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Polyimine Vitrimers with Tunable Mechanical and Dynamic Properties via a Rigid-Flexible Strategy

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Abstract:

A series of polyimine vitrimers (TBD-x) based on dynamic imine bonds were synthesized via a rigid-flexible synergistic design strategy and systematically characterized. By adjusting the molar ratio between the rigid monomer 3,3'-DDS and the flexible siloxane monomer BAPT, the mechanical, thermal, and dynamic properties of the materials were effectively tuned. Increasing the 3,3'-DDS content raised the tensile strength from 40.3 to 78.3 MPa, the storage modulus from 1695.2 to 2777.6 MPa, and T_g from 98.2 to 160.7 °C, while the elongation at break decreased from 30.9% to 9.6%. In contrast, increasing the BAPT content lowered the activation energy for dynamic imine exchange from 68.50 to 32.92 kJ/mol and generally reduced T_v, indicating improved reprocessability. After three recycling cycles, all samples retained over 90% of their original tensile strength and elongation at break. Furthermore, TBD-5 attained a limiting oxygen index (LOI) of 30.1% and achieved a UL-94 V-0 rating. Among all compositions, TBD-3 showed the best overall balance of mechanical performance, thermal stability, and dynamic exchange behavior. This study provides an effective approach for developing recyclable polyimine vitrimers with tunable mechanical properties and balanced overall performance.

1. Introduction

Thermosetting polymers are widely used in aerospace, electronic packaging, and automotive manufacturing due to their excellent mechanical properties, thermal stability, and solvent resistance. However, their permanently cross-linked network structure makes them difficult to recycle after use, typically ending up in landfills or incinerators, which not only wastes resources but also causes severe environmental pollution^[1]. In contrast, while thermoplastic polymers can be remelted and reprocessed, they often suffer from insufficient heat resistance and dimensional stability. Therefore, developing novel polymeric materials that combine the superior performance of thermosets with the recyclability of thermoplastics has become a crucial research direction in polymer science.

Vitrimers are a class of emerging dynamic cross-linked polymeric materials, first conceptualized by Leibler et al. in 2011^[2]. These materials feature three-dimensional networks constructed through dynamic covalent bonds (e.g., disulfide bonds, ester bonds, imine bonds). Under specific stimuli (such as heat or light or pH), these dynamic bonds can undergo reversible exchange reactions, leading to rearrangement of the network topology and macroscopically exhibiting plasticity and reprocessability akin to thermoplastics. When the stimulus is removed, the material retains the structural stability of a cross-linked network, displaying characteristics of thermosets^[3,4]. This unique property enables vitrimers to bridge the gap between thermosetting and thermoplastic materials, offering a revolutionary approach to designing sustainable polymers.

Among various dynamic covalent bonds, the imine bond (-C=N-) has attracted significant attention due to its simple synthesis, high reactivity, fast exchange kinetics, and well-understood mechanisms^[5,6]. Through imine exchange reactions, polyimine vitrimers can achieve efficient self-healing, reshaping, and physical recycling. However, most reported polyimine vitrimers primarily employ rigid aromatic monomers as building blocks to

pursue high thermal stability and strength, often resulting in high brittleness and low elongation at break, which limits their application in scenarios requiring certain toughness^[7,8]. Furthermore, like many polymeric materials, polyimines are inherently flammable. Traditional additive flame retardants can enhance flame resistance but often disrupt the homogeneity of the dynamic network, hinder chain segment mobility, and severely degrade the dynamic properties such as stress relaxation, self-healing, and reprocessability of vitrimers^[9]. Therefore, a key scientific challenge for the practical application of polyimine vitrimers is how to simultaneously endow them with good comprehensive mechanical properties (high strength and high toughness) and good flame retardancy while preserving their excellent dynamic performance^[10,11].

Based on the above considerations, this study adopts a rigid-flexible synergistic design strategy to construct polyimine vitrimers^[12]. A novel symmetric tri(4-formyl-2-methoxyphenyl) phosphate monomer (TMP) was synthesized from biomass-derived vanillin and phosphorus oxychloride and used as a multifunctional cross-linker^[13,14]. The rigid aromatic diamine 3,3'-diaminodiphenyl sulfone (3,3'-DDS) and the flexible siloxane diamine 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane (BAPT) were selected as comonomers. By varying the ratio of these two diamines, a series of polyimine vitrimers (TBD-x) were prepared through dynamic imine chemistry. The effects of composition on the mechanical properties, dynamic behavior, thermal stability, recyclability, and combustion-related performance of the materials were systematically evaluated^[15]. This work aims to develop high-performance polyimine vitrimers with balanced mechanical properties and good reprocessability, thereby providing useful guidance for the design of sustainable and recyclable polymeric materials^[16,17].

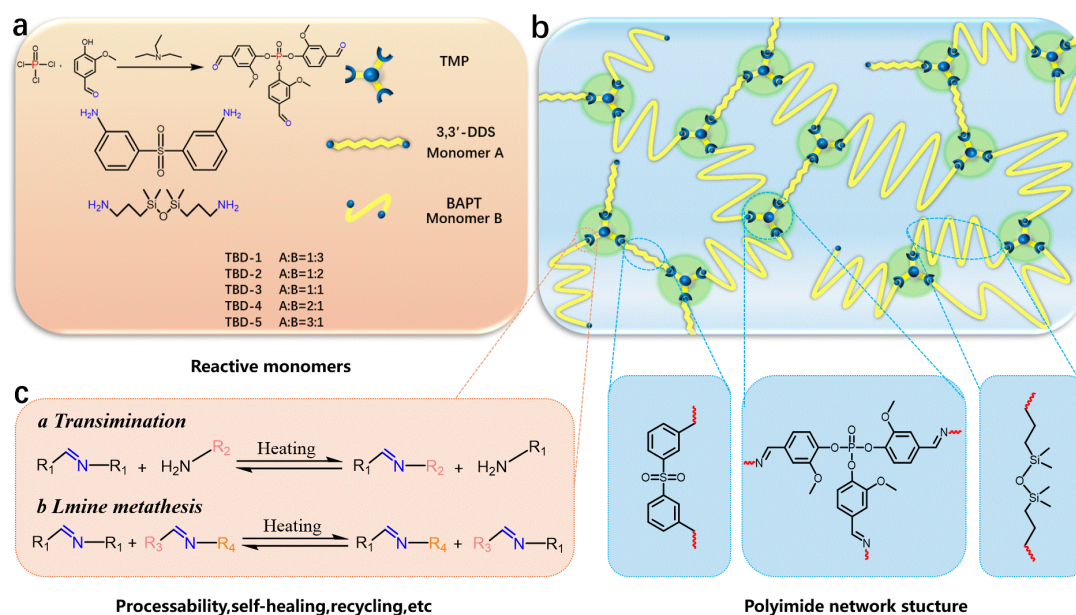


Figure 1. (a) Synthesis method of TMP, preparation of TBD-x. (b) Description of the microscopic composition and structure of TBD-x membranes. (c) And schematic diagram of the imine exchange mechanism.

2. Experimental Section

2.1 Materials

All chemical reagents and solvents, including vanillin, phosphorus oxychloride (POCl₃), 3,3'-diaminodiphenyl sulfone (3,3'-DDS), 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane (BAPT), Dimethylacetamide (DMAc), chloroform, petroleum ether, absolute ethanol (EtOH), triethylamine, methanol (MeOH), acetone (ACE), toluene (TOL), ethyl acetate (EtOAc), tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), and dichloromethane (DCM) were purchased from Shanghai Macklin Biochemical Technology Co., Ltd. Unless otherwise specified, all reagents were used as received without further purification.

2.2 Synthesis of the TMP

The TMP was synthesized from vanillin and phosphorus oxychloride following previously reported procedures^[18]. In a typical synthesis, vanillin (35.90 g, 236 mmol), triethylamine (23.88 g, 236 mmol), and chloroform (100 mL) were added to a 250 mL three-necked flask and stirred at room

temperature until complete dissolution (Figure 1a). The mixture was cooled to 0 °C in an ice bath, and a solution of phosphorus oxychloride (11.95 g, 78 mmol) in chloroform (30 mL) was added dropwise over 30 min under vigorous stirring. After stirring at 0 °C for an additional 30 min, the reaction was heated to 80 °C and refluxed for 5 h. Upon completion, the mixture was poured into 200 mL of petroleum ether to precipitate the product. The white precipitate was collected by filtration, washed thoroughly with absolute ethanol, and dried under vacuum at 80 °C to constant weight. The final product was obtained as a white solid with a yield of 93.5%. ¹H NMR (400 MHz, CDCl₃, δ ppm) : 9.91 (s, 3H), 7.48 (d, *J*=3.7, 1.8 Hz, 6H), 7.41 (d, *J*=8.5 Hz, 3H), 3.99 (q, *J*=7.1 Hz, 1H), 3.83 (s, 9H), 1.95 (s, 2H), 1.14 (t, *J*=7.1 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃, δ ppm): 56.1(–O–CH₃), 111.2(Ar), 121.6(Ar), 124.5(Ar), 134.6(Ar), 144.3(Ar), 151.4(Ar), 190.7(C=O); ³¹P NMR (240 MHz, CDCl₃, δ ppm): 18.65(P=O).

2.3 Preparation of Polyimine Vitrimers (TBD-x)

A series of polyimine vitrimers, denoted as TBD-x, were prepared by reacting the biomass-derived TMP serving as the cross-linking node with the rigid aromatic diamine 3,3'-DDS and the flexible siloxane diamine BAPT. The network formation mechanism involves an initial step-growth polymerization forming low-molecular-weight, linear or branched prepolymers, followed by an increase in cross-linking density as the reaction proceeds, ultimately leading to a three-dimensional cross-linked network structure^[8] (Figure 1). All polymers were designed with a fixed molar ratio of aldehyde groups (–CHO) to amine groups (–NH₂) at 1:1. By varying the molar feed ratio of the rigid (3,3'-DDS) to flexible (BAPT) diamine monomers, five compositions were synthesized and named TBD-1 to TBD-5. The specific feed molar ratios (BAPT : 3,3'-DDS) were 3:1, 2:1, 1:1, 1:2, and 1:3, respectively (Table 1).

Taking the representative sample TBD-3 as an example, the detailed preparation process is as follows: TMP (4 g, 8 mmol), 3,3'-DDS (1.48 g, 6 mmol), and BAPT (1.49 g, 6 mmol) were precisely weighed and dissolved

in 8 mL of DMAc with vigorous stirring to form a homogeneous solution. The solution was then transferred into a flat glass Petri dish. The dish was placed in a vacuum oven and heated at 100°C for 2 hours to initially form a transparent gel-like prepolymer. A stepwise heating protocol was subsequently applied for complete curing and solvent removal: 120°C for 1 hour, 150°C for 1 hour, and finally 160°C for 2 hours. This process ensured the complete formation of imine bonds and the solidification of the three-dimensional network, resulting in a transparent polyimine vitrimer film^[19,20].

Table 1. The molar feed ratio of BAPT to 3,3'-DDS in different TBD-x samples.

Mole ratio of BAPT and 3,3'-DDS		
Samples	BAPT	3,3'-DDS
TBD-1	3	1
TBD-2	2	1
TBD-3	1	1
TBD-4	1	2
TBD-5	1	3

2.4 Physical Recycling of TBD-x

The physical recycling of TBD-x was conducted via a hot-pressing method. Specifically, the TBD-x film was first cut into small pieces. These fragments were then sandwiched between two layers of aluminum foil. According to the glass transition temperature of each sample, appropriate recycling conditions were selected: TBD-1, TBD-2, TBD-3, TBD-4, and TBD-5 were hot-pressed at 100°C, 120°C, 140°C, 160°C, and 170°C, respectively, under a pressure of 15 MPa for a duration of 20 minutes. After the thermal treatment, the sample was allowed to cool down to room temperature, yielding a regenerated TBD-x film^[20,21]. The schematic of this recycling process is illustrated in Figure 2.

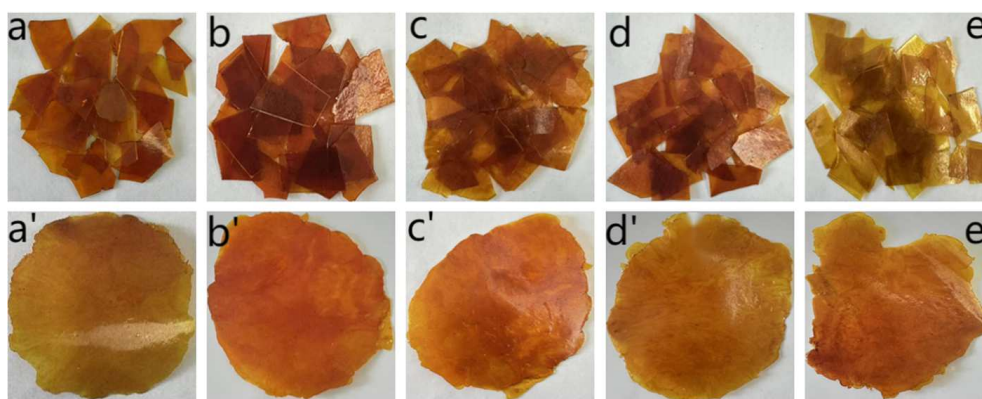


Figure 2. Fragments of TBD-1, TBD-2, TBD-3, TBD-4, TBD-5 and the smooth film obtained by hot pressing.

2.5 Characterization and Instrumentation

The ^1H NMR, ^{13}C NMR, and ^{31}P NMR spectra were recorded using deuterated chloroform (CDCl_3) as the solvent on Agilent 400 MHz (for ^1H NMR), 101 MHz (for ^{13}C NMR), and 240 MHz (for ^{31}P NMR) NMR spectrometers, respectively. The structural characterization of the film samples was performed by Fourier transform infrared (FT-IR) spectroscopy using a Thermo Fisher Nicolet 6700 spectrometer in reflection mode, with a scanning range of 400 to 4000 cm^{-1} . Mechanical properties were tested using a computer-controlled electronic universal testing machine (MTS Industrial Systems (China) Co., Ltd.) with dumbbell-shaped specimens (dimensions: $12\text{ mm} \times 4\text{ mm} \times 300\text{ }\mu\text{m}$) at a tensile rate of 2 mm/min . Stress relaxation tests were conducted on a TA Instruments Q800 dynamic mechanical analyzer (DMA), where the sample was stretched by 1% under an axial force of 0.001 N and the strain was held constant. Dynamic mechanical analysis (DMA) was performed using a TA Q850 instrument to determine the storage modulus and loss factor ($\tan \delta$) at a frequency of 1 Hz and a heating rate of $10\text{ }^\circ\text{C/min}$. Thermogravimetric analysis (TGA) was carried out on a Mettler Toledo TGA1 instrument under a nitrogen atmosphere (flow rate: 50 mL/min) with a heating rate of $10\text{ }^\circ\text{C/min}$ from 30 to $800\text{ }^\circ\text{C}$. The fracture morphology of the dumbbell-shaped specimens was observed using a JEOL JSM5510LV scanning electron microscope (SEM) at an accelerating voltage of 10 kV . The morphology of the

residual carbon layer was characterized by a Hitachi S4800 field-emission scanning electron microscope (FE-SEM) at an accelerating voltage of 5 kV, and its elemental composition was analyzed using a Horiba EMAX energy-dispersive X-ray spectroscopy (EDS) system with a resolution of 129 eV.

3. Results and Discussion

3.1 Synthesis and Characterization of TMP

Following the procedure described in Section 2.2, a biomass-derived triaromatic trialdehyde monomer (TMP) with a phosphorus oxychloride backbone was successfully synthesized. Its chemical structure was confirmed by nuclear magnetic resonance (NMR) spectroscopy, including ^1H NMR, ^{13}C NMR, and ^{31}P NMR (Figure 3).

The ^1H NMR spectrum (Figure 3b) revealed the following signals: a strong peak at $\delta = 3.83$ ppm with an integrated area corresponding to 9.06 protons, assigned to the nine hydrogen atoms of the three methoxy groups (H5); signals at $\delta = 7.48$ ppm and $\delta = 7.41$ ppm (split into a doublet due to spin-spin coupling) corresponding to three types of aromatic protons in different chemical environments (H2, H3, H4); and a singlet at $\delta = 9.91$ ppm attributed to the three aldehyde protons (H1). The ratio of the integrated peak areas was $\text{H1} : (\text{H2}+\text{H3}) : \text{H4} : \text{H5} \approx 3.0 : 6.1 : 3.07 : 9.06$, consistent with the expected proton distribution in the target structure.

The ^{13}C NMR spectrum (Figure 3c) further supported the structural framework: signals at $\delta = 56.1$ ppm and 190.7 ppm were assigned to the methoxy carbon (C8) and aldehyde carbon (C1), respectively; signals at $\delta = 111.2, 121.6, 124.5, 134.6, 144.3$, and 151.4 ppm were all attributed to the six carbon atoms of the aromatic rings. Additionally, the ^{31}P NMR spectrum (Figure 3d) displayed a single peak at $\delta = 18.65$ ppm, confirming the presence of phosphorus and indicating the successful incorporation of the phosphorus moiety into the TMP molecule^[18].

The main functional groups of TMP were analyzed by Fourier transform

infrared (FT-IR) spectroscopy (Figure 3a). The spectrum showed a strong absorption band at 1703 cm^{-1} , characteristic of the carbonyl (C=O) stretching vibration of the aldehyde group; a weak band at 2720 cm^{-1} was assigned to the C–H stretching vibration of the aldehyde group. Weak absorptions at 2950 cm^{-1} and 2870 cm^{-1} corresponded to the asymmetric and symmetric stretching vibrations of the methyl ($-\text{CH}_3$) groups, respectively. Strong peaks at 1197 cm^{-1} and 1028 cm^{-1} were identified as the asymmetric and symmetric bending vibrations of the C–O–C bonds. Furthermore, absorption bands in the range of $1595\text{--}1440\text{ cm}^{-1}$ were characteristic of aromatic ring skeletal vibrations, while bands in the $976\text{--}631\text{ cm}^{-1}$ region belonged to the fingerprint region of the aromatic rings^[22,23]. All spectroscopic data were in full agreement with the expected structure of TMP, confirming its successful synthesis.

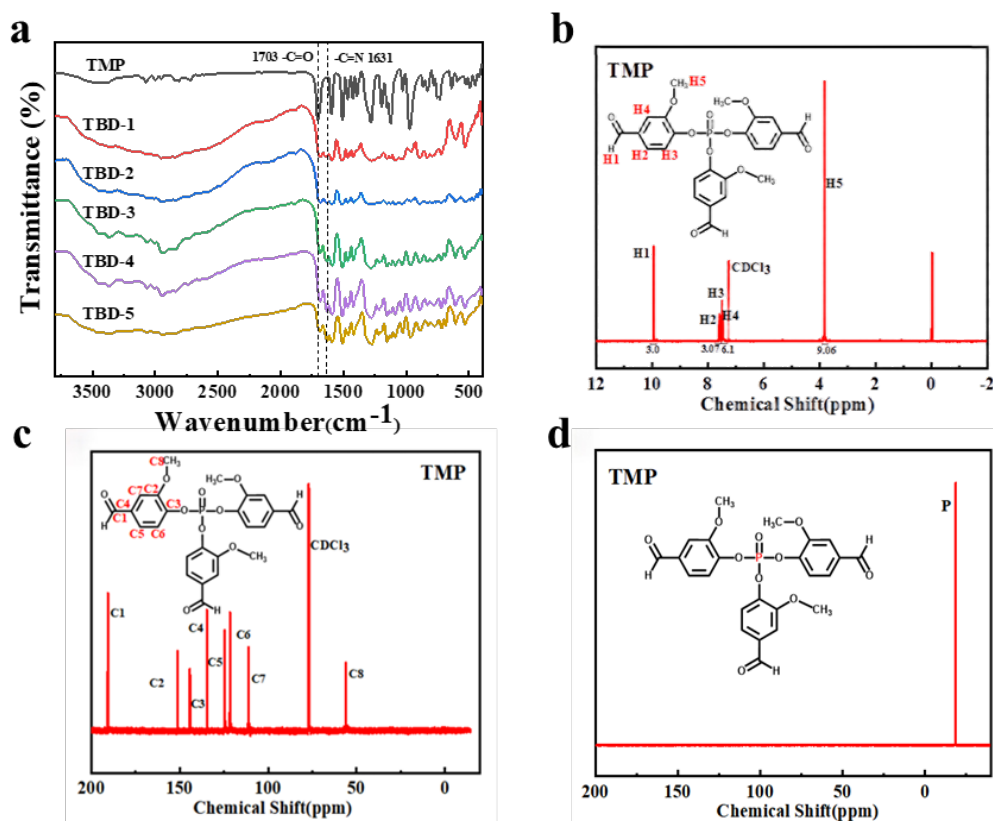


Figure 3. FT-IR of TMP and TBD-x(a), ^1H NMR spectrum of TMP (b), ^{13}C NMR spectrum of TMP (c), and ^{31}P NMR spectrum of TMP (d).

3.2 Preparation of Imine-Based Vitrimers TBD-x

A series of imine-based vitrimers, designated as TBD-x, were prepared by curing the trialdehyde monomer TMP with varying molar ratios of 3,3'-DDS and BAPT. Taking the synthesis of TBD-3 as an example: first, the reaction mixture was treated at 100°C for 2 hours to perform pre-curing and remove the solvent, yielding a transparent gel-like prepolymer. Subsequently, a stepwise heating program was applied, maintaining the temperature at 120°C and 150°C for 1 hour each to promote further curing and eliminate residual solvent. Finally, the sample was held at 160°C for 2 hours to complete the final cross-linking and ensure complete removal of the solvent DMAc. To enhance material densification and obtain samples suitable for testing, the resulting products TBD-1, TBD-2, TBD-3, TBD-4, and TBD-5 were hot-pressed at 100°C, 120°C, 140°C, 160°C, and 170°C, respectively, under a pressure of 15 MPa for 20 minutes, ultimately yielding smooth and transparent films^[13].

The chemical structures of all cured TBD-x samples were characterized using FT-IR, and the spectra were compared with that of the starting material TMP. As shown in Figure 3a, TMP exhibited a distinct characteristic absorption peak of the aldehyde group (-CHO) at 1703 cm^{-1} , while no significant absorption was observed near 1631 cm^{-1} . In contrast, all five TBD-x samples showed a strong absorption peak at 1631 cm^{-1} , attributed to the stretching vibration of the imine bond (-CH=N-). Simultaneously, the characteristic aldehyde peak at 1703 cm^{-1} was significantly weakened or nearly absent. This change indicates that the aldehyde groups were fully consumed during the curing process and converted into imine bonds.

The FT-IR analysis results demonstrate that the cured TBD-x films contain only trace amounts of aldehyde groups, with the majority having been converted into corresponding imine bonds via the Schiff base reaction. This confirms that the imine-based vitrimers were formed through the condensation reaction between -CHO and -NH_2 groups, and the reaction proceeded to near completion, indicating a high conversion of aldehyde groups into imine linkages.

3.3 Mechanical Properties of TBD-x

Dog-bone-shaped specimens with various component ratios and recycling cycles were prepared in large quantities. For each group, five defect-free specimens were selected and tested for tensile properties using a universal testing machine. Statistical analysis of the data was performed, and stress-strain curves were plotted, revealing a clear composition-dependent structure-property relationship^[24,25]. As shown in Table 3, the maximum tensile strengths of TBD-1 to TBD-5 were 40.3MPa, 45.3 MPa, 67.9 MPa, 72.5 MPa, and 78.3 MPa, respectively, while their elongation at break values were 30.9%, 19.5%, 11.8%, 10.9%, and 9.6%, respectively. With increasing content of the rigid monomer 3,3'-DDS, both tensile strength and elastic modulus gradually increased. In contrast, higher content of the flexible monomer BAPT led to significantly improved elongation at break and a distinct cold-drawing stage in the stress-strain curves. These differences in mechanical behavior originate from the distinct contributions of BAPT and 3,3'-DDS molecular structures to the characteristics of the dynamic cross-linked network^[26].

In TBD-1 and TBD-2, which contain higher BAPT content, the abundant siloxane segments reduce the internal rotational energy barrier and increase free volume, endowing the chain segments between cross-links with spring-like flexibility. As shown in Figure 4(a), these samples exhibit lower elastic modulus, a prolonged cold-drawing stage after yielding, and eventual ductile fracture, demonstrating high elongation at break and fracture energy — characteristics of a "soft yet tough" mechanical profile. Conversely, in TBD-4 and TBD-5, where 3,3'-DDS dominates, the highly conjugated rigid aromatic structures are arranged in a centrosymmetric manner, significantly increasing the internal rotational energy barrier and reducing free volume, thereby enhancing the rigidity of chain segments between cross-links. As shown in Figure 4(a), these samples display higher elastic modulus, brief yielding, and rapid brittle fracture, representing a "strong yet brittle"

mechanical behavior. Notably, when the BAPT to 3,3'-DDS ratio is 1:1 (TBD-3), the material forms an interpenetrating rigid-flexible cross-linked network. The rigid segments provide load-bearing capacity, while the flexible segments dissipate external energy through limited motion, achieving an optimal balance of strength and toughness^[27,28]. As shown in Figure 4(a), TBD-3 maintains relatively high elastic modulus and tensile strength while retaining a certain degree of plastic deformation capability, exhibiting a "strong yet tough" mechanical profile.

SEM analysis of fracture surfaces after tensile testing further revealed the fracture mechanisms at the microscopic level^[29]. As shown in Figures 4(e) and 4(f), the fracture surfaces of TBD-1 and TBD-2 exhibit typical dimple morphology—cup-shaped pits with dark centers and bright edges—indicating microvoid coalescence and plastic deformation during fracture, characteristic of ductile failure. The dimples in TBD-1 are smaller and more uniformly distributed than those in TBD-2, implying greater energy dissipation during plastic deformation, consistent with its higher elongation at break. In contrast, the fracture surfaces of TBD-4 and TBD-5 are smooth and display river-like patterns, with markings aligned in the direction of crack propagation, consistent with brittle fracture characteristics^[30] (Figures 4(g) and 4(h)). The surface of TBD-4 is slightly rougher than that of TBD-5, corresponding to its slight yielding during stretching, whereas TBD-5 underwent almost no yielding before brittle fracture. The fracture surface of TBD-3 shows a mixed brittle-ductile morphology (Figure 4(i)), with shallow dimples in some regions interspersed with river-like patterns^[20].

In summary, by adjusting the molar ratio of 3,3'-DDS to BAPT, the cross-linked network structure of imine-based vitrimers can be effectively tailored, enabling precise design of mechanical properties to achieve a balanced material system that combines high tensile strength with high elongation at break.

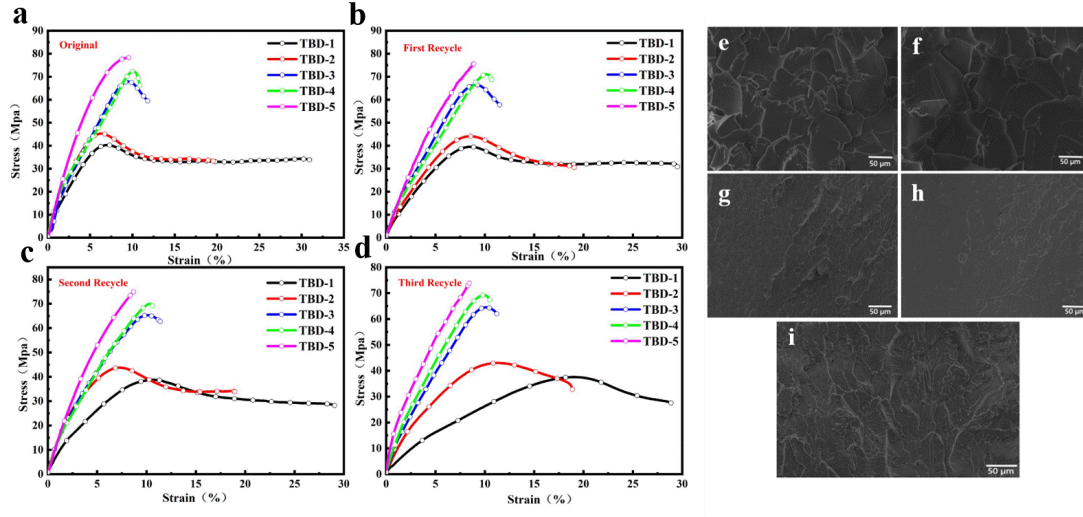


Figure 4. Stress-strain curves of TBD-1, TBD-2, TBD-3, TBD-4, and TBD-5 without recovery(a) and three cycles(b-d). SEM images of the fracture surfaces of tensile test specimens of TBD-1(e), TBD-2(f), TBD-4(g), TBD-5(h) and TBD-3(i).

3.4 Ductility and Dynamic Properties of TBD-x

The glass transition temperature (T_g) is a key thermodynamic parameter that determines the ductility and processability of materials, and it is closely related to the exchange capability of dynamic covalent bonds. Stress relaxation testing is an important method for characterizing the dynamic behavior of vitrimers. By measuring the time required for stress to decay to $1/e$ of its initial value (τ), the activation energy (E_a) of the dynamic bond exchange reaction can be calculated, thereby evaluating the material's reprocessability.

Stress relaxation tests conducted on the TBD-x series at different temperatures showed that for the same composition, increasing temperature significantly shortened the relaxation time τ , indicating that high temperature promotes the dynamic exchange reaction of imine bonds. The activation energy of the imine exchange reaction can be obtained by fitting the Arrhenius equation^[31,32]:

$$\ln \tau = \frac{E_a}{RT} - \ln A \quad (1)$$

where T is the absolute temperature, A is the pre-exponential factor, and

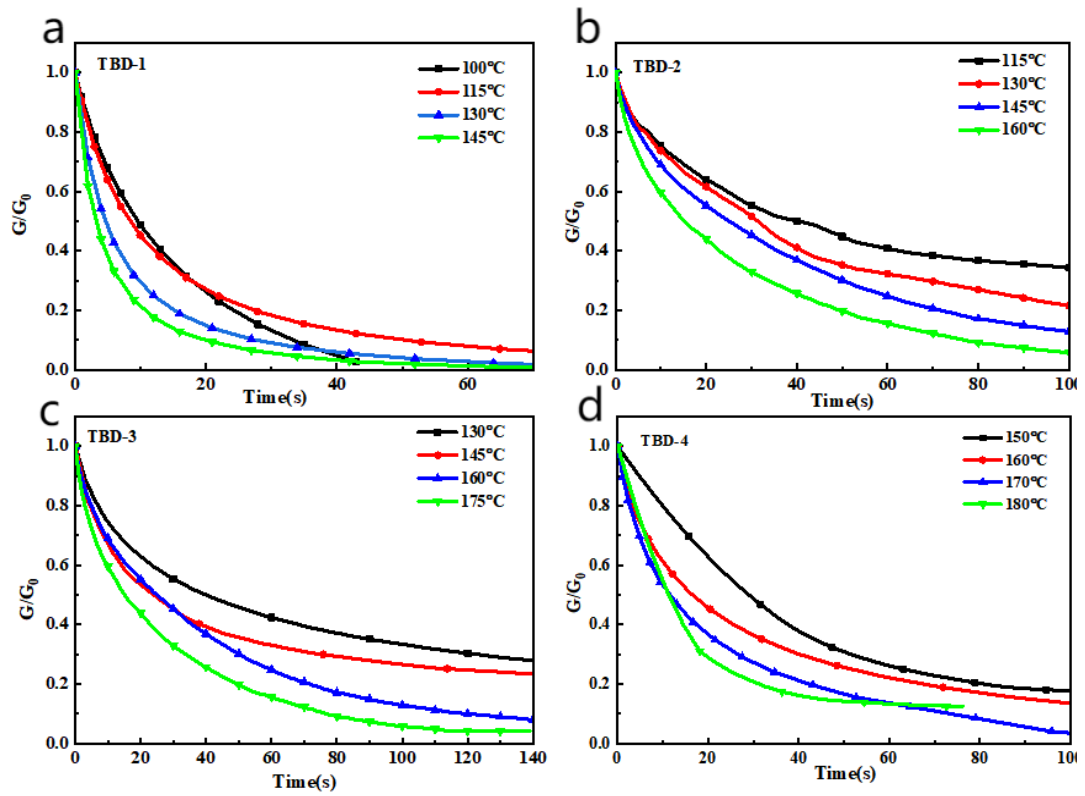
R is the molar gas constant. The slope k is obtained through linear fitting, and the activation energy is calculated as $E_a = kR$. As shown in Table 2, the activation energies of TBD-1 to TBD-5 are 32.92 kJ/mol, 33.59 kJ/mol, 35.83 kJ/mol, 53.62 kJ/mol, and 68.50 kJ/mol, respectively. The activation energy exhibits clear composition dependence: as the proportion of BAPT increases and that of 3,3'-DDS decreases, the activation energy gradually decreases (Figure 5).

The reduction in activation energy can be attributed to the following three mechanisms: (1) "Dilution Effect" of Chemical Bond Energy: The original rigid network is mainly formed by the reaction of TMP and 3,3'-DDS, with cross-linking points consisting of aromatic imine ($\text{Ar}-\text{CH}=\text{N}-\text{Ar}$) and phosphate ester bonds ($\text{Ar}-\text{O}-\text{P}$), which have high bond energies (C=N bond ~ 615 kJ/mol, P-O bond ~ 335 kJ/mol) and are constrained within the rigid aromatic network, requiring high energy to break. Introducing siloxane soft segments ($\text{Si}-\text{O}-\text{Si}$) replaces some aromatic imines with aliphatic imines connected to siloxane ($-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{N}=\text{CH}-$), which have lower C=N bond energy. Although the Si-O-Si bonds in the siloxane backbone have relatively high bond energy (~ 460 kJ/mol), their unique bond length and bond angles confer high flexibility and easy torsional mobility. This allows thermal energy to concentrate more easily on weaker bonds such as Si-C bonds (~ 318 kJ/mol) or aliphatic C=N bonds during heating, making them initiation weak points for thermal exchange. Higher siloxane content increases the proportion of low-bond-energy, easily breakable chemical bonds in the network, thereby lowering the average exchange activation energy of the entire network^[33]. (2) Free Volume and Stress Concentration Effects in Topological Structure: The pure 3,3'-DDS system is a highly cross-linked rigid network with small free volume and restricted molecular chain segment mobility. Under heating, internal stress is difficult to release, requiring accumulation of substantial energy to initiate cooperative bond breakage across the rigid network. Introducing siloxane flexible spacers, particularly long and flexible siloxane

chains with tetramethyl substitution (which have large steric hindrance and excellent flexibility), significantly increases free volume and reduces overall cross-link density^[34]. Under heating, flexible siloxane segments can dissipate energy through conformational changes and motion, avoiding excessive stress accumulation. Simultaneously, the interface between the rigid aromatic domains (composed of 3,3'-DDS and TMP) and the flexible siloxane domains becomes a stress concentration zone due to structural mismatch. These interfacial defects and local high stress serve as preferential initiation weak points for thermal exchange, thereby lowering the macroscopically measured overall activation energy. (3) "Promotion Effect" of Thermal Conduction and Local Overheating: The thermal conductivity of polysiloxanes is generally higher than that of aromatic polymers. Higher siloxane content can improve internal heat conduction, allowing heat to transfer faster and more uniformly throughout the material rather than accumulating locally to form "hot spots." More uniform and rapid heat transfer means the material can reach its exchange temperature more quickly, kinetically manifesting as a reduction in apparent activation energy—thermal exchange no longer requires overcoming a high local energy barrier to initiate.

As shown in Table 2, the activation energy for dynamic exchange of imine bonds in the TBD-x series increases significantly with higher 3,3'-DDS content. TBD-1, TBD-2, and TBD-3 all exhibit relatively low activation energies (<36 kJ/mol), primarily due to the lower reversible exchange activation energy of aliphatic imine bonds derived from BAPT, which dominate the network. However, when the 3,3'-DDS content further increases, the activation energy of TBD-4 (53.62 kJ/mol) shows a significant jump compared to TBD-3, indicating that the exchange reaction of aromatic imine bonds with higher activation energy has become the dominant process. Notably, the TBD-3 sample, which exhibits the best overall mechanical performance, also possesses a relatively low activation energy (35.83 kJ/mol). This indicates that while maintaining excellent mechanical properties, it still

demonstrates good recyclability and reprocessing potential, showing promising prospects for practical applications^[35].



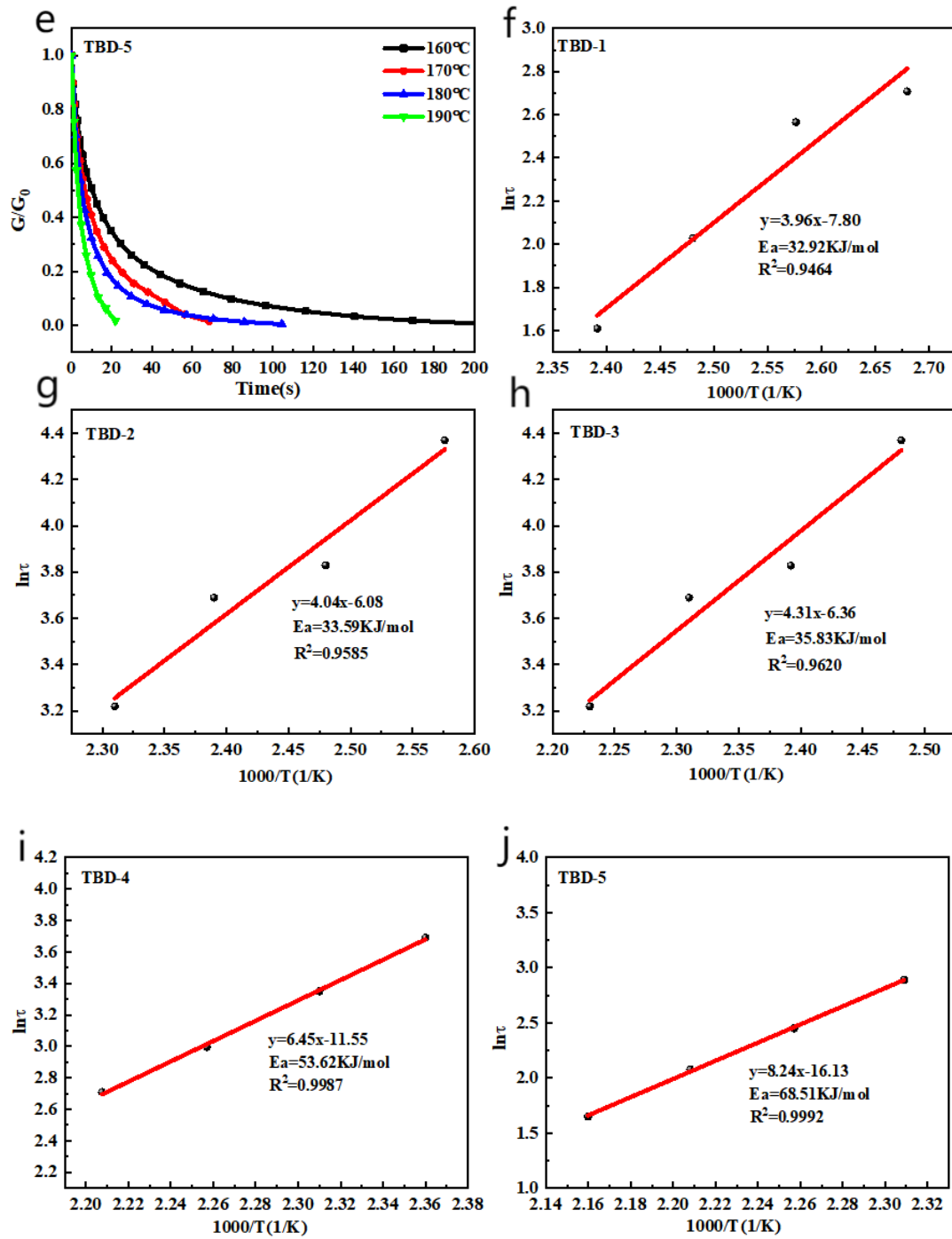


Figure 5. (a, b, c, d, e) represent the stress relaxation of TBD-x at different temperatures, and (f, g, h, i, j) represent the fitted activation energies.

Table 2. The time required for the stress relaxation of TBD-x to decrease to 1/e of the initial value at different temperatures, and the fitted activation energy.

Samples	Relaxation times (s)	Relaxation times (s)	Relaxation times (s)	Relaxation time (s)	Ea (kJ/mol)
TBD-1	15.0/100°C	13.0/115°C	7.6/130°C	5.0/145°C	32.92
TBD-2	79.0/115°C	46.0/130°C	40.0/145°C	25.0/160°C	33.59
TBD-3	78.9/130°C	46.1/145°C	39.9/160°C	25.0/175°C	35.83
TBD-4	40.1/150°C	28.5/160°C	20.0/170°C	15.0/180°C	53.62
TBD-5	18.0/160°C	12.6/170°C	8.0/180°C	5.2/190°C	68.51

3.5 Recyclability and Reprocessability of TBD-x

To evaluate the physical recycling capability of the TBD-x series, sample fragments were placed in a plate vulcanizer and hot-pressed under 15 MPa for 20 minutes at temperatures tailored to each composition: 100 °C for TBD-1, 120 °C for TBD-2, 140 °C for TBD-3, 160 °C for TBD-4, and 170 °C for TBD-5, successfully obtaining uniform and smooth regenerated films (Figure 2). This macroscopic phenomenon indicates that dynamic imine bonds underwent effective exchange reactions during hot-pressing, allowing the material to reform a complete three-dimensional cross-linked network. All five sample groups demonstrated good recyclability and reprocessability^[30].

By comparing the mechanical properties of the original samples with those of each generation of recycled samples, the potential for cyclic utilization of the materials was systematically evaluated. Figure 6 shows the stress and strain recovery efficiencies obtained from the stress-strain tests. After the first recycling, the maximum fracture strength of each sample remained highly similar to the original values: the stress recovery rates for TBD-1 to TBD-5 were 98.0%, 97.4%, 97.9%, 98.1%, and 96.6%, respectively, with a maximum strength loss of only 3.4%. The strain recovery rates were 95.5%, 97.9%, 97.5%, 98.2%, and 92.7%, respectively (Table 3). Except for TBD-5, the strain recovery rates of the other samples remained at relatively

high levels, which is related to the dominance of highly reactive imine bonds derived from BAPT in the system. Overall, TBD-x can effectively restore its initial network structure through reprocessing while largely retaining its original mechanical properties.

After the second and third recycling cycles, the mechanical strength and flexibility of TBD-x showed slight declines. This is primarily attributed to two factors: first, moisture in the air during processing may cause reversible hydrolysis of imine bonds, while oxygen may induce oxidation reactions, with both effects synergistically partially damaging the dynamic cross-linked network; second, repeated hot-pressing may further increase the cross-link density of imine bonds, enhancing network rigidity and consequently reducing elongation at break.

Although the overall mechanical performance of TBD-x gradually declined with increasing recycling cycles, after three cycles, both stress and strain recovery efficiencies remained above 90% of the original values, demonstrating excellent mechanical stability. This characteristic indicates that this material system holds significant potential for applications requiring high recycling efficiency.

Table 3. Data on the maximum stress and elongation at break of TBD-x without recycling and after three recycling cycles.

Samples	Original		1st Recycled		2nd Recycled		3rd Recycled	
	σ_m /MPa	ε_b /%	σ_m /MPa	ε_b /%	σ_m /MPa	ε_b /%	σ_m /MPa	ε_b /%
TBD-1	40.3	30.9	39.5	29.5	38.8	29.1	37.5	28.9
TBD-2	45.3	19.5	44.1	19.1	43.8	18.9	43.1	18.9
TBD-3	67.9	11.8	66.5	11.5	65.3	11.4	64.5	11.2
TBD-4	72.5	10.9	71.1	10.7	69.8	10.6	69.2	10.5
TBD-5	78.3	9.6	75.6	8.9	74.9	8.8	73.9	8.7

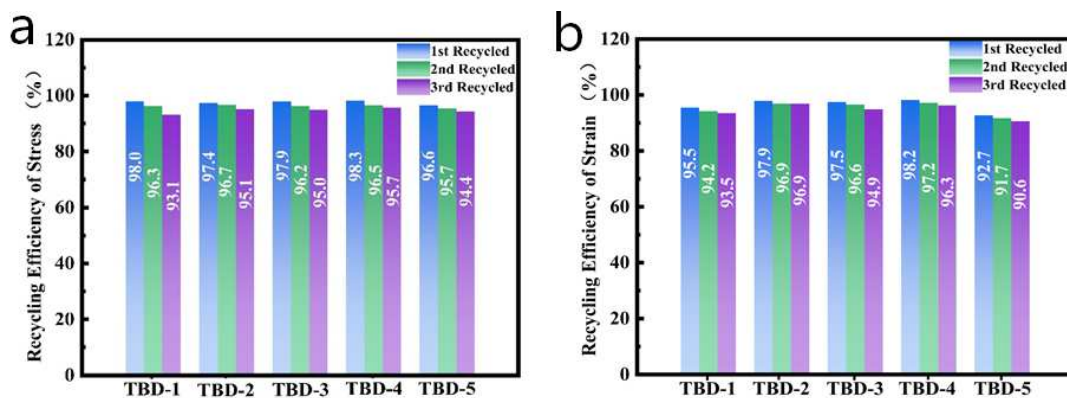


Figure 6. Cycling efficiency of stress (a) and strain (b) for TBD-x after three cycles.

3.6 Thermal Properties of TBD-x

The thermal and mechanical properties of the TBD-x were systematically investigated using DMA. The results indicate that as the proportion of the 3,3'-DDS component increases and the proportion of the BAPT component decreases, T_g shows a significant upward trend. Further DMA testing yielded T_g values of 98.2°C, 104.3°C, 136.7°C, 153.8°C, and 160.7°C. The variation in T_g is primarily attributed to differences in molecular chain structure: the flexible siloxane groups (-Si-O-) in the BAPT backbone facilitate internal rotation, enhancing the mobility of polymer chain segments and thereby lowering T_g . In contrast, the diphenyl sulfone structure in 3,3'-DDS contains two non-coplanar benzene rings, resulting in significant steric hindrance that restricts single-bond rotation, reduces chain segment mobility, and leads to an increase in T_g ^[36,37].

According to the DMA test results (Figure 7(a-e)), the storage modulus curves of TBD-x exhibit only a single transition from the glassy state to the viscoelastic state, with no secondary transition plateau observed^[26,28]. Simultaneously, the loss factor ($\tan \delta$) curves all display a single peak, indicating a homogeneous cross-linked network structure within the materials. In the glassy region, the storage moduli of TBD-1 to TBD-5 are 1695.2, 1921.2, 2050.7, 2697.5, and 2777.6 MPa, respectively, while the loss moduli are 97.2, 101.7, 111.1, 160.1, and 182.5 MPa, respectively (Table 4). As the content of 3,3'-DDS increases, both storage modulus and loss modulus rise

significantly, indicating enhanced material rigidity. This trend is consistent with the results from static mechanical testing and stress relaxation analysis.

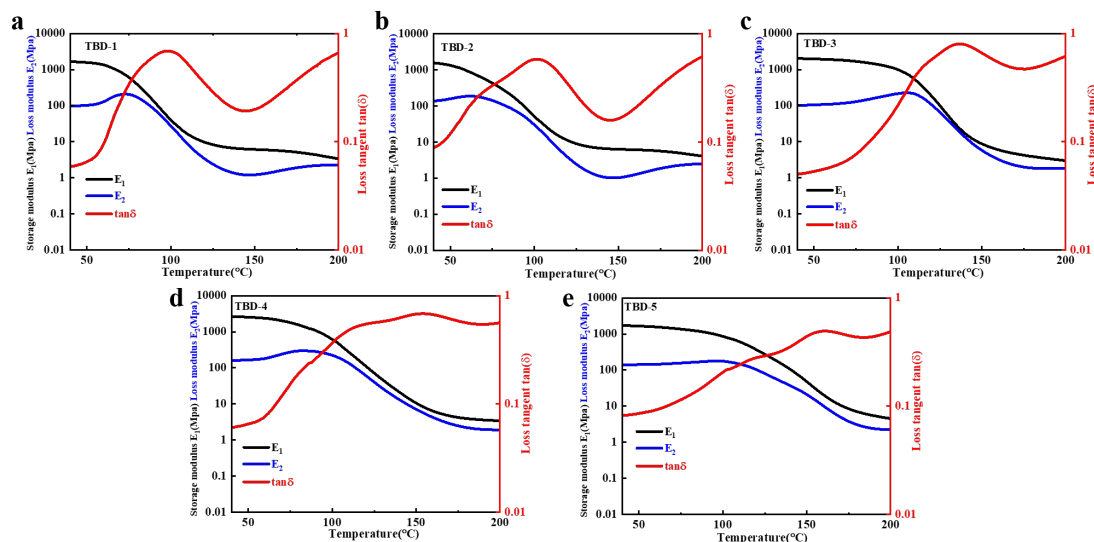


Figure 7. DMA curves of TBD-x, TBD-1(a); TBD-2(b); TBD-3(c); TBD-4(d); (e) TBD-5(e).

Table 4. Storage modulus, loss modulus, and Tg determined from the tan δ peak of TBD-x.

Samples	Storage modulus E_1 (Mpa)	Loss modulus E_2 (Mpa)	Tg from tan δ peak ($^{\circ}$ C)
TBD-1	1695.2	97.2	98.2
TBD-2	1921.2	101.7	104.3
TBD-3	2050.7	111.1	136.7
TBD-4	2697.5	160.1	153.8
TBD-5	2777.6	182.5	160.7

The thermal decomposition behavior of the TBD-x series was investigated using TGA, and DTG curves were plotted based on the mass loss rate data (Figure 8). All samples began to decompose at approximately 200 $^{\circ}$ C, with their thermal stability showing clear composition dependence. The T_{5%} values for TBD-1 to TBD-5 were 314 $^{\circ}$ C, 318 $^{\circ}$ C, 316 $^{\circ}$ C, 308 $^{\circ}$ C, and 275 $^{\circ}$ C,

respectively. At 800°C, the residual mass fractions were 53.2%, 58.9%, 60.4%, 64.7%, and 63.8%, respectively. Before 335 °C, TBD-1 showed the highest residual mass, indicating better resistance to early-stage thermal decomposition. However, above 335 °C, TBD-4 and TBD-5 retained more mass than the other samples, whereas TBD-1 exhibited the lowest residual mass at high temperature. This result suggests that TBD-1 possesses relatively better initial thermal stability, while TBD-4 and TBD-5 exhibit stronger high-temperature carbonization ability. This phenomenon stems from the different thermal decomposition characteristics of the two structural units: the rapid decomposition range of pure 3,3'-DDS is 250–280°C, while the main decomposition temperature range of BAPT is 300–350°C. From the DTG curves, it can be observed that the thermal decomposition process of all samples consists of two stages. The first stage (205–270°C) corresponds to the initial cleavage of the 3,3'-DDS structural units, during which the cross-linked network remains relatively intact overall. The decomposition rate in this stage increases with higher 3,3'-DDS content, with TBD-5 exhibiting the fastest decomposition rate due to its highest proportion of 3,3'-DDS. The second stage (280–420°C) is the main decomposition phase, involving the breakage of BAPT structural units, leading to severe damage to the network structure and a significant increase in mass loss rate. The decomposition rate in this stage and the residual mass fraction at 800°C are closely related to the BAPT content: higher BAPT proportions result in greater mass loss rates in this stage and lower final residual mass fractions. The above results indicate that by adjusting the ratio of 3,3'-DDS to BAPT, the thermal decomposition behavior and char-forming ability of imine-based vitrimers can be effectively regulated, providing a design basis for their application in high-temperature environments.

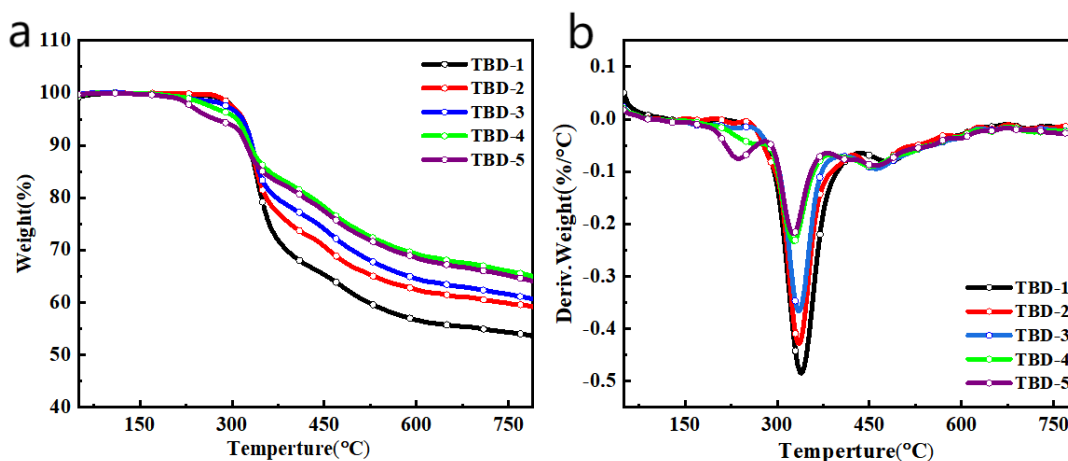


Figure 8. TG and DTG curves of TBD-x.

Based on Equation (1), with the characteristic relaxation time set to $\tau = 100$ s, the topological freezing transition temperatures (T_v) for TBD-1 to TBD-5 were calculated as 46.0°C, 104.9°C, 119.8°C, 126.1°C, and 124.2°C, respectively (Table 5). It is noteworthy that although TBD-5 exhibits a higher activation energy (68.50 kJ/mol) than TBD-4 (53.62 kJ/mol), its T_v (124.2 °C) is slightly lower than that of TBD-4 (126.1 °C). This indicates that T_v is not solely determined by E_a . According to the Arrhenius equation, $T_v = E_a/[R \cdot \ln(\tau/\tau_0)]$, the pre-exponential factor τ_0 also plays a critical role. The highly rigid aromatic network of TBD-5 imposes greater conformational constraints on chain segments in the ground state. Upon reaching the transition state for imine exchange, a larger gain in conformational freedom results in a more favorable activation entropy, leading to a smaller τ_0 that partially offsets the higher E_a . Consequently, TBD-5 requires a slightly lower temperature than TBD-4 to achieve the same relaxation time, highlighting the importance of both energetic and entropic contributions in governing the reprocessability of vitrimers.

T_v can serve as an indicator to evaluate the difficulty of material reprocessing: a higher T_v indicates that the material requires greater energy input during reprocessing, correspondingly increasing the difficulty of recycling and reshaping^[41]. However, lowering T_v typically leads to a

reduction in the material's thermal stability, manifested as a simultaneous decrease in the T_g. As shown in Table 5, the sample with the lowest T_g corresponds to the lowest T_v, and T_v increases with rising T_g, but the rates of increase differ between the two. This asynchronous variation provides the possibility of designing vitrimers with both low T_v (high recyclability) and high T_g (high thermal stability) through compositional tuning. Comparing the T_g and T_v of the five compositions reveals that the T_v of all samples is lower than their corresponding T_g, indicating that these materials can be recycled and their networks reconstituted under conditions below their service temperature. Notably, TBD-1, TBD-4, and TBD-5 exhibit a larger difference between T_g and T_v, while the values for TBD-2 and TBD-3 are relatively close. For TBD-1, efficient recycling can be achieved at low temperatures below 100°C while still maintaining thermal stability that meets practical application requirements. This phenomenon suggests that, provided the thermal performance meets usage requirements, systems with a larger T_g–T_v gap are more amenable to low-temperature reprocessing, offering important design insights for balancing the reprocessability and thermal stability of recyclable polyimine vitrimers^[38].

Table 5. T_g data of TBD-x, temperature at 5% weight loss, residual mass percentage at 800 °C, and topological freezing transition temperature.

Samples	T _g /°C	T _{5%} /°C	Char residues	T _v /°C
			at 800°C(%Wt)	
TBD-1	98.2	314	53.2	46.0
TBD-2	104.3	318	58.9	104.9
TBD-3	136.7	316	60.4	119.8
TBD-4	153.8	308	64.7	126.1
TBD-5	160.7	275	63.8	124.2

The TBD-3 sample, which exhibits the best overall performance, was compared with similar materials reported in the literature, as summarized in Table 6. TBD-3 demonstrates not only high mechanical strength and thermal stability but also a low activation energy for dynamic exchange reactions and a relatively low topological freezing transition temperature. This combination achieves an optimal balance between rigidity and flexibility, successfully resolving the inherent trade-off between high thermal stability and easy recyclability^[39].

Table 6. Comparative analysis of the properties of TBD-3 and similar materials reported in the literature.

Sample	Tg ^a /°C	Tg ^b /°C	T _{5%} /°C	Ea/kJ/mol	Tensile strength and strain	Ref
BioSi- PABZ-4	-	98	200~23 0	53.6	28.0 MPa / >60%	[19]
CTM- 2.875	138	167	423	67.9	50.0 MPa / 12%	[20]
VNTMSi- EP/DDM	72	-	-	50.6	49.0 MPa / 13%	[38]
LP-40%	-	78	322	49.6	18.4 MPa / 11%	[39]
HVPA/G DE	82	117.6	-	74.5	50.0 MPa / 5%	[40]
TBD-3	-	136.7	316	35.83	67.9 MPa / 11.8%	This work

^a by DSC test. ^b by DMA test.

3.7 Solvent Resistance of TBD-x

To evaluate the solvent resistance of TBD-x, TBD-3 with balanced mechanical properties and good reprocessability was selected and machined into standard dumbbell-shaped specimens. These were immersed in 10 common organic solvents at room temperature for 24 hours^[40]. The

experimental results show that the samples exhibited no significant changes in MeOH, EtOH, ACE, TOL, or EtOAc; slight swelling occurred in THF, DMSO, DMF, and DMAc; only in DCM did significant swelling occur, accompanied by a loss of mechanical properties (Figure 9). This phenomenon can be attributed to the strong interaction between solvent molecules and the permanent dipole moment of the imine groups in the polymer. This polarity-matching effect surpasses simple polar interactions, and the small molecular size of DCM facilitates its penetration into the cross-linked network, significantly enhancing swelling efficiency. The above results indicate that TBD-x exhibits good solvent resistance in non-polar solvents, alcoholic solvents, and highly polar solvents such as DMF, DMAc, and DMSO.



Figure 9. TBD-3 immersed in different solvents at room temperature for 0 hours (a) and 24 hours (b).

3.8 Flame Retardancy of TBD-x

To enhance the practical application of the TBD-x series, its flame retardancy was preliminarily evaluated using LOI and UL-94 tests. As shown in Table 7, the LOI values of TBD-1 to TBD-5 are 22.6%, 23.8%, 28.4%, 28.6%, and 30.1%, respectively, exhibiting a clear upward trend with increasing 3,3'-DDS content. TBD-5 achieves an LOI of 30.1%, exceeding the 28% threshold generally recognized for flame-retardant materials^[13]. In the

UL-94 vertical burning test, TBD-1 and TBD-2 failed to achieve a rating and were classified as NR. TBD-3, with a substantially improved LOI of 28.4%, attained a V-1 rating. TBD-4 and TBD-5 both achieved a V-0 rating, self-extinguishing within 10 s after ignition without dripping that ignited the cotton indicator (Figure 10(a)(b)). These results demonstrate that the flame-retardant performance of TBD-x is effectively tunable through the monomer ratio, with higher 3,3'-DDS content consistently leading to improved flame retardancy^[37,38].

The observed composition dependence suggests that the flame-retardant properties of TBD-x are primarily associated with the phosphorus-containing TMP and the aromatic 3,3'-DDS building blocks. The phosphate ester structure in TMP contributes to char formation during combustion, which helps to suppress heat and mass transfer. Meanwhile, the aromatic structure of 3,3'-DDS promotes carbonization at elevated temperatures, leading to a higher char yield and a more compact char layer, as reflected by the increasing LOI values and improved UL-94 ratings with higher 3,3'-DDS content. To gain preliminary insight into the charring behavior, the residual char of TBD-5 was examined by SEM and EDS^[17,20]. The SEM image (Figure 10(c)) reveals a continuous and dense char surface without obvious cracks or pores, confirming the formation of an effective physical barrier. EDS analysis confirms the presence of phosphorus in the char residue, consistent with the incorporation of TMP.

Table 7. LOI values and UL-94 ratings of TBD-x.

Sample	LOI(%)	UL-94
TBD-1	22.6	NR
TBD-2	23.8	NR
TBD-3	28.4	V-1
TBD-4	28.6	V-0
TBD-5	30.1	V-0

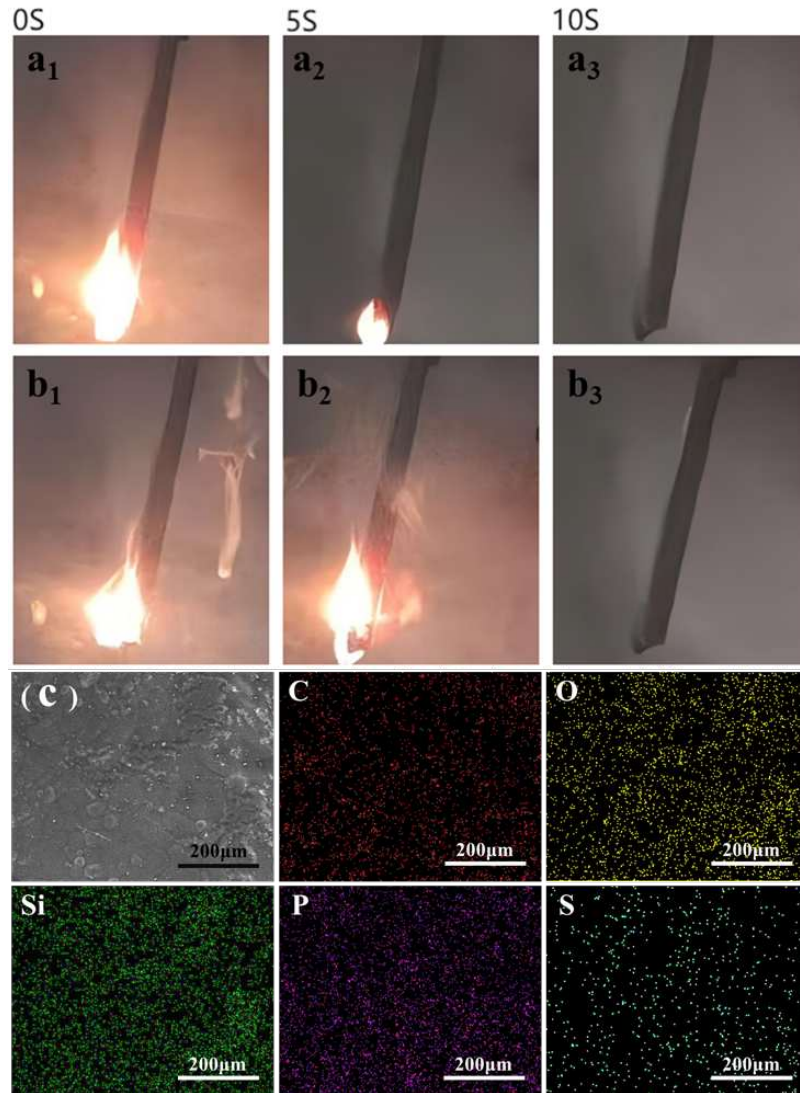


Figure 10. TBD-5(a) and TBD-4(b) self-extinguished within 10 seconds after ignition in the vertical burning test. SEM (c) images and EDS spectral analysis of the post-combustion residual carbon layer in TBD-5.

4 Conclusions

In conclusion, a series of imine-based vitrimers (TBD-x) with tunable properties were successfully synthesized via a rigid-flexible molecular design strategy. The results demonstrate that the mechanical properties of the materials can be effectively tailored by varying the ratio of 3,3'-DDS to BAPT. As the 3,3'-DDS content increased, the tensile strength and stiffness increased markedly, while the elongation at break decreased, indicating a clear transition from ductile to rigid behavior. At the same time, T_g increased significantly, whereas increasing the BAPT content lowered the activation energy for dynamic imine exchange and generally reduced T_v , thereby facilitating network rearrangement and reprocessing. After three recycling cycles, all samples retained over 90% of their original tensile strength and elongation at break, confirming good recyclability. Flame-retardant testing further showed that the LOI increased from 22.6% to 30.1%, and the UL-94 rating improved from NR to V-0 across the series. Among the investigated compositions, TBD-3 exhibited the most balanced overall performance, with a tensile strength of 67.9 MPa, a T_g of 136.7 °C, an activation energy of 35.83 kJ/mol, and a UL-94 V-1 rating. Overall, this study provides an effective approach for constructing recyclable polyimine vitrimers with adjustable mechanical performance and favorable comprehensive properties.

Conflicts of interest

There are no conflicts to declare.

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