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Sustainable polyimine vitrimers derived from biological resources with high performance and self-healing properties

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ABSTRACT

Thermosetting polymers are characterized by high mechanical performance, thermal resistance, chemical resistance, and good dimensional stability during processing. However, their inability to be repaired and recycled creates an environmental burden. Vitrimers are an important technique to overcome this issue. In this study, a vitrimer derived from biological resources was developed and can be a candidate to replace thermosetting polymers. First, a trifunctional aldehyde was synthesized by nucleophilic substitution of vanillin derived from lignin with 1,3,5-tris(bromomethyl)benzene. Subsequently, it was reacted with commercially available amines to prepare a series of polyimine vitrimers. Dynamic mechanical analysis showed that when the aldehyde and amine were reacted at the stoichiometric ratio, the obtained vitrimer had the largest storage modulus (8.80 GPa) and crosslinking density (1.18 mol/L). Self-healing test showed that the tensile strength of the vitrimer can remain as high as 70.16 MPa after two repair cycles. These characteristics exhibit superior performance in comparison with prior studies. This study successfully developed the vitrimers derived from biological resources with excellent mechanical property and self-healing effect, which is renewable and has a strong potential to replace thermosetting polymers in the future.

Keywords: Biological resources, Vanillin, lignin, Self-healing.

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1. INTRODUCTION

Traditional covalently crosslinked thermosetting polymers are characterized by high mechanical performance, thermal resistance, chemical resistance, and good dimensional stability during processing. Therefore, they are widely used in many applications such as coatings, adhesives, tires, and the electronics industry (Ma et al., 2016). However, the permanent crosslinking in thermosetting polymers prevents reprocessing, contributing to a growing environmental burden due to increased disposal rates and a larger carbon footprint (Wu et al., 2025). In contrast, thermoplastics consist of linear polymer chains that are recyclable, but they generally exhibit lower thermal and chemical resistance than thermosets. Vitrimers, a novel class of materials, bridge the gap between thermosets and thermoplastics by combining the mechanical durability of thermosets with the reprocessability and malleability of thermoplastics. A key feature of vitrimers is their permanent network structure formed through dynamic covalent bonds, which underlie their unique chemical and physical properties (Rai et al., 2025). In recent years, the self-healing property of materials has also been highly valued. It can be applied in various fields such as coatings, wearable devices, electrochemical sensors, and biomedical materials (Zhu et al., 2020). Self-healing materials have two main mechanisms: extrinsic repair type and intrinsic repair type. Extrinsic repair involves methods such as microcapsules and microvascular systems. Intrinsic repair, on the other hand, relies on reversible chemical bonds (covalent or non-covalent) and intermolecular forces for the healing process (Hia et al., 2016; Wang et al., 2020). Although the self-healing mechanisms of microcapsule repair or vascular repair systems can achieve successful self-repair, they have the following limitations: Firstly, the healing agents contained within them are limited, so once the healing agent is depleted, it cannot repair again. Secondly, since the healing agent flows through capillary action, it requires a certain

level of fluidity to complete the repair within a short period of time. Thirdly, the production of microcapsules, vascular channels, or the selection of catalysts and healing agents involve high time and cost. Therefore, in recent years, research on self-healing has shifted towards intrinsic repair methods (Hia et al., 2016). Intrinsic repair is based on specific structures of polymers, where appropriate energy (such as temperature, UV light, or solvent) is applied as an external stimulus when damage occurs. This stimulus allows the molecular chains to move and repair the damaged area. After the removal of the external stimulus, the material can maintain properties similar to the original state. Intrinsic repair is mainly divided into non-covalent bonding types and reversible dynamic covalent bonds. Non-covalent bonding refers to repair mechanisms based on supramolecular chemistry, such as hydrogen bonding, metal coordination, or π-π stacking (Burattini et al., 2009; Syrett et al., 2010; Fiore et al., 2011; Garcia et al., 2014). However, although these supramolecular chemistry crosslinked materials are recyclable and can repair damaged areas under external stimuli, their mechanical properties are weaker compared to materials with covalent crosslinking. This limitation restricts their industrial applications. Therefore, the concept of dynamic covalent bonds has been widely discussed (Hayashi, 2020). In 2011, Montarnal et al. proposed the concept of "vitrimer", which introduced dynamic covalent bonds to enable the material to undergo reversible reactions under external stimuli. This rearranges the crosslinked structure without affecting the crosslinking density, allowing the material to possess self-healing capabilities and reprocessability similar to thermoplastic materials (Denissen et al., 2016; Gu et al., 2018).

The network formed by crosslinking with dynamic covalent bonds is referred to as Covalent Adaptive Networks (CANs). CANs have two main advantages compared to regular covalent bonds. Firstly, they can effectively break and reform bonds under external stimuli such as heat, UV light, or solvents. This property enables the material to possess repairability and recyclability. The lower bond energy of dynamic covalent bonds compared to regular covalent bonds contributes to this characteristic (Samanta et al., 2021). The second advantage is that the bonds in CANs remain stable and frozen in the absence of external stimuli, allowing them to retain the same properties as regular covalent bonds. CANs enable materials to maintain good mechanical properties within a certain temperature range while possessing characteristics such as repairability, recyclability, and weldability. Furthermore, the repairs performed on CANs do not cause significant damage to the mechanical properties of the material (Alabiso and Schlögl, 2020; Huang et al., 2020). Recently, the types of vitrimers have expanded from the initial ester exchange reaction to include disulfide bonds, imine bonds, urethane, siloxane, and others (Wang et al., 2019). Among them, the imine bond exchange reaction, also known as Schiff base, can be conducted under mild conditions without the need for catalysts. It involves the condensation reaction of aldehyde or ketone with an amine, resulting in the formation of imine bonds (Gu et al., 2018). In 2014, Taynton et al., first prepared vitrimers based on polyimine systems. They initially formed a crosslinked network by combining different amine monomers with aldehyde monomers. The crosslinking density could be controlled by adjusting the content of different amine monomers. The results showed that the material exhibited rapid stress relaxation properties. The wetted powder could be pressed into a film at room temperature, indicating that the partial hydrolysis of imine groups could promote the exchange reaction of imine bonds (Taynton et al., 2014).

Agro-waste, which is rich in lignocellulosic materials, holds great potential for the conversion of waste into valuable products such as biofuels, biochemicals, and bioplastics, owing to its abundance and low cost (Panakkal et al., 2024). Vanillin, when derived from petroleum-based synthetic processes, presents several drawbacks, including the generation of undesirable byproducts and relatively low yields. In contrast, residual lignocellulosic biomass offers a renewable source of aromatic compounds that can be utilized as raw materials for vanillin synthesis. Latorre et al. (2025) proposed a sustainable method for vanillin production from lignocellulosic biomass, highlighting its high selectivity, environmental friendliness, and cost-effectiveness. This approach not only promotes the valorization of biomass waste but also enables the large-scale production of vanillin, which is widely used in the medical, pharmaceutical, cosmetic, fragrance, and fine chemical industries. Owing to the scarce natural occurrence of aldehydes, vanillin and structurally related compounds are commonly employed as key sources (Zhao et al., 2024). In 2018, Geng et al. (2018) synthesized a dialdehyde monomer by combining vanillin with 1,4-dibromobutane. They then reacted this dialdehyde monomer with an amine monomer to form a dynamic imine bond system. After three cycles of thermal reprocessing, it can be observed that the tensile strength and elongation of the obtained vitrimers remain virtually unchanged. In 2019, Tao et al. prepared a polyimine vitrimer using the sol-gel method. This material not only can undergo thermal pressing for reprocessing but also possesses the self- healing ability through solvent-induced welding at room temperature. Moreover, it could withstand a weight of 700 g while maintaining a tensile strength of 55 MPa. In 2020, Hajj et al. developed a series of polyimine vitrimers with adjustable mechanical properties by altering the proportions of triamines and diamines as well as the molecular weight of the diamine. It was observed that an increase in crosslinking density resulted in an increase in the Young's modulus and fracture stress, while the elongation decreased. This demonstrates that the vitrimer-based system can possess properties similar to those of a permanent crosslinked network.

In this study, a novel tri-functional aldehyde was

synthesized from the bioresource vanillin. This tri-functional aldehyde possesses four benzene rings in its structure, aiming to enhance the mechanical properties and thermal stability of the material. It was then reacted with amine monomers to prepare polyimine vitrimers. And the influence of different proportions of amine monomers on the material's mechanical properties, thermal properties, viscoelasticity, self-healing, and recyclability properties was investigated. The vitrimers developed in this study are derived from bio-based resources and are expected to exhibit excellent mechanical properties and self-healing capabilities. Being renewable and recyclable, they hold strong potential to replace conventional thermosetting polymers.

2. MATERIALS AND METHODS

2.1 Materials

1,3,5-Tris(bromomethyl)benzene was obtained from Jie En Reagent Co., Ltd., located in Taiwan. 4-Hydroxy-3-methoxybenzaldehyde (vanillin, 98%), potassium carbonate (≥ 99%), and diethylenetriamine (99%) were purchased from Uni-Onward corp. All of these chemicals were of reagent grade and used without further purification.

2.2 Synthesis of Vanillin-derived Trifunctional Aldehyde

The synthesis of the trifunctional aldehyde derived from vanillin is analogous to the procedure reported previously (Shah et al., 2016). First, dissolved approximately 1.5060 g of vanillin in a 50 mL acetone solution. Weighed approximately 3.7315 g of potassium carbonate and dissolved it in the vanillin solution. Stirred the mixture for 30 s. Then, added 1.0704 g of 1,3,5-tris(bromomethyl) benzene and 50 mL acetone solution to the vanillin solution and stirred for another 30 s. Refluxed the reaction mixture at a temperature of 40°C and a stirring speed of 500 rpm for a duration of 3 hrs. After the reaction was complete, allowed the mixture to cool to room temperature. Poured the reaction mixture into ice water to stop the reaction and performed filtration. The resulting white solid was recrystallized and purified using ethanol. The reaction scheme was shown in Fig. 1, and the obtained vanillin-derived trifunctional aldehyde was named BV (Yield: 75.3%). The structural identification results of BV can be found in our previous study (Shih et al., 2022).

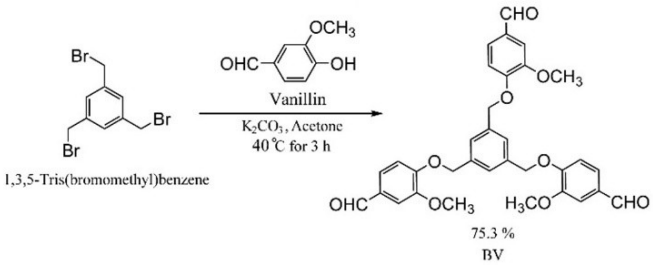

Fig. 1. Reaction scheme of vanillin-derived trifunctional aldehyde

2.3 Preparation of Polyimine Vitrimer (BVD)

The synthesis of polyimine vitrimer was conducted based on our previous study (Shih et al., 2022). First, the aldehyde solution was prepared by dissolving 1.1418 g of BV in a 12 mL solution of dimethylformamide (DMF) at 80°C. The amine solution was prepared by dissolving 0.2063 g of diethylenetriamine (DA) in 3 mL of ethanol. The aldehyde solution was then added dropwise into the amine solution while vigorously stirring at room temperature for approximately 3 min. The mixture was then transferred to a glass culture dish and allowed most of the solution to evaporate at room temperature in a fume hood. The resulting film was pre-cured by placing it in an 80°C oven for 1 hr. This step was necessary to remove residual solvents

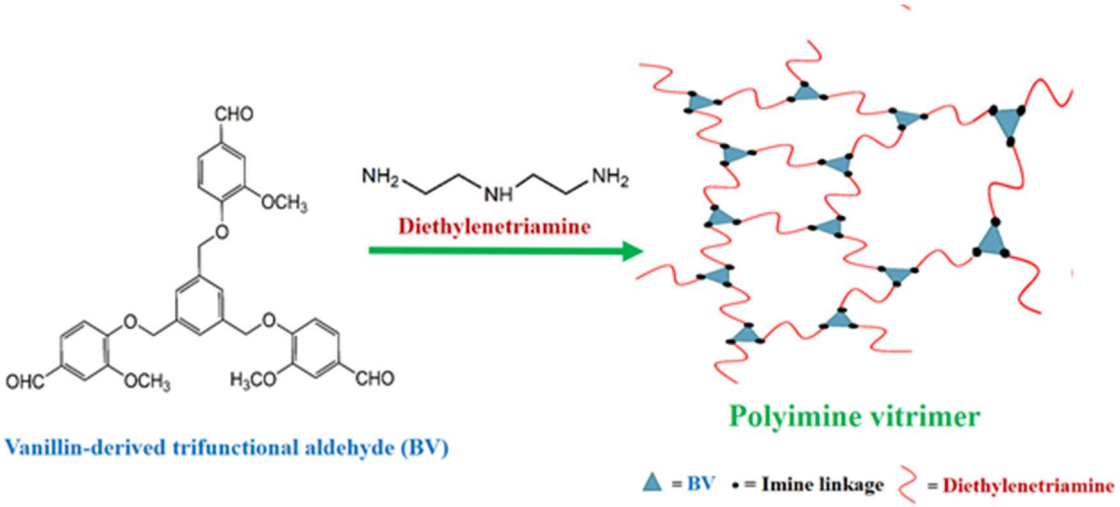

Fig. 2. Reaction scheme of polyimine vitrimer

and ensure proper curing of the film. Next, the film was cured at 85°C for 24 hrs, followed by curing at 120°C for 20 hrs to complete the curing process. A yellow polyimine vitrimer film was obtained (BVD-2). The film was removed from the glass culture dish and various tests were conducted on it. BVD-2 was prepared by reacting BV with DA at an equimolar ratio. Additionally, different formulations were prepared by varying the BV/DA ratio to demonstrate that the properties of the final material can be tailored based on the ratio. BVD-3 and BVD-4 correspond to the molar ratios of BV:DA at 2:3 and 2:4, respectively, as shown in Table 1. The reaction scheme of the polyimine vitrimer is depicted in Fig. 2. The structural identification results of BVD can be found in our previous study (Shih et al., 2022).

Table 1. Sample compositions

Sample	Vanillin-derived trifunctional aldehyde (mole)	Diethylenetriamine (mole)
BVD-2	2	2
BVD-3	2	3
BVD-4	2	4

2.4 Preparation of the Polyimine Vitrimer Aample for Self-healing Test

First, two pieces of polyimine vitrimer films were partially overlapped and placed between two steel plates. The assembly was then inserted into a hot press machine preheated to 120°C and maintained under these conditions for 10 min. Afterward, the films were removed and allowed to cool to room temperature. The resulting films (referred to as the 1st Reprocessed) were then subjected to tensile testing. The same procedure was repeated using the 1st Reprocessed films to produce the 2nd Reprocessed films, which were also tested for their tensile properties.

2.5 Characterization

The stress relaxation behaviour of polyimine vitrimer was analyzed using a dynamic mechanical analyzer (DMA; TA Instruments, Q800) with a heating rate of 3°C/min. The amplitude and frequency of the dynamic oscillatory loading were set at 20 μm and 1 Hz, respectively. To examine the self-healing effect of the polyimine vitrimers, a polarizing optical microscope (POM; Carl Zeiss, Axio Scope A1) was utilized. Tensile test was conducted in accordance with ASTM D368 specifications using a universal testing machine (Hung Ta Instrument, HT-9102) at a rate of 30 mm/min.

3. RESULTS AND DISCUSSION

3.1 Dynamic Mechanical Analysis of Polyimine Vitrimers

Fig. 3(a) and Table 2 present the results of the storage modulus (E') analysis for polyimine vitrimers. From Table

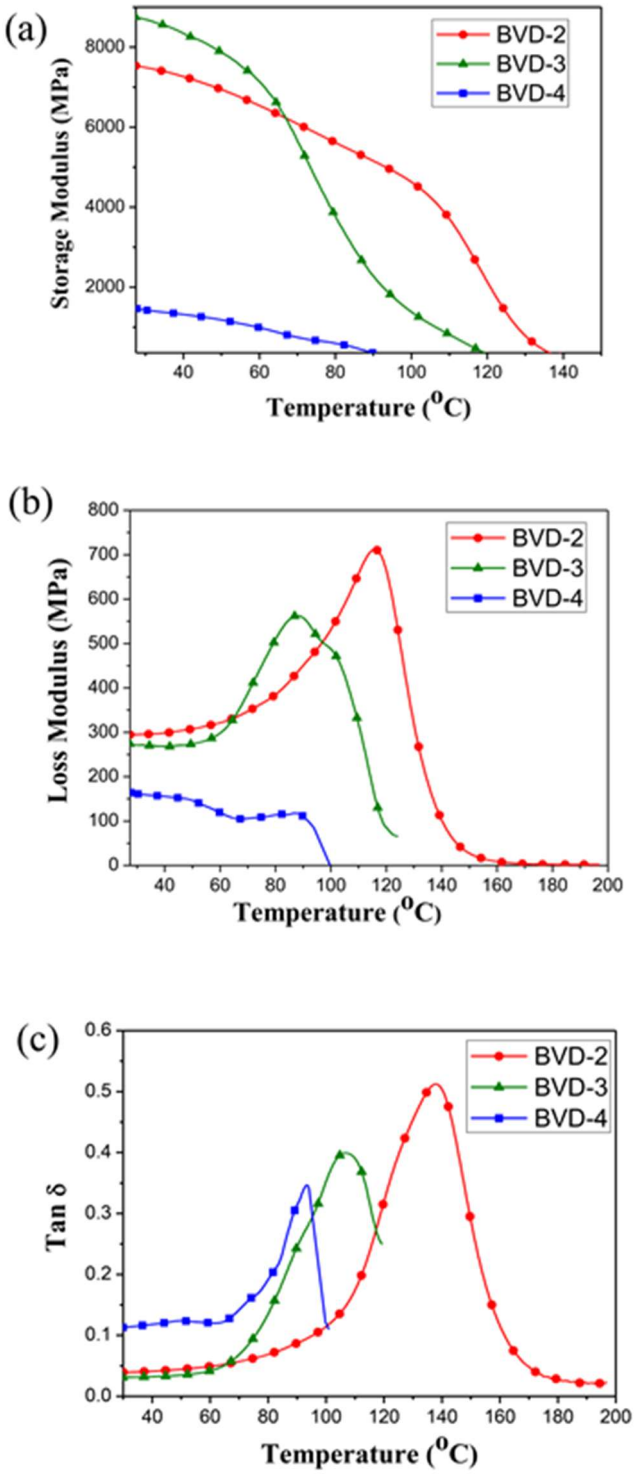

Fig. 3. DMA analysis of polyimine vitrimers (a) Sorage modulus (b) Loss modulus

2, it is evident that BVD-3 exhibits the highest storage modulus of 8.80 GPa. This is likely attributed to its preparation using a stoichiometric ratio, which results in a higher proportion of imine bonds and manifests as superior

Table 2. Results of DMA analysis

Sample	E' (GPa)	E'' (MPa)	Tg (℃)*	ve (mol/L)
BVD-2	7.57	712.01	137.85	1.01 ± 0.06
BVD-3	8.80	562.81	106.72	1.18 ± 0.03
BVD-4	1.46	164.10	93.47	0.19 ± 0.03

mechanical strength. Conversely, BVD-2 has a storage modulus of 7.57 GPa, indicating a lower crosslinking density compared to BVD-3, potentially due to a lower proportion of amine monomer added relative to the stoichiometric ratio. BVD-4, characterized by an excessive proportion of amine monomer, demonstrates a decrease in storage modulus due to structural damage caused by an excessive amount of residual amine monomer. The crosslinking densities of polyimine vitrimers were calculated based on the equation as follow (Sun et al., 2022):

$$\nu_e = \frac{E\prime}{3RT} \quad (1)$$

Where ν_e represents the crosslinking density per unit volume, E' represents the storage modulus, R represents the gas constant (8.314 J/mol-K), and T represents the absolute temperature (K). The calculated crosslinking densities for BVD-2, BVD-3, and BVD-4 are 1.01 ± 0.06, 1.18 ± 0.03, and 0.19 ± 0.03 mol/L (Table 2), respectively. This confirms that BVD-3, prepared using the stoichiometric ratio, has the highest crosslinking density and proportion of imine bonds. Fig. 4 shows no significant difference between BVD-2 and BVD-3; however, both differ significantly from BVD-4, indicating that excessive amine content has a critical impact on crosslinking density. Additionally, the standard deviation of BVD-3 (0.03) is lower than that of BVD-2 (0.06), indicating better uniformity in BVD-3.

Fig. 3(b) and Table 2 showed that BVD-2 has the highest loss modulus of 712.01 MPa. The loss modulus of BVD-3 is 562.81 MPa, as it has the highest crosslinking density, which restricts molecular chain rotation and increases rigidity while reducing toughness relatively. Moreover, when amine monomers remain in the crosslinked network, they can disrupt the formed crosslinked structure, leading to a decrease in toughness. Therefore, BVD-4 has a loss modulus of 164.10 MPa, indicating a decrease in both rigidity and toughness when an excessive amount of amine monomer is added beyond the stoichiometric ratio (Choudhury et al., 2011; Denissen et al., 2016).

Fig. 3(c) and Table 2 present the results of the Tan δ analysis and the determined glass transition temperature (T_g) from the Tan δ plot for polyimine vitrimers. It can be observed that as the proportion of amine monomers increases, the glass transition temperature decreases. The T_g values for BVD-2, BVD-3, and BVD-4 were found to be 137.85, 106.72 and 93.47℃, respectively.

Fig. 5 is the stress relaxation analysis plot of polyimine vitrimers. The relaxation time can determine the rate of exchange reactions and follows the Arrhenius law, which is expressed by the following equation (Kuang et al., 2017):

$$\ln(\tau) = \frac{\mathrm{Ea}}{\mathrm{RT}} - \ln(A) \quad (2)$$

Where τ is the relaxation time (s); Ea is the activation energy (kJ/mol); R is the gas constant (8.314 J/mol-K); T is the absolute temperature (K); and A is a constant. Therefore, the activation energy (Ea) of exchange reactions can be calculated. Fig. 6 represents the Arrhenius plot based on the relaxation time of polyimine vitrimers. The activation energies of BVD-2, BVD-3, and BVD-4 were calculated from the slope of the graph, which were 33.12, 96.44 and 143.99 kJ/mol, respectively. The activation energy of dynamic covalent bonds is lower compared to traditional covalent bonds, with a range of approximately 28 to 157 kJ/mol (Elling et al., 2020; Samanta et al., 2021). This confirms the successful introduction of exchangeable dynamic covalent bonds in polyimine vitrimers.

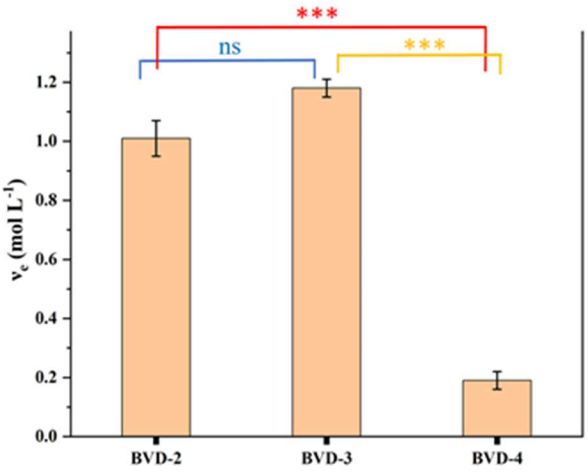

Fig. 4. Quantitative analysis of crosslinking densities across different groups (n = 3)

In addition, vitrimers have a unique characteristic temperature known as the topology freezing transition temperature (Tv). It represents the temperature at which the material transitions from a viscoelastic solid to a viscoelastic liquid and is defined as the temperature at which the viscosity exceeds 1×10^{12} Pa·s (Lei et al., 2020). First, the storage modulus of the material in the rubbery plateau region is determined. The storage moduli for BVD-

2, BVD-3, and BVD-4 in the rubbery plateau region are determined to be 6.0234, 4.7819 and 3.2822 MPa, respectively. These values are then substituted into the following equation:

$$\eta = \frac{1}{3} E' \times \tau^* \quad (3)$$

Where η is 1×10^{12} Pa·s; E' is the storage modulus (Pa) in the rubbery plateau region; τ* is the relaxation time (s) at a viscosity of 1×10^{12} Pa·s. From the above calculations, it can be determined that when the viscosity reaches 1×10^{12} Pa·s, the relaxation times for BVD-2, BVD-3, and BVD-4 are 4.98×10^5, 6.27×10^5 and 9.14×10^5 s, respectively. By using the Arrhenius equation and extrapolation, the respective Tv temperatures can be calculated (Lei et al., 2020). Based on the calculations, the Tv values for BVD-2, BVD-3, and BVD-4 are -45.81℃, 8.83℃, and 16.25℃, all of which are lower than their glass transition temperatures. This indicates that these materials can undergo rapid exchange reactions and stress relaxation. Additionally, as the proportion of amine monomers increases, the presence of unreacted amine monomers that are not fully crosslinked with aldehyde monomers can lead to the cleavage of imine bonds. This results in a decrease in the quantity of dynamic exchange bonds, leading to longer relaxation times and higher Tv values and activation energy. Fig. 6(c) shows that the linear regression coefficient (R2) value for BVD-4 (0.7694) is lower as compared to those of BVD-2 and BVD-3. This is likely due to the excess amine monomers causing the cleavage of imine bonds, resulting in a less uniform distribution of crosslinking bonds in the structure.

3.2 Self-Healing Test of Polyimine Vitrimers

To investigate the self-healing behavior of BVD-2 at the molecular level, the samples were cut into two pieces and pressed together at 120°C for 5 min. When the broken pieces were joined with a 200 g load, the material re-healed without any visible interface and was able to support a 1 kg weight (Fig. 7). These results confirm that the imine metathesis reaction was successfully carried out and that the material could largely recover through the application of heat and pressure. Fig. 8 displays the microscopic images of the repair process for BVD-2. After creating a scratch on the material's surface, the healing process was observed using polarized optical microscopy (POM) at 120°C. From Fig. 8(a), it can be observed that the initial scratch width was approximately 95.36 μm. After heating for 10 min, the scratch started to become shallower with a width of around 27.63 μm (Fig. 8(b)), indicating the beginning of healing. After 15 min of heating, the scratch width reduced to approximately 25.22 μm (Fig. 8(c)). Finally, after 60 min of heating, the scratch was completely healed (Fig. 8(d)). This confirms the high self-healing efficiency of polyimine vitrimers, as they can undergo complete repair even without the application of pressure or the addition of catalysts. This is attributed to the rapid rearrangement of the crosslinking network in the damaged region at high temperatures, allowing the polyimine vitrimer to effectively repair itself.

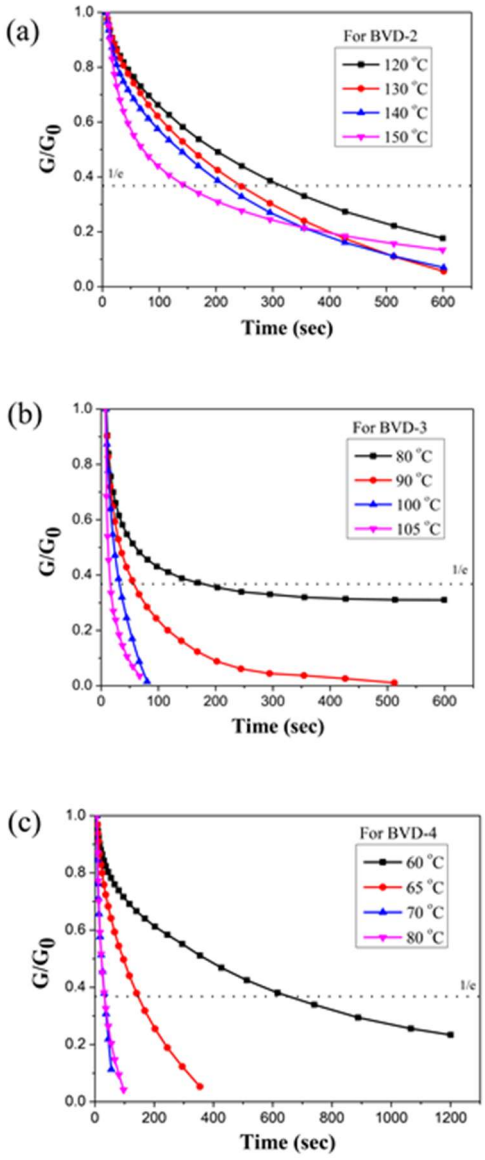

Fig. 5. Stress relaxation analysis of polyimine vitrimers (a) BVD-2 (b) BVD-3 (c) BVD-4

Table 3 present the tensile test results of the original and repaired polyimine vitrimers. It can be observed that the tensile strengths of BVD-2 and BVD-3 are 67.90 and 71.34 MPa, respectively. The high mechanical strength of BVD-2 and BVD-3 can be attributed to the presence of numerous aromatic structures along the polymer chains. Aromatic structures possess symmetry and high bond energy, resulting in excellent mechanical strength and rigidity. Furthermore, BVD-3 was prepared based on the chemical equivalent ratio, leading to a slightly higher crosslinking However, BVD-4 has a tensile strength of only 29.44 MPa, which may be due to an excess of amine monomers reducing the crosslinking density of the vitrimer. The

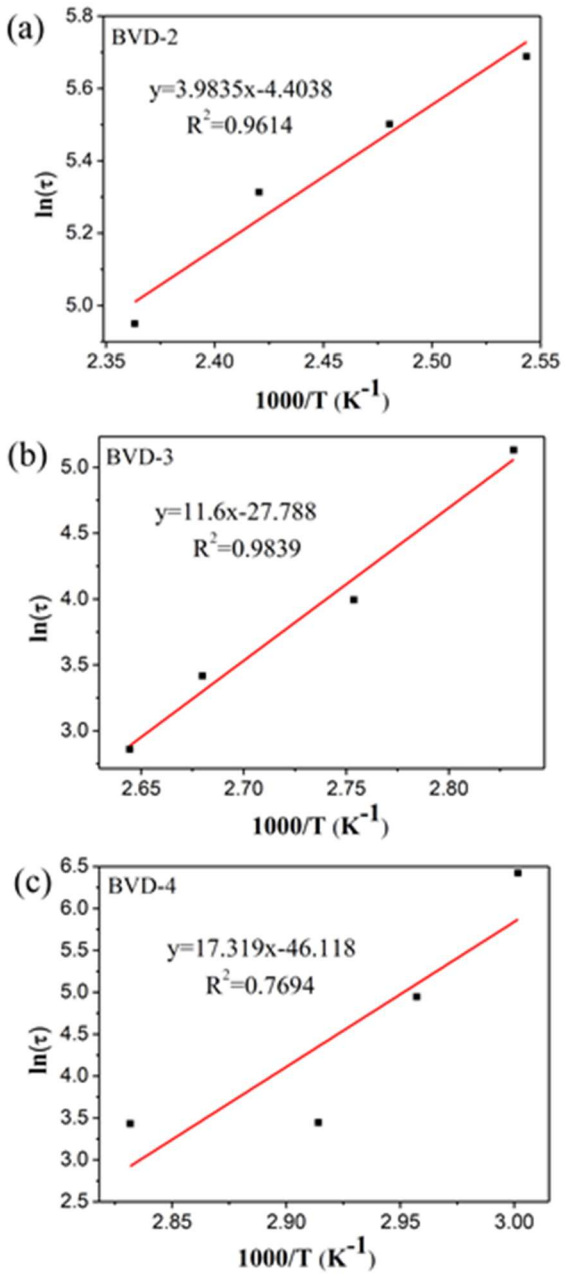

Fig. 6. Arrhenius plot of polyimine vitrimers (a) BVD-2 (b) BVD-3 (c) BVD-4

associative mechanism of vitrimers requires the association of two polymer chains before a crosslink can be exchanged. Nevertheless, the stoichiometry of reactants plays a crucial role in determining the properties of vitrimers (Guerre et al., 2020). Studies on epoxy ester vitrimers have shown that elongation at break of 14.88%, which is higher than those of BVD-3 and BVD-4 (4.73% and 0.73%), indicating superior ductility. The decreased elongation of BVD-3 (4.73%) is likely attributed to its higher crosslinking density, which makes the material stiffer and reduces the ductility. As for BVD-4, its elongation is only 0.73%, mainly because the excessive addition of amine monomers results in a lower crosslinking density, leading to a decrease in both mechanical strength and fracture elongation.

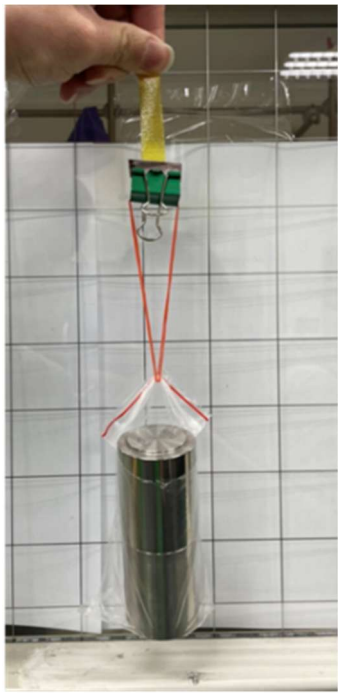

Fig. 7. Macroscopic image of the repaired BVD-2

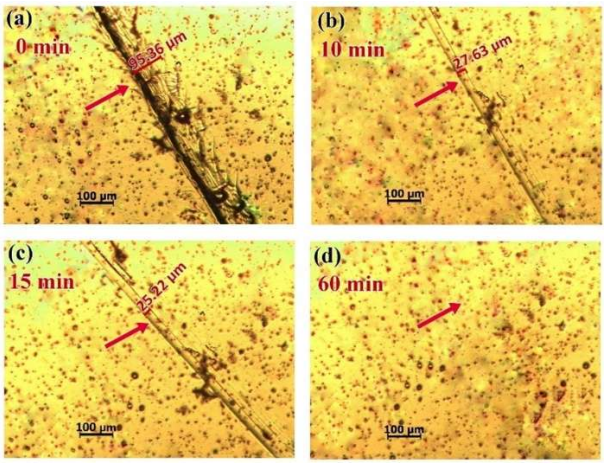

Fig. 8. POM images of the repair process for BVD-2 (a) Create scratches on the material surface, and then heating at 120°C for (b) 10 min (c) 15 min (d) 60 min

After one repair cycle, the tensile strength of BVD-2 increased from 67.90 to 71.35 MPa, BVD-3 increased from71.34 to 74.89 MPa, and BVD-4 increased from 29.44 to 30.63 MPa. One possible reason for the increase in tensile strength is that during the repair process, thermal compression can further promote the formation of imine linkage. Another reason could be the occurrence of side reactions, where at high temperatures, imine bonds undergo crosslinking reactions to form nitrogen-containing heterocycles, thereby increasing the crosslinking density

Table 3. Tensile test results of the original and repaired polyimine vitrimers

Sample	Tensile strength (MPa)	Elongation at break (%)
Original BVD-2	67.90 ± 1.92	14.88 ±1.43
1st Reprocessed BVD-2	71.35 ± 1.30	10.93 ±0.53
2nd Reprocessed BVD-2	65.19 ± 1.35	7.38 ± 1.47
Original BVD-3	71.34 ± 1.32	4.73 ± 0.12
1st Reprocessed BVD-3	74.89 ± 1.44	4.40 ± 0.69
2nd Reprocessed BVD-3	70.16 ± 1.49	2.66 ± 0.83
Original BVD-4	29.44 ± 2.32	0.73 ± 0.07
1st Reprocessed BVD-4	30.63 ± 1.44	0.53 ± 0.12
2nd Reprocessed BVD-4	22.75 ± 1.62	0.16 ± 0.10

Table 4. Performance of various polyimine vitrimers

Vitrimer type	Reactants	Tensile strength (MPa)	Modulus (GPa)	Reference
Polyimine vitrimers	Terephthaldehyde, m-xylylene diamine, and tris (2-aminoethyl) amine as crosslinker	49	-	Zheng et al., 2018
Biobased polyimine vitrimers	A dialdehyde or trialdehyde derived from vanillin and a commercial biobased aliphatic amine	5.09	0.0035	Zhou et al., 2020
Polyimine vitrimers	Terephthaldehyde, m-xylylenediamine dimer, and triethylene tetramine.	45	1.56	Zheng et al., 2019
Cellulose-based polyimine vitrimer	Introducing dynamic imine bonds between cellulose molecular chains using Schiff-base reaction	46.3	2.9	Su et al., 2023
Fluorinated polyimine vitrimer	Terephthaldehyde, 4-phenyl ether-1, 3-diamine, and 1, 4-bis(4-amino-2-trifluoromethylphenoxy) benzene	64	1.2	Yu et al., 2023
Biobased polyimine vitrimer	Trialdehyde derived from vanillin and diethylenetriamine	29.44–71.34	1.16–8.80	This study

(Schoustra et al., 2024). Moreover, it is noted that the tensile strength of all three test samples increased. However, BVD-4 exhibited the smallest increase in comparison to BVD-2 and BVD-3. After two repair cycles, the tensile strength of BVD-2 decreased from 71.35 to 65.19 MPa, BVD-3 decreased from 74.89 to 70.16 MPa, and BVD-4 decreased from 30.63 to 22.75 MPa. BVD-2, BVD-3, and BVD-4 show recovery rates of 96.00%, 98.34%, and 77.27%, respectively. BVD-2 and BVD-3 exhibit tensile strengths very similar to the original values, and the welded repair sections did not fracture during the tensile test. This suggests that effective reversible reactions occur at the imine bonds in the welded regions. The poorer recovery of BVD-4 may be attributed to the dissociation of dynamic covalent bonds.

Furthermore, it can be observed that as the number of repair cycles increases, the elongation at break decreases gradually. This indicates that during the repair process, the ductility of the material deteriorates. This is likely due to the increase in crosslinking density during the thermal repair cycles or the formation of a less complete structure, leading to increased brittleness of the material and a decrease in fracture elongation.

Vanillin is obtainable on a large scale from lignin at a reasonable cost. Furthermore, the vanillin-based vitrimers reported in this study demonstrate enhanced performance relative to most comparable systems, as presented in Table 4.

4. CONCLUSION

In this study, a trifunctional aldehyde was successfully synthesized by nucleophilic substitution reaction between the renewable resource vanillin and 1,3,5-tris(bromomethyl) benzene. A series of polyimine vitrimers were then prepared by controlling the proportions of different amine monomers. The results showed that BVD-3, with an equivalent ratio of aldehyde and amine monomers, exhibited the highest storage modulus and crosslinking density. However, when the amine content is excessive, the unreacted amine monomers led to the cleavage of imine bonds, resulting in a decrease in the number of dynamic exchange bonds. This led to poorer mechanical properties, longer relaxation times, increased Tv values, and higher activation energies.

Additionally, the polyimine vitrimer films prepared in this study, which possessed multiple benzene rings, exhibited excellent tensile strength of over 70 MPa, indicating their high rigidity. The self-healing tests also demonstrated that these obtained polyimine vitrimers could undergo repair under temperature stimulus without the need for additional pressure or catalysts. The damaged areas of the films underwent rapid metathesis reactions, enabling effective material restoration. Moreover, the mechanical strength of the repaired materials was comparable to that of the original materials. The polyimine vitrimers developed using vanillin as a renewable resource not only exhibited excellent mechanical strength and self-healing capabilities but also offered recyclability and reprocessability. These vitrimers exhibit potential as alternatives to thermosetting polymers and for use in self-healing material systems. Therefore, it makes a substantial contribution to the circular economy and sustainable environment. In addition, future efforts to advance these vitrimers may focus on: (1) introducing dual dynamic bonds to optimize the balance between reprocessability and network stability; (2) incorporating bio-based nanofillers to improve mechanical performance without compromising recyclability; and (3) replacing high-purity vanillin or expensive diamines with industrial-grade or waste-derived alternatives to lower overall production costs.

DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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