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Biobased Polystyrene Vitrimers for Thermoset Circularity

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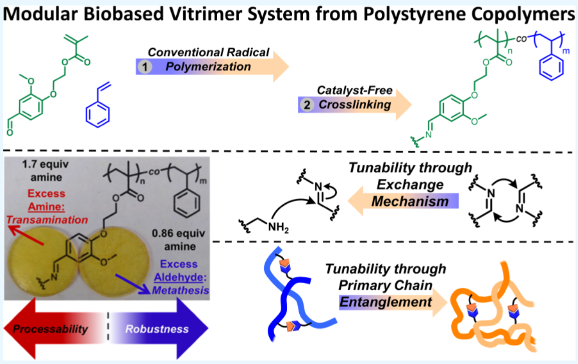

ABSTRACT: Thermoset polymers, known for their robust thermomechanical and chemical durability, suffer from poor recyclability due to their covalent cross-linking. This study explores the tunability of covalent adaptable networks (CANs), specifically prepolymer-derived vitrimers, which offer both durability and recyclability through dynamic covalent cross-links. By utilizing biobased vanillin methacrylate (VnMA) and Priamine cross-linkers, we synthesized polystyrene (PS) vitrimers with readily tunable viscoelastic properties. The vanillin-derived PS copolymer was cross-linked with varying equivalents of Priamine to favor different exchange mechanisms: transamination for rapid processability and metathesis for enhanced dimensional stability. Extending the prepolymer chain length above the entanglement threshold also introduced physical cross-links that significantly improved creep resistance. Our findings highlight a versatile approach for creating biobased, reprocessable thermosets with high thermomechanical performance. The incorporation of primary chain entanglement and the ability to tune exchange mechanisms offer a promising pathway for sustainable and durable polymer materials suitable for various applications. This methodology enhances the recyclability and sustainability of PS-based materials, broadening their commercial utility.

KEYWORDS: *biobased, covalent adaptable networks, vitrimers, recyclable thermosets, radical polymerization*

INTRODUCTION

Thermoset polymers are characterized by a covalently cross-linked network structure, which provides enhanced thermomechanical and chemical durability.[1,2] In contrast, thermoplastics are composed of discrete, physically entangled polymer chains. The increased durability provided by covalent cross-links inherently compromises their mechanochemical recyclability, generally precluding a circular economy for commodity thermoset materials.[3,4]

The emergence of covalent adaptable networks (CANs), particularly associative networks or "vitrimers", has offered a promising synthetic pathway for consolidating robustness and renewability in thermosets.[5−7] The dynamic covalent cross-links in associative networks allow for predictable viscoelastic flow through segmental rearrangement, achievable via a wide range of exchange chemistries and network architectures.[8,9] Furthermore, biobased vitrimers represent a favorable avenue for departing from reliance on virgin petrochemicals and achieving thermoset sustainability and circularity.[10] Nevertheless, the inherent dynamicity of a vitrimer material poses a challenge, as elevated creep deformation is difficult to combat.[11] Current research into mitigating material creep within vitrimers has primarily focused on control of exchange kinetics,[12−14] dual-network enhancement through orthogonal cross-links,[15−17] and architectural control of the polymer matrix.[18−20]

Polyimine networks have gained popularity in various CANs and reticular materials due to their rapid bond exchange and the availability of monomers or precursors.[21−24] Vanillin, a lignin-based biofeedstock, is widely used in polyimine networks because it can be easily derived into multifunctional aldehydes.[25−27] However, the rapid exchangeability of a polyimine-based network can result in undesirable creep at elevated temperatures. Polyimine exchange can be tuned to favor three general mechanisms: rapid transamination,[28,29] dissociative hydrolysis via adventitious water,[21] or metathesis.[30] While the rapidity of transamination enables facile network (re)processability, it can also lead to increased creep susceptibility. Conversely, imine metathesis offers enhanced dimensional stability and creep resistance because of its relatively slow kinetics but limits network mobility at moderate temperatures, thus diminishing material recyclability. Moreover, recent studies by Carden et al. suggest that metathesis of imines is not feasible at temperatures below polymeric decomposition.[31] Therefore, alternative methods to expand control over network dynamics are needed, particularly within

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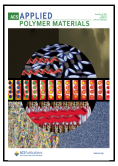

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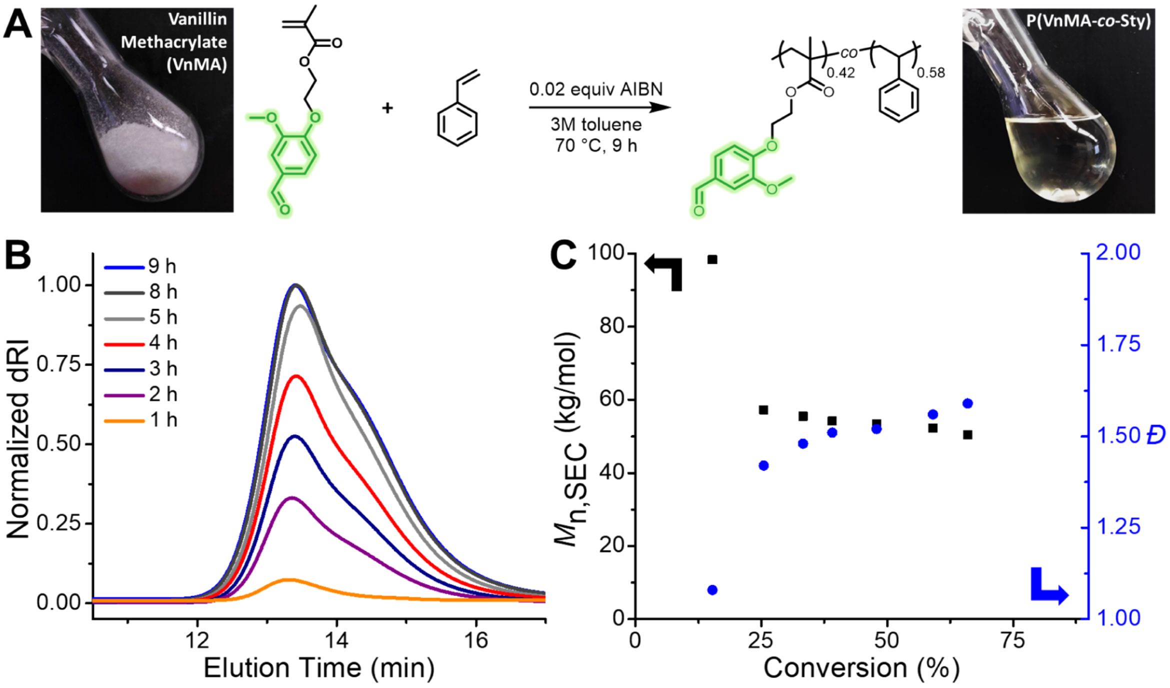

Figure 1. (A) Copolymerization scheme of vanillin methacrylate (VnMA) and styrene (Sty), with crystalline VnMA monomer (left) and resultant copolymer [P(VnMA-*co*-Sty)] solution (right). (B) Size-exclusion chromatography (SEC) traces of P(VnMA-*co*-Sty) over time. (C) Number-average molecular weight determined by SEC ($M_{n,SEC}$) and dispersity values ($Đ$) versus conversion.

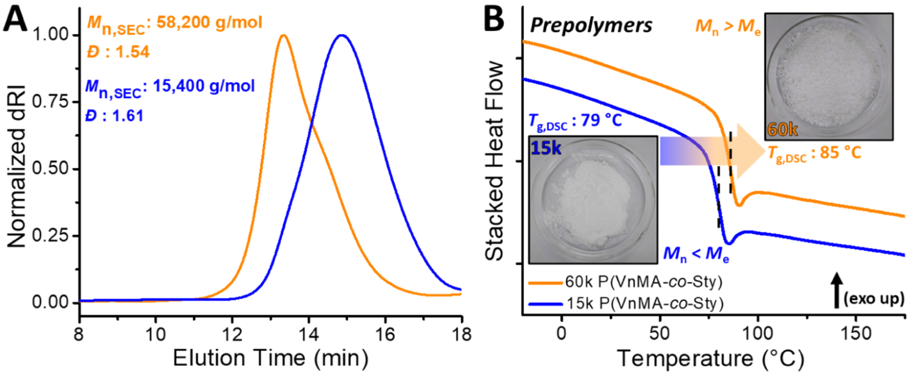

Figure 2. (A) Size exclusion chromatography (SEC) traces of 15.4 kg/mol copolymer [P(VnMA-*co*-Sty)$_{15k}$] and 58.2 kg/mol copolymer [P(VnMA-*co*-Sty)$_{60k}$] following purification. (B) Differential scanning calorimetry (DSC) thermograms of the P(VnMA-*co*-Sty)$_{15k}$ (left inset image) and P(VnMA-*co*-Sty)$_{60k}$ (right inset image) displaying a slight elevation in glass transition temperature (T_g) for the entangled prepolymer.

polyimine vitrimers derived from macromolecular building blocks.

Recent efforts from our group have demonstrated that tunability within vinylogous urethane vitrimers derived from polymethacrylate and polystyrene (PS) copolymers bearing pendent β-ketoesters can be readily achieved.[32−34] These studies have demonstrated that block copolymer-based networks exhibit superior creep resistance compared to their statistical copolymer counterparts, attributable to phase separation and sequestration of the network segments.[35,36] We have also shown how increasing the primary chain length of reactive prepolymers can enhance creep resistance by introducing physical entanglements that act as secondary cross-links reminiscent of a dual network.[37]

This report details an expansion on our previous work, leveraging the straightforward synthesis of a biobased PS copolymer featuring a pendent vanillin moiety on the methacrylic comonomer, achieved through conventional radical polymerization. This copolymer is cross-linked with a variable mole percentage of Priamine, a 100% biomass-derived multiamine, to tune network dynamics by favoring transamination or metathesis-like cross-link exchange. Additionally, by extending the chain length of the prepolymer, a dramatic increase in the creep resistance of the transaminative vitrimers was observed as compared to copolymers with chain lengths predominately below the entanglement threshold. By utilizing a more entangled prepolymer, the elevated creep characteristic of imine transamination can be mitigated, while maintaining efficient stress relaxation and reprocessability—features that are largely precluded when favoring metathesis-driven imine exchange. Such holistic tailorability within a heavily biomass-derived vitrimer network offers an attractive platform for encompassing robustness, recyclability, and renewability within a commodity thermoset.

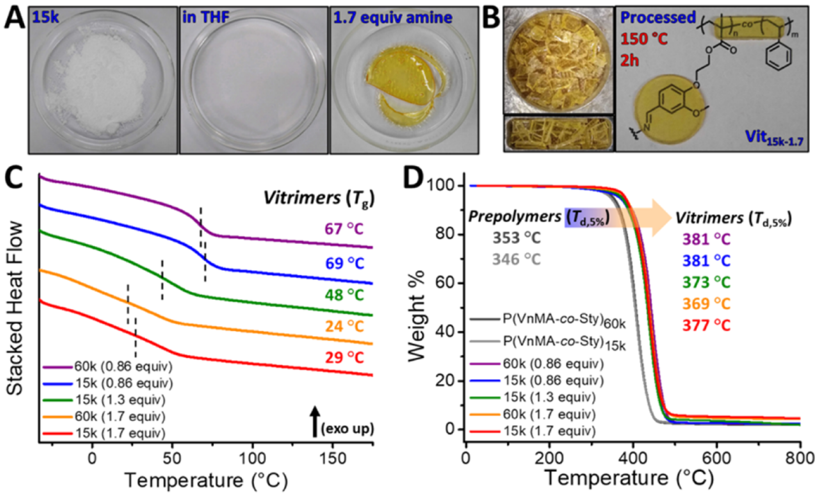

Figure 3. (A) Solution casting of the 70% excess amine content vitrimer derived from the 15k prepolymer ($\text{Vit}_{15\text{k-1.7eq}}$) and final cured network film (left to right). (B) Compression molding of the $\text{Vit}_{15\text{k-1.7eq}}$ into disc and bar geometries for rheology; specimens showed pristine clarity and were defect-free following 2 h at 150 °C under reduced pressure. (C) Differential scanning calorimetry (DSC) thermograms of the polystyrene-based vitrimers derived from two primary chain lengths showing tunable T_g values based upon amine equivalence (curves reflect third heating cycle). (D) Thermogravimetric analysis (TGA) of polystyrene copolymers and vitrimer networks showing excellent thermal stability following dynamic cross-linking with Priamine.

RESULTS AND DISCUSSION

The vanillin-containing PS copolymer was prepared in similar fashion to our previously reported system for fabricating enaminone cross-linked networks.[33] However, the reactive comonomer (bearing a β-ketoester) was replaced with that of vanillin methacrylate (VnMA), synthesized according to previous literature reports (Figures S1 and S2).[30,38] Copolymerization of styrene (Sty) and VnMA was performed with $[\text{VnMA}]_o/[\text{Sty}]_o$ 40:60 at 70 °C for 9 h (Figure 1A). The copolymerization displayed typical conventional radical polymerization kinetics, maintaining generally consistent number-average molecular weights (M_n) and elevated dispersity values ($Đ$) following the early stages of the copolymerization (Figure 1B,C).

The copolymer ($\text{P(VnMA-}co\text{-Sty)}_{60\text{k}}$) was purified by precipitation into cold methanol and was afforded in multigram yields (58.2 kg/mol, $Đ$ = 1.54, 42% VnMA incorporation; Figure S3). Seeking to investigate the tunability of the vitrimer flow behavior through primary chain length dependence, we repeated the copolymerization with a higher equivalence (0.08 equiv) of exogenous initiator to favor shorter chain lengths. In this manner, we were able to limit M_n of the final copolymer to 15.4 kg/mol ($\text{P(VnMA-}co\text{-Sty)}_{15\text{k}}$, $Đ$ = 1.61, 43% VnMA incorporation; Figures 2A and S4). Given the entanglement molecular weight (M_e) of PS is reported between 16–18 kg/mol,[39−41] the

$\text{P(VnMA-}co\text{-Sty)}_{15\text{k}}$ serves as an adequate comparator for a minimally entangled system. Moreover, the copolymer likely possesses a higher M_e than homopolymeric PS due to the longer pendant length of the VnMA comonomer, leading to an increase in free volume.[37,42] This hypothesis is supported by differential scanning calorimetry (DSC), which revealed glass transition temperatures (T_g) significantly lower than that of PS (∼100 °C) (Figure 2B). Moreover, the $\text{P(VnMA-}co\text{-Sty)}_{60\text{k}}$ displayed a higher T_g (85 °C) than that of $\text{P(VnMA-}co\text{-Sty)}_{15\text{k}}$ (79 °C), which we believe may be attributed to the polymer chains above the entanglement threshold.

We initially explored the viscoelastic tunability of the vitrimers by manipulating the mechanism of exchange between imine cross-links, achieved by cross-linking $\text{P(VnMA-}co\text{-Sty)}_{15\text{k}}$ in three different molar ratios of Priamine 1074, a 100% biomass-derived bisamine that provides plasticity and flexibility within the final vitrimer network (Scheme S1).[43] Three networks were prepared via solution casting in tetrahydrofuran (THF) with 1.7, 1.3, and 0.86 equiv of amine to VnMA ($\text{Vit}_{15\text{k-1.7}}$, $\text{Vit}_{15\text{k-1.3}}$, and $\text{Vit}_{15\text{k-0.86}}$, respectively) (Figures 3A and S5−S14). $\text{Vit}_{15\text{k-1.7}}$ and $\text{Vit}_{15\text{k-1.3}}$ served as model networks for varying levels of transaminative cross-link exchange, whereas the $\text{Vit}_{15\text{k-0.86}}$ was deliberately prepared by maintaining a stoichiometric excess of aldehyde to favor a predominately metathesis-like network rearrangement. The final vitrimer films were cured at 80 °C for 4 h under reduced pressure, showing good clarity and ductility. The films were broken into shards and subsequently compression molded at 150 and 165 °C (2 h, reduced pressure) for the excess amine and amine-deprived networks, respectively, yielding pristine vitrimer specimens with no defects and excellent clarity (Figures 3B and S7). DSC analysis displayed clear shifts toward higher T_g values as the Priamine content decreased, ranging from 29 to 69 °C for $\text{Vit}_{15\text{k-1.7}}$ and $\text{Vit}_{15\text{k-0.86}}$, respectively, (Figure 3C). Finally, the $\text{P(VnMA-}co\text{-Sty)}_{60\text{k}}$ was cross-linked with 1.7 and 0.86 equiv of amine to VnMA ($\text{Vit}_{60\text{k-1.7}}$ and $\text{Vit}_{60\text{k-0.86}}$, respectively) to study the effect of primary chain-entanglement within the two distinctive exchange regimes (Figures S5−S7). The networks exhibited T_g values in agreement with their $\text{Vit}_{15\text{k}}$ counterparts. Thermogravimetric analysis (TGA) of the networks displayed excellent thermal stabilities (temperature at 5% mass loss, $T_{d,5\%}$) ranging from 369−381 °C, with a notable increase in the thermal stabilities compared to the prepolymers (Figure 3D). Furthermore, the thermal stabilities of the networks are significantly higher than those of previous vinyl polymer-based vitrimers,[32,35] making the largely styrenic backbone a favorable platform for increasing thermooxidative robustness as compared to other prepolymer-based CANs.

We then investigated the viscoelastic flow behavior of the vitrimer networks by performing dynamic mechanical analysis

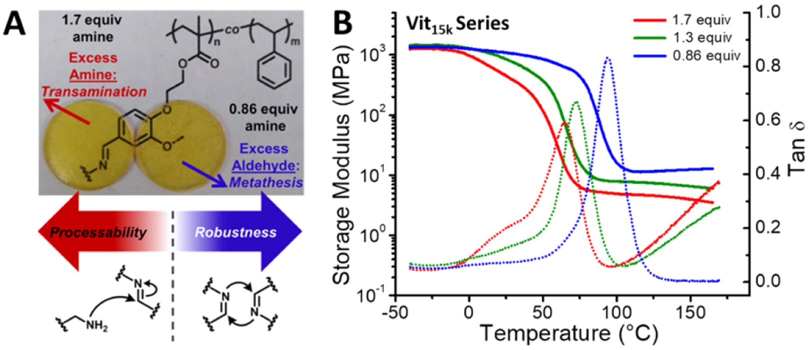

Figure 4. (A) Compression molded disc geometries of Vit$_{15k\text{-}1.7}$ and Vit$_{15k\text{-}0.86}$ corresponding to networks driven by transamination or metathesis, respectively. Such exchange dynamics allow for tailorability between network processability and dimensional robustness. (B) Dynamic mechanical analysis (DMA) thermograms of the Vit$_{15k}$ series demonstrating readily tunable cross-link densities and T_g values (taken at the peak of tan δ) within networks derived from a single, partially biobased prepolymer.

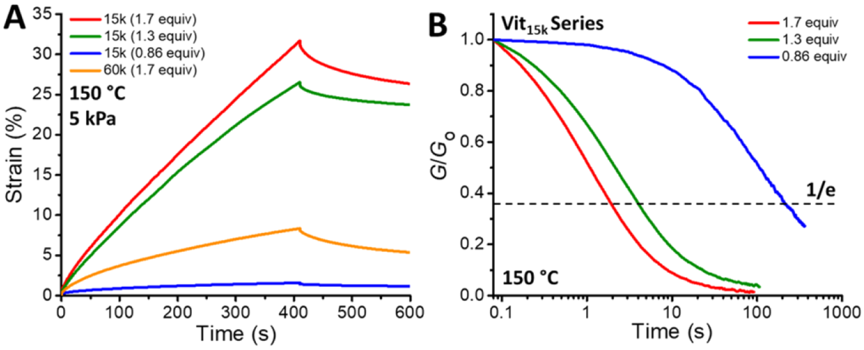

Figure 5. (A) Creep-recovery experiments of Vit$_{15k}$ series demonstrating a dramatic increase in creep resistance when network dynamics are dictated by imine metathesis (0.86 equiv amine) or within transaminative networks (1.7 equiv amine) when utilizing a prepolymer above the entanglement threshold. (B) Stress-relaxation curves of the Vit$_{15k}$ networks at 150 °C displaying disparate flow behavior between the operative exchange mechanisms.

(DMA), creep-recovery, and stress-relaxation experiments to elucidate the balance between rapid processability (transamination) and dimensional robustness (metathesis) (Figure 4A). DMA thermograms of the Vit$_{15k}$ networks displayed three distinct rubbery plateau moduli in good agreement with the variable cross-link densities of the vitrimers (Figure 4B). Moreover, the networks displayed a clear transition to a more uniform mode of energy dissipation (taken as the curve of tan δ) as well as increasing $T_{g,\mathrm{DMA}}$ (taken at the maximum of tan δ) values as the Priamine content decreased and the network cross-link density increased. These discrete cross-link densities were further supported by swelling studies (conducted in THF), with higher swelling ratios and lower gel contents in the networks with excess amine than that of the amine-deprived vitrimer (Table S1; eqs S1 and S2). In this way, these significantly Priamine-based vitrimers can be readily tuned to access a range of thermomechanical properties that may be required under different service conditions.

Next, we demonstrated a clear distinction between metathesis and transamination imine exchange through creep-recovery and stress relaxation experiments. The disparate flow behavior was profoundly reflected in the creep behavior (conducted at 150 °C under 5 kPa of constant force), with significant creep observed in the excess Vit$_{15k}$ networks and negligible creep in the amine-deprived counterpart (Figures 5A and S15−S18). Notably, the Vit$_{15k\text{-}1.3}$ (30% excess amine content) displayed only a slight decrease in material creep as compared to the Vit$_{15k\text{-}1.7}$ (70% excess amine content), reflective of the rapid nature of polyimine transamination at such elevated temperatures. While the Vit$_{15k\text{-}0.86}$ enables outstanding creep resistance due to its sluggish flow behavior and elevated T_g, its limited flow behavior would ultimately undermine reprocessing lifetimes and network circularity. Gratifyingly, the primary chain entanglement that resulted from using a higher molecular weight prepolymer significantly bolstered the creep resistance of the final vitrimer even when operating under 70% excess amine content (Vit$_{60k\text{-}1.7}$).

In this way, we can access the conditions amenable to facile reprocessability (transamination) while enriching dimensional stability by introducing secondary, physical cross-links (primary chain entanglement). This supramolecular contribution of primary chain entanglement is well supported, given that the Vit$_{60k}$ networks and their respective Vit$_{15k}$ counterparts exhibited nearly identical cross-link densities as determined by DMA (Figure S19). Moreover, the Vit$_{60k}$ networks were shown to be highly moisture resistant, with virtually no difference in material behavior as determined by DMA following 8 days of immersion in DI water (Figure S20). As the Vit$_{60k}$ networks displayed augmented creep resistance and hydrolytic robustness, we further characterized these materials by tensile testing, with the materials displaying minimal extensibility and Young's moduli of 11.8 and 4.5 MPa for Vit$_{60k\text{-}0.86}$ and Vit$_{60k\text{-}1.7}$, respectively (Figure S21). Next, stress relaxation experiments were conducted to quantify the disparate flow behavior of the two exchange mechanisms as well as the dependence on primary chain length. The Vit$_{15k}$ and Vit$_{60k}$ networks were

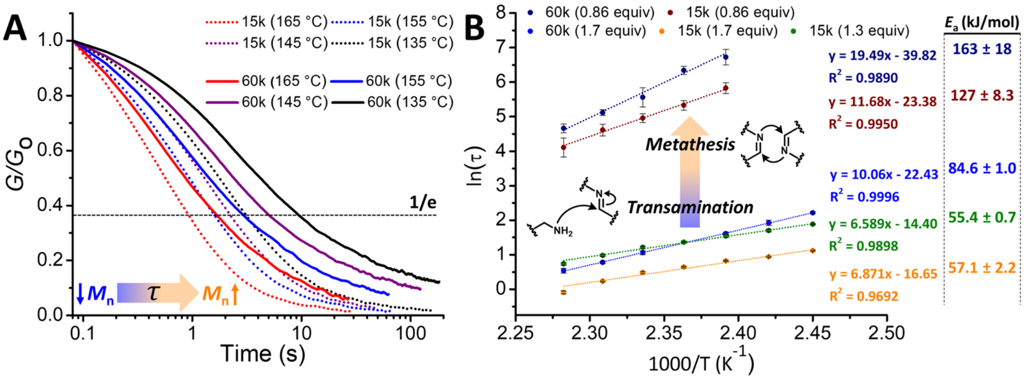

Figure 6. (A) Stress-relaxation curves of the Vit$_{60k}$ (solid) and the Vit$_{15k}$ (dotted) when cross-linking with 1.7 equiv amine. Data clearly indicates increased characteristic times at all temperatures when primary chain entanglement is introduced within the dynamic network, supporting the increased creep resistivity of the Vit$_{60k}$ networks. (B) Arrhenius plot of PS-based vitrimer systems from stress relaxation experiments with energy of activation (E_a) values, clearly demonstrating multifaceted viscoelastic tunability directed by both mechanism of exchange and prepolymer chain length.

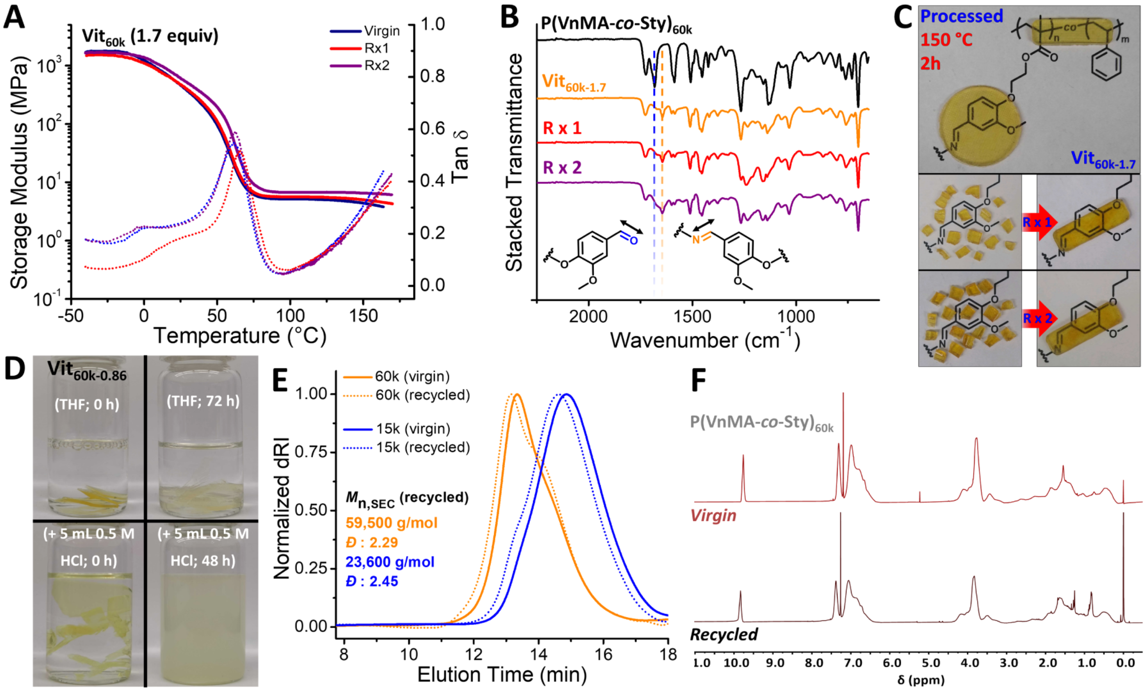

Figure 7. (A) Dynamic mechanical analysis (DMA) thermograms of the Vit$_{60k-1.7}$ over two reprocess cycles showing good recyclability and consistent rubbery plateau moduli. (B) FTIR spectra of P(VnMA-*co*-Sty)$_{60k}$ prepolymer, the initial vitrimer network derived therefrom, and two cycles of reprocessed material. Spectra showed a clear disappearance of the aldehyde stretching (blue dotted line) and an increase of the imine stretching (orange dotted line) over the lifetime of the vitrimer network. (C) Pictures of original disc and bar geometries of Vit$_{60k-1.7}$ compression molded at 150 °C for 2 h, with each destruction and healing cycle shown below. Reprocessing conditions were identical to those of initial processing. (D) Chemical recycling of the Vit$_{60k-0.86}$ vitrimer utilizing acidic hydrolysis showing efficient degradation under mild conditions. (E) Overlaid SEC traces of the recycled P(VnMA-*co*-Sty) prepolymers with the virgin materials showing slight increase in copolymer molecular weights and a significant increase in dispersity values, possibly indicating residual imines and polymer branching. (F) ^{1}H NMR spectra of recycled P(VnMA-*co*-Sty)$_{60k}$ and the virgin prepolymer showing conservation of the main characteristic polymer signals.

subjected to a 0.3% displacement, and their relaxation behavior was studied at temperatures ranging from 135 to 165 °C (Figures S22−S29). The mechanistic dependence on viscous flow was clearly evidenced, as Vit$_{15k-1.7}$ and Vit$_{15k-1.3}$ exhibited rapid flow at elevated temperatures with characteristic relaxation times (τ, when $G/G_0 = 1/e$) less than 10 s at 150 °C (Figure 5B). Conversely, the Vit$_{15k-0.86}$ operating principally through imine metathesis required 209 ± 29 s and displayed unique relaxation behavior compared to the networks with excess amine content. Given recent studies refuting imine metathesis feasibility,[31] it is possible that the observed network dynamics attributed to imine metathesis could arise from residual, kinetically trapped amines percolating the network or via low levels of imine hydrolysis by adventitious water. Nevertheless, our deliberate preparation of vitrimers containing excess aldehyde moieties indicate that network dynamics can be tuned over a wide range of viscoelastic flow. Clear chain-length dependence on network relaxation was demonstrated, as the Vit$_{60k-1.7}$ exhibited slower relaxation dynamics at all temperatures compared to the Vit$_{15k}$ counterpart (Figure

6A), agreeing well with previous reports on pendent-cross-linked vitrimer networks.[37,44,45] This mechanistic tunability of the networks through chemical and architectural means was quantified by fitting stress relaxation data for all vitrimer networks to Arrhenius law (by plotting τ versus temperature).

These data provided the energy of activation for viscous flow (E_a), a value describing the viscous flow sensitivity of the network with respect to temperature changes (Figures 6B and eq S3−S5). As expected, the $\text{Vit}_{15k\text{-}1.7}$ and $\text{Vit}_{15k\text{-}1.3}$ networks displayed significantly lower E_a values (57.1 ± 2.2 and 55.4 ± 0.7 kJ/mol, respectively) than that of $\text{Vit}_{15k\text{-}0.86}$ (127 ± 8.3 kJ/mol), demonstrating higher energy requirements to facilitate flow within metathesis-driven networks. The similarity in the E_a values of the Vit_{15k} networks with excess amine content is expected, as the reduction in residual nucleophile limits the extent of transamination (reflected as an increase in τ at each temperature) rather than the temperature-sensitivity of the exchange mechanism. However, when a secondary cross-link was introduced through primary chain entanglement ($\text{Vit}_{60k\text{-}1.7}$), the τ values were comparable to $\text{Vit}_{15k\text{-}1.3}$ but indicated a clear increase in the E_a (84.6 ± 1.0 kJ/mol), with a more rapid increase in network viscosity at temperatures below 150 °C. This entanglement effect was further demonstrated in the vitrimers governed by metathesis, with the Vit_{60k} showing a distinctive increase in both τ and E_a (163 ± 18 kJ/mol) in comparison to the Vit_{15k}. These results highlight a versatile methodology for achieving tunable viscoelastic flow behavior in the PS-based vitrimers systems through an interplay of exchange mechanism and architectural enhancement through primary chain entanglement.

The circularity of this biobased vitrimer system was demonstrated through mechanical and chemical recyclability studies. $\text{Vit}_{60k\text{-}1.7}$, selected for its balance between efficient network exchangeability and resistance to creep deformation, was subjected to two cycles of destruction and remolding. Reprocessed specimens (Rx1 and Rx2) displayed rheological behavior consistent with the virgin material, with moderate increases in rubbery plateau moduli and $T_{g,\text{DMA}}$ values over each iteration (Figures 7A and S30). FTIR analysis indicated good conservation of the vitrimer spectra compared to the original sample, with an increased C = N band at ~1650 cm^{-1}, suggesting more complete network formation after reprocessing (Figures 7B and S31). The vitrimer samples maintained excellent clarity and displayed minimal discoloration, with no evidence for accumulation of material defects (Figure 7C). Chemical remediation of the PS vitrimers was demonstrated through network depolymerization facilitated by acidic hydrolysis (Figure 7D) of the amine-deprived $\text{Vit}_{60k\text{-}0.86}$ and $\text{Vit}_{15k\text{-}0.86}$ networks. Following depolymerization of the vitrimers, the isolated copolymers displayed SEC traces and^{1}H NMR spectra that were generally consistent with the original P(VnMA-*co*-Sty) building blocks (Figures 7E and F; Figures S32 andS33), albeit with higher dispersity values (2.29−2.45) and slightly elevated M_n values. We hypothesize that this may be attributable to low amounts of residual, oxidized amine adducts with the polymer that are resistant toward acid-catalyzed hydrolysis, supported by additional^{1}H NMR signals in the region of 0−2.0 ppm. Nevertheless, this study demonstrates that the robust vitrimer networks can be readily depolymerized under mild conditions for end-of-life remediation.

CONCLUSION

This study presents a flexible and sustainable method for producing biobased PS vitrimer materials using vanillin methacrylate and Priamine cross-linkers. By adjusting the molecular weight of the prepolymers and refining the cross-link exchange processes, we achieved an optimal balance between reprocessability and creep resistance, leading to enhanced dimensional stability without sacrificing network dynamics. Considering the extensive applications and cost-efficiency of styrene-based polymers, incorporation into a highly bioderived, reprocessable network with excellent thermomechanical and solvochemical properties broadens the utility and sustainability of PS materials. This methodology improves the longevity and durability of these materials and provides for more circular thermosets through mechanical and chemical recyclability. Our findings highlight the potential for scalable, durable, and renewable PS thermoset materials suitable for a wide range of commercial uses.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsapm.4c01900.

Materials and instrumentation, polymer synthesis and characterization, vitrimer synthesis, rheology, and references (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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