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Recyclable vitrimer epoxy coatings for durable protection

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ABSTRACT

In this research, the synthesis and application of vitrimer epoxy coatings for long-term corrosion protection of metal surfaces are described. To that end, a polyamine curing agent based on vinylogous urethanes (VUs) was developed to add repairability, recyclability and recoatability to thermosetting materials. Thin films with excellent resistance to water penetration and damage could be obtained by combining the dynamic hardener with existing epoxy resins, resulting in good barrier properties. Various formulations were investigated yielding transparent coatings with durable corrosion protection, even after being scratched, exposed to saltwater, and subjected to steam condensation. Furthermore, stress-relaxation experiments revealed sufficient material flow at 150 °C, which could be significantly slowed down below 100 °C. Optical microscopy was used to demonstrate the healing ability of the vitrimer coatings, resulting in the restoration of barrier properties after scratching. The dynamic properties of the epoxy resin were used to recoat an aluminium plate as a proof of concept, demonstrating that the thin layer could be adhered to a surface again in its cured state. As a result, the service life of epoxy coatings and protected metals could be extended while maintaining excellent mechanical properties, opening the door to a wide range of potential applications such as marine coatings and concrete bonding.

1. Introduction

Epoxy coatings are thermosets with superior performance characteristics in terms of strength, toughness, thermal and adhesive properties, making them ideal for a variety of bonding, structural, and protective applications [1–3]. Epoxies, in particular, are arguably one of the most commonly used industrial barrier coatings to prevent corrosion of metal surfaces, thereby avoiding significant economic losses [4]. However, after prolonged environmental exposure or mechanical damage, the protective layer may fail, exposing the metal surface. To withstand these stringent requirements, new types of cross-linkers with improved performance have been developed. For two-component epoxy coatings, the most popular compounds in this regard are (poly)amines and reactive amidoamines, which offer the advantage of flexibility and high hydrophobicity [5–7]. Nevertheless, like all covalently cross-linked materials, epoxy resins do not flow and cannot be healed, reshaped or recycled, and are thus discarded after damage or failure. As a result, there has been an increasing interest in the synthesis and application of robust, but responsive hardeners for dynamic polymer networks in recent years in order to (re)use epoxy materials more efficiently [8–13].

Vitrimers are an important subclass of dynamic materials in which rapid exchange of cross-links results in material flow upon heating without losing connectivity [14]. In this sense, the nature of the dynamic exchange reaction primarily determines the obtained material properties, which has been the subject of several dedicated reviews [15–19]. Consequently, several cross-linkers based on (polyfunctional) amine curing agents, have been modified to obtain epoxy vitrimer materials [20–28]. For example, our research group prepared a straightforward type of amine curative, based on vinylogous urethane (VU) bonds, for the fast (re)processing of high T_g epoxy networks [29]. Despite the fact that the use of epoxy vitrimers has been demonstrated frequently for bulk applications, their use for 'smart' coating systems has had limited

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Abbreviations: BAC, 1,3-bis(aminomethyl)cyclohexane; BADGE, Bisphenol A diglycidyl ether; BDAA, 1,4-butanediol diacetoacetate; bp, boiling point; DSC, differential scanning calorimetry; FTIR, Fourier-transform infrared spectroscopy; GU, gloss units; TGA, thermogravimetric analyses; T_g, glass transition temperature; THF, tetrahydrofuran; VU, vinylogous urethane; VUE, vinylogous urethane epoxy; WLF, Williams-Landel-Ferry.

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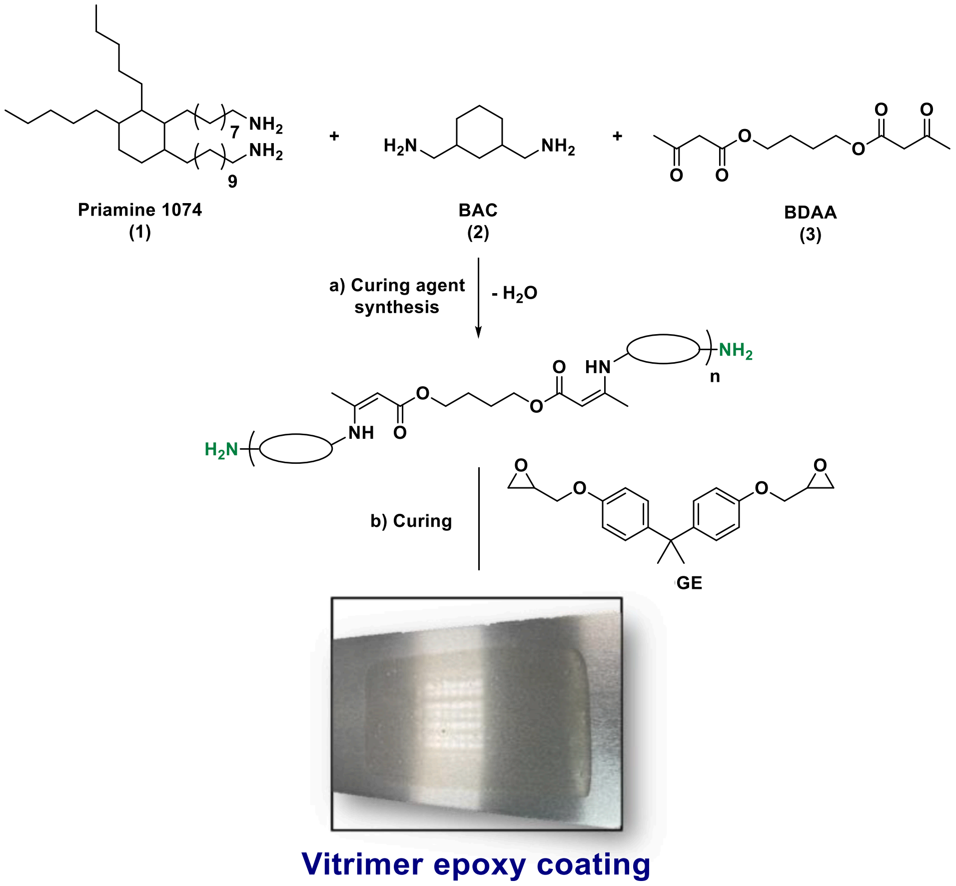

Fig. 1. Design concept of vitrimer epoxy coatings. a) Polycondensation reaction resulting in a vinylogous urethane-based polyamine curing agent. b) Application of the two-component epoxy formulation on an anodised aluminium panel.

success [30–34]. This can be explained by the required use of additives, catalysts, or hardeners, which results in formulations with (physico)-chemical properties that are quite different from those found in existing formulations. Therefore, an increasing demand exists for more appropriate methods to introduce damage-tolerant epoxy coatings without sacrificing durability or performance [35].

In this work, we report the design and synthesis of vitrimer epoxy coatings with intrinsic damage resistance and repairability. To accomplish this, an amine-acetoacetate mixture was prepolymerised to obtain an oligomeric vinylogous urethane-based amine curing agent (Fig. 1a), which was then mixed with commercially available epoxy monomers and cured as a thin layer on an aluminium substrate (Fig. 1**b**). Various monomer compositions were tested using this scalable approach to determine the effect of dynamic bonds on adhesion, hardness, wetting, and repairability. We show that the transparent coatings retained their water-repellent barrier properties, even after being scratched, cut, exposed to saltwater, and subjected to steam condensation. Furthermore, the efficiency of dynamic bond exchange was demonstrated by performing healing and recoating tests as well as stress-relaxation measurements on bulk samples.

2. Results and discussion

Because one of the primary goals of this research was to develop a dynamic (poly)amine curing agent with competitive properties compared to a readily used polyamidoamine hardener (Ancamide 2864), the starting point of this research effort was the selection of appropriate monomers. Generally, polyamidoamines are obtained by reacting a bio-based fatty acid with an amine mixture [6], whereby good flexibility and hydrophobicity are mainly attributed to the dimer compound. Analogously, when preparing the VU-based curing agent (see Fig. 1), the fatty acid derived Priamine 1074 (**1**) was selected for its hydrophobic nature and mixed with 1,3-bis(aminomethyl)cyclohexane (BAC, **2**) and 1,4-butanediol diacetoacetate (BDAA, **3**). To this end, a fixed ratio of 3:7 Priamine to BAC was determined (as primarily based on T_g analysis by DSC, *vide infra*) for good mechanical stability and flexibility, while different ratios of amine:acetoacetate (NH_2/AA), ranging from 1.1 to 1.4, were used to determine the most preferred composition. Polycondensation was done at 80 °C for 24 h in a vacuum oven to remove the water condensate, according to a previously reported procedure [29].

In a next step, coating formulations were obtained by mixing the aforementioned curing agents with bisphenol A diglycidyl ether (BADGE) in an epoxide-to-amine (E/NH) ratio of 0.95 at 60 °C for 15 min. Importantly, the calculated 5 mol% excess of pendant amines serves three different purposes: promote VU exchange reactions [29], inhibit corrosion (*i.e.* adsorption barrier for corrosive species) [36], and enhance adhesion to the metal surface [7]. Without addition of any solvent or diluent, viscosities of the curatives ranged from 5 to 40 Pa.s at 100 °C, which was too high compared to Ancamide 2864 (0.05 Pa.s, 100 °C). The significant difference in viscosities can be explained by the presence of up to 50 wt% of benzyl alcohol in Ancamide 2864. As this high boiling solvent (bp = 205 °C) cannot be easily removed upon curing, which was expected to interfere with thermal and rheology measurements of the vitrimer coatings, up to 50 wt% of ethyl acetate (bp = 77 °C) was added to the formulations. This was found to ensure good wetting upon film application (see SI for details on film application). After drying for 24 h at 100 °C, tack-free transparent films with a coating thickness of 20 to 40 μm could be obtained, further referred to as VUE-1.1, VUE, 1.2, VUE-1.3 and VUE-1.4 with the numbers referring to

Table 1
Overview of composition and physical properties of (vitrimer) epoxy coatings.

Coating	T_g[a] (°C)	$T_{d5\%}$[b] (°C)	Swel. Rat.[c] (%)	Sol. Frac.[d] (%)	Thickness (μm)[e]	Adhesion[f]	θ[g] (°)	H/E[h]
VUE-1.1	17	295	317 ± 8	11.4 ± 2.7	20–30	5B	80	0.6
VUE-1.2	23	287	176 ± 5	4.4 ± 0.5	25–32	5B	79	1.7
VUE-1.3	39	289	273 ± 25	5.4 ± 0.7	25–32	5B	77	2.6
VUE-1.4	41	301	257 ± 13	5.1 ± 0.5	27–33	5B	82	4.3
Reference	36	-[i]	340 ± 12	5.8 ± 1.2	34–39	5B	69	4.8

[a] Determined from the second heating in DSC analysis (10 °C.min^{-1}).
[b] TGA onset temperature after 5 % weight loss ($T_{d5\%}$).
[c] Obtained from a four-sample measurement in THF at rt for 24 h.
[d] Obtained from Soxhlet extraction in THF for 24 h.
[e] Dry film thickness was confirmed using an elcometer 345 coating thickness gauge.
[f] Determined by cross-hatch adhesion test (ASTM D3359).
[g] Measured *via* static water contact angle measurements.
[h] Hardness (H) and elasticity (E) values obtained by nanoindentation.
[i] Interference by evaporation of benzyl alcohol (diluent) did not allow accurate determination.

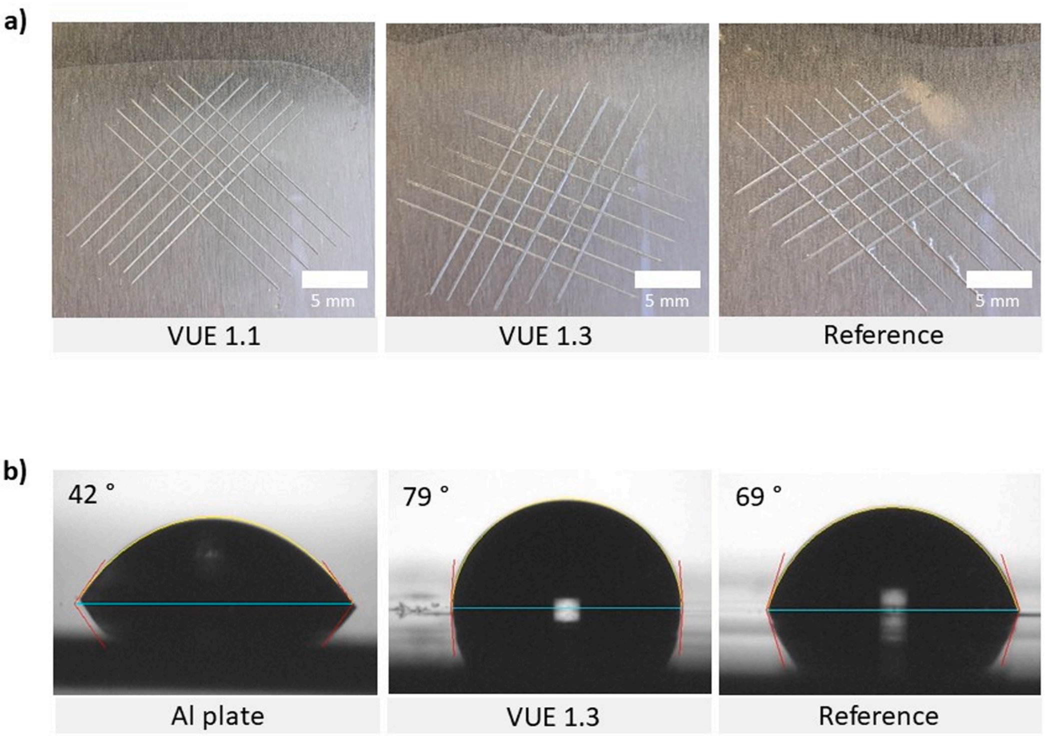

Fig. 2. a) Photographs of the epoxy vitrimer and reference coatings after a cross-cut adhesion test. b) Static water contact angle measurements of plain (uncoated) aluminium sheet and coated samples, indicating an increase in hydrophobicity after coating.

the NH$_2$/AA ratio (**Fig. S1**). The obtained materials had a relative variable amount of dynamic VU bonds ranging from 83 to 56 mol%, which were necessary to introduce sufficient (re)processability to the final material [29,37]. Using an E/NH ratio of 1.0, Ancamide 2864 was mixed with BADGE to obtain a reference material with no visual difference and similar film thickness (**Fig. S2**). The transparency of all films was confirmed *via* light reflectance, showing high gloss values of ca. 120 GU.

2.1. Thermal and barrier properties

To ensure that the dynamic cross-linker was incorporated as intended, completion of curing was confirmed *via* IR analysis, indicating the presence of distinct VU signals at 1648 cm^{-1} and 1602 cm^{-1}, while no residual signals corresponding to epoxide groups could be detected at 910 cm^{-1} (**Fig. S3-S4**). Moreover, as determined by DSC analysis, no further exothermic reactions were observed in the first heating scans, while T_g values ranging from 17 °C to 41 °C could be obtained for the epoxy vitrimers and reference material (Fig. S5–S6). Since healing of the coatings is expected to be activated upon heating, further thermal characterisation included TGA measurements, yielding relatively high decomposition temperatures in the range of 285 °C to 300 °C (**Fig. S7-S8**). In addition, no significant mass loss (<1%) could be detected from isothermal TGA analysis after heating at 160 °C over a period of 2 h (**Fig. S9**). In contrast, a large mass loss was measured for the reference material, which is attributed to evaporation of the (high boiling) additive benzyl alcohol (**Fig. S10**). Further, good network integrity was confirmed *via* Soxhlet extraction and swelling experiments in THF for 24 h (Table 1).

Having determined the materials' thermal properties after curing, the barrier properties of the cured epoxy film could subsequently be studied. To assess adhesion to the metal substrate, a standard cross-cut adhesion test (ASTM D3359-02) was first performed (**Fig. S11-S12**).

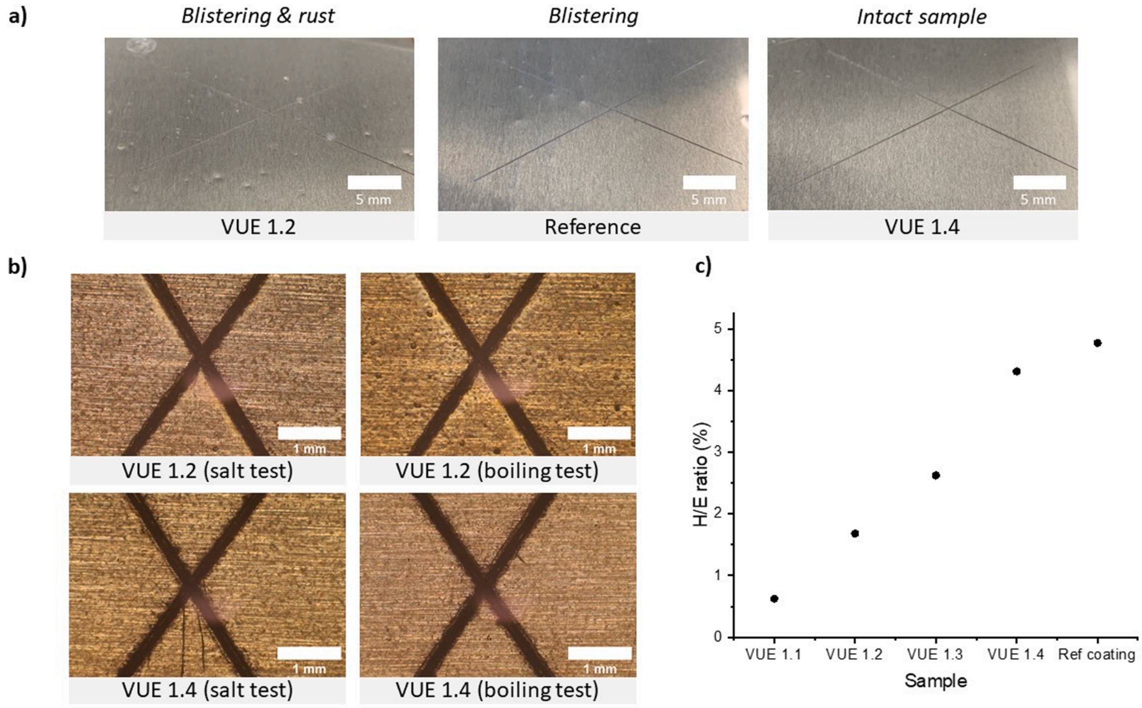

Fig. 3. a) Camera images and b) Optical microscope images of epoxy vitrimer and reference coatings, having undergone a boiling water adhesion test after corrosion resistance experiment for 30 days. c) Calculated hardness and elastic moduli (H/E) ratio of all coated samples.

Excellent adhesion of both the vitrimers and benchmark samples could be concluded from the intact edges without any coating detachment, as shown in the photographs in Fig. 2**a** (5B rating). Following that, static water contact angle measurements were performed to determine the hydrophobicity of the adhered films in comparison to the plain metal surface (**Fig. S13**). When comparing the reference material to the epoxy vitrimers, the contact angle (θ) increased from 67° to 76-82°, which were both significantly higher values than for the uncoated sample (θ = 43°) (Fig. 2**b**).

Motivated by the increased hydrophobic character of the vitrimer system, the coatings were immersed in a water solution to evaluate the coating stability. After immersion for one day, no signs of delamination could be observed. Because water did not pass through the barrier easily, the corrosion resistance of the coated samples was qualitatively investigated by cutting St. Andrew's crosses along the surface and soaking the samples in a 5 M NaCl solution at room temperature for one month. After a visual inspection every 5 days, no signs of corrosion on the metal surface of any of the tested coatings could be found (**Fig. S14-S18**). However, blistering could be observed as a result of water penetration in VUE 1.1, VUE 1.2 and the reference coating, leading to reduced adhesion and eventually delamination over time. The effects were even more dramatic when the same samples were subjected to a boiling water adhesion test (**Fig. S19-S23**). Significant corrosion and blistering were indeed found in VUE 1.1 and VUE 1.2, resulting in poor corrosion resistance under boiling water conditions (Fig. 3**a**). Although blistering was found in the reference coating, no macroscopic corrosion could be detected. On the other hand, VUE 1.3 and VUE 1.4 exhibited no blistering or corrosion, indicating excellent corrosion resistance, even when exposed to boiling water. The improved performance of VUE 1.3 and VUE 1.4 over the other two coatings was rationalised by the larger epoxy content, resulting in a higher cross-linking density and stronger adhesion (*i.e.* more hydroxyl groups available to interact with the surface) [38]. Moreover, optical microscope images were taken to confirm the difference in blistering behaviour (Fig. 3**b** and **Fig. S24-S25**).

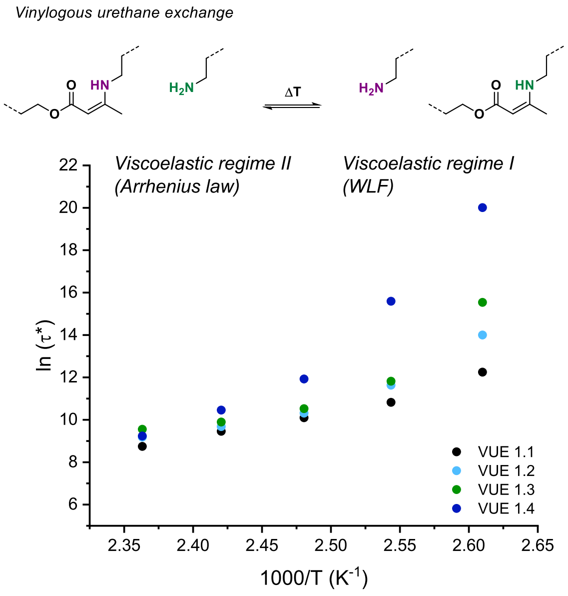

Fig. 4. Temperature dependence of material flow for VUE materials, highlighting two viscoelastic regimes where relaxation is first controlled by diffusion (WLF) and then by exchange kinetics (Arrhenius law).

Nanoindentation experiments were carried out to further evaluate the mechanical properties. For the VUE coatings, it was observed that a higher cross-linking degree resulted in an increased coating hardness (H), while yielding relatively similar elasticity (E) (**Fig. S26**). Due to differences in composition, absolute values of the vitrimer and reference coatings are not comparable, but competitive values for a H/E ratio could be obtained (Fig. 3**c**), indicating that resilient thin films have been obtained. These encouraging findings, that ultimately could be further supported by a more quantitative description of the barrier properties, indicate that the vitrimer coatings produced equivalent barrier properties in comparison to the commercial resin.

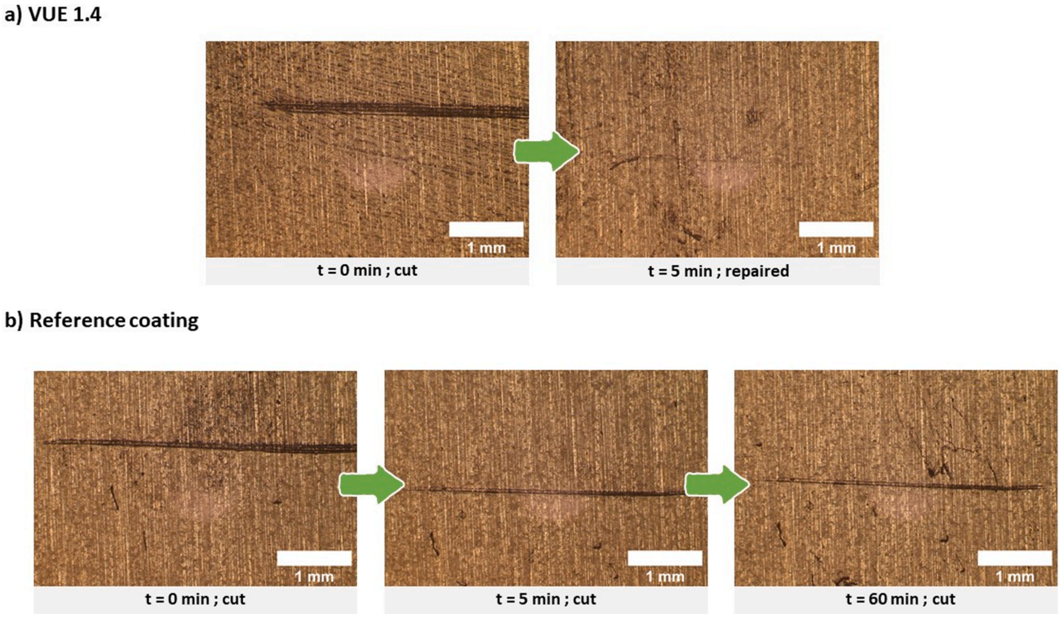

Fig. 5. Scratch healing performance of the a) vitrimer coating VUE 1.4 and the b) reference coating, as characterised by optical microscopy after scratching and repairing at 160 °C under 2 tons of pressure.

2.2. *Material flow & repairability*

A preliminary assessment of the possibility of activating material flow of the cured resins at higher temperatures was performed using stress-relaxation experiments on separate disc-shaped samples from 150 °C to 110 °C (**Fig. S27**). This experiment was preceded by a compression moulding (*i.e.* thermo-mechanical recycling) step at 150 °C with a slight variation in reprocessing time, ranging from 25 to 45 min when transitioning from VUE 1.1 to VUE 1.4. Prior to analysing the relaxation data, it was critical to consider the theoretical model that was used to fit the data. Traditionally, relaxation curves of vitrimers have been fitted to a single-exponential decay model (single Maxwell element, **Equation S3**), assuming that the chemical environment of each bond in the system is more or less identical [14,39]. However, the chemical environment of the herein reported material was expected to be heterogeneous due to sample stoichiometry variation and the combination of dynamic VU and static epoxy bonds. Therefore, all relaxation data were fitted to a stretched exponential decay model (also known as Kohlrausch – Williams – Watts, **Equation S4**), that includes a factor $0 < \beta \leq 1$ that represents the breadth of the distribution of relaxation times (**Table S1**) [37,40]. An example of fitting the experimental data to both models was added to the supporting information for comparison, which also supports the need to use the stretched exponential decay model (**Fig. S28**). When comparing the high and low temperature intervals on an Arrhenius plot, a non-linear viscoelastic behaviour could be observed (Fig. 4 and **Fig. S29**). To account for this behaviour, it is assumed that during the heating of the vitrimer coatings, relaxation was first dominated by segmental motion (*i.e.* super-Arrhenian or WLF viscosity behaviour), which was followed by a scenario where relaxation was dominated by dynamic bond exchange (*i.e.* Arrhenian viscosity behaviour) [16,41]. Such a thermal transition is common when a glassy solid is heated and transforms into a viscoelastic liquid. Moreover, drastic reduction in relaxation due to limited segmental motion results in materials with improved creep resistance [37]. Interestingly, the decreased segmental mobility at lower temperatures had no significant effect on the reprocessability of the samples, as relatively similar relaxation times (τ^*) could be measured at higher temperatures with τ^* values at 150 °C ranging from 6000 to 14000 s. We hypothesise that the comparable relaxation rate can be explained by the fact that the rate determining step of bond rearrangement relies on the availability of reactive functional groups (*i.e.* dangling primary amines), which was calculated to be the same for every VUE material [13,42].

To gain additional experimental insight into the macroscopic healing capacity of the vitrimer coatings, controlled surface scratches were

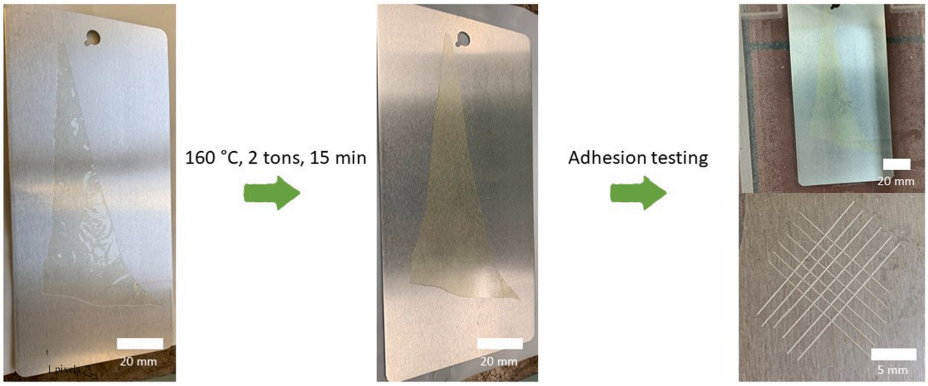

Fig. 6. Proof of concept recoating procedure of a vitrimer coating on aluminium plate. After heating at 160 °C and 2 tons of pressure for 15 min, the thin film adhered to the surface again, showing no delamination after a cross-cut adhesion test.

applied to VUE 1.4 and the reference coating, using an Elcometer cross hatch cutter. Healing could be easily monitored using optical microscopy after heating the damaged samples in a hydraulic press at 160 °C under 2 tons of pressure (**Fig. S30**). Already after 5 min, the damaged area of approximately 4 mm in length vanished for the vitrimer coating VUE 1.4 (Fig. 5**a** and **Fig. S31**). This was in stark contrast to the reference coating, which showed no significant signs of healing, even after 1 h of heating at 160 °C (Fig. 5**b**), highlighting the potential of the dynamic covalent bonds to substantially extend the lifetime of the presented epoxy coatings.

Another intriguing result of incorporating dynamic covalent bonds into epoxy coatings is the ability to reactivate surface wetting *via* material flow, which promotes the formation of adhesive interactions between the protective layer and the substrate [43,44]. This process is conceptually similar to the application of powder coatings, in which the solid contents of the powder melt and wet the surface in its viscoelastic liquid form [45]. To test the ability to apply the vitrimer coating starting from a thin film, a VUE 1.4 sample was first coated onto a glass plate (Fig. 6). The cured layer was carefully removed from the surface and transferred to an aluminium sheet, which was sandwiched between two metal plates weighing approximately 1 kg. The setup was transferred to a hydraulic press at 160 °C and 2 tons of pressure for 15 min to initiate surface wetting to the metal. To confirm that good adhesion of the layer to the new substrate had occurred, the metal sheet was first immersed in water for 48 h, which revealed no delamination. Following that, a cross-cut adhesion test revealed excellent adhesion to the substrate with no coating delamination, indicating that the coating barrier properties could be regained (5B rating).

3. Conclusion

Polycondensation of an amine-acetoacetate mixture in various stoichiometric ratios resulted in the successful synthesis of dynamic curing agents, used for the preparation of vitrimer epoxy coatings. By comparing adhesive, hydrophobic, corrosion and deformation resistance properties, successful samples could be identified. Interestingly, even after boiling water tests, hydrolysis of VU bonds was not detected, indicating the robustness of the vitrimer coatings. As a result, competitive barrier properties could be obtained when compared to a reference coating. The stress-relaxation data of the bulk samples revealed a clear transition from WLF to Arrhenius behaviour, resulting in an apparent non-linear viscosity profile. This resulted in significantly different relaxation behaviour at the higher and lower investigated temperatures. The ability of the vitrimer coatings to recover barrier properties after damage was investigated by monitoring the disappearance of surface scratches for 5 min at 160 °C under 2 tons of pressure. Furthermore, the reapplication of a used vitrimer coating on an aluminium substrate was demonstrated by applying the sample at 160 °C under 2 tons of pressure for 15 min, with no signs of delamination. Importantly, real applicability and industrial adaptation will mainly depend on the design of technologies that are able to apply heat across large structures during use. In summary, we can conclude that this straightforward approach enabled us to demonstrate the applicability of vitrimer epoxy coatings for corrosion protection of metals with competitive, if not superior, properties when compared to a commercial coating. Moreover, the added dynamic bond features offer the possibility to repair damages and restore barrier properties without the need for stripping and complete reapplication of the coating material.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

CRediT authorship contribution statement

Filip Van Lijsebetten: Investigation, Writing – original draft. **Stéphanie Engelen:** Investigation. **Erwin Bauters:** Investigation, Resources. **Wim Van Vooren:** Resources. **Maarten M.J. Smulders:** Supervision, Writing – review & editing, Funding acquisition. **Filip E. Du Prez:** Supervision, Writing – review & editing, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Data availability

The raw and reprocessed data needed to replicate these results are available upon request from the corresponding author.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.eurpolymj.2022.111426.

References

[1] H.Q. Pham, M.J. Marks, Epoxy resins, in: Ullmann's Encyclopedia of Industrial Chemistry; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2005, pp 156–244.

[2] A.J. Kinloch, Mechanics and mechanisms of fracture of thermosetting epoxy polymers, in: Epoxy resins and composites I; Springer, Berlin, Heidelberg, 1985, pp 45–67.

[3] R. Jain, P. Kukreja, A.K. Narula, V. Chaudhary, Studies of the curing kinetics and thermal stability of epoxy resins using a mixture of amines and anhydrides, J. Appl. Polym. Sci. 100 (5) (2006) 3919–3925.

[4] T.L. Metroke, R.L. Parkhill, E.T. Knobbe, Passivation of metal alloys using sol–gel-derived materials—a review, Prog. Org. Coatings 41 (4) (2001) 233–238.

[5] W.R. Ashcroft, Curing agents for epoxy resins, Chem. Technol. Epoxy Resins (1993) 37–71.

[6] M. Pramanik, M. Early, S. Wand, D. Gottschalk, S.K. Mendon, J.W. Rawlins, Amidoamine: synthesis, disparity in cure with epoxy resins between bulk and solvent systems, and structure-property relationships of its epoxy-based coatings, Polym. Eng. Sci. 59 (S1) (2019) E69–E81.

[7] T.H. Wu, A. Foyet, A. Kodentsov, L.G.J. Van Der Ven, R.A.T.M. Van Benthem, G. De With, Wet adhesion of epoxy-amine coatings on 2024–T3 aluminum alloy, Mater. Chem. Phys. 145 (3) (2014) 342–349.

[8] C.J. Kloxin, C.N. Bowman, Covalent adaptable networks: smart, reconfigurable and responsive network systems, Chem. Soc. Rev. 42 (17) (2013) 7161–7173.

[9] N. Zheng, Y. Xu, Q. Zhao, T. Xie, Dynamic covalent polymer networks: A molecular platform for designing functions beyond chemical recycling and self-healing, Chem. Rev. 121 (3) (2021) 1716–1745.

[10] F. Van Lijsebetten, J.O. Holloway, J.M. Winne, F.E. Du Prez, Internal catalysis for dynamic covalent chemistry applications and polymer science, Chem. Soc. Rev. 49 (23) (2020) 8425–8438.

[11] F. Van Lijsebetten, Y. Spiesschaert, J.M. Winne, F.E. Du Prez, Reprocessing of covalent adaptable polyamide networks through internal catalysis and ring-size effects, J. Am. Chem. Soc. 143 (38) (2021) 15834–15844.
[12] M.M. Obadia, A. Jourdain, P. Cassagnau, D. Montarnal, E. Drockenmuller, Tuning the viscosity profile of ionic vitrimers incorporating 1,2,3-triazolium cross-links, Adv. Funct. Mater. 27 (45) (2017) 1703258.
[13] F. Van Lijsebetten, K. De Bruycker, Y. Spiesschaert, J.M. Winne, F.E. Du Prez, Suppressing creep and promoting fast reprocessing of vitrimers with reversibly trapped amines, Angew. Chemie Int. Ed. 61 (9) (2022).
[14] D. Montarnal, M. Capelot, F. Tournilhac, L. Leibler, Silica-like malleable materials from permanent organic networks, Science 334 (6058) (2011) 965–968.
[15] G.M. Scheutz, J.J. Lessard, M.B. Sims, B.S. Sumerlin, Adaptable crosslinks in polymeric materials: resolving the intersection of thermoplastics and thermosets, J. Am. Chem. Soc. 141 (41) (2019) 16181–16196.
[16] W. Denissen, J.M. Winne, F.E. Du Prez, Vitrimers: permanent organic networks with glass-like fluidity, Chem. Sci. 7 (1) (2016) 30–38.
[17] M. Guerre, C. Taplan, J.M. Winne, F.E. Du Prez, Vitrimers: directing chemical reactivity to control material properties, Chem. Sci. 11 (19) (2020) 4855–4870.
[18] N.J. Van Zee, R. Nicolaÿ, Vitrimers: permanently crosslinked polymers with dynamic network topology, Prog. Polym. Sci. 104 (2020), 101233.
[19] D.J. Fortman, J.P. Brutman, G.X. De Hoe, R.L. Snyder, W.R. Dichtel, M.A. Hillmyer, Approaches to sustainable and continually recyclable cross-linked polymers, ACS Sustain. Chem. Eng. 6 (9) (2018) 11145–11159.
[20] A. Ruiz de Luzuriaga, R. Martin, N. Markaide, A. Rekondo, G. Cabañero, J. Rodríguez, I. Odriozola, Epoxy resin with exchangeable disulfide crosslinks to obtain reprocessable, repairable and recyclable fiber-reinforced thermoset composites, Mater. Horizons 3 (3) (2016) 241–247.
[21] G.C. Tesoro, V. Sastri, Reversible crosslinking in epoxy resins. I. Feasibility studies, J. Appl. Polym. Sci. 39 (7) (1990) 1425–1437.
[22] V.R. Sastri, G.C. Tesoro, Reversible crosslinking in epoxy resins. II. New approaches, J. Appl. Polym. Sci. 39 (7) (1990) 1439–1457.
[23] X. Xu, S. Ma, H. Feng, J. Qiu, S. Wang, Z. Yu, J. Zhu, Dissociate transfer exchange of tandem dynamic bonds endows covalent adaptable networks with fast reprocessability and high performance, Polym. Chem. 12 (36) (2021) 5217–5228.
[24] H. Memon, Y. Wei, L. Zhang, Q. Jiang, W. Liu, An imine-containing epoxy vitrimer with versatile recyclability and its application in fully recyclable carbon fiber reinforced composites, Compos. Sci. Technol. 199 (2020), 108314.
[25] H. Memon, H. Liu, M.A. Rashid, L. Chen, Q. Jiang, L. Zhang, Y. Wei, W. Liu, Y. Qiu, Vanillin-based epoxy vitrimer with high performance and closed-loop recyclability, Macromolecules 53 (2) (2020) 621–630.
[26] Xiao Wu, Xin Yang, Ran Yu, Xiao-Juan Zhao, Ying Zhang, Wei Huang, A facile access to stiff epoxy vitrimers with excellent mechanical properties via siloxane equilibration, J. Mater. Chem. A 6 (22) (2018) 10184–10188.
[27] N. Lorwanishpaisarn, N. Srikhao, K. Jetsrisuparb, J.T.N. Knijnenburg, S. Theerakulpisut, M. Okhawilai, P. Kasemsiri, Self-healing ability of epoxy vitrimer nanocomposites containing bio-based curing agents and carbon nanotubes for corrosion protection, J. Polym. Environ. 30 (2) (2022) 472–482.
[28] M. Jouyandeh, F. Tikhani, N. Hampp, D. Akbarzadeh Yazdi, P. Zarrintaj, M. Reza Ganjali, M. Reza Saeb, Highly curable self-healing vitrimer-like cellulose-modified halloysite nanotube/epoxy nanocomposite coatings, Chem. Eng. J. 396 (2020), 125196.
[29] Y. Spiesschaert, M. Guerre, I. De Baere, W. Van Paepegem, J.M. Winne, F.E. Du Prez, Dynamic curing agents for amine-hardened epoxy vitrimers with short (Re) Processing times, Macromolecules 53 (7) (2020) 2485–2495.
[30] J. Han, T. Liu, C. Hao, S. Zhang, B. Guo, J. Zhang, A catalyst-free epoxy vitrimer system based on multifunctional hyperbranched polymer, Macromolecules 51 (17) (2018) 6789–6799.
[31] J. Han, T. Liu, S. Zhang, C. Hao, J. Xin, B. Guo, J. Zhang, Hyperbranched polymer assisted curing and repairing of an epoxy coating, Ind. Eng. Chem. Res. 58 (16) (2019) 6466–6475.
[32] T. Liu, S. Zhang, C. Hao, C. Verdi, W. Liu, H. Liu, J. Zhang, Glycerol induced catalyst-free curing of epoxy and vitrimer preparation, Macromol. Rapid Commun. 40 (7) (2019) 1800889.
[33] S. Wang, J. Dai, N. Teng, J. Hu, W. Zhao, X. Liu, Synthesis of mechanically robust and self-healing UV-curable materials from renewable feedstock, ACS Sustain. Chem. Eng. 8 (45) (2020) 16842–16852.
[34] T. Shen, H. Zeng, Z. Chen, S.-R. Zhao, H.-C. Yang, W. Li, Recyclable and self-repairable epoxy anticorrosion coatings with curing-controlled thermoplasticity, ACS Appl. Polym. Mater. 2022, acsapm.1c01487.
[35] H. Memon, Y. Wei, C. Zhu, Recyclable and reformable epoxy resins based on dynamic covalent bonds – present, past, and future, Polym. Test. 105 (2022), 107420.
[36] H. Kaesche, N. Hackerman, Corrosion inhibition by organic amines, J. Electrochem. Soc. 105 (4) (1958) 191.
[37] L. Li, X. Chen, K. Jin, J.M. Torkelson, Vitrimers designed both to strongly suppress creep and to recover original cross-link density after reprocessing: quantitative theory and experiments, Macromolecules 51 (15) (2018) 5537–5546.
[38] S. Abbott, Sticking Together: The Science of Adhesion, Royal Society of Chemistry, 2020.
[39] S.P.O. Danielsen, H.K. Beech, S. Wang, B.M. El-Zaatari, X. Wang, L. Sapir, T. Ouchi, Z. Wang, P.N. Johnson, Y. Hu, D.J. Lundberg, G. Stoychev, S.L. Craig, J.A. Johnson, J.A. Kalow, B.D. Olsen, M. Rubinstein, Molecular characterization of polymer networks, Chem. Rev. 121 (8) (2021) 5042–5092.
[40] L.E. Porath, C.M. Evans, Importance of broad temperature windows and multiple rheological approaches for probing viscoelasticity and entropic elasticity in vitrimers, Macromolecules 54 (10) (2021) 4782–4791.
[41] Y. Nishimura, J. Chung, H. Muradyan, Z. Guan, Silyl ether as a robust and thermally stable dynamic covalent motif for malleable polymer design, J. Am. Chem. Soc. 139 (42) (2017) 14881–14884.
[42] J.M. Winne, L. Leibler, F.E. Du Prez, Dynamic covalent chemistry in polymer networks: A mechanistic perspective, Polym. Chem. 10 (45) (2019) 6091–6108.
[43] L. Li, X. Chen, J.M. Torkelson, Covalent adaptive networks for enhanced adhesion: exploiting disulfide dynamic chemistry and annealing during application, ACS Appl. Polym. Mater. 2 (11) (2020) 4658–4665.
[44] N.D. Blelloch, H.J. Yarbrough, K.A. Mirica, Stimuli-responsive temporary adhesives: enabling debonding on demand through strategic molecular design, Chem. Sci. 12 (46) (2021) 15183–15205.
[45] E.G. Belder, H.J.J. Rutten, D.Y. Perera, Cure characterization of powder coatings, Prog. Org. Coatings 42 (3–4) (2001) 142–149.