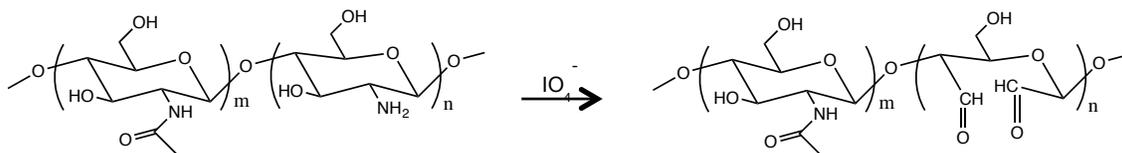


Squid Beak Inspired Water Processable Chitosan Composites with Tunable Mechanical Properties

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Scheme S1. Periodate induced chitosan oxidation mechanism, where periodate ions attack the amine groups in chitosan, leading to dialdehyde formation, and chitosan becomes partially oxidized.

Reaction Cascade and Chemistry of the Cross-Link

In Scheme1 of the paper, product c or d or both are a result of the cross-linking reaction between oxidized L-dopa and Chitosan. Here we use FTIR and UV-Vis to confirm the molecular structure, however, we could not exclude possibility of formation of c (Michael-type adducts) or d (Schiff-base) for the following reasons.

In UV-Vis spectra, a peak at 460nm is employed as the evidence for Michael-type adducts^{1,2}. While the UV-Vis does not give an obviously distinguishable peak, (Fig. 2) we hypothesize that it is due to the strong absorbance at around 300-320nm, which overshadows the weak peak of 460nm. Nevertheless, this result agrees with previous studies that the 460nm peak of Michael-type adducts is only observed for small molecule models¹.

An FTIR spectra (Fig.S2) also provides chemistry evidence of Schiff-base cross-linking leading to imine-type functionality formation. It is shown previously that for highly deacetylated chitosan, amide I band from C=O stretching at around 1635cm⁻¹ is rather weak^{3,4}. We observed an increasing absorbance at 1660 cm⁻¹, which according to literature, corresponds to formation of C=N bond, confirming the presence of imine functionality⁵. It is noted, however, that C=O cannot be excluded from this peak, and that the dialdehyde formation resulting from chitosan oxidation⁶ may also contribute to the intensity increase of this peak.

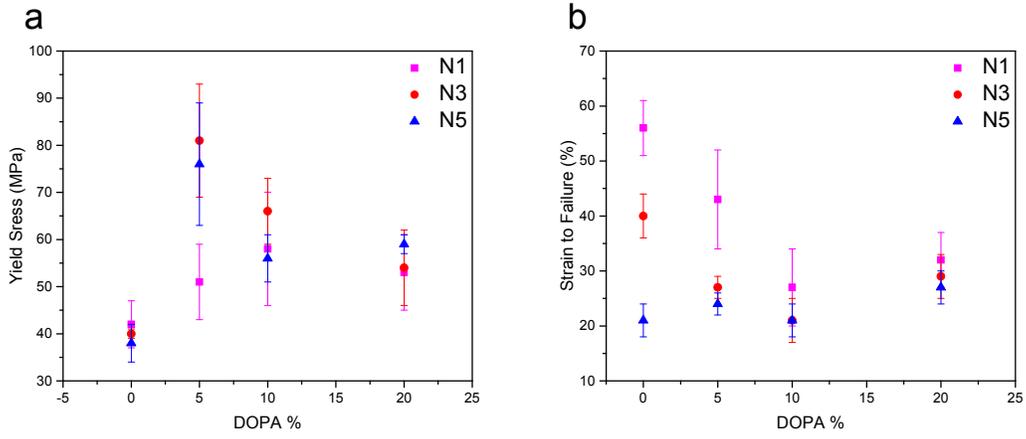


Fig S1. (a) Yield strength and (b) strain to failure of ChitoDX composites. For ChsDXN1, ChsDXN3, and ChsDXN5, the change in mechanical properties relates to the amine content change summarized in Table S1, where a higher amine content change indicates a more extensively reacted cross-linking.

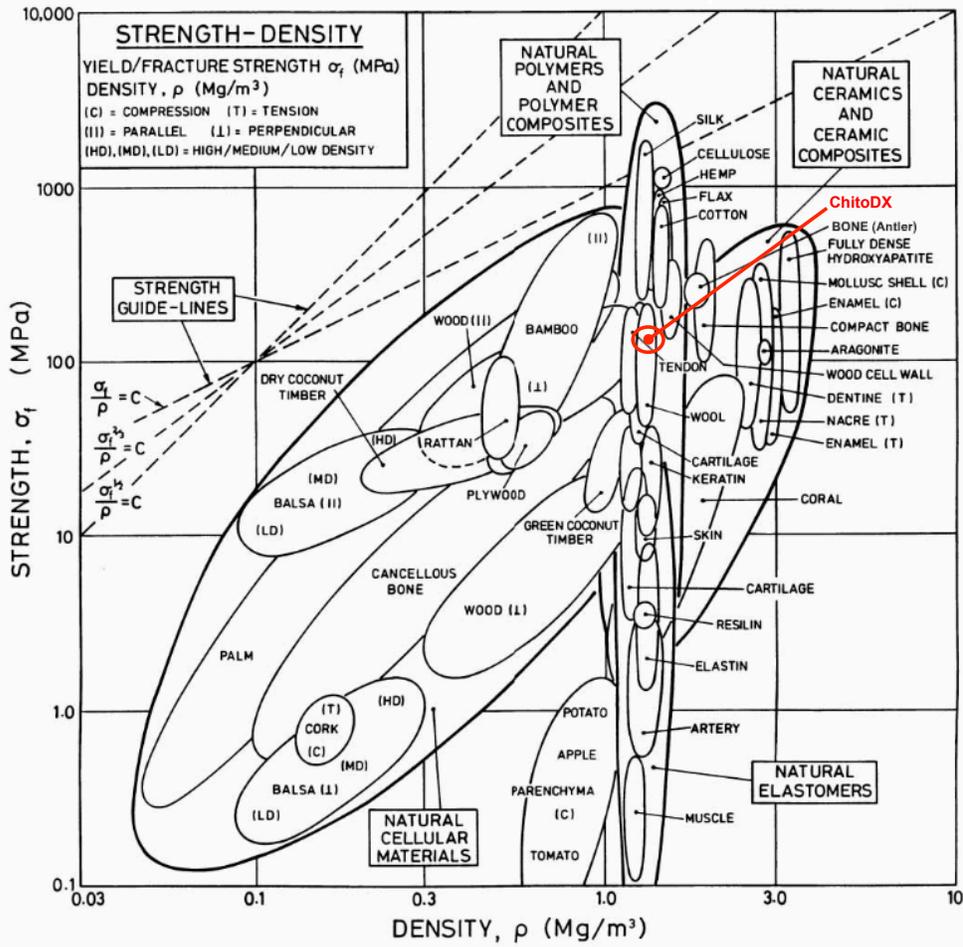


Fig S2. Ashby plot for natural materials plotting strength against density, showing ChitoDX is mechanically efficient sitting in the upper regime of natural polymer and polymer composites. The plot is adapted from a publication by U.G.K. Wegst and M.F. Ashby,⁷ reprinted by permission of the publisher, Taylor & Francis Ltd.

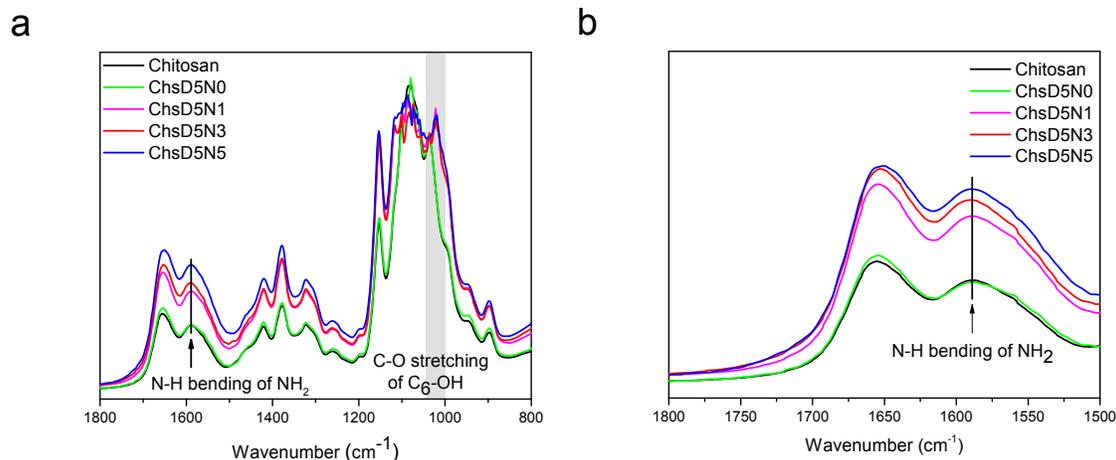


Fig S3. FTIR spectra for chitosan and ChsD5NY. Spectra are normalized with respect to the peak for C-O stretching of C₆-OH, which we see a visual absorbance intensity difference regarding N-H bending of NH₂, indicating increasing NH₂ groups consumption along with increasing oxidant composition during the reaction cascade.

In order to further confirm the cross-linking reaction and quantify the extent of cross-linking, we perform Fourier Transformed Infrared Spectroscopy (FTIR) on ChsD5NY composites (Figure S2). In ChsD5NY composites, we hypothesize that increasing the amount of oxidant leads to more amines being reacted with L-Dopa as expected. We quantify the extent of this increase by adapting a procedure previously published for determining the chitosan degrees of deacetylation, or the ratio between the number of D-glucosamine units and D-glucosamine+ N-acetyl-D-glucosamine.⁸ For pure chitosan, N-H bending of the primary amine (NH₂) shows at 1560 cm⁻¹ and C-O stretching of C₆-OH group shows at 1030 cm⁻¹.⁹ The ratio between these two peaks indicates the relative amount of primary amines in the chitosan. We used this procedure in the past to determine the degree of functionalization of chitosan with maleic, proline, and pyridine groups.¹⁰⁻¹² Here, we use it to determine how many primary amines in the chitosan have reacted with the L-Dopa as part of the cross-linking reaction that does not involve the C₆-OH group. The values shown in Figure 4a are also in agreement with an alternate procedure⁸ that involves analyzing the FTIR absorbance at 1560 cm⁻¹ (Figure S1a). From FTIR, we also infer that Schiff-base cross-linking (Scheme 1d) occurs during the process leading imine-type functionality formation showing as C=N stretching at 1660 cm⁻¹ (Figure S2b).¹³

L-dopa wt%	Oxidant wt%	Change in Amine Content (%)
5	1	7
10		10
20		2
5	3	13
10		9
20		7
5	5	25
10		11
20		14

Table S1. This table summarizes the change in amine content along with increasing concentrations of L-dopa based on FTIR spectra. Calculations are based on the method to determine the degree of deacetylation as described in literature. The change in amine content closely relates to the mechanical performance of the composites as discussed in Figure 4.

Moreover, for the case with constant oxidant, increasing L-Dopa concentration increases change in amine content to a certain extent since there is the other competing reaction of polydopamine formation (Scheme 1e). L-dopa molecules are much smaller, thus diffuse and react faster. Therefore with excessive amount of L-dopa, polydopamine formation is the dominating reaction, consuming most oxidant, leading to smaller percent of cross-linking reaction (amine content change)

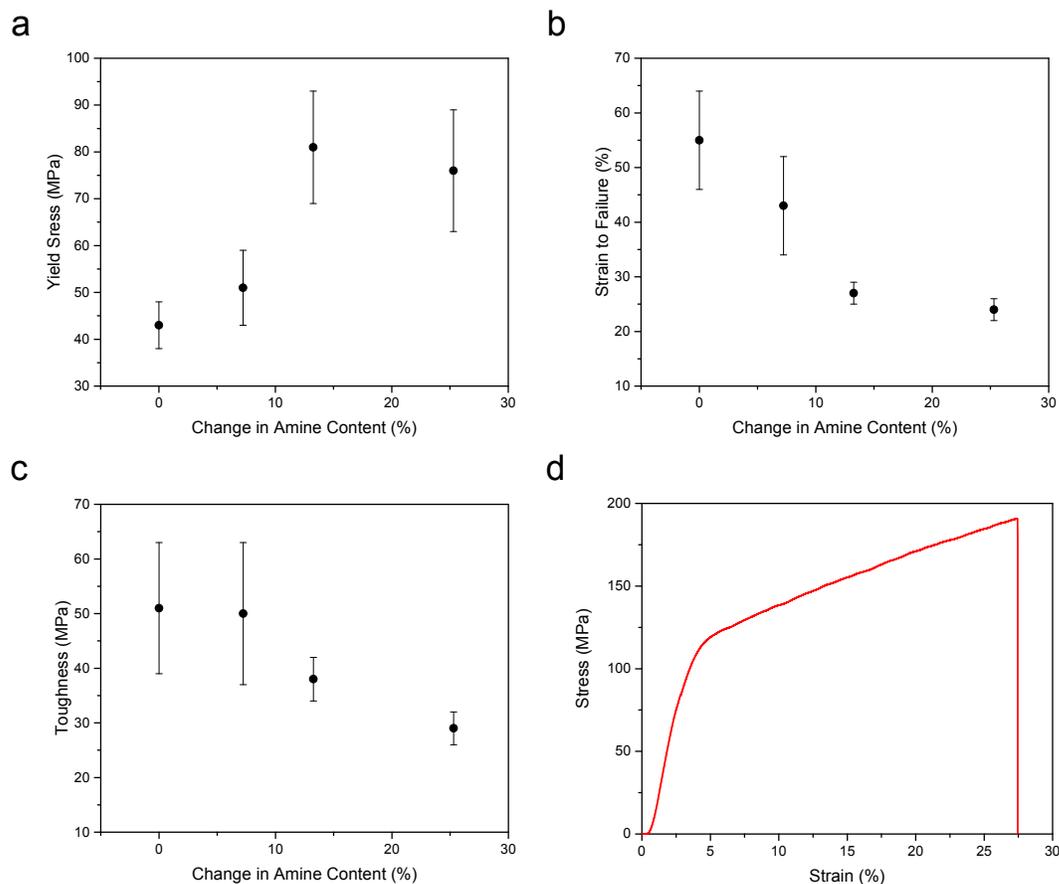


Fig S4. Mechanical characterization for ChsD5NY composites under dry conditions. (a) Yield strength increases as an increasing amount of NH_2 groups reacted up to ChsD5N3, following the same trend as the elastic modulus and ultimate tensile strength. As the cross-linking density increases, the polymer network becomes more rigid, resulting decreasing (b) strain to failure. With a combination effect of stiffness enhancement and maximum strain reduction, toughness decreases at a slower rate along with NH_2 consumption. (d) A stress-strain curve for ChsD5N3 showing the elastic and prolonged plastic deformation.

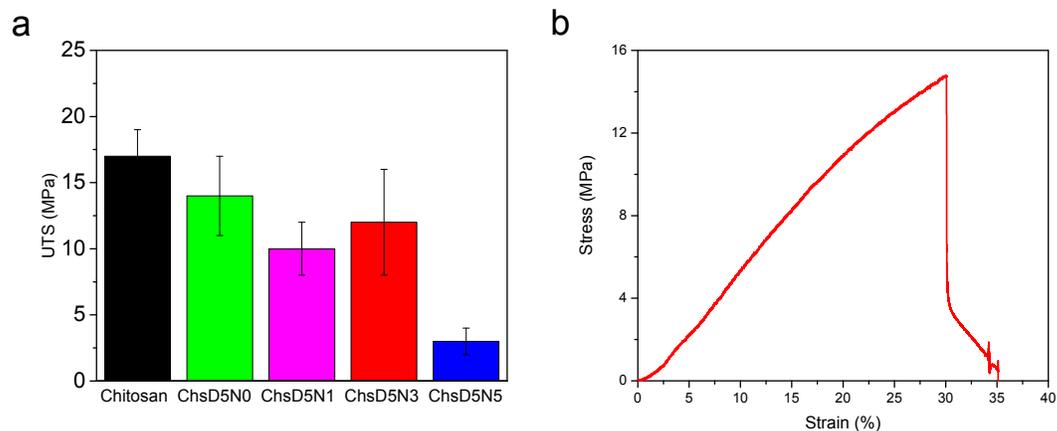


Fig S5. (a) UTS for hydrated ChsD5NY after immersion in water for 24 hours. (b) A stress-strain curve for hydrated ChsD5N3.

Here we notice that both chitosan and ChsD5N0 have higher UTS compared to cross-linked ChsD5NY composites under hydrated conditions. Upon immersion in water for 24 hours, chitosan film absorbs water in a free swelling situation. Cross-linking restricts the chitosan network swelling to a limited amount until equilibrium.¹⁴ Nevertheless, the L-dopa cross-linking also drives water molecule out of the chitosan network with localized dehydration.¹⁵ This results a non-homogenous structure on a molecular scale. When the sample is subject to the uniaxial tensile stress, such inevitable mechanical mismatch between the soft, swelling chitosan network with locally stiff, hydrophobic cross-links causes micro-cracks,¹⁶ leading to materials failure.

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