetics model is essentially a mathematical expression of the dependence of the reaction rate – the time-derivative of the degree of cure – on an Arrhenius temperature-dependent rate constant, $K(T)$, and a fractional conversion-dependent mechanism, $f(\alpha)$, and is expressed phenomenologically as:

$$\frac{d\alpha}{dt} = K(T)f(\alpha) \quad (2.2)$$

The Arrhenius temperature dependence is given by:

$$K(T) = Ae^{-\frac{E}{RT}} \quad (2.3)$$

where A is a pre-exponential factor, which is independent of temperature, E is the reaction activation energy and R is the universal gas constant ($8.314 \text{ Jmol}^{-1}\text{K}^{-1}$). Altogether, $f(\alpha)$, A and E constitute the kinetics triplet embodying the factors governing the progress of the curing reaction, the accurate determination of which is essential to the processing conditions of the resin [172].

Shen [170] employed the popular Kissinger model for dynamic experiments – for which the maximum reaction rate corresponds to the peak temperature of the cure exotherm, T_p :

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{E}\right) - \frac{E}{RT_p} \quad (2.4)$$

– and isoconversional analysis, which uses the dependence of reaction rate on temperature at a constant conversion, expressed by holding $f(\alpha)$ constant in the logarithmic derivative of Eq.2.2:

$$\left[\frac{\partial \ln(d\alpha/dt)}{\partial T^{-1}}\right]_{\alpha} = \left[\frac{\partial \ln K(T)}{\partial T^{-1}}\right]_{\alpha} + \left[\frac{\partial \ln f(\alpha)}{\partial T^{-1}}\right]_{\alpha} \quad (2.5)$$

yielding:

$$\left[\frac{\partial \ln(d\alpha/dt)}{\partial T^{-1}} \right]_{\alpha} = \left[\frac{\partial \ln K(T)}{\partial T^{-1}} \right]_{\alpha} \quad (2.6)$$

to quantify the values of E for various epoxy/dicarboxylic acid vitrimers and assessed the effects of catalyst and acid chain length on the value of E and thus the reaction rate. This is achieved by combining Eq.2.2 and 2.6 to obtain:

$$\left[\frac{\partial \ln(d\alpha/dt)}{\partial T^{-1}} \right]_{\alpha} = -\frac{E_{\alpha}}{R} \quad (2.7)$$

Eq.2.7 highlights the isoconversional activation energy, E_{α} , determined based on Arrhenius dependence only, without any modelling assumptions [173,174] by applying to various temperature profiles to ascertain the temperature dependence of the reaction rate under constant conversion and correct the oversimplification implied by a single temperature (T_p) Kessinger model expressed by Eq.2.4. This approach which led to the derivation of three popular isoconversional activation energy models: Flynn-Wall-Ozawa (FWO), Kissinger-Akahira-Sunose (KAS), and Starink [175–177], with general form of:

$$\ln \frac{\beta}{T_{\alpha}^K} = -A \frac{E_{\alpha}}{RT_{\alpha}} + C \quad (2.8)$$

was utilised by Shen [170] to obtain more reliable values of isoconversional activation energy for various epoxy dicarboxylic acid vitrimers. In this analysis, the pre-exponential factor is determined leading to different approximate solutions [178,179]. The activation energy was found to decrease substantially towards the later stages of the reaction, suggesting a transition from a chemical-controlled kinetics to one controlled by diffusion due to an increasingly minimal diffusion coefficient of the monomers corresponding to the creation of mobility-limiting three-dimensional network [180]. Therefore, the system was modelled using an autocatalytic model incorporating a logistic function to account for the chemical-to-diffusion controlled kinetics in the way suggested in [181]:

$$\frac{d\alpha}{dt} = \frac{Ae^{\left(-\frac{E_a}{RT}\right)} \alpha^m (1-\alpha)^n}{1+e^{C[\alpha-(\alpha_{c0}+\alpha_{cT}T)]}} \quad (2.9)$$

Yielding an average 84 % goodness of fit. In Eq.2.9, C is a coefficient controlling the breadth of the transition to diffusion-controlled kinetics, and α_{c0} and α_{cT} are coefficients controlling the critical degree for diffusion as a function of temperature.

In another development, the cure kinetics of an epoxy/anhydride resin in the presence of a zinc catalyst was modelled solely on the basis of the model-free approach for determining activation energy, approximating the pre-exponential factor without accounting for the influence of diffusion as a rigid three-dimensional network is established during crosslinking, transitioning kinetics from a chemically controlled phenomena to one controlled by diffusion [171]. This provides an insight into the cure behaviour of the vitrimer, but not the processing characterisation for manufacturing purposes.

Recently, the popular aeronautical epoxy resin, RTM6, supplied by Hexcel was vitrimerised by replacing the RTM6-2 part B curing agent with 4-aminophenyl disulphide, yielding an aerospace-grade epoxy vitrimer with glass transition temperature of 233°C [182]. The Kamal-Sourour model:

$$\frac{d\alpha}{dt} = (K_0 + k_1\alpha^m)(1 - \alpha)^n \quad (2.10)$$

– which is normally used to model the cure kinetics of epoxies and unsaturated polyesters [183,184], applicable to both autoclave[185] and liquid moulding epoxy systems [186,187] – was successfully used to simulate the cure behaviour of the RTM6 vitrimer [182] with an acceptable degree of accuracy. However, this model needs to utilise an assumption of temperature-dependent reaction orders, which is vulnerable to overfitting. In Eq.2.10, K_0 and K_1 are Arrhenius temperature-dependent reaction rate constants. A comparison of cure kinetics and rheology – accompanied by physicochemical characterisation enabling the construction of a temperature-time-transformation (TTT) diagram (**Figure 2.26**) – permitted optimal processing of the vitrimer composite with a major drawback; the reported alpha relaxation temperature of 243°C and TGA 5% weight loss of 291°C point

to the impossibility of reprocessing the vitrimer without degradation due to the narrow temperature window between alpha relaxation and material degradation.

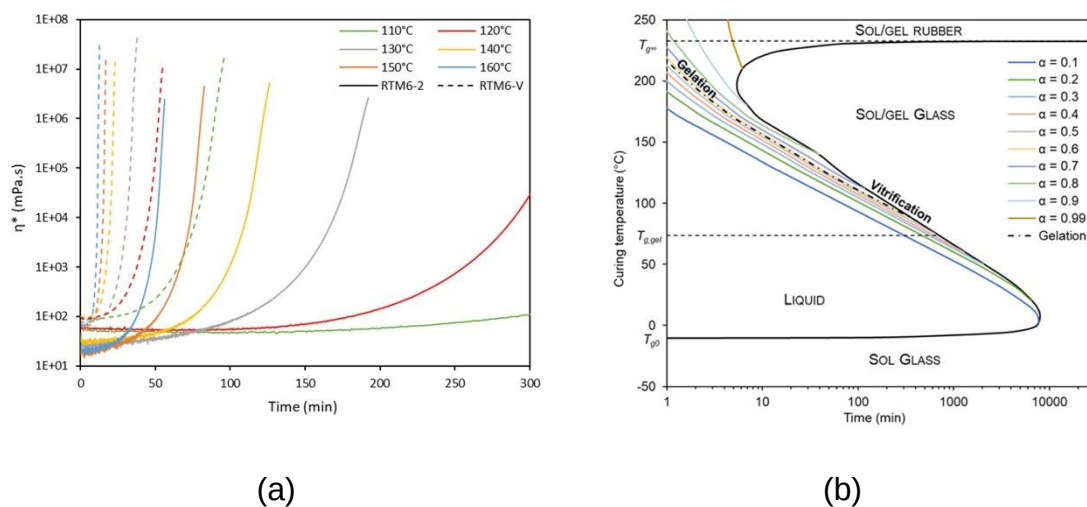


Figure 2.26. Chemoviscosity evolution (a) and TTT diagram of RTM6 vitrimer. Reprinted with permission from [182]. Copyright (2023) American Chemical Society.

2.6 Vitrimer composites

2.6.1 Vitrimer composites processing

Vitrimer composites have been manufactured with a variety of reinforcements, including carbon fibres, glass fibres, carbon nanotubes, graphene, carbon black, nanodots, activated carbon, cellulose-based reinforcements, silicon and aluminium-oxide-based fillers, and polyhedral oligomeric silsesquioxane (POSS) fillers [188]. Amongst these reinforcements, carbon fibre vitrimer composites feature prominently, due to their high-performance structural applications, made possible by their excellent mechanical properties, chemical resistance, and high-strength-to-weight ratio. This study uses carbon fibre as reinforcement for vitrimer composite fabrication. Therefore, this section reviews the processing of carbon fibre reinforced vitrimer composites.

The successful use of vitrimers for fabricating composites hinges on their compatibility with existing composite manufacturing techniques, mostly

represented by pultrusion, resin transfer moulding (RTM), vacuum assisted resin transfer moulding (VARTM), prepregging, resin film infusion (RFI) and autoclave [189]. The selection of a manufacturing method to produce composite parts relies on multiple factors, including the materials used, the specific forms of these materials, cure kinetics, viscosity and chemoviscosity of matrix, the desired mechanical properties, the required production rates, and cost considerations [190].

Of all the vitrimers reported in literature, only a few systems have made it to composites manufacturing trials, because vitrimeric systems are not commercially available [191], and composite manufacturers lack the cure and chemorheological information to establish their optimal manufacturing routes [191]. For manufacturability of vitrimer composites, the viscosity of the vitrimer must be compatible with the industrially relevant manufacturing processes such as RTM, VARTM, RFI or, prepregging. The glass transition temperature must be located reasonably above the service temperature of the intended application. In addition to this, the reprocessing temperature must be sufficiently above the glass transition to permit sufficient segmental mobility of the polymer chain as well as sufficiently below the degradation temperature to avoid the risk of degradation reaction occurring during reprocessing thereby compromising material mechanical properties.

Odriozola *et al.* [14] manufactured the first carbon fibre epoxy vitrimer composite based on exchangeable disulphide bond using RTM. Recyclability of the composite was demonstrated by reprocessing in a zig-zag mould using a hot press to obtain 3D composite. Due to the comparable mechanical properties of disulphide-based epoxy vitrimers with conventional epoxy thermosets, reasonable attention has been paid to this class of functional resin systems in terms of optimising their applicability in real industrial manufacturing. A disulphide bond-based epoxy vitrimer has also been tuned and applied to pultrusion by substituting an anhydride crosslinker with 4-aminophenyl disulphide, which modifies the curing process by slowing down the kinetics [190]. The reprocessing of vitrimer powder into continuous solid by Leibler and his coworkers [11] within

3 minutes through compression moulding under 10 bar and 240 °C, investigated further by Yu *et al.* [192] led to the manufacturing of the first vitrimer composites by hot pressing woven carbon fibres and vitrimer powder [193]. Essentially, the process involves sandwiching carbon fibre fabric within two layers of the vitrimer powder in a flat mould and subjecting the stack to a heat press under 250°C, and 9.6 bar for 5 minutes. A commercial vitrimer, Vitrimax T100™, having a T_g of 100°C is supplied in form of resin films which have been used to manufacture composites through RFI, vacuum bagging and curing in autoclave at 135°C and 1 bar and for 30 minutes followed by 6.5 bar for 30 minutes [194]. Recently, the processing of vitrimer composite by hand lay-up, lamination and consolidation in autoclave, followed by post cure in the oven was reported [195]. None of the manufacturing routes of vitrimers cited herein addressed process optimisation through chemorheological modelling to control manufacturing issues such as resin flow, viscosity, and gelation in order to minimise processing defects such as voids, occurrence of resin-rich or resin-poor areas, or uneven fibre distribution within the composite. The current study seeks to close this gap by providing accurate chemoviscosity models for the vitrimer matrices studied and by manufacturing the composites based on these models.

2.6.2 Self-healing and mechanical resilience in vitrimer composites

Amongst the various self-healing strategies, disulphide bond-enabled epoxy vitrimers have drawn attention due to their ability to reversibly undergo uncatalysed intramolecular dynamic disulphide bond exchanges over the matrix T_g , a network topology rearrangement that enables fast self-healing recovering original mechanical properties [14,18,167]. It has been demonstrated that tuning these vitrimers by increasing the concentration of disulphide bond enhances the self-healing of the fibre composites [19,47]. The application of self-healing to carbon fibre-reinforced polymer composites presents a compelling opportunity to enhance their durability and mechanical performance.

The mechanical recovery of damaged vitrimer composite structures after self-healing is an emerging topic. Self-healing efficiency in vitrimer composites has

been studied by interlaminar shear strength (ILSS), with recovery efficiency of 92% reported after the first healing cycle of a carbon fibre (CF) epoxy vitrimer composite [196]. Biobased self-healing recycled carbon fibre composites perform much like the virgin composites with tensile strength and ILSS amounting to 80% and 81%, respectively, of their original values [197–199]. A transesterification-based vitrimer incorporating polycaprolactone-diol (PCL-diol) as an external healing agent, was shown to exhibit healing from wide-opened cracks with efficiency ranging from 41 % to 58% as the fracture/healing cycle increases [200]. Glass fibre-reinforced vitrimer composites featuring healing efficiency of 60-90% after low velocity impact, healing, with efficiency improved by the incorporation of a shape memory alloy [201]. Using lap shear tests, mechanical strength recovery in the range of 61- 84% was reported for a Zn^{2+} catalyst-based epoxy vitrimer composite [195]. An epoxy vitrimer composite comprising a stoichiometric combination of diglycidyl ether of bisphenol A and 4-aminophenyl disulphide featuring T_g of 173.8°C, reinforced with glass fibre twill 2/2 fabrics, was investigated using 4-end notched flexure tests, showing average fracture toughness recovery of 89 % of the original after the first delamination/healing cycle and 50 % after several repair cycles [202]. Flax fibre-reinforced commercial Vitrimax T100™ exhibits an interfacial shear strength recovery of 50-70% after failure and healing at 6.9 bar and 120°C for 5 min [194].

A study of the mechanical performance of a disulphide bond-enabled epoxy vitrimer composite using a re-processable, repairable, and recyclable (3R)-resin in comparison to the traditional RTM6 epoxy resin, reveals some quantitative evidence of the viability of vitrimers as self-repairing structural composite matrices [203]. Inter-laminar shear strength (ILSS) and low-velocity impact tests reveal a small knockdown effect of 4%, with ILSS repair efficiency at 72 %. Low-velocity impact specimens show significant recovery at 91 % for average maximum load and 87 % for absorbed energy, at 9 J impact energy level whilst for 15 J energy level, the maximum load and absorbed energy recoveries are 100%. The knockdown ranges between 2-4% for both energy levels.

The first study on interlaminar fracture toughness of carbon fibre-reinforced vitrimer composite using mode I double cantilever beam (DCB) testing [204] did not focus on healing efficiency. Using tapered dual cantilever beam (TDCB) and uniaxial-tension specimens. Fracture toughness and tensile strength recovery in an epoxy vitrimer based on transesterification chemistry, reach values of about 75% and 63 [205] respectively, with unidirectional fibre composite laminates exhibiting efficiencies of 100 % in interlaminar toughness and strength, following 2 cycles of loading. The healing efficiency in interlaminar properties of a transesterification-based vitrimeric composite reaches values over 8 % after healing at 200°C and 100 bar for 4 hours [206]. This pressure is very high compared to the consolidation pressure of composites manufacturing, usually in the range of 1-7 bar, and thus may not be practicable for industrial manufacturing purposes, whilst the 4 hours healing time may be too long for optimal reprocessing without degradation at this temperature. Throughout the literature, there is currently limited research on the delamination and healing efficiency of carbon fibre vitrimeric composites. The present study aims to further the understanding of composites self-healing by assessing the effectiveness of the self-healing mechanism in restoring fracture toughness.

2.7 Concluding remarks on research gap

The literature is lacking relevant processing characterisation of vitrimers, especially for the manufacturing of composites. Producing fibrous vitrimer composites in industrially relevant ways requires the development of understanding of the behaviour of vitrimeric matrices during manufacturing, generation of the corresponding datasets and representation in appropriate material models capturing the cure kinetics and chemorheological behaviour. These can facilitate the optimisation of processing conditions with respect to filling or consolidation effects as well as curing and development of process stress and strain to allow the adaptation of current composites manufacturing strategies for the production of vitrimer matrix fibrous materials. The processing of composites is accompanied by phenomena governed by cure behaviour such as residual

stress development, leading to microcracking which ultimately affects the final product quality, or exothermic heat generation, that can cause temperature overshoots and degradation of material quality, whilst generation of defects, such as porosity and dry spots, is governed by the rheological behaviour of the matrix system and its evolution during the process. Therefore, this study develops cure kinetics, glass transition advancement and chemoviscosity models for both establish and novel vitrimeric systems, towards optimising their manufacturing.

Since the discovery of vitrimers, research has delt predominantly with epoxy formulations which, though dominating thermosetting market, do not always cover all desirable functionalities fully. For example, polybenzoxazines and phenolic resins feature excellent fire retardancy due to their aromatic rings. Polybenzoxazines show near zero shrinkage and non-release of toxic volatiles, as well as excellent structural stability and molecular design flexibility. Whilst polybenzoxazine vitrimers are recognised as promising options for achieving multiple functionalities such as self-healing, recyclability, fire retardancy, hydrophobicity, and high thermal stability, there is currently no known product meeting these criteria through a traditional, cost-effective, solventless one-pot method of benzoxazine synthesis. The reported high-temperature polybenzoxazine vitrimers do not meet all of these requirements and are produced through complex routes involving intermediate purification steps before the final synthesis of benzoxazine monomers. These processes are complex and not cost-effective. The current research aims to address this gap by synthesising and manufacturing a high-temperature polybenzoxazine vitrimer that not only exhibits high fire retardancy, but also has very low water absorption capacity for effective operation in wet environments.

There is currently lack of data on the self-healing of damaged vitrimer fibrous composites. The reported studies on self-healing vitrimers mainly focus on matrices other than those incorporating well-established epoxy/amine chemistry, limiting the industrial relevance of the results presented. Moreover, the emphasis has been mainly on the resins, with limited data reported for composites to date. The works on vitrimeric composites cover the gap only partially. For example,

epoxy/amine vitrimer composites have been reprocessed at practically unrealistic pressures in the order of 100 bar. Also, the literature lacks data on the development of self-healing of damaged vitrimer composite. This research, therefore, seeks to close these gaps by achieving self-healing of damaged vitrimer composites within the level of pressure, temperature and time limits that are industrially realistic, as well as provide an understanding of the mechanism of mechanical property recovery in a damaged vitrimer composites during healing.

Chapter Three

3 Methodology

3.1 Introduction

This chapter introduces the materials, synthesis, and manufacturing procedures as well as characterisation and testing techniques employed in this study. The materials used include precursor chemicals used for vitrimer synthesis, the carbon fibre used for polymer reinforcement and ancillary materials such as solvents, glass casting plates, silicone paper, razor blade and porous media. Vitrimer synthesis procedures involve stoichiometric reactions of the precursor chemicals according to established chemistries of individual resin system, whilst manufacturing methods involve resin infusion and vacuum oven curing. The characterisation techniques for resins include Fourier Transform Infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), rheometry, and dynamic mechanical analysis (DMA). The self-healability of vitrimer systems is quantified by profilometry, whilst dual cantilever beam (DCB) testing was utilised for mechanical characterisation. Consolidation pressure for composite self-healing was provided by a press or a C-clamp assembly designed to apply uniform consolidation pressure on the healed specimen. Modelling methodologies for the cure kinetics and viscosity development of the vitrimer systems are also presented in this chapter.

3.2 Materials

Diglycidyl ether of bisphenol A - DGEBA (D.E.R. 332; epoxy equivalent mass of 170.2, molecular weight of 340.4 g mol^{-1}) [207], paraformaldehyde ($\leq 100 \%$) [208] and ethanol (99.8 %) [209] were supplied by Sigma Aldrich/Merck. 4-aminophenyl disulphide (4-APDS) (98%), an aromatic diamine with molecular weight of 248.4 g mol^{-1} and amine equivalent mass of 62.1 [210], manufactured by Oakwood Products, Inc., USA, was supplied by Fluorochem Ltd, UK. Bis (4-hydroxyphenyl) disulphide (98 %) was purchased from AmBeed USA [211].

Aniline (99.8 %) [212], acetone (99.8 %) [213], N,N-dimethylformamide (DMF) (99+% extra pure) [214] and dimethyl sulfoxide (DMSO) (99.5 %) [215] were purchased from Thermo Fisher Scientific. Tenax HTA 5131 pseudo-UD carbon fibre, with area weight of 185 gsm, width of 100 mm was purchased from Havel composites [216] and used as the reinforcement in this study. DGEBA was cured with 4-APDS to produce the epoxy vitrimer according to the chemistry described in the next section. Bis (4-hydroxyphenyl) disulphide, paraformaldehyde and aniline were used to synthesise the novel benzoxazine vitrimer. Ethanol, acetone, DMSO and DMF were used in this study alongside room temperature and hot water (75°C) as solvents for testing the swelling of the new polybenzoxazine vitrimer. All chemicals were used as received without any treatment.

3.3 Synthesis and oven cure of vitrimers

3.3.1 Synthesis of DGEBA/4-APDS epoxy vitrimer

Stoichiometric amounts of DGEBA and 4-aminophenyl disulphide (**Figure 3.1**) (2:1 epoxy/amine mole ratio or 2.74:1 epoxy/amine weight ratio) were used to formulate DGEBA/4-APDS epoxy vitrimer. To prepare a batch, 10 g DGEBA was measured into a 100 mL beaker and 3.65 g of 4-aminophenyl disulphide was added. The mixture was stirred on a hot plate at 80°C for 20 minutes, after which the resin was stored in the freezer at -20°C for future use.

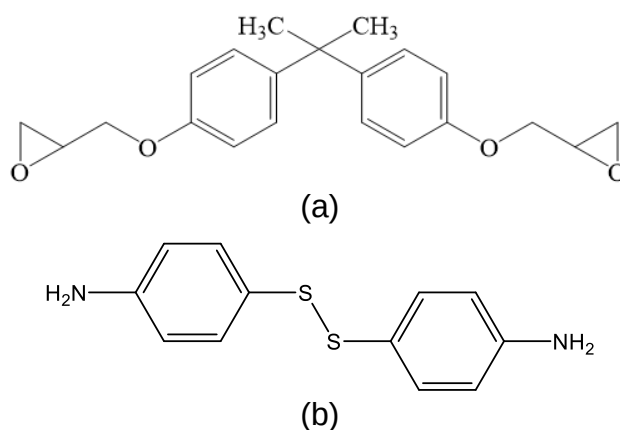


Figure 3.1. Chemical structures of (a) DGEBA (D.E.R. 332), (b) 4-aminophenyl disulphide.

3.3.2 Synthesis of BH-A benzoxazine vitrimer

The benzoxazine monomer, 1,2-bis(3-phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-yl)disulphane, which is coded BH-A, was synthesised by the solventless Mannich condensation reaction [165] involving stoichiometric amounts of aniline, paraformaldehyde, and bis(4-hydroxyphenyl) disulphide (**Figure 3.2**) at 2:4:1 molar ratio. 3.72 g (39.94 mmol) aniline was measured into a 150 ml beaker. 2.40 g (79.88 mmol) paraformaldehyde was added and stirred with a magnetic stirrer for 10 minutes at room temperature. 5 g (19.97 mmol) bis(4-hydroxyphenyl) disulphide was added to the mixture and stirred for another 1 minute at room temperature. The mixture was then placed in a silicone oil bath maintained at 90°C, shielded to avoid heat losses and stirred for 30 minutes. A brown viscous benzoxazine monomer, BH-A (92 % yield) was obtained, requiring no further purification. The beaker was then removed from the silicone bath, cleaned with tissue paper, placed in a sample bag, labelled and stored in the freezer at -20°C for future sampling.

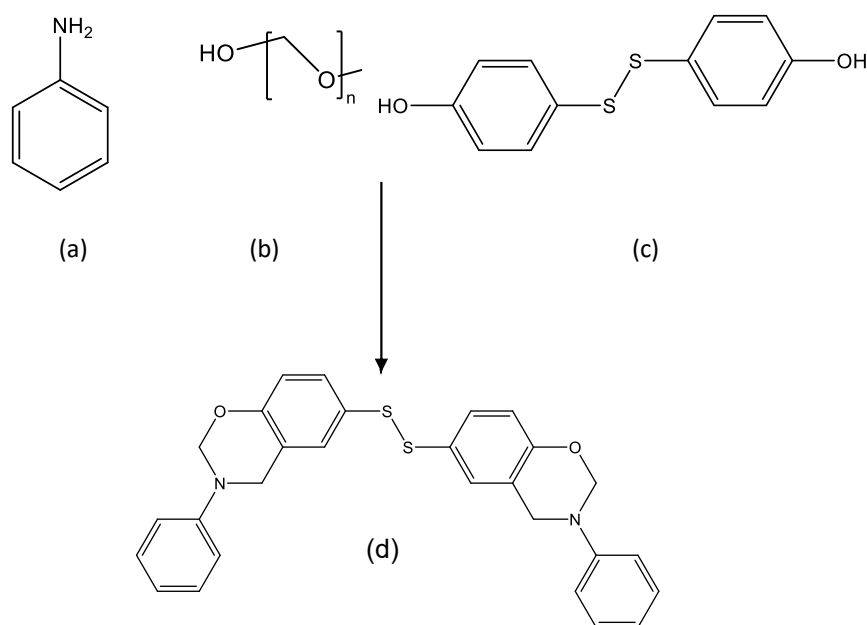


Figure 3.2. (a) Aniline. (b) Paraformaldehyde. (c) Bis(4-hydroxyphenyl) disulphide. (d) Benzoxazine vitrimer

3.3.3 Casting and oven curing of neat resins

DGEBA/4-APDS epoxy and BH-A benzoxazine vitrimers were cast using a mould consisting of 2 glass plates with a sandwiched silicone rubber which creates the borders of the casting. The glass mould was cleaned with acetone and treated with a Chemlease PMR-90 EZ semi-permanent release agent to aid easy removal of the polymer after curing. DGEBA/4-APDS epoxy resin was removed from the freezer and heated on a hot plate at 80°C for about 5 minutes. It was degassed at 80°C for 10 minutes and poured into the mould, clamped to avoid resin leakage and placed in an OV301 precision composite curing vacuum oven (Easy Composites). It was cured using the program: 180°C for 4h; 200°C for 1h; 220°C for 30 min. A TC-08 thermocouple data logger (Pico Technology) equipped with an RS PRO Type K Thermocouple, running on a picolog data logging software was used to record real-time ambient, tool and specimen temperatures during cure.

BH-A is a rubbery solid at room temperature. The rubbery monomer of BH-A was placed in an acetone-cleaned glass plate treated with release agent and bounded by silicone rubber to form a mould. The glass plate was gradually heated to 80°C on a hot plate to allow the material transition into a fully viscous liquid and spread in the glass plate up to the boundary created by the silicone rubber. A second glass plate was used to close the casting and the mould was clamped as described previously and placed in the vacuum oven. The resin was degassed in vacuum oven at 110°C for 10 minutes, after which the vacuum pump was turned off and the temperature of the oven ramped to the cure temperature. The curing program of BH-A was 170°C for 2h followed by 190°C for 30 min. **Figure 3.3** shows the casting.

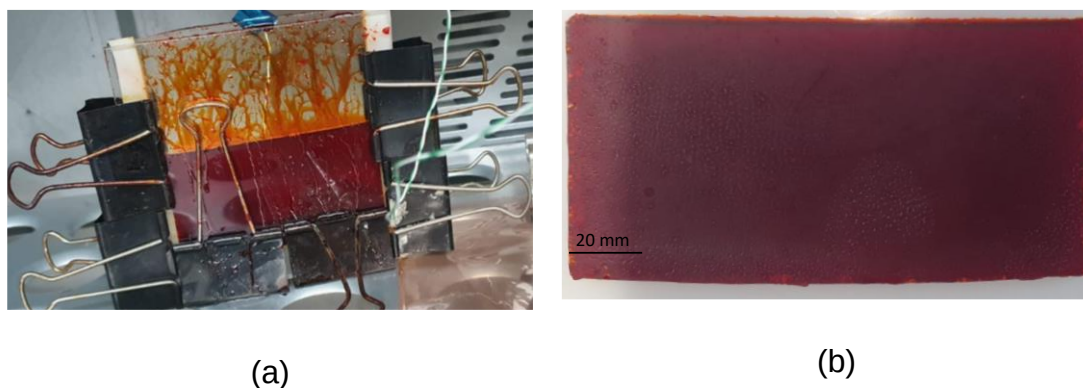


Figure 3.3. (a) Casting and curing. (b) Cured resin.

3.4 Composite manufacturing

Two different fabrication methods were employed in manufacturing epoxy and benzoxazine vitrimer composites based on the knowledge of the feasible infusion and consolidation windows dictated by the chemoviscosity of each resin system: vacuum-assisted resin transfer moulding (VARTM) used for the epoxy system and resin film infusion (RFI) used for the benzoxazine system. The geometry of the composites was chosen to conform to the specific mechanical test to be carried out (DCB). sixteen plies of the fibre, each 290 mm long were used for manufacturing the composites for both epoxy and benzoxazine composites.

3.4.1 Vacuum-assisted resin transfer moulding (VARTM)

Vacuum-assisted resin transfer moulding (VARTM) process was used to manufacture epoxy vitrimer composites. The preform was prepared by laying 16 plies of the fibre, alternating front and back sides of the plies for each successive layer to ensure geometric uniformity of the preform. Teflon films of length of 60 mm and thickness of 0.013 mm were inserted in the midplane of the plies, from the two ends of the plies (DCB), to create a pre-crack. The layup was covered with an aluminium plate and allowed to stay for 24 hours to pre-consolidate. After 24 hours, an aluminium mould was cleaned with acetone and release agent was applied to the mould to enhance debonding of the laminate after curing. The preform was placed in the mould as shown in **Figure 3.4** for resin infusion. The

preform was covered with a peel ply to aid debonding and prevent excess resin from coming into direct contact with the mould surface. This was then covered with a porous flow media and vacuum-bagged. The inlet and outlet resin transfer lines were fixed on both sides of the preform, and the whole setup was sealed with tacky tape. The vitrimer was then degassed and injected into the preform under vacuum pressure of 1 bar, tool temperature of 95°C and resin temperature of 90°C. Based on the chemoviscosity of the DGEBA/4-APDS epoxy vitrimer, the viscosity at this temperature, remains below 200 mPas, which is the range of infusion viscosity commonly used for liquid composite moulding [217,218], achieving good flowability up to 60 minutes of infusion and consolidation time. However, the infusion was complete and full fibre wet out achieved within the first 30 minutes of infusion. When the infusion was completed, the temperature of the tool was ramped up to 180°C and the program: 180°C for 4h, 200°C for 1h and 220°C for 30 min was applied, as used for the neat resin, before cooling down to room temperature. The composite was then removed from the vacuum bag and stored.

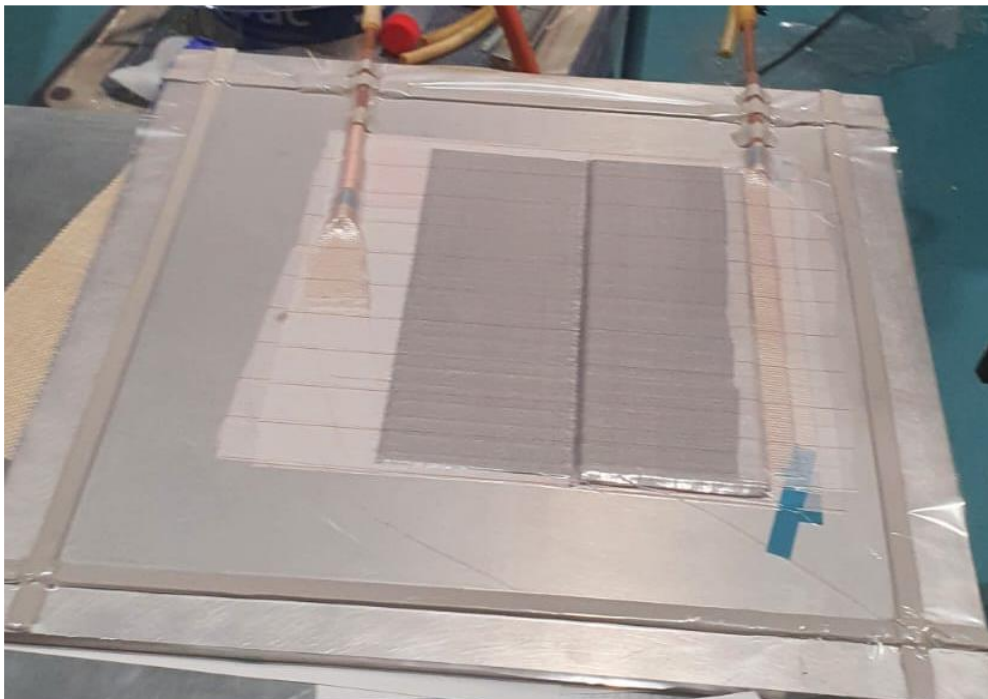


Figure 3.4. VARTM fabrication process.

3.4.2 Preparation of resin film and resin film infusion (RFI)

The BH-A composite was fabricated by RFI. The preference of RFI in the case of BH-A composite against VARTM used to fabricate DGEBA/4-APDS composite was informed by the fact that the infusion window for liquid moulding of BH-A based on its chemorheological behaviour indicates a narrow infusion time of about 1 minute at 130°C, whilst temperatures below 130°C results in viscosities higher than the practicable infusion viscosity of 200 mPas. The resin is appropriate for either impregnation (prepreg making) or RFI.

The resin films were made with a 3570/2 doctor blade (Elcometer UK), on a hot plate set at 70°C and monitored with an external thermocouple, and a carrier plate covered with a silicone-coated PTFE release paper. The doctor blade was set to a film thickness of 300 µm. To control the fibre volume fraction of a preform, the film thickness was adjusted by adjusting the doctor blade, based on cumulative fibre volume fraction determined during fibre layup. After filming, the temperature was adjusted to 50°C. The film was then covered with another silicone-coated release paper. A cylindrical steel rod was rolled on the silicone paper-covered film to ensure evenness of the surface. The carrier plate was removed and allowed to cool down to room temperature and the top release paper was removed.

The first layer of fibre fabric (290 mm × 100 mm), weighing 5.5 g was laid on the film and covered by the release paper. The plate was then placed on the hot plate and the temperature increased to the filming temperature of 70°C, with the steel rod rolling over it for 1 minute to allow adhesion of the resin film onto the fabric. This was more effective than removing the film and laying it on the fabric, which results in shattering the film due to the brittleness of the resin. After rolling the steel rod for 1 minute, the release paper was then removed, and the resin and reinforcement were removed from the lower release paper and weighed to obtain the weight of the resin and calculate the fibre volume fraction based on the value of resin density of 1.23 g/cm³ determined using a cuboidal cured BH-A sample. This process was repeated to produce subsequent layers of resin film and fabric.

Layer-by-layer determination of cumulative weight was necessary to ensure that the fibre volume fraction of the final 16-layer resin film and reinforcement (DCB specimens) did not fall outside the range of 0.50 – 0.60. The final fibre volume fraction was 0.53. After laying the fabric, the preform was vacuum-bagged as described in the VARTM process, excluding resin transfer lines and porous flow aid mesh as these are not needed in this case. The set up was then placed in the vacuum oven and consolidated with a vacuum pressure of 1 bar, during which the following thermal profile was applied: 3°C/min to 170°C followed by an isothermal segment for 2 h, equilibration at 190°C, isothermal segment for 30 min and cool down to 50°C. The various stages involved in the RFI, consolidation and curing are shown in **Figure 3.5**.

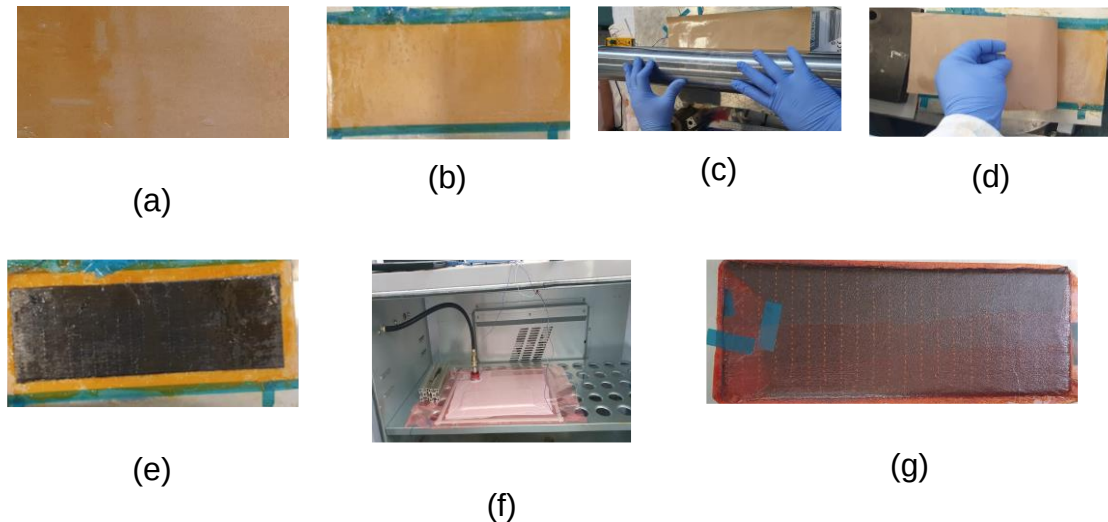


Figure 3.5. Stages of RFI and curing of BH-A benzoxazine composite.

3.5 Characterisation

3.5.1 Neat resin and composites self-healing

A scratch was manually made on a cured specimen using a T5016 heavy duty single edge razor blade (Agar Scientific). The depth of the scratch was measured using a Bruker Dektak XT profilometer with a stylus range of 524 μm , scan length of 1500 μm and scan resolution of 0.25 μm . The specimen was subsequently clamped between two flat pieces of aluminium and placed in the oven at 190°C

for 30 minutes, followed by cooling down. The depth of the scratch was remeasured with the profilometer and compared with the results obtained before healing.

Delaminated specimens of polyDGEBA/4-APDS were healed in a LABPRO 1000 Fontijne presses (Fontijne Grotnes BV, The Netherlands) at 220°C, pressure of 50 bar and healing time of 90 minutes. The pressure of 50 bar is high compared to the consolidation pressure of the order of 1-7 bar commonly used in composite manufacturing. However, in the literature a pressure of 100 bar has been applied in healing a similar epoxy vitrimer system [14], whilst attempts were made to heal the composite with a pressure of 7 bar and of 20 bar which were unsuccessful.



Figure 3.6. A system of 4 C-clamps.

The new polybenzoxazine vitrimer, (polyBH-A) was found to exhibit macroscopic flow at elevated temperature with little pressure, indicative of a better platform for low pressure self-healing. First attempt was made to heal BH-A composite with vacuum pressure of 1 bar, but this did not yield the desired result. From experience with the material, typical consolidation pressure in the range 2 – 5 bar would be good for healing the material. The force required to exert this pressure was very low for a press, leading to non-uniformity in the application of the pressure and ultimately undesired result. Based on this challenge, a system of 4 C-clamps shown in **Figure 3.6** was designed to exert a uniform pressure across the area of the composite specimen. Each clamp was calibrated using a FIRSTINFO H5177 ultra precision certified torque limiting screwdriver, 1/4 inch universal hex quick release bit holder, torque range 5-60 cNm (FIRSTINFO Tools) and a DBBSMM-50kg-002-000 load cell (Applied Measurements Ltd) –

running on a DSCUSB Toolkit software – to establish the torque corresponding to various clamping forces, generating the force versus torque calibration curve, a straight-line graph with intercept of 0 and coefficient of determination of 0.998. The force versus torque measurement was repeated 4 times to assess the variabilities for each clamp. The average of the 4 measurements was taken. The variabilities within each clamp were found to be greater than the differences measured between clamps. It was, therefore, more appropriate to use a single calibration curve for all the clamps based on a slope determined by all the datasets put together as shown in **Figure 3.7**. This to the following equation for the clamps:

$$F = 263.1T_o \quad (3.1)$$

where F is the force (N) and T_o is the torque (Nm).

Based on Eq.3.1, the force was generated corresponding to a consolidation pressure of 4 bar based on the dimensions of the rectangular composite specimens. PolyBH-A composite was healed using this pressure (4 bar) at 190°C for 30 minutes.

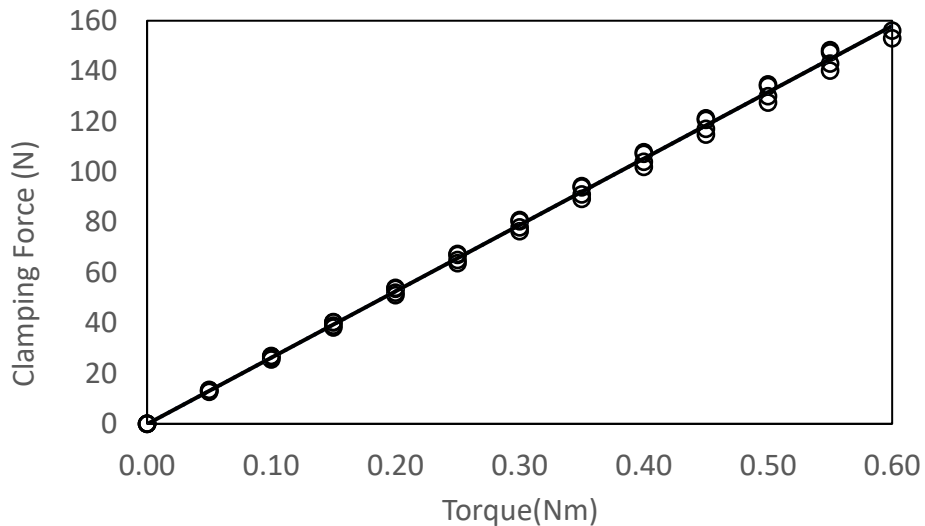


Figure 3.7. Clamp calibration curve.

3.5.2 Spectroscopy

Fourier Transform Infrared (FTIR) spectroscopy was performed in transmission mode with a SMART iTR Nicolet iZ10 spectrometer (Thermo Fisher Scientific) from 600 to 4000 cm^{-1} . The FTIR spectroscopy was carried out on the new benzoxazine monomer and its polymer to identify the key benzoxazine spectral bands and functional groups associated with the unique structure of BH-A. Each FTIR spectroscopy involves two distinct steps: in the first step, 100 background scans were performed without any sample in the sample holder, with a resolution of 4.0 cm^{-1} , sample gain of 8.0, optical velocity of 0.4747 and aperture of 80.0. The role of the background scan is to record the baseline signal of the instrument. This signal serves as the baseline correction capturing the inherent noise and systematic errors in the instrument. After the background scan, a sample of BH-A or polyBH-A was loaded on the sample holder and covered. The second scan was then performed. The machine automatically subtracts the contribution from the background signal and records the sample signal, thus improving the signal-to-noise ratio. FTIR spectroscopy of BH-A was performed each time a batch was synthesised throughout the study, and there were no differences in the spectra collected in each occasion. Similarly, each time a sample of BH-A was cured, an FTIR spectrum was collected to assess the disappearance of spectral bands due to benzoxazine ring.

3.5.3 Swelling behaviour

Swelling experiments were performed using deionised water (DI water), ethanol, acetone, dimethyl formamide (DMF), dimethyl sulfoxide (DMSO) at room temperature ($22 \pm 2^\circ\text{C}$) and hot DI water at 75°C . In these tests, samples of fully cured polymer of about 50 mg were immersed in 10 mL of solvent for 31 days (744 h). The samples were removed at 5, 24, 72, 240, 408, 567 and 744 h, surface-cleaned with tissue paper and weighed to obtain the swelling ratio (W) using:

$$W = \frac{m_s}{m_i} - 1 \quad (3.2)$$

where m_i and m_s are the initial and swollen sample masses, respectively. After each measurement, the sample was returned to the solution as fast as possible. The samples were removed after 31 days, dried in an oven at 50°C for 24 hours and weighed to obtain the dry mass after swelling. The soluble fraction (M) was calculated using:

$$M = 1 - \frac{m_d}{m_i} \quad (3.3)$$

where m_d is the mass of the sample after drying. To ensure statistical reliability of the swelling data, 4 samples of the polymer were used for each solvent and average result used for data analysis.



(a)



(b)

Figure 3.8. Swelling tests (a) Solvents at room temperature. (b) Hot water at 75°C.

3.5.4 Thermal and rheological analyses

3.5.4.1 Differential scanning calorimetry

The cure behaviours of DGEBA/4-APDS and BH-A were studied using a DSC 250 Discovery (TA Instruments) equipped with an RCS cooling system under nitrogen purge at 50 mL/min, running on Trios software. An amount of resin in the range 5-10 mg was encapsulated in a Tzero aluminum pan and used to perform each DSC experiment. Two modes of DSC runs with varying thermal profiles were performed: dynamic DSC and isothermal DSC.

Dynamic DSC experiments were performed at 1.25°C/min, 2.5°C/min, 5°C/min and 10°C/min heating rates for DGEBA/4-APDS and BH-A to assess the characteristic resin cure parameters, namely the uncured resin glass transition temperature, T_{g0} , exothermic cure onset temperature, T_{onset} , cure peak temperature, T_{poly} , offset temperature, T_{offset} , and heat of reaction, ΔH . Isothermal DSC experiments were carried out at 140°C, 150°C, 160°C, 170°C, 180°C, 190°C and 200°C for DGEBA/4-APDS. The temperatures for the isothermal DSC of BH-A are 150°C, 160°C, 170°C, 180°C and 190°C. For all isothermal DSC runs, the samples were brought to the desired temperature of the reaction using 10°C/min heating rate from -50°C and the isothermal conditions were maintained until the DSC heat flow signal reached a plateau, signifying the end of the reaction. This was followed by quenching to -50°C and reheating up to 250° at 10°C/min to identify any residual cure.

The initial reaction enthalpy value was considered in the integration of isothermal experiments, estimated using the results of the dynamic experiment at 10°C/min. The total enthalpy of the reaction (ΔH) was calculated by averaging the total enthalpy of all experiments for which the residual reaction upon re-heating was negligible. A linear baseline was used to integrate DSC signals in all dynamic and isothermal experiments to calculate the reaction enthalpy, with the difference that in dynamic runs, the double point linear baseline type was selected whereas in isothermal runs, horizontal (from right) linear baseline type was selected. At the end of each run, the cured resin was rescanned at 10°C/min to measure the cured polymer glass transition temperature, T_g .

The development of glass transition temperature (T_g) during cure was investigated using partially cured samples with 17 different thermal histories – in the case of DGEBA/4-APDS – comprising material cured dynamically at 1.25°C/min up to 130°C, 136°C, 140°C, 145°C, 150°C, 160°C, 170°C, 180°C and 190°C, dynamically up to 170°C at rates of 2.5°C/min, 5°C/min and 10°C/min, isothermally at 150°C for 10 minutes, 20 minutes, 30 minutes and 40 minutes as well as a fully cured sample (cured at 150°C for 100 minutes) and an uncured

sample. The partially cured samples were reheated from -50°C to 250°C at 10°C/min in the DSC and the T_g was identified as the inflection point of the transition step in heat flow curves. The uncured sample was heated from -50°C to 220 °C at 1.25°C/min, during which the uncured sample T_g was identified alongside the full cure exotherm.

In the case of BH-A, 10 dynamic DSC runs corresponding to different degrees of cure were used to prepare the samples for T_g measurement, including materials cured dynamically at 1.25°C/min from -50°C to 146°C, 153°C, 158°C, 162°C, 167°C, 173°C, 179°C, 185°C, 194°C, 240°C, material equilibrated at 170°C and scanned isothermally for 120 minutes and materials equilibrated at 190°C and scanned isothermally for 30 minutes. The degree of cure evolution was computed using:

$$\alpha(t) = \frac{H(t)}{\Delta H} \quad (3.4)$$

where $H(t)$ is the integral of the DSC heat flow signal. The reaction rate evolution was computed by differentiating numerically degree of cure with respect to time. The integrated cure kinetics DSC data were utilised to obtain the degree of cure corresponding to the partially cured samples.

3.5.4.2 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed on a TGA 550 Discovery (TA Instruments) under nitrogen purge (60 mL/min) running Trios software at 10°C/min heating rate from 35 – 373°C (polyDGEBA/4-APDS) and from 50 – 910°C (polyBH-A). The wide gap in the choice of the temperature range for polyDGEBA/4-APDS and polyBH-A is due to the difference in purpose of each of the experiments. For polyDGEBA/4-APDS, the purpose is to measure the thermal stability of the material only, whereas for polyBH-A, there are two purposes, which include measuring thermal stability and obtaining char yield at 850°C for limiting oxygen index determination. An amount of resin in the range of 10-15 mg in a 100 µL platinum pan was used for all TGA measurements. The instrument was

initially zeroed by tarring. After this, the polymer was sampled into the furnace, and the machine was equilibrated to 35°C or 50°C before ramping to 373°C or 910°C as described earlier. The Limiting Oxygen Index (*LOI*) of the polymer, which can be used as an indication of flame retardance, is approximated according to the van Krevelen empirical relationship [219]:

$$LOI = 17.5 + 0.4CR_{850} \quad (3.5)$$

where CR_{850} is the char yield in weight % at 850°C.

3.5.4.3 Dynamic mechanical analysis

Two modes of dynamic mechanical analysis were performed in this study: single frequency temperature ramp and stress relaxation experiments. DMA data were recorded on a DMA Q800 (TA Instruments) in tension mode (Figure 3.4) using a single cantilever. Specimens of dimensions $35 \pm 0.5 \text{ mm} \times 8 \pm 0.2 \text{ mm} \times 2 \pm 0.05 \text{ mm}$ (polyDGEBA/4-APDS) and $35 \pm 0.5 \text{ mm} \times 8 \pm 0.2 \text{ mm} \times 3 \pm 0.12 \text{ mm}$ (polyBH-A) were cut from plates cured in the oven as described in subsection 3.2.3. Oscillatory DMA in temperature ramp mode with a single frequency of 1 Hz, amplitude of 15 μm , heating rate of 3°C/min at 32-246°C (polyDGEBA/4-APDS) and 35-217°C (polyBH-A) were utilised to measure the storage and loss moduli as function of temperature to determine the glass transition temperatures of each polymer.

Stress relaxation experiments were conducted at five isothermal temperatures of 180°C, 190°C, 200°C, 210°C, and 220°C for polyDGEBA/4-APDS vitrimer and 175°C, 180°C, 185°C, 190°C, and 195°C for polyBH-A benzoxazine vitrimer. The specimens were preloaded with a force of 0.001 N to ensure straightness prior to deformation, equilibrated to the desired isothermal temperature and subsequently deformed to an applied strain of 1 % and 2 % for polyDGEBA/4-APDS and polyBH-A, respectively. The decay of relaxation modulus with time was recorded and the relaxation time was estimated as the time required for the modulus to drop from its plateau value by 1/e.

3.5.4.4 Rheology

The viscosity development of the DGEBA/4-APDS and BH-A systems was measured using an AR2000ex rheometer (TA Instruments) equipped with a water-cooling system. A cone and plate configuration with 2° cone of 40 mm diameter and truncation depth of 54 μm was used. The gap setting in the rheometer was equal to the truncation of the cone. Measurement of chemoviscosity of DGEBA/4-APDS system comprises five isothermal experiments at 80°C, 90°C, 100°C, 110°C and 120°C, whilst chemoviscosity development in BH-A was studied using five isothermal experiments at 100°C, 105°C, 110°C, 120°C and 130°C. A constant shear rate of 300 s^{-1} was used to deform the resin in both epoxy and benzoxazine cases. The sample was loaded onto the lower plate of the rheometer, which was at ambient temperature, the gap was closed and the temperature was equilibrated for 30 s before shearing.

3.5.5 Mechanical testing

To access the mechanical performance of both epoxy and benzoxazine vitrimer composites and thus the fracture toughness recovery after autonomous damage repair, mode I delamination using dual cantilever beam specimens was the mechanical testing technique employed in this study to quantify composite mechanical property.

3.5.5.1 Mode I DCB specimen preparation and delamination

The standards (BS ISO 15024:2001 and ASTM D5528 - 01) recommend mode I DCB specimen dimensions of 125 mm $\times$ 20 mm $\times$ 3 mm for carbon fibre polymer composites [220,221]. However, ASTM D5528/D5528M-21 recommends specimen dimensions of 140 mm $\times$ 20 mm $\times$ 3 mm [222]. The difference in length is a matter of convenience. In this study, the BS ISO 15024:2001 standard method was adopted, with a slight adjustment in length for convenience: 135 mm $\times$ 20 mm $\times$ 3 mm. The specimens were machined to size. The specimens were provided with load-blocks such that the distance from the loading centre to the tip of the precrack is 50 mm. The two edges of each specimen were calibrated in

millimetres with a white marker to enable visual tracking of crack propagation, starting from the tip of the precrack up to 70 mm to the direction of the expected crack growth. Mode I DCB specimens of DGEBA/4-APDS epoxy vitrimer are shown in **Figure 3.9**, representing all DCB specimens used in this study since they are the same in dimensions.



Figure 3.9. Mode 1 DCB specimens of DGEBA/4-APDS composite.

Mode I DCB delamination experiments were performed on a Zwick Z000 TMZ010/TN2S electromechanical universal testing machine (Zwick GmbH & Co. KG, Germany) using a 100 N static load cell. The delamination involved two stages: a crack initiation stage and a crack propagation stage. The first stage involved crack initiation from the insert film tip up to a crack length of about 3 – 5 mm using a constant crosshead speed of 1mm/min. Crack lengths were measured along the edge of the specimen using a video camera. The loading was stopped as soon as the crack was seen to move on the edge of the specimen, and the specimen was completely unloaded at a constant crosshead speed of 5 mm/min. Following this procedure, the specimen was reloaded from the mode I precrack at a constant crosshead speed of 1 mm/min. The crack lengths were measured, in intervals of every 1 mm up to the first 5 mm, then every 5 mm up to the desired crack length. The loading was then stopped, and the specimen unloaded at a constant crosshead speed of 5 mm/min. The load-displacement curves were generated. The coordinates of the load-displacement curves corresponding to the recorded crack lengths were used to calculate the

strain energy release rate. Three mode I DCB specimens – marked as specimens 1, 2 and 3 – were tested for each resin system.

In the first cycle of the multi-cycle DCB experiment, the loading was stopped as soon as a crack propagated up to about 80 mm and then unloaded. The delaminated specimen was then healed using the procedure described in section 3.5.1. The specimen was then re-delaminated in a second cycle, as described previously up to a crack length of about 90 mm and re-healed. Finally, the specimen was re-delaminated in a third cycle up to about 100 mm crack length and re-healed. After each cycle of delamination and healing, the fracture toughness of the composite was analysed by calculating the strain energy release rate from the experimental data generated. For healed specimens, the strain energy release rate is compared with that of the pristine specimen, thus determining the efficiency of fracture toughness recovery achieved after healing the material.

The strain energy release rate (G_{IC}) of a mode I DCB specimen is calculated using the corrected beam theory [206,223] as:

$$G_{IC} = \frac{3P\delta}{2b(a+|\Delta|)} \frac{F}{N} \quad (3.6)$$

where P , δ , a and b are the applied load, loading point displacement, crack length and DCB specimen width, respectively. In Eq.3.6, $|\Delta|$, F and N are crack length correction factor, large displacement correction factor and load-block correction factor, respectively, all determined experimentally.

The analysis of fracture toughness recovery in the DCB specimen after a delamination and healing cycle is performed by considering the relationship between G_{IC} recovery efficiency and historical crack opening that occurred in the healed portion of the material prior to healing. The historical crack opening is derived from beam deflection theory, for which the deflection, $\delta(x)$, of a suspended beam of length, L , under the influence of a point load, P , at a distance, x from its fixed end is given by:

$$\delta(x) = \frac{Px^2(3L-x)}{6EI} \quad (3.7)$$

where E is the flexural modulus of the material and I is its moment of inertia. At the free end, $\delta(x)$ has a maximum value of Δ , whilst $x = L$. Therefore, Eq.3.7 becomes:

$$\delta(x) = \frac{PL^3}{3EI} \quad (3.8)$$

Dividing Eq.3.7 by Eq.3.8, making $\delta(x)$ the subject gives:

$$\delta(a) = \frac{x^2(3L-x)\Delta}{2L^3} \quad (3.9)$$

For a delaminating dual cantilever beam, with crack length, a , and maximum crack length, a_{max} , $L = a_{max}$ and $x = a_{max} - a$. Substituting these parameters into Eq.3.9 gives:

$$\delta(a) = \frac{(a_{max}-a)^2(3a_{max}-(a_{max}-a))\Delta}{2a_{max}^3} \quad (3.10)$$

where δ is historical crack opening, a_{max} is the historical maximum crack length, Δ is the historical maximum crack opening. In this analysis, the average G_{IC} recovery across all specimens – determined by averaging the G_{IC} across all points of the crack propagations, excluding crack initiation values – is expressed as a function of historical crack opening. The resulting exponential decay is modelled with a Kohlrausch–Williams–Watts (KWW) relaxation function:

$$f(\delta) = (1 - c) \left[c + e^{-\left(\frac{\delta}{d}\right)^\beta} \right] \quad (3.11)$$

where δ is the historical crack opening, d is the constant opening displacement obtained by fitting Eq.3.8 into the experimental data, β is the stretching parameter, obtained by fitting Eq.3.8 and c is a constant also obtained by fitting Eq.3.8. The model values of the G_{IC} recovery are calculated using Eq.3.8, whilst the relative error between experimental and model values, expressed as:

$$\varepsilon = \sum_{j=1}^n \frac{|r_j - \hat{r}_j|}{r_j} \quad (3.12)$$

– where r_j and $\hat{r}_j$ are experimental and model toughness recoveries at point j and n is the number of datapoints – is minimised using the Generalised Reduced Gradient Nonlinear Optimisation method of Microsoft Excel Solver, thereby obtaining the values of the fitting parameters of model Eq.3.8.

3.6 Cure modelling, T_g advancement and chemoviscosity

A phenomenological modelling method – involving mapping of reaction rate on temperature and degree of cure – was used to model the cure behaviour of both DGEBA/4-APDS and BH-A, capturing all effects occurring during cure such as chemical effects controlled by frequency of molecular collisions, diffusion and vitrimer dynamic bond exchange where this plays a role. The following model was selected for modelling DGEBA/4-APDS system [181]:

$$\frac{d\alpha}{dt} = \frac{Ae^{\left(-\frac{E}{RT}\right)}\alpha^m(1-\alpha)^n}{1+e^{C[\alpha-(\alpha_{c0}+\alpha_{cT}T)]}} \quad (3.13)$$

where n is n -th reaction order, m is autocatalytic reaction order, E_1 is the activation energy, A_1 the pre-exponential factor, C is the coefficient controlling the breath of transition from chemical to diffusion-controlled kinetics, α_{cT} and α_{c0} are coefficients controlling the critical degree for diffusion as a function of temperature and R is the universal gas constant.

The following model was used to model the cure behaviour of BH-A [224]:

$$\frac{d\alpha}{dt} = \frac{A_1e^{-E_1/RT}(1-\alpha)^{n_1} + A_2e^{-E_2/RT}\alpha^m(1-\alpha)^{n_2}}{1 + e^{C[\alpha-(\alpha_{c0}+\alpha_{cT}T)]}} \quad (3.14)$$

where n_1 and n_2 are two n -th reaction orders, A_1 and E_1 are first reaction rate constant pre-exponential factor and activation energy and A_2 and E_2 are second reaction rate constant pre-exponential factor and activation energy. The kinetics data were used to identify the parameters of the cure kinetics models developed. The minimisation of model error was carried out using the Generalised Reduced Gradient Nonlinear Optimisation method implemented in the Solver of Microsoft Excel [225]. The error minimised is:

$$\varepsilon = \sum_{i=1}^{ne} \sum_{j=1}^{np_i} \frac{|r_j^i - \hat{r}_j^i|}{np_i r_{max}^i} \quad (3.15)$$

where r_j^i is the reaction rate of point j of experiment i , r_{max}^i is the maximum reaction rate of experiment i – used to scale the error so that high rate experiments do not dominate the fitting, np_i is the number of datapoints in experiment i , ne is the number of experiments – 11 in the case of DGEBA/4-APDS and 7 in the case of BH-A, and $\hat{r}_j^i$ is the reaction rate computed by the model for point j . Experimental analysis and cure modelling were carried out assuming an initial degree of cure of 1% in both epoxy and polybenzoxazine vitrimer systems. This is commonly used in systems where the peak reaction rate is associated with an intermediate conversion [226,227] to facilitate the utilisation of autocatalytic kinetics. This assumption does not affect the results as it is merely a numerical adaptation to allow initiation of the reaction from a finite degree of cure; setting this initial degree of cure to a value within a similar order of magnitude yields the same behaviour with slightly different model parameters. The initial value acts as the initial condition that accompanies the cure kinetics model and its parameters.

The Di Benedetto equation [246,247] was used to model the advancement of glass transition temperature during the cure:

$$T_g(\alpha) = T_{go} + \frac{\lambda\alpha(T_{g\infty} - T_{go})}{1 - \alpha(1 - \lambda)} \quad (3.16)$$

where T_{g0} is the glass transition temperature of the prepolymer, $T_{g\infty}$ is the ultimate glass transition temperature of the polymer (fully cured) and λ is a fitting parameter that determines the convexity of the dependence of glass-transition temperature on the fractional conversion. The T_g -degree of cure coordinates, of partially cured materials were used to identify the parameters of the Di Benedetto equation, using the same procedure as for the fitting of the cure kinetics model described previously, with the difference that the minimisation function was computed as the sum of absolute error over all data points.

The viscosity of a curing resin in liquid state is influenced by two phenomena, the increase in molecular size as the network develops which leads to a decrease in mobility, hence increase in viscosity and the effect of temperature on molecular mobility. An approach which uses an inverse temperature exponential dependence of viscosity [228] was utilised here:

$$\eta = \eta_r e^{D\left(\frac{1}{T} - \frac{1}{T_r}\right)} \quad (3.17)$$

alongside the following kinetics applied to the logarithm of viscosity:

$$\frac{d\ln\eta_r}{dt} = A e^{-\frac{E}{RT}} \left(\ln \frac{\eta_r}{\gamma}\right)^l \quad (3.18)$$

where coefficient D governs the temperature sensitivity, A is the pre-exponential factor, E and l the activation energy and order of the kinetics respectively, and γ a fitting parameter that must be lower than the initial value of reference viscosity, has been used successfully to model commercial liquid composite moulding aerospace systems [228]. The viscosity was modelled by fitting the experimental data to identify the values of the parameters of the viscosity model following the procedure described previously for the T_g and kinetics models. The minimisation error was computed as the sum of absolute differences between experimental and model logarithm of viscosity over all data points.

Chapter Four

4 Cure kinetics, glass transition evolution, chemorheology and stress relaxation of DGEBA/4-APDS epoxy vitrimer

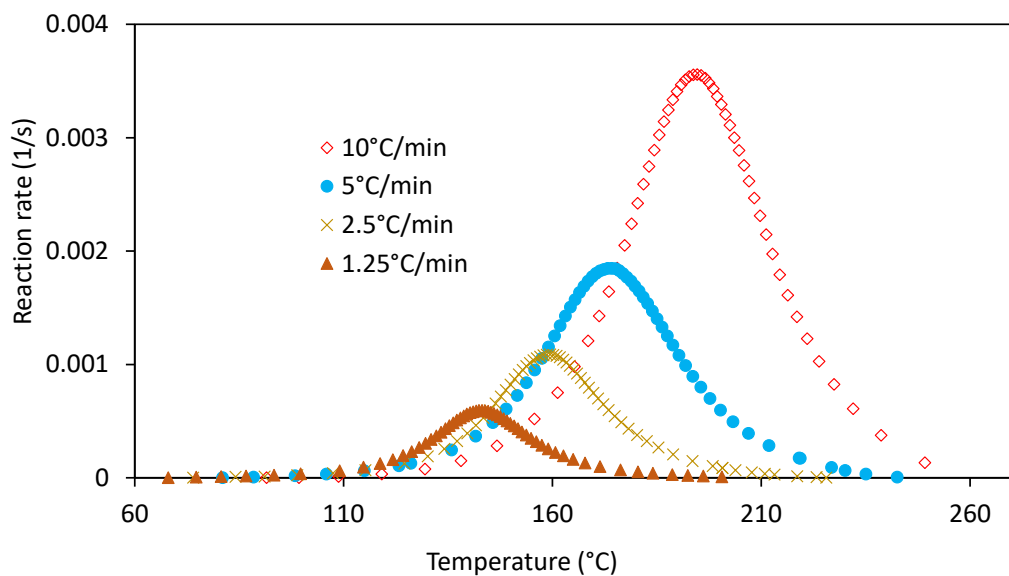
4.1 Introduction

In this chapter, the cure kinetics, glass transition advancement and chemorheological modelling of DGEBA/4-APDS epoxy vitrimer – which guides the manufacturing of the composite – is presented. The cure kinetics of DGEBA/4-APDS epoxy vitrimer was simulated using an autocatalytic model which incorporates a logistic function accounting for diffusion effects that dominate the kinetics as a rigid three-dimensional network is established during the curing reaction. Also presented in this chapter is the chemorheology of DGEBA/4-APDS epoxy vitrimer which focuses on a low degree of cure window, addressing the infusion and consolidation step of the vacuum assisted resin transfer moulding process, for which an inverse temperature exponential dependence of viscosity is utilised as the underlying variable of the viscosity model, rather than degree of cure, as explained in chapter three. Furthermore, the evolution of glass transition temperature – modelled using the Di Benedetto equation as well as the stress relaxation behaviour of this vitrimer leading to the determination of its topology freezing transition temperature – are presented.

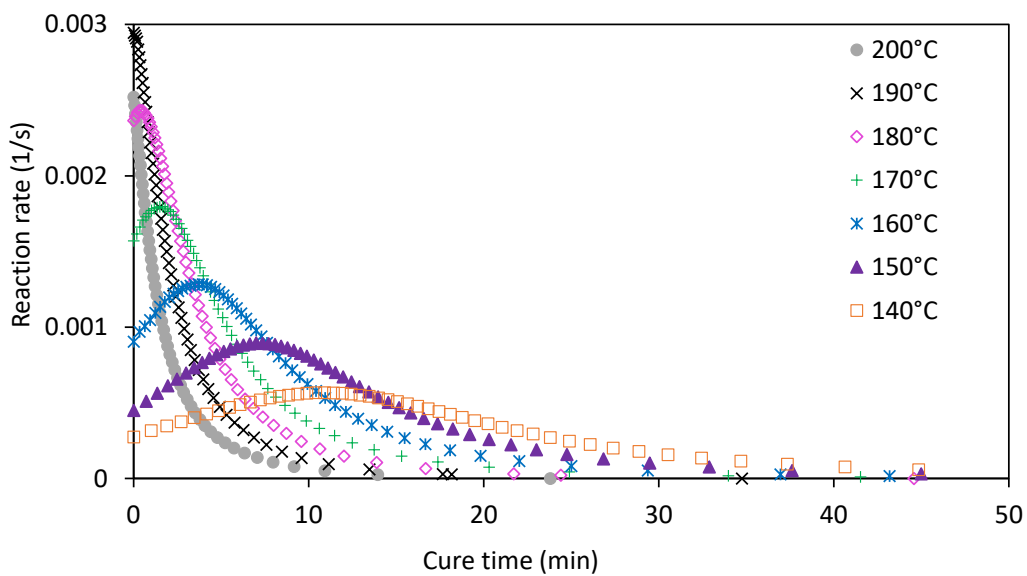
4.2 Cure kinetics of DGEBA/4-APDS epoxy vitrimer

The reaction rate curves for the isothermal and dynamic experiments of DGEBA/4-APDS epoxy vitrimer are illustrated in **Figure 4.1**. All dynamic and isothermal DSC experiments, with the exception of the 140°C test, result in full cure of the material. The total heat of the reaction of the DGEBA/4-APDS system is 454.9 ± 9.9 J/g. The enthalpy measured corresponds only to the curing epoxy-

amine reaction, as any energy exchange due to disulphide bond metathesis has a zero net effect.



(a)



(b)

Figure 4.1. Experimental cure kinetics of DGEBA/4-APDS system: (a) reaction rate versus temperature in dynamic DSC experiments; (b) reaction rate versus cure time in isothermal DSC experiments.

In dynamic data, a peak in reaction rate is observed at an intermediate conversion during the cure. This is due to the combined effects of temperature changes and of progression of the reaction. Initially, as the temperature increases, reaction rate increases due to enhanced kinetic energy of reacting groups. As the reaction progresses, the concentration of reactants declines leading to a reduction of the rate of collisions of reacting groups. Therefore, the reaction rate increases with temperature until it reaches a maximum at an intermediate conversion point at which the decline in reactant concentration dominates the kinetics. The position of the reaction peak shifts to higher temperatures as the heating rate increases, with the reaction peak increasing from 140°C at 1.25°C/min to 190°C at 10°C/min, due to the shorter exposure to a specific temperature range with increasing rate. Similarly, the maximum rate increases with increasing rate from $5.9 \times 10^{-4} \text{ s}^{-1}$ at 1.25°C/min to $3.5 \times 10^{-3} \text{ s}^{-1}$ at 10°C/min, due to the occurrence of the maximum at a greater temperature and the Arrhenius dependence of rate constants on temperature.

The reaction rate curves for isothermal experiments reported in **Figure 4.1(b)** show peak values at intermediate conversions, which is indicative of an autocatalytic mechanism. The isothermal reaction peak shifts to shorter times for higher temperatures, whilst the initial reaction rate has a finite and increasing value with increasing temperature. Maximum rates under isothermal conditions range from $5.7 \times 10^{-4} \text{ s}^{-1}$ at 140°C to $2.9 \times 10^{-3} \text{ s}^{-1}$ at 190°C. This behaviour is attributed to the Arrhenius dependence of rate constants on temperature. The increasing part of isothermal curves, from the beginning of isothermal cure to the peak, diminishes with increasing temperature to the extent that for higher temperatures, such as 190°C and 200°C, the peak disappears completely, and maximum reaction rate occurs at the start of the isothermal cure. This is attributed to the fact that the material cures during the heating ramp to reach the isothermal temperatures. Knowledge of the evolution of the cure from the corresponding dynamic test at 10°C/min allows the calculation of the initial degree of cure for the isothermal tests, which is reported in **Table 4.1**. The isothermal cure at high temperatures starts from degrees of cure exceeding 40%, which explains why the

autocatalytic character is not manifested as maximisation of reaction speed at intermediate times as it is the case at lower temperatures. Furthermore, at the highest temperature of 200°C the reaction starts at 65%, which is well past the location of the reaction rate peak. Therefore, the rate at the beginning of the 200°C isothermal segment is lower than the corresponding reaction rate for the 190°C, which occurs at an initial degree of cure of 46%, which is closer to the point of the reaction rate peak.

Table 4.1. Initial degree of cure of isothermal experiments reported in **Figure 4.1(b)**; isothermal temperature reached at a rate of 10°C/min.

Isothermal temperature (°C)	140	150	160	170	180	190	200
Initial degree of cure (-)	0.03	0.04	0.08	0.15	0.28	0.46	0.65

The basis for modelling cure kinetics using an expression that maps reaction rate onto degree of cure-temperature space is the assumption that reaction rate is a unique function of degree of cure and temperature. This means that reaction rate shows no path dependence when mapped onto the degree of cure – temperature space, i.e., once a point in this space is reached, the reaction rate is the same irrespective of thermal history. Testing the validity of this assumption involves superimposing the results obtained for identical degree of cure – temperature points reached under isothermal and dynamic conditions [229]. This involves interpolating results of 1.25°C/min, 2.5°C/min, 5°C/min and 10°C/min dynamic experiments at the isothermal temperatures of 140°C, 150°C, 160°C, 170°C, 180°C, 190°C and 200°C and overlaying reaction rate – degree of cure points reached dynamically with the isothermal curves as depicted in **Figure 4.2**. The dynamic results at the corresponding temperatures are in close agreement with the isothermal curves over the whole range. The average absolute difference between dynamic and isothermal rate data is $3.4 \times 10^{-5} \text{ s}^{-1}$, whilst the average relative difference is 5.9%. This result confirms the validity of the assumption of reaction rate being a function of temperature and degree of cure and allows application of a phenomenological model to represent the kinetics of DGEBA/4-APDS cure by expressing reaction rate as a function of degree of cure and

temperature only. This result also validates the assumption that the enthalpy measured by DSC provides a quantitative metric of the degree of conversion that is uniquely mapped to the state variables of the reaction. Based on these observations, Eq.3.10, expressing autocatalytic behaviour with diffusion limitations in the way proposed in [181] was selected for modelling the cure of the DGEBA/4-APDS system, expressed as:

$$\frac{d\alpha}{dt} = \frac{A_1 e^{-E_1/RT} \alpha^m (1 - \alpha)^n}{1 + e^{C[\alpha - (\alpha_{cT}T + \alpha_{co})]}} \quad (4.1)$$

where E_1 is the activation energy, A_1 the pre-exponential factor and α_{cT} and α_{co} are coefficients controlling the critical degree for diffusion as a function of temperature and R is the universal gas constant. The role of the denominator in Eq.4.1 is to incorporate mobility and diffusion limitations as the polymer approaches the glass transition during crosslinking. The fitting involving the seven parameters of Eq.4.1 was carried out using the procedure described in section 3.5 to minimise the error expressed by Eq.3.12. The cure kinetics parameters identified are reported in **Table 4.2**.

Table 4.2. DGEBA/4-APDS kinetics parameters values for the model represented by Eq.4.1; α_o is the initial degree of cure used in the analysis.

α_o (-)	A_1 (s ⁻¹)	E_1 (J mol ⁻¹)	m (-)	n (-)	C (-)	α_{cT} (K ⁻¹)	α_{co} (-)
0.01	27,190	55,810	0.697	1.53	29.5	0.0095	-3.07

Figure 4.3 provides a comparison of experimental and model data for dynamic and isothermal experiments. Both dynamic and isothermal data are reproduced successfully by the cure kinetics model. The model underestimates slightly the reaction rate at the later stages of the 10°C/min experiment, which corresponds to temperatures over 200°C, whilst it overestimates slightly the rates in the 190°C and 200°C isothermal experiments, which coincide with the later stages of cure at these temperatures. This is consistent with the superposition data presented in **Figure 4.2**, in which isothermal reaction rates at the highest temperatures tend

to be lower than the corresponding data points. The model fitting finds a compromise between these two, which results in slight overestimation of isothermal rates and slight underestimation of dynamic rates in this region of the temperature-degree of cure space. The rest of the experimental data are followed very closely by the model, including the partial completion of cure, at about 0.88, in the lowest isothermal cure at 140°C. **Table 4.3** summarises the average absolute and relative error in reaction rate for each experimental condition. The absolute error ranges from $1.8 \times 10^{-5} \text{ s}^{-1}$ to $12.4 \times 10^{-5} \text{ s}^{-1}$, which in terms of relative error translate to 2.3 % to 9.3 %. The average absolute error over all conditions is $5.0 \times 10^{-5} \text{ s}^{-1}$ and the relative error 5.2 %. A comparison with the superposition average absolute and relative differences of $4.2 \times 10^{-5} \text{ s}^{-1}$ and 7.2 % respectively shows the optimal performance of the model as it represents the experimental results with an accuracy similar to the inherent consistency of the dataset, without overfitting or significant model deviations.

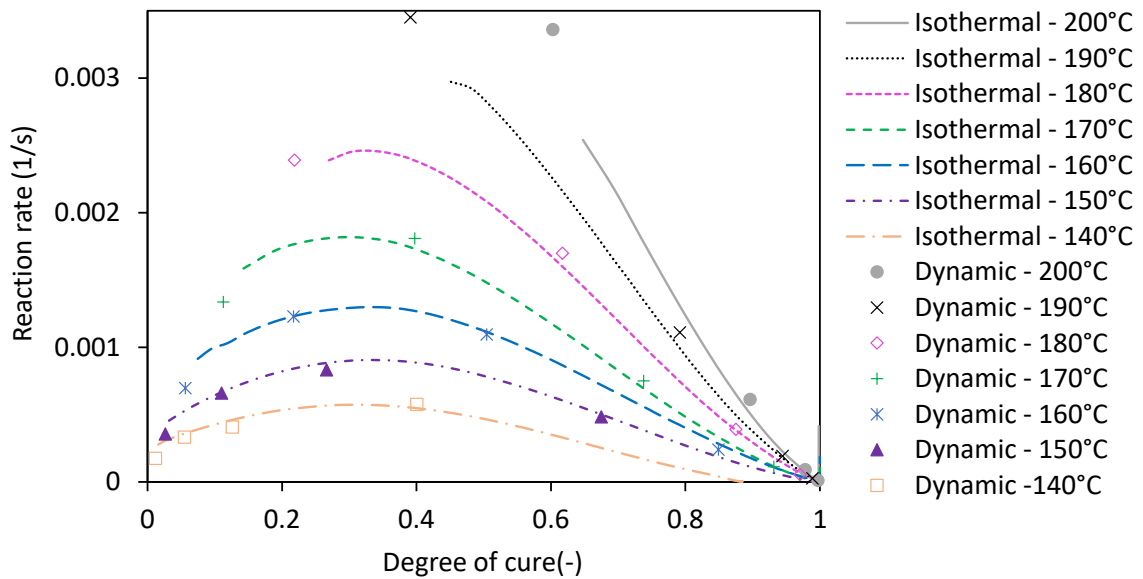


Figure 4.2. Superposition of dynamic and isothermal reaction rate versus degree of cure data for DGEBA/4-APDS vitrimer.

The validity of the cure kinetics model can be tested further by using it to predict the evolution of degree of cure under isothermal and dynamic cure conditions. This involves integrating the reaction rate computed using Eq.4.1 for the thermal

profile of the corresponding experiment and comparing model to experiment degree of cure. **Figure 4.4** illustrates the comparison of the model predictions of the degree of cure with experimental values for dynamic and isothermal conditions. The model reproduces the evolution of degree of cure in DSC experiments very closely. Given the fitting of the kinetics model expressed by Eq.4.1 was carried out on the reaction rate data, this reinforces the model validity.

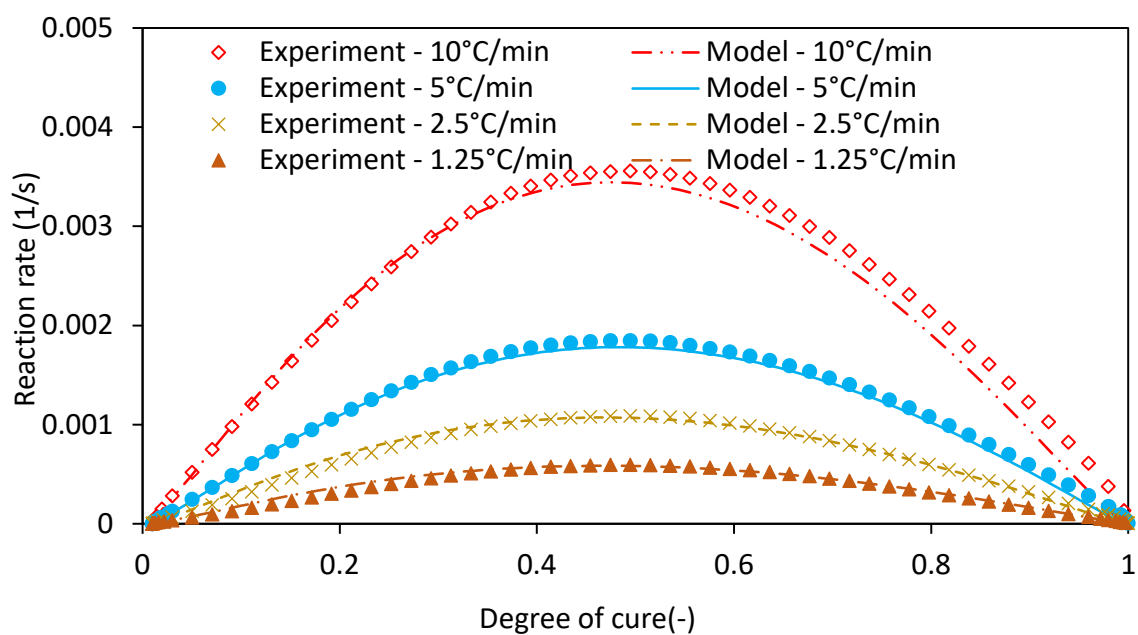
Some small deviations are observed in the initial stages of low-rate dynamic experiments and the final stages of low temperature isothermal tests. This relates to the fact that the data is denser in the areas where most of the cure reaction occurs, making the regions of low temperature – intermediate degree of cure and low temperature – high degree of cure to have a weaker contribution to the determination of the kinetics parameters. Lower prioritisation of these regions is also consistent with practicalities of cure, in which under a typical ramp-dwell profile the material is expected to attain intermediate and high degrees of cure at greater temperatures than those corresponding to these regions. The level of accuracy of the model in reproducing the evolution of degree of cure is confirmed by the average absolute and relative error reported in **Table 4.3**. The absolute error in degree of cure ranges from 0.0035 to 0.025 with the corresponding relative error in the 0.4 % to 8.7 %. The overall average absolute error in degree of cure across all experiments is 0.01, corresponding to an overall relative error of 3%. This accurate model can form the basis of process development for the DGEBA/4-APDS system based on the stoichiometric formulation utilised here.

In the cure kinetics of the DGEBA/4-APDS epoxy vitrimer, modification of the formulation by altering the epoxy-to-amine ratio would lead to kinetics similar to the one presented in this study with changes in the values of the cure kinetics model parameters. Similarly, the model reported in this study is specific to the dynamic bonds involved in this formulation and captures their overall effect, in terms of both occurrence of exchange reaction and effects on the crosslinking polymer structure; as the curing process reaches the topology freezing transition temperature of the system, the activation energy for dynamic bond exchanges is overcome. Thus, disulphide bond exchanges begin to occur simultaneously as

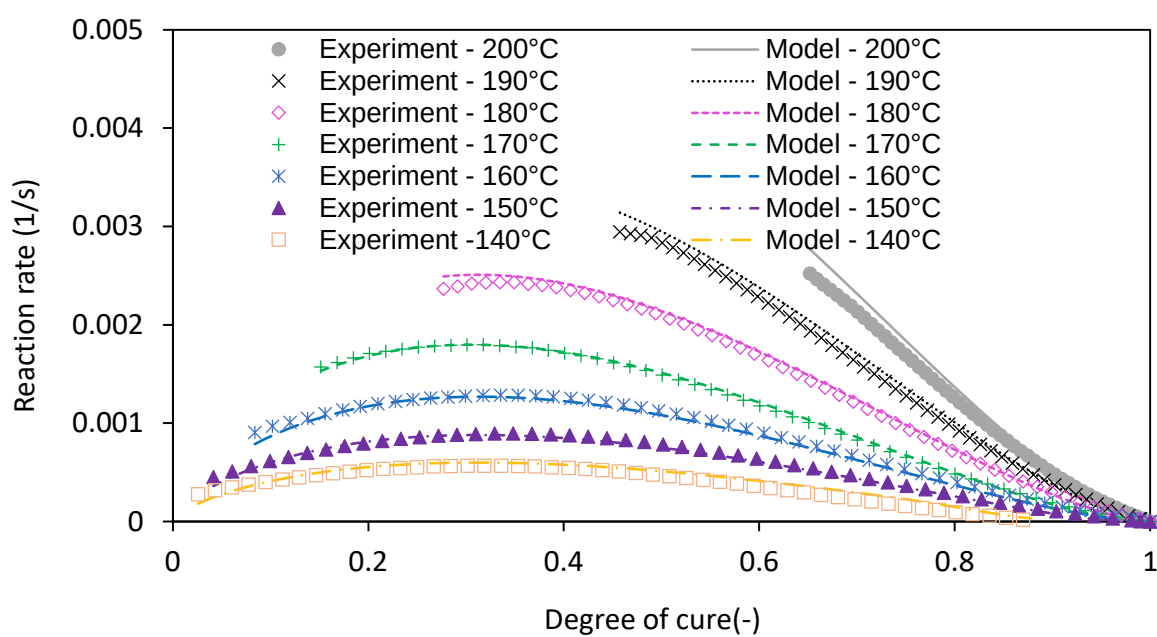
the curing reaction proceeds, with the result that the total energy of disulphide bond breakage equals the total energy of its reformation, giving rise to net zero contribution of the bond metathesis to the measurable polymerisation exotherm of the vitrimer.

Table 4.3. Average absolute error and average relative error in reaction rate and degree of cure of the cure kinetics model of DGEBA/4-APDS. Relative error computed over experimental points exceeding reaction rate of 2.5×10^{-4} .

Experiment	Reaction rate		Degree of cure	
	Absolute error	Relative error	Absolute error	Relative error
1.25°C/min	$1.8 \times 10^{-5} \text{ s}^{-1}$	4.5 %	12.5×10^{-3}	5.4 %
2.5°C/min	$2.5 \times 10^{-5} \text{ s}^{-1}$	4.2 %	13.1×10^{-3}	7.0 %
5°C/min	$4.4 \times 10^{-5} \text{ s}^{-1}$	4.4 %	8.2×10^{-3}	3.9 %
10°C/min	$12.4 \times 10^{-3} \text{ s}$	7.9 %	8.5×10^{-3}	8.7 %
140°C	$4.1 \times 10^{-5} \text{ s}^{-1}$	9.3 %	24.9×10^{-3}	4.0 %
150°C	$2.4 \times 10^{-5} \text{ s}^{-1}$	4.1 %	14.6×10^{-3}	1.7 %
160°C	$3.3 \times 10^{-5} \text{ s}^{-1}$	4.3 %	14.0×10^{-3}	1.6 %
170°C	$3.1 \times 10^{-5} \text{ s}^{-1}$	3.7 %	3.5×10^{-3}	0.4 %
180°C	$4.2 \times 10^{-5} \text{ s}^{-1}$	2.3 %	6.7×10^{-3}	0.7 %
190°C	$7.1 \times 10^{-5} \text{ s}^{-1}$	4.7 %	5.5×10^{-3}	0.5 %
200°C	$9.8 \times 10^{-5} \text{ s}^{-1}$	7.5 %	5.5×10^{-3}	0.5 %

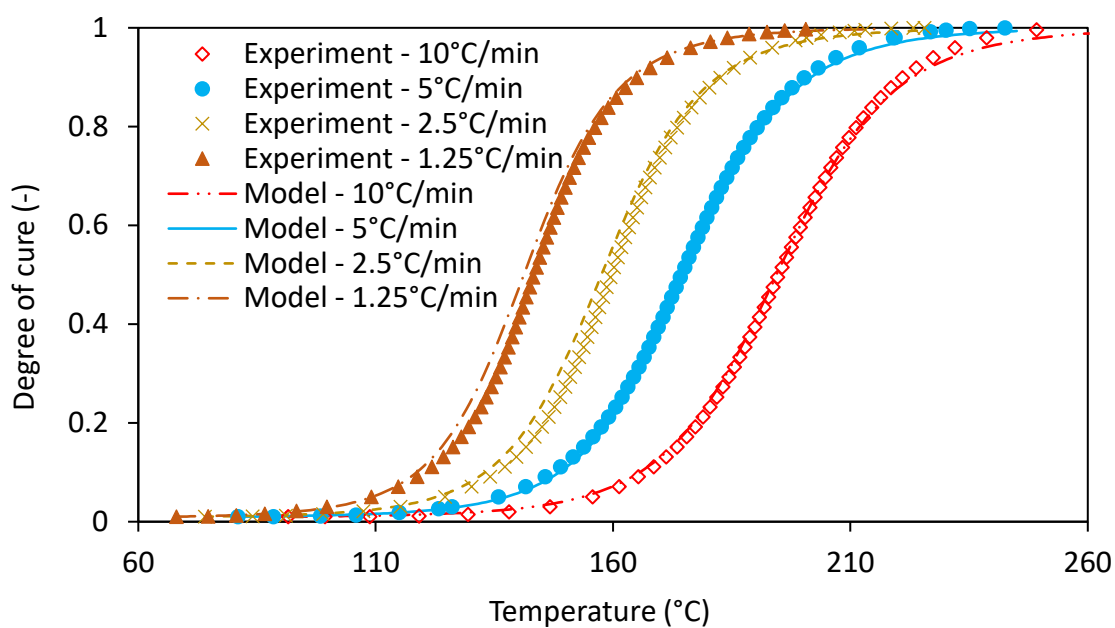


(a)

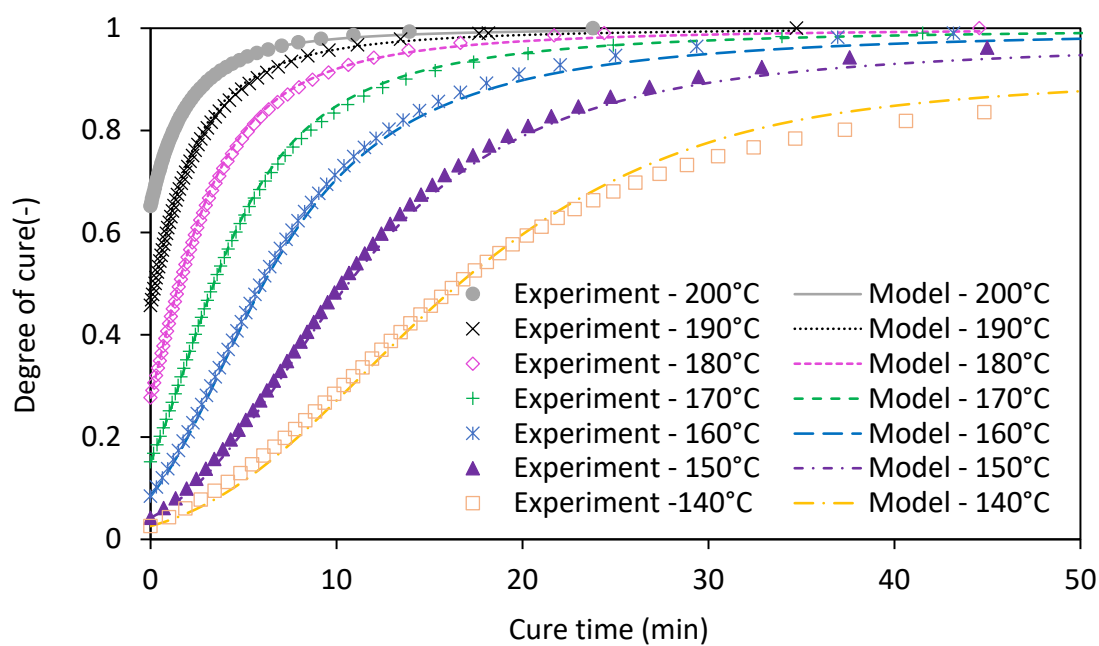


(b)

Figure 4.3. Cure kinetics modelling of DGEBA/4-APDS: Comparison of model and experiment reaction rate in dynamic (a) and isothermal (b) conditions.



(a)



(b)

Figure 4.4. Cure kinetics modelling of DGEBA/4-APDS: Comparison of model and experiment degree of cure evolution in dynamic (a) and isothermal (b) conditions.

4.3 Glass transition evolution of DGEBA/4-APDS epoxy vitrimer

The experimental measurements of T_g for different states of cure of the DGEBA/4-APDS vitrimer are illustrated in **Figure 4.5**. The points correspond to a variety of thermal histories for reaching the partial cure state isothermally or dynamically, with the values of T_g following a single curve supporting the conclusion that material state can be captured by the degree of cure reached in the study of cure kinetics. The T_g varies over a wide temperature range from -18°C in the uncured state to 162.6°C in the fully cured state. The low value of -18°C for the uncured material T_g points to a desirably low viscosity at typical infusion temperatures, whilst the high value of 162.6°C at full cure is characteristic of the aromatic ring of amine curing agents. The evolution of the glass transition temperature is modelled using the Di Benedetto equation as follows:

$$T_g = T_{go} + \frac{\lambda\alpha(T_{g\infty} - T_{go})}{1 - \alpha(1 - \lambda)} \quad (4.2)$$

where $T_{g\infty}$ and T_{go} are the values of the glass transition temperature of the fully cured and uncured system respectively and λ is a parameter controlling the convexity of the evolution curve, whilst α is the degree of cure. **Table 4.4** reports the values of the three model parameters obtained by fitting, whilst the Di Benedetto curve is also shown in **Figure 4.5**. The average error of the fitting of the model is 3.5°C. The model follows very closely experimental values at high degrees of cure with the experimental $T_{g\infty}$ being identical to the model value obtained. Greater deviations are observed at low degrees of cure with the experimental T_{go} at -18°C being lower than the model value.

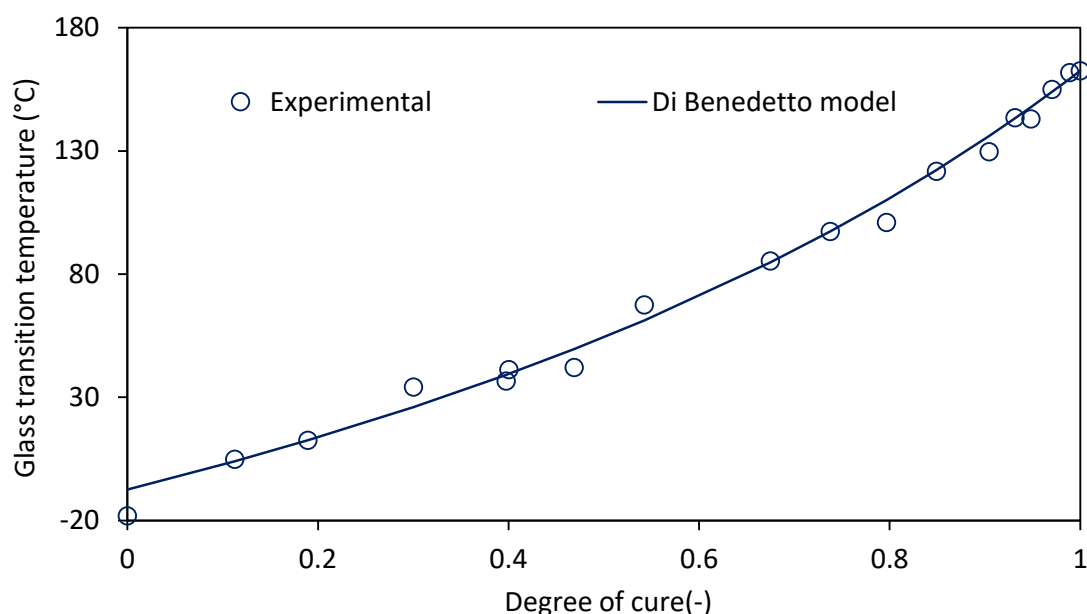


Figure 4.5. Development of the glass transition temperature of the DGEBA/4-APDS vitrimer as a function of the degree of cure.

Table 4.4. DGEBA/4-APDS Di Benedetto T_g development model parameters and error.

$T_{g\infty}$ (°C)	T_{go} (°C)	λ (-)	Average absolute error (°C)
162.6	-7.5	0.572	3.5

4.4 Chemorheology of DGEBA/4-APDS epoxy vitrimer

The development of viscosity of the DGEBA/4-APDS system in the temperature range of infusion processing is illustrated in **Figure 4.6**. The results window is selected up to viscosities of 1 Pas, which is significantly greater than the levels required for liquid moulding, usually in the range of 10-200 mPas [59,60]. The initial viscosity decreases with increasing temperature as a result of enhanced molecular mobility, with an initial viscosity of 12 mPas at 120°C and of 53 mPas at 80°C. The increase of viscosity with time is exponential, whilst the realistic infusion times, before the viscosity increases beyond values that would make

reinforcement impregnation challenging, are in the range of around 20 min at 120°C to around 100 min at 80°C. The time spent at low viscosity is a decreasing function of temperature as a result of the acceleration of cross-linking with increasing temperature. This causes a trade-off as, at high temperatures, infusion can be fast due to the low initial viscosity; however, the processing time over which infusion becomes challenging due to the increasing viscosity is shorter. At low infusion temperatures the situation is reversed, with an inherently slower process due to the greater initial viscosity, but a significantly greater time window over which the process can be completed without issues. The rheological behaviour of the system is simulated by combining Eqs.3.14 and 3.15 in a single differential equation to facilitate integration:

$$\frac{d\eta}{dt} = Ae^{-\frac{E}{RT}} \eta \left[\ln\eta + D \left(\frac{1}{T_r} - \frac{1}{T} \right) - \ln\gamma \right]^l - \frac{D\eta}{T^2} \frac{dT}{dt} \quad (4.3)$$

Here, all temperatures are in K and the initial condition of the integration is:

$$\eta_{t=0} = \eta_r^o e^{D \left(\frac{1}{T_{t=0}} - \frac{1}{T_r} \right)} \quad (4.4)$$

where η_r^o is the initial viscosity at the reference temperature (T_r). The results of the fitting are illustrated in **Figure 4.7**, whilst the parameters of the model are summarised in **Table 4.5** where A is the preexponential factor, E is the activation energy, l is the order of the kinetics, γ is a fitting parameter that has to be lower than the initial value of the reference viscosity and D is the coefficient that governs the temperature sensitivity of viscosity. The fitting is very close to the experimental data for all curves, with deviations observed only for the 100°C experiment, for which the model underestimates viscosity at the later stages of the process. The error of the model is summarised in **Table 4.6** for the different experiments. The average absolute error is in the 1 - 17 mPas range, whilst the relative error is 1.0 - 10.1 %. The average absolute error over all tests is 6.5 mPas and the average relative error 4.8 %. The highly accurate representation of effects in the low viscosity range demonstrates the advantages of the model utilised here, which allows effects of early cure represented very closely to experimental

behaviour for the window of temperature – material state most relevant to liquid composite moulding.

Table 4.5. DGEBA/4-APDS viscosity development parameter values for the model represented by Eq.4.3. Fitting performed for viscosity levels up to 500 mPas.

η_r^o (mPa·s)	A (s ⁻¹)	E (J mol ⁻¹)	l (-)	γ (mPas)	D (K ⁻¹)
53.6	14,300	55,410	1.4	17.3	5,180

Table 4.6. Average absolute error and average relative error of the viscosity model of DGEBA/4-APDS.

Experiment	Absolute error	Relative error
80°C	1.2 mPas	1.0 %
90°C	8.0 mPas	4.7 %
100°C	18 mPas	10.8 %
110°C	4.1 mPas	6.7 %
120°C	1.0 mPas	1.1 %

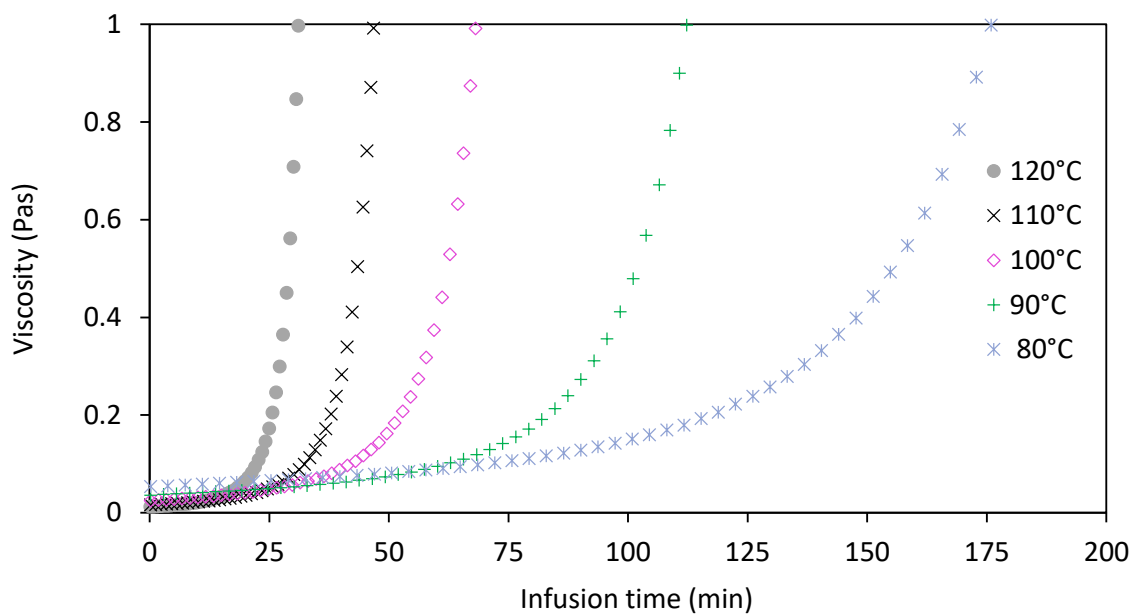


Figure 4.6. Viscosity evolution of the DGEBA/4-APDS vitrimer as a function of time at different isothermal infusion temperatures.

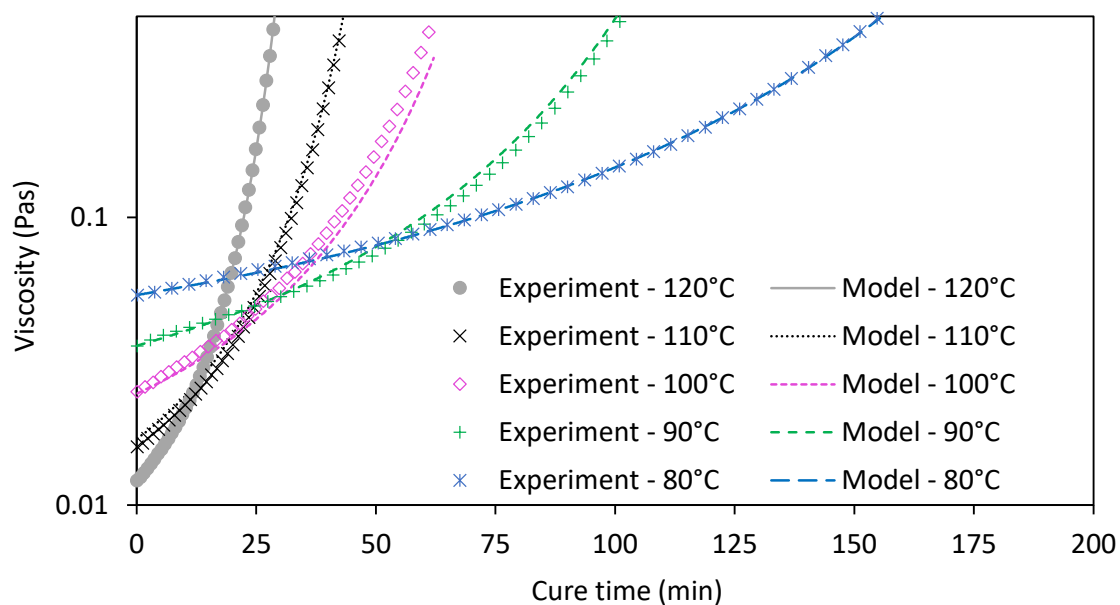


Figure 4.7. Viscosity development model of the DGEBA/4-APDS system: Comparison of modelling and experimental results.

4.5 Stress relaxation and topological transition temperature

Figure 4.8 reports the isothermal stress relaxation curves of the DGEBA/4-APDS system, whilst **Figure 4.9** presents the normalised stress relaxation curves. The relaxation modulus follows a behaviour close to an exponential decay as indicated by the step drop in a logarithmic time scale. The plateau relaxation modulus depicted in **Figure 4.8** increases marginally with increasing temperature from 180°C up to 200°C, due to the entropic contribution in the elastic behaviour of the rubbery material, which is indicative of a retention of the thermosetting character of the system. Beyond 200°C, this trend reverses as the thermosetting character of the vitrimer becomes weaker. The relaxation times estimated using the time required to reach a reduction in modulus by $1/e$ are reported in **Figure 4.10**, alongside the fitting of an Arrhenius dependence of the inverse of relaxation time on temperature. The coefficient of determination of the fitting is 0.99, and the activation energy is 196.8 kJ/mol. This activation energy for the disulphide bond exchange varies depending on the molecular structure of the chemical. To determine the T_v , the rubbery modulus of the material was approximated by averaging the initial relaxation modulus over the five experiments. The value found is 24 MPa, which for the assumed viscosity of 10^{12} Pas at transition, corresponds to a relaxation time of 41700 s. T_v is determined as the temperature at which the Arrhenius dependence reported in **Figure 4.10** reaches this value and is equal to 149.5°C. It should be noted that the T_v found here is higher than that reported in the literature for a similar epoxy-4-aminophenyl disulphide system [15]. This can be attributed to differences in the epoxy prepolymer and relative fraction of APDS. T_v falls within the temperature region of active polymerisation in the material based on the kinetics. This is an indication of active bond metathesis during the curing of the material. However, since T_v is sufficiently higher than the chemoviscosity modelling temperatures, bond metathesis activation energy is not overcome during the chemorheology, and there is no bond exchange within the low degree of cure window of chemoviscosity modelling.

The T_v of 149.5°C for DGEBA/4-APDS is lower than its T_g . Therefore, the system can be reprocessed over its T_g , a behaviour that is desirable as the matrix system maintains its thermosetting character up to its maximum functional temperature at the T_g , whilst over this it attains its functionality as a vitrimer. Although bond metathesis is possible at temperatures above T_v and below the T_g , lack of molecular mobility makes it very slow; once T_g is reached, rate and mobility limitations are lifted, and bond exchanges occur at high rates, allowing healing and reprocessing.

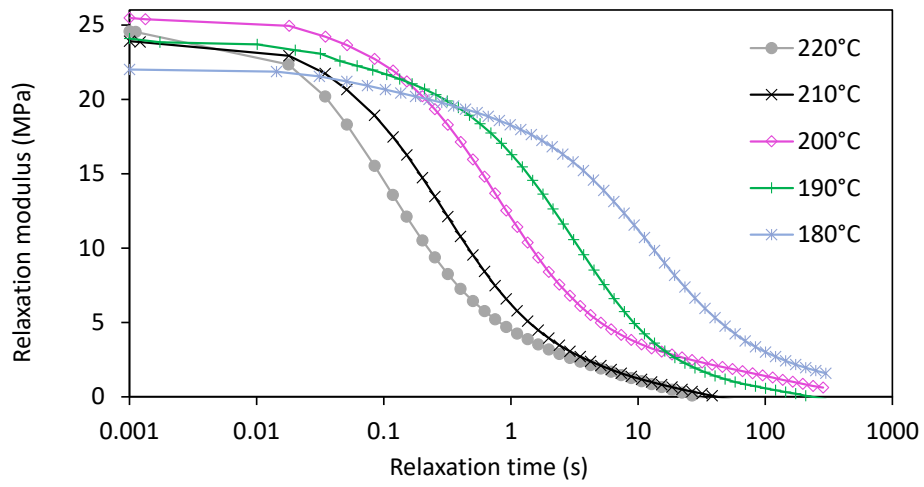


Figure 4.8. Stress relaxation curves of DGEBA/4-APDS system.

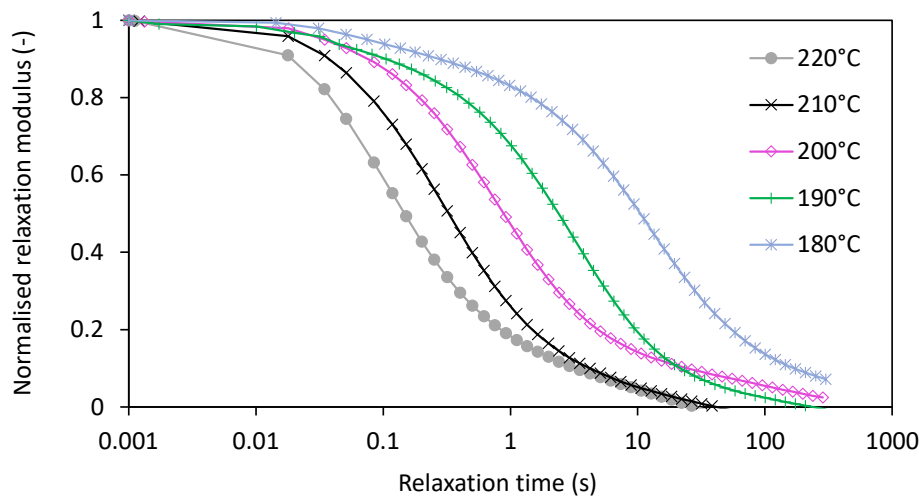


Figure 4.9. Normalised stress relaxation curves.

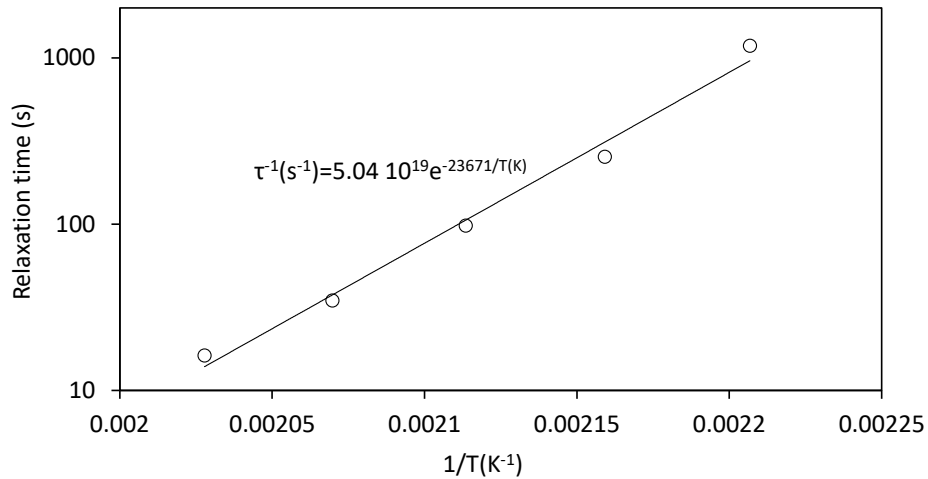


Figure 4.10. Relaxation time as a function of temperature.

4.6 Concluding remarks

The autocatalytic model with diffusion term accurately replicates the DGEBA/4-APDS epoxy vitrimer cure behaviour with minimal average absolute and relative errors. The Di Benedetto equation represents the vitrimer glass transition advancement, and the chemoviscosity model represents resin rheology accurately. This cure kinetics model characterises the unique combination of disulphide bond and epoxy/amine crosslinking based on the stoichiometry of the system. Also, the chemorheological model presented in this chapter guides the selection of boundary conditions – temperature, viscosity and time – for optimal liquid moulding of DGEBA/4-APDS fibrous composite described in chapter 3 and mechanically tested, healed and retested in chapter 7. Finally, it is shown that at 220°C, polyDGEBA/4-APDS vitrimer fully relaxes stress within 16 seconds, triggering dynamic disulphide metathesis with an activation energy of 197 kJ/mol, making it a self-healable polymer matrix.

Chapter Five

5 Synthesis and characterisation of BH-A benzoxazine vitrimer

5.1 Introduction

This chapter presents the synthesis and characterisation of the new benzoxazine vitrimer described in section 3.2.2. Spectroscopic results involving identification and assignment of key benzoxazine and associated functional group spectral bands in both monomer and fully polymerised material are presented. This is followed by DSC results showing the monomer glass transition temperature, cure exotherm and polymer glass transition temperature. DMA and TGA results are also presented in this chapter, illustrating the glass modulus of the vitrimer, its viscoelastic behaviour, glass transition temperature, thermal stability, and fire retardancy potential. Furthermore, the swelling behaviour of the material, which demonstrates its thermosetting character as well as stress relaxation behaviour demonstrating flow capability over the glass transition temperature – leading to dynamic bond rearrangement – are presented. Finally, profilometric measurements of surface profiles of a scratched and healed specimen of the polybenzoxazine vitrimer are reported, demonstrating its self-healing behaviour within practically realistic temperatures, pressures and time constraints.

5.2 Synthesis and polymerisation of BH-A

Successful synthesis of the benzoxazine monomer (BH-A) based on bis (4-hydroxyphenyl) disulphide and aniline as described in chapter 3 – illustrated in reaction **Figure 5.1** – is confirmed by FTIR results (**Figure 5.2**). The aromatic ring stretches of C=C bonds of primary amine and benzoxazine are observed at 1599 cm^{-1} and 1571 cm^{-1} , respectively. The peaks at 1495 cm^{-1} and 1479 cm^{-1} are assigned to C–C stretching vibrations of the disubstituted aromatic ring of the amine and substituted aromatic ring of the benzoxazine ring, respectively. CH₂ wagging of oxazine is observed at 1320 cm^{-1} . C–O–C asymmetric and symmetric

stretches of the oxazine ring are observed at 1230 cm^{-1} and 1082 cm^{-1} , respectively, whilst the oxazine ring C–N–C stretch is observed at 1121 cm^{-1} . The oxazine ring mode and out-of-plane bending vibration of C–H bond of the benzene ring attached to oxazine is observed at 934 cm^{-1} , thus confirming successful synthesis of the benzoxazine monomer. The bands from 871 cm^{-1} to 755 cm^{-1} are assigned to aromatic C–H bending vibrations.

The polymerisation was carried out using 8 mg sample in a $10^{\circ}\text{C}/\text{min}$ dynamic DSC run from -50°C to 240°C and confirmed by the disappearance of key benzoxazine monomer bands at 1230 and 934 cm^{-1} in the FTIR spectrum of polyBH-A. The ring-opening polymerisation is shown in **Figure 5.3**, whilst the DSC thermograms of BH-A and its polymer (polyBH-A) are shown in **Figure 5.4**, indicating a monomer T_g of 22°C , polymerisation onset at 110°C , symmetrical cure exotherm due to ring-opening polymerisation of the benzoxazine vitrimer with a single peak at 192°C , and T_g of 155°C for the cured polymer.

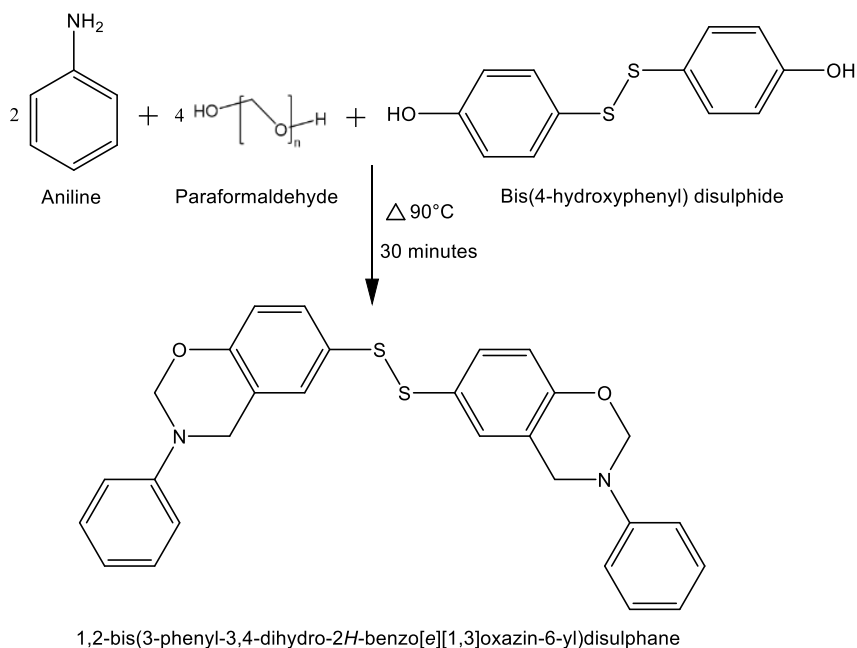


Figure 5.1. Synthesis of 1,2-bis(3-phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-yl)disulphane (BH-A).

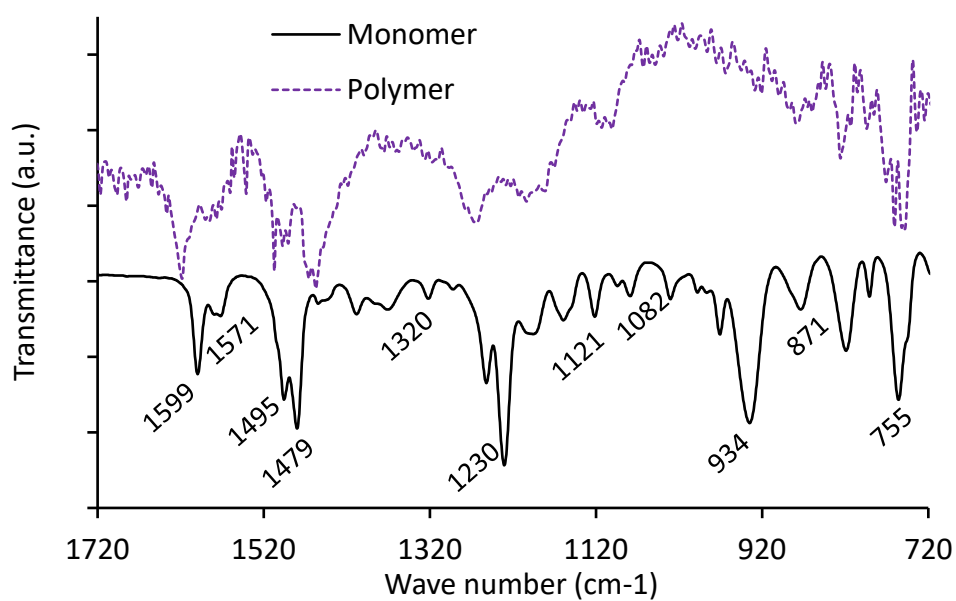


Figure 5.2. FTIR spectrum of BH-A.

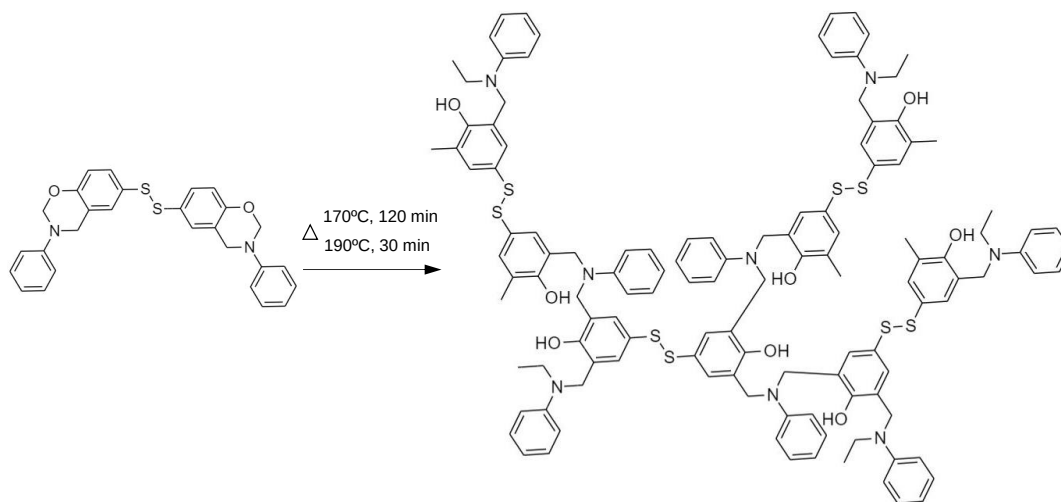


Figure 5.3. Ring-opening polymerisation of BH-A.

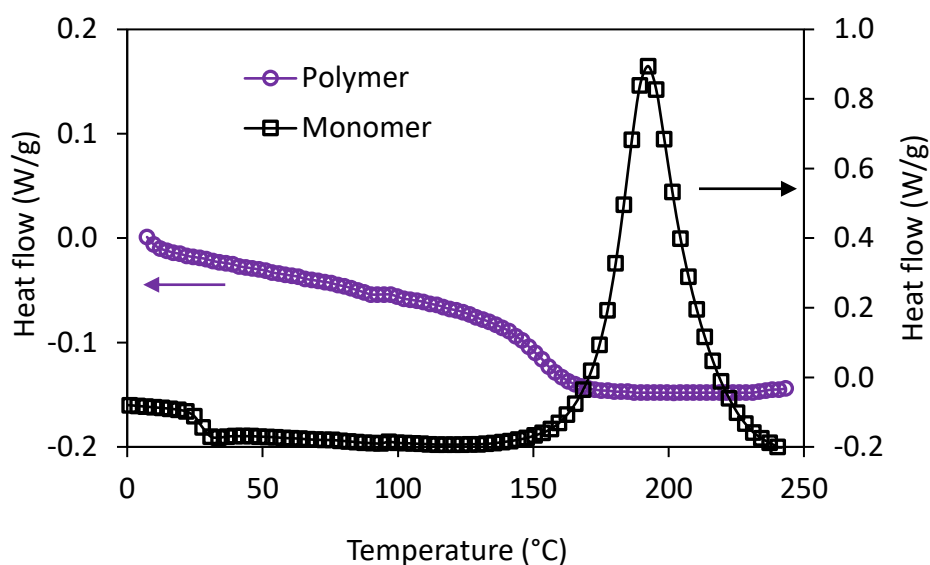


Figure 5.4. DSC thermograms of BH-A and polyBH-A showing monomer T_g of 27°C, cure enthalpy and polymer T_g of 155°C.

5.3 Thermomechanical characterisation and fire retardancy

Figure 5.5 illustrates the results of DMA dynamic testing. PolyBH-A features a storage modulus of around 3.6 GPa in the glassy state, which is typical of polybenzoxazines [230]. The glass transition temperature of polyBH-A determined by the inflection in storage modulus is 164.2°C. This is comparable with the glass transition temperature determined by DSC, with the difference between the two values attributed to differences in inherent frequency of the measurement, in thermal lag due to sample size and in the type of excitation.

The result of thermogravimetric analysis of polyBH-A is illustrated in **Figure 5.6**. A 5% weight loss temperature of 293°C is recorded, indicating a greater thermal stability compared to a similar polybenzoxazine vitrimer which has a value of 252°C [16]. PolyBH-A features a high char residue of 57.4% at 850°C which, according to Eq.3.5, corresponds to an LOI of 40.5%. Materials with LOI above 21% are generally considered flame-retardant. The best fire-retardant polybenzoxazine in literature has an LOI of 45.9% based on char yield measured at 800°C [231], with the greatest majority of benzoxazine formulations having

values below the level achieved by polyBH-A [231]. The intrinsic flame retardance of polyBH-A is attributed to the presence of many aromatic groups in the polymer structure, as shown in **Figure 5.3**.

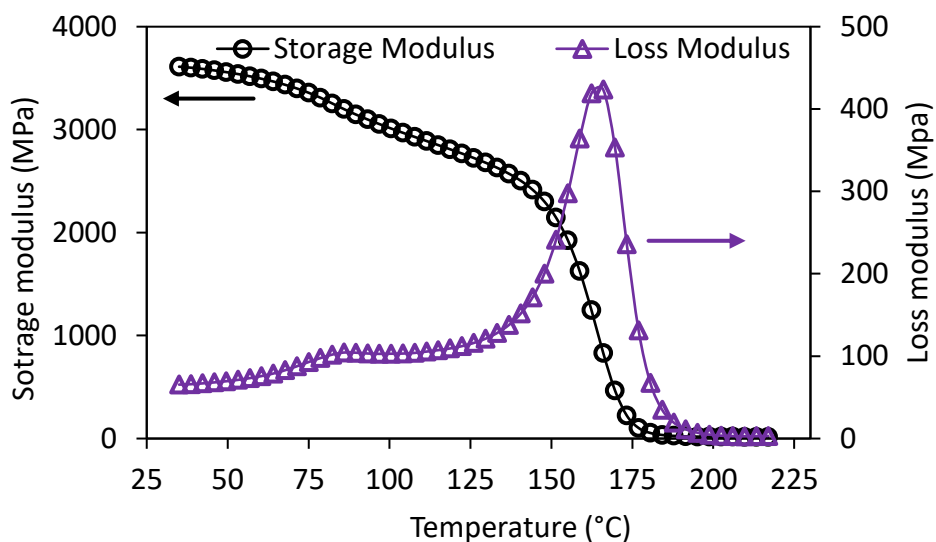


Figure 5.5. Dynamic mechanical scan of polyBH-A showing storage modulus and loss modulus.

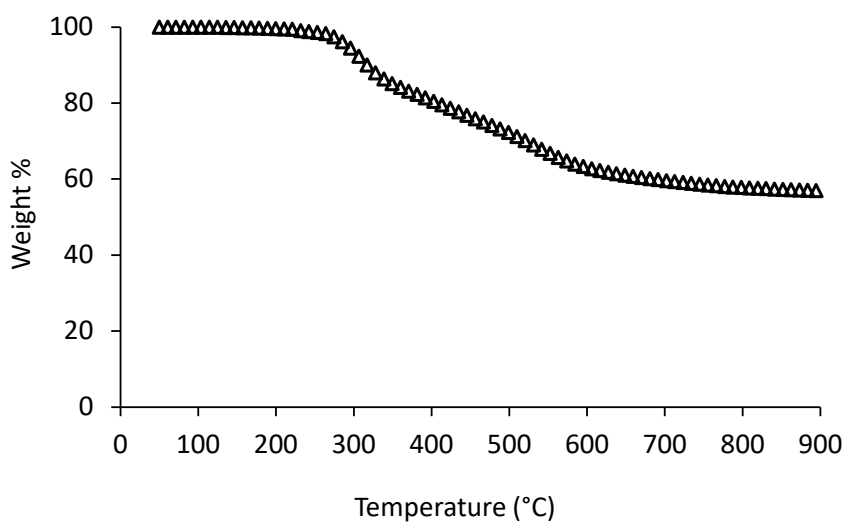


Figure 5.6. TGA thermogram of polyBH-A.

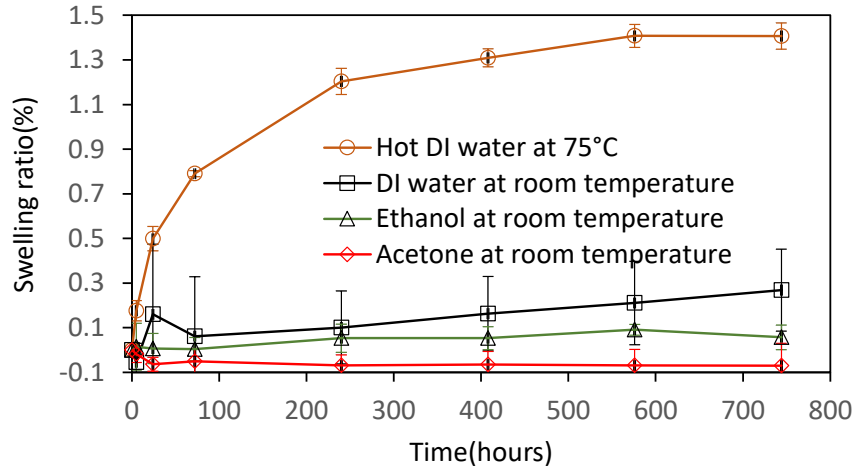
5.4 Swelling behaviour

The swelling behaviour of polyBH-A in different solvents – described in subsection 3.4.3– is illustrated in **Figure 5.7** and summarised in **Table 5.1**. PolyBH-A absorbs 0.27 % water at room temperature ($22 \pm 2^\circ\text{C}$) after immersion for 31 days. This is lower compared to characteristic values for high-temperature epoxy thermosets with T_g similar or greater than that of polyBH-A which show water uptake in the 1.5 – 2% range over equivalent periods [232]. After 31 days immersion at an elevated temperature of 75°C , polyBH-A swells by 1.4 %. This is better performance compared to high- T_g epoxy resins, which undergo swelling in the 1.2 – 2.8% range in water at elevated temperatures in similar or less severe conditions [233,234]. The superior water absorption resistance of polyBH-A compared to high- T_g epoxies is attributed to the lower polarity, compared to epoxies, of aromatic rings present in benzoxazines which increases hydrophobicity. The water resistance of polyBH-A is also comparable to that of high- T_g polybenzoxazine composites which undergo swelling of about 1.7 – 2% after immersion in water at 80°C [235,236]. The soluble fraction of polyBH-A in DI water after soaking for 31 days at room temperature and at 75°C is 0.03% and 0.04% respectively.

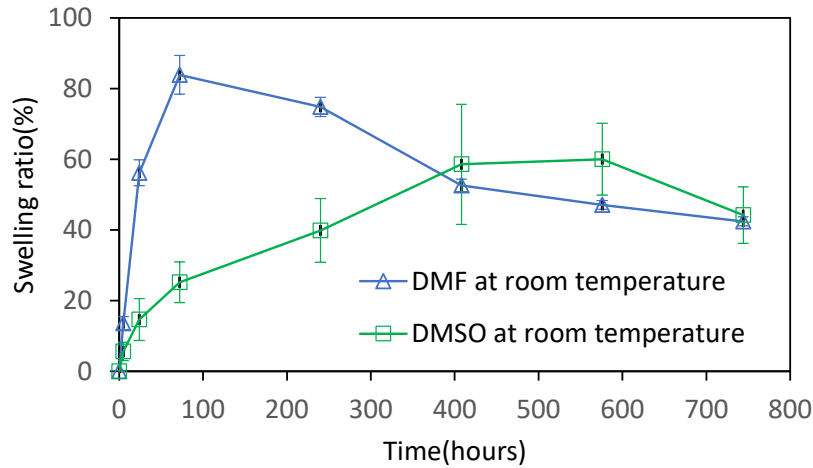
PolyBH-A is resistant to both ethanol and acetone, featuring uptakes of 0.06% and -0.07%, respectively in these solvents after soaking for 31 days. The negative value in the case of acetone is attributed to dissolution dominating solvent uptake, as more solute particles go into solution than solvent is absorbed by the solute. The swelling behaviour of polyBH-A in ethanol and acetone is similar or better compared to epoxy thermosets which are reported to exhibit swelling ratio ranging from 0.3 to 12% at 35°C [237]. After 31 days of soaking at room temperature, polyBH-A has a dissolved fraction of 0.15% in acetone whilst ethanol has dissolved fraction of 0.08%.

Figure 5.7(b) indicates that after 3 days of soaking at room temperature, polyBH-A is saturated by DMF with a swelling ratio of 83.9% and begins to lose weight due to gradual dissolution of the material. At this point, mass uptake in DMSO

continues increasing with swelling of 25.2%. It takes about 17 days for DMSO to saturate polyBH-A, plateauing at a swelling ratio of about 60% at 21 days before weight loss due to dissolution. DMF and DMSO are both strong aprotic solvents, degrading a wide range of thermosetting polymers. For example, carbon fibre epoxy composite swelling ratios of 83.6%, and 85.0% have been reported after 1 hour immersion at 120°C in DMF and DMSO, respectively [238].



(a)



(b)

Figure 5.7. Swelling behaviour of polyBH-A in various solvents. Error bars correspond to one standard deviation.

Figure 5.8 shows immersed polyBH-A samples and the solvents after soaking for 31 days. In the case of room temperature DI water, ethanol, acetone and water at 75°C the solvents remain colourless which indicates negligible to low dissolution. Samples in DMF and DMSO which substantially swell and dissolve change the colour of the solvents after the 31 days immersion period from colourless to brown. The change in colour indicates that the polymer is gradually dissolving/degrading in these two solvents.

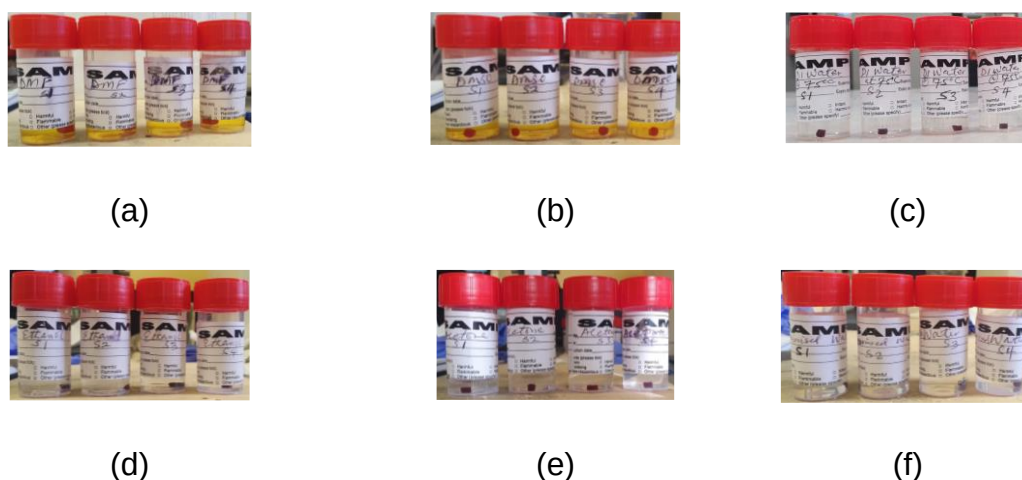


Figure 5.8. Images of BH-A in different solvents after 31 days of swelling tests: (a) DMF; (b) DMSO; (c) hot water; (d) ethanol; (e) acetone; (f) water at room temperature.

Table 5.1. Swelling behaviour of polyBH-A after 31 days immersion.

Solvent	Water	Water	Ethanol	Acetone	DMSO	DMF
Temperature (°C)	22	75	22	22	22	22
Swelling ratio (%)	0.27	1.41	0.06	-0.07	44.17	42.42
Soluble fraction (%)	0.03					
		0.04	0.08	0.1	54.7	52.4

5.5 Stress relaxation and T_v determination

The isothermal stress relaxation behaviour of polyBH-A is shown in **Figure 5.9** and the normalised stress relaxation data in **Figure 5.10**. The relaxation follows an exponential decay with the relaxation time corresponding to the time required for the modulus to drop by $1/e$ of its plateau value. The relaxation time as a function of inverse absolute temperature is illustrated in **Figure 5.11** alongside the corresponding Arrhenius dependence fit. The exponential fit follows the experimental data closely with a coefficient of determination of 0.998. The activation energy of the bond exchange is 127 kJ/mol. The activation energy of disulphide bond exchange in BH-A is lower than that of DGEBA/4-APDS epoxy vitrimer due to the additional flexibility of the molecular structure.

The complex rubbery modulus of polyBH-A from the dynamic single frequency temperature ramp DMA results shown in **Figure 5.5**, which is 14.9 MPa, can be used to calculate the topological transition temperature (T_v), taken as the temperature at which the viscosity becomes 10^{12} Pas, corresponding to a relaxation time of 201800 s. T_v is determined as the temperature at which the Arrhenius dependence reported in **Figure 5.11** reaches this value and is equal to 78°C. The T_v and activation energy of polyBH-A are similar to those of a disulphide bond-enabled epoxy vitrimer which has a T_v of 75°C and dynamic bond exchange activation energy of 126 kJ/mol [15,25] as well as another set of disulphide bond-based epoxy vitrimers having topological transition temperatures of 85.7°C and 141.1°C and activation energies of 128.9 kJ/mol and 165.6 kJ/mol, respectively [20]. Like other metathesis vitrimers, T_v of polyBH-A is below its T_g of 155°C, meaning a high bond exchange potential is frozen in the material between T_v and T_g . Upon reaching the glass transition temperature, fast dynamic bond exchange is triggered, enabling reprocessing to be carried out.

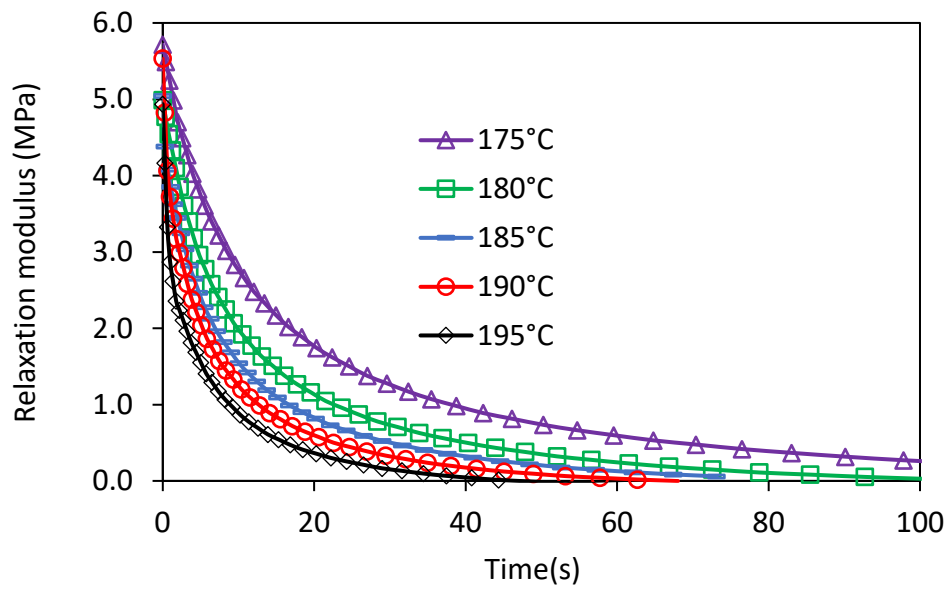


Figure 5.9. Stress relaxation curves of polyBH-A.

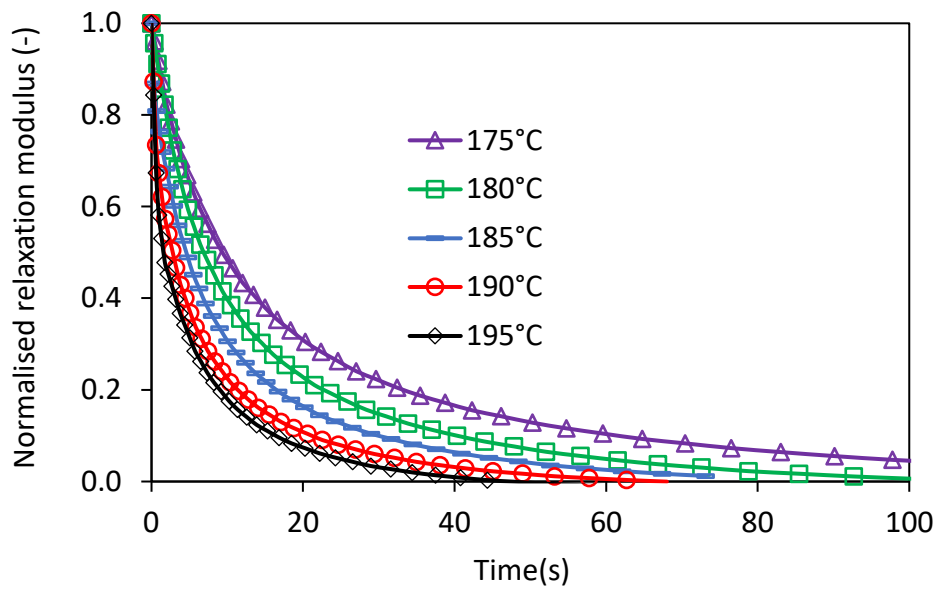


Figure 5.10. Normalised stress relaxation curves of polyBH-A.

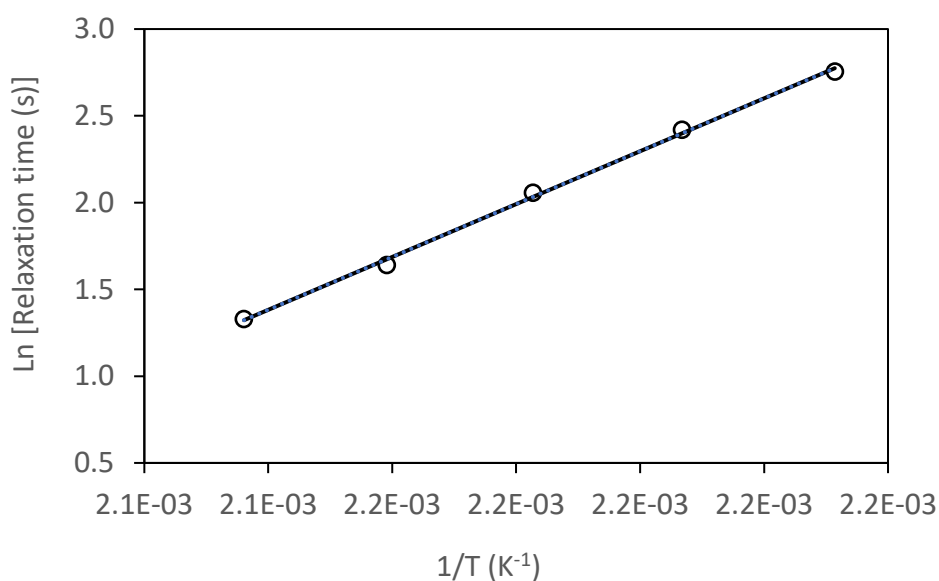


Figure 5.11. Arrhenius temperature dependence of relaxation time.

5.6 Demonstration of self-healing

The surface profiles of scratched polyBH-A measured before and after healing at 190°C for 30 minutes – as described in subsection 3.4.1 – are shown in **Figure 5.12**. The scratch has an approximate width of about 100 μm and a depth of about 25 μm . Its lips have a height of 30 – 40 μm and a base of about 70 μm . The approximate cross-sectional areas affected by the scratch are reported in **Table 5.2**. The scratch is almost fully recovered after the healing. The overall recovery of the scratch is about 88%, indicating very effective healing, within timelines and temperatures compatible with composite manufacturing strategies.

Table 5.2. Surface areas affected by scratching before and after healing polyBH-A.

	Unhealed	Healed	% Recovery
Lips (μm^2)	2694	213	92.1
Valley (μm^2)	2542	435	82.9
Overall (μm^2)	5236	648	87.6

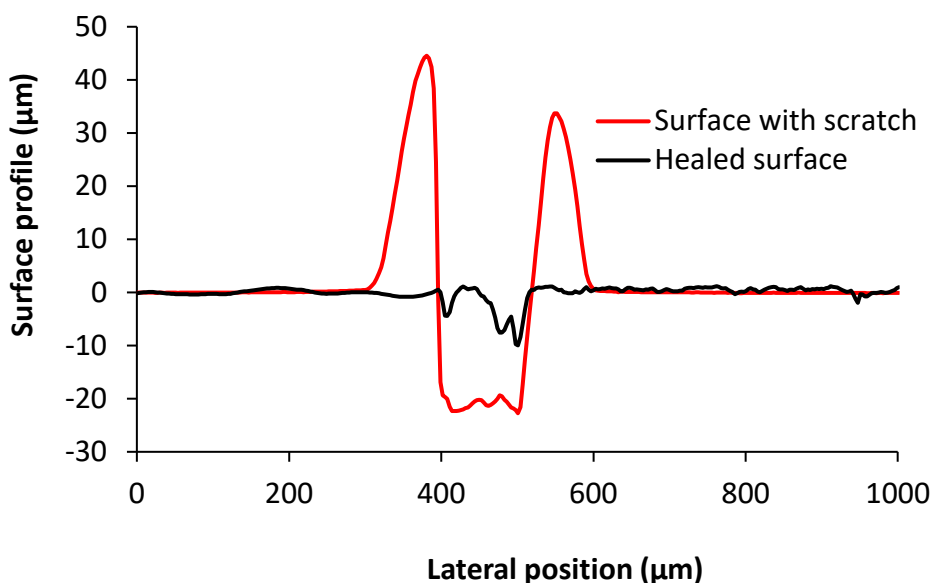


Figure 5.12. Surface profiles of unhealed and healed polyBH-A specimen.

5.7 Concluding remarks

The benzoxazine system reported in this work, polyBH-A, is the second benzoxazine vitrimer to be successfully synthesised by a cost-effective solventless one-pot method involving Mannich condensation, with the advantage of being the first high-temperature benzoxazine vitrimer formulated using this strategy. The PolyBH-A glass transition temperature and glassy modulus are 155°C and 3.6 GPa, respectively. The system features a high fire retardancy as indicated by an *LOI* of 40.5%, relatively high thermal stability with $T_{d5\%}$ of 293°C, high environmental resistance, represented by equilibrium water uptake of only 1.4% around its topology freezing transition temperature, and solvent resistance. PolyBH-A has a T_v of 78°C, which is below its T_g , meaning that a fast reversible bond exchange occurs with the onset of T_g . Thus, polyBH-A can be reprocessed at 190°C, following a fast stress relaxation enabled by reversible disulphide bond exchanges. The properties of polyBH-A reported in this work position it as a functional polymer for a broad spectrum of functionalities, such as self-healing, high-temperature, fire retardancy, environmentally resistant applications for aerospace, corresponding well to the future requirements for matrix system of

sustainable composites for the aerospace, marine and energy sectors. Comparing the characteristics of polyBH-A with DGEBA/4-APDS epoxy vitrimer in terms of healability, environmental and solvent resistance, storage modulus, and fire retardancy, polyBH-A stands out as a preferable material with attractive properties, surpassing the reported properties of known disulphide bond-based epoxy vitrimers.

Chapter Six

6 Cure kinetics, glass transition evolution and chemorheology of BH-A

6.1 Introduction

This chapter presents the cure kinetics, glass transition advancement and chemorheology of BH-A, providing information to guide the manufacturing of BH-A fibre composites. The cure kinetics is modelled by the Karkanas equation as explained in section 3.5. Like the chemorheological modelling of DGEBA/4-APDS epoxy vitrimer presented in chapter 4, the chemoviscosity of BH-A utilises the low degrees of cure inverse temperature exponential dependence of viscosity. The glass transition temperature development of BH-A is modelled with the Di Benedetto equation.

6.2 Cure kinetics

The dynamic and isothermal reaction rate curves of BH-A are illustrated in **Figures 6.1.** and **6.2**, respectively. All dynamic and isothermal DSC experiments, except the 150°C test, result in full cure of the material. The total heat of the reaction of the BH-A system is 231 ± 17 J/g, corresponding only to the enthalpy of the ring-opening polymerisation of the benzoxazine, as the energy contribution from disulphide bond exchange during crosslinking has a zero net effect on the kinetics. In dynamic data, a peak in reaction rate is observed at an intermediate conversion during the cure, attributed to the combined effects of temperature ramp and progression of the reaction. At the beginning of the reaction, reaction rate increases as a function of increasing temperature, due to enhanced internal energy. The decline in the concentration of the reactants leads to a reduced frequency of molecular collisions. Therefore, the reaction rate increases with temperature until it reaches a maximum at an intermediate conversion point where the decline in reactant concentration dominates the kinetics. Increasing the heating rate shifts the position of the reaction peak to the right of the

thermogram, with the reaction peak temperature increasing from 169°C at 2.5°C/min to 191°C at 10°C/min, due to the shorter exposure to a specific temperature range with increasing heating rate. Similarly, the maximum rate increases with increasing rate from $1.2 \times 10^{-3} \text{ s}^{-1}$ at 2.5°C/min to $5.3 \times 10^{-3} \text{ s}^{-1}$ at 10°C/min, due to the occurrence of maxima at higher temperatures and the Arrhenius temperature dependence of the rate constant.

The autocatalytic character of BH-A is confirmed from the peak values of the reaction rate curves for isothermal experiments reported in **Figure 6.2** observed at intermediate conversions. The duration of the isothermal reaction peaks decreases at higher temperatures, whilst the initial reaction rate has a finite value that increases with temperature. Maximum rates under isothermal conditions range from $3.8 \times 10^{-4} \text{ s}^{-1}$ at 150°C to $3.5 \times 10^{-3} \text{ s}^{-1}$ at 190°C, with the increasing trend attributed to the Arrhenius temperature dependence of the rate constant. As with the epoxy system presented in chapter four, the calculation of the initial degree of cure for the isothermal experiments, reported in **Table 6.1**, was performed using the knowledge of the evolution of the cure from the corresponding dynamic test at 10°C/min. The isothermal cures at 180 and 190°C start from degrees of cure of 29 % and 52 %, respectively; prior to attaining these degrees of cure, the reaction has proceeded past the peak rate during the dynamic ramp, thus eclipsing the manifestation of the autocatalytic character as a maximisation of reaction speed at intermediate times, as observed at lower temperatures.

Table 6.1. Initial degree of cure of isothermal experiments reported in Figure 6.2; isothermal temperature reached at a rate of 10°C/min.

Isothermal temperature (°C)	150	160	170	180	190
Initial degree of cure (-)	0.03	0.05	0.08	0.29	0.52

The superposition of the dynamic data onto the isothermal data is illustrated in **Figure 6.3**, confirming no path dependence of the system. The dynamic results at the corresponding temperatures are in close agreement with the isothermal

curves over the whole range. The average absolute difference between dynamic and isothermal rate data is $1.6 \times 10^{-4} \text{ s}^{-1}$, whilst the average relative difference is 16.7%. This result confirms the validity of the assumption of unique dependence on degree of cure and temperature and allows application of a semi-empirical model to represent the kinetics of BH-A cure by expressing reaction rate as a function of degree of cure and temperature. It also validates the assumption that the enthalpy measured by DSC provides a quantitative metric of the degree of conversion that is uniquely mapped to the state variables of the reaction. Based on these observations and a suspicion of a secondary mechanism at the later stages of slow dynamic cures, Karkanis equation with diffusion term, Eq.3.11, was selected to improve accuracy at the later stages of the reaction.

$$\frac{d\alpha}{dt} = \frac{A_1 e^{-E_1/RT} (1 - \alpha)^{n_1} + A_2 e^{-E_2/RT} \alpha^m (1 - \alpha)^{n_2}}{1 + e^{C[\alpha - (\alpha_{c0} + \alpha_{cT} T)]}} \quad (6.1)$$

expressing autocatalytic behaviour with diffusion limitations [181]. The fitting involving the ten parameters of Eq.6.1 was carried out using the procedure described in section 3.5 to minimise the error expressed by Eq.3.12. The cure kinetics parameters are reported in **Table 6.2**.

Table 6.2. BH-A kinetics parameters for the model represented by Eq.6.1

Table 6.3. BH-A kinetics parameters for the model represented by Eq.6.1				
$A_1(1/s)$	$E_1(J/mol)$	n_1	m	C
$1.21 \cdot 10^{14}$	$1.45 \cdot 10^5$	1.32	1.81	6.21
$A_2(1/s)$	$E_2(J/mol)$	n_2	α_{c0}	$\alpha_{cT}(1/K)$
$5.48 \cdot 10^{10}$	$1.03 \cdot 10^5$	4.63	1.34	$1.44 \cdot 10^2$

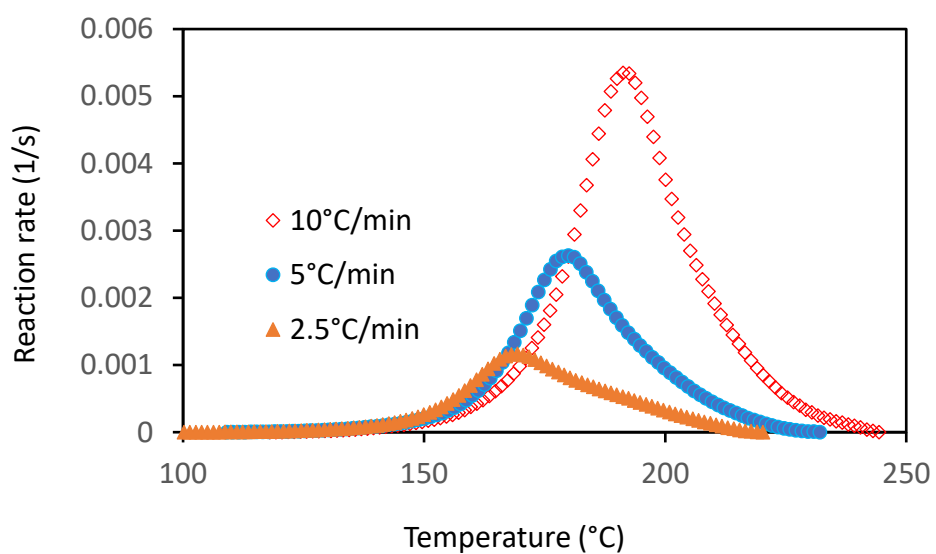


Figure 6.1. Reaction rate versus temperature in dynamic DSC experiments.

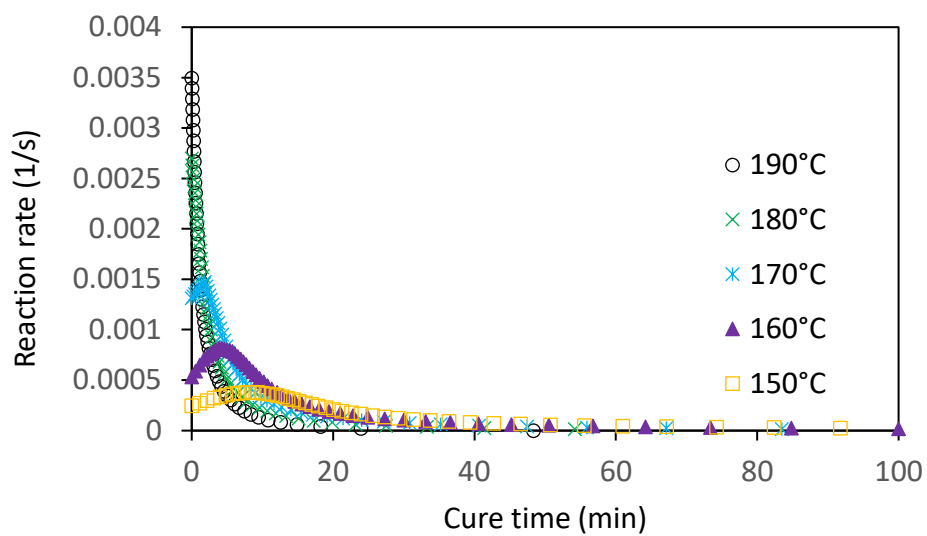


Figure 6.2. Reaction rate versus cure time in isothermal DSC experiments.

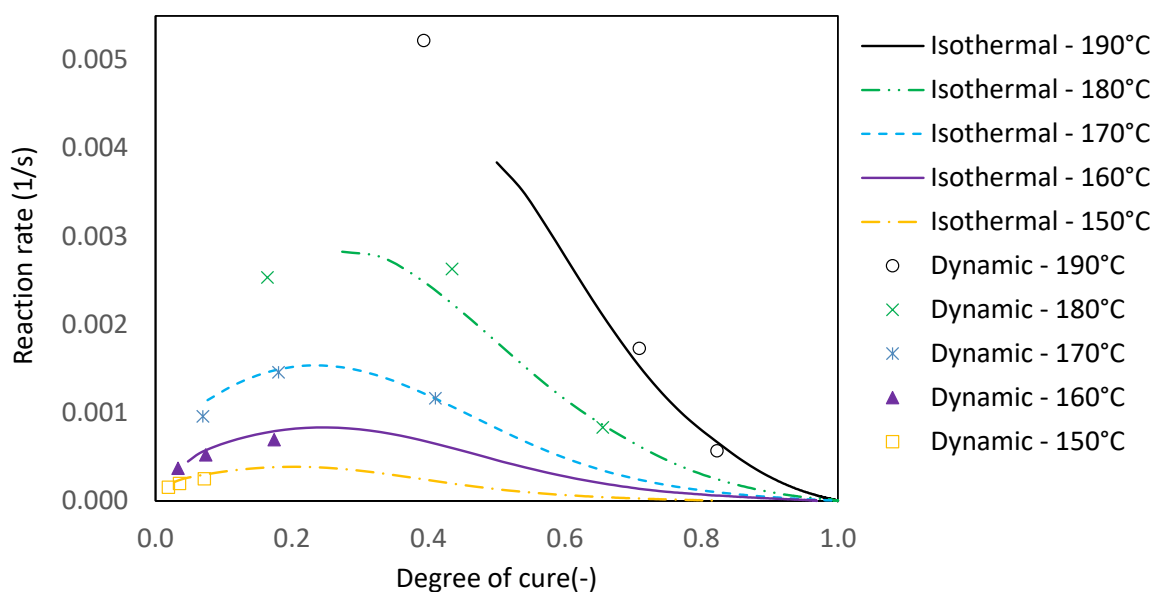


Figure 6.3. Superposition of dynamic and isothermal reaction rate versus degree of cure data for BH-A vitrimer.

Figures 6.4 and **6.5** provide comparisons of experimental and model data for dynamic and isothermal experiments. Both dynamic and isothermal data are reproduced successfully by the cure kinetics model. The model fitting overestimates the reaction rate at the beginning of high dynamic heating rates and underestimates it at higher temperatures to compensate for the initial overestimation. This is consistent with isothermal reaction rates in which the model estimates higher reaction rates at the beginning of the isothermal segments of high temperature experiments (180°C and 190°C) but adjusts closely to the experimental values as the reaction nears completion. This is in agreement with the superposition data presented in **Figure 6.3**, in which isothermal reaction rates at the highest temperatures of 180°C and 190°C tend to be lower than the corresponding dynamic data points. The model compromises between these two by slightly overestimating the isothermal reaction rates whilst underestimating the dynamic reaction rates within this temperature-degree of cure space. The model tracks the rest of the experimental points closely, including the partial completion of cure, at about 0.82, in the lowest isothermal cure at 150°C. **Table 6.3** summarises the average absolute and relative error in reaction rate for each experimental condition. The absolute error ranges from 6.2

$\times 10^{-6} \text{ s}^{-1}$ to $1.9 \times 10^{-4} \text{ s}^{-1}$, which in terms of relative error translate to 5.0 - 27.4%. The average absolute error over all conditions is $4.2 \times 10^{-5} \text{ s}^{-1}$ and the relative error 14.1 %. These errors are close to the superposition average absolute and relative differences of $1.6 \times 10^{-4} \text{ s}^{-1}$ and 16.7 % respectively, indicating good performance of the model, as its accuracy is similar to the consistency of the dataset.

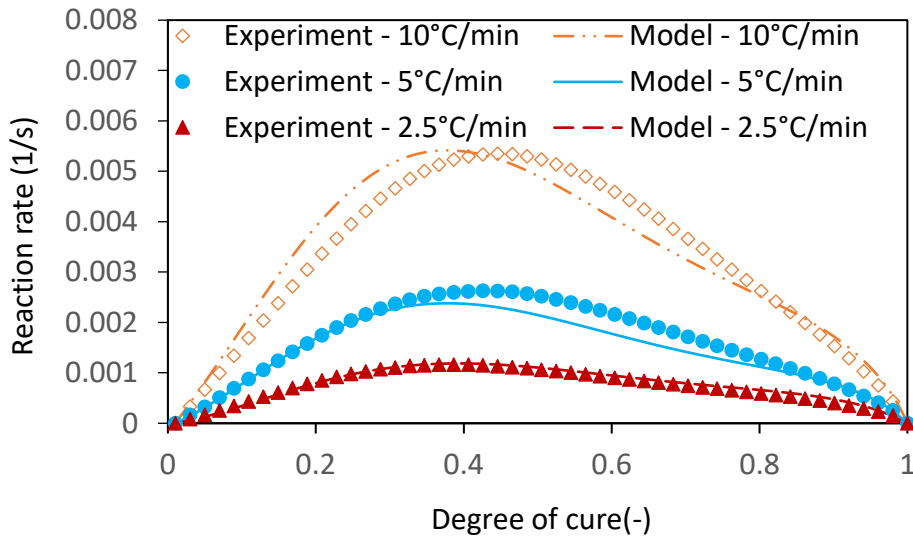


Figure 6.4. Comparison of cure kinetics model and experiment reaction rate versus degree of cure in dynamic experiments.

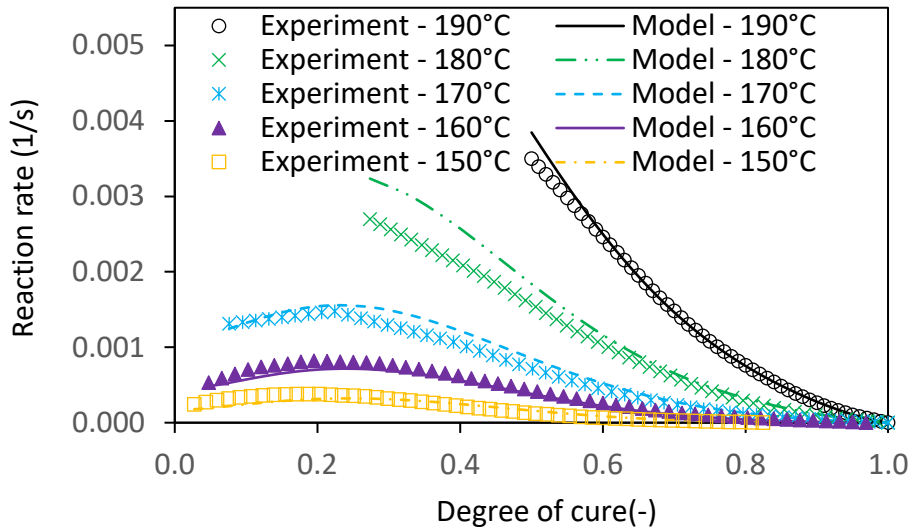


Figure 6.5. Comparison of cure kinetics model and experiment reaction rate versus degree of cure in isothermal experiments.

Table 6.4. Average absolute error and average relative error in reaction rate and degree of cure of the cure kinetics model of BH-A. Relative error computed over experimental points exceeding reaction rate of 2.5×10^{-4} .

Experiment	Reaction rate		Degree of cure (-)	
	Absolute error	Relative error	Absolute error	Relative error
2.5°C/min	$2.4 \cdot 10^{-5} \text{ s}^{-1}$	13.3 %	0.012	10.7 %
5°C/min	$6.8 \cdot 10^{-5} \text{ s}^{-1}$	11.2 %	0.009	5.7 %
10°C/min	$1.9 \cdot 10^{-4} \text{ s}^{-1}$	18.0 %	0.010	5.7 %
150°C	$1.2 \cdot 10^{-5} \text{ s}^{-1}$	22.3 %	0.031	5.2 %
160°C	$1.9 \cdot 10^{-5} \text{ s}^{-1}$	27.4 %	0.041	5.0 %
170°C	$6.2 \cdot 10^{-6} \text{ s}^{-1}$	5.0 %	0.010	1.2 %
180°C	$9.2 \cdot 10^{-6} \text{ s}^{-1}$	10.8 %	0.009	1.1 %
190°C	$1.3 \cdot 10^{-5} \text{ s}^{-1}$	4.8 %	0.003	0.3 %

The validity of the cure kinetics model is tested further by using it to predict the degree of cure evolution under isothermal and dynamic cure conditions, achieved by integrating model degree of cure using reaction rate computed from Eq.6.1 for the thermal profile of each experiment and comparing the model degree of cure with the corresponding experimental degree of cure. **Figures 6.6 and 6.7** illustrate these comparisons for dynamic and isothermal conditions, respectively.

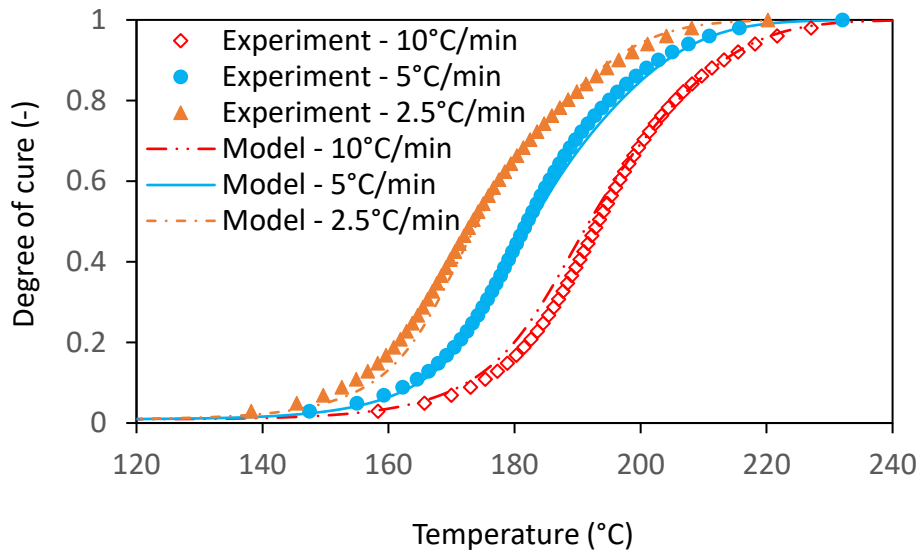


Figure 6.6. Cure kinetics modelling of BH-A: Comparison of model and experiment degree of cure evolution in dynamic conditions.

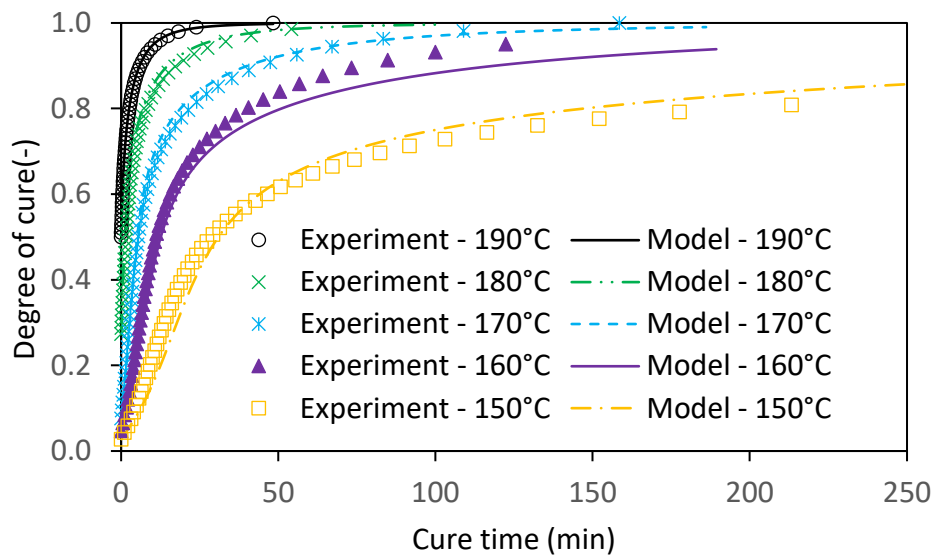


Figure 6.7. Cure kinetics modelling of BH-A: Comparison of model and experiment degree of cure evolution in isothermal conditions.

The results show that the model reproduces closely the evolution of degree of cure in DSC experiments. The model validity is reinforced by the fact that the fitting of the kinetics model expressed by Eq.6.1 was carried out on the reaction rate data. The absolute error in degree of cure ranges from 0.003 to 0.041 with the corresponding relative error in the 0.3 % to 10.7 % range. The overall average absolute error in degree of cure across all experiments is 0.016, corresponding to an overall relative error of 4.4 %. Consequently, the model has a good level of accuracy in predicting both the instantaneous reaction rate and cumulative progress of cure, making it appropriate for use in the development of manufacturing process for the BH-A vitrimer system.

6.3 Glass transition temperature evolution

The experimental measurements of T_g for different states of cure of the BH-A vitrimer are illustrated in **Figure 6.8**, with experiments corresponding to 12 dynamic thermal histories for attaining the partial cure state. The values of T_g follow a single curve reinforcing the conclusion that material state is defined by the degree of cure reached in the study of cure kinetics. The T_g varies over a wide temperature range from a monomer T_g of 22°C to an ultimate T_g of 155.2°C for the fully cured polymer. The value of 22°C for the uncured material T_g is indicative of a high viscosity at ambient or slightly elevated temperatures, pointing to manufacturing based on a film or prepreg route rather than liquid moulding. The high ultimate T_g of 155.2°C is characteristic of polybenzoxazines and renders the material applicable to high-temperature applications. The evolution of the glass transition temperature is modelled using the Di Benedetto model (Eq.4.2). **Table 6.4** reports the values of the three model parameters obtained by fitting the Di Benedetto model following the procedure described in section 3.5. The T_g evolution curve is illustrated in **Figure 6.8** with average model error of 0.8°C. The model reproduces experimental values closely with a concave curve corresponding to λ value which is greater than 1.

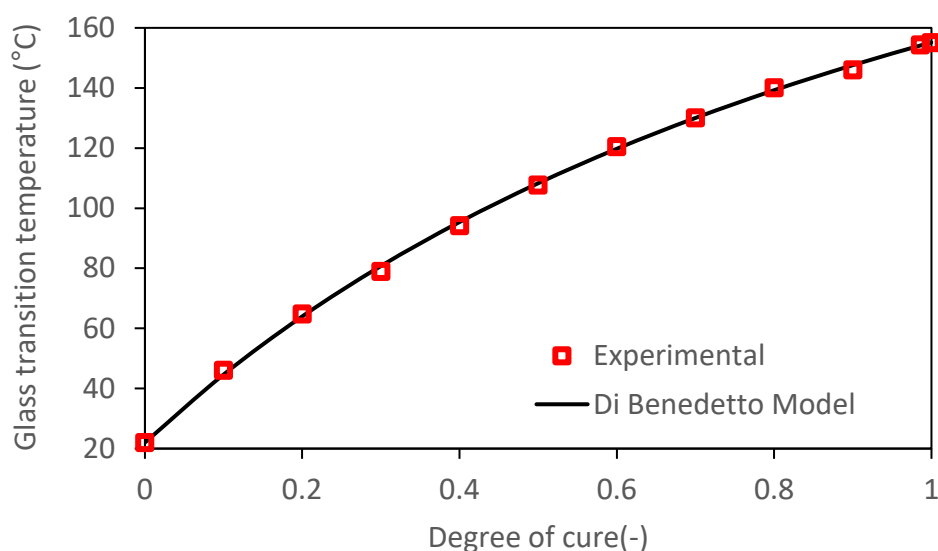


Figure 6.8. Development of the glass transition temperature of the BH-A vitrimer as a function of the degree of cure.

Table 6.5. BH-A Di Benedetto T_g development model parameters and error.

$T_{g\infty}$ (°C)	T_{go} (°C)	λ (-)	Average absolute error (°C)
155.2	22.0	1.84	0.8

6.4 Viscosity development

The evolution of viscosity of BH-A is illustrated in **Figure 6.9** up to viscosities of 10 Pas. Due to increased molecular mobility with increasing temperature, the initial viscosity decreases with increasing temperature. The initial viscosity at 100°C is 1.12 Pas, whereas at 130°C the initial viscosity is 145 mPas. The increase of viscosity with time is exponential, whilst the time spent at low viscosity is a decreasing function of temperature due to the acceleration of cross-linking with increasing temperature. In 100°C, 110°C and 120°C the viscosity is greater than what is typically required for liquid moulding (10-200 mPas). The material viscosity at 130°C is initially below 200 mPas, but exceeds this limit within 2

minutes at temperature, essentially making processing of this system using liquid composite moulding impracticable. Thus, other manufacturing technologies such as prepregging and resin film infusion (RFI) are recommended.

Similarly to the epoxy system in chapter 4, the chemorheological behaviour BH-A is simulated using:

$$\frac{d\eta}{dt} = Ae^{-\frac{E}{RT}} \eta \left[\ln\eta + D \left(\frac{1}{T_r} - \frac{1}{T} \right) - \ln\gamma \right]^l - \frac{D\eta}{T^2} \frac{dT}{dt} \quad (6.2)$$

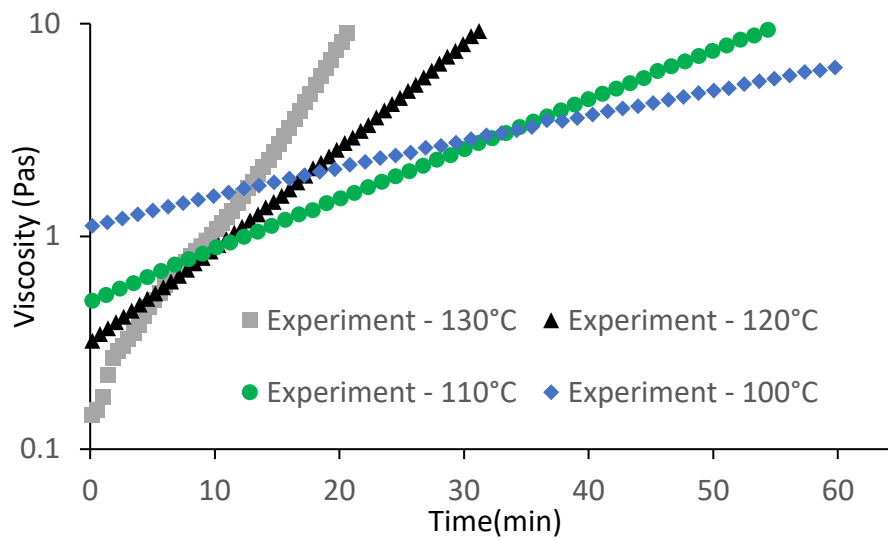


Figure 6.9. Viscosity evolution of the BH-A vitrimer as a function of time at different isothermal infusion temperatures.

The results of the fitting are presented in **Figure 6.10**, with model parameters summarised in **Table 6.5**. The fitting, which was obtained by minimising the error defined by the sum of absolute logarithm of model-to-experimental viscosity ratios over all datapoints of the experiments using the Generalised Reduced Gradient Nonlinear Optimisation method implemented in Microsoft Excel Solver, follows closely the experimental data for all curves, with deviations observed only for the 110°C experiment, for which the model overestimates viscosity at the later stages of the process. The error of the model is summarised in **Table 6.6** for the different experiments. The average absolute error is in the range of 14-94 mPas,

representing relative error in the range of 3.4-24.4 %. The average absolute error over all tests is 38 mPas whilst the average relative error 9.4 %.

Table 6.6. BH-A viscosity development parameters for the model represented by Eq.6.2. Fitting performed for viscosity levels up to 10,000 mPas.

T_r (K)	η_r^o (mPas)	A (s ⁻¹)	E (J mol ⁻¹)	l (-)	γ (mPas)	D (K ⁻¹)
373.15	1198.96	386,061	74,750.97	1.43	0.015	8,900

Table 6.7. Average absolute relative error of the viscosity model of BH-A

Experiment	Absolute error	Relative error
100°C	18.6 mPas	4.2 %
110°C	24.7 mPas	5.6 %
120°C	94.0 mPas	24.4 %
130°C	14.9 mPas	3.4 %

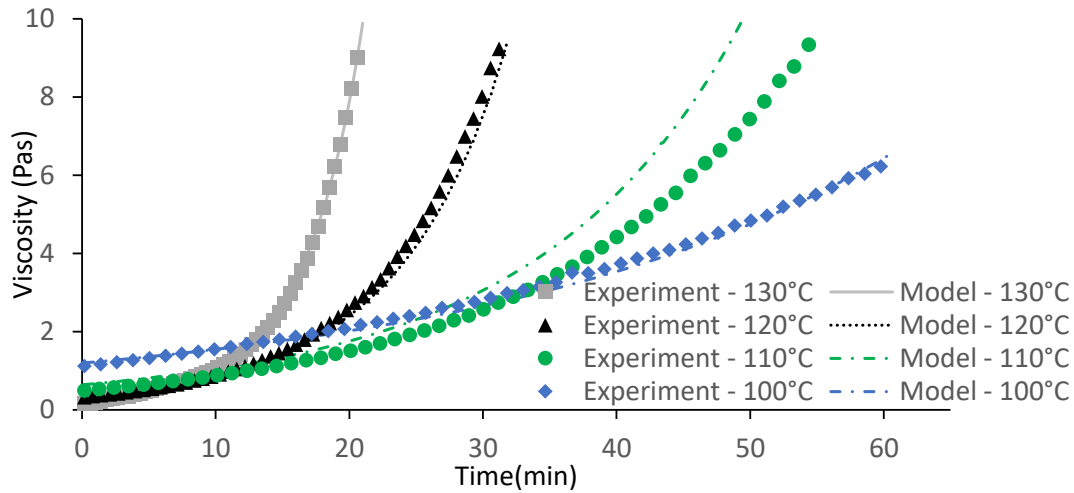


Figure 6.10. Viscosity development model of the BH-A system: Comparison of modelling and experimental results.

6.5 Concluding remarks

The cure kinetics results presented in this chapter shows that the polymerisation kinetics of BH-A is autocatalytic, adequately simulated by Karkanas equation with logistic function to account for the transition of the kinetics from a chemically controlled process to one controlled by diffusion. The glass transition temperature evolution in BH-A follows the Di Benedetto equation with a concave behaviour. The chemorheological model of BH-A reported herein represents the evolution of chemoviscosity in the resin as a function of time and temperature which guides the decision regarding BH-A composites manufacturing. Liquid moulding of pure BH-A is not practically feasible. This is because the material has typical infusion viscosities (10-200 mPas) for about 2 minutes. BH-A is, therefore, amenable to alternative manufacturing technologies such as prepregging and resin film infusion, rather than RTM or VARTM. This outcome informs the choice of resin film infusion which was used to manufacture carbon fibre-BH-A composite as described in section 3.3.2.

Chapter Seven

7 Delamination and self-healing of DGEBA/4-APDS carbon fibre composite material

7.1 Introduction

In this chapter, the results of cyclic mode I DCB delamination experiments carried out with DGEBA/4-APDS epoxy vitrimer carbon fibre composite as described in subsection 3.4.5.1 are presented. The average toughness of the pristine material is compared with that of the undamaged part of the healed material. Also, toughness recovery is evaluated on a specimen-by-specimen basis. The average toughness of the healed material is compared with the average toughness of the pristine material. The healing efficiency of the first and second healing cycles is assessed, and the average efficiency is modelled using a Kohlrausch–Williams–Watts (KWW) exponential decay as a function of crack opening before healing.

7.2 Mode 1 DCB experimental results and analysis

The force-displacement curves for the three delamination cycles of the three composite specimens are shown in **Figures 7.1** through **7.3**. Each of these figures reveals two different reproducible scenarios for the pristine and healed materials. In the pristine material, the trajectory of delamination is characterised by two regions – a region of no delamination due to linear response of the material and another region of crack initiation and propagation due to attainment of critical strain energy release rate. In the case of healed materials, there are four distinct regions in the delamination evolution: the first region of no delamination represented by linear response, indicative of toughness recovery up to the point marked by the vertical red line in **Figures 7.1** through **7.3**, a second region of early delamination – between the red and green vertical lines, where the strain energy release rate is insufficient for the material to resist crack due to incomplete toughness recovery, a third region of crack arrest due to healing accompanied by partial crack propagation, which is bordered by red and black vertical lines and a

fourth region of full crack propagation as the material ultimate strain energy release rate is overcome, corresponding to the parts of the curves after the black vertical lines.

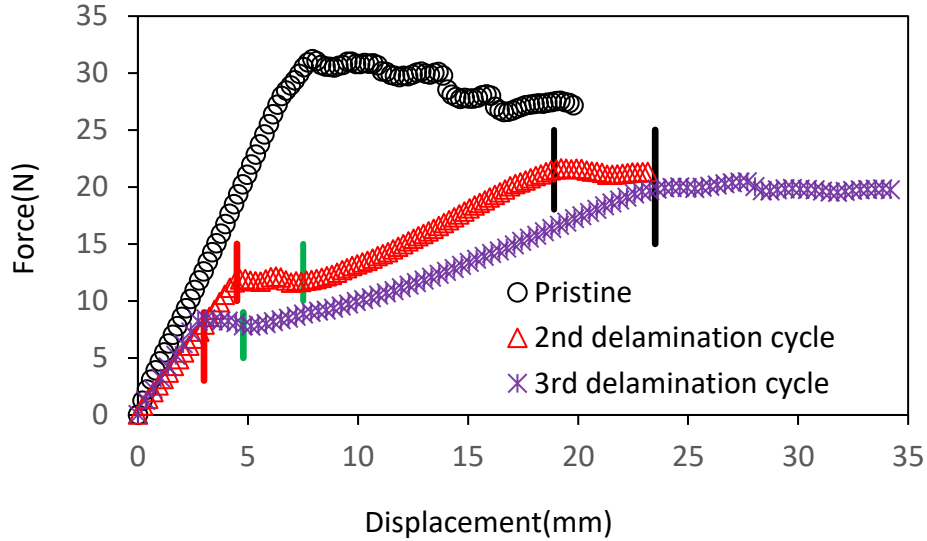


Figure 7.1. Force-displacement curves of specimen 1.

The resistance curves (R-curves) of the delamination of the pristine composites are presented in **Figure 7.4**. The G_{IC} of the material, which is the measure of toughness of the matrix, starts from a lower value after crack initiation and increases due to fibre bridging leading to the crack front encountering fibres of different orientation approaching closer to the through thickness direction. The average G_{IC} of the carbon fibre-DGEBA/4-APDS composite is $347 \pm 59 \text{ J/m}^2$ with a coefficient of variation of 17 %. The error bars in **Figure 7.4** represent the associated standard deviation of 59 J/m^2 . The results illustrated in **Figure 7.4** indicate that all specimens follow closely the same behaviour, represented by the average R-curve.

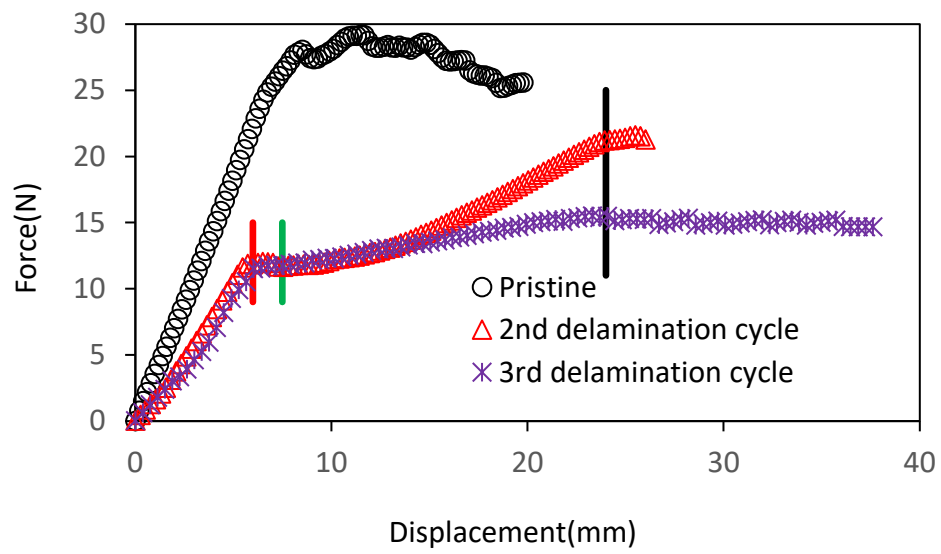


Figure 7.2. Force-displacement curves of specimen 2.

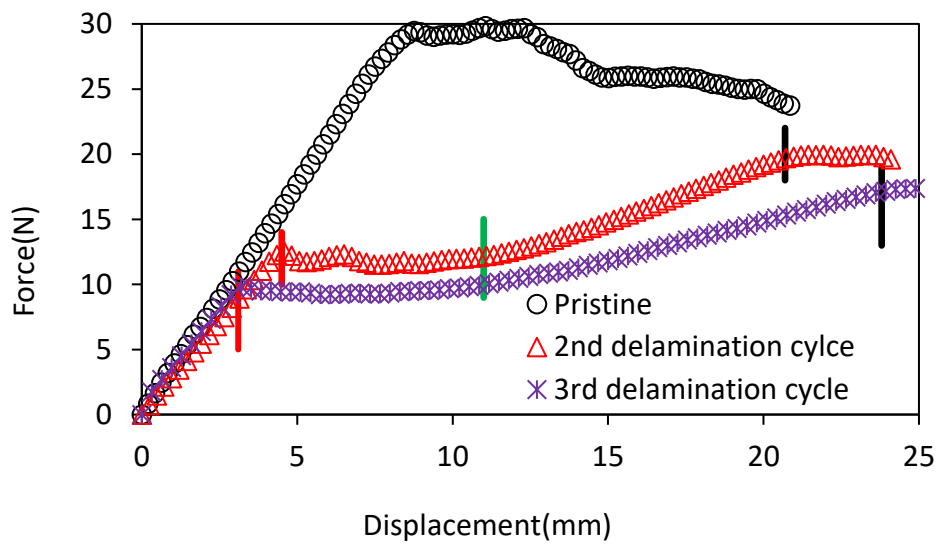


Figure 7.3. Force-displacement curves of specimen 3.

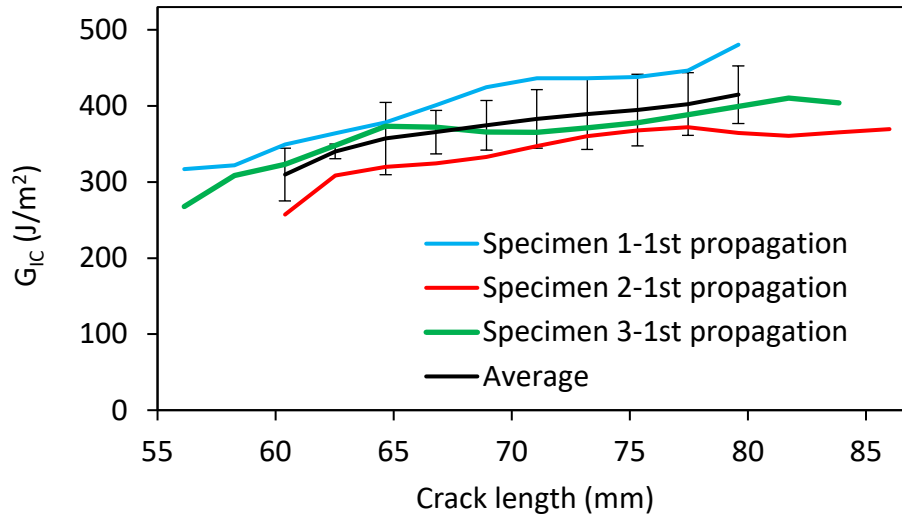


Figure 7.4. R-curves of pristine material.

The R-curves of the second delamination cycle are presented in **Figure 7.5** in which the G_{IC} has an initial value of from about 20 % of pristine G_{IC} at initiation and grows up to 100 % at the position of the previous crack tip. The low toughness recovery region corresponds to early delamination between the red and green vertical lines described previously in **Figures 7.1** through **7.3**. Bridging effects during the first delamination mean that healing of the delaminated material is characterised by regions of resin-to-resin contact that are dominant near the previous crack tip due to good alignment of fibres in this zone, regions of resin-to-fibre contact, corresponding to moderate fibre alignment further away from the previous crack tip and regions of fibre-to-fibre contact due to total fibre misalignment mostly near the crack initiation zone. In contrast, in the pristine materials delamination occurs mostly through resin-to-resin interfaces. The healing in any region depends on the level of resin-to-resin contact in that region. This explains why the healing is more efficient in the regions closer to the crack tip and less efficient further away from it. **Figure 7.5** presents the optical micrographs of a delaminated specimen showing the region healed once, the region healed twice and the unhealed region. The micrographs show evidence of fibre damage by fibre pullout. These contribute to increased bridging and fibre

misalignment, leading to different degrees of resin-to-resin contact for different regions of the material during healing. The greater the number of delamination and healing cycles a region of the material has been subjected to, the more the fibre misalignment and lower the resin-to-resin contact. Due to the pressure of the press, the fibres appear compressed without aligning properly. These factors result in partial toughness recovery observed in the healed material.

On average, the G_{IC} of the results shown in **Figure 7.6** has a value of 112 ± 29 J/m² in the 55-65 mm crack length range, corresponding to 32% average toughness recovery in the region of early delamination of **Figure 7.1** through **7.4**. This grows gradually to an average of 208 ± 65 J/m² in the 65-75 mm crack length, signifying 60% toughness recovery in the crack arrest and partial delamination region of **Figure 7.1** through **7.4**. On reaching the crack length range of 75-85 mm, which corresponds to the previous delamination crack tip, the material ultimate G_{IC} is reached, signifying full 100 % fracture toughness recovery of the material in this region. These results are presented in **Table 7.1** which compares the average G_{IC} of pristine specimens with that of various locations on the healed specimens which, for each cycle of delamination and healing, depicts the average toughness recovery efficiency of the four regions of **Figure 7.1** through **7.4**.

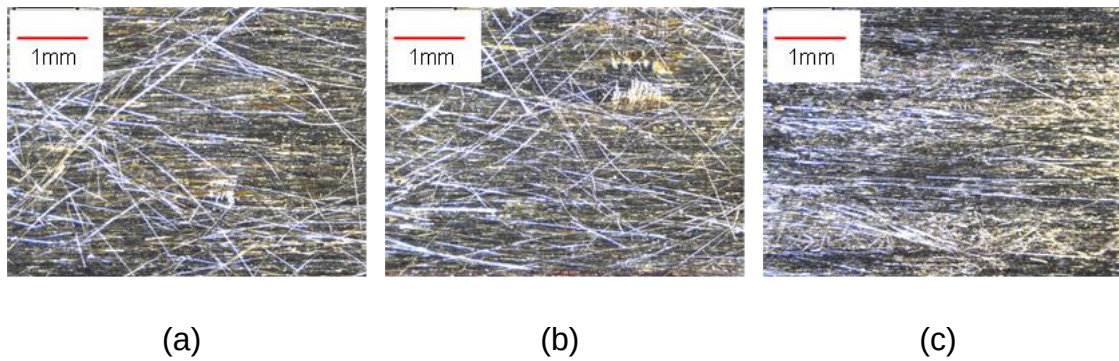


Figure 7.5. Micrographs of damaged DGEBA/4-APDS epoxy vitrimer composites. (a) Unhealed region of specimen. (b) Region of specimen healed once. (c) Region of specimen healed twice.

Table 7.1. Average G_{IC} and recovery after each delamination cycle

Region	1st healing		2nd healing	
	$G_{IC}(J/m^2)$	Recovery (-)	$G_{IC}(J/m^2)$	Recovery (-)
55-65 mm	112±29	0.32	66±20	0.19
65-75 mm	208±65	0.60	120±33	0.35
75-85 mm	332±67	0.96	248±91	0.71
85-95 mm	–	–	359±36	1.04
Pristine	347±59	–		–

To fully visualise the response and assess the reproducibility of the results, the G_{IC} is plotted as a function of shifted crack length with respect to the previous crack position before healing. This is illustrated in **Figure 7.7** and carried out by subtracting the maximum crack length attained in the delamination before healing from the crack lengths recorded in the delamination being analysed so that zero implies previous crack tip for all specimens and negative values represent healed regions. The G_{IC} was interpolated for the same crack position to allow a clearer visualisation and more accurate comparison of the results. Since zero signifies the beginning of fresh undamaged interface, all curves in **Figure 7.7** express full G_{IC} immediately before or upon reaching this position. Whilst the error bars in **Figure 7.7** represent the standard deviation, it is clear that all specimens follow closely a common curve, which is indicative of reproducibility of the behaviour.

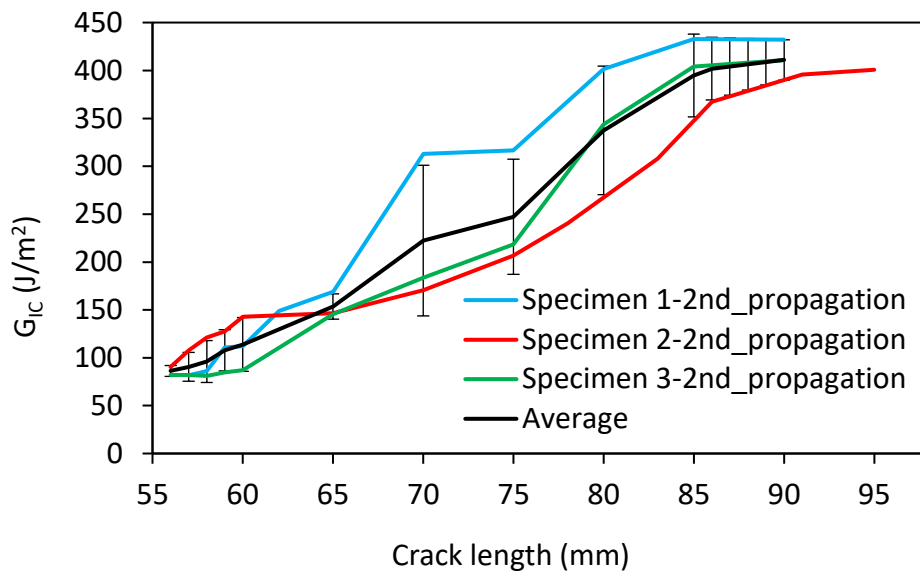


Figure 7.6. R-curves after first healing.

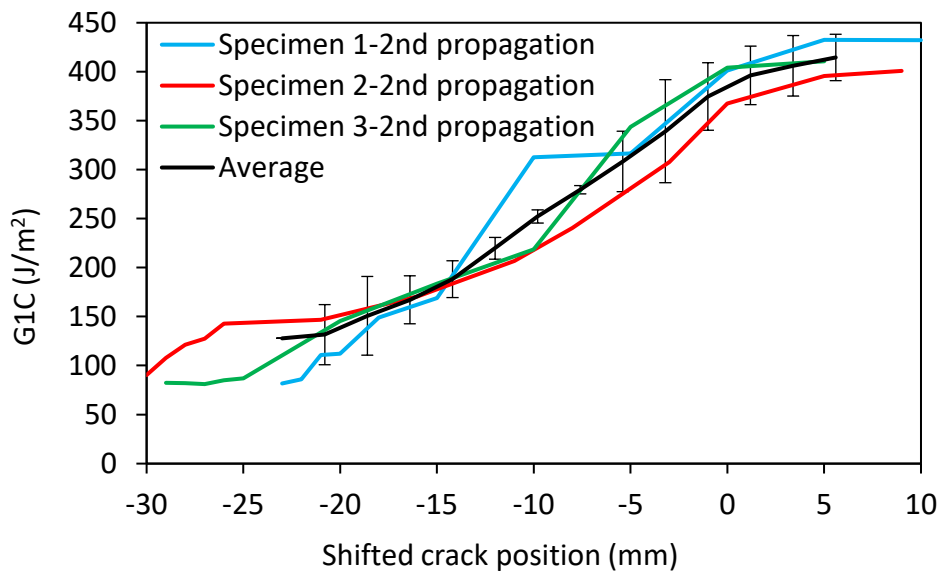


Figure 7.7. Normalised R-curves after first healing.

The result of the delamination after the second healing cycle is illustrated in the R-curves of **Figure 7.8** and shifted R-curves of **Figure 7.8**, in which the error bars represent to associated standard deviation. The recovery of fracture toughness associated with the second healing starts from an average G_{IC} of 66 ± 20 J/m² near

the crack initiation which translates to 19 % recovery in the 55-65 mm crack length range and gradually evolves up to 120 ± 33 in the 65-75 mm crack length, corresponding to 35 % recovery in this region of early crack arrest and partial delamination. The later stage of crack arrest and partial delamination features an average G_{IC} of 248 ± 91 , which represents 71 % fracture toughness recovery. As in the case of delamination after first healing, the material has its full G_{IC} near the crack tip, meaning 100% toughness recovery. The shifted R-curves of **Figure 7.9** allow a better visualisation of the healing result. In this figure, all specimens tend to show similar G_{IC} at the same relative crack position, with each specimen attaining G_{IC} up to 80 % of pristine G_{IC} about 8-10 mm away from the previous crack tip. The average curves in **Figures 7.7** and **7.9** are plotted on the same axes to allow comparison in **Figure 7.10**. It is observed that the curves in **Figure 7.10** are close, revealing a universal behaviour, independent of the number of healing cycles, whereby each average R-curve tracks closely a common trajectory, demonstrating the existence of a master curve for the recovery.

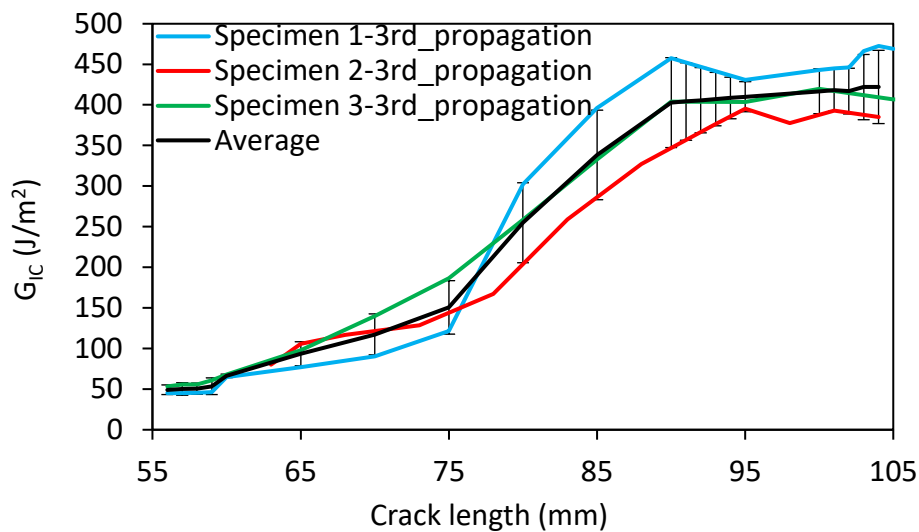


Figure 7.8. R-curves of specimens 1, 2 and 3 after second healing.

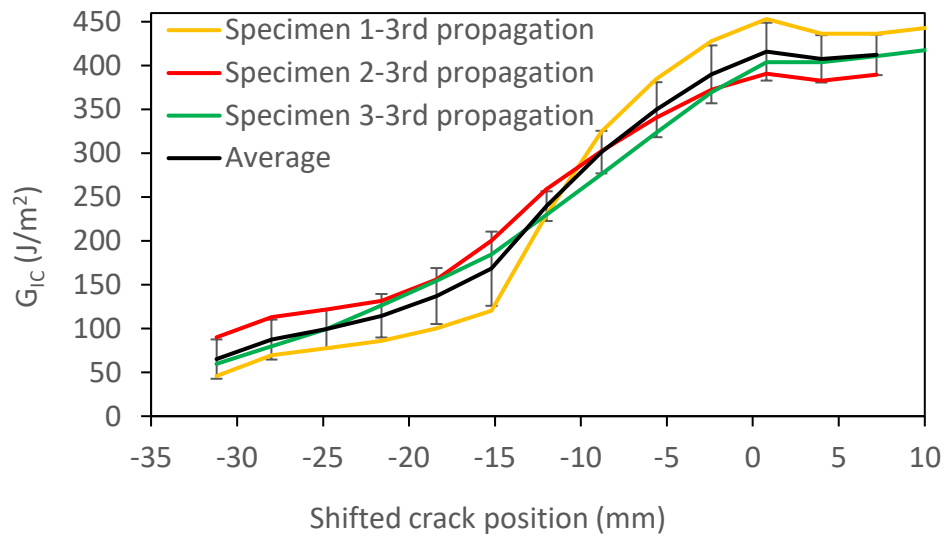


Figure 7.9. Normalised R-curves after second healing.

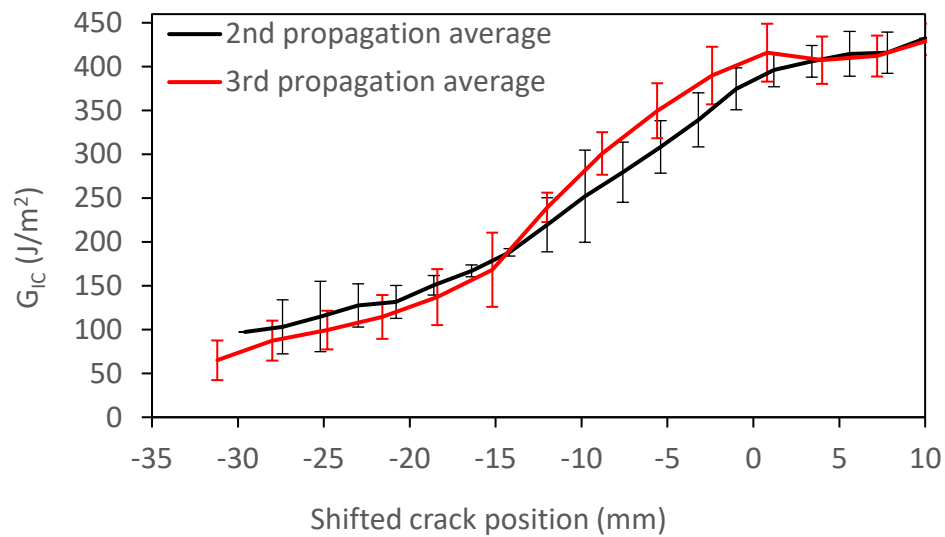


Figure 7.10. Comparison of shifted average R-curves of delamination after first and second healings cycles.

The self-healing of the disulphide-based epoxy/amine vitrimer composite can be achieved at a pressure of 50 bar used in this study. This pressure is half the pressure used in the case of a similar epoxy/amine vitrimer composite healing achieved at 100 bar [14]. Although 50 bar is too high for practical manufacturing applications, this result shows that this vitrimer composite system is healable at pressures lower than those previously reported in the literature.

The toughness recovery as a function of previous crack opening is presented in **Figures 7.11 and Figure 7.12** for first and second healing, respectively. The historical crack opening in the first and second delamination experiments are calculated using Eq.3.10 and used to express G_{IC} . In both cases, it is found that toughness recovery increases gradually from a level of about 15% when two surfaces of the material have been completely separated with an opening of 4.5 mm to 100% close to the point of fresh interface with historical opening of about 0.01 mm. The recovery of toughness is controlled by the maximum historical crack opening that occurred at a particular position along the interface. This dependence of toughness recovery shown in **Figures 7.11 and 7.12** is suggestive of an exponential decay. For clarity of the relationship between the first healing and second healing fracture toughness recovery responses of the system, the average recovery data are interpolated for eight datapoints as shown in **Figure 7.13** for the two healing cycles. **Figure 7.13** shows that in the delamination after first healing, the maximum historical crack opening of 3.2 mm starts with a higher recovery of 20% whilst the delamination after second healing which has a higher historical crack opening of 4.5 mm, with a corresponding lower recovery of 15%. The two healing curves are close, in agreement with the result of **Figure 7.10**, suggesting the existence of a master curve for the toughness recovery. Therefore, the number of healing cycles is inconsequential as toughness recovery follows the same behaviour. The dependence of healing efficiency on historical crack opening shown in this study is an important consideration for the future design of self-repairing composite structures [209]. Other factors that affect the healing efficiency of the composite include healing pressure, healing temperature and healing time. This study did not optimise these factors. Under optimal conditions of these factors, the effect of historical opening and crack length would be better understood.

Due to the observed exponential behaviour of toughness recovery in this system, the fracture toughness recovery result was modelled with KWW stretched exponential decay:

$$f(\delta) = (1 - c) \left[c + e^{-\left(\frac{\delta}{d}\right)^\beta} \right] \quad (7.1)$$

The stretching parameter, β in Eq.7.1 allows capturing the variations in the decay behaviour not accounted for by a simple exponential function where β is 1, whereas d , is the characteristic crack opening at which the toughness recovery amounts to $(1 - c)(c + \frac{1}{e})$. Minimising the relative error for this analysis yields a value of 0.066 for c and 1.16 mm for d . The model fitting is illustrated in **Figure 7.14**, comparing experimental and model results and has relative error of 1.5 %. The model parameters are reported in **Table 7.2**. This system is associated with a half-length of 0.77 mm, at which the model predicts toughness recovery is of 50 %.

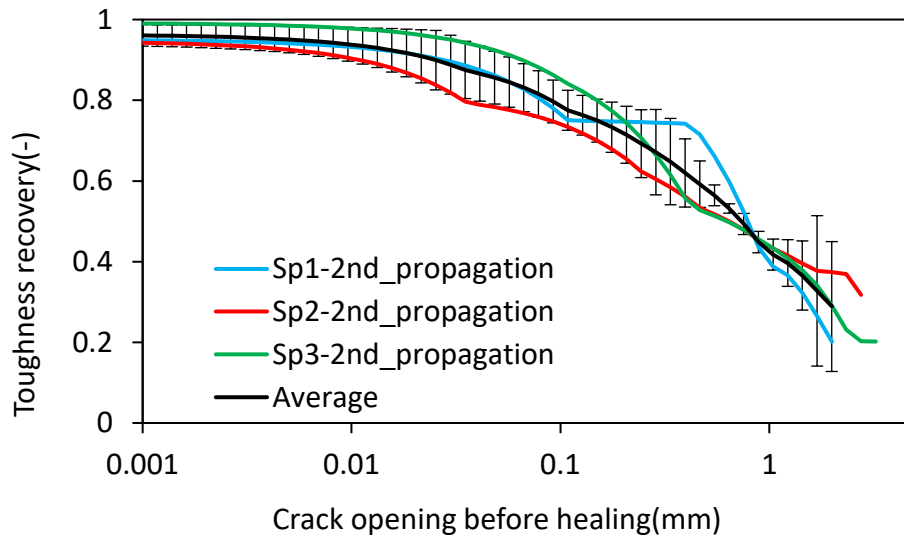


Figure 7.11. First healing recovery efficiency versus previous crack opening.

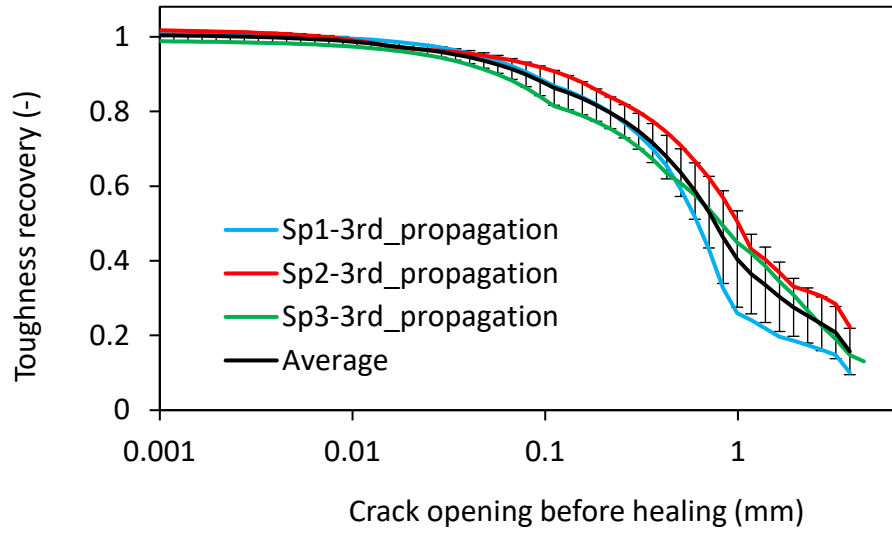


Figure 7.12. Second healing recovery efficiency versus previous crack opening.

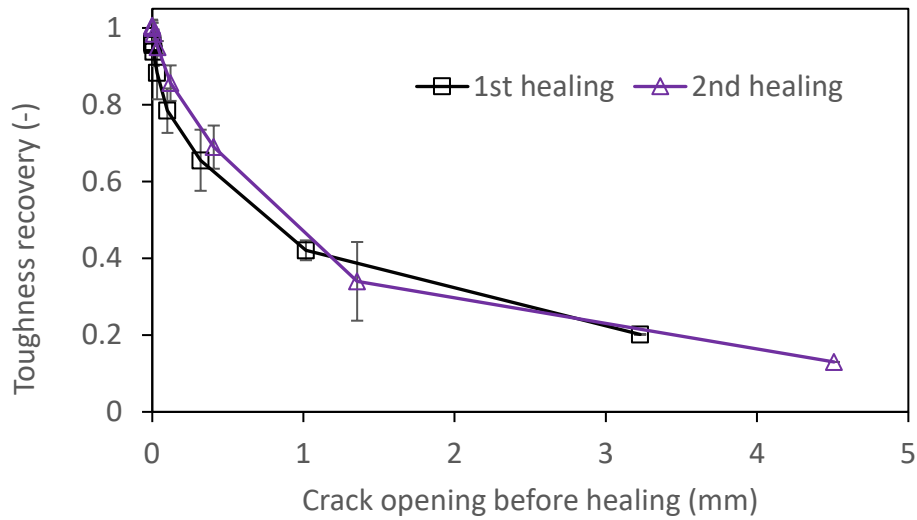


Figure 7.13. Average healing efficiency versus historical crack opening.

Table 7.2. Model parameters of G_{IC} recovery in DGEBA/4-APDS composite.

Parameter	Unit	Value
c	—	0.066
β	—	0.691
d	mm	1.16

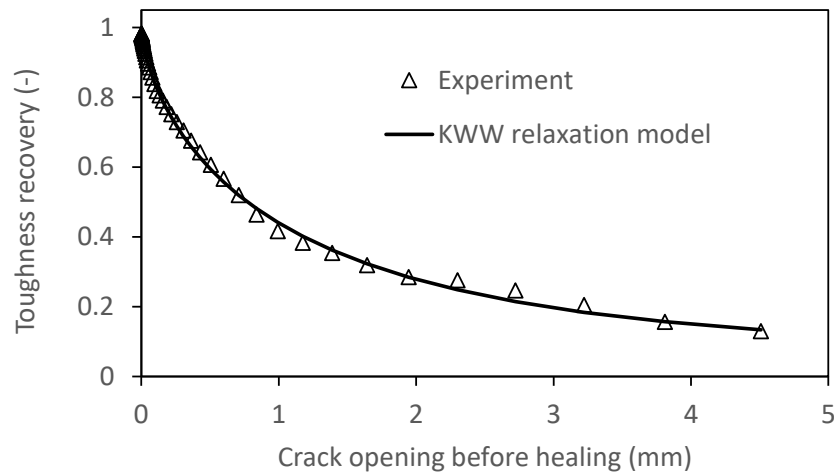


Figure 7.14. KWW relaxation modelling of healing efficiency as a function of previous crack opening in DGEBA/4-APDS epoxy vitrimer fibrous composite.

7.3 Concluding remarks

Prior to this study, the understanding was that if a composite specimen heals, it does so by attaining a certain degree of healing at every location in the material [206]. The results presented here show instead, the healing depends on the amount of crack opening in the material prior to healing. Thus, for effective healing of a composite structure, it is important that the crack must be small. This is illustrated in the multicycle delamination and healing of the composite studied herein in which after the healing, recovery efficiency decays exponentially from 100% at the fresh interface, to 37 % at 1.2mm crack opening down to about 20% at maximum previous opening. This conclusion is reinforced by the fact that the maximum previous opening associated with first healing is 3.2 mm giving healing efficiency of 20% at this point, whereas in the second healing, the maximum previous opening is 4.5 mm, accounting for the lesser healing efficiency of 13 % at this point. This behaviour does not depend on the number of delamination and healing cycles the material has experienced.

Chapter Eight

8 Delamination and self-healing of polyBH-A carbon fibre composite material

8.1 Introduction

This chapter reports the cyclic mode I DCB delamination of the new benzoxazine vitrimer carbon fibre composite as described in subsection 3.4.5.1. The analysis followed is the same as that for the delamination of DGEBA/4-APDS epoxy vitrimer composite reported in chapter 7. The recovery of fracture toughness from mode I delamination after two delamination and healing cycles is quantified. Average toughness recovery of the healed composite is determined as the percentage of the pristine toughness measured in the healed material. The mechanism of toughness evolution in the healed composite is modelled using a Kohlrausch–Williams–Watts (KWW) exponential decay as a function of crack opening before healing.

8.2 Mode 1 DCB experimental results and analysis

Figures 8.1 through **8.3** illustrate the delamination cycles of three BH-A carbon fibre composite specimens. In each figure, distinct and reproducible scenarios are observed for both the pristine and healed materials. In pristine material, the delamination trajectory exhibits two regions: a segment characterised by a lack of delamination due to the linear response of the material, followed by another region indicating crack initiation and propagation upon reaching the critical strain energy release rate. For healed materials, the delamination evolution encompasses four distinct regions in much the same way as observed and reported in chapter 7 for the epoxy system. The first region signifies no delamination and is marked by a linear response, indicating toughness recovery up to the point denoted by the vertical red line in **Figures 8.1** through **8.3**. The second region, located between the red and green vertical lines, represents early delamination where the strain energy release rate is insufficient for the material

to resist crack due to incomplete toughness recovery. The third region, bordered by red and black vertical lines, indicate crack arrest attributed to healing accompanied by partial crack propagation. The fourth region illustrates full crack propagation as the material ultimate strain energy release rate is exceeded, corresponding to the segments of the curves beyond the black vertical lines.

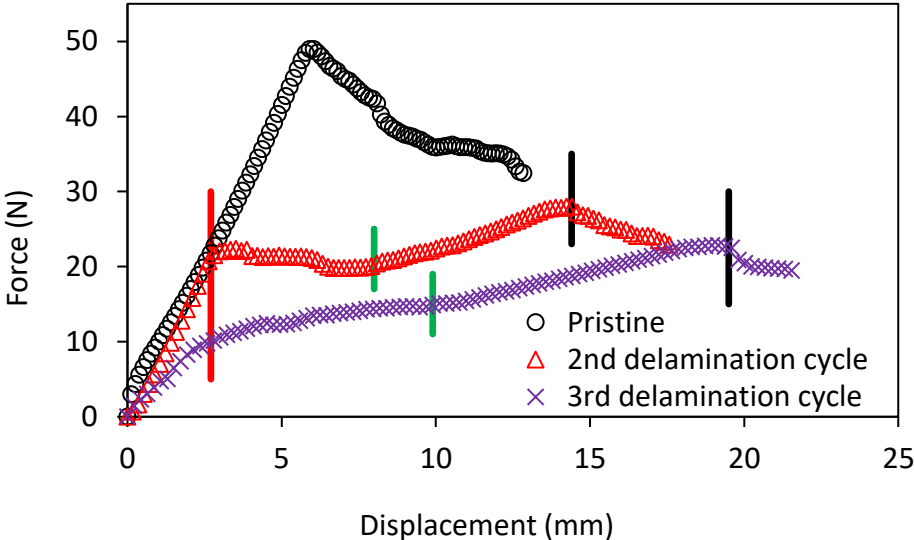


Figure 8.1. Force-displacement curves of specimen 1.

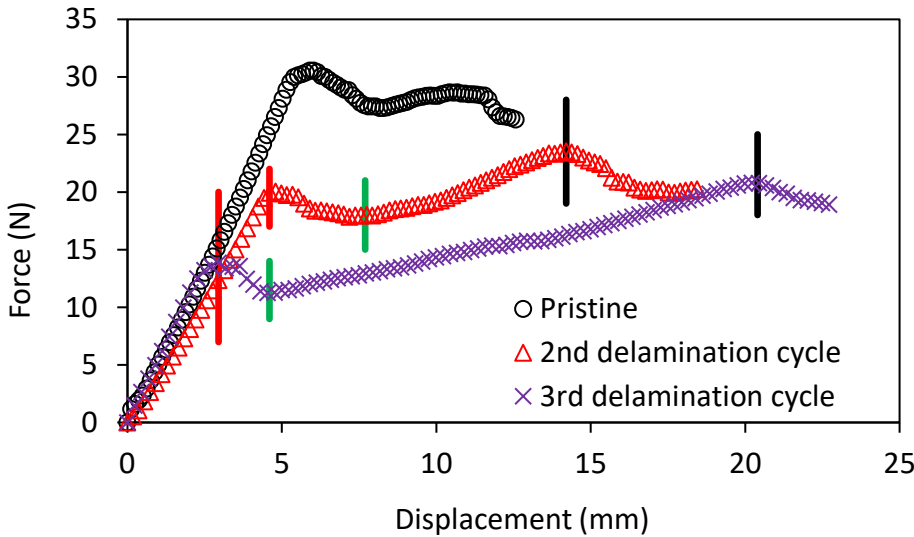


Figure 8.2. Force-displacement curves of specimen 2.

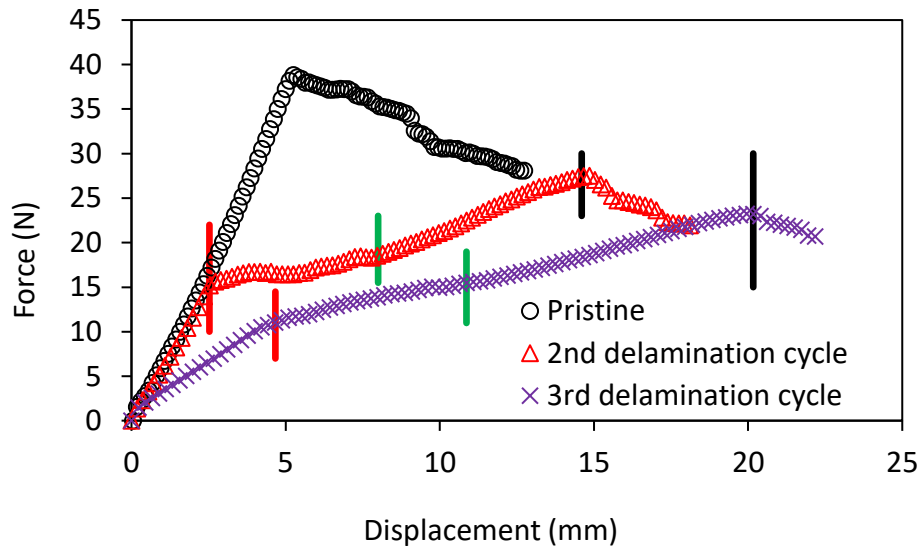


Figure 8.3. Force-displacement curves of specimen 3.

Figure 8.4 shows the R-curves of mode I behaviour of the pristine composites. The observed crack propagation within these curves features a degree of stability. Specifically, the average G_{IC} for the carbon fibre-BH-A composite studied is $295 \pm 46 \text{ J/m}^2$, showing a coefficient of variation of 15 %. The error bars depicted in **Figure 8.4** correspond to the standard deviation. These curves collectively highlight a consistent behaviour across the specimens, with observed deviations primarily attributed to the inherent variability in material properties and experimental error.

Figure 8.5 presents the R-curves of the second delamination cycle, where G_{IC} initiates at approximately 30 % of the pristine G_{IC} value and progresses to 100% at the position of the previous crack tip. The segment of low toughness recovery is attributed to early delamination, spanning the region marked by the red and green vertical lines in **Figures 8.1** through **8.3**. The complexity of healing in the delaminated material, resulting from bridging effects during the initial delamination, manifests in distinct regions of resin-to-resin contact near the previous crack tip, resin-to-fibre contact with moderate fibre alignment farther away, and fibre-to-fibre contact due to total fibre misalignment, primarily in the crack initiation zone. These regions of varying resin presence in the healing

material, absent in pristine material due to the resin complete wet-out during initial manufacturing, contribute to the observed variations in healing efficiency across different regions. Optical micrographs shown in **Figure 8.6**. indicate that these results are similar to those of epoxy vitrimer composite DCB specimens with evidence of non-uniform bridging associated with different degrees of fibre damage leading to fibre misalignment, leading to partial healing.

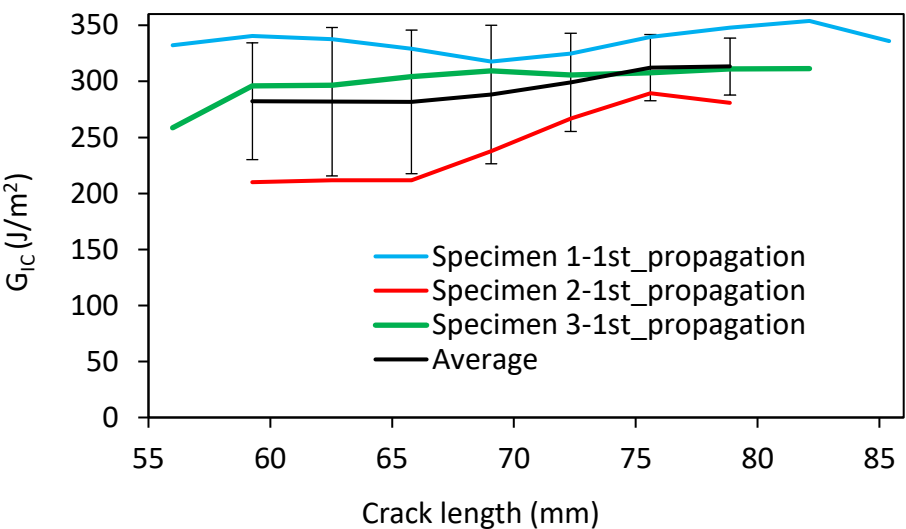


Figure 8.4. R-curves of pristine material.

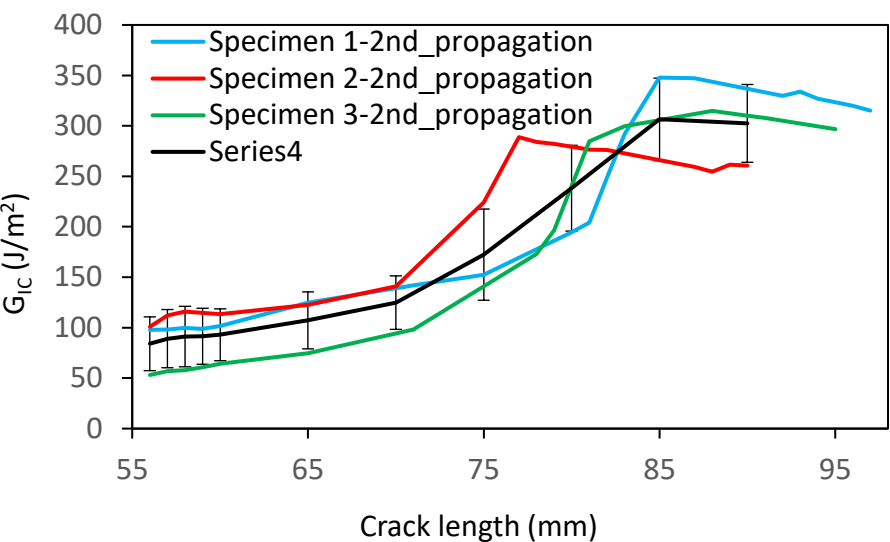


Figure 8.5. R-curves after first healing.

On average, G_{IC} has a value of $93 \pm 25 \text{ J/m}^2$ within the 55-65 mm crack length range, indicating a 31% average toughness recovery in the early delamination region illustrated in **Figures 8.1** through **8.3**. This figure progressively increases to an average of $135 \pm 42 \text{ J/m}^2$ in the 65-75 mm crack length range, signifying a 46% toughness recovery in the crack arrest and partial delamination region of **Figures 8.1** through **8.3**. As the crack length extends to the range of 75- 85 mm, the G_{IC} reaches 248 J/m^2 , corresponding to a recovery of 84 %. This recovery further evolves to 96% within the 95 -97 mm crack length range before reaching a 100 % G_{IC} recovery around the previous delamination crack tip. These results are summarised in **Table 8.1**. The R-curves generated by plotting interpolated G_{IC} as a function of shifted crack length with respect to the crack position prior to healing are illustrated in **Figure 8.7**. Curves closely are close to each other showing that a common behaviour.

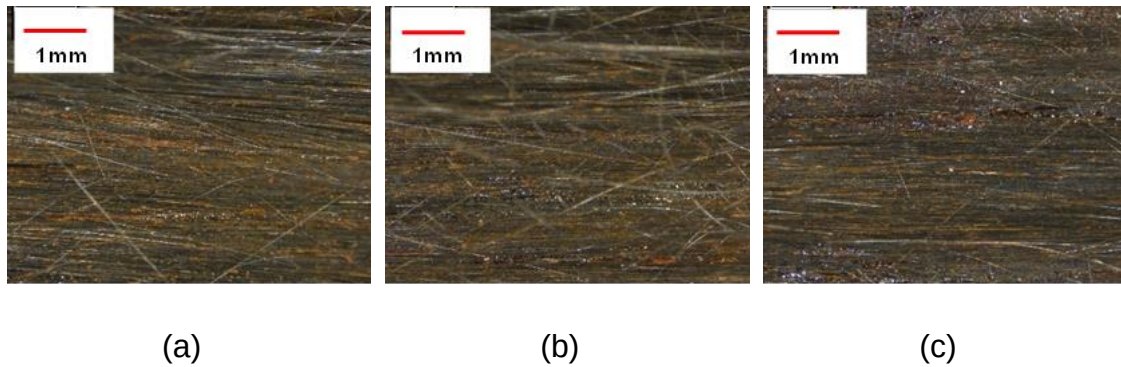


Figure 8.6. Micrographs of damaged BH-A vitrimer composites. (a) Region of specimen healed twice. (b) Region of specimen healed once. (c) Unhealed region of specimen.

Table 8.1. Average G_{IC} and recovery after each delamination cycle

	1st healing		2nd healing	
Region	G_{IC} (J/m ²)	Recovery (-)	G_{IC} (J/m ²)	Recovery (-)
55-65 mm	93±25	0.31	51±20	0.17
65-75 mm	135±42	0.46	72±33	0.24
75-85 mm	248±57	0.84	116±90	0.39
85-95 mm	284±49	0.96	234±36	0.79
95-97 mm	-	-	292±30	0.99
Pristine	295±46	—		—

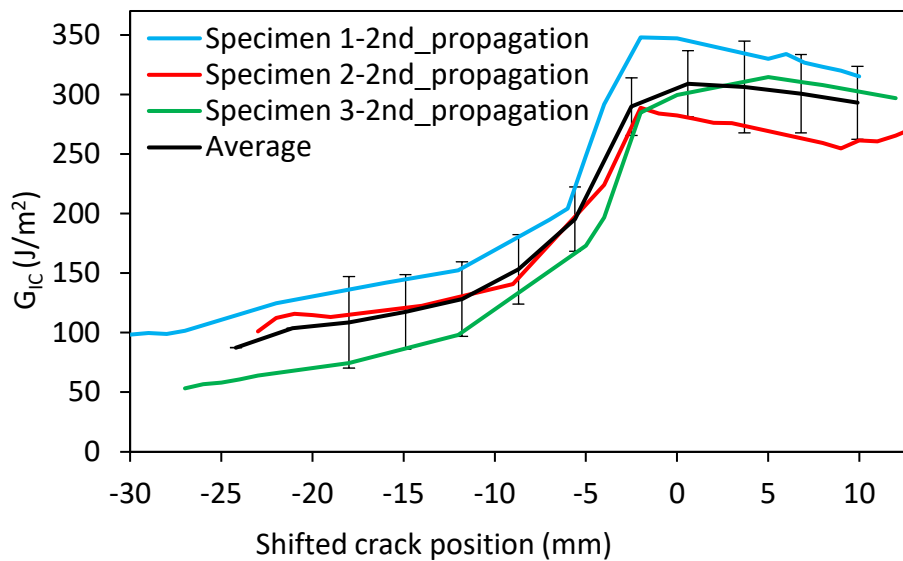


Figure 8.7. Normalised R-curves after first healing.

The outcomes of the delamination tests following the second healing cycle are illustrated in the R-curves shown in **Figure 8.8**, with shifted R-curves, together with error bars representing the associated standard deviation, presented in **Figure 8.9**. The recovery of fracture toughness, as indicated by the second healing result in **Figure 8.8**, features an average G_{IC} of 66 ± 20 J/m² in the

proximity of the crack initiation. This value corresponds to 19% of the pristine G_{IC} within the 55-65 mm crack length range. The toughness progressively rises to 120 ± 33 J/m² in the 65-85 mm crack length range, signifying a 35% recovery in this region characterised by early crack arrest and partial delamination. The later stage of crack arrest and partial delamination has an average G_{IC} of 248 ± 91 J/m², representing an 81% recovery in fracture toughness. Similarly, to the delamination after the first healing cycle, the material attains its full G_{IC} near the crack tip, signifying 100 % toughness recovery. In **Figure 8.9** all specimens manifest comparable G_{IC} values at identical crack positions. Each specimen consistently achieves G_{IC} up to 80% of the pristine value approximately 8-10 mm away from the previous crack tip. To facilitate comparison, the average curves from **Figures 8.7** and **8.9** are plotted on the same axes, as illustrated in **Figure 8.10**. The average R-curves follow closely each other, pointing to the existence of a master curve for the recovery process. This consistent trend reinforces the robustness and reliability of the observed recovery phenomenon.

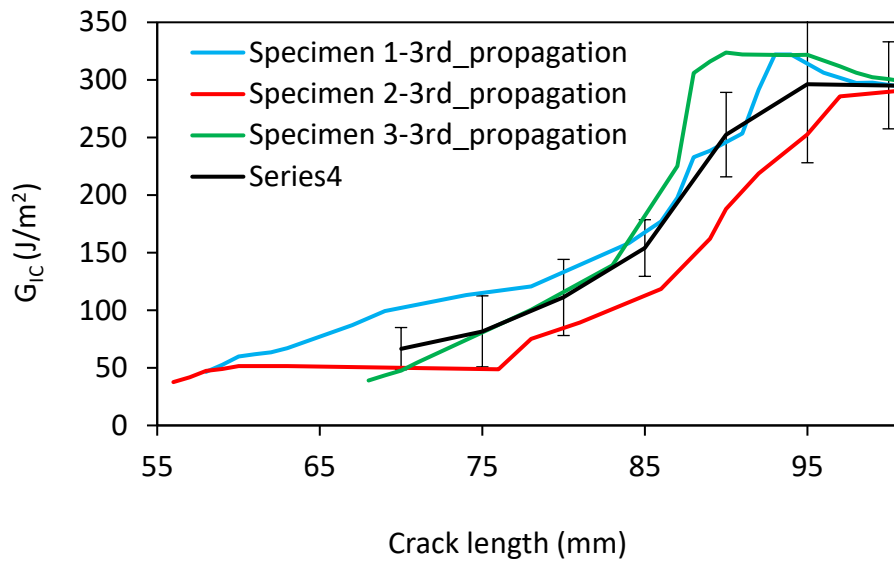


Figure 8.8. R-curves of specimens 1, 2 and 3 after second healing.

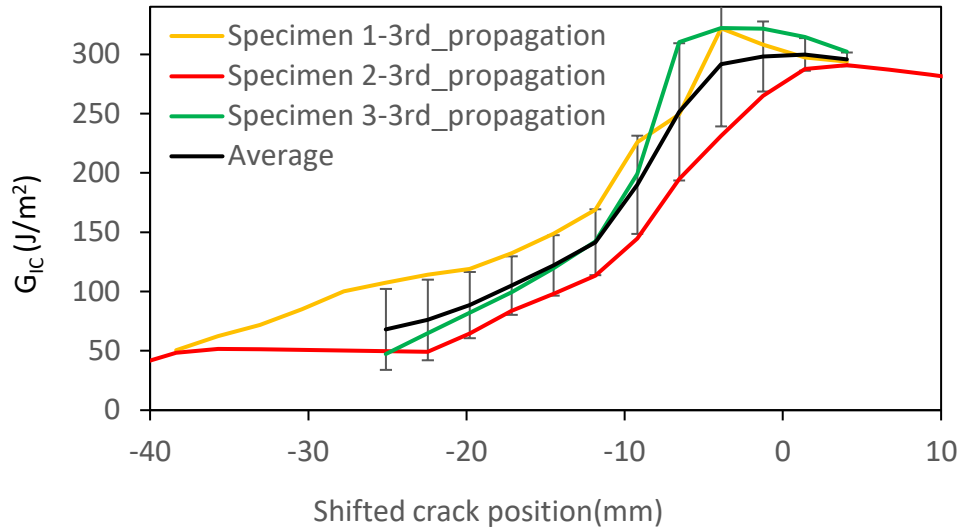


Figure 8.9. Normalised R-curves of specimens 1, 2 and 3 after second healing.

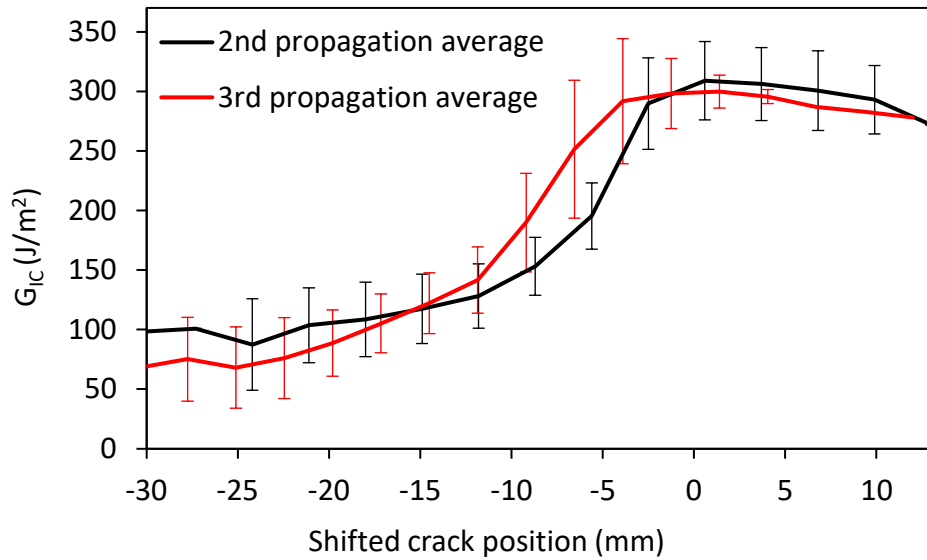


Figure 8.10. Comparison of normalised average R-curves of delamination after first and second healings cycles.

Figures 8.11 and 8.12 depict the recovery of toughness for the first and second healing cycles as a function of previous crack opening, respectively. Gradual

increase in toughness from an initial value at approximately 20% is observed when two surfaces of the material have undergone complete separation, resulting in an opening of 4.2 mm, to 100% recovery near the point of a fresh interface. As observed in the epoxy system results reported in chapter 7, the recovery of toughness is linked to the maximum historical crack opening observed in the material. **Figures 8.11** and **8.12** illustrate this dependence, showing an exponential decay. To elucidate the relationship between the fracture toughness recovery responses in the first and second healing cycles, the average recovery results are interpolated for eight datapoints, as illustrated in **Figure 8.13** for both cycles. This figure underscores the fact that in the delamination after the first healing, the maximum historical crack opening of 2.2 mm exhibits a higher initial recovery of 30% compared to the delamination after the second healing, which features a greater maximum historical crack opening of 4.2 mm and a corresponding lower recovery of about 20%. The healing curves closely mirror each other, aligning with the findings of **Figure 8.10** and reinforcing the evidence for the existence of a master curve for toughness recovery in the BH-A composite. The observed dependence of healing efficiency on historical crack opening in this benzoxazine vitrimer composite is similar to the findings in the epoxy system reported in chapter 7, with pressure, temperature and time as factors that need to be optimised to facilitate a better understanding of the effect of historical opening and crack length on healing efficiency.

The fracture toughness recovery in this system was modelled with KWW exponential function:

$$f(\delta) = (1 - c) \left[c + e^{-\left(\frac{\delta}{d}\right)^\beta} \right] \quad (8.1)$$

using the average of delamination data after first and second healing cycles as in the case of the epoxy system. The values of the fitting parameters of Eq.8.1 are reported in **Table 8.2**. The characteristic crack opening, d , for this system is 0.62 mm, corresponding to toughness recovery of 43%. The model fitting has an average relative error of 6.7 % and is illustrated in **Figure 8.14**. This half-length

of this vitrimer composite system, for which the composite has 50% toughness recovery is 0.44 mm.

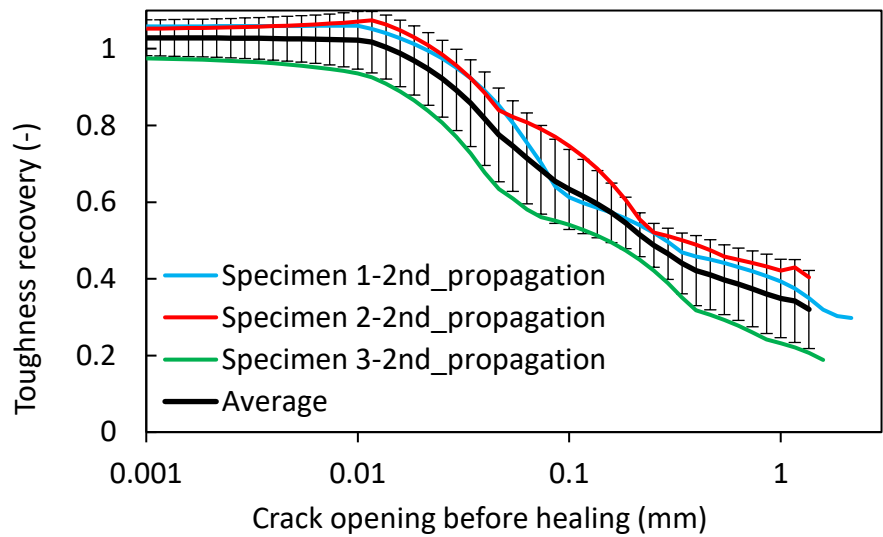


Figure 8.11. First healing recovery efficiency versus previous crack opening.

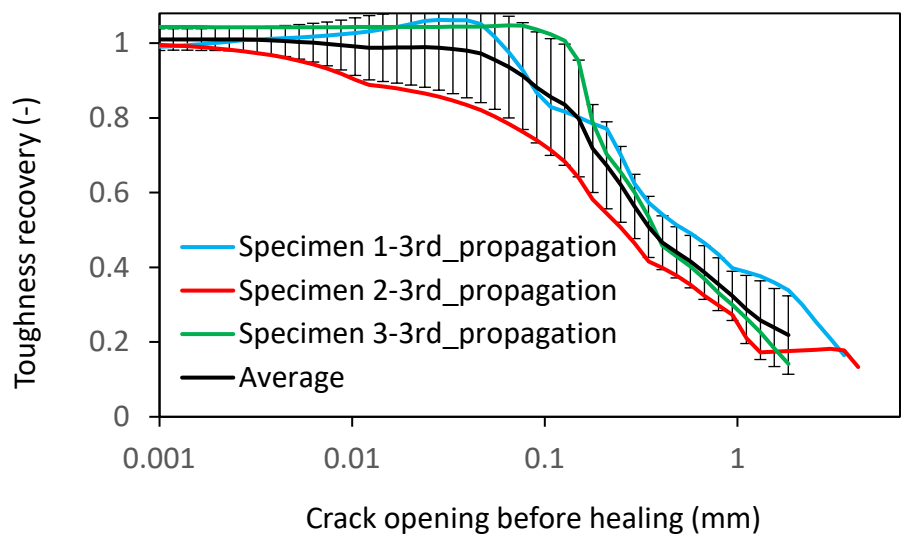


Figure 8.12. Second healing recovery efficiency versus previous crack opening.

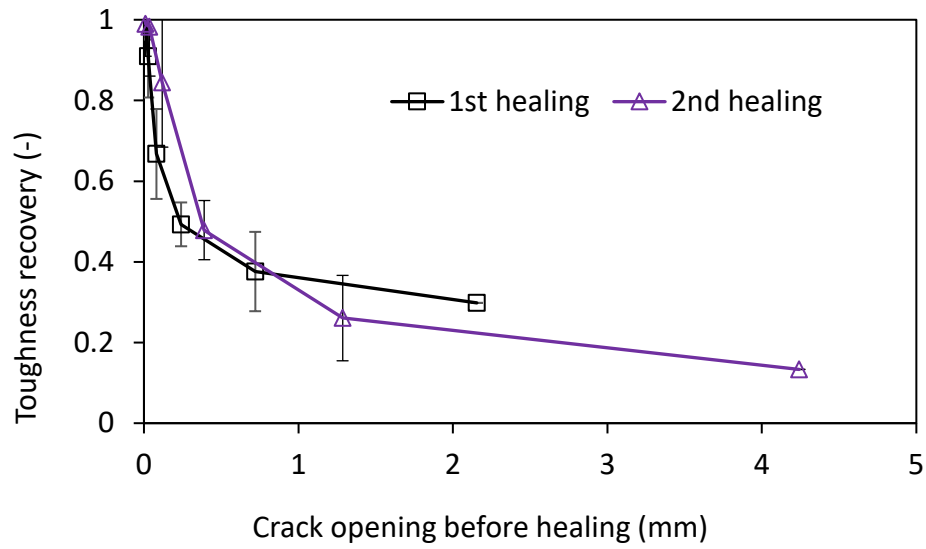


Figure 8.13. Average healing efficiency versus historical crack opening.

Table 8.2. KWW model parameters of G_{1C} recovery in BH-A composite.

Parameter	Unit	Value
c	—	0.116
β	—	0.640
d	mm	0.620

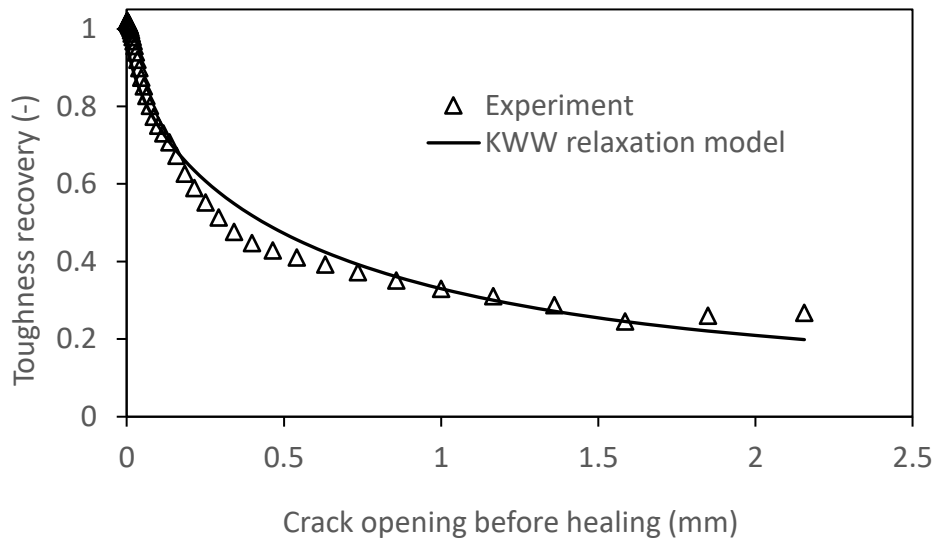


Figure 8.14. KWW relaxation modelling of healing efficiency as a function of previous crack opening in BH-A benzoxazine vitrimer fibrous composite.

8.3 Concluding remarks

The results of cyclic mode I delamination and healing of the new polybenzoxazine vitrimer presented in this chapter are in agreement with the conclusion in chapter 7. The damage is quantified by the amount of separation or opening that has occurred in the material prior to healing. Therefore, the material at a location that has been damaged to a small extent heals more effectively than one in which the damage is more severe. In the case of the benzoxazine vitrimer fibrous composite reported in this chapter, the recovery efficiency is full near the crack tip and it decays exponentially to a half-length of 0.44 mm where the efficiency is 50 % and to 27% at maximum previous opening of 2.2 mm used in the modelling fitting. The maximum previous opening of 4.2 mm associated with first healing therefore results in a lower healing efficiency of 13 % compared to a lower maximum historical crack opening of 2.2 mm associated with the second healing with a higher efficiency of about 30 %, reinforcing the existence of a universal law governing the process.

Chapter Nine

9 General Discussion

9.1 Introduction

In this chapter, the overall discussion of the results presented in chapters 4, 5, 6, 7 and 8 is carried out. The key outcomes of each chapter are discussed with respect to the progress in the underlying objectives of the study. Comparisons are made between the two materials of the study, the epoxy and benzoxazine matrices, which determined their processing routes, as well as mechanical response and recovery of healing of each fibrous composite system. Furthermore, the limitations of the study are discussed, pointing out areas that may lead to potential improvement. Finally, the impact of the study is discussed.

9.2 Overall discussion

Autocatalysis with a diffusion term accurately simulates the cure behaviour of both resin systems. DGEBA/4-APDS is accurately modelled using a simple autocatalytic model with logistic function, yielding degree of cure average absolute and relative errors of 0.01 and 3%, respectively, whilst BH-A is modelled using Karkanis equation which ensures more accurate representation of the curing reaction in the later stages of the autocatalysis, leading to a model with degree of cure prediction absolute and relative errors of 0.016 and 4.4%, respectively. For both vitrimer systems, the Di Benedetto equation models accurately the glass transition temperature evolution. Whilst DGEBA/4-APDS has a convex glass transition advancement curve, characteristic of most resins studied in the literature, BH-A has a concave T_g evolution curve. The chemorheology of the two systems reveals that DGEBA/4-APDS is a liquid moulding vitrimer due to the availability of reasonable infusion time during the low viscosity phase of its viscosity evolution, whilst the chemoviscosity of BH-A does not permit the desired infusion window during the low viscosity phase rendering it amenable to manufacturing strategies such as prepreg and resin film infusion.

Thus, whilst DGEBA/4-APDS composite was manufactured by VARTM, BH-A composite was manufactured by RFI in this study. Both resins are high temperature systems with similar T_g in which topology transition over T_g is enabled by disulphide metathesis. The results presented guide the application of these vitrimers in composites manufacturing in terms of optimising the composites fabrication process.

The novel high- T_g benzoxazine vitrimer, BH-A, synthesised through an easy cost-effective solventless one-pot method presents unique combination of properties. Of all the known polybenzoxazine vitrimers, none combines the advantages of high-temperature performance and solventless one-pot method. Besides this advantage over known polybenzoxazine vitrimers, polyBH-A features two additional advantageous characteristics. First, it exhibits a very high char yield, resulting in high limiting oxygen index, which is an indicator of excellent fire retardancy. The *LOI* of polyBH-A is at par with the class of the best known fire-retardant conventional polybenzoxazines. Apart from polyBH-A, there is no known benzoxazine vitrimer with such level of fire retardancy. Second, the environmental resistance of polyBH-A, expressed by its excellent low water uptake signature, represents one of the best environmental resistance results of any resin system, positioning it as an excellent material solution for extreme environment applications, such as in aerospace, marine or energy sectors. PolyBH-A exhibits glass transition temperature of 155°C, glassy modulus of 3.6 GPA, 5% weight loss temperature of 293°C, topology freezing transition temperature of 78°C, and *LOI* of 40.5 %.

In literature, damage repair in DGEBA-based epoxy/amine vitrimer composite has been carried out using high pressures of about 100 bar [14], which is very high. In this study, it has been demonstrated that the pressure can be halved, and healing achieved at 50 bar. PolyBH-A composite is by far a better healable material because its healing can be achieved within practically realistic manufacturing conditions. It requires a low pressure such as 4 bar used in this study to heal within as little time as 30 minutes, compared to DGEBA/4-APDS

composite which requires up to 90 minutes at 50 bar to achieve similar healing efficiency. In both vitrimer systems, there is partial but significant recovery of toughness after healing a delaminated surface, with the degree of toughness recovery affected by fibre misalignment resulting from bridging effects that creates non-uniform interface between the two healed parts of the interface. The use of a multicycle DCB specimen delamination with incremental crack opening and repair per cycle has produced an insight into the understanding of the factors upon which mechanical property recovery after healing a delaminated composite laminate depends. The maximum historical crack opening prior to healing; the governs the healing efficiency achieved.

9.3 Progress with respect to objectives

This study set out with seven objectives as presented in section 1.2. All the seven objectives have been addressed.

The first objective of the study was to synthesise and characterise a high-temperature reference epoxy vitrimer based on established chemistry as a baseline for comparison. Essentially, this objective was accomplished with successful synthesis and characterisation of the DGEBA/4-APDS epoxy vitrimer. DGEBA/4-APDS vitrimer features T_g of 162.6°C, T_v of 149.5°C activation energy of 196.8 kJ/mol, and relaxation time of 16 s at its reprocessing temperature of 220°C, which is broadly an improvement over its literature counterpart with T_g of 130°C, T_v of 75°C activation energy of 126 kJ/mol and relaxation time of 20 seconds at 200°C, with fibre composite reprocessed at 100 bar [14,15].

The second objective of this research was to develop and validate models for simulating the cure kinetics, glass transition evolution and chemoviscosity of the synthesised epoxy vitrimer for optimal manufacturing. This objective has been realised with the development of the first cure kinetics, glass transition advancement and chemorheological models of DGEBA/4-APDS, setting the scene for the development of fibrous composites of this epoxy/amine vitrimer

system. The models developed are accurate in predicting material behaviour during polymerisation, with small errors.

The third objective of this study concerning the design and synthesis of sustainable/cost-effective high-performance novel benzoxazine vitrimer was achieved. The benzoxazine vitrimer synthesised through a catalyst-free cost-effective solventless one-pot method, combines excellent thermosetting character below its T_g , exemplified by high environmental resistance and thermoplastic flow over its T_g leading to topological transition, whilst exhibiting excellent fire retardancy potential, not yet reported of any vitrimer.

The fourth objective of this study was to characterise the novel high-performance benzoxazine vitrimer. Given successful synthesis, the objective of characterising BH-A was pursued. DSC was used to study the cure behaviour of BH-A and identify its monomer glass transition temperature of 22°C, its cure temperature, polymerisation heat of reaction and cured polymer glass transition temperature of 155°C. TGA was employed to characterise the polyBH-A's thermal stability, which apart from revealing a 5 % weight loss temperature of 293°C, also revealed a high char yield which was used to characterise its fire retardancy through the determination of its *LOI* of 40.5 %. Furthermore, dynamic DMA measurements were used to obtain polyBH-A's glassy modulus of 3.6 GPa and T_g , whilst transient DMA measurements were employed to study the stress relaxation of polyBH-A, leading to the determination of its T_v of 78°C and dynamic bond exchange activation energy of 127 kJ/mol.

Similar to the cure modelling of the DGEBA/4-APDS vitrimer, the development and validation of analytical/numerical models for simulating the cure kinetics, glass transition advancement and chemoviscosity of the novel benzoxazine vitrimer for optimal manufacturing was set out as the fifth objective of this study. This objective was achieved with the successful modelling of the cure kinetics, glass transition advancement and chemoviscosity of BH-A. The models developed accurately simulate the thermal and rheological events accompanying

the curing reaction, as well as track the degree of cure given known T_g and vice versa. This has set the scene for optimal manufacturing of BH-A composites.

Following successful modelling of the cure, T_g development and chemoviscosity of DGEBA/4-APDS and BH-A, the manufacturing of sustainable and functional fibre-reinforced composites of the two vitrimers was pursued as the sixth objective of this study and fully addressed. The models led to an understanding of the manufacturing methods suited for each resin system. The fibrous composite of DGEBA/4-APDS epoxy vitrimer was successfully manufactured by VARTM, whilst the BH-A benzoxazine composite was manufactured by RFI. The composites showed good surface finish due to good infusion and fibre wet out, whilst the fibre volume fraction was within the desired range of 0.5 – 0.6, with no visible defects such as surface voids, resin-rich and resin-poor areas.

Finally, the seventh objective of this study – validation of functionality of manufactured vitrimeric composites – was realised by a series of multicycle mechanical tests involving DCB experiments, healing and retesting. DCB specimens were delaminated on an incremental crack propagation basis as detailed. The vitrimeric functionality of the epoxy and benzoxazine vitrimer composites is validated by self-healing which enabled recovery of the delaminated composite laminates, achieving partial but significant degrees of fracture toughness recovery in each case.

9.4 Limitations of the study

With aerospace industry as the target, to synthesise a reference epoxy vitrimer, the search was centred on high temperature epoxy resins for aerospace applications. At the time of carrying out this research, no commercial aerospace resin had been vitrimerised, limiting the choice of reference epoxy vitrimer to non-commercial systems which need to undergo different qualification tests before consideration for industrial application. Due to the emphasis on high glass transition temperature, aromatic amines were the favoured option since they produce high- T_g epoxy resins compared to their aliphatic counterparts. Also, the

choice of vitrimer chemistry is a limiting factor in the sense that catalyst-free fast stress relaxation is desired for fast healing/reprocessing, narrowing down the search of curing agents to aromatic amines with catalyst-free dynamic covalent bond exchange chemistry, for which disulphide bond stands out. 2-aminophenyl disulphide and 4-aminophenyl disulphide were available in the market as at the time of search for suitable commercial precursors. Epoxy vitrimers based on 2-aminophenyl disulphide had not been reported, whereas epoxy vitrimer based on 4-aminophenyl disulphide had been reported with its properties. This informed the decision to use 4-aminophenyl disulphide, an expensive material, as curing agent to synthesise the reference epoxy vitrimer. This produced a vitrimer with T_g in the range of 162.6 - 178°C depending on the measurement method, which is not in the highest T_g range for aeronautic application. Typical aeronautical structural resins normally have T_g above 170°C; therefore, the results obtained with DGEBA/4-APDS, although insightful, may not represent the best option for the aerospace industry due to the requirement of higher T_g than that of DGEBA/4-APDS. The T_g of DGEBA/4-APDS epoxy vitrimer can be increased by incorporating a controlled amount of a tri-epoxy monomer to increase the crosslink density without permanently freezing the network, whilst the T_g of the benzoxazine vitrimer can be increased by altering the molecular architecture of the benzoxazine in favour of increased crosslink density. This can be done by either copolymerising with epoxy or by incorporating a crosslinking functional group during benzoxazine synthesis without leading to a permanently frozen network after curing. Vitrimers created from the commercially available aerospace resins with similar thermomechanical performance, would attract the interest of the aerospace industry faster than the results of the current research.

Although, BH-A is a sustainable material due to its proven self-healing and recyclability potential, none of its three precursors – bis-4(hydroxyphenyl) disulphide, paraformaldehyde and aniline – is biobased; they are all synthetic chemicals. Efforts were made to synthesise high-performance benzoxazine vitrimers through solventless one-pot method by using biobased precursors such as vanillin, eugenol, vanillin alcohol and guaiacol. To do this, 4-aminophenyl

disulphide was the available amine endowed with the desired dynamic covalent bond chemistry. However, 4-aminophenyl disulphide, being a diamine, poses difficulty in benzoxazine synthesis, due to undesired side reactions that limit oxazine ring formation, necessitating the use of solvents and various stages of purification. Moreover, benzoxazines synthesised using these precursors, as well as their derivatives, exhibit early degradation characteristics due to decarboxylation associated with the carbonyl group of these phenolic precursors, requiring further combination with another precursor to knock off the carbonyl group from the benzoxazine. Benzoxazines with similar functionality could be created from biobased resources, given molecular versatility of benzoxazines.

To manufacture the epoxy composite, VARTM process was easy to carry out without challenges. However, the same is not the case for the benzoxazine composite, which was fabricated by RFI. The major limitation in manufacturing the benzoxazine composite stems from the brittle nature of the resin. When the film is made, it cannot be removed and laid on the fibre without shattering; therefore, laying the fabric on the film whilst still on the filming plate, increasing the temperature to the filming temperature to allow resin and fibre to stick together was necessary. This may not have yielded the best quality for the composites compared to traditional standalone films. Also, microscopy was not performed to assess surface finish and porosity of the final composite, which if present, would affect the toughness recorded for both epoxy and benzoxazine composites.

In carrying out the mechanical testing, healing and retesting of composite specimens, there is a limitation to the results presented in this work due to the small number of DCB specimens. An increased number of test specimens would have reduced the uncertainty and given a more accurate robust of healing and mechanical property recovery phenomena in a delaminated fibrous vitrimer composite laminate. Another major limitation encountered in mechanical testing and healing of the composites relates to the healing of benzoxazine vitrimer composite, which requires low healing pressure typical of consolidation pressure of composites manufacturing.

9.5 Impact

This study can make significant impact towards the progress of vitrimer science and its industrial application. Since vitrimers were discovered, literature is saturated with many reported vitrimeric systems mostly focussing on the formulation of novel systems, predominantly epoxy resins. The application of vitrimeric matrices to composites manufacturing remains relatively unexplored, whilst the manufacturing route for any vitrimer and its processing conditions are not known. This study provides the first processing characterisation of an epoxy/amine-based vitrimer to guide the selection of manufacturing route and the and fabrication process parameters towards optimised fibrous vitrimeric composite manufacturing. The dominance of epoxy vitrimers in the literature means that the benefits inherent in the use of vitrimers are not yet fully unlocked. Polybenzoxazines can out-perform epoxies in terms of environmental resistance and fire retardancy. Motivated by this possibility, this study puts forward the first known high-temperature catalyst-free polybenzoxazine vitrimer produced through a cost-effective solventless one-pot method. This polybenzoxazine vitrimer is the first vitrimer to meet the high environmental resistance and fire retardancy requirements of an aerospace resin. Beyond developing the new high-performance benzoxazine, this study provides the cure and chemorheological modelling of the new system to facilitate its early application to healable composites manufacturing. Furthermore, this study demonstrates that the healing of vitrimer composites can be achieved under practically realistic composite manufacturing conditions of temperature, pressure, and time, whilst providing a useful insight into the mechanism of toughness recovery in a delaminated and healed fibrous vitrimer composite, not previously known. It is shown that healing depends on the maximum historical crack opening that occurs in the material prior to healing and in the case of the epoxy and benzoxazine fibrous composites investigated in this study can be modelled with a stretching exponential decay function, with a high level of accuracy. This sets the scene for the defining the type of damage that can be easily healed in vitrimer composites, potentially leading to future design criteria for self-healing structures.

Chapter Ten

10 Conclusions and future work

10.1 Conclusions

The main conclusions of this study are as follows:

Synthesis of benzoxazine vitrimer

- A high-performance polybenzoxazine vitrimer can be synthesised using established bond exchange chemistries discussed in this study.
- PolyBH-A features a T_g of 155°C, a glass modulus of 3.6 GPa, high fire retardancy as indicated by an LOI of 40.5%, relatively high thermal stability with 5% weight loss temperature of 293°C.
- PolyBH-A has a T_v of 78°C, which is below its T_g , and can therefore, be reprocessed above its T_g , at 190°C, with full relaxation happening within 5 s.

Cure kinetics, T_g evolution and chemorheology

- The cure kinetics of DGEBA/4-APDS is accurately stimulated by autocatalytic model with a logistic function for diffusion effects.
- The cure behaviour of polyBH-A can be modelled by Karkanis model with logistic function for diffusion effects.
- Effects of dynamic covalent bond exchanges that may occur during the polymerisation of a vitrimer does not change the forms of established phenomenological cure kinetics models.
- The chemoviscosity of DGEBA/4-APDS and polyBH-A can be modelled using a model that expresses viscosity evolution in terms of its inverse temperature exponential dependence, rather than using degree of cure as an underlying model variable.
- T_g evolution in vitrimers follows the Di Benedetto model.

Delamination behaviour and self-healing in vitrimer composites

- The DGEBA/4-APDS epoxy vitrimer composite can be healed at 50 bar, which is half of the pressure reported in literature for reprocessing this system.
- PolyBH-A is healable at 190°C, 4 bar and 30 minutes, conditions which are compatible with practical manufacturing conditions of temperature, pressure, and time.
- The degree of healing after delamination is governed by the previous crack opening that a specific location has undergone.
- The dependence of toughness recovery on previous crack opening follow an exponential law with half lengths of 0.77 mm and 0.44 mm for the polyDGEBA/4-APDS and PolyBH-A, respectively.

10.2 Future work

Although the T_g of polyDGEBA/4-APDS and polyBH-A – 163°C and 155°C, respectively – fall within aerospace acceptable T_g range which is typically above 150°C, they are not optimised for aerospace structural application which utilises resins with T_g about 170°C and above. It is recommended to increase the T_g of the two systems to about 170°C and above by incorporating selected amounts of suitable crosslinkers into the polymer network, increasing crosslink density. Similarly, as highlighted in chapter 9, the development of BH-A left room for improvement. It is suggested that benzoxazines from sustainable biobased vanillin, guaiacol, eugenol, vanillin and alcohol be investigated by combining with different polyether amines, with a view of effectively replacing carbonyl groups with dynamic imine bonds to address the problem of early degradation due to decarboxylation and improve the vitrimeric character. This will make benzoxazine vitrimer chemistry more sustainable. Furthermore, other biobased phenolic precursors should be investigated with disulphide bonds, imine bonds and other dynamic bonds to fully unlock the potentials of benzoxazine vitrimer chemistry towards more sustainable composites future. It is suggested that the crosslinking density of BH-A be improved by careful combination with furfurylamine and/or

allylamine to increase the T_g . Moreover, it is suggested to formulate an epoxy-endowed BH-A by mixing with an epoxy system to yield a copolymer with improved toughness.

As highlighted in chapter 9, the multicycle DCB tests and healing results presented are based on three specimens per matrix system, which leaves room for improvement. It is therefore recommended to increase the number of test specimens as this would reduce the associated errors of the experiment and present a more accurate presentation of the scenario. Moreover, bridging effects lead to different degrees of fibre alignment during healing which affects the healing process. It is therefore recommended to design a way of suppressing bridging effects in this kind of study so that the fibres can always remain closely aligned after delamination with a view to ascertaining whether healing efficiency would exhibit the same or different behaviour under more idealised conditions. Equally important and thus recommended is the inclusion of scanning electron microscopy in the study to provide a detailed insight into the microstructure and quality of the manufactured vitrimer composites before and after delamination and healing cycles as well as to observe the influence of bridging on recovery.

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