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Artificial reproduction of chitinous mechanical versatility through metal doping and its use in resource-efficient product design

Akshayakumar Kompa^a and Javier G. Fernandez  ^{*ab}

Structural biomaterials achieve diverse mechanical functions by reconfiguring a small chemical palette, often *via* metal–ligand coordination in hydrated matrices. Despite biology's extensive use of such coordination in water-rich environments, engineered polysaccharide systems have primarily focused on mitigating moisture sensitivity rather than using hydration as a mechanical control parameter. Here we show that chitosan can be mechanically programmed by introducing divalent transition-metal ions (Cu, Zn, and Ni) and activating amines as inner-sphere donors through a simple post-casting neutralization. Multiscale characterization reveals metal-specific coordination states and water partitioning. These molecular differences produce distinct macroscopic behaviours: Zn increases dry strength and stiffness, Cu yields a more compliant and ductile response, and Ni inverts the hydration response, with immersion increasing modulus and strength. Because a single renewable backbone can span a wide mechanical range with minimal compositional changes, the approach reduces materials complexity in both manufacturing and end-of-life processing. Using only these minimal modifications, we fabricate a mechanically graded origami structure that integrates soft and stiff regions, demonstrating that coordination-mediated hydration control provides a scalable route to diverse mechanical designs from a single renewable biopolymer.

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Introduction

Modern product design often relies on combinations of polymers, fillers, and additives to meet application-specific performance requirements. This property-by-formulation model has enabled rapid technological development, but it also multiplies material grades, processing routes, and supply chains. Products assembled from chemically dissimilar materials are difficult to sort and recover at end of life, contributing to low recycling rates and the accumulation of unmanaged solid waste.

Biological systems offer a contrasting strategy. Under resource constraints, functional diversity is often achieved from a limited set of building blocks whose interactions and organization are tuned locally, an evolutionary principle described as the “survival of the cheapest”.¹ Arthropod cuticles exemplify this economy: compliant joints, resilient surfaces, and specialized tools are integrated within a continuous hierarchical chitin–protein matrix whose local crosslinking and inorganic content vary with function.² It is, however, built as a single, continuous, hierarchical chitin–protein system with variations in local crosslinking and small fractions of inorganic components.

Translating this strategy into engineering materials remains challenging because natural and synthetic material systems are organized and processed according to different principles.³ Chitin is abundant, renewable, and integrated into natural material cycles, yet its use in product design has often relied on chemical modification, blending, and additives intended to reproduce the processing and performance of conventional polymers.^{4,5} Such approaches can increase compositional complexity and complicate established recycling or composting routes.⁶

Here, we show that metal doping with Cu, Zn, or Ni, followed by neutralization of pH-responsive groups, can broaden the mechanical response of chitosan without further covalent modification of its backbone. The resulting films span markedly different combinations of stiffness, strength, and deformation behavior under dry and wet conditions. Because these properties are obtained from a common chitosan formulation and processing route, mechanically differentiated regions can be integrated within a continuous material, streamlining both their production and end-of-life.

The use of these metals is not arbitrary; their use in chitinous structures is well established in natural systems. In arthropod chitinous cuticle, localized metal enrichment is a known strategy for hardening critical features (*e.g.*, fang and claw tips); however, these interactions have historically been attributed primarily to cuticular proteins *via* histidine residues, rather

^aInstitute for Bioengineering of Catalonia, Barcelona, Spain. E-mail: jgomez@ibecbarcelona.eu

^bICREA, Barcelona, Spain

than to the polysaccharide matrix itself. Direct metal-ion binding is well established for chitosan, a partially deacetylated derivative of chitin with an amine-to-acetyl ratio above 50%. Its accessible primary amine groups can participate in metal-polymer coordination, while its solubility in acidic aqueous media allows metal ions to be incorporated before casting into continuous films. Subsequent alkaline neutralization changes the protonation state of the amines, providing a means of modifying metal-polymer interactions without further covalent modification of the chitosan backbone. Chitosan is typically produced by deacetylating chitin recovered from crustacean processing residues and is widely used, for example, as a flocculant for metal-ion removal in bioremediation and wastewater treatment. This metal sequestration by chitinous polymers has also been reported in fungi and leveraged to remediate heavy-metal-contaminated soils. These biological examples provide conceptual inspiration rather than a model that is directly replicated in the present material. Native chitin fibrils and processed chitosan films differ substantially in molecular organization, charge state, and available metal-binding groups. Only recently has the role of metal coordination in chitosan supramolecular assembly begun to be elucidated, enabling advances such as room-temperature fabrication of functional metallic structures and the first biomaterial that exploits environmental water to increase mechanical strength. Building on our previous mechanistic study of the Ni-chitosan hydration response,⁷ the present work examines whether metal identity can serve as a broader mechanical-design variable within a common chitosan platform. By comparing Cu, Zn, and Ni at the same nominal molar loading and under the same casting and neutralization conditions, we identify distinct dry- and wet-state mechanical responses and apply this differentiation to a construct containing locally compliant and load-bearing regions.

Results and discussion

Metal-modified chitosan films were prepared by dissolving chitosan (3 wt%) in 1% acetic acid and stirring for 48 h to achieve complete dissolution. Cu, Zn, or Ni precursors were then added, and the solutions were cast and dried at 40 °C to form free-standing films (Fig. 1a). The films were subsequently neutralized in 4% NaOH and thoroughly rinsed. This treatment removes residual acid and acetate and converts the amines from predominantly protonated to predominantly deprotonated states, increasing their capacity to act as electron donors in metal coordination. Neutralized samples are denoted by the suffix “-N” throughout.

Theoretical and computational work on chitosan-metal complexation, much of it developed in the context of metal sequestration and flocculation, provides a useful framework for interpreting how the deprotonation of the amine groups biases the system toward specific binding modes. Previous experimental and computational studies of chitosan-metal complexation provide a framework for interpreting the effect of amine deprotonation. Proposed binding motifs include coordination of a metal ion to an amine and a neighbouring hydroxyl group

on the same chain, with water or hydroxide completing the coordination sphere, as well as coordination between donor groups on adjacent chains, which may increase interchain cohesion.⁸ Solution studies also indicate that hydroxide/water participate in completing the coordination sphere and that neutral amines become increasingly available as pH rises. Similarly, at the atomistic level, DFT studies using glucosamine/*N*-acetylglucosamine as chitosan/chitin motifs find stable complexes in which divalent ions (Ni^{2+} , Cu^{2+} , Zn^{2+}) engage the amine nitrogen together with a proximal oxygen donor, and they emphasize that hydration can change relative stabilities and even preferred geometries (notably for Zn^{2+}). Therefore, the neutralization of the amine groups included in our workflow can be interpreted as establishing a coordination-competent state for the polymer, enabling the inner-sphere metal-amine binding under aqueous conditions.

The first qualitative observation of a successful incorporation/entrapment of the metals within the chitosan films was their macroscopic appearance: the salts impart distinct colors to the vitrified films (Fig. 1a), consistent with metal retention within the matrix rather than complete loss during processing. At the supramolecular level, X-ray diffraction (XRD) reveals the characteristic chitosan reflections near 10° and 20°,⁹ which shift and broaden upon metal incorporation, indicating changes in polymer packing and increased structural disorder. No additional sharp reflections attributable to a major crystalline metal-containing phase were detected in the neutralized samples (Fig. 1c). This indicates that the bulk films are not dominated by large, well-crystallized precipitated metal phases, although low-abundance, nanoscale, or poorly crystalline species cannot be excluded by XRD.¹⁰ The three formulations were prepared using the same nominal molar amount of divalent metal per unit mass of dry chitosan, allowing the effects of metal identity to be compared at a constant initial metal-to-polymer ratio.

SEM images of the neutralized films show generally continuous surfaces without a widespread population of large precipitated particles (Fig. S1). Localized crystalline features are nevertheless visible, particularly in the Cu- and Ni-containing samples, and are attributed to local precipitation of metal salt species during alkaline neutralization and washing. Their limited surface distribution and absence as distinct XRD reflections indicate that they do not constitute a major detectable bulk crystalline phase. The films are therefore interpreted as containing metal ions associated with the chitosan matrix, together with localized, precipitated, metal-containing species.

Hydration plays a central role in chitosan-metal interactions. The initial TGA mass-loss region differed markedly among the formulations (Fig. 1d): Cs-N, CsZn-N, CsCu-N, and CsNi-N exhibited losses of 10.15%, 11.28%, 12.54%, and 21.58%, respectively. These values indicate metal-dependent differences in water retention, with CsNi-N containing the largest water-associated fraction. The metal-containing films also decomposed at lower temperatures than Cs-N (~170 °C for CsCu-N, ~220 °C for CsZn-N, and ~195 °C for CsNi-N, compared with ~250 °C for Cs-N), consistent with altered

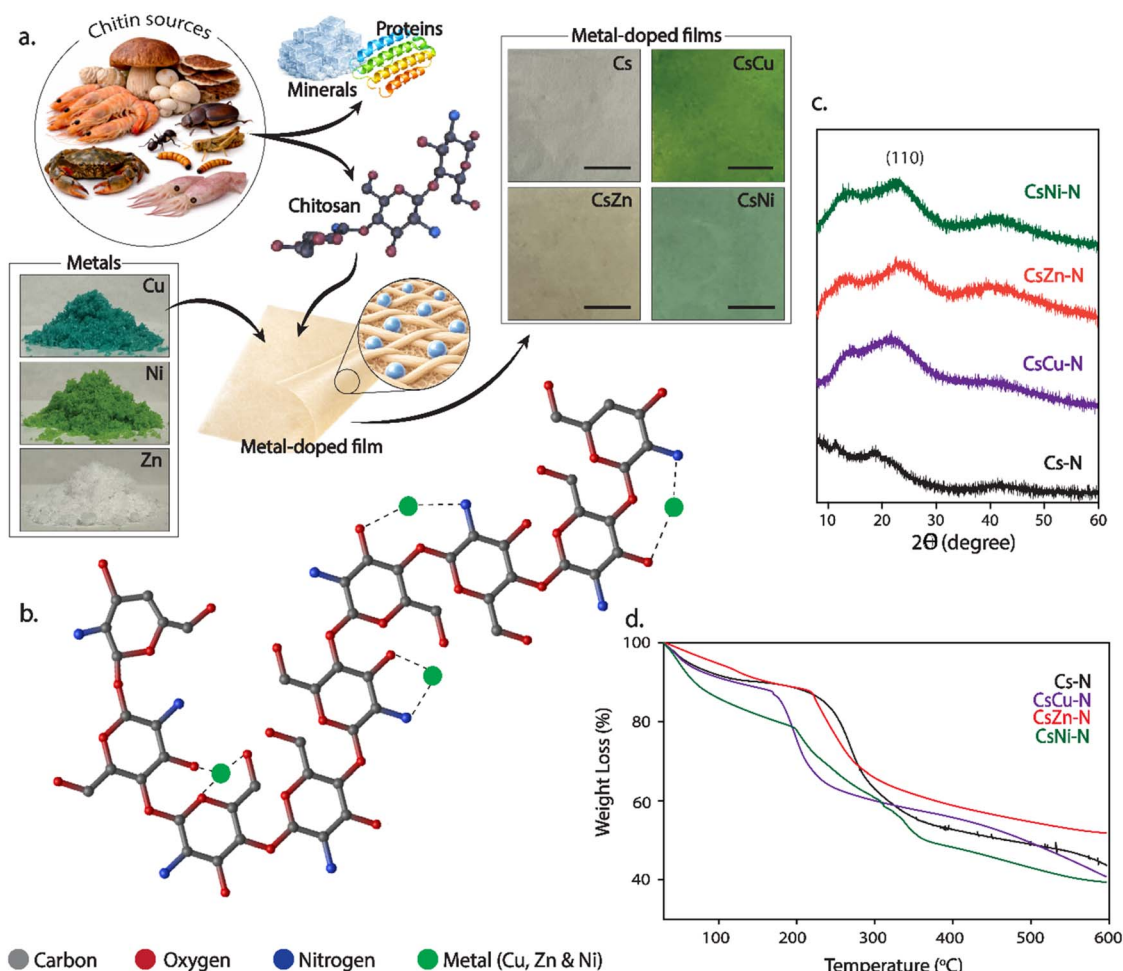


Fig. 1 Fabrication and structural characterization of metal-modified chitosan films. (a) The schematic illustrates the use of chitosan, extracted from local sources, to fabricate chitosan–metal composite films via a traditional solution-based method, with transition metal ions (Cu, Zn, and Ni) added. Optical images (scale bar = 10 mm) reveal that the transition metal salts introduced distinct colors to the final film. (b) 2D Schematic representation of possible metal-ion interaction sites in chitosan. The illustration identifies accessible amine and hydroxyl donor groups that may participate in metal coordination. (c) Structural characterization through X-ray diffraction (XRD) confirmed the successful formation of chitosan and its subsequent deformation upon the incorporation of metal ions. The XRD patterns showed an increase in amorphous content and a shift of the major peak (110) to a higher angle, indicating deformation of the chitosan structure. Importantly, no peaks associated with impurities were observed, indicating that most of the metal ions were effectively crosslinked with the chitosan molecules. (d) Thermogravimetric analysis (TGA) revealed distinct decomposition temperatures for the pure chitosan and its composite films. The initial weight loss, corresponding to the moisture adsorbed by the samples, was notably higher in the CsNi-N film, indicating a higher moisture content than in the others.

polymer packing and/or metal-catalysed degradation pathways.¹¹

The FTIR spectra of all metal-doped films retain the canonical chitosan signatures (broad O–H/N–H stretching envelope; amide bands; and carbohydrate skeletal vibrations), indicating preservation of the polysaccharide backbone (Fig. 2a). The main high-wavenumber band (O–H/N–H stretching, sensitive to hydrogen bonding and local coordination¹²) is centered at $\sim 3280\text{ cm}^{-1}$ in pristine chitosan and shifts to $\sim 3301\text{ cm}^{-1}$ (Cu), $\sim 3265\text{ cm}^{-1}$ (Zn), and $\sim 3311\text{ cm}^{-1}$ (Ni), evidencing metal-specific reorganization of the hydrogen-bonding/solvation environment around the donor groups engaged in complexation.¹³ In this region, a unique shoulder/peak at $\sim 3434\text{ cm}^{-1}$ appears in the Cu-doped sample, which in Cu-containing materials is usually associated with a hydroxyl–Cu population

introduced or stabilized during neutralization (observed as crystalline features in the surface morphological studies). In the mid-IR, the band at 1556 cm^{-1} (amide II/N–H bending contributions in partially deacetylated chitosan) remains present,¹⁴ supporting that metal incorporation perturbs donor environments without introducing new covalent cheoxyl-rich environment,¹³ and in our case, consistent with a minor Cu–OH and hydroxylated chemistry in the backbone. In the fingerprint region, the characteristic chitosan C–O–C/C–O bands (commonly assigned near $\sim 1150\text{ cm}^{-1}$, with contributions also around $\sim 1100\text{ cm}^{-1}$) are markedly attenuated in the Cu-doped film, coincident with the appearance of a Cu-associated feature at 821 cm^{-1} , consistent with overlap by Cu–O/O–Cu–O vibrations. Below 800 cm^{-1} , the metal-doped samples show enhanced spectral contributions, including a band near

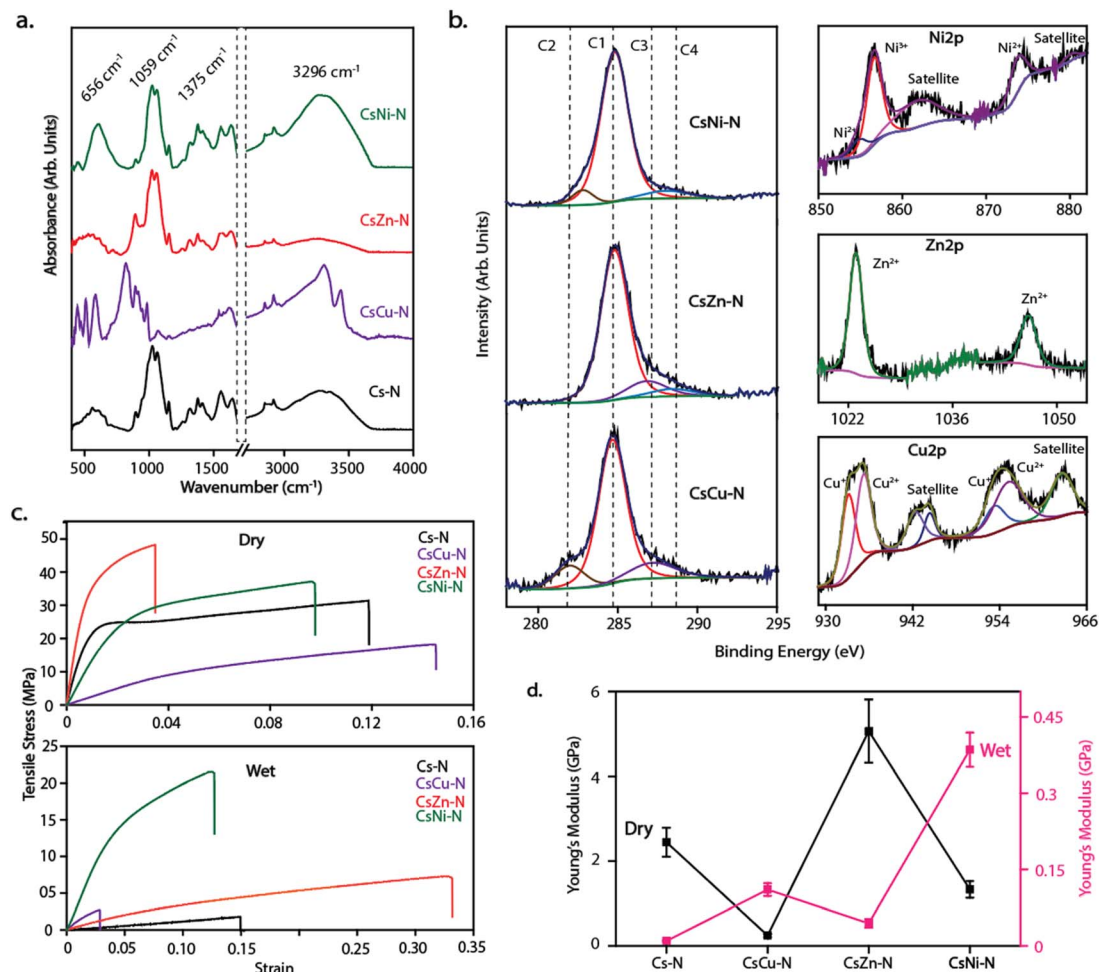


Fig. 2 Supramolecular level insights and mechanical properties of metal-modified chitosan films. (a) Infrared (IR) spectroscopy results further confirmed the role of chitosan as the primary component of the doped samples. Additionally, (a) prominent peak at 3434 cm^{-1} confirmed the strong stretching of Cu–OH, emphasizing the interaction between the chitosan matrix and the metal ions. (b) X-ray photoelectron spectroscopy (XPS) was used to examine changes in the carbon backbone of chitosan upon incorporation of metal ions. Narrow-scan of copper, zinc, and nickel ions provided insights into the oxidation states of the metals, which, in turn, indirectly confirmed the nature of bonding between the chitosan functional groups and the metal ions. (c) The mechanical properties of the chitosan composite films were evaluated by measuring their tensile strength in dry and wet conditions. The freshly prepared dry films demonstrated high tensile strength, but this decreased after wetting. (d) Among the metal-doped samples, CsZn–N exhibited the highest Young's modulus under dry conditions and the lowest Young's modulus under wet conditions.

656 cm^{-1} that is particularly pronounced for Cu and Ni and is often assigned to N–H wagging/out-of-plane modes and related deformations resulting from changes in the local environment of amine/hydroxyl groups,¹⁵ consistent with increased coupling of these donor sites to the metal ions.¹⁶ Therefore, the FTIR signature presents a superimposition of (i) a predominant fraction of the metal stabilized within the polymer that reorganizes the O–H/N–H hydrogen-bond network (common to the three metals), and (ii) a small fraction hydroxide/oxide-associated metal formed under NaOH treatment, which is only observable in Cu spectra (but cannot be ruled out in Zn and Ni) and consistent with the surface crystallites seen by SEM.

To obtain molecular-level insight into the near-surface chemical environments induced by metal incorporation, we performed X-ray photoelectron spectroscopy (XPS). In the high-resolution C 1s region (Fig. 2b), four components were resolved

at 284.8 eV (C1), 281.87 eV (C2), 287.07 eV (C3),¹⁷ and 288.59 eV (C4).¹⁸ The dominant C1 (284.8 eV) corresponds to C–C/C–H environments and reflects the intact carbon skeleton of chitosan.^{18,19} The C3 component at 287.07 eV is consistent with carbon bound to heteroatoms (C–O and/or C–N), in our case, the hydroxyl- and amine/amide-adjacent environments that are expected to be perturbed when metal ions are coordinated within the polymer network. The C4 contribution at 288.59 eV falls within the range associated with carbonyl-containing motifs and supports retention of the chitosan chemical scaffold while allowing for local electronic redistribution near functional-group-rich sites. The low-binding-energy component C2 at 281.87 eV is typical for polysaccharides; its presence is most conservatively interpreted as a minor carbon environment strongly influenced by a proximate metal-rich fraction at or near the surface.²⁰

The metal narrow scans further support metal-dependent near-surface speciation. In the Cu 2p region (Fig. 2b), components at 932.82 eV (Cu^+) and 935.23 eV (Cu^{2+}) are accompanied by shake-up satellites at 942.27, 945.27, and 962.86 eV, consistent with the presence of Cu(II)-containing species and compatible with Cu-O/Cu-OH-rich local environments.²¹ Together with the Cu-specific FTIR signatures and the pronounced Cu-associated surface crystallites by SEM, these data support a Cu population comprising both coordination-stabilized Cu within the chitosan matrix and a smaller hydroxide/oxide-associated Cu-rich fraction in the near-surface region. The Zn spectra exhibit the characteristic Zn 2p doublet at 1023.02 eV and 1046.20 eV, consistent with Zn(II) as the dominant oxidation state and coordination to electron-donor functional groups of chitosan.²² Similarly, Ni shows a dominant Ni^{2+} component at 854.59 eV together with an additional higher-binding-energy component at 856.67 eV, consistent with a more oxidized or hydroxide-associated near-surface environment.²³ Collectively, the XPS data are consistent with the functional-group perturbations identified by FTIR, confirming that, upon incorporation, metal coordinates to chitosan donor groups, while also producing a smaller population of hydrolyzed/oxide/hydroxide-associated species that can form in less ligand-protected regions during alkaline processing.

The molecular- and supramolecular-scale differences introduced by metal incorporation, namely changes in local coordination environment and in how water is partitioned between weakly associated and more structured/coordination-coupled populations, propagate directly to the material's macroscopic mechanical response (Fig. 2c and Movie S1). This framing is consistent with DFT results showing that hydration can reorder preferred binding configurations (C1 vs. C4) and alter local coordination environments in a metal-dependent manner,⁸ with Zn^{2+} exhibiting particularly hydration-sensitive coordination (including tetrahedral/hexa-coordinated motifs as water ligands are introduced) relative to $\text{Ni}^{2+}/\text{Cu}^{2+}$. In this sense, we demonstrate that a single biopolymer platform can access a broad mechanical design space with minimal synthetic complexity: the polymer backbone is held constant, while the identity of the divalent ion and the protonation state of chitosan donor groups (set by neutralization) select which coordination/hydration motifs dominate under load.

Related studies on TEMPO-oxidized cellulose nanofibril films have shown that multivalent ions can improve wet mechanical integrity by promoting associations between charged fibril surfaces, thereby restricting interfibrillar separation and sliding.²⁴ Subsequent work attributed this behavior to a combination of ion-ion correlations, specific-ion effects, and the resulting connectivity of the fibrillar network.²⁵ The present chitosan system shares the general principle of ion-mediated noncovalent association but differs in its structural organization and donor chemistry. Here, the relevant structural units are chitosan chains rather than carboxylated cellulose fibrils, and the transition-metal ions interact with amine and hydroxyl donor environments whose availability is altered by neutralization. Metal-mediated associations between neighboring chitosan chains may therefore restrict chain mobility and

contribute to the mechanical response, although their relative contribution is not directly resolved by the present measurements.

Under dry conditions, pristine chitosan exhibits a tensile strength of ~ 31.29 MPa,²⁶ whereas Zn incorporation increases strength to ~ 48.14 MPa at the expense of ductility, consistent with a more constrained network that resists chain mobility.²⁶ In contrast, Cu incorporation produces a different dry-state phenotype, characterized by lower ultimate strength (~ 18.07 MPa) but substantially higher elongation at break, consistent with a mechanically more compliant network in which a larger fraction of interactions are effectively plasticizing or less load-bearing. CsNi-N falls between these in dry strength (~ 37.21 MPa), underscoring that the same processing route can yield either stiff/strong or compliant/ductile behavior solely through metal selection (Table S1).

Hydration then acts as a stringent functional probe, separating metal-specific mechanisms. In typical chitosan films and hydrogel-like networks, water reduces modulus and strength through plasticization and swelling-driven softening. Consistent with that expectation, pristine chitosan, as well as CsCu-N and CsZn-N, weakens under wet conditions. Among the metal-doped samples, CsZn-N exhibited the lowest Young's modulus under wet conditions and the highest Young's modulus under dry conditions (Fig. 2d), while CsNi-N exhibited the highest wet-state strength and modulus. It also showed the largest initial water-related mass loss by TGA, indicating that its wet-state performance is not associated with a lower water content. The Ni-specific interaction with water was investigated in detail in our previous study,⁷ where metal-release measurements, electrolyte screening, chelation experiments, and water-retention analysis supported a mechanism involving retained Ni-chitosan coordination coupled to water-mediated intermolecular interactions. The present study complements that mechanistic investigation by comparing Cu, Zn, and Ni under the same processing framework and showing how metal identity produces distinct dry- and wet-state mechanical responses within a single chitosan platform. Taken together with the FTIR/XPS evidence for metal-donor interactions and metal-dependent hydroxyl/oxo fractions, these mechanical results establish the central outcome of the study: a single biopolymer can be "programmed" to soften, rubberize, or strengthen upon hydration, not by changing the polymer chemistry, but by selecting the ion and donor activation state that determine whether water primarily lubricates chain motion or instead becomes incorporated into a reversible, load-bearing, coordination-coupled cohesion mechanism.

The mechanical responses emerging from these coordination and hydration environments reflect a recurring principle in structural biomaterials: substantial functional diversity can be achieved by reorganizing a limited chemical palette through local compositional and environmental changes. In biological structures, transition metals are used in different ways to modify the mechanical behaviour of polymer-rich matrices. Zinc and manganese enrichment, for example, contribute to the hardening and stiffening of arthropod cuticle and tool-like structures without extensive bulk mineralization.²⁷ In

polychaete jaws, Zn-mediated coordination can provide load-bearing and reversible interactions, whereas copper in *Glycera* jaws is associated with localized copper-containing mineral phases that contribute to abrasion resistance. Similarly, metal coordination in mussel byssus contributes to combinations of stiffness, extensibility, and damage recovery.^{28,29} Although these biological systems differ substantially from the present chitosan films, they illustrate how metal identity and local chemical environment can modulate mechanical properties without changing the principal structural polymer. In the present system, metal selection, alkaline neutralization, and hydration provide related design variables, producing distinct tensile responses from a common chitosan platform (Fig. 3a).

To illustrate this concept in a simple, manufacturable form, we selected two compositions with markedly different Young's

modulus in water: neutralized chitosan (Cs-N), which is comparatively compliant when hydrated, and neutralized Ni-doped chitosan (CsNi-N), which retains the highest wet-state modulus among the compared formulations (Fig. 3b). We fabricated an origami-inspired structure with localized metal-doped regions, yielding soft and stiff regions within a single construct, analogous to biological foldable architectures that exploit stiffness gradients to enable reversible folding and deployment (Fig. 3c and Movie S2). The films were neutralized and thoroughly washed after shaping to ensure aqueous stability and to establish the coordination-competent donor state that governs their mechanical contrast; under these standardized conditions, CsNi-N functions as the load-bearing element while Cs-N provides the compliant hinge-like regions.

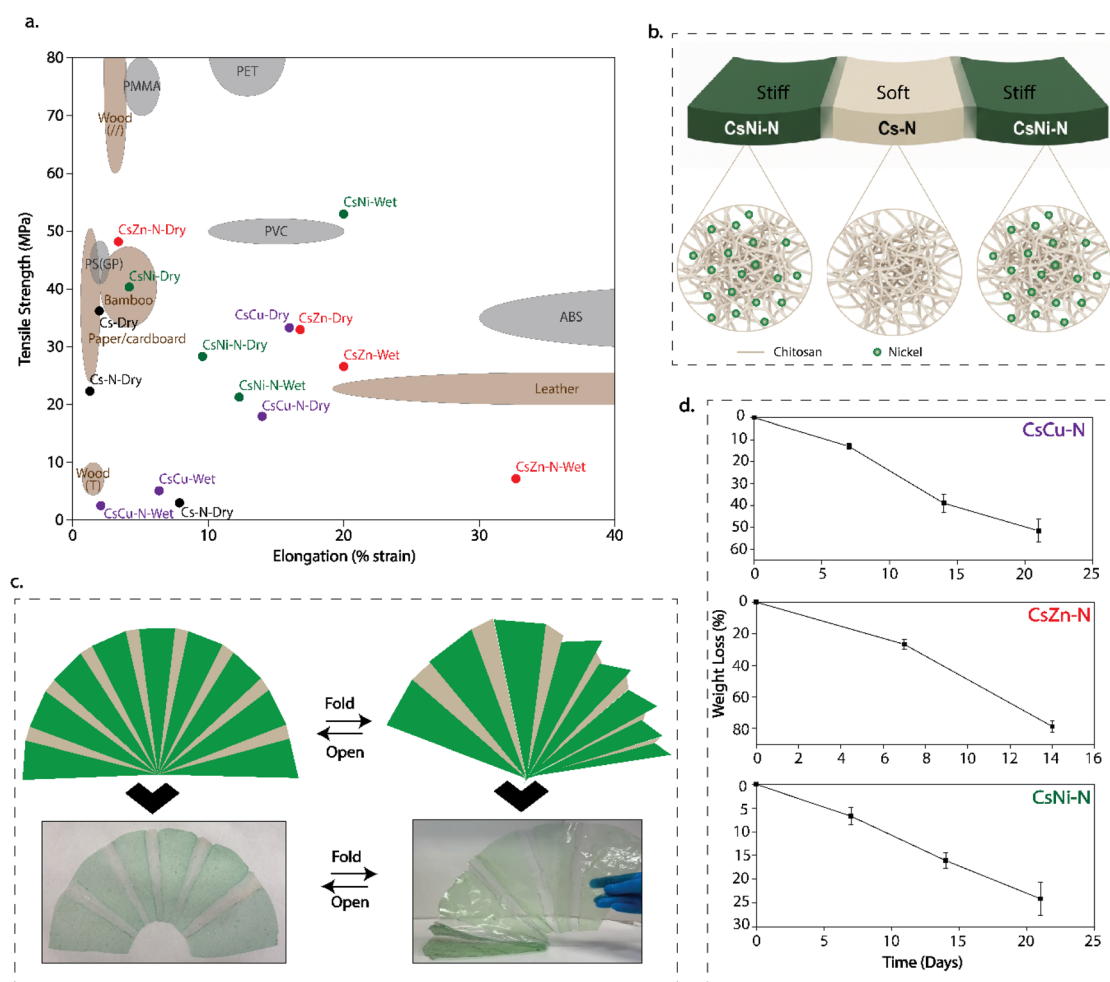


Fig. 3 Mechanical properties, origami fabrication, and biodegradation of metal-modified chitosan films. (a) The tensile strengths of chitosan samples treated with different metal ions, both neutralized and non-neutralized, were compared under both dry and wet conditions. This plot enables the selection of a biomaterial with specific strength characteristics suitable for various applications. (b) Schematic for a combination of chitosan-based material with different strengths after neutralization; pure chitosan retains its flexibility, while CsNi-N became stiffer after neutralization. (c) An origami structure was fabricated using a stiff (CsNi-N) and soft (Cs-N) material. This structure was inspired by the foldable wings of insects, which have varying mechanical strengths that enable them to fold and open easily. The fabricated structure mimics this phenomenon, providing potential for real-world applications to replace multi-material designs (Movie S2). (d) A soil burial test was conducted to assess the degradation of the materials. Among the composite samples, CsZn-N degraded within three weeks, while CsCu-N and CsNi-N degraded by 54% and 24%, respectively, over the same period.

In the preliminary soil-burial experiment, the metal-containing films showed composition-dependent mass loss, with CsNi-N exhibiting the lowest mass loss over the experimental period. CsNi-N also exhibited the lowest swelling and the highest wet-state modulus among the compared formulations, which is consistent with a more water-stable network and may contribute to its lower mass loss. However, the soil-burial experiment does not distinguish biological degradation from dissolution, fragmentation, or metal release. Dedicated leaching, mineralization, and ecotoxicity studies would therefore be required to assess degradation mechanisms and environmental safety (Fig. 3d). This proof of concept demonstrates that regions with distinct wet-state mechanical properties can be combined within a single chitosan-based construct. Further work is required to evaluate interface durability, repeated actuation, manufacturability, and application-specific performance.

In conclusion, this study establishes a coordination-based strategy using unmodified, bio-derived chitosan for reproducing a hallmark of structural biomaterials: large mechanical diversity from a single chemical platform. Cu, Zn, and Ni ions were introduced into chitosan films using a common solution-processing and neutralization procedure. The resulting materials exhibited metal-dependent mechanical responses: CsZn-N showed the highest dry-state modulus among the metal-containing films, CsCu-N showed a more compliant dry-state response, and CsNi-N retained the highest wet-state strength and modulus among the formulations examined. Structural and spectroscopic measurements were consistent with metal-dependent changes in polymer organization and donor-group environments. These outcomes were achieved using a common chitosan platform, enabling diverse local mechanical properties within a single construct, as demonstrated here by producing origami-inspired objects that combine soft and stiff areas on a continuous surface. Finally, soil burial tests confirmed the unassisted biodegradability and revealed that metal identity can also tune degradation kinetics. Together, the results provide a general, experimentally grounded framework for designing mechanically heterogeneous materials from a single unmodified renewable feedstock, an approach directly aligned with scalable circular-materials design.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article, including the experimental data underlying the figures and SI figures, have been included as part of the supplementary information (SI). Additional information required to reproduce the work is provided in the Experimental section and SI. Supplementary information: materials and methods, two additional figures, and two videos. See DOI: <https://doi.org/10.1039/d6ta04260k>.

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