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Flexible and Stretchable Vitrimers for Sustainable Electronics

Agni K. Biswal, Peter Hong, Zhihan Zhang, Yiwen Zheng, Surabhit Gupta, Dhriti Nepal, Vikram Iyer, and Aniruddh Vashisth*

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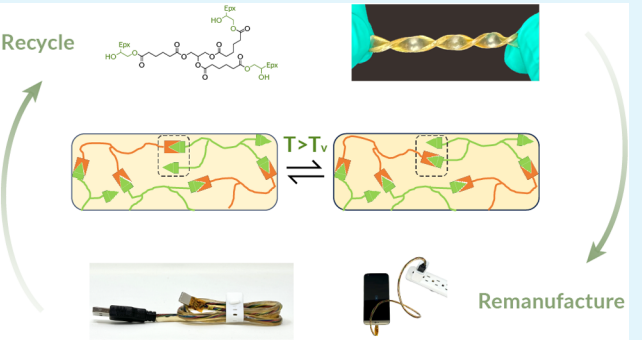
ABSTRACT: The rapid increase in electronic waste (e-waste) necessitates sustainable materials that combine functionality with recyclability. Here, we introduce a novel approach for creating flexible vitrimers—reprocessable polymers with dynamic covalent bonds—for use in electronic applications, such as wiring and connectors. By extending polymer chains and employing transesterification reaction, we develop vitrimers that exhibit tunable viscoelastic properties, high stretchability (over 250% tensile strain), and enhanced toughness (up to 466 J/m^3). Our vitrimers demonstrate a topological freezing temperature (T_v) of 185−248 °C, adjustable through catalyst concentration and chain length. The materials are synthesized by using a two-step process involving widely available industrial chemicals. Molecular dynamics simulations provide insight into how chain extension and network topology affect viscoelasticity, supporting the experimental findings. Using transesterification, covalent bonding between flexible and rigid vitrimers can be achieved. We prototype a functional USB cable that successfully transfers power and data, showcases repairability, and is recyclable through a solvent-based process. These results highlight the potential of flexible vitrimers in reducing e-waste and advancing sustainable electronic manufacturing.



KEYWORDS: *flexible vitrimers, transesterification, thermomechanical properties, sustainable electronics, polymer recycling, molecular dynamic*

1. INTRODUCTION

Engineered polymers are used extensively in the electronics industry due to their processability, low relative permittivity, corrosion resistance, exceptional flexibility, fatigue strength, thermal resistance, and electrical resistivity.[1−3] Their versatility allows them to be used in a wide range of applications, from the rigid, high stiffness materials that make up printed circuit boards (PCBs) to the softer, flexible polymers required for wires and interconnects. From common Universal Serial Bus (USB) and power cables to novel wearable devices and soft actuators, numerous flexible and highly stretchable elastomeric materials[4] have been developed for diverse electronics applications.[5−7]

The ubiquitous use of polymers in electronics, however, means they also become a part of electronic waste (e-waste) when outdated or damaged products reach end-of-life.[8] For example, studies have shown that as much as 40% of data cable waste comes from the polymers[9] used to create their insulation and housing. E-waste is among the fastest growing global waste streams, and the staggering 62 million metric tons produced in 2022[10] underscores the need for sustainable polymers. In this work, we seek to develop recyclable polymers with tunable thermomechanical properties for flexible electronics.

Achieving this goal is, however, challenging as thermoset polymers have permanently cross-linked covalent networks that prevent them from being reprocessed or recycled. While thermoplastics can be reprocessed at elevated temperatures, the polymers cannot form new bonds, meaning that their properties, such as mechanical strength, degrade substantially with each successive recycling attempt. In contrast, a new class of polymers called vitrimers possess a unique ability to undergo associative rearrangement reactions while maintaining structural integrity.[11] This dynamic property arises from the presence of dynamic covalent bonds that can break and reform above a certain topological freezing temperature T_v, allowing the material to flow and adapt to external stimuli.[12−14] Vitrimers exhibit healing capabilities, making them repairable after damage occurs.[15−17] When exposed to mechanical stress or other environmental factors causing bond breakage, vitrimers can be repaired using the dynamic exchange nature of the polymeric network.[18] Researchers have explored the

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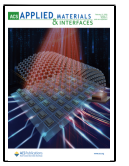

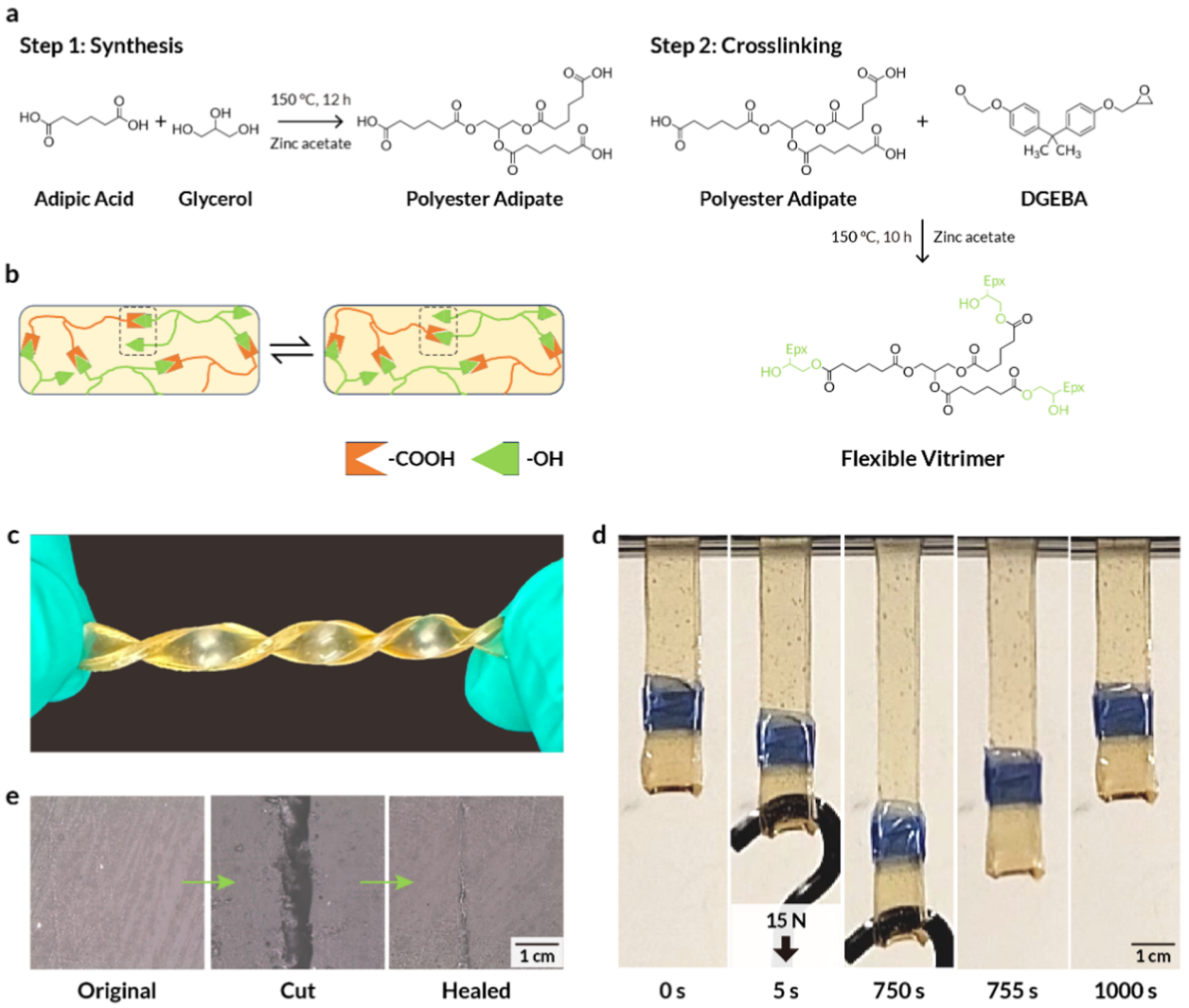

Figure 1. (a) Reaction and synthesis of polyester adipate and the consequent cross-linking with bifunctional epoxides; (b) rearrangement schematic of the transesterification reaction in flexible vitrimer; (c) visual representation of vitrimer flexibility strand by twisting; (d) stretchability representation of polymer using load of 1.5 kg (~15 N); and (e) the healability properties of flexible vitrimer at 1 MPa pressure and 150 °C for 1 h.

potential of vitrimers in applications such as coatings, composites, adhesives, and biomedical devices.[19−21]

Recent work has successfully used vitrimers to create recyclable composites for electronics applications such as printed circuit boards.[22] These materials are, however, rigid and cannot be used in the many electronics applications like wire insulation that require flexibility. While flexible vitrimer chemistries with various dynamic bond exchange reactions, including transesterification, imine exchange,[12] transcarbamoylation,[23] and silyl-ether exchange reactions,[24] have been synthesized, these materials require complex synthesis processes and high barrier energy.

To address these challenges, we take a different approach. We observe that the toughness and flexibility of thermosets can be tuned by cross-linking epoxies with a thermoplastic segment like diacid or dithiols[25] to transition these chemistries to have elastomeric behavior. The chain extension in these chemistries enables greater viscoelasticity by reducing the number of covalent bonds and increasing the weak intramolecular interactions.[26,27] Inspired by this approach, we explore whether chain extension can be used as a means to tune the thermomechanical properties of vitrimers to create flexible materials with customizable viscoelasticity. In addition to the ability to leverage simplified synthesis processes using widely available industrial chemicals, we hypothesize that this approach has a second key advantage: the similarity between rigid and flexible chemistries combined with their ability to perform bond exchange reactions will enable strong bonding at hard−soft material interfaces. This approach addresses a common failure mode of flexible materials, such as cables, at the interface between the flexible insulation and rigid connector. These parts are typically bonded with adhesives or approaches such as friction welding, which are both far weaker than covalent bonds in the materials.

In this study, we synthesized flexible vitrimers from a polyester adipate, demonstrating the ability to create extended polymer chains and epoxides in the presence of a transesterification catalyst. Our material requires a simple two-step synthesis process (Figure 1a) using widely available industrial chemicals. We show through thermomechanical characterizations that this approach allows for tuning the chain length and results in highly flexible and stretchable materials (Figure 1b,c). We further show that even combinations of rigid and flexible materials can be bonded together with high mechanical

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strength. To examine the molecular effect of varying chain lengths in vitrimers, we carried out accelerated reactive molecular dynamics (MD) (ReaxFF) simulations to cross-link and develop a virtual specimen. These virtual specimens were examined in extension loading to understand the effect of varying network topology on the resulting viscoelasticity. We combine these findings to create an end-to-end demonstration of an electronic USB cable with a vitrimer jacket, showing it can successfully charge a smartphone, send data to a laptop, and be recycled.

2. MATERIALS AND METHODS

A combination of epoxides, acids, polyols, and catalysts was used to synthesize the flexible materials. Varying the stoichiometry of these components allows the resulting vitrimer material properties to be tailored for different applications by tuning the chain length.

2.1. Materials. The required materials for the synthesis of polymers, such as adipic acid, glycerol, and catalyst zinc acetate, were purchased from Sigma-Aldrich. A diglycidyl ether of bisphenol A (DGEBA) epoxide (EPON 828) was purchased from SkyGeek, USA. Solvents were procured from Fisher Scientific. Other lab consumables, including adhesive Teflon sheets for molds and high-temperature Kapton tape, were purchased from McMaster.

2.2. Experimental Procedure. *2.2.1. Synthesis of Polyester Adipate.* Our key hypothesis is that extension of chain lengths between the reactive ends of the vitrimer polymer will modify its viscoelasticity, stretchability, and toughness. We synthesized flexible vitrimers in a two-step process to evaluate this, as shown in Figure 1a. First, we synthesized polyester adipates with carboxyl terminations from adipic acid and glycerol. To synthesize the extended chain polyester adipate, the required amount of adipic acid (60 mmol) and glycerol (30 mmol) with zinc acetate (0.2 wt % of acid) were charged into a dried Schlenk round-bottom flask with a magnetic stirrer that was fitted with a condenser.[28] The flask was kept in an oil bath at 150 °C and heated continuously for 12 h under a nitrogen flow to displace water generated from the reaction. Finally, the resulting waxy polyester adipate materials were collected, dissolved in methanol, and precipitated into water to remove the excess unreacted excess acids. This yielded a clear, viscous liquid of polyesters, which was further confirmed by NMR (Figure S1) and FTIR spectra (Figure S2)

2.2.2. Synthesis of Vitrimer. In the second step, the polyester adipate synthesized above was cross-linked with the epoxide to yield the completed flexible vitrimers. An equivalent amount of polyester adipate (7 g) and epoxide (DGBEA, 7 g) were mixed with the required amount of zinc acetate catalyst (2−5 mol % of catalyst relative to the epoxide content) in a 100 mL beaker using a magnetic stirrer at temperature 150 °C for 10−15 min. The homogenized mixture was then transferred into a preheated mold of dimension 4″ × 4″ to cure at 150 °C for 10 h. Before curing, the resin containing mold was kept under vacuum for 2 min for degassing. These vitrimers synthesized by cross-linking polyester adipate with bifunctional epoxides are termed flexible vitrimers. Control vitrimer specimens were synthesized using only adipic acid and epoxide (without glycerol) with a catalyst (Rigid Vitrimer). The film was cut into the required dimensions for mechanical and other characterization.

2.2.3. Determination of Swelling Ratio and Soluble Fraction. The swelling ratio and soluble fraction of the cross-linked vitrimers containing 2 mol % and 5 mol % catalyst were determined using tetrahydrofuran (THF).[29] Preweighed (m_0) samples were immersed in THF overnight to allow swelling and the dissolution of any uncured components. The samples were then removed, dried overnight at room temperature in a vacuum oven to eliminate the solvent, and reweighed (m_f). The soluble fraction was calculated using the equation $((m_0 - m_f)/m_0) \times 100$ and the swelling ratio was calculated from the initial mass and swollen mass. All of the experiments were performed in triplicate.

2.2.4. Fabrication of Cable. A prototype USB cable was fabricated by casting the flexible vitrimer resin in a mold. A mold for the vitrimer-encased wire was created from a 30 cm long Teflon tube with a diameter of 5 mm (Figure S3). Braided wires for USB were placed at the center of the tube. One end of the tube was then wrapped with Kapton tape to create a closed end and prevent leakage. Vitrimer resin was poured into the mold with the braided cables centered. The mold with cables was placed in an oven at 150 °C for a 10 h cure cycle. The resulting cable was soldered to USB connectors to create a functional USB cable.

2.3. Characterization. *2.3.1. Fourier-Transform Infrared Spectroscopy and NMR Spectroscopy.* Synthesized polyesters in $CDCl_3$ using internal standard trimethylsilane were characterized by using ^{1}HNMR (Bruker Advance AV-III, 400 MHz). Fourier-transform infrared spectroscopy (FTIR) (Bruker Vertex 70) scan was performed on the synthesized polyester adipates and cross-linked vitrimer products following wavelength range from 4000 to 400 cm^{-1}, and the measured data were averaged over 32 scans at a resolution of 4 cm^{-1}.

2.3.2. Thermal Analysis. Thermal analysis of these polymers was carried out using a TA Instruments Q2000 for differential scanning calorimetry (DSC) and a TA Instruments Q200 for thermogravimetric analysis (TGA). DSC experiments were carried out within the temperature range of −20 to 200 °C at the heating rate of 5 °C/min under nitrogen flow to determine the glass transition temperature (T_g) of the synthesized polymers using the tangent for the second heating curves. TGA was carried out on the polyester adipates to determine the thermal stability of the cross-linked polymer. The polymer was scanned from room temperature to 900 °C at 10 °C/min.

2.3.3. Viscoelastic Analysis. Dynamic mechanical analysis (DMA) was carried out using an ElectroForce 3200 (TA Instruments). Rectangular specimens of dimensions 6 mm (width) × 0.5 mm (thickness) were laser cut (LPKF Protolaser U4) from the vitrimer sheets. DMA experiments were done by scanning a temperature range from −20 to 120 °C at a heating rate of 2 °C/min using 1 Hz frequency at 0.1% strain. The resulting storage modulus, loss modulus, and tan δ values were recorded.

Thermomechanical responses of the flexible vitrimers were evaluated using thermomechanical analysis (TMA) (PerkinElmer, TMA7). Circular disc samples were placed under a mechanical static force of 0.1 N using a 2 mm diameter quartz glass probe. The heating range was room temperature 0 to 300 °C at heating rates of 2 °C/min, 5 °C/min, and 10 °C/min. The thermal transitions that demonstrate a drop in dimensional expansion of the vitrimer are indicative of flowability at topological freezing temperature (T_v).

2.3.4. Lap Shear Test. The cured samples were cut into the dimensions of 70 mm × 5 mm × 2 mm, and lap shear specimens were prepared with an overlapped length of 25 mm. The lap area was welded through 1 h at 150 °C under a load of 20 N. The welded samples were tested using an Instron mechanical testing machine with a 2 kN load cell at a 2 mm/mm strain rate. The shear deformations were recorded by using a video extensometer.

2.3.5. Toughness Test. Toughness of the vitrimer was determined by measuring the crack propagation of notched samples in tensile deformation mode. Samples with 30 mm length (10 mm gauge length), a cross-section width of 10 mm, and 1.5 mm thickness were prepared from the vitrimer sheet.[30] The samples were notched in the middle of the gauge length with a 2.5 mm razor blade cut. Experiments were carried out using a 2 kN load cell at a 0.5 mm/min strain rate. The toughness energy for the specimens was calculated from the area under stress−strain curve for at least three samples.

2.3.6. Electrical Characterization. To conduct electrical characterization for flexible vitrimer, two 25 μm-thick sheets of copper foil (McMaster-Carr) were first cut to the appropriate size and placed on both sides of the vitrimer. The laminate was then heat-pressed at 50 °C and 2 MPa for 10 min.

2.3.6.1. Dielectric Constant. The dielectric constant test was conducted with a vector network analyzer (VNA, Anritsu MS2036C) using the parallel plate method. Test specimens were trimmed to a rectangular shape with dimensions of 10 mm × 10 mm × 1.5 mm. An SMA connector was used to connect the specimen to a VNA S11

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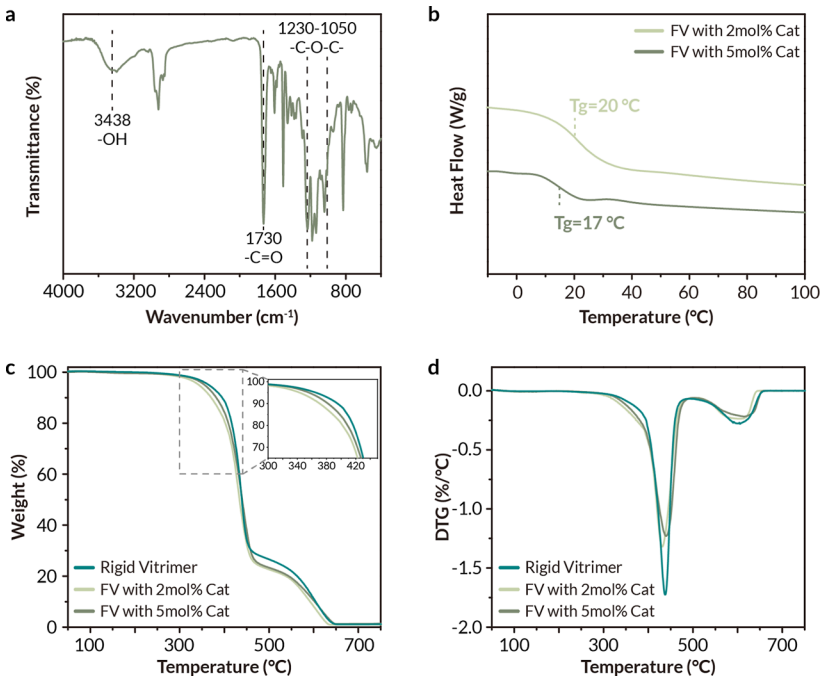

Figure 2. (a) FTIR showing fully cured cross-linked vitrimer confirming the evolution of ether peaks and the disappearance of epoxy. (b) Representative DSC scan for the cross-linked vitrimers showing only T_g of vitrimer polymers. (c) Decomposition TGA curves for flexible and rigid vitrimers with an inset showing weight loss between 300 and 420 °C. (d) TGA thermal decomposition curve showing the derivative of the thermal decomposition curve with respect to temperature. (Note: FV, flexible vitrimer).

port, with the signal pin of the SMA connector soldered to one side of the copper layer of the laminate and the ground pins soldered to the other side. The capacitance of the parallel plate was measured at a frequency of 1 MHz. The dielectric constant of the vitrimer was determined using the following eq 1

$$k = \frac{C.\ t}{\varepsilon_0 A} \tag{1}$$

where C is the capacitance reading from the VNA, t is the effective thickness of the specimen, ε_0 is the vacuum permittivity, and A is the area of the specimen.

2.3.6.2. Resistivity. Volume resistivity tests were conducted using a SourceMeter (Keithley 2470) on samples with similar dimensions to those used for dielectric properties. The volume resistance was measured by connecting the SourceMeter to each side of the laminate. The current was measured while applying 40 V DC across the specimen at room temperature. The volume resistivity of the vitrimer was calculated using eq 2

$$r = \frac{R.\ A}{t} \tag{2}$$

where R is the measured resistance, A is the effective area of the surface, and t is the average thickness of the specimen.

2.4. ReaxFF Molecular Dynamics Simulations. We carried out MD simulations to understand the molecular mechanisms leading to enhanced flexibility due to chain elongation. Various methods have been utilized to model the cross-linking of epoxy networks via MD. Traditional approaches often rely on the "cutoff" distance method, which determines the likelihood of reactions between sites based solely on their proximity, neglecting the actual reaction pathway.[31] In contrast, our study adopts a novel technique[32,33] for polymer simulating cross-linking within the reactive MD framework (ReaxFF) that uses the concept of "bond boost"[34] to accelerate reactions with slow kinetics. This method is referred to as accelerated ReaxFF; it considers first the prescribed proximity conditions for a reaction to be feasible (similar to the cutoff method), but these reactive sites are then provided with additional energy when the first condition is satisfied. This additional energy or "boost energy" is equivalent to or slightly exceeds the energy barrier of the reaction, facilitating the cross-linking at lower, more realistic temperatures and thereby replicating chemical reaction conditions more accurately. This strategy helps prevent undesirable reactions that typically occur at higher temperatures and allows for the selective rejection of reactions with high energy barriers.

For virtual characterization, two types of vitrimer specimens were synthesized by reacting bisphenol A with either adipic acid or polyester adipate in a 1:1 molar ratio. It is important to note that in these epoxy−acid vitrimers, catalysts are used to manage the rate of exchange reactions, but in our simulations, we focus exclusively on the polymerization reactions, omitting the catalyst for ease of modeling. The accelerated ReaxFF algorithm requires determining two key parameters: the distance range between reactive sites and the force constants that supply the necessary bond boost energy (Supporting Information). These parameters (i.e., F_1, F_2, and R_{12}; see Supporting Information) were optimized for three different sets of atomic groupings through an iterative process to minimize the required input energy. A comprehensive explanation of the cross-linking process can be found in Vashisth et al.[17,32] After cross-linking, the virtual specimens were annealed to remove local heterogeneities and then tested in tension loading; the segment lengths in each chain were analyzed in the direction of loading to evaluate chain unfolding.

3. RESULTS AND DISCUSSION

3.1. Synthesis of Polyester Adipate and Its Vitrimer. The flexibility of a cross-linked polymer can be tuned by changing the polymer chain length of the reactants.[35,36] In our previous work,[22] we synthesized vitrimers with adipic acid, which have carboxylic functional groups to react with bifunctional epoxides that follow a transesterification bond exchange mechanism in the presence of a catalyst under external stimuli. In this work, we extended the polymer chain lengths between the reactive sites to achieve increased flexibility and viscoelasticity; additionally, we used a branched polymeric structure to enhance toughness. The reaction schemes for synthesized polyester adipate with carboxylic

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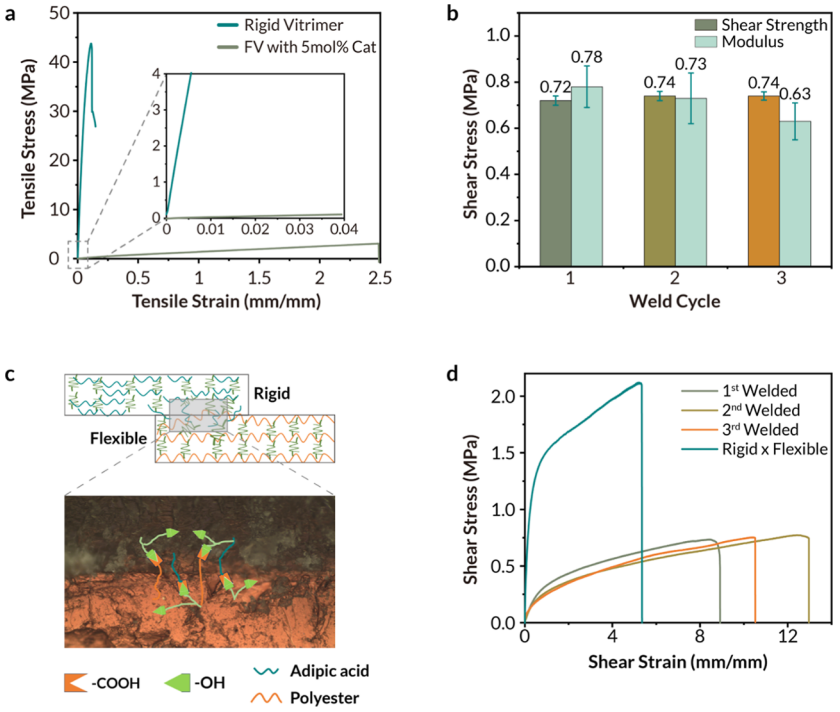

Figure 3. (a) Comparative mechanical study for the adipic acid−epoxy vitrimer, and flexible vitrimer. (b) Mechanical properties of welded flexible vitrimer. (c) Mechanism for the bond diffusion at the rigid and flexible vitrimer interface and their optical microscopic image. (d) Welding properties of flexible vitrimer with rigid vitrimer made from adipic acid and epoxy; first, second, and third welds for flexible-flexible lap joints.

terminated polymers are shown in Figure 1a. The synthesized polymer was characterized using NMR (^{1}HNMR 400 MHz, Chloroform-D) 1.71−1.63 ppm (m, $OCOCH_2CH_2$), 2.43−2.31 ppm (m, $OCOCH_2CH_2$), 4.39−4.15 ppm (m, H from glycerol ester), and 5.26 ppm (s, H from the free hydroxyl) (Figure S1). FTIR analysis of the synthesized polymer resulted in peaks at 3402 cm^{-1} (corresponds to O−H stretch from carboxylic acid end-groups), 2914 and 2846 cm^{-1} (C−H saturated), 1739 cm^{-1} (C═O ester), 1604 cm^{-1} (C═O acid end-group), and 1170 cm^{-1} (C−O stretch), and the results confirm the formation of polyester (Figure S2). The NMR and FTIR spectra show the chain-extended polyester containing carboxylic end groups which can actively participate in the cross-linking process with epoxide molecules.

The cross-linking reaction between polyester and epoxides was carried out in the presence of varying amounts of transesterification catalyst (2 and 5 mol %). The cross-linking process was carried out for 10 h at 150 °C to ensure a high degree of cross-linking. The cross-linked polymers were verified using FTIR, where the characteristic peaks for ether associated with epoxies were observed at 1050−1230 and 1730 cm^{-1} for ester linkage. No peaks were observed at 900 cm^{-1}, indicating that all epoxide functionalities were utilized in the cross-linking reactions. Also, other peaks with ester linkages around 1400−1650 cm^{-1} show the formation of ester linkages between the polyester and epoxies. The FTIR spectrum is shown in Figure 2a.

The soluble fraction of the synthesized flexible vitrimers was determined by THF swelling to dissolve the uncured moieties. The results showed soluble fraction values of 8.08% and 4.65% for the vitrimers with 2 and 5 mol % catalyst, respectively. The corresponding swelling ratios were calculated as 151% and 102% for 2 and 5 mol % catalyst, respectively. These stable swelling ratios and low soluble fraction indicate significant cross-link densities comparable to those of traditional thermoset materials. As expected, higher catalyst concentrations promoted the cross-linking mechanism in vitrimer polymers, leading to increased cross-link density.

We examined the recoverability and healing ability of these flexible vitrimers next. Two millimeter thick flexible vitrimer sheets were fabricated using a custom mold. The cured sheets were flexible in nature, and the stretchability of these polymers is shown in Figure 1b under 1.5 kg (14.7 N) loading. A flexible vitrimer sample with a cross-sectional area of 12 mm^2 was deformed under 1.5 kg tensile load to display the flexibility and extensibility of these novel vitrimer polymers. Figure 1d displays the extension of the material from 4.1 to 6.5 cm (160%) over time, followed by contraction back to its original length. The same contraction properties were also seen in the twisting experiment (Figures 1c and S4). Entropic forces influence the extensibility and flexibility of these rubbery materials. In their natural, unstressed state, polymer chains adopt a coiled random configuration to maximize their entropy. When these chains are stretched, their configurations become more ordered. The system inherently resists this reduction in entropy, which manifests as an elastic restoring force that attempts to return the chains to their coiled state. The T_g of these polymers is below room temperature (discussed later); this allows the chains to overcome intermolecular forces and return to their original, coiled configuration, driven by entropic elasticity at room temperature under zero stress. Next, healability of these vitrimer polymers was tested by creating a cut mark with a razor blade, which was healed for 1 h at 150 °C and 1 MPa pressure; the healing process was examined using an optical microscope, as shown in Figure 1e.

3.2. Thermal Characterization. Next, thermal analysis was carried out on the vitrimer polymers using DSC and TGA.

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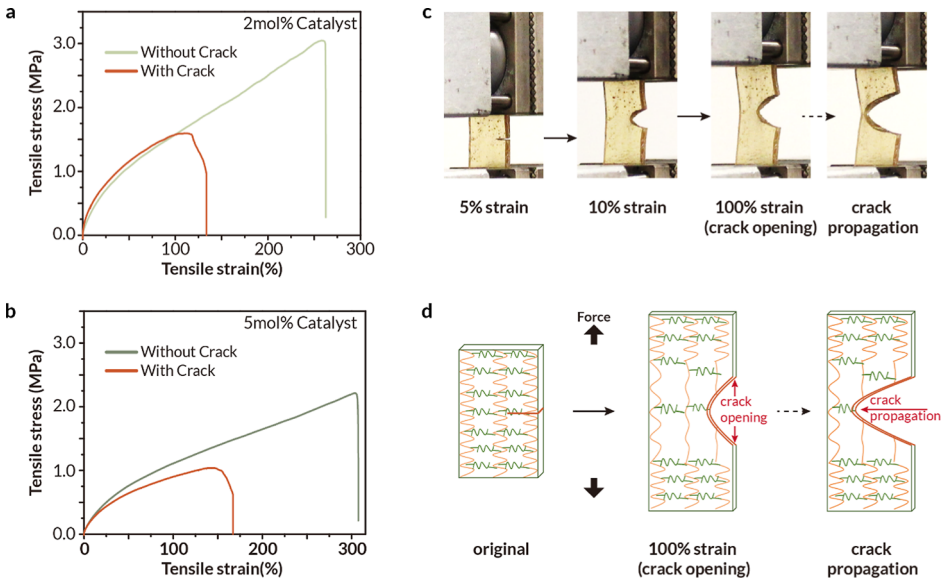

Figure 4. Tensile toughness of the flexible vitrimers with varying catalyst concentrations, with and without a crack (flaw). Representative tensile stress−strain curves for measuring the tensile toughness with (a) 2 mol % and (b) 5 mol % catalyst concentration. (c) Crack propagation in notched samples after different strains. (d) Schematic showing crack opening and propagation delayed by the flexible nature of the polymer due to extended chains.

The glass transition temperature (T_g) using DSC analysis was found to be 17° and 20 °C (Figure 2b) for the 2 and 5 mol % catalyst samples, respectively, which is below room temperature. Polymers transition into a rubbery state at temperatures above T_g and exhibit an enhanced viscoelastic nature due to time-dependent deformation and recovery processes. Next, TGA was performed to determine the thermal stability of cross-linked systems. Figure 2c and d shows weight loss percentage versus temperature and derivative of TGA curves. The initial degradation measured by the 5% weight loss temperature (T_{d5}) was found to be 343 and 356 °C for 2% and 5 mol % catalyst, respectively, for flexible vitrimer; 75 weight % loss was at 521 °C. The T_{d5} for 5 mol % is slightly higher than that for the 2 mol % vitrimer due to higher cross-linking in the 5 mol % vitrimer. Additionally, the rigid vitrimer had a degradation temperature of T_{d5} = 365 °C.

3.3. Mechanical Characterization. The mechanical properties of the flexible and rigid vitrimers were measured and analyzed (Figure 3a). Three specimens were tested for measuring the mechanical properties; additionally, all specimens were kept in a desiccant chamber between synthesis and testing to ensure minimum moisture uptake. All the lap shear and tensile testing to measure the quasi-static modulus and strength was done at room temperature to mimic the environment of consumer electronics. The rigid vitrimer had a tensile strength of 44.0 ± 2.04 MPa and a modulus of 3.12 ± 0.28 GPa with an extension at failure of 1.46%. The flexible vitrimer with 2 mol % catalyst had a tensile strength of 3.16 ± 0.13 MPa and a modulus 3.94 ± 0.53 MPa with an extension of 256%, comparable to that of stretchable elastomers.[37,38] The higher catalyst concentration (5 mol %) showed a lowered mechanical performance with 2.36 ± 0.13 MPa strength and 2.73 ± 0.31 MPa modulus. Interestingly, it can be seen that by chain extension coupled with a branched polymeric network, a rigid vitrimer can transition into an elastomer (flexible vitrimers) with an 8× increase in the strain to failure. The tensile strength ratio of rigid to flexible is 13.9 and 18.6 for 2 and 5 mol %, respectively, whereas the modulus ratio of rigid to flexible was 792 and 1130 for 2 and 5 mol %, respectively. The elongated chain lengths and branched structure increase the system's entropy because the chains have more possible configurations. When stretched, these chains can uncoil more and the material exhibits greater elasticity (higher strain to failure). In the flexible vitrimer material, the prior reaction of glycerol with adipic acid increased its polymer chain length and hence increased the extension in the cross-linked polymer. Figure S5 compares the mechanical modulus versus failure strains for various transesterification vitrimers; the figure highlights how polymer chain length and monomer composition variations impact the mechanical properties of vitrimers. This analysis shows the contributions of our study, particularly in achieving tunable flexibility and mechanical performance by changing the chain structure.

In support of the healing properties of the vitrimers under a microscope for a crack (Figure 1e), we further evaluated the lap shear properties of welded coupons (Figure 3b). The lap shear modulus and strength of pristine flexible-flexible vitrimers were 0.72 ± 0.02 MPa and 0.78 ± 0.19 MPa, respectively. Further, to assess repeatability, failure surfaces were welded again and tested. The lap shear strength of the second and the third weld was 0.74 ± 0.02 MPa and 0.74 ± 0.02 MPa, respectively; the shear modulus for the second and third weld was 0.73 ± 0.26 MPa and 0.63 ± 0.08 MPa. All specimens failed at the lap interface (Figure 3b), and there was minimal change in the lap shear modulus and strength for repeated welding.

Similarly, we also demonstrated welding rigid-flexible vitrimers; since both are transesterification vitrimers, we expected covalent bonding at the interface due to rearrangement reactions. Additionally, bonding between hard and soft materials is critical for electronic applications, where flexible cables are connected to a rigid housing containing the connector. Welding rigid-flexible vitrimers is exciting since traditional approaches like adhesives or friction welding are used in the electronic industry for soft−hard interfaces; these fail at the interface due to fatigue damage from repeated use

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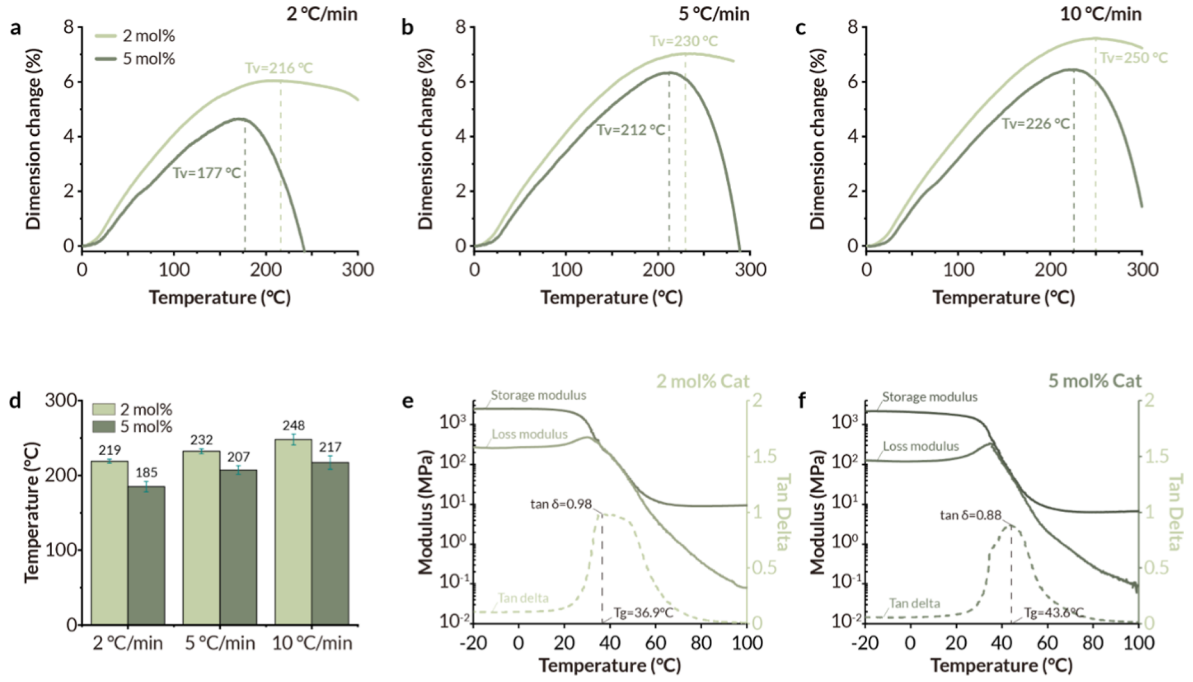

Figure 5. TMA on the samples with varying catalyst % from 2 mol % to 5 mol % at different heating rates: (a) 2 °C/min, (b) 5 °C/min, and (c) 10 °C/min, and (d) transitions temperature occur at flow termed as T_v. (e,f) DMA for tan δ, storage modulus E', and loss modulus E''.

and are difficult to repair. We welded rigid-flexible vitrimers, and microscopy images (Figure 3c) show a well-bonded interface. The lap-shear strength and modulus for rigid-flexible vitrimer was 2.13 ± 0.15 MPa and 6.18 ± 0.55 MPa (Figure 3d). An overlaid schematic in Figure 3c shows a trans-esterification mechanism with carboxylic and hydroxyl linkages on both sides of the interface that take part in the same reaction. Additionally, the shear stress−strain curves for first, second, and third weld for flexible-flexible lap specimens is shown in Figure 3d.

Next, we examined the change in the toughness properties of these vitrimers (Figure 4). We carried out mechanical toughness experiments on notched and un-notched specimens with varying catalyst concentrations for flexible vitrimers, and three specimens were tested for each experiment. Specimens were strained to failure, and the resulting stress−strain curves were analyzed; the area under this curve was measured to determine the tensile toughness. We observed that an increased catalyst concentration (5 mol %) improved its flexibility and yielded a failure strain, ε_f = 307.1 ± 6.3% compared to the samples with 2 mol % with ε_f = 255.7 ± 7.9% for un-notched specimens. The tensile toughness of un-notched flexible vitrimers with 2 mol % and 5 mol % was found to be 466.25 ± 5.44 J/m^3 and 415.82 ± 5.55 J/m^3, respectively. Samples with a 2.5 mm notch over a 10 mm width had a tensile toughness of 146.82 ± 8.59 J/m^3 for 2 mol % catalyst (ε_f = 130.5 ± 12.5%) and 128.07 ± 4.67 J/m^3 for 5 mol % (ε_f = 157.2 ± 5.5%). Two competing mechanisms play a role in tensile toughness with increasing catalyst concentration: higher catalyst concentration would increase the cross-link density but concurrently cause a more significant plasticizing effect in the network, causing chain sliding. During these experiments on notched specimens, delayed crack propagation was observed. This delay would be due to chain uncoiling before rupture at the crack tip, which has high stress concentrations.

3.4. Thermomechanical and Viscoelastic Properties.

The topological freezing temperature of vitrimers can be measured by nonisothermal creep,[39] dilatometer,[40,41] and fluorescence[42] methods. Out of these methods, TMA is a straightforward method in terms of time and sample mass required compared with other methods. Here, we performed TMA to measure T_v for these polymers (Figure 5a−d), in line with a previous work that extensively showed the feasibility of this method.[41] Dimensional change is tracked as the temperature is ramped up; the initial change in dimension indicates the transition from the solid to the rubbery phase, representing the T_g of the polymer. For the temperature regime where $T_g < T < T_v$, the polymer chains partially overcome the intermolecular forces, allowing greater molecular mobility. This increased mobility results in thermal expansion and an increase in deformations. The slope for the dimensional change represents the thermal expansion coefficient (α) of the vitrimer. Transesterification exchange reactions occur in the polymer network in the temperature regime above T_v; the polymer exhibits viscous flow characteristics as it deforms under a constant load. Different heating rates 2 °C/min, 5 °C/min, and 10 °C/min were used for TMA testing. The T_v of the polymer is characterized by the concave downward point in the deformation-temperature plot, indicating increased flowability due to rearrangement reactions.

For varying parameters, T_v was observed to range from 185° to 248 °C. For increasing heating rates, the average T_v value increases from 219 to 248 °C for 2 mol % catalyst and 185 to 217 °C for 5 mol % catalyst. It should be noted that T_v is lower for higher catalyst mol % for similar heating rates; this happens as the catalyst is more readily available for the trans-esterification reversible reactions at higher concentrations, which lowers the energy barrier for the dynamic reactions and hence shows lower thermal transition representing maximum dynamics happening in these complex network systems. Further, we observe that increasing the heating rate also

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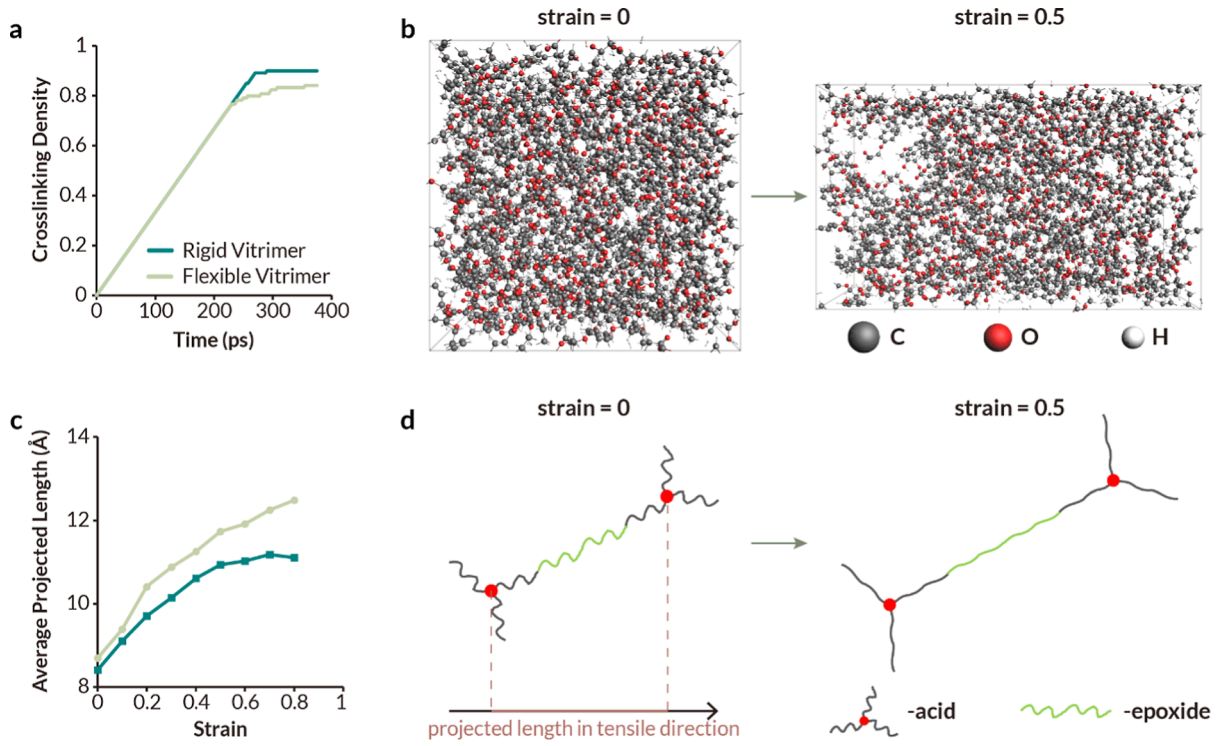

Figure 6. ReaxFF MD simulations of vitrimers. (a) Cross-linking density of acid−epoxy vitrimer and flexible vitrimer. (b) Snapshots of flexible vitrimer at 0 and 0.5 strain. (c) Schematic representation of unfolding polymer chain segments of flexible vitrimer during tension. (d) Average segment length projected in the tensile direction of acid−epoxy vitrimer and flexible vitrimer.

increases the T_v of the vitrimer polymers. This happens because the reactive sites have less time for rearrangement reactions to reduce local relaxations.[41]

The DMA was carried out to verify the storage modulus, corresponding loss modulus, and damping factor tan δ for the vitrimers (Figure 5e,f). DMA is a reliable technique for measuring bulk thermo-mechanical properties over a wide temperature range. The tan δ values are obtained by dividing the loss modulus by storage modulus, and the peak signifies the T_g. This study showed T_g values of 36.9 and 43.6 °C for catalysts 2 and 5 mol %, respectively. We compare the T_g calculated from DMA (tan δ) and DSC; the T_g from DMA is consistently 15−20 °C higher than the DSC measurements. The difference in T_g from DSC and DMA arises due to the different physical phenomena and sensitivities each technique measures. DSC measures the heat flow associated with the glass transition, which reflects changes in heat capacity as the polymer transitions from a glassy to a rubbery state. It provides an average T_g. DMA on the other hand measures the mechanical response of the polymer to an oscillatory stress or strain, which results from the changes in molecular mobility.

3.5. ReaxFF Simulations. We use MD simulations to study the phenomena resulting from the changed molecular topology and how the structure affects the resulting properties. Using accelerated ReaxFF, two virtual specimens were fabricated by cross-linking DGBEA with (a) adipic acid and (b) adipate ester in 1:1 molar ratios of epoxides and acids. The CHON_2017_weak_bb force field[32] was used for all simulations, and four atoms were marked and used for bond boost; the selected force parameters are shown in Figure S6. The evolution of cross-linking over 0.375 ns simulations is shown in Figure 6a; the cross-linking density (i.e., ratio of number of formed cross-links to the maximum number of theoretical cross-links) converged at 90% and 84% for rigid and flexible vitrimers, respectively. Next, the system was annealed to remove local heterogeneities though NPT simulations at 1 atm pressure with temperature cycles from 100 to 600 K over 8 cycles. The annealed virtual specimen is shown in Figure 6b.

Next, these annealed systems were tested with tensile loads up to 80% strain at a 10^{10} s^{-1} strain rate; a schematic of the tensile tested specimen is shown in Figure 6b. Next, we calculated the projected segment lengths in the tensile direction for these two types of polymers to highlight unfolding and mobility of chain segments (Figure 6c). Segments were described as the repeating units for the polymer network; for the rigid vitrimer, segments constituted one epoxide and one acid, whereas flexible vitrimer segments included the polymer chain between two consecutive carbon atoms at the center of polyester adipates. These segments were measured throughout the tensile test of the virtual specimens, and it was observed that the average segment length for rigid vitrimers plateaus, whereas the segments for the flexible vitrimer are able to unfold much more (Figure 6d), which contributes to the flexibility of vitrimer. In addition, the reduced elastic modulus observed in flexible vitrimers can be attributed to their lower polymer strand density compared with rigid vitrimers. According to affine network theory for ideal cross-linked polymer networks, both shear and elastic moduli are proportional to polymer segment density.[43] The extended segment length between cross-links in flexible vitrimers results in reduced segment density per unit volume, leading to lower moduli and enhanced flexibility.

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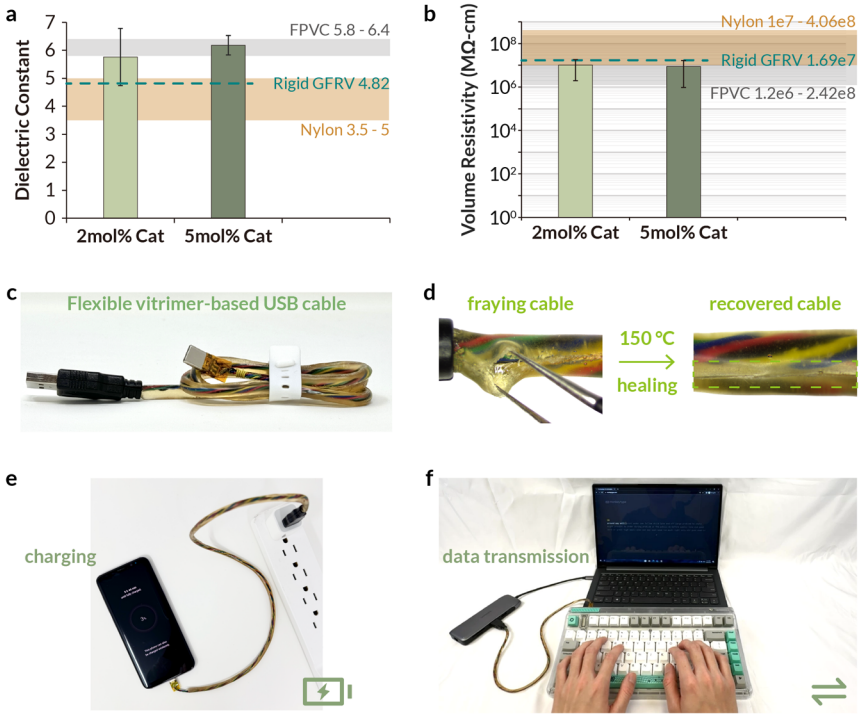

Figure 7. Measured (a) dielectric constant and (b) volume resistivity for the flexible vitrimers containing 2 mol % and 5 mol % catalyst. Fabricated cable used for electronics: (c) cable made from flexible vitrimer with USB heads; (d) healing properties of vitrimer cables; (e) charging a mobile using the cable; and (f) data transfer capability of cable.

4. APPLICATIONS TO ELECTRONICS

The results above show that our vitrimers can achieve both high flexibility and toughness, which are critical for insulating electrical wiring. We leverage these findings to create an end-to-end demonstration of an electronic USB cable with a vitrimer jacket. This adaptable application of vitrimers in creating durable electronic cables opens up new possibilities. The dielectric constants of the flexible vitrimer with 2 mol % and 5 mol % catalysts were 5.76 and 6.18, as shown in Figure 7a. Additionally, we found the volume resistivity to be 1.03×10^7 MΩ cm for 2 mol % catalyst and 8.83×10^6 MΩ cm for 5 mol % catalyst flexible vitrimers (Figure 7b). Our experiments showed no dielectric breakdown of these polymers at 1 kV during resistivity measurements, suggesting high insulating properties. These properties are comparable to commercial flexible PVC or PE polymers used in electrical cables.[44]

We develop an in-house fabrication technique to prototype cables using 5 mm diameter Teflon tubes as molds and placing five strands of copper wire in the center as conductors. We cast the resin in the mold and cured the assembly at 150 °C for 10 h to create the cable. The exposed conductors were then soldered to standard USB A and C connectors to create the samples shown in Figures 7c and S3. Next, we verified the functionality of the cables for power and data transfer. Figure 7e illustrates the practical application of our prototype cable as it charges an LG smartphone. In Figure 7f, we demonstrate the data transfer between a keyboard and laptop, all made possible by our vitrimer cable prototype. Below, we describe how the unique properties of the vitrimer enable it to reduce common failure modes, heal damage to repair frayed cables, and recycle them at their end of life, providing a practical solution to industry challenges.

4.1. Combining Rigid and Flexible Vitrimers. Cables and interconnects demand a unique blend of mechanical properties. The cable's length should be flexible, while connectors require a rigid material due to their handling and insertion into a device. We demostrate welding of rigid and flexible vitrimers under ∼1.2 MPa at 150 °C for 1 h. Rigid-flexible interfaces are common point of mechanical failure;[45] in contrast, our vitrimer formulation allows for creating materials with tunable stiffness by variations in chain length to form strong covalent bonds with one another. Figure 3d demonstrates that the combination of a rigid and flexible material welded together can withstand a shearstrain of up to 5.66. Figure 3c shows a microscopic image of the bond interface with an overlay illustration of the chemical bonds, showcasing how the rigid and flexible vitrimers flow together and seamlessly bond across this interface to form a single material.

4.2. Repair and Recycling. In addition to strengthening the material interface to prevent failures, using vitrimers enables repair to extend the cable's lifetime and recycling further when it reaches the end of life. We first evaluate the repairability by creating a cut in the cable to emulate fraying in the insulation, as shown in Figure 7d. The damaged cable was simply pinched together using tweezers, heated to 150 °C for 1 h, and cooled at room temperature. Figure 7d shows a close-up image of the repaired cable, demonstrating only a slight marking of the area where the damage occurred. Next, we investigate the recyclability of our cables. Because these vitrimers have cross-linked carboxylic acid functional groups with epoxides that yields ester linkages similar to our previous work,[22] we test the same recycling method. We examined acetone, chloroform, DMF, ethanol, and THF (Figure S7) and found that THF and DMF were able to swell the material within 24 h. DMF is considered more toxic than THF; therefore, we used THF. We recently found that ∼91% of the

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THF can be reused and reclaimed for recycling vitrimer composites.[22]

Segments of cable were immersed in a sealed container of THF, as shown in Figure S8a, for 24 h. As seen in the time-lapse images, THF swells the polymer network and enables the complete removal of metal cables. After separating the metal, the polymer was dried and reprocessed into films using a heat press at 150 °C under a pressure of 1 MPa (Figure S8b). Mechanical testing on the recycled samples revealed a tensile strength of 2.28 ± 0.11 MPa, a modulus of 2.45 ± 0.99 MPa, and a strain to failure of 301 ± 4% (Figure S9a). For comparison, the pristine polymer exhibited a tensile strength of 2.36 ± 0.13 MPa, a modulus of 2.73 ± 0.31 MPa, and a similar flexibility. Additionally, TMA analysis showed that the topological freezing temperature (T_v) of the recycled vitrimers ranged from 183 to 187 °C, compared to 185° to 217 °C for the pristine samples (Figure S9b). These findings confirm that the recycled vitrimers retain their mechanical and thermal properties, demonstrating their durability and consistency after reprocessing. This experiment shows the practical implications of our research, demonstrating that vitrimers can enable a circular manufacturing cycle for cables.

5. CONCLUSIONS

This study demonstrates that the polymer chain extension of our transesterification vitrimers can unlock a range of properties, including tunable flexibility, stretchability, and increased toughness. When combined with the healing and reprocessability of vitrimers, these materials could substantially reduce the environmental impact of the cables and wiring. We characterize the materials through a series of thermomechanical analyses determining its T_v to be 180−250 °C and tolerant of strains from 250 to 300% for catalyst concentrations of 2−5 mol %. We further exploit the ability to tune polymer chain lengths to create strongly bonded flexible and rigid materials, which opens the door for new fabrication techniques. We use this material to prototype a fully functional USB cable capable for power and data transfer. We further verified the ability to heal the materials by applying heat and showed they can still tolerate high strain, which is on par with pristine materials. These properties, when combined, could enable substantial extensions in the lifetime of cables by reducing failures and enabling repair. Additionally, we have shown that the polymer can be easily separated from the metal for recycling by immersing the material in THF. We hope future research can build on these results to establish a circular manufacturing cycle for electronic cables.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.4c16995.

NMR spectra for the synthesized polyester, FTIR for polyester adipate, fabrication process for the USB cable, visual representation of the flexibility at room temperature, tensile modulus and tensile strain at failure for various transesterification vitrimers, labelled atoms, distance ranges, and force parameters used in the accelerated ReaxFF method and the density of the flexible vitrimer during annealing, swelling properties of flexible vitrimers in solvents, recycling of vitrimer from cable in THF for 24 h, thermo-mechanical characterization, and details on accelerated ReaxFF simulations (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Aniruddh Vashisth − *Mechanical Engineering, University of Washington, Seattle, Washington 98195, United States;* orcid.org/0000-0002-4740-1296; Email: vashisth@uw.edu

Authors

Agni K. Biswal − *Mechanical Engineering, University of Washington, Seattle, Washington 98195, United States*

Peter Hong − *Materials Science and Engineering, University of Washington, Seattle, Washington 98195, United States*

Zhihan Zhang − *Paul G. Allen School of Computer Science & Engineering, University of Washington, Seattle, Washington 98195, United States*

Yiwen Zheng − *Mechanical Engineering, University of Washington, Seattle, Washington 98195, United States;* orcid.org/0000-0002-6908-3436

Surabhit Gupta − *Mechanical Engineering, University of Washington, Seattle, Washington 98195, United States*

Dhriti Nepal − *Materials and Manufacturing Directorate, Air Force Research Laboratory, Dayton, Ohio 45433, United States;* orcid.org/0000-0002-0972-9960

Vikram Iyer − *Paul G. Allen School of Computer Science & Engineering, University of Washington, Seattle, Washington 98195, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acsami.4c16995

Notes

Vikram Iyer holds concurrent appointments as an assistant professor in the Paul G. Allen School of Computer Science and Engineering at the University of Washington and as an Amazon Visiting Academic. This paper describes work performed at the University of Washington and is not associated with Amazon.

The authors declare no competing financial interest.

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■ REFERENCES

(1) Rimdusit, S.; Ishida, H. Development of New Class of Electronic Packaging Materials Based on Ternary Systems of Benzoxazine, Epoxy, and Phenolic Resins. *Polymer* **2000**, *41* (22), 7941−7949.

(2) Bur, A. J. Dielectric Properties of Polymers at Microwave Frequencies: A Review. *Polymer* **1985**, *26* (7), 963−977.

(3) Madi, A.; He, Y.; Jiang, L.; Yan, B. Surface Tracking on Polymeric Insulators Used in Electrical Transmission Lines. *IJEECS* **2016**, *3* (3), 639.

(4) *Advances in Elastomers I: Blends and Interpenetrating Networks*; Visakh, P. M., Thomas, S., Chandra, A. K., Mathew, A. P., Eds.;

Advanced Structured Materials; Springer Berlin Heidelberg: Berlin, Heidelberg, 2013; Vol. *11*..
(5) Oh, J. Y.; Rondeau-Gagné, S.; Chiu, Y.-C.; Chortos, A.; Lissel, F.; Wang, G.-J. N.; Schroeder, B. C.; Kurosawa, T.; Lopez, J.; Katsumata, T.; Xu, J.; Zhu, C.; Gu, X.; Bae, W.-G.; Kim, Y.; Jin, L.; Chung, J. W.; Tok, J. B.-H.; Bao, Z. Intrinsically Stretchable and Healable Semiconducting Polymer for Organic Transistors. *Nature* **2016**, *539* (7629), 411−415.
(6) Morin, S. A.; Shepherd, R. F.; Kwok, S. W.; Stokes, A. A.; Nemiroski, A.; Whitesides, G. M. Camouflage and Display for Soft Machines. *Science* **2012**, *337* (6096), 828−832.
(7) Acome, E.; Mitchell, S. K.; Morrissey, T. G.; Emmett, M. B.; Benjamin, C.; King, M.; Radakovitz, M.; Keplinger, C. Hydraulically Amplified Self-Healing Electrostatic Actuators with Muscle-like Performance. *Science* **2018**, *359* (6371), 61−65.
(8) Abdelbasir, S. M.; Hassan, S. S. M.; Kamel, A. H.; El-Nasr, R. S. Status of Electronic Waste Recycling Techniques: A Review. *Environ. Sci. Pollut. Res.* **2018**, *25* (17), 16533−16547.
(9) Suresh, S. S.; Mohanty, S.; Nayak, S. K. Composition Analysis and Characterization of Waste Polyvinyl Chloride (PVC) Recovered from Data Cables. *Waste Manage.* **2017**, *60*, 100−111.
(10) Global e-Waste Monitor 2024. *Electronic Waste Rising Five Times Faster than Documented E-Waste Recycling*; United Nations Institute for Training and Research (UNITAR). https://www.unitar.org/about/news-stories/press/global-e-waste-monitor-2024-electronic-waste-rising-five-times-faster-documented-e-waste-recycling.
(11) Samanta, S.; Kim, S.; Saito, T.; Sokolov, A. P. Polymers with Dynamic Bonds: Adaptive Functional Materials for a Sustainable Future. *J. Phys. Chem. B* **2021**, *125* (33), 9389−9401.
(12) Montarnal, D.; Capelot, M.; Tournilhac, F.; Leibler, L. Silica-Like Malleable Materials from Permanent Organic Networks. *Science* **2011**, *334* (6058), 965−968.
(13) Krishnakumar, B.; Sanka, R. P.; Binder, W. H.; Parthasarthy, V.; Rana, S.; Karak, N. Vitrimers: Associative dynamic covalent adaptive networks in thermoset polymers. *Chem. Eng. J.* **2020**, *385*, 123820.
(14) Zheng, N.; Xu, Y.; Zhao, Q.; Xie, T. Dynamic Covalent Polymer Networks: A Molecular Platform for Designing Functions beyond Chemical Recycling and Self-Healing. *Chem. Rev.* **2021**, *121* (3), 1716−1745.
(15) Alabiso, W.; Schlögl, S. The Impact of Vitrimers on the Industry of the Future: Chemistry, Properties and Sustainable Forward-Looking Applications. *Polymers* **2020**, *12* (8), 1660.
(16) Ye, C.; Li, W.; Voet, V. S. D.; Folkersma, R.; Pei, Y.; Loos, K. Flexible Vitrimers for Self-healable Triboelectric Nanogenerators. *Adv. Mater. Technol.* **2023**, *8* (8), 2201670.
(17) Kamble, M.; Vashisth, A.; Yang, H.; Pranompont, S.; Picu, C. R.; Wang, D.; Koratkar, N. Reversing Fatigue in Carbon-Fiber Reinforced Vitrimer Composites. *Carbon* **2022**, *187*, 108−114.
(18) Van Zee, N. J.; Nicolaÿ, R. Vitrimers: Permanently Crosslinked Polymers with Dynamic Network Topology. *Prog. Polym. Sci.* **2020**, *104*, 101233.
(19) Sharma, H.; Krishnakumar, B.; Dickens, T. J.; Yun, G. J.; Kumar, A.; Rana, S. A Bibliometric Survey of Research Trends in Vitrimer. *Heliyon* **2023**, *9* (6), No. e17350.
(20) Biswal, A. K.; Nandi, A.; Wang, H.; Vashisth, A. Ultrasonic Welding of Fiber Reinforced Vitrimer Composites. *Compos. Sci. Technol.* **2023**, *242*, 110202.
(21) Schenk, V.; Labastie, K.; Destarac, M.; Olivier, P.; Guerre, M. Vitrimer Composites: Current Status and Future Challenges. *Mater. Adv.* **2022**, *3* (22), 8012−8029.
(22) Zhang, Z.; Biswal, A. K.; Nandi, A.; Frost, K.; Smith, J. A.; Nguyen, B. H.; Patel, S.; Vashisth, A.; Iyer, V. Recyclable Vitrimer-Based Printed Circuit Boards for Sustainable Electronics. *Nat. Sustainable* **2024**, *7* (5), 616−627.
(23) Yan, P.; Zhao, W.; Fu, X.; Liu, Z.; Kong, W.; Zhou, C.; Lei, J. Multifunctional Polyurethane-Vitrimers Completely Based on Transcarbamoylation of Carbamates: Thermally-Induced Dual-Shape Memory Effect and Self-Welding. *RSC Adv.* **2017**, *7* (43), 26858−26866.
(24) Nishimura, Y.; Chung, J.; Muradyan, H.; Guan, Z. Silyl Ether as a Robust and Thermally Stable Dynamic Covalent Motif for Malleable Polymer Design. *J. Am. Chem. Soc.* **2017**, *139* (42), 14881−14884.
(25) White, J. E.; Silvis, H. C.; Winkler, M. S.; Glass, T. W.; Kirkpatrick, D. E. Poly(hydroxyaminoethers): A New Family of Epoxy-Based Thermoplastics. *Adv. Mater.* **2000**, *12*, 1791−1800.
(26) Lessard, J. J.; Stewart, K. A.; Sumerlin, B. S. Controlling Dynamics of Associative Networks through Primary Chain Length. *Macromolecules* **2022**, *55* (22), 10052−10061.
(27) Nakka, J. S.; Jansen, K. M. B.; Ernst, L. J. Effect of Chain Flexibility in the Network Structure on the Viscoelasticity of Epoxy Thermosets. *J. Polym. Res.* **2011**, *18* (6), 1879−1888.
(28) Zhang, T.; Howell, B. A.; Smith, P. B. Thermal Degradation of Glycerol/Adipic Acid Hyperbranched Poly(Ester)s Containing Either Hydroxyl or Carboxyl End-Groups. *J. Therm. Anal. Calorim.* **2015**, *122* (3), 1221−1229.
(29) Guerre, M.; Taplan, C.; Nicolaÿ, R.; Winne, J. M.; Du Prez, F. E. Fluorinated Vitrimer Elastomers with a Dual Temperature Response. *J. Am. Chem. Soc.* **2018**, *140* (41), 13272−13284.
(30) Wang, Z.; Xiang, C.; Yao, X.; Le Floch, P.; Mendez, J.; Suo, Z. Stretchable Materials of High Toughness and Low Hysteresis. *Proc. Natl. Acad. Sci. U.S.A.* **2019**, *116* (13), 5967−5972.
(31) Varshney, V.; Patnaik, S. S.; Roy, A. K.; Farmer, B. L. A Molecular Dynamics Study of Epoxy-Based Networks: Cross-Linking Procedure and Prediction of Molecular and Material Properties. *Macromolecules* **2008**, *41* (18), 6837−6842.
(32) Vashisth, A.; Ashraf, C.; Zhang, W.; Bakis, C. E.; van Duin, A. C. T. Accelerated ReaxFF Simulations for Describing the Reactive Cross-Linking of Polymers. *J. Phys. Chem. A* **2018**, *122* (32), 6633−6642.
(33) Vashisth, A.; Ashraf, C.; Bakis, C. E.; van Duin, A. C. T. Effect of Chemical Structure on Thermo-Mechanical Properties of Epoxy Polymers: Comparison of Accelerated ReaxFF Simulations and Experiments. *Polymer* **2018**, *158*, 354−363.
(34) Miron, R. A.; Fichthorn, K. A. Accelerated Molecular Dynamics with the Bond-Boost Method. *J. Chem. Phys.* **2003**, *119* (12), 6210−6216.
(35) Jiang, Z.; Dou, W.; Sun, T.; Shen, Y.; Cao, D. Effects of Chain Flexibility on the Conformational Behavior of a Single Polymer Chain. *J. Polym. Res.* **2015**, *22* (12), 236.
(36) Dutta, K.; Karak, N. Exchangeable Disulfide Bond Containing Highly Flexible Epoxy Vitrimers with Shape-memory, Self-healing, and UV Shielding Attributes. *Polym. Adv. Technol.* **2024**, *35* (1), No. e6286.
(37) Stoyanov, H.; Kollosche, M.; Risse, S.; Waché, R.; Kofod, G. Soft Conductive Elastomer Materials for Stretchable Electronics and Voltage Controlled Artificial Muscles. *Adv. Mater.* **2013**, *25* (4), 578−583.
(38) Shim, H. J.; Sunwoo, S.; Kim, Y.; Koo, J. H.; Kim, D. Functionalized Elastomers for Intrinsically Soft and Biointegrated Electronics. *Adv. Healthc. Mater.* **2021**, *10* (17), 2002105.
(39) Capelot, M.; Unterlass, M. M.; Tournilhac, F.; Leibler, L. Catalytic Control of the Vitrimer Glass Transition. *ACS Macro Lett.* **2012**, *1* (7), 789−792.
(40) Kim, H.; Cha, I.; Yoon, Y.; Cha, B. J.; Yang, J.; Kim, Y. D.; Song, C. Facile Mechanochemical Synthesis of Malleable Biomass-Derived Network Polyurethanes and Their Shape-Memory Applications. *ACS Sustainable Chem. Eng.* **2021**, *9* (20), 6952−6961.
(41) Hubbard, A. M.; Ren, Y.; Sarvestani, A.; Picu, C. R.; Varshney, V.; Nepal, D. Thermomechanical Analysis (TMA) of Vitrimers. *Polym. Test.* **2023**, *118*, 107877.
(42) Yang, Y.; Zhang, S.; Zhang, X.; Gao, L.; Wei, Y.; Ji, Y. Detecting Topology Freezing Transition Temperature of Vitrimers by AIE Luminogens. *Nat. Commun.* **2019**, *10* (1), 3165.
(43) Rubinstein, M.; Colby, R. H. *Polymer Physics*; Oxford University PressOxford, 2003; ..

https://doi.org/10.1021/acsami.4c16995
ACS Appl. Mater. Interfaces 2025, 17, 9736−9747

(44) *Technical Information Handbook - Wire and Cable*, 2013; p 328. https://www.rmelectricsolutions.com/uploads/8/7/8/4/87841322/wire____cable_technical-handbook-en-us.pdf.
(45) Lampman, S. *Characterization and Failure Analysis of Plastics*; ASM International: Materials Park, OH, 2003.

https://doi.org/10.1021/acsami.4c16995
ACS Appl. Mater. Interfaces 2025, 17, 9736−9747