S’Inspirer des Matériaux de la Nature – des Structures Multi-Echelles Mènent à des Nouvelles Propriétés

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How Can We Make Strong, Stiff, Tough, Lightweight Materials?

- State of the art engineering problems require a new generation of lightweight materials.

- But they also need to have superior mechanical properties, e.g., in impact resistance.
Contents

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1 Mechanical Properties of Materials
• first elastic deformation (reversible), then plastic deformation (irreversible shape change)
• **stiffness** (slope = modulus, GPa) is force required to make a material undergo elastic deformation.
• **strength (MPa)** is stress representing a material's resistance towards irreversible deformation
• ductility (strain at break) is the maximum strain tolerated by the material before fracture
- **toughness (kJ/m$^2$)** is the resistance to fracture, measured as total energy needed for fracture.
Toughness of Brittle, Ductile, and Rubbery Materials

- **toughness** is optimal for ductile materials, but high strength and ductility mutually exclusive.
Mechanical Properties of Ceramics and Metals

- ceramics are very stiff, reasonably strong, but brittle; metals are reasonably stiff, strong, ductile
- some polymers brittle, some very ductile, but all have relatively low strength, stiffness

Toughness of Typical Polymers

- plexiglass
- nylon
- polypropylene
- polyethylene
- metals dominate strong and tough structure materials, polymer composites too brittle
• high density of metals makes it difficult to design strong, tough, lightweight materials
Hierarchical Structure Formation and Properties of Silk Materials
## Properties of Spider Silk versus the Best Manmade Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Strength $\sigma_{\text{max}}$ / GPa</th>
<th>Toughness / kJ m$^{-2}$</th>
<th>Stiffness / GPa</th>
<th>Energy at Break / kJ kg$^{-1}$</th>
<th>Ductility $\varepsilon_{\text{max}}$ / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spider Silk</td>
<td>1.1</td>
<td>160</td>
<td>10</td>
<td>100</td>
<td>27</td>
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<tr>
<td>Nylon</td>
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<td>80</td>
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<td>15</td>
<td>18</td>
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<tr>
<td>Kevlar</td>
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<td>50</td>
<td>100</td>
<td>30</td>
<td>3</td>
</tr>
<tr>
<td>Steel</td>
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<td>6</td>
<td>200</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Rubber</td>
<td>1–10</td>
<td>1–100</td>
<td>0.001</td>
<td>10</td>
<td>1000</td>
</tr>
</tbody>
</table>

high performance fibers are very strong but brittle; spider silk close in strength and very ductile
What is Hierarchical Structure Formation?

- hierarchical structures are “order” and “structures” on distinctly different length scales

- macroscopic hierarchical structures are used in engineering for lightweight, sturdy construction
the main component of spider silk is a protein named major spidroin I (molecular weight 750 kDa)
only small segments of the protein are known (each letter represents an amino acid)

highly regular structure of hydrophobic alanine-rich and hydrophilic glycine-rich segments
alanine-rich segments are well-defined AAA-AAA runs flanked by GGA or GAG (or similar)
hydrophilic segments are regularly repeated GGX sequences (X = hydrophilic amino acid)
Self-Assembly of the Phase-Segregated Hydrophobic Segments

- self-assembly of alanine-rich segments into tape-like structures by hydrogen bonding

- helical molecular conformation is translated into supramolecular helicity of the tapes
Further Self-Assembly into Hierarchically Structured Nanofibrils

\[ \beta - \text{sheet tape} \rightarrow \text{interfacial energy} \rightarrow \text{nanofibrils (2–6 stacked } \beta \text{-sheets)} \]

- interfacial energy
- oligopeptide length (aggregation enthalpy)
- helicity / conformation (energy penalty bc/ helix pitch increase)
- polymer chain length (frustration; chain extension entropy)
soluble proteins are produced in the spinning glands in the spider’s abdomen

shear forces and active water removal in the spinning duct result in liquid-crystalline phase

finally, “cold extension” (by means of the spider’s legs) results in highly oriented fiber
Hierarchical Structure of Spider Dragline Silk

- like a “nanocomposite” of a polymer reinforced with short fibrils of nanometer dimensions
- spider silk is a hierarchically structured material, several levels of structure formation

- well-defined amino acid sequence (impossible to achieve in synthetic polymers)
- phase segregation between alanine-rich runs and the other segments
- formation of well-defined nanofibrils (with periodic structure), “string of beads”, and matrix
in most cases, increasing the strength in nanocomposites decreases toughness and vice versa
• ordered domains (nanofibrils) disordered, order-disorder gradient from center to periphery
• disordered domains (flexible matrix) with a lot of residual order (defined conformations)

Balance of Order and Disorder on the Nanoscale in Spider Dragline Silk

• complex, carefully designed balance of order and disorder on the nanometer length scale
• purpose is to avoid interfaces, and guide stresses onto different components at different loads
• nanofibrils for stiffness at small loads, unfolding of beads at larger loads for toughness
Hierarchical Structures of Bone, Wood, and Nacre
The hierarchical structure of bone is characterized by its ability to remodel itself to repair damage. Bone is composed of osteons and Haversian canals, which have a lamellar structure with individual lamella consisting of fibers arranged in geometrical patterns. The fibers surround blood vessels, and osteocytes (osteoblasts that have become trapped within the bone) communicate with each other through canaliculi, which are the means by which the signaling that promotes bone repair occurs.

Crack growth in bone is a complex process that involves both intrinsic and extrinsic toughening mechanisms. Intrinsic toughening occurs at small length scales through microcracking, while extrinsic toughening is observed at larger scales, such as the cement lines. Crack bridging and crack delection are two major toughening mechanisms that serve to blunt crack tips, thereby reducing the driving force for further cracking.

As in most materials, plasticity and the resultant ductility provide a regime of dissipative deformation once plastic yielding has begun. However, an even larger contribution to the fracture resistance of bone is made by the intrinsic toughness, which is required to propagate the crack further. Indeed, it is because of the small-scale intrinsic and larger-scale extrinsic toughening that the fracture toughness of bone, which in the longitudinal direction is typically 1–5 MPa√m, can be many times higher in the transverse direction, where cracks delection and bridging are effectively used in natural materials.

Bone, like other materials, is not static but evolves over time in response to both intrinsic and extrinsic factors. The signaling that promotes such repair, as the microcracks are thought to severe the canaliculi, which are the means by which the bone alternatively dissipates energy at higher stress levels and is formed by microcracking.

Biological factors (such as altered collagen crosslinking due to age) are generated at small length scales through intrinsic processes. When the intrinsic toughness, genetically encoded at small length scales through biological factors, is coupled with extrinsic processes, the bone alternatively dissipates energy at higher stress levels and is formed by microcracking.

This makes possible a large increase in strength and toughness. However, an even larger contribution to the fracture resistance of bone is made by the intrinsic toughness, which is required to propagate the crack further. Indeed, it is because of the small-scale intrinsic and larger-scale extrinsic toughening that the fracture toughness of bone, which in the longitudinal direction is typically 1–5 MPa√m, can be many times higher in the transverse direction, where cracks delection and bridging are effectively used in natural materials.
Hierarchical Structure of Bamboo Wood

Hierarchical Structure of Nacre

Proteins + chitin

-30 nm grains

Breaking of mineral bridges

Inelastic shearing resisted by nano-asperities

Organic layer acting as viscoelastic glue

Tablet interlocking during sliding

Conclusions
• hierarchical structure formation in biomaterials results from competing interactions on various length scales

• hierarchical structure formation allows biomaterials to use different materials components and decouple their individual materials properties

• this gives rise to new materials with unusual property combinations

• biomaterials “play” with disorder in their ability to create perfect materials from a self-sorting mixture of imperfect parts

• synthetic organic and polymer materials should strive to mimic hierarchical structures formation and the role of disorder