13. Composites, bio-inspired materials and self assembly

Introduction - composites

Composites: engineered materials made from 2 (or more) different constituents that remain separate and distinct on macroscopic level (in contrast to solution)

2 classes of constituent materials: matrix & reinforcement

Matrix surrounds and supports reinforcement by maintaining its relative positions

Reinforcement provides special and desired physical properties (e.g. mechanical, electrical and optical)

Synergism between matrix and reinforcement can produce properties unavailable from single-component materials!

Wide variety of available matrix and reinforcement materials → design potential enormous

Nature full of inspirational composite materials…
13. Composites, bio-inspired materials and self assembly

...a few examples of natural composites:

**Wood (dry)**

Composed of 2 most common organic materials on Earth:

*Strong & stiff (polymeric) cellulose fibers in hierarchical structure* (= reinforcement, ~70%)

*Dispersed in soft polymer lignin* (= matrix, ~30%)
13. Composites, bio-inspired materials and self assembly

Bone! Relatively hard, slightly elastic & lightweight composite made from:

- Ca$_3$(PO$_4$)$_2$ plate-shaped micro-crystals (~50*25*2 nm$^3$ called calcium hydroxyapatite): in pristine form brittle ceramic with high stiffness (k=F/δ; δ = deformation)

- Various organic “glue” components allow for elastic properties of bone: mainly collagen fibers ← much finer (80–100 nm diameter) collagen fibrils ← aligned and packed triple-helical collagen molecules

- Bone cells (osteocytes)

Bone either: (i) woven (quick growth/replacement → random collagen fiber orientation → low strength) or (ii) lamellar (slow growth → parallel fibers → high strength)

Lamellar bone (shown here) often replaces quickly formed woven bone as bone growth progresses
Mankind have used primitive composites for long time

Example: For building of houses (and other supporting structures) we have used -- and still use -- bricks, which can be composites containing straw (reinforcement) and mud (matrix)

(Already ancient Egyptians used mud bricks on regular basis; in Bible it is mentioned as a punishment to be forced to make bricks without straw!)

But, even though straw (hollow tubular form of cellulose) as reinforcement has triple advantage of being cheap, readily available, and easy to handle, it is neither very stiff, stable, nor strong (mainly since cellulose molecules poorly aligned)

Last ~50 years: high-performance reinforcement materials developed with high stiffness, stability & strength, due to better understanding of “structure-property” relationships …
**Design criteria for functional reinforcement materials - 1**

1. **Stiffness** depends on inter-atomic forces, which can be extracted from plot of binding potential ($U$) vs. inter-atomic separation:

$$F = \nabla U \ (= k\delta; \ \delta = \text{deformation})$$

→ desirable to employ materials with steep (& deep) binding-potential curves. Often found in atoms/molecules bound together by chemical covalent bonds (or by metal bonds or, to a lesser degree, by large collection of hydrogen bonds)

Moreover, covalent bonds particularly stiff if formed between light atoms (e.g. Be, B, C, N, O), since outer valence electrons less shielded from nucleus with few core electrons

∴ Stiffness benefits from strong, inflexible bonds between light elements
13. Composites, bio-inspired materials and self assembly

Design criteria for functional reinforcement materials - 2

2. Stability: 3 desired key properties:

✓ *High melting temperature.* Typical characteristic of materials with strong (covalent or metal) bonds

✓ *Low thermal expansion.* Direct consequence of symmetric binding-potential curve: typical feature of materials with strong bonds & deep binding potential wells

✓ *High resistance towards chemical oxidation.* Compact materials with strong (covalent) bonds will minimize its exposure to (oxidizing) environment

∴ *Compact* materials made from *strong* bonds often exhibit good stability
13. Composites, bio-inspired materials and self assembly

Design criteria for functional reinforcement materials - 3

3. High strength

Important: Strong bonds always requirement for strong material, but it is not a sufficient criteria in itself!

Minimizing number of flaws in material also critical, since flaws will concentrate stress and promote propagation of cracks

∴ Certain individual fibers exceptionally strong, since they can be synthesized (in facile manner) without any significant flaws

Some collection of fibers -- in combination with appropriate matrix -- (i.e. bulk materials) exhibit desired combination of large stiffness, good stability, and high bulk strength 😊

A few examples…
13. Composites, bio-inspired materials and self assembly

Modern fiber-type reinforcement materials:
- Glass
- Carbon
- Nylon
- Kevlar
- Steel
- Carbon nanotubes

in combination with matrix material of:
- Rubber
- Polyimide
- Epoxy
- Cement
- Aluminium

Can form highly functional synthetic composites…
13. Composites, bio-inspired materials and self assembly

Examples of functional (and complex) synthetic composites

Rubber tyres rather complex laminar composites: parallel fiber bundles (“the cords”) interleaved with layers of rubber

Properties of tyres can be changed significantly by choice of materials...

Matrix: Type of rubber, and amount of cross-linking, determine, e.g., operational temperature range

Reinforcement: Choice of cord material (kevlar, steel, nylon, glass,...) and cord-winding geometry determine the strength and resilience of tyre, as well as the behaviour of the car on the road

Essential that cord (reinforcement) material is stiff, strong, light-weight, cheap, mix well and bond with rubber,, not reacts with sulfur, not is susceptible to fatigue, etc.
Examples of functional (and complex) composites

Pole used by pole vaulters: illustrative example of functionality of designed composite

Before 1960: Bamboo poles and then Al poles used, and WR stabilized at ≈ 5m

Why no further improvement?

\[ E_k = \frac{1}{2} mv^2 = E_p = mgh \rightarrow h = \frac{v^2}{2g} + v \approx 10 \text{ m/s (really fast!)} \rightarrow h \approx 5 \text{ m} \]

So how to find some extra energy that can be transformed into more \( E_p \)?

What about if vaulter makes pre-jump (inspired by high jumpers)?

Very difficult with a pole in hands!
13. Composites, bio-inspired materials and self assembly

Functional alternative: Bend pole with muscle power when it is planted → make use of release of stored bending energy when pole straightens

Important: (i) pole appropriately stiff (to allow for storage of significant energy), (ii) pole has high elastic strength limit (so it not fractures or deforms during bending)

Elasticity requirement impossible to fulfil with old Al poles (not elastic enough) and bamboo poles (fail easily during compression) …

but with the advent of “fiberglass” composite pole it was possible

→ WR over 6 m

Today: variation in amount & type of carbon and glass fibers allow for individually designed poles
13. Composites, bio-inspired materials and self assembly

Self-healing materials

Possible to fabricate high-strength composites which are self-healing towards undesired formation of small cracks

Trick: addition of (i) small microcapsules filled with “glue” and (ii) large number of catalyst grains

When crack reaches capsule → capsule ruptures and its “glue” content (monomers or oligomers) leaks into crack

When monomers come in contact with catalyst → solid polymer forms → crack is closed!

Major damage cannot be repaired, but idea is to prevent build-up of microscopic cracks that often lead to material disintegration
13. Composites, bio-inspired materials and self assembly

Introduction – self assembly

In order to design new functional materials on molecular level (for nano-electronics, molecular electronics, etc.): critical to employ additive **bottom-up** fabrication methods (e.g. AFM manipulation described in lecture 9)

Such methods are/will be distinctly different than conventional subtractive **top-down** photolithography approach used in fabrication of microelectronic circuits (i.e. application of photoresist, UV curing using photomask, selective dissolution, etching, etc.)

<table>
<thead>
<tr>
<th>Example stages of photolithography:</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Wafer is oxidized.</td>
</tr>
<tr>
<td>2. Oxidized wafer is covered with photoresist.</td>
</tr>
<tr>
<td>3. Wafer is exposed to UV light through a photomask.</td>
</tr>
<tr>
<td>4. Unexposed photoresist is dissolved in developer solution.</td>
</tr>
<tr>
<td>5. Oxide now unprotected by photoresist is etched away in hydrofluoric acid.</td>
</tr>
<tr>
<td>6. The rest of the photoresist is removed. Wafer is now ready for doping.</td>
</tr>
</tbody>
</table>
Self-assembly: Langmuir-Blodgett deposition

One functional bottom-up method for nanofabrication of ultra-thin films is Langmuir-Blodgett deposition.

If molecules with hydrophilic ("water-loving") heads and hydrophobic ("water-hating") tails are dispersed into water → self-organization can take place resulting in "heads" pointing down into water and "tails" accumulating at surface.

Self-assembled mono-layers of such molecules will form on water surface, and may be picked up on substrate by slowly and gently pulling substrate up through the surface.

The deposition can be repeated (and direction reversed) a number of times to produce molecular films with very well-defined thickness and order.
Self-assembly: selective chemical reactivity

Another route towards self-assembled monolayers (SAMs) is to use selective chemical reactivity:

e.g. S (in thiol compounds) reacts strongly with Au

If $n$-alkane thiol ($\text{CH}_3\text{(CH}_2\text{)}_n\text{SH}$ molecules) compound added to ethanol solution (0.001 M), and Au substrate subsequently is immersed into solution:

SAM structure forms relatively rapidly, which typically is sufficiently ordered to exhibit a lattice structure
13. Composites, bio-inspired materials and self assembly

Introduction – bio-inspired materials

Alternative approach towards functional advanced materials is to learn and become inspired from bottom-up approach of nature.

We have talked about fascinating double-helix structure of DNA and its functions, but the material that it codes for is also inspirational:

Proteins -- “the principal machinery of life” -- are polymers with very complex structures, which allows for their many important and diverse functions.

But how are they organized?
13. Composites, bio-inspired materials and self assembly

Bio-inspiring materials: structure of proteins

**Primary structure:** order in which 20 amino acids are chemically (covalently) connected within one single polymer unit

**Secondary structure:** chain conformations within one single protein polymer unit (established by hydrogen bonding); can either be alpha helix, beta sheet, or disordered coil; many different secondary structures exist in one single protein molecule…

**Tertiary structure:** spatial relationship of secondary structures within one single protein molecule that define the overall molecular shape

**Quaternary structure:** global structure that results from union of several protein molecules
13. Composites, bio-inspired materials and self assembly

Bio-inspired materials

Inspired by hierarchical structure of proteins (and other bio-molecules), scientists currently try to produce self-assembling materials built from synthetic polymers

The primary structure of such synthetic polymers can be relatively well controlled

Example: copolymers consisting of chemically connected blocks, each with well-defined length and distinctly unique chemical composition, now routinely prepared

Phase separation of chemically different regions → preparation of nanostructures over large areas

If these nanostructures directed by template → functional (and commercially interesting) nanostructures formed
13. Composites, bio-inspired materials and self assembly

**Bio-inspired materials**

Chemists also capable of synthesizing a manifold of polymers that adopt well-defined secondary structure

Particularly helical structures (similar to alfa-helix of proteins and double helix of DNA) are commonplace

Helical polymers can be divided into 2 classes depending on their helix inversion barrier…

In solution at room temperature: stiff helical polymers having large helix inversion barriers (> 20 kcal/mol) exist as stable helices, while more flexible helical polymers exist as dynamic polymer chains in which helix reversal regions move along the backbone
13. Composites, bio-inspired materials and self assembly

Bio-inspired materials

At the higher -- tertiary & quaternary -- structural levels, lot of interesting science currently going on

Example: single dendritic molecules form conical or wedge-shaped building blocks

Large number of such dendritic building blocks can self-assemble into spherical and cylindrical nano-objects (in similar manner to virus assembly in nature)

By functionalizing dendritic molecules and chemically stabilizing the self-assembled nano-objects: possible to attain specifically tuned materials with high electron mobility (useful in molecular electronics) or specific inner diameter and chemical environment (useful for, e.g., drug delivery)
Reminder: course information

1. All solutions to problems handed in before 27/5 (unless you are already approved; check home page!)

2. Laboratory projects approved before 27/5

3. Project… oral presentation 25/5!

Written exam!

Time: 2/6 9.00, Place: Östra paviljongerna, room 5