Electronic Supplementary Material –

On optimal hierarchy of load-bearing biological materials

ESM Text

A. Tension-Shear Chain Model and Recursive Formulae for $E_n$, $S_n$, and $\Gamma_n$.

Based on the tension-shear chain model (Jager & Fratzl 2000; Gao et al. 2003; Ji & Gao 2004), the recursive expressions for Young’s modulus $E_n$, strength $S_n$ and fracture energy $\Gamma_n$ in a bottom-up designed hierarchical material have been discussed in the literature (Gao 2006; Yao & Gao 2007). Here, we only give a brief overview of the main formulae. As figure S1 shows, the composite at level $n$ contains hard inclusions at level $(n-1)$ arranged in a regular staggered pattern. Assuming that the structure and properties of the $(n-1)$-th level has been determined, the effective Young’s modulus at the $n$-th hierarchical level, $E_n$, can be calculated by generalizing a simple formula for the Young’s modulus of the staggered nanostructure (Gao et al. 2003; Ji & Gao 2004) as

$$E_n = \left[ \frac{4(1-\varphi_{n-1})}{G_{n-1}^p \varphi_{n-1}^2 \rho_{n-1}^2} + \frac{1}{\varphi_{n-1} E_{n-1}} \right]^{-1}, \quad (S1)$$

where $G_{n-1}^p$ denotes the shear modulus of soft matrix at the $n$-th level, and $\varphi_{n-1}$, $\rho_{n-1} = \frac{l_{n-1}}{h_{n-1}}$, $E_{n-1}$ denote the volume fraction, aspect ratio and Young’s modulus of hard inclusions at the $n$-th level, respectively.

From simple load balance, the tensile strength of composite at the $n$-th level is calculated as

$$S_n = \frac{1}{2} \varphi_{n-1} \rho_{n-1} \tau_{n-1}^p, \quad (S2)$$

in which $\tau_{n-1}^p$ is the shear strength of soft matrix at the $n$-th level.

In the fracture process of load-bearing biological materials, the strain energy is primarily dissipated through deformation of the soft matrix (Menig et al. 2000; Menig et al. 2001; Meyers et al. 2008). Thus, the fracture energy at the $n$-th level can be expressed as
\[ \Gamma_n \approx (1 - \varphi_{n-1})l_{n-1}^p \Theta_{n-1}^p = (1 - \varphi_{n-1})l_{n-1} \rho_{n-1} \tau_{n-1}^p \Theta_{n-1}^p, \]  

(S3)

where \( \Theta_{n-1}^p \) denotes the failure shear strain of the soft matrix at the \( n \)-th level.

Fracture in load bearing biological materials is usually characterized by a diffused process/damage zone in front of a crack tip (Ji & Gao 2004). As a conservative estimate, the width of the fracture process zone is taken to be the length of the hard inclusion, \( l_{n-1} \).

**B. About the Assumption of “Identical Soft Matrix at All Hierarchical Levels”**. In the main text, we have assumed that the soft matrix is identical throughout all hierarchical levels, i.e., equation (2.5). This assumption can be relaxed without affecting the main conclusions of our model. To demonstrate this, two types of soft materials are adopted; one is collagen (with properties \( G_p = E_m/1000 = 0.1 \text{ GPa} \) and \( \tau_p = \sigma_m/50 = 1/15 \text{ GPa} \) ) distributed in the 1\(^{st}\) level microstructure; a non-collagenous protein with properties \( G_p = E_m/2000 = 0.05 \text{ GPa} \) and \( \tau_p = \sigma_m/100 = 1/30 \text{ GPa} \) is adopted as soft matrix at higher hierarchical levels (i.e., the 2\(^{nd}\)-\( N \)-th levels). The failure shear strain of the soft matrices is still taken to be between \( \Theta_p = 35\% \) and \( \Theta_p = 100\% \). From the calculated results shown in figure S2, one can see that the trends of the plots are not affected. The optimal number of hierarchical levels are 4 for \( \Theta_p = 35\% \) and 5 or 6 for \( \Theta_p = 100\% \), which are in good agreement with the original results (figure 4), 4 for \( \Theta_p = 35\% \) and 6 for \( \Theta_p = 100\% \), respectively. The adoption of two different types of soft matrix allows us to achieve much better agreement between the theoretically predicted strain ratios and corresponding experimental measurements for the first 3 hierarchical levels, as shown in figure 5. Table S2 lists the predicted size and properties of the two-soft-matrix hierarchical material at different hierarchical levels for \( \Theta_p = 35\% \) up to the optimal level \( N = 4 \).

**C. About the Assumption of “Identical Volume Fraction of Hard Inclusions at All Hierarchical Levels”**. In the main text, we have assumed that the volume fraction of hard inclusions is identical throughout all hierarchical levels, i.e., equation (2.6). This
assumption can also be relaxed without affecting the main conclusions of our model. To demonstrate this, the volume fractions of hard inclusions at hierarchical levels $2-N$ are set to be $\varphi_i = ... = \varphi_{N-1} = 85\%$, while the volume fraction of hard inclusions at the 1st level is taken to be $\varphi_0 = 0.15/0.85^{N-1}$. In this case, the volume fraction of hard inclusions at higher hierarchical level is larger than that at the elementary level for $N \leq 10$ (Fratzl et al. 2004). From the calculated results shown in figure S3, we can see that relaxing this assumption does not affect the basic trends of the plots. The optimal number of hierarchical levels are shown to be 5-7 (depending on $\Theta_p$), compared to the original results of 4-6 (figure 4).

**D. Calculated Results for Bone and Shell.** The calculated results for bone ($\Phi = 45\%$) and shell ($\Phi = 95\%$) are shown in figure S4 and figure S5, respectively.

ESM Figures:

Figure S1. A generalization of the tension-chain model (Jager & Fratzl 2000; Gao et al. 2003; Ji & Gao 2004) to quasi-self-similar hierarchical materials. (a) A unit cell with staggered hard inclusions (blue) embedded in a soft matrix (yellow), and (b) the path of load transfer under uniaxial tensile load.

Figure S2. Calculated properties of biocomposites based on 2 different soft matrices as a function of the hierarchical level $N$. (a) Young’s modulus, (b) strength, (c) toughness, and (d) size of an $N$-level quasi-self-similar hierarchical material with mineral volume fraction $\Phi = 15\%$. 
Figure S3. Calculated properties of biocomposites based on 2 different volume fractions of hard inclusions at different structural levels as a function of the hierarchical level $N$. (a) Young’s modulus, (b) strength, (c) toughness, and (d) size of an $N$-level quasi-self-similar hierarchical material with mineral volume fraction $\Phi = 15\%$.

Figure S4. Variations of (a) Young’s modulus, (b) strength, (c) toughness, and (d) size of an $N$-level quasi-self-similar hierarchical material with mineral volume fraction $\Phi = 45\%$. 
Figure S5. Variations of (a) Young’s modulus, (b) strength, (c) toughness, and (d) size of an N-level quasi-self-similar hierarchical material with mineral volume fraction $\Phi = 95\%$.

**ESM Tables:**

Table S1. Variations of inclusion aspect ratio and length at different hierarchical levels in a fiber of mineralized tendon.

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Table S2. The predicted size and properties at different hierarchical levels of the mineralized tendon fiber based on 2 different soft matrices and $\Theta_p=35\%$.

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