

Contents lists available at ScienceDirect

Progress in Organic Coatings



journal homepage: www.elsevier.com/locate/porgcoat

Solvent-free coatings based on bio-sourced benzoxazines resins with healing, repair, and recycling capabilities

Louis Van Renterghem^{a,*}, Roya Malekkhouyan^b, Leila Bonnaud^a, Romain Tavernier^a, Marjorie Olivier^b, Jean-Marie Raquez^a

^a Laboratory of Polymeric and Composite Materials (LPCM), Center of Innovation and Research in Materials, Materia Nova Research Center University of Mons (UMONS), Place du Parc 20, Mons 7000, Beleium

^b Materials Science Department, University of Mons, Place du parc 20, Mons 7000, Belgium

ARTICLE INFO

Keywords: Benzoxazines coatings Aluminum coatings Anticorrosion

ABSTRACT

Conventional benzoxazine resins, in spite of their excellent thermo-mechanical properties and good solvent resistance, suffer from high curing temperatures and limited self-healing/ reprocessability. In this frame, biosourced phenol (Phloretic acid), various diols (Dodecandiol/PEG200/Ethylene glycol), and amine (monoethanolamine) have been used in appropriate proportions to synthesize innovative benzoxazine precursors bearing exchangeable ester functions following a solventless method. They can be directly handled and used for coating applications without using any solvent. The overall synthesis was followed by Nuclear Magnetic Resonance and Fourier transform infrared spectroscopy (FT-IR). The reduced curing temperature, thermal stability, good thermo-mechanical performance, and ester bond exchange-ability system were demonstrated by Differential Scanning Calorimetry (DSC), thermogravimetric analysis (TGA), and Dynamic mechanical analysis (DMA - stress relaxation testing), respectively. The elaborated resins were applied on etched aluminum 1050 without solvent and the corrosion resistance of the coatings was investigated by electrochemical impedance spectroscopy (EIS). The electrochemical results showed proper corrosion protection on aluminum substrates. The best result was obtained with Dodecandiol-based benzoxazine coating due to its longer aliphatic chain and hydrophobic property. Comparing this coating with an epoxy-based benchmark showed enhanced corrosion resistance for the benzoxazine for thure industrial use.

1. Introduction

Aluminum (Al) alloys have different applications in industrial technologies like aircraft, buildings, automobiles, and chemical plants due to their low cost, form-ability, weld-ability, durability, and high strengthto-weight ratio properties [1,2]. The corrosion resistance of Al alloys is relatively stable due to the formation of an oxide layer, but this layer cannot sustain in the case of very aggressive chemical attacks [3]. Different strategies can be performed for enhancing the corrosion resistance of Al alloys like chromating, cathodic protection, and organic coating [4]. Among them, the low-cost application of organic coatings is preferred for industry and it is estimated that by 2024 the global coating market would be increased to USD 218 billion [5]. Organic coatings can protect the substrates by creating a barrier layer between the corrosive environment and the surface. For this purpose, epoxy [6,7], epoxy/ polyamide [8], and conducting polymers like polyaniline [9], and polypyrrole [10] were used. Polybenzoxazine, a new type of phenolic resin, has recently attracted attention for coating applications by presenting outstanding properties of low dielectric constant, thermal stability, alkaline resistance, hydrophobic behavior, and slight shrinkage after curing [1,4,11–18]. Benzoxazine resins are commonly obtained from the ring-opening polymerization of 1,3-benzoxazine precursors. The latter can be straightforwardly synthesized at high yield (>90 wt%) by a Mannich- like condensation of an amine, a phenol, and formalde-hyde [13,15,19–21].

With regard to benzoxazine-based coatings, in previous studies our group developed and studied benzoxazine- based PhenolparaPhenyleneDiAmine (P-pPDA) [4,16] and benzoxazine-based 4-ethylphenol-para-phenylenediamine (4EP-pPDA) [1] coatings applied to various aluminum-based substrates treated in different ways. In all cases, these benzoxazine-based systems significantly improve the corrosion resistance of aluminum-based metal substrates, and it was

* Corresponding author. *E-mail address:* louis.vanrenterghem@umons.ac.be (L. Van Renterghem).

https://doi.org/10.1016/j.porgcoat.2024.108316

Received 6 December 2023; Received in revised form 24 January 2024; Accepted 5 February 2024 0300-9440/© 2024 Elsevier B.V. All rights reserved.

found that 4EP-pPDA resin, which has a much lower viscosity than PpPDA, enables deeper impregnation of the substrate [1]. Another study also showed that the addition of nanoparticles such as *B*-trimethysityl-*N*triphenylborazine at different concentrations to P-pPDA resin further enhanced the corrosion resistance of metal substrates [14]. However, despite their good performance, this type of precursor has a number of environmental drawbacks. More specifically, they are synthesized from petro-sourced reagents, and a three-dimensional covalent network that is difficult to repair or recycle is formed during polymerization. What's more, these precursors are solid at room temperature, and a solvent that is generally toxic to the environment (e.g. chloroform) must be used to apply them as coatings. Alternative, more sustainable and eco-circular approaches are therefore desirable.

In this context, this study proposes new benzoxazine precursor structures that are synthesized from reagents that can be derived from renewable resources, that incorporate functionality enabling resin repair and recycling after curing via the formation of a covalent adaptive network (CAN) [22], and that can be sufficiently fluid to be applied directly in the absence of solvent by the dry coating technique.

Interestingly, the literature reports numerous examples of the preparation of benzoxazine precursors from biobased or biobasable compounds [18-21,23,24]. One study even shows that it is possible to synthesize water-soluble benzoxazine precursors for water-borne coating [18]. The dry-coating technique already used for epoxy systems is even more eco-friendly, as no solvents are used [22]. To our knowledge, no benzoxazine coating has yet been tested using this technique. Very recently, a number of new benzoxazine precursor structures with interchangeable functions for the manufacture of CANs, including transcarbamoylation [24], transesterification [25], dioxoborolane [26], disulfide bonds [27], have also been developed. In particular, tertiary amines are known to catalyze and promote transesterification reactions by nucleophilic activation of hydroxyl groups [28]. The intrinsic presence of tertiary amines on the benzoxazine backbone makes transesterification a particularly well-suited tool for introducing exchangeable functions into a benzoxazine network. The literature also shows that it is possible to obtain benzoxazine precursors that are liquid and therefore very fluid at room temperature or at relatively low temperatures, by incorporating long chain groups (such as alkyl or ether-alkyl chains, for example) into the precursor structure [20,23]. It was on the basis of these various elements that the reagents were selected to design the benzoxazine precursors of this study.

More specifically, ester functions were introduced into the benzoxazine network by Fischer esterification between a low-viscosity natural phenolic compound bearing an acid group and various biobased diols of different chain lengths to modulate viscosity. Few phenols that have both low viscosity and acid functionality can be biobased. For instance, Diphenolic acid which has been already used in the synthesis of benzoxazine monomers, was ruled out as too viscous [25]. Furthermore, in order to reduce the polymerization temperature of the monomers, the chosen phenol must be free in the ortho position [29]. For this reason, ferulic acid was excluded [30]. Arslan has demonstrated the synthesis of a low-cure benzoxazine precursor with gallic acid due to the presence of three alcohol functions that can catalytically lower the temperature during polymerization [31], but it cannot be used for the design of solvent-free bio-based monomers due to its high melting temperature.

Similarly, coumaric acid and para-hydrodxybenzoic acid could be used for the synthesis of polybenzoxazine precursors, but the monomers obtained suffered from a significant loss of mass visualizable by TGA, which limits their use [30,32]. Finally, phoretic acid, a naturally occurring phenolic compound which can be produced by the hydrogenation of p-coumaric acid or from a by-product of apple tree leaves (e.g. phloretin), was chosen for its better temperature resistance, its low viscosity/melting temperature, which allows both monomer synthesis and solvent- free application to the metal substrate, and the presence of its acid function for the development of CANs by transesterification [33]. With regard to the biobased diols contributing to the tuning of the viscosity of the benzoxazine precursors and needed to generate the ester exchangeable groups by Fischer esterification with phoretic acid, 3 compounds were selected for this study: PEG200, ethylene glycol and 1,12-dodecandiol. The latter has a molecular weight similar to that of PEG200, and was chosen to compare the influence of polarity on the coating. Furthermore, to facilitate exchange reactions between ester functions, additional free hydroxyl pendant groups were incorporated into the resin structure with mono-ethanolamine (mea), a biologically derived amine obtained by decarboxylation of L-serine [34].

In addition to the synthesis and detailed characterization of these 3 new eco-friendly and eco-circular benzoxazine precursors, their use in dry-coating to protect 1050 aluminum substrates is also being studied in depth in this study.

2. Material and methods

2.1. Sample preparation

2.1.1. Materials

Phloretic Acid (>98 %) was purchased from TCI. 1,12- Dodecandiol (99 %), Ethylene glycol (99,8 %), para- toluenesulfonic acid (98,5 %), Methyl Ethyl Ketone, Dioxolane and paraformaldehyde were obtained from VWR. Polyethylene glycol (PEG 200) and ethanolamine were purchased from Merck. The commercial resin Epikote 828 (Brenntag) with an equivalent weight of 185–192 g/eq was used as epoxy resin. Diluent Epotec RD 106 (ThaiEpoxy group) with an equivalent weight of 220–250 g/eq was added to reduce the viscosity of the resin. The amine curing agent was Ancamine 2753 (Air product) with an equivalent weight per active H of 153 g/eq. All chemicals were used without any further purification.

2.1.2. Synthesis of phloretic ester

The syntheses of PA-PEG₂₀₀, PA-dd and PA-EG were performed according to Fig. 1. The operating conditions were the same for all the samples. The synthesis protocol for the PA-PEG₂₀₀ is explained as an example. Phloretic acid (20.0 g, 120 mmol), polyethylene glycol 200 (14,4 g, 72 mmol) and paratoluenesulfonic acid (0,17 g, 1 mmol) were placed into a 250 ml beaker equipped with a stirring bar. The mixture was stirred at 130 °C for 24 h at 150 rpm. After cooling to room temperature, the crude product was solubilized in 200 ml of methyl Ethyl Ketone. Then, the solution was washed with deionized water three times to remove the catalyst. The organic solvent was dried under vacuum overnight to obtain a dark red viscous liquid yield of 95 %. ¹H NMR (DMSO-d₆,ppm): PA-PEG₂₀₀: 9.17 (Ar-OH*), 6.99 (Ar*-OH), 6.66 (Ar*-OH), 4.12 (O=C-O-CH2*), 3.57(O=C-O-CH2-CH2*), 3.51 (PEG CH2*-CH2*-O), 2.73 (HO-AR-CH2*), 2.56 (HO-AR-CH2-CH2*). PA-dd: 9.18 (Ar-OH*), 6.97(Ar*-OH), 6.67(Ar*-OH), 3.98 (O=C-O-CH2*), 2.75 (HO-AR-CH2*), 2.55 (HO-AR-CH2-CH2*), 1.53 (O=C-O-CH2-CH2*), 1.25 (DD -CH2*-CH2*-). PA-EG: 9.17 (Ar-OH*), 7.02 (Ar*-OH), 6.67 (Ar*-OH), 4.19 (O=C-O-CH2*), 2.74 (HO-AR-CH2*), 2.56 (HO-AR-CH2-CH2*).

2.1.3. Synthesis of Phloretic benzoxazine

The syntheses of PA-PEG₂₀₀-mea, PA-dd-mea, and PA-EG-mea were performed according to Fig. 1. The operating conditions were the same for all the samples. The synthesis protocol for the PA-PEG₂₀₀-mea is detailed as an example. Phloretic ester (29,0 g, 58,5 mmol), mono-ethanolamine (7,14 g,117 mmol) and paraformaldehyde (7,0 g, 234 mmol) were placed into a 250 ml beaker equipping with a stirring bar. The mixture was stirred at 85 °C for 150 min and 30 min at 90 °C at 150 rpm. The resulting product was a dark red viscous liquid. ¹H NMR (DMSO- d_6 ,ppm): PA-PEG₂₀₀-mea: 6.93–6.62 (Ar*-oxazine) $\int 2.17$, 4.79 ($N - CH_2^*$ -O-Ar) $\int 0.95$, 4.13(O = C - O - CH_2^*) $\int 1.34$, 3.96($N - CH_2^*$ -Ar) $\int 0.94$, 3.57(= C - O - CH₂-CH₂* + HO-CH₂*-CH₂) $\int 2.38$, 3.52($P EGCH_2^*$ -CH₂*-O) $\int 3.60$, 2.71($AR - CH_2^*$ + HO-CH₂-CH₂*) $\int 2.32$, 2.58($AR - CH_2$ -CH₂*) $\int 1.00$. P A-dd-mea : 6.92–6.63(Ar * -oxazine) $\int 2.54$, 4.79($N - CH_2^*$ -O-Ar) $\int 1.12$, 4.51(impurity), 3.98(O)



Fig. 1. Synthesis of pPA-DD-mea, pPA-PEG-mea and pPA-EG-mea.

 $= C - O - CH_2^*) \int 1.28, \ 3.93(N - CH_2^* - Ar) \int 1.06, \ 3.56(HO - CH_2^* - CH_2^* - Ar) \int 1.06, \ 3.56(HO - CH_2^* - CH_2^* - Ar) \int 1.06, \ 3.56(HO - CH_2^* -$ CH₂) ∫ 1.38, 2.72(AR - CH₂* + HO- CH₂-CH₂*) ∫ 1.84, 2.55(AR - CH₂- CH_2^*) $\int 1.00, 1.51(O = C - O - CH_2 - CH_2^*) \int 1.59, 1.23(DD - CH_2^* - CH_2^*)$ CH_2^* -) $\int 7.91.PA-EG - mea : 6.93-6.63(Ar * -oxazine) \int 2.83, 4.77(N)$ $- CH_2^*-O-Ar) \int 0.94, 4.21(O = C - O - CH_2^*) \int 1.07, 3.92(N - CH_2^*-CH_2^$ Ar) $\int 0.94$, 3.56(HO - CH₂*-CH₂) $\int 0.96$, 2.71(AR - CH₂* + HO- CH₂- CH_2^*) $\int 2.10, 2.57(AR - CH_2-CH_2^*) \int 1.00.FTIR(cm^{-1})$: PA-PEG₂₀₀mea: 1731 (C=O stretching from the ester), 1230 (C-O-C stretching assymmetric), 1116 (C-H inplane bending mode 18a and 18b), 1031 (C-O-C stretching symmetric), 937 (C-H out of plane bending vibration bands oxazine mode 10a and trisubstituted benzene). PA-dd-mea: 1700, 1230 (C-O-C stretching asymmetric), 1118 (C—H inplane bending mode 18a and 18b), 1034 (C-O-C stretching symmetric), 937 (C-H out of plane bending vibration bands oxazine mode 10a and trisubstituted benzene). PA-EG- mea: 1730 (C=O stretching from the ester), 1231 (C-O-C stretching asymmetric), 1143 (C-H inplane bending mode 18a and 18b), 1049 (C-O-C stretching symmetric), 934 (C-H out of plane bending vibration bands oxazine mode 10a and trisubstituted benzene).

2.1.4. Curing of benzoxazine thermoset

All monomers were poured into square Teflon molds (5/5/0,1 cm), then degassed under pressure in an oven at 100 °C (15 min). Afterward, samples were heated at 160 °C for 2 h to obtain the corresponding polymerized products: pPA-PEG-mea, pPA-dd-mea, pPA-EG-mea. As follows: FTIR (cm⁻¹) pPA-PEG-mea: 1729 (C=O stretching from the ester), 871 (out-of-plane, out-of-phase hydrogen wagging node for the 1,2,3,5-tetrasubstituted aromatic ring). pPA-dd- mea:1729 (C=O stretching from the ester), 875 (out-of-plane, out-of-phase hydrogen wagging node for the 1,2,3,5- tetrasubstituted aromatic ring). pPA-EG-mea: 1729 (C=O stretching from the ester), 873 (out-of-plane, out-of-phase hydrogen wagging node for the 1,2,3,5- tetrasubstituted aromatic ring). pPA-EG-mea: 1729 (C=O stretching from the ester), 873 (out-of-plane, out-of-phase hydrogen wagging node for the 1,2,3,5- tetrasubstituted aromatic ring).

2.1.5. Coating preparation

A1050 Al alloy substrates with dimensions 150 mm * 100 mm * 1.0 mm were first etched with NaOH 1 M solution at 60 °C for 2 min and with nitric acid for 1 min after rinsing. These substrates were further washed with deionized water and dried.

PA samples were degassed at 100 °C for 15 min and applied with a

bar coater on the metallic substrate at 100 $^{\circ}$ C without solvent. All samples were heated at 160 $^{\circ}$ C for 2 h to obtain the corresponding polymerized products. The thickness of the coatings was determined using SEM images of the cross-section.

2.2. Characterization

2.2.1. Chemical and morphological characterization

Fourier transform infrared (FTIR) spectra were recorded using a Fourier Transform Tensor (FTIR) 27 Spectrometer from Brüker $600-4000 \text{ cm}^{-1}$, with 2 cm⁻¹ resolution and an accumulation of 32 scans.

Nuclear magnetic resonance (NMR) measurement was performed on a Bruker AVANCEII-500 (Karlsruhe, Germany) at room temperature. The solvent was DMSO.

Gel content (GC) tests were performed in water and dioxolane by immersion at room temperature of 0.3 g of the material in 25 ml of solvent for 14 days. The samples were further dried at 100 °C in an oven for 24 h. The gel content is determined according to the Eq. (1).

$$GC(\%) = \frac{m_i - m_d}{m_i} \cdot 100$$
 (1)

With m_i and m_d being the initial and the dried mass, respectively.

Swelling ratio water (W) tests were performed in water by immersion at room temperature of 0.3 g of the material in 25 ml of solvent for 14 days. The samples were further wiped clean and weighed. The Swelling ratio water is determined according to the Eq. (2).

$$W(\%) = \frac{m_i - m_s}{m_i} \cdot 100$$
 (2)

With m_i and m_s being the initial and the swollen mass, respectively. The reported values are an average of three measurements.

Scanning Electron Microscopy (SEM) experiment was carried out by a STEM FEG SU8020 instrument invented by Hitachi. The resolution was 5.0 nm in general mode, and its resolution can reach 2.0 nm at 5 kv. The accelerated voltage ranged from 0.1 to 30 kV, and the magnification varied from 20 to 800k.

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2.2.2. Surface wettability test

Contact angle measurements were performed with a DSA 10 Mk2 drop shape analysis system (Krüss) in a three- phase system consisting of the coating surface, air, and a drop of water. Concretely, water droplets (5 μ l) were dispensed onto the surface of each coatings. Images were captured using a digital camera (2 \times magnification, white light, 5500 K).

2.2.3. Thermal analyses

Thermogravimetric analyses (TGA) were performed using a TGA Q50 TA Instruments device. About 10 mg of each sample was scanned from 25 to 800 °C at a heating rate of 10 °C/min under N_2 gas at a flow rate of 60 ml/min.

Differential scanning calorimetry (DSC) thermograms were recorded by means of a MDSC 2920 TA Instruments apparatus operating under an inert atmosphere (N_2) with a linear heating ramp from -40 to 250 °C at 10 °C/min rate on a sample of about 10 mg.

2.2.4. Mechanical and thermo-mechanical properties

Dynamic rheological analyses (DRA) were realized on a compact and modular MCR 302 instrument from Anton Paar equipped with a temperature control device and disposable aluminum plate-plate configuration. Temperature ramp tests were performed in oscillatory mode at a frequency of 1 Hz at 10 % strain using 2.5 cm diameter plate and a gap of 1 mm.

Dynamic mechanical analyses (DMA) were conducted on a DMA Q800TA Instruments analyzer. 2 types of tests were realized: temperature ramp and stress relaxation. For temperature ramp test, DMA were performed on rectangular sample (40/13/1 mm) in tensile mode with an amplitude of 2 μ m at a frequency of 1 Hz, with a heating rate at 3 °C/min from 25 °C to 200 °C. The crosslinking density (ν) was calculated using Eq. (3).

$$v_{E'} = \frac{E'_R}{3RT_R} \tag{3}$$

where E' is the storage modulus at rubber state (MPa), T_R the temperature at 60 °C above Tg (K) and R the gas constant. Stress relaxation test were carried out using specimens with the same dimensions as those used for DMA tests. A constant 2 % strain was applied for each test and the relaxation modulus was recorded. The stress relaxation behavior was studied at different temperatures in the range between 150 °C and 180 °C. Results were fitted using a two-phase Maxwell model using Eq. (4).

$$\tau^* = \tau_1 e^{\frac{E_a}{RT}} + \tau_2 e^{\frac{E_a}{RT}} \tag{4}$$

2.2.5. Electrochemical properties

The electrochemical impedance spectroscopy (EIS) measurements were performed in 0.1 M NaCl solution using Parstat Model 2273 equipment controlled by Powersuit® software. A classical three-electrode system, which consisted of a platinum counter electrode, an Ag/AgCl (sat. KCl) reference electrode, and Al alloy samples, as working electrodes with an exposed area of 7 cm² were used. EIS measurements were performed in a frequency range from 100 kHz to 100 mHz with 60 points using a 30 mV peak-to-peak sinusoidal voltage. Each experiment was performed at least three times.

2.2.6. Adherence properties

The cross-cut adhesion test was carry out according the ISO 2409 standard. The coating was incised by three parallel knife to produce a grid. An adhesive was applied 30 s on the coating and quickly remove. The aspect of the coating was further analyse by microscopy and compare with the standard class.

3. Results and discussions

3.1. Characterization and curing behavior of benzoxazine monomer

The esterification of the Phloretic acid with three different diols (PEG₂₀₀, ethylene glycol, and 1,12 dodencandiol) was confirmed by HNMR (Fig. 2). The characteristic peaks of the ester appeared at 2.75 and 3.98 ppm for the PA- PEG corresponding respectively to the methylene protons adjacent to the carbonyl moieties β - and α - positions. The chemical shifts in the range of 6.67-6.97 ppm are associated with the aromatic ring. All the products were washed to remove the catalyst and reacted with monoethanolamine and paraformaldehyde to synthesize the monomer. The chemical shifts of the oxazine moieties, attributed to the O-CH₂-N and Ar-CH₂-N, appeared respectively at 4.79 and 3.93 ppm. Furthermore, the disappearance of the phenolic peak at 9.18 ppm confirmed the completion of the reaction. In order to verify the NMR results, FTIR analyses were performed. The shift from acid function to ester was observed between 1700 and 1732 cm^{-1} . The formation of benzoxazine ring was also validated by the peak at 934, 1229, 1116, and 1031 cm⁻¹, corresponding respectively to the out-of-plane bending of H-C-H, C-X stretching mode 13 + C-O-C aromatic asymmetric stretching, CH in-plane bending mode 18a/b and C-O-C stretching symmetric [35].

The ring-opening polymerization of benzoxazine groups was followed by FTIR, DSC, and rheological experiments. The complete polymerization was confirmed by the disappeared characteristic peaks of benzoxazine at 930 and 1230 cm⁻¹ and the apparition of the out-ofphase hydrogen wagging node for the 1,2,3,5-tetrasubstituted aromatic ring at 875 cm^{-1} (Fig. 3). From the DSC thermograms, the completeness of the polymerization was confirmed by the disappearance of the first exothermic peak at 189, 210, and 193 °C of PA-PEG-mea, PAdd-mea, and PA-EG-mea respectively (Fig. 4a/b/c). The ring-opening polymerization (ROP) at a relatively low temperature is provided by the free hydroxyl function held by the monoethanolamine, which can react with zwitterionic intermediates appearing during the polymerization [36]. This catalytic effect affords a lower curing step (160 °C 2 h), by contrast with common biobased benzoxazine, synthesized with stearylamine or furfurylamine, requiring more time and/or energy (220 °C) [37,38]. This curing temperature is the main limiting parameter that affects the thermo-mechanical properties of the resulting metallic substrate. The second exotherm is correlated with the degradation of the monomer, confirmed by TGA analysis. In order to verify the DSC measurement and to identify the best temperature for applying the monomer to the metal substrate, the evolution of the complex viscosity of the benzoxazine during the ROP was also monitored by rheological analysis. First, the sharp increase in viscosity (around 170 °C), corresponding to monomer crosslinking for each sample, is consistent with the DSC results. In addition, the PEG and DD samples unequivocally showed the lowest viscosity due to the long aliphatic chain. In order not to create any defects during the application of the organic coating, the temperature chosen for each formulation was set at 100 °C, which is the best compromise between the lowest viscosity and the onset of ROP. All the results can be found in the Fig. 4 and the Table 1. Finally, gel content test verified the formation of cross-linked polymer with only a portion of soluble part inside the polymer matrix lower than 6 % for each sample (Table 2).

3.2. Properties of benzoxazine polymers

Due to the basic requirements for polymer coatings, the thermal, thermo-mechanical, and swelling/solubility behaviors were investigated at first. As expected, samples with a longer carbon structure (like PEG and dodecandiol) are more flexible and show a lower cross-linking density. All polymers showed good thermal behavior with a T5%, T10%, Tmax, and char yield of $\pm 265 / 290 / 405$ °C and 30 % which were comparable to other biobased benzoxazine with self- healing features



Fig. 3. a) FTIR spectra of PolyPA-DD-mea, b) FTIR spectra of PolyPA-EG-mea, c) FTIR spectra of PolyPA-PEG-mea.

[25,26,39]. The decomposition of these systems was mainly due to the thermal degradation of the main chain, occurring at 300–400 °C. As shown in Fig. 5, the glass transition temperature of the system was determined to be 65 / 69 / 127 °C from DMA thermograms for pPA-PEG-mea, pPA-dd-mea and pPA-EG-mea respectively. In addition, the benzoxazine polymers that were synthesized with ethylene glycol exhibited good mechanical properties. The storage modulus at the glassy state was $\pm 1,85$ GPa and 20,6 MPa at rubber state (60 °C above Tg), respectively. These results, especially in the area of biobased covalent adapted networks synthesized and applied without any solvent, are competitive

with other resins manufactured for anticorrosion applications. [40-42].

3.3. Self-healing, ester bond exchange and reprocessability of benzoxazine polymers

The self-healing behavior of the benzoxazine systems was assessed by analyzing the surface morphology recorded by a Leica optical microscope (Fig. 6). The coatings were cut on the surface with a razor blade. All the samples were further heated at 160 °C for 2 h without any external pressure and the final width of the damaged area was measured



Fig. 4. a) DSC, TGA and rheological behavior of PA-DD-mea, b) DSC, TGA and rheological behavior of PA-PEG-mea, c) DSC, TGA and rheological behavior of PA-EG-mea.

Table 1

thermal and rheological behavior of PA-PEG-mea, PA-DD-mea and PA-EG-mea monomers.

Samples	onset exotherm DSC (°C)	Max exotherm DSC (°C)	Enthalpy (J/ g)	Initial curing temperature (rheology) (°C)	Complex Viscosity at 100 °C (PA*s)	T5% (°C)
PA-PEG-	126	189	53.9	179	0.05	212
mea						
PA-DD-mea	173	210	50.0	179	0.01	226
PA-EG-mea	161	193	95.2	154	0.11	243

Table 2

Properties of PA-PEG-mea/PA-DD-mea/PA-EG-mea polymers.

Samples	Gel content dioxolane (%)	Storage modulus RT (MPa)	Tg DMA (°C)	Storage modulus rubber state (MPa)	Crosslinking density (mol/l)	T5% (°C)	Char Yield (%)	Swelling ratio water (%)
pPA- PEG-	94.9	640	65	7.0	0.7	267	29	17.6
pPA-DD-	97.0	660	69	7.6	0.8	239	25	4.1
pPA-EG-	98.7	1850	127	20.6	1.8	260	41	6.2



Fig. 5. a) TGA and DMA behavior of pPA-DD-mea, b) TGA and DMA behavior of pPA-PEG-mea, c) TGA and DMA behavior of pPA-EG-mea.

(Table 3). As expected, flexibility induced by DD aliphatic diols leads to the best results with 69 % self-healing. Similarly, EG, which has the highest Tg due to its short chain, revealed the lowest result with 46 %. Surprisingly, polarity seems to limit the ability of polymers to repair their scars as shown, by the lower value of the PEG sample.

The recyclability of the materials was evaluated mechanically and chemically as shown in Fig. 7 Chemically, the samples were first degraded with acetic acid solution due to the protonation of the tertiary amine present after ring- opening polymerization [43]. The system residue was washed with deionized water until a neutral pH was reached. The wet samples were then dried overnight at 100 °C in an oven. Mechanically, the ground samples can rebuild the network through the transesterification mechanism. Finally, chemically and mechanically damaged polymer was filled into different square mold and pressed at 160 °C for 1 h at 3 metric tons.

The thermo-mechanical properties of the as-recycled samples were then evaluated by dynamic mechanical tests in tensile mode. As shown in Supplementary information, Figs. 13, 14, 15, all reprocessed samples exhibit an apparent and single alpha transition, highlighting the homogeneity of the reshaped network. However, the nature of the diol seems to have a significant impact on the recyclability of the material. While the hydrophobic pPA-DD-mea sample showed a decrease in the tan delta value, the pPA-PEG-mea and pPA-EG-mea showed no significant mechanical evolution. In all cases, the retention of Tg remains better than 83 %. Similar to the Tan-Delta results, the nature of the diols influenced the evolution of the crosslinking densities. Thus, mechanical and chemical reprocessing of the flexible dodecandiol and PEG 200 networks tended to increase the crosslinking density, while the more rigid EG network seemed to decrease it. In parallel, the storage modulus was also increased for all systems. Such behavior could be related to a



Fig. 7. a) Evolution of Max Tan delta after chemical and mechanical reprocessing of each benzoxazine polymers, b) Evolution of cross-link density after chemical and mechanical reprocessing of each benzoxazine polymers.



Fig. 8. Transesterification mechanism occurring in the polybenzoxazine network.



Fig. 9. a) Stress relaxation curve of pPA-DD-mea, b) Stress relaxation curve of pPA-PEG-mea, c) Stress relaxation curve of pPA-EG-mea, d) Arhenius fit of pPA-DD-mea, e) Arhenius fit of pPA-PEG-mea, f) Arhenius fit of pPA-EG-mea.

a)



Fig. 10. a) SEM pictures of benzoxazines coating b) Cross-cut adhesion test of pPA-DD-mea.



Fig. 11. Water contact angles of polybenzoxazine coatings.

post-curing effect induced by the applied pressure and temperature [44,45].

Stress relaxation experiments were performed to characterize the dynamic of ester bond exchange of polybenzox- azine resins (Fig. 8). Ea and τ^* were calculated by DMA in tensile mode applying 2 µm of amplitude at a frequency of 1 Hz at a higher temperature than Tg's polymers (Fig. 9). Several models can be used to fit our experimental data (Maxwell model, Kohlrausch-Williams-Watts model, ...), but the two-phase Maxwell model (or a two-phase exponential decay function with time constant parameters) was preferred due to the presence of different types of alcohol moieties in the network (alkyl hydroxyl and phenoxy), which could result from different transesterification rates. The two phases Maxwell model consists of a sum of two terms in A exp. $(-t/\tau)$, that can be attributed to the alkyl hydroxyl and phenoxy. This

multi-element model has already been used to fit transesterification reaction in epoxy network [46] and imine exchange [47]. Two relaxation times (T1 and T2) were obtained for each curve obtained at different isothermal temperatures. All relaxation times are reported in SI (Tables 1–3).

Clearly, the nature of the diols used has an impact on the relaxation behavior, specifically on the two relaxation time, and the activation energies. For example, T2 at 160 °C, corresponding to the relaxation time for the second relaxation, was 348.4 s, 102.9 s, and 134.3 s for pPA-EG-mea, pPA-DD-mea, and pPA-PEG-mea, respectively. Thus, the lower mobility network provided by the small aliphatic chain of EG showed the highest relaxation time for each temperature. Furthermore, the strain can be completely relaxed provided the efficiency of the transesterification reaction. The low relaxation time may be obtained by the abundance of tertiary amine in the network which may favor the nucleophilic substitution of the ester by the free hydroxyl group carried by the monoethanolamine [28]. The activation energies were measured by the slope of the Arrhenius equation obtained by the linear fitting of ln (τ) versus 1/T. Calculated Ea (Table 4) are all coherent with dynamic covalent bond mechanisms, since they are in the range of transesterifications, especially in an internally-catalyzed network [25,28,48]. Captivatingly, the activation energies tend to increase as the crosslinking density decreases, which may be related to the amount of OH groups. For example, when pPA-DD- mea exhibited low crosslinking density with 800 mol/l, both activation energies reached 143.5 and 105.6 KJ/mol. Conversely, pPA-EG-mea showed a lower value with 58.1 and 49.1 KJ/mol. Finally, the polarity of the network also seems to have an impact on stress relaxation. The activation energy changes by a factor of 2 for the DD and PEG motifs, even though they revealed the same thermo-mechanical behavior.

3.4. Polybenzoxazine coatings

The three benzoxazines were applied on a heat plate with a Teflon bar without solvent. The samples were first degassed at 110 $^{\circ}$ C under pressure for 30 min and applied at 100 $^{\circ}$ C on etched aluminum 1050



Fig. 12. Bode plots of a) Epoxy, b) pPA-PEG, c) pPA-EG, d) pPA-DD coated, after immersion in 0.1 NaCl for 1 day, 7, and 50 days.

substrate. The coating was further heated in an oven at 160 $^\circ C$ for 2 h to completely cure monomers. The thickness was measured by SEM analysis and showed a width of $\pm 70~\mu m$ (Fig. 10).

To assess the polymerization of the monomers, the behavior of the coatings against common solvents was evaluated. The coatings were immersed in different solvents and stirred at 200 rpm for 24 h. All results can be found in the SI (Table 4). Only acetic acid could damage the pPA-EG-mea coating by the protonation of the tertiary amine [43]. For the other polymers, due to the presence of long spacer between the esters moieties, the ability of the solvent to remove the coating is also correlated by the aptness to swell the polymer.

To evaluate the adhesion between the metal substrate and the organic coating, a standard cross-cut adhesion test (ISO 2409) was performed. Excellent adhesion of both systems could be obtained from the intact edges without any coating detachment, as shown in the photographs in Fig. 10 (5B rating).

The water contact angles of polybenzoxazine samples on aluminum plates are shown in Fig. 11 which illustrates the importance of the diols used in the synthesis. For example, the long alkyl chain of dodecandiol imparts a more hydrophobic character, as shown by the water contact angle of 101.3°, whereas the PEG200 and EG networks are more hydrophilic (94.7 and 94.0, respectively).

3.5. Electrochemical behavior of benzoxazine coatings on A1050 Al alloy

Fig. 12 shows Bode plots of coated substrates with benzoxazine and epoxy (as a reference [49, 50]) coatings at different immersion times in

0.1 M NaCl solution. The Bode phase diagram for epoxy, and DD has one time constant and the phase angle at high frequency is around -87° reflecting both capacitive behavior and good barrier property of the coatings [51]. This time constant could cover a wide range of frequencies for DD even after 50 days of immersion. However, for the epoxy sample after 50 days of immersion and EG sample, another time constant was added at low frequencies showing a decrease in the barrier properties of the coating. For PEG, the phase angle at high frequency is around -70° , representing less protectivity of the coating in comparison to the other samples. The impedance modulus at low frequency of 0.1 Hz, as the representation of the system's resistance [52], is the highest for DD and epoxy, and after that EG and PEG, respectively. The impedance at low frequency for the epoxy sample was almost constant after 7 days of immersion $(2.7 \times 10^{10} \,\Omega.\text{cm}^2)$ until it was decreased to $6.5 \times 10^9 \,\Omega.\text{cm}^2$ after 50 days. For DD, the impedance at low frequency increased from 6.8 \times 10⁹ $\Omega.cm^2$ to 1.1 \times 10¹⁰ $\Omega.cm^2$, and for PEG from $3.8\times10^5\,\Omega.cm^2$ to $7.3\times10^5\,\Omega.cm^2$ after 50 days of immersion. While in the bode diagram of EG, this amount decreased from $3.8 \times 10^9 \,\Omega.\text{cm}^2$ to $5 \times 10^8 \,\Omega.\mathrm{cm}^2$ after the same immersion time. The impedance modulus of samples at low frequency along with immersion time is shown in Fig. 13(a).

The EIS data were fitted by different equivalent circuits presented in Fig. 14 [49,53]. As the coatings show non- ideal behavior, constant phase element (CPE) was used for fitting data. The impedance for CPE is shown by eq. $Z_{CP \ E} = [Y_0.(i.\omega)^n]^{-1}$ in which Y_0 and n are characteristic parameters of CPE. The parameter n can have values between 0 for a pure resistor and 1 for a pure capacitor [14]. Circuit (a) was used for



Fig. 13. (a) Impedance at low frequency (|Z|), (b) pore resistance of coatings (R_{coat}), and (c) capacitance of coatings (C_{coat}), obtained from fitting EIS data after immersion in 0.1 M NaCl solution.



Fig. 14. Equivalent circuits used for fitting EIS data of samples with coating.

fitting epoxy and DD samples in which R_{coat} and CPE_{coat} are related to the pore resistance and capacitance of the coating, respectively. For fitting EG at different immersion times and epoxy after 50 days of immersion, another loop with CPE_{dl} as double layer capacitance and R_{ct} as charge transfer resistance was added to the circuit (Fig. 14 (b)) due to the metal/electrolyte interface representing a reduction in corrosion resistance. Moreover, for PEG, corrosion products on the surface caused the addition of a loop to the circuit with CPE_{cor} and R_{cor} (Fig. 14 (c)). Obtaining the n value higher than 0.97 represents the capacitor behavior of the coatings. Fig. 13 (b), (c) show R_{coat} and C_{coat} evolution with time for all of the samples, respectively. According to Fig. 13 (b), the most R_{coat} after 50 days of immersion was observed for DD ($1.6 \times 10^{10} \Omega.cm^2$) and after that for epoxy coating ($5.9 \times 10^9 \Omega.cm^2$). However, the R_{coat} of EG and PEG are in the order of $10^3-10^4 \ \Omega.cm^2$. For DD, the amount of R_{coat} was first increased from $7.1 \times 10^9 \ \Omega.cm^2$ to $2.3 \times 10^{11} \ \Omega.cm^2$ and then decreased to $1.6 \times 10^{10} \ \Omega.cm^2$ which is more than the amount of R_{coat} at 1 h immersion. The same trend was seen in C_{coat} for this sample but in an inverse way (first decrease from $9.5 \times 10^{-11} \ \Omega^{-1} s^n cm^{-2}$ to $5.7 \times 10^{-11} \ \Omega^{-1} s^n cm^{-2}$ and then increase to $9.5 \times 10^{-11} \ \Omega^{-1} s^n cm^{-2}$ after 50 days of immersion). This may be due to the self-healing ability of the coatings and retrieving corrosion resistance. The same behavior was observed for PEG but for this sample, the existence of corrosion product can also affect the increase in corrosion resistance [54] (the value of these parameters can be found in Fig. 13). With increasing immersion time for epoxy and EG, R_{coat} was diminished, and the amount of C_{coat} increased due to the penetration of electrolyte in the coating [55]. The



Fig. 6. Self healing behavior of benzoxazine polymers.

Table 3	
Self healing behavior of benzoxazine polyme	rs.

Samples	Initial width (μm)	Width after 1 h (µm)	Self- healing 1 h (%)	Width after 2 h (µm)	Self- healing 2 h (%)
pPA-PEG- mea	168 ± 9	127 ± 11	24	82 ± 5	51
pPA-DD- mea	117 ± 11	45 ± 9	61	36 ± 5	69
pPA-EG- mea	139 ± 11	93 ± 8	33	75 ± 9	46

Table 4

Transesterification activation energies of each polybenzoxazine network.

Samples	$R_{ln\tau_1}^2$	$Ea_{ln\tau_1}$	$R_{ln\tau_2}^2$	$Ea_{ln\tau_2}$
pPA-PEG-mea	0.993	78.9	0.994	43.9
pPA-DD-mea	0.999	143.5	0.997	105.6
pPA-EG-mea	0.981	58.1	0.983	49.1

value of C_{coat} can be estimated by the equation below:

$$C_{coat} = \varepsilon \varepsilon_0 \frac{A}{d} \tag{5}$$

In this equation, ϵ and ϵ_0 stands for the electrical permittivity of the corrosive medium and vacuum, and A and d show the area and the thickness of the coating, respectively. With passing time, water can penetrate coatings and increase ϵ , as the water relative permittivity is 80 (while this amount is between 2.5 and 10 for the organic coatings). According to Fig. 13 (c), C_{coat} increase from 5.7 \times 10⁻¹¹ to 6.8 \times 10⁻¹¹ $\Omega^{-1} s^n cm^{-2}$ and from 9 \times 10⁻¹¹ to 1 \times 10⁻¹¹ $\Omega^{-1} s^n cm^{-2}$ for epoxy and EG, respectively after 50 days of immersion.

The better corrosion resistance of DD can be attributed to the longer carbon chain (in comparison to EG) and the hydrophobic property of this sample. The existence of more phenolic functions in EG than in DD facilitates the interactions with water by hydrogen bonds which increase the hydrophilicity. Besides, the hydrophile PEG, as the result of C—O bond in the chemical structure [56], does not have proper barrier property and swells as it is also visually observed.

In the study of Golru et al. [8], epoxy/polyamide coating with a

thickness of 40 µm was used for A1050 alloy substrate. The impedance modulus at low frequency for this sample was around $1 \times 10^9 \ \Omega.\mathrm{cm}^2$ after 3 days and reduced to $<10^8 \ \Omega.\mathrm{cm}^2$ after 60 days [8]. Bandeira et al. [9] used polyaniline coating on A1050, and their best protective coating was obtained for intermediate-thickness coatings (18–23 µm) due to having lower roughness with the impedance of around $10^7 \ \Omega.\mathrm{cm}^2$ at low frequency after 1 day. Polybenzoxazine synthesized from commercial bisphenol A, revealed impedance at low frequency in the order of $10^8 \ \Omega.\mathrm{cm}^2$ after 30 days of immersion (thickness around $10 \ \mu\mathrm{m}$) [17] and the impedance of P-pPDA benzoxazine was in the order of $10^6 \ \Omega.\mathrm{cm}^2$ after 21 days [14]. Even though the thickness of the coatings in the current study is larger than the abovementioned studies, the protectivity and corrosion resistance of DD sample is high enough and could maintain its anti-corrosive properties after 50 days of immersion.

4. Conclusion

In this study, three solventless bio-sourced benzoxazine polymer coatings exhibiting healing ability via dynamic covalent bond exchange were reported. Proton NMR spectra confirmed the successful preparation of precursors as indicated by the presence of oxazine ring and their polymerizability by ROP was evidenced by DSC/FTIR analyses. The properties of the resulting resins were largely found to be dependent on the type of diols used for their synthesis. More precisely, the structure with the shorter chain (i.e. EG) led to the more rigid system with higher Tg, higher storage modulus at room temperature, higher crosslink density and better solvent resistance whereas the structures bearing longer aliphatic moieties (i.e. PEG and DD) resulted in higher chains mobility allowing enhanced self-healing and mendable properties. In addition, the three resins were found to be reprocessable with no loss of mechanical properties and thus paving the way to their recyclability. Specifically for coating applications, thanks to their low viscosity, all precursors could be applied directly to etched A1050 substrates in the complete absence of solvent, which is an asset in achieving a more environmentally friendly solution. EIS results highlighted that the corrosion resistance of both PEG and DD-based coatings increased with immersion time due to dynamic bond exchanges promoting enhanced substrate protection. The DD-based system was found to display the best corrosion behavior after 50 days of immersion, making it a suitable candidate for industrial applications.

CRediT authorship contribution statement

Louis Van Renterghem: Writing – original draft, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Roya Malekkhouyan: Writing – original draft, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Leila Bonnaud: Writing – review & editing, Supervision, Resources, Conceptualization. Romain Tavernier: Software, Methodology, Formal analysis, Data curation. Marjorie Olivier: Writing – review & editing, Supervision, Resources, Conceptualization. Jean-Marie Raquez: Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare no conflict of interest.

Data availability

No data was used for the research described in the article.

Acknowledgements

The authors wish to thank the Wallonia-Brussels Federation, Wallonia, and the European Community for general support in the frame of the Concerted Research Action program (ARC 2020 - PROCOMAG project). L.B. also want to thank the INTERREG V FWVL program (ATHENS project) and PIT AERO (WINGS project). JMR is FRS-FNRS senior research associate.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.porgcoat.2024.108316.

References

- Alexis Renaud, Yoann Paint, Alex Lanzutti, Leïla Bonnaud, Lorenzo Fedrizzi, Philippe Dubois, Marc Poorteman, Marie Georges Olivier, Sealing porous anodic layers on AA2024-T3 with a low viscosity benzoxazine resin for corrosion protection in aeronautical applications, RSC Advances 9 (29) (2019) 16819–16830.
- [2] Niloofar Hosseiny, Ali Shabani, Mohammad Reza Toroghinejad, Effect of bimodal microstructure on texture evolution and mechanical properties of 1050 Al alloy processed through severe plastic deformation and subsequent annealing, Mater. Sci. Eng. A 820 (2021) 7.
- [3] Ruohan Zhao, Patrick Rupper, Sabyasachi Gaan, Recent Development in Phosphonic Acid-Based Organic Coatings on Aluminum 9, 2017.
- [4] Alexis Renaud, Marc Poorteman, Julien Escobar, Ludovic Dumas, Yoann Paint, Leïla Bonnaud, Philippe Dubois, Marie Georges Olivier, A new corrosion protection approach for aeronautical applications combining a phenolparaPhenyleneDiAmine benzoxazine resin applied on sulfo-tartaric anodized aluminum, Prog. Org. Coat. 112 (2017) 278–287, 11.
- [5] Shuaipeng Wang, Wu Yonggang, Jinyue Dai, Na Teng, Yunyan Peng, Lijun Cao, Xiaoqing Liu, Making organic coatings greener: renewable resource, solvent-free synthesis, UV curing and repairability, Eur. Polym. J. 123 (2020) 1.
- [6] J. M. Hu, J. Q. Zhang, and C. N. Cao. Determination of water uptake and diffusion of Cl- ion in epoxy primer on aluminum alloys in NaCl solution by electrochemical impedance spectroscopy. Prog. Org. Coat., 46(4):273–279, 6 2003.
- [7] J.B. Bajat, V.B. Mišković-Stanković, Z. Kačarević-Popović, Corrosion stability of epoxy coatings on aluminum pretreated by vinyltriethoxysilane, Corros. Sci. 50 (7) (2008) 2078–2084, 7.
- [8] S. Sharifi Golru, M.M. Attar, B. Ramezanzadeh, Effects of surface treatment of aluminium alloy 1050 on the adhesion and anticorrosion properties of the epoxy coating, Appl. Surf. Sci. 345 (2015) 360–368.
- [9] Rafael Marinho Bandeira, Julia van Drunen, Amanda Cristina Garcia, Germano Tremiliosi-Filho, Influence of the thickness and roughness of polyaniline coatings on corrosion protection of AA7075 aluminum alloy, Electrochim. Acta 240 (2017) 215–224, 6.
- [10] Jie He, Dennis E. Tallman, Gordon P. Bierwagen, Conjugated polymers for corrosion control: scanning vibrating electrode studies of polypyrrole-aluminum alloy interactions, J. Electrochem. Soc. 151 (12) (2004) B644.
- [11] Carlos H. Carlos, Mauro R. Mauro, Alessandra F. Baldissera, Carlos A. Ferreira, A new benzoxazine-based intumescent coating for passive protection against fire, Prog. Org. Coat. 137 (2019), 12.

- [12] Deepak M. Patil, Ganesh A. Phalak, and S. T. Mhaske. Enhancement of anticorrosive performances of cardanol based amine functional benzoxazine resin by copolymerizing with epoxy resins. Prog. Org. Coat., 105:18–28, 4 2017.
- [13] Hatsuo Ishida, Tarek Agag, Amsterdam Boston, Heidelberg, London, New, York • Oxford, Paris • San, Diego • San, Francisco • Sydney, and • Tokyo. Handbook of Benzoxazine Resins Edited by. Technical report.
- [14] Alexis Renaud, Leïla Bonnaud, Ludovic Dumas, Tao Zhang, Yoann Paint, Francesco Fasano, Olesia Kulyk, Eva Pospisilova, Bernard Nysten, Arnaud Delcorte, Davide Bonifazi, Philippe Dubois, Marie Georges Olivier, Marc Poorteman, A benzoxazine/substituted borazine composite coating: a new resin for improving the corrosion resistance of the pristine benzoxazine coating applied on aluminum, Eur. Polym. J. 109 (2018) 460–472, 12.
- [15] N.N. Ghosh, B. Kiskan, Y. Yagci, Polybenzoxazines-new high performance thermosetting resins, Synthesis and properties 11 (2007).
- [16] Marc Poorteman, Alexis Renaud, Julien Escobar, Ludovic Dumas, Leïla Bonnaud, Philippe Dubois, Marie Georges Olivier, Thermal curing of para-phenylenediamine benzoxazine for barrier coating applications on 1050 aluminum alloys, Prog. Org. Coat. 97 (2016) 99–109, 8.
- [17] Julien Escobar, Marc Poorteman, Ludovic Dumas, Leïla Bonnaud, Philippe Dubois, Marie Georges Olivier, Thermal curing study of bisphenol A enzoxazine for barrier coating applications on 1050 aluminum alloy, Prog. Org. Coat. 79 (C) (2015) 53–61.
- [18] Ludovic Dumas, Leïla Bonnaud, Marjorie Olivier, Marc Poorteman, Philippe Dubois, Arbutin-based benzoxazine:: En route to an intrinsic water soluble biobased resin, Green Chem. 18 (18) (2016) 4954–4960.
- [19] Ludovic Dumas, Leila Bonnaud, Marjorie Olivier, Marc Poorteman, Philippe Dubois, Chavicol benzoxazine: ultrahigh Tg biobased thermoset with tunable extended network, Eur. Polym. J. 81 (2016) 337–346, 8.
- [20] Zhibin Wen, Leïla Bonnaud, Rosica Mincheva, Philippe Dubois, Jean-Marie Raquez, Materials Development of Low-Viscosity and High-Performance Biobased Monobenzoxazine from Tyrosol and Furfurylamine, 2021.
- [21] Ludovic Dumas, Leïla Bonnaud, Marjorie Olivier, Marc Poorteman, Philippe Dubois, Eugenol-based benzoxazine: from straight synthesis to taming of the network properties, J. Mater. Chem. A 3 (11) (2015) 6012–6018, 3.
- [22] Damien Montarnal, Mathieu Capelot, François Tournilhac, Ludwik Leibler, Silicalike malleable materials from permanent organic networks, Science 334 (6058) (2011) 965–968, 11.
- [23] Leïla Bonnaud, Benjamin Chollet, Ludovic Dumas, Aurélien A.M. Peru, Amandine L. Flourat, Florent Allais, Philippe Dubois, High- performance bio-based benzoxazines from enzymatic synthesis of diphenols, Macromol. Chem. Phys. 220 (1) (2019), 1.
- [24] Zhibin Wen, Leïla Bonnaud, Philippe Dubois, and Jean Marie Raquez. Catalyst-free reprocessable crosslinked biobased polybenzoxazine- polyurethane based on dynamic carbamate chemistry. J. Appl. Polym. Sci., 139(19), 5 2022.
- [25] Antoine Adjaoud, Acerina Trejo-Machin, Laura Puchot, Pierre Verge, Polybenzoxazines: a sustainable platform for the design of fast responsive and catalyst-free vitrimers based on trans-esterification exchanges, Polym. Chem. 12 (22) (2021) 3276–3289, 6.
- [26] Caiying Bo, Ye Sha, Fei Song, Meng Zhang, Hu Lihong, Puyou Jia, Yonghong Zhou, Renewable benzoxazine-based thermosets from cashew nut: investigating the selfhealing, shape memory, recyclability and antibacterial activity, J. Clean. Prod. 341 (2022), 3.
- [27] Mustafa Arslan, Baris Kiskan, Yusuf Yagci, Recycling and self-healing of polybenzoxazines with dynamic sulfide linkages, Sci. Rep. 7 (1) (2017), 12.
- [28] Facundo I. Altuna, Cristina E. Hoppe, Roberto J.J. Williams, Epoxy vitrimers with a covalently bonded tertiary amine as catalyst of the transesterification reaction, Eur. Polym. J. 113 (2019) 297–304, 4.
- [29] Meng Wei Wang, Ru Jong Jeng, Ching Hsuan Lin, Study on the ring-opening polymerization of benzoxazine through multisubstituted polybenzoxazine precursors, Macromolecules 48 (3) (2015) 530–535, 2.
- [30] Marc Comí, Gerard Lligadas, Juan C. Ronda, Marina Galià, Virginia Cádiz, Renewable benzoxazine monomers from "lignin-like" naturally occurring phenolic derivatives, J. Polym. Sci. A Polym. Chem. 51 (22) (2013) 4894–4903, 11.
- [31] Mustafa Arslan, Synthesis and characterization of novel bio-based benzoxazines from gallic acid with latent catalytic characteristics, React. Funct. Polym. 139 (2019) 9–16, 6.
- [32] Riyad Mahfud, Tarek Agag, Hatsuo Ishida, Sohel Shaikh, Syed Qutubuddin, Synthesis and evaluation of novel anionic polymeric surfactants based on polybenzoxazines, J. Colloid Interface Sci. 407 (2013) 339–347, 10.
- [33] Acerina Trejo-Machin, Pierre Verge, Laura Puchot, Robert Quintana, Phloretic acid as an alternative to the phenolation of aliphatic hydroxyls for the elaboration of polybenzoxazine, Green Chem. 19 (21) (2017) 5065–5073.
- [34] Mirjam Foti, Rosario Médici, Harald J. Ruijssenaars, Biological production of monoethanolamine by engineered pseudomonas putida S12, J. Biotechnol. 167 (3) (2013) 344–349.
- [35] J. Dunkerst, H. Ishida, Vibrational assignments of N,N-bis(3,5-dimethyl-2hydroxybenzyl)methylamine in the fingerprint region, Technical Report 5 (1995).
- [36] Ryoichi Kudoh, Atsushi Sudo, Takeshi Endo, A highly reactive benzoxazine monomer, 1-(2-hydroxyethyl)-1,3-Benzoxazine: activation of benzoxazine by neighboring group participation of hydroxyl group, Macromolecules 43 (3) (2010) 1185–1187, 2.
- [37] Kan Zhang, Lu Mengchao Han, Han, and Hatsuo Ishida., Resveratrol-based trifunctional benzoxazines: synthesis, characterization, polymerization, and thermal and flame retardant properties, Eur. Polym. J. 116 (2019) 526–533, 7.

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- [38] Hongjie Yao, Lu Xin, Zhong Xin, Xiu Li, Chen Chen, Yuzhu Cao, Two novel eugenol-based difunctional benzoxazines: synthesis and properties, Colloids Surf. A Physicochem. Eng. Asp. 616 (2021), 5.
- [39] Acerina Trejo-Machin, Laura Puchot, Pierre Verge, A cardanol-based polybenzoxazine vitrimer: recycling, reshaping and reversible adhesion, Polymer Chemistry 11 (44) (2020) 7026–7034, 11.
- [40] Shaoheng Yang, Heng Fang, Hai Li, Fangning Shen, Xudong Chen, Hu Yang, Zhuohong Yang, Synthesis of tung oil-based vinyl ester resin and its application for anti-corrosion coatings, Prog. Org. Coat. 170 (2022), 9.
- [41] Xiang Wang, R.M. Weiqi Leng, Oshani Nayanathara, Eugene B. Caldona, Liyang Liu, Lei Chen, Rigoberto C. Advincula, Zhao Zhang, Xuefeng Zhang, Anticorrosive epoxy coatings from direct epoxidation of bioethanol fractionated lignin, Int. J. Biol. Macromol. 221 (2022) 268–277, 11.
- [42] Filip Van Lijsebetten, Stéphanie Engelen, Erwin Bauters, Wim Van Vooren, Maarten M.J. Smulders, Filip E. Du Prez, Recyclable vitrimer epoxy coatings for durable protection, Eur. Polym. J. 176 (2022), 8.
- [43] Jacob Song Kiat Lim, Chee Lip Gan, Hu. Xiao Matthew, Unraveling the mechanistic origins of epoxy degradation in acids, ACS Omega 4 (6) (2019) 10799–10808, 6.
- [44] Chiara Di Mauro, Samuel Malburet, Alain Graillot, Alice Mija, Recyclable, repairable, and reshapable (3R) thermoset materials with shape memory properties from bio-based epoxidized vegetable oils, ACS Appl. Bio Mater. 3 (11) (2020) 8094–8104, 11.
- [45] Hafeezullah Memon, Haiyang Liu, Muhammad A. Rashid, Li Chen, Qiuran Jiang, Liying Zhang, Yi Wei, Wanshuang Liu, Yiping Qiu, Vanillin-based epoxy vitrimer with high performance and closed-loop recyclability, Macromolecules 53 (2) (2020) 621–630, 1.
- [46] Yang Yang, Guirong Peng, Wu Shu, Wenguang Hao, A repairable anhydride-epoxy system with high mechanical properties inspired by vitrimers, Polymer 159 (2018) 162–168, 12.
- [47] Sybren K. Schoustra, Timo Groeneveld, Maarten M.J. Smulders, The effect of polarity on the molecular exchange dynamics in imine-based covalent adaptable networks, Polymer Chemistry 12 (11) (2021) 1635–1642, 3.

- [48] Florian Cuminet, Dimitri Berne, Sébastien Lemouzy, Éric Dantras, Christine Joly-Duhamel, Sylvain Caillol, Éric Leclerc, Vincent Ladmiral, Catalyst-free transesterification vitrimers: activation via *a*-difluoroesters, Polymer Chemistry13 (2022) 2651–2658.
- [49] M. Toorani, M. Aliofkhazraei, M. Mahdavian, R. Naderi, Superior corrosion protection and adhesion strength of epoxy coating applied on AZ31 magnesium alloy pre-treated by PEO/Silane with inorganic and organic corrosion inhibitors, Corros. Sci. 178 (2021), 1.
- [50] Adolphe Foyet, A. Te Hui Wu, Leo G. Kodentsov, Van der Ven, Gijsbertus De With, Rolf A. Van Benthem, Absorption of water and corrosion performance of a clear and pigmented epoxy coating on Al-2024 alloy, ECS Trans. 25 (29) (2019) 31–39, 12.
- [51] Jéssica V. Nardeli, Cecílio S. Fugivara, M.F. Maryna Taryba, Montemor, and Assis V. Benedetti., Self-healing ability based on hydrogen bonds in organic coatings for corrosion protection of AA1200, Corros. Sci. 177 (2020), 12.
- [52] Su Caina, Wu Wei, Zuopeng Li, Yong Guo, Prediction of film performance by electrochemical impedance spectroscopy, Corros. Sci. 99 (2015) 42–52, 10.
- [53] I.C.P. Margarit-Mattos, EIS and organic coatings performance: revisiting some key points, Electrochim. Acta 354 (2020), 9.
- [54] Suyun Liu, Li Liu, Xinxin Wei, Bo Zhang, Fandi Meng, Fuhui Wang, Oxide film formed on Al alloy beneath sulfosalicylic acid doped polyaniline incorporated into epoxy organic coating, Appl. Surf. Sci. 512 (2020), 5.
- [55] Jorge Andrés Calderón-Gutierrez, Franky Esteban Bedoya-Lora, BARRIER PROPERTY DETERMINATION AND LIFETIME PRE- DICTION BY ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY OF A HIGH PERFORMANCE ORGANIC COATING DETER- MINACIÓN DE PROPIEDADES BARRERA Y DE PREDICCIÓN DE TIEMPO DE VIDA POR ESPECTROSCOPÍA DE IMPEDANCIA ELECTROQUÍMICA DE UN RECUBRIMIENTO ORGÁNICO DE ALTO RENDIMIENTO 81(183), 2014, pp. 97–106.
- [56] Ken Kojio, Yoshitaka Mitsui, Mutsuhisa Furukawa, Synthesis and properties of highly hydrophilic polyurethane based on diisocyanate with ether group, Polymer 50 (15) (2009) 3693–3697, 7.