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This study unveils a sustainable, easily recyclable biocomposite, leveraging the dynamic nature of covalently adaptive bonds in a vitrimer matrix. The fabrication involved a fatty acid-derived vitrimer as the polymer matrix and multi-layered, nonwoven flax mat as reinforcing scaffold. The incorporation of these fibers significantly improved the mechanical performance of the vitrimer matrix uniformly. The ester-based covalently adaptive network plays a crucial role in enabling exceptional fiber-matrix bonding, as well as recyclability. The vitrimer matrix dissolves in ethylene glycol through transesterification, facilitating complete material recovery and biocomposite recycling without compromising the original properties of the matrix and reinforcing fibers.

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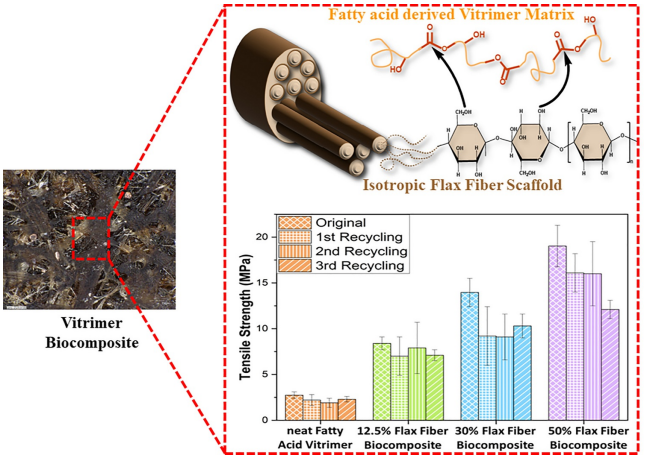

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Additive Manufacturing of Functional and Smart Composites
Research Letter

Flax fiber-reinforced fatty acid vitrimer biocomposite with enhanced chemical recyclability

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Abstract

This study unveils a sustainable, easily recyclable biocomposite, leveraging the dynamic nature of covalently adaptive bonds in a vitrimer matrix. The fabrication involved a fatty acid-derived vitrimer as the polymer matrix and multi-layered, nonwoven flax mat as reinforcing scaffold. The incorporation of these fibers significantly improved the mechanical performance of the vitrimer matrix uniformly. The ester-based covalently adaptive network plays a crucial role in enabling exceptional fiber-matrix bonding, as well as recyclability. The vitrimer matrix dissolves in ethylene glycol through transesterification, facilitating complete material recovery and biocomposite recycling without compromising the original properties of the matrix and reinforcing fibers.

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Introduction

Over recent decades, escalating acknowledgment of the link between greenhouse gas emissions and global warming has substantially increased awareness regarding the pivotal contribution of bio-based feedstocks to the development of emerging high-performance materials.[1–5] This heightened ecological consciousness has sparked a revived interest in the creation of economically feasible, biodegradable materials endowed with enhanced properties. Conventionally, the incorporation of fibers and fillers into polymer matrices serve a dual purpose—reducing costs while simultaneously enhancing or customizing the properties of the resulting materials. These improvements span a spectrum of characteristics, encompassing strength, modulus, hardness, as well as rheological and thermal properties.[6–8] The evolution of polymer composites, with a particular focus on fiber-reinforced thermosets, has garnered considerable attention within the industry. However, the escalating utilization of fiber-reinforced polymer composites has led to a substantial increase in waste materials, including off-cuts generated during manufacturing and end-of-life components. This surge in waste has sparked environmental concerns and heightened economic awareness, underscoring the pressing need for recycling fiber-reinforced polymer composites.

The design of environmentally friendly and sustainable fiber-reinforced composites demands a comprehensive approach. It extends beyond merely incorporating cellulosic or lignocellulosic materials like cellulose, sisal, jute, and wood fibers into polymer matrices. It requires meticulous design considerations to achieve full recyclability for both polymer matrix and utilized fibers in composites. This objective, however, presents notable challenges. Firstly, a considerable obstacle lies in efficiently separating the polymer from embedded fibers to facilitate their reclamation. The existing mechanical and thermo-mechanical recycling methods employed for various fiber-reinforced thermosets prove cumbersome. These processes often entail demanding conditions, rendering them unsuitable for a diverse range of fibers. Furthermore, recycled constituents frequently result in lower value applications, as the original fibers cannot be fully recovered due to length shortening and property degradation.[9,10] Secondly, thermosetting polymers that are inherently non-recyclable yet extensively favored in fiber-reinforced composites for their exceptional chemical resilience, stability, and superior mechanical performance arising from their permanent crosslinked network pose a formidable challenge to conventional processing or forming/molding methods.[11,12] The inherent permanence of cross-linkages within thermoset materials hinders their (re)processability

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through conventional means. Many of these challenges associated with fiber-reinforced thermosetting composites can be effectively mitigated by strategically incorporating dynamic covalent bonds within crosslinked networks. This integration introduces precise mechanisms for bond exchange triggered by external stimuli such as light, heat, or pH.[13,14] Remarkably, temperatures required for bond exchange consistently remain well below the degradation temperatures of the polymer backbone. This unique attribute empowers networked structures to undergo seamless processing and reprocessing, aligning with the versatility typically associated with thermoplastics.

In this study, we fabricated an environmentally friendly, sustainable, and readily recyclable biocomposite by harnessing the dynamic characteristics of covalently adaptive bonds. The biocomposite was comprised a fatty acid-derived vitrimer as the polymer matrix and non-woven, isotropic flax fibers serving as reinforcing scaffold. The incorporation of isotropic flax fibers led to a substantial enhancement in the mechanical performance of the inherently soft and elastomeric vitrimer matrix, exhibiting improvements consistently in all directions. Notably, the dynamic nature of the ester-based covalently adaptive network is pivotal in enabling exceptional fiber-matrix bonding and recyclability of the flax fiber-reinforced biocomposite. The fatty acid vitrimer showcased a remarkable ability to dissolve fully in ethylene glycol solvent, engaging in bond exchange reactions with the alcohol moieties of the solvent through transesterification. This unique phenomenon allows for the dissolution of the vitrimer matrix without causing damage to the reinforcing fibers and enabling complete recycling of both the vitrimer matrix and reinforcing fibers without compromising their original properties.

Experimental

Materials

In our study, we prepared an ester-based covalently adaptive network. The synthesis involved a mixture (23% di-functional and 77% tri-functional) of carboxylic fatty acids (Pripol-1040, supplied by Cargill Bioindustrial, Wayzata, MN, USA), diglycidyl ether of bisphenol A (DGEBA, Sigma-Aldrich, St. Louis, MO, USA), and metal catalyst Zinc acetylacetonate hydrate ($Zn(acac)_2$, Sigma-Aldrich, St. Louis, MO, USA). ACS grade acetone (Sigma-Aldrich, St. Louis, MO, USA) was a diluent for the monomer precursors. Ethylene glycol (Sigma-Aldrich, St. Louis, MO, USA) was used for recycling experiments. All chemicals were utilized without additional purification. The flax fibers usedtilize in our research were non-woven isotropic fibers provided by Endeavor Composites, Knoxville, TN, USA.

Fabrication of fatty acid vitrimer and its biocomposite

A polyester-based vitrimer matrix was synthesized through a chemical reaction involving carboxylic acid functionalities in fatty acids and epoxy functional groups of DGEBA. This reaction was catalyzed by $Zn(acac)_2$ vitrimer catalyst. The preparation of polyester-based vitrimer matrix maintained a stoichiometric feed ratio of carboxylic acid to epoxide functional groups, set at 1:1. The detailed experimental procedure for synthesizing the fatty acid-derived vitrimer matrix can be found in previously reported work.[15,16] Briefly, a mixture of fatty acids and $Zn(acac)_2$ (at 5 mol% relative to -COOH groups) was heated at 150°C for 30 min in a dried glass vial to obtain a homogenous solution. Subsequently, this fatty acid/$Zn(acac)_2$ solution was mixed with DGEBA at 40°C and manually stirred until homogeneity and translucency were achieved. To ensure thorough and uniform mixing, the solution underwent further homogenization in a SpeedMixer (FlackTek, SC) at 2500 rpm for 10 min. The resulting solution was then transferred to a custom-made polytetrafluoroethylene (PTFE) mold, subjected to vacuum degassing, and cured at 130°C for 6 h in an oven.

To fabricate the vitrimer biocomposite, carboxylic acid and epoxy-based monomer precursors, i.e., fatty acid and DGEBA, were pre-mixed with vitrimer catalyst $Zn(acac)_2$, following the previously mentioned procedure. Acetone (60 ml) was introduced as a diluent in the monomer precursor solution. The solution was stirred using a magnetic bead to ensure complete homogeneity of the reaction mixture. A non-woven isotropic flax fiber mat was utilized as a reinforcing scaffold for the vitrimer biocomposite. Before fabricating the multi-layered biocomposite laminate, the flax fiber scaffold was dried for 12 h at 80°C and subsequently weighed. The fibrous scaffold was impregnated with the reaction mixture by immersion in diluted fatty acid/DGEBA/$Zn(acac)_2$ solution for 10 min to ensure saturation of the scaffold with monomer precursors. The fibrous scaffold exhibited immediate absorption of the solution, ensuring appropriate dispersion of reactive moieties. Subsequently, the solution-dipped fibrous scaffold was transferred to a convection oven and heated at 60°C for 12 h to completely evaporate the acetone diluent, followed by assembling the layered laminate and curing at 130°C for 6 h under pressure (5 atm) using a Carver hydraulic laboratory press. The vitrimer biocomposite was weighed following the curing process, and the fiber weight percentage (wt.%) was subsequently determined. Schematic illustration of fabrication procedure of the vitrimer biocomposite is presented in Figure S1, ESI.

Physical, thermal, and mechanical characterization

Room temperature FTIR spectra were obtained using a Frontier FT-IR/NIR Spectrometer (PerkinElmer, SC) for the neat fatty acid vitrimer, vitrimer biocomposite, and neat flax fiber to elucidate the functional groups and analyze the chemical structure. The measurements were conducted using attenuated total reflection (ATR) mode, with spectra and data collected as averages of 32 scans within the absorbance range of 4000 to 600 cm^{-1} at a spectroscopic resolution of 4 cm^{-1}. The thermal stability and degradation of the neat fatty acid vitrimer, biocomposite, and neat flax fiber were characterized through a thermogravimetric analyzer (TGA, Q500 TA Instruments, New Castle, DE) under nitrogen purge. Each

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sample was heated from 25°C to 700°C at a heating rate of 10°C/minute, and the corresponding change in weight percent was recorded as a function of time. The dynamic mechanical properties for each vitrimer were analyzed on a Dynamic Mechanical Analyzer (DMA, Q800 TA Instruments, New Castle, DE) in tension mode. A strain rate of 0.1%, a frequency of 1 Hz, and a heating rate of 5°C/minute were employed over a temperature range of -50°C to 200°C. Each specimen had a dimension of 20 mm × 10 mm cut from the cured fatty acid vitrimer and biocomposite films. Additionally, the frequency sweep experiment was also performed on each vitrimer sample at 25°C from 0.01 Hz to 100 Hz at a strain rate of 0.02%. DMA was employed to determine the storage modulus and Tan δ for neat vitrimer and biocomposite samples. Differential Scanning Calorimetry (DSC) was performed to determine the glass transition temperature (T_g) of the neat vitrimer and biocomposite samples. The DSC analysis was performed using a heat/cool/heat thermal cycle on a Q2000 (TA Instruments, New Castle, DE), between -50 to 200°C with a heating and cooling rate of 5°C/minute. For each run, ~ 10 mg of the sample was added to a T-Zero aluminum pan.

Uniaxial tensile tests were performed to analyze the mechanical properties of all the neat vitrimer and vitrimer biocomposite systems using an MTS Criterion model 42 tensile frame with dog-bone specimens, following ASTM-D638. The tensile measurements were performed using a 5000 N load cell at a 5 mm/min strain rate. The dog-bone specimens were precisely cut using a water-jet cutter (ProtoMAX, Kent, WA) to maintain uniform dimensions (98.0 mm × 6.8 mm × 1.0 mm). The gauge and thickness dimensions were measured for each specimen prior to testing, and a minimum of four specimens were tested for each sample. Young's modulus was calculated from the slope of the stress–strain curve between the strain value of 0.1% and 0.2% for each sample. The mechanical properties of the recycled samples were performed on rectangular specimens (30.0 mm × 7.5 mm × 1.0 mm) using the same conditions.

Results and discussion

In this study, we fabricated a vitrimer biocomposite reinforced with natural fibers, employing a polyester-based vitrimeric matrix and isotropic flax fiber non-woven as the reinforcing scaffold. The synthesis of the polyester-based vitrimeric resin involved a classical ring-opening condensation copolymerization between monomer precursors containing carboxylic acid and epoxy functionalities catalyzed by $Zn(acac)_2$. The crosslinking reaction, initiated by hydrated $Zn(acac)_2$, triggered nucleophilic attacks of carboxylate ions on epoxy groups, leading to the formation of β-hydroxy groups and ester moieties. These groups activate transesterification exchange reactions (TERs) at elevated temperatures in the presence of Zinc (II) catalyst.[17] $Zn(acac)_2$ serves as a dual role in the epoxy-acid polymerization, facilitating crosslinking between epoxy and acid while promoting bond exchange between ester linkages and neighboring β-hydroxy groups within the matrix.[16,18] These thermally stimulated TERs-induced topological rearrangements in the overall matrix, causing changes in the viscoelastic properties of the vitrimer. Consequently, the vitrimer biocomposite was endowed with traits such as malleability and recyclability, which are absent in traditional thermoset networks. Figure 1(a) illustrates a representative reaction between carboxylic acid-containing fatty acids and epoxy-containing DGEBA, culminating in the formation of an ester-based covalently adaptive network. This network undergoes topological rearrangement through transesterification, facilitated by functionalities like β-hydroxy groups and unreacted carboxylate groups. A range of flax fiber-reinforced vitrimer biocomposites was systematically crafted by adjusting the flax fibers' weight fraction in the matrix's solvated monomeric precursor. After the curing stage, the vitrimer biocomposites underwent weighing, disclosing distinct flax fiber weight fractions of 12.5%, 30% and 50% (w/w).

The crosslinking reaction between the carboxylic acid and epoxy species in the vitrimer and biocomposite systems was meticulously characterized using FTIR analysis. The DGEBA presented a distinctive epoxy ring stretching vibration at 915 cm^{-1}, and the fatty acids displayed a characteristic -C=O stretching peak at 1710 cm^{-1} (see Figure S2). The confirmation of the crosslinking reaction between these reactive moieties was evident from the disappearance of these peaks and the appearance of distinctive ester linkages, as indicated by the emergence of two characteristic peaks. Specifically, these peaks were identified at 1740 cm^{-1}, representing the carbonyl C=O stretching, and 1230 cm^{-1} for C–O–C ether stretching. Both distinctive ester peaks were unequivocally observed in the neat vitrimer and the biocomposite spectra, as illustrated in Fig. 1(b). In addition to the ester peaks, a distinctive feature of the crosslinking reaction between the monomer precursors is the emergence of a broad O–H stretching peak at 3400 cm^{-1}. In the case of the neat fatty acid vitrimer, this broad O–H stretching peak is attributed to the formation of β-hydroxy groups during the crosslinking reaction between the epoxy and acid moieties. As flax fiber comprises cellulose, hemicellulose, pectin, and lignin building blocks, the neat flax fiber exhibited a broad inter and intramolecular O–H stretching band ranging from 3100 to 3600 cm^{-1}. Biocomposite featuring higher fiber loading (50 wt%) exhibited a reduction in FTIR spectra intensity, attributed to the heightened rigidity and diminished transparency associated with increased fiber content, resulting in the suppression of the peak intensity of the biocomposite. As hydroxyl groups introduced through fillers contribute to transesterification kinetics and interfacial adhesion, the peak intensity ratio of hydroxyl to ester groups in a biocomposite was assessed relative to the weight fraction of flax fibers (Figure S3, ESI).[17,19] The FTIR spectra of the vitrimer biocomposite revealed a systematic increase in the peak intensity ratio of hydroxyl groups to ester groups with an augmentation in the weight fraction of flax fiber. The increase in the peak intensity ratio with higher fiber loading suggests a greater potential for productive exchange and interactions between hydroxyl and

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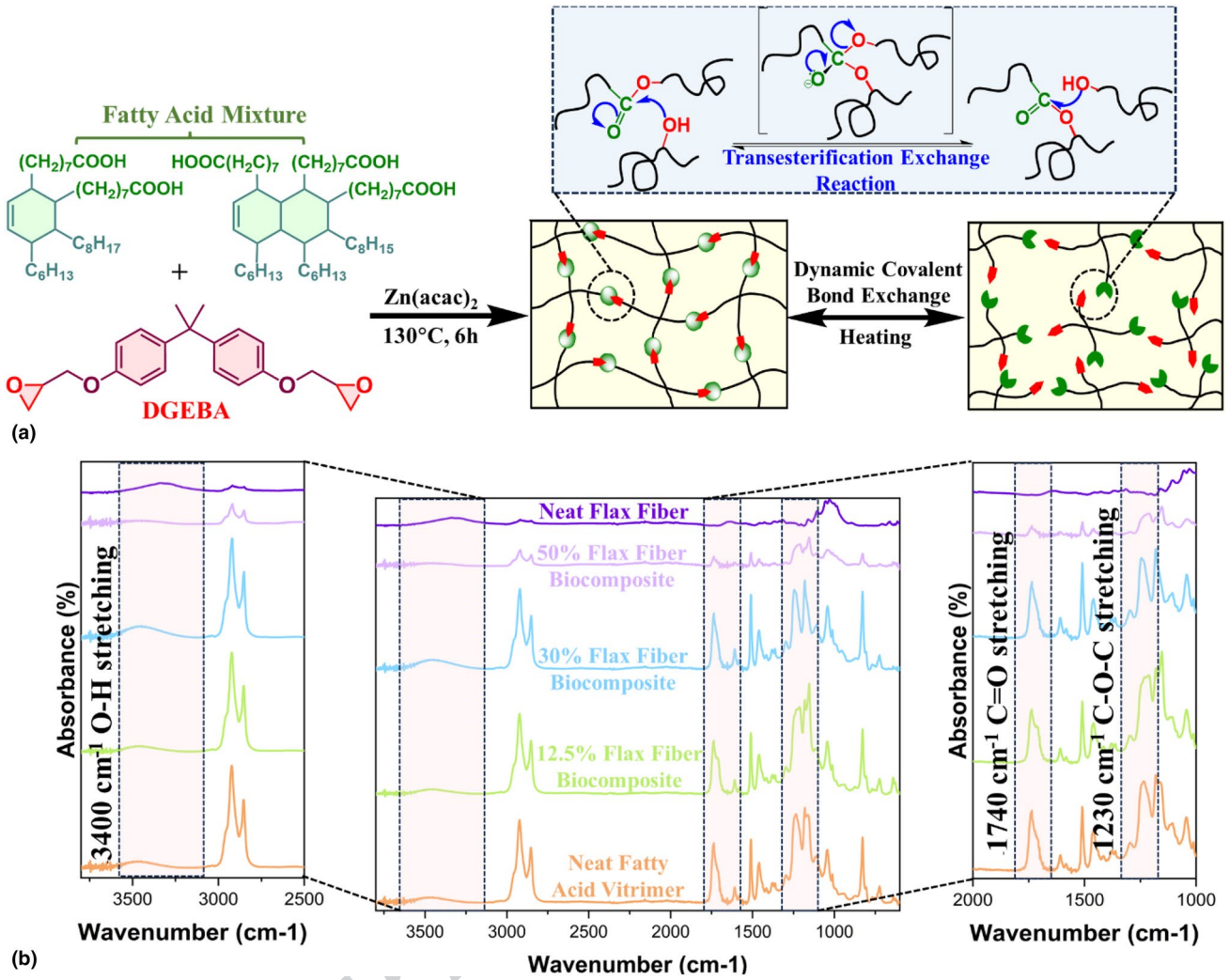

Figure 1. (a) Schematic illustration of the formation of covalently adaptive networks through topological transesterification in the product formed by reaction between fatty acids and DGEBA. (b) FTIR spectra for neat fatty acid vitrimer, vitrimer biocomposite with different wt.% of flax fiber loading, and neat flax fiber.

ester groups, leading to the enhancement of the biocomposite's tensile strength as elaborated in the subsequent section.

The thermal stability of the neat flax fiber, fatty acid vitrimer, and biocomposite was assessed through TGA experiments, as depicted in Fig. 2(a). The results underscored a substantial enhancement in the thermal stability of the flax fiber upon the incorporation of the vitrimer matrix. Specifically, the neat flax fiber scaffold exhibited a 5% weight loss temperature ($T_{d5\%}$) of 160°C, a value that witnessed a significant increase to a range between 284 and 340°C as the flax fiber content decreased from 50% (w/w) to 12.5%(w/w). For the neat fatty acid vitrimer, a $T_{d5\%}$ of 353°C was observed. Notably, the biocomposites formulated with these fatty acid vitrimers demonstrated markedly superior thermal stability compared to previously reported bio-derived vitrimeric systems and conventional thermoset materials, which typically initiated thermal degradation within the temperature range of 190 to 220°C.[20,21]

Additionally, the temperature-dependent storage moduli of both fatty acid vitrimer and vitrimer biocomposite were performed to unravel the nuanced reinforcing effects of fillers [Fig. 2(b)]. In a general trend, the storage moduli of both matrix and flax fiber-reinforced biocomposites exhibit a diminishing trend with increasing temperatures. Remarkably, the neat fatty acid vitrimer displayed a storage modulus of 166.5 MPa at 25°C, escalating systematically to 2790 MPa, 3880 MPa, and 3340 MPa for the 12.5% (w/w), 30% (w/w), and 50% (w/w) flax fiber-reinforced vitrimer biocomposites, respectively. The observed surge in the storage modulus with an augmented loading of flax fibers originates from a restriction in the molecular mobility of polymer chains. This constrained mobility contributes to increased stiffness and rigidity within the material. As the fiber concentration rises, the reinforcing impact becomes notably pronounced, resulting in a discernibly higher storage modulus for the composite material. Noteworthily, the observed

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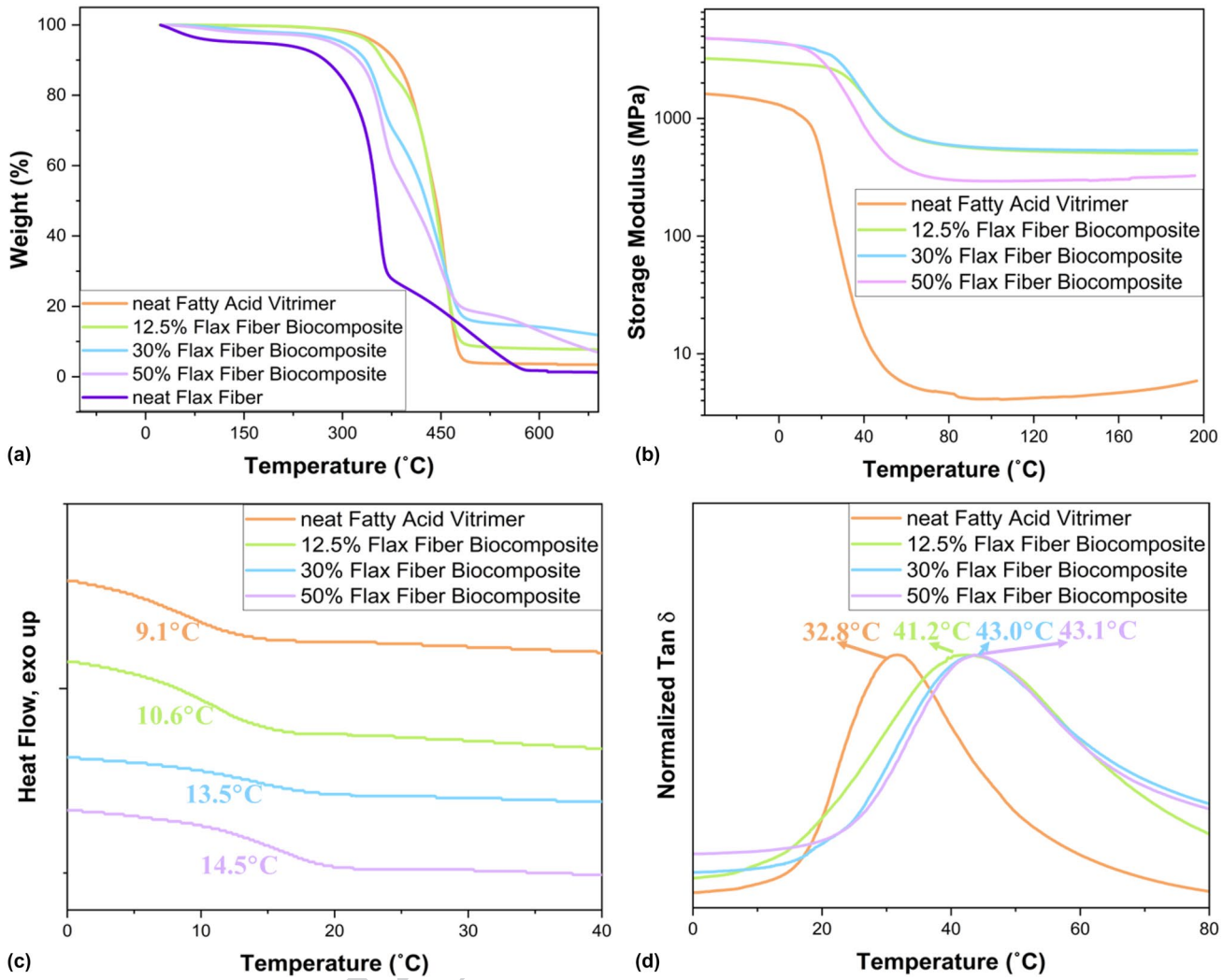

Figure 2. (a) TGA thermograms of neat fatty acid vitrimer, vitrimer biocomposite with different wt.% of flax fiber loading and neat flax fiber. (b) storage modulus, (c) DSC thermograms, and (d) normalized Tan δ of neat fatty acid vitrimer, vitrimer biocomposite with different wt.% of flax fiber loading.

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high-temperature rubbery modulus drops slightly in the 50% flax fiber biocomposite. This drop in high-temperature modulus for highly reinforced composites can be attributed to several factors. During the fabrication process, the curing of monomer precursors in a biocomposite happens while being impregnated in the fibrous scaffold. The hydroxyl functionalities present in the fibers also compete and interact covalently with the epoxy monomer in the precursors. Consequently, as the weight fraction of flax fibers increases, the high degree of interaction with the hydroxyl functionalities of fiber results in reduction in the matrix molecular weight and degree of the network formed within the matrix. While the contribution from chemically bonded fiber fraction leads to a higher T_g and tensile strength for the 50% w/w vitrimer biocomposite, it also results in a slight drop in modulus beyond the T_g of the material.

Furthermore, the impact of fiber loading on the glass transition temperature of the biocomposite was discerned by analyzing DSC thermograms and normalized *Tan* δ plots, as illustrated in Fig. 2(c) and (d), respectively. Both data sets revealed a gradual elevation in the glass transition temperature (T_g) of the biocomposite with an increasing flax fiber loading. This observation phenomenon can be attributed to the reinforcement effect resulting from heightened fiber loading, which, in turn, reduces the free volume available for polymer chain movement, consequently leading to an augmentation in T_g. For the neat fatty acid vitrimer, the T_g was determined to be 9.1°C and 32.8°C from the DSC and *Tan* δ analysis, respectively. As the fiber loading increased, a systematic rise in the T_g was evident in the DSC thermograms, escalating from 10.6°C to 14.5°C for 12.5% (w/w) and 50% (w/w) flax fiber loading. This trend was similarly reflected in the *Tan* δ where the T_g increased from 41.2°C for the 12.5% (w/w) loading to 43.1°C for the 50% (w/w) flax fiber vitrimer biocomposite (Table I).

The assessment of mechanical properties is crucial in determining the recyclability of natural fillers within a polymer composite, as the thermodynamic incompatibility of their components often results in suboptimal mechanical characteristics. Figure 3(a) illustrates representative stress–strain curves derived from unidirectional tensile testing for neat fatty acid vitrimer and vitrimer biocomposites, encompassing various flax fiber loadings up to 50% w/w. The subsequent data on tensile strength, tensile modulus, and toughness are detailed in Fig. 3(b) and (c). The neat fatty acid vitrimer exhibited a tensile strength and modulus of 2.8 MPa and 22 MPa, respectively. Notably, the incorporation of higher weight fractions of flax fibers in the biocomposite led to a significant enhancement in both the tensile strength and modulus of the biocomposite. Among all the compositions, the 50% w/w flax fiber biocomposite demonstrated the highest tensile strength and modulus, reaching 19.0 MPa and 1016.9 MPa, respectively. However, this biocomposite exhibited a brittle failure with only 5% elongation at break. In contrast, the 30% and 12.5% flax fiber biocomposite displayed a relatively higher strain to failure, 8% and 25%, respectively, accompanied by respective peak stress of 13.9 MPa and 8.4 MPa. The incorporation of fibers into a polymer composite typically enhances its tensile strength by promoting uniform load distribution, augmenting stiffness, and facilitating crack arrest and deflection. Consequently, this increase significantly amplifies the overall tensile strength of the composite. Additionally, the higher tensile strength observed in all flax fiber-reinforced vitrimer biocomposite can be attributed to the substantial improvement in interfacial adhesion resulting from the ester exchange reactions between the vitrimer matrix and the hydroxyl functionalities present on the flax fibers.[19,22] Furthermore, the impregnation of fibers with the vitrimer matrix led to a noteworthy increase in secondary hydrogen bonding interactions, further enhancing tensile strength, as observed in various hydrogels and elastomeric samples.[23,24] Overall, while increasing fiber loading tends to amplify the tensile strength of a composite, it often entails a trade-off with a decrease in toughness.[25,26] This decrease can be attributed to an improved fiber-matrix interface resulting from the increased fiber loading that lowers matrix ductility and enhances composite brittleness.[27] Since the matrix material plays a crucial role in providing ductility and energy absorption mechanisms, higher volume fraction of rigid fibers diminishes matrix ductility. This, in turn, fosters a more brittle behavior, thereby contributing to the observed decrease in toughness, as elucidated in higher flax fiber biocomposites (30, 50% w/w). Crucially, the isotropic nature of the flax fibers introduced into our biocomposite resulted in uniform properties across all directions of the material.

The investigation into the recyclability of the flax fiber-reinforced vitrimer biocomposite followed an experimental protocol established by Yu et al., which was originally designed for the dissolution of fatty acid vitrimer in carbon fiber-reinforced composite.[28] The initial step involved immersing the original flax fiber biocomposite in ethylene glycol and subsequently heating the solution to 180°C. At this elevated temperature, the ester-based vitrimer matrix engaged in a transesterification reaction with the hydroxyl functional groups of ethylene glycol, leading to a gradual dissolution of the matrix (see Figure S4). As a result, the flax fiber scaffold disintegrated in the ethylene glycol solution. The suspended flax fibers were separated via filtration. These separated fibers can be used in non-woven scaffold manufacturing for its second life. In the solvated depolymerized matrix, due to the inherent incompatibility between the alcohol solvent and dissolved fatty acid derivatives, it becomes straightforward to access the excess ethylene glycol. Following this, the vitrimer solution underwent additional heating to evaporate the ethylene glycol. A fresh isotropic flax fiber scaffold was utilized in this study to fabricate a biocomposite

Table I. Composition and properties of fatty acid-derived vitrimer and its biocomposites.

Sample	Fatty Acid Vitrimer (wt.%)	Flax Fiber (wt.%)	T_g[a] (°C)	T_g[b] (°C)	$T_{d5\%}$[c] (°C)	T_s[d] (°C)	Tensile Strength (MPa)	Tensile Modulus (MPa)	Toughness (MJ/m^3)
Neat Fatty Acid Vitrimer	100	0	9.1	32.8	353	192	2.7±0.4	21.9±6	155.6±13.1
12.5% Flax Fiber Biocomposite	87.5	12.5	10.6	41.2	340	189	8.4±0.7	157.0±28	155.1±19.5
30% Flax Fiber Biocomposite	70	30	13.5	43.0	300	169	13.9±1.5	614.9±30.5	74.8±4.8
50% Flax Fiber Biocomposite	50	50	14.5	43.1	284	162	19.0±2.2	1016.9±87.3	45.8±6.0
Neat Flax Fiber	0	100	–	–	160	129	–	–	–

[a]Glass transition temperature (T_g) from DSC thermogram curves [Fig. 2(c)].

[b]T_g from loss tangent spectra (DMA data) [Fig. 2(d)].

[c]Temperature corresponding to 5% mass loss.

[d]Static heat resistant temperature (T_s) calculated from equation A1 (shown in ESI).

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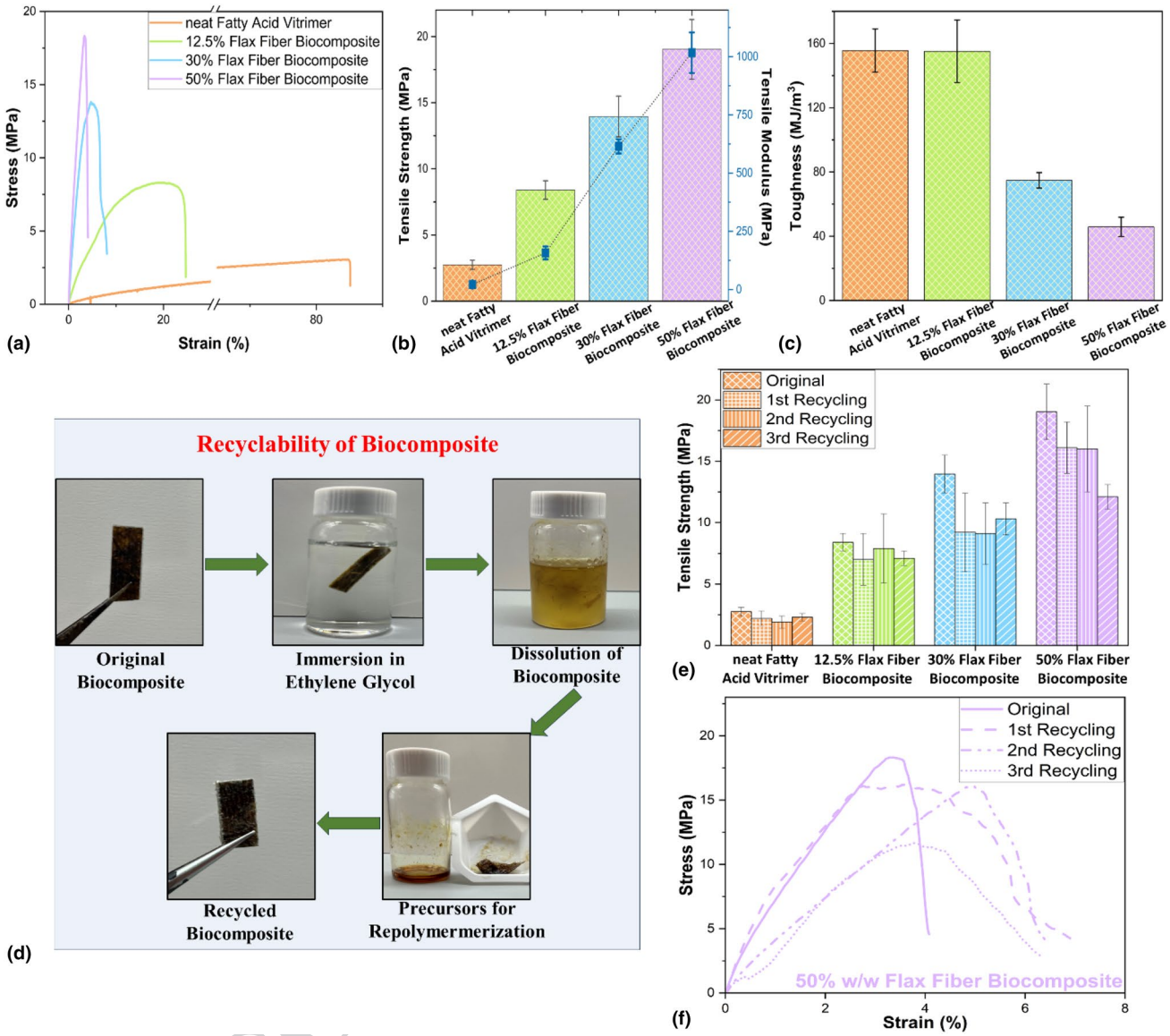

Figure 3. Mechanical characterization of flax fiber-reinforced biocomposite: (a) stress–strain curves; (b) tensile strength and modulus; (c) toughness, estimated as the area under the stress–strain curves of neat fatty acid vitrimer, vitrimer biocomposite with different wt.% of flax fiber loading; (d) steps depicting biocomposite recycling through the recovery of fibers and matrix followed by repolymerized composite fabrication; (e) tensile strength of original and "recycled" biocomposites; and (f) representative stress–strain plots of original and "recycled" biocomposites containing 50% w/w flax fibers.

using the recovered fatty acid derivative as a precursor for matrix repolymerization.

Figure 3d depicts the procedural steps of the recyclability experiment conducted on neat fatty acid vitrimer and biocomposites with varying flax fiber loading. The biocomposite matrix underwent depolymerization (via transesterification with solvents) in excess ethylene glycol, resulting in matrix dissolution within 5 h at 180°C, allowing reclamation of dispersed flax fibers. Subsequent heating of the vitrimer solution for an additional 3 h facilitated the evaporation of excess ethylene glycol solvent. The resultant vitrimer solution, now devoid of excess solvent, served as a precursor for repolymerization. This vitrimer solution was then transferred to a mold containing a fresh isotropic flax fiber scaffold positioned at the center. After heating at 180°C for approximately 10 h (without adding an additional catalyst), the precursors underwent repolymerization, completing the recycling process of the biocomposite. The recycled biocomposite demonstrated over 80% recovery in mechanical performance compared to the original biocomposite. Tensile strength data for neat fatty acid vitrimer and biocomposites with various flax fiber loadings are outlined in Figs. 3(e), (f) and S5. The slight decrease in tensile strength and increased toughness observed in the recycled biocomposites can be attributed to several factors. First, the glycolyzation of

the matrix material and incomplete rearrangement metathesis within the reinforced polyester matrix during material recovery (via thermal evaporation of residual solvents) play significant roles.[29] Furthermore, the depolymerization of the ester-based matrix in ethylene glycol solvent yields precursors for repolymerization with slightly longer chain lengths (see Fig. S4) compared to the starting monomers.[28] This results in an overall chain extended softer matrix for recycling as compared to the original biocomposite. Additionally, the presence of hydroxyl functionalities on the surface of flax fibers also forms covalent interactions with ester functionalities present in the matrix solution, along with the catalyst. Consequently, this diminishes the networked structure of the matrix, leading to increased toughness, higher elongation at break, albeit with a slight reduction in the tensile strength of the biocomposite.

Conclusions

This study has successfully introduced a sustainable and easily recyclable biocomposite, capitalizing the covalently adaptive bonds within a polyester vitrimer matrix. A fatty acid-derived vitrimer in combination with non-woven isotropic flax fiber as the reinforcing scaffold resulted in a significantly improved mechanical property of the matrix across all directions. Neat vitrimer, exhibiting a tensile strength of 2.7 MPa and a modulus of 22.8 MPa, delivered flax fiber-reinforced biocomposite (50 wt.% fiber) with 19.0 MPa tensile strength and 1016.9 MPa tensile modulus. The dynamic nature of the ester-based covalently adaptive network played a crucial role in achieving exceptional fiber wetting, significantly enhanced tensile strength, modulus, and T_g, in addition to subsequent chemical recyclability. The vitrimer matrix's dissolution in ethylene glycol through transesterification allowed for the complete recovery of materials without compromising the original properties of the matrix and reinforcing fibers. This research represents a significant stride towards environmentally conscious and sustainable material design in the domain of fiber-reinforced composites.

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Authors contributions

SSR: conceptualization, methodology, investigation, writing—original draft. ZY: conceptualization, writing—review and editing. LTK: conceptualization, writing—review and editing, supervision. MDT: conceptualization, writing—review and editing. HKG: conceptualization, methodology. AKN: conceptualization, writing—reviewing, supervision, funding acquisition.

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Data availability

Data that support the findings of this study are available from the lead and corresponding authors upon reasonable request. Additional data have been added to supplementary information.

Declarations

Conflict of interest

Coauthor Hicham K. Ghossein is CEO and Founder of Endeavor Composites, Inc. For the rest of the authors, there is no conflict of interest.

Supplementary Information

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