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Flexible Vitrimers for Self-healable Triboelectric Nanogenerators

Chongnan Ye, Wenjian Li, Vincent S.D. Voet, Rudy Folkersma, Yutao Pei, and Katja Loos*

Despite rapid advancements in the development of triboelectric nanogenerators (TENG), mechanical defects generated during their working condition limit the service lifetime of these devices. Polyester-based vitrimers can offer a solution to solve this issue via their dynamic bond exchange reactions. However, they often require high temperatures and a long time to crosslink, rendering them not useful for large-scale TENG fabrication. To solve these issues, a self-healable vitrimer-based triboelectric nanogenerator (VITENG) is developed based on diacrylate poly(dimethylsiloxane) (AA-PDMS) via a fast thiol-Michael reaction. By including 2,3-dihydroxypropyl methacrylate (DHPMA), hydroxy end dangling side chains are generated in the matrix, which increase the PDMS network's flexibility and transesterification efficiency. Efficient transesterification occurs on the abundant dynamic β -hydroxy ester bonds in the PDMS network, resulting in 100% efficient mechanical damage repair. The VITENG demonstrates a good performance with an output voltage of 135 V under a load of 10 N, demonstrating the potential for mechanical energy harvesters with long lifetimes and high design flexibility.

boelectric nanogenerators (TENG) seems to provide a viable solution and therefore they have been widely and rapidly studied over the last decade.^[3b,5] TENGs convert mechanical stimuli to electrical impulses and surpass other nanogenerator devices in terms of output performance.^[5b] In addition to the easy manufacturing and low cost, TENGs display excellent conversion efficiency and extensive adaptability to a range of different kinds of mechanical energies such as vibration,^[6] human motion,^[7] wind,^[8] and water currents.^[9] However, due to their inherent working mechanism, large deformations usually generate small structural defects such as grazes, cracks, damage of microstructure, etc., resulting in failure of their self-charging power and suppression of their output performance and longevity.^[10]

To address this issue, the concept of self-healing TENGs based on dynamic

interactions has been introduced.^[5d,6,11] Due to their reversible nature, dynamic interactions such as supramolecular interactions, especially hydrogen bonding, have been widely utilized to endow a repair mechanism into TENGs.^[12] However, as a result of their weak structure, the resultant self-healing TENGs demonstrate poor mechanical characteristics and low-temperature resistance, causing devices to decrease in terms of robustness and durability after they are damaged by frequent mechanical impact.^[13]

The development of vitrimers provides a promising way to solve these problems. Vitrimers are a set of polymer networks that are crosslinked by dynamic covalent bonds and they can elegantly provide a solution to the above-mentioned challenges.^[14] Several attempts have been made to develop self-healing vitrimer elastomers (utilized in healable TENGs), such as dynamic imine couplings with polydimethylsiloxane (PDMS),^[5d] disulfide bonded polyethylene glycol (PEG) networks,^[11] or polyurethane-based shape memory polymers.^[12b] The self-healing behavior in these systems relies on metathesis exchange reactions by dynamic bonds in the polymer network, in response to an external stimulus.^[15] However, the particular networks are usually sensitive to humidity,^[16] which lowers their output significantly compared with the conventional (non-healable) TENGs. Additionally, complicated synthesis routes and a high price limits their practical application.

Polyester-based vitrimers, initially coined by Leibler et al. in 2011, are a type of novel associative covalent adaptive network in which dynamic connections only break when a new bond in another part of the network is formed.^[17] Due to their constant crosslink density, this category of vitrimers has a higher

1. Introduction

The rapid growth of soft electronics has changed human life, driving the demand for highly deformable electronic devices such as transistors,^[1] sensors,^[2] energy-storage devices,^[3] and light-emitting diodes (LEDs).^[4] To further demonstrate their conformability and stretchability, a mechanically reliable and healable power source is highly desired. The emergence of tri-

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tolerance to chemical solvents, allowing them to swell but not dissolve, even at high temperatures.^[18] Nevertheless, the rigid polyester moieties, at the same time, lower the flexibility of the network and restrict its applicability in TENG fabrication.

To address these issues, we have developed a stretchable and self-healable vitrimer triboelectric nanogenerator (VITENG) with high stretchability and good healability enabled by the use of an elastomeric PDMS-based vitrimer (VPDMS). In contrast to polyester-based vitrimers, the PDMS moieties in our network reduce stiffness while increasing stretchability. Simultaneously, the ester bonds not only enable self-healing and reprocessability but also increase the durability and robustness of VITENG, as compared with previously reported supramolecular self-healing TENGs. Additionally, quantified hydroxy dangling end chains are incorporated in VITENG to further increase flexibility and healing rate significantly. To realize the concept, a diacrylate PDMS resin featuring hydroxy ester moieties was produced, resulting in a self-healing TENG with high output. This work presents a realistic approach for multipurpose soft power sources that will be valuable for next-generation soft electronics.

2. Results and Discussion

2.1. Fabrication of Dynamic Polyester-based PDMS Networks

To effectively harvest energy from a variety of mechanical inputs (bending, twisting, pressing, sliding, etc.), a flexible material is required for the development of TENGs, especially for application in human wearable devices.^[5d] An end-group functionalized PDMS, bearing ester bonds and hydroxy groups, was selected for the VITENG due to its flexibility and low glass transition temperature, above which the increasing number of collision events between free hydroxy groups and ester bonds speeds up bond exchange reactions.^[19]

Typically, transesterification is not a rapid process,^[20] which means that the synthesis of the network will require high temperatures and long curing times. To address this problem, a reaction of acrylic acid with diepoxidized PDMS (DE-PDMS) was carried out, yielding diacrylate PDMS (AA-PDMS) (Figure 1). While the epoxy moieties were opened by acrylic acid, β -hydroxy ester bonds were formed and acrylate moieties were incorporated into the PDMS backbone, simultaneously. The high reactivity of the acrylate enables a fast curing potential of the target vitrimer and the β -hydroxy ester bonds benefit the transesterification since the hydroxy group is close to the ester bond.^[21] To further make the network flexible and speed up the bond exchange reaction of the target vitrimer, 2,3-dihydroxypropyl methacrylate (DHPMA), a hydroxy dangling monomer, was synthesized by a simple hydrolysis process of glycidyl methacrylate.

The successful substitution of acrylate and hydrolysis of epoxy rings are validated by ¹H-NMR, where the signals of acrylate double bonds (6.39, 6.11, and 5.82 ppm.) were observed whereas the signals contributing to epoxy protons (3.12, 2.77, and 2.58 ppm.) disappeared for both DE-PDMS and GMA (Figure 2). Furthermore, ¹³C-NMR and heteronuclear single quantum coherence spectroscopy (HSQC) measurements were used to demonstrate complete conversion (Figure S1, Supporting Information).

The vitrimer network was created by mixing the AA-PDMS and DHPMA in ethanol with pentaerythritol tetra(3-mercaptopropionate) (PETMP) via a thiol-Michael addition reaction (see Figure 1). Since the thiol-Michael reaction is a rapid and quantitative uniform crosslinking reaction,^[22] a quantified amount of DHPMA (0.25 to the thiol group molar ratio) was introduced into the network. The inclusion of DHPMA does not only directly relate to the degree of flexibility of the network, in which the bulky dangling chains acted as spacers controlling the stiffness and elasticity of the network, but also provides β -hydroxy ester groups, which facilitate the network self-healing process.^[21] The triazabicyclodecene (TBD) here works as a catalyst, not only increasing the rate of crosslinking during this process but also activating the transesterification for the vitrimeric transition later. The Fourier transform infrared spectroscopy (FTIR) spectra of reactants and product in Figure S2 (Supporting Information), reveal signals associated to S–H and C=C stretching modes at 2570 and 1610 cm⁻¹, respectively, which were monitored to determine the extent of crosslinking. Both the S–H and C=C stretching signals vanished in the VPDMS after the curing step, suggesting successful crosslinking.

Owing to the PDMS segments, VPDMS shows a quite low glass-transition temperature ($T_g = -48.7$ °C), resulting in a flexible and stretchable network at room temperature (Figure S3, Supporting Information). The integration of the DHPMA (0.25mole of total thiol groups of PETMP) further increases the mobility of the network by generating dangling chains (Figure 1). As revealed in Figure S3 (Supporting Information), the T_g of the VPDMS when adding DHPMA in the synthetic procedure equals -51.48 °C, which is lower in comparison to VPDMS without DHPMA.

2.2. The Self-Healing of VPDMS Networks

In addition to thermal analysis, tensile tests revealed that the introduction of the DHPMA reduced the network stiffness while sacrificing the strength to a limited extent. The fracture stress of pure VPDMS was ≈ 600 KPa at 96% strain, as indicated in Figure 3a, while the addition of DHPMA to the formulation made the sample more stretchy and softer (stress 465 KPa at 124% strain). Based on its working principle,^[13] the more contacted area of TENG achieved while applying force, the higher the energy-harvesting efficiency. Consequently, in this study, DHPMA was chosen to be incorporated in the VPDMS formulation to achieve the highest flexibility based on this requirement.

Due to the well-designed molecular structure of AA-PDMS and DHPMA, dynamic ester bonds are introduced into the VPDMS network. When heated, the dynamic bonds undergo reversible exchange reactions via associative bond exchange of polymeric chains resulting in topological rearrangements, as schematically shown in Figure 3b. A temperature-dependent stress relaxation test was used to evaluate the dynamic adaptive feature of VPDMS via rheology. With increasing temperature, the normalized stress relaxation modulus decreases radially over time as shown in Figure S4 (Supporting Information). The dynamic covalent network was capable of relaxing stress for an extended period of time because the catalyst utilized for the curing reaction also serves as a catalyst for transesterification.

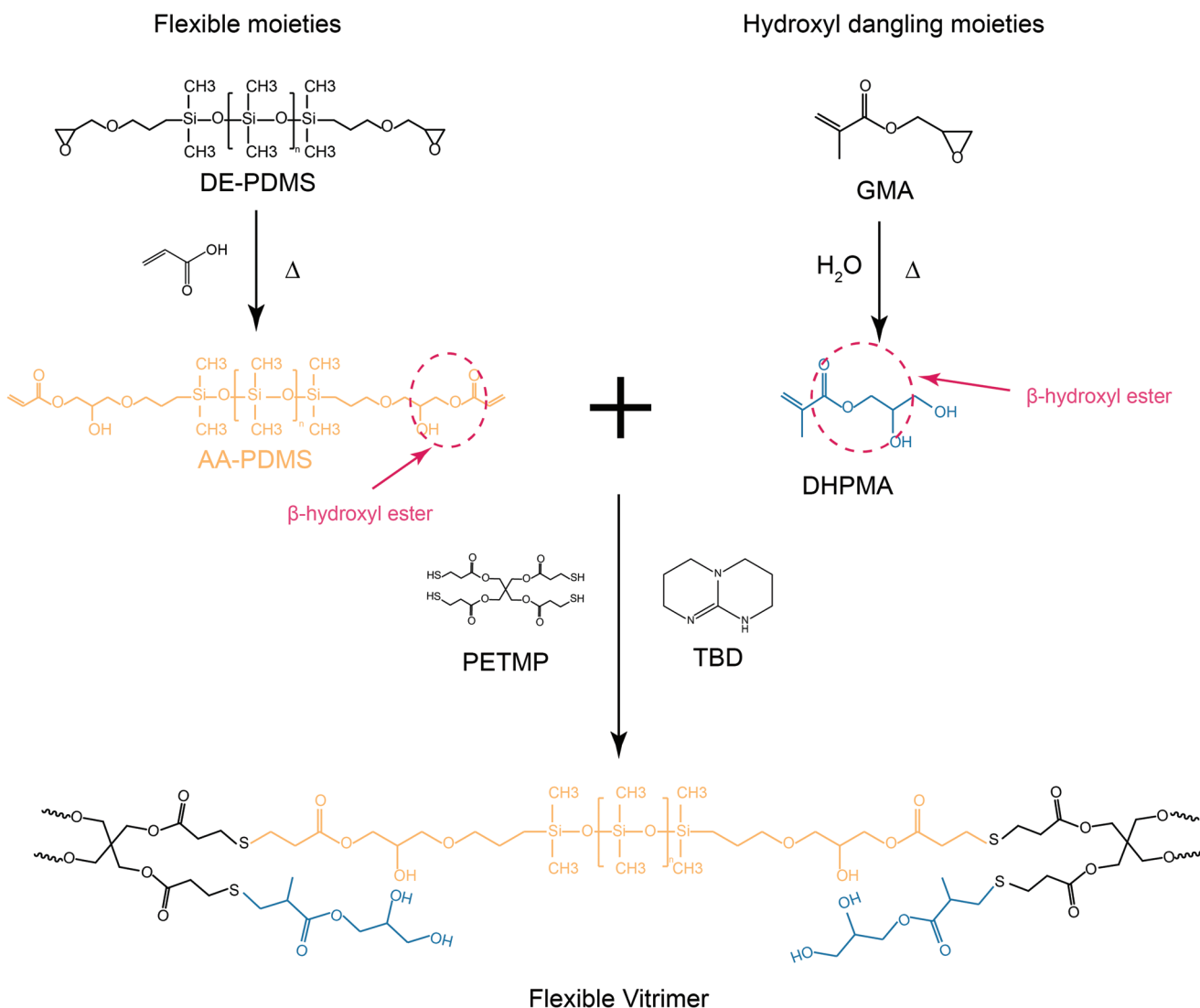


Figure 1. Synthetic approach for the preparation of AA-PDMS, DHPMA, and crosslinking of the AA-PDMS via thiol-Michael reaction with PETMP in the presence of TBD (3 mol% to the ester bond), leading to a flexible covalent adaptable network (vitriimer).

Relaxation times were defined by using Maxwell's model for viscoelastic fluids as the time required to relax to $1/e$ of the original stress or modulus.^[23] With temperature increasing from 130 °C to 170 °C, the relaxation period was observed to decrease sharply from more than 4 h to 2.6 h, which indicates higher temperature results in increased bond exchange processes.

The VPDMS's self-healing capability is enabled by the dynamic ester bond exchange reactions. Tensile testing was carried out to evaluate the mechanical healing performance, and fracture strain recovery was used to quantify healing efficiency. The dried films cast in a Teflon mold at room temperature were sliced into two pieces and joined together. Due to the surface tension, the dried films suffered from a curved shape after solvent evaporation, which limited the contact area during the healing process. To address this issue, a piece of Teflon plate of 300 g weight was used to compress the curved two strips at the joint, resulting in complete contact with each other. Healing between two strips occurred as a result of transesterification after being

heated at 150 °C for a certain time period, while it can't take place for the sample without DHPMA under the same conditions. The stress-strain curves of the original and healed samples at healing times from 15 – 60 min are shown in Figure 3c. In comparison with the conventional rigid polyester-based vitriimer systems, our VPDMS exhibited a high healing efficiency (84%) in a short period of time (15 min).^[24] Longer healing durations resulted in better recovery, with >100% recovery after 1 h of healing at 150 °C. Because the number of bond exchange reactions increases with a longer healing time, the defect will be healed more effectively within the network until it has vanished.

2.3. Energy-Harvesting Performance of the VITENG

With hydroxy and amine (TBD) playing an important role in dynamic bond exchange reactions, they enable VPDMS to perform as the triboelectric positive material while commercial

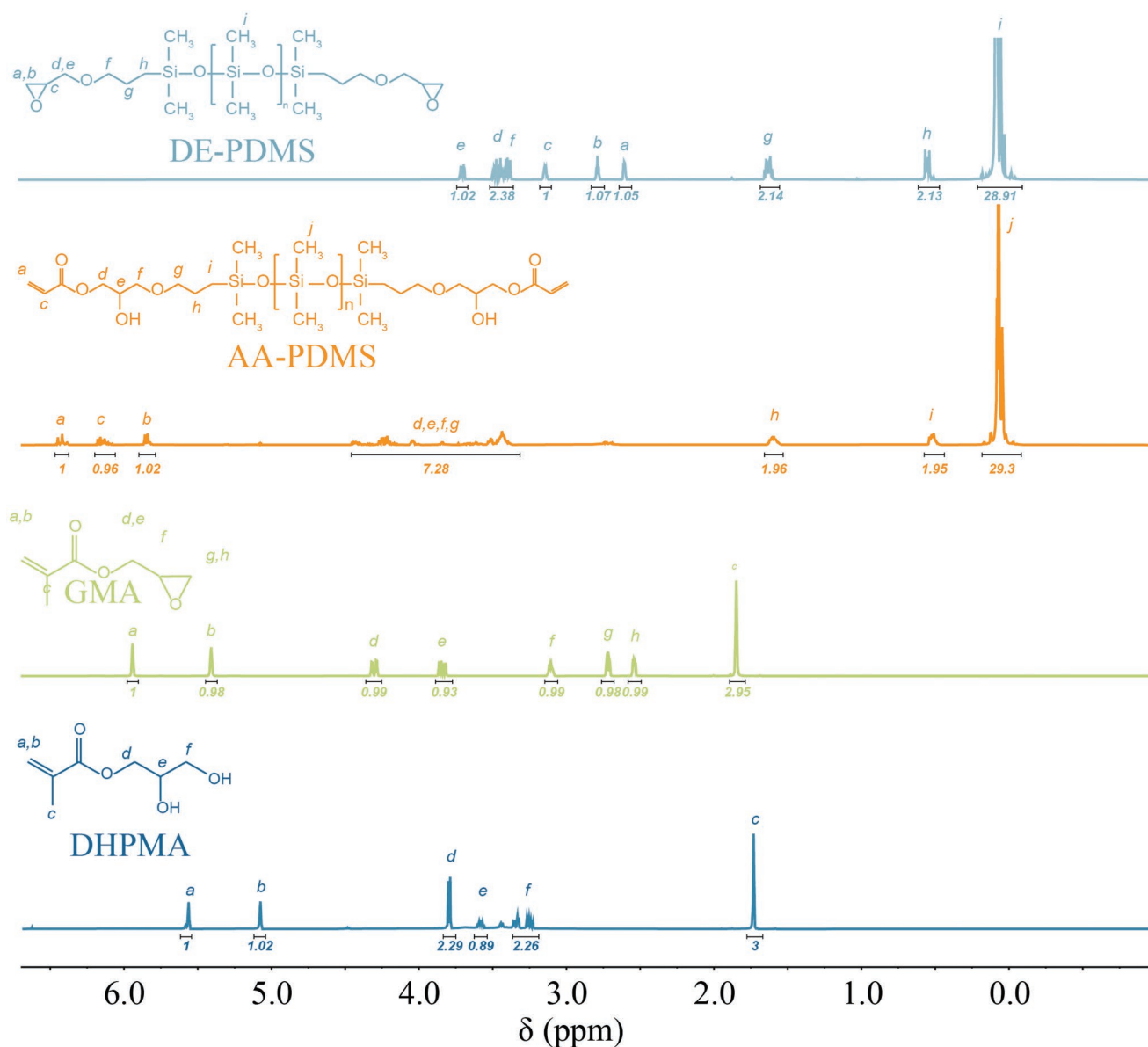


Figure 2. ^1H NMR spectra of DE-PDMS, AA-PDMS, GMA, and DHPMA. The signals associated with the epoxy moieties in both DE-PDMS and GMA were not observed after the synthesis process.

PDMS was employed as the triboelectric negative material due to its relative electronegativity.^[5a] As shown in **Figure 4a**, the complete VITENG device was assembled using two working in pairs electrodes, which are coated with VPDMS and PDMS respectively. Surface charge transfer occurs between the two layers when they get in contact because of the difference in electron affinities. Following the first contact, the separation initiated an electrostatic field between the two charged surfaces resulting in an electron flow between the two electrodes owing to the electrostatic induction. The electrons flow continuously until the two surfaces completely separate where the new electrostatic equilibrium is reached (Figure S5, Supporting Information).^[25]

To investigate our VITENG performance, typical electrical output was measured, and the data from five subsequent cycles is shown in Figure 4b,c, which demonstrates VITENG's high

and stable electrical output. The open circuit voltage (V_{oc}) and transferred charge (Q_{sc}) both exhibited a dependent output with VITENG's periodic operation (touch-detaching cycle), with maximum values of 130 V and 35 nC, respectively. The output open-circuit voltage of VITENG was recorded from 0.25 to 1.5 Hz in Figure 4d to study its performance at different frequencies. The output open-circuit voltage slightly increased with the increase of frequency and finally saturated $\approx 160\text{V}$ at 1.5 Hz, which is the maximum output V_{oc} . In contrast to other generators, the V_{oc} of VITENG remains high at low-frequency conditions, even more than 100V at 0.25 Hz, which shows its advantage in scavenging irregular low-frequency mechanical energy.^[26] The V_{oc} of the developed VITENG is as high as the V_{oc} of previous dynamic network-based TENGs, but without complicated synthesis routes, which shows the great potential of our polymer

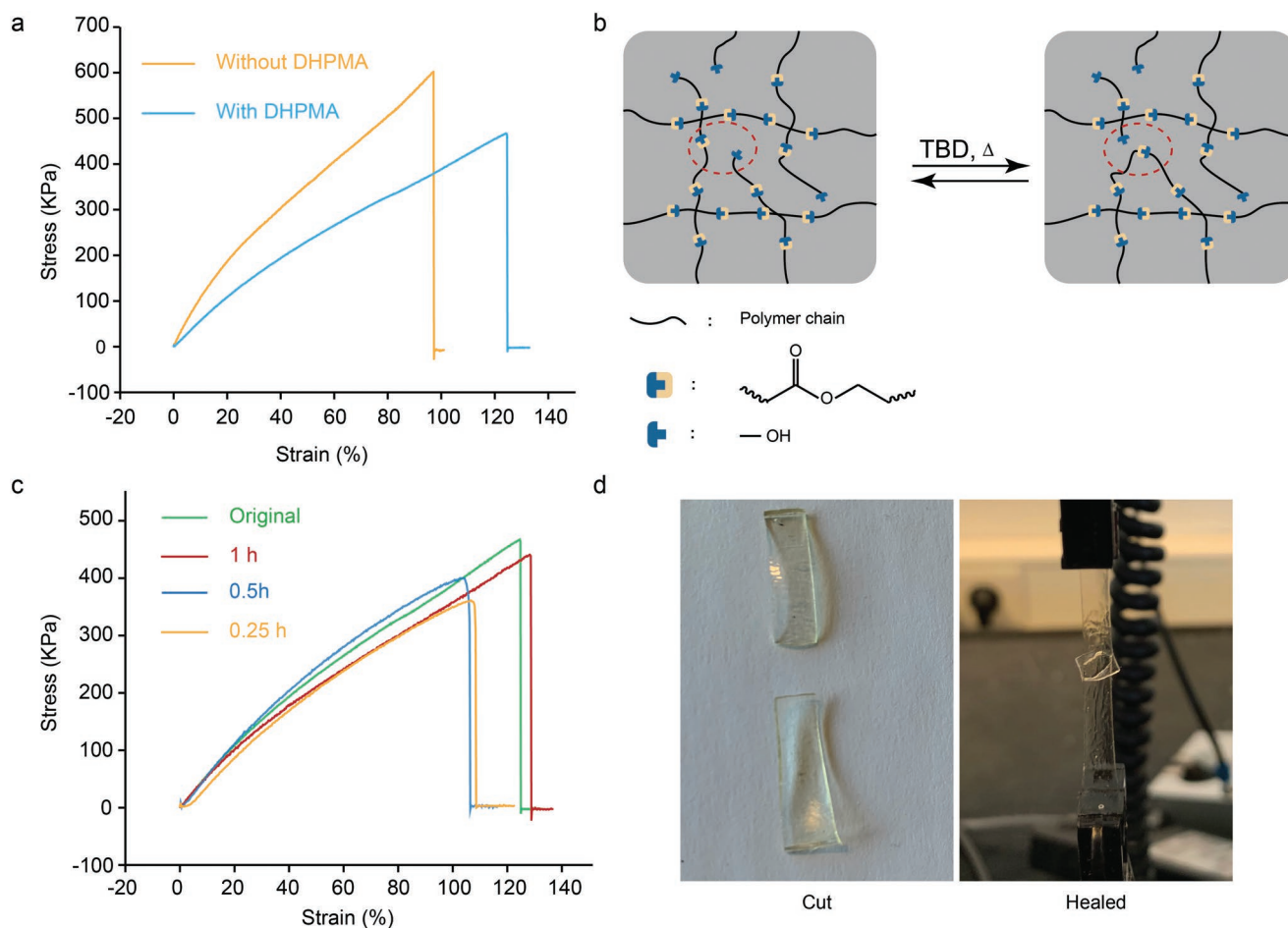


Figure 3. Mechanical property and self-healing behavior. a) Typical tensile stress-strain curves of the samples with and without DHPMA. b) Transesterification-based dynamic bonds' associative exchange reactions within the network between the (dangling) hydroxy groups and ester bonds in VPDMs. c) Tensile stress-strain curves of virgin and healed VPDMs at 150 °C for different time periods. d) Images showing the typical self-healing behavior: a rectangular sample was first cut by blade, then healed at 150 °C for 1 h before being tested.

for future application.^[5d,7,15,27] As revealed in Figure 4e, pressure is another effect on V_{oc} that increases with increasing applied force, particularly in the low force area (from 2 N to 4 N), but its rate decreases and eventually trends to saturation. Because triboelectric charges are highly related to material deformation, VPDMs thin film deformation will reach its limit with increased pressure and eventually result in a saturated V_{oc} . To visualize the electric energy generated from the VITENG, ten green light-emitting diodes (LEDs) were connected to VITENG and lighted up as shown in Figure 4a and Movie-S1 (Supporting Information). Owing to its dynamic bonds, VITENG can recover its energy harvesting performance after damage to the VPDMs layer. Following an easy healing process, the V_{oc} and Q_{sc} values recovered to nearly pre-damage values (118 V and 42 nC respectively) – see Figure S6 (Supporting Information).

3. Conclusion

A self-healing, stretchable, and transparent elastomer was designed, that can be deformed and recovered from damage with the aid of heat and pressure. As a self-healing polymer

based on dynamic transesterification, the developed VPDMs achieved a high healing efficiency (84%) in a short period of time (15 min), contrasting it from the conventional polyester-based vitrimer systems reported in literature.^[24] According to our findings, the dangling hydroxy end chains benefit not only the flexibility and stretchability of the material but also the self-healing ability, since the low T_g system promotes efficient collision of the dynamic bonds exchange process.

In addition, VPDMs proposes a realistic solution for soft power sources. The choice of an energy-conversion approach is uncommon due to the required high flexibility, transparency, and healing ability. Our transparent TENG has a healing effectiveness of 100%, and a stretchability of 125%. The excellent output performance (135 V) in low frequencies and applied forces suggest that the developed VITENG is a highly efficient energy harvester, making it very promising for powering a wide range of soft devices.

4. Experimental Section

Preparation of AA-PDMS and DHPMA: AA-PDMS: PDMS-diglycidyl ether terminated (16 g, 20 mmol), acrylic acid (5.76 g, 80 mmol), triphenylphosphine (1% w/w, 0.22 g), and mequinol (0.2% w/w, 0.045 g)

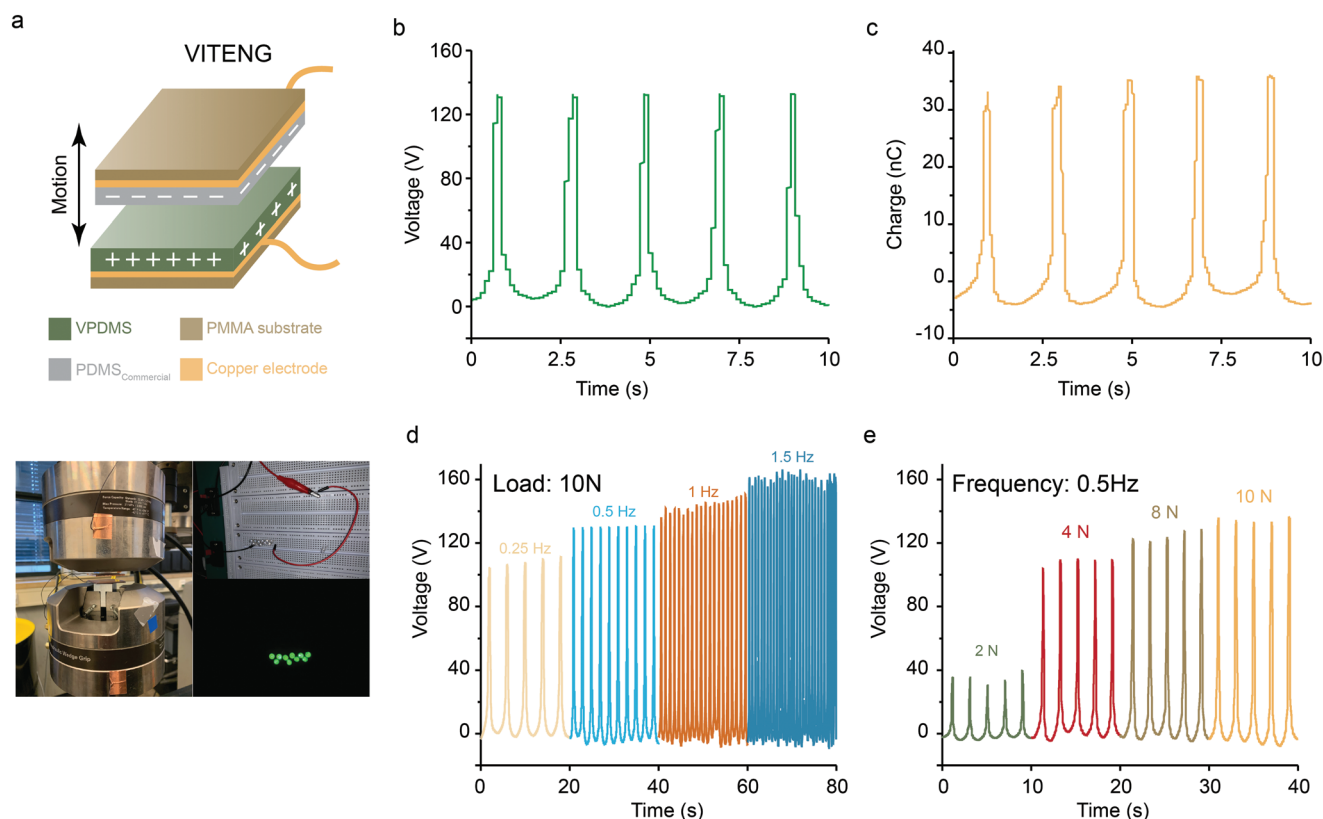


Figure 4. Energy-harvesting performance. a) Up: Schematic diagram of the complete stack of stretchable and healable VITENG, in which VPDMs is used as the positive triboelectric layer, and commercial PDMS is used as the negative triboelectric layer. Down: Digital photos of VITENG (left) and lighting LEDs powered by VITENG tapping (right). The performance of VITENG subjected to a load of 10 N at a frequency of 0.5 Hz: b) Output voltage (V_{oc}), and c) transferred charge density (Q_{sc}). d) Open-circuit voltage of VITENG with different frequencies. e) Open-circuit voltage of VITENG with different force loading.

were added in a 100 mL round bottom flask. The mixture was stirred at 105 °C for 16 h. After completion, the reaction was diluted with 50 mL of DCM and washed with a 5% sodium bicarbonate aqueous solution (200 mL, three times). Then the excess solvent was evaporated under an air flow to yield the final product. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ): 6.45, 6.18, 5.85 (3H, $\text{CH}_2=\text{CH}-$), 4.49–3.46 (5H; CH and CH_2), 1.60 (2H, CH_2), 0.52 (2H, CH_2), 0.05 (27H, CH_3)

DHPMA: Glycidyl methacrylate (1.42 g, 10 mmol) was added to deionized water (14 mL, $\approx 10\%$ w/w solution) in a 50 mL round-bottomed flask equipped with an oxygen balloon to avert polymerization of monomer. Then, the emulsion was vigorously stirred at 80 °C overnight. Obtained homogeneous aqueous solution was extracted with ethyl acetate (3×50 mL). Combined organic layers were washed with brine (2×20 mL), dried over Na_2SO_4 , and concentrated under reduced pressure. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 6.09 (s, 1 H), 5.56 (s, 1 H), 4.16 (d, $J = 5.6$ Hz, 2 H), 3.90 (m, 1 H), 3.77 (m, 2 H), 3.69 (m, 1 H), 3.64 (m, 1 H), 3.54 (m, 1 H), 1.89 (s, 3 H) ppm

Fabrication of Stretchable and Healable PDMS-based Vitriimer and VITENG: The vitriimer system was obtained by a straightforward process: first AA-PDMS (0.235 g, 0.25 mmol), DHPMA (0.04 g, 0.25 mmol), and TBD (15 mg) were dissolved in 1 mL ethanol solution to obtain $\text{AA}_{\text{solution}}$. Then PETMP (0.09 g, 0.1875 mmol) was first dissolved in 200 μL acetone and then diluted with the same 0.8 mL ethanol solution to obtain $\text{SH}_{\text{solution}}$. Finally, by mixing $\text{AA}_{\text{solution}}$ and $\text{SH}_{\text{solution}}$ in a PTFE mold, a piece of gel was obtained after solvent evaporation.

The vitriimer system without DHPMA was produced by the following process: first AA-PDMS (0.235 g, 0.25 mmol), and TBD (10 mg) were dissolved in 1 mL ethanol solution to obtain $\text{AA}_{\text{solution}}$. Then PETMP (0.06 g, 0.125 mmol) was first dissolved in 200 μL acetone and then

diluted with the same 0.8 mL ethanol solution to get $\text{SH}_{\text{solution}}$. Finally, by mixing $\text{AA}_{\text{solution}}$ and $\text{SH}_{\text{solution}}$ in a PTFE mold, a piece of PDMS gel was obtained after solvent evaporation.

VITENG was fabricated as follows: Positive electrode (VPDMs): first AA-PDMS (0.235 g, 0.25 mmol), DHPMA (0.04 g, 0.25 mmol), and TBD (15 mg) were dissolved in 0.5 mL ethanol solution to obtain $\text{AA}_{\text{solution}}$. Then PETMP (0.09 g, 0.1875 mmol) was dissolved in 1 mL acetone to get $\text{SH}_{\text{solution}}$. Finally, $\text{AA}_{\text{solution}}$ and $\text{SH}_{\text{solution}}$ were mixed and immediately casted on a copper tap-coated PMMA substrate. Negative electrode (PDMS): 10 g of the elastomer and curing agent (Sylgard 184, Dow Corning) in a mass ratio of 10:1 was mixed and poured into the Teflon mold to degas the air bubbles via a vacuum pump. Then, the mixture was added dropwise on a copper-coated PMMA substrate and cured in the oven at 85 °C for 1 h.

Self-Healing, Tensile Testing, Energy-Harvesting Measurement, and LEDs Lighting Demonstration: The mechanical properties of hybrid elastomers were characterized using a Low Force Universal Testing Systems Instron 5565 (USA) with a 100 N load cell. Samples were cut from the film that had been peeled off from the PTFE mold. The samples have a dimension of 21 mm in length, 5 mm in width, and 0.23 mm in thickness. Mechanical tensile stress and mechanical self-healing tests were performed at room temperature with a strain rate of 10 mm min^{-1} . Damaged samples were given 15, 30, or 60 min to heal under 150 °C.

Energy-harvesting measurements were performed on VITENG samples using Low Force Universal Testing Systems Instron 5565 (USA) with a 100 N load cell. The VITENG (length 4 cm, width 4 cm) was placed on the down stage of the testing systems, and a 4×4 cm^2 PDMS film was affixed to the end of the moving head to provide periodic vertical contact with the VITENG. For the healing test, the VPDMs layer was scratched

by a lancet while still being clamped in the machine. After testing the damaged layer, the electrode with the damaged layer was removed from the clamp and placed in an oven at 150 °C for 1 h. After heating, it was transferred to the lab desk for cooling. After the temperature of the material reached room temperature, the healed electrode was installed on the same system as mentioned above and tested without further treatment. To produce a frequency of 0.5 Hz, the separation distance was set to 5 mm and the motion speed was set to 0.5 mm s⁻¹. The electrical signal was collected by system electrometer Keithley 6514 (USA).

LEDs lighting demonstration: 10 LEDs were connected to the two electrodes of the VITENG by using wires directly. The VITENG was working at 1.5 Hz and 10 N conditions.

Material Characterization: Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance II 400 or Bruker Ascend 600 FT-NMR spectrometer at 25 °C in deuterated solvent as indicated.

Fourier-transform infrared spectroscopy (FTIR) measurements were conducted on a Bruker IFS88 FTIR spectrometer.

Differential Scanning Calorimetry (DSC) was carried out on a TA DSC Q1000 instrument in a dry N₂ atmosphere. Samples were analyzed in a range from -90 °C to 180 °C by performing heating-cooling-heating scans with heating and cooling rates of 10 °C min⁻¹.

Rheology experiments were performed on an Anton Paar MCR 302. The experiments were performed in parallel plate geometry using 8 mm sample disks. Unless otherwise specified, the experiments were performed using a normal force of 1 N, an oscillating frequency of 1 rad s⁻¹, and a strain of 1% was applied.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

vitrimers, transesterification, self-healing, TENG

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