Reversible hetero-Diels-Alder amine hardener as drop-in replacement for healable epoxy coatings

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Reversible hetero-Diels-Alder amine hardener as drop-in replacement for healable epoxy coatings

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Abstract

We describe a new amine-hardener that enables intrinsic thermally activated healing in epoxy-amine coatings. A hetero-Diels Alder (HDA) adduct bridges biosourced fatty acids and serves as the thermoreversible linker. We validated the thermal reversion of the adduct in solution and the HDA-containing diamine served as a drop-in replacement for commercial hardeners.

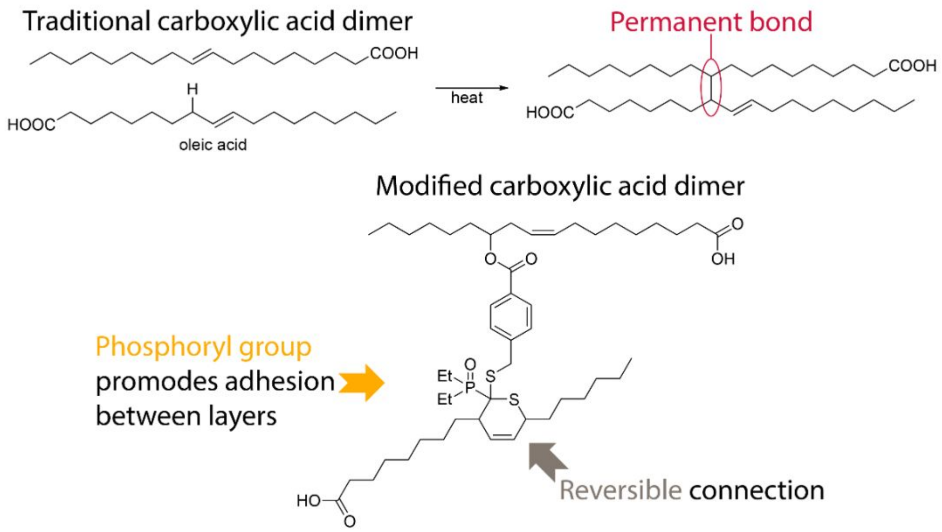
1. Introduction

Healable materials have the inherent capacity to repair physical and/or chemical damage to regain their integrity and associated properties,[1–7] following two main strategies: extrinsic[8–11] and intrinsic healing.[12–15] The former relies on pre-assembled healing agents (such as unreacted monomer, catalyst and solvent), which are incorporated into the material during fabrication. Various methodologies for sequestering the healing agents have been demonstrated, such as capsules or vasculature, which release their cargo upon damage allowing for new monomers to react and repair physical damage. The intrinisic method hinges upon reversible interactions within the system, such as in supramolecular interactions[16,17] or dynamic covalent chemistry (associative[18,19] or dissociative[20]). These systems can either repair autonomously[21,22] (i.e. as a result of the damage), or in response to an external stimulus.[23,24] Depending on the intended end-use (e.g. operational temperature, kinetic considerations), the content of reversible motifs embedded into matrix can vary greatly.

Intrinsic healing is inherently amenable to multiple repairs as opposed to extrinsic methods which are spatiotemporally constrained by healing agent availability. Non-covalent interactions such as hydrogen bonding,[25,26] π–π stacking,[27–29] and electrostatic interactions[30] constitute ideal building blocks to bestow mendability upon materials on account of their reversible character. Concomitantly, cross-linked polymeric networks containing dynamic covalent bonds, *viz.* disulfide bonds,[31] thermally cleavable alkoxyamines,[32,33] ester linkages,[34,35] dioxaborolanes,[36] oximes linkages,[37,38] and Diels-Alder (DA) bonds,[39,40] have emerged as a promising path to extend the life cycle of polymeric materials.[41] DA reactions excel thanks to their simplicity, 100% atom economy, repeatability, and thermal tunability. As such, maleimide-furan bond,[42,43] maleimide-anthracene,[44] anthracene-anhracene,[45,46] and other hetero-DA (HDA) reaction[47] have been employed in the fabrication of healable materials. Barner-Kowollik and coworkers have extensively used HDA units in supramolecular and polymeric architectures.[47–50]

From a commercial perspective, epoxy-based polymers are relevant to the fields of aerospace, transportation, civil engineering, home and office goods, and coatings.[51–54] They generally possess high T_g, strength, and toughness, while maintaining excellent moisture, chemical and corrosion resistance. Furthermore, their final properties can be readily tuned thanks to a wide range of commercially available monomers. Also, the absence of toxic emissions upon curing makes for scalable manufacturing processes. Recently, Zhang et al. reviewed healing strategies employed in epoxy-polymers,[52] whereby both extrinsic[55] and intrinsic strategies have been used. Intrinsic methods have ranged from photo- or thermoreversible disulfide bridges[56,57] to the use of supramolecular 2-ureido-4[1H]-pyrimidinone (UPy) units capable of strong H-bonding.[58]

Scheme 1. Graphical depiction of traditional carboxylic acid dimers versus the proposed HDA containing carboxylic acid dimer.



In the present study, we use phosphoryl dithiocarbonyl methyl benzoic acid (PDTMBA) as a dienophile and a conjugated C-18 fatty acid as diene to form HDA-adduct (Scheme 1). Industrial amine hardeners for epoxy coatings often contain dimerized unsaturated fatty acids, whereby the dimer forms a permanent covalent bond connecting amine functionalities. We hypothesized that the incorporation of PDTMBA within the dimer acid units used in commercial systems would yield coatings capable of healing upon the application of heat, while minimally impacting the formulation of known epoxy resins. We demonstrated the importance of the type of amine in the healing behavior and confirmed that the HDA linkages enabled healing in epoxy coatings cast onto aluminum plates. The present study opens the door for the implementation of modified fatty acids for repairable epoxy coatings and materials.

2. Results and Discussion

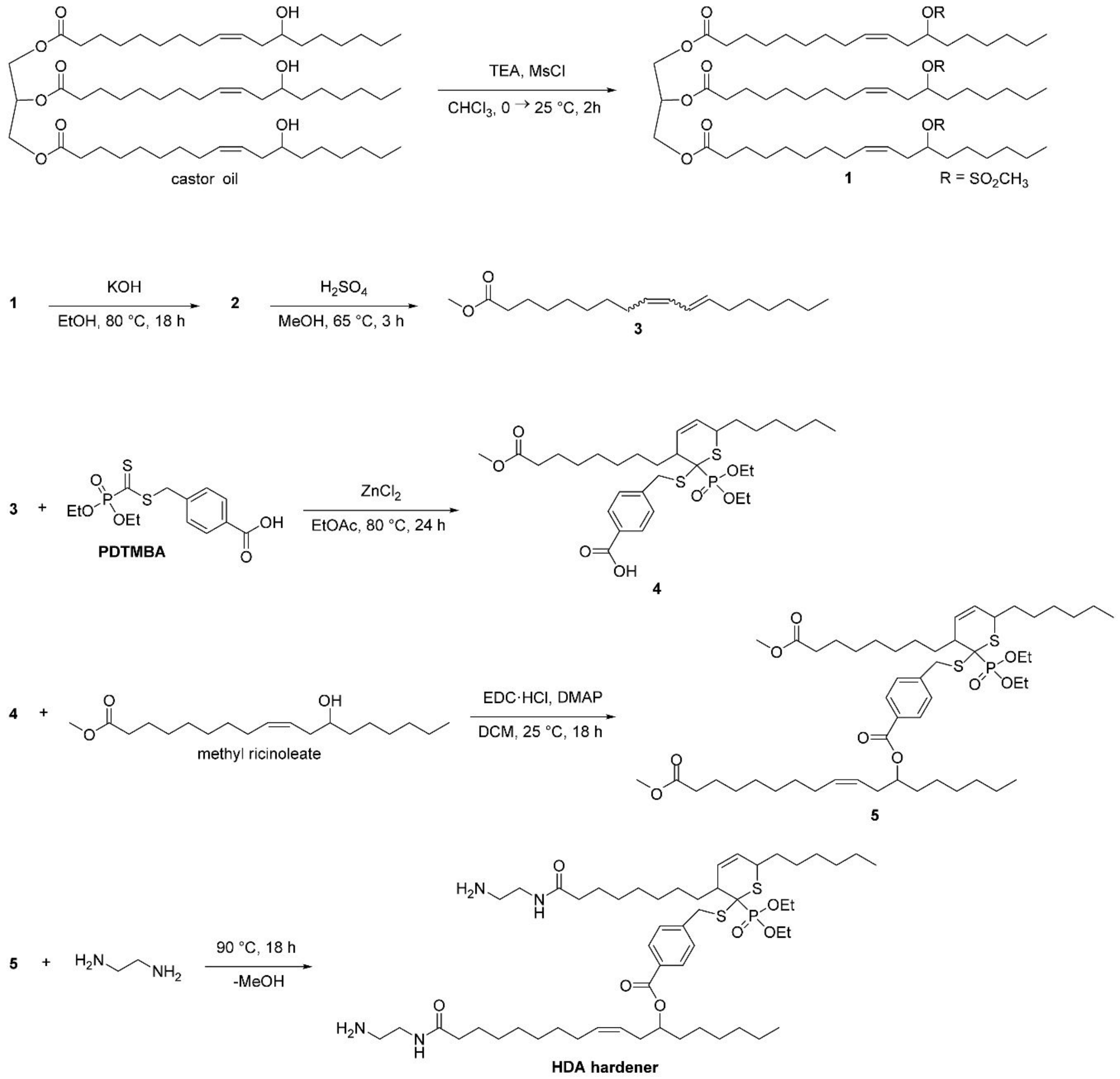
2.1. Synthesis of the HDA-based drop-in hardener

Castor oil is renewably sourced from the *Ricinus communis* plant grown primarily in India, Africa, and South America.[59] Although inedible, castor oil is widely used in the chemical industry for applications including alkyd resins[60] and biodiesel production,[61] with global demand increasing to 610,000 tons in 2010.[62] About 90% of castor oil's chemical content is ricinoleic acid, which bears a hydroxy group on the C-18 fatty acid chain. As such, it can be readily converted into conjugated linoleic acid diene, which could be further reacted via a concerted cylic addition pathway. Realizing this possibility, we mesylated castor oil (Scheme 2, Figures S1 and S2) to obtain the trimesylated triglyceride (**1**), which underwent upon one-pot saponification and desulfonylation/elimination using KOH in ethanol to afford linoleic acid (**2**) in quantitative yield. The saponification reaction could be monitored through the loss of glycerol peaks at 4.28 and 4.17 ppm (Figure S3). Due to various de-sulfonylation possibilities, the product obtained was a mixture of isomers. Note that ethanol could potentially react with the acid functionality revealed by the saponification to form an ethyl ester. However, in the subsequent step, the acid-catalyzed esterification reaction of **2** in methanol produced the corresponding linoleate methyl ester (**3**) in excellent yield (Figure S4 and S5).

$ZnCl_2$-catalyzed cycloaddition reaction of PDTMBA (synthesized following literature precedent,[49] Figure S6) and **3** yielded the fatty acid ester HDA adduct (**4**) in good yield (Scheme 2, Figure S7).[50] The CH_3 end-terminus and the methyl ester are easily identifyiable at 0.89 and 3.67 ppm, respectively, and both integrated to 3H. In addition, the aryl peaks at 8.20 and 7.47 ppm integrated to 4H, and the alkene signals of the 3,6-dihydro-2*H*-thiopyran moiety are observed at 5.92 and 5.70 ppm and integrate to 2H. Together, these signals and their integrations confirm that **4** was synthesized and isolated.

Using the aryl carboxylic acid on adduct **4** and the free alcohol of commercially available and biosourced methyl ricinoleate, we performed an esterification using carbodiimide coupling and obtained the desired HDA-dimerized fatty acid dimethylester (**5**) in high yield (Scheme 2, Figure S8). Similarly to **4**, the two ω-CH_3 and the two methyl esters remain at 0.88 and 3.66 ppm, respectively, but now correspond to 6H, while the integration of the aryl peaks at 8.20 and 7.47 ppm integrates for 2H. Likewise, the alkene peaks of the 3,6-dihydro-2*H*-thiopyran remain unaltered. For the synthesis of the amine hardener, we heated **4** with ethylene diamine at 90 °C overnight while removing byproduct methanol *via* vacuum yielding the amine-terminated dimerized HDA (**HDA hardener**, Figure S9). We wanted to take advantage of the higher reactivity of the methyl ester in comparison to the aryl ester, which should allow for preferable amidation of at the methyl ester. We can see complete conversion of **5** to the **HDA hardener** by monitoring the loss of the methyl ester signal at 3.66 ppm, while retaining the two ω-CH_3 at 0.88 ppm. A new peak at 2.78 ppm appears corresponding to the $NH_2C\mathit{H_2}CH_2$ of the reacted ethylene diamine, which integrates to 6, rather than the expected 4. The $P(OC\mathit{H_2}CH_3)_2$ and the methylene bridge between the sulfur and the aromatic ring in the PTMBA moiety had appeared within the 4-4.5 ppm range in **5** integrating to 6 protons. However, upon reaction with the ethylene diamine, the integration between 4-4.5 ppm only corresponds to 2.3 protons. Together these results indicate that there coud be instances where the **HDA hardener** is slightly polymeric having undergone multiple reactions with ethylene diamine or having replaced the remaining ester bond with an amide. In either case, the functionality of the HDA would remain intact and would theoretically still fuction as a thermo-reversible unit.

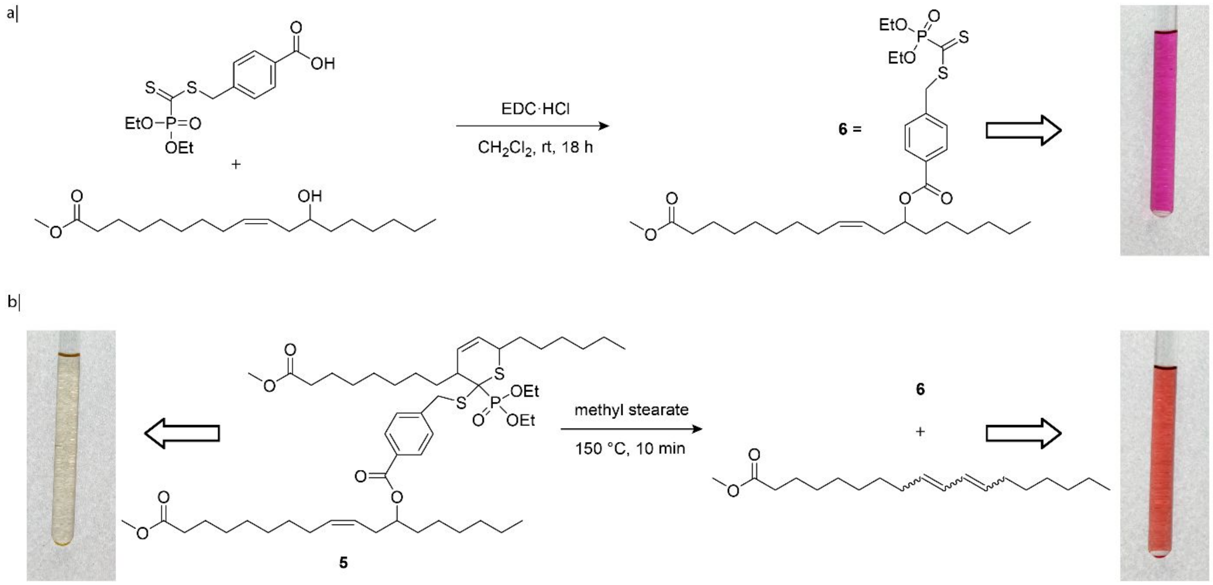
Scheme 2. Synthesis the **HDA hardener** from castor oil, methyl ricinoleate and PDTMBA.



2.2. Thermal reversibility analysis of HDA dimer acid ester (**5**)

Upon retro-DA, we predicted that the **HDA hardener** would dissociate into methyl linoleate and PDTMBA-derivative, **6** (Scheme 3a). To this end, we retrosynthesized **6** *via* EDC·HCl coupling of PDTMBA with methyl ricinoleate (Figure S10 and S11). Knowing that structurally similar adducts undergo retro-DA at around 160 °C,[63] we heated **5** in methyl stearate, an inert colorless solvent (mp 39.1 °C, bp 443 °C), at 150 °C for 10 minutes and observed a visible color change from light-yellow to a dark orange (Scheme 3b, Figure S12). The reaction vial was quench-cooled by immersion into liquid nitrogen, to minimize the adduct re-formation. The quenched reaction mixture was dissolved in dichloromethane and the non-polar components were removed using a silica plug and 5 vol% ethyl acetate in hexanes. The polar fractions were then eluted with ethyl acetate and dried *in vacuo*.

Scheme 3. a| Retrosynthesis of the retro-DA product and b| retro-DA reaction in methyl stearate at 150 °C with inset pictures of the solutions of the reagents and products for both reactions.



Analysis by ^{1}H NMR spectroscopy revealed that the polar fraction contained a 1:1.2 mixture of the dissociated product (**6**) to the undissociated (**5**) (Figure S13). Diagnostic peaks utilized were the characteristic peaks of methylene bridge between the thioester at 4.56 ppm in **6** and the alkyene and the 3,6-dihydro-2*H*-thiopyran at 5.92 and 5.70 ppm in **5** (Figure 1). The cleavage at the HDA seen in this test reaction represents a successful retro-DA reaction, which we can leverage allow for thermal healability.

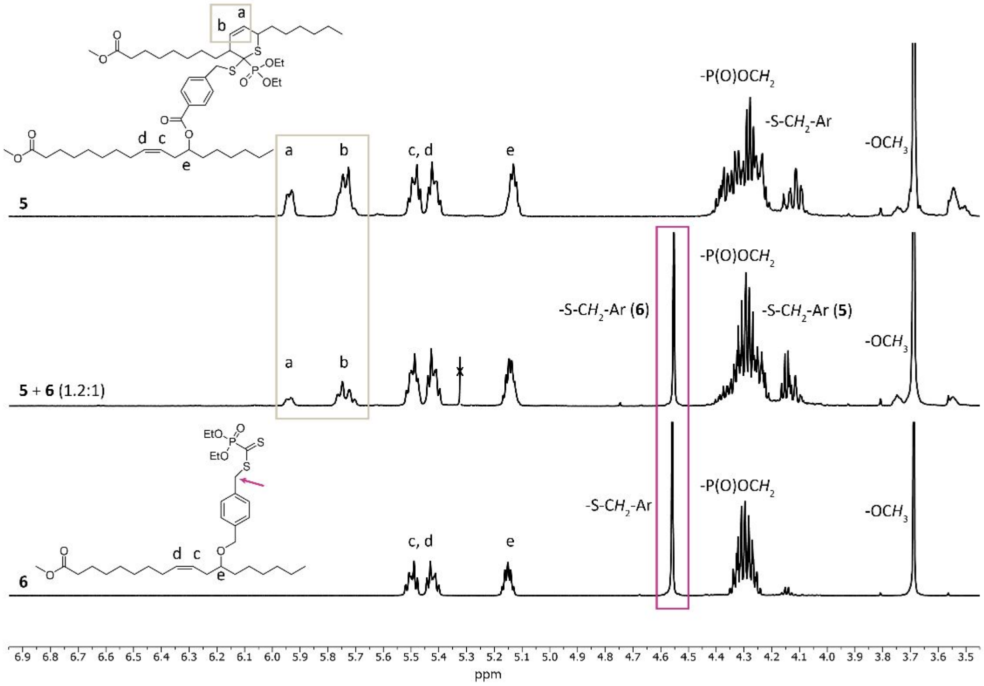


Figure 1. Partial ^{1}H NMR spectra showing the comparison of the top| starting compound, **5**, middle| the retro-Diels-Alder reaction products along and bottom| the synthesized control product, **6**.

2.2 Scratch healing of epoxy coat

Upon successful demonstration of the retro-DA reaction, we used **HDA hardener** and EPON 872, a modified BPA-based epoxy resin with an equivalent epoxy weight (EEW) of 675 (see ESI for detail) to create our healable epoxy coatings. The **HDA hardener** was found to have an amine hydrogen equivalent weight (AHEW) of 304 by titration (see ESI for detail). Blends were made with a 1:1 epoxy amine stochiometry by blending EPON 872, **HDA hardener**, 4-nonylphenol, and 2-heptanone. The coatings were blended until uniform and applied to aluminum panels using a drawdown bar at an 8 wet mills thickness. The coatings were cured at room temperature for 2 days, then heated at 60 °C for 1 h in oven to ensure full cure and removal of volatiles. The coatings formed were clear with a light yellow tint and a smooth untacky finish. Differential scanning calorimetry (DSC) measurements confirmed that coatings were fully cured and further revealed a broad glass transition centered at 20 °C (Figure S26). For comparison, a control coating was made (**control-coating**) using a non-healable diamine (**control-amine**) (see ESI for synthesis).

Both the **HDA**- and the **control-coatings** were scribed within a guide ink mark with a sharp knife (Figure 2a and b). Both coatings were then heated at 95 °C for 15 min in a pre-heated oven. The **HDA-coating** showed significant scratch repair, leaving only a faint trace of the previous damage (Figure 2c). To monitor the effect of heating duration, the same panels were further heated for a further 30 minutes at 95 °C, which did not lead to obvious improvement (Figure S19). After heating, the coatings remained stable when submerged in acetone, indicating reformation of the HDA adduct (Figure S20). Throughout all of the heating tests, the **control-coating** did not show any signs of scratch healing, as expected (Figure 2d). Furthermore, we performed König hardess tests on HDA-coatings heated for 30 min at 95 °C which exhibited greater hardness 43.5 ± 1.4 s than the corresponding control 23.8 ± 0.1 s (Table S1), further alluding to the retention of network properties upon thermal treatment. Also, note that the functionality of the amine used is critical as initial tests performed with triethylenetetramine-based (TETA-based) hardener (Figure S21) did not show any healing even after prolonged heating (30 min) at temperatures up to 200 °C (with EPON 825, 872, 1007 with or without $ZnCl_2$), probably on account of additional crosslinks through the secondary amines (Figures S22-S24). Based on the number of available amines per TETA-based HDA hardener, we can evaluate that 89% of the crosslinks in said networks are permanent. These absence of healing is therefore consistent with the report of Li et al. who showed that the reprocessability of covalent adaptable networks was ineffective upon introduction of 60% of permanent crosslinks.[64] For the TETA-based coatings, the controls were made with a commercial Ancamide 2445 resin. Interestingly, the EPON 872 systems the HDA turned burnt orange indicating irreversible retro-DA. These results show the importance of molecularly engineering the reversible connectors in dynamic covalent networks.

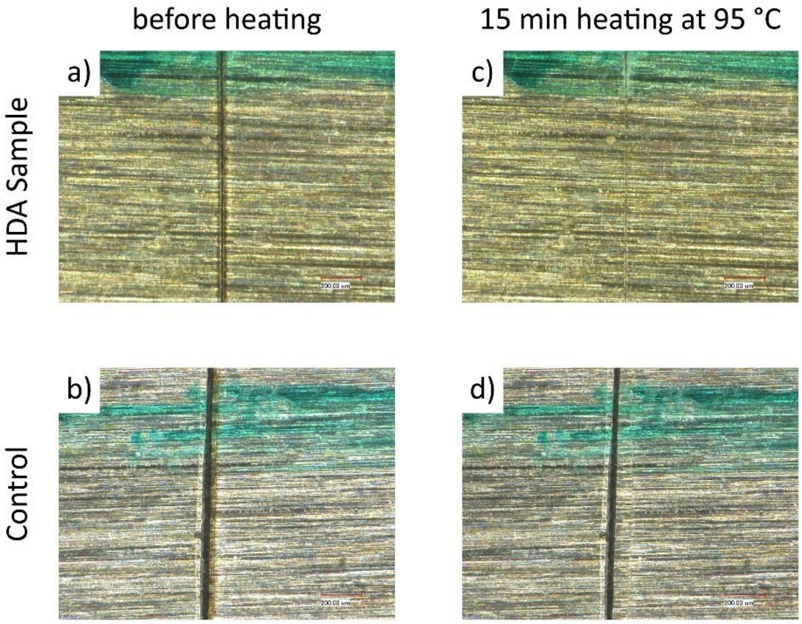


Figure 2. OM image of scratch before and after heating. Top row (a, c): healable **HDA-coating**. Bottom row (b, d): non-healing **Control-coating**. All images are taken at 200x magnification.

3. Conclusion

Looking to create a drop-in replacement for epoxy-amine coatings with temperature-triggered healing, we synthesized an amine-terminated HDA adduct. The long-chain fatty acids (ricinoleic acid) used in this synthesis are commercially available and biosourced. With simple chemical reactions, the ricinoleic acid could be converted to a conjugated linoleic acid, the diene component of the cycloaddition and reacted with the PDTMBA to form the HDA fatty acid adduct. The thermal reversibility in solution of the HDA adduct was confirmed by NMR analysis. Reaction with a diamine yielded an amine-terminated HDA adduct which was incorporated into an epoxy-amine coating. The HDA-based epoxy-amine coating showed excellent scratch-healing properties upon heating at 95 °C compared to a corresponding inert control coating. These observations are significant for the development of new thermally-repairable coatings and open up the door to new (partially or fully) biosourced healable materials.

Author Contributions

S. C. R. developed the methodology pertaining to the synthesis of the different building blocks and led the investigation of the coatings. B. J. D. aided with the characterization of the materials and compiled the results into a manuscript form. I. T. D. helped with the hardener synthesis. T. L. T. helped define the scope of the project and assisted in the project administration. J. J. P. helped revise the manuscript. Y. C. S. conceived and supervised this work.

Conflicts of interest

There are no conflicts to declare

Notes and references

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