A Degradable and Self-Healable Vitrimer Based on Non-isocyanate Polyurethane

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Developing degradable and self-healable elastomers composed of reusable resources is of great value but is rarely reported because of the undegr adable molecular chains. Herein, we report a class of degradable and self-healable vitrimers based on non-isocyanate polyurethane elastomer. Such vitrimers are fabricated by copolymerizing bis(6-membered cyclic carbonate) and amino-terminated liquid nitrile rubber. The networks topologies can rearrange by transcarbonation exchange reactions between hydroxyl and carbonate groups at elevated temperatures; as such, vitrimers after reprocessing can recover 82.9–95.6% of initial tensile strength and 59–131% of initial storage modulus. Interestingly, the networks can be hydrolyzed and decarbonated in the strong acid solution to recover 75% of the pure di(trimethylolpropane) monomer. Additionally, the elastomer exhibits excellent self-healing efficiency (∼88%) and fracture strain (∼1,200%) by tuning the monomer feeding ratio. Therefore, this work provides a novel strategy to fabricate the sustainable elastomers with minimum environmental impact.

Keywords: vitrimer, non-isocyanate polyurethane, acid-degradation, strain-rate response, self-healing

INTRODUCTION

Elastomers are a class of the most important polymer materials that have diverse applications in automobile, biomedical, and aerospace industries, as well as our daily life. Traditional covalently cross-linked elastomers display excellent mechanical properties and thermal and chemical stability (Tee et al., 2012; Tadakaluru et al., 2014; Wang and Loh, 2017). However, the irreversibility of chemical network prevents the recycling, reprocessing, and degradability of elastomer products, which puts a huge burden on ecology and environment.

One effective way to address this issue is to introduce dynamic covalent bonds into elastomer networks (Scott et al., 2005; Jin et al., 2013; Kloxin and Bowman, 2013; Garcia and Smulders, 2016; Chen et al., 2019; Jiang et al., 2020). The resulting dynamic networks can rearrange their topologies via exchange reactions under external stimuli, which imparts the elastomers with reprocessability and damage healability. Among various dynamic chemistries, vitrimers, a concept pioneered by Röttger et al. is particularly attractive because of associative topological rearrangement of the dynamic covalent networks (Montarnal et al., 2011; Röttger et al., 2017). As such, they hold huge potential in a variety of applications, such as recyclable thermoset polymers and self-healable polymers (Yang et al., 2014, 2016; Ube et al., 2016; Shi et al., 2017; Zhang and Xu, 2017). The fascinating performance of vitrimer was first demonstrated in a carboxylic acid cured epoxy network, which
undergoes transesterification under catalytic Zn(OAc)$_2$
(Montarnal et al., 2011). Currently, a variety of strategies
have been adopted to design vitrimer or vitrimer-like materials,
including carboxylate transesterification (Cromwell et al.,
2015; Chen et al., 2018; Liu et al., 2018; Wang et al., 2019),
transalkylation of triazolium salts (Obadia et al., 2015),
transcarbamoylation (Fortman et al., 2015), olefin metathesis
(Fortman et al., 2015), disulfide exchange (Jian et al., 2018;
Zhou et al., 2018), sulfoxide silanol exchange (Zheng and McCarthy,
2012), transamination (Denissen et al., 2017), etc. These strategies impart the
vitrimer materials with reprocessable, recyclable, and repairable
properties via bond exchange reactions at elevated temperatures;
however, the products are usually non-degradable and insoluble,
which causes serious ecological and environmental pollution at
the end of the vitrimer service life. Therefore, developing a degradable and self-healable vitrimer material is of great public value.

In this article, we develop a novel and efficient path to prepare a
degradable and self-healable vitrimer based on non-isocyanate polyurethane elastomer (PU$_E$) by introducing carbonates that
can undergo transcarbonation exchange reactions in Figure 1.
The prepared elastomer can rearrange the network topology via transcarbonation exchange reactions, thus endowing the
elastomer with vitrimer behaviors. In addition to being reprocessable and repairable, the networks can be hydrolyzed and decarboxylated in hydrochloric acid solution to recover the di(trimethylolpropane) monomer and Pre-PU$_E$.

**EXPERIMENTAL**

**Materials**

Amino-terminated liquid nitrile rubber (ATBN, Mn =
402 g mol$^{-1}$) was purchased from Shandong Jining benoke
Biotechnology Co., Ltd. Chloroformic acid–propylester (98%),
n-methyl pyrrolidone (NMP), anhydrous tetrahydrofuran
(THF), and di-trimethylolpropane (98%) were provided by
Shanghai TITAN Technology Co., Ltd. Ethanol (AR grade), butyl
titanate (C$_{16}$H$_{36}$O$_4$Ti), and triethylamine (Et$_3$N, AR grade)
were supplied by Kelong Reagent Corp. (Chengdu, China). All of the
raw materials were dried before use.

**Synthesis of bis(6-Membered Cyclic Carbonate) (Bcc)**

Bcc was successfully synthesized from di(trimethylolpropane)
and chloroformic acid–propylester reaction procedure in Figure 1A. The details of the preparation were as follows: di-trimethylolpropane (10.0 g, 40 mmol) was dissolved in THF
(250 mL) and transferred to three-neck round bottom flask with
magnetic stirring 1 h under N$_2$ at 25°C, and then chloroformic
acid–propylester (26 mL) was step-by-step drop added into a
three-neck flask during stirring. Subsequently, catalyst Et$_3$N
was added dropwise when the reaction temperature cooled to
0°C. Then, the reaction mixture was magnetic stirring for 5 h
to form a white precipitate and removed by vacuum filtration,
and solvent was removed via under rotary evaporation to yield
a white solid. Finally, the white solid was recrystallized in THF
(10 mL) to attain the pure product Bcc.

**Preparation of Polymer PU$_E$**

Attributing to the long molecular chain structure of ATBN, the
end amino groups in long-chain molecule were surrounded by
ATBN molecular chains, leading to a limited reactivity between
amino and bis(6-membered cyclic carbonate). To improve the
reactivity of the reaction, the low-molecular-weight ATBN was
first chosen. Bcc (0.5 g, 1.65 mmol) and ATBN (29 g, 60 mmol)
were added into three-neck round bottom under nitrogen
atmosphere. Then, the reaction solvent NMP (60 mL) was added
into the mixture, after nucleophilic addition reaction at 100°C
with magnetic stirring for 24 h and formed prepolymer. Bcc can serve as cross-linker to realize cross-linking existed catalyst.
For details, the cross-linked PU$_E$ was synthesized by a one-step
copolymerization existed catalyst C$_{16}$H$_{36}$O$_4$Ti and THF
at 25°C. Finally, the polymer PU$_E$ was successfully prepared
(Figure 1B). Because of existed substantial hydrogen bonds
formed by hydroxyl and carbonate groups, dual cross-linked
networks were thus formed during polymer preparation process in
Figure 1C. Because the content of cross-linker Bcc and physical cross-links directly influences the polymer cross-linking
density and thus has impact on the mechanical properties, a
series of samples were synthesized by tuning the feed ratio. The feed ratios of PU$_E$—X (X = 1, 2, 3, 4, 5) are summarized in Supplementary Table 1.

**Preparation of Polymer PU$_E$ Film**

The product PU$_E$ solution was first put into a Teflon mold (30
× 50 × 10 mm) with a glass plate and was subsequently placed in
an oven for 12 h at 40°C. Second, the product solution was heated
from 40 to 50°C for 12 h. Additionally, the resulting polymer film
was dried under vacuum at 50°C for 24 h. Finally, the film was
taken out and cut into rectangles of 2 × 25 mm for further testing.

**Characterization Methods**

Prior to this, polymer PU$_E$ samples were vacuum-dried at 50°C
for 12 h.

**Fourier Transform–Infrared Spectrometry (FT-IR)**

FT-IR spectral analysis was recorded on a Fourier transform
infrared spectrometer (Nicolet iS50) in a range of wavenumbers
from 4,000 to 500 cm$^{-1}$.

**Nuclear Magnetic Resonance Spectroscopy (NMR)**

NMR spectra were recorded on a Bruker AV400 spectrometer
(400 MHz, Germany) with dimethyl sulfoxide-d$_6$ and deuterated
chloroform as the solvents and tetramethyl silane as the internal
reference.

**Dynamic Mechanical Analysis (DMA)**

The dynamic mechanical analysis was studied using DMA Q800
(TA Instruments, USA), at a frequency of 1 Hz and then a heating
rate of 3°C min$^{-1}$ from −100 to 100°C.

**Differential Scanning Calorimetry (DSC)**

DSC was performed with a DSC-Q200 (TA Instrument, USA)
over the temperature range from −60 to 60°C at a heating rate
of 5°C min$^{-1}$ under N$_2$ and empty aluminum as the reference.
Scanning Electron Microscope (SEM)
A scanning electron microscope (Nova NanoSEM450) was used to trace the healing process of scratch immediately after making scratch by a blade.

Static Tensile Tests
The mechanical properties of the samples were investigated on an Instron Universal Testing Machine (Model 5967, Instron Crop) at a stretching rate of 0.083 s$^{-1}$ at room temperature. The thickness and width of the specimens were 0.70 and 4 mm, respectively. The length of the sample between the two pneumatic grips of the testing machine was 20 mm. Three dumbbell-shaped specimens were tested in each sample.

Acid-Degradation Studies
To conduct swelling test, 0.5-g sample of polymer film was submerged in THF (15 mL) and then stirred for 24 h at room temperature until no obvious changes appear. It was shown that the cross-linked network only was swollen. For degradation studies, the same 0.5-g PU$_E$ sample films were immersed in sealed vials containing 10 mL of HCl (1 M), KOH (1 M), and H$_2$O, respectively. The vial was heated in a drying oven to 100$^\circ$C for 24 h. The sample was cleaned containing HCl solution with n-butanol (20 mL). The solvent was removed by rotary evaporation, and finally, the di(trimethylolpropane) monomer was obtained.

Reprocessing Recovery
To reprocess the PU$_E$ materials, the sample films were ground to small pieces first, and second placed in a hot press at 130$^\circ$C under the pressure of 5 to 10 MPa. These pieces were thermally equilibrated for 30 min and removed from the press to check for homogeneity of the film and then once again placed in a hot press at 130$^\circ$C for 2 h under same pressure. Finally, uniaxial tensile tests and dynamic mechanical thermal analysis were carried out to determine the recovery efficiency of mechanical properties.

Self-Healing Tests
The elastomer sample was cut into two pieces at the center using a razor blade; the two pieces rejoin together to form nearly complete elastomer when contacting with each other at 100$^\circ$C. Uniaxial tensile test was performed to determine the mechanical properties and healing efficiencies.

Polymer Characterization
The chemical structure of Pre-PU$_E$ and PU$_E$ samples was characterized using FT-IR spectra, as shown in Supplementary Figure 3. It can be found that the prepolymer sample exhibits several characteristics peaks: the absorption peak at 3,840 cm$^{-1}$ indicates the presence of $-\text{OH}$; the peaks at 2,980 cm$^{-1}$ can be attributed to the N-H bending vibration of the carbamate groups ($-\text{NHCOO}$) (Fan et al., 2019), and the peaks at 1,460 and 1,741 cm$^{-1}$ can be assigned to the C–O stretching vibration and C = O stretching vibration of linear carbonate,
RESULTS AND DISCUSSION

Thermal Properties and Dynamic Nature of the Networks

The thermal properties of polymer materials play a dominant role in their topological rearrangement of networks. Therefore, differential scanning calorimetry (DSC) is performed. Figure 2A displays the DSC curves of PU_E samples. The relevant thermal parameters and their corresponding values are summarized in Supplementary Table 2. It is evident that the glass transition temperature (T_g) of PU_E samples increases with the increasing cross-linker Bcc amount. This suggests that the enhancement of the degree of cross-linking greatly restricts the mobility of chain segments, as shown in Supplementary Figure 5A. As is expected, there is no endothermic peak above T_g, which indicates that the material is amorphous. In addition, it can be found from Supplementary Figure 5A that the T_g values are lower than room temperature, indicating the material is an elastomer rather than plastic at room temperature. Meanwhile, thermogravimetric analysis measurements are conducted, and the values of thermal degradation temperatures are summarized in Supplementary Table 2. The elastomer network first lose mass around 214°C (5% mass loss), which is well above the temperature required for transcarbonation exchange reaction in Supplementary Figure 5B.

To better determine the network topology rearrangement via transcarbonation exchange reactions between free hydroxyl and carbonate groups at elevated temperatures and the rate of exchange reactions, the stress–relaxation measurements are performed by stretching the samples to a strain of 50% from 50 to 120°C. The strain is then maintained for 12 min, and the stress is recorded as a function of time in Figure 2B. The network characteristic relaxation time (τ) is defined as the time required for the elastomer to reach 1/e (37%) of the initial stress and is used as a measure of the rate of transcarbonation exchange reactions under the testing conditions (Snyder et al., 2018). As illustrated by Figure 2B, it can be seen that PU_E-4 has a stress relaxation time of 547 s at 90°C. As the temperature increases to 120°C, the relaxation time decreases to 132 s. The result demonstrates that the exchange rate of elastomer network rearrangement largely depends on the temperature. As shown in Figures 2B,C, the temperature dependence of the relaxation time of PU_E-4 follows Arrhenius’ law (Wu et al., 2020). According to Arrhenius’ law:

\[ \ln \tau = \ln \tau_0 + \frac{E_a}{RT} \]  

The activation energy of the rearrangement network is determined to be 55.09 kJ mol⁻¹. As the temperature rises, the adaptivity of the PU_E-4 network is activated as a result of exchange reaction. Simultaneously, the samples with different cross-linker amount are fixed at 100°C and then maintained for 12 min; it can be seen that the residual stress of these samples lower than 1/e of the initial stress undergoes stress relaxation within 4 min, illustrating that the network topologies of all these samples can be rearranged at elevated temperature in Supplementary Figure 6. Moreover, the storage modulus (E′) and the loss factor (tanδ) of the elastomers as a function of temperature are recorded by DMA, as shown in Figure 2D and Supplementary Figure 5D. The samples exhibit a marked decrease of E′ when the temperature exceeds T_g in Figure 2D. Interestingly, the rubber modulus decreases with temperature, indicating the dissociation of hydrogen bonds prior to dynamic network change. Not surprisingly, the sample with the higher cross-linker Bcc content possesses a higher E′ value. According to the E’ value at T_g + 30°C (Tang et al., 2020), the cross-linking density can be calculated in Supplementary Equation 1 and shown in Supplementary Table 2.

Mechanical Properties

To investigate the mechanical properties of the elastomer, static tensile measurements are performed at a strain rate of 0.083 s⁻¹. Figure 3A displays the typical stress–strain curves for these samples, and mechanical properties are summarized in Figure 3B and Supplementary Table 4. PU_E-1 exhibits a tensile strength about 0.79 MPa and a strain at break of 1,696%, as illustrated by Figure 4A. Interestingly, the stress–strain curves of these samples are relatively non-linear, and there is yielding point, which represents a non-classical rubberlike behavior. To further explore the non-linear relationship between deforming and mechanical properties, we selected PU_E-4 as an example to perform the tensile tests at various straining rates, from 0.004 to 0.3 s⁻¹. Figure 3C manifests a unique strain-rate–responsive yield phenomenon. The yield stress strikingly with increasing strain rate, and meanwhile the Young's modulus...
obtained from the initial linear region of the stress–strain curves increases from 1.04 to 4.64 MPa in Figure 3D. Such a phenomenon demonstrates that the elastomers possess a self-stiffening ability with increasing strain rate (Wu et al., 2019). To explain the underlying mechanism governing this increasing yield phenomenon with strain rate, we need to consider the inherent (stress-free) dissociation rate constant \( k_p \) of the hydrogen bonds (Hu et al., 2017). At room temperature, \( k_p \) of the hydrogen bonds is much smaller than the strain rate. As a result, higher strain rates (>0.004 s\(^{-1}\)) tend to enhance the strain localization and thus promote yielding, which induces a slight drop in stress.

Additionally, the stretchability is highly dependent on the straining rate in Supplementary Figure 7, which is consistent with most elastomers (Li et al., 2016; Son et al., 2018; Lai et al., 2019). Surprisingly, unlike other super-stretchable elastomers with large residual strain after deformation, the non-isocyanate PU\(_E\) displays an excellent elastic behavior and can nearly completely restore its original shape even after they are subjected to large deformations. For an example, PU\(_E\)-4 can be stretched to a strain of 1,700%. After releasing the stress, the instantaneous residual strain is 70%, and it gradually decreases as a function of time, as shown in Supplementary Figures 8A,B. Prolonging the waiting time, the sample almost fully recovers its original shape without evident residue strain, which suggests both the robustness of the covalent network and reversibility of the physical network formed by hydrogen bonds. The performance comparison between this material and the existing literatures PU elastomer has been put into the (Supplementary Figure 9).

**Acid-Degradation and Reprocessing**

Compared with traditional isocyanate-based PU\(_E\)s, one degradation process allows the PU\(_E\) to recover the di(trimethylolpropane) monomer under acid hydrolysis condition at the end of service life. To illustrate the degradation process, the sample films of 0.5 g are immersed in sealed vials containing 10 mL of HCl (1 M), NaOH (1 M) and H\(_2\)O, respectively. The vials are heated in an oven to 100\(^\circ\)C for 24 h. The sample films show no obvious changes in aqueous solution (H\(_2\)O) and slight degradation in basic solution (NaOH), while in strong acid solution (HCl), the sample can be fully dissolved into a homogenous solution after heating.
in Figure 5A. The acid-degradation mechanism is shown in Figure 4B: the carbonate bonds are broken in the strong acid solution. Extracting the acid-degraded solution containing HCl with n-butanol (20 mL) leads to 75% recovery of the pure di(trimethylolpropane) monomer. The product structure is not destroyed, as verified by NMR characterization in Supplementary Figure 10. In addition to being acid-degradable, the dynamic cross-linked network can reform once again at elevated temperatures owing to transcarbonation exchange reactions via free hydroxyl and carbonate groups. As such, the...
samples can be reprocessed. For example, the damaged samples are cut into small pieces and then hot pressed at 130°C under a pressure of 5 to 10 MPa. The sample can be fully restored after hot pressing in Figure 5B, indicating the excellent recyclability of the dynamically cross-linked elastomer.

The reprocessing mechanism relies on transcarbonation exchange reaction and is illustrated in Figure 1D: a hydroxyl nucleophile reacts with a carbonate at elevated temperature, forming an associative intermediate, and then the exchanged carbonate and hydroxyl groups are released, denoting completion of the network rearrangement process. Dynamic mechanical analysis and uniaxial tensile tests are carried out to determine the recovery efficiencies of the tensile strength and plateau storage modulus after reprocessing. The storage modulus of the samples after reprocessing as a function of temperature is recorded by DMA in Figure 5C. Figure 5D exhibits the plateau storage modulus at 50°C before and after reprocessing. The performance of the reprocessed material, which was better than its original form. Similar results have been found in previous literature (Snyder et al., 2018), and the mechanism is still unclear. Exploring the questions will require model networks of more controlled network structure and molar ratio between reversible
Self-Healing Properties

To demonstrate the self-healing behavior, tensile tests before and after self-healing are performed. As shown in Figure 6A, the healed sample can sustain a large strain after healing at 100°C for 12h, indicating the excellent self-healing ability of the PU samples. Figure 6C exhibits the typical stress–strain curves of PU-4 healed at 85 and 100°C for various times. The self-healing efficiency is quantified by the ratio of the fracture stress of the healed to the pristine sample in Supplementary Equation 3. After being healed for at 85°C for 12h, the healing efficiency is 34.9%. Significantly, the healing efficiency further increases to 62.8% and 88.4% after being healed at 100°C for 6 and 12h, respectively. The self-healing fully demonstrates the reconstructing ability of network topologies and hydrogen bonds. Figure 6D shows the healing efficiencies of different PU samples. It is worth noting that the healing efficiency does not change monotonously with cross-linking density, and PU-4 sample exhibits the highest efficiency. In general, higher crosslinking density indicates restricted chain mobility, which is unfavorable for wetting and diffusion of rubber chains at interface and consequently leading to poor healing behavior (Cao et al., 2019). However, a higher crosslinking density means more carbonate bonds, which indicates that more covalent linkages can be reformed at interface via transcarbonation exchange reaction. The competition of these two effects leads to the highest healing efficiency of PU-4. To investigate the healing from microscopic scale, we prepare a scratch on a sample film and characterize the evolution of the scratch with scanning electron microscope (SEM). Figure 6B exhibits that the scratch on the film almost completely disappears after healing at 100°C for 12h. This once again indicates the good self-healing behavior of the obtained PU samples.
CONCLUSIONS

In summary, we have designed and fabricated a novel acid-degradable and self-healable vitrimer based on non-isocyanate PU. Interestingly, the elastomer manifests a unique strain-rate-responsive yield phenomenon during stretching. The yield stress increases with increasing strain rate, as the increasing high strain rate (>0.004 s⁻¹) tends to enhance the strain localization and promote yielding. Elevating the temperature can alter the networks topologies of the elastomer, which results in excellent reprocessing and self-healing behaviors. Simultaneously, the elastomer containing the dynamic networks can be hydrolyzed and decarboxylated in the strong acid solution (HCl) to recover 75% of the pure di(trimethylolpropane) monomer. Therefore, we can envision that this non-isocyanate-based PU will manifest longer service life and decreased pollution to the environment.

DATA AVAILABILITY STATEMENT

All datasets generated for this study are included in the article/Supplementary Material.

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AUTHOR CONTRIBUTIONS

HWu carried out experiment and wrote the manuscript. JW supervised the project and mainly revised the paper. All authors extensively reviewed the manuscript and approved the final version of the manuscript to be submitted.

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SUPPLEMENTARY MATERIAL

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

The reviewer LC declared a past co-authorship with one of the authors JW to the handling editor.

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