Nanocomposites

Lecture 14

OUTLINE

- Why nanocomposites?
- Can polymer based composites be strong?
- How to produce polymeric nanocomposites?
- What polymeric nanocomposites are good for?
Why do we need composites?

**Composites**: Multiphase material with significant proportions of each phase.

Combine materials with the objective of getting a more desirable combination of properties.

**Principle of combined action**
– Mixture gives “averaged” properties
**Dreamliner**

**Motivation:** increasing efficiency and thereby decrease fuel costs.

**Requirement:** to incorporate lighter and stronger materials into airplanes.

**Solution:** In 2009, Boeing completed the first successful test flight of the Boeing 787 Dreamliner. One of the primary innovations of the Boeing 787 is the extensive use of **composite materials**; composites are formed by incorporating multiple phase components in a material in such a way that the properties of the resultant material are unique and not otherwise attainable. Composite materials comprise half of the Dreamliner’s total weight. For example, the fuselage of the Boeing 787 is made from carbon fiber-reinforced plastic (a composite of carbon fiber in an epoxy matrix). The carbon fibers impart strength and stiffness to the material, and the epoxy matrix binds the fibers together.
Constituent phases are:
- Chemically dissimilar;
- Separated by distinct interface

**Matrix:**
-- The continuous phase
-- Purpose is to:
  - transfer stress to other phases
  - protect phases from environment
-- Classification: MMC, CMC, PMC

Metal Matrix  Ceramic Matrix  Polymer Matrix

Concrete is a particulate composite containing coarse sand or gravel in a cement matrix.
The properties of composites are a function of the properties of the constituent phases, their relative amounts, and the geometry of the dispersed phase.

- **Dispersed phase:**
  - **Purpose:** enhance matrix properties.
    - **MMC:** increase yield stress, tensile strength, creep resistance
    - **CMC:** increase fracture toughness
    - **PMC:** increase modulus, yield stress, tensile strength, creep resistance.
  - **Classifications:** Particle, fiber, structural
Common particle reinforcements/geometries and their respective surface area-to-volume ratios

- **Particulate materials**
  \[ \frac{3}{r} \]

- **Fibrous materials**
  \[ \frac{2}{r} + \frac{2}{l} \]

- **Layered materials**
  \[ \frac{2}{t} + \frac{4}{l} \]
The properties of composites are a function of
- the properties of the constituent phases;
- their relative amounts;
- the geometry of the dispersed phase

Shape of the particles; size; distribution; orientation
What are nanocomposites?

- **Nanocomposites** are a class of materials in which **one or more phases** with **nanoscale** dimensions (0-D, 1-D, and 2-D) are embedded in a metal, ceramic, or polymer matrix.
- The **general idea** behind the addition of the nanoscale second phase is to create a **synergy** between the various constituents, such that novel properties capable of meeting or exceeding design expectations can be achieved.
- The **properties** of nanocomposites rely on a range of variables, particularly the matrix material, which can exhibit nanoscale dimensions, loading, degree of dispersion, size, shape, and orientation of the nanoscale second phase and interactions between the matrix and the second phase.
Polymer nanocomposites

Why nanocomposites?

- Nanoparticle properties
- Multifunctional capabilities
- Chemical functionalization
- Huge interphase zone

Potential to replace/augment traditional (micron) composites

Qian, Dickey, et al. 2000
Polymers viscoelasticity

Some properties of solids: occupy fixed volume/shape
Some properties of liquids: flow under force
  - E.g. Creep: apply $\sigma(t) = \sigma_0 H(t-t_0)$

![Diagram showing elastic and viscous responses]

$J(t) \rightarrow$ creep compliance
Polymer-matrix nanocomposites

- **Polymer-matrix nanocomposites** consist of a matrix made from a polymeric material.
- The **second phase** (usually a few percent by weight, wt%), which is dispersed within the matrix, has nanoscale dimensions.
- The small size of this phase leads to unique properties.
- Due to the nanoscale size of the reinforcing phase, the interface-to-volume ratio is significantly higher than in conventional composites. As a result, the volume fraction of the second phase can be reduced, without degradation of the desired properties.
Multifunctionality

Multifunctional NEW material with <1% nanoparticles in traditional polymers

- Transparent, flexible, electrical conducting polymer
- Increased environmental stability: diffusion constants increased
- Increased durability: 100x improved wear resistance
- Increased toughness and strength, altered fracture modes
- Thermal stability increased 30°C
The polymer matrix system can be a thermoplastic, thermoset, or elastomer.

A thermoplastic polymer will soften when heated above the glass transition temperature ($T_g$) and thus can be moulded into a particular shape upon cooling.

This process is repeatable, which makes thermoplastic materials reprocessable and recyclable.
Polymer matrix – thermosetting and elastomer

- **Thermosetting** materials become permanently hard through cross-linking when heated above $T_g$. Thus thermosetting polymers cannot be molded by softening. Instead, they must be fabricated during the cross-linking process.

- **Elastomer** resins are lightly crosslinked polymer systems and have properties that lie between thermosets and thermoplastics.
Reinforcing phase

- The nanoscale reinforcing phase can be grouped into three categories, namely, nanoparticles (0-D), nanotubes (1-D), and nanoplates (2-D).
- In the case of nanoparticles, the particle size and distribution are of great importance.
- Depending on the type of nanoparticles added, the mechanical, electrical, optical, and thermal properties of polymer nanocomposites can be altered.
- In the field of mechanical properties, the changes in modulus and strength depend strongly on the degree of interaction between the particle and the polymer.
Advantage of reinforcements

- Advantage of using nanoparticles as reinforcement is that their size is smaller than the critical crack length that typically initiates failure in composites.
- As a result, nanoparticles provide improved toughness and strength.
- However, agglomeration of nanoparticles should be prevented at all costs.
- In fact, several investigations have shown that small levels of agglomeration can decrease the strain-to-failure by several tens of percent.
- Nanoparticles can also significantly affect Tg.
- Typically this occurs because nanoparticles influence the mobility of the polymer chains due to bonding between the particles and the polymer and bridging of the polymer chains between the particles.
The electrical and optical properties of polymer-matrix nanocomposites can be improved by the addition of nanoparticles. With respect to electrical properties, the nanoparticles seem to act in a variety of ways. First, the smaller the nanoparticles, the shorter the distance between the particles, provided the volume is kept constant. This in turn leads to percolation at lower volume fraction, resulting in higher electrical conductivity.
Electrical properties of polymer-matrix nanocomposites (2)

- Even for nanocomposites embedded with insulating nanoparticles, the electrical conductivity of the nanocomposite seems to increase due to a better compactness of the polymer, leading to enhanced coupling among the nanoparticles through the grain boundaries.

- In some cases, such as in polypyrrole nanocomposites filled with Fe2O3 nanoparticles, the so-called variable range-hopping (VRH) mechanism seems to explain the enhancement in DC current. The VRH mechanism involves exchange of charges between the nanoparticles and the polymer matrix.
Optical properties

- There is a large interest in developing transparent nanocomposites with enhanced mechanical and electrical properties.
- To achieve transparency, scattering must be minimized, which means that the nanoparticles should be as small as possible while the index of refraction should remain as similar as possible to the matrix.
- Excellent use of nanoparticles in polymer nanocomposites is in controlling the index of refraction, which can be achieved by tailoring the volume fraction of nanoparticles.
- In addition, using active optical nanoparticles and changing the particle size, distribution, and shape, the color of the nanocomposite can be tuned. This behavior has been shown in polyethylene polymer films filled with silver nanoparticles.
Changes in transmittance in polyimide nanocomposites

- The addition of nanoparticles of silica to polyimide has been used to control the transmittance in these nanocomposites.
1-D nanomaterials reinforcements

- The use of CNTs in composites has received wide attention due to their extraordinary physical and mechanical properties.
- Several critical factors need to be addressed:
  - (1) uniform dispersion of carbon nanotubes within the polymer matrix,
  - (2) alignment of CNTs in the nanocomposite, and
  - (3) good interfacial bonding between the CNTs and the polymer matrix.
Dispersion of CNTs

- CNTs exhibit smooth surfaces and intrinsic Van der Waals interactions, which tend to promote clustering when dispersed in a polymer matrix.

- If agglomeration occurs, the CNTs are less adhered to the matrix and will slip against each other under an applied stress, with drastic consequences for the mechanical properties.

Typical agglomeration of carbon nanotubes

M. Ashby, P. Ferreira, D. Schodek; Nanomaterials, Nanotechnologies and Design; Copyright 2009 Elsevier Ltd.
Methods to disperse CNTs

- **sonication** of CNTs,
- **shear mixing** (for rubbery epoxy resins, for which 1 wt% of CNTs led to an increase by 27% in the tensile modulus and by 100% in the tensile strength),
- **surfactant-assisted processing**, and
- **chemical functionalization** (partial separation of SWCNTs from the bundles by means of an acidic solution), and
- **in situ polymerization**.
Chemical functionalization

- Chemical modification of nanoparticles
  - Specific to polymer matrix
  - Enhance interaction with polymer chains
  - Increase interphase zone

a-SWNT + PMMA

PMMA tethered to a-SWNT
Reinforcements orientation

- A crucial aspect for providing optimal reinforcement is to properly **orient** the CNTs.
- Because of their **aspect ratio**, CNTs possess highly **anisotropic** mechanical properties.
- To take advantage of their load carrying efficiency along the axial direction, it is essential that CNTs are well aligned within the matrix.
Methods to align the CNTs

- **Extrusion** is a popular technique, in which a polymer melt reinforced with CNTs is extruded through a die and drawn under tension before solidification.
- Due to the fact that CNTs exhibit high electrical conductivities, the application of a **magnetic field** or **electric field** has also been used to induce CNT alignment.
Interfacial bonding between the CNTs and the polymer matrix

- It is believed that the efficiency of load transfer in nanocomposites is controlled by the interfacial characteristics of the reinforcing phase and the matrix.
- It is believed that the main mechanisms of load transfer include mechanical interlocking, chemical bonding, and nonbonded interactions between the CNTs and the matrix.
- In particular, it is believed that the key factor in forming a strong bond lies in the polymer morphology, especially its ability to form large diameter helices around individual CNTs.
- The strength of the interface is then due to molecular-level entanglements of CNTs and matrix as well as long-range order of the polymer.
Surface area increases $10^3 \times$

- Altered mobility & chain conformation
- Trapped entanglements
- Altered crystallinity
- Decreased interparticle distance
- Crosslink density
Hierarchically structured composites

- Hierarchically designed, self-assembled, nanostructured, chemically tuned polymer nanocomposites affect \textbf{bulk} response:
  - Glass transition
  - Thermal Stability
  - Aging rate
  - Diffusion
  - Environmental robustness
  - Toughness

\textbf{DURABILITY +}
Thermal properties

- The inclusion of CNTs can be used to improve the thermal conductivity.
- The CNTs create a percolation network that allows the nanocomposite to conduct heat with conductivities up to 3.5 times the conductivity of the pristine polymer.
- However, the thermal conductivity of a nanocomposite is still far from the theoretical value for an isolated CNT, which has been predicted to be on the order of $10^3$ W/m.K.
- The main reason for this discrepancy is the large thermal resistance that exists between the polymer matrix and the CNT surface.
- Because CNTs possess high surface-to-volume ratios, when CNTs are dispersed in the polymer matrix, the large interfacial area creates a significant resistance.
- This effect has been attributed to differences in phonon frequency between the CNTs and the polymer matrix.
2-D second-phase nanomaterials

- **Platelike** layered materials with a thickness on the order of 1 nm but with an aspect ratio of 25 or above.
- The most common are **layered silicates**.
- When these are added to polymer-matrix nanocomposites, a **wide** array of property enhancements can be achieved, such as **increased stiffness and strength**, **improved UV resistance** and **gas permeability**, **greater dimensional stability**, and **superior flame resistance**.
- Remarkably, these **enhancements** in properties are obtainable at extremely **low-filler concentrations** (2-5% vol), a fraction of what is typically needed in conventional composite materials (30-40% vol).
Layered silicates

- Among the layered silicates, mica and smectic clays are the most used.
- **Mica** consists of large sheets of silicate with **strong** bonds between the layers.
- The **smectic clays** exhibit **weak** bonds between the layers.
Scheme of three main types of layered silicates in polymer matrix
Polymer nanocomposite synthesis

1. **PMMA in NMP**
2. **SWNT in NMP**

3. **Sonicate @40°C for 1h**

4. **Anti-solvent for precipitation of the composite**
   - Filtered and dried @80°C under vacuum

5. **Methanol**

6. **Hot Press molding**
   - Thin films pressed @ 2000 pounds at 210°C for 10 mins
FGS: Functionalized Graphene Sheets

Graphite $\xrightarrow{\text{oxidize, expand}}$ Graphite Oxide $\xrightarrow{\text{reduce, exfoliate}}$ FGS

Elemental Analysis

<table>
<thead>
<tr>
<th>Element</th>
<th>Percentage</th>
</tr>
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<tbody>
<tr>
<td>Carbon</td>
<td>77%</td>
</tr>
<tr>
<td>Oxygen</td>
<td>22%</td>
</tr>
</tbody>
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- No functionality
- Hydrophilic
- Some functionality
Current applications

Displays

Thin Film Transistor (TFT) backplane on polyester substrates