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Benzoxazine/amine-based polymer networks featuring stress-relaxation and reprocessability

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Amines as additives in benzoxazines are known to beneficially affect the polymerization temperature and furthermore to allow for partially reversible reaction steps yielding however a non-dynamic polybenzoxazine network. This contribution proves that the polymerization behavior of a two-component polymer of the polyetheramine Jeffamine[®] ED-600 and a bisphenol-A-based benzoxazine features stress-relaxation and reprocessability usually known from vitrimers. With the aim to gain a deeper understanding of the material properties of this system and the corresponding polymer structure, the reaction mechanism of a monofunctional benzoxazine and monoamine model system was studied revealing at first primary, and then secondary amine induced opening of oxazine rings, leading at first to linear polymer chains and then to covalently crosslinked networks. Both consist of repeated phenolic benzoxazine/amine motifs with permanently incorporated polyetheramine chains that do not impact the mechanical properties, compared to pure polybenzoxazine. Thermal, spectroscopic, and extraction analyses show that the addition of Jeffamine[®] reduces the polymerization temperature and introduces material properties such as reprocessability at the same time. Stress-relaxation measurements support the assumption that the reprocessability point to vitrimer-like molecular processes. The material shows rapid stress-relaxation of up to 11 s, a corresponding bond-exchange activation energy of 146 kJ/mol, and a topology freezing temperature of 97°C.

KEYWORDS

benzoxazine, vitrimer network, polyetheramine (PEA), stress-relaxation behavior, reprocessability

1 Introduction

Materials research and development in the field of thermosets encounters an almost inexhaustible potential for innovations and improvements in the chemistry of polybenzoxazines. Characterized by design flexibility at the molecular level and thus a broad spectrum of physical and chemical properties at the macroscopic level, benzoxazines form a class of thermosets whose properties outperform those of typical phenols and epoxides. (Ishida and Agag, 2011).

Despite having tremendous advantages in terms of chemical and mechanical stability, the biggest shortcoming of thermosets is their inability to be malleable after polymerization

due to their three-dimensionally crosslinked molecular structure. This strongly limits the possibilities of reuse and recycling, especially when they are used in combination with reinforcing fibres. (Witik et al., 2013). To overcome these drawbacks, vitrimers open up new opportunities for the sustainable and smart use of thermosets. Vitrimers are associative covalent adaptive networks and form a new polymer class alongside thermosets and thermoplastics. (Montarnal et al., 2011; Fortman et al., 2018). Covalent adaptive networks are defined by reversible chemical bonds that allow a temporary or permanent change in the network structure through an appropriate stimulus, such as temperature. This reaction is macroscopically associated with a change in the stress-strain state in the plastic region of the material without loss of network integrity or density. (Kloxin et al., 2010). Hence, this ability allows thermosets to overcome their limitation and make them malleable, healable and, depending on the system, recyclable. (Luzuriaga et al., 2016).

Benzoxazines featuring vitrimeric properties pose a challenge due to the high thermal properties of benzoxazines and the temperature range for vitrimeric behavior between the glass transition temperature and the initial degradation of the polymer. (Anagwu et al., 2022). Up to now, covalent adaptive benzoxazine systems are based on boronic ester exchange reaction (Gulyuz et al., 2022; Wang et al., 2022), dioxaborolane metathesis (Bo et al., 2022), disulfide metathesis (Trejo-Machin et al., 2020), transcarbamoylation (Wen et al., 2022) and transesterification (Adjaoud et al., 2022).

A characteristic of vitrimers is their reprocessability, which can be based on the dynamic exchange reactions, but it is well known that such properties are not exclusive to vitrimers. (Arslan et al., 2018). However, the reprocessability is often presented in crushing- or cracking-reforming cycles, evaluated with mechanical tests. For true vitrimers, Wang et al., 2022 show that polybenzoxazines can reprocess via dynamic boronic ester bonds. In tensile tests, strengths at break decreased by up to 15% after three cycles. Ručigaj et al., 2020 developed a diphenolic acid-based benzoxazine. The reprocessability was determined by compact tensile tests. After a single cycle, specimens achieved 40%–50% of the fracture toughness of virgin specimens. Other approaches to develop polybenzoxazine-based reprocessable polymers are realized, for example, via a cardanol-based polybenzoxazine vitrimer (Trejo-Machin et al., 2020), with biobased poly (benzoxazine-co-urethane) (Sriharshita et al., 2020), with isosorbide-based polybenzoxazine (Adjaoud et al., 2022), and by means of a catalyst-free trans-esterification in benzoxazines (Adjaoud et al., 2021). In contrast to the chemistry of the systems, the reprocessability of benzoxazine/amine polymers has not been studied, yet.

Polymerization of benzoxazines in presence of amines have been investigated by several groups in the last years, mainly with the aim to lower benzoxazines high polymerization temperatures. (Sun et al., 2015; Zong and Ran, 2019; Zhang et al., 2020). However, the resulting structures are reported to strongly depend on the chemical reactivity of the respective benzoxazine and amine. (Sun et al., 2015; Zong and Ran, 2019; Zhang et al., 2020). Mechanistical studies of benzoxazines with amines suggest the formation of several consecutive reaction steps with increasing reaction temperature that partially can be reversible. The total reaction is, however, reported to be irreversible and non-dynamic. (Sun et al., 2015). Furthermore, oligomeric amines such as the polyetheramine Jeffamine® are used for toughening aside the

impact on polymerization temperature. (Yagci et al., 2009; Gonçalves et al., 2022; Gulyuz et al., 2022). The synthesis of a polyetheramine-based main chain polybenzoxazine was developed by Agag et al. (2010). Typically, the polyether diamine is incorporated into the network structure by using the amine as the amine component for the benzoxazine monomer synthesis. The resulting benzoxazine consists of linear oligomers which are liquid at room temperature and can be thermally crosslinked into flexible thermosets. Based on this pioneering work, further research has been conducted. Khan et al., 2018 investigated the gas permeability of main chain polybenzoxazines based on Jeffamines® of different molecular weights. Liu et al., 2016 reported a polyetheramine-bearing polybenzoxazine with thermally induced shape memory properties. Various responsive Jeffamine®-based polybenzoxazines have been reported. However, the responsive effects, such as self-healing, did not result from the presence of Jeffamine®, but from additional functional groups allowing for, e.g., light-induced oxoketene formation (Arslan et al., 2018), boronic ester exchange reactions (Gulyuz et al., 2022), photoinduced dimerization of coumarin (Kiskan and Yagci, 2014) or supramolecular hydrogen-bond formation (Ručigaj et al., 2020). Gonçalves et al. (2022) described a benzoxazine and cardanol-doped polyaniline coating for corrosion protection. In their work, Jeffamine® acts as catalytic curing agent and flexibilizer. Puozzo et al. (Puozzo et al., 2022) used the flexibilizing properties of high molecular weight Jeffamine® to prepare an elastomeric benzoxazine for pressure-sensitive applications. So far, a neat benzoxazine/polyetheramine copolymer has not yet been described to yield a covalent adaptive network.

Against this background, this contribution presents a benzoxazine/polyetheramine based polymer network resulting from bisphenol-A and aniline-based benzoxazine (BA-a) and Jeffamine® as a polyetheramine that exhibits vitrimeric properties. Stress-relaxation measurements and multiple reprocessability proved the dynamic character of the benzoxazine/amine copolymer. The impact of the polymerization parameters was studied on overall but in particular vitrimeric properties. With the aim to elucidate structure-property relation, monofunctional benzoxazine monomer with primary monoamine was studied as a model reaction. In a second step, polymer networks resulting from bifunctional benzoxazines and diamines were characterized in terms of crosslinking densities and the state of polyetheramine incorporation into the polybenzoxazine network. Insights regarding the molecular structure were then correlated to derive a reaction mechanism and the corresponding polymer structure of the vitrimer-like benzoxazine/amine network.

2 Experimental part

2.1 Materials

Bisphenol-A and aniline-based benzoxazine, Araldite® MT 35600 (BA-a) was provided by Huntsman Advanced Material (Huntsman International LLC, Texas, United States). *para*-cresol, aniline, Jeffamine® M-600 and Jeffamine® ED-600 were purchased from Merck KGaA (Darmstadt, Germany). Paraformaldehyde,

Na₂SO₄, ethanol and butan-2-one were purchased from Carl Roth GmbH & Co. KG (Karlsruhe, Germany). Chloroform and NaOH were supplied from VWR International GmbH (Darmstadt, Germany). CDCl₃ and DMSO-d₆ were purchased from Deutero GmbH (Kastellaun, Germany). All chemicals were used without further purification. Casting moulds for the sample manufacturing were coated with the release agent ACMOScoat 82-9101 (ACMOS CHEMIE KG, Bremen, Germany).

2.2 Synthetic procedures and sample preparation

2.2.1 Synthesis of *para*-cresol and aniline-based benzoxazine (*pC*-a)

pC-a was synthesized according to Takeichi *et al.* (Takeichi *et al.*, 2004) *para*-cresol (25.0 g, 231 mmol), aniline (19.6 g, 210 mmol), and paraformaldehyde (13.9 g, 462 mmol) were placed in a round bottom flask under an atmosphere of N₂, slowly heated to 100°C and kept at that temperature for 1 h. The resulting pale-brown liquid was cooled to room temperature, dissolved in 200 mL of chloroform, and washed three times with 150 mL of aqueous NaOH (1 mol L⁻¹). The organic phase was dried over Na₂SO₄, and the solvent was removed under reduced pressure at 60°C. The resulting pale-brown oil that can solidify with time, was dissolved in 400 mL boiling ethanol, and stored for 24 h at -20°C for recrystallization. The resulting white crystals were melted at 75°C and dried under high vacuum for 30 min.

pC-a was obtained as a pale-yellow solid, 32.6 g (yield = 69%) ¹H-NMR (600 MHz, DMSO-d₆, 296 K): δ/ppm = 7.23 (t, *J* = 8.0 Hz, 2H, *H*^{ar}), 7.11 (d, *J* = 7.7 Hz, 2H, *H*^{ar}), 6.91 (s, 1H, *H*^{ar}), 6.88 (d, *J* = 8.2 Hz, 1H, *H*^{ar}), 6.85 (t, *J* = 7.3 Hz, 1H, *H*^{ar}), 6.62 (d, *J* = 8.2 Hz, 1H, *H*^{ar}), 5.40 (s, 2H, H^{OCH₂N}), 4.60 (s, 2H, H^{CCH₂N}), 2.19 (s, 1H, H^{CH₃}). ¹³C{¹H}-NMR (151 MHz, DMSO-d₆, 296 K): δ/ppm = 151.7, 147.9, 129.1, 128.1, 127.3, 120.9, 120.4, 117.3, 115.9 (C^{ar}), 78.6 (C^{OCH₂N}), 48.9 (C^{CCH₂N}), 20.2 (C^{CH₃}). IR-ATR: wavenumber/cm⁻¹: 3042 (C^{ar}H), 3027 (C^{ar}H), 3013 (C^{ar}H), 2914, (CH₂/CH₃), 1600, 1579, 1493 (PhR₃), 1454, 1446, 1356, 1220 (C^{ar}OCH₂), 1204, 1168, 1141, 1119, 1042, 942 (oxazine ring), 915.

2.2.2 Copolymerization procedure of *pC*-a and Jeffamine[®]

An equimolar mixture of *pC*-a and Jeffamine[®] M-600 in a glass vial closed with a PP lid was mixed and stirred at 50°C in an oil bath for 13 days. For the following high-temperature cascade reactions (120°C, 150°C, 180°C) new mixtures of unreacted *pC*-a and Jeffamine[®] M-600 were heated in open glass vials and stored in a convection oven for 2 h for each single temperature step (Supplementary Scheme S1).

2.2.3 Copolymerization procedure of BA-a and Jeffamine[®]

BA-a and Jeffamine[®] ED-600 were mixed at molar ratios of 1: 0.25, 1:0.50 or 1:1 (BAa:Jeffamine[®]), liquefied and homogenized at 120°C in a convection oven (Heraeus 19 Function Line, UT 6 P/ UT 20 P, 250°C, Thermo Fisher Scientific Inc., Waltham, United States). The mixture was degassed for 30 min in a vacuum oven (Heraeus Vacutherm VT6025, Thermo Fisher Scientific Inc., Waltham, United States). The BA-a/Jeffamine[®]

mixtures were filled in casting molds and polymerized in a convection oven at 120, 150, and 180°C, respectively. The neat BA-a was polymerized according to the manufacturer information at 180 and 200°C. For the further course of this work, the polymerization conditions, as shown in Table 1, will be indicated in roman numbers I–V. The sample composition will be abbreviated as BA-a/J for mixtures of BA-a and Jeffamine[®] ED-600 and *pC*-a/J for mixtures of *pC*-a with Jeffamine[®] M-600. The appropriate molar ratio (benzoxazine:amine) will be indicated in brackets after the abbreviation. Specimens of the resulting polymers were cut using a wet cut-off sander (Conrad Apparatebau GmbH, Clausthal-Zellerfeld, Germany).

2.3 Material characterization

2.3.1 Spectroscopic measurements

NMR experiments were performed on an AVANCE NEO 600 MHz spectrometer (Bruker Corporation, Massachusetts, United States). All spectra were referenced against the residual solvent signal of the respective NMR solvent. IR-ATR spectra were recorded on an ALPHA II (Bruker Corporation, Massachusetts, United States) with a platinum-ATR unit. Recording range: 400–4000 cm⁻¹; resolution: ±2 cm⁻¹; 32 scans.

2.3.2 Gel content determination

Polymerized samples of BA-a/Jeffamine[®] ED-600 copolymers, as well as reference samples of neat BA-a were subjected to Soxhlet extraction. Prior to the experiments, the Soxhlet sleeves were dried for 24 h at 80°C in a convection oven. Crushed polymer samples were extracted for 24 h with butan-2-one (MEK, 100 mL) (oil bath temperature 100°C). Afterwards, the solvent was removed under reduced pressure and the extracts as well as the residual polymer samples were dried at 60°C to mass constancy in a vacuum oven. The gel contents were determined (Eq. 1) and the mass-losses in the sleeves were related to the masses of amine originally placed in the polymer mixture (Eq. 2) from mass *m*, amount of substance *n*, molar mass *M*, of initial sample before extraction *S_i*, or final residual sample in the sleeve after extraction and drying *S_f*.

$$\text{gel content} = \frac{mS_i - mS_f}{mS_i} \quad (1)$$

$$\frac{\Delta m_{\text{extr.}}}{m_{\text{amine}}} = \frac{(mS_i - mS_f)}{\left(\frac{m_{\text{amine}} \cdot M_{\text{amine}}}{n_{\text{BA-a}} \cdot M_{\text{BA-a}}}\right) S_i} \quad (2)$$

2.3.3 Thermal analysis

Polymerization behavior was characterized with differential scanning calorimetry (DSC), using a Discovery DSC (TA Instruments, New Castle, Delaware, United States). The sample weight was between 1.5 mg and 3 mg, the heating rate was 10 K/min from -20 to 350°C. Thermogravimetric analysis (TGA) measurements were conducted under ambient atmosphere, using a TGA Q5000 V3.17 Build 265 calorimeter (TA Instruments, New Castle, Delaware, United States). The sample weight was between 1.2 and 3 mg and the measurements were performed with a heating rate of 10 K/min from 34 to 800°C.

TABLE 1 Heating temperatures and durations in the polymerization of benzoxazine/amine mixtures and neat benzoxazine. The table shows three formulations (column) and the used polymerization program (row). The individual samples are defined by the row. A missing formulation in the row means that the sample was not examined.

Benzoxazine formulations			Temperature/°C	Time/h
Bifunctional Benzoxazine	Bifunctional Benzoxazine/Jeffamine ED-600	Monofunctional Benzoxazine/Jeffamine M-600		
BA-a-I	BA-a/J-I	pC-a/J-I	120	2
BA-a-II	BA-a/J-II	pC-a/J-II	120, 150	2, 2
	BA-a/J-III		120, 150	2, 4
BA-a-IV	BA-a/J-IV	pC-a/J-IV	120, 150, 180	2, 2, 2
BA-a-V			180, 200	2, 2

2.3.4 Thermo-mechanical testing

Thermo-mechanical behaviour was characterized by dynamic mechanical analysis (DMA) with a RSA-G2 Solid Analyzer (TA Instruments, New Castle, Delaware, United States). The samples were tested in the dual cantilever mode, at a frequency of 1 Hz, from 25 to 250°C, using a heating rate of 2 K/min. The specimen size was 50 mm × 10 mm × 3 mm.

2.3.5 Stress-relaxation behavior

Stress-relaxation measurements were performed on rectangular specimens (50 mm × 10 mm × 3 mm), polymerized at 120°C for 2 h and 150°C for 4 h (BA-a/J-III), with a Discovery Hybrid Rheometer (TA Instruments, New Castle, Delaware, United States) in torsion-mode. The specimens were selected because they showed the best mechanical properties in preliminary tests and parametric studies. The samples were heated to the respective temperature (BA-a/J: 120°C, 130°C, 140°C, 150°C, 160°C, 170°C) and were kept at that temperature for 5 min. Then, a strain of 1.5% for BA-a/J was applied and the decrease in tension was recorded as a function of time. Relaxation times $\tau(T)$ were determined, as defined as the time by which the original relaxation modulus was reduced to a factor of 1/e. According to the Arrhenius law (Eq. 3), with τ^0 as a factor describing the bond lifetime and R as the gas constant, $\ln \tau(T)$ values were plotted against the inverse temperature T^{-1} , and from the slope of the linear regression the activation energy E_a of the exchange reactions was determined.

$$\ln(\tau(T)) = \ln(\tau^0) + \frac{E_a}{R \cdot T} \quad (3)$$

2.3.6 Determination of reprocessing properties

To investigate the reprocessability and remoulding ability of the material, specimens were pressed multiple times in a manual, hydraulic bench-top laboratory press (Paul-Otto Weber GmbH, Remshalden, Germany). The two-part mould was made of aluminium alloy and five samples, each 50 mm × 10 mm × 3 mm, were produced in one operation. The semi-permeable release agent was refreshed after three press-cycles. In the press, original or healed materials were crushed into 1–3 mm sized particles. The open mould was heated to 155°C for 20 min, before the upper mould was inserted. The samples were pressed for 30 min at 155°C with 15 kN (approximately 6 MPa at each

sample). Three series of tests were carried out: one, three and five crushing-pressing cycles. To evaluate the mechanical recycling or the healing ability, the original and pressed samples were tested in a three-point bending test in accordance with DIN EN ISO 604, using a Zwick/Roell Z020, 20 kN (ZwickRoell GmbH & Co. KG, Ulm, Germany).

3 Results and discussion

3.1 Reaction mechanism of benzoxazine with amines

The presence of amines during the ring opening reaction of benzoxazines is known to affect the polymerization progress in particular to decrease the polymerization temperature. However, the resulting structures are reported to strongly depend on the chemical reactivity of the respective benzoxazine and amine. Furthermore, it is not understood if the amines act as catalyst, or get incorporated into the polymer network. (Sun et al., 2015; Zong and Ran, 2019; Zhang et al., 2020). It is assumed that the benzoxazine/amine reaction follows the formation of several consecutive reaction steps with increasing reaction temperature. However, type of starting materials and applied reaction conditions affect the resulting molecular structure and reversibility of the single reaction steps. With the aim to understand the mechanism of the polymerization reaction a model system was studied. The insight in reaction pathways was then transferred to the bifunctional benzoxazine/amine system.

3.1.1 Molecular structure determination with a benzoxazine/amine model system

A monofunctional benzoxazine based on *para*-cresol and aniline (pC-a) was used as a model system with monoamine Jeffamine® M-600 to elucidate the reaction mechanism and to unveil the resulting molecular structures. Due to the monofunctional nature of the benzoxazine and the single primary amine group of Jeffamine®, the formation of low molecular weight products was observed that were soluble in common solvents and that were thus accessible to conventional 2D-NMR spectroscopy. At the same time, the system was assumed to inherit similar chemical reactivity to the insoluble, high molecular weight product resulting from bifunctional BA-a and diamine Jeffamine® ED-600.

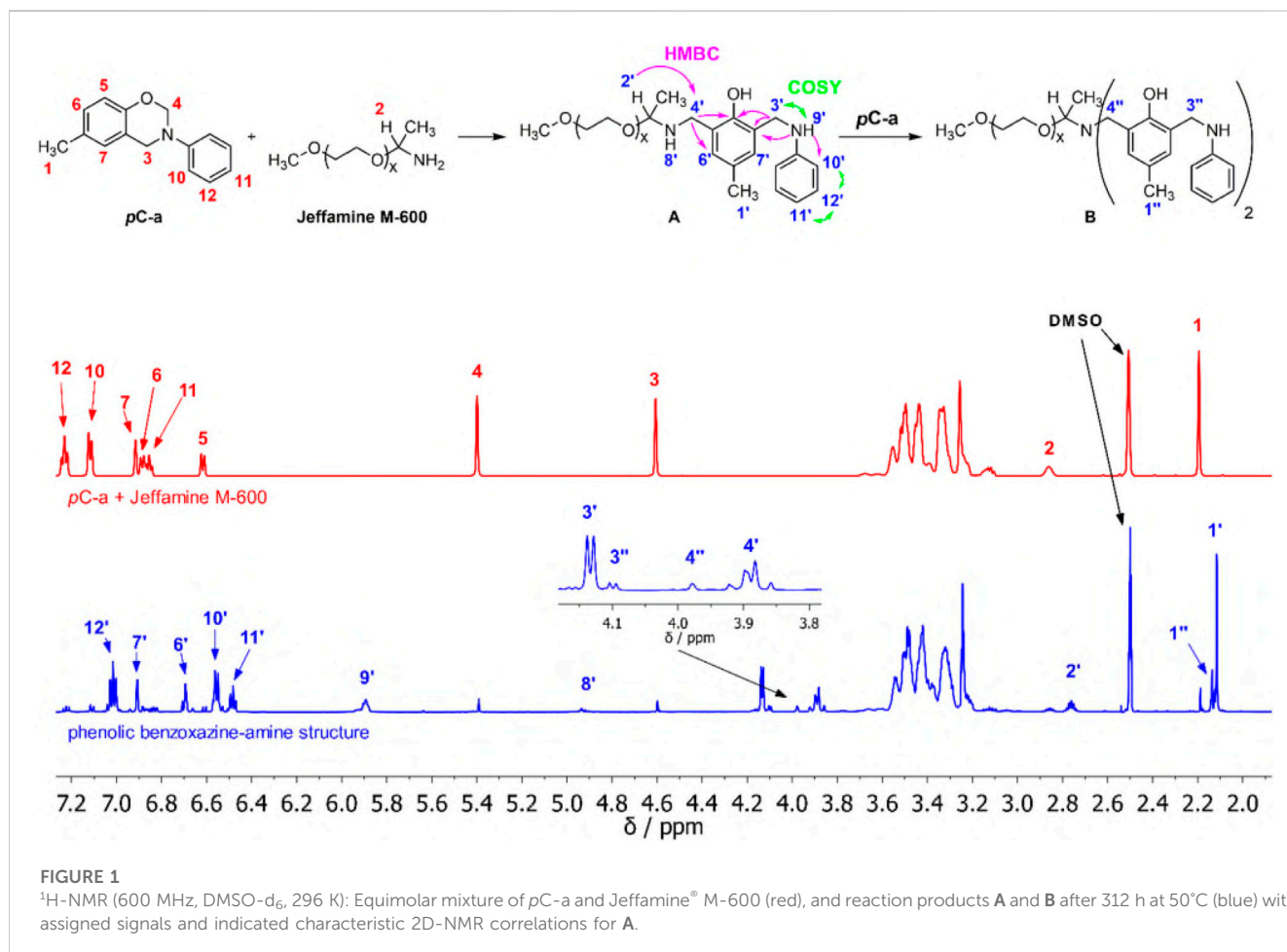
The reaction of *pC*-a and monoamine was carried out in bulk to avoid influences from a solvent. Previous mechanistic studies in the literature suggest that several consecutive reaction steps occur with increasing reaction temperature. (Sun et al., 2015). To be able to observe as many of these steps as possible, the equimolar reaction of *pC*-a and Jeffamine[®] M-600 was first investigated at 50°C, the empirical lowest temperature at which a homogeneous mixture could be obtained. The reaction was monitored in regular intervals via NMR spectroscopy to ensure high conversion of the reactants. The integrals of the signals in the ¹H-NMR spectra were normalized by the sum of the integrals of signals corresponding to all methyl groups 1 and 1' (and 1'') present. The low reaction temperature resulted in a very slow reaction rate with saturation of conversions at 92% for *pC*-a and of 85% for Jeffamine[®] M-600 after 13 days, respectively (Figure 1). A continuous integral decrease of the characteristic signals that were assigned to *pC*-a (methylene bridge-signals 3 and 4) and Jeffamine[®] M-600 (single-proton signal 2) indicated the opening of the oxazine ring and the consumption of Jeffamine[®]. At the same time new signals appeared that suggested the formation of a main product A (74% yield of *pC*-a) and a side product B (10% yield of *pC*-a).

The structure of A was solved using 1D- and 2D-NMR spectroscopy. The characteristic ¹H-NMR 1,2,4-trisubstitution pattern of the phenolic benzene ring in *pC*-a relative to the oxygen atom (doublets 5, 6, singlet 7) changed into a

tetrasubstitution pattern (singlets 6', and 7'). Signals 3' and 4' correspond to the newly formed methylene bridges that formerly formed the oxazine ring and 2' corresponds to the single proton in the former Jeffamine[®]. A multitude of 2D-correlations prove the constitution of the ring-opened phenolic benzoxazine/amine structure (benzoxazine:amine = 1:1), in which the former amine is attached via methylene bridge 4' in *ortho*-position to the hydroxyl group and which thus has a 1, 2, 4, 6-tetrasubstituted phenolic benzene ring. Signals 8' and 9' show the formation of two secondary amine groups in the product. Signals 10' (doublet 2 H), 11' (triplet 1 H) and 12' (triplet 2 H) with corresponding COSY correlations indicate the intact monosubstituted *N*-phenyl moiety attached to 9'.

Due to its low quantity in the product mixture, the structure of side product B could not be fully described. However, chemical shifts, multiplicities, and relative integrals of signals 3'' (doublet 2 H) and 4'' (singlet 2 H) suggest the presence of molecule B that was formed in a reaction of A with a second equivalent of *pC*-a (benzoxazine:amine = 2:1). This assumption is further supported by the fact that a higher conversion was detected for *pC*-a than for Jeffamine[®] M-600. This secondary amine induced opening of oxazine-rings has also been recently reported in literature. (Zhang et al., 2020).

Sun et al. (2015) reported a mechanism for the reaction of benzoxazines with amines. A simplified version of this mechanism is



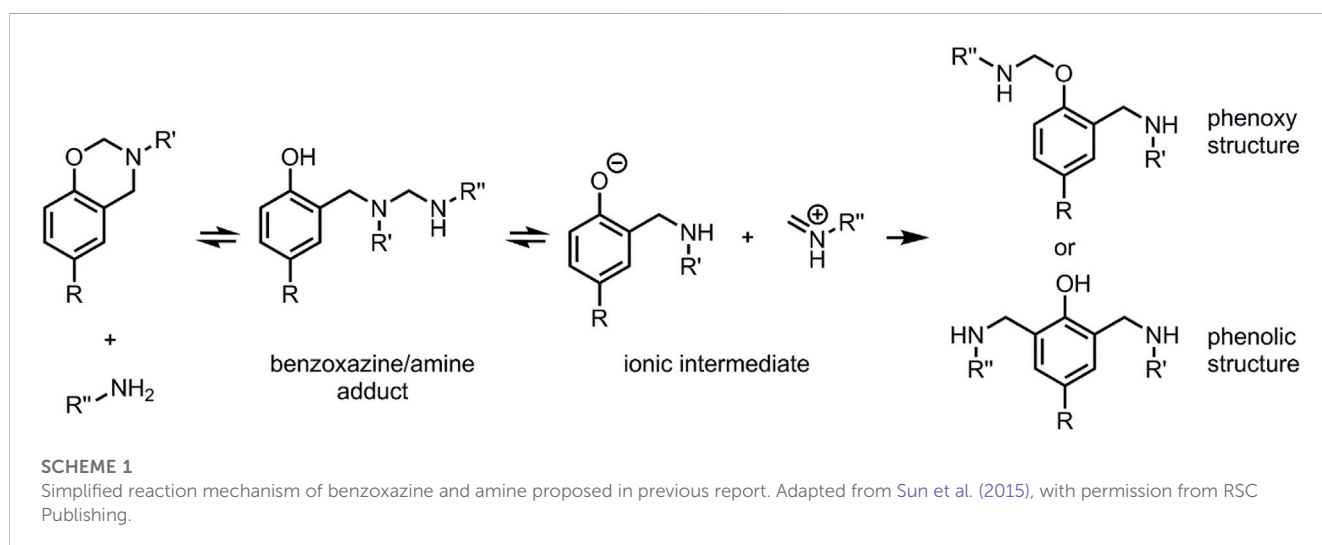
shown in Scheme 1. In a first step, the lone pair of the amine attacks the electrophilic carbon atom of the OCH₂N moiety of the benzoxazine, inducing opening of the oxazine ring and leading to a covalently bonded benzoxazine/amine adduct. This adduct thermally decomposes at higher temperatures into ionic pair of phenolate and iminium ion. Two potential different final products are reported. On the one hand, the reaction of phenolate oxygen with the iminium ion can lead to a phenoxy structure. On the other hand, electrophilic aromatic substitution of the aromatic *ortho*-hydrogen of the phenolic benzene ring with the iminium ion can lead to a phenolic benzoxazine/amine structure. In literature, it is assumed that the reversible reactions of the adduct and intermediate product result a reaction equilibrium that breaks down by further heating with a subsequent crosslinking process. (Wang et al., 2016).

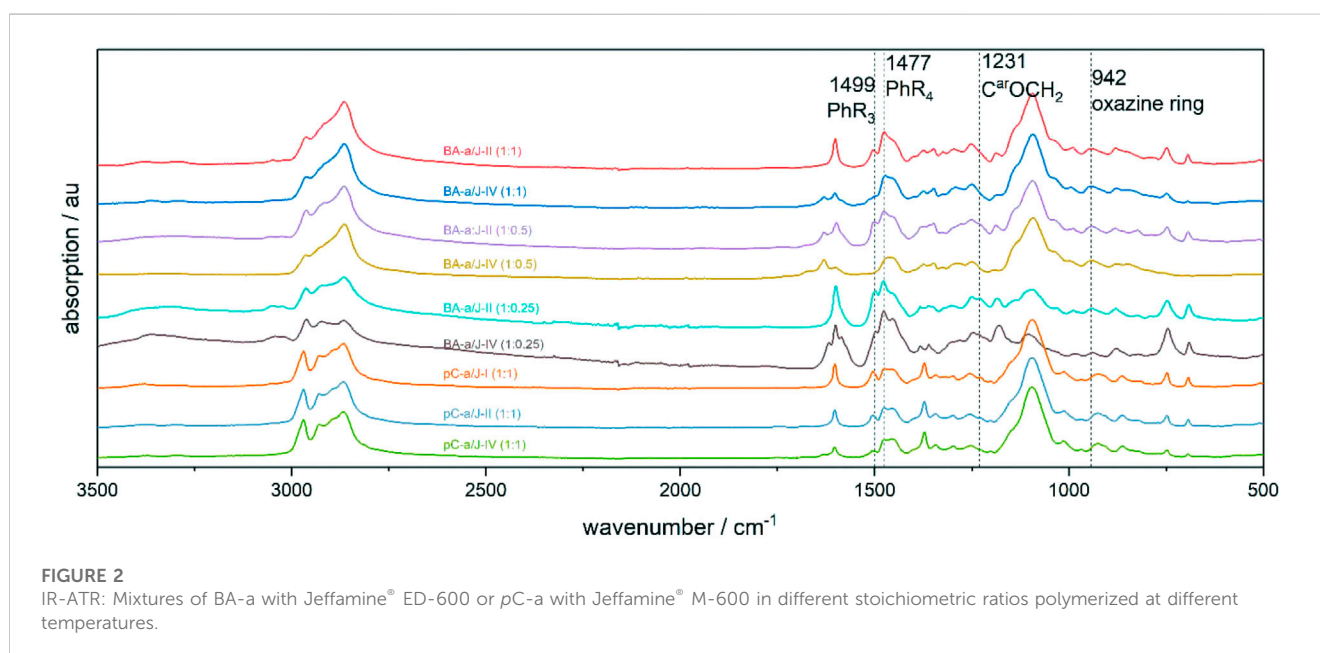
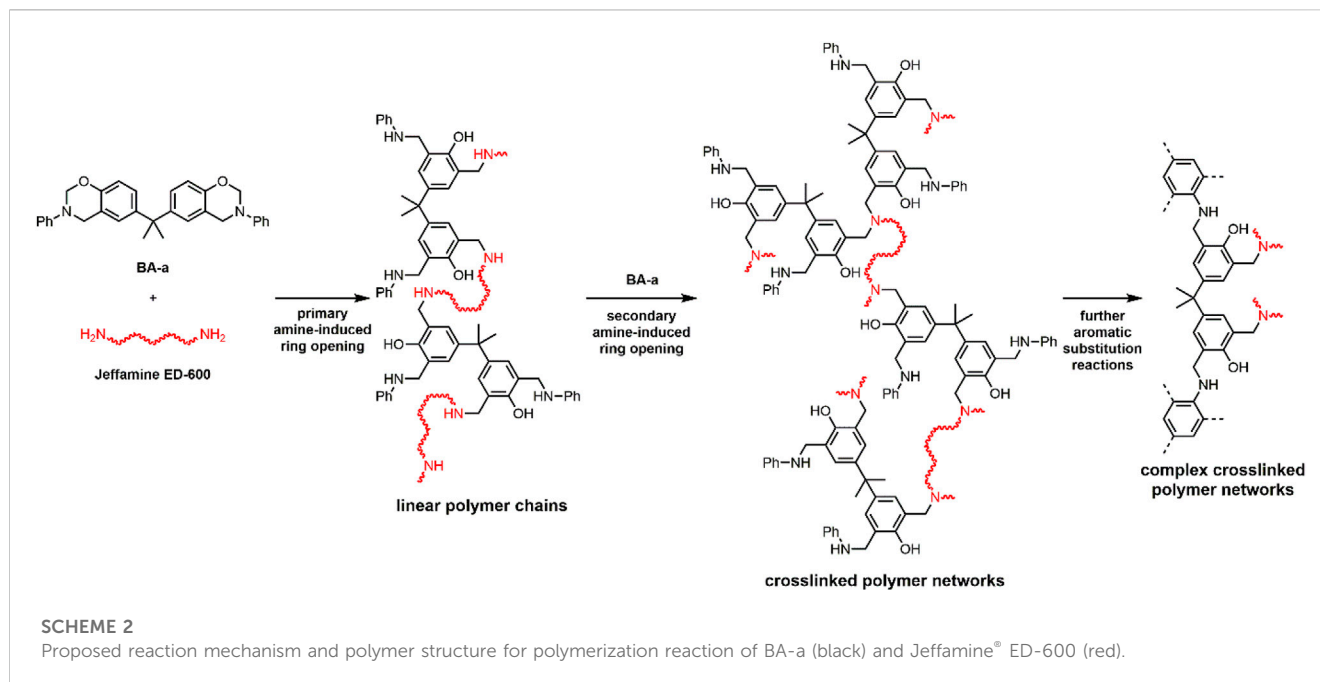
In contrast to the mechanism suggested by Sun *et al.* and Wang *et al.*, solely the formation of **A** and **B** was observed, which are analogous to the reported phenolic structures. Neither the benzoxazine/amine adduct, nor the ionic intermediates were observed at any stage of the reaction, despite the very low reaction temperature at 50°C. However, they can be assumed as logical intermediates or transition states. The evidence of analogous benzoxazine/amine structures in the literature was gathered in solution-based reactions. (Sun et al., 2015; Zong and Ran, 2019). It is assumed that potential intermediates resulting from the *pC*-a/amine reaction possess a lower thermodynamic stability in absence of a solvent favouring the formation of product **A**. The observed effects might also be explained by electronic influences of the polyether chain on the stability of the intermediates. The proposed phenoxy structure was not observed here, either. The formation of this structure was recently reported to be favoured in *ortho* blocked benzoxazines. (Zhang et al., 2019). The absence of such *ortho*-blocking substituents in *pC*-a led to an exclusive formation of the phenolic structure. The newly formed secondary amine group 8' itself can induce opening of further oxazine rings of unreacted *pC*-a, leading to phenolic benzoxazine/amine structure **B**. This has also been reported by Zhang et al., 2020. **A** is formed in higher amounts than **B**, which can probably be explained by steric hinderance of secondary amine 8' through the polyether chain. At higher temperatures and at different stoichiometric ratios of benzoxazine and amine the secondary amine induced reaction may play a more important role.

The reaction was also studied at higher reaction temperatures in a cascade of three successive stages at 120, 150, and 180°C for 2 hours, respectively. At the first stage (120°C), phenolic products **A** and **B** are formed as determined at the low temperature experiment, as observed by the presence of all the characteristic signals in ¹H-NMR spectra (Supplementary Figure S1). At higher temperatures (up to 180°C), however, these signals decrease in magnitude and a multitude of further, broad signals are observed. These indicate the formation of various oligomers through a complex set of reactions. At the same time, the relative sums of integrals corresponding to aromatic protons decrease from 8 H (unreacted mixture of *pC*-a and Jeffamine[®] M-600) to 5 H at the last stage of the reaction. This indicates the occurrence of further substitution reactions, probably in the *N*-phenyl moieties of the former benzoxazine. (Martos et al., 2020). Another possible explanation for the observed effect is thermal degradation of the polymer accompanied by oxidation reactions in aromatic structures or evaporation of volatile aromatic fragmentation products like aniline. (Zhao et al., 2018). The reformation of free primary Jeffamine[®], as described in the literature for different amines (Zhang et al., 2020), was not observed, indicating the permanent incorporation of Jeffamine[®] into the reaction product.

3.1.2 Proposed polymer structure of BA-a/ Jeffamine[®] ED-600 systems

Based on the results of the model reaction (*pC*-a and Jeffamine[®] M-600), a general reaction polymerization mechanism and a polymer structure are proposed for the reaction between BA-a and Jeffamine[®] ED-600 (Scheme 2). In a first step, the primary amine groups in Jeffamine[®] ED-600 probably induce opening of the oxazine rings of BA-a, which leads to linear polymer chains, showing repeated phenolic benzoxazine/amine motives, analogous to **A**. The interaction between benzoxazine and primary amine reduces the overall polymerization temperature compared to the neat benzoxazine. The polymer chains are probably then crosslinked via secondary amine induced opening of oxazine rings. The crosslinking density presumably depends on the polymerization temperature and the stoichiometric ratio of benzoxazine and amine. Higher relative benzoxazine contents probably lead to increased crosslinking density. Further crosslinking reactions assumedly occur, for example, via substitution reactions in the





N-phenyl moieties (Martos et al., 2020) or other complex reactions, yielding a highly crosslinked three-dimensional polymer network.

3.2 Polymerization of benzoxazine/Jeffamine® mixtures

3.2.1 Network formation in benzoxazine/Jeffamine® polymers

Samples of BA-a/Jeffamine® ED-600 mixtures with stoichiometric benzoxazine:amine ratios of 1:1, 1:0.5 and 1:0.25 were polymerized at 120, 150°C for 2 h (BA-a/J-II) respectively, or at 120, 150, 180°C for 2 h

(BA-a/J-IV), respectively. The corresponding IR spectra of the BA-a/Jeffamine® ED-600 reaction products are qualitatively similar to those of the *pC*-a/Jeffamine® M-600 mixtures, thermally treated at the same conditions (Figure 2, Supplementary Figure S2). Especially the presence of the absorption band 1477 cm⁻¹, corresponding to the tetrasubstituted benzene ring, indicates the formation of similar phenolic benzoxazine/amine structures as observed in the model reaction. This further proves that the reaction of BA-a and Jeffamine® ED-600 and the model reaction of *pC*-a and Jeffamine® M-600 follow a similar reaction mechanism.

Above-mentioned polymerized samples of BA-a/Jeffamine® ED-600 mixtures, as well as reference samples of neat BA-a, polymerized

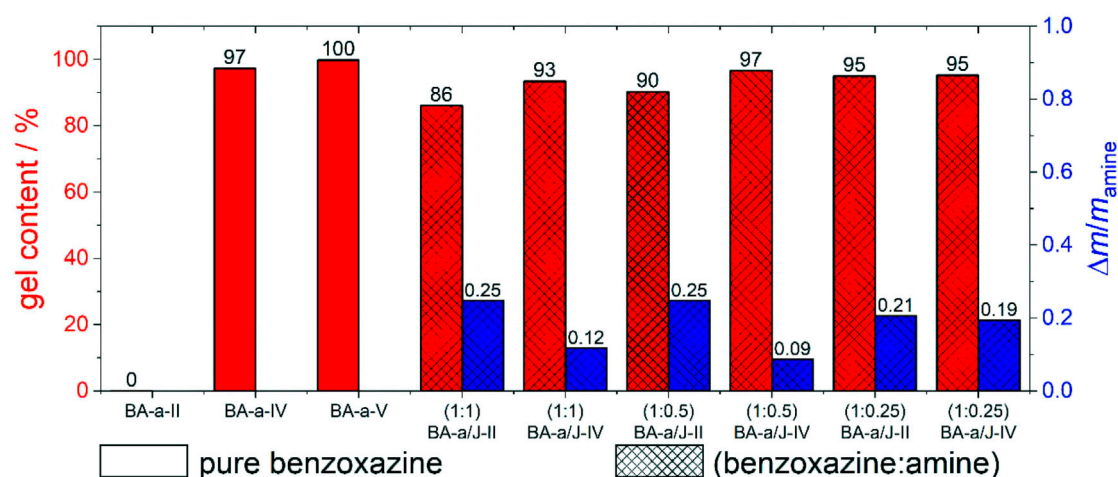


FIGURE 3

Gel content (red), and $\Delta m/m_{\text{amine}}$ ratios (blue) determined via Soxhlet extraction experiments for BA-a/Jeffamine[®] ED-600 mixtures of different stoichiometries (X:Y) (crossed pattern), and pure BA-a (no pattern) polymerized at different temperatures.

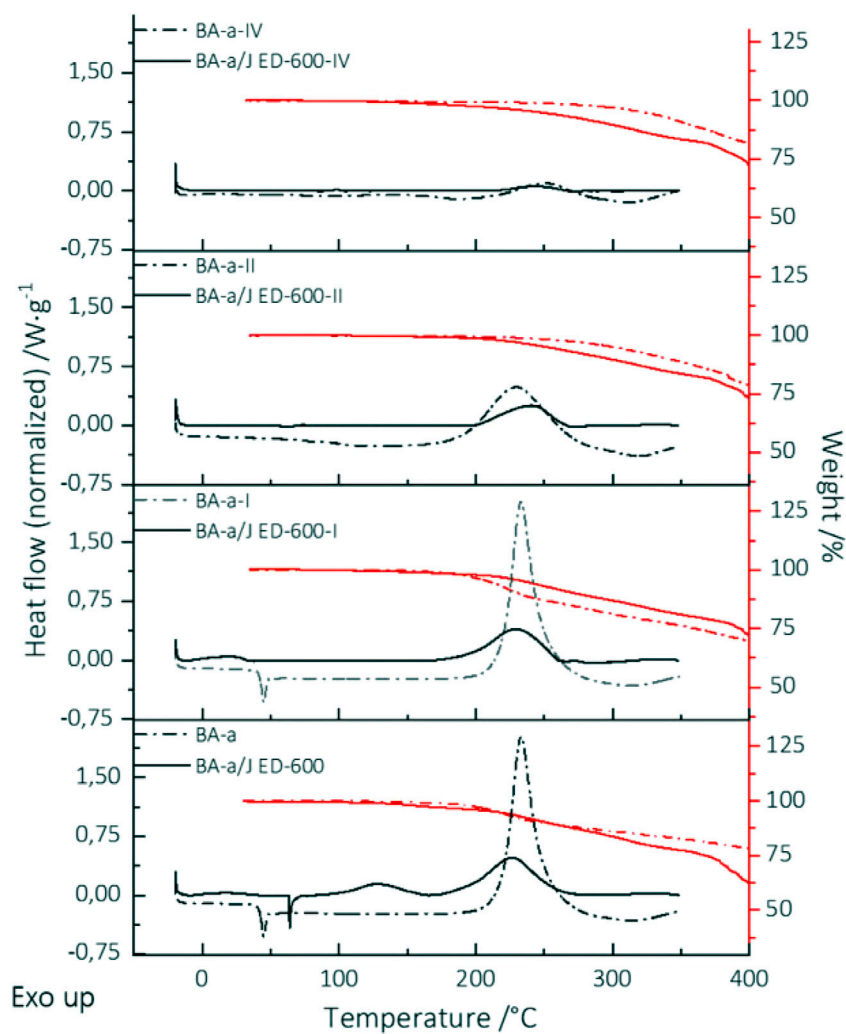
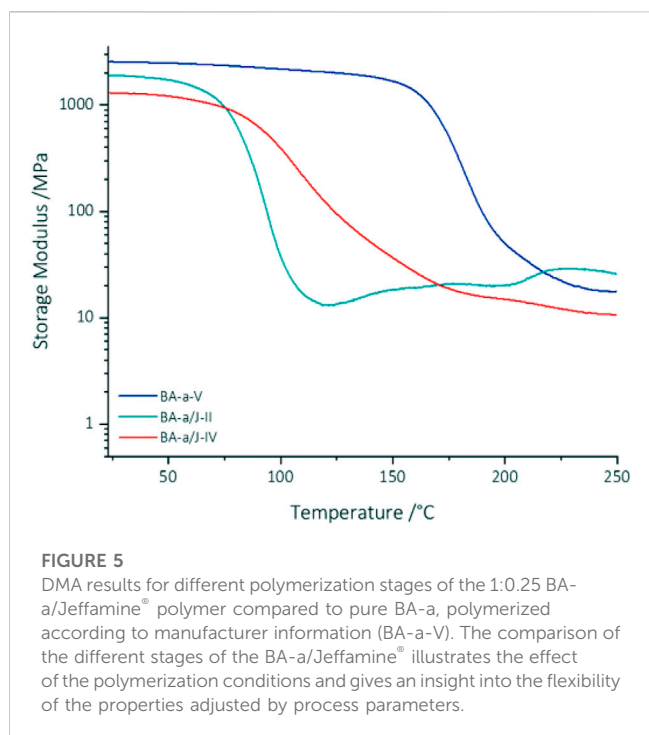


FIGURE 4

DSC and TGA thermograms for the BA-a/Jeffamine[®] ED-600 system and pure BA-a at different polymerization stages. The addition of Jeffamine[®] influences the polymerization behavior of the benzoxazine. The ring-opening reaction induced by Jeffamine[®] already occurs at 120°C and therefore generally reduces the residual enthalpy of the BA-a between 200°C and 250°C.



at either the same conditions (BA-a-II, BA-a-IV) or 180, 200°C for 2 h (BA-a-V), respectively, were subjected to Soxhlet extractions. The gel contents were calculated and the determined mass-losses during extraction were related to the masses of amine, $\Delta m/m_{\text{amine}}$, that were initially added to the respective polymer mixtures (Figure 3).

For the neat polymerized benzoxazine BA-a-II, a gel content of 0% is determined, indicating that the applied polymerization temperatures were too low to initiate polymerization. In contrast, all samples that included Jeffamine[®] (BA-a/J-II) show an unexpected high gel content of 86%–95%, indicating that polymerization takes place at low polymerization temperatures and includes already the secondary amine induced ring opening and by this crosslinking reaction at a significant degree. The sample with a benzoxazine:amine ratio of 1:1 shows the lowest gel content, which can probably be explained by a lower crosslinking density and a higher content of flexible polyether chains. Increasing the reaction temperature up to 180°C (BA-a/J-IV) leads to high gel contents of 93%–97% for all benzoxazine:amine ratios, indicating further progress of the polymerization reaction at these conditions. The reference samples of pure BA-a also showed high gel contents at polymerization temperatures above 180°C (BA-a-IV, BA-a-V). It can therefore be assumed that the observed gel content of the BA-a/J-IV samples at these high temperatures results from both, the network formation via benzoxazine/amine copolymerization and homopolymerization of residual unreacted oxazine rings of BA-a. With the aim to elucidate the role of the amine, the determined mass losses during extraction were related to the masses of amine that were initially placed in the respective reaction mixtures. The obtained $\Delta m/m_{\text{amine}}$ values reach up to 0.25 indicating that at least 75% of the amine remains in the polymer network, even in an assumed extreme case that the extracted material was pure Jeffamine[®]. However, spectroscopic analyses (Supplementary Figures S3, S4) show that

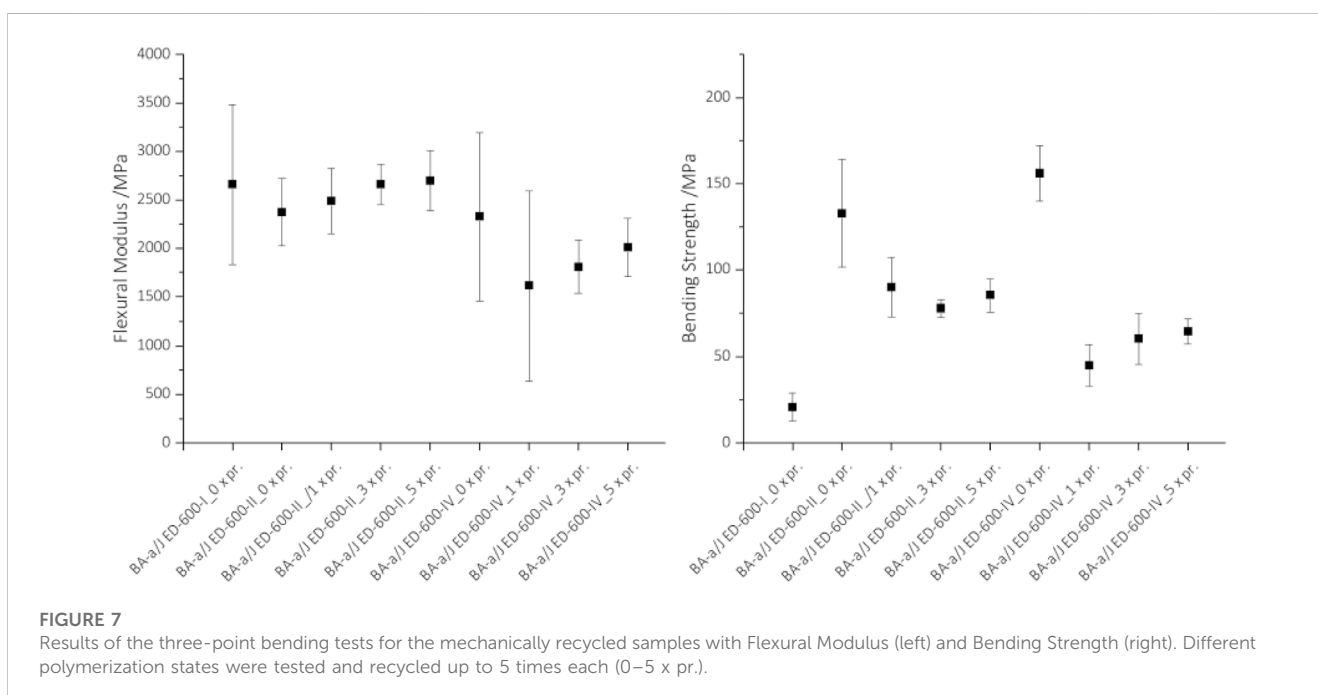
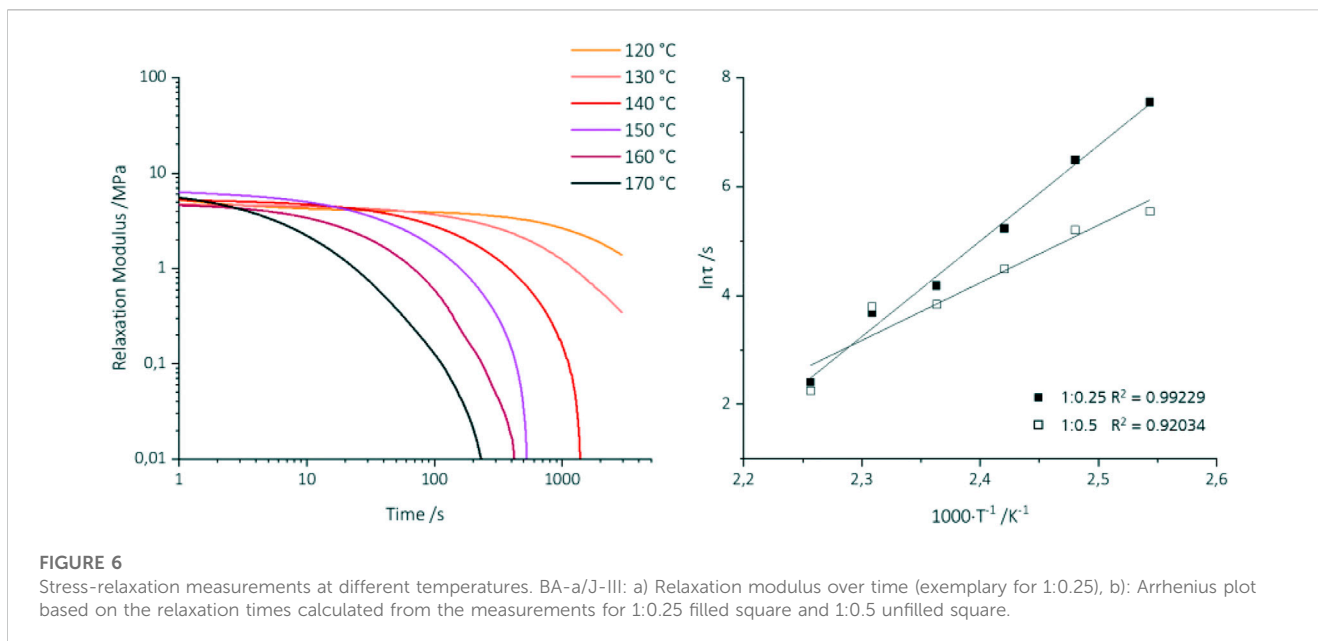
all extracts did not contain intact Jeffamine[®] ED-600 chains. They contained a multitude of fragments of both the polyether chain and the benzoxazine backbone that were probably abstracted from the polymer scaffold during the extraction process. This, again, suggests that the amine stays covalently incorporated into the polymer network, even at elevated reaction temperatures.

3.2.2 Thermal properties of benzoxazine/Jeffamine[®] copolymers

The polymerization and thermo-mechanical behavior of BA-a was studied in presence of the amine bearing polyether Jeffamine[®], in a stoichiometric ratio of 1:0.25 (BA-a: Jeffamine[®] ED-600). Basically, the presence of an amine significantly reduces the polymerization temperature of BA-a. Comparison of the DSC of the non-polymerized BA-a monomer and the BA-a/J mixture shows that two endothermic peaks occur in the presence of Jeffamine[®]. The first peak at about 120°C is associated with the ring opening reaction with the amine. The second peak at about 220°C is attributed to the opening reaction of the remaining closed oxazine rings. (Gonçalves et al., 2022). Moreover, the absolute residual enthalpy ΔH_R is already relatively low for BA-a/J-IV: $\Delta H_R = 16.0 \pm 2.7$ J/g, compared to BA-a-IV: $\Delta H_R = 56.7 \pm 2.1$ J/g (Figure 4). The thermal behavior of the polymerization of BA-a/Jeffamine[®] mixture compared to neat BA-a is in agreement with the results of Sun et al., 2015, who investigated different benzoxazine/amine polymers and showed comparable DSC results. Consistent with Sun et al., BA-a/Jeffamine[®] mixture did not melt after being thermally treated at 120°C for 2 hours (BA-a/J-I) as can be seen in Figure 4, by the absence of any endothermic peak. This can be explained with the progressed polymerization and crosslinking process at that low temperature. Furthermore, the residual reaction enthalpy between 200 and 250°C is much lower compared to neat BA-a after heating at 120 and 150°C for 2 hours, respectively.

The various polymerization steps affected the thermal stability of the resulting BA-a/Jeffamine[®] polymers as was shown by TGA experiments. The first step, sample BA-a/J-I polymerized at 120°C, shows a higher thermal stability compared to BA-a-I, which is probably due to the higher crosslink density respective a higher polymerization degree as a result of the lowering of the polymerization temperature by Jeffamine[®]. A higher polymerization temperature reverses the effect as ring opening polymerization of BA-a takes place at 150°C to a significant extent. Up to a polymerization temperature of 150°C, the BA-a/J-II exhibits with $T_{5\%} = 256.6 \pm 6.1$ °C a lower thermal stability, in comparison to the corresponding BA-a-II with $T_{5\%} = 304.6 \pm 5.6$ °C. Sun et al., 2015 reported similar results for benzoxazine/amine mixtures with aliphatic amines. They have attributed the lower degradation temperatures of the resulting benzoxazine polymer networks to the presence of thermally less stable aliphatic chains.

As expected, polyether chains impact thermo-mechanical properties determined by DMA experiments. Figure 5 shows a strong decrease of the glass transition temperatures (T_g) of the BA-a/J polymers. Compared to the fully polymerized BA-a, ($T_g = 188.2 \pm 2.34$ °C), the polymers BA-a/J-II and -III exhibit $T_g = 97.2 \pm 0.4$ °C and $T_g = 108.1 \pm 0.4$ °C, respectively. The aliphatic polyether chains of the Jeffamine[®] cause a decrease in polymer network density lowering the T_g accordingly, which is in agreement with TGA results. These results are also in an agreement with studies



performed by Ni et al., 2002 on the influence of different isomeric cyclohexane diacids in polyurethanes.

Despite the strong impact of Jeffamine on the thermal behavior, the storage modulus did not change significantly. For BA-a/J-II ($E' = 2280 \pm 350$ MPa) the storage modulus is in the same range as for the polymerized BA-a ($E' = 2300 \pm 300$ MPa).

In contrast to BA-a/J-IV, the increase in storage modulus for sample BA-a/J-II between 140°C and 250°C is likely due to post-curing processes and/or further aromatic substitutions. This indicates the complexity and temperature dependency of the

polymer network and is in line with the molecular studies on polymer network formation.

3.3 Vitramer-like behavior of benzoxazine/Jeffamine® polymers

3.3.1 Characterization of stress-relaxation behavior

Rheological tests proved that BA-a/Jeffamine® copolymers feature vitrimeric properties such as stress relaxation and

reprocessing ability. All BAa/J-III specimens (BAa:Jeffamine[®] ratio of 1:0.25 and 1:0.5) were heated to the respective temperature and kept at that temperature for 5 minutes before applying the strain and stress relaxation measurement. Figure 6 shows exemplarily the stress relaxation modulus in dependence of time and temperature treatment for sample BAa/J-III (1:0.25) (Figure 6, left). The initial modulus varies slightly for the studied temperatures due to standard deviation determined on three independent samples and rheology measurements (Supplementary Figure S6). All samples show similar initial relaxation moduli at temperatures above the glass transition temperatures ($T_g = 97.2 \pm 0.4^\circ\text{C}$ for a ratio of 1:0.25 and $T_g = 50.3 \pm 0.2^\circ\text{C}$ for 1:0.5), followed by quick relaxation of stress (Figures 6A, B). The relaxation times for the BA-a:Jeffamine[®] ratio of 1:0.25 vary with test-temperature, from 11 s at 170°C to 1895 s at 120°C , and follow the Arrhenius law. For the mixture-ratio of 1:0.5, the relaxation times range from 9 s at 170°C to 256 s at 120°C ; the higher the amine content, the faster stress-relaxation. Based on the linear dependency of the temperature and relaxation time, the activation energy for the 1:0.25 samples was determined with $E_a = 145.8 \text{ kJ/mol}$. The activation energy depends on several parameters, like the glass transition temperature and the bond exchange mechanism. Values in the range of 46 kJ/mol to 181 kJ/mol have been reported. (Anagwu et al., 2022; Adjaoud et al., 2023). In comparison to other vitrimeric bond exchange activation energies, the E_a of the BA-a/Jeffamine[®] copolymers is relatively high. This could be due to the stoichiometric BAa:Jeffamine[®] ratio of only 1:0.25. An increase of Jeffamine[®] by varying the stoichiometry yields a decrease in E_a . The activation energy for the 1:0.5 samples is 88.0 kJ/mol. If the molar ratio of Jeffamine[®] increases, the concentration of covalent adaptive bonds increases, leading to a decrease in E_a .

Based on the Arrhenius plot, the topology freezing temperature T_v can be calculated using Maxwell's equation (Supplementary Eqs 1–5). (Dhers et al., 2019). The T_v for the BA-a/Jeffamine[®] system 1:0.25 is 94°C , which is in the range of T_g . A similar T_v - T_g relationship is also shown for a BA-a/Jeffamine[®] ratio of 1:0.5, where the $T_v = 39^\circ\text{C}$ is also in the range of the T_g . In general, vitrimers are distinguished into two classes. Those with T_v above T_g and *vice versa*. (Anagwu et al., 2022). A material with a similar relationship of T_v and T_g was reported by Adjaoud et al. (Adjaoud et al., 2022) for a lignin-based benzoxazine exhibiting T_v and T_g in the same range of about 182°C .

The reaction mechanism, gel content and thermo-mechanical experiments prove that the benzoxazine/amine reaction yields a phenolic aminomethyl structure in a reaction equilibrium at low temperatures. Temperature treatments at 150 and 180°C result a crosslinked structure originating from an amine induced ring-opening reaction. The resulting vitrimeric behavior was not expected as the subsequent curing at temperatures higher than 120°C were reported to be irreversible. The deviating observations could result from two facts: 1) the reaction was performed without the use of solvents and 2) the applied amine bears oxypropylene units in contrast to the studied aromatic and aliphatic hydrocarbon-based amines. As Sun et al., 2015 we assume that the electrophile substitution reaction leading to phenolic structure A is irreversible. Based on the Arrhenius-like stress-relaxation behavior, we propose a possible dynamic reaction which is based on an associative mechanism that involves

exchange reactions between primary and secondary amines in an addition elimination reaction involving methylene units with positive partial charges. However, further extensive research is needed to prove this hypothesis and to reveal the nature of the dynamic reaction that is responsible for the vitrimer-like behavior of this benzoxazine/Jeffamine[®] system.

3.3.2 Reprocessing characteristics

The BA-a/Jeffamine[®] ED-600 polymer was shown to exhibit vitrimer-like behavior in stress-relaxation measurements. Hence, it should be possible to crush and heal the polymer multiple times, similar to a mechanical recycling process of a thermoplastic material. The results of the three-point bending test after the cyclic crushing-pressing process are shown in Figure 7. Crushing-pressing cycles do not seem to have any effect on the flexural modulus and the values for all crushing-pressing cycles are in the same range of 2300–2700 MPa for the specimens with polymerization condition 120, 150°C each 2 h (BA-a/J-II) and 1600–2000 MPa for 120, 150, 180°C each 2 h (BA-a/J-IV). In general, the high temperature conditions at 120, 150, 180°C for 2 h each, negatively influence the flexural modulus, which is also observed in the storage modulus in the DMA.

In contrast to the modulus, the strength is strongly affected by the mechanical recycling process. After the first crushing-pressing step, the flexural strength decreases, which could be due to defects in the material, such as particle boundaries. Residues of the release agent could also have a significant influence on the bonding process. It adheres to the specimen after the pressing process, and thus also to the interfaces of the pressed particles. After the pressing cycles, the flexural strength of the specimens polymerized at 180°C (BA-a/J-IV) is reduced by about 30% compared to the specimens polymerized at 120°C and 150°C for 2 h each (BA-a/J-II). This could be explained by the occurrence of a temperature-dependent molecular structure or initial degradation processes in Jeffamine[®] at high temperatures.

4 Conclusion

Material characterization and structure elucidation have been merged for the first time for a dynamic benzoxazine/polyetheramine using Jeffamine[®] ED-600 to gain better understanding of the resulting polymer network. Mechanical studies on a model system based on a monofunctional benzoxazine and monoamine proved that the initial step corresponds to the amine mediated opening of the oxazine rings of BA-a. Bifunctional benzoxazine and diamines result linear polymer chains with repeated phenolic benzoxazine/amine motifs. Moreover, the polymer chains are crosslinked by secondary amine-induced opening of oxazine rings and the introduced amine remains covalently incorporated into the polymer network, as proven by extraction experiments. The mechanical properties of the polymers are similar to those of pure polymerized BA-a, but thermal properties are strongly affected by the Jeffamine[®] as the glass transition temperature is reduced significantly. The addition of Jeffamine[®] and by this the presence of amines reduce the polymerization temperature and introduce vitrimeric behavior as proven by stress-relaxation tests; the latter enables reprocessability. The activation energy of the

bond exchange reaction for a BA-a:Jeffamine[®] ratio of 1:0.25 was calculated to be 146 kJ/mol, and the topology freezing temperature was determined to be 97°C. The high E_a in comparison to other vitrimers could be explained by the very low amine ratio. At a higher Jeffamine[®] ratio (1:0.5), the activation energy and topology freezing temperature decrease to 88.0 kJ/mol and 39°C, respectively. Thus, E_a and T_v as well as general material properties could be adjusted with ratio of benzoxazine and amine. Further research should address the effect of the polymerization parameters and the stoichiometry on the thermo-mechanical properties, to gain a better understanding of the structure-property-relationship of this vitrimer. The dynamic reaction is possibly based on an associative addition elimination mechanism involving primary and secondary amines as well low field shifted methylene units. However, additional research is needed to fully reveal the nature of the dynamic reaction enabling the vitrimeric properties.

Data availability statement

The original contributions presented in the study are included in the article/[Supplementary Material](#), further inquiries can be directed to the corresponding author.

Author contributions

LP and AW planned, performed, and evaluated the experiments; prepared the figures; wrote the manuscript. LP was responsible for the characterization of the thermal properties, the vitrimer behavior and the reprocessing characteristics. AW was responsible for determination of the reaction mechanism and the development of the structure model. Both have contributed equally in first authorship to this work. KK and TU guided the research. KK was responsible for the funding and supervision of the project

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary material

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/frsfrm.2023.1197868/full#supplementary-material>

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