Title: Mechanochemical Synthesis of Dynamic Hybrid Polymer Networks using Whole Biomass

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Abstract:

Whole plant biomass from non-agricultural sources and waste biomass from processing agricultural products are promising feedstocks for biopolymer production because they are abundant and do not compete with food production. However, their processing steps are notoriously tedious with the final materials often displaying inferior performance and limited scope in their properties. Here, we report a strategy to integrate whole-cell spirulina, a green-blue algae, into mechanically robust hybrid biomass-polyimine networks by leveraging mechanochemistry. This strategy provides a greener synthetic approach to conventional solution-phase methods for polyimine synthesis, and it simultaneously overcomes persistent constraints encountered in biomass processing and derivatization. The hybrid algae-based materials retain adaptability and recyclability imparted by the underlying dynamic covalent polymer matrix and display enhanced mechanical properties compared to their all-synthetic equivalents. These advantageous properties are attributed to differences in morphology between 1) the all-synthetic material and the hybrid materials and 2) their respective synthetic methods (solution-phase vs mechanochemical). Substituting spirulina with alternative biomass sources such as waste agricultural products also yields robust hybrid materials, thus highlighting the generality of this mechanochemical approach.

INTRODUCTION

Renewable feedstocks are central to achieving a more sustainable polymer economy. Raw biomass is generally converted into renewable building blocks (over multiple reaction steps), which are then used as monomers to synthesize bio-based polymers.[1-3] Alternatively, native biopolymers, such as starch and cellulose[4,5], lignin[6,7], or chitin[8] may be simply extracted and/or lightly functionalized to generate semi-synthetic[9] biopolymers. Despite these advances, there are persistent constraints to achieving efficient biomass processing or derivatization. Moreover, the resultant synthetic biopolymers may complicate recycling waste streams[10,11] and commonly show unpredictable environmental degradability.[12-14]

Whole, or raw, biomass from non-agricultural sources is another attractive feedstock for polymeric materials production as it introduces renewable content into materials without competing with food production.[15] Bacterial[16,17], fungal[18,19], and algal[20] biomass is converted into novel materials with minimal pre-processing, thus offering significant economical and emissions gains compared to typical extraction and chemical processing[21] techniques for lignocellulosic biomass conversion. When surveying whole biomass feedstock sources, algae is particularly attractive and versatile as it grows rapidly in non-arable lands (i.e. marine environments) and can also be efficiently cultured.[22,23]

Raw biomass-based materials, including algae, are typically performance-limited compared to commodity polymers. They are regularly formulated into composites, often with added plasticizers, to improve their mechanical properties.[24,25] A rare exception is a recent study by Roumeli and co-workers where they describe strong and stiff bioplastics obtained directly from hot-pressing of whole-cell spirulina without additives.[26] Nevertheless, the history of algal biomass predominantly focuses on blending with conventional non-degradable thermoplastics, such as polyolefins, where the algae is a filler component in the composite.[27-29] These examples also typically feature additives and employ a reactive extrusion process to attain a homogeneous morphology and thus adequate mechanical properties. Furthermore, their blended structure likely renders the composite plastics incompatible with equivalent polymer waste streams, i.e. non-recyclable, while also compromising their environmental degradability.

Considering prior work with algae composites, there is interest to replace polyolefins with alternative polymer matrices that can mitigate end-of-life concerns without compromising mechanical performance and/or requiring additives. Dynamic covalent polymer networks (DCPNs) are an ideal continuous polymer matrix to assess due to their mechanical likeness to thermosets combined with thermoplastic-like recyclability owing to their transient network.[30,31] To our knowledge, there are no prior reports that use dynamic covalent polymer networks as the matrix for algal biomass composites, nor any other raw biomass composites in general. Herein, we describe the synthesis of robust, adaptable, and recyclable hybrid biomass polymer networks that are formed from combining whole-cell algae (spirulina) and a dynamic polyimine network via a rapid mechanochemical synthesis (Fig. 1). This synthetic approach is highly modular as other biomass sources are efficiently substituted for spirulina to also produce strong polymeric materials.

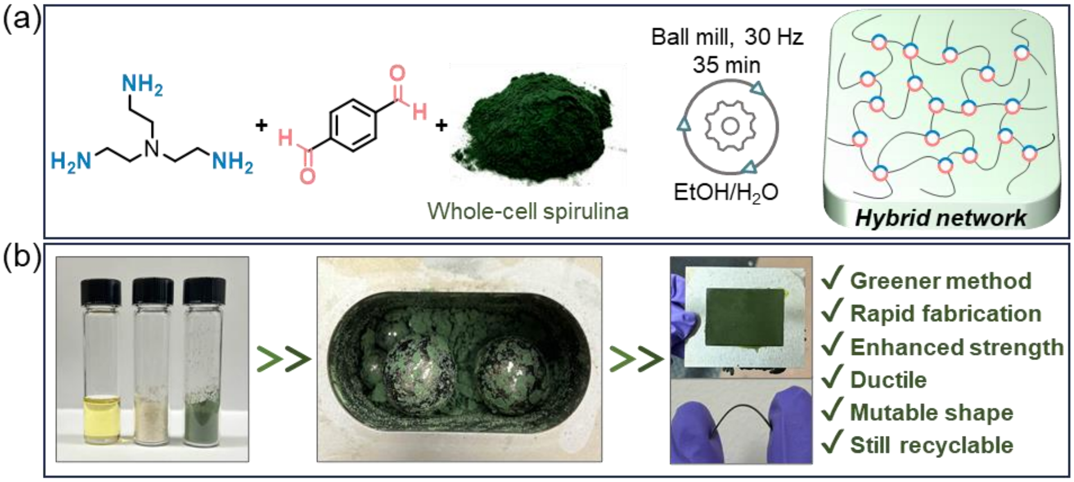

Figure 1. Mechanochemical synthesis of spirulina-polyimine hybrid network using whole-cell spirulina. (a) Reaction scheme showing ball milling of synthetic and biomass precursors. (b) Photographs illustrating the synthetic process to produce polymer films.

RESULTS & DISCUSSION

Synthesis of spirulina-polyimine hybrid networks

We selected polyimine as the polymer matrix due to its rapid relaxation kinetics, wide structure-property scope and relatively simple fabrication methods.[32-39] Spirulina was also selected as a benchmark biomass as it is economical with a high protein content.[40] Furthermore, we hypothesized that the amino acids from the protein in spirulina would serve as a complementary amino nucleophile and integrate into the polyimine network by reacting with aldehyde precursors[41,42], thus enhancing the homogeneity and mechanical properties of the final material.

We initially surveyed conventional solvent-based methods to synthesize biomass-polyimine networks from terephthalaldehyde (TA), tris(2-aminoethyl)amine (TREN), and whole-cell spirulina (Fig. S1a-c).[32,35] Although these methods were operationally simple, they required an carefully optimized solvent mixture (ethanol/water) to dissolve both the spirulina and the organic components due to their opposing solubilities. Further, the synthetic process required a multi-stage curing procedure, taking several days to obtain heterogeneous films (Fig. S1d). After subsequent processing, we obtained a homogeneous film (Fig S1e), but it possessed relatively poor mechanical properties (*vide infra*).

To mitigate these synthetic challenges, we explored ball milling as a greener mechanochemical technique to fabricate hybrid networks. Ball milling is gaining prominence in organic and polymer synthesis as it typically requires little or no solvent, often achieves rapid reaction rates (compared analogous solution-phase methodologies), and can even enable unique reaction pathways.[43,44] For the mechanochemical synthesis, we initially combined TA, TREN, and spirulina in a stainless steel ball mill jar (50 mL volume) equipped with stainless steel milling balls (ø=20 mm × 2; ø=10 mm × 3) and milled the sample for 35 min at 30 Hz. The resultant sample appeared as a homogeneous green powder. However, subsequent hot pressing of the material produced a heterogeneous film with macroscopic defects (Fig S2).

We then repeated the reaction (30% wt spirulina) but added a few drops of water/ethanol (1:1 v/v) to facilitate the clumping and homogenizing processes during milling. Liquid-assisted grinding (LAG) is known to enhance reaction conversion in some milling processes, particularly when using solid substrates.[45] The LAG milling method yielded a crude sample that appeared as large flakes (1-2 cm), distinct from the solvent-free ball mill method. FTIR spectroscopy of the milled sample indicated full conversion of the monomers as evidenced by the disappearance of the aldehyde signal (1750 cm^{-1}, C=O bond) and concomitant appearance of a new signal at 1640 cm^{-1} (C=N bond) assigned to the imine species (Fig. S11). The crude polymer flakes were then hot-pressed using a dynamic temperature ramp (80–120 °C, Δ10 °C/5 min) to achieve a uniform film (Fig. 1b, Fig. S3) suitable for assessing thermomechanical properties. Here, the small amount of water present from the milling process likely also activates dynamic imine exchange when hot-pressing the sample. These procedures were repeated for various formulations ranging from 0–60 wt% spirulina and yielded homogeneous films.

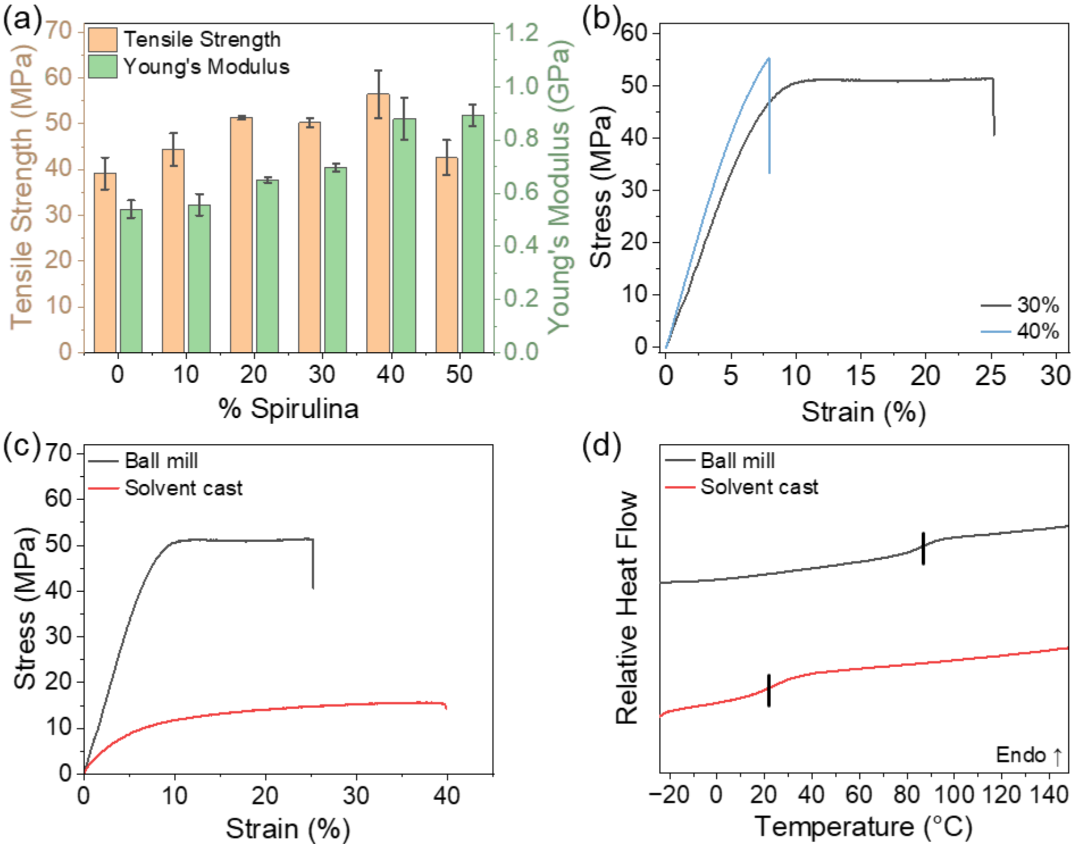

Figure 2. Thermomechanical properties of biomass-polyimine hybrid networks. (a) Plot of tensile strength and modulus for various networks (0–50% spirulina content) synthesized using ball mill method. (b) Representative stress vs strain curve for 30% spirulina network compared to 40% spirulina network synthesized using ball mill method. (c) Representative stress vs strain curve for 30% spirulina network synthesized by ball mill or solvent cast method. (d) DSC thermograms for 30% spirulina network synthesized by ball mill or solvent cast method.

Bulk material properties and morphology of hybrid networks

The thermomechanical properties of the films were assessed using uniaxial tensile testing. Interestingly, we observed a positive correlation between spirulina content and mechanical properties (Fig. 2a, S5-10, Table S1). In fact, the 30% spirulina sample showed a significant increase in Young's modulus (30%), tensile strength (28%), and elongation at break (92%) compared to the synthetic polyimine sample (Fig. S8, Table S1). The 40% spirulina sample was the strongest sample of the series (Fig. S9, Table S1); however, the material was highly brittle and broke before the yield point (Fig. 2b). Thus, the 30% spirulina sample was chosen for further analysis. The thermal properties of the hybrid networks were more ambiguous, where the 10% sample showed a significant reduction in glass transition temperature (T_g) compared to the polyimine sample ($\Delta T_g = 25$ °C) (Fig. S18). However, as spirulina content increased, we observed a positive correlation with T_g according to differential scanning calorimetry (DSC); it possible that the spirulina plasticizes the network more severely at low content.[46] The 30% spirulina sample possessed a degradation temperature ($T_{d5\%}$) greater than 200 °C, which is between values obtained for samples of pure spirulina and polyimine (Fig. S15).

To quantify differences between the two synthetic methods, we compared the thermomechanical properties between the solvent cast and ball milled samples at 30% spirulina content using uniaxial tensile testing (Fig 2c, 2d). We observed significant differences in their mechanical profiles, where the ball milled sample displayed a five-fold increase in Young's modulus compared to the solvent cast material (Fig. 2c, Fig. S11). This is likely due to their differences in thermal properties as the solvent cast sample possessed a lower T_g value (45 °C vs 95 °C) (Fig. 2d). Considering these results, the mechanochemical synthesis afforded materials with superior thermomechanical properties, even for the polyimine sample compared to its solvent cast analogue. This suggests that ball milling methods could be generally beneficial in the synthesis of other synthetic DCPN materials.

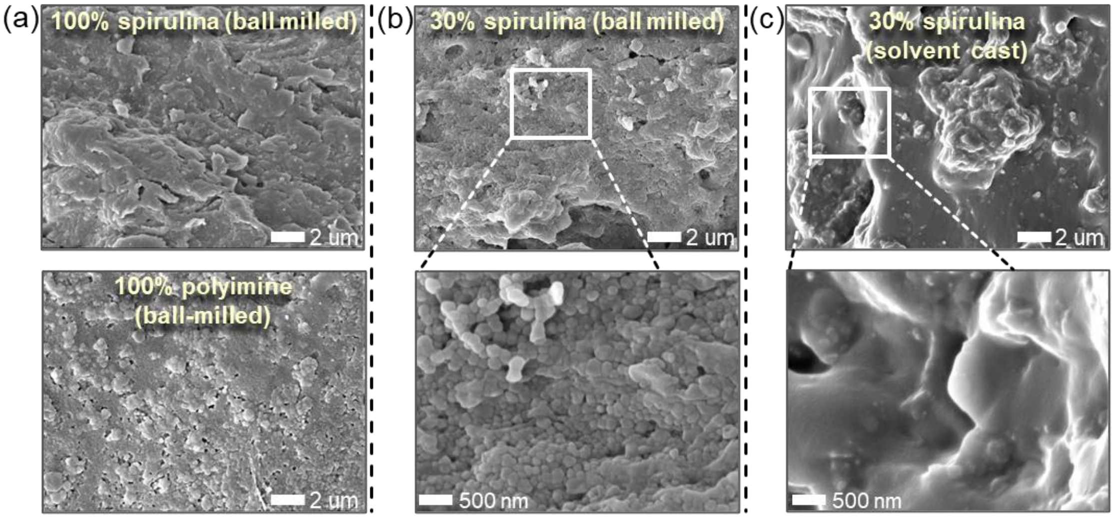

Figure 3. SEM micrographs of biomass-polyimine hybrid networks. (a) Comparison of 100% spirulina sample and 0% spirulina sample (polyimine) after ball milling. (b) 30% spirulina network synthesized from ball mill method. (c) 30% spirulina synthesized from solvent cast method.

We then investigated the morphological differences using scanning electron microscopy (SEM) to provide insight on the enhanced bulk properties that were observed in the ball milled samples. We found uniform nano-spherical features in the ball milled polyimine sample (Fig. 3a). This was consistent with a prior report that showed spherical features in a linear (non-network) polyimine sample synthesized by ball milling.[47] In contrast, the pure spirulina showed a heterogeneous, undefined morphology after ball milling. The 30% spirulina sample showed nano-spherical features, like polyimine (Fig. 3b). This indicated that morphology of the polyimine was conserved, and that spirulina integrated into the bulk sample without disrupting continuity of the network. However, the 30% spirulina material obtained from the conventional solvent cast method showed a heterogeneous morphology devoid of nanoscale features (Fig. 3c). High energy milling techniques are historically well known and used for particle size reduction of various materials.[48] It is reasonable to expect a similar reduction in particle sizes for spirulina and organic components alike during the ball milling process. In effect, this increases their surface area and likely promotes better interfacial contact among the particles to enable more efficient network formation. These morphological data corroborate the observed mechanical properties, which indicates that milling is a critical factor to obtaining materials with enhanced performance.

The information learned from bulk material properties and microscopic imaging also suggests that spirulina may serve a dual role in this hybrid material. Whole-cell spirulina is composed of approximately 60–70 % protein, 20% carbohydrates, and 6-8% fats, among other minerals and vitamins.[49] First, animo acids with a primary amino side chain (such as lysine) may crosslink[41] the protein domains to the polyimine network, improving strength and stiffness of the bulk material. It is also possible that some proteins may be denatured during milling and/or hot pressing, thus generating other reactive amino species for crosslinking. Simultaneously, carbohydrates and fats likely plasticize the bulk sample,[46,50] which lowers the T_g and increases the ductility of the hybrid networks (10-30% spirulina content) compared to the polyimine. For networks containing ≥ 40% spirulina content, these synergistic effects become less evident and the materials embrittle, resembling properties that are closer to 100% spirulina bioplastics.[26]

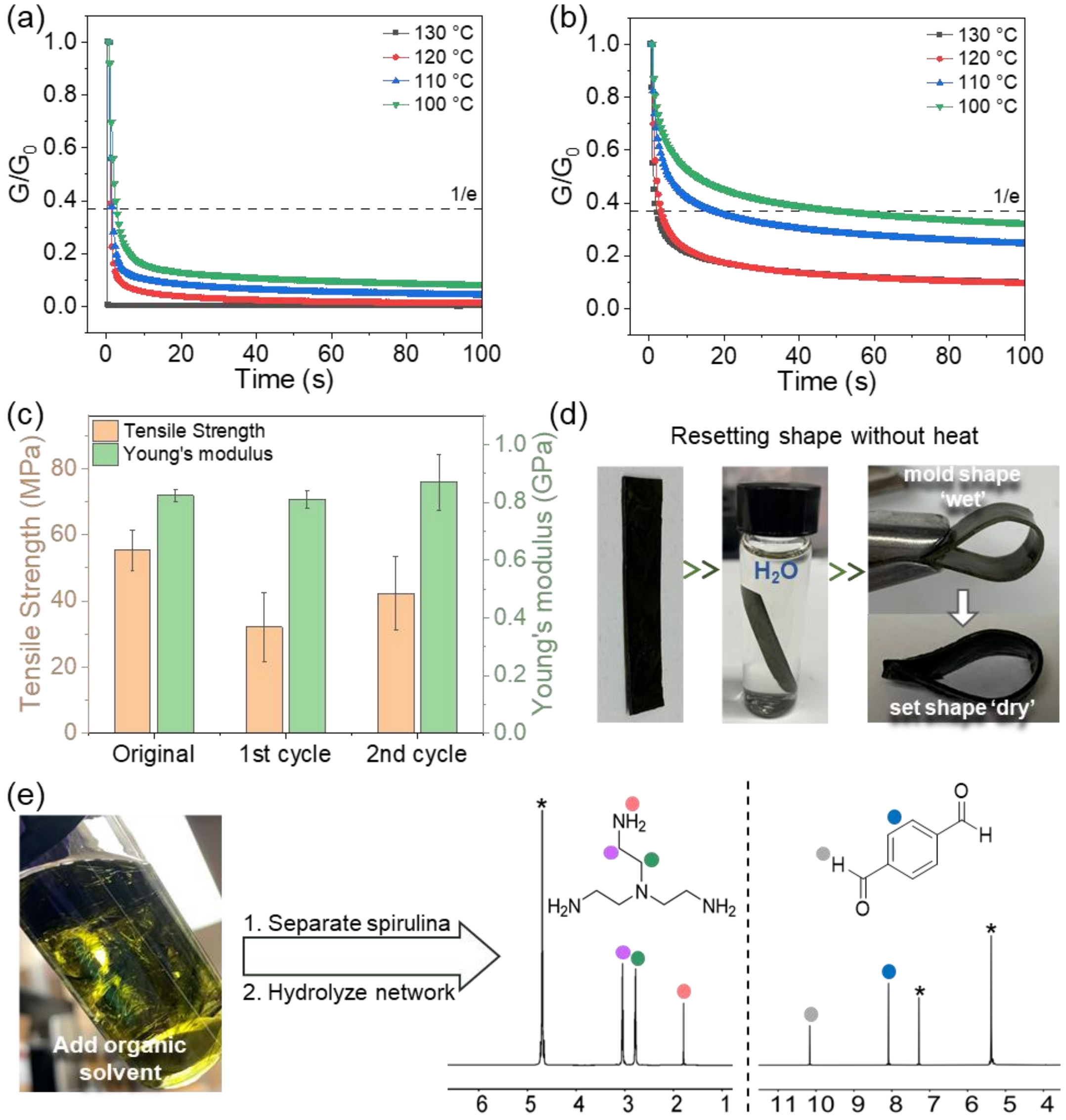

Figure 4. Processing and recycling of biomass-polyimine hybrid networks. Stress relaxation using shear oscillatory rheology at various temperatures for (a) 0% spirulina sample and (b) 30% spirulina sample. (c) Tensile strength and Youngs' modulus of 30% spirulina sample after repeated heated-compression molding. (d) Shape transformation of 30% spirulina film using water-assisted molding. The wet film became highly malleable and was set into a new permanent shape after subsequent drying. (e) Chemical recycling or depolymerization of the network (left) and ^{1}H NMR spectra of recovered aldehyde and amine monomers (right). *Indicates solvent ($CHCl_3$ and CH_2Cl_2 respectively).

Reprocessing and recycling of hybrid networks

Next, we assessed the viscoelastic properties of the 30% spirulina sample using shear oscillatory rheology, providing insight on the adaptability and recyclability of bulk hybrid material. Stress relaxation experiments were performed as a proxy for hot press molding. The synthetic polyimine network displayed rapid relaxation kinetics, like previous work[32,35], where full relaxation (*i.e.* where the material theoretically flows for reprocessing) occurred within < 5 s at 100 °C (Fig. 4a). The full relaxation time is defined when the normalized relaxation modulus (G/G_0) reaches ($1/e$) or ∼37% of the initial stress value on based on the Maxwell model.[51] At the same temperature, the spirulina-polyimine hybrid network relaxed approximately one order of magnitude slower (~50 s) (Fig. 2b). Although the relaxation is slower, this value indicates adequate activation of imine bonds[52] throughout the hybrid material and suggests it is readily processable by standard hot pressing methods.

Informed by the rheology data, we synthesized a 30% spirulina network and then subsequently hot-pressed the material for two additional cycles to create remolded the samples (Fig. 4c). After the first cycle, the material possessed a similar stiffness ($\sigma = 0.81 \pm 0.02$) but was weaker (UTS = 32.1 ± 8.5 MPa) and more brittle ($\varepsilon_{break} = 4.6 \pm 1.5$ %) compared to the original sample. However, we then added a small amount of water before the second pressing cycle and the resultant material more closely matched the original network (UTS = 41.8 ± 10.4 MPa; $\varepsilon_{break} = 8.8 \pm 4.5$). These data indicate that the hybrid materials retain suitable reprocessability.

Polyimines are known to undergo water-assisted reshaping[32], which is analogous to heat-assisted thermoforming of thermoplastics. We conducted a similar water-reshaping experiment on the 30% spirulina hybrid network (Fig. 4d). A rectangular film was placed in water for 1 h, then removed and reshaped using a metal clip. The sample was then dried while deformed in the metal clip to set a new “permanent” shape. This malleability is advantageous as it provides another simple method to reprocess the material without heat and pressure.

Finally, we examined the full chemical recycling of the 30% spirulina hybrid network (Fig. 4e). First, we pulverized 30% spirulina film into a fine powder using a ball milling process. Then, we added chloroform to dissolve the polyimine network, as previously reported by Smulder and co-workers[53]. Spirulina is insoluble in organic solvents, so it was subsequently filtered and reclaimed. Then, the polyimine network was depolymerized by dilute HCl solution to regenerate spectroscopically pure TREN and TA components (Fig. S32, S33). Importantly, this separation-depolymerization process was complete within 1 h, again providing another simple method to recycle the hybrid material.

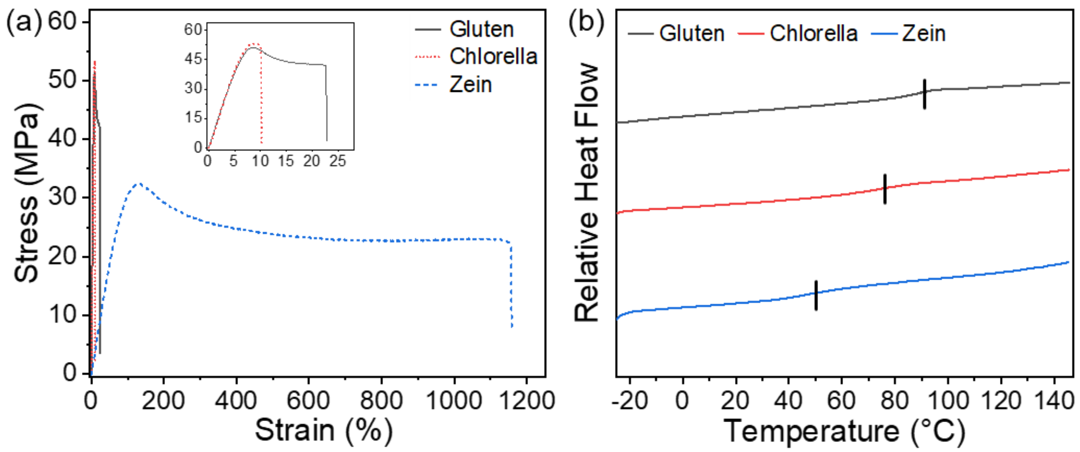

Figure 5. Thermomechanical properties of biomass-polyimine hybrid networks (gluten, chlorella, or zein) synthesized using ball milling method. (a) Stress vs strain curves for 30% biomass samples. (b) DSC thermograms for 30% biomass samples.

Assessing biomass scope

We then evaluated other biomass substrates using the same mechanochemical synthetic method. Chlorella, gluten, and zein were substituted for spirulina to create analogous biomass-polymine hybrid networks at 30% biomass content. Chlorella was chosen as a control, since it is a different algae species that also possesses high protein content. Gluten and Zein were assessed because they are protein-rich biomass materials that are regarded as agricultural waste products.[54] Although the gluten hybrid network was significantly more ductile than the chlorella-based material, both featured mechanical profiles that were similar to the benchmark spirulina network as evidenced by their high strength (UTS > 50 MPa) and Young's modulus (> 0.8 GPa) (Fig. 5a). The zein hybrid network was comparatively soft and less strong, however the ductility was dramatically enhanced ($\varepsilon_{\text{break}} > 1100\%$) compared to all other materials resulting in a material with extreme toughness (Fig. 5a). All samples were in a glassy state (testing temperature < T_g) during mechanical analysis (Fig. 5b) which makes the exceptional mechanical properties of the zein material even more remarkable. These proof-of-concept experiments reveal the broad versatility of this ball milling approach for fabricating robust biomass-hybrid materials with tunable thermomechanical properties using diverse biomass sources.

CONCLUSION

In summary, we outline a modular and efficient mechanochemical synthesis for constructing biomass-polyimine hybrid materials. This approach addresses prior constraints associated with synthesizing biomass-based composites. It simultaneously improves the mechanical properties of polyimine networks compared to existing solution-phase methods while mitigating waste generation. A brief survey of additional proteinaceous biomass sources using the optimized ball milling method reveals that it is broadly applicable, yielding robust materials with diverse thermomechanical properties. In future work, we will assess a more diverse range of biomass products and investigate different dynamic polymer networks.

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Author contributions: JCW conceived the work and directed the research. JCW, MJ, and EB designed the experiments. JCW, MJ, EB, WH performed and analyzed experiments. JCW and MJ prepared the manuscript, and all authors contributed to manuscript revisions.

Competing interests: None

Data and materials availability: All data are available in the manuscript or the supplementary information.

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