**High glass transition catalyst-free fire-retardant polybenzoxazine vitrimer through solventless one-pot method**

Festus Ifeanyi Anagwu*, Alex A. Skordos

Composites and Advanced Materials Centre, School of Aerospace, Transport and Manufacturing, Cranfield University, Cranfield, MK43 0AL, United Kingdom

E-mail: f.i.anagwu@cranfield.ac.uk (F.I. Anagwu); a.a.skordos@cranfield.ac.uk (A.A. Skordos)

*Corresponding author E-mail address: f.i.anagwu@cranfield.ac.uk (F.I. Anagwu).

## Abstract

A high-temperature polybenzoxazine vitrimer has been synthesised by a solventless one-pot method involving the Mannich condensation of a phenolic disulphide, paraformaldehyde and aniline. The polybenzoxazine has a glass transition temperature of 155°C and exhibits thermosetting behaviour below the glass transition temperature. Dynamic bond exchange enabled by disulphide metathesis associated with a topological freezing temperature of 78°C results in healing over the glass transition temperature. The system is reprocessable at 190°C, has a glassy modulus of 3.6 GPa, and a limiting oxygen index (LOI) of 40.5%. The combination of thermosetting character, ease of synthesis, good processability, fire retardancy and reprocessability of this polybenzoxazine vitrimer system make it an attractive candidate material solution as a matrix for recyclable and self-repairable aerospace thermosetting continuous fibre composites.

**Keywords:** Composites, benzoxazine, vitrimer, self-healing

## 1. Introduction

Vitrimers have attracted the attention of the polymer science community in the last decade due to their combination of thermosetting performance, including environmental resistance,

high mechanical strength and thermoplastic reprocessability without compromising the material structural integrity. Since their discovery [1], epoxy vitrimer systems are the most widely studied class [2–5] due to the current dominance of epoxy systems in the composites industry relative to other resins such as phenolics, benzoxazines, bismaleimides, and polyimides. There is currently a research focus on the design of polybenzoxazine vitrimers as alternatives to epoxies, motivated by the advantages of polybenzoxazines compared to both epoxies and phenolics in terms of thermomechanical and hygrothermal performances, fire retardancy, low cure shrinkage, molecular design flexibility, dimensional stability, and compatibility with sustainable precursors.

Established reprocessable polybenzoxazines with high thermomechanical properties incorporate boronic ester bond [6] and transesterification exchange chemistry [7,8]. The synthesis of the benzoxazine vitrimer crosslinked with boronic ester bond involves the use of toluene as solvent in a time-consuming three-pot strategy that includes a purification step. The synthesis of established 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. This strategy has been applied to synthesise formulations involving the purification of the esterified precursor prior for use in benzoxazine synthesis [7–9], yielding moderate to high glass transition temperature ($T_g$) systems, with transesterification bond exchange catalysed by the benzoxazine tertiary amine. Other reprocessable polybenzoxazines featuring dynamic covalent bond exchanges incorporate dioxaborolane metathesis [10] and transcarbamoylation [11], with low glass transition temperatures of 29°C and 55°C respectively, and formulations involving more than one-pot method; whilst, the former is synthesised by mixing a cardanol-based benzoxazine thermoset with 1,4-phenylenebisboronic acid and water at ambient temperature followed by treatment with magnesium sulphate, introducing boronic bond into the monomer, the latter involves

reacting hexamethylene diisocyanate with crude benzoxazine monomer made from tyrosol, dodecylamine, and paraformaldehyde in the presence of dibutyltin dilaurate catalyst, producing a hybrid polybenzoxazine-polyurethane vitrimer system. Similarly, self-healability of polybenzoxazine main chain is achieved by mixing benzoxazine with phenyl boronic acid in chloroform prior to curing; this has been successfully applied in synthesising a low temperature system [12].

A polybenzoxazine obtained by the polymerisation of a two-component mixture of main-chain benzoxazine and polyether amine features characteristic stress-relaxation, dynamic bond exchange between primary and secondary amines, and reprocessability of vitrimeric systems with moderate $T_g$ (97 – 108°C) and topology freezing transition temperatures in the range 39 – 97°C [13] depending on polyether amine content, whilst a set of imine bond-enabled polybenzoxazine vitrimers with $T_g$ in the range of 34 - 160°C [14] are synthesised via a solventless approach that involves multiple steps, more complex than the traditional benzoxazine synthesis route [15]. A high-temperature benzoxazine vitrimer has been formulated from a main-chain benzoxazine and an epoxide-functionalised polyrotaxane, yielding a mechanically interlocked network and a covalent adaptable network with improved ductility and toughness, and bond exchange by a tin (II) 2-ethylhexanoate-catalysed transacetalation [16].

Disulphide metathesis is an effective bond exchange for catalyst-free vitrimers. Vitrimers incorporating disulphide bonds feature a fast evolution of stress relaxation modulus at moderate temperature and have been achieved with benzoxazine using a simple implementation of one-pot solventless Mannich condensation reaction [17], resulting in a vitrimer appropriate for low temperature applications due to 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 temperature benzoxazine vitrimers following the established cost-effective solventless one-pot Mannich

condensation method [15], incorporating fast catalyst-free bond exchange. The hypothesis in this work is that this is achievable if the phenolic and amine precursors are endowed with molecular structural functionalities that could translate into moderate-to-high crosslinking density upon polymerisation of the potential benzoxazine monomer, and the precursors exhibit a high level of solvency without solidifying prior to the end of the anticipated synthesis reaction. Combined with disulphide chemistry, this would deliver a benzoxazine system featuring high glass transition and fast catalyst-free stress relaxation leading to vitrimeric functionalities. A formulated monomer following this route is characterised using FTIR spectroscopy whilst calorimetric analyses of both monomer and polymer are carried out to establish the curing behaviour and glass transition temperature. The degradation behaviour and fire retardancy potential of the polymer are investigated using thermogravimetric analysis, applying the van Krevelen model for limiting oxygen index (LOI) calculation. Furthermore, swelling experiments are performed to establish the thermosetting character of the polymer. Dynamic mechanical analysis (DMA) is used to measure the glassy modulus and glass transition temperature, whereas stress relaxation is used to estimate the vitrimer topological freezing transition temperature. Scratching and self-healing experiments – quantified through profilometric analysis of surface profiles before and after healing a scratched specimen – are utilised to demonstrate the functionality of the vitrimer as an autonomously repairable matrix system.

## 2. Experimental

*2.1 Raw materials and synthesis of 1,2-bis(3-phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-yl)disulphane (BH-A)*

Bis (4-hydroxyphenyl) disulphide (98 %) was purchased from AmBeed USA [18]. Aniline (99.8 %) was purchased from Fisher Scientific [19], and paraformaldehyde was purchased from Sigma Aldrich/Merck [20]. All chemicals were used as received without any further treatment.

The benzoxazine monomer, 1,2-bis(3-phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-yl)disulphane (BH-A), was synthesised following the solventless method [15]. Stoichiometric amounts of aniline, paraformaldehyde, and bis(4-hydroxyphenyl) disulphide (2:4:1 mole ratio) were used for the synthesis. An amount of 3.72 g (40 mmol) of aniline was measured into a 150 ml beaker, 2.40 g (80 mmol) of paraformaldehyde was added and stirred with a magnetic stirrer for 10 minutes at room temperature and 5 g (20 mmol) of bis(4-hydroxyphenyl) disulphide was added to the mixture and stirred for another one minute at room temperature. The mixture was then placed in a silicone oil bath maintained at 90°C and was stirred at 300 rpm for 30 minutes. A brown viscous benzoxazine monomer, BH-A (92 % yield) was obtained, requiring no further purification. The reaction is shown in **scheme 1**.



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

## 2.2 Casting and curing of BH-A

BH-A is a rubbery solid at room temperature. To cast plates of the polymer for dynamic mechanical testing, the rubbery monomer was placed on a glass plate, bounded by silicone rubber. The glass plate was gradually heated to 80°C on a hot plate to allow the material transition into a viscous liquid and spread in the glass plate up to the boundary created by the silicone rubber. A second glass plate was used to form the casting cavity and the assembly was

then clamped and placed into an OV301 precision composite curing vacuum oven (Easy composites). The resin was degassed at 110°C for 10 minutes, after which the vacuum was turned off and the temperature of the oven ramped to the cure temperature. The resin was cured at 170°C for 2 hours and post-cured at 190°C for 30 minutes.

## 2.3 Characterisation

Fourier Transform Infrared (FTIR) spectroscopic data were acquired in transmission mode with a SMART iTR Nocolet iZ10 spectrometer (Thermo Fisher Scientific) from 600 to 4000 cm$^{-1}$. One hundred background and sample scans were performed with a resolution of 4.0, sample gain of 8.0, optical velocity of 0.4747 and aperture of 80.0.

The cure behaviour of BH-A was studied by differential scanning calorimetry (DSC), using a DSC 250 Discovery (TA Instruments) equipped with an RCS cooling system under nitrogen purge at 50 mL/min. DSC experiments were conducted by encapsulating resin in a Tzero aluminium pan and scanning at 10°C/min from -50°C to 240°C to measure the uncured material glass transition, exothermic cure onset temperature, cure peak temperature and heat of reaction. The cured sample was rescanned at 10°C/min to measure the cured polymer glass transition temperature.

Thermogravimetric analysis (TGA) was performed on a Discovery TGA 550 (TA Instruments) under nitrogen (60 mL/min) at 10°C/min heating rate from 50°C to 910°C. Samples were placed in a 100 μL platinum pan. The Limiting Oxygen Index ($LOI$) of the polymer, which can be used as an of indication of flame retardance, was approximated according to the van Krevelen empirical relationship [21]:

$$LOI = 17.5 + 0.4CR_{850} \tag{1}$$

where *CR$_{850}$* is the char yield in weight % at 850°C.

Dynamic mechanical analysis (DMA) and stress relaxation experiments were carried out on a Q800 DMA (TA Instruments) in tension mode using single cantilever (2-point bending).

The dimensions of specimens were $35 \pm 0.5$ mm $\times$ $8 \pm 0.2$ mm $\times$ $2 \pm 0.05$ mm. DMA testing with a heating rate of 3°C/min in the 30 – 250°C range, frequency of 1 Hz and amplitude of 15 µm was utilised to measure the storage and loss moduli as functions of temperature and identify the glass transition temperature. Stress relaxation experiments were conducted at five isothermal temperatures of 175°C, 180°C, 185°C, 190°C, and 195°C. The specimens were preloaded with a force of 1 mN and subsequently deformed to an applied strain of 2 % after equilibration to the desired isothermal temperature. 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. Results and discussion

### 3.1 Synthesis of BH-A

Successful synthesis of the benzoxazine monomer based on bis (4-hydroxyphenyl) disulphide and aniline – represented in **scheme 1** – is confirmed by FTIR results (**Figure 1**). 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. CH$_2$ 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.

**Figure 1**. FTIR spectrum of BH-A.

*3.2 Polymerisation and thermomechanical characterisation*

The polymerisation of BH-A is confirmed by the disappearance of key benzoxazine monomer bands at 1230 and 934 cm$^{-1}$ in the FTIR spectrum of polyBH-A (**Figure 1**). The ring-opening polymerisation reaction is shown in **scheme 2**. The DSC 10ºC/min dynamic thermograms of BH-A and polyBH-A are shown in **Figure 2**, indicating a monomer glass transition temperature of 25°C, polymerisation onset at 110°C, symmetrical cure exotherm due to ring-opening polymerisation of benzoxazine with a single peak at 192°C, and $T_g$ of 155°C for the cured polymer. The measured heat of reaction determined using a sigmoidal baseline for integration of the heat flow signal is 206 J/g.

**Scheme 2**. Ring-opening polymerisation of BH-A

**Figure 3** 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 [22]. The glass transition temperature of polyBH-A determined by the peak of tan delta is 178°C. The difference between this value and that measured by DSC is attributed to differences in inherent frequency of the measurement, in thermal lag due to sample size and in the type of excitation.



**Figure 2**. DSC thermograms of BH-A and polyBH-A showing monomer $T_g$ of 27°C, cure enthalpy and polymer $T_g$ of 155°C.

**Figure 3**. Dynamic mechanical scan of polyBH-A showing storage modulus, loss modulus and tan delta.

The result of thermogravimetric analysis of polyBH-A is illustrated in **Figure 4**. 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 [17]. PolyBH-A features a high char residue of 57.4% at 850°C which, according to Eq.1, 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 [23], with the greatest majority of benzoxazine formulations having values below the level achieved by polyBH-A [23]. The intrinsic flame retardance of polyBH-A is attributed to the presence of many aromatic groups in the polymer structure, as shown in **scheme 2**.

**Figure 4**. TGA thermogram of polyBH-A.

*3.3 Stress relaxation*

The isothermal stress relaxation behaviour of polyBH-A is shown in **Figure 5**(a) and the normalised stress relaxation data in **Figure 5**(b). 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 6** 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.

(a)



(b)

**Figure 5**. Stress relaxation curves of polyBH-A. (a) Relaxation modulus versus time (b) Normalised relaxation modulus versus time.

The complex rubbery modulus of polyBH-A from dynamic single frequency temperature ramp DMA results shown in **Figure 3**, 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 $10^{12}$ Pa.s, corresponding to a relaxation time of 201800 s. $T_v$ is determined as the temperature at which the Arrhenius dependence reported in **Figure 6** 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 [4,24] 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 [5]. Like other metathesis vitrimers, $T_v$ of polyBH-A is below its $T_g$ of 155°C, meaning a high potential of stress relaxation is frozen in the material when the temperature is below the $T_g$. Upon reaching the glass transition temperature, fast dynamic bond exchange is triggered, enabling reprocessing to be carried out.



**Figure 6**. Arrhenius temperature dependence of relaxation time

*3.4 Self-healing*

The surface profiles of scratched polyBH-A measured before and after healing at 190°C for 15 minutes are shown in **Figure 7.** The scratch has an approximate width of about 100 μm and a depth of about 25 μm ad its lips 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 1**. 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 fully compatible with composite manufacturing strategies.



**Figure 7**. Surface profiles of unhealed and healed polyBH-A specimen.

**Table 1.** Surface areas affected by scratching before and after healing of polyBH-A.

|  | Unhealed specimen | Healed specimen | % Recovery |
|---|---|---|---|
| Lips ($\mu m^2$) | 2694 | 213 | 92.1 |
| Valley ($\mu m^2$) | 2542 | 435 | 82.9 |
| Overall ($\mu m^2$) | 5236 | 648 | 87.6 |

## 4. Conclusions

The benzoxazine system reported in this work, coded polyBH-A, is the second benzoxazine vitrimer to be successfully synthesised by the cost-effective solventless one-pot method involving Mannich condensation, with the advantage of being the first high-temperature benzoxazine vitrimer formulated using this strategy. It 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 $T_{d5\%}$ of 293°C. 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 applications for aerospace, which aligns with the future requirements for matrix system of sustainable composites for the aerospace, marine and energy sectors.

## Acknowledgements

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