

Lecture 8

Composites

The idea behind nanocomposites is to use building blocks with dimensions in the nanometre range to design and create new materials with unprecedented flexibility and improvements in their physical properties. This concept is exemplified in many naturally occurring materials, such as **bone**, which is a hierarchical nanocomposite built from ceramic tablets and organic binders. When designing the nanocomposite, scientists can choose constituents with different structures and composition and, hence, properties, so that materials built from them can be **multifunctional**.

As a general definition, a nanocomposite is a conventional material reinforced by nanoscale particles or nanostructures which are dispersed throughout the bulk material. The base material itself generally consists of non-nanoscale matrices. **Nanocomposites typically consist of an inorganic (host) solid containing an organic component or vice versa or two (or more) inorganic/organic phases in some combinatorial form. At least one component must be nano-sized.** In general, **nanocomposite materials can demonstrate different mechanical, electrical, optical, electrochemical, catalytic and structural properties which are different from those of the individual components.** Apart from the properties of the individual components, **interfaces** in a nanocomposite play an important role in determining the overall properties of the material. Due to the high surface area of nanostructures, nanocomposites present many interfaces between the intermixed phases and, often, the special properties of the nanocomposite are a consequence of the interaction of its phases

at interfaces. In comparison, the interfaces in conventional composites constitute a much smaller volume fraction of the bulk material.

In this lecture, nanocomposites are subdivided in **two main groups: inorganic nanocomposites**, which are characterised by an inorganic matrix (e.g. ceramic) reinforced by nanoscale particles or nanostructures of inorganic (e.g. metal) or organic (e.g. carbon-based) nature; and **polymer nanocomposites**, which are characterised by an organic matrix (e.g. polymer) reinforced by nanoscale particles or nanostructures by inorganic (e.g. clay) or organic nature.

1. Inorganic nanocomposites

High-performance ceramics are sought in many applications, such as highly efficient gas turbines, aerospace materials, cars, etc. The field of ceramics that focuses on improving their mechanical properties is referred to as **structural ceramics**.

Nanocomposite technology is also applicable to **functional ceramics** such as ferroelectric, piezoelectric, varistor and ion-conducting materials. In this case, the properties of these nanocomposites relate to the dynamic behaviour of ionic and electronic species in electro-ceramic materials. Among these materials, in this document, the review is limited to **nanocomposite with enhanced magnetic properties**.

➤ Structural nanocomposites

Presently, even the best processed ceramics pose many unsolved problems such as **poor resistance to creep, fatigue and thermal shock; degradation of mechanical properties at high temperatures; and low fracture toughness and strength. To solve these problems, one approach** has been to incorporate a

second phase such as particulates, platelets, whiskers or fibres in the micron-size range at the matrix grain boundaries. However, the results obtained with these methods have been generally disappointing. Recently, the concept of nanocomposites has been considered, where **nanometre-size second-phase dispersions** are inserted into ceramic matrices. Large improvements in both the fracture toughness and the strength of a ceramic can often be achieved with nanometre-range particles embedded in a matrix of larger grains at their grain boundaries. These can involve the incorporation of a **nano-ceramic in a bulk ceramic, a nano-metal in a ceramic, or a nano-ceramic in a metal**. Another possibility is the incorporation of a polymer in a ceramic. Without going into too much detail, the following are examples of inorganic **nanocomposites that have improved structural properties**.

- ❖ The incorporation of **fine SiC and Si₃N₄ nanoparticles in an alumina matrix** (Al₂O₃, a structural ceramic material) first demonstrated the concept of structural nanocomposites. The dispersion of these particles has been shown to improve the fracture toughness from 3 to 4.8 MPa m^{1/2} and the strength from 350 to 1050 MPa at only 5 vol. % additions of SiC.
- ❖ One possibility for the fabrication of advanced structural ceramics is the dispersion of **metallic second-phase particles into ceramics** which improves their mechanical properties, such as fracture toughness, and influences other properties including magnetic and optical properties. Nanocomposites of this type are Al₂O₃/W or MgO/Fe. **Granular films** can also be made with a ceramic phase embedded with nano-size metal granules (such as Fe/Al₂O₃, Fe/SiO₂). Such films often show **unusual or enhanced transport, optical and magnetic properties**. The inclusion of nano-sized

metals in a thin ceramic film can transform it **from an insulator to a conductive film.**

❖ Another possibility is to add fine, **rigid ceramic reinforcements to a ductile metal or alloy matrix** (metal matrix composites or MMCs). The reinforcement can be either in the form of particles (e.g. silicon carbide, aluminium oxide), fibres (e.g. silicon oxide, carbon) or a mixture of both (hybrid reinforcement). Materials produced by this method are particularly useful in the aerospace, automotive and aircraft industries. The advantage of MMCs is that they **combine metallic properties (ductility and toughness) with ceramic characteristics (high strength and modulus)**, leading to materials having greater strength to shear and compression and to higher working temperature capabilities. The properties of MMCs are controlled by the size and volume fraction of the reinforcements as well as by the nature of the matrix/ reinforcement interface. **The attention is now oriented towards the incorporation of nanoparticles and nanotubes for structural applications, since these materials exhibit even greater improvements in the physical, mechanical and tribological properties compared to MMCs with micron-size reinforcements.**

❖ Nanoscale ceramic powders with **carbon nanotubes** provide another method for creating dense ceramic-matrix composites with enhanced mechanical properties. For instance, **hot pressed alumina with mixed carbon nanotubes results in lightweight composites with enhanced strength and fracture toughness compared to polycrystalline alumina.** The processing conditions greatly influence the properties of this material, though. In metal matrix composites (MMCs), the incorporation of carbon

nanotubes is considered very promising since these materials have higher strength, stiffness and electrical conductivity compared to conventional metals.

➤ **Nanocomposites with enhanced magnetic properties**

Materials with outstanding magnetic properties are in high demand as these are employed in nearly all important technical fields including electrical power, mechanical power, high-power electromotors, miniature motors, computer elements, magnetic high-density recording, telecommunications, navigation, aviation and space operations, medicine, sensor techniques, magnetic refrigeration, materials testing and household applications. Recent developments in the field of magnetic materials have involved materials with a nanocrystalline structure or, in the case of thin films, layers of nanometre thickness.

Nanostructuring of bulk magnetic materials leads to soft or hard magnets with improved properties. One example is the Finemet **nanocrystalline soft magnetic alloys**, which consist of melt-spun Fe-Si-B alloys containing small amounts of niobium and copper. When annealing at temperatures above the crystallisation temperature, the Fe-Si-B-Nb-Cu amorphous phase transforms to a crystalline solid with grain size of about 10 nm. These alloys have excellent magnetic induction and large permeability, and a very small coercive field.

Nano-sized magnetic powders can have extreme properties and have no hysteresis at any temperature. These materials are called **superparamagnetic** and one example is nano-sized powders of a Ni-Fe-Co alloy.

Nanostructuring has also been studied in the context of **hard magnets** (permanent magnets). **The strongest known magnets are made of neodymium (Nd), iron and boron (e.g. $\text{Nd}_2\text{Fe}_{14}\text{B}$). In these materials, it has been found that the coercive field decreases significantly below approximately 40 nm and the remnant magnetisation increases.** Another approach to improving the magnetisation curve of permanent magnets has been to **fabricate nanocomposites made of hard magnetic phases, such as $\text{Nd}_2\text{Fe}_{14}\text{B}$ and $\text{Sm}_2\text{Fe}_{17}\text{N}_3$, within soft magnetic matrices (e.g. soft phase of iron). The effect of the inclusion of a soft iron mixed in with a hard material is to increase the remnant field.**

The **grain size of the material** also influences the magnetisation saturation point. For instance, the magnetisation of ferrite increases significantly below a grain size of 20 nm. Thus, **reducing the size of the grains in the magnet increases the energy product (which is the product of magnetisation and coercivity).** The coercivity also increases with decreasing the grain sizes. In the case of nanocomposite magnetic films, this is true if the grains are isolated (no interaction), but when the grains are in contact and exchange interaction kicks in, the coercivity falls rapidly with grain size. The coercivity is thus highest at percolation, when the grains just start touching each other. This effect is important in the context of designing thin-film nanocomposites (**magnetic multilayer nanocomposites**), for instance for high magnetic density recording.

2. Polymer nanocomposites

Polymer composites are materials where a polymer is filled with an inorganic synthetic and/or natural compound in order to increase several properties, such as heat resistance or mechanical strength, or to decrease other properties, such as electrical conductivity or permeability for gases like oxygen or water vapour. Materials with synergistic properties are used to prepare composites with tailored characteristics; for instance, high-modulus but brittle carbon fibres are added to low-modulus polymers to create a stiff, lightweight polymer composite with some degree of toughness. Current polymer composites are really filled polymers, since these materials lack an intense interaction at the interface between the two mixed partners. Progress in this field has involved moving from macroscale fillers to micron-scale fillers, to even smaller fillers.

In recent years, scientists have started to explore a new approach to the production of polymer composites with the use of **nanoscale fillers**, in which the filler is below 100 nm in at least one dimension. Nanoscale fillers include: nanoparticles; nanotubes; and layered (also called ‘plate-like’) inorganic materials such as clays (**Figure 27**).



Figure 27: Schematic representation of nanoscale fillers

Although **some nano-filled composites have been used for more than a century**, such as carbon-black and fumed-silica-filled polymers, researchers have only recently started to systematically produce and study these materials. The motivation has been the realisation of the exceptional combined properties that have been observed in some polymer nanocomposites. This, together with substantial development in the chemical processing of nanoparticles and in the *in situ* processing of nanocomposites, has led to unprecedented control over the morphology of these materials.

One of the most common reasons for adding fillers to polymers is to improve their mechanical performance. In traditional composites, this often compromises the ductility of the polymer and, in some cases, negatively impacts its strength because of stress concentration caused by the fillers. **Well-dispersed nano-fillers, such as nanoparticles or nanotubes, can improve the modulus and the strength and maintain (or even improve) ductility because their small size does not create large stress concentration. For all nano-fillers, a key requirement is the homogeneous dispersion of the filler within the polymer matrix.** As discussed in the following sections, this is a challenge in many cases, and a topic of intense research.

Although the scientific community has made remarkable progress in this field in the last years, **polymer nanocomposites have just started to be explored**, and many research questions still need to be addressed. What is clear so far is that the use of nanoscale fillers opens the way for the development of materials with exceptional properties. For instance, nanoparticles do not scatter light significantly, thus it is possible to make polymer composites with altered electrical or mechanical properties that remain **optically clear**. Nanoparticles are also of

interest not just for their small size, but for their inherent unique properties. Carbon nanotubes, for instance, display the highest values so far seen of elastic modulus, as high as 1 TPa, and strengths that can be as high as 500 GPa. This could allow, for example, the fabrication of polymeric composites with exceptional strength and flexibility.

Another outstanding property that the use of nanoscale fillers confers on nanocomposites is an exceptionally **large interfacial area**. The increase of surface area below 100 nm is dramatic. The interface controls the degree of interaction between the filler and the polymer, and is thus responsible for the composite properties. Thus, the largest challenge in nanocomposite science is learning to control the interface.

Nanoscale fillers can potentially allow the creation of a vast range of different polymeric materials with advanced properties. In general, macroscopic reinforcement elements have the limitation of always containing imperfections, but as the reinforcements become smaller and smaller, structural perfection could be reached. The ideal reinforcements would have atomic or molecular dimensions and be intimately connected with the polymer. The use of nanoscale fillers, however, also introduces a series of **fabrication challenges**. **Because of their small size and high surface area, nanoscale fillers such as nanoparticles have a strong tendency to agglomerate rather to disperse homogeneously in a matrix. This leads to particle-matrix mixtures with high viscosities, which can make the processing of those materials quite challenging.** The result is that even the most exciting polymer nanocomposites have very low fractions of particle content, and relatively weak mechanical properties when compared to those predicted in theory. Therefore, polymer nanocomposites are an exciting type of advanced materials that

hold great promise in many application, but which are still mainly in a development stage. The intense research efforts in this area suggest, however, that these materials will become more readily accessible in the near future.

➤ **Nanoparticle-polymer nanocomposites**

Nanoparticles are a type of nano-filler that offer the opportunity of developing polymers with new or advanced properties. As already discussed, the size of a nanoparticle affects its properties: for instance, gold nanoparticles have different optical absorption spectra depending on the particle size. **One of the advantages of using nanoparticles in polymer composites is that the particle size and distribution can be tuned.** Materials that cannot be grown easily as single crystals can be used at the nanoscale and dispersed in a polymer to take advantage of the single-crystal properties.

In general, **nanoparticle-filled polymers display better mechanical properties, at least at low volume fractions and if well dispersed in the polymer. The reason is that nanoparticles are much smaller than the critical crack size for polymers and thus do not initiate failure. Thus, nanoparticles provide a way for simultaneously toughening and strengthening polymers. Proper dispersion is critical,** however, in achieving this.

The size scale of nanoparticle-polymer composites ranges from hybrid nanocomposites, in which the polymer matrix and the filler are so intimately mixed that they are no longer truly distinct, to discrete particles in a continuous matrix. Hybrid nanocomposites often arise from the use of block copolymers.

In terms of properties, the use of nanoparticles in filling polymers can influence not only the polymers' mechanical properties, but also the **polymers' mobility**

and relaxation behaviour, which, in turn, are connected to the glass transition temperature of the polymer (T_g) (i.e. the temperature at which a polymer becomes brittle on cooling or soft on heating). In general, adding well-dispersed, exfoliated nano-filler increases the T_g of the polymer. Nanoparticle-filled polymers also show an **increase in the abrasion resistance** of the composite.

One of the most exciting prospects of using nanoparticles in polymer composites is to create composites with **combined functionalities**, such as electrically conducting composites with good wear properties that are optically clear: this is possible because nanoparticles do not scatter light.

➤ **Carbon nanotubes in polymer composites**

Carbon nanotubes have very distinct properties compared to graphite, as summarised in **Table 2** in the section on mechanical properties. In the context of nanocomposites, **SWNTs are the most promising nanotube fillers. Some properties are particularly interesting: in particular their flexibility under mechanical stress, behaviour under high temperature conditions and electrical properties.** As with other applications that make use of carbon nanotubes, it has been observed that, in composites, the processing conditions ultimately affect the properties of the nanotubes and, as a consequence, the purity of the composite, as well as the purity of the nanotubes. Carbon nanotubes can also be doped, for example with nitrogen and boron, which changes their surface reactivity. For instance, nitrogen atoms inserted into the lattice of nanotubes makes them more dispersed in solution (carbon nanotubes are insoluble in water). Modified nanotubes present different electrical and optical properties and hence their use could lead to composites with novel properties.

It should be noted that the inclusion of carbon nanotubes in a polymer does not necessarily improve its mechanical properties. Although, in theory, the modulus of nanotubes is much higher than any graphite fibre, and hence the composite should have outstanding mechanical properties, it has been demonstrated that a number of variables influence this outcome. **For SWNT composites, the SWNTs are in a bundle; until SWNTs are isolated from the bundles or the bundles are cross-linked, the modulus of composites made of these materials will be limited.** For this reason, researchers are concentrating on developing processing methods that make it possible to obtain significant volume fractions of **exfoliated nanotubes**. As will be discussed later concerning clay-polymer nanocomposites, **the structural arrangement of the nano-filler within the polymer is also important: if the nanotubes are not straight when placed in the composite, the modulus of the composite significantly decreases.**

Apart from the mechanical enhancement of polymers, **nanotubes are also of interest for their electrical properties.** Carbon nanotubes are inherently more **conductive than graphite**. It has been found, for instance, that nanotube-PPV composites show a large increase in electrical conductivity, compared to simple PPV (poly(p-phenylene vinylene), of nearly eight orders of magnitude. Recently, an improvement of 4.5 orders of magnitude in the electrical conductivity of nanotube-PVA nanocomposites has been reported.

Finally, nanotube-polymer composites are promising in the context of light-emitting devices. These devices were developed after the discovery of electroluminescence from conjugated polymer materials (such as PPV). The practical advantages of polymer-based LEDs are their low cost, low operating voltage, ease of fabrication and flexibility. Small loadings of nanotubes in

these polymer systems are used to tune the colour of emitted light from organic LEDs.

➤ **Polymer-clay nanocomposites**

In the late 1980s, it was discovered that adding 5 % by weight of nano-sized clays to Nylon 6, a synthetic polymer, greatly increased its mechanical and thermal properties. Since then, polymer-clay nanocomposites have been widely studied and many commercial products are available. These hybrid materials are made of organic polymer matrices and clay fillers. **Clays are a type of layered silicates that are characterised by a fine 2D crystal structure**; among these, mica has been the most studied.

Mica is made up of large sheets of silicate held together by relatively strong bonds. Smectic clays, such as montmorillonite, have relatively weak bonds between layers. Each layer consists of two sheets of silica held together by cations such as Li^+ , Na^+ , K^+ and Ca^{2+} . The presence of the cations is necessary to compensate for the overall negative charge of the single layers. The layers are 20–200 nm in diameter laterally and come into aggregates called tactoids, which can be 1 nm or more thick. Naturally occurring clays include montmorillonite (MMT) and hecrite, and their synthetic equivalents are saponite and laponite respectively.

For these layered silicates to be useful as fillers in nanocomposites, **the layers must be separated, and the clay mixed thoroughly in the polymer matrix.** This is not trivial as silicate clays are inherently hydrophilic, whereas polymers tend to be hydrophobic. The solution is to exchange the cations that keep the layers in the silicate together with larger inorganic ions that can thus open the galleries between the layers (intercalation). When the silicate layers are completely separated, the

material is said to be exfoliated. In the case of intercalation, extended polymer chains are present between clay layers, resulting in a multilayer structure with alternating polymer/clay phases at repeated distances of a few nanometres: in the exfoliated state, the silicate layers are totally separated and dispersed in a continuous polymer matrix.

As already mentioned, the fabrication of a **polymer-clay nanocomposite requires mixing two components that are intrinsically non-compatible**. Surfactants are ionic, and thus interact well with the clay, but not with the polymer. An ideal solution is the use of ‘macro-surfactants’ such as block copolymers combining hydrophilic and hydrophobic blocks that can interact with the clay and the polymer respectively. For instance, poly(ethylene oxide) (PEO) is an excellent intercalation material.

Although homogeneous dispersion of the filler in the polymer is an important parameter, another important aspect is the **packing (or alignment) of the filler in the polymer**. To understand this concept, it is useful to consider a natural nanocomposite, bone. The unique properties of bone are a list of apparent contradictions: rigid, but flexible; lightweight, but solid enough to support tissue; mechanically strong, but porous. In order to meet these different demands, bone has a hierarchical structure that extends from the nanoscale to the macroscopic length scale. *The hierarchical structure of bone is responsible for its load transfer ability*. Nanoparticle-filled polymer composites have mechanical properties that are actually disappointing compared to theoretical predictions, and this is due to the **difficulty in obtaining well-dispersed large volume fractions of the reinforcing nanomaterial and a lack of structural control**. Taking this into consideration, some scientists have recently reported the fabrication of ultra-strong and stiff

layered polymer nanocomposites. In this work, bottom-up assembly of polymer-clay nanocomposite allowed the preparation of a homogeneous, transparent material, where the clay nanosheets have planar orientation. It was found that the stiffness and tensile strength of these multilayer nanocomposites are one order of magnitude greater than those of analogous nanocomposites.

Nanoclays are also used as fillers in polymers to increase the **thermal stability of polymers**. This property was first demonstrated in the late 1960s for montmorillonite-PMMA composites. The dispersion of the clays is critical to increasing the thermal stability (that is, raising the degradation temperature) of the polymer.

In addition to thermal stability, the **flammability properties** of many polymer-clay nanocomposites are also improved. Combining traditional flame retardants with intercalated or, better, exfoliated clays can result in further improvements in flame retardancy.

Finally, polysaccharide-clay nanocomposites are a class of materials that are important especially to the **food industry**. These composites make use of naturally occurring polymers, such as starch, mixed with clay to make a biopolymer film with enhanced properties, in particular permeability to water vapour.

Reference:

- Luisa Filipponi and Duncan Sutherland, Nanotechnologies: Principles, Applications, Implications and Hands on Activities, Edited by the European Commission Directorate-General for Research and Innovation Industrial technologies (NMP) programme, 2013, Chapter 5.