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Vitrimerization of Rigid Thermoset Polyurethane Foams: A Mechanochemical Method to Recycle and Reprocess Thermosets

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RESEARCH ARTICLE

Vitrimerization of rigid thermoset polyurethane foams: A mechanochemical method to recycle and reprocess thermosets

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Abstract

Polyurethane (PU) thermosets are extensively used in different applications and recycling the large amount of PU thermoset waste remains a universal challenge. Recycling the thermoset waste through vitrimerization is a feasible, cost-effective, and environmental-friendly approach. In this work, triazabicyclodecene (TBD) is used as organocatalyst in the vitrimerization process to recycle and reprocess thermoset rigid polyurethane foams. The results show that the permanent crosslinked structure of the PU thermoset foam is converted to a dynamic network upon vitrimerization. The vitrimerized network can rapidly relax the stress in 10 s at temperatures as low as 120°C. The topology rearrangement happens through the carbamate exchange reaction, mainly via a dissociative mechanism. The vitrimerized network retains high mechanical strength with Young's Modulus of 2.7 GPa and tensile strength of 76.4 MPa and can be reprocessed for a second time without addition of extra catalyst and without loss in mechanical properties. The vitrimerized network can also be foamed by applying small pressure at high temperatures.

KEYWORDS
recycling, rigid polyurethane foam, thermoset waste, vitrimerization

1 | INTRODUCTION

Polyurethane (PU) thermosets accounting for 31% of the thermoset market are extensively used in different applications such as furniture, construction, automobile, sound, and thermal insulation. PUs are versatile materials used as adhesives, coatings, elastomers, and foams.[1] The growing quantities of PU thermoset waste causes significant environment challenges and consequently technologies to recycle the thermoset PUs have attracted significant attention. However, the recycling of thermoset PUs is limited due to their permanent cross-linked structure which prevents melt reprocessing.[2] Common methods for recycling these materials are mechanical recycling and chemical degradation. In the mechanical approach, the materials are crushed and used as filler in other applications. However, using these recyclates as fillers above certain limits decreases the mechanical properties and prevent processing because of the increased viscosity of the compound. In the chemical approach, the PU thermosets are recycled into polyols or other small molecules via catalyzed glycolysis.[3–5] Both these methods have low efficiency and high energy requirements. Therefore, it is essential to design a practical and efficient method for recycling PU thermoset wastes directly into similar or higher-value products.

One promising approach to overcome these challenges is to involve covalent adaptive networks (CANs) in the system whereby the crosslinked network undergoes an exchange reaction with topology rearrangement at high temperature. CANs possess the ability to be reprocessed like thermoplastics while keeping the robust mechanical strength associated with traditional thermosets.[6–11] Leibler and

coworkers adopted the dynamic covalent network chemistries in crosslinked polyester networks using the Zn^{2+}-catalyzed transesterification reaction and they attributed the rapid stress relaxation to the efficient exchange reactions allowing topological rearrangements while preserving the network integrity.[12] Many dynamic networks such as carbonate,[13] vinyL‍ogous urethane,[14] disulfides,[15,16] and boronate esters[17] have been investigated and showed the stress relaxation allowing bulk reprocessing. Consequently, most of the synthesized CANs can be reprocessed through traditional thermoplastic techniques such as extrusion,[18] melt blowing,[19,20] compression molding,[21] and injection molding.[12]

Recently, Wang et al[22] synthesized thermally processable PU foams by making the dynamic PU network using the dynamic disulfide bonds. They showed that the topology rearrangement of the network happens due to the exchange reaction of disulfide bonds at high temperatures making the PU foams malleable and thermally processable. The authors reported that the mechanical properties of recycled PU foams are comparable to the original ones and they can be reprocessed several times without significant loss in mechanical properties. However, formulation and design of new materials with dynamic networks does not alleviate the problem of recycling the existing thermoset waste present in the market. To overcome this challenge, Sheppard et al[23] made PU thermoset foams reprocessable by introducing dibutyltin dilaurate as a carbamate exchange catalyst into the PU network through a solvent swelling method. The authors showed that the crosslinked PU foam can be continuously reprocessed into film through twin-screw extrusion. However, reprocessing of the PU foams through compression molding was inefficient due to the trapped air in the reprocessed materials. The main drawback for the solvent swelling method is long processing times and the use of toxic solvents.

Xie and coworkers[24] synthesized thermoset shape memory PU with 0.5–2 wt% dibutyltin dilaurate (DBTDL) and showed that the aliphatic thermoset rapidly relax stress at 130°C due to transcarbamoylation reactions. In another study, Dichtel and coworkers[25] explored the effect of various types of Lewis acid catalysts in PU and demonstrated fast stress relaxation at 140°C. However, due to the harmful impact of the metal-based catalyst on the environment, there is a significant interest toward using organocatalysts in the synthesis of PU which can perform as effective as tin-based catalyst.[26] In addition, it has been shown that these catalysts can affect the dynamic character of vinyL‍ogous urethanes.[14]

Recently, we developed a new technique to convert the permanent crosslinked structure of thermosets into dynamic networks through a mechanochemical approach labeled vitrimerization.[27–29] In this method, a mechanochemical process is used to form exchangeable linkages via ball milling the thermoset network with an appropriate catalyst.[30–32]

In this study, the carbamate exchange reaction is utilized for the vitrimerization of thermoset rigid PU foams. Moreover, we used the triazabicyclodecene (TBD) as organocatalyst for the vitrimerization of rigid PU foams. TBD is in solid state at room temperature enabling its use in a mechanochemical process. We explore the effect of different catalyst concentration on the mechanisms of exchange reactions (associative and dissociative) and on the final properties of vitrimerized network. Vitrimerization is a feasible, cost effective, environment-friendly, and commercially scalable process that can pave the way for thermoset recycling. This work enables to design an efficient method for recycling rigid PU thermoset foam wastes to high value-added products.

2 | EXPERIMENTAL SECTION

2.1 | Materials

Commercial rigid PU foam was kindly provided by Stepan Company. The Triazabicyclodecene (TBD) was purchased from Sigma-Aldrich and used as catalyst.

2.2 | Vitrimerization process

The fine particles (<500 μm) of the PU foams were obtained by grinding small pieces of the PU foams. The ultrafine powder mixtures were obtained by ball milling the PU fine particles and the catalyst (TBD) in a ball mill tank (Fritsch pulverisette 6), purged with N_2. Each run for the ball milling process was for 40 min with 8 cycles of grinding for 5 min at a speed of 570 rpm and an intermediate cooling for 15 min. The compression molding of the ball milled powder mixtures was performed at 110°C and 20 MPa with 10 min preheating and 60 min heating in a mold, to obtain vitrimerized samples (Figure 1). Reprocessing of the vitrimerized samples was performed with the same procedure except that no catalyst was added during the ball milling.

2.3 | Characterization

2.3.1 | Dynamic mechanical analysis

TA Instruments Q800 was used to measure the dynamic mechanical properties, storage modulus (E'), and tan (δ). The measurements were performed in tensile mode with a strain amplitude of 0.05% at constant frequency of 1 Hz and scanning rate of 5°C min^{-1} from 25 to 200°C. The glass transition temperature (T_g) of samples was determined by the peak of tan (δ) curves. Dilatometry was performed in tension and controlled force mode. Two different constant forces of 0.2 and 0.75 N were used with a heating rate of 5°C min^{-1} from 25 to 200°C. The strain was measured during the test.[33]

2.3.2 | Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) analyses were carried out using an Agilent Cary 630 FTIR spectrophotometer in a spectral range of 4000–600 cm^{-1}.
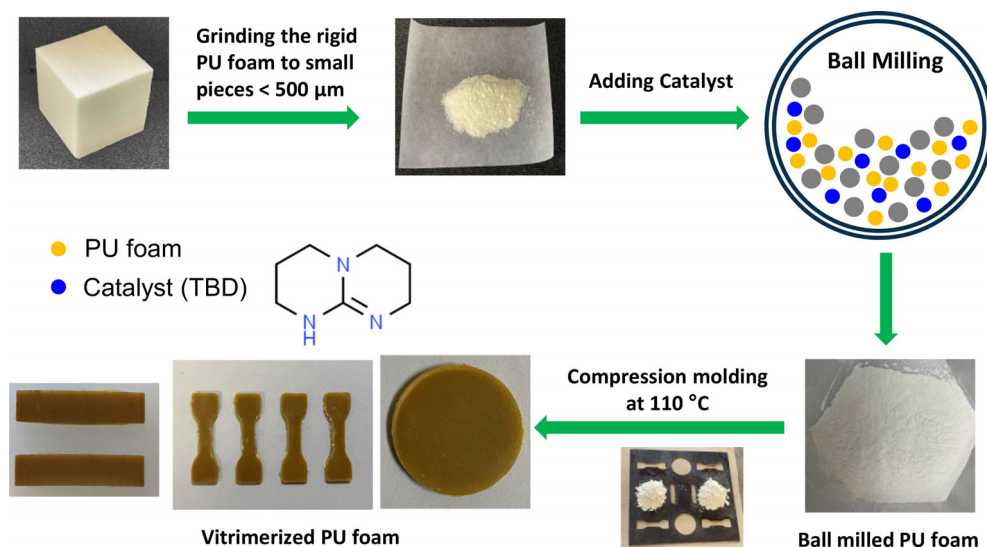
FIGURE 1 Vitrimerization of rigid polyurethane foam

2.3.3 | Mechanical testing

Stress–strain curves were obtained on an MTS Insight tensile instrument in tensile mode. The samples size was 1.2 mm × 5.4 mm × 15 mm (thickness, width, gage length) and the strain rate was 5 mm min^{-1}.

2.3.4 | Rheology

Stress relaxation tests were performed on a TA ARES-G2 rheometer with a 25 mm parallel plate geometry on samples with average thickness of 1.2 mm. After a 10 min temperature equilibrium, a 0.1% strain strep was applied. A constant normal force of 10 N was applied during the test to avoid the gap between the sample and the plate.

2.3.5 | Thermogravimetric analysis

TA Instruments Q500 with an aluminum pan was used to study the thermal stability. Around 10 mg sample was used for each run with a heating rate of 10°C min^{-1} from room temperature to 700°C under nitrogen flow.

2.3.6 | Scanning electron microscopy

ThermoFisher Apreo2 SEM Scanning Electron Microscope was used to characterize the morphology of the PU foams and vitrimerized samples.

3 | RESULTS AND DISCUSSION

3.1 | Network reforming

The vitrimerization process is shown schematically in Figure 1. The mixture of grinded PU foam and different concentrations of catalyst

(2, 5, and 10 wt%) are ball milled under nitrogen atmosphere. It should be noted that the melting temperature of TBD is 125°C, therefore, to avoid the catalyst melting during compression molding, as illustrated by preheating the powders at 120°C (Figure S1a), the powders were vitrimerized at 110°C. Increasing the temperature to 200°C for the ball milled powder with catalyst results in sample degradation during compression molding (Figure S1b).

As shown in Scheme 1, the exchange reaction in the urethane linkage can occur through associative and dissociative mechanisms.[34] The rapid drop in viscosity due to the dissociative exchange reaction increases the efficiency of reprocessing.[10,35,36] However, the dissociative mechanism creates free isocyanate groups which can result in secondary reactions and stable byproducts that can reduce the dynamic character of the network.[37,38]

The FTIR results for the initial, vitrimerized and ball milled PU foams (Figure 2) show that by introducing the catalyst and increasing the concentration to 5 and 10 wt% there is a split for the absorbance of the urethane carbonyl groups (C═O) in 1718 and 1650 cm^{-1}. This splitted absorbance has been attributed to the stretching vibrations of the non-hydrogen-bonded and hydrogen-bonded carbonyl groups. It has been shown that the carbonyl stretching vibration can shift to an absorbance of tens of cm^{-1} in the lower wavenumber direction of the spectrum due to the hydrogen bonding.[39,40] In addition, the absorbance at around 3340 cm^{-1} is related to the N—H stretching vibrations of the urethane groups[39,40] and increasing the catalyst concentration results in hydrogen bonding of the N—H groups. The FTIR results show that increasing the catalyst concentration results in more hydrogen bonding in the structure of vitrimerized PU foams, which can improve the mechanical properties of vitrimerized samples.

3.2 | Dynamic mechanical analysis

The DMA results (Figure 3A) show similar values for the storage modulus of vitrimerized PU foams with different catalyst concentration at room temperature followed by an abrupt drop with increasing

SCHEME 1 Schematic representing the dissociative and associative mechanisms during the carbamate exchange reaction

Dissociative Mechanism
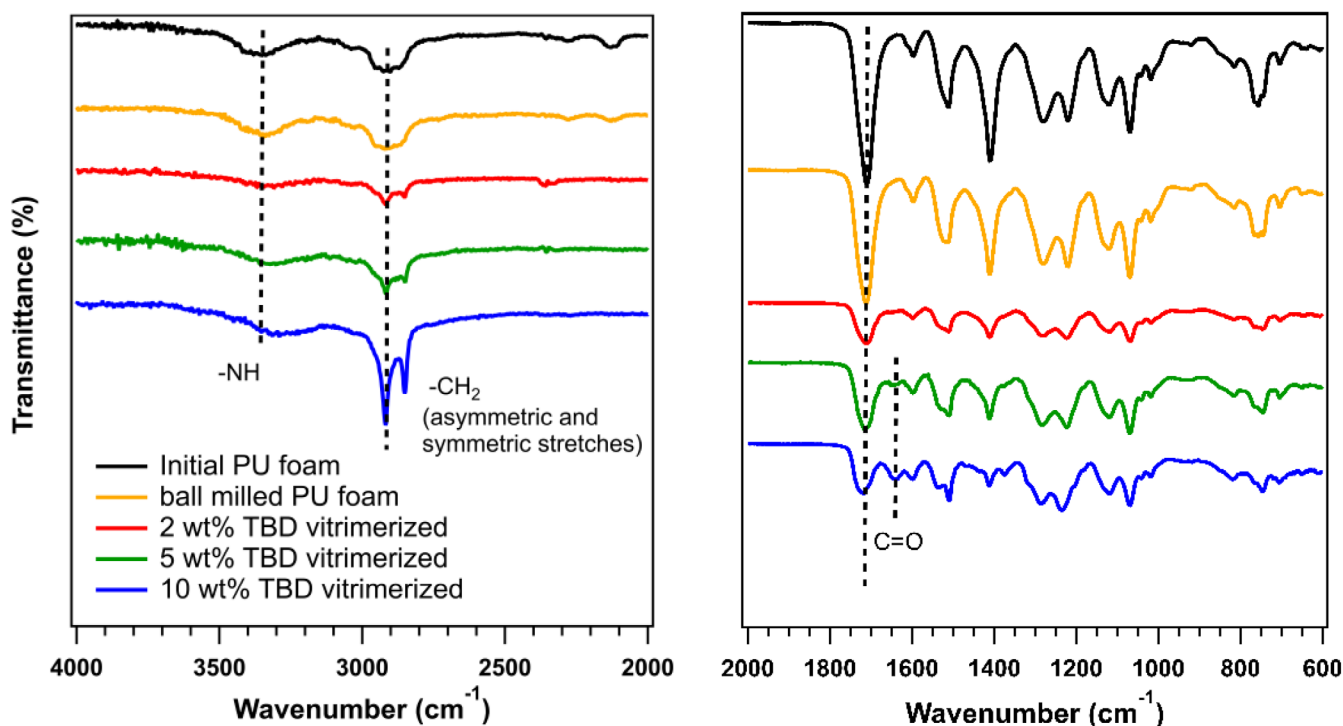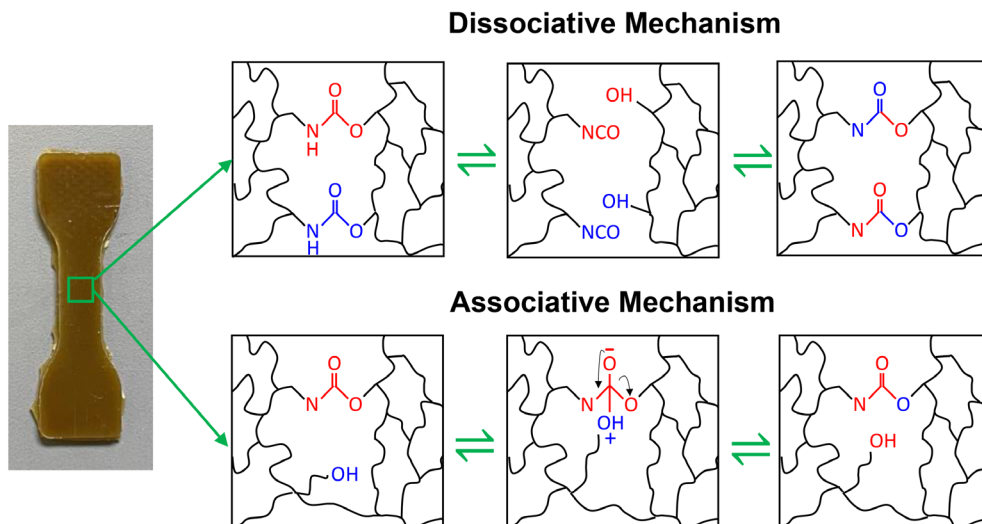
Associative Mechanism

FIGURE 2 FTIR spectra of initial and vitrimerized PU foam with different concentrations of catalyst. FTIR, Fourier transform infrared spectroscopy; PU, polyurethane

temperature and reaching a plateau region at elevated temperatures. The storage modulus at plateau region decreases with increasing the catalyst concentration in the vitrimerized samples suggesting primarily a dissociative mechanism for the exchange reaction. It should also be noted that at higher temperatures (around 170°C) the vitrimerized samples with 5 and 10 wt% catalyst exhibit an abrupt decay in storage modulus. As shown in Figure S2, at this temperature these vitrimerized samples start foaming. This phenomenon may indicate the occurrence of side reactions of the free isocyanate groups. Such groups form potentially during the exchange reaction through a dissociative mechanism (Scheme 1).

3.3 | Thermal properties of the vitrimerized networks

The thermal behavior of the vitrimerized networks was investigated and compared with the initial PU foam. The DSC results (Figure 3C) show a weak transition around 50°C which is not affected by the vitrimerization and a much sharper transition around 90°C for the initial PU foam which occurs at higher temperatures (110–120°C) for the vitrimerized samples. This second transition shifts to higher temperatures for the vitrimerized samples due to the more compact crosslinked networks in the vitrimerized samples. The DSC results show
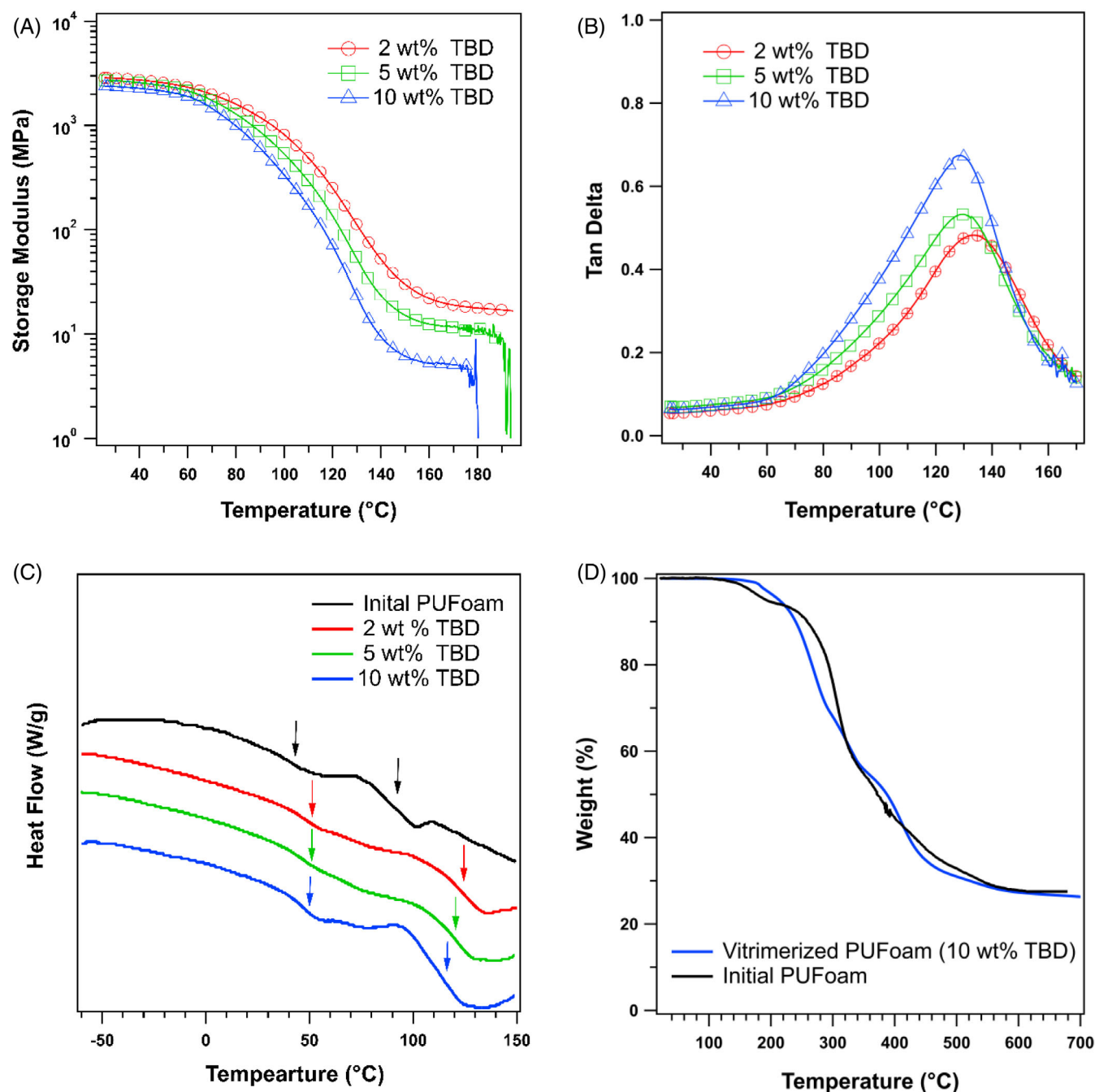
FIGURE 3 (A) Storage modulus and (B) Tan δ of vitrimerized networks. (C) DSC curves, and (D) thermogravimetric analysis curves of weight loss

the same trend with the tan delta results presented in Figure 3B and point out to a small shift in the glass transition temperature of the vitrimerized samples with increasing catalyst concentration. These results reiterate the plausible dissociative mechanism of exchange reaction at high temperatures increasing with catalyst concentration. The thermogravimetric analysis (TGA) results (Figure 3D) show that the vitrimerized PU foams are stable up to 200°C, which is appropriate for most of the PU-based material applications.

3.4 | Stress relaxation

In the presence of catalyst, topology rearrangement and stress relaxation for the vitrimerized samples occur due to the exchange reactions, which are activated at elevated temperatures. As shown in Figure 4A, B, increasing the catalyst concentration accelerates the exchange reaction rate due to the formation of more dynamic linkages in the network. The Arrhenius equation $\tau^*(T) = \tau^*_0(T)\, exp\, (E_a/RT)$ is used to
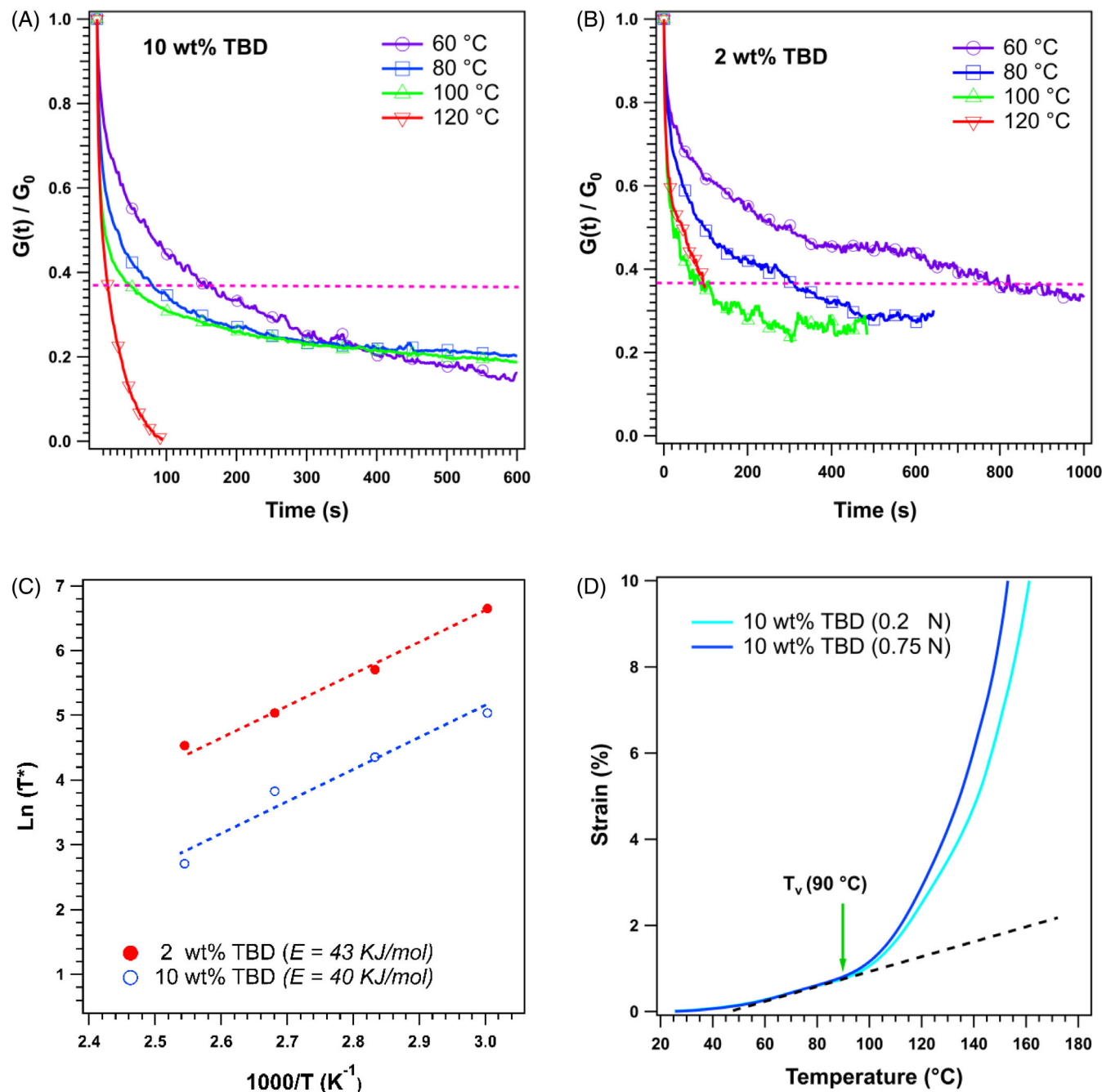
FIGURE 4 (A,B) Stress relaxation curves of vitrimerized samples at different temperatures for 2, and 10 wt% triazabicyclodecene, (C) Arrhenius plot of the relaxation times at various temperatures, (D) Dilatometry results for vitrimerized network

obtain the activation energy (Ea) for the exchange reactions. The relaxation time τ^* is defined as the time for relaxing 63% of the initial stress. The results show that the activation energy for the vitrimerized network with 2 wt% catalyst is 43 kJ/mol and with 10 wt% TBD is 40 KJ/mol.

The dynamic covalent bonds in the vitrimerized network introduce a temperature-dependent behavior and the chemical exchange reactions control the viscosity.[11] Therefore, the vitrimers can be

processed without losing the network integrity due to the controlled viscosity by exchange reactions. The topology freezing point (T_v) defines the viscoelastic phase transition in vitrimers. The exchange reaction happens slow and fast below and above the T_v, respectively. The topology freezing point, measured in a dilatometry experiment performed using two different constant forces of 0.20 and 0.75 N to ensure reproducible results, is around 90°C for the vitrimerized sample with 10 wt% TBD (Figure 4C).

(A)

Density = 0.01 g/cm³ — *Vitrimerization* → Density = 1.38 g/cm³ — *Foaming* → Density = 0.56 g/cm³
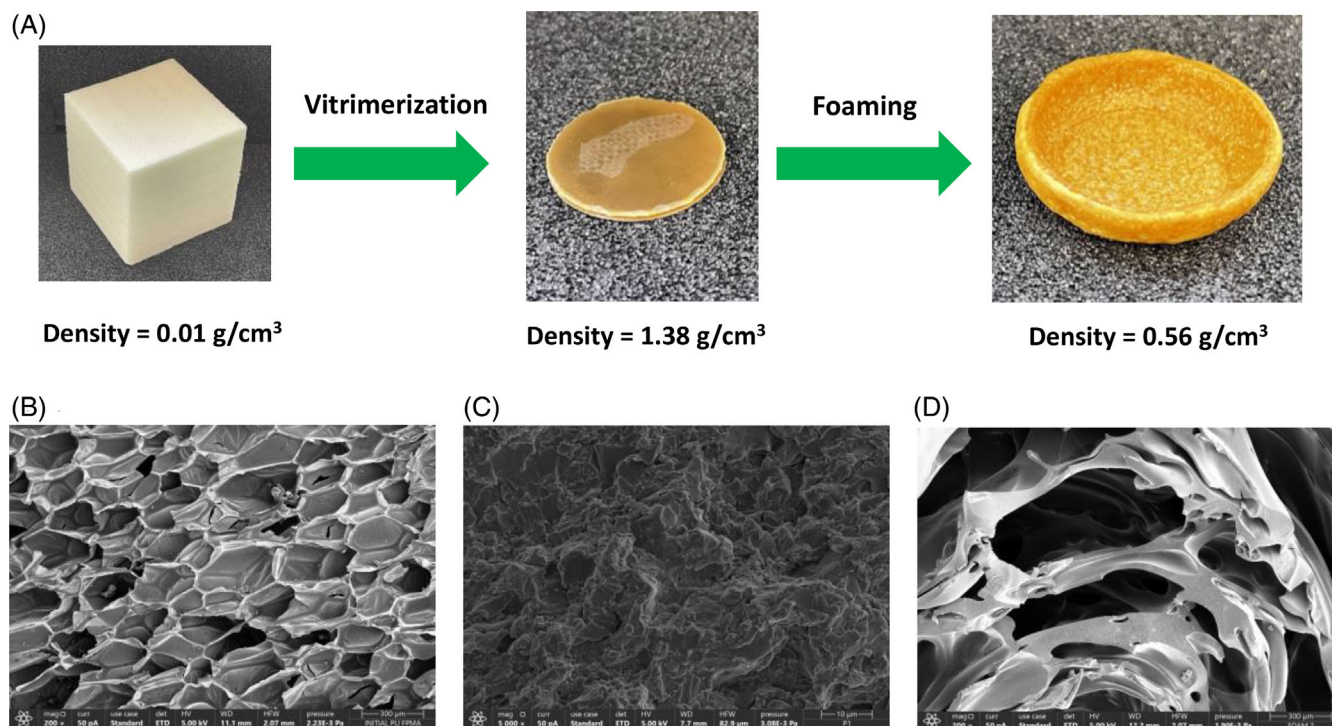
(B) **(C)** **(D)**

FIGURE 5 (A) Foaming the vitrimerized network by applying pressure and heating at 170°C. Cross section SEM images of (B) initial PU foam, (C) vitrimerized network with 10 wt% TBD, and (D) foam produced from vitrimerized network with 10 wt% TBD. PU, polyurethane; SEM, scanning electron microscopy; TBD, triazabicyclodecene
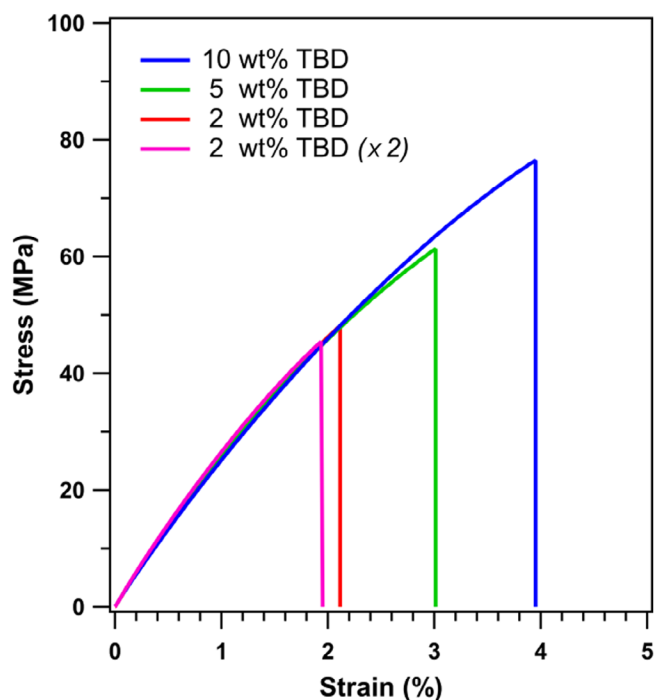

FIGURE 6 Strain–stress curves of vitrimerized polyurethane foams

3.5 | Foaming of vitrimerized network

As mentioned before, the vitrimerized network can be foamed again by applying heat and small pressure. Figure 5A shows that by applying 10 N force at temperature of 170°C foaming occurs in the vitrimerized network. The SEM images show that the initial foam has cell size around 250 µm and the cell size for the foam produced from the vitrimerized network is in the range of 200–500 µm. It should be noted that the work presented here for the foaming is an exploratory study and no process optimization was attempted. Further optimization will allow tailoring the density and cell structure of the foam.

3.6 | Mechanical properties of vitrimerized network

The mechanical properties of vitrimerized PU foam are evaluated by tensile tests, and the results are displayed in Figure 6. Significantly more rigid networks are obtained upon vitrimerization (Young's Modulus ≈ 2.7 GPa, tensile strength ≈ 76.45 MPa for the sample with 10 wt% TBD) compared to the initial PU foam (Young's Modulus ≈ 4 KPa, tensile strength ≈ 170 KPa as shown in Figure S3). Details of mechanical properties are summarized in Table S1. The tensile

strength (σ_{max}) and elongation at break (ϵ_b) both increase with increasing the catalyst concentration, attributed to increased hydrogen bonding in the network at higher catalyst concentrations as revealed by the FTIR results (Figure 2).

The vitrimerized network was reprocessed for the second time through grinding and ball milling without addition of any catalyst. The results (Figure 6) indicate that the vitrimerized network can be reprocessed without loss in the mechanical properties.

4 | CONCLUSION

Rigid PU foams can be recycled through vitrimerization using an organocatalyst (TBD). Stress relaxation results show that the vitrimerized network can relax stress rapidly. The dynamic networks have low activation energy (as low as 40 KJ/mol for 10 wt% TBD) which makes this vitrimerized material processable using common processing techniques such as injection molding and extrusion. The dynamic mechanical analysis indicates that the carbamate exchange reaction in the vitrimerized network is mainly occurring through a dissociative mechanism. The formation of free isocyanate during the exchange reaction at high temperatures (170°C) and under small pressure results in foaming of the vitrimerized network. The mechanical properties of the vitrimerized network are significantly higher compared to previous reported values in the literature for recycled PU foams. The vitrimerization process shows potential for converting the rigid PU foam waste already existing in the market into higher value-added products. This work can pave the way to overcome the challenges in recycling PU thermoset waste and tune the properties of vitrimerized network with minimum environmental impact.

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.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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