

Chemically Recyclable and Upcyclable Epoxy Resins Derived from Vanillin

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Chemically Recyclable and Upcyclable Epoxy Resins Derived from Vanillin

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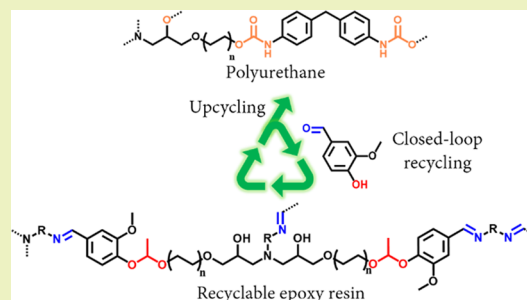
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ABSTRACT: Epoxy resins constitute a very significant portion of all high-performance plastics due to their excellent thermal and mechanical properties that appear in a wide range of applications. Nevertheless, traditional epoxy networks show limitations regarding chemical recycling due to their covalently crosslinked structures. The current methods to recycle epoxy resins are not indeed through sustainable ways, but this issue could be solved by developing smart monomers with functional groups, which can be switched between polymerized and depolymerized states. Herein, we developed two bio-based liquid monomers based on vanillin structures containing aldehyde, acetal, and oxirane-ring functionalities. These monomers were polymerized in solvent-free conditions using commercially available diamines, resulting in double-dynamic imine-acetal-containing thermosets. These networks combine the excellent properties of the traditional epoxy systems and dynamic polymers. Most importantly, such thermosets were fully depolymerized into vanillin, which can be reused for the preparation of original epoxy monomers, and a mixture of well-defined polyols, which was upcycled into high-performance polyurethane.

KEYWORDS: epoxy, imine, chemical recycling, upcycling, vanillin



INTRODUCTION

Epoxy resins constitute a significant portion of all high-performance thermosets due to their excellent thermal and mechanical properties that appear in a wide range of applications such as aerospace and automotive industries, high-performance adhesives, coatings, floorings, and wind turbine blades.^{1,2} Seventy-five percent of the current epoxy-based crosslinked polymers are traditionally cured from the commercially available diglycidyl ether of bisphenol A (DGEBA).³ Due to its high aromatic content and rigidity, the epoxy thermosets produced with this monomer have excellent thermal and mechanical properties.^{4,5} However, this petroleum-based monomer is synthesized from bisphenol A (BPA), which is known as a reprotoxic and endocrine disruptor.⁶ Consequently, there is a huge demand for exchanging DGEBA with monomers obtained from bio- or renewable sources.⁷ Vanillin and its derivatives are therefore great candidates for incorporation into the epoxy networks due to their rigid aromatic structures.⁸

More importantly, superior mechanical and thermal properties of traditional epoxy resins result in significant limitations in their closed-loop recycling and reprocessability options.^{9,10} A large amount of such epoxy resins and their carbon fiber-reinforced composites are therefore landfilled or incinerated, which creates vital problems such as waste of resources and environmental pollution.^{11,12} Current viable methods to reduce the epoxy waste include mechanical recycling, pyrolysis,

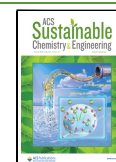
and chemical and thermal degradation.^{9,13} Mechanical recycling is applied on an industrial scale, and grinded materials could be used as cheaper reinforcers in the new composites.¹⁴ Except mechanical recycling, all other methods are basically based on degradation of the network and require harsh conditions (i.e., high temperature, high pressure, etc.), demonstrating that they are energy-intensive and harmful to the environment and degraded products are very complex mixtures of oligomers that cannot be reused or upcycled.^{15–21}

Given that the ultimate purpose of recycling is to reduce the carbon footprint of plastics, one has to consider the technical feasibility and economic viability (i.e., total energy consumption of the recycling) when discussing the recycling options. An innovative design of monomers and the target polymers will enable circularity, which is useful in many environmental and economic aspects.²² Incorporation of dynamic and cleavable imine or acetal bonds to achieve dynamic crosslinking provides an interesting approach to circularity.^{23–31} For instance, a vitrimeric vanillin-based epoxy network, which was hardened with isophorone diamine,

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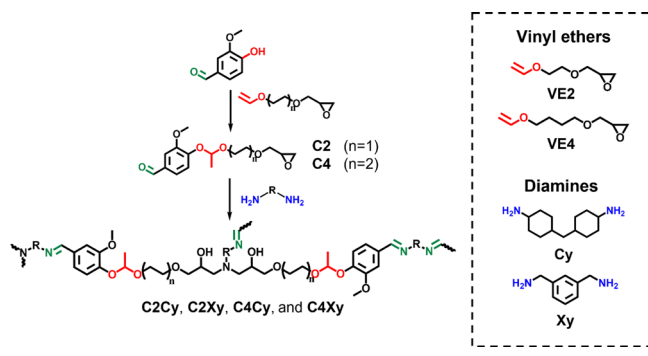
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showed a tensile strength at 65.0 MPa with a 4.4% elongation at break, which had reprocessability without loss of mechanical performance, and could be degraded into oligomeric structures under acidic conditions.³² In another work, a series of acid-degradable vanillin-based epoxy vitrimers were prepared with Jeffamine D-400 and isophorone diamine and the solution of the acid-degraded products was upcycled into a composite film with responsive structural color.³³ Similarly, a vanillin-based epoxy vitrimer cured with 4,4'-methylenebis(cyclohexanamine) showed a tensile strength of 81 MPa, which could be easily reprocessed, and carbon fibers could be recovered non-destructively upon treatment with dilute acid from its carbon fiber composites.³⁴ In another approach, an imine-containing di-epoxy monomer was developed, which was then polymerized with 4,4'-diaminodiphenylmethane to obtain a high-performance network with a T_g of 206 °C and a tensile strength of 122 MPa.³⁵ However, in above-mentioned systems, the polymerization was performed in organic solvents (i.e., DMF and DCM) due to the selection of solid monomers, which is in contradiction with the principles of green chemistry and limits its applications in industry.

Even though closed-loop recycling for bio-based epoxy-imine resins was achieved through depolymerization into oligomeric structures in most of the previous works, a full depolymerization toward the initial building blocks has not been demonstrated.^{36–43} There are several studies based on acetal-containing epoxy networks synthesized from petroleum-based DGEBA in which recovery of monomers or reinforcing agents could be achieved upon acidic depolymerization;^{44–47} however, synergistic use of dynamic acetal and imine functionalities has never been exploited in epoxy systems. Obviously, there is a need for high-performance epoxy systems based on bio-renewable monomers, which could achieve closed-loop recycling.⁴⁸ Therefore, herein, we developed two liquid epoxy precursors, which are lignin derived, based on vanillin bearing acetal, aldehyde, and oxirane functionalities, which could be cured with commercial diamines under solvent-free, green conditions (Scheme 1). The obtained vanillin-based

Scheme 1. Synthesis Pathway toward Vanillin-Based Epoxy Networks



recyclable epoxy networks have tensile strength in the range between 50 and 70 MPa, whereas their elongation at break values lie between 10 and 20%. In addition, the epoxy networks built herein could be reprocessed readily and depolymerized under mild acidic conditions. Due to simultaneous hydrolysis of acetal and imine groups, an initial building block, vanillin, can be obtained in high yield and purity. Given that its production from lignin requires harsh conditions with low yields,⁴⁹ our work provides an easy and

elegant pathway to recover vanillin. As a side product of acidic depolymerization, we obtained a mixture of well-defined polyols, which could be upcycled into high-performance thermosetting polyurethane.

RESULTS AND DISCUSSION

Structure Characterization of C2 and C4. The syntheses of monomers C2 and C4 were performed using a catalyst-free, click-type addition reaction between vanillin and vinyl ether precursors.⁵⁰ The structures of the monomers were confirmed by ¹H and ¹³C NMR (Figures S1–S4), which was supported by FTIR (Figure 1). As indicated by the ¹H NMR

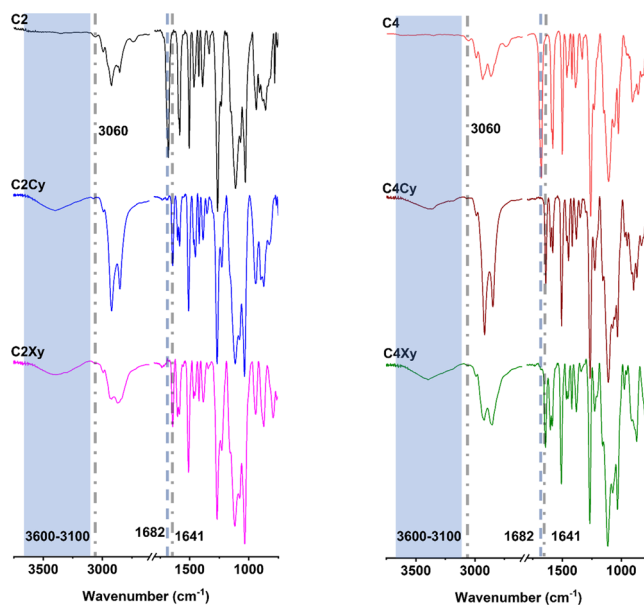


Figure 1. Normalized FTIR spectra of epoxy monomers and networks.

spectra (Figures S1 and S3), C2 and C4 gave one singlet belonging to their aldehydic protons at $\delta = 9.87$ ppm, whereas their acetal protons appeared as quartets of doublets at $\delta = 5.59$ and 5.54 ppm for C2 and C4, respectively. Due to the stereocenter on the oxirane ring, the same carbon protons (protons *g* and *k* for both monomers) were not equivalent and split into two peaks. Furthermore, aromatic aldehyde stretching (C=O) at 1682 cm^{-1} , O–C–O stretching of the acetal moiety at 1265 cm^{-1} , C–H stretching of the oxirane ring at 3060 cm^{-1} , and C–O stretching of the oxirane ring at 911 cm^{-1} were observed for both monomers, proving the successful incorporation of the epoxide ring to the vanillin moiety via acetal formation (Figure 1).^{51,52}

Curing and Characterization of Vanillin-Derived Epoxy Networks. All networks were cured in bulk, solvent-free, single-step conditions. A homogeneous mixture of monomers was heated to 100 °C under N_2 flow for 24 h. Figure 1 shows the FTIR spectra of the cured networks and monomers. Upon curing, the aldehyde stretching vibration at 1682 cm^{-1} disappeared, whereas the imine peak was observed at 1641 cm^{-1} . Furthermore, the appearance of comparably wide –O–H stretching peaks between 3600 and 3100 cm^{-1} and a significant decrement of the intensity of the C–H stretching of the oxirane ring at 3060 cm^{-1} showed that networks were formed successfully.

Thermal and Mechanical Characterization of Epoxy Networks. Thermal properties of the networks were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under nitrogen flow. Figure 2A,B indicates

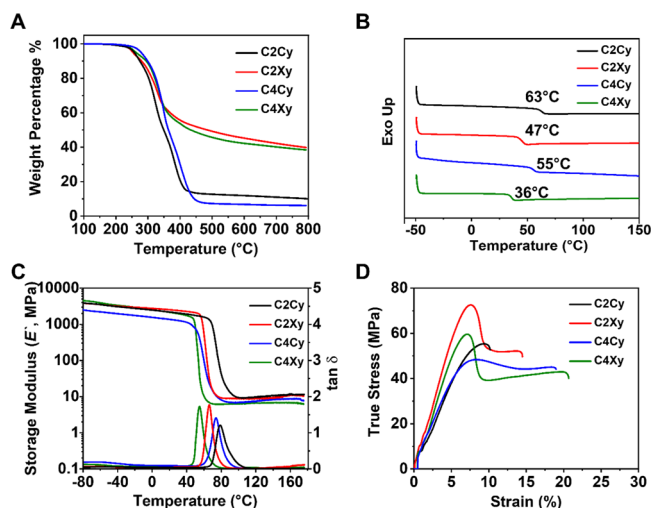


Figure 2. Thermal and mechanical characterization of the epoxy networks: TGA (A), DSC (B), DMA (C), and tensile tests (D).

the TGA and DSC thermograms of the epoxy networks. All networks showed good thermal stability under N_2 with two main degradation steps, and their onset degradation temperatures ($T_{d5\%}$) ranged between 251 and 279 °C (Table 1 and

Table 1. Thermal and Mechanical Properties of the Epoxy Networks^a

	C2Cy	C2Xy	C4Cy	C4Xy
$T_{d5\%}$ (°C)	258	251	279	263
$T_{d30\%}$ (°C)	318	333	339	338
R_{800} (%)	10.1	39.9	6.2	38.5
$T_{g,DSC}$ (°C)	63	47	55	36
$T_{g,DMA}$ (°C)	78	65	63	56
$E_{30'}$ (MPa)	2050	2406	1273	1966
ν_e (mol/m ³)	985.03	943.61	745.05	697.27
σ_m (MPa)	55.3 ± 1.1	72.7 ± 0.8	49.0 ± 0.6	56.5 ± 3.1
ϵ_b (%)	12.3 ± 2.0	13.9 ± 1.8	18.6 ± 1.8	21.5 ± 0.8
E (MPa)	918.7 ± 54.7	1249.6 ± 91.7	928.0 ± 51.7	1136.7 ± 75.1

^a $T_{d5\%}$ and $T_{d30\%}$: temperatures of 5 and 30% weight loss, respectively. R_{800} : char residue at 800 °C. $T_{g,DSC}$ and $T_{g,DMA}$: glass transition temperatures obtained from DSC and DMA, respectively. $E_{30'}$: storage modulus at 30 °C obtained from DMA. ν_e = crosslinking densities obtained by DMA. σ_m , ultimate tensile strength; ϵ_b , elongation at break; E , Young's modulus.

Figure S5). Furthermore, their 30% weight loss ($T_{d30\%}$) was observed between 318 and 339 °C (Table 1). C4-based networks have slightly better thermal stabilities ($T_{d5\%}$ and $T_{d30\%}$) than C2-based networks when comparing the same amine spacers. Additionally, the char residues of C2Xy and C4Xy are 39.9 and 38.5%, respectively, which are significantly larger than those for C2Cy (10.1%) and C4Cy (6.2%) at 800 °C. This was attributed to the higher aromatic content in the former.^{53,54}

The glass transition temperatures obtained from DSC ($T_{g,DSC}$) were 36 and 55 °C for C4Xy and C4Cy, whereas the T_g of the C2Xy and C2Cy were 47 and 63 °C, respectively

(Figure 2B and Table 1). Reducing the carbon spacer from 4 to 2 within the same amine spacer resulted in a decrease in the flexibility of the backbone, which elevated the T_g . Conversely, C2Xy showed lower glass transition temperatures than C2Cy though having an aromatic amine spacer. A similar trend was obtained between C4Xy and C4Cy, which is consistent with the previously published literature.^{55,56}

Thermomechanical properties of the networks were determined by DMA (Figure 2C, Figure S6, and Table 1). The storage moduli of the C4Cy and C4Xy networks at 30 °C ($E_{30'}$) were found to be 1273 and 1966 MPa, respectively. Conversely, the values for the C2Cy and C2Xy networks were larger (2050 MPa for C2Cy and 2406 MPa for C2Xy). This could be attributed to the flexibility/rigidity and the ratio of the aromatic units.⁵⁷ As the aromatic unit ratio increases and the chain length decreases, the stiffness of the material increases, which results in a larger storage modulus. Furthermore, the maxima of the $\tan \delta$ vs temperature plots were denoted as T_g values of the networks (Figure 2C and Table 1). The values obtained from DMA followed the same trend with the results from DSC. Additionally, C4Cy and C2Cy gave the lower intensities for $\tan \delta$ curves showing the slower movement of these networks compared with C4Xy and C2Xy due to their higher rigidity.³⁴ Furthermore, the calculated crosslinking densities of the networks were 985.03, 943.61, 745.05, and 697.27 mol/m³ for C2Cy, C2Xy, C4Cy, and C4Xy, respectively. As expected by their structures, C2Cy and C2Xy have significantly higher crosslinking densities due to the shorter aliphatic chain on C2 compared with C4. The gel fractions obtained in THF and DMF were in the range of 76 to 100%, which supported high crosslinking densities obtained by DMA (Table S1).

The mechanical characterization of the epoxy networks was performed with tensile tests (Figure 2D and Figure S7). The tensile strength of the new networks ranged from 50 to 70 MPa with 10–20% elongation. Accordingly, the C2Xy network had the highest tensile strength of 72.7 MPa with an elongation at break of 13.9%, while the C2Cy network gave a tensile strength of 55.3 MPa with a 12.3% elongation at break. The same trend was obtained in the tensile strength values of C4Xy (56.5 MPa) and C4Cy (49.0 MPa). Clearly, the use of shorter chains had a positive impact on the tensile strength values and a decrease in elongation at break due to the decreased flexibility.³⁵ The Young modulus of C2Xy was 1249.6 MPa, whereas that of C2Cy, C4Xy, and C4Cy was 918.7, 1136.7, and 928.0 MPa, respectively. This clearly indicated that the use of an aromatic amine hardener resulted in stiffer networks, which supports the storage modulus trend.

Reprocessability of the Networks. Traditional epoxy networks are highly crosslinked thermosets with permanent covalent bonds; consequently, it is not possible to reshape or reprocess them.^{52,58,59} Since imine and acetal functional groups are known to be dynamic and reversible,^{23,60,61} the designed epoxy networks could be potentially malleable. The vitrimeric behavior of the networks was investigated with stress-relaxation experiments (Figure 3 and Figure S8). By changing the diamine hardener and alkyl spacer, a significant difference in relaxation times was observed at 120 °C with $\tau^* = 730$ s for C2Cy, 14.5 s for C2Xy, 679 s for C4Cy, and 4.6 s for C4Xy. The activation energy (E_a) was calculated using the Arrhenius equation and found to be 53.0 kJ/mol for C2Cy, 40.2 kJ/mol for C2Xy, 55.0 kJ/mol for C4Cy, and 36.7 kJ/mol for C4Xy, which is typical for polyimine-based structures.^{62,63} Apparently,

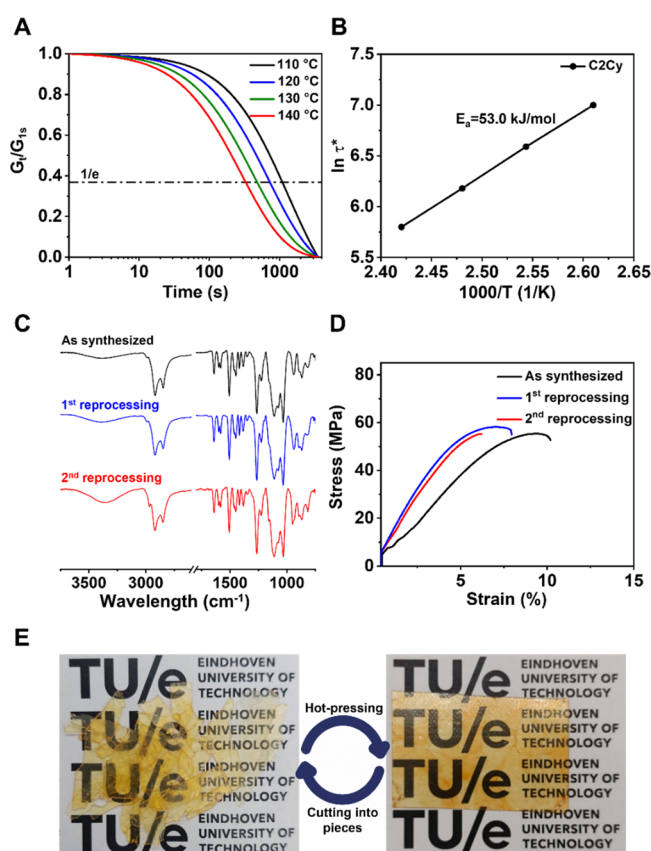


Figure 3. Normalized stress-relaxation curves of C2Cy (A). The stress-relaxation curves of the other networks are provided in the Supporting Information (Figure S8). Fitted curve for C2Cy between $1000/T$ and characteristic relaxation time ($\ln \tau^*$) according to the Arrhenius law (B). Comparison of the FTIR spectra (C) and mechanical properties (D) of as-synthesized and reprocessed C2Cy. Photographs of the reprocessing cycle of C2Cy (E): chopping off the C2Cy film into small pieces, followed by reprocessing via hot-pressing at 120 °C and 75 kN pressure for 1 h. The university logos were adapted with the permission from the Eindhoven University of Technology.

the use of a rigid cycloaliphatic hardener resulted in higher T_g and therefore higher activation energies and longer relaxation times as compared with a slightly more flexible hardener, which is consistent with the previously published literature.^{28,64,65} It is also noteworthy to emphasize that the calculated E_a values are much lower than similar structured vanillin-based epoxy-imine networks (90–103 kJ/mol).^{32,34}

Furthermore, to prove the malleability of the material, we tried to remold the network with the highest T_g (C2Cy). Remolding was performed by hot-pressing the chopped pieces of the C2Cy film with a 75 kN pressure at 120 °C for 1 h, which was followed by vacuum drying for 12 h at 80 °C. The FTIR spectra and the mechanical properties before and after the reprocessing procedure did not show any significant difference, proving the excellent reprocessing ability of the networks (Figure 3C–E and Figures S9 and S10). Indeed, after the first hot-pressing cycle, we observed a significant increase in the Young modulus from 918.7 to 1381.7 MPa along with a decrease in elongation at break from 12.3 to 7.3% while keeping the tensile strength nearly constant (55.3 MPa before press and 56.5 MPa after press). This could be attributed to the plasticizer effect by the remaining trace amount of water

present before the first hot-pressing cycle.⁶³ Upon second reprocessing, the tensile properties were nearly identical with a tensile strength value of 54.9 MPa, an elongation at break of 6.2%, and a Young's modulus of 1221.2 MPa. Also, the T_g (DMA) was slightly raised from 78 to 84 °C after second reprocessing possibly due to the complete removal of a trace amount of water within the matrix (Figure S10).

Closed-Loop Recycling and Upcycling. The incorporation of reversible imine and acetal bonds into the epoxy network enables efficient chemical depolymerization and thus paves the way for establishing a partial closed-loop recycling scheme. As a proof of concept, we performed the depolymerization of C4Cy and C4Xy in the mixture of THF/1 M HCl (2/8 by volume) at 65 °C (Figure 4 and Figure S11).

A full depolymerization was observed within 2 h for both cases. After liquid–liquid extraction with chloroform, vanillin was obtained as a pure solid with 93 and 91% yields from the depolymerization of C4Cy and C4Xy networks, respectively (Figure S12). The remaining water-soluble, acidic part was neutralized with 2 M NaOH. After removal of water from the mixtures, the solids were dispersed in DMF and filtered to remove salts. The obtained parts are a mixture of well-defined polyols and a minor amount of diamine, which could not be separated due to the similar polarity and solubility. The stretching peaks of carbonyl compounds at 1682 cm^{-1} (aldehyde) and 1641 cm^{-1} (imine) were not observed in the polyols. Also, the peak at 1265 cm^{-1} belonging to the acetal structure disappeared (Figure S13). It could be concluded that the depolymerization took place efficiently. Moreover, ESI-MS showed that the epoxy networks depolymerized into well-defined structures (Figures S14–S16 and Tables S2 and S3).

Following the acidic hydrolysis of the networks, we directly determined the total hydroxyl/amine value for the mixtures (492 mg KOH/g for the polyol mixture of depolymerized C4Cy and 380 mg KOH/g for the polyol mixture of depolymerized C4Xy). Such polyols could be utilized in the synthesis of value-added polyurethanes (Figure 4); this process is defined as upcycling.⁶⁶ Polyurethanes are a very important class of high-performance polymers due to their wide range of application areas such as adhesives, sealants, flexible and rigid foams, coatings, insulation, and elastomers.^{67,68} Also, they can be readily recycled by several chemical recycling methods such as glycolysis and acidolysis.^{69,70} The polyol mixture obtained from the depolymerization of C4Xy was reacted stoichiometrically with an isocyanate prepolymer of 12.4% NCO content based on 4,4'-methylenebisphenyl diisocyanate (MDI) and poly(propylene glycol) having a molecular weight of 2000 g/mol to form a crosslinked polyurethane network. The characterization of the film was performed using FTIR (Figure S17). The disappearance of the isocyanate stretching vibration ($\text{N}=\text{C}=\text{O}$) at 2259 cm^{-1} and the formation of $\text{N}-\text{H}$ stretching at 3293 cm^{-1} proved the successful incorporation of the polyol in the final polyurethane. The formed polyurethane was further characterized using TGA, DMA, and mechanical testing (Figure S18). The onset thermal degradation of the upcycled polyurethane was 249 °C, whereas the glass transition temperatures were -32 and 126 °C. The lower T_g is dominated by the soft segments (PPG 2000), and the higher T_g is dominated by the hard segments, which is mainly based on the reaction product of MDI and upcycled polyol structures. It is a transparent, tough material with Young

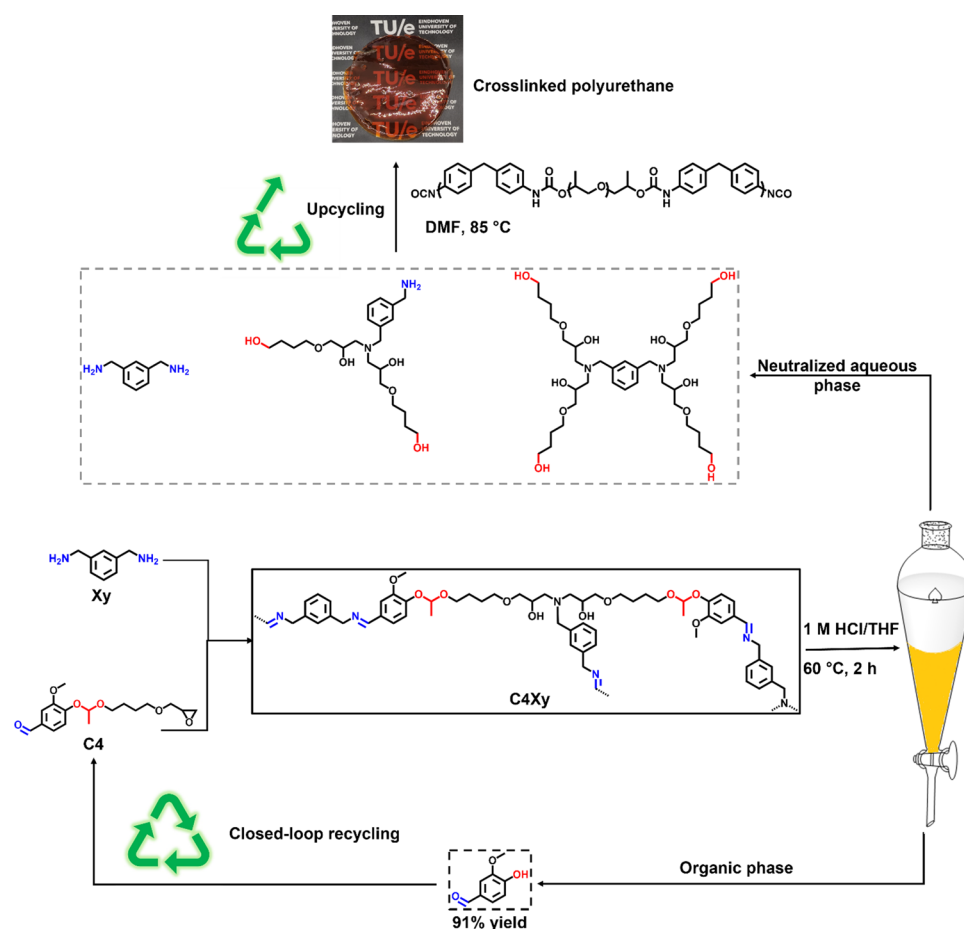


Figure 4. Schematic representation of depolymerization of C4Xy, partial closed-loop recycling toward vanillin, and upcycling into polyurethane. Some of the polyol structures are omitted for clarity. All possible polyol structures are shown in Figure S16. The university logos were adapted with the permission from the Eindhoven University of Technology.

modulus, stress at break, and elongation at break values of 263.4 MPa, 85.8 MPa, and 208.2%, respectively.

CONCLUSIONS

Two monomers for recyclable, upcyclable, and malleable epoxy systems were developed based on vanillin structures bearing aldehyde, acetal, and oxirane-ring functionalities. Polymerization of these monomers was performed in bulk without use of any organic solvents, thanks to their liquid state, which is in line with the principles of green chemistry. Curing this monomer with common, commercial epoxy hardeners (i.e., diamines) resulted in high-performance, dual-dynamic imine-acetal-containing thermosetting materials, which combines the excellent properties of the traditional epoxy systems and dynamic networks. The tensile strength values of the epoxy networks herein are in the range of 50–70 MPa, which are comparable to the commercial epoxy systems. As an advantage, the end thermosetting material is malleable and could be fully depolymerized into the vanillin monomer, achieving a partial closed-loop recycling and yielding well-defined value-added polyols. Such polyols could be upcycled into polyurethanes with excellent properties. This kind of epoxy resins could have a great potential for the development of composites that could be recycled.

EXPERIMENTAL SECTION

Materials. Chemicals were used as received without further purification. Vanillin, epichlorohydrin, ethylene glycol vinyl ether, tetrabutylammonium bromide, and sodium hydroxide were obtained from Merck, whereas *m*-xylylenediamine and 4,4'-methylenebis(cyclohexylamine) were purchased from Tokyo Chemical Industry (TCI). 4-Hydroxybutylvinylether, poly(propylene glycol) (MW = 2000 g/mol), and 4,4'-methylenediphenyl diisocyanate (MDI) were obtained from BASF. Ethyl acetate, petroleum ether, dimethylformamide (DMF), and toluene were purchased from Biosolve B.V. Deuterated CDCl₃ was obtained from Cambridge Isotope Laboratories for ¹H NMR and ¹³C NMR analyses. 2-((2-(Vinyl-oxymethyl)oxirane)ethoxy)methyl)oxirane (VE2) and 2-((4-(vinyl-oxymethyl)butoxy)methyl)oxirane (VE4) were synthesized using the reported procedures.⁷¹

Methods. The ¹H NMR and ¹³C NMR spectra were recorded on a Bruker UltraShield (400 MHz) using CDCl₃ as the solvent. Mass spectroscopy of the compounds was performed with a Bruker Autoflex III TOF/TOF MALDI analyzer and LCQ Fleet ESI-MS (Thermo Fisher Scientific). The FTIR spectra were recorded on a Thermo Scientific NICOLET iS20 FTIR spectrometer as an average of 8 scans over the wavenumber range of 450–4000 cm⁻¹.

TGAs were performed using a TA Instruments TGA550, in which 5–10 mg of the samples was heated from 100 to 800 °C under N₂ atmosphere. DSC measurements were performed on a TA Instruments Q2000. The samples (5–15 mg) were placed in an Aluminum-Hermetic pan. The experiments were carried out from –50 to 180 °C at a rate of 10 °C/min under N₂ atmosphere. Glass transition temperatures (*T*_g) were determined by taking the midpoint of the reversible endotherm of the second heating.

Dynamic mechanical analysis (DMA) measurements were performed on a TA Instruments DMA850. The experiments were carried out from -80 to 150 °C at a heating rate of 3 °C/min under an oscillatory strain of 0.1% and a frequency of 1 Hz. The glass transition temperature (T_g) was recorded as the maximum value of $\tan \delta$. The presence of crosslinking networks in the epoxy systems was proved by the storage modulus value at the rubbery plateau using the following equation:³²

$$E' = 3\nu_e RT \quad (1)$$

where E' corresponds to the storage modulus of the resin at the rubbery plateau ($T_g + 40$ °C), R refers to the universal gas constant, and T is the absolute temperature.

The crosslinking densities obtained by DMA were further supported by gel fraction experiments. All monomers, hardeners, and possible oligomers are soluble in THF and DMF; therefore, gel fraction experiments were conducted in both solvents using the static method. Gel fractions were calculated using the equation below, where GF stands for gel fraction, W_0 refers to the initial weight of the thermoset, and W_1 is the weight of the thermoset after drying:³²

$$GF = 100 \times \frac{W_1}{W_0} \quad (2)$$

Stress-relaxation analysis was performed on a Discovery TA Instruments HR20. The relaxation modulus ($G(t)$) was followed over different time periods for a constant applied strain of 1% at the constant temperature (from 110 to 140 °C). The relaxation modulus (G) was normalized by the initial value ($G_{0.1s}$ or G_{1s}).

The total hydroxyl/amine value of the polyol mixture was determined by using a Metrohm 916 Ti-Touch titrator according to the ASTM E222-17 standard method. The experimental free isocyanate content of the prepolymer was determined by using a Metrohm 916 Ti-Touch titrator according to the ASTM D5155-19 standard method.

Synthesis of the Monomers. 2-((2-(Vinylloxy)ethoxy)methyl)oxirane (VE2) and 2-((4-(vinylloxy)butoxy)methyl)oxirane (VE4) were synthesized using the reported procedure with slight modification.⁷¹

2-((2-(Vinylloxy)ethoxy)methyl)oxirane (VE2). Ethylene glycol vinyl ether (35.24 g, 0.40 mol) and tetrabutyl ammonium bromide (4.2 g, 13 mmol) were dissolved in 240 mL of the toluene/NaOH (50 wt %) mixture ($1:1$ by volume) in a 250 mL three-necked round-bottom flask equipped with a reflux condenser, an Ar inlet, and a dropping funnel, and the mixture was cooled to 0 °C. Epichlorohydrin (59.28 g, 0.64 mol) was added dropwise over 1 h. After completion of the addition, the reaction temperature was raised to room temperature and the mixture was allowed to stir for 24 h at this temperature under Ar flow. The reaction mixture was extracted with distilled water and dried over magnesium sulfate. Upon removal of the solvent, the crude product was purified upon distillation under reduced pressure to give a colorless liquid with a yield of 54.8 g, 95.0% . $^1\text{H NMR}$ (400 MHz, chloroform- d) δ 6.50 (dd, $J = 14.3$, 6.8 Hz, 1H), 4.20 (dd, $J = 14.3$, 2.2 Hz, 1H), 4.02 (dd, $J = 6.8$, 2.2 Hz, 1H), 3.88– 3.70 (m, 5H), 3.45 (dd, $J = 11.7$, 5.9 Hz, 1H), 3.18 (ddt, $J = 5.7$, 4.1 , 2.8 Hz, 1H), 2.81 (dd, $J = 5.0$, 4.1 Hz, 1H), 2.62 (dd, $J = 5.0$, 2.7 Hz, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 151.83, 86.88, 72.16, 69.85, 67.34, 50.93, 44.31. MS (ESI-TOF) m/z : $[2\text{M} + \text{Na}^+]^+$ calculated for $\text{C}_{14}\text{H}_{24}\text{NaO}_6^+$ 311.15, found 311.17.

2-((4-(Vinylloxy)butoxy)methyl)oxirane (VE4). 4-Hydroxybutylvinylether (23.24 g, 0.20 mol) and tetrabutyl ammonium bromide (2.1 g, 6.5 mmol) were dissolved in 120 mL of the toluene/NaOH (50 wt %) mixture ($1:1$ by volume) in a 250 mL three-necked round-bottom flask equipped with a reflux condenser, an Ar inlet, and a dropping funnel, and the mixture was cooled to 0 °C. Epichlorohydrin (30.64 g, 0.33 mol) was added dropwise over 1 h. After completion of the addition, the reaction temperature was raised to room temperature and the mixture was allowed to stir for 24 h at this temperature under Ar flow. The reaction mixture was extracted with distilled water and dried over magnesium sulfate. Upon removal of the solvent, the crude

product was purified upon distillation under reduced pressure to give a colorless liquid with a yield of 32.7 g, 94.8% . $^1\text{H NMR}$ (399 MHz, chloroform- d) δ 6.46 (dd, $J = 14.3$, 6.8 Hz, 1H), 4.17 (dd, $J = 14.4$, 1.9 Hz, 1H), 3.97 (dd, $J = 6.8$, 1.9 Hz, 1H), 3.75– 3.67 (m, 3H), 3.53 (m, 2H), 3.38 (dd, $J = 11.5$, 5.8 Hz, 1H), 3.14 (ddt, $J = 5.8$, 4.2 , 2.8 Hz, 1H), 2.79 (dd, $J = 5.0$, 4.1 Hz, 1H), 2.61 (dd, $J = 5.0$, 2.7 Hz, 1H), 1.81– 1.62 (m, 4H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 152.03, 86.46, 71.59, 71.24, 67.84, 51.02, 44.42, 26.40, 25.94. MS (ESI-TOF) m/z : $[2\text{M} + \text{Na}^+]^+$ calculated for $\text{C}_{18}\text{H}_{32}\text{NaO}_6^+$ 367.25, found 367.21.

3-Methoxy-4-(1-(2-(oxiran-2-ylmethoxy)ethoxy)ethoxy)benzaldehyde (C2). Vanillin (4.93 g, 32.4 mmol) and 2-((2-(vinylloxy)ethoxy)methyl)oxirane (7.01 g, 48.6 mmol) were mixed in a 100 mL three-necked round-bottom flask equipped with a reflux condenser and an Ar inlet, and the mixture was heated to 95 °C for 24 h under Ar flow. After cooling to room temperature, the obtained crude product was purified using column chromatography with ethyl acetate and petroleum ether as eluents. The C2 monomer was obtained as a yellow liquid with a yield of 5.05 g, 52.6% . $^1\text{H NMR}$ (400 MHz, chloroform- d) δ 9.87 (s, 1H), 7.42 (m, 2H), 7.28 (s, 1H), 5.59 (q, $J = 5.4$ Hz, 1H), 3.92 (s, 3H), 3.91– 3.87 (m, 1H), 3.79– 3.61 (m, 4H), 3.38 (m, 1H), 3.12 (m, 1H), 2.77 (t, $J = 4.4$ Hz, 1H), 2.63– 2.52 (m, 1H), 1.59 (d, $J = 5.4$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 191.14, 151.62, 150.95, 131.33, 126.30, 117.02, 109.96, 100.83, 72.06, 70.58, 65.14, 56.11, 50.91, 44.27, 19.95. MS (MALDI-TOF) m/z : $[M + \text{Na}^+]^+$ calculated for $\text{C}_{15}\text{H}_{20}\text{NaO}_6^+$ 319.12, found 319.12.

3-Methoxy-4-(1-(4-(oxiran-2-ylmethoxy)butoxy)ethoxy)benzaldehyde (C4). Vanillin (3.79 g, 24.9 mmol) and 2-((4-(vinylloxy)butoxy)methyl)oxirane (6.43 g, 37.3 mmol) were mixed in a 100 mL three-necked round-bottom flask equipped with a reflux condenser and an Ar inlet, and the mixture was heated to 95 °C for 24 h under Ar flow. After cooling to room temperature, the obtained crude product was purified using column chromatography with ethyl acetate and petroleum ether as eluents. The C4 monomer was obtained as a yellow liquid with a yield of 5.52 g, 68.4% . $^1\text{H NMR}$ (399 MHz, chloroform- d) δ 9.87 (s, 1H), 7.41 (m, 2H), 7.22 (d, $J = 8.0$ Hz, 1H), 5.53 (q, $J = 5.4$ Hz, 1H), 3.92 (s, 3H), 3.80– 3.73 (m, 1H), 3.69 (dd, $J = 11.5$, 3.0 Hz, 1H), 3.49 (m, 3H), 3.33 (dd, $J = 11.5$, 5.8 Hz, 1H), 3.11 (ddt, $J = 5.8$, 4.1 , 2.8 Hz, 1H), 2.78 (t, $J = 5.0$, 4.1 Hz, 1H), 2.58 (dd, $J = 5.0$, 2.7 Hz, 1H), 1.66– 1.61 (m, 4H), 1.57 (d, $J = 5.3$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 191.14, 151.88, 150.88, 131.11, 126.32, 116.62, 109.95, 100.73, 71.58, 71.25, 65.85, 56.11, 50.99, 44.35, 26.48, 26.39, 20.02. MS (MALDI-TOF) m/z : $[M + \text{Na}^+]^+$ calculated for $\text{C}_{17}\text{H}_{24}\text{NaO}_6^+$ 347.15, found 347.15.

Preparation of Epoxy Networks. Epoxy-imine networks were prepared in solvent-free conditions, where a homogeneous mixture of monomers was heated to 100 °C in an inert environment for 24 h.

C2Cy. The C2Cy network was prepared by homogenizing the bulk mixture of C2 (3.50 g, 11.8 mmol) and 4,4'-methylenebis(cyclohexylamine) (1.86 g, 8.9 mmol) at room temperature. The resultant liquid was cured in a N_2 oven at 100 °C for 24 h.

C2Xy. The C2Xy network was prepared by homogenizing the bulk mixture of C2 (3.49 g, 11.8 mmol) and *m*-xylylenediamine (1.20 g, 8.8 mmol) at room temperature. The resultant liquid was cured in a N_2 oven at 100 °C for 24 h.

C4Cy. The C4Cy network was prepared by homogenizing the bulk mixture of C4 (3.0 g, 9.3 mmol) and 4,4'-methylenebis(cyclohexylamine) (1.46 g, 6.9 mmol) at room temperature. The resultant liquid was cured in a N_2 oven at 100 °C for 24 h.

C4Xy. The C4Xy network was prepared by homogenizing the bulk mixture of C4 (2.09 g, 6.4 mmol) and *m*-xylylenediamine (0.66 g, 4.8 mmol) at room temperature. The resultant liquid was cured in a N_2 oven at 100 °C for 24 h.

Reprocessing of the C2Cy Network. The C2Cy film was chopped into small pieces. Remolding was performed by hot-pressing the chopped pieces with a 75 kN pressure at 120 °C for 1 h, which was followed by vacuum drying for 12 h at 80 °C. This process was performed twice to observe the changes in the structure and mechanical properties caused by hot-pressing.

Depolymerization of Epoxy Networks. The network film (4 g) (C4Cy or C4Xy) was cut into small pieces and dispersed in 40 mL of

the solvent mixture containing THF/1 M HCl (2/8 by volume). The mixture was heated to 65 °C until a clear solution was obtained (roughly within 2 h). Following that, THF was evaporated and the acidic aqueous part was extracted with chloroform (2 × 20 mL). The chloroform layer was then separated and dried with MgSO₄. After filtration and evaporation of the organic solvent, vanillin was obtained as a pure solid (1.20 g, 93% for C4Cy and 1.28 g, 91% for C4Xy). ¹H NMR (399 MHz, CDCl₃) δ 9.83 (s, 1H), 7.50–7.34 (m, 2H), 7.05 (d, *J* = 8.5 Hz, 1H), 6.16 (s, 1H), 3.97 (s, 3H) (Figure S12). The remaining acidic aqueous solution, which was free of vanillin, was neutralized with 2 M NaOH, and water was evaporated under reduced pressure. The solid residue was sonicated in DMF and then filtered. A viscous liquid was obtained upon evaporation of the organic solvent, which contains the mixture of constituent diamine and well-defined polyols (Figures S15 and S16).

Synthesis of the Isocyanate Prepolymer. Poly(propylene glycol) (MW = 2000 g/mol) (28 g) and 4,4'-methylenediphenyl diisocyanate (MDI) (22 g) were reacted in bulk conditions at 80 °C under continuous Ar flow for 2.5 h. The reaction product with a free isocyanate content of 12.4% was used without any further purification.

Synthesis of the Upcycled Polyurethane. The polyol mixture obtained from the depolymerization of C4Xy (1.0 g) was dissolved in DMF (7.5 mL) in a stainless steel metal mold. In another vial, the isocyanate prepolymer with an NCO content of 12.4% (2.4 g) was dissolved in DMF (7.5 mL) and was added to the polyol solution dropwise and stirred vigorously. The reaction solution was placed in a N₂ oven at 80 °C for 12 h, and the resultant film was dried in a vacuum oven at 80 °C overnight.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.3c00761>.

Additional experimental data including: ¹H NMR and ¹³C NMR characterization of monomers; thermal, thermomechanical and mechanical characterization of the pristine and reprocessed networks; gel fractions; stress-relaxation experiments; ¹H NMR, FTIR and ESI-MS characterizations of the recovered products after depolymerization; FTIR characterization, thermal, thermomechanical, and mechanical properties of the upcycled network (PDF)

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Author Contributions

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

Notes

The authors declare no competing financial interest.

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